REGULAR ARTICLE



Single site MIL-101 for novel low-temperature liquid-phase toluene methylation

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Abstract. P-xylene is one of petrochemical products eagerly in demand. Until recently, the process for preparing of p-xylene was done *via* gas-phase toluene methylation reaction at high temperature using a strong acid catalyst. In this work, high surface area, shape-selective and single-site MIL-101(Cr) was used as a catalyst to perform toluene methylation reaction in a liquid phase at low reaction temperature (60-120 °C). Toluene conversion and p-xylene selectivity are up to 50% and 90%, respectively. Under the optimum operating conditions; 1:1 toluene: methanol molar ratio, the reaction temperature is 120 °C. The catalyst was synthesized *via* the hydrothermal method and the MIL-101 structure was confirmed by different analytical techniques: TGA, XRD, FTIR and BET surface area. The remarkably high toluene conversion and xylene selectivity at a low reaction temperature, in comparison to previous research, was attributed to the suppression of side reactions that could convert methanol to linear hydrocarbons, and to the inhibition of p-xylene isomerization. This suppression can be attributed to the single site properties and to the uniform pore size distribution of the prepared MIL 101 catalyst.

Keywords. Cr-MOF; liquid phase alkylation of toluene; shape selective; single site.

1. Introduction

Friedel-Crafts alkylation is an important process in petroleum and chemical industries due to the synthesis of substituted aromatic compounds.¹⁻³ Friedel–Crafts alkylations by adding alkyl chains to aromatic rings through the use of a strong Lewis acid, generally BF₃, AlCl₃, FeCl₃, TiCl₄ and protonic acid-like HF, H₂SO₄, as a catalyst, which is highly toxic and corrosive, create a large amount of waste and cause difficult purification of the products.^{4,5} Therefore, the efficient solid acid catalyst should be largely motivated in these acid-catalyzed reactions,^{6,7} those solid acid catalysts must offer sufficient active site and pore design possibilities. The active site in the catalyst and its interaction with reactant indicate the rate of reaction and selectivity of a certain product at relatively mild conditions compared to the non-catalyzed reaction. So, the description of type and number of active sites in heterogeneous catalysts is of high controversial.⁸

Among all the solid catalysts, Metal Organic Frameworks (MOFs) are a class of porous crystalline materials whose crystal structure is composed of inorganic nodes (metal atoms) and poly-dentate organic linkers.^{9–11} An important feature of MOFs is a high content of active metal sites; all of them are uniformly spatially distributed and are accessible for reactants, provided the size of pore entrances allows penetration of the reactant molecules. It is composed of isolated metal atoms or clusters linked by polydentate organic ligands, resulting in a rigid porous network, hence, the structure of MOFs meets the general requirements of single-site catalysts.^{12,13} Single-site catalysts are expected to combine the merits of both homogeneous (activity and selectivity) and heterogeneous (simplicity of recovery and recycling)

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catalysts. In addition, MOFs have many advantages like, uniform three-dimensional structures with very high surface area, tunable pore sizes, and low density.^{14,15}

Moreover, MIL 101 MOF can be considered of type I single-site catalysts (commonly referred to as open metal sites (OMSs)). In this type, active sites are created by using the structurally embedded metal nodes, which are geometrically undercoordinated—this is clearly only possible in the case of MOFs.¹⁶

So in this work, we decided the utilization of MIL 101 as a single site-heterogeneous catalyst to achieve high activity and selectivity of the desired product (p-xylene) during liquid phase alkylation of toluene with methanol.

2. Experimental

2.1 Materials

Chromium(III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, \geq 99%), 1,4-Benzenedi-carboxylic acid (H₂BDC \geq 98%), hydrochloric acid (HCl), toluene (C₆H₅CH₃ \geq 99.8) and methanol absolute (CH₃OH, 99.9%) were purchased from Sigma-Aldrich and used without purification. Water used in all experiments was deionized.

