Chemical Engineering Journal 145 (2008) 328–334

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

The benzylation of xylenes using heterogeneous catalysts from rice husk ash silica modified with gallium, indium and iron

Farook Adam*, Adil Elhag Ahmed

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

ARTICLE INFO

Article history:
Received 28 March 2008
Accepted 18 August 2008

Keywords:
Benzylation
Xylene
Rice husk silica
Heterogeneous catalyst
Sol–gel

ABSTRACT

Rice husk ash (RHA) was used to synthesize RHA-Ga, RHA-In and RHA-Fe catalysts by direct incorporation of the respective ions into rice husk ash silica at room temperature. The prepared catalysts were used to catalyze the benzylation of *p*-xylene (*p*-Xyl) with benzyl chloride (BC). The catalysts had a BET specific surface area of ca. 272–347 $m^2\,g^{-1}$. The catalytic activity increased with a decrease in the *p*-Xyl/BC molar ratio. However, the selectivity towards the mono-benzylated product decreased. RHA-Fe showed the highest catalytic activity whereas RHA-In and RHA-Ga gave higher selectivity to 2,5-dimethyldiphenylmethane (2,5-DMDPM). The catalytic activity followed the order: RHA-Fe > RHA-In > RHA-Ga. The activity of RHA catalyst towards Xyl isomers was found to follow the order: *o*-Xyl > *m*-Xyl > *p*-Xyl whereas the selectivity for DMDPM products decreased in the order: *m*-Xyl > *p*-Xyl > *o*-Xyl.

1. Introduction

The production of dielectric fluid [1] involves the use of dimethyldiphenyl methane's (DMDPM's) as intermediates. One of the starting materials for DMDPM's is the series of xylene (Xyl) isomers. These xylenes are benzylated to yield the respective DMDPM's. Benzylation of xylenes with benzyl chloride (BC), which is a typical example of Friedel-Crafts alkylation, is generally known to proceed over homogenous Lewis acid catalyst, i.e. $AlCl_3$ [2].

Many problems are associated with the use of homogeneous Lewis acid catalysts such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, $GaCl_3$ and $InCl_3$. These include their handling (highly hygroscopic), the necessity of using large amount of substrates (required in stoichiometric amounts) and the difficulty in the separation from the products. In addition, these halides being strong Lewis acids also catalyze other undesirable reactions like alkyl isomerization and transalkylation [3]. For these reasons, considerable efforts have been directed towards the replacement of conventional problematic homogenous acid catalysts with heterogeneous solid acid catalysts for the Friedel-Crafts reaction. The solid acid catalysts that have been studied include: Lewis acids supported on mesoporous molecular sieves [4–8], zeolites (e.g. ZSM-5 [9], Hβ [10]), clays [11–13], alumina [14], or poly acid salts [15,16] as well as rice husk ash (RHA) silica [17–19].

All these catalysts were tried mainly for the benzylation of benzene or toluene. However, only few of them [5,6,10] were used for the benzylation of *p*-Xyl as part of the benzylation study. The activity towards this aromatic at 80 °C was observed to be less than that of benzene and toluene. However, at the refluxing temperature of 139 °C, *p*-Xyl was reported to be more active than benzene and toluene over Lewis acid supported apatite [15,16]. With In-Mg-hydrotalcite anionic clay [11], *p*-Xyl was found to be less active than toluene at the toluene refluxing temperature of 110 °C for the benzylation reaction. A detailed study for the liquid-phase benzylation of *o*-, *m*- and *p*-Xyl over zeolite catalysts was reported by Singh et al. [20]. For the benzylation of *o*-Xyl over zeolite H-beta with *o*-Xyl/BC molar ratio of 5:1 at 90 °C, only 33.5% BC conversion and 92.2% selectivity to mono-benzyl *o*-Xyl products were obtained. The major product was 3,4-DMDPM. However, about 1% of 2,3-DMDPM was also detected. Lower rates of reactions were found for *m*-Xyl (24%) and *p*-Xyl (11%) reactions at the same reaction conditions.

In this work we report the catalytic activity of the heterogeneous catalysts which were prepared by the direct incorporation of some Lewis acids (In^{3+}, Ga^{3+} and Fe^{3+}) onto silica from RHA. These catalysts showed high activity and selectivity to DMDPMs for the benzylation of *o*-, *m*- and *p*-xylenes at 80 °C (a temperature much lower than the Xyl refluxing temperature of ∼140 °C). It is noteworthy that the activities of these catalysts are superior to all other catalysts reported so far. These catalysts are also comparable to that of our recently reported catalyst for the benzylation of benzene [18].

