

# Electrostatic Immobilization of Ionic Liquids onto SBA-15 as Heterogenized Catalysts for Esterification of Oleic Acid with Trimethylolpropane

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## Abstract

To overcome the drawbacks of homogeneous catalysts in the synthesis of trimethylolpropane trioleate (TMPTO), ionic liquids with different acidity were electrostatically immobilized onto SBA-15 to obtain heterogenized catalysts. The catalytic performance of the as-prepared two catalysts (IL1/SBA-15 and IL2/SBA-15) was investigated at different temperature (100 -140oC) and molar ratio of oleic acid (OA) to trimethylolpropane (TMP) (3:1 to 5:1) at fixed catalyst dosage of 3 wt. % and reaction time of 20h; where the catalyst IL1/SBA-15 with higher acidity exhibits higher activity. The optimum temperature (at OA: TMP = 3: 1) was obtained at 130oC, where the total conversion was 86.1% and 70% with selectivity towards TMPTO of 95.6% and 92.96% for IL1/SBA-15 and IL2/SBA-15, respectively. Above this temperature, the selectivity began to decrease. The effect of OA: TMP molar ratio showed the increase of conversion (92.7% and 79.1%) with the increase of OA: TMP molar ratio up to 4.5. Further increase in OA concentration results in a damping of the catalytic efficiency of the two catalysts. Through six consecutive runs, the periodicity test refers to the relative stability of the employed catalysts with slightly decrease in activity. All results were interpreted and discussed in detail

## 1. Introduction

Today, as the world continues to grow rapidly and extensive use of mineral oil has caused fear in large fields of growth. This is due to decline in the quantity of mineral oil which would take millions of years to replenish. Also, the contamination caused by mineral oils has also led to many studies into the option of using alternative lubricants as more eco-friendly or green materials (Mahmud, 2014). It was established from the early production and uses of special application lubricants that polyol esters of fatty acid have equal or even better technical properties than mineral oils<sup>2</sup>. Consequently, vegetable oils are the perfect choice for replacing mineral oil (Lathi, 2007). In spite of the excellent lubricating properties (high viscosity index, low volatility and high shear stability), the vegetable oils have several drawbacks that cause their instability and tend to be easily damaged and have restricted their application in the lubricants industries (Wang, 2019). The poor oxidation stability is owing to the contamination of polyunsaturated fatty acids in its composition (Campanella, 2010). Many chemical and biological studies were conducted to reduce the content of polyunsaturated fatty acids and increase the monounsaturated fatty acids (Li, 2012). However, the esterification reaction of fatty acid and polyhydric alcohols as an effective industrial method to obtain desirable polyhydric esters seems to be the favored (Zhang, 2004). Of all these polyesters, in recent years TMPTO have been given considerable attention due to their high thermal and hydrolytic stability due to the absence of  $\beta$ -H (Miles, 1998). Meanwhile, oleic acid (OA) is chosen as a cheap monounsaturated fatty acid for synthesis the polyhydrate ester. The esterification of OA with possesses difficulties among them

is the molecular inherent hindrance of the components of the reaction (Karimi, 2012). At the industrial scale, according to our knowledge, the homogenous acidic catalysts are the most employed. The advantages of the homogeneous catalysts are the high catalytic activity and high selectivity as a result of well-defined molecularly structure. This system of homogeneous catalysis requires additional steps to isolate and purify the final product (Kuzminska, 2015). Using of heterogeneous catalysts could overcome the latter problem but with low activity and selectivity.

Our work is an attempt to solve this problem. Modified catalysts, namely "heterogenized homogeneous catalysts", which possess both advantages of homogeneous and heterogeneous catalyst were applied in OA esterification with TMP. In the synthesis of these catalysts, the ionic liquids (as homogeneous catalyst) were electrostatically immobilized onto SBA-15 to be loosely as Brønsted acids in viscous medium of the reaction.