2.2 Catalyst preparation

MIL-101(Cr) was synthesized *via* the hydrothermal reactions of Cr(NO₃)₃·9H₂O with terephthalic acid (TPA), concentrated hydrochloric acid (HCl), and deionized water following the reported method¹⁷ under autogenous pressure at 200 °C for 12 h. The green product of MIL-101(Cr) was obtained by centrifugation. Further, the solvothermal treatment of synthesized MIL-101(Cr) was carried out by washing several times with DMF and then washing with ethanol. The final product was dried at 75 °C for overnight.

2.3 Catalyst characterization

Thermal gravimetric analysis (TGA) was performed using a SETARAM Labsys TGDSC16 equipment with a heating rate of 10 °C/min in N₂ atmosphere. X-ray Diffraction Analysis (XRD) was carried out to investigate the crystal phase structure using Shimadzu XD-1 diffractometer with Cu-target and Ni-filtered radiation (λ = 1.540 Å). The specific surface area was measured from the N₂ adsorption-desorption isotherms at liquid nitrogen temperature (-196 °C) using Quantachrome Nova 3200 S automates gas sorption apparatus. Prior to such measurements, all samples were perfectly degassed at 150 °C for overnight. Fourier-transform infrared spectroscopy (FT-IR) spectrum

was recorded between 4000 and 500 cm⁻¹ with an FTIR spectrometer Perkin Elmer (model spectrum one FT-IR spectrometer, USA). Samples were prepared using the standard KBr pellets. Scanning electron microscopy (SEM) was performed on Quanta 250 field emission gun (FEG) attached to an EDS unit, with an accelerating voltage of 30 kV was used to characterize the morphology of the sample.

2.4 Catalytic activity and regeneration

Catalytic toluene methylation over the prepared Cr-MOF catalyst was simply performed in a magnetically stirred round bottom flask fitted with a reflux condenser at a temperature ranged from 60 to 120 °C. In the reaction container, a mixture of toluene and methanol with different molar ratio (1:1, 1:2 and 1:3) was added into the flask containing, the catalyst amount (0.01, 0.02 and 0.04 gm). The resulting mixture was stirred for 2–8 h. The catalyst was separated from the reaction mixture by centrifuge, washed and dried under vacuum for the reusability tests. The petrochemical products were subjected to gas chromatographic (Perkin-Elmer GC) with a hydrogen flame ionization detector for analysis.

3. Results and Discussion

3.1 Catalyst characterization

TGA curve Figure 1 shows two weight loss stages. The first weight loss (~35 wt%) at temperature ~300 °C corresponds to the loss of surface moisture water molecules from the large and/or middle cage (pores) of the structure MIL-101. The second weight loss at temperature ~420 °C, corresponds to the decomposition of the organic ligands in the framework with a complete transformation into Cr_2O_3 .¹⁷ This data indicates the high thermal stability of the prepared MIL-101 structure, as the sample can be heated safely up to 400 °C during the regeneration process.



Figure 1. TGA analysis of the as-synthesized Cr-MOF sample.



Figure 2. XRD patterns of the as-synthesized Cr-MOF fresh (a) and after the reaction (b).

The XRD (X-ray diffraction) pattern of synthesized MIL-101(Cr) is illustrated in Figure 2. The main diffraction peaks at $2\theta = 5.27$, 8.55, 9.16, 16.63 corresponding to the MIL-101(Cr) crystal plane^{17,18} is observed, which confirmed that MIL-101(Cr) crystals were successfully synthesized.¹⁷

