# EVALUATION OF MESOPOROUS MODIFIED FERRIERITE ZEOLITE PERFORMANCE IN PRODUCTION OF DIGLYCEROL FROM GLYCEROL

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Preparation of the ion exchanged Ferrierite zeolites with alkali metals cations (Li^+, K^+, Rb^+, Cs^+) as a basic heterogeneous catalyst and examination of their activities in selective etherification reaction of glycerol to diglycerol were investigated in this paper. The prepared catalysts were characterized by X-ray diffraction (XRD), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), X-ray Fluorescence (XRF), Scanning electron microscopy (SEM) and Burnauer-Emmett-Teller (BET) techniques. Under our experimental conditions, the ion exchanged Ferrierite zeolite containing caesium cation (Cs-FER) has shown the best activity and selectivity to diglycerol in comparison to other catalysts which were prepared with (Li^+, K^+, Rb^+) cations. Results studies show the catalyst activities of prepared samples were directly depended on the basicity of catalyst.
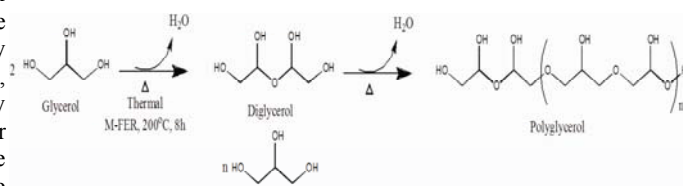
INTRODUCTION

Glycerol can be obtained from different processes as a byproduct such as soap manu-facturing from fats and oils, fermentation of sugars like glucose, hydrolysis of biomass, and methanolysis of trigly-cerides.[1] Glycerol is the most important byproduct of transesterification of fatty acids into biodiesel, and can also be synthesized from propylene oxide.[2] Development of some processes such as pyrolysis, selective oxidation, selective hydro-genolysis, selective dehydration, selective transes-terification, selective etherification, and polymerization, which convert producing glycerol into valuable chemical products are remarkably attractive from economical point of view.[3-5]

Selective glycerol etherification is one of the most important processes for production of diglycerol (DG), triglycerol (TG) and tetraglycerol, among which DG is the most valuable. DG has numerous applications in cosmetics and pharmaceutical industry, production of fatty acid ester emulsifiers, food additives, production of plasticizer in polyvinyl alcohol films, the manufacture of polyurethanes and polyesters, biodiesel additive, etc.[6] Selective etherification could be catalyzed in the presence of homogeneous and heterogeneous[7] acidic and basic catalysts. Because of the production of undesirable by-products such as acrolein in the presence of acidic catalysts, basic catalysts are more preferred.[8,9] Also, heterogeneous basic catalysts have some advantageous over the homogeneous ones.[10] The basic-catalyzed conversion reaction of glycerol over heterogeneous alkali earth oxides have been investigated by several research groups.[11,12] Among the examined heterogeneous alkaline catalysts,

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porous materials such as crystalline nanoporous zeolites [13] are preferred due to the easy usage, easy handle and recovery, no waste or disposal problems, ion-exchange ability, high thermostability, selectivity based on shape and size, high surface area and uniform porosity. Barrault *et al*. discovered that basic mesoporous materials are quite selective catalysts for the direct synthesis of DG and TG from glycerol.[14] Cottin used zeolite Beta (Si/Al = 12) as a catalyst in oligomerization of glycerol. Also, NaX zeolite has been reported as a catalyst for the selective production of DG.[15] In this way, the ion exchange property of zeolites can be used to substitution with basic-cations such as Li^+, Na^+, etc. and basic-modified zeolites could be obtained. The effects of alkali cations on the base strength of zeolites are in the order $Cs^+>Rb^+>K^+> Na^+>Li^+$.[16,17]