## 2. Experiment

### 2.1. Materials

All main chemicals used are of analytical grade and the mentioned purity according to the manufacturer and were used without further purification. Tetraethyl orthosilicate (TEOS, Aldrich, 99.999%) and (3-mercaptopropyl) trimethoxysilane (85%, Acros) were used, as silica and organosulfonic acid precursors. Pluronic P123 (with the PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub> molecular structure, M.wt =5800) as a pore regulator was obtained from (BASF Co., USA). 1,4-butane sultone (99%) was purchased from Beijing HWRK Chem. Co., Ltd. Trimethylolpropane (TMP) 98%, 1-methylimidazole and oleic acid were obtained from (Sigma Aldrich). All other chemicals and reagents (hydrochloric acid, hydrogen peroxide, sulfuric acid, 1,4-dioxane, ethyl ether, acetonitrile, butyl bromide, methanol, toluene, and potassium hydroxide) were obtained from Jiangtian Chemical Reagents Co. (Tianjin, China) and used as received.

### 2.2. Preparation Procedures

#### 2.2.1. Preparation of SBA-15

The mesoporous SBA-15 silica with tuned geometrical structure was prepared using the method described elsewhere (Zhao, 1998). Pluronic P123 (8 g) was dissolved in 60 ml demineralized water and 2 M HCl (240 g) solution under vigorous stirring at 50 °C for 16 h. After the mixture became clear, in a closed vessel, TEOS (17 g) was added dropwise into the solution with continuous stirring at 50 °C for 20 h and then aged at 100 °C for 24 h. The formed solid product was separated by centrifugation, washed repeatedly with de-ionized water and dried at ambient temperature. Controlled removal of the template was managed through the calcination at 550°C for 6h with temperature ramping of 1°C min<sup>-1</sup>.

#### 2.2.2. Propyl sulfonic acid functionalized SBA-15

For surface functionalization of SBA-15 with sulfonic groups, of SBA-15 was firstly dispersed in toluene, and of 3-mercaptopropyl- trimethoxysilane was added portion wise to the suspension (Wang, 2018). The suspension was then stirred at for 8 h in nitrogen atmosphere. Then, the mixture was filtered off and the surface modified SBA-15 with thiol (-SH) groups was washed three times with ethanol to remove the residual solvent and unreacted reagent. The obtained white solid was dried at under vacuum for 12 h and denoted as SBA-15-TH. The anchored thiol groups (SBA-15-TH) were oxidized with dilute H<sub>2</sub>O<sub>2</sub> in methanol under argon atmosphere for 4h (Karimi, 2012). Then, the solution was filtered off and washed with ethanol/water solution. The wet material was suspended in 1M H<sub>2</sub>SO<sub>4</sub> for 2h. Finally, the functionalized silica was washed several times with ethanol/water solution and dried at 60°C under vacuum overnight, *Scheme 1*.

#### 2.2.3. Synthesis of ionic liquids

##### i) Synthesis of 1-(4-sulfonate)-butyl-3-methyl imidazolium zwitterion

1-Methylimidazole and 1,4-butane sultone were mixed in equal molar ratio in an ice bath. Firstly, 1-methylimidazole was dissolved in acetonitrile and 1,4-butane sultone was added dropwise to the solution. Then, the solution was stirred at 40 °C for 24 h in N<sub>2</sub> atmosphere, and the obtained white solid was collected

and washed three times with acetonitrile to remove the unreacted materials. The solid was dried at 60 °C under vacuum for 12 h to form 1-(4-sulfonate)-butyl-3-methyl imidazolium zwitterion which denoted as IL<sub>1</sub>, <sup>1</sup>H NMR (400MHz, MeOD) δ: 1.8 (m, 2H), 2.06 (m, 2H), 2.9 (t, 2H), 3.97 (s, 3H), 4.3 (t, 2H), 4.67 (s, 1H), 7.57 (s, 1H), 7.64 (s, 1H).

<sup>13</sup>C NMR (101MHz, MeOD) δ: 21.56, 28.65, 35.23, 47.09 – 50.33, 122.34 – 122.38, 123.63 – 123.67, 136.21 – 136.88.

