METAL OXIDE CATALYSTS FOR THE CO$_2$-ASSISTED PROPANE OXIDATIVE DEHYDROGENATION

by

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A dissertation submitted to the

School of Graduate Studies

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

Graduate program in Chemical and Biochemical Engineering

Written under the direction of

George Tsilomelekis

And approved by

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New Brunswick, NJ – January 2022
ABSTRACT OF THE DISSERTATION

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Propylene is one of the most crucial building blocks in chemical and petrochemical industry. In the big picture of shale gas revolution and global warming, the CO$_2$-assisted propane oxidative dehydrogenation exhibits its unique advantages and stands out as a ‘on-purpose’ propylene production technique. In this work, we endeavor to present a catalyst design idea for both propane and CO$_2$ activation with high efficiency. Cerium oxide has been well-established with superb oxygen mobility and abundant surface oxygen vacancies, which can be further improved with a transition metal dopant such as Fe, thus giving it great potential to serve as active sites and to maintain long-lasting constant performances. Furthermore, we investigated and evaluated the possibility of anchoring CrO$_x$ on top of Fe-doped cerium oxide surface and discussed the structure-reactivity relationship of Cr/Fe-CeO$_2$ catalysts.

Catalytic performances and kinetics of CO$_2$-assisted propane oxidative dehydrogenation was studied over Fe-doped ceria supported Cr oxides. The catalysts were synthesized via co-precipitation of Fe, Ce, and wetness impregnation of Cr. A pseudo-binary phase Cr/Fe-
CeO$_2$ structure was confirmed after combining Raman, XRD and TEM analysis. H$_2$-TPR experiments confirmed that the addition of Cr oxides altered original surface oxygen sites and enhanced the reducibility of the catalyst. The Cr-related catalysts outperformed Fe-doped ceria at low reaction temperature range, but as temperature increases the propane dry reforming plays a dominate role and diminished differences in catalytic performance of Fe-CeO$_2$ and supported Cr catalysts. A Mars-van-Krevelen kinetic model was developed based on 14 elementary steps and successfully predicted the reaction output. All catalysts exhibited excellent stability during 24-hour continuous reaction without regeneration in between. Especially, 10Fe-CeO$_2$ appeared to be the most stable and promising catalyst with minimal coke accumulation after 24-hour reaction test. Stability analysis revealed that Cr-related catalysts are even more stable than Fe-CeO$_2$ in the early 10 hours due to the dual redox circle of Ce($^{IV}$/Ce($^{III}$) and Fe($^{III}$/ Fe($^{II}$) but suffered from C-C scissoring side reactions and coke formation after 12 hours TOS.

Key words: Propane oxidative dehydrogenation; CO$_2$ activation; Fe-doped cerium oxide; Mars-van-Krevelen kinetic model; Catalyst stability and deactivation
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1. Introduction

1.1 Background

The US Shale gas revolution has been playing a profound role over the past decade in US energy and chemical industrial structures. According to a recent statistical study shown in Figure 1, light hydrocarbon paraffins’ annual production exhibited a stationary point in the late 2000s and doubled in less than 10 years from 15 million BOE to 30 million BOE\(^1\). Correspondingly, the boosted propane supply over the past decade has led to a significant drop in the price of natural gas liquids (NGLs) and decoupled their prices from the more expensive oil derivatives such as naphtha. Instead of a byproduct from crude oil or natural gas, the massive storage of propane in shale gas provided an alternative industrial routine as well as a profitable market choice. As a result, the shifting to cheaper propane resources offers an incentive among not only industrial investors, but also the entire research

![Figure 1](image_url)

Figure 1. Reprint: US production of crude oil, dry methane, and the natural gas liquids ethane and propane, since 1985, presented in equivalent barrels (BOE) of crude oil (146). One BOE is equal to 5.8 MMBtu.
community to develop new technologies for propane conversion into more complex downstream products.

Particularly, propylene is one of the most important building blocks for downstream petrochemical production. Propylene, with linear formula CH\(_3\)CH\(_2\)CH\(_2\), CAS No. 115-07-1, features one of the simplest organic chemical structures. Unlike the relative stable sp\(^3\) hybridized carbon from propane, propylene molecule contains two sp\(^2\) hybridized carbon and a C=C double bond, which is known to be quite active in oxidation, addition, cyclization and polymerization reactions, to produce corresponding products such as acrylonitrile\(^2\), propylene oxide\(^3\), cumene\(^4\) and isopropyl alcohol\(^5\). While traditional naphtha-fed steam crackers and fluidized catalytic cracking\(^6\) (FCC) units still consist of a great percentage in global propylene production, the growing trend of propylene demand has been attracting more concerns from both academia and industry to develop direct and propylene-oriented production techniques, also known as ‘on-purpose’ propylene (OPP). Up to now, mature OPP manufacture techniques feature metathesis\(^7\), methanol-to-olefin\(^8\) (MTO) and propane direct dehydrogenation (PDH). Table 1 below summarized industrial known PDH technologies, including the most representative Honeywell UOP Oleflex process and CB&I Catofin Lummus process\(^9\). The PDH process is governed by the chemical reaction:

\[
C_3H_8 \rightarrow C_3H_6 + H_2 \quad \Delta H^o = +123.9 \text{ kJ/mol}
\]

Although PDH technology has been widely applied in manufacture, the overall catalytic performance is still facing great challenges:

**(1) Thermodynamic considerations.** Standard molar reaction enthalpy change of PDH is +124kJ/mol, which requires significant amount of energy input in order to achieve considerable propane conversion. This mere fact is responsible for typical PDH to operate at reaction conditions usually above 873K. Meanwhile, reaction equilibrium towards
propylene formation is not favored at low or mild temperatures, thus restricting process single way (non-cyclic) reactant conversion\textsuperscript{10}. It still remains a big challenge in obtaining high reactivity with not so harsh reaction conditions.

\textbf{(2) Side reactions and catalyst deactivation.} Propane cracking and coke formation remains a common problem\textsuperscript{11}. Typically, propane tends to be further oxidized to carbon species and migrate to surface active sites, which is known as carbon deposition or coke formation. Severe coke formation can block active sites easily and result in loss of apparent activity. Weckhuysen et al. simulated PDH reaction under industrial reaction conditions with 10 dehydrogenation-regeneration cycles\textsuperscript{12} and reported that propane conversion reduces drastically within 6 hours in single cycle. Worse still, regeneration can barely recover initial activity as shown from their results. Significant effort that has been placed on product separation and catalyst regeneration is still in need to improve the productivity and to reduce the costs.
Table 1. Reprint: currently known propane dehydrogenation industrial techniques.

<table>
<thead>
<tr>
<th>Technology name</th>
<th>CATOFIN</th>
<th>Oleflex</th>
<th>Uhde STAR process</th>
<th>FBD</th>
<th>PDH</th>
<th>FLOTU/Tsinghua</th>
<th>SABIC</th>
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<tr>
<td>Licensor/developer</td>
<td>CB&amp;I-ABB</td>
<td>Lumus</td>
<td>UOP LLC</td>
<td>Krupp-Uhde</td>
<td>Varsinte-Snamprogetti</td>
<td>Linde-BASF-Statoil</td>
<td>Tsinghua</td>
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<tr>
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<td>Adiabatic fixed bed</td>
<td>Adiabatic moving bed</td>
<td>Honeywell</td>
<td>Ohad + PDH</td>
<td>Isothermal fixed bed</td>
<td>University Bimodal fluidized bed</td>
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<td>$C_3C = C_3C$</td>
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<td>$C_3C = C_3C$</td>
<td>$C_3C = C_3C$</td>
<td>$C_3C = C_3C$</td>
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<td>$Pt-Sn/Al_2O_3$ with alkaline promoter</td>
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<td>0.3–0.5</td>
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<td>Cycle time</td>
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<td>Commercial</td>
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<td>Commercial</td>
<td>Pilot plant</td>
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</table>

While the thermodynamics and technical barrier make PDH less economically attractive, oxidative dehydrogenation of propane (ODH) has become an attractive alternative for many researchers across academia and industry. Oxygen is the most common oxidant in this field ($O_2$-ODH):

$$2C_3H_8 + O_2 \rightarrow 2C_3H_6 + 2H_2O \quad \Delta H^0 = -235.8 \text{ kJ/mol}$$

Oxygen as a strong oxidant can overcome the aforementioned problems. As Carrero et al.\textsuperscript{13} pointed out, the participation of oxygen completely changes the overall reaction to an exothermic one due to $H_2$ combustion (formation of water) with favorable equilibrium at mild temperatures. At the same time, $O_2$ has a direct effect on coke gasification, which prolongs catalyst mean life and provides a relatively more stable catalytic performance.
However, it is of great difficulty to control oxygen selective activating C-H bond rather than fully combustion process, which results in an unsatisfactory overall yield/productivity of propylene in ODH-O₂ process. Alternative choices of oxidants, such as N₂O¹⁴-¹⁶, has been investigated over the past decades.
1.2 CO₂-assisted Propane oxidative dehydrogenation

CO₂ has been identified as a promising alternative oxidant for ODH reaction. The overall reaction of propane and CO₂ proceeds with the following equation:

\[ \text{C}_3\text{H}_8 + \text{CO}_2 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2\text{O} + \text{CO} \quad \Delta H^\circ = +165.1 \text{ kJ/mol} \]

In the CO₂-ODH reaction, there are two well-acknowledged pathways:

(1) Direct dehydrogenation coupled with reverse water-gas shift reaction (RWGS)\(^{17,18}\):

\[ \text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2 \quad \Delta H^\circ = +123.9 \text{ kJ/mol} \]

\[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \quad \Delta H^\circ = +41.2 \text{ kJ/mol} \]

This pathway acknowledges direct dehydrogenation as major routine in the microscopic view, with no direct participation of oxygen atoms in the dehydrogenation step. At the same time, H₂ is consumed in the consecutive reverse water-gas shift reaction, thus resulting in a shift in PDH equilibrium towards reaction equation right hand side to achieve higher conversion or selectivity.

(2) Oxidative hydrogenation coupled with CO₂ splitting\(^{19,20}\):

\[ \text{C}_3\text{H}_8 + \text{O}_{\text{surface lattice}} \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} + \text{surface vacancy} \]

\[ \text{CO}_2 + \text{surface vacancy} \rightarrow \text{CO} + \text{O}_{\text{surface lattice}} \]

Propane dissociative adsorbs on active sites and reacts with surface oxygen atoms leaving a vacancy behind; then CO₂ molecule splits on the surface and refills the vacancy. Mars-van-Krevelen mechanism is generally accepted to describe surface oxygen atoms behavior. Along this approach, it is required that the metal oxide catalyst exhibits redox cycle(s) with low oxygen diffusion barrier. Specifically, conventional irreducible supports such as SiO₂,
Al₂O₃ or zeolites are not likely to donate lattice oxygen to adsorbed reactants while reducible metal oxides such as TiO₂ and CeO₂ benefits from this pathway.

In both routines, CO₂ molecule does not participate in the C-H bond activation directly, and CO₂ activation is identified as the rate-determining step for overall reaction²¹. Besides, as Zangeneh et al. pointed out, both pathways are limited at low temperatures: RWGS is thermodynamically limited while MvK is limited by low oxygen mobility²². However, high temperature is only a tradeoff option: elevating propane conversion while sacrificing propylene selectivity by combust ing reactant or products. Thus, a long-standing goal is to find a material capable of dissociating CO₂ with superb oxygen mobility at moderate temperature.

On the other hand, side reactions and by-products are unavoidable throughout medium temperature hydrocarbon reaction system. Among all possible side reactions, propane cracking and dry reforming are highlighted most frequently in CO₂-ODH system, which can be expresses as:

\[
C_3H_8 \rightarrow C_2H_4 + CH_4 \quad \Delta H^\circ = +81.5 \text{ kJ/mol}
\]

\[
C_3H_8 + 3CO_2 \rightarrow 4H_2 + 6CO \quad \Delta H^\circ = +621.4 \text{ kJ/mol}
\]

These different propane conversion pathways are widely identified and addressed in propane ODH publications as part of the concern since they are possibly associated with various surface active sites and often exhibit different kinetic behavior. From a thermodynamic point of view, Gibbs free energy change of these reactions suggests their simultaneous occurrence with high possibility as compared to the main ODH reaction, which will be discussed in detail in later chapter.

Apart of the above discussed, coke formation is conventionally considered responsible for catalyst deactivation and deviation in carbon balance from outlet stream analysis. Normally
the reaction can be expressed as:

\[ C_3H_8 \rightarrow 2C(s) + CH_4 + 2H_2 \]

\[ C_3H_8 \rightarrow C(s) + C_2H_4 + 2H_2 \]

Technically, however, the structure of coke can be not pure carbon or graphite species, but also close to aliphatics or poly-aromatics\(^{23}\). Accordingly, coke deposition could be partially removed in the presence of the soft oxidant, CO\(_2\), also known as reverse reverse Boudouard reaction:

\[ C(s) + CO_2(g) \rightleftharpoons 2CO(g) \]

\[ \text{Coke} + \ CO_2 \rightleftharpoons \text{CO} + \text{coke} - O \]

From quite a long time, coke formation has been identified as the primary reason of catalyst deactivation. The presence of CO\(_2\) in the reaction system could mitigate or reduce coke deposition to some extent, but the coke gasification process is not thermodynamically favored by such a soft oxidant like CO\(_2\). In this work, Raman spectroscopy was applied to study coke deposition on different catalysts and X-ray Photoelectron Spectroscopy (XPS) was applied to semi-quantify coke concentration and to reveal the possible existing nanostructures.

The comparison table of PDH, O\(_2\)-ODH and CO\(_2\)-ODH pathways is shown below.
Table 2. A comparison of PDH, O₂-ODH and CO₂-ODH

<table>
<thead>
<tr>
<th>PATHWAY</th>
<th>PDH</th>
<th>O₂-ODH</th>
<th>CO₂-ODH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scheme</strong></td>
<td>C₃H₆ ↔ C₃H₆ + H₂</td>
<td>C₃H₈ + ½O₂ ⇌ C₃H₆ + H₂O</td>
<td>C₃H₈ + CO₂ ⇌ C₃H₆ + H₂O + CO</td>
</tr>
<tr>
<td><strong>Advantages</strong></td>
<td>Mature industrial technology; High productivity; Simple product purification process;</td>
<td>Exothermic reaction; Thermodynamically unrestricted; Low operating temperature; Minimal coke formation;</td>
<td>Promote conversion via RWGS; Mild reaction conditions; Reduce CO₂ emission; Co-production of syngas;</td>
</tr>
<tr>
<td><strong>Challenges</strong></td>
<td>Severe coke formation; High energy input;</td>
<td>Deep oxidation; Low propylene selectivity;</td>
<td>High activation barrier of CO₂; CO₂ hinders C₃H₆ adsorption on surface</td>
</tr>
<tr>
<td><strong>Reaction temperature</strong></td>
<td>Above 823K;</td>
<td>723 to 823K;</td>
<td>773 to 873K</td>
</tr>
<tr>
<td><strong>Side reactions</strong></td>
<td>Coke formation;</td>
<td>Total combustion of propane;</td>
<td>Propane dry reforming;</td>
</tr>
</tbody>
</table>
1.3 Determination of catalytic system and principles of choosing active species

In the history of propane dehydrogenation studies, oxide supported metal/metal oxide are most commonly investigated as the heterogeneous catalysts because of the following advantages: (1) ease of laboratory synthesis; (2) high-temperature/pressure tolerance; (3) high surface area. Meanwhile, great challenges remain in the hydrocarbon catalytic system, i.e. low propylene yield/productivity and quick deactivation due to coke formation or irreversible reduction in metal oxidative states during reaction process, etc. Consequently, one major part of this work is to rationally design a stable catalyst, which is active for propane ODH towards propylene production as well as possessing a strong oxygen mobility that could recover the surface sites while it is consumed and thus achieving long-lasting constant conversion and selectivity.

Cerium oxide was identified in this work as a promising catalyst support. Compared with conventional oxide supports like silica, alumina, zeolites and TiO$_2$, synthetic CeO$_2$ has decent specific surface area and is well acknowledged as a metal oxide with promising oxygen mobility and oxygen storage capacity (OSC). According to some experimental evidence as well as DFT calculations$^{24, 25}$, the energy barrier for oxygen diffusion from bulk to surface is much lower compared to traditional metal oxide supports and shows promising ability to replenish consumed surface lattice oxygen or to re-oxidize reduced metal oxide species during the reaction process, even without extra regeneration treatment within a long time. Besides, CeO$_2$ can be partially re-oxidized by CO$_2$ and maintained at Ce$^{4+}$/Ce$^{3+}$ redox equilibrium$^{26}$. This dynamic equilibrium is achieved by creation and consumption of ceria lattice/surface vacancies$^{27}$.

Furthermore, a dopant of tri-valent ion in the ceria lattice enhances oxygen mobility by lowering activation energy barrier of oxygen migration$^{24}$. After extensive literature research, Fe was chosen as a dopant since that apart from dopant effect, Fe also proves to be active for both propane oxidative dehydrogenation$^{17, 28}$ as well as CO$_2$ splitting$^{19, 28, 29}$. 
It is expected that the synergistic effect of Ce and Fe could provide with high activity as well as maintaining stable conversion and selectivity.

On the other hand, we need to be aware of the fact that commonly synthetic CeO$_2$ does not have periodic and regular pore structure, nor extremely high surface area. The lack of high active sites density could possibly result in lower propane consumption rate per unit mass of catalyst (mol/s/g$_{\text{cat.}}$). To overcome this problem, we need a third surface anchoring metal oxide species with proven high activity to set a reference and conclude what can be achieved, either high activity or high stability, or both. In light of the available literature, it is expected that dispersed chromium oxide could exhibit a great potential as active site in an effort to achieve high conversion and selectivity. It is widely believed that the reaction follows a Mars-van Kreleven mechanism based on Cr redox cycle. XANES and XPS results for spent catalysts have shown that during the reaction process, Cr$^{6+}$ undergoes a rapid reduction to Cr$^{3+}$/Cr$^{2+}$, which is crucial for catalytic activity$^{30-36}$. With CO$_2$ being a soft oxidant, reduced Cr species can be partially re-oxidized to higher oxidative states$^{33}$. To the best of the author’s knowledge, chromium is the most active metal species for propane ODH with CO$_2$ in terms of propane conversion and propylene selectivity comparing to all other metal oxide species at comparable reaction conditions. Consequently, Cr has been evaluated as part of this dissertation work to identify its reactivity on the novel FeCeOx support and to confirm if there is any possible interactions between surface Cr and FeCeOx support, for instance, redox cycle, atomic migration, electron transfer, etc.

While Cr-based catalysts generally provides promising activity, deactivation remains a big problem. According to several literature reports, Cr-based catalysts suffer in general from severe and rapid deactivation within a short time, regardless of sample preparation, reaction conditions and reactor design. More specifically, according to literature data (see figure 2), a 20~30% activity loss within 360 minutes is usually observed$^{30-34, 36-43}$. The proposed reasons behind the severe deactivation encompassing potential coking$^{32, 34, 39, 44}$, collapse of catalyst mesoporous structure$^{39}$, agglomeration of reduced Cr to Cr$_2$O$_3$ crystal$^{45}$, etc. On
the other hand, Zhang et al. believe that reduction of Cr(VI) to Cr(III)/Cr(II) is the main reason causes deactivation\textsuperscript{38}.

**In this dissertation, the author is trying to design a stable and industrially appealing catalyst for the simultaneous propane ODH as well as CO\textsubscript{2} splitting.** The major catalyst of our interest is made by doping Fe into ceria lattice and anchoring Cr on the support surface. Furthermore, we tested the catalytic performance with knowledges from thermodynamics and kinetics, investigated surface structures and properties by several techniques and then tried to resolve the structure-reactivity relationship.

![Relative loss of propane initial conversion among literature reported Cr-based catalysts. The relative loss of conversion was calculated as 100\% minus (final propane conversion versus initial propane conversion).](image)

Figure 2.
2. literature review

While the rapid development in propane direct dehydrogenation industrial technology has been playing a predominate role in global propylene supply, oxidative dehydrogenation is considered as one of the promising alternatives to be industrialized. Despite of the well-known oxidants such as oxygen, sulfur oxides (SO\textsubscript{x}) and nitrogen oxides (NO\textsubscript{x}), CO\textsubscript{2} has been also investigated as a mild oxidant. To the best of author’s knowledge, the earliest publication dates backs to 1996, when Takahara and Saito\textsuperscript{37} discussed the promotional effect of CO\textsubscript{2} in propane hydrogenation over SiO\textsubscript{2} supported Cr catalysts. Starting from that, CO\textsubscript{2} has become a heated topic attracting a great amount of endeavor from worldwide researchers. Over the past 25 years, many groups worldwide have studied a variety of catalysts and supports for the CO assisted propane ODH. In general, light alkane ODH catalysts can be categorized into four main groups: (1) non-oxide materials such as carbide\textsuperscript{46, 47}, nitride\textsuperscript{48-50} and boride\textsuperscript{51} materials; (2) non-redox metal oxide catalysts including Ga\textsubscript{2}O\textsubscript{3}/In\textsubscript{2}O\textsubscript{3}\textsuperscript{52-56}, ZnO\textsuperscript{57} and MgO\textsuperscript{58}; (3) supported transition metal oxide species and (4) supported metals\textsuperscript{59, 60} such as Pt, Pd, Rh, Ru and Ir. Since transition metals present multiple oxidative states associated also with different interconvertible surface structures, altering, or controlling their redox properties has been highlighted to affect propane ODH. In the open literature concerning propane ODH with CO\textsubscript{2}, Cr\textsuperscript{31, 41, 61-63}, V\textsuperscript{20, 21, 64}, Ni\textsuperscript{19, 28}, Fe\textsuperscript{17, 28, 65} and Mo\textsuperscript{18, 46} were proved as the most active and easy to regenerate catalysts. It is believed that the presence of higher/lower oxidative states serve as the required oxidant/reductant pair in the reaction process\textsuperscript{20, 33, 66}. On the other hand, the choice of support is crucial in providing additional physicochemical properties such as specific surface area\textsuperscript{67}, mechanical strength\textsuperscript{68}, thermostability\textsuperscript{69}, surface acidity\textsuperscript{52} and oxygen mobility\textsuperscript{70}. A good support usually requires good thermal conductivity in order to avoid the formation of local hot spots which in turn might lead to side reactions. Specifically, pure silica\textsuperscript{40, 66, 71}, mesoporous zeolites (MCM\textsuperscript{18, 30, 72}, ZSM\textsuperscript{38, 73}, SBA\textsuperscript{39, 43}) and Al\textsubscript{2}O\textsubscript{3}\textsuperscript{64, 74} have been well-established for high temperature heterogeneous catalysis. In addition, ZrO\textsubscript{2}\textsuperscript{61, 74,
$\text{Ga}_2\text{O}_3^{76}$ and $\text{CeO}_2^{19,28,65,77,78}$ have been studied extensively to reveal the support effect on catalytic performance.

In this section, also before formally started introducing my PhD research, a thorough examination into current literatures will be discussed. This whole section is mainly focused on the role of CO$_2$ over different catalysts observed and reported among propane ODH community. Although the reaction process of propane and carbon dioxide has been successfully fulfilled with promising performances (e.g. propane conversion, propylene selectivity, stability, etc), it is still undetermined the exactly effect of CO$_2$ in the reaction process from microscopic point of view. In fact, the role of CO$_2$ can be quite ambiguous, sometimes even completely opposite from different research groups. In order to fully understand the current research progress and prevailing ideas, the literature review will be mainly focused on the discussion of CO$_2$ into the molecular level and to summarize the interactions between CO$_2$ and C$_3$H$_8$, as well as CO$_2$ and catalyst surface.
2.1 ODH reaction network and thermodynamic analysis

Prior to any discussion on the role of carbon dioxide on ODH performance, it is necessary to discuss possible competitive reactions that may occur in the overall network and evaluate/consider relevant thermodynamic restrictions. The overall CO\textsubscript{2} assisted propane ODH reaction written as: (ODH-CO\textsubscript{2}): \[ C_3H_8 + CO_2 \rightarrow C_3H_6 + H_2O + CO \]

is usually accompanied by various competitive side reactions that intrinsically limit olefin selectivity. Those competitive side reactions are described from previous section.

It should be noted that in CDP and RBD reactions, C(s) is denoted as surface deposited carbonaceous species, and indeed, the actual structure for coke is much complicated and features aromatic rings, graphitic and/or disordered carbon-hydrogen-oxygen molecules\textsuperscript{79,80}. In this review work, the thermodynamic equilibrium analysis considers all reactants and products in gas phase as a closed system, neglecting carbon fixation and mass exchanges (mostly oxygen exchanges) between catalyst and gas phase composition. Without further introducing complex hydrocarbon molecules as potential by-products, a parallel-consecutive reaction network is built with only propane and carbon dioxide as input, hydrogen and propylene can be regarded as secondary reactants.