For example, glycerol was converted to di-, tri- and tetra glycerol with selectivity about 62%, 33% and 4% respectively and conversion about 70% over Cs-exchanged zeolite X as a catalyst.[18] On the other hand, influence of pore size and the basicity of the porous catalysts in the oligo-merization reaction are proved by the use of basic MCM-41 as catalyst. Clacens *et al*. Modified mesoporous MCM-41 zeolite by impregnation with different metals and they observed Cs-impregnated zeolites show the best results.[3,5]

In this research, the two-dimensional and medium-pore Ferrierite (FER) zeolite was modified with alkali metal ions and used as catalyst for etherification reactions. The effect of different basic cations on the yield of produced DG was compared and the best base-modified catalyst was chosen according to the obtained results.

EXPERIMENTAL

Synthesis of FER zeolite

The ferrierite zeolite was prepared according to the procedure reported in the literature.[19] 24.44 g of silica sol was mixed with 6.94 g aqueous solution of aluminium sulfate (Al_2O_3 = 7.49%, H_2O = 74.9%) to form a mixture. Then 1.69 g of NaOH and 13.25 g of deionized water were added to the mixture. A homogeneous gel of the reactant was formed after 3.71 g of THF were added into the mixture with vigorous stirring. The synthesis was carried out in a teflon-lined stainless steel autoclave at 200°C for 1 day in static condition. The resulting solid powder was then separated from the liquid by centrifugation, washed several times with distilled water, and dried at 120°C overnight to obtain ferrierite in sodium form. To eliminate the template, the temperature was increased to 550°C in air with a ramp rate of 10°C/min and maintained at this temperature for 12 h. The calcined sample was converted into alkali ion forms by two-fold ion-exchange with 1.0 mol/L aqueous solutions of MNO_3 (M=Li^+, K^+, Rb^+, Cs^+). 4 g of zeolite

was dispersed and stirred at 80°C for 12 h in a solution of the respective salts. After washing with distilled water, the ion-exchanged zeolites were dried at 120°C for 12 h. The above described procedure was repeated twice to achieve the maximum ion-exchange for all the metal ions. Finally the catalyst was calcined at 550 °C for 4 h.

Characterization

Phase purity identification of the synthesized parent zeolite and ion-exchanged zeolites was made by Philips model PW1729-X-ray diffractometer using Cu Kα radiation at 30 kV and 24 mA. The scanning range of 2θ was between 5 to 50 degrees. The silica to alumina ratio of parent zeolite was determined by XRF (PW2404, PHILIPS), with lithium tetraborate as a flux. Amount of metals loaded in ion-exchanged FER were determined by an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) system. The nitrogen adsorption/desorption isotherms were determined at liquid nitrogen temperature on an automatic analyzer (BELSORP mini-II).

The surface morphology of the catalysts was observed by a SEM (Zeiss, DSM 960 A) with an acceleration voltage of 10 kV. The high performance liquid chromatography (HPLC) technique for confirming the products formation was recorded on a refractive index detector (RID). Analysis conditions: isocratic acetonitrile/water (80/20) as a mobile phase, column temperature at 40°C, flow cell temperature at 40°C and 0.1% of each oligomer in mobile phase as standard.

Reaction procedure

In a round-bottomed flask which was connected with a Dean-Stark trap to collect formed water of reaction, 50 g glycerol was exposed to etherification reaction in the presence of 2 Wt % of M-FER catalyst, in solvent free condition. The flask equipped with a magnetic stirrer was kept at 200°C with vigorous mixing for 8h under argon (Ar) flow. After completion of reaction, the oligomeric reaction products were centrifuged, separated and analyzed by HPLC.

RESULTS AND DISCUSSION

Analysis of parent FER zeolite

Comparison of the X-ray pattern of prepared FER zeolite with standard sample (Fig. 1) shows the diffraction peaks of ferririte that obviously appeared at 2θ = 9.8°, 13.5°, 16°, 22.3°, 23.6°, 24.4°, 25.7°, 26.3° and 30.9° are similar to the standard one.[19]

Also XRF analysis of parent sample shows Silicon to aluminum ratio is equal to 11.5. The elemental contents of the zeolite are shown in Table 1.