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**Scheme 1** . Functionalization of SBA-15 and electrostatic immobilization of IL<sub>1</sub>

#### ii) Synthesis of butyl methyl imidazolium bromide

The ionic liquid was prepared following the procedures stated in literature (Huddleston, 2001). 1-Methylimidazole and 1-bromobutane were mixed in a molar ratio of 1:1 in three-necked round bottom flask and refluxed under stirring at 70 °C till two phases (layers) were formed. After removing the unreacted materials the obtained liquid was washed repeatedly with ethyl acetate to remove the unreacted material. Then, the remaining solvent was removed by heating at 70 °C. The pale yellow liquid was distilled under vacuum and the obtained ionic liquid was dried under vacuum at 80 °C and denoted as IL<sub>2</sub>, *Scheme 2*. <sup>1</sup>H NMR (400MHz, MeOD) δ: 1.0 (t, 3H), 1.41 (m, 2H), 1.91 (m, 2H), 4.02 (s, 3H), 4.31 (t, 2H), 4.68 (s, 1H), 7.64 (d, 1H), 7.7 (d, 1H).

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<sup>13</sup>C NMR (101MHz, MeOD) δ: 12.66, 19.14, 31.87, 35.64, 47.14-48.42, 49.31, 122.4-122.44, 123.63-123.67, 136.57.

**Scheme 2** . Synthesis and immobilization of IL<sub>2</sub>

#### 2.2.4. Electrostatic immobilization of ionic liquids onto SBA-15 - functionalized sulfonic acid

The concentration of H<sup>+</sup> in the functionalized SBA-15 was determined as described in our previous work (Shalaby, 2018). The method of alteration and immobilization was set out in *Scheme 1* and *2*. SBA-15 with surface sulfonic groups was dispersed in toluene and equal mole of IL<sub>1</sub> or IL<sub>2</sub> in 1,4-dioxane was added portion wise at ambient temperature. After that, the temperature of the reaction mixture was ramped slowly up to 90°C and stirred for 2h and then, the mixed solvent was removed under vacuum at 90°C (Zhang, 2009). The obtained heterogenized catalyst was washed with ethanol, dried under vacuum at 60°C and denoted as IL<sub>1</sub>/SBA-15 or IL<sub>2</sub>/SBA-15.

#### 2.3. Catalytic Performance

The catalytic activity of IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15 catalysts was investigated via esterification of OA and TMP. The effect of temperature (100°C – 140°C) and molar ratio of OA to TMP (3:1- 5:1) on the ester percentage yield were studied at fixed catalyst dosage of 3 wt. % (weight percent based on palmitic acid) and reaction time of 20h. The esterification was performed as follows: the catalyst, IL<sub>1</sub>/SBA-15 or IL<sub>2</sub>/SBA-15, OA and TMP (in molar ratio under study) were charged into a 150 mL three neck round bottom flask containing toluene (as a water removing agent) with a reflux condenser and a magnetic stirrer. Then the reaction was allowed to proceed under nitrogen atmosphere and the chosen temperature for 20 h. At the

end of each run, the exploited catalyst separated from the reaction mixture by centrifugation, washed with methanol and n-hexane and dried under vacuum at 80 °C to obtain the recovered catalyst.

From practical and economic point of view, the periodicity of the catalysts was studied. The recovered catalysts were directly applied in esterification of OA with TMP, in six consecutive runs, at the optimized conditions as will be discussed in section 3.

## 2.4. Analytical Procedures

### 2.4.1. Characterization of the As-prepared Sample

Characterization of the ionic liquids using <sup>1</sup>H NMR and <sup>13</sup>C NMR were performed on a Bruker High Performance Digital FT – NMR Spectrometer Avance 111 400MHz (Micro-analytical unit, NMR Laboratory of Pharmaceutical Collage, Cairo University, Egypt). All spectra were recorded in MeOD and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. High-resolution transmission electron microscopy (HR-TEM) images were obtained with a (JEM- 2100CX, JEOL, Japan) operated at 200 kV. The HR-TEM specimens were prepared by dispersing a small amount of sample in ethanol, ultrasonicated for 15 min, dropped on a carbon-coated copper grid, dried and photographed. Thermal gravimetric analysis (TGA) was carried out on 0.2 g of each sample which was heated in air flow of 50 cm<sup>3</sup>/min at heating rate of 5 °C min<sup>-1</sup>. The TGA curve was recorded during the temperature range of 40–600 °C using a simultaneous TGA – DSC model SDT Q600 apparatus (USA). The BET surface areas for the specimens were measured by N<sub>2</sub> adsorption/desorption isotherms at 77 K using Autosorb 1, Quantachrome instrument.