Du et al.\textsuperscript{81} discussed the thermodynamic equilibrium of ODH-CO\textsubscript{2}, PDH, RWGS, CRK and RBD via calculation of molar Gibbs free energy change of reaction ($\Delta rG_m$) along 300–500\textdegree C range as shown in figure 3. The calculated $\Delta rG_m$ of all reactions exhibit similar decreasing trend with elevated temperature, but still that of ODH-CO\textsubscript{2} cannot reach a negative value at 500\textdegree C where the main reaction is expected to occur. Interestingly, it seems though that the oxidative dehydrogenation of C\textsubscript{3}H\textsubscript{8} using CO\textsubscript{2} appears more feasible than certain molecular structures of C\textsubscript{4}, highlighting its potential use. According to figure 3(b), it was shown that only CRK can reach a negative value of $\Delta rG_m$ within temperature range, indicating the spontaneity towards lower hydrocarbon products. Given that equilibrium
constant $K$ is calculated from $\Delta rG_m$:

$$K^\ominus = \exp \left(-\frac{\Delta_r G_m^\ominus}{RT}\right)$$

The equilibrium composition is not favored towards high propylene yield through either ODH-CO$_2$ or PDH. Particularly, Chen et al.$^{28}$ calculated equilibrium gas composition (figure 4) and confirmed the promotional effect of CO$_2$ in propane conversion at 1:1 CO$_2$/C$_3$H$_8$ ratio as compared to that of PDH pathway. Careful examination of the equilibrium curve revealed that at temperature below 823K, although a significant conversion of propane and CO$_2$ can be observed, propylene yield is still very low and CO accounts for the majority of carbon source from CO$_2$ and C$_3$H$_8$. This result clearly indicates the occurrence of propane dry reforming that transferring carbon atoms from propane to COx. Thus, the addition of CO$_2$ can be seen as a ‘trade-off’ option: promoting propane conversion while decrease propylene selectivity due to DRF reaction. In an effort to address this challenge, research endeavors have been devoted in developing new materials capable of promoting C-H cleavage and CO$_2$ activation rather than C-C bond cleavage to suppress cracking and dry reforming reactions. In the next sections, we review the effect of CO$_2$ on catalyst stability, selectivity, and overall performance with the intention to provide the reader a different perspective on the aforementioned “trade-off” practices.

Figure 3. Left: $\Delta rG_m$ of ODH of light alkanes in the presence if CO2 at 300 to 500°C. Right: $\Delta rG_m$ of PDH, RWGS, CRK and RBD reactions in the modelled system, at 300-500°C.
Potential side reactions were demonstrated earlier in the introduction part, among which propane oxidative dehydrogenation (ODH) and propane dry reforming (DRF) are two distinct pathways that may simultaneously occur with essential propane conversion at medium temperature reaction conditions. According to the thermodynamic calculations, the Gibbs free energy change of the ODH-CO₂ and DRF at 823K equals to +23.8kJ/mol and -55.9kJ/mol, respectively. The huge difference suggests that DRF is favored and may occur spontaneously towards syngas products, while ODH pathway is strictly limited in propane conversion. However, careful examination on the stoichiometric coefficient of ODH and DRF shows that CO₂/C₃H₈ feed ratio may be a key factor determining the relative reaction pathways. Namely, if CO₂ and propane are fed with 1:1 ratio, it is expected that propylene will take up a relative larger percentage from overall products. Consequently, the CO₂ partial pressure becomes a trade-off option: either increasing propane conversion at the expense of sacrificing propylene selectivity, or maintaining high selectivity, but productivity will be rather low. This issue can be even more complicated though, considering the standard Gibbs free energy of formation (ΔG°) of CO₂ to be -394kJ/mol.
Figure 5 shows the equilibrium composition of propane and carbon dioxide with different feed ratio and different reaction temperatures. The thermodynamic discussion was performed by the authors that provides complementary information. In order to build up an equilibrium system reflecting multi-reaction pathways, the most commonly identified products from ODH, DRF and RWGS were addressed in the equilibrium analysis. Namely, propylene, CO, hydrogen, and water were included with zero initial concentration. Propane and carbon dioxide co-feed was diluted in nitrogen with total flow of 20mL/min and fixed propane partial pressure at 5%. It should be noted that the results calculated below can only be applied to user defined reaction conditions, since molarity is extensive variable and the existence of unreacted diluent gas to some extent determines final partial pressure of each active gas component. Accordingly, the lower partial pressure of the active reactants, the higher theoretically conversion can be achieved.

The first observation regarding temperature effects shows that propane conversion as well as apparent CO\textsubscript{2} conversion increases at high temperature, highlighting the endothermic feature for both ODH and DRF pathways. Typical propane ODH reaction occurs at a temperature range of 823K to 873K, where a propane equilibrium conversion of 72.5% to 86.5% can be reached under 1:1 feed ratio. In addition, the ODH pathway is more favored as compared to dry reforming at higher temperatures. Minor propylene selectivity is observed at low temperature initially but is improved monotonically as a function of temperature. Correspondingly, syngas products reach a plateau at above 723K. In summary, propane dry reforming could easily occur at lower temperature range, however, equilibrium selectivity to ODH pathway outpaces that of DRF pathway at medium to high temperature range in the thermodynamic view.

Next, we extended the equilibrium analysis to various propane/CO\textsubscript{2} feed ratio in order to further optimize reaction conditions. Particularly, 1:3, 1:1 and 1:0.2 with fixed propane partial pressure were discussed to mimic dry reforming, oxidative dehydrogenation and CO\textsubscript{2} deficient scenarios, respectively. It is obvious from the Le Chatelier’s principle that
additional CO₂ promotes propane conversion, in spite of a great loss of propylene selectivity. Besides, as pointed out by J.G. Chen et al., equilibrium conversion of CO₂ in dry reforming reaches over 95% in all feed ratio at temperature above 800K, which could in turn reduce coke formation and recover catalyst surface. Propylene equilibrium yield is also favored at lower CO₂ partial pressure, with 40% yield at 823K and 1:1 feed ratio. Consequently, theoretical analysis suggests high temperature and low CO₂ partial pressure to maximize propylene yield. Meanwhile, it should be noted that the intrinsic mechanism of ODH and DRF pathways are quite different: ODH process requires selective C-H bond activation via an oxygen insert mechanism, while DRF process is associated with C-C cleavage. In order to promote ODH contribution to the overall propane conversion, Cr is chosen as an active species supported on the Fe-doped ceria, since it has been extensively studied as an active and selective element for ODH reaction process.

It should be noted that thermodynamics only discuss and conclude the final state of reaction system with identified gaseous species, regardless of the activation energy barrier, reaction conditions or reactor configuration. Also, a specific active site could promote ODH reaction while suppress DRF from a kinetic point of view, which may also break the thermodynamic anticipated results. Most importantly, in thermodynamic predictions we discuss a closed system (or isolated system), while in practice the continuous flow reactor is an open system, suggesting that the thermodynamic conclusions can only be applied to very limited reactor scenarios. But still, thermodynamics plays an instructive and leading role for us to foresee and anticipate possible outcomes in a reasonable and logic way, so that we can clearly understand how far we are from ‘optimum’ propane conversions, and how can the catalyst contribute to the overall efficiency of the system.
Figure 5. Thermodynamic analysis of equilibrium composition of propane-CO$_2$ co-feed under different temperature and feed ratio.
2.2 The role of CO\(_2\) in catalytic performance

Any efforts to investigate molecular level implications of CO\(_2\) in reported ODH-CO\(_2\) performance data in the open literature should be accompanied with data relevant to PDH and/or ODH-O\(_2\) under the similar reaction conditions and catalytic systems. Herein, we review the overall performance from the same catalyst by grouping them in pairs (ODH-CO\(_2\) versus PDH, and ODH-CO\(_2\) versus ODH-O\(_2\)) to evaluate the basic catalytic performances and further advantages that CO\(_2\) offers as a mild oxidant. It is of great importance to compare activity data in a strict manner to guarantee identical reaction conditions such as catalyst synthesis, reaction parameters, reactor configuration and systematic deviation, thus leaving oxidant as the only variable in the system. For this reason, this review is focused initially on a smaller set of catalytic systems with the intention to draw general conclusions applicable to a larger subset.

**ODH-CO\(_2\) versus PDH**

The approach to evaluate the ability of CO\(_2\) to serve as an oxidant, in many publications, usually utilizes a set of controlled ODH experiments in the presence as well as absence of CO\(_2\) under identical reaction conditions. Three sets of catalytic active phases supported on various supports and evaluated at similar reaction conditions have been combined in Figure 6. A comparison is made on the relative changes in reaction activity in the presence or absence of CO\(_2\)^{17, 33, 37, 39, 41, 52, 82}. In figure 6(a), it is confirmed that the promotional effect of CO\(_2\) exerts both on catalyst activity and selectivity over mesoporous SiO\(_2\)-based supports\(^{72}\) (and also alkaline metal-promoted silica supports\(^{66}\), see SI). However, in the case of oxide supports that belong to the aluminum family, an adverse effect is reported highlighting that Al\(_2\)O\(_3\) and Ga\(_2\)O\(_3\) supports do not unlock the potential of CO\(_2\) in propane ODH reaction\(^{83, 84}\). According to Shishido et al.\(^{85}\), the reduced propane conversion can be attributed to the preferential adsorption of CO\(_2\) on alumina surface that strongly inhibiting propane from being adsorbed on the catalyst surface, i.e. competitive adsorption. When
ZrO₂ support is considered, interestingly, propane conversion is hampered while propylene selectivity is evidently enhanced. According to Wu et al.⁴¹, CrOₓ/ZrO₂ catalytic performance in the presence and absence of CO₂ is also TOS-dependent: Initially ODH-CO₂ outperformed PDH in propylene selectivity and underperformed PDH in propane conversion. As TOS proceeds, a sharp increase in selectivity (60% to 95% within 1 hour TOS) was observed in the absence of CO₂, accompanied by a rapid deactivation in propane conversion (75% down to 5% throughout reaction time). On the contrary, the CrOₓ/ZrO₂ behaves much more stable under CO₂-oxidizing environment, which is considered more appealing in continuous manufacture with steady-state propylene productivity. It could be argued that due to the lack of an effective oxidant, Cr(VI) underwent rapid reduction in the initial period by propane molecules to Cr(III), which provides additional PDH selectivity. By comparing CrOₓ supported over different oxide supports (non-metal oxide, non-redox metal oxides, redox metal oxides), it may be underscored that competitive pathways toward olefin occur over oxidic supports that promote oxygen mobility. However, since the comparison discussed herein pertains to identical reaction conditions and not same alkane conversion, any attempt to unravel CO₂ effects on olefin selectivity should be careful.
Contrary, ODH activity over supported Ga$_2$O$_3$ and FeO$_x$ revealed a negative effect of CO$_2$ when in contact with Al$_2$O$_3$ and MgO. Similarly, Chen et al.$^{56}$ also reported a reduced propane conversion with In$_2$O$_3$/Me$_x$O$_y$ (Me = Al, Zr). TiO$_2$ appears to be the only support that positively promotes gallium activity on propane conversion, but olefin selectivity is reduced followed by increasing amounts of cracking products, primarily ethylene and methane. Furthermore, the initial conversion of CO$_2$ over five catalysts followed the sequence of TiO$_2$ ≈ ZrO$_2$ >> Al$_2$O$_3$ > MgO > SiO$_2$, evidently indicating the direct participation of CO$_2$ in dehydrogenation over Ga$_2$O$_3$/TiO$_2$ and Ga$_2$O$_3$/ZrO$_2$ (see reprinted table 3). This result is consistent with the fact that TiO$_2$ has a strong tendency to activate
Unsupported Fe₂O₃ and FeOₓ supported on active carbon(AC) behaved actively in the propane-CO₂ co-feed, by which Michorczyk et al.¹⁷ argued that the promotional effect of CO₂ is correlated with the mechanism of reduction of Fe(III) present in the catalyst. This argument was further strengthened by temperature-programmed-reduction (TPR-H₂) experiments, showing very similar reduction profiles between Fe₂O₃ single phase and Fe₂O₃/AC. On the other hand, Al₂O₃ and MgO stabilizes Fe₂O₃ by dispersing Fe(III) into its matrix and forming FeAl₂O₄/MgFe₂O₄ phases. During this process, Fe³⁺ ion is reduced to Fe²⁺ and strongly stabilized within MgO or Al₂O₃ matrix, which affects the redox property of Fe active sites and eventually leads to a decrease in both propane conversion and propylene selectivity in ODH-CO₂ pathway.

Table 3. Reaction data in the presence of CO₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₃H₈</td>
<td>CO₂</td>
</tr>
<tr>
<td>G₂O₃/TiO₂</td>
<td>32</td>
<td>30</td>
</tr>
<tr>
<td>G₂O₃/Al₂O₃</td>
<td>26</td>
<td>5.2</td>
</tr>
<tr>
<td>G₂O₃/ZrO₂</td>
<td>30</td>
<td>9</td>
</tr>
<tr>
<td>G₂O₃/SiO₂</td>
<td>6.4</td>
<td>3.1</td>
</tr>
<tr>
<td>G₂O₃/MgO</td>
<td>4.3</td>
<td>4.2</td>
</tr>
</tbody>
</table>

a Reaction time: 10 min.

In general, the promotional effect of CO₂ depends on both active sites and support, as well as their synergistic effect. Disentangling the effect of the support is not always an easy task since many metal oxides are highly reactive at the reaction conditions of propane ODH interest. Al group metals are known to exhibit single oxidation state (+3) and thus unlikely to donate surface lattice oxygen and participate to the ODH-MvK reaction pathway, as showcased earlier. Although the addition of CO₂ can potentially enhance the catalytic performance by participating to the RWGS reaction, the overall propane conversion is still suppressed due to the competitive adsorption of CO₂ and propane molecules. Silica-based supports (amorphous silica, mesoporous silica²⁰, zeolites with low Al/Si ratio⁵⁷, ⁶³, ⁷³) are commonly safe choices for promoting ODH-CO₂ because of their high surface area and
low acidity/basicity. The dependence of CO₂ promoting effect on support was further investigated in PtSn/SiO₂ and PtSn/Al₂O₃ catalytic systems⁸⁵. In this case, the probability of redox cycle is low and ideally, CO₂ could increase propane conversion solely via RWGS reaction. In reality, the difference in activity is hardly found over PtSn/SiO₂ while a decrease is seen over PtSn/Al₂O₃. In later section, a discussion on the relationship between support acid/base properties and CO₂/C₃H₈ will be presented in more detail.

*ODH-CO₂ versus ODH-O₂*

To evaluate the oxidizing efficiency, ODH-CO₂ has been studied alongside ODH-O₂ or with a co-feed of CO₂ and O₂. Figure 7 shows a representative study of propane ODH over Cr/MCM-41³¹. Switching from oxygen to carbon dioxide, a decrease of propane conversion but increase in propylene yield is reported. Such observation is expected and is strongly associated with the fact that oxygen is a more efficient oxidizing agent without thermodynamic limitations; however, deep oxidation/total combustion is the main shortcoming that hampers olefin selectivity. Additionally, an increase in ethylene yield indicates that cracking is also promoted. It could be either homogeneous propane activation by oxygen, or unselective surface oxygen species generated upon dissociative adsorbed oxygen from gas phase during the reaction process. Further examination on the yield of C₂H₄ as a function of time strengthened the latter, since direct O₂-C₃H₈ interaction is supposed to be less affected with time-on-stream. During the course of reaction, the catalyst is expected to be reduced and upcoming oxygen dissociates to produce adsorbed O of which the concentration accumulates with time. Interestingly, when O₂ is co-fed with CO₂ the system behaves the worst in terms of propylene yield. According to Botavina et al., the fact that ethylene became the major product in CO₂+O₂ might be resulted from enhanced cracking of propane, also responsible for the production of a larger excess of CH₄.³¹,⁸⁹ In additional, Botavina et al. also reported a decrease in total olefin selectivity from 95% to 75%, indicating the prevailing oxidation of propylene in the presence of O₂.
In addition, for catalytic tests of ODH-O\textsubscript{2} versus ODH-CO\textsubscript{2} over NiMoO\textsubscript{4} catalyst\textsuperscript{90}, it is reported that 3\% CO\textsubscript{2} in the feed resulted in an increase in propane conversion with lower propylene selectivity. Furthermore, a comparison of 0.5\%O\textsubscript{2} versus 0.5\%O\textsubscript{2}+10\%CO\textsubscript{2} at 450\textdegree C revealed that no propylene was detected under 0.5\% oxygen environment, and the addition of CO\textsubscript{2} decreased propane conversion from 84\% down to 2\%. Dury et al. argued that such significant difference could be attributed to the contribution of CO\textsubscript{2} in maintaining $\alpha$-NiMoO\textsubscript{4} in fully oxidized state which possesses only octahedrally coordinated Mo\textsuperscript{90,91}.

This unusual behavior reminds us of that CO\textsubscript{2}-assisted propane ODH depends strongly on the nature of surface active sites and structural properties of catalyst itself. No simple predictions or conclusions can be drawn just by examining the type and quantity of oxidant without considering a priori physicochemical factors such as change in the surface area, formation of new complex products/unique side reactions brought by CO\textsubscript{2}, modification of surface acid/basic sites and surface reconstruction.
The ratio of CO₂/C₃H₈ and syngas ratio

The ratio of CO₂/C₃H₈ in the feed has been studied extensively as part of the optimization of reaction conditions. Shishido et al. investigated the effect of CO₂ partial pressure over Cr/SiO₂ and Cr/Al₂O₃. CO₂ has been systematically varied over different catalysts, namely, from its absence up to 20% CO₂ in the feed (partial pressure of propane was fixed at 12%), where a monotonic increase in propylene yield was observed over Cr/SiO₂ while a monotonic reduce was reported over Cr/Al₂O₃. Besides the possibility of competitive adsorption, Shishido et al. pointed out that the reaction order of partial pressure of CO₂ over Cr/SiO₂ and Cr/Al₂O₃ was estimated to be 0.14 and -0.16, respectively. The feed ratio was extended up to 10:1 by Michorczyk et al. over Cr/SBA-1 catalysts and consistent
promoting effect at higher CO$_2$ partial pressure was reported. On the contrary, Ren et al.$^{57}$ studied the variation of feed ratio over ZnO/HZSM-5 catalysts with Si/Al atomic ratio to be 160, where propylene yield increased initially with feed ratio up to 2, and then decreased upon further increase of the feed ratio. The authors ascribed this promoting effect to the RWGS reaction that accelerates the formation of dehydrogenation products. As CO$_2$ partial pressure increases, adsorbed propane is displaced to a larger extent. Given that propane dissociatively adsorbs on the zinc oxide surface to produce H$^+$ and C$_3$H$_7$$^{92}$, CO$_2$ as an acidic gas tends to titrate the basic sites that in turn inhibit propane dissociation.

In the reaction network, the co-production of syngas is also an appealing factor from an industrial point of view. By examining the stoichiometric ratio of both PDH+RWGS and ODH-MvK pathways, H$_2$ and CO should ideally be produced with 1:1 molar ratio. Another reaction pathway that could alter H$_2$/CO ratio is said to be propane dry reforming, with a direct production of 2:3 molar ratio. According to Sandupatla et al.$^{64}$, H$_2$/CO ratio at thermodynamic equilibrium should decrease with increasing CO$_2$/C$_3$H$_8$ feed ratio. Among the publications in the open literature, hydrogen selectivity/formation rate is hardly considered as a major part of catalyst evaluation, neither the syngas ratio. However, reviewed articles with available syngas ratio has represent a wide range of both active sites and support, including Cr/SBA-1$^{39}$, In$_2$O$_3$-Al$_2$O$_3$,$^{53,55}$ Rh/Al$_2$O$_3$,$^{60}$ and Cr/MCM-41$^{30}$. In all these cases, the negative correlation between CO$_2$ partial pressure and syngas ratio was observed with no exception. More specifically, hydrogen selectivity/formation rate was kept basically stable, while CO formation is greatly enhanced with addition of more CO$_2$ in the gas phase$^{30,53}$. As Michorczyk et al.$^{39}$ pointed out, the syngas ratio between 1:1 to 3:1 is widely applied in industry including F-T synthesis, methanol/dimethyl ether production and hydroformylation. Besides feed ratio, the syngas ratio is also dependent on the reaction temperature, affinity between CO$_2$ and catalyst surface, and catalyst efficiency on reverse water-gas shift reaction. Setting a reference at 1:1 feed ratio, the outcome syngas
ratio usually fluctuates around 0.7 to 2.1 at 550°C over different ODH catalysts. In general, the self-attaining syngas ratio within applicable range is a unique advantage associated with ODH-CO$_2$ reaction, which is regarded as a solid basis for co-production of propylene and syngas downstream chemicals from industrial point of view.
2.3 The role of CO₂ in catalyst deactivation and regeneration

Effect of CO₂ on carbon deposition

Coke formation is almost unavoidable in heterogeneous catalysis with hydrocarbon chemicals as reactants, primarily due to the unselective C-C or C-H bond break to produce intermediates/coke precursors including carbocation, carbanion and hydrocarbon free radicals. In the ODH-CO₂ literature, it has been reported that contrary to propane direct dehydrogenation, catalyst stability is greatly enhanced with the addition of CO₂. Conventionally, it is well-accepted that the introduction of an oxidizing agent as reactant co-feed or regeneration of spent catalysts is very effective for removal of surface carbon deposition. Similar idea was also proposed in the propane ODH community that the coke gasification process via CO₂ can be generally expressed by the reserve Boudouard reaction. Simultaneously, the amount of coke formation over spent catalysts were thoroughly studied over in-situ Raman and TGA analysis, claiming a relatively lower amount in the presence of CO₂ as compared to that in the absence of CO₂. From Figure 8, it is confirmed that deposited carbonaceous species over CrOₓ/ZrO₂ catalytic system is removed under flowing CO₂ in less than 180 minutes after 230 minutes continuous reaction. It should be noted that, the time scale cannot indicate the rate of coke removal to be faster than that of coke accumulation, since in the catalyst regeneration experiment, the partial pressure of CO₂ is 10% as compared to 2% propane in the reactant feed. On the other hand, however, one cannot neglect the probability that coke formation rate is suppressed in the CO₂ atmosphere instead of coke being gasified directly. It has been predicted that the formation of carbon deposition species is indeed very unreactive to CO₂. In this case, rather than direct reacting with coke, the most dominating effect of CO₂ is to inhibit coke formation rate by reacting with coke precursors. Actually as Xie et al. and Ge et al. pointed out, the rate of CO₂ elimination of coke is pretty low. Alenazey et al. studied coke removal kinetics with various gasifying agents and predicted that the intrinsic reactivity coefficient of coke gasification with O₂ is two order of magnitude higher than
that of CO$_2$. In the view of both kinetics and thermodynamics, coke gasification with CO$_2$ through RBD reaction features lower reaction rate and endothermic reaction pathway, which are generally not expected to play a major role in coke removal. Unfortunately, such information and research is missing in the ODH open literature community, and there is no agreed conclusion on whether CO$_2$ contributes more in the coke precursor decomposition process or coke gasification process.

On the contrary, different observations claiming that Cr/AC deactivates faster in CO$_2$-rich rather than inert atmosphere have been also reported$^{95}$. The authors argued that in the presence of CO$_2$ the yield to propene is higher, which could potentially be a precursor of inactive coke on the surface given the fact that the $\Delta rG_m$ of propylene is lower than that of propane, indicating higher possibility of cracking$^{81}$. On the other hand, CO$_2$ is too mild to effectively remove the deposited carbonaceous species. The authors also confirmed a higher coke accumulation rate over Cr/SBA-1 in the CO$_2$ environment with in-situ UV-vis DRS$^{34}$. Similar result have been also observed by Chen et al.$^{56}$ over In-Al mixed metal oxide catalysts. Furthermore, in a very recent publication regarding Cr/Zr catalysts, Xie et al.$^{75}$ proposed that CO$_2$ can also be a potential source of coke as revealed via in-situ Raman
reactions with 2%H₂ and 4%CO₂ as co-feed reactants. It turned out that reverse water-gas shift reaction can also lead to carbon deposition on the surface, which has been neglected in the past two decades when people investigate ODH-CO₂ reaction. They further discussed two requirements to produce coke from CO₂: the first is reduced Cr species with abundant H species to fix carbon dioxide; the second is carbon chain growth and aromatization when reaction temperature exceeds 300°C.

In summary, CO₂ has exhibited opposite effect in formation and suppression of coke. Although CO₂ could suppress coke formation and enhance catalyst stability in some cases, still it can be an adverse factor under specific reaction conditions. It is still unclear whether such discrepancy dependents on the nature of catalyst, reactor configuration or reaction conditions thus underscoring that this is an uncharted area for future research endeavors. It is worthwhile and essential to develop a systematic study to further investigate coke formation and its dependence on CO₂ in the field of propane ODH catalysis.