Figures 3a, 3b illustrated the specific surface area, and pore size distribution of the prepared MIL-101 was estimated by N₂ adsorption/desorption isotherms at T=77K. The BET surface area of synthesized MIL-101 was 1783 m² g⁻¹, which is closer to the reported value,¹⁹ total pore volume (V_p) of Mill-101 is calculated to be 0.8877 cc/g at the relative pressure (p/p_o) of 0.98 and the pore size distribution curve showed one type of pore size at (12A°). FTIR pattern of MIL-101(Cr) is presented in Figure 4. Figure 4 illustrates vibrational band at 1635 cm⁻¹ which indicates the presence of adsorbed water molecules on the surface of MIL-101, and a strong band at 1397 cm⁻¹ due to the symmetric (O–C–O) vibrations of dicarboxylate within the framework of MIL-101.²⁰ The other bands between 600 and 1600 cm⁻¹ were due to benzene ring. The band at 1510 cm⁻¹ was attributed to the (C=C) stretching vibration and several small peaks occurring in the range of 1250–1010 cm⁻¹ correspond to the C–H group present in the benzene ring of the BDC linker (benzenedicarboxylic).²¹

The scanning electron microscopy (SEM) image Figure 5 represented the morphology of synthesized



Figure 3. (a), (b) Nitrogen adsorption-desorption isotherms and pore size distribution of the as-synthesized Cr-MOF sample.



Figure 4. FTIR spectra of the as-synthesized Cr-MOF fresh (**a**) and after the reaction (**b**).



Figure 5. SEM micrographs images of the as-synthesized Cr-MOF sample.

Cr-MOF; the structure is octahedral with dual-sided pyramidal type geometry.

3.2 Catalytic activity

The main propose of this research paper is to track the activity and selectivity of the prepared MIII-101-Cr as a heterogeneous catalyst in a highly important acidcatalyzed and shape-selective reaction, toluene alkylation with methanol to produce p-xylene as the main product. In this study, the reactions were performed in a liquid phase at different reaction condition: reaction temperature (60–120 °C), contact time (2–8 h), amount of catalyst (0.01–0.04 gm), and toluene: methanol molar ratio (1:1, 1:2 and 1:3) and for four cycles in the reusability test. The data was illustrated in Figures 1–5 and manipulated in Table S1 listed in the Supplementary Information. The reaction products were found to be: (1) xylenes (o-xylenes and p-xylenes) as a primary product produced by ring alkylation of toluene by methanol, (2) ethylbenzene as secondary product, produced by side-chain alkylation reaction, and finally (3) styrene which is the possible product of intermolecular dehydration of ethylbenzene (Figure 6).

3.2a Effect of reaction *temperature*: In the beginning, the study took place using 0.01 gm catalyst and 1:1 toluene: methanol molar ratio, at different temperature (60-120 °C) for 2 h, the catalyst showed neglected toluene conversions at low reaction temperature (0.02% at 60 °C) and then increased to moderate value as the reaction temperature increased to reach 15% at 120 °C (Figure 7). This is a new and good result, where the previous study 23,24 reported that the methylation of toluene could be carried out as a gas phase reaction in the temperature range of (200-400 °C). The high activity of MIL-101-Cr (at milder reaction conditions) than those solid acid catalyst reported for alkylation reaction may be attributed to its specific pore size and volume, great BET surface area, as well as hydrophilic functional which favors adsorption of reactant. groups, Moreover, the better isolation and accessibility of the metal site is another reason for the good activity of the prepared catalyst. At a low reaction temperature and low toluene conversion (Figure 8), the catalyst was more selective toward side-chain alkylation reaction to produce ethylbenzene. While as the conversion increased at a high reaction temperature, the catalyst was selective toward ring alkylation reaction; xylenes were the major reaction products. This may be attributed to the increase of BrÖnsted acid sites: Lewis acid sites ratio occurred due to the water molecules by-product produced during the toluene methylation reaction. Moreover, the absence of benzene even at high temperatures means that the disproportionation of toluene is negligible.