### 2.4.2. Products Analysis and Performance Evaluation

Products were analyzed using gas chromatographs (GC) (Agilent 6890 plus HP) on the capillary column (HP-30 50% phenyl/50% dimethyl polysiloxane, 30 meter in length, 0.53 mm in internal diameter and 0.32 mm in film thickness) and a flame ionization detector (FID) with nitrogen as the carrier gas and isopropanol was used as the internal standard.

All samples were transformed into silane derivatives with BSA (N,O-bis (trimethylsilyl) acetamide). The program involved holding the temperature at 80°C for 2 min, then heating to 340°C at 5°C/min, and then finally holding at 340°C for 5 min. The injector was held at 300°C, while the detector was at 360°C.

$$\text{Selectivity (\%)} = \frac{\text{Obejective product \%}}{\text{Total conversion \%}} \times 100 \dots\dots\dots(1)$$

$$\text{Total Conversion} = 100 - (\text{Final \% of TMP} + \text{Final \% of OA}) \dots\dots\dots(2)$$

Kinematic viscosity was measured at 40 and 100°C using calibrated Ubbelohde Viscometer tubes. Viscosity and viscosity index (VI) were calculated using ASTM D 445 and ASTM D 2270 methods, respectively. All viscosity measurements were run in duplicate and the average value was reported. Pour points were determined according to ASTM D 97. Sample temperature was measured in 3 °C increments at the top of the sample until it stopped pouring.

## 3. Results and Discussion

Basically, this study reports the *electrostatic* immobilization of molecular imidazolium cation, with different substituents, on the functionalized silica surface. The different substituents on the imidazolium ring induce different acidity strength which affects the catalyst activity. These catalysts were employed in the esterification of OA with TMP; and study the temperature and the substrate proportions as process effective parameters.

### 3.1. Textural Analysis

The textural characteristics of the as-prepared samples were studied by BET surface analysis, and their constituent morphologies were analyzed by HR-TEM. Figure 1 shows  $N_2$  adsorption-desorption isotherms and pore size distribution (PSD) over the pristine SBA-15 as a reference material, SBA-15 immobilized ionic liquids  $IL_1/SBA-15$  and  $IL_2/SBA-15$ . No marked difference can be noticed in the isotherms for pristine silica SBA-15,  $IL_1/SBA-15$  and  $IL_2/SBA-15$ . All isotherms are predominately of type IV, exhibiting IUPAC type H1 hysteresis loop which is a characteristic of porous materials consisting of agglomerates or particles of uniform and regularly packed materials (Gu, 2007). The results of TEM images (Fig.2) and PSD curves support these findings. The immobilization of ionic liquids onto SBA-15 surface seemed to change the adsorption characteristics of  $IL_1/SBA-15$  and  $IL_2/SBA-15$  through the remarkable modification in the pore structure. This may be due to the existing organic layer screening Si-O-Si bonds and thus impeding the adsorption process. Such findings can be demonstrated in terms of the pore dimension and surface area values (Table 1), where the specific surface area decrease from about  $668\text{m}^2/\text{g}$  for SBA-15 to about  $484\text{m}^2/\text{g}$  and  $502\text{m}^2/\text{g}$  for  $IL_1/SBA-15$  and  $IL_2/SBA-15$ , respectively. The pore volume  $V_P$ , also decrease in the same manner. In opposite to this result, the average pore diameter ( $D_p$ ) increased with immobilization of the ionic liquids due to the decrease in population of pore fractions centered at 3.6 nm which increase the average pore diameter, *see* PSD curves.

Figure 2 shows the constituent morphologies of the presented structures in this article. From the image, the pure SBA-15 possesses a regular pore system with a two-dimensional, long-range hexagonal, ordered open-frame structure that confirms to the results of BET surface analysis. The pore lengths seem to be nearly straight and can be estimated by matching with the image scale ( $\sim 150\text{nm}$ ). The straight path length of the pores of the support surface, promotes the catalytic activity by diminishing the diffusional limitation. It is difficult to observe the pore dimensions after the loading of ionic liquids due to the coverage of support surface with the functionalizing sheet.