Control of oxidation states and CO₂ dissociative adsorption

Exhibiting interconvertible multi-oxidation states is well accepted as one of the most important criteria for an effective catalyst in propane ODH. The stable nature of CO₂ creates a top concern whether it maintains the dynamic redox equilibrium at an effective level. The major approach is through dissociative adsorption, leaving CO and oxygen species adsorbed O(a) on the surface and further O(a) to fill up oxygen defects for active sites. In a recent DTF study of ethylbenzene dehydrogenation with CO₂ over Ce₂Zr₂O₈ catalyst²⁵, it is claimed that the CO₂ activation need to overcome a barrier of 1.82eV as compared to 0.56eV for C-H bond activation, and it could be roughly estimated that the rate of C-H activation is about seven order of magnitude faster than that of oxygen replenishment by CO₂ at 550°C. It is expected that the rate of CO₂ re-oxidation is much
slower than that of propane reduction over typical propane ODH-CO₂ catalysts which in turn leads to deactivation. The condition could be more harsh considering a potential agglomeration of reduced active sites during the course of reaction.

There is a large number of publications concerning ODH that have applied XPS, XANES, TPR, Raman and UV-vis DRS to characterize supported Cr and V active sites in pre-reaction, post-reaction as well as in-situ conditions. In the cases of Cr-based catalysts, there is a broad consensus that Cr(VI) tetrahedral species is reduced to Cr(III) or Cr(II) octahedral species under propane-CO₂ cofeed environments. Michorczyk et al.³⁵ performed in-situ UV-vis to monitor the change in Cr oxidation states. As shown in Figure 9, two bands at 260 and 370nm indicate the presence of Cr(VI) at the beginning of the reaction; after 30 seconds time-on-stream, the peak intensity rapidly dropped to baseline level and a new band at 700nm rise up simultaneously thought a uphill and reached steady state. This result clearly indicates that CO₂ is not capable of maintaining a majority of Cr⁶⁺ under reaction conditions. Botavina et al. applied in-situ XANES under different propane ODH reaction conditions and found a broad pre-edge peak around 5996eV, and two weak pre-edge peaks at 5988eV and 5990eV (Figure 10), indicating the average oxidation state of Cr is 2⁺ in the presence of CO₂.³¹ Alternating H₂-TPR and CO₂-TPO experiments are widely utilized to investigate the regeneration of active sites with CO₂. The results revealed that the fraction of Cr(VI) for CO₂ regenerated samples are at least 70% lower than that of the as-calcined samples, indicating that CO₂ could only partially recover the reduced Cr back to Cr(VI)⁶¹, ⁶². On the other hand, similar observations were reported for V-based catalysts. Ascoop et al. proposed a silsesquioxane model of active sites of VOₓ/SiO₂ catalyst to demonstrate the reaction pathway for ODH, PDH and RWGS reaction. The model suggested that an active site consists of a V⁵⁺/V³⁺ dimer connected with oxygen bridging bond supported on SiO₂ surface (see Scheme 1). For both ODH and RWGS pathways, they believed that the V³⁺/V⁵⁺ redox cycle could be looped by CO₂ dissociative adsorption, but they also provided isothermal hydrogen reduction data and quantified its
regeneration efficiency to be only 45% as compared to O\textsubscript{2} regeneration. In addition, Sandupatla et al. performed XPS experiments and de-convoluted V\textsubscript{2p3/2} scans for fresh, O\textsubscript{2}-regenerated and CO\textsubscript{2}-regenerated samples. The average oxidation state for V fresh sample is +4.77, while after O\textsubscript{2} and CO\textsubscript{2} regeneration, the average oxidative state is brought back to +4.78 and +4.58, respectively.

Figure 9. Reprint of in situ UV–vis DRS results recorded during initial step of propane dehydrogenation with CO\textsubscript{2} at 550 °C. (A) Spectra collected during first minute of process. (B–D) The variation of intensity of the band at 260 nm, 370 nm and 700 nm during 2 min on-stream. Reaction conditions: CO\textsubscript{2}:C\textsubscript{3}H\textsubscript{8}:He molar ratio = 5:1:9; Total flow rate = 30 cm\textsuperscript{3} min\textsuperscript{-1}; catalyst weight = 200 mg. The spectra were collected at regular interval 2s.
Figure 10. Reprint: Normalized XANES spectra of the 1.0-Cr/DHS sample after treatment under different propane dehydrogenation reaction conditions: a) only C₃H₈ (green curve), b) C₃H₈ + CO₂ (blue curve), c) C₃H₈ + O₂ (red curve) and d) C₃H₈ + CO₂ + O₂ (orange curve). The spectrum of Cr₂O₃ is shown as a reference for comparison (grey curve).

Scheme 1. Reprint of catalytic circle of propane ODH in the presence of CO₂. Gibbs free energies in kJ/mol at 600°C are reported next to the reaction arrows. Underlined numbers correspond to the highest Gibbs free energy barrier of the catalytic circle.

As Dury et al. pointed out, it is believed that the equilibrium of CO₂ dissociative adsorption to CO and adsorbed oxygen denoted O(a) shifts to the right when CO₂ comes to a reduced oxide catalyst, since the reduced surface has a remarked tendency to rapidly accommodate monoatomic oxygen species. However, they also mentioned that they failed to capture the amount of CO as an indirect indicator of O(a) quantity. Fortunately, Norwicka et al.
performed temporal analysis of products experiments with CO$_2$ pulses over Pd/CeZrAlO$_x$ pre-reduced by repeated H$_2$ pulses and observed CO formation within 0.2 second$^{27}$. They successfully proved that CO$_2$ dissociative adsorbed over Ce-based catalyst surface and replenished surface oxygen vacancies$^{70}$. According to Dury et al., if the concentration of CO is regarded as equal to O(a) concentration, considering the effect of O(a) and free oxygen in gas phase, O(a) should indeed by extremely more active than O$_2$. The role of O(a) should lie in three aspects: (1) modify the nature of active site, maintaining a higher oxidation state; (2) react directly with adsorbed propane, giving propylene and non-selective products; (3) react with coke precursors and leaving those non-selective sites exposed again to reaction atmosphere.
2.4 Competitive adsorption

Most of the poisoning effect of CO\textsubscript{2} resulted from its competitive adsorption with propane molecules on the catalyst surface. It depends not only on the chemical identity of the surface and adsorbates, but also the order in which the molecule is exposed to the surface. In 2006, Xu et al.\textsuperscript{52} investigated the effect of CO\textsubscript{2} on propane chemisorption over Ga\textsubscript{2}O\textsubscript{3} supported on a series of oxide supports. As shown in Table 4, the quantity of propane adsorbed on the surface decreased in all cases except for Ga/SiO\textsubscript{2}, which initially exhibited a very low adsorption ability to propane. Given that CO\textsubscript{2} is a much more acidic gas than propane, it has been proposed that the adsorption of CO\textsubscript{2} mainly favors basic sites rather than acidic sites\textsuperscript{52, 61, 96}, consistent with the fact that SiO\textsubscript{2} is generally considered as a neutral and inert surface. In this case, it is not hard to understand the fact that the addition of CO\textsubscript{2} cannot necessarily lead to an increase in propane conversion over Al\textsubscript{2}O\textsubscript{3}, MgO and ZrO\textsubscript{2}. By studying the effect of CO\textsubscript{2} over ZnO/HZSM-5 catalysts, Ren et al.\textsuperscript{57} argued that propane adsorbed on the surface to produce C\textsubscript{3}H\textsuperscript{7} on acidic sites and protonate basic sites, thus CO\textsubscript{2} could certainly reduce the probability of propane dissociation. Ideally if CO\textsubscript{2} is capable of removing H\textsuperscript{+} effectively via RWGS reaction, it is reasonable to expect a positive role of CO\textsubscript{2}, however, the rate of CO\textsubscript{2} dissociation and propane activation could not match each other, and H\textsubscript{2}O, as a RWGS reaction product, could also strongly adsorbed on the surface to block the active sites\textsuperscript{85}. In 2018, Chen et al. discussed the rate of propane consumption under different CO\textsubscript{2} partial pressure, and concluded that in the very low CO\textsubscript{2} concentration regime (0.9kPa), propane rate is less affected or even increases slightly depending on the nature of active sites, but once jump out of this region, the propane rate drops drastically\textsuperscript{28, 78}. In conclusion, competitive adsorption has been attested as one of the major negative causes of poison effect. It depends more on the surface acidity/basicity and less on the surface area. With increasing partial pressure of CO\textsubscript{2} introduced into the system, one could expect a higher CO\textsubscript{2} dissociation rate, but still competitive adsorption becomes over-dominant and exhibits an overall negative effect.
Table 4. Reprint: Amount of propane chemisorbed in the absence and presence of CO$_2$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount in the absence of CO$_2$ (µmol/g)</th>
<th>Amount in the presence of CO$_2$ (µmol/g)</th>
<th>Decreasing ratio (%)$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$_2$O$_3$/TiO$_2$</td>
<td>4.2</td>
<td>2.5</td>
<td>40</td>
</tr>
<tr>
<td>Ga$_2$O$_3$/Al$_2$O$_3$</td>
<td>5.3</td>
<td>3.7</td>
<td>30</td>
</tr>
<tr>
<td>Ga$_2$O$_3$/ZrO$_2$</td>
<td>8.1</td>
<td>5.9</td>
<td>27</td>
</tr>
<tr>
<td>Ga$_2$O$_3$/SiO$_2$</td>
<td>1.1</td>
<td>1.1</td>
<td>0</td>
</tr>
<tr>
<td>Ga$_2$O$_3$/MgO</td>
<td>2.0</td>
<td>1.5</td>
<td>25</td>
</tr>
</tbody>
</table>

$^{a}$ Decreasing ratio = (1 – amount in the presence of CO$_2$)/(amount in the absence of CO$_2$) × 100%.
2.5 Conclusion

The discussion on the role of CO\textsubscript{2} in propane ODH is quite divergent among community researchers. CO\textsubscript{2} is indeed a ‘trade-off’ option in propane oxidative dehydrogenation reaction. We are expecting CO\textsubscript{2} to serve as an oxidant, a regenerating agent and a stabilizer, at the cost of competitive adsorption with propane and a potential source of coke formation. Kinetically speaking, the rate of CO\textsubscript{2} dissociation and surface replenishment have a strong dependence on higher CO\textsubscript{2} partial pressure, however, thermodynamics concluded that higher CO\textsubscript{2} value could improve propane conversion while introduce other side reaction including dry reforming and propylene decomposition. Moreover, support effect also plays a crucial role in determining CO\textsubscript{2} behavior. The abundance of acid sites generally determines the amount of propane chemisorbed on a plain surface; while the concentration of basic sites could be an indicator of how severe the competitive adsorption is. Still, for the purpose of unravelling the comprehensive effect of CO\textsubscript{2}, more comparative and systematic studies over specific catalysts are needed.
3. Experimental

3.1 Material synthesis

Metal oxide supports (CeO$_2$, Fe-CeO$_2$) are synthesized batchwise via the precipitation/co-precipitation from metal oxide precursor aqueous solution as reported elsewhere$^{97-99}$. Ce(NO$_3$)$_3$·6H$_2$O (99.99%) and Fe(NO$_3$)$_3$·9H$_2$O (99.95%) were purchased from Sigma Aldrich and used without further purification. In a typical synthesis, certain amount of Fe and Ce precursors were weighed, dissolved in 60mL of water in a three neck round flask according to the required stoichiometric ratio of Ce and Fe atoms. After that, the mixed precursor solution was kept heating in an oil bath until temperature reached 70°C. Initial pH value was measured at 70°C, which generally locates in a range of 1.6 to 1.9, depending on the concentration of Fe and Ce precursor. When temperature and pH maintained stable, ammonium hydroxide solution (NH$_3$·H$_2$O, Sigma 30%) was added dropwise into the mixed precursor solution. During this step, the solution system was controlled under very strong stirring/agitation (600 revolutions per minute, RPM) in order to ensure a uniform pH value throughout the entire solution volume. When pH was elevated to 7.5, the solution was kept under the same temperature, pH and stirring for 1 hour stabilization. Later on, NH$_4$OH was added dropwise for the second time until pH reached 10.5. Upon this moment, stirring was reduced to 100rpm, and the suspension was kept at T = 70°C, pH = 10.5, RPM = 100 with cooling water at room temperature for 24 hours. After 24 hours, the suspension was filtrated out with vacuum filtration and a membrane filter. Usually the sample was washed with two batches of 500mL DI water, together with 200mL of pure ethanol in between. After that, the sample was collected in a vial and dried in 110°C oven overnight. The dried sample was calcined for 5 hours at 600°C and/or 800°C, with heating rate 2K/min and 50cc/min air flow. I denote the support as $x$FeCe$T$, where $x$ stands for percentage of moles of Fe atoms with respect to Ce atoms in the lattice ($x = n$(Fe)/$n$(Ce)*100%); $T$ stands for calcination temperature in degree Celsius. Up to the current work, where we haven’t investigated the effect of iron dopant amount, most studied ratio is 10% Fe dopant in ceria
lattice. Such catalyst support is denoted 10FeCe600. Synthesis of pure CeO$_2$ follows the same procedures described above, except the addition of Fe precursor.

During the synthesis of support, upon first drop of NH$_4$OH added into the mixed precursor solution, semi-transparent, light brown particles were observed. These particles are believed to be Fe/Ce hydroxide nuclei. Meanwhile, pH increased drastically, with a pH jump from 2.7 to 6.5. As solution became more basic, more particles precipitated out of liquid phase and the suspension became more condensed. After 24 hour stabilization, the color of particles turned from grey-brown to light yellow, which is known to be Ce(IV). As is known from literature, Ce(OH)$_3$ is unstable and extremely sensitive to oxygen$^{100}$, thus it can be oxidized by both NO$_3^-$ $^{101}$ and dissolved O$_2$ $^{102}$ during co-precipitation process.

Chromium is supported on the surface via different approaches. According to literature research, we chose Cr(NO$_3$)$_3$·9H$_2$O (99.99%, sigma) as chromium precursor and follow the standard procedures of incipient wetness impregnation (IWI). Firstly, test of wetness point of the synthesized support is needed. 0.5g of support and 5g of DI water were measured accurately and transferred into two separate vials. Next, DI water was added dropwise into the sample vial with a pipet gun, and spread each water drop all over particles with a spatula. Gradually, the sample turned wet, with more particles stick together. Until the sample felt like ‘toothpaste’ and we no longer felt strong resistance to spatula stirring, the difference in the weight of the DI water vial is calculated. This step was repeated 3 times and we average these three results as final wetness point. Secondly, we took certain amount of support, chromium precursor and water based on calculation and our need, dissolved Cr precursor in water and added Cr precursor solution dropwise to support. Finally, we kept the ‘toothpaste-like’ samples in 110°C oven dried overnight and calcine the catalyst at 600°C for 5 hours with 2K/min ramping rate, 50cc/min air flow. The sample is denoted as $n$Cr-xFeCe$T$, where $n$ stands for atomic density (Cr/nm$^2$). The calculation of desired surface atomic density is calculated based on the following equation:
\[ n \left( \frac{Cr}{nm^2} \right) = \frac{wt_{Cr} \% \times N_A}{100 \times AW_{Cr} \times S_{BET} \times 10^{18}} \]

Where,

- \( n \) stands for atomic density, atom/nm\(^2\);
- \( wt_{Cr} \% \) stands for weight percent of chromium atoms over total mass of catalyst;
- \( N_A \) stands for Avogadro constant;
- \( AW_{Cr} \) is atomic weight of Cr;
- \( S_{BET} \) is BET surface area of the support.

Besides the aforementioned procedures, commercial cerium(IV) oxide is also used directly as a support without further purification or treatment. The purpose of using commercial support is to benchmark our system and prove that our catalytic reaction system functions well and the data we collected are similar to what has been reported in literatures under the same reaction conditions.
3.2 Characterization of catalysts and lab techniques

In order to fully understand the structures and surface properties of the catalyst, and changes of surface during the reaction, we were trying actively to find resources and collaborations for different characterization techniques which help us to identify crystalline structure, surface active sites, surface area, etc. In this section, a detailed description is provided for all the experimental techniques in order to show my understanding and the necessity of these techniques.

BET surface area

The primary purpose of the BET theory is to measure the specific surface area, pore distribution and full adsorption isotherm by physical adsorption of gas molecules (nitrogen is common cases) on a solid surface. The BET model of multilayer adsorption is an extension of Langmuir theory, where it assumes that: (1) gas molecules only interact with the adjacent layers; (2) the enthalpy of adsorption for the first layer is constant and higher than the second (higher) layer; (3) the enthalpy of adsorption of second (higher) layer equals to enthalpy of liquefaction. Based on these assumptions, the resulting BET equation is:

$$\frac{1}{v[(p/p_0) - 1]} = \frac{c - 1}{v_mc} \left(\frac{p}{p_0}\right) + \frac{1}{v_mc}$$

Where, \(v\) stands for adsorbed gas quantity, in volume units;
\(v_m\) stands for monolayer adsorbed gas quantity, in volume units;
\(p_0, p\) are saturation pressure and equilibrium pressure of adsorbates, respectively.
\(c\) is BET constant.

When \(p/p_0\) locates in the range of 0.05 to 0.35, the BET plot \((p_0/p)/(p/p_0)-1\) vs. \(p/p_0\) forms a straight line. The slope and intersection of this line can be used to calculate monolayer adsorbed gas quantity \((v_m)\) and BET constant \((c)\). Together with the known size
of gas adsorbate, BET specific surface area can be calculated as:

\[
S_{\text{BET}} = \frac{v_m N s}{V a}
\]

Where, \(N\) stands for Avogadro’s number;
\(s\) stands for cross section area of adsorbate molecule;
\(V\) stands for molar volume of gas adsorbate;
\(a\) stands for the mass of solid sample.

The BET data are collected using Micromeritics TriStar 3000 (Serial # 2111) system. Usually 30mg of catalyst is weighed accurately and loaded into the instrument. Prior to BET analysis, the samples were degassed at 150C for 8 hours in order to remove physisorbed molecules (e.g. H\(_2\)O from atmosphere) from the surface. It should be noted that careful consideration is needed to make sure of no irreversible changes occurring during degas. Sample must be reweighed after the degas to capture any loss of mass. In a normal BET surface area measurement, 13-point measurement is applied, from 0.05 to 0.3 p/p\(_0\) with 0.02 increment.

**Raman Spectroscopy**

Raman spectroscopy is one of the most applied techniques in catalysis, especially for understand the bulk and surface structures of the catalyst material. When an incident laser beam is scattered by the sample surface, most quantity of scattered laser features the same wavelength (the same color) as the incident beam, which is known as Rayleigh scattering. However, a very small amount (1/10\(^9\)) of scattered laser wavelength was changed by the chemical structures of the sample, which is called Raman scattering. Raman scattering has two different transition energy state differences, Stokes scattering and anti-Stokes
scattering (as shown in Scheme 1), and they locate symmetrically beside Rayleigh scattering, with a shift of plus/minus specific photon energy ($\Delta \nu$). Although the wavenumber of Raman scattering lines changes with incident laser line, $\Delta \nu$ is only a function of vibrational modes of the sample, which is a fingerprint related to its unique chemical structures. Thus, Raman spectroscopy is a useful tool for analyzing chemical structures, phase transformation, crystallinity and molecular interactions.

![Scheme 2](image)

Scheme 2. Schematic description of Rayleigh Scattering, Stokes Scattering and anti-Stokes Scattering.

According to Quantum Chemistry and Group Theory, in order for a sample to be Raman-active, it must have such vibration modes that the polarizability is changed during the vibration process. For a typical diatomic oscillator, there are two factors determining vibrational frequency: force constant ($K$) and reduced mass ($\mu$). The former depends on bond strength, electronic cloud density, etc; while the latter is more relevant to atomic weight. As for polyatomic vibrations, it is proved that any of a complicated vibration can be expressed as a superposition of a set of independent diatomic vibrations.

The Raman spectra are collected with a Horiba Scientific LabSpec HR Raman spectrometer equipped with 532nm solid-state laser line, Synapse CCD detector ($-70^\circ$C) and three objectives (10x, 50x and 100x). On-site Raman, in-situ/operando Raman and liquid phase Raman modes are performed in order to adapt to different experimental scenarios. On-site Raman is most common applied to analyze samples at ambient
temperature and pressure. The biggest advantage of on-site Raman is that we can usually achieve the highest resolution and the best Raman signal intensity within short acquisition time. However, in order to investigate the real-time changes of surface structures under reaction conditions, in-situ/operando Raman is most commonly applied to record Raman spectra at elevated temperatures and with continuous gas flow. With in-situ/operando Raman technique, we are able to observe surface species behaviors under propane ODH conditions and also study Raman spectrokinetics to investigate oxidation/reduction rates of surface active sites. High temperature chamber from Harrick Scientific is used as a reactor to allow gas flow, hold the sample and maintain reaction at desired temperature. Besides, liquid phase Raman approach helps to analyze the behavior and structure of metal precursors in aqueous. Unlike on-site or in-situ/operando Raman approach, liquid phase Raman technique passes laser not through an objective but through a L-shaped channel with mirrors to focus laser to the center of a cuvette containing liquid phase samples. It is useful in understanding how pH and ionic concentration affect agglomeration of metal precursor species in liquid solution during the synthesis step.

*Powder X-ray Diffraction (XRD)*

X-ray Diffraction (XRD) helps to identify atomic and molecular structure of a crystal. When incident beam of X-ray strikes crystal surface, it is scattered by regular arrays of atoms to many directions through constructive interference, which is determined by Bragg’s law:

\[ 2dsin\theta = n\lambda \]

Where, d is the spacing between incident plane; 
\( \theta \) is incident angle;
n is any integer number;
λ is the wavelength of the incident beam.

X-ray is used to produce diffraction pattern since the wavelength of X-ray is usually the same order of magnitude as place spacing d. The position and intensity of these diffraction lines are uniquely related to the crystalline structure. By examining the diffraction pattern, people are able to collect information including crystalline phase, size of unit cell, chemical bonding and crystallographic disorder.

In this work, XRD analysis are performed with PANalytical Phiips X’Pert X-Ray diffractometer to determine crystallinity and phase composition. The XRD facility is equipped with a Cu Kα source at 40 kV and 40 mA and angular incidence 2θ between 20° and 90° with 0.05° step and 4.0 s/step. The phase composition is analyzed by whole pattern fitting (WPF) refinement 2-phase analysis with relative error R% targeted below 15%. Silicon is used as an external standard reference to determine any possible peak shift caused by instrument.

**X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy is one of the most commonly applied surface techniques in catalysis to quantify element composition and investigate its oxidative states/chemical binding environment. When a sample surface absorbs a photon with an energy in excess of the binding energy of deep core level electrons, a photoelectron is ejected out from the atom with kinetic energy closely related to its binding energy according to Einstein Equation:

\[ E_B = h\nu - E_K \]
Where, \( E_B \) stands for binding energy of the emitted core level electron; 
\( E_K \) is the term for kinetic energy of the emitted core level electron; 
\( h \nu \) is incident photon energy.

By analyzing the small variations in kinetic energy, people are able to identify the chemical states of each elements. Normally for a solid sample, XPS probes 2 to 20 atom layers, corresponding to 5 to 50 angstroms. XPS is supposed to be performed under ultra-high vacuum (UHV) chamber, since the mean free path to electrons depends on pressure and it is crucial to make sure that ejected electrons reaches detector without being scattered by background gas environment.

XPS analysis are performed with Thermo Fisher K-Alpha XPS instrument quipped with a monochromatic Al K\( \alpha \) line with photon energy of 1486.7eV. Estimated X-ray spot area is 5\( \mu \)m\(^2\) and penetration depth is 5nm. C 1s peak at 284.8eV is collected with each sample as a standard reference to binding energies. Each elemental analysis is repeated with 10 scans to improve the spectrum quality.

Transmission Electron Microscopy (TEM)

TEM and related techniques detect transmitted electrons and radiation. In TEM experiment, a thin solid specimen (usually less than 200nm thick) is bombarded in vacuum with a highly-focused, monoenergetic electron beam. The beam is of sufficient energy to propagate through the specimen. A series of electromagnetic lenses then magnifies this transmitted electron signal. Diffracted electrons are observed in the form of a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons from images from small regions of sample that contain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample. Analysis of transmitted electron images yields information both about atomic structure and about defects present in the material.

In this work, the TEM experiments are performed by our collaborator Dr. Weiqing Zheng and his group in Delaware University. The Transmission electron microscopy (TEM) images were acquired with a JEM-2010F (JEOL, Japan) transmission electron microscope equipped with a field emission gun emitter.

Scanning Transmission Electron Microscopy (STEM)

STEM is one of the most frequently applied techniques in catalysis characterization. Unlike conventional Transmission Electron Microscopy (TEM), STEM analyzes sample by scanning over sample surface focused with converged electron beams in UHV chamber. When the electron beam passes through a very thin specimen, the direction and energy will be changed due to elastic and inelastic scattering, and this information is collected with annular detectors behind the specimen. According to different scattering angles, scattered
electrons produce annular bright field, ABF ($\theta<10$ mrads) and annular dark field, ADF (10mrads$<\theta<50$mrads). Meanwhile, as electron beam pass through a sample, some electrons in the beam lose energy via inelastic scattering interactions with electrons in the sample. Such electron energy loss is measured using an electron spectrometer, which is known as electron energy loss spectroscopy (EELS). EELS can be used for chemical mapping and element mapping to provide an elemental distribution around the sample surface.

