

Mesoporous Silica Nanomaterial-Supported Fe(III) Catalysts for Epoxide Ring-Opening Reaction: Effects of Functionalization Solvents and Ligand on Catalysis

By

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ABSTRACT OF THE THESIS

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The interest in the development of new heterogeneous catalysts remains unabated because of their long proven uses in industries as well their prospects of applications in several new and existing industrial and commercial processes. In this respect, mesoporous silica nanomaterials provide a unique advantage for making new and better heterogeneous catalysts because of their surface silanols, which allow for not only for further functionalization but also as catalytic moieties themselves. However, the lack of full knowledge regarding their structure-property relationship has often limited the synthesis of mesoporous silica-based heterogeneous catalysts for a range of catalytic applications. In this project, the effects of different solvents on the density of grafted catalytic groups on mesoporous silica (SBA-15) and the catalytic activity of the resulting materials have been investigated by grafting *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (diamine) and 2-(diphenylphosphino)ethyltriethoxysilane (pph₂) in toluene and 2-propanol. This procedure produced two materials with diamine and pph₂ ligands, respectively. The materials were then coordinated with Fe(III), and the catalytic properties and activities of

the resulting materials were tested for epoxide ring opening reaction. The effect of the ligands as well as the indirect influence of solvent dependent grafting has been discussed.

Dedication

I dedicated this work to all the people of Iraq, my great father, wonderful mother, adorable daughter (Amalbanen), lovely wife (Nooralhuda), my brothers (Rafid, Haider, Hussein) and my sister (Noor).

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Abbreviations

°C	Degree Celsius
%	Percent
Å	Angstrom
cc	Cubic centimeter
g	Gram
mg	Milligram
GC	Gas Chromatography
TEM	Transmission Electron Microscopy
BET	Brunauer-Emmett-Teller
TOF	Turn Over Frequency
h	Hour
h ⁻¹	Inverse hour
IPA	Isopropanol
nm	Nanometer
m ² /g	Meter square per gram
Tol	Toluene
en / diamine	<i>N</i> -(2-aminoethyl)-3-aminopropyltrimethoxysilane
pph ₂	ethyl (diphenylphosphine)
N ₂	Nitrogen
EA	Element Analysis
TEOS	Tetraethyl orthosilicate
mL	Milliliter
mmol.....	Millimolar

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1. Introduction

In this universe an unlimited number of chemical, biological, or biochemical reactions occur every single moment, and many of these chemical reactions almost always need energy to take place. This energy is called activation energy (EA). There are two definitions of activation energy. The first definition is the energy required to convert the reactant molecules to the active state, and the second definition is the least amount of energy a molecule needs to undergo the reaction. In this context, there is an important question that needs to be addressed in the interest of energy conservation: is it possible to reduce the amount of activation energy or the energy required for the reactions? The answer is yes, as it is achievable with the help of catalysts or via catalysis! Among the most important properties that characterize the typical catalysts or catalysis, the catalyst does not change its qualities during the interaction, and it enters and leaves the reaction processes with the same composition and qualities, without undergoing changes or alterations. Figure 1 shows the EA (activation energy) of the reaction with a catalyst, which is lower than that of without a catalyst.¹

The term catalyst was first coined by Berzelius in 1836 to explain a new entity capable of promoting reactions and their production of a given chemical product.² Since then, the field of “catalysis” has progressed immensely that today there is hardly any process available and a commercial chemical product which does not use a catalyst.³

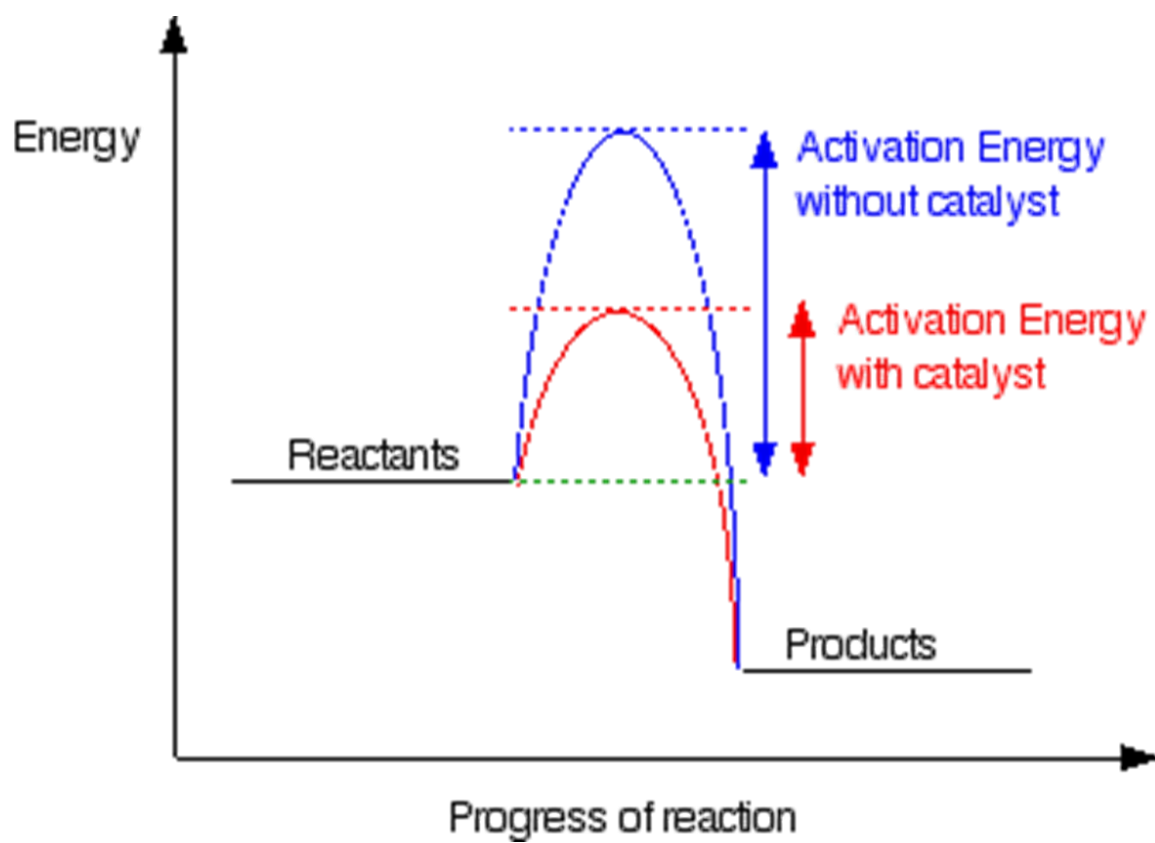


Figure 1. The activation energy of the reaction with and without a catalyst.¹

1.1. Types of Catalysts

In general, catalysts can be divided into two categories: heterogeneous and homogeneous. A homogeneous catalyst is one that is in the same phase as those of the reactant, while a heterogeneous catalyst is one that is in different phase (typically solid) as those of the reactant. As such there are many differences between homogeneous and heterogeneous catalysts.²

1) Recyclability. A heterogeneous catalyst can be easily recycled and reused compared to homogeneous catalyst. Thus, the latter is relatively more expensive.

2) Thermal stability. A heterogeneous catalyst tends to be relatively more stable in harsh reaction conditions, for example at temperatures higher than 250 °C; conversely, a homogeneous catalyst has limited stability under similar conditions.

3) Separation of the catalyst. To separate homogeneous catalyst from a reaction's product is difficult, costly and requires more effort and processes to capture and recycle. On the other hand, separation of heterogeneous catalysts is more easily attainable and relatively cheaper.²

4) Surface properties. By using different synthetic procedures, heterogeneous catalysts can be prepared with better surface properties (*e.g.*, higher surface area) and provide unique advantages over homogeneous version. Improved surface properties and higher surface area often lead to better transport of reactant/products, making the catalytic systems more reactive.¹² These aforementioned advantages of heterogeneous catalysts are among the reasons for their choice of heterogeneous catalysts for various industrial applications as well as for environmental remediation.

1.2. Nanoporous Materials

According to the International Union of Pure and Applied Chemistry (IUPAC) classification, nanoporous materials can be subdivided into three main types based on their pore size: microporous, mesoporous and macroporous materials.^{4,24,25} Microporous materials are nanoporous materials that have pore size between 0 to 2 nm whereas macroporous materials are at the other end with pore sizes, in the range of 50-1000 nm. In between these two classes, mesoporous materials are nanoporous materials that have 2-50 nm pore size. Figure 2 further explains the three types of nanoporous materials, along with some examples for each type of material.

Besides pore size, another most important feature of mesoporous materials is their large surface area. Moreover, many nanoporous materials, especially composed of metal oxides, are stable under a wide pH range. Additionally, they have exceptional thermal stability, are harmless and relatively inexpensive. These unique properties bolster their importance many nanoporous materials and account for the great interest to these materials by the scientific community.

For instance, their large desorption capacity and ordered pore structure make many mesoporous materials important for the development of heterogeneous catalyst for the oil industries.⁵ Common types of mesoporous materials that are considered for such applications include mesoporous alumina and mesoporous silica. Mesoporous silica is also considered for many other applications such as sensors, electronics device, and a drug delivery.⁸

Among many types of mesoporous materials reported so far, MCM-41 (Mobile Composition of Matter)⁶ and SBA-15 (Santa Barbara Amorphous)⁷ constitute the two most widely studies and useful important kinds of mesoporous metal oxides. Furthermore, the materials provide a host of applications for catalysis and separations, especially by supporting metal catalytic groups in their channel pores.^{9,10} For example, Newalker and his colleagues successfully showed the ability of SBA-15 for adsorption of light hydrocarbons.¹¹ Das et al. showed that SBA-15 has a distinct nanometer pore which makes it used as a supported material for catalyst.¹²

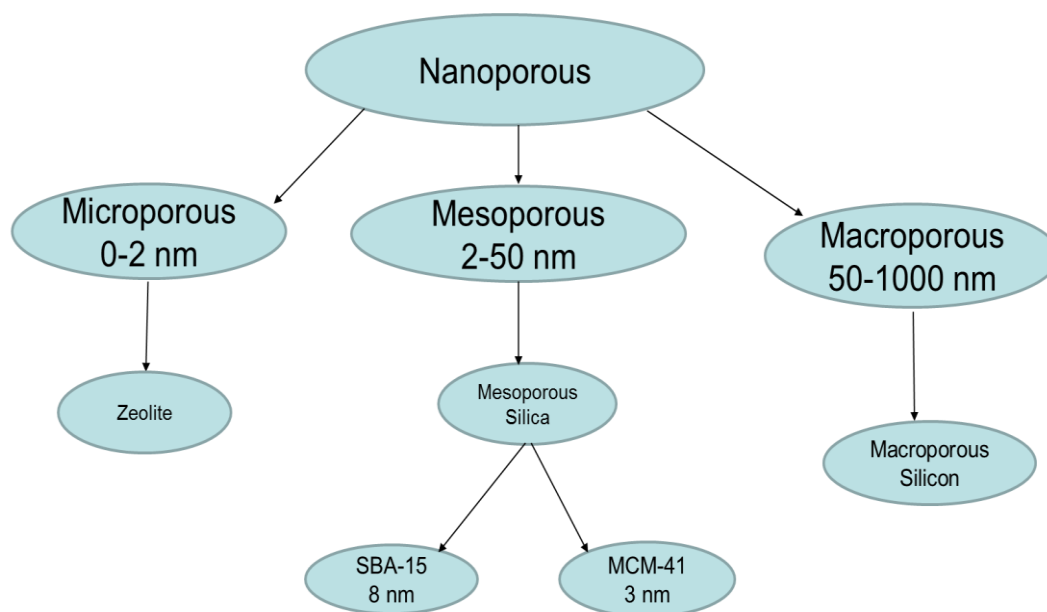


Figure 2. The classification of nanoporous materials and some examples for each class of material.