On the other hand, within xylene isomers, the selectivity to o-xylene decrease as the reaction temperature increased from 51.46 at 60 °C to 8.93 at 120 °C, while the selectivity to p-xylene increased from 48.54 at 60 °C to 91.07 at 120 °C (Figure 8). This can be discussed as: toluene methylation reaction produces only p-xylene which isomerizes over the acid site on the external catalyst surface to produce secondary product o- and m-xylene,^{25,26} so, the increase



Figure 6. Schematic illustration for Fridel-Crafts Toluene Methylation reaction.²²



Figure 7. Effect of reaction temperature on product selectivity over Cr-MOF catalyst.

of p-xylene selectivity with the increase of reaction temperature (more than the thermodynamic equilibrium (ca. 25%) value), can be attributed to the decrease in the external acid sites character due to the adsorbed molecule during methylation reaction, which inhibits p-xylene isomerization reaction. Moreover, the unique pore size (12 Å) structure of the prepared MIL-101-Cr catalyst favors the diffusion of p-xylene molecules and enhances p-xylene selectivity.^{27,28}

3.2b *Effect of reaction time*: Moreover, the study took place with reaction mixture containing 0.01 gm catalyst and 1:1 toluene: methanol molar ratio at a constant temperature of 120 °C, aliquots were withdrawn at intervals, then analyzed. The toluene conversion was increased sharply with time until it reached 40.58% after 8 h (Figure 9a) and the xylenes were still the major products, whereas, p-xylene exhibits the higher selectivity of the converted products (Figure 9b); o-xylene was also detected in trace amounts. The increase of p-xylene selectivity with time may be attributed to the reduction of pore mouth to prevent the diffusion of o- and m-substitution out of the pores, and also to the coverage of active



Figure 8. Effect of reaction temperature on xylenes selectivity over Cr-MOF catalyst.



Figure 9. (a), (b) Effect of reaction time on toluene methylation (0.01 gm Cr-MOF, 1:1 toluene: methanol molar ratio, 120 °C).

sites on the catalyst external surface which suppresses the isomerization of p-isomer.²⁹

3.2c *Effect of catalyst weight*: With such results in hand, we encourage to study the effect of different reaction parameters trying to enhance the performance of the prepared Cr-MOF catalyst toward liquid phase methylation reaction. The effect of catalyst amount (0.01, 0.02 & 0.04 gm) on reaction conversion was investigated for reactant mixture of 1:1 toluene: methanol molar ratio at 120 °C for 2 h. As expected, increasing the catalyst amount enhances the toluene conversion (Figure 10), so, the reaction could afford 54.42% toluene conversion in the presence of 0.04 gm catalyst and the p-xylene product was still observed at high selectivity within all reaction products. From this data, we can conclude that this amount of catalyst is as small vis-à-vis the conversion, as compared by the data previously reported in the alkylation reaction. This may be attributed to the acidic character of the prepared MOF catalyst which effectively reduces the amount of catalyst for toluene methylation reactions.³⁰ 3.2d *Effect of toluene: methanol molar ratio*: From another point of view, the alkylation reaction of toluene with methanol occurred in the absence of the solvent. It was previously reported that 1:3 toluene: methanol molar ratio is usually required for high p-xylene selectivity.²² In this work, it was found that the methanol toluene reaction could proceed with significantly low toluene: methanol molar ratio of 1:1 and 1:2. The reaction using 1:1 toluene: methanol molar ratio in the presence of 0.01 gm catalyst at 120 °C for 2 h afforded a conversion of only 15% with 58% xylene selectivity and 91.07% p-xylene in total xylene product (Figure 11).

3.2e *Catalyst regeneration*: Regeneration is one of the benefits of solid catalysts and we wish to prove the reusability of MIL-101(Cr) under optimized reaction conditions. For this study, the toluene methylation reaction over the prepared MIL-101(Cr) catalyst was carried out for four cycles at the same reaction condition; at 120 °C for 2 h in the presence of 0.01 gm catalyst and 1:1 toluene: methanol molar ratio. After



Figure 10. (a), (b) Effect of catalyst weight on toluene methylation reaction (1:1 toluene: methanol molar ratio, 2 h, and 120 °C).