### 3.2. Thermal Stability

The thermal stability of the functionalized samples derived from SBA-15, exemplified by  $IL_1/SBA-15$  and  $IL_2/SBA-15$ , had to be investigated for application. As shown in Fig. 3, the TGA-DSC curve for functionalized silica samples shows a small endothermic peak at  $100^\circ\text{C}$  with some weight loss ( $\sim 4.7\%$  and  $7.5\%$  for  $IL_1/SBA-15$  and  $IL_2/SBA-15$  respectively) up to  $110^\circ\text{C}$ , mainly referring to the evolution of adsorbed retained water. In the temperature range from  $\sim 110^\circ\text{C}$  to  $280^\circ\text{C}$ , the observed slight weight loss of 2-2.5 % may be attributed to the removal of loosely linked ionic liquid moieties, ensuring the formation of stable and compact functionalizing sheet of ionic liquids (Cao, 2013). The decomposition of the organic sheet on the surface of SBA-15 observed in the  $280^\circ\text{C} - 380^\circ\text{C}$  region, with a weight loss of  $\sim 6\%$ , probably due to the evolution of the charred organic residue. The last stage of weight loss up to  $500^\circ\text{C}$  (with  $\sim 1\%$  loss) correlated with a broader endothermic peak is likely due to dehydroxylation and/or collapse of silanol sets in the surface network (Cao, 2013).

### 3.3. Catalytic Performance

In this work, the main target is the preparation of heterogenized catalysts by *electrostatic* immobilization of ionic liquids onto the SBA-15. The obtained catalysts have the advantages of both homogeneous and heterogeneous catalysts; where the immobilized ionic liquids move loosely in the reaction medium and become easily accessible for the reactants. The esterification of oleic OA with TMP for bio-lubricant production was employed to measure the catalytic activity. In general, no significant difference in textural characteristics or content of ionic liquids of the two catalysts can be observed. The difference is only in the acidity strength of the tow catalytic systems which originated from the different inductive effects of the substituents on the imidazolium molecular cation.

#### a) Effect of Temperature

To study the temperature effect, experiments were performed at fixed conditions of molar ratio of reactants (OA: TMP of 3:1), reaction time of 20 h and catalysts dosage of 3 wt.% . Figure 4 depicts the variation of catalytic behavior over the temperature range from  $100^\circ\text{C}$  to  $140^\circ\text{C}$ . For the two catalysts, the activity (total

conversion) increased with temperature, reaching a maximum of 87.2% and 71.73% at 140°C for IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15, respectively. Meanwhile, the selectivity of the two catalysts, it is increased with the temperature towards the objective product (TMPTO) up to 130°C (95.6% and 92.9% for IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15, respectively). Above this temperature, the selectivity begins to decrease with increasing of di-ester that may have been the result of the backward reaction, *viz.*, breakdown of tri-ester to di-ester (Xm, 2011). Through the studied temperature range, IL<sub>1</sub>/SBA-15 exhibits higher activity than that of IL<sub>2</sub>/SBA-15. This is due to stronger acidity of IL<sub>1</sub>/SBA-15 than that of IL<sub>2</sub>/SBA-15, induced by the variance of substituents on the imidazolium ring.

Beside the GC analysis, the obtained product was investigated by kinematic viscosity analysis. Of all the methods used for the study of used oil, none have better repeatability or accuracy of methods than viscosity. The lubricants with high viscosity require more energy to flow, and in the same time, low viscosity may not reduce friction (Wu, 2013). Hence, the optimum viscosity value can be defined as the least viscosity reducing friction between surfaces in mutual contact. From Table 2, the viscosity of the obtained TMPTO is lower than that of a commercial oil at 40°C; indicating that the produced bio-lubricant is appropriate for low load conditions (Qiao, 2017). The TMPTO viscosity index is obviously higher than that of the commercial oil, which means that TMPTO has improved viscosity-temperature properties, *viz.*, TMPTO will retain good viscosity on condition that the temperature obviously changes. The pour point of TMPTO is low enough to satisfy the requirements of lubrication oil.