2. Description of Previous Works

In their paper entitled “Epoxide Ring-Opening Reaction with Mesoporous Silica-Supported Fe(III)”¹⁷ Das et al. reported as to why the epoxide ring-opening reaction is an important class of a useful industrial reaction and how it can be catalyzed by mesoporous silica based heterogeneous catalysts. The reaction (Figure 3, with styrene oxide as epoxide and alcohol ROH as nucleophile), which is typically catalyzed by Lewis acid catalysts, allows for the production of valuable commodity chemicals and many pharmaceutically useful compounds such as 1-phenyl-1,2-ethanediol and 2-alkoxy-2-phenylethanol from the reactions between the styrene oxide and water or alkyl alcohol.^{13,14} Furthermore, these products of the reaction can potentially lead to various antibiotic and antibacterial agents.^{15,16}

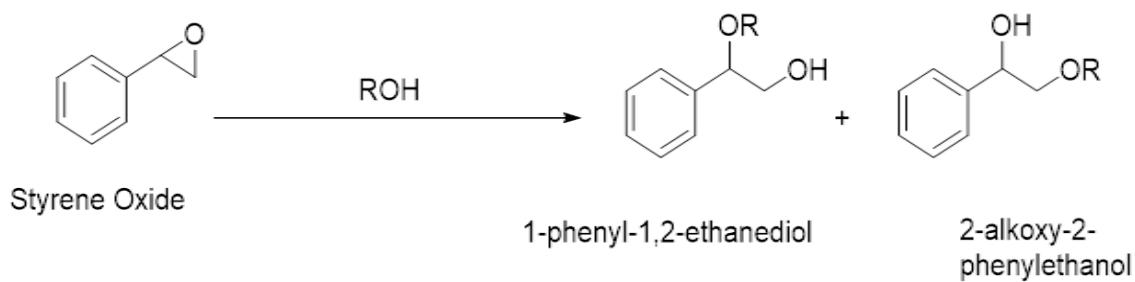


Figure 3. Ring-opening reaction of styrene with alcohol.

To obtain a desirably high yield for such reactions, efficient catalysts need to be used. As documented in Das et al., the reaction can be enhanced by different nucleophiles in the presence of metals.¹⁸⁻²¹ Unfortunately, however, these materials have disadvantages due to their high toxicity, less earth abundance, and high cost.¹⁷ To overcome this issue,

the development of catalytic systems from earth-abundant, inexpensive metals is highly desirable.

Considering this, the use of iron-based catalysts for such reactions is highly appealing as iron is more eco-friendly, inexpensive, and a non-noble metal that is proven to catalyze many reactions.¹⁷ To produce iron-based heterogeneous catalyst, a common strategy involves coordination of the active iron catalytic groups with solid support materials, especially those that have high surface areas. Compared with polymers or zeolite that have such needed high surface areas, mesoporous silica is more attractive for this purpose (or to serve as a good support material for various catalytic groups) because of not only its large surface area but also its physical stability and tunable and bigger pore sizes (compared to those of zeolites).¹⁷ This should result in iron-based mesoporous silica catalysts that can encompass the advantages of both the metal (inexpensiveness, nontoxicity, etc.) and the support material (high surface area, physical stability, etc.).¹⁷

Das et al. reported that the synthesis of mesoporous silica (SBA-15) supported iron catalysts for this reaction. In the work, SBA-15 was grafted with organoamine group as ligands to produce SBA-15-en (amine-grafted SBA-15) by using 3-aminopropyltrimethoxysilane in toluene. This was followed by coordination of iron(III) on the surface of the resulting amine-functionalized mesoporous material, to produce a material denoted as SBA-15-en-Fe(III). This material was successfully used as a catalyst in epoxide ring-opening reaction.^{12,17} Figure 4 details the synthetic steps used to make Ext-SBA-15 and Ext-SBA-15-en-Fe(III).

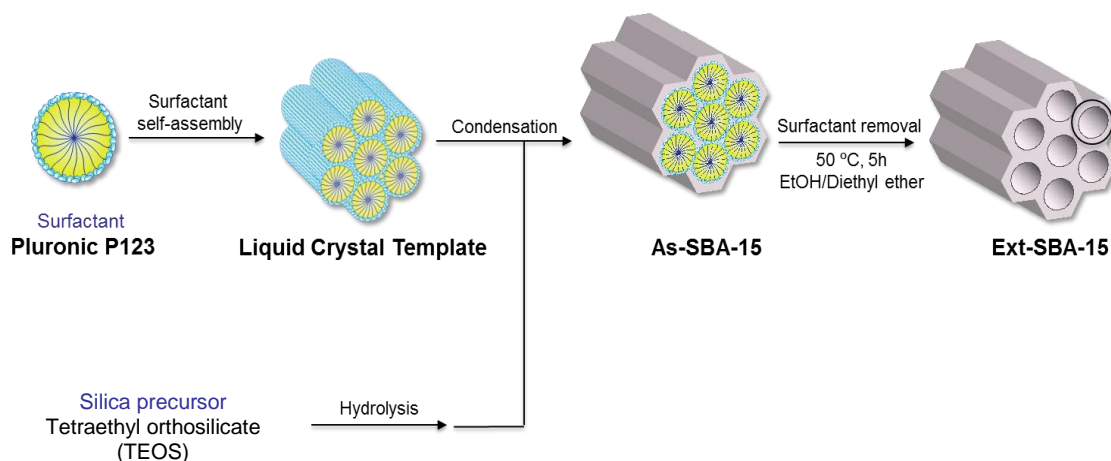


Figure 4. Synthesis of SBA-15 mesoporous silica.¹²

Next, the authors grafted organoamine ligands on the SBA-15 materials using *N*-(2-aminoethyl-3-aminopropyltrimethoxysilane) and toluene as a grafting solvent. This produced a material grafted with diamine groups, denoted as Ext-SBA-15-en. In the final step of this process, they stirred the dried Ext-SBA-15-en in a solution of iron(III) nitrate nonahydrate and distilled water. The resulting, iron(III)-grafted SBA-15 material was noted as Ext-SBA-15-en-Fe(III).¹⁷ Figure 5 shows all the steps used to make this material or catalyst.

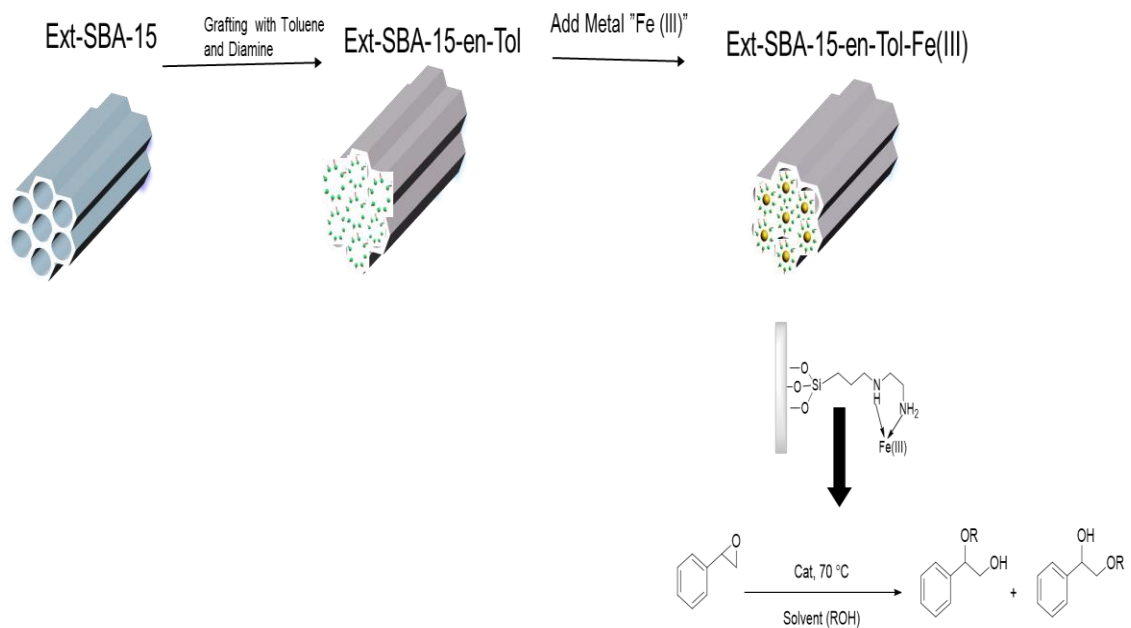


Figure 5. Grafting Ext-SBA-15 with diamine groups using toluene as a solvent, and then coordinating iron(III) on the resulting diamine-grafted SBA-15 material.

In Figure 5, the abbreviation (Tol) refers to toluene, which was used as the solvent for grafting the ligands on the surfaces of the SBA-15 material. Its effect and implications on the catalytic activities and properties of the material will be explained later in the Aim and Significant sections of this thesis.

The catalytic activities of the materials thus prepared were tested in epoxide ring-opening reaction as shown in Figure 5. In the typical reaction, the catalyst Ext-SBA-15-en-Fe(III) was added into a solution of styrene oxide and alcohol, in which the alcohol served both as a solvent and a reactant. Gas chromatography (GC) was used to quantify the ratios of products and reactants as the reaction takes place and to determine the yield reaction as well as relative catalytic activity of the material. As additional experiments, other

nucleophiles (alcohols, water, etc.) were also tested. Furthermore, all the necessary control experiments were carried out. While there is no reaction between the styrene oxide and methanol in room temperature without the catalyst in 5 h, quantitative conversions was achieved in 6 h with the catalyst. In addition, they determined that different types of alcohol were found to give different yields (*e.g.*, methanol gave a yield of about 100% in 6 h in room temperature but ethanol gave a yield of about 100% in longer reaction time of 9 h). On the other hand, when water was used, the reaction was took place much faster compared with the alcohols, giving about 100% yield in 2 h.¹⁷ Additionally, they observed that there was no reaction upon using Ext-SBA-15 instead of Ext-SBA-15-Fe(III); this fact confirmed that iron(III) does all the work while the Ext-SBA-15 serves as a support material.