Figure 11. Effect of toluene: methanol molar ratio on toluene methylation reaction (0.01 gm Cr-MOF, 2 h, 120 °C).

each cycle, the catalyst MIL-101(Cr) was separated from the reaction mixture by centrifuge, washed several times with methanol, dried under vacuum before it was ready for reuse in the next run, in order to remove adsorbed products that can block active sites and thus decrease the activity; the results are shown in Table S1 (Supplementary Information). After the chromatographic analysis, it can be concluded that the catalyst can easily separate, has high stability and durability. MIL-101(Cr) did not lose its activity and selectivity for the four runs during the toluene methylation reaction (Figure 12). On the other hand, the structural stability of the catalyst was also investigated by X-ray diffraction and IR spectroscopy. Figures 2 and 4 display that MIL-101(Cr) had appropriate structural stability to be used again (Figure 13).



Figure 12. Regeneration of Cr-MOF for toluene methylation reaction (120 °C for 2 h in presence of 0.01 gm catalyst and 1:1 toluene: methanol molar ratio).



Figure 13. Schematic illustration Ring alkylation mechanism over the prepared Cr-MOF.²⁹

3.2f *Reaction mechanism*: The reaction of toluene methylation is explained according to ring alkylation and side-chain alkylation mechanisms:

- In ring alkylation mechanism: the reactants are adsorbed on the BrÖnsted acid sites bridging hydroxyl. Methanol strongly adsorbs on the catalyst acidic site before it reacts with the toluene which weakly interacts with the solid acids (Eley-Rideal type mechanism).³¹ The methanol directly attaches to the acidic proton sites on the catalyst *via* its oxygen atom and the CH₃ group is immediately chemisorbed to the oxygen of the hydroxyl group,³² then the methyl group attached to toluene forms π -complex with the metals. After π - σ conversion, a proton of toluene is given back to catalyst to form a new bridging hydroxyl group, and the xylenes and water are produced *via* the adsorption-desorption process.
- On the hand, the side chain alkylation mechanism,³³ requires the complete absence of Brönsted acid sites, since these would catalyze ring

alkylation at a much higher rate.^{34,35} In this mechanism, the role of the catalyst is twofold. First, it promotes the dehydrogenation of methanol to formaldehyde (step (1)). In step (2), styrene is formed from toluene and formaldehyde. This reaction maybe enhanced through polarization of the methyl group of toluene by the catalyst which leads to a carbanion structure. In step (3), styrene is hydrogenated to ethylbenzene with the generated H in step (1).

$$CH_3OH \rightarrow HCHO + H$$
 (1)

 $C_6H_5CH_3 + HCHO \rightarrow C_6H_5CH = CH_2 + H_2O \qquad (2)$

$$C_6H_5CH = CH_2 + H_2 \rightarrow C_6H_5CH_2CH_3$$
(3)

4. Conclusions

This research demonstrated that the metal-organic framework Cr-MIL-101 is an efficient catalyst for liquid-phase toluene alkylation reaction with methanol at low reaction temperature. This is a good and important new result compared to previous literature data. The selectivity was reached 76% at 120 °C with 33% conversions that can be accomplished using Cr-MIL-101. The content of p-xylene in xylenes is still at a relatively high level, which induces low separation cost in the industry.

Supplementary Information (SI)

Table S1 is available at www.ias.ac.in/chemsci.