Both the imaging and electron energy loss (EEL) data were acquired by a Nion UltraSTEMTM 100. The microscope was operated at 60 kV with a probe convergence semi-angle of 35 mrad and an energy loss collection semi-angle of 34 mrad. The EEL spectrum image (SI) data was processed using Hyperspy1, a python-based microscopy analysis package. After background removal, the intensity of each element in the SI data was normalized to its maximum value in the SI map such that one can visualize the spatial distribution of the elements in the acquired area.

**Temperature-programmed experiments (TPE)**

Temperature programmed reduction/oxidation (TPR/TPO)

TPR/TPO is an analytical technique that examines the surface chemistry of metal oxides under varying thermal conditions, an important factor in catalysis studies. TPR/TPO is originally used in the field of heterogeneous catalysis to determine the most suitable and efficient reaction conditions. In a typical TPR experiment, certain amount of an oxidizing catalyst is placed in a reactor. A reducing gas (normally H$_2$) mixed in carrier gas is flowed through the packed bed, under a pre-determined temperature ramping rate. In TPO tests, reducing catalyst or reduced catalyst will be examined with an oxidizing agent. Depending on the research project, TPR and TPO experiments can be performed when catalyst features
superb redox property.

Besides investigating optimal reaction conditions, TPR/TPO experiments are also applied as an auxiliary method in distinguishing surface redox species with semi-quantified abundance. In this work, as stated before, the synthetic Fe-doped cerium oxide (fully calcined FeCe) contains various surface oxidizing sites with different oxidizing ability and activity. Furthermore, Cr-FeCe catalysts might introduce at least one more new oxidizing site, while the surface anchoring bond or bridging bond might block or eliminate current existing FeCe surface oxidizing features.

In this work, the output of the reactor was analyzed by an in-line mass spectrometer. When H$_2$ was chosen as reducing agent, mass 2 (m/e = 2) and mass 18 (m/e = 18) will be focused representing the consumption of hydrogen and production of H$_2$O since oxygen can be the only active site on the clean metal oxide surface. As for CO$_2$, mass (m/e = 44, 28, 12, 16) was obtained.

In-situ temperature-programmed reduction

Meanwhile, we also performed in-situ TPR experiments with Raman spectra coupled in order to monitor the real-time changes occurred on the catalyst surface under TPR experiment conditions. In this case, the same amount of catalyst was packed into the high temperature Harrick reaction chamber (will be shown below). Gaseous flowrate and temperature ramping rate will be also adjusted to keep consistent with conventional TPR. Especially, we may need to pay attention on two things: first, in-situ Raman spectra can only provide an ‘average’ signal of the catalyst, since the surface kept changing during the reaction and standard spectra collection time was set to be at least 10 minutes, within which the temperature will be different by 100K from the beginning point until last second before spectra finishes. In fact, the change between different spectra is of greater importance than single spectra itself. Second, Harrick reactor configuration is different than that of U-tube
reactor in TPR, in terms of the height of packed bed, residence time distribution, etc. In order to deal with this problem, a pulse system was applied to calibrate the difference between conventional and in-situ TPR.

Cyclic TPR experiments

Due to the unique redox property of FeCe oxides, single process of H₂-TPR can only reveal the reduction activity of FeCe and Cr/FeCe oxides, but not the re-oxidation half circle. As compared to conventional TPO experiments to investigate the re-oxidation ability, cyclic TPR experiments can better manipulate an actual reaction scenario, where reduced catalysts after first H₂-TPR experiment will be re-oxidized immediately at 873K with flowing air for 30 minutes, followed by a duplication of second H₂-TPR experiments. Again, the reduce catalyst is then regenerated with CO₂ and followed by a third H₂-TPR experiment. All these experiments must be performed in a row or the FeCe oxide will undergo reconstruction and change its surface redox property. The cyclic TPR experiments can provide complementary information about active oxidation sites on the reduced FeCe surface, as well as a comparison on oxidation ability between oxygen and CO₂. Besides, the third H₂-TPR can also be regarded as an implication of the role of CO₂ in catalyst reduction/ODH conditions.

In practice, 50mg of the catalyst will be packed into the U-tube quartz reactor. The sample is always pretreated with flowing air and temperature ramping to 873K in order to obtain fully dehydrated and fully oxidized conditions. Then the reaction furnace is cooled down to room temperature with flowing inert gas. Through repeated trial and error tests, the total flowrate is finally decided to be 30mL/min, with 1% Hydrogen and balancing Ar. Temperature ramping rate is fixed at 10K/min, from 373K (373K is far below activation temperature for reaction of H₂ and catalysts) up to 923K (923K is at the brink of changing the crystal structure or surface structure of our catalyst, as will be demonstrated in the result and discussion part). When the ramp finishes, the reaction will be hold isothermally at
Mass Spectrometry (MS)

Mass spectrometry (MS) is an analytical technique that is used to measure the mass-to-charge ratio of ions. The results are typically presented as a mass spectrum, a plot of intensity as a function of the mass-to-charge ratio. Mass spectrometry is used in many different fields and is applied to pure samples as well as complex mixtures. A mass spectrum is a plot of the ion signal as a function of the mass-to-charge ratio. These spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to elucidate the chemical identity or structure of molecules and other chemical compounds.

In a typical MS experiment, a sample, which may be solid, liquid, or gaseous, is ionized, for example by bombarding it with a beam of electrons. This may cause some of the sample's molecules to break up into positively charged fragments or simply become positively charged without fragmenting. These ions (fragments) are then separated according to their mass-to-charge ratio, for example by accelerating them and subjecting them to a magnetic field: ions of the same mass-to-charge ratio will undergo the same amount of deflection. The ions are detected by a mechanism capable of detecting charged particles, such as an electron multiplier. Results are displayed as spectra of the signal intensity of detected ions as a function of the mass-to-charge ratio. The atoms or molecules in the sample can be identified by correlating known masses (e.g. an entire molecule) to the identified masses or through a characteristic fragmentation pattern.
All mass spectra shown in this work are collected with MKS Cirrus™ Mass spectrometer which can scan from m/e =1 to m/e = 300 and is equipped with dual detector: electron multiplier and Faraday cup. Before each experiment, the MS was calibrated with Ar at 101.3kPa as zero gas. Detector scan speed was normally fixed at 5 accuracy and 193 data points can be collected within 10 minutes at 10K/min temperature ramping rate.

*Gas Chromatography (GC)*

Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. In typical GC measurements, samples are vaporized and directed through a certain column. Gas chromatography is the process of separating
compounds in a mixture by injecting a gaseous or liquid sample into a mobile phase, typically called the carrier gas, and passing the gas through a stationary phase. The mobile phase is usually an inert gas or an unreactive gas such as helium, argon, nitrogen or hydrogen. The stationary phase is a microscopic layer of viscous liquid on a surface of solid particles on an inert solid support inside a piece of glass or metal tubing called a column. The surface of the solid particles may also act as the stationary phase in some columns. The composition at outlet will be tested by a detector, either FID (flame ionized detector) or TCD (thermal conductivity detector).

Specifically, in our continuous gas-phase reaction, the reactor output is not injected but instead, bypassed microGC during the idle time. When a microGC measurement starts, the pump will be activated and sucks gas into a pre-column for injection preparations. Three columns (Molecular sieve 5A, poraplot U and poraplot Q) and two carrier gases (Argon, nitrogen) were equipped in order to fully analyze the reaction composition. Single GC measurement takes approximately 3 minutes, and thus time-on-stream reaction performances are conducted every 15 minutes, with two replicates for one data point in order to flush the gases trapped between bypass inlet and pump inlet.
3.3 Infrastructure setup of in-situ Raman and catalytic reactor

In order to fulfill mechanistic study and catalytic analysis, different experimental setups were built incorporated with Raman spectrometer and high-temperature catalytic reactor.

To design an in-situ Raman setup in our lab (figure 11), all different gas components, including inert gas (N₂, He, Ar), oxidant (O₂, air, CO₂) and reductant (H₂, C₃H₈) were delivered at a constant temperature, pressure and flowrate thought Alicat mass flow controller (MFC). After each MFC, a check valve is mounted in-line to eliminate back pressure damage or back flow contamination of the MFCs. After the check valve, gases are mixed though several Tee units and delivered in single 1/4-inch tube into high temperature reaction chamber from Harrick Scientific. Rear nozzle of Harrick cell was connected as gas inlet; while middle nozzle was connected as gas outlet so that a downflow through the catalyst packed bed can be guaranteed. A bypass through the reactor was also assembled in order to monitor the accurate number of initial flow and gas composition. The outlet/exhaust gas was then connected to a mass spectrometer from MKS, Circus™ 3-XD, with accuracy level 6, standard ionization energy. Since mass spectrometer requires
20mL/min constant flow all the time, another branch was built up before MS inlet in case of any total flow greater than 20mL/min damaging the instrument. MS exhaust was connected to the hood as indicated from standard operating procedures. All tubing, fittings, valves, Tees, elbows, reducers, etc were purchased Swagelok. 1/4-inch tube was used as primary gas transfer tube. In the case of specific requirements, 1/8-inch tube was used on the purpose of flexibility and space occupancy considerations.

Scheme 5 shows a process flow diagram of catalytic reactor setup. Similarly, all gas components were delivered individually in 1/8-inch tube through an MFC. Check valves, ball valves were assembled in each line to control gas flow. Gas feed was transferred into a 20-inch long quartz tube reactor with quartz frizz (90 to 150 microns) blow inside in order to hold catalyst sample in place. The isothermal quartz tube reactor was hold inside a vertical configured Lindberg/Blue M Mini-Mite™ Tube Furnace, 1100°C from Thermo Scientific. All the furnace openings were blocked with quartz wools to minimize heat loss. The reactant mixture was feed from the top into the quartz tube reactor and product mixture was collected from the bottom. Outlet gas was analyzed with 490 MicroGC from Agilent. Bypass were designed from both reactor and microGC so that we were able to control the system and response at the earliest time of any emergency. All major gas transfer lines were built with 1/4-inch tube; in the case of MicroGC inlet, 1/8-inch and 1/16-inch tube were used instead to reduce dead volume.
Scheme 5. Experimental setup of the fixed-bed reactor used for the catalytic measurements.
3.4 Catalytic performance test

Catalytic performance tests are conducted with the aforementioned system. In all experiments, 200mg of catalysts were loaded into a fixed bed quartz tube reactor with 1g quartz sand as diluent. The samples were preheated in the furnace at a ramping rate of 10K/min under 20cc/min pure oxygen flow in order to fully oxidize and dehydrate the surface active sites. After temperature reached desired setpoint, reactor is closed with pure oxygen isolated inside and we started to flow reactant mixture (propane, carbon dioxide and balancing nitrogen) through bypass. Meanwhile, concentration of propane and carbon dioxide were monitored simultaneously until the flow reached equilibrium with constant partial pressure of propane and CO₂. After that, reactant mixture flow was switched to reactor and started to collect and calculate outlet concentration every 15 minutes. Gas concentration at each time point is collected with two replicates; only the second replicate was trusted for analysis in order to eliminate the effect of dead volume right before microGC inlet. Volumetric flow of each reactant is controlled by Alicat MC-series mass flow controllers which were pre-calibrated by using a bubble flow meter with 4 times repeated experiments. Total flows for bypass and reactor were also monitored at the system exit with the bubble flow meter in order to calculate conversion, selectivity as well as carbon balance.

Concentration of each outlet gas component were collected via an Agilent 490 microGC equipped with Molecular Sieve-5A (MS5A, for hydrogen, carbon monoxide, oxygen and methane analysis) and PoraPlot Q (PPQ, for ethane, ethylene, propane, propylene and carbon dioxide analysis) columns. Single GC analysis is performed with the following parameters: MS5A: 120°C column temperature, 110°C injection temperature, 5.0s backflush time; PPQ: 120°C column temperature, . The microGC was calibrated with all possible outlet component gases including H₂, CO, O₂, CH₄, CO₂, C₂H₆, C₂H₄, C₃H₈, C₃H₆, and N₂. Single-point calibration is applied for each component with point-to-point fitting. Each calibration line is forced through zero.
Catalytic tests were performed with three major parts: stability test, determination of activation energy and effects of different parameters. Stability tests were performed at 550°C, with a reactant mixture of 5% propane, 5% carbon dioxide in balancing nitrogen. Each catalytic run was hold for 12 or 24 hours with continuous gas flow without regeneration in between. Conversion (X) to each reactant, selectivity (S) to each product and propylene yield (Y) were calculated as the following:

\[ X_{C_3H_8} = \frac{F_{in,C_3H_8} - F_{out,C_3H_8}}{F_{in,C_3H_8}} \times 100\% \]

\[ X_{CO_2} = \frac{F_{in,CO_2} - F_{out,CO_2}}{F_{in,CO_2}} \times 100\% \]

\[ S_{C_3H_6} = \frac{F_{C_3H_6}}{F_{in,C_3H_8} - F_{out,C_3H_8}} \times 100\% \]

\[ S_{CxHy} = \frac{x}{3} \cdot \frac{F_{CxHy}}{F_{in,C_3H_8} - F_{out,C_3H_8}} \times 100\% \]

\[ Yield = X_{C_3H_8} \times S_{C_3H_6} \]

In practice, many repeated measurements were conducted and equimolar flow at inlet and outlet of the reactor was confirmed to simplify the calculations of conversion and selectivity. In the case the change is concentration completely reflects the change in volumetric flow. The final equations simplified as:

\[ X_{C_3H_8} = \frac{C_{in,C_3H_8} - C_{out,C_3H_8}}{C_{in,C_3H_8}} \times 100\% \]

\[ X_{CO_2} = \frac{C_{in,CO_2} - C_{out,CO_2}}{C_{in,CO_2}} \times 100\% \]
\[ S_{C_3H_6} = \frac{C_{C_3H_6}}{C_{\text{in,C}_3H_8} - C_{\text{out,C}_3H_8}} \times 100\% \]

\[ S_{C_xH_y} = \frac{\frac{x}{3} \cdot C_{C_3H_6}}{C_{\text{in,C}_3H_8} - C_{\text{out,C}_3H_8}} \times 100\% \]

Where all concentration can be read directly from microGC data.

Catalyst stability is quantified and expressed with catalyst mean life. Calculation of catalyst mean life follows the first-order deactivation model:

Deactivation constant \( k_d \):
\[ k_d = \frac{\ln\left(\frac{1-x_{C_3H_8,\text{final}}}{x_{C_3H_8,\text{final}}}\right) - \ln\left(\frac{1-x_{C_3H_8,\text{initial}}}{x_{C_3H_8,\text{initial}}}\right)}{\tau} \]

Mean Catalyst life \( t_m \):
\[ t_m = k_d^{-1} \]

Where \( X \) represents propane conversion at initial or final reaction time-on-stream, and \( \tau \) represents the overall reaction time-on-stream.
4. Results and discussion

4.1 Fe-doped cerium oxide (FeCe)

In this section, a full characterization as well as the complete catalytic performances will be presented and discussed. As a novel catalyst which has not been studied over the past two decades in the field of propane dehydrogenation, the author endeavors to explore such material from very fundamental aspects to practical applications under the instruction of surface science, thermodynamics, kinetics and catalysis. The research protocols are pre-determined after a detailed literature research within the past 20 years and in order to get a sense of topics that has been fully investigated and those not been thoroughly discussed. Meanwhile, in order to realize the similarities and differences in surface properties, catalytic performances, stability, etc, corresponding experiments must be controlled with three pre-requisites: (1) **All experiments must be conducted with solid fundamental references and rigorous design of each step and approach.** For example, In most cases the reaction temperature cannot surpass the calcination, or it will induce thermal sintering and surface/crystal structural changes; Raman laser intensity must be controlled below a certain temperature dependent range so that the surface is not over heated or burnt; etc. (2) **Experimental conditions must be comparable to most works inside community so that we can acknowledge the improvements as well as shortcomings between my catalyst and materials reported in open literature.** (3) **Experimental data must be processed or normalized with the same scale.** For instance, it is known that in reaction engineering people normally accept two definitions of selectivity. Overall selectivity refers to the ratio of desired product over total converted reactants; meanwhile it can be quite complex when there are multiple reactants in the feed, and especially when we deal with hydrocarbon or organic molecules. In this case, except for unifying selectivity, total carbon balance (sometimes even oxygen balance and hydrogen balance) has to be examined to provide more convincing results. In this work, the author is always trying to perform a solid study that meets all these prerequisites and details.
4.1.1 Structural analysis of fresh materials

Calcination temperature is crucial for phase transformation and crystalline growth, as well as removal of surface hydroxyl groups and possible carbon-based organics. In this work, starting from an primitive metal oxide catalyst, the purpose of calcination is to form a highly crystalline cerium oxide with Fe ions partial substitution periodically, without local agglomeration or formation of iron oxide crystal phase. Also, it is expected that all metal species are oxidized to their highest oxidation state during calcination process with convective air flow.

Since typical propane ODH reaction take places at temperature range of 823 to 873K, it is crucial to guarantee that calcined samples are thermally stable (mesoporous structure not collapsing, no chemical changes between active species and supports, etc) at or above this temperature. Under this circumstance, Fe-doped ceria from the same synthesis batch were calcined at 873K and 1073K for 5 hours and then characterized by BET, Raman and XRD. Characterization results are shown in the following table and graphs. From Figure 12, it is clearly observed that although 10FeCe800 features much shaper and narrower peak (smaller FWHM), hematite phase is also observed indicating a phase separation between ceria and hematite after 1073K calcination. In contrast, we were still able to achieve highly crystalline ceria at 873K calcination with no hematite phase identified. The 2-Theta value for 10FeCe800 main peak (111) shifted to higher Bragg angle as compared to 10FeCe600, which is a direct proof of Fe-substitution inside ceria lattice, since Fe$^{3+}$ is of smaller size than Ce$^{4+}$, which results in lower d-spacing and higher 2-Theta angle according to Bragg function.

Table 5. XRD fitting analysis and BET analysis of surface area, 2-Theta shift, size of unit cell and hematite phase quantification.

<table>
<thead>
<tr>
<th>Phase</th>
<th>BET $^2$ m/g</th>
<th>2-Theta (111) $^\circ$</th>
<th>Cell Å</th>
<th>Hematite content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Ceria</td>
<td>-</td>
<td>28.55</td>
<td>5.41134</td>
<td>-</td>
</tr>
</tbody>
</table>
Similarly, ex-situ Raman spectra (figure 13) showed peaks at 220cm$^{-1}$, 287cm$^{-1}$ and 459cm$^{-1}$, assigned to hematite $A_{1g}$, $E_{g}$ vibrational mode and ceria $F_{2g}$ mode respectively, indicating two separate bulk phases. Besides, a red shift to 453cm$^{-1}$ of ceria $F_{2g}$ peak is observed in 10FeCe600. It should be noted that although strong laser intensity might induce such red shift in Fe-doped ceria samples, repeated trials and explorations of neutral density filter proved that at 5% of the total laser power, the nature of the ceria photon vibration properties is free from laser-induced effect or temperature effect. In addition, BET results showed that the specific surface area of 10FeCe800 is reduced by almost an order of magnitude than that of 10FeCe600, indicating severe collapse of mesoporous structure of the catalyst during high temperature calcination. Consequently, 873K is chosen as most suitable calcination conditions.

<table>
<thead>
<tr>
<th></th>
<th>10FeCe800</th>
<th>10FeCe600</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 ppm</td>
<td>9.6</td>
<td>70</td>
</tr>
<tr>
<td>Specific Area</td>
<td>28.59</td>
<td>28.61</td>
</tr>
<tr>
<td>BET</td>
<td>5.41055</td>
<td>5.41076</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BDL</td>
</tr>
<tr>
<td></td>
<td>2.4%</td>
<td></td>
</tr>
</tbody>
</table>

Figure 12. XRD analysis of 10FeCeOx calcined at 873K and 1073K, respectively. Insert: amplified 10FeCe800 from 2-Theta = 20 to 70°
Next, a series of Fe-doped ceria catalyst were characterized with XRD, Raman and BET. X-ray diffractograms of the various Fe-doped ceria materials are shown in Figure 14. Upon calcination at 600°C, all the materials show that cerianite is the main crystalline phase (reference cerianite phase lines are also included). As compared to the reference cerianite, all diffraction peaks of the Fe-doped ceria samples shift to higher Bragg angles underscoring the formation of Fe-Ce solid solution, where Ce\(^{4+}\) cations are partially substituted by smaller Fe\(^{3+}\) ions inside cubic ceria structure. The small shift as well as observed broadening of the diffraction peaks indicate also possible changes of the crystallite sizes of cubic CeO\(_2\); however, the average crystallite size of cubic CeO\(_2\) as estimated from the corresponding (111) diffraction peak by means of the Debye-Scherrer equation (See Table 6) appears to be within the 8-12nm without a monotonic behavior across different samples. In addition, this type of partial substitution of Ce ions has the potential to result in different local environments of the oxygen atoms such as oxygen from the main ceria lattice phase, oxygen surrounded by Ce/Fe cations (Ce-rich) and/or oxygen surrounded by Fe/Ce cations (Fe-rich). The diverse nature of oxygen atoms and/or vacancies created within the surface of CeO\(_2\) have been highlighted as important active...
sites for propane activation. It is worth mentioning here that crystalline hematite (α-Fe₂O₃) phase was not detected by XRD for any of the samples tested indicating a good dispersion of Fe in the ceria lattice. The possibility of very small α-Fe₂O₃ crystals that lie below the detection limit of the XRD cannot be excluded.

Figure 14. X-ray diffractograms of Fe-doped ceria calcined at 873K with varying Fe atomic ratio from 1% to 15%.

Figure 15 shows the Raman spectra of the fresh catalysts after calcination. The spectral envelope in the 200-800cm⁻¹ range displays a very strong band located at 460cm⁻¹ which is associated with the F₂g vibrational mode of CeO₂. Upon increasing of Fe, a very small shift was observed to lower wavenumbers that is ascribed to the gradual doping of CeO₂ lattice with Fe and is consistent with the XRD results discussed at an earlier section. A
closer look shows a monotonic increase in intensity of a broad peak (Figure 15-inset) located at 592cm\(^{-1}\) which is associated with the presence of sub-stoichiometric CeO\(_{2-x}\) units underscoring an increase in oxygen vacancies\(^{104}\). The relative intensity ratio of 592cm\(^{-1}\) and 460cm\(^{-1}\), I\(_{592}/I_{460}\), has been routinely used in the open literature as an indicator of the presence of oxygen vacancies in CeO\(_2\) based materials\(^{105-107}\). The I\(_{592}/I_{460}\) is summarized in table 6. We observe that the I\(_{592}/I_{460}\) reaches a maximum at high Fe/Ce catalysts. In the recent computational publication where Zr-doped cerium oxide was studied, it is stated that although the Zr-O bond is stronger than Ce-O bond, the relaxation energy of Zr-O*-Ce (Ce-rich) is much lower than that of Ce-O*-Ce sites. Consequently, the formation energy of Zr-doped ceria is lower than pure cerium oxide. Assuming an analogy can be applied where Fe dopant provides similar effect as Zr, it can be concluded the promotional effect of creating oxygen vacancies on the Fe-Ce oxide surface.
Table 6. Summary of BET, XRD and Raman analysis results of fresh Fe-doped catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET $m^2/g$</th>
<th>2-Theta (111) $^\circ$</th>
<th>Crystallite size nm</th>
<th>$I_{592}/I_{460}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1FeCe600</td>
<td>59.9</td>
<td>28.600</td>
<td>12</td>
<td>0.0435</td>
</tr>
<tr>
<td>2.5FeCe600</td>
<td>53.9</td>
<td>28.641</td>
<td>9.8</td>
<td>0.0547</td>
</tr>
<tr>
<td>5FeCe600</td>
<td>65.5</td>
<td>28.659</td>
<td>10.7</td>
<td>0.0829</td>
</tr>
<tr>
<td>10FeCe600</td>
<td>62.2</td>
<td>28.770</td>
<td>8.7</td>
<td>0.1108</td>
</tr>
<tr>
<td>15FeCe600</td>
<td>65.2</td>
<td>28.722</td>
<td>8.6</td>
<td>0.1068</td>
</tr>
</tbody>
</table>

Figure 15. Raman Spectra of a series of Fe-doped ceria fresh catalysts calcined at 873K. Insert: enlarged spectra centered at 590cm$^{-1}$.
The TEM images (figure 16) of 10FeCe oxides also provides complementary information to XRD and Raman information. From all six images we can tell that the overall crystallite size centered around 5 to 10 nanometers. From locally focused images it can be clearly observed that atomic arrays and crystalline are highly ordered with hexagonal structure. The edge of the FeCe crystals is also well defined indicating that we have a clean and flat FeCe surface. From analyzing the distance between atomic layers, we concluded that the exposed facet of 10FeCe is (111).
Next, we performed TPR reactions and cyclic TPR reactions with synthetic cerium oxide (synthesized based on the same co-precipitation method as FeCe oxides, except for the absence of Fe precursor) as reference. As stated before, in cubic structure of cerium oxide, when Ce atoms are substituted by the smaller size Fe atoms, a series of physicochemical parameters of the oxygen atoms will be altered including bond length, binding energy, migration energy barrier and activation energy, etc. The TPR and cyclic TPR reactions here aim at unravelling the differences in surface active oxygen sites upon increasing Fe dopant concentration in cerium oxide lattice. As discussed in our previous work, the FeCe mesoporous structure will severely collapse upon calcination at above 600°C, meanwhile phase separation of cerianite and hematite also occurs. Consequently TPR experiment were performed up to 650°C to maintain a relative consistency in surface and bulk structure.  