In order to prove that the iron(III)-containing materials they obtained had similar structural properties as pure mesoporous silica, they characterized all the materials with nitrogen adsorption, TEM and TGA to determine the materials' structural features. Figure 6 shows that all the materials give type IV adsorption isotherms, suggesting that all the materials have the similar ability to adsorb nitrogen or have similar structural features.¹⁷

Moreover, the BET surface area and pore size of the Ext-SBA-15 functionalized with organomine group and iron(III) (*i.e.*, Ext-SBA-15-en) was found to be lower than those of original Ext-SBA-15 (Table 1). This suggests that the grafting synthetic procedure was successful in incorporating organoamine groups and iron(III) moieties in the pores of the SBA-15 material.¹⁷ Figure 7 shows the results clearly.

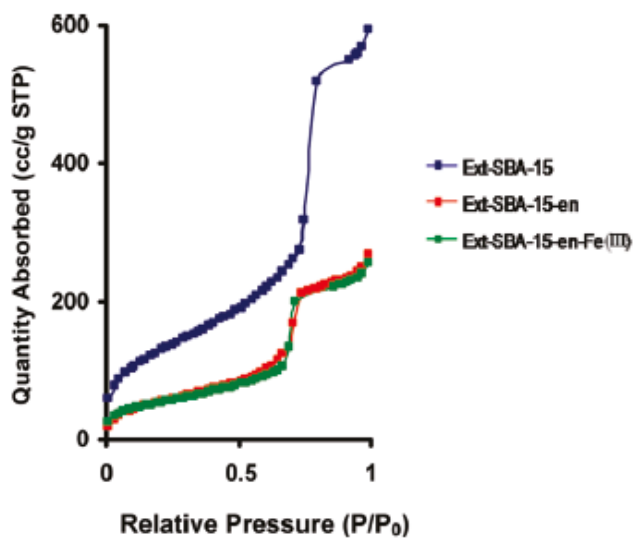


Figure 6. Nitrogen gas adsorption isotherm of Ext-SBA-15, Ext-SBA-15-en and Ext-SBA-15-en-Fe(III).^{12,17}

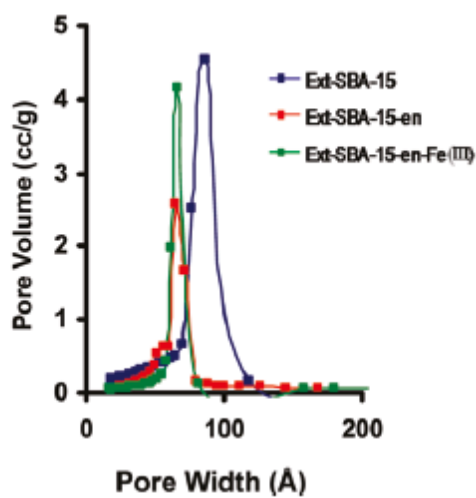


Figure 7. Pore size distribution of Ext-SBA-15, Ext-SBA-15-en and Ext-SBA-15-en-Fe(III).^{12,17}

Table 1. The surface area and pore size of mesoporous material and the Ext-SBA-15-en-Fe (III).

Sample	Surface area(m ² /g)	Pore Size (Å)
Ext-SBA-15	470	72
Ext-SBA-15-en	204	67
Ext-SBA-15-Fe(III)	194	67

Moreover, TEM images (Figure 8) showed that the materials have similar hexagonally ordered structure and channel pores, both before and after grafting with organic groups and Fe(III) species. This suggests that the mesostructured properties such as pore structure and monodispersity did not change after the grafting with amine groups and immobilization with Fe(III) moieties.¹⁷

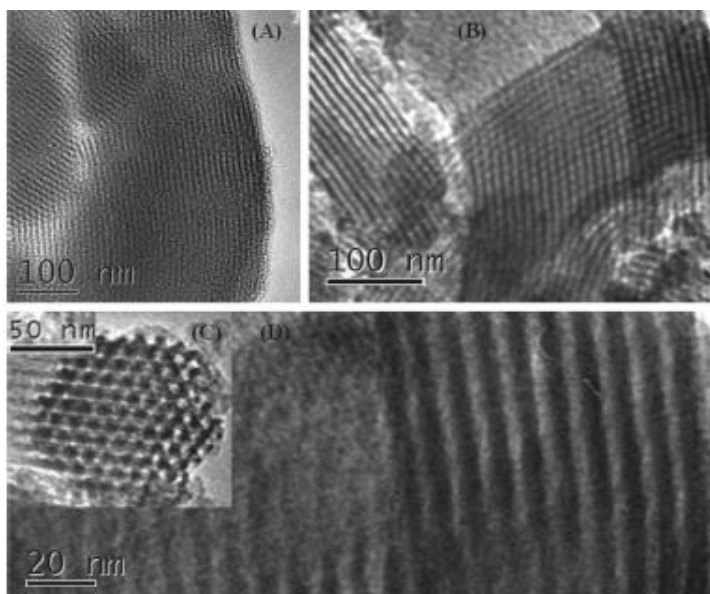


Figure 8. TEM images of (A) Ext-SBA-15 and (B-D) Ext-SBA-15-en-Fe (III).¹⁷

The thermogravimetric analysis (TGA) results (Figure 9) showed that all the materials lost some weight around 100 °C due to absorbed water. Moreover, the amine grafted materials lost weight after around 300 °C, which could be attributed to the loss of organoamine groups from the materials.

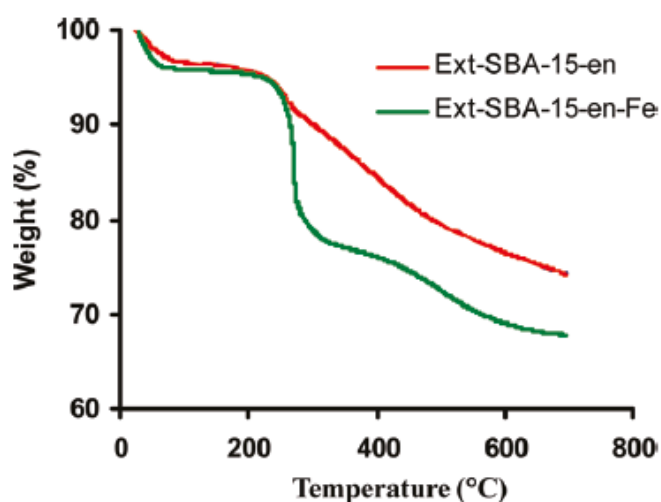


Figure 9. Thermogravimetric of Ext-SBA-15-en and Ext-SBA-15-en-Fe(III).¹⁷

In their paper entitled “Direct synthesis and catalytic application of ordered large pore Aminopropyl-Functionalized SBA-15 Mesoporous Materials”, Wang et al. followed a similar synthetic strategy to make SBA-15-based catalysts and showed their catalytic activity.²² They indicated that the surface area of SBA-NH₂ was smaller than pure SBA-15 because of the presence of amine group in the former. Moreover, they found that the surface areas of the materials decreased as the relative amount of amine groups increased. Their structural features are compiled in Table 2.

Table 2. The structure properties of SBA15, 5% SBA-NH₂, 10% SBA-NH₂, 15% SBA-NH₂ and 20% SBA-NH₂.²²

Sample	Pore diameter (Å)	Surface area (m ² /g)	Wall Thickness (Å)
Pure SBA-15	78	769	29.9
5% SBA-NH ₂	73	723	39.0
10% SBA-NH ₂	67	664	39.5
15% SBA-NH ₂	59	443	46.0
20% SBA-NH ₂	91	290	48.3

However, TEM images (Figure 10 below) showed that all the materials have the same structure as well as a structure similar to that of SBA-15. In addition, all the materials were found to have similar shape and morphology.²²

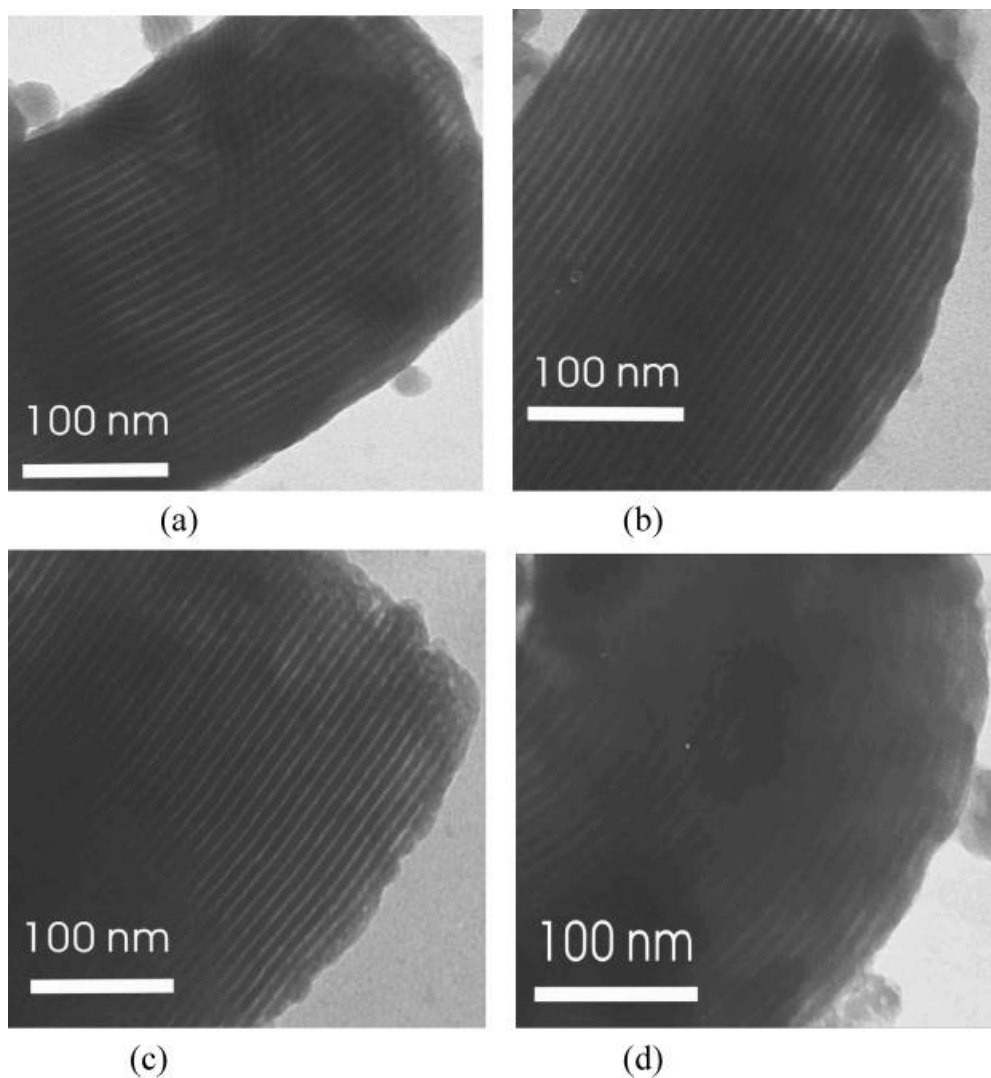


Figure 10. TEM of a) SBA15, b) 10% SBA-NH₂, c) 15% SBA-NH₂, and d) 20% SBA-NH₂.