References

- Shimizu K, Niimi K and Satsuma A 2008 Polyvalentmetal salts of heteropolyacid as catalyst for Friedel-Crafts alkylation reactions *Appl. Catal. A: Gen.* 349 1
- 2. Olah G A 1964 *Friedel-Crafts and related reactions* (New York: Wiley–Inter Science) p. 1
- Shrinivas V Gh and Uma V Ch 2015 Friedel–Crafts alkylation and acylation of aromatic compounds under solvent free conditions using solid acid catalysts *Int. J. Chem. Studies* 2 27
- De Noronha R G, Ferrandes A C and Roao C C 2009 MoO₂Cl₂ as a novel catalyst for Friedel–Crafts acylation and sulfonylation *Tetrahedron Lett.* 50 1407
- 5. Nguyen L T L, Le K K A and Phan N T S 2012 A Zeolite Imidazolate Framework ZIF-8 Catalyst for Friedel-Crafts Acylation *Chin. J. Catal.* **33** 4
- 6. Zhichao M, Jin Zh, Jinping Zh, Dandan L, Xu B, Lingjun Ch and Shuping Zh 2017 A novel mesoporous sulfated zirconium solid acid catalyst for Friedel–Crafts benzylation reaction *Appl. Surf. Sci.* **411** 419

- Ahmed K A, Ateyya A A, Salwa A G, Samia A H and Ahmed E A 2012 Catalytic para-xylene maximization. Part X: Toluene disproportionation on HF promoted H-ZSM-5 catalysts *Egypt. J. Pet.* **21** 119
- Cook T R, Zheng Y-R and Stang P J 2013 Metal– Organic Frameworks and Self-Assembled Supramolecular Coordination Complexes: Comparing and Contrasting the Design, Synthesis, and Functionality of Metal–Organic Materials *Chem. Rev.* **113** 734
- Nagaraj A and Amarajothi D 2017 Cu₃(BTC)₂ as a viable heterogeneous solid catalyst for Friedel-Crafts alkylation of indoles with nitroalkenes *J. Colloid Interf. Sci.* 494 282
- Abd El Salam H M, Younis S A, Ali H R and Zaki T 2017 Statistical modeling and optimization of phenol adsorption from water by modified Cu₃(BTC)₂: Kinetic, isotherm, and thermodynamic analysis *Micropor. Mesopor. Mater.* 241 210
- Abd El Salam H M and Zaki T 2018 Removal of hazardous cationic organic dyes from water using nickel-based metal-organic frameworks *Inorg. Chim. Acta* 471 203
- Maksimchuk N V, Zalomaeva O V, Skobelev I Y, Kovalenko K A, Fedin V P and Kholdeeva O A 2012 Metal–organic frameworks of the MIL-101 family as heterogeneous single-site catalysts *Proc. R. Soc. A* 468 2017
- Li H, Eddaoudi M, O'Keeffe M and Yaghi M 1999 Design and synthesis of an exceptionally stable and highly porous metal–organic framework *Nature* 402 276
- Rowsell J L C and Yaghi O M 2004 Metal–organic frameworks: a new class of porous materials *Micropor*. *Mesopor. Mater.* 73 3
- 15. Li Z-Q, Qiu L-G, Xu T, Wu Y, Wang W, Wu Z-Y and Jiang X 2009 Ultrasonic synthesis of the microporous metal–organic framework Cu₃(BTC)₂ at ambient temperature and pressure: an efficient and environmentally friendly method *Mater. Lett.* **78** 63
- 16. Rogge S M J, Bavykina A, Hajek J, Garcia H, Olivos-Suarez A I, Sepulveda-Escribano A, Vimont A, Clet G, Bazin P, Kapteijn F, Daturi M, Ramos-Fernandez E V, Llabres i Xamena F X, Van Speybroeck V and Gascon J 2017 Metal–organic and covalent organic frameworks as single-site catalysts *Chem. Soc. Rev.* **46** 3134
- Sibnath K, Baichuan S and Anutosh Ch. 2015 Study of metal–organic framework MIL-101(Cr) for natural gas (methane) storage and compare with other MOFs (metal–organic frameworks) *Energy* **91** 772
- Razieh F, Hamid A, Majid M and Mona M 2013 Nanorod catalysts: Building MOF bottles (MIL-101 family as heterogeneous single-site catalysts) around vanadium oxide ships *J. Mol. Catal. A: Chem.* **374** 46
- Pham D D, Huynh T M T, Thuy C T, Ho S T, Mai X T, Tran N T, Tran T H and Dinh Q K 2019 Metal-Organic Framework MIL-101: Synthesis and Photocatalytic Degradation of Remazol Black B Dye J. Nanomater. 15 1
- 20. Prasanth K and Johnny D 2015 Hydrogen adsorption in lithium doped MIL-101 and MIL-53(Al) at 77 and 298 K up to 100 bar: effect of lithium concentration *J. Porous Mater.* 22 1073