As shown in figure 17, H$_2$-TPR data for representative catalysts are presented. Synthetic cerium oxide shows a broad peak centred at 620°C, which is attributed to the reduction of reactive surface oxygen species. Since the total reduction of CeO$_2$ to Ce$_2$O$_3$ is only expected in the temperature range of 800 to 900°C, the broad reduction band suggests the creation of oxygen defects and exposure of Ce$^{3+}$ on the surface.  

Figure 16. TEM images of the 10FeCe samples at different resolutions and different transmission spots.
further strengthened by coupled in-situ Raman study. As shown in figure 34, two evidence were observed for partial reduction of CeO$_2$. Firstly, the peak at 245cm$^{-1}$ represents transverse acoustic mode of surface oxygen$^{111}$, which gradually flattened out during H$_2$-TPR. In addition, the inserted graph showed peak ratio between 600cm$^{-1}$ and 460cm$^{-1}$, which is regarded qualitatively as an indication of oxygen vacancy concentration$^{105}$. The existence and abundance of this oxygen sites guarantees the oxygen mobility and redox properties of CeO$_2$. Upon doping of Fe into cerium oxide lattice, the main peak shifted greatly to lower temperatures, indicating the enhanced surface reducibility as compared to primitive CeO$_2$$^{25}$. As stated before$^{65}$, the surface oxygen to FeCe oxide should be predominately involved in two types of structures: Fe-rich sites (Fe-O-Ce) and Fe-free sites (Ce-O-Ce). Incorporation of Fe converts Fe-free sites into Fe-rich sites and promotes the appearance of peak 400$^\circ$C, depending on the relative Fe abundance in the ceria lattice, the peak shift features a monotonic increase from 5FeCe to 10FeCe. In this following figure, the shoulder at 431$^\circ$C and 362$^\circ$C corresponds to 5FeCe and 10FeCe, respectively.

In the cyclic H$_2$-TPR reactions, 5FeCe and 10FeCe are studied with three status: fresh, oxygen regenerated (30 minutes) and CO$_2$ regenerated (30 minutes). Cyclic H$_2$-TPR experiments were performed to investigate the stability and reversibility of catalysts under different oxidizing agents. According to Fig 18(left), the relative signal intensity at ~380$^\circ$C and 600$^\circ$C revealed that O$_2$ could properly replenish surface oxygen sites coordinated in Fe-O-Ce structures, while CO$_2$ exhibited a preference over Fe-free oxygen sites. While Fe dopant effect enhances the easiness of oxygen donation under reducing environment, the reaction enthalpy change of CO$_2$ splitting to refill the oxygen vacancy is increased simultaneously$^{25}$. Due to its endothermicity, the activation energy barrier must be consistently increased. Comparing to O$_2$ that unselectively oxidizing oxygen vacancies from Fe-rich and Fe-free sites, CO$_2$ was facing a harsh environment when encountering a Fe-rich oxygen site. Consequently, although generally regarded as a mild oxidant, CO$_2$ presented its effectiveness in diminishing Fe-free oxygen vacancies and the peak at 600$^\circ$C
became more appealing after CO$_2$ re-oxidation as compared to O$_2$. Besides, the peak feature at 473°C in figure 18(left) seems not to be reversible after 30 minutes regeneration. According to Wu et al.$^{105}$, this peak feature could be assigned as surface oxygen clusters that occupy the oxygen vacancies, particularly oxygen peroxide (O$_2^{2-}$) or oxygen superoxide (O$_2^-$). As in the case of 5FeCe, such species presented a strong peak at 587°C. These oxygen species only exist on the very fresh Ce-based catalysts and are usually generated during the calcination process. The consumption of dioxygen species is not reversible after short time regeneration process, since it was proved that oxygen molecules will preferably dissociate over reduced ceria surface rather than forming dioxygen species directly. Only when oxygen encounters an oxidized surface with vacancies at high temperature the formation of dioxygen species can be observable, which could be addressed by the 5 hours calcination process at 600°C during synthesis of Fe-CeO$_2$.

![Figure 17. H$_2$-TPR experiments with MS signal at m/e = 18 of pure synthetic CeO$_2$, 5FeCe and 10FeCe catalysts. Catalyst loading: 50mg. Flow rate: 1% H$_2$ in balancing Argon, with total flow at 30mL/min. Temperature ramping rate: 10K/min.](image)
Figure 18. Cyclic H₂-TPR experiments with MS signal at m/e = 18 of 5FeCe (left) and 10FeCe (right) catalysts. Catalyst loading: 50mg. Flow rate: 1% H₂ in balancing Argon, with total flow at 30mL/min. Temperature ramping rate: 10K/min. Regeneration: 20% O₂/CO₂ with total flow of 40mL/min, lasting 30 minutes.
4.1.2 Initial screening of catalytic performance

In Figure 19 (a), we present the catalytic evaluation screening, as referred to propane conversion and olefin selectivity for all catalysts synthesized. The data reported in Figure 19 pertain to initial reaction conditions, 20ml/min total flow (w/F=0.6 g.s/cc) and constant temperature at 550°C. The data collected for commercial CeO$_2$, Fe$_2$O$_3$ as well as their physical mixture (Fe$_2$O$_3$/CeO$_2$ = 1:20 molar ratio) are also included for comparison. The commercial CeO$_2$ shows very low conversion, less than 5%, with propylene selectivity to reach around 40%. Fe$_2$O$_3$ shows slightly higher propane conversion while the propylene selectivity decreased dramatically due to the formation of carbon oxides as discussed later. A physical mixture of the commercial CeO$_2$ and Fe$_2$O$_3$ resulted to almost double propane conversion (as compared to pure CeO$_2$) with the propylene selectivity to reach almost that of pure CeO$_2$. Although moderate temperature treatment (close to the reaction temperature, i.e. 550°C) of CeO$_2$ and Fe$_2$O$_3$ physical mixtures does not alter significantly the local structure of the individual oxides, it is reported that the performances and overall redox properties can be enhanced just through their physical contact$^{112}$. The incorporation of small amount of Fe (1FeCeO$_2$) in ceria structure as dopant leads to a significant increase in propane conversion while propylene selectivity slightly decreases as compared to pure CeO$_2$. Upon increasing of Fe content, a monotonic increasing trend in propane conversion was observed from 6.5% (1FeCeO$_2$) to 21.5% (15FeCeO$_2$). Interestingly, although the conversion increases, the same behaviour was observed for the selectivity towards the propylene, reaching a maximum of around 47% for the 10FeCeO$_2$ catalyst. The increase in propane conversion can be partially associated with the increase in surface area of the catalysts. A maximum in propylene selectivity and propane conversion is achieved between 10FeCeO$_2$ and 15FeCeO$_2$ with the initial yield to reach ~10% for the 15FeCeO$_2$ catalyst at 550°C. Besides the slightly higher surface area, the results suggest that there is a promotional effect of Fe as dopant on the activity of C-H bond activation. This effect can be associated to relative changes induced in active species with different local oxygen
environments. As Fan et al.\textsuperscript{25} demonstrated in a recent DFT study of ethylbenzene ODH on ZrCeO\textsubscript{x}, the C-H bond activation is positively correlated with charge transferred from adsorbed hydrocarbon species to catalyst surface. It is likely that higher Fe concentration benefits the formation of Fe-rich oxygen sites rather than Ce-rich or Ce lattice oxygen species, which in turn results in advantages from two different aspects: lowering of reaction activation energy barrier and favoring the formation of oxygen vacancies in ceria surface lattice. The former has the potential to improve the catalytic activity, i.e. propane conversion, while the latter is observed to be closed associated with propylene selectivity, which is discussed in later section. On the other hand, the propylene selectivity behavior on different Fe-doped catalysts is closely related with the density of surface oxygen vacancy. Figure 20 provides additional information of the trend of selectivity to each product as a function to the $I_D/I_{F2g}$ intensity on Fe-doped ceria. A relationship is observed between propylene selectivity and $I_D/I_{F2g}$ ratio thus highlighting the possible participation of oxygen vacancies to the selective ODH reaction pathways towards the formation of propylene. However, we have to underscore that this is a phenomenological relationship and more direct experimental or computational evidence at the molecular level is needed in the future to further demonstrate the actual chemistry behind this observation. Correspondingly, one of the crucial and meaningful research direction is to tune the surface density of oxygen vacancies and study of oxygen vacancy-catalytic performance relationship.
Figure 19. (a) Propane and apparent CO$_2$ conversion as well as propylene selectivity and (b) selectivity to ethylene and methane of all synthesized catalysts. Data pertain to initial reaction conditions, 20ml/min total flow (w/F=0.6 g.s/cc) and constant temperature at 550°C.

Figure 20. $I_{CO2}/I_{460}$ as a function of different catalysts and relevant product selectivity
In Figure 19(b), the selectivity patterns to methane and ethylene are also shown. A monotonic decrease in the formation of methane and ethylene is clear as more Fe is incorporated in the catalyst structure. The most straightforward propane conversion pathway towards ethylene and methane is the catalytic cracking (reaction 6) which stoichiometrically results in 1:1 molar ratio between these hydrocarbon products. In low Fe content catalysts, the molar ratio of methane-to-ethylene is very close to 1 (See Figure 21), up to 5FeCeO$_2$ indicating that selectivity loss is associated to propane cracking. On the other hand, methane-to-ethylene molar ratio increased by two-fold over 10FeCeO$_2$ and 15FeCeO$_2$, which suggests that additional reaction pathways may exist that lead to the formation of excess methane. Among the possible reaction pathways towards methane, the propane decomposition to carbon deposition (reaction 8) is likely to occur at the temperature range of our experiments. Meanwhile, CO$_2$ methanation reaction$^{113}$
\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (11)
\]
cannot be excluded. The former reaction is expected to severely affect the stability of these catalysts and will be discussed in more detail at a later section. However, the total selectivity of methane and ethylene decrease significantly at high Fe content indicating that these pathways do not dominate the catalytic performance under these reaction conditions.
Figure 21. Molar ratio of methane-to-ethylene of all Fe doped CeO2 catalysts. Data pertain to initial reaction conditions, 20ml/min total flow (w/F=0.6 g.s/cc) and constant temperature at 550°C.

The improved catalytic performance of the 10FeCeO2 and 15FeCeO2 catalysts is associated with the lower amount of other hydrocarbon by-products present under our reaction conditions. Considering that the overall carbon balance as calculated based on the total carbon flow of all gaseous reactants/products is usually above 98-99%, the rest carbon flow pertains to carbon oxides, CO and CO2. It must be highlighted here that the majority of carbon oxides pertains to CO that is also consistent with previous reports 28, 114, 115.

Although CO2 formation from deep oxidation is plausible, CO2 readily reacts over the catalytic surface under our reaction conditions as shown also in Figure 19a. It is evident that the addition of Fe in the ceria shows a monotonic increase in the CO2 conversion that resembles the propane conversion behavior. The maximum CO2 conversion (~30%) was observed for the 15FeCeO2 catalyst. In carbon dioxide assisted alkane oxidative dehydrogenation reaction it is well recognized that CO2 participates mainly in the RWGS reaction which in turns favors propane conversion as discussed earlier. According to literature studies, the ratio between propane conversion and CO2 conversion is below unity in most cases even if the feed ratio is extrapolated to 1:1, indicting the advantages in CO2
activation ability for our FeCe oxides. The catalytic behavior presented here for the Fe-doped CeO$_2$ catalysts appears to be consistent with the aforementioned reaction scheme, but the difference in product selectivity across different catalysts underscores the complexity of the reaction network that exists. In addition, a recent report$^{113}$ highlighted also the possibility of CO$_2$ participation in methanation (reaction 11) as well as in propane dry reforming reaction (reaction 7).

Very recently, the concept of CO$_2$ dissociation over reduced metal oxides was also introduced in light of re-oxidizing surface oxygen vacancies$^{27}$ according to the reaction 5-2. However, it is hard to clearly distinguish the actual selectivity to CO and/or CO$_2$ due to the uncertainty of relative contribution of CO production from either propane combustion, reverse water gas shift reaction, dry reforming, reverse Boudouard reaction or CO$_2$ splitting. Future experimental endeavors towards the establishment of kinetic and mechanistic understanding can shed light on the actual role of CO$_2$ on the activity, stability and/or deactivation of the catalyst reported herein.
4.1.3 Effect of temperature, residence time and reactants partial pressure

Next, we evaluate the effect of temperature, residence time as well as propane/CO$_2$ partial pressure on the catalytic performance of the most selective, 10FeCeO$_2$, catalyst. Specifically, we assess the catalyst activity in the 450°C–600°C temperature range while we also varied the total flow of reaction mixture within the 10-30ml/min range. Figure 22 compares relevant results for the propane conversion as well as hydrocarbon selectivities and propylene yield. Upon increasing temperature and/or reducing residence time (W/F), the propane conversion increases significantly reaching a maximum of 52% at 600°C and 0.33g$_{\text{cat.}}$/h/L. The selectivity to propylene is monotonically reduced upon increasing the residence time which is associated with consecutive paraffin/olefin oxidation to CO$_x$. Propylene selectivity reaches a maximum upon increasing temperature around 500-550°C while a decrease is observed at higher temperature. Furthermore, examination on the product selectivity distribution as a function of reaction temperature might indicate different reaction pathways in the propane ODH with CO$_2$ reaction system. In the lower temperature range between 450 to 500°C, as predicted from figure 5(a), the selectivity to propylene is expected to increase with temperature in ODH and DRF reaction system. On the other hand, when further increasing the reaction temperature, the reaction rate of cracking is also significantly improved, which results in an increasing percentage of cracking products in the overall selectivity and making the ODH pathway less competitive. The above discussion is further strengthened by an examination on experimental data shown in Figure 23, where it is clearly observed that the ratio of selectivity to propylene over carbon oxide raises up from 450 to 550°C temperature range (from 0.85 to 1.40), while such ratio is decreased from 1.40 to 1.16 up to 600°C. Together with the observed monotonic increase in propane cracking products as a function of reaction temperature, it might also suggest that the negative effect of cracking exerts mainly on ODH pathway rather than DRF pathway. Thermodynamic analysis of standard Gibbs free energy change of light alkanes and olefins cracking shows that spontaneity of olefin cracking outweigh alkane
cracking, especially at high temperatures\textsuperscript{81}. This is also consistent with our experimental results presented in figure 22 which showed a monotonic increase in selectivity to ethylene and methane, the major products of C\textsubscript{3} cracking. Under similar reaction conditions, Nijhuis et al. reported the formation of coke deposits at different positions of the catalyst bed as revealed by in-situ Raman and thermogravimetric studies. They found that significantly less coke was observed at the top catalyst layers than the middle and bottom parts of the catalyst bed\textsuperscript{116}. In conclusion, from experimental data combined with thermodynamic analysis, it is believed that ODH dominates over DRF thermodynamically at higher temperatures, while the cracking pathway is favored kinetically at higher temperatures and probably through a direct competition with ODH.

The effect of the C\textsubscript{3}H\textsubscript{8}/CO\textsubscript{2} in the feed on the catalytic performance of the most selective catalyst identified, i.e. 10\%FeCeO\textsubscript{2}, was studied under 550°C and total flow of 20ml/min. Relevant results concerning propane conversion and propylene selectivity are summarized in Figure 24. Our data show that higher partial pressure of CO\textsubscript{2} in the feed resulted in slight decrease in conversion for feeds rich in propane and almost no change for low propane initial concentration. In all cases, a marked decrease in propylene selectivity was observed. The highest propylene selectivity exceeded 60\% for 5:1 C\textsubscript{3}H\textsubscript{8}/CO\textsubscript{2} ratio in the reaction feed while propane conversion was maintained at \textasciitilde18\% resulting in a maximum of 11\% propylene yield. In spite of a vast collection of literatures where researchers emphasized the positive role of CO\textsubscript{2} in the system—in most cases propane/CO\textsubscript{2} is fed as 1:5 ratio to promote propane conversion, the propylene selectivity is generally not much affected with extra CO\textsubscript{2} feed. However, similar negative effect of CO\textsubscript{2} on catalyst performance has been discussed by Wang et al. and Kocon et al.\textsuperscript{84,117} showing that when Al\textsubscript{2}O\textsubscript{3} is used as support, the presence of CO\textsubscript{2} suppresses propane conversion and propylene yield. Gomez et al.\textsuperscript{28} studied effect of CO\textsubscript{2} partial pressure on propane rate for FeNi/CeO\textsubscript{2} system. The decline of rate was attributed to less available active sites for propane, which points out that the competitive adsorption of CO\textsubscript{2} and propane on the active sites might play a major role.
Furthermore, a very recent article discussed a possibility of consecutive oxidation of propylene with the following equation:\(^{75}\):\[ C_3H_6 + 3CO_2 \leftrightarrow 5CO + H_2O + CH_4 \] (12)

In a nutshell, CO\(_2\) hampers selective propane conversion to propylene for the following reasons: (1) promotion of propane dry reforming pathway; (2) competitive adsorption with propane and (3) consecutive oxidation of propylene to by-products. However, due to the complex reaction network occurring simultaneously, conclusions regarding the intrinsic effect of CO\(_2\) at the molecular level cannot be drawn and thus future efforts on kinetic studies together with advanced characterization can shed light into the actual effect of carbon dioxide on our catalysts. In later sections, we will further develop and discuss a MvK-based surface reaction model. The model will further discuss the role of CO\(_2\) in surface activation process.

Figure 22. Effect of temperature as well as residence time on (a) propane conversion, (b) propylene selectivity and (c) propylene yield, (d) methane selectivity, (e) ethylene selectivity, (f) ethane selectivity of the most selective, 10FeCeO\(_2\), catalyst. Data pertain to initial reaction conditions.
Figure 23. Selectivity distribution of propylene, carbon oxide, ethylene, ethane and methane as a function of reaction temperature. Catalyst: 10FeCe600. Reaction parameters: 20mL/min total flow with 5%C₃ and 5%CO₂, 200mg catalyst loading.
Figure 24. Effect of propane and/or carbon dioxide partial pressure on the catalytic performance. Catalyst: 10FeCe600. Reaction conditions: 550°C, 20mL total flow, 200mg catalyst loading.
4.1.4 Time-on-stream catalytic performance and deactivation

Figure 25. Time-on-stream catalytic performance of (a)1FeCeO₂, (b)5FeCeO₂, (c)10FeCeO₂, (d)2.5FeCeO₂ and (e)15FeCeO₂ catalyst. Data pertain to 20ml/min total flow (w/F=0.6 g.s/cc) and constant temperature at 550°C.

Figure 25(a-e) displays the propane conversion and selectivity of major products on five Fe-doped CeO₂ samples with time-on-stream. The stability of catalysts was tested for 20-24hr time-on-stream. We observe that the selectivity to propylene appears to be stable for most of the catalytic materials tested. With a closer look at the Fe-doped catalysts with large Fe/Ce ratio, an increase in propylene selectivity is observed within in propane conversion from 17.5% to 14%. Similar behavior was observed for the 15FeCe catalyst. Contrary, for low Fe concentration catalysts, the propane conversion is more stable with time-on-stream; the best stability performance was observed for the 5FeCe catalyst. More specifically, the conversion for the 1, 2.5 and 5FeCe catalysts was found to be stable up to 6, 10 and 15 hours respectively while for the rest catalysts a monotonic decrease is observed.

It is worth mentioning here that for the low Fe concentration catalysts, the gradual decrease of propane conversion at very long time-on-stream is accompanied by a simultaneous increase in the selectivity of ethylene and methane. This result suggests that the observed deactivation observed is also associated probably with consecutive paraffin and/or olefin
cracking that can lead to lighter hydrocarbons and/or coke. On the other hand, even though a monotonic decrease in propane conversion was observed for the catalysts with large Fe/Ce ratio, no significant change was noticed in methane and ethylene selectivity. These results underscore that between low and high Fe/Ce catalysts, different deactivation mechanisms may exist that directly affect the stability in their catalytic performance.
4.1.5 Characterization of post-reaction catalysts

To further investigate the reasons behind the observed deactivation, thorough characterization of post reaction catalysts was performed via Raman spectroscopy. Figure 26 shows the presence of two broad and intense peaks located at 1344 cm\(^{-1}\) and 1598 cm\(^{-1}\) which are associated with the G and D bands of carbon deposits\(^{23, 118, 119}\). Quite intense D and G peaks are observed at low Fe content (below 5%), at extreme cases the peak intensity of D and G bands is even stronger than that of ceria F\(_{2g}\) band, indicating a very thick layer of carbon deposition on the surface. In contrast, coke formation is greatly suppressed at 10% and 15% Fe-doped ceria catalysts. Similar results were observed in a recent published article\(^{74}\), where CrO\(_x\)/CeO\(_2\) was studied with Raman spectra and showed minimal coke after ethane ODH-CO\(_2\) reaction. To the best of the author’s knowledge, there is no systematic study (either experimental or computational work) to explain this finding. However, it is believed that the enhanced surface oxygen mobility and reactivity promotes oxidation of coke precursors and further reduces coke formation.

It is worth mentioning that the nature of coke formation and propane cracking processes are very similar: they both require C-C bond cleavage at specific active sites or certain reaction conditions. In this point of view, the coke analysis is highly consistent with catalytic data where high selectivity to methane and ethylene (cracking products) were observed at low Fe loading samples.
Figure 26. Raman spectra of post-reaction FeCe600 catalysts from low Fe loading to high Fe loading.

In addition, ex-situ XPS was applied to investigate the chemical states of highly ordered carbon nanostructures deposited over fresh and spent iron-cerium oxides. Symmetrical sp3 peak (284.6~284.8eV) and asymmetrical sp2 peak (284.2~284.3eV) was fitted to the C1s main feature for post-reaction catalysts. The detailed deconvolution is shown in the Figure 27. An apparent increase was observed in C/O ratio for up to 5FeCeO2 spent catalysts as opposed to fresh material, where the C/O basis was estimated within 20~30%. A major contribution of this carbon amount lies in the advent of sp2 peak fitted on the basis of the invariant sp3 peak, revealing aromatic structure as primary chemical states of coke. As higher Fe-dopant concentration was reached, C/O ratio decreases together with sp2 peak area percentage, observation that is consistent with our Raman data. Particularly, C/O ratio
fell into the range of reference fresh material, which is a strong proof of minor carbon deposition after 24-hour ODH reaction. Although the suppressed formation of coke deposits appears to be associated with the higher propylene selectivity observed, the reasons behind the monotonic decrease in the conversion for the high Fe/Ce catalysts is still inconclusive.
Figure 27. Ex-situ XPS analysis of C1s peak deconvolution for a series of fresh and spent Fe-doped ceria catalysts.
Table 7. XPS analysis and quantification of surface carbon and oxygen atomic percentage and C/O ratio for fresh/spent Fe-doped ceria catalysts.

| Fe content | pre-reaction | | | post-reaction | | |
|---|---|---|---|---|---|
| | C atomic % | O atomic % | C/O ratio | C atomic % | O atomic % | C/O ratio |
| 1 | 11.3 | 56.9 | 0.20 | 28 | 48.9 | 0.57 |
| 2.5 | 13.4 | 57.8 | 0.23 | 28.9 | 46.7 | 0.62 |
| 5 | 11.7 | 55.2 | 0.21 | 23.1 | 51.3 | 0.45 |
| 10 | 16.5 | 55.3 | 0.30 | 14.3 | 57.2 | 0.25 |
| 15 | 16.3 | 52.8 | 0.31 | 15.7 | 54.2 | 0.29 |

Table 8. Peak table for carbon chemical state quantification based on deconvolution of XPS C1s scans of spent Fe-doped ceria catalysts. (sp²: coke/carbon deposition; sp³: adventitious carbon contamination)

<table>
<thead>
<tr>
<th></th>
<th>sp² Area %</th>
<th>sp³ Area %</th>
<th>C-O Area %</th>
<th>COO Area %</th>
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In an effort to gain more insight into the observed catalytic behavior of the 10FeCeO₂, samples before and after reaction were investigated using a scanning transmission electron microscope (STEM). Typical catalyst particles before and after reaction are shown in Figure 28(a-c). It is observed that the particle size before the reaction is less than 10 nm (consistent with XRD results) while the particle size after the reaction is in general larger than 15 nm. This result points to the decrease in specific surface area due to sintering as one possible reason behind the observed catalyst deactivation as seen from the conversion
of propane in time-on-stream. In addition, element mapping was carried out for the after-reaction sample. As shown in Figure 28c, iron is found in two localized areas in the mapped area. The result suggests that, besides CeO₂ sintering, iron also migrates to localized areas instead of keeping its initial solid solution form during the reaction indicating a significant change in morphology of the catalysts which can in turn affect the overall catalytic performance.
Figure 28. High resolution STEM images of the 10%FeCeO2 catalyst particles before (a) and after (b) reaction. (c) The dashed box indicates the element mapping area and its corresponding oxygen, iron, and cerium distribution maps.
4.2 Chromium supported iron-cerium oxide (CrO$_x$-FeCeO$_2$)

In this section, Cr supported FeCe oxides will be discussed. The idea of Cr serving as active species comes from the fact that Cr is well acknowledged as one of the most active and selective transition metals in propane DH and ODH reactions. Cr over alumina has been industrialized as propane direct dehydrogenation catalyst by Catofin Lummus process, one of the biggest commercial propane manufacture technologies. Cr has also been extensively studied as an active site when supported on silica, zeolites and various metal oxides in propane oxidative dehydrogenation reactions. In our case, the FeCe oxide itself was treated as a conventional support with clean and flat surface (surface area around 70m$^2$/g) and well-defined crystalline structure. Besides, the thermal stability and mechanical strength of FeCe oxides can also meet the basic requirements as a potential support.