Table 1

Percentages (wt%)
of silicon and aluminum in sample ferririte

Analyte	Concentration
Al_2O_3	6.73 wt%
SiO_2	91.32 wt%

Characterization of modified catalysts

The XRD diffraction of the catalysts is shown in Fig. 2. The framework of the FER zeolite had no changes after ion-exchanging with alkali metal ions. Slight changes in the peak intensities of the modified FER zeolites were observed due to the filling of metals inside the FER. All samples exhibited. the characteristic peaks of FER, indicating that the crystallinity of M-FER maintained well during the cation exchange.

However, the characteristic diffraction peak positions of M-FER have been slightly changed after M cation-exchanges. For K-FER and Li-FER, as shown, the diffraction peaks at 2θ = 22.3 and 30.9 shift to lower angles in comparison to that of Na-FER, as well as at 2θ = 30.9 change in the intensity peak of Rb-FER and Cs-FER was observed which is attributed to the larger ionic radius of Rb+ and Cs+ than that of Na+. These also indicated the M cations are successfully exchanged into the M-FER. The extent of cation-exchange in all samples of M-FER were measured by inductively coupled plasma (ICP), and listed in Table 2.
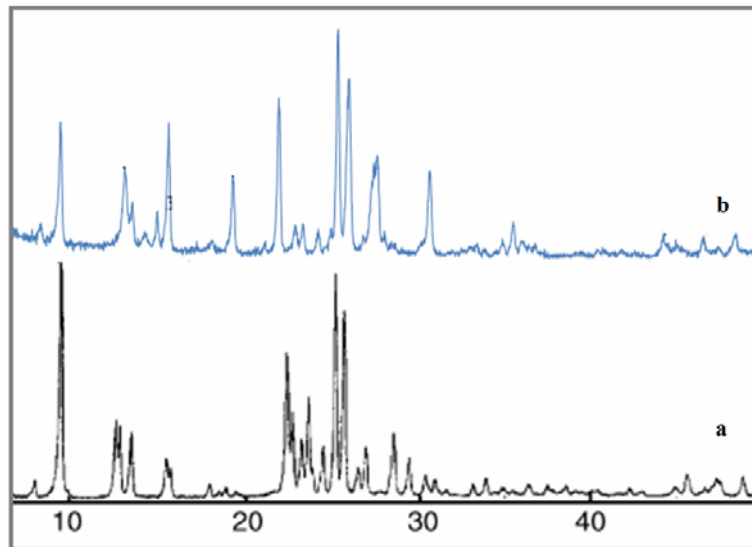

Fig. 1. – XRD Patterns of a) standard and b) parent FER zeolite (Na-FER).
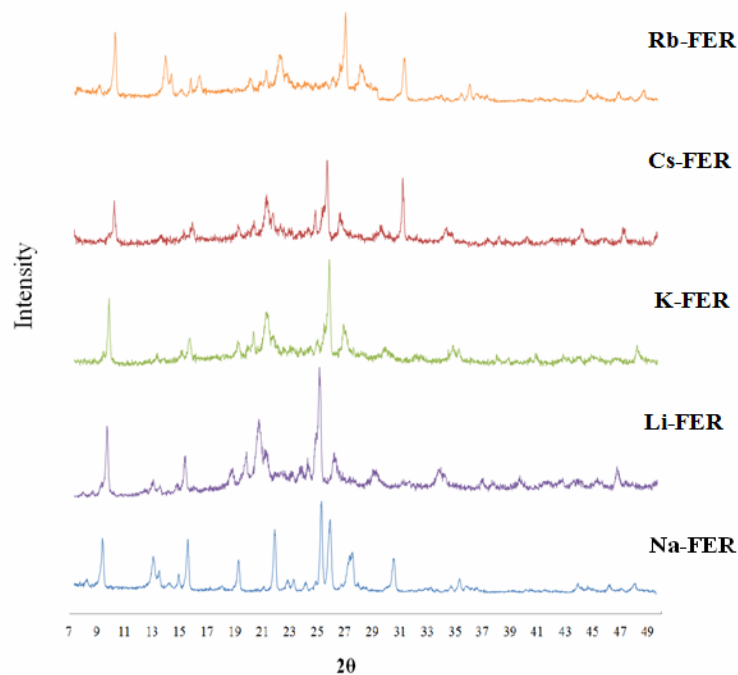