Moreover, TGA traces showed the weight loss below 100 °C due to the loss of absorbed water in the materials, whose amount is approximately the same for the different materials. Furthermore, some weight loss have been seen in the temperature range of 100-250 °C which is due to the loss of amine groups.²²

3. Goals, Objectives and Significance

3.1 Goals

The synthesis of the Ext-SBA-15 and the grafting of the organoamine ligand on it using organic solvents were described previously. Specifically, in the previous work by Das et al., only *N*-(2-amino ethyl-3-aminopropyltrimethoxysilane) was used as a ligand and toluene as a solvent for grafting Ext-SBA-15 in order to place the Fe(III) on the surface of mesoporous silica.¹⁷ The final product successfully catalyzed the epoxide ring opening reaction between styrene oxide and alcohol. The motivation for the current project includes investigation of the types of ligand and solvents used for grafting step on the materials properties and catalytic activities for epoxide ring opening reaction. These ligands are anchored using different solvents and then iron(III) ions were coordinated on the ligands. The resulting materials were tested for heterogeneous catalysis of epoxide ring opening reaction between styrene oxide and alcohol. From the results in order the best possible combination of ligand and solvent for grafting in the catalytic process and the effect of ligands were assessed.

First, Ext-SBA-15 was taken as silica support and the grafting was carried out with toluene and diamine groups following the procedure reported in Das et al.¹⁷ In order to determine the effect of solvent, here another material was also prepared by using 2-propanol as a solvent for grafting the same aminosilane under the same reaction conditions. In parallel, another set of samples were prepared using 2-diphenylphosphino (ethyltriethoxysilane) as the silane precursor and both toluene and 2-propanol as solvents. These resulting four different materials were then immobilized with iron(III) ions.¹⁷ These gave four different samples that allowed the investigation of the effect of solvent on the

grafting and the affinity of the two different ligands in the materials toward Fe(III) ions. The catalytic activities of these four different materials were then tested for epoxide ring-opening reaction in alcohol. For further comparison, and also to serve as a reference, the same substrates (*i.e.* styrene oxide and alcohols) and same reaction conditions, as reported by Das et al., were employed in the studies. The catalytic activity of the materials was then correlated with the grafted ligands, solvents used for grafting and the structures of the materials. These results might provide further insights into the mechanistic details of similar silica-supported heterogeneous reactions in the future as well. Figure 11 illustrates the experiments performed for the current project.

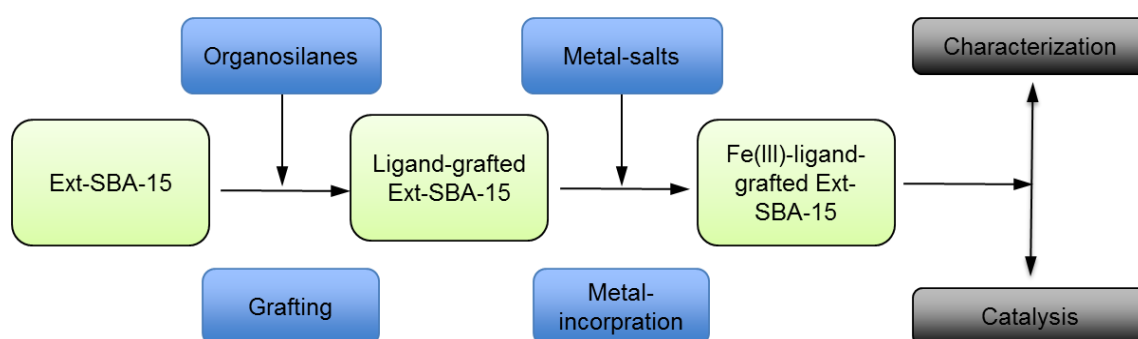


Figure 11. The synthetic steps used for making the materials/catalysts, which include the synthesis of SBA-15, grafting of ligands, and coordination of metal ions on the ligands.

Figure 12 shows the digital images of the four samples obtained by the changing of the synthetic conditions. Specifically, compared with the work in Das et al. the following points summarize the major differences and the grounds for the studies conducted here.

1. Grafting solvent: (2-Propanol) besides toluene was used (2-propanol was tested for the first time to make these materials/catalysts).

2. Ligand types: A diphenylphosphinoethyl group (pph2) was also studied besides (*N*-2-amino ethyl-3-amino propyltrimethoxysilane) (Diamine). It is also worth noting here that diphenylphosphinoethyl group was used for the first time to make such materials and catalysts.

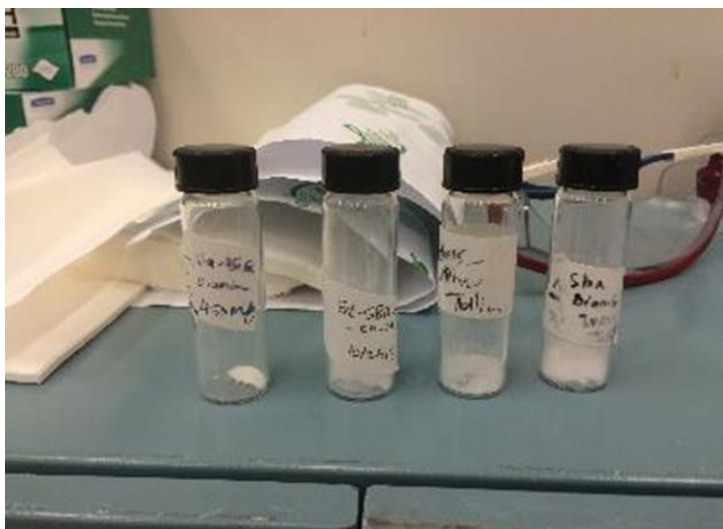


Figure 12. Digital images of the four samples obtained by the changing of the synthetic conditions (ligands or solvents) as described above.

After the synthesis accordingly, four different catalysts obtained were labeled as:

1. Ext-SBA-15-en-Tol-Fe(III) (using toluene as a solvent and diamine as ligand)
2. Ext-SBA-15-en-IPA-Fe(III) (using isopropanol as a solvent and diamine as ligand)
3. Ext-SBA-15-pph2-Tol-Fe(III) (using toluene as a solvent and diphenylphosphine as ligand)
4. Ext-SBA-15-pph2-IPA-Fe(III) (using isopropanol as a solvent and diphenylphosphine as ligand)

3.2 Objectives and Significance

The current study involved the synthesis, characterization and evaluation of catalytic activity of new types of Fe(III)-organofunctionalized-SBA samples. After the four materials mentioned above were obtained, they were characterized by various techniques to verify whether these materials had the similar structure and physical properties to each other as well as to as the reference material (*i.e.*, SBA-15). After the characterization, their catalytic activity was investigated. The ultimate purpose of this present work was to identify the important features needed to make the best possible catalysts for epoxide ring opening reactions for various commercial processes. The steps taken to reach this included: (1) synthesis and characterization of different materials by changing the ligands and the solvents used to place the ligands and (3) evaluation of the catalytic activity for the materials. For characterization of the materials, two main techniques were used: (1) Nitrogen adsorption and an accompanying BET (Brunauer-Emmett-Teller) method to examine the surface area and N₂ adsorption and (2) TEM (transmission electron microscope) imaging to check the structure of the materials. The catalytic conversion was assessed *via* gas chromatography and elemental analysis was used to determine the catalytic turn-over-frequency of the materials. Figure 13 shows a schematic representations of the methods employed for this work.

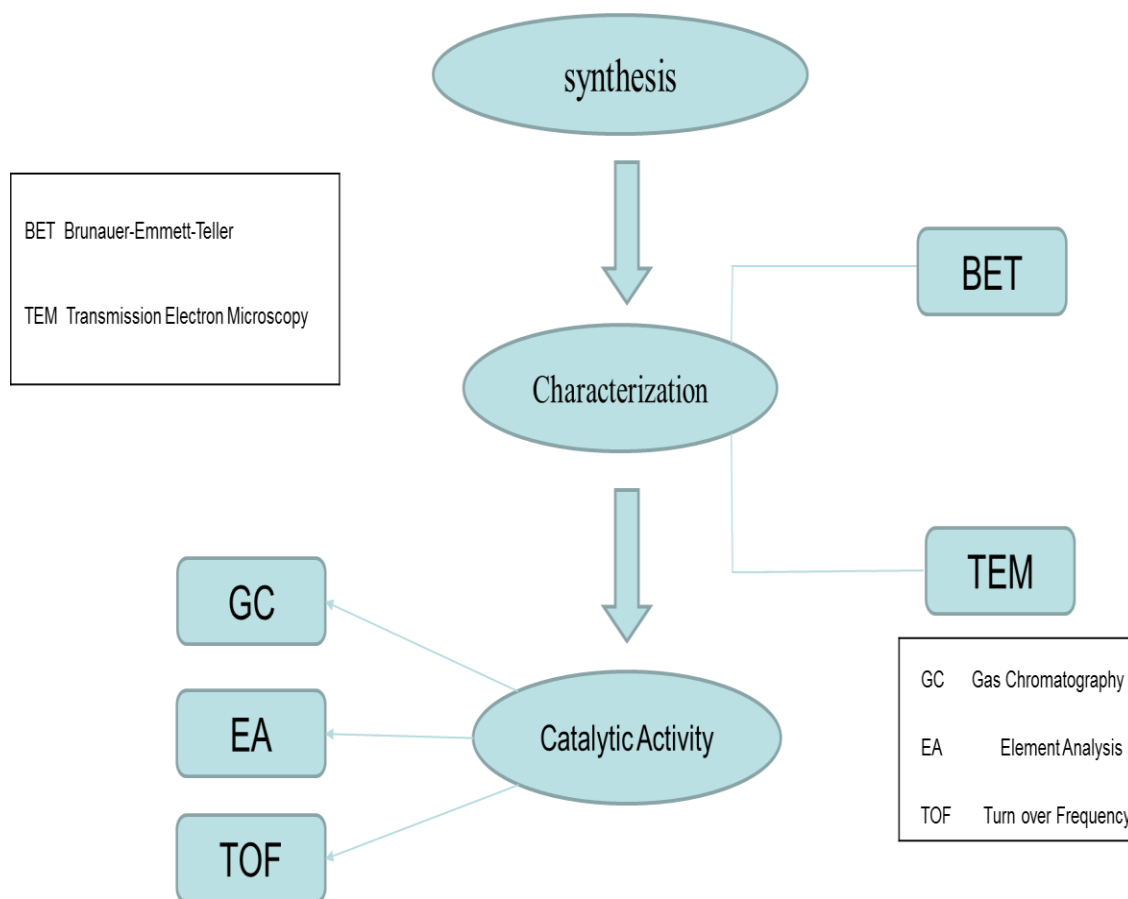


Figure 13. A flow chart representing the steps involved in the current work.