Upon impregnating Cr over FeCe surface, several anticipations can be stated before the discussion begins. The primary purpose is certainly to improve the overall propane conversion and propylene selectivity. Since the synthesis of Cr was performed over pre-calcined FeCe oxides with incipient wetness impregnation, Cr is not likely to migrate into the bulk lattice. On the other hand, Cr sites will remain on the surface layers and alters original active oxygen sites by covering those sites with its anchoring bond (Ce-O-Cr/Fe-O-Cr) or bridging bond (Cr-O-Cr). While the previously identified active oxygen sites are less selective towards propane ODH, the Cr-O or Cr=O bond are expected to perform a better job.

In addition, the design idea also depends on the interactions between FeCe surface layers (mostly supported Cr oxides) and FeCe bulk lattice. The most explicit interaction occurs through oxygen diffusion from sufficient space to deficient space. Baron et al.$^{121}$ argued with DFT study that when transition metal is anchored on the CeO$_2$ surface, the surface reconstruct itself so that an oxygen vacancy will be created at sub-atomic layer below the anchoring area. Electrons from Cr 3d orbital transfer to Ce 4f orbitals and converting Ce$^{4+}$
into Ce$^{3+}$. Under non-reactive conditions, Cr maintains at high oxidation state with Ce partially reduced, generating oxygen vacancies below. Under reactive or reduction conditions, the surface loses oxygen heavily so that bulk lattice will back donate its oxygen to the surface under oxygen concentration driving force and re-oxidize reduced Cr sites. If the above assumptions hold, we are able to create an active and very stable Cr/FeCe oxide catalysts for propane ODH reaction. To the best of the author’s knowledge, the catalyst deactivation has always been a severe problem in hydrocarbon reactions, especially in propane ODH reactions, the Cr supported catalysts suffered a lot from rapid deactivation. As can been seen from figure 2, most catalysts lost more than 20% of its initial propane conversion in the overall time-on-stream runs. The time scale of individual tests is controlled within 10 hours. More detailed information will be presented and discussed in later section. Herein, we endeavor to create a Cr-based catalyst that can provide much more stable catalytic performance at longer time scale.
4.2.1 *Structural analysis of Cr/FeCe oxides*

BET analysis of surface area, pore size distribution and texture properties. Table 9 below summarized information of surface area, pore width and pore volume of 10FeCe and Cr anchored 10FeCe oxides. Upon anchoring Cr over 10FeCe surface, several textural changes can be observed. First, surface area has been greatly reduced with increasing Cr loading. Similar observations can be found widely and repeatedly in the open literatures. Average pore width is increased monotonically with Cr loading as seen from table as well as pore size distribution (figure 29). Combining the reduced pore volume at higher Cr loading catalysts, it can be inferred that the anchoring Cr species mostly blocked smaller pores with 220 to 300Å. Particularly, the from figure 29 we can tell that pore volume in the range of 220 to 300Å was reduced from 0.2 to 0.05cm³/g. Figure 30 showed a representative adsorption/desorption isotherm of 10FeCe oxides. According to IUPAC, 10FeCe isotherm belongs to type IV. The Type IV isotherm is irreversible and exhibits a hysteresis loop, which is associated with capillary condensation taking place in mesopores. This isotherm also is characterized by limiting uptake over a range of high p/pₒ. The initial part of the Type IV isotherm is much like a Type II isotherm and is attributed to monolayer–multilayer adsorption. Type IV isotherms are found for many mesoporous industrial adsorbents.

Table 9. Summary of BET and BJH analysis of 10FeCe and 10FeCe supported Cr oxides.

<table>
<thead>
<tr>
<th></th>
<th>Surface area</th>
<th>Pore width</th>
<th>Pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m²/g</td>
<td>Å</td>
<td>cm³/g</td>
</tr>
<tr>
<td>10FeCe</td>
<td>78.67</td>
<td>199.6</td>
<td>0.410</td>
</tr>
<tr>
<td>1Cr/10FeCe</td>
<td>56.53</td>
<td>234.9</td>
<td>0.338</td>
</tr>
<tr>
<td>2Cr/10FeCe</td>
<td>52.34</td>
<td>324.2</td>
<td>0.413</td>
</tr>
</tbody>
</table>
Figure 29. Pore size distribution of 10FeCe and 10FeCe supported Cr oxides via BJH analysis.
X-ray diffractograms of the support and Cr-based catalyst with varying loadings are shown below in figure 31. As can be observed from the graph, the synthesis of Cr/FeCe oxides do not change the bulk lattice structure of the support itself. Throughout the scan angle from 20° to 85°, all peaks appeared pertain to cerianite phase, with main peak centered at 29.23° as cerianite (111). In other words, no Fe or Cr oxide related crystalline phases were detected from XRD, which leads to three major conclusions: (1) the incipient wetness impregnation of Cr successfully disperse Cr over the FeCe surface without severe clustering or crystallization in local area. The monolayer coverage of Cr over pure cerium oxide was expected to be around 4Cr/nm². As of our FeCe material, the uniform matrix of Fe substituting Ce may not change the diatomic distance between adjacent Cr atoms, consequently Cr monolayer atomic density can be considered as around 4Cr/nm² as well. (2) Fe doped inside ceria lattice was very stable without re-crystallization or reacting with Cr. The previous synthesis of FeCe oxides has been identified as a stable and highly crystalline solid solution. When adding Cr as a third component, the overall material can be regarded as pseudo-binary system. Due to the limited lab resources, we are not able to
further investigate the interactions between Fe and Cr. On the other hand, no direct evidence or phenomena has been observed as potentials of Fe-Cr links. In this work, we will try not to discuss too much on this part. (3) No solid reactions observed between Cr and Ce. It has been widely reported that in metal oxide materials, the surface anchoring species might react with the bulk support phase through solid-state reaction at temperature (or during calcination process) to create a third stable crystalline structure. Especially for CeO₂, because of its unique inter-convertible redox pair with low energy barrier, when being anchored with a transition metal (e.g. Vanadium), the interaction of transition metal V⁵⁺ and Ce³⁺ actively produces cerium vanadate CeVO₄ phase and it is irreversible. According to Banares et al.¹²², the active site was V⁵⁺-O-Ce³⁺ for both systems. Consequently, in the case of Cr, our Cr/FeCe oxide is free from any binary or ternary metal/metal oxide reactions. The catalyst is marked as a thermally stable and pseudo-binary metal oxide material ready to be tested for other characterizations and propane ODH reaction.

Figure 31. XRD data of 10FeCe oxides and 10FeCe supported Cr oxides.

Raman characterizations of the Cr/FeCe materials are presented in the figure below. In Figure 32, we report the in-situ Raman spectra of fully oxidized and fully dehydrated Cr-
10FeCe catalysts at 550°C, with 1, 2 and 4 Cr/nm² atomic surface densities. The most intense peak centred around 450cm⁻¹ corresponds to the F₂g vibrational mode of ceria, with a red shift of approximate 10cm⁻¹ (depending on Fe/Ce atomic ratio) due to the incorporation of Fe dopants inside ceria lattice. The band that appears at 590cm⁻¹ is assigned as oxygen defect-related band and the ratio of peak intensity I₄₅₁/I₅₉₀ can be regarded as an indirect indicator of the relative abundance of oxygen vacancies. Chromium related peaks appear at 539cm⁻¹, 837cm⁻¹, 998cm⁻¹ and 1026cm⁻¹. Wachs et al. have assigned the peaks at 998cm⁻¹ and 1026cm⁻¹ to di-oxo and mono-oxo Cr=O vibrations respectively. The broad band located around 837cm⁻¹ remains controversial among different publications: it could be either symmetric stretching of O-Cr-O or Cr-O-Cr (845cm⁻¹) structure; however, there is a consensus that this peak is associated with the presence of polymeric species. Our Raman results are consistent with this assignment considering that the integrated peak area under 840cm⁻¹ from 2Cr- and 4Cr-10FeCe is much larger as compared to 1Cr-10FeCe, indicating oligomerizing of tetrahedral Cr(VI)O₄ species at high Cr loading. Besides, a sharp peak arose at 539cm⁻¹ over 4Cr-10FeCe oxide pertains to A₁g symmetric vibrational mode of chromium oxide (R3c space group), which is also known as the characteristic peak for Cr₂(III)O₃ crystals. The normalized peak intensity for ceria F₂g vibration decreases over 4Cr-10FeCe oxide. These results suggest the formation of inert chromium crystalline phases when Cr surface density reached 4Cr/nm², indicating the overreach of monolayer coverage on FeCe oxide surface. While not observed by XRD, the Cr₂O₃ crystal phase from 4Cr/10FeCe was captured with Raman Spectroscopy. Such apparent paradox can be resolved by the synthesis procedure of the catalyst. The impregnation of Cr causes surface reconstruction upon the formation of anchoring oxygen bonds, without alternating atomic arrays of FeCe in the bulk phase. As a result, those nanosized Cr oxide crystal structures on the surface locale could be captured by sensitive Raman Spectroscopy. On the other hand, when X-ray beam penetrates surface and sub-surface atomic layers into the bulk phase, no Cr₂O₃ phases could be found. In most discussion topics below, especially kinetic discussion, only those samples free from Cr₂O₃ crystals
will be addressed since the actual surface density of active sites is undeterminable upon the formation of crystals. In addition, no solid-state reaction or phase transformation over Cr-Fe-Ce oxides is identified under calcination and reaction conditions. Raman spectra and Cr peak information at different reaction temperatures can be found in Figure 32-supp.

Figure 32. In-situ Raman spectra of 10FeCe and 10FeCe supported Cr oxides. Spectra were collected at 550°C in continuous air flow.

Figure 32-supp. In-situ Raman spectra of 10FeCe and 10FeCe supported Cr oxides. Spectra were collected at 450, 500 and 600°C in continuous air flow.

Next, TEM analysis was performed with Cr/FeCe samples and shown in figure 33 below. TEM images for 10FeCe support can be found in previous section. Upon anchoring Cr over FeCe surface, several changes can be observed after comparing those TEM images. First, it can be obviously observed that with increasing amount of Cr loading, the FeCe oxides were gradually losing its original sharp angle at the edge of the particles. For Cr loading at
1Cr/nm² in figure 33, the features related to 10FeCe were partially retained, including sharp corners and flat edges. Meanwhile, at some local area the particles are already re-shaped with rounded corners. When further increasing Cr loadings as in figure 33, the particles were evolving heavily into spheres. When approaching the Cr monolayer coverage, it can be clearly observed a coated layer of amorphous Cr oxides with no more sharp corners and flat edges, and meanwhile highly crystalline FeCe bulk phase can still be identified. From 1Cr/FeCe to 4Cr/FeCe, the overall crystallite size was gradually also reduced. Unlike the co-precipitation of Fe and Ce which produces a solid solution, the impregnation process could not make supported Cr to penetrate and attack into deep atomic layers but rather interacting actively and strongly especially at high temperatures (during calcination process) and reconstruct the FeCe oxide surface. It is commonly acknowledged that for a well-defined crystal material, the atoms at corners and edges are generally not saturatedly coordinated, and electron density around surface layers oscillates around surface layers known as Friedel oscillation shown in scheme 6. In such case, the Cr at high oxidation state as a strong Lewis acid tends to attack electron enriched surface and forming strong Cr-O-Ce known as surface anchoring bond.

On the other hand, it is still not very clear if Cr substitutes partially into Ce lattice, at least for limited surface layers. Currently known reliable technique to test is Secondary Ion Mass Spectrometry (SIMS). SIMS is capable of profiling element concentration as a function of probing depth up to 10 microns. Imaging the case that Cr penetrates into sub-atomic layers and partially substitutes Ce, it is not difficult to fully explain the surface reconstruction observed from 10FeCe to Cr/FeCe. However, it’s not of crucial importance to explain the differences in catalytic performances and kinetics between FeCe and Cr-supported FeCe materials.
Figure 33. TEM analysis of 10FeCe supported Cr catalysts. Top row: 1Cr/10FeCe; mid row: 2Cr/10FeCe; bottom row: 4Cr/10FeCe. Sample images are collected at different transmission spots with different resolutions.

Scheme 6. Friedel oscillation: the electron density near surface oscillates before decaying exponentially into vacuum.

Last but not least, we performed H₂-TPR and cyclic H₂-TPR experiments as described in previous FeCe section. Furthermore, the H₂-TPR experiments are coupled with operando Raman in order to observe and unravel the structural changes under reduction environments. Figure 34 (a) to (d) showed cyclic TPR results for Cr loading on 5FeCe and 10FeCe with various surface atomic density. If recalling the cyclic TPR data presented in section 4.1.1, by comparing 1Cr/10FeCe and FeCe supports, it can be found that the ‘irreversible’ peak shifted to reduced temperatures, indicating the lowering of activation energy barrier so that those peroxides and superoxides can be activated at milder reaction
conditions. In the case of 2Cr/10FeCe, such peak center shifted dramatically to less than 500°C. Meanwhile, the relative peak intensity as compared to its adjacent peak signal is also decreased. Given that the surface solid state interaction of Cr and FeCe reconstructs the original clean and flat FeCe surface into curved plane and eliminating corners and edges from FeCe crystals, it may be discreetly argued that the irreversible (or it could be non-redox) oxygen sites concentrated at the edges and corners of FeCe crystals. According to the previous analysis and author’s lab experience, the formation of non-redox oxygen sites only occurs under continuous flowing oxygen environment at a longer time scale (normally expected to be over 10 hours) and preferably concentrated around corners and edges where atoms and particles are under-coordinated. Chromium preferably modified FeCe crystals and consumed those non-redox sites. If such analysis holds, the TEM and TPR data can be consistent in explaining surface active oxygens for FeCe and Cr/FeCe materials.

In the next experiments, H₂-TPR experiments coupled with in-situ Raman were performed in order to capture the temperature-dependent changes during the whole reduction process. Speaking of the reaction setup, Harrick high temperature reaction chamber with quartz window was utilized instead of the conventional U-shape reactor for spectroscopic purposes. It should be noted that the residence time distribution of Harrick cell and U-shape reactor is quite different, which might affect reaction kinetics and thus the relative reactor output intensity (in other words the integrated area). However, TPR peak centers are not expected to shift. The most challenging part is to seek for the balancing point between acquisition time and Raman spectra quality. Due to the specialty of FeCe oxides, practical in-situ Raman spectra requires around 10 minutes to collect the range of CeO₂ and supported Cr species simultaneously. During this time, the temperature will rise by 100K. Consequently, the Raman spectra dynamically changes with each accumulation and the final outcome spectra can be only considered as an average information of structural changes within 100K ramping.

The in-situ Raman spectra of 1Cr/10FeCe and 2Cr/10FeCe are shown below. As can be
seen in 1Cr/10FeCe, the Cr-O-Cr bridging bond starts to be activated in the temperature range of 350 to 450°C, corresponding to the 445°C peak shoulder in figure 35. In the range of 450 to 550°C, the Cr=O terminal bond was completely reduced by hydrogen. Upon increasing Cr loading, we observed a dramatic increase in the Raman intensity of Cr-O bridging bond, and such peak did not completely disappear in the range of 350 to 450°C. During the next Raman spectra period, however, both the bridging bond and the terminal bond are reduced by hydrogen. The reduction of these two structures corresponds to the 431°C peak and 491°C shoulder according to figure 36. Meanwhile, by plotting the Raman peak intensity ratio of I_{590}/I_{460}, it can be seen that the oxygen vacancy concentration is increasing with elevated activation temperature. The creation of oxygen vacancies can be explained in two ways. The normal thought is that FeCe oxide is emitting O_2 under oxygen deficient conditions. Apart from this, it could also be that since Cr oxides covered the FeCe surface, oxygen vacancies might be filled with bridging oxygen. After reduction those oxygen sites are removed so that oxygen vacancies are exposed again. Such argument is also consistent with the temperature range where Cr Raman bands begin to disappear. The reduction of oxygen vacancy density upon anchoring Cr is further supported by Wu’s work\textsuperscript{105}, where they applied 325nm laser line and provided spectroscopic evidence. The above experiments provide not only insights into the surface changes during the H_2-TPR, but also a sense of relative activity between Cr bridging bonds and Cr terminal bonds. Transition metals, especially in Cr group and V group, are capable of forming the unique surface anchoring structure with one or two terminal M=O bonds (as known as mono-oxo and di-oxo) and several bridging bonds due to the readiness of emptying its d electron orbitals and reaching high oxidation states (normally +5 or +6). Over the past years lots of research resources have been put into studying the differences in catalytic performances between these two structures. For instance, one of the PhD researcher in the author’s group studied Mo supported over CeTi oxides and concluded that Mo=O bond to be more active than Mo-O bridging bonds. In this work, however, opposite behaviors were observed. In fact, the relative activity can be quite complicated outcome of a few determinants, such as
support effect, neighbor effect, surface reconstruction, etc. Regardless of the relative selectivity, from comparing TPR graphs of FeCe and Cr/FeCe, we can tell that Cr-related structures are independently activated on the surface from the conventional active oxygen sites identified for FeCe samples. Together with TEM images, it is not hard to conclude that Cr species reconstructed FeCe surface involving the conventional active oxygen sites, resulting in a direction towards more uniform structure and activity. At higher Cr loadings, the previous FeCe TPR peak for peroxides and superoxides completely disappeared, instead the Cr sites played an independent role in the reaction other than a collaborative role between Cr sites and FeCe oxygen sites. Considering the propane ODH reaction, since propane molecules has larger steric hindrance than H₂, it is even less likely for propane to reach those sites H₂ cannot reach. In such case, For Cr-based materials, we can safely unify its propane oxidation sites into one kind rather than treating the whole Cr/FeCe separately as Cr sites and FeCe sites.

After H₂-TPR experiments, the author further performed a series of re-oxidation experiments especially for Cr surface structures. Firstly, 5% CO₂ in balancing argon was fed into the reactor at 550°C with a total flow of 50mL/min. However, the Raman spectra of reduced Cr/FeCe materials remained unchanged, even after 24 hours’ continuous CO₂ flow. Next, the oxidizing agent was switched to air at the same reaction conditions, and Cr surface species reappeared instantly after the very first spectra acquisition finished within 10 minutes. From the reduction experiments, we can exclude the probability of CO₂ directly oxidizing catalysts during the propane ODH with CO₂. In other words, the way CO₂ keeping catalyst alive is not through direct oxidation of Cr, and the reduced Cr can also be active in propane ODH, which has also been reported by a few research groups.
Figure 34. Cyclic H₂-TPR experiments of 1Cr/10FeCe (left) and 2Cr/10FeCe (right) catalysts.

Figure 35. Cyclic H₂-TPR experiments of 1Cr/5FeCe and 2Cr/5FeCe catalysts.

Figure 36. In-situ Raman spectra of 1Cr/10FeCe (left) and 2Cr/10FeCe (right) catalysts coupled with H₂-TPR experiments. Insert: peak ratio of I₅₉₀/I₄₆₀ at different stages of TPR experiments.
4.2.2 Discussion on the catalytic performance

In this section, a general discussion on the basic catalytic performances of Cr-based samples as well as comparison to FeCe supports will be presented. All data are collected under normal catalytic regime.

As displayed in Table 10, the addition of Cr active sites below monolayer coverage presented a promotional effect to both propane conversion (from 2.2% to 3.3%) and propylene selectivity (44.6% to 65.9%) at low temperature regime. On the other hand, however, it was noticed that Cr-based catalysts performed worse than 10FeCe towards selective propane activation when focusing on 550 to 600°C. Given the fact that supported Cr structures remained the same (see Figure 32) and no identifiable binary or ternary Cr/Fe/Ce crystalline phases formed during the catalyst preparation, it is quite contradictory to see reduced activities of Cr-based catalysts, since Cr-O and Cr-O-M stretching of surface anchored mono/poly-chromate species over a wide range of metal oxide supports (including: zeolites, silica, alumina, titania, zirconia) has been confirmed as effective structures for propane C-H activation. Consequently, such discrepancy could be resulted from changes in the surface redox properties or electronic properties brought by Cr-O-Ce anchoring bond. Michoreczyk et al. argued that fully oxidized Cr$^{6+}$ is rather a precursor than real active sites for propane dehydrogenation, since Cr sites reduce rapidly during the initial period of the reaction. Botavina et al. examined Cr oxidation states with in-situ XANES method and reported an average of Cr$^{2+}$ during the reaction process. As an analogy to Cr/FeCe oxides, it can be inferred that Cr remains Cr(VI) or Cr(V) due to the strong oxygen migration provided by ceria oxygen storage capacity (OSC). At the same time, original surface active oxygen sites are partially alternated by surface anchoring Cr-O-Ce bonds. Moreover, surface area decreases with chromium loading compared to oxide bare support, resulting in a reduction of total available sites for propane dehydrogenation. This approach tends to explain the drawbacks of Cr/10FeCe through 550 to 600°C, however,
it fails to resolve chromium promotional effects between 450 and 500°C.

Table 10. Catalytic performance of 10FeCe600 and Cr supported 10FeCe catalysts. Exp. paramters: 550°C, 1atm, 20mL/min total flow with 5% propane and 5% carbon dioxide, 200mg catalyst loading. Data collection time: 30min TOS

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C3H8</td>
<td>CO2</td>
</tr>
<tr>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10FeCe</td>
<td>2.2</td>
<td>0</td>
</tr>
<tr>
<td>0.5Cr</td>
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<td>10FeCe</td>
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</tr>
<tr>
<td>0.5Cr</td>
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</tr>
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</tr>
<tr>
<td>1Cr</td>
<td>35.4</td>
<td>41.7</td>
</tr>
</tbody>
</table>
On the other hand, it should always be noted that the above discussion was based on a general reaction conditions in accordance with our previous work in order to provide a consistent comparison of Cr-based materials. But still the lack of understanding deep into intrinsic kinetic regime must be re-considered to reveal the actual temperature influence. Figure 37 below described temperature dependent conversion/selectivity under kinetic regime for 10FeCe, 1Cr/10FeCe and 2Cr/10FeCe. It is noticed that despite the local differences arose during the examination (e.g., At 550°C, 10FeCe behaved the worst in propane conversion among all catalysts under kinetic regime, while under 20mL/min total flow, 10FeCe provided best conversion and selectivity), the overall trend conveyed a clear message that 10FeCe oxide was chasing behind Cr-based catalysts with a much higher increment in propane conversion and finally surpassed Cr-based catalysts at 590°C. ODH selectivity is decreasing with temperature as expected from our previous investigation, where Cr-based catalysts underwent a drastic drop from 80% to less than 60% and 10FeCe catalyst remained less affected at elevated temperatures. Based on the above observations, it could be deduced that [Cr(VI)O₄]²⁻ structures provided unique surface properties which are kinetically more favourable at low temperature conditions. In order to clarify the effect of chromium species, a kinetic model will be built with detailed discussions in later sections.

As for the performances of 5FeCe and corresponding Cr-based samples, the temperature-dependent performances are basically similar to that of 10FeCe series. As discussed in previous section, the 10FeCe catalyst outperformed 5FeCe both in propane conversion and propylene selectivity. The reason, as stated before, the surface Fe rich oxygen sites serve as a selective site to propane dehydrogenation and improves the overall performances. When Cr sites were anchored on the FeCe oxide surface, it can be found that the behavior
of Cr samples are basically the same within experimental derivations, e.g. Cr atomic density, particle size distribution, reactant flowrate fluctuations, etc. The fact that regardless of the Fe loadings in the FeCe oxides, Cr samples output constant performance further strengthened the assumption that the original oxygen sites pertaining to FeCe oxides are completely altered or covered by surface Cr oxide species. Even if considering the probability that FeCe oxygen sites and Cr oxygen sites co-exists on the catalyst surface, still the overall performances proved that Cr oxygen sites plays a dominate role in either propane adsorption or propane reaction rate, or even both. The differences between two kinds of oxygen sites can be expressed from the changes in physicochemical parameters, but in the case of Cr-based catalysts, it is actually plausible to consider only one kind of oxygen sites that assumes the catalytic functions while original FeCe oxygen sites are either physically eliminated or kinetically negligible in this study.