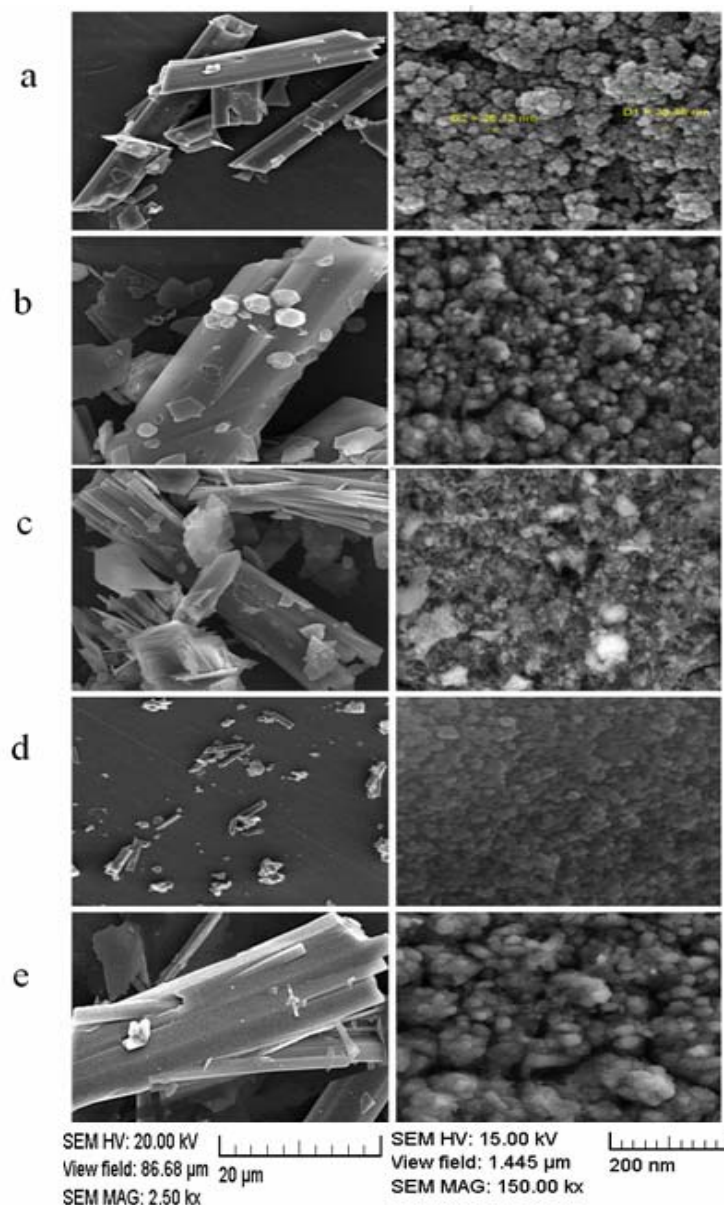Fig. 2. – Powder XRD patterns of catalysts.

Fig. 3. – SEM images of a) Na-FER, b) Li-FER, c) K-FER, d) Cs-FER, e) Rb-FER.

Scanning electron microscopy (SEM) images of prepared catalysts showed rod-like morphology for all samples (Fig 3). Also, no noticeable change in their morphology is detected from SEM measurement.