4. Experimental Part

4.1. Chemical and Reagents

Pluronic P123 surfactant with an average molecular weight of 5800 was obtained from BASF (USA). Tetraethyl orthosilicate (98%, TEOS), toluene, styrene oxide (97%), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was purchased from Sigma-Aldrich, USA. HCl (36.5%) was obtained from Fisher scientific (USA). Ethanol, 2-propanol (also called isopropanol), diethyl ether was purchased from Alfa Aesar (USA). *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane, and 2-(diphenylphosphino)ethyltriethoxysilane were obtained from Gelest Inc. (USA).

4.2. Synthesis of the Catalysts

4.2.1. Synthesis of SBA-15 and Ext-SBA-15

The mesoporous particle was synthesized using Pluronic P123 as the templating agent and a mass ratio of P123/HCl/TEOS/ H_2O = 2:12:4.3:26.^{17,23} First, HCl and distilled water were added to Pluronic P123, and the mixture was stirred for 1 hour and 40 °C in a plastic container. Afterwards or after all the Pluronic was completely dissolved, TEOS was added and the mixture was stirred at 40 °C for 24 h. Eventually, the solution was aged in an oven at 65 °C for 24 h. Subsequently, the solution was filtered, and the solid product was washed with a large amount of water several times. The resulting material was noted as as-synthesized SBA-15 (As-SBA-15).

In order to remove the Pluronic P123 templates from the material, the material was stirred with ethanol and diethyl ether. A 4 g of As-synthesized SBA-15 (4 g) was stirred with (400 mL) ethanol and (400 mL) diethyl ether for 5 h at 50 °C. This procedure was done twice in order to ensure the removal of the pluronics P123 templates from the material. The resulting mixture was filtered, and the solid product was washed with ethanol. The solid product was dried in an oven producing mesoporous silica (or denoted here as Ext-SBA-15).¹⁷

4.2.2. Synthesis of Ext-SBA-15-en-Tol.

To make Ext-SBA-15-en-Tol, first Ext-SBA-15 was mixed and stirred with (*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane) to in the presence of toluene. A 500 mg of Ext-SBA-15, 3.68 mmol of the diaminesilane precursor, and 100 mL of toluene were stirred at 80 °C for 6 h. The mixture was filtered, and the solid washed with 20 mL ethanol and 60 mL toluene. The dried result was labeled as (Ext-SBA-15-en-Tol).¹⁷

4.2.3. Synthesis of Ext-SBA-15-en-IPA

The synthesis of this material was done by the same way as previously reported, except isopropanol (2-propanol) was used as a solvent instead of toluene. The mixture was filtered, and the solid product washed with 20 mL of ethanol and 60 mL of isopropanol. The dried material was denoted as Ext-SBA-15-en-IPA.

4.2.4. Synthesis of Ext-SBA-15-en-Tol-Fe(III) and Ext-SBA-15-IPA-Fe(III)

A 200 mg Ext-SBA-15-en-Tol was added to an aqueous solution of iron(III) solution was prepared by dissolving 400 g of the salt $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ in 100 mL distilled water. The mixture was stirred at room temperature for 6 h.¹⁷ It was then filtered, and the solid product was washed with 1000 mL of water to remove non-coordinated, free iron(III) off of the material. The resulting dried materials were denoted as Ext-SBA-15-en-Tol-Fe(III). The same synthetic strategy was also applied to make Ext-SBA-15-en-IPA-Fe(III). Figure 14 the presents the details of the syntheses of two catalyst products, which were obtained and then used as a catalyst in the further ring-opening of epoxide reaction.

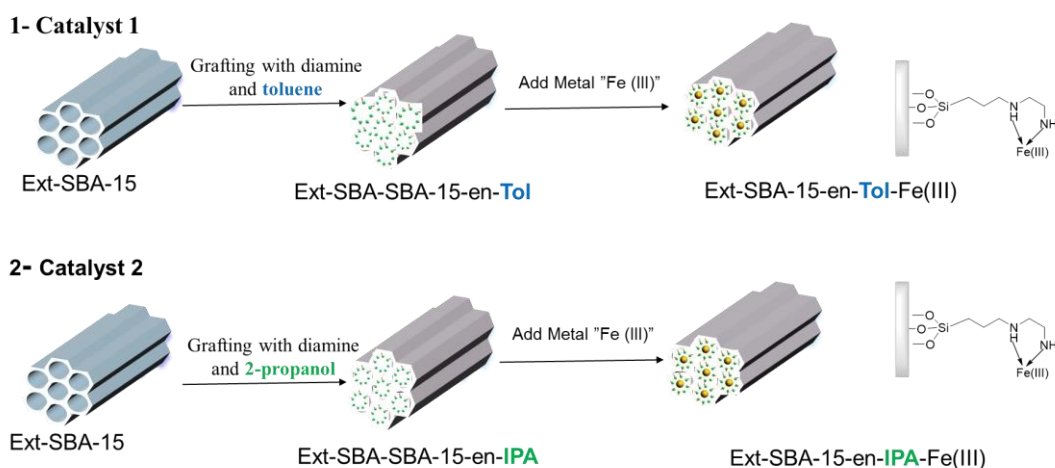


Figure 14. Schematic representation of the preparation of Ext-SBA-15-en-Tol-Fe(III) and Ext-SBA-15-en-IPA-Fe(III).

4.2.5. Synthesis of Ext-SBA-15 -pph2-Tol

This synthesis of Ext-SBA-15-pph2-Tol was achieved by grafting 2-diphenylphosphino(ethyltriethoxysilane) on Ext-SBA-15 material. After adding Fe(III) ions to the materials, the two desired catalysts: Ext-SBA-15-pph2-Tol-Fe(III) and Ext-SBA-15-pph2-IPA-Fe(III) were obtained. The catalytic properties of the two materials were also evaluated in epoxide ring-opening reaction. Figure 15 illustrates the procedure by which these materials were synthesized.

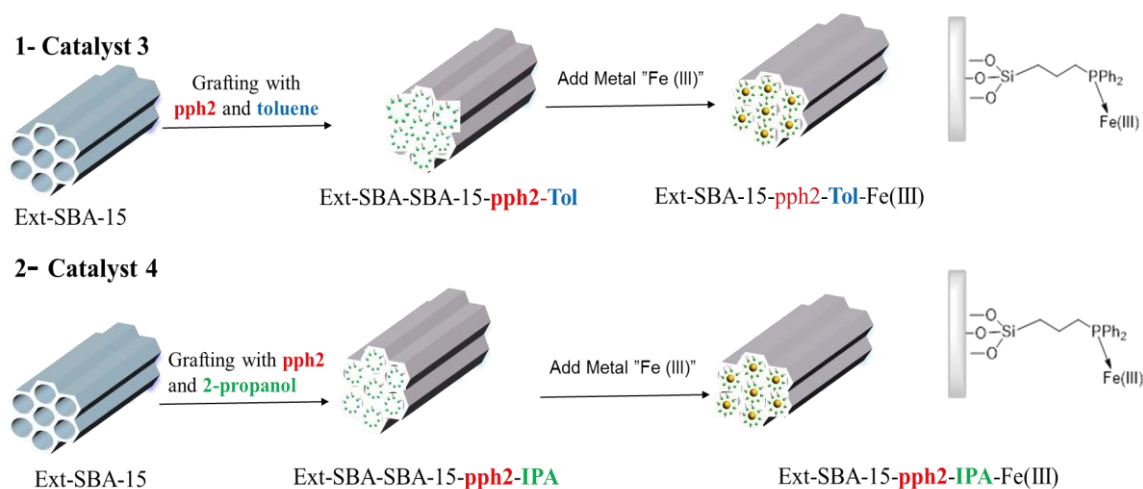


Figure 15. Schematic to prepare Ext-SBA- 15-pph2-Tol-Fe(III) and Ext-SBA-15-pph2-IPA-Fe(III).

4.3. Catalysis

The four materials/catalysts prepared above were then tested in the epoxide ring-opening reaction. Typically, 20 mg of Ext-SBA-en-Tol-Fe (III), 0.9 mmol of styrene oxide and 5 mL of ethanol were mixed and stirred together at 70 °C.¹⁷ The same procedure was followed for the other catalysts as well, namely, Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-15-pph2-Tol-Fe(III) and Ext-SBA-15-pph2-IPA-Fe(III). While the reaction mixture is under stirring, samples were taken from it at different time intervals to check reactant conversion using gas chromatography. Specifically, the samples were taken during 0, 1, 2, 3, 6, 10, 13, 14, and 24 h in order to check the progress of the catalytic reaction and to ultimately evaluate the catalytic activity of each catalyst. Furthermore, styrene oxide and ethanol (without any material or catalyst) was stirred with same ratio previously mentioned to verify if the reaction can take place without the catalyst.

5. Results and Discussion

5.1 Characterization

After the materials have been synthesized, their characterization provides details about their structures and properties. Transmission electron microscopy (TEM) and BET (Brunauer-Emmett-Teller) were particularly used to determine physical features of the materials. These two techniques gave clear information about the physical properties and material structure. Specifically, TEM enabled determination of the structure of the materials while N₂ adsorption enabled determination of the surface area, pore size and pore volume of the materials.

5.1.1. N₂ Gas Adsorption/Desorption Isotherms

The SBA-15 and the four catalysts prepared (Ext-SBA-15-en-Tol-Fe(III), Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-15-pph2-Tol-Fe(III) and Ext-SBA-15-en-IPA-Fe(III)) were all characterized by the nitrogen gas adsorption method using liquid nitrogen with a Micrometrics Tristar 3000 instrument. Prior to the measurement and before the samples were subjected to adsorption of nitrogen, the materials were degassed at 80 °C for 24 h. The N₂ adsorption results indicated that all materials had similar type IV isotherm with hysteresis loops, which is indicate of mesoporous structure. Figure 16 shows that when the relative pressure increases, the quantity of adsorbed N₂ also increases. Similar results have been reported for mesoporous materials previously.^{17,22} These results verify that the four materials/catalysts (Ext-SBA-15-en-Tol-Fe(III), Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-

15-pph2-Tol-Fe(III) and Ext-SBA-15-en-IPA-Fe(III) remain mesoporous, even after functionalization with ligands and iron(III) species is attached on the surfaces of SBA-15.