---

* Corresponding author. Tel.: +60 4 6533567; fax: +60 4 6574854.
E-mail address: farook@usm.my (F. Adam).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.08.028

2. Experimental

2.1. Raw material

Indium nitrate monohydrate and gallium nitrate monohydrate (from Alfa Aesar, 99.99%) and iron granules (Aldrich, 99.999%) were used as the source for indium, gallium and iron respectively. Other materials used were sodium hydroxide and nitric acid (Systerm, 99 and 65% respectively), BC (Fluka, 99%), *o*-, *m*- and *p*-Xyl (Acros, 99% or higher). Rice husk (RH) was obtained from a rice mill in Penang, Malaysia. All chemicals used were of AR grade or higher purity and were used directly without further purification.

2.2. Methods

2.2.1. Catalyst preparation

The treatment of RH and the preparation of the catalysts were done following published procedures [18]. In a typical run, the treated RHA was dissolved in 1.0 M NaOH and filtered. The filtrate was titrated with 3.0 M HNO_3 or 3.0 M HNO_3 containing 5 wt% of Fe^{3+}, Ga^{3+} or In^{3+} ions, with constant stirring to pH 5. The gel formed was aged for 24 h. The precipitate was filtered, washed thoroughly with distilled water and dried at 100 °C for 18 h. The silica or metal ion modified silica xerogel was ground to powder and labeled as RHA-SiO_2, RHA-Fe, RHA-Ga and RHA-In. Catalysts labeled RHA-10%In and RHA-15%In were also prepared by loading 10 and 15 wt% of In^{3+} ions respectively.

2.2.2. Characterization of the catalysts

The prepared samples were characterized using the previously reported physico-chemical techniques [18], i.e. FT-IR spectroscopy, N_2 sorption analysis, powder X-ray diffractometry, scanning electron microscopy (SEM), energy dispersive spectrometry (EDX), and GC/GC–MS chromatography (for product detection and confirmation).

Gas chromatograms of the benzylation products were obtained using Clarus 500 (PerkinElmer) gas chromatograph with a VB-1 non-polar capillary column, 30-m length and 0.32-mm inner diameter and equipped with an FID detector.

2.2.3. Catalytic benzylation reactions

Liquid phase Friedel-Crafts benzylation reactions of xylenes over the prepared catalysts were carried out in a magnetically stirred 50.0 mL two-neck round bottom flask fitted with a reflux condenser. The temperature of the reaction vessel was maintained precisely using an oil bath. The reactions were carried out under the continuous flow of argon gas to avoid the effect of moisture.

In a typical reaction, 1.0 mL of dodecane (as internal standard) and 23.5 mL of *o*-, *m*- or *p*-xylene were added to 0.1 g of RHA-Ga, RHA-In or RHA-Fe catalyst (which had been activated overnight at 100 °C and flushed with argon for 1 h). The reaction mixture was maintained for about 30 min at the predetermined temperature. This was followed by the addition of 1.5 mL of BC to obtain the required Xyl/BC molar ratio of 15:1. Reactions over the catalysts of higher metal loading, i.e. RHA-10%In and RHA-15%In were carried out under the same conditions using *p*-Xyl. The effect of other molar ratios of ca. 5:1 and 25:1 was also studied with *p*-Xyl over RHA-In catalyst. Samples for analysis (~0.50 mL) were withdrawn at regular intervals from the reaction mixture and analyzed by gas chromatography. The products were confirmed by GC–MS.

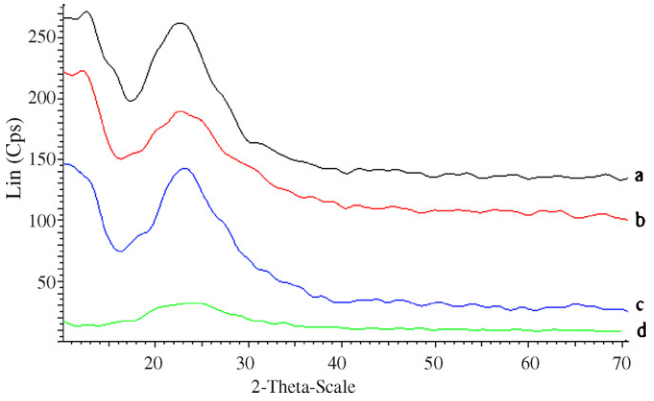

Fig. 1. The powder X-ray diffraction spectra of (a) RHA-SiO_2, (b) RHA-In, and (c) RHAGa and RHA-Fe.

Reusability experiments were conducted by running the reaction successively with the same catalyst (RHA-In) according to the published procedure [18,21]. A leaching experiment was carried out for RHA-In catalyst for *p*-Xyl reaction by separating the solid catalyst after 15 min by filtration at the reaction temperature (80 °C) using a micro membrane filter. The filtrate was quickly returned to the original flask allowing the reaction to proceed further. The products were analyzed in the usual manner.

All experiments were repeated three times to confirm the repeatability of the experimental data obtained.