The XRD patterns and SEM images of the modified materials confirmed good crystallinity and phase purity of zeolites.

ICP analysis results and metals content are shown in Table 2. The degree of ion-exchange of the metal ions were slightly changed. It is clearly observed that ion-exchange was accomplished above 90% .The lower degree exchange of Li+ and K+ cations might be due to the fact that Li+ and K+ cations prefer to form hydrated lithium

and potassium cations with large diameter, resulting in the lower diffusion rate to the cation-exchange sites located within the channels.

Table 2

Metals content based on ICP analysis

Catalyst	Alkali metal content (Wt %)
Li-FER	16.3
Na-FER	17.2
K-FER	16.2
Rb-FER	16.7
Cs-FER	16.9

Nitrogen adsorption and desorption isotherms obtained at 77K were classified as type IV for all

samples, which corresponded to mesoporous materials according to the BDDT classification.[20] Results of surface area measurements for the catalysts are given in Table 3.

Table 3

Textural properties of catalysts

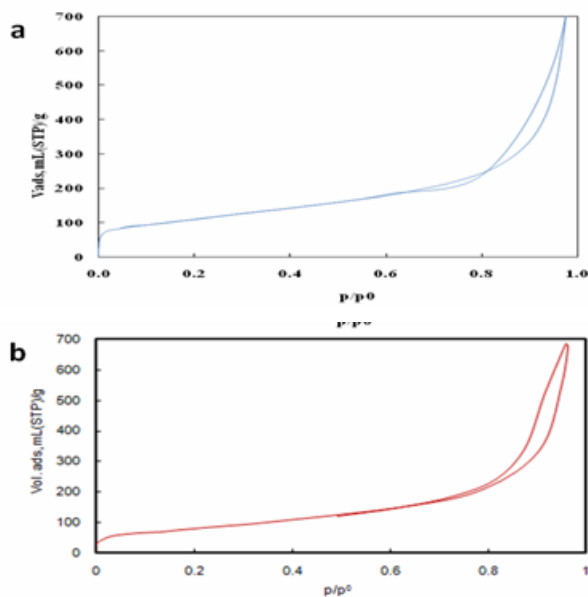| Sample	BET surface area (m²/g)	Average pore diameter (nm)
Li-FER	327	2.34
Na-FER	389	2.33
K-FER	312	2.36
Rb-FER	289	2.46
Cs-FER	286	2.47

Fig. 4. – Nitrogen adsorption and desorption isotherms for a) Na-FER and b) Cs-FER.

Gas adsorption was indicated that all of the catalysts are highly porous and zeolite modification practically does no effect on the isotherm. For instance, Gas adsorption isotherms are shown in Fig. 4 for Na-FER and Cs-FER.

It was observed that the surface areas of M-FER decreased significantly after cation-exchange. For Rb-FER and Cs-FER, it is reasonable that their surface areas were smaller than those of the original Na-FER owing to the increasing size of alkali metal cations. Differently, the reason of the relatively small surface areas of Li-FER and K-FER might be that the Li+ and K+ cations were not totally exchanged to the location of the original Na+ cation and consequently partially blocked the channel of the M-FER.

Evaluation of synthesized catalyst in glycerol etherification reaction

The aim of this work was to peruse the selective synthesis of diglycerol by avoiding the formation of higher oligomers of glycerol in selective etherification of glycerol reaction on modified zeolites with two-dimensional channels (FER).

Glycerol was dehydrated in the free solvent condition in the presence of modified FER zeolite with different alkali metals to produce the corresponding oligomers. Since the presence of oxygen greatly influences the yield of desired product of the reaction, the experiments were carried out under argon atmosphere.[21]

In the present study conversions of glycerol and DG selectivity that were obtained by HPLC analyses were shown in Table 4. The highest conversion (57%) and selectivity (92%) were obtained over Cs-FER for the glycerol selective etherification. These results show that the activity of catalyst is directly dependent on the nature of the exchanged cation. Zeolites with Rb and Cs cations are much more active than Na- form zeolite. This is due to the basicity properties of Rb and Cs. In other words, the rate of reaction increases as basicity is raised. In fact, we have shown from the results that there was a direct relationship between the activity and the basicity of the catalysts. Triglycerol was also detected during the reaction but its selectivities were lower than 16%. Comparison of the results showned that increasing weight of the alkali metals causes decrease of oligomers larger than DG.