![Figure 37. Temperature dependent catalytic performance of 5FeCe (left) and 10FeCe (right) oxides and their supported Cr catalysts at kinetic regime. Catalyst loading: 100mg. Flow: 5% propane and 5% carbon dioxide in balancing Helium, total flow of 100mL/min.](image)
4.2.3 Effect of partial pressure of $C_3H_8$ and $CO_2$

The effect of partial pressure of propane and carbon dioxide of different chromium loading catalysts were shown in figure 38. Figure 38 (a) and (b) illustrated the change of propane consumption rate and propylene formation rate per unit mass of 10FeCe catalyst as a function of low propane feed ratio under three fixed $CO_2$ feed ratio: 0, 5% and 25% (excess $CO_2$). Relative rates over Cr-based catalysts were included in figure 38 Regardless of the experimental variations, propane rates were fitted via a power law function with the power index valued around (100±7)% of reaction order reported above. Propylene formation rates were fitted with a linear function approaching origin point according to the rate law of PDH reaction. Propane rates remained invariant even under extreme $CO_2$ partial pressure (25%) while propylene formation rates decreased monotonically with increasing $CO_2$ partial pressure, clearly indicating a shift between the relative contributions of parallel PDH and DRF pathways. Provided that propane molecules are only converted through dissociative adsorption on the surface oxygen active sites, it may be concluded that $CO_2$ partial pressure is not a determinant in rate controlling of propane activation under low partial pressure situation where competitive adsorption has not yet begun to play a significant role. Particularly, propane dissociative adsorption, where first methylene $C-$H bond is activated to produce $(CH_3-CH-CH_3)-C_o$ and $H-C_o$, is identified as a rate limiting step in the reaction network$^{21,25}$. 

From the aspect of $CO_2$ activation, the redox pair of $Ce^{4+}$ and $Ce^{3+}$ plays a decisive role in improving the $CO_2$ utilization efficiency. An oxygen defect/vacancy ($C_v$) will be created once hydrocarbon adsorbate/intermediate evolves and extracts an oxygen atom from CeO$_2$ surface, which has a great potential to be replenished by the following $CO_2$ dissociation$^{27}$. On the other hand, the negative effect of $CO_2$ on propylene formation was observed from figure 38 for all catalysts. One of the most straightforward and well-acknowledged reason is that DRF is thermodynamically favored than PDH at high $CO_2/C_3H_8$ feed ratios (see
figure 5 for thermodynamic predictions of system composition at various initial partial pressure). Since propane activation rate is pre-determined by C-H activation step, extra CO₂ co-feed provides abundant surface reactive oxygen adsorbates that stimulates further decomposition of C₃H₇⁺ into light hydrocarbon pieces and reduces the chance for secondary C-H cleavage. When CO₂ is absent as a feed in the reaction system, propane can be activated at almost the same rate, suggesting two independent activation routes for propane and carbon dioxide in the overall reaction network. Moreover, it is noticed from Table 11 that propane individual feed will produce CO₂ at initial time-on-stream and CO₂ decays rapidly within 10 minutes, indicating the existence of unselective surface oxygen species produced from calcination or regeneration steps.

Table 11. Comparison of catalytic performances of 10FeCe and 2Cr/10FeCe in the kinetic regime in the presence/absence of CO₂.
Figure 38. Propane consumption rates and propylene formation rates as a function of propane partial pressure and carbon dioxide partial pressure. (a-c) pertains to 10FeCe, (d-f) pertains to 1Cr/10FeCe, (g-i) pertains to 2Cr/10FeCe. In the test of propane and propylene rates, three different CO\textsubscript{2} feed conditions were tested, which are 5\% CO\textsubscript{2}, excess CO\textsubscript{2} (25\%) and in the absence of CO\textsubscript{2}. 
4.2.4 Analysis of catalyst stability and deactivation

The stability of Cr-10FeCe catalysts were examined at 550°C with a total flow of 20mL/min. Figure 39 showed propane conversion and selectivity to major hydrocarbon products in the system. The reason of deactivation of 10FeCe oxide was investigated in our previous work and STEM results suggested that Fe dopants were reduced and migrated together, which is consistent with another independent study from Chen et al. The deactivation patterns of Cr-FeCe oxides behaved similarly: a rapid initial decrease followed by stable platform and then deactivating at a faster rate (slope of conversion curve grew more negative). The initial deactivation could be explained by a rapid reduction of Cr valence state. Unlike the most commonly reported exponential decay of propane conversion curve over Cr-based catalysts (Cr supported on silica, alumina, titania and zeolites), Cr-FeCe catalysts kept stable performance for 600 minutes. Finally, as carbon deposition accumulated, Cr-FeCe further lost its activity and broke C-C bonds and C-H bonds unselectively, meanwhile increased amount of methane and ethylene was also observed. The main catalyst life at 600- and 1200-minute TOS were calculated according to Serrano-Ruiz et al. and listed in Table 12. Although Cr-based catalysts deactivate faster in the long term, up to 600 minutes Cr-catalysts maintained a highly stable performance, which could possibly rely on the formation of dual redox cycle of Cr and Ce demonstrated with scheme 7. The dehydrogenation of propane consumes hexavalent Cr to trivalent Cr species, which is further re-oxidized by oxygen donation from CeO₂ lattice, and a local oxygen vacancy is created. The oxygen vacancy can be replenished in two approaches: splitting CO₂ or being re-filled by oxygen migrated from CeO₂ sub-atomic layers. Such dual redox cycle guaranteed constant propane conversion and selectivity within 10hours. Unfortunately, coke formation is still an evitable problem over Cr-containing catalysts and finally deactivation is observed.
Figure 39. Stability test of 10FeCe, 1Cr/10FeCe and 2Cr/10FeCe catalysts. Reaction conditions: 5% propane and 5% CO\textsubscript{2} in balancing Helium with total flowrate of 20mL/min. Catalyst loading: 200mg. Reaction temperature: 823K. Overall TOS: 1200min.

Table 12. Catalyst mean life calculated at 600 minutes and 1200 minutes.

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<tr>
<th></th>
<th>(T_{m,1200\text{TOS}}) (h)</th>
<th>(T_{m,600\text{TOS}}) (h)</th>
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<td>10FeCe</td>
<td>78.67</td>
<td>215.8</td>
</tr>
<tr>
<td>1Cr-</td>
<td>49.90</td>
<td>233.5</td>
</tr>
<tr>
<td>2Cr-</td>
<td>28.70</td>
<td>245.8</td>
</tr>
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</table>
In order to explicitly show the supreme stability of our catalyst design idea, we investigated open literatures over the past two decades in the field of CO$_2$-assissted propane dehydrogenation catalysis. Expect for those that did not report time-on-stream catalytic data, in the table 13 below we summarized mostly cited and mostly relevant works in the community with comparable reaction conditions and parameters. It should be noted that the calculation of selectivity to FeCe and Cr-FeCe catalysts in this work is based on the definition of propylene over detected hydrocarbon species, where especially CO as a side product is not included. In these calculations we use the same set of raw data as what reported in section 4.2.2. As a result, the values appear to be different between selectivity reported at two sections, and the reason to do so is just to normalize our data with the same criteria that has been mostly applied in the community to provide a direct sense of comparison.

Among all the catalysts design ideas and catalytic outcomes, we emphasize our achievement in comparing the catalyst mean life especially for Cr-based samples. The catalyst mean life is defined with a first-order deactivation model, which is quite suitable

![Scheme 7. Proposed dual redox cycle of surface Ce and Cr during the reaction process.](image-url)
for our catalyst time-on-stream behavior with slight linear decay of propane conversion as shown above. As for Cr-based samples, while most Cr catalysts features exponential decay of reaction rates, we are managed to achieve more or less constant propane conversion rates over the beginning 10 hours, when most other catalysts were not even reported with corresponding data and deactivated already.

The reason behind long lasting propane dehydrogenation performance could be ascribed to the dual redox cycle between Ce$^{4+}$/Ce$^{3+}$ and Cr$^{6+}$/Cr$^{3+}$ as argued above. As compared to most conventional supports where Cr sites are anchored on, for instance high SSA silica, alumina and various type of zeolites, the most essential difference of FeCe oxides is obviously the well-established and supreme oxygen mobility of ceria which has been further enhanced by Fe substitution. While from TEM analysis we deduced that original oxygen sites are no longer accessible by propane molecules, those oxygens could still serve as redox sites in responsible for regenerating reduced Cr sites back to its higher oxidation state. On the other hand, it has been reported extensively that when Cr serves as active sites, the reduced Cr$^{3+}$/Cr$^{2+}$ are in fact more active than the Cr$^{6+}$ sites. Due to the redox effect and oxygen migration of FeCe, the average oxidative state of Cr active sites are expected to be higher than Cr supported over non-redox supports (although currently we are not able to test such hypothesis since in-situ XPS experiments are rather demanding and beyond our accessibility). Consequently, the redox cycles kept stabilizing a constant reactor at the expense of losing the best activity of Cr sites. This analysis also explains further why supported Cr catalysts reduces propane conversion at normal reaction conditions.

Table 13. Reaction conditions, catalytic performances and catalyst mean life collected and normalized from open literature resources and a comparison to this work.

<table>
<thead>
<tr>
<th>journal</th>
<th>Catalyst</th>
<th>temperature(°C)</th>
<th>initial conversion</th>
<th>selectivity</th>
<th>TOS(min)</th>
<th>Mean life (h)</th>
</tr>
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<tbody>
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<td>10FeCe</td>
<td>550</td>
<td>17.4%</td>
<td>85.0%</td>
<td>600</td>
<td>215.8</td>
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<td>14.1%</td>
<td>84.5%</td>
<td>600</td>
<td>233.5</td>
</tr>
<tr>
<td>this work</td>
<td>2Cr-10FeCe</td>
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<td>13.0%</td>
<td>85.6%</td>
<td>600</td>
<td>245.8</td>
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<td>-----------------</td>
<td>------------</td>
<td>-----</td>
<td>-------</td>
<td>-------</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>2018 ACS catal\textsuperscript{27}</td>
<td>Pd/CeZrAlOx</td>
<td>500</td>
<td>10.0%</td>
<td>90.0%</td>
<td>180</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>Pd/CeZrAlOx</td>
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<td>16.0%</td>
<td>80.0%</td>
<td>9000</td>
<td>82.5</td>
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<tr>
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<td>Ni3Pt1/CeO2</td>
<td>550</td>
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<td>800</td>
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<td>360</td>
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<tr>
<td></td>
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<td>550</td>
<td>59.3%</td>
<td>77.8%</td>
<td>360</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>Cr2/Al2O3</td>
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<td>12.1%</td>
<td>92.4%</td>
<td>360</td>
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<td></td>
<td>Cr-K/SiO2</td>
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<td>Cr-Ca/SiO2</td>
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<td>Cr-Ba/SiO2</td>
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<td>2011 micro meso\textsuperscript{38}</td>
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<td>77.8%</td>
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<td>14.6%</td>
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<td>360</td>
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<td>600</td>
<td>54.0%</td>
<td>38.2%</td>
<td>600</td>
<td>30.1</td>
</tr>
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</table>
5. Kinetic analysis and developing kinetic models

Upon previous discussion, it has been found that the temperature dependent catalytic behavior of the FeCe oxides and Cr-based catalysts were quite different. The addition of Cr did not provide marked improvements to the overall catalytic performances, but in fact it behaved worse while we tried to investigate the material at higher temperatures. Similar results are concluded when we increase the reactant flowrate to eliminate the external mass transfer limitation and discuss in the intrinsic kinetic regime. It is quite beyond anticipation that Cr-FeCe oxides does not boost up propane conversion, due to the fact that Cr as active sites has been industrialized. Questions arise when we put some thoughts into the possible reaction pathways. Industrial Cr/Al₂O₃ catalyzes propane direct dehydrogenation, with propane as the only reactant feed into the system (sometimes steam will be added in order to suppress coke formation, but H₂O does not participate in the reaction). Herein, the addition of CO₂ might have changed the apparent reaction to oxidative dehydrogenation so that PDH reaction coordination is no longer processed in ODH system.

On the other hand, however, if we examine the stepwise reaction pathways as summarized previously in the introduction section, it is not hard to find that no matter in DH+RWGS or in ODH-MvK, CO₂ seems not to directly participate in the reaction steps where propane is activated. In other words, CO₂ and C₃H₈ could be independently activated at different active sites and the overall reaction still proceeds as CO₂-assisted ODH. It could be, although not directly, supported by the fact that several research groups reported the apparent reaction order of CO₂ in propane ODH reaction is zero. If this argument holds, the catalytic behavior of Cr active sites in ODH should resemble that in PDH. Under certain circumstance, support effect might play a decisive role in controlling ODH activity of Cr sites. According to a recent DFT study, Cr substituted CeO₂ (111) surface exhibited some unique physicochemical properties. In their work, they divided all surface oxygens around Cr sites into three parts as shown in figure 40, which are oxygen atoms nearest to Cr sites (green balls); oxygen atoms next-nearest to Cr at surface layer (pink balls); and oxygen
atoms nearest to Cr at subsurface layers (blue balls). DFT calculation showed that all nearest surface oxygen atoms have smaller formation energy of oxygen vacancies. On the other hand, however, the formation energies of oxygen vacancies of all next-nearest surface oxygen sites are larger ($E_{Ov} > 2.36eV$) as compared to ideal CeO$_2$ (111) surface (2.25eV). The formation energy of oxygen vacancy basically provides the energy information that needed to break the current oxygen-metal bond in order to create such vacancy. In other words, while the activity of surface nearest oxygen atoms are unstable and easier to be activation upon Cr doping, the surface next-nearest atoms are relatively stabilized and become less active in oxidative reactions. Up to this point, however, it still cannot be determined quantitively that whether Cr improves or inhibits ODH reaction rates from overall view.

In order to resolve the question and provide some insights into the structure and activity of Cr on the molecular level, a steady state kinetic study towards the FeCe and Cr/FeCe catalyzed CO$_2$-assisted propane ODH reaction system will be presented in this section. The primary purpose of this study is to figure out an explanation why Cr sites over FeCe support cannot improve the overall performances. Firstly, a power-law kinetic model will be regressed from catalytic data in the kinetic regime to unravel the partial pressure dependent rate performances of FeCe oxides and Cr-based catalysts. Apart from that, a Langmuir-Hinshelwood reaction mechanism will be proposed with detailed elementary steps to describe the complex reaction network containing propane dehydrogenation, reverse water gas shift reaction and propane dry reforming reaction. To the best of author’s knowledge, no one has ever performed such kinetic study for a complex reaction network in the field of propane-CO$_2$ ODH system. Langmuir-Hinshelwood mechanism can resolve not only the elementary steps but also adsorption changes before and after anchoring Cr sites.
Figure 40. Reprint: Surface structures of Cr-CeO$_2$(111) surface. Green balls represent surface O atoms nearest to the dopant(O1 ~ O3), pink balls are the three next-nearest surface O atoms (O4 ~ O6) and light blue balls are the nearest subsurface O atoms (O7 ~ O9).

Figure 41. Test of kinetic regime and elimination of external mass transfer limitation. All tests were performed at 823K, varying flowrate from 20mL/min to 100mL/min with constant propane and CO$_2$ partial pressure.
5.1 Power-law kinetics

The first examination on kinetic data revealed apparent propane reaction order from the power law kinetic expression: $-r_{C_3H_8} = k_{app}P_{C_3H_8}^{\alpha}P_{CO_2}^{\beta}$. In order to decouple the individual influence of propane or carbon dioxide, the other reactant was kept at excess feed ratio (25% : 5%) so that it was considered constant and lumped with ln($k_{app}$) in the log form. Figure 42 and table 14 reported the apparent order of individual reactants over 10FeCe and 2Cr/10FeCe catalysts. It is shown that the apparent propane reaction order for 10FeCe, 1Cr/10FeCe and 2Cr/10FeCe are 0.71, 0.74 and 0.64, respectively. The actual apparent order is expected between 1 and 0.33 depending on the relative weight of PDH and dry reforming contributions. The overall $C_3H_8$ consumption rate can be regarded as a linear combination of $r_{DH}$ and $r_{DRF}$, which exhibit an apparent reaction order of 1 and 1/3 (demonstrated in the following kinetic model), respectively. According to a recent related study, Shishido et al.\textsuperscript{85} tested reaction orders of partial pressure of propane over Cr/SiO$_2$ and Cr/Al$_2$O$_3$ catalysts, and they reported 0.65 and 0.59, respectively. Reaction orders of CO$_2$ partial pressure over different chromium loadings located between 0 to -0.1, indicating a slight negative dependence of CO$_2$ in current reaction scenarios. Particularly, all these kinetic data were collected at low partial pressure regime (from 0.5% to 5%), where competitive adsorption of propane and CO$_2$ was not taken into account. According to Jingguang Chen et al.\textsuperscript{28}, competitive adsorption and reduction of $C_3H_8$ reaction rates occurs severely when CO$_2$ partial pressure exceeds certain partial pressure threshold (generally above 30% but also depending on the type of active sites and support surface). The data for Arrhenius plot were collected from 450°C to 575°C with an increment of 25°C in the kinetic regime. By impregnating Cr sites, the apparent activation energy reduced from 70kJ/mol down to 65kJ/mol and remained approximately the same at various Cr loadings. The result suggests that the addition of Cr species generates or promotes active sites in propane activation.
Table 14. Summary of apparent reaction orders of propane consumption rate and propane overall activation energy

<table>
<thead>
<tr>
<th></th>
<th>C$_3$H$_8$ reaction order (a)</th>
<th>CO$_2$ reaction order (b)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10FeCe</td>
<td>0.71</td>
<td>-0.06</td>
<td>70.45</td>
</tr>
<tr>
<td>1Cr-</td>
<td>0.74</td>
<td>-0.03</td>
<td>65.29</td>
</tr>
<tr>
<td>2Cr-</td>
<td>0.64</td>
<td>-0.02</td>
<td>65.37</td>
</tr>
</tbody>
</table>

Figure 42. Log-log plot and propane rates as a function of propane partial pressure (left) and CO$_2$ partial pressure (middle), and Arrhenius plot (right).
5.2 Langmuir-Hinshelwood kinetic model for FeCe and Cr/FeCe

In order to fully describe the potential reaction pathways to match our experimental results, a number of reactions need to be considered which makes the overall reaction network complex and occasionally redundant. A full list of possible reactions can be found in section 1.2. However, in a real kinetic application, it is not wise to take into account every reaction pathway due to the following reasons: first, it is not likely to disintegrate and trace the contribution to every component from its complete set of all possible reactions; second, some of the products (e.g., C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and CH\textsubscript{4}) consists of extremely small content as compared to major products in the reaction. Due to the limitation of experimental facilities, not enough significant digits can be recorded, where deviations can be exaggerated and leads to inaccurate or even unreliable regression results. Particularly, above 95% of the total carbon sources flow to C\textsubscript{3}H\textsubscript{6} as well as CO, indicating propane dehydrogenation and dry reforming as predominant reaction pathways. From the conventional prospect, no matter DH+RWGS or ODH-MvK, propane and CO\textsubscript{2} are converting with 1:1 molar ratio according to the stoichiometric coefficient of the overall reaction (C\textsubscript{3}H\textsubscript{8} + CO\textsubscript{2} \rightleftharpoons C\textsubscript{3}H\textsubscript{6} + CO + H\textsubscript{2}O). However, the reaction may not proceed strictly with 1:1 consumption ratio, since C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2} molecules are activated successively rather than simultaneously on the same sites. Meanwhile, considering the strong oxygen mobility and relaxation of FeCe crystal surface, oxygen defects can be buried at sub-atomic layers and stay unexposed to incoming CO\textsubscript{2} molecules\textsuperscript{25}. Besides, the absence of CO\textsubscript{2} did not enhance nor mitigate propane conversion according to our previous results, which further strengthened the fact that CO\textsubscript{2} is activated independently from C\textsubscript{3}H\textsubscript{8}. In this way, ODH reaction misdescribes the overall performance by over-estimating the contribution of CO\textsubscript{2} dissociation. In this work, in order to avoid the ambiguity of ODH expression, PDH and DRF were defined as major propane reaction pathways along with RWGS reaction serving as a shift of partial pressure of by-products to reach equilibrium. Based on the understanding from above analysis and reported literatures, a reaction pathway is put forward and illustrated in
The incoming C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2} molecules are independently adsorbed and activated on the surface oxygen sites and oxygen vacancies, respectively. One of the C\textsubscript{3}H\textsubscript{8} decomposition adsorbate, C\textsubscript{3}H\textsubscript{7}*, is then evolved via two branches: secondary dehydrogenation or C-C scissoring, corresponding to PDH and DRF/cracking, respectively. The light hydrocarbon pieces are further evolved through two approaches depending on the participation of oxygen sites: if combined with oxygen atoms (either from CO\textsubscript{2} or from CeO\textsubscript{2}), the final product will be dry reforming products; if not, it is likely to produce coke precursors and migrate to form coke and block certain active sites. In light of the interconversion of low hydrocarbon pieces, it was used to believed that they further decompose to atomic carbon and then oxidized to form CO\textsuperscript{134,135}. Recently however, it was proposed by computational works that before totally reduced to atomic carbon, low hydrocarbon species (CH\textsubscript{x}) can be involved in the surface elementary reaction with O* or -OH to form alcoholic and formate species (CH\textsubscript{x}O\textsuperscript{136-138}). In this work, the latter is considered more realistic since the FeCe oxides is believed to have very reactive surface oxygen site that could readily oxidizing low hydrocarbon intermediates before they completely turned to atomic carbon. In addition, our previous work showed minimum coke formation over 10FeCe surface, which further reduces the possibility of atomic carbon formation. On the other hand, CO\textsubscript{2} is adsorbed independently on the surface. The activation of CO\textsubscript{2} is fulfilled via two possible approaches: direct dissociation to generate adsorbed CO and O*\textsuperscript{27,65,139,140} or combined with adsorbed hydrogen atoms (mostly generated via propane C-H activation step) and form carboxyl intermediates(-COOH), which further decompose to CO and hydroxyl group(-OH). The latter is also known as associative mechanism of reverse water-gas shift reaction\textsuperscript{140-143}. 
In order to derive the kinetic model, a few assumptions must be declared first in order to simplify the model in a reasonable manner. (1) Reactions are performed at low propane conversion, preferably below 15% in order to guarantee differential reactor conditions. (2) Intrinsic kinetic conditions were guaranteed by adjusting the total mass flow rate of the feed at constant $C_3H_8$ and $CO_2$ partial pressure. As shown in figure 41, linear correlations approaching origin points were fitted when total flow rate exceed 50mL/min, indicating intrinsic condition can be safely considered at above 50mL/min total flow. (3) Carbon balance is a key point to ensure the accuracy of kinetic analysis and parameter regression\(^\text{13}\). In this work, carbon balance of all individual experiments maintained at level above 99.4%. (4) Volumetric flow from upstream and downstream of the reactor was regarded equivalent due to the excess feed of inert gas (over 90% in most cases) and low conversion of reactants in the kinetic regime.

In order to develop a steady-state kinetic model, several assumptions must be declared based on the understanding of the nature of FeCe oxide. (1) Two types of active sites were identified from previous works\(^\text{25, 27, 65, 144}\): surface active oxygen sites ($S_1$) and oxygen vacancies ($S_2$). (2) No migrations of adsorbed intermediates between $S_1$ and $S_2$ sites. (3) Single site adsorption. (4) Langmuir-Hinshelwood Hougen-Watson (LHHW) surface reaction mechanism was applied to describe the reaction networks composed of PDH, DRF.
and RWGS assuming a primary rate-limiting step (p-rds) and two secondary rate-limiting steps (s-rds).

Fourteen elementary steps were identified for the whole model:

s1: $C_3H_8(g) + 2S_1 \rightleftharpoons C_3H_7S_1 + H_S1$

s2: $C_3H_7S_1 \rightleftharpoons C_3H_6(g) + H_S1$

s3: $2H_S1 \rightleftharpoons H_2(g) + 2S_1$

s4: $CO_2(g) + S_2 \rightleftharpoons CO(g) + S_1$

s5: $CO_2(g) + S_2 + H_S1 \rightleftharpoons COOH_S2 + S_1$

s6: $COOH_S2 \rightleftharpoons CO(g) + HO_S2$

s7: $2HO_S2 \rightleftharpoons H_2O(g) + S_1 + S_2$

s8: $C_3H_7S_1 + S_1 \rightleftharpoons CH_3CH_S1 + CH_3S_1$

s9: $CH_3CH_S1 + S_1 \rightleftharpoons CH_3S_1 + CH_S1$

s10: $CH_3S_1 \rightleftharpoons CH_3O_S2$

s11: $CH_S1 \rightleftharpoons CHO_S2$

s12: $CH_3O_S2 + S_1 \rightleftharpoons CH_2O_S2 + H_S1$

s13: $CH_2O_S2 + S_1 \rightleftharpoons CHO_S2 + H_S1$

s14: $CHO_S2 + S_1 \rightleftharpoons CO(g) + H_S1 + S_2$
It should be noted that in the elementary step, S\textsubscript{1} and O\textsubscript{S}\textsubscript{2} is generally considered as equivalent without considering the local effects of oxygen vacancy sites. Similarly, H\textsubscript{S}\textsubscript{1}\&OH\textsubscript{S}\textsubscript{2}, CH\textsubscript{x}S\textsubscript{1}\&CH\textsubscript{x}O\textsubscript{S}\textsubscript{2} are regarded as ‘redox pairs’ that represents oxygen removal and replenishment processes during the reaction, which is consistent with the oxygen exchange phenomena among reactants (CO\textsubscript{2}), catalytic surface and products (CO and H\textsubscript{2}O) observed and concluded from previous analysis. Meanwhile, S\textsubscript{1} and S\textsubscript{2} sites are inter-convertible in these elementary steps and total amount of site (S\textsubscript{1, tot} and S\textsubscript{2, tot}) are in dynamic equilibrium.