- Qing L, Liqi N, Shudong Zh. Mengna T, Yao Sh. and Yi H 2013 Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contamina *Rep.* **3** 2916
- Abd Elhafiz D R, Ebiad M A and Mekhail S 2015 Shape Selective Pillared Clay Catalysts for P-Xylene Production J. Adv. Mater. Proc. 3 35
- Changq L, Seungjun L, Wookdong K and Ryong R 2017 High utilization of methanol in toluene methylation using MFI zeolite nanosponge catalyst *Catal*. *Today* 303 143
- 24. Liu H Y, Zhu J, Wang Y D, Yu O B and Xu T J 2017 Effect of operating conditions on alkylation of toluene with methanol *Petrol. Sci. Technol.* **35** 148
- 25. Sotelo J L, Uguina M A, Valverde J L and Serrano D P 1993 Kinetics of toluene alkylation with methanol over Mg-modified ZSM-5 *Ind. Eng. Chem. Res.* 32 2548
- 26. Sotelo J L, Uguina M A, Valverde J L and Serrano D P 1994 Deactivation of toluene alkylation with methanol over magnesium-modified ZSM-5 Shape selectivity changes induced by coke formation *Appl. Catal. A: Gen.* **114** 273
- 27. Chuanfu W, Qi Zh, Yufei Zh, Dongke Zh, Jingyun Ch. and Fou-Kuo Ch. 2017 p-Xylene selectivity enhancement in methanol toluene alkylation by separation of catalysis function and shape-selective function *Mol. Catal.* 433 242

- 28. Chen N Y, Kaeding W W and Dwyer F G 1979 Paradirected aromatic reactions over shape-selective molecular sieve zeolite catalysts *Am. J. Chem. Soc.* **101** 6783
- 29. Luqman A, Abdullah M A and Sulaiman al-kh 2015 Experimental and kinetic studies of ethyltoluenes production via different alkylation reactions *Chem. Eng. Res. Des.* **95** 34
- 30. Phan N T S, Le K K A and Tuan D Ph 2010 MOF-5 as an efficient heterogeneous catalyst for Friedel–Crafts alkylation reactions *Appl. Catal. A: Gen.* **382** 246
- Binitha N N and Sugunan S 2008 Shape selective toluene methylation over chromia pillared montmorillonites *Catal. Commun.* 9 2376
- 32. Blaszkowski S R and Van santen R A 1997 Theoretical Study of the Mechanism of Surface Methoxy and Dimethyl Ether Formation from Methanol Catalyzed by Zeolitic Protons *J. Phys. Chem. B* **101** 2292
- Itoh H, Miyamoto A and Murakami Y 1980 Mechanism of the side-chain alkylation of toluene with methanol *J. Catal.* 64 284
- 34. Song L, Li Z, Zhang R, Zhao L and Li W 2012 Alkylation of toluene with methanol: The effect of K exchange degree on the direction to ring or side-chain alkylation *Catal. Commun.* **19** 90
- 35. Kohantorabi M and Gholami M R 2018 Cyclohexene oxidation catalyzed by flower-like core-shell Fe₃O₄@-Au/metal organic frameworks nanocomposite *Mater*. *Chem. Phys.* 213 472