Table 4

Summary of the HPLC analysis to activity and selectivity of modified FER zeolite catalysts

Catalyst Evaluated parameters	Li-FER	Na-FER	K-FER	Rb-FER	Cs-FER
Glycerol conversion (%wt)	35	37	40	46	57
Diglycerol selectivity (%wt)	77	79	80	83	92
Triglycerol selectivity (%wt)	16	12	13	13	6
Tetraglycerol selectivity (%wt)	5	6	5	3	1
Polyglycerol selectivity(%wt)	2	3	2	1	1
Yield (%)=(Conversion × Selectivity(%wt)	28	29	33	38	52

Stability of Cs-FER

In view of the highest catalytic activation of Cs-FER among the M-FER, we evaluated the stability of Cs-FER in such liquid phase reaction. The XRD pattern of the Cs containing catalyst before and after etherification for one cycle is shown in Figure 5, rather similar XRD pattern was observed for the catalyst before and after reaction. However, it can be seen that the intensity of peaks was decreased after the reaction. The similar PXRD patterns for the fresh and recycled catalysts further illustrated Cs-FER retaining its structural identity. Cs metal content before and after reaction was identified 14.9 and 14.7 wt% by ICP, respectively.

The results showed that the basic strength and surface area of the Cs-FER catalyst were high enough to effectively catalyze the mentioned reaction. Due to large pore size of mesoporous zeolites over glycerol molecule (0.515 nm), bulk reaction seems to mainly occur inside the pores of the catalyst.[22,23] On the other hand, the performance of the Ferrierite zeolites critically depends on the Si/Al molar ratio. The higher molar ratio of aluminium to silicon causes the higher hydrophilicity property. So, diffusion of glycerol into the zeolite pores is affected by this property directly. On the other hand, the presence of alkali cations modifies the hydrophilic property of zeolite and cosnsequently the adsorption rate of glycerol.
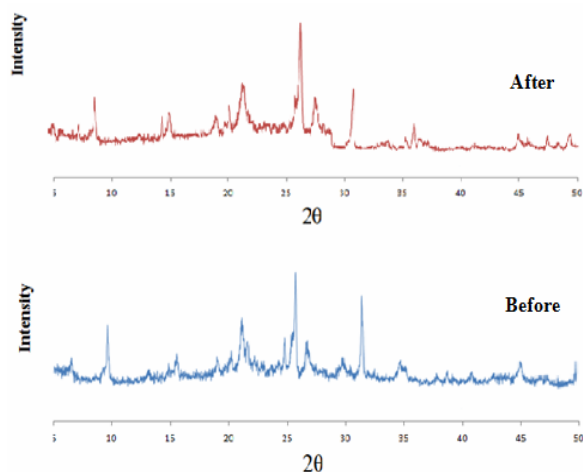

Fig. 5 – XRD pattern of Cs-FER
before and after reaction.

CONCLUSIONS

Selective etherification of glycerol is an alternative reaction for production of diglycerol.

In this study, a series of ion-exchanged FER zeolites with alkali cations were prepared and tested as catalyst for solventless etherification of glycerol to DG. It has been successfully demonstrated that glycerol can be converted to diglycerol using modified Ferrierite zeolites. The main conclusion to be drawn from this study showed that among these catalysts, Cs-FER catalyst had the highest activity for glycerol etherification, giving 57% glycerol conversion with 92% selectivity toward DG. In addition, this catalyst can limit the production of large oligomers to desired DG formation. The higher glycerol conversion suggested that the basicity could significantly affect the product selectivity. This result also suggested that the shape-selective reaction might have taken place mostly in the internal pores rather than on the external surface of the catalyst.