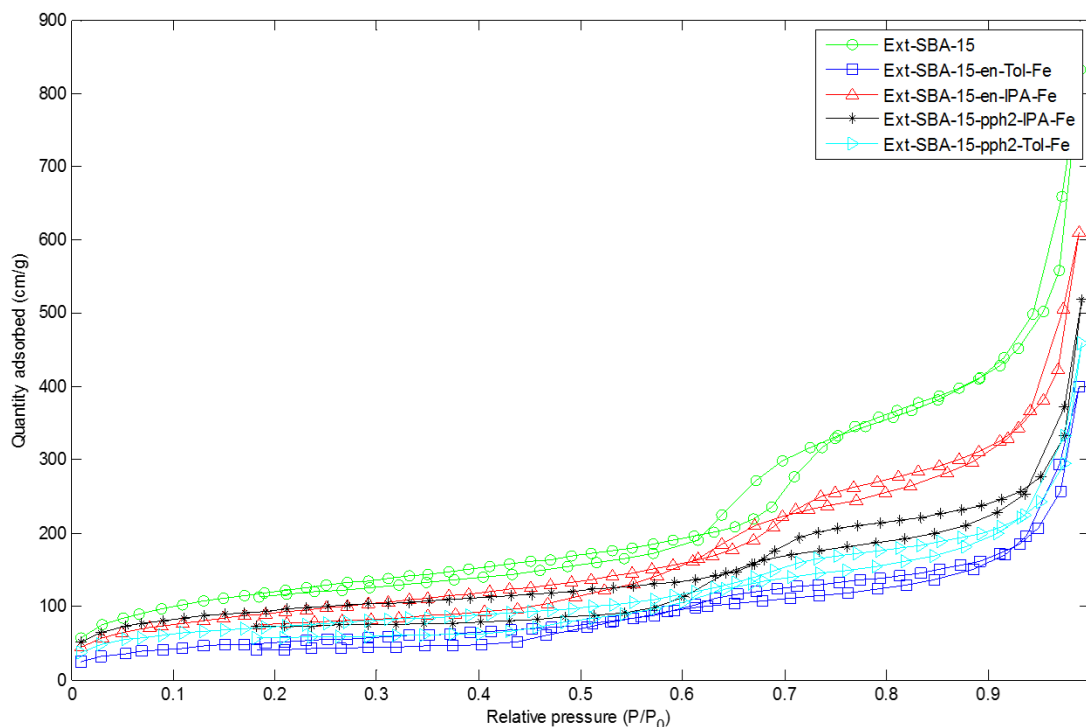


Figure 16. Nitrogen gas adsorption-desorption isotherms of samples: Ext-SBA-15-en-Tol-Fe(III), Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-15-pph2-Tol-Fe(III) and Ext-SBA-15-en-IPA-Fe(III).

5.1.2. BET Surface Area

The BET surface area was also determined for all samples. The BET surface area for Ext-SBA-15, Ext-SBA-15-en-Tol-Fe(III), Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-15-pph2-Tol-Fe(III), and Ext-SBA-15-en-IPA-Fe(III) were found to be 434 m²/g, 250 m²/g, 250 m²/g, 250 m²/g, and 250 m²/g, respectively.

300 m²/g, 318 m²/g, and 325 m²/g, respectively. In addition, the pores sizes were found to be 75 Å, 68 Å, 71 Å, 72 Å, and 70 Å, respectively, and the pores volume were found to be 1.2 cm³/g, 0.9 cm³/g, 0.9 cm³/g, 0.85 cm³/g, and 0.74 cm³/g, respectively. These results are further compiled in Table 3 and Figure 17.

Table 3. The BET surface area, pore sizes and pore volume of Ext-SBA-15 and the four mesoporous catalysts synthesized.

Sample	Surface Area (m ² /g)	Pore Size (Å)	Pore Volume (cm ³ /g)
Ext-SBA-15	434	75	1.2
Ext-SBA-15-en-Tol-Fe(III)	250	68	0.9
Ext-SBA-15-en-IPA-Fe(III)	300	71	0.9
Ext-SBA-15-pph2-Tol-Fe(III)	318	70	0.85
Ext-SBA-15-pph2-IPA-Fe(III)	325	72	0.74

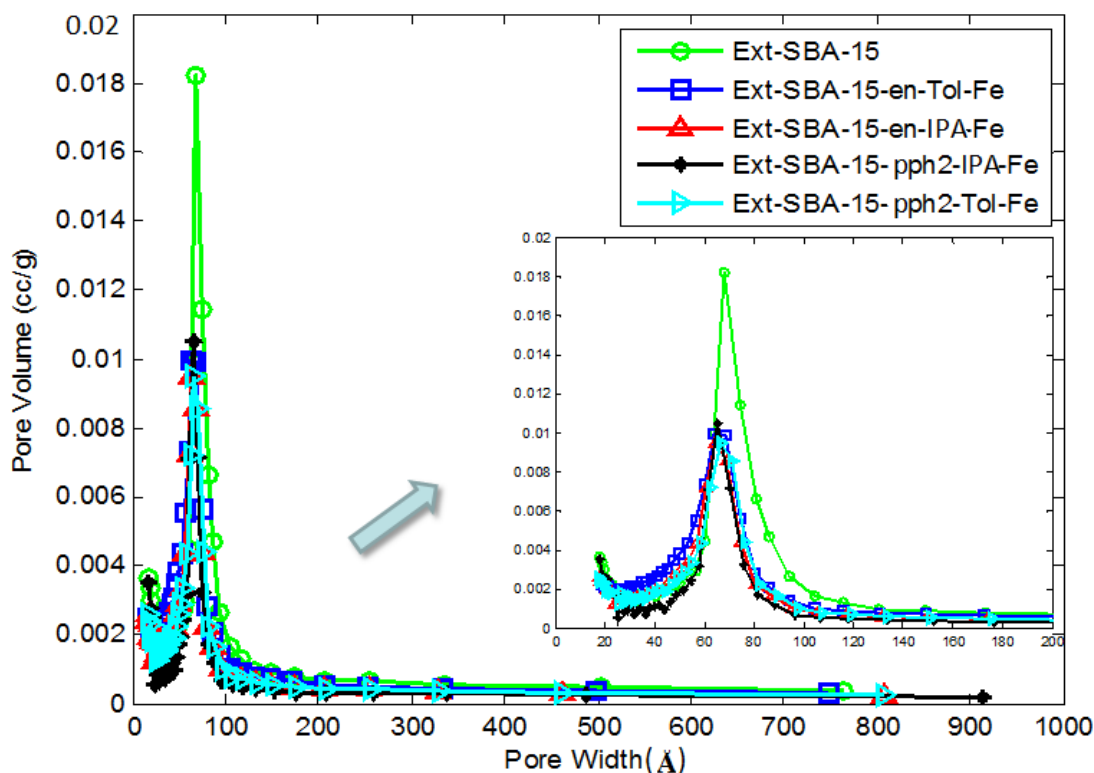


Figure 17. Pore size distribution of Ext-SBA-15 and the four mesoporous catalysts.

The results also indicate that the surface area of the four mesoporous catalysts decreased because of the presence of the organoamine and diphenylphosphine groups and iron(III) species, which occupied the pores of the mesoporous material. The presence of these functional groups in the pores of the materials is also responsible for the lower pore size and pore volume of the mesoporous catalysts compared with Ext-SBA-15; i.e., catalyst 1 (Ext-SBA-15-en-Tol-Fe(III)) and catalyst 2 (Ext-SBA-15-en-IPA-Fe(III)) compared with Ext-SBA-15 as well as catalyst 3 (Ext-SBA-15-pph2-Tol-Fe(III)) and catalyst 4 (Ext-SBA-15-pph2-IPA-Fe(III)) compared with Ext-SBA-15. Similar results were also reported in previous works for related materials.^{17,22}

5.1.3. Transmission Electron Microscopy (TEM)

A JEOL 2010F HR-TEM was used to acquire the TEM images of the materials. The TEM images showed that all materials had not only mesoporous structures but also one that is similar in all cases (Figure 18). In other words, the mesoporous structure of the original, non-functionalized Ext-SBA-15 did not change after grafting with *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane or diphenylphosphino groups and subsequent functionalization with iron(III) moieties. The four catalysts also had similar morphology (monodispersity and mesoporosity) as the original material (Ext-SBA-15).

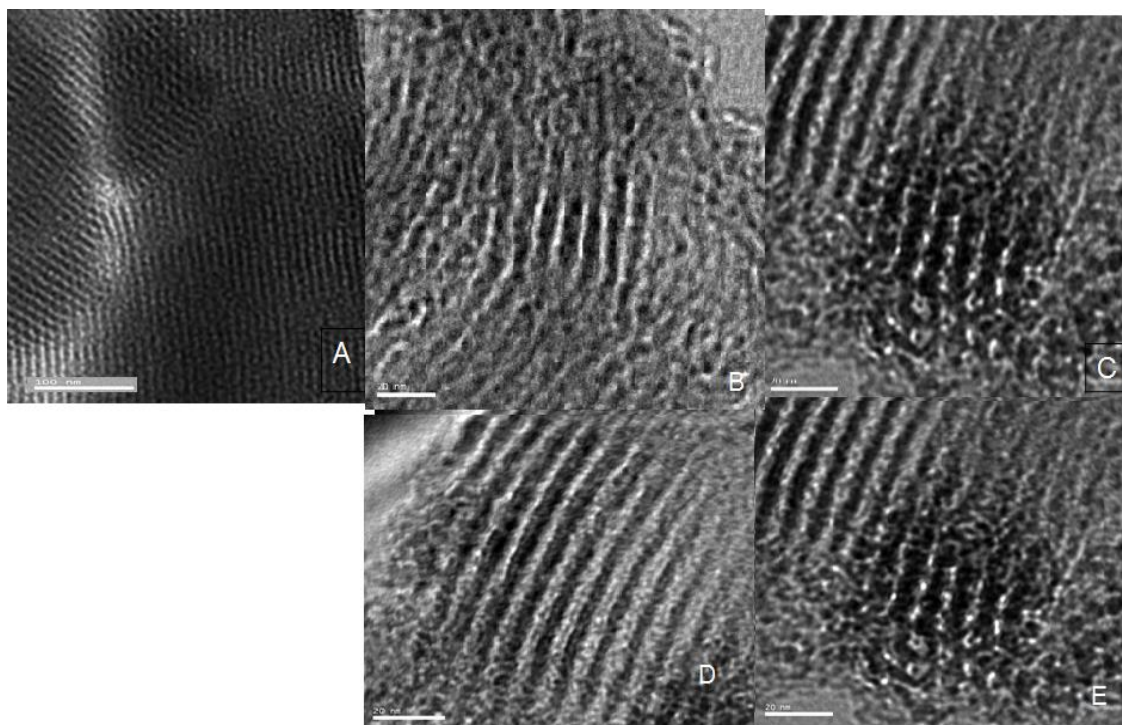


Figure 18. TEM images of A) Ext-SBA-15, B) Ext-SBA-15-en-Tol-Fe(III), C) Ext-SBA-15-en-IPA-Fe(III), D) Ext-SBA-15-pph2-Tol-Fe(III) and E) Ext-SBA-15-pph2-IPA-Fe(III).