Site balance:

\[
\frac{S\textsubscript{1,tot}}{S\textsubscript{1}} = (1 + \frac{S\textsubscript{1,C3H7}}{S\textsubscript{1}} + \frac{S\textsubscript{1,H}}{S\textsubscript{1}} + \frac{S\textsubscript{1,CH3}}{S\textsubscript{1}} + \frac{S\textsubscript{1,CH3CH}}{S\textsubscript{1}})
\]

\[
\frac{S\textsubscript{2,tot}}{S\textsubscript{2}} = (1 + \frac{S\textsubscript{2,COOH}}{S\textsubscript{2}} + \frac{S\textsubscript{2,OH}}{S\textsubscript{2}} + \frac{S\textsubscript{2,CHO}}{S\textsubscript{2}} + \frac{S\textsubscript{2,CH3O}}{S\textsubscript{2}} + \frac{S\textsubscript{2,CH2O}}{S\textsubscript{2}})
\]

Assuming highly reactive and unstable surface adsorbates including CH, CH\textsubscript{3}, CH\textsubscript{3}CH, CH\textsubscript{3}O and CH\textsubscript{2}O, the site balance were simplified to:

\[
\frac{S\textsubscript{1,tot}}{S\textsubscript{1}} = (1 + \frac{S\textsubscript{1,C3H7}}{S\textsubscript{1}} + \frac{S\textsubscript{1,H}}{S\textsubscript{1}}), \text{ and } \frac{S\textsubscript{2,tot}}{S\textsubscript{2}} = (1 + \frac{S\textsubscript{2,COOH}}{S\textsubscript{2}} + \frac{S\textsubscript{2,OH}}{S\textsubscript{2}} + \frac{S\textsubscript{2,CHO}}{S\textsubscript{2}})
\]

Reactor design equation:

\[
T_{C3H8} = \frac{dX_{C3H8}}{d(w/F_{C3H8})}
\]
\[ \frac{dX_{C_3H_8}}{d(w/(F_{tot}P_{C_3H_8}))} \approx \frac{\Delta X_{C_3H_8}}{\Delta (w/(F_{tot}P_{C_3H_8}))} \]

\[ = \frac{X_{C_3H_8, final} - X_{C_3H_8, ini}}{(w/(F_{tot}P_{C_3H_8}))_{final} - (w/(F_{tot}P_{C_3H_8}))_{ini}} \]

Assuming s14 as primary rate-limiting step, s1 and s4 as secondary rate-limiting step, overall PDH, DRF and RWGS rates were expressed as:

\[ r_{DH} = \frac{k_{DH}}{1 + K_2^{-1}P_{C_3H_6}(K_{H_2}P_{H_2})^{0.5} + (K_{H_2}P_{H_2})^{0.5}} \]

\[ r_{RWGS} = \frac{k_{RWGS}}{1 + K_5P_{CO_2}(K_{H_2}P_{H_2})^{0.5}(1 + \frac{K_5}{P_{CO}} + \frac{K_{CHO}P_{C_3H_6}^{1/3}P_{CO_2}}{P_{CO}(P_{H_2})^2})} \]

\[ r_{DRF} = \frac{k_{DRF}}{1 + K_5P_{CO_2}(K_{H_2}P_{H_2})^{0.5}(1 + \frac{K_5}{P_{CO}} + \frac{K_{CHO}P_{C_3H_6}^{1/3}P_{CO_2}}{P_{CO}(P_{H_2})^2})} \]

\[ k_{DH} = k_2S_{1, tot}K_{C_3H_8}K_{H_2}^{-1/2} \]

\[ K_{DH} = \frac{K_{C_3H_8}}{K_2^{-1}K_{H_2}} \]

\[ k_{RWGS} = k_7S_2^{2, tot}K_5^{2}K_{H_2}K_6^{2} \]
\[ K_{RWGS} = \frac{k_5^2 K_{H_2} K_6^2}{K_{H_2 O}} \]

\[ k_{DRF} = k_{14} S_{1,tot} S_{2,tot} K_{CHO} K_{C_3H_8}^{1/3} K_4 K_{H_2}^{-5/6} \]

\[ K_{DRF} = K_{14} K_{CHO} K_4 K_{H_2}^{-5/6} \]

\[ K_{CHO} = (K_5 K_9 K_{10} K_{11} K_{12} K_{13})^{1/3} K_4 K_{C_3H_8}^{1/3} K_{H_2}^{1/2} \]

It should be noted that the derived expression lumped all possible parameters from elementary steps and site balance. While \( K_2, K_5 \) and \( K_6 \) stands for the equilibrium constants for each elementary step, most other constants are dismissed from the final expression, due to either the fact that rate-limiting steps are not considered to approach their equilibrium, or the equilibrium constants are essentially lumped together. Details of lumped parameters could be found in the supporting information. PDH equilibrium constant was expressed as: \( K_{DH} = \exp (16.858 - 15934/T + 148728/T^2) \), RWGS equilibrium constant was expressed as: \( K_{RWGS} = 10^{2.4198 - 0.0003855 \times T + 2180.6/T} \) and dry reforming equilibrium constant \( K_{DRF} \) is considered much larger in the order of magnitude than partial pressure terms on the numerator according to thermodynamic equilibrium examination in the supporting information figure 5. Reaction rate constants \( k_{rxn} \) and adsorption constants for certain reaction components \( K_{cpn} \) (cpn in subscript will be denoted as different reaction components, including both reactants and products) were expressed by linearized Arrhenius equation and linearized van-Hoff equation with a reference temperature at 550°C (823K):

\[ k_{rxn} = k_{rxn,0} \left( \frac{-E_{a,rxn}}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right) \]

\[ K_{cpn} = K_{cpn,0} \left( \frac{-\Delta H_{cpn}}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right) \]
With all derived rate expressions of DH, RWGS and DRF, the next step is to resolve the differences between rate of reactions and the rate of reactants, which can be directly observed from the reaction output. For three main reactions, we included the rate of propane and carbon dioxide into the calculation, as well as propylene the desired product. Through observing the stoichiometric coefficients in DH, RWGS and DRF, we can express the rate of each composition with rate of all reactions that participates. Then the rate expressions can be alternated into the following:

\[
\begin{align*}
    r_{C_3H_8} &= r_{DH} + r_{DRF} \\
    r_{C_3H_6} &= r_{DH} \\
    r_{CO_2} &= r_{RWGS} + 3r_{DRF}
\end{align*}
\]

Here we applied the concept of the extent of reaction into the calculation in order to satisfy mass conservation. The above expressions help to create a matrix, with rate of reaction as column vectors and rate of components as row vectors, denoted reaction coordination (RC):

\[
RC = \begin{pmatrix} 1 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 3 \end{pmatrix}
\]

Taking the inverse of RC, we get the rate of reactions as a function of the rate of components:

\[
\begin{pmatrix} r_{DH} \\ r_{RWGS} \\ r_{DRF} \end{pmatrix} = RC^{-1} \times \begin{pmatrix} r_{C_3H_8} \\ r_{C_3H_6} \\ r_{CO_2} \end{pmatrix}
\]

\[
\begin{align*}
    r_{DH} &= r_{C_3H_6} \\
    r_{RWGS} &= -3r_{C_3H_8} + 3r_{C_3H_6} + r_{CO_2} \\
    r_{DRF} &= r_{C_3H_8} - r_{C_3H_6}
\end{align*}
\]
Thus, the direct experimental observation are converted into the model input. Another part of model input is the partial pressure of all reactants and products, as expressed in the LH rate expressions. The major model output are pre-exponential factors and activation energies for each reaction, as well as the adsorption constants of different reactants and products.
5.3 Model regression, prediction, and discrimination

For all parameters to be fitted, the initial values are calculated from several different DFT calculations\textsuperscript{135, 138, 146, 147} on propane dehydrogenation and dry reforming reactions. Kinetic data was fitted via MATLAB nonlinear regression function and model accuracy was optimized by maximizing adjusted R squared:

\[
R^2 = 1 - \frac{RSS}{TSS} = 1 - \frac{\sum (r_{exp} - r_{cat})^2}{\sum (r_{exp} - \bar{r}_{exp})^2}
\]

In order to visualize the accuracy of model regression, a parity plot of predicted rates with respect to observed rates for 10FeCe, 1Cr/10FeCe and 2Cr/10FeCe was displayed is figure 43. Details of the regressed kinetic parameters are summarized in table 15. Meanwhile, activation energies of propane dehydrogenation and dry reforming over similar catalyst system has been summarized in Table 16 for clarifying the consistency. As seen from Table 15, the true activation energy for propane CO\textsubscript{2}-assisted propane dehydrogenation is 109 kJ/mol. Upon impregnating Cr on the FeCe surface, the activation energy was decreased drastically down to 44.4 and 28.4kJ/mol, depending on the Cr surface density. The differences in activation energy implies that as compared to the bare support surface, propane molecules are preferably activated on the Cr active sites. On the other hand, the activation energies of propane dry reforming is less affected by supported Cr species, indicating that dry reforming pathway is contributed mostly from FeCe oxide while Cr active sites is more selective towards propane dehydrogenation, which is also consistent with high selectivity reported in most Cr-related catalyst (Cr/Silica\textsuperscript{32, 33, 35}, Cr/SBA\textsuperscript{39, 148}, Cr/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{148}, etc) in the CO\textsubscript{2}-assisted propane dehydrogenation. In addition, when taking the second order derivative of the linearized Arrhenius equation with respect to temperature,

\[
\frac{d^2 k(T)}{dT^2} = \frac{-2k_0Ea}{RT^3}
\]
The numeric value of the second derivative is negative for all reaction temperature above absolute zero, indicating that the higher activation energy, the smaller rate constant increment with respect to temperature. In other words, although Cr-related catalyst exhibited higher propane reactivity in the low temperature range, the rate constant for 10FeCe catalyst increases faster and finally outpaces that of CrO\textsubscript{x} catalysts. In this case, propane conversion is expected to be higher over FeCe oxides, which is consistent with our aforementioned observations in Table 11 and figure 19.

Figure 44 compares the result of kinetic model with catalytic data reported previously as a function of propane partial pressure. It is evident that based on the set of kinetic parameters regressed from the model, both predicted propane consumption rates and propylene production rates fitted well with experimental observations. Along with the essential activation energy from open literature summarized in Table 16, the consistency and validity of the model could be guaranteed. However, it should be noted that the current kinetic model is not capable of precisely predicting the catalytic performance far outside reaction conditions discussed above. For instance, as stated several times previously, competitive adsorption of propane and CO\textsubscript{2} will be non-ignorable at high partial pressure regime (above 15%), which for sure alters the adsorption constants of both propane and CO\textsubscript{2}, thus nullifying the previous regression. Besides, as temperature keep increasing approaching 800°C, the net rate of C-C cracking and coke formation\textsuperscript{146} will be boosted and lead to a deficiency in total carbon balance and hydrogen balance. In that case, an additional deactivation model is required to better describe the reaction system.

<table>
<thead>
<tr>
<th>Reaction rate constants and activation energies</th>
<th>PDH</th>
<th>DRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>k0, Ea (kJ/mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10FeCe</td>
<td>1.49*10\textsuperscript{-5} 109.4</td>
<td>2.57*10\textsuperscript{-5} 140.1</td>
</tr>
</tbody>
</table>
Table 16. Activation energies of propane PDH reported from open literature obtained with different methods.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PDH, Ea (kJ/mol)</th>
<th>Catalyst</th>
<th>DRF, Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Sn/CeO$_2$</td>
<td>41.48</td>
<td>Co$_3$Pt$_1$/CeO$_2$</td>
<td>126</td>
</tr>
<tr>
<td>Cr/Al$_2$O$_3$</td>
<td>35.5</td>
<td>Co-Ni/Al$_2$O$_3$</td>
<td>92.3</td>
</tr>
<tr>
<td>NbO$_4$/CeO$_2$</td>
<td>45.2-69.2</td>
<td>Ni$_3$Pt/CeO$_2$</td>
<td>119</td>
</tr>
<tr>
<td>Cr/SiAlO$_x$</td>
<td>up to 40</td>
<td>Ni/Mg(Al)O$_x$</td>
<td>93</td>
</tr>
</tbody>
</table>

Figure 43. Parity plot of propylene rates fitted and experimentally observed.
Figure 44. Model predictions of propane consumption rate and propylene formation rates under 823K with varying propane partial pressure.
6. Conclusions

With the relatively simple structure and unique double bond, propylene can participate in many types of organic reactions, and its downstream products can be found everywhere in daily life and making modern life much easier for people. Behind the role of propylene, propane dehydrogenation technique is undoubtedly one of the most important pathways to produce propylene and has been industrialized for many years. But still, the inner pursuit of humankind would not stop here, as they are always looking for alternating pathways with better performances, higher productivity, and more economic benefits. Herein, we found CO$_2$-assisted propane dehydrogenation as a very promising and competitive pathways, due to multiple reasons and considerations. At the same time, the utilization of CO$_2$ is also favored in the big picture of global warming and green house effect. CO$_2$ activation has always been and will continue to be a most heated topic for the following decades, especially with the great ambition to fulfill ‘carbon neutral’, meaning that the net balance between carbon emission to nature and carbon retrieving from nature is zero.

On the other hand, both academic and industrial field are facing technical and scientific problems, for instance, the low productivity and high energy cost in propylene manufacture; the difficulties to overcome CO$_2$ activation energy barrier; the severe coke formation and inevitable catalyst poison and deactivation. As a result, governments and universities and research institutions have been investing large amount of money in the field. As for individual researchers, we feel great responsibility for the chances to investigate and explore in this field to make our own contributions. Particularly, the author’s work is to develop new catalysts for CO$_2$-assisted propane dehydrogenation to propylene (CO$_2$-ODH), to validate the feasibility and potentials of the catalyst design idea, and to explain the chemistry behind.

After a thorough literature research, we found that Mars-van-Krevelen mechanism has been quite frequently and commonly agreed to be adapted to explain the propane activation
process over metal oxide catalysts. Especially, transition metals with multiple oxidation states and redox cycle can be utilized in CO$_2$-ODH, including CrO$_x$, VO$_x$, MoO$_x$, WO$_x$, etc. Speaking of redox cycle, however, we cannot forget about the rare-earth metal—cerium. Cerium oxide is featured by its superb oxygen mobility and oxygen storage capacity, as well as its non-stoichiometry often exhibited as oxygen vacancies under multiple gas phase environments. Furthermore, transition metal dopants inside cerium oxide lattice can form massive amount of ‘hybrid’ oxygen sites (Fe-O-Ce structures) and enhance the redox properties of CeO$_2$, making the oxygen migration much easier with lower energy barrier. In this case, we were very curious about how the dopant effect functions in CO$_2$-ODH reaction. At the same time, supported transition metal oxides was also investigated in this work.

From the periodic table, we picked Fe as dopant and successfully synthesized FeCe and CrO$_x$/FeCe catalysts with conventional co-precipitation and incipient wetness impregnation methods. As a first move, we focused on the textual and structural analysis of all the materials. Based on our lab facilities and collaborating with other groups, we tested the samples with a wide variety of characterization techniques, including BET, XRD, XPS, Raman, TEM, STEM/EELS and TPR. A single cerianite crystalline phase was observed for all Fe-doped CeO$_2$ samples without even nano-sized hematite phase, indicating that Fe ions are uniformly dissolved inside ceria lattice. With the impregnation of CrO$_x$ no other crystalline phases were introduced, but we did observe the very strong surface interaction between FeCe and CrO$_x$, and the surface interaction originated from high temperature calcination process reconstructed the catalyst surface. The ternary Cr-Fe-Ce catalytic system could be in fact treated as a pseudo-binary system, with well-defined FeCe oxides in the bulk and supported CrO$_x$ on the surface. Besides, the H$_2$-TPR and extended experiments confirmed that the reducibility of FeCe improved with increasing amount of Fe loading. When switching to CrO$_x$/FeCe, the signature Fe-O-Ce structure disappeared, and Cr-O sites dominated instead.
In the test of catalytic activity with standard and normalized reaction parameters obtained from open literature in the community (550°C, 20mL/min total flowrate with 5% C₃H₈ and 5% CO₂, 200mg catalyst loading), we found a monotonic increase in both propane conversion and propylene selectivity with increasing amount of Fe dopants, starting from the inert synthetic CeO₂ all the way up to 22% propane conversion with 50% propylene selectivity. At the same time, the CO₂ conversion for higher FeCe samples is even above propane conversion, which is a big achievement comparing to many peers work in this field. On the other hand, the CrOₓ catalyst exhibited its unique advantages at lower operating temperatures below 500°C but outperformed by FeCe oxides at high temperatures. Furthermore, we investigated the effect of reaction temperature, residence time and C₃H₈/CO₂ feed ratio, and found that those behaviors are basically consistent with the thermo and kinetic perspective viewpoint: we can achieve promoted conversions at higher temperature and high residence time (lower gas flow rates), and we can improve selectivity at lower CO₂ feed ratios. Particularly, the propane conversion is not affected by CO₂ feed ratio, indicating that the surface propane and CO₂ activation process is relatively independent from each other.

In order to further explore our catalyst system and provide molecular level of information in the reaction process, we stimulated differential reactor in the kinetic regime, studied catalytic behaviors in the kinetic regime and developed a Mars-van-Krevelen surface reaction kinetic model for the catalytic system. The study of partial pressure dependence revealed that the propane consumption rate is positively correlated with its initial partial pressure, while the propylene formation rate features a linear relationship. The apparent activation energy is slightly reduced with CrOₓ catalyst. A brief power-law kinetic study revealed that reaction order of propane located in the range of 0.65 to 0.75, while CO₂ appeared as zero order in the reaction system. The negative role of CO₂ was found in propylene formation rate. Especially in the kinetic regime, CrOₓ activities at lower temperatures is much greater than FeCe oxides, but a greater thermal promotional effect
over FeCe oxides is also clearly observed. As a result, at 600°C the FeCe oxides once again outperformed CrOx, which is to some point consistent with the catalytic studies as described before.

After the discussions in kinetic regime, we developed a MvK surface reaction kinetic model, with focuses over ODH, DRF and RWGS in the complex reaction network. Based on literature research (computational and mechanistic study) and our own experimental data and understanding, we proposed fourteen elementary steps including adsorption, desorption and surface reactions, derived rate expressions for ODH, DRF, RWGS, and regressed important kinetic parameters including rate constants, intrinsic activation energy and equilibrium adsorption constants. From low FeCe to high FeCe, the activation energy remained the same while rate constants almost increased proportionally with Fe concentration, suggesting that the increasing Fe enriched Fe-O-Ce sites with the same structure over FeCe materials. As for Cr samples, the rate constants were promoted, but a dramatic decrease in the activation energy suggested that the nature of active sites diverged from the original Fe-O-Ce structure. DRF pathway was suppressed in both high FeCe and Cr cases, which is consistent with the elevated propylene selectivity in corresponding scenarios.

As the last part of our work, we tested the catalyst stability and studied the cause of deactivations. 5FeCe and 10FeCe exhibited very promising stability, with just slight decrease in propane conversion after 24 hours TOS, while most catalysts in this field suffered from severe deactivation even after less than 6 hours. As for Cr oxides, they were even more stable with first 10 hours without deactivation, but out of which a severe deactivation was observed. In this case, we proposed a dual redox cycle for Ce^{IV}/Ce^{III} and Cr^{VI}/Cr^{III} to explain the unique deactivation patterns for Cr oxides. In the post-reaction material characterizations, we found that coke formation was still a major problem for low FeCe oxides, but from 10FeCe we observed very limited coke formation after 24 hours continuous reaction, which is very rare in the alkane conversion studied. Combining XPS,
Raman, STEM/EELS results, we finally confirmed coke formation as major cause of deactivation for low FeCe and CrOₓ oxides, while the Fe migration/aggregation and sintering as a major deactivation reason for 10FeCe samples.
7. Discussion of future works

Up to now, we have presented a relative complete study of FeCe oxide materials in propane CO$_2$-ODH. However, there are still several aspects that worth further investigation.

First of all, although FeCe oxides can be regarded as a promising catalyst, the very limited surface area prevents itself from becoming a good support choice for surface CrO$_x$ species. There are some literatures discussing the synthesis of CeO$_2$ with high surface area, but few of them could be applied as our synthesis strategy. The so-called high surface area CeO$_2$ is merely 100 m$^2$/g as compared to our cases (~70 m$^2$/g), which is not really an essential improvement. In most cases, the CeO$_2$ is reported with high surface area because of a relative low calcination temperature (at maximum 500°C), which certainly cannot be applied in our cases since our temperature range were set to be 450 to 600°C and we need to minimize the physical and mechanical changes to the samples due to thermal effect. Also, those reports mostly pertain to pure cerium oxide, it is not certain if FeCe has been adapted in the cases. Regarding these limitations, it could be of great importance to introduce and collaborate with new synthesis techniques. For instance, we can put more efforts in developing synthesis techniques for high surface area Fe-doped CeO$_2$, or making materials more uniform with hydrothermal methods, or controlling particle morphologies including nanorods, nanotubes and nanospheres to investigate in the facet-dependent activities and if possible, to combine with a DFT study and show some consistency.

Secondly, we already have some inspection and postulation that propylene selectivity is correlated with surface oxygen vacancy concentration qualitatively. However, the reason behind is still ambiguous. It could be due to the oxygen defect itself, but also it can be the nearest neighbour effect of oxygen defects on the neighbouring oxygen atoms, making it active and selective only for ODH pathway. On the other hand, while selectivity can be accurately calculated, the concentration of oxygen defects is still based on a relative
indication from Raman Spectroscopy. Our current method may not fully support an accurate determination of non-stoichiometry. Regarding this obstacle, we could possibly try electron paramagnetic resonance (EPR). By studying the spin state and unpaired electrons, we could possibly determine in percentage level of Ce\(^{III}\) and Ce\(^{IV}\) over the FeCe materials and determine the non-stoichiometry. XPS could be rather challenging especially considering the Ce\(^{III}\) percentage might be super low and deconvoluting triplet Ce\(^{IV}\) peaks and doublet Ce\(^{III}\) peaks simultaneously could cause huge deviations in final results and data interpretations. If we are capable of determining the non-stoichiometry of CeO\(_2\) further with in-situ techniques, we can even combine the kinetics of reaction with the kinetics of oxygen diffusion and oxygen sites consumption/replenishment over FeCe catalysts.

Last but not least, doped ceria with transition metals exhibited a periodic trend in oxygen vacancy formation and C-H bond activation according to Janik’s group\(^{149}\). Dopants in groups IV and V alter the reducibility of the surface and dopants in groups X–XII become the reduction center. The optimal M/CeO\(_2\) dopant for methane conversion to CO or CO\(_2\) follows a volcano relationship with oxygen vacancy formation: Highly reducible surfaces will be limited by re-oxidation, whereas surfaces difficult to reduce will show high barriers for C–H bond activation. Transition metal dopants near the peak region of the volcano are Pd, Co, Ni, and Mn. These new materials will also be very interesting to study.
ACKNOWLEDGEMENT

First of all, I’d like to acknowledge my advisor Dr. George Tsilomelekis and all the group members. My whole PhD period was instructed by Dr. Tsilomelekis, starting from his provisions in determining my PhD program, along an insightful path of discussions and feedback in methodology and experimental data, ended with my PhD degree and two independent research papers. During this years’ study, all group members provided me with support in negotiating experimental schedules, building lab facilities, discussing ideas and data.

Besides, we also have very important collaborators, including Dr. Fuat Celik, Dr. Alexander Neimark, Dr. Teddy Asefa from Chemical Engineering department, Dr. Phil Baston from Physics department and Dr. Weiqing Zheng from University of Delaware. These professors and their group provided me with various lab instruments and valuable data interpretation and feedback.

Last, I want to express my thanks to my family and my friends. It was not easy at the beginning to study in another country far from home, but they always encourage me and give me endless support. Even at the most frustrated moments, it feels so great to have them watching myself from the back.

Sincerely,

Hedun Wang
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