REFERENCES

1. C.-H. C. Zhou, J. N. Beltramini, Y.-X. Fan and G. Q. M. Lu, *Chem. Soc. Rev.*, **2008**, *37*, 527–549,.
2. D. Liang, J. Gao, H. Sun, P. Chen, Z. Hou and X. Zheng, *Applied Catal. B, Environ.*, **2011**, *106*, 423–432.
3. J. Clacens, Y. Pouilloux and J. Barrault, *Appl. Catal.*, *A*, **2002**, *227*, 181–190.
4. G. L. Brett, Q. He, C. Hammond, P. J. Miedziak, N. Dimitratos, M. Sankar, A. A. Herzing, M. Conte, J. A. Lopez Sanchez and C. J. Kiely, *Angew. Chemie*, **2011**, *123*, 10318–10321.
5. J. Barrault, J.-M. Clacens and Y. Pouilloux, *Top. Catal*, **2004**, *27*, 137–142.
6. K. A. Oudhoff, F. A. Vandamme and E. P. C. Mes, *J. Chromatogr. A*, **2004**, *1046*, 263–269.
7. K. Klepáčová, D. Mravec and M. Bajus, *Chem. Pap.*, **2006**, *60*, 224–230.
8. M. J. Franco, R. Alcantara, L. Canoira and A. Navarro, *React. Funct. Polym.* **2000**, *43*, 97–104.
9. R. Eckelt, M. Schneider, Y. K. Krisnandi, R. Eckelt, M. Schneider and A. Martin, *Chem. Sus. Chem*, **2008**, *1*, 835-844.
10. A. M. Ruppert, J. D. Meeldijk, B. W. M. Kuipers, B. H. Ernø and B. M. Weckhuysen, *Chem. Euro P. J.*, **2008**, *14*, 2016–2024.
11. M. A. Medeiros, M. H. Araujo, R. Augusti, L. C. A. de Oliveira and R. M. Lago, *J. Braz. Chem. Soc.*, **2009**, *20*, 1667–1673.
12. F. Jørôme and Y. Pouilloux, *Chem. Sus. Chem.*, **2008**, *1*, 586–613.
13. J. Clacens, Y. Pouilloux, J. Barrault, C. Linares and M. Goldwasser, *Poly. Glycerols*, **1998**, *118*, xxx.
14. P. J. Kunkeler, D. Moeskops and H. van Bekkum, *Microporous Mater.*, **1997**, *11*, 313–323.
15. H. Hattori, *Chem. Rev.*, **1995,** *95*, 537–558.
16. A. Martin and M. Richter, *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 100–117.

17. R. C. Deka, R. K. Roy and K. Hirao, *Chem. Phys. Lett.*, **2000**, *332*, 576–582.

18. P. Cañizares and A. Carrero, *App. Cat. A*, **2000**, *190*, 93–105.

19. G. Guo-Qing Guo, *S.* Yao-Jun and L. Ying-Cai, *Chem. Commun.*, **2000**, 1893–1894.

20. K. S. W. S. S. J.Gregg, "Adsorption, Surface Area and Porosity." Academic Press, New York, 1982, p. 40–100.

21. T. Chemical, E. Journal, M. Ayoub, U. Teknologi, A. Zuhairi, A. Universiti, B. Production, W. F. Oil, M. C. K-, U. S. M. Golden and G. View, *Chem. Eng. J.*, **2013**, *225*, 784-789.

22. A. Martin, M. P. Checinski and M. Richter, *Catal. Commun.* **2012**, *25*, 130–135.

23. M. Ayoub, A. Z. Abdullah, M. Ahmad and S. Sultana, *J. Taibah Univ. Sci.*, **2014**, *8*, 231–235.