5.2. Catalytic Activity

5.2.1. Gas Chromatography

Gas chromatography (GC) was used to measure the conversion of the reactants in time intervals. An Agilent Technologies 6850 GC instrument was used for the experiment. As mentioned previously in the experiment part, the reaction was carried out between the styrene oxide and the ethanol in the presence of the catalysts prepared. After the reaction mixtures were stirred at different times (0, 1, 2, 3, 6, 10, 13, 14 and 24 h), they were measured with GC to calculate the yield for each case.

Five reactions were examined; four of them contained the four catalysts prepared and one without a catalyst (to serve as a reference). All reactions were stirred at 70 °C. The reactions, which contained the catalyst Ext-SBA-15-pph2-IPA-Fe(III) gave the highest reactant conversion and yield. It gave a yield of 35%, 45%, 65%, 75%, 95%, 100%, 100% and 100% in 1, 2, 3, 6, 10, 13, 14 and 24 h, respectively. However, the sample which contained the catalyst Ext-SBA-15-en-Tol-Fe(III) gave a lower yield as it gave 10%, 15%, 20%, 30%, 45%, 60%, 63% and 73% yield in 1, 2, 3, 6, 10, 13, 14 and 24 h, respectively. On the other hand, the sample without catalyst gave no reaction from for almost 10 h, and then only a very low yield of 4%, 7% and 12% in 13 h, 14 h, and 24h. In the case of catalyst Ext-SBA-15-en-IPA-Fe(III), a yield of 26%, 40%, 55%, 70%, 90%, 100%, *ca.* 100% and *ca.* 100% were obtained in 1, 2, 3, 6, 10, 13, 14 and 24 h, respectively. On the other hand, the catalyst Ext-SBA-15-pph2-Tol-Fe(III) gave a yield of 15%, 20%, 25%, 60%, 80%, 90%, *ca.* 100%, and *ca.* 100% in 1, 2, 3, 6, 10, 13, 14 and 24 h, respectively. The results indicated that the reaction mixtures containing catalysts took place significantly faster than those without catalysts. However, these GC-based results alone were not enough to indicate

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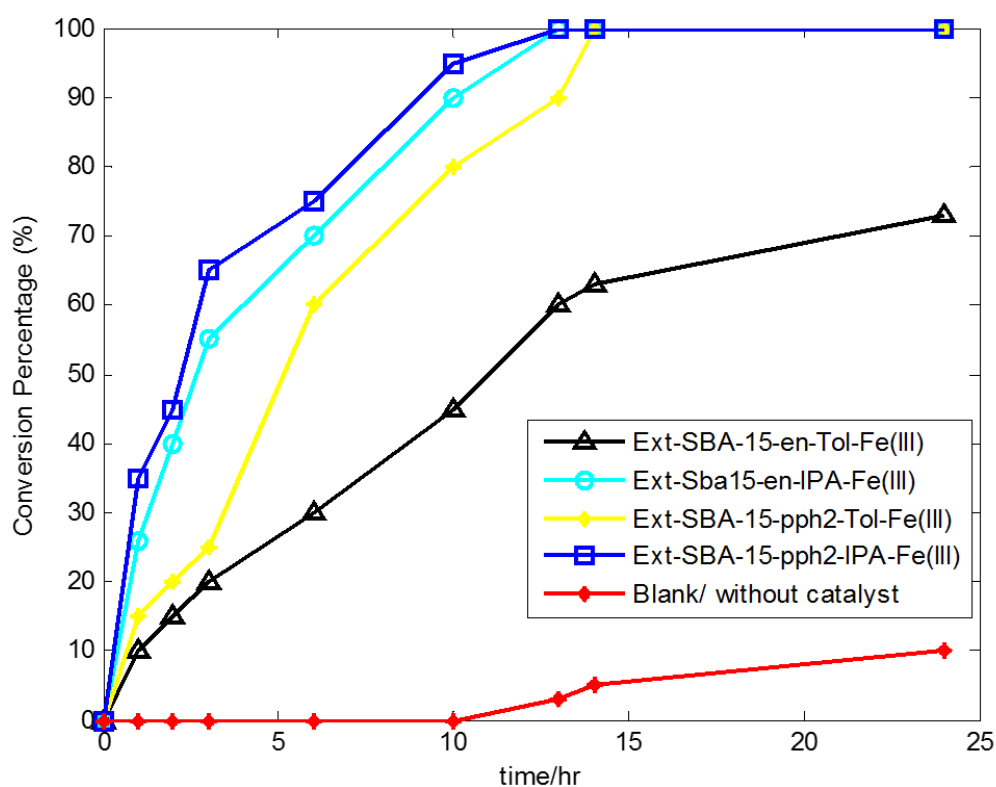


Figure 19. Graphs of catalytic conversion obtained with GC versus reaction time for the four different catalysts synthesized and the reference, where no catalyst was used.

5.2.2. Element Analysis (EA)

The elemental analysis of the four catalysts was obtained at Robertson Microlit Laboratories located at Ledgewood, New Jersey. The element analysis measured all the elements in the samples such as carbon, hydrogen, phosphorus, nitrogen and iron. The results were calculated by ICP-OES analysis. The results indicated that the weight percent (wt. %) of Fe in Ext-SBA-15-en-Tol-Fe(III), Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-15-pph2-Tol-Fe(III) and Ext-SBA-15-pph2-IPA-Fe(III) were 0.15%, 0.32%, 0.31%, and

0.69%, respectively. On the other hand, the wt. % of nitrogen were 3.1% and 5.2% for Ext-SBA-15-en-Tol-Fe(III) and Ext-SBA-15-en-pph2-Fe(III), respectively. However, the wt. % of phosphorous were 0.55% and 0.21% for Ext-SBA-15-pph2-Tol-Fe(III) and Ext-SBA-15-pph2-IPA-Fe(III), respectively. Finally, the wt. % carbon were 12.9%, 8.6%, 6.67% and 5% for Ext-SBA-15-en-Tol-Fe(III), Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-15-pph2-Tol-Fe(III) and Ext-SBA-15-pph2-IPA-Fe(III), respectively. Moreover, the wt. % of hydrogen was 2.9%, 2%, 1.36% and 1.9%, respectively. These results are compiled in Table 5 below.

Table 5. The elemental analysis results for catalysts.

Materials	C%	H%	N%	P%	Fe(III)
Ext-SBA-15-en-Tol-Fe(III)	12.9	2.9	5.2	–	0.15
Ext-SBA-15-pph2-Tol-Fe(III)	8.6	2	3.1	–	0.32
Ext-SBA-15-en-Tol-Fe(III)	6.67	1.36	–	0.55	0.31
Ext-SBA-15-pph2-IPA-Fe(III)	5	1.9	–	0.21	0.69

5.2.3. Catalytic Turn over Frequency (TOF)

After all the results for the catalysts with GC and EA were obtained, the TOF values for the catalysts was calculated to gain insights regarding the intrinsic catalytic efficiency of the materials synthesized for this current study. The TOF values were calculated by using equations 1 and 2.

$$\text{Equation 1} \quad \text{TOF}(h^{-1}) = \frac{\text{Number of moles of product}}{\text{Number of moles of Catalyst} * \text{time}}$$

Equation 2

$$\text{TOF}(h^{-1}) = \frac{\text{Number of moles of styrene oxide} * \text{yield}\%}{\text{Number of moles of iron(III)} * \text{percentage in EA} * \text{time}}$$

During three hours of reaction times, the reaction yields were 20%, 55%, 25% and 65% for Ext-SBA-15-en-Tol-Fe(III), Ext-SBA-15-en-IPA-Fe(III), Ext-SBA-15-pph2-Tol-Fe(III), and Ext-SBA-15-pph2-IPA-Fe(III), respectively. So based on the calculations, Ext-SBA-15-en-IPA-Fe(III) catalyst was found to have the highest TOF, with a value of 68.85 h^{-1} , while Ext-SBA-15-pph2-Tol-Fe(III) was found to have the lowest, with a value of 32.78 h^{-1} . The TOFs of Ext-SBA-15-en-Tol-Fe(III) and Ext-SBA-15-pph2-IPA-Fe(III), on the other hand, were found to have values of 54.18 h^{-1} and 38.28 h^{-1} , respectively. The results are further described in Figure 20 below.

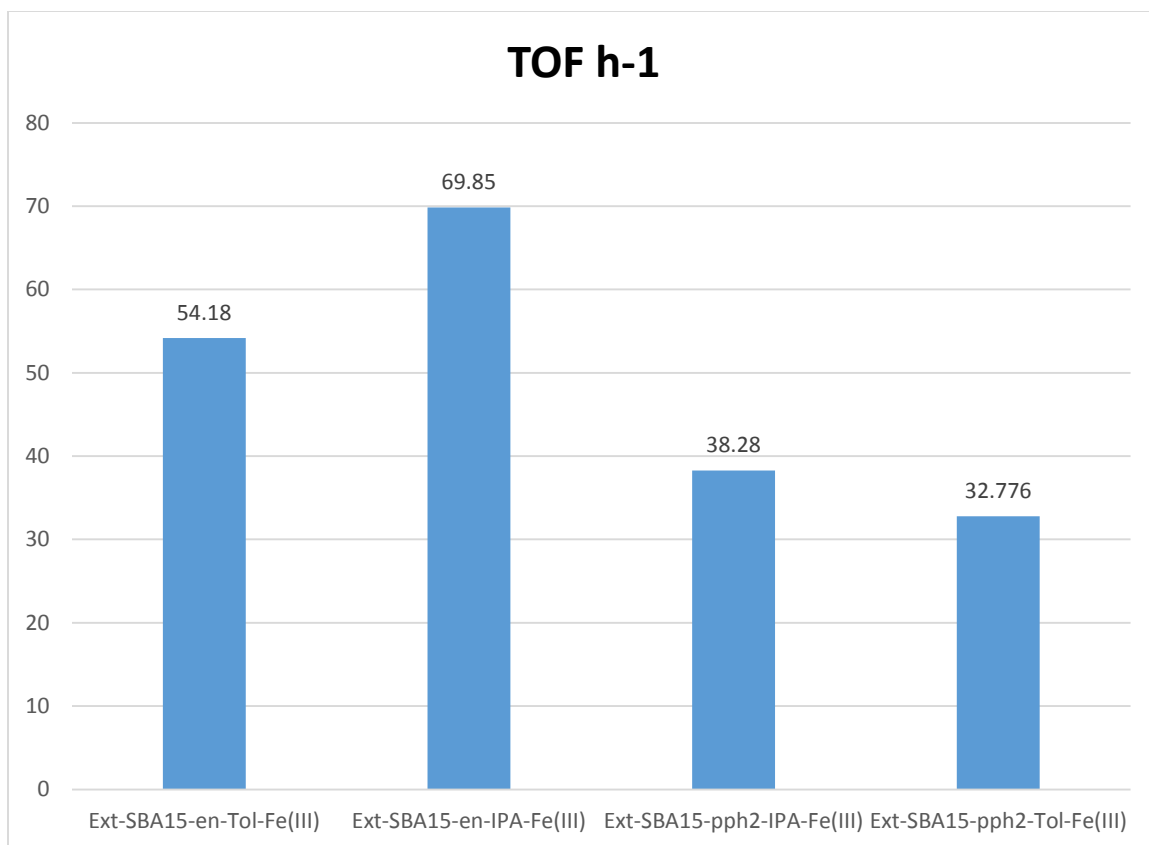


Figure 20. Comparative results of catalytic turn-over-frequency (TOF) for the different iron(III)-based catalysts synthesized with different ligands and by using different solvents.