### b) Effect of OA:TMP molar ratio

For reversible reactions, an excess of a reactant drives the forward reaction generating more products to restore a new equilibrium point. In the case of catalytic reversible reactions, where the reactants must collide the catalyst active site on the same time, this concept is limited to a certain excess reactant concentration. The increase of a reactant concentration will dilute the other reactant and diminish the probability to meet each other on the catalyst surface. This research may confirm this concept where the catalytic performance was investigated over the molar ratio of OA: TMP range from 3:1 to 5:1 at fixed: temperature of 130°C, reaction time of 20h and catalyst dosage of 3 wt.%. Figure 5, shows the increase of total conversion with increase of OA/TMP molar ratio up to 4.5:1 to begin dramatically decrease with further increase of OA/TMP molar ratio. The same result was reported by Li et al (Li, 2012). It is noticeable that the increase of OA/TMP has a significant effect on the increase of the total conversion at the beginning and diminishes gradually till reaches the minimal increase at 4.5:1. This result runs in harmony with the previous concept.

### c) Periodicity

In applied catalysis, the catalyst reusability is the most important after the catalytic performance. The reusability of the tow employed catalysts was studied at the previously optimized reaction conditions, *viz.*, at 130°C, OA/TMP molar ratio of 3:1, catalyst dosage 3wt. % and reaction time of 20h. At these optimized circumstances, any change in the catalytic behavior will be easily detectable. Figure 6 illustrates the observed results during six consecutive runs where the recorded catalytic activity of each run is slightly less than the previous one. The decrease in catalytic activity most probably attributed to the slight leaching of acidic protons or the adsorption of reactant molecules on the active sites (Li, 2012). In general, the yield of TMPTO is maintained at the level of 83.40% and 65% for IL<sub>1</sub>/SBA and IL<sub>2</sub>/SBA-15 referring that the catalysts are relatively stable during the reaction.

## 4. Conclusion

We developed new powerful heterogenized Brønsted acid catalysts via a new route of immobilization of ionic liquids onto silica surface. By the electrostatic immobilization, the obtained catalysts with the loosely movement of the supported imidazolium cation, as a molecular catalyst, in the reaction medium makes the catalysts to possess both the advantages of homogeneous and heterogeneous ones. The prepared catalysts displayed strongly reasonable catalytic behavior with relative stability at mild temperature (130°C) and stoichiometric ratio (OA: TMP = 3:1) in direct esterification of OA with TMP for production of bio-degradable lubricant.

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### Captions to Tables

**Table 1** . BET surface area and pore dimensions of SBA-15, IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15.

**Table 2** . Physical properties of the bio-lubricant produced over IL<sub>1</sub>/SBA-15 at OA/TMP molar ratio of 3:1, catalyst dosage of 3wt.% and reaction time 20h in comparing with a commercial one.

**Table 1** . BET surface area and pore dimensions of SBA-15, IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15.

Item	SBA-15	IL <sub>1</sub> /SBA-15	IL <sub>2</sub> /SBA-15
V <sub>P</sub> (cc/g)	0.751	0.585	0.582
D <sub>P</sub> (nm)	3.648	5.320	5.270
S <sub>BET</sub> (m <sup>2</sup> /g)	668.644	484.433	502.232

**Table 2** . Physical properties of the bio-lubricant produced over IL<sub>1</sub>/SBA-15 at OA/TMP molar ratio of 3:1, catalyst dosage of 3wt.% and reaction time 20h in comparing with a commercial one (Qiao, 2017).

Property	Trioleate Ester	Mobil CF-415W-40
Viscosity at 40 C (cSt)	61.63	106
Viscosity at 100 C (cSt)	14.20	14.2
Viscosity index	242	136
Pour point (°C)	- 18	-27

### Captions to Figures

**Fig.1.** The nitrogen adsorption-desorption isotherm and PSD of SBA-15, IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15.

**Fig.2.** HR-TEM images of: a) SBA-15, b) IL<sub>1</sub>/SBA-15 and c) IL<sub>2</sub>/SBA-15.

**Fig.3.** TGA and DSC curves of IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15.

**Fig.4.** The catalytic behavior of IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15 as a function in temperature.

**Fig.5.** Catalytic performance of IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15 as a function in reactants molar ratio.

**Fig.6** . Relative stability of IL<sub>1</sub>/SBA-15 and IL<sub>2</sub>/SBA-15 during the reusability test.

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