It is worth adding here that the amount of ligands in the catalysts based on the diamine were significantly larger than those based on pph2, by about 10 times where toluene was used as a solvent and by about 15 times where 2-propanol was used as a solvent. However the catalytic activity for the materials based on the pph2 were only half times lower than those of the activity of the materials based on the diamine, despite the former had much less ligands than the latter. Figure 21 below shows the differences based on the ligands.

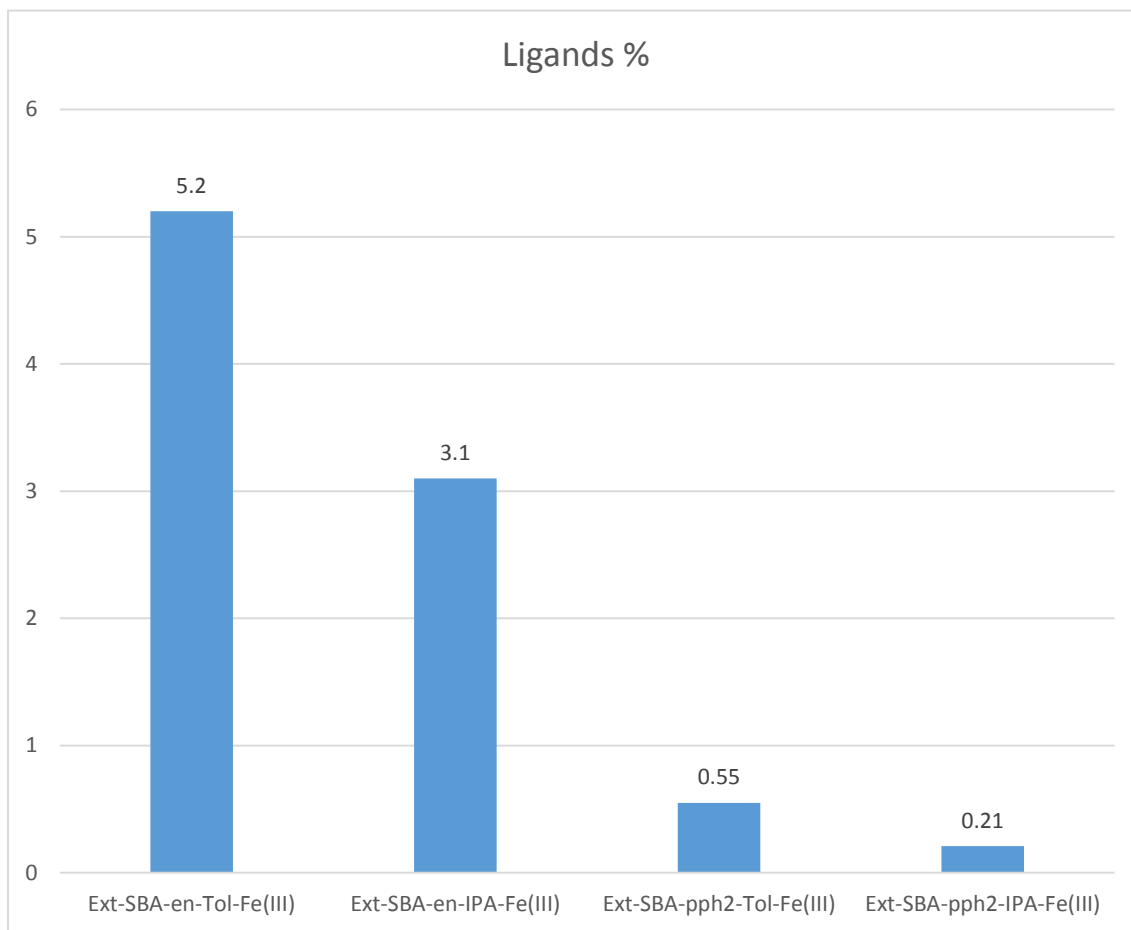


Figure 21. The amount of ligands in each catalyst.

In order to clarify the effects of ligands and the relative catalytic activities of the four different materials, the TOF values obtained above were further normalized based on ligands, besides the amount of iron(III) using the equation below.

$$\text{TOF}(h^{-1}) = \frac{\text{Number of moles of styrene oxide} * \text{yield}\%}{\text{Number of moles of ligands} * \text{percentage in EA} * \text{time}}$$

In this case, catalyst Ext-SBA-15-pph2-IPA-Fe(III) was found to have the highest TOF with a value of 112.96 h^{-1} , whereas catalyst Ext-SBA-15-en-Tol-Fe(III) was found to have the lowest catalytic activity with a value by 4.56 h^{-1} . However, Ext-SBA-15-en-IPA-Fe(III) and Ext-SBA-15-pph2-Tol-Fe(III) were found to have relatively lower values of 7.65 h^{-1} and 43.132 h^{-1} , respectively. So, it appears that the catalytic activities of the samples containing pph2 were much better than those containing diamine where the results were normalized with the ligands besides iron(III) species. These results are compiled in Figure 22.

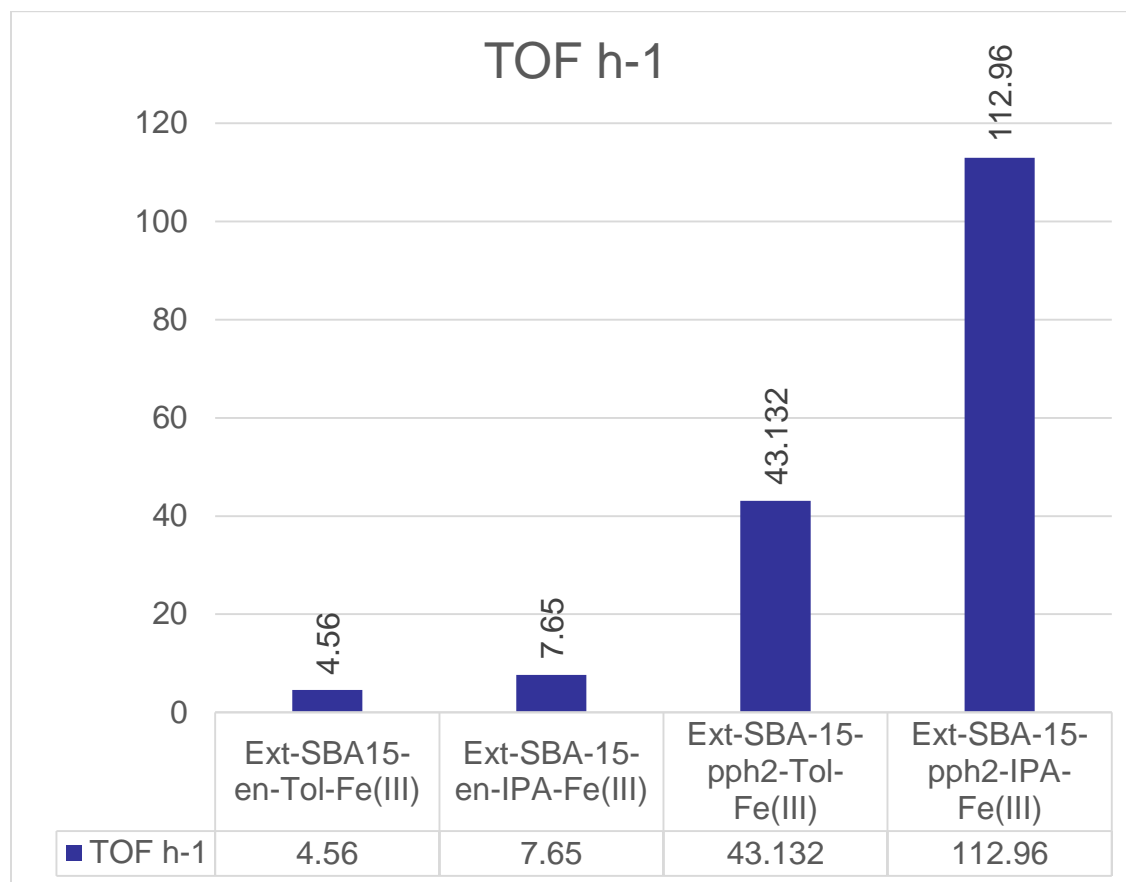


Figure 22. The TOF results based on ligands instead of iron(III)

In fact, the catalyst based on pph₂ has 20 times less ligands compared to the corresponding material based on diamine. In both sets of studies, 2-Propanol was found to be the best grafting solvent for obtaining the best catalyst. Given the fact that many types of ligands are costly, making heterogeneous catalysts with significantly higher catalytic activity using smaller amount of ligands and a solvent that gives optimum grafting, as demonstrated here, is a great approach to deliver efficient catalysts for many industrially important reactions.

Conclusion

Mesoporous silica materials/catalysts that comprised SBA-15, various ligands and iron(III) species for epoxide ring opening reactions were synthesized and their structures and catalytic properties were investigated. Specifically, four samples were obtained using two different ligands and two different solvents. This was followed by anchoring iron (III) to the ligands onto the four different materials. The two types of ligands included *N*-(2-aminoethyl)-3-aminopropyl and diphenylphosphinoethyl groups whereas the two types of solvents included toluene and 2-propanol. The four different materials/catalysts obtained were characterized and the results showed that all the four materials have similar structural features and morphology. The catalytic properties of the four catalysts were then investigated in epoxide ring-opening reaction involving styrene oxide and ethanol. The results of the catalytic activity tests showed that the materials with *N*-(2-aminoethyl)-3-aminopropyl ligand gave the highest TOF. However, despite the materials based on pph₂ gave half as much activity as those based on diamine, the former possessed much less or about 10 times less ligands than the latter. Moreover, it was found that the materials made using 2-propanol as a solvent generally showed better catalytic activity than the corresponding materials made using toluene as a solvent. So, with these results as well as given the higher costs of many types of ligands, the work here has revealed that rational design of catalysts with proper ligands, sustainable precursors (e.g., SBA-15 and iron salt) and the right solvents can lead to highly efficient, cost effective and sustainable heterogeneous catalysts for industrially important reactions and chemical processes.

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