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1 shows the X-ray diffraction of the catalysts prepared in this work. The X-ray diffraction patterns of RHA-SiO_2 as well as RHA-In, RHA-Ga and RHA-Fe catalysts, indicated the absence of any ordered crystalline structure. All the catalysts had similar diffraction patterns, i.e. a broad peak centered at 2θ angle of around 22° which confirmed the amorphous nature of the samples. These results were consistent with our previous studies [17–19].

Nitrogen adsorption–desorption isotherms of these catalysts had been reported earlier [18]. These catalysts exhibit the same isotherm shapes and hysteresis loops indicating almost similar tex-

Table 1
The N_2 adsorption surface analysis parameters and metal contents for RHA-SiO_2, RHA-In, RHA-Ga and RHA-Fe

Sample	Specific surface area ($m^2\,g^{-1}$)	Average pore volume ($cm^3\,g^{-1}$)	Average pore diameter, D (nm)	Average content of metal ions ($mmol\,g^{-1}$)[a]
RHA-SiO_2	347	0.87	10	–
RHA-Ga	332	0.82	10	0.29 (0.36)[b]
RHA-Fe	284	1.10	15	0.67 (0.66)
RHA-In	272	0.87	13	0.35 (0.24)
RHA-10% In	208	0.99	15	0.98 (0.73)
RHA-15% In	114	0.42	13	1.25 (1.04)

[a] The values shown are from EDX analysis.

[b] The values in brackets are the actual amounts of metal ions determined by ICP-MS spectrometer (PE-SCIEX-ELAN 6100).

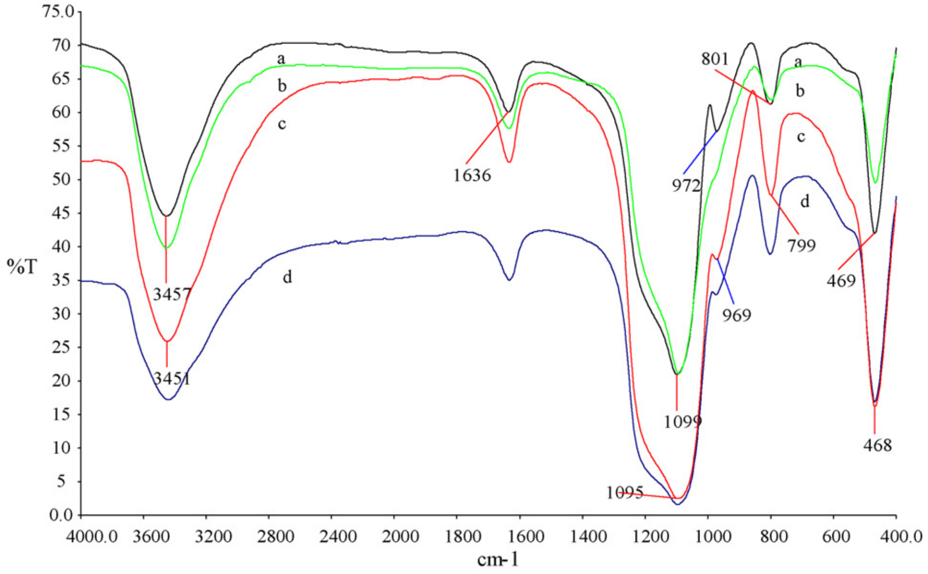

Fig. 2. The FT-IR spectra of RHA silica and metal modified silica (a) RHA-SiO_2, (b) RHA-Fe, (c) RHA-In and (d) RHA-Ga.

tural properties. The corresponding specific BET surface areas, pore sizes and pore volumes are shown in Table 1. All the metal ion modified silica samples, i.e. RHA-In, RHA-Ga and RHA-Fe as well as the silica support, RHA-SiO_2 showed a type (IV) isotherm. Type (IV) isotherms are normally exhibited by porous materials. The hysteresis loops were of type H1 (IUPAC classification), which is a characteristic of porous materials consisting of agglomerates or having nearly uniform and regularly packed pores. The shapes of these isotherms are similar to those synthesized from the optimized concentration of alkali, i.e. 1.0 M NaOH solution as reported previously [18]. For RHA-In with varying metal composition, it was found that the specific surface area decreased linearly with a linearity coefficient of 0.988 (graph not shown) as the metal content increased.

This decrease in the specific surface area is probably due to the metal filling up the inter-particle voids by the formation of –O–M–O– bonds ($M = Fe^{3+}$, In^{3+} or Ga^{3+}).

Fig. 2 shows the FT-IR spectra of RHA-SiO_2, RHA-Ga, RHA-In and RHA-Fe. The absorption bands at about 470, 800 and 1099 cm^{-1} were attributed to the stretching vibrations of SiO_4 tetrahedra [22]. The peak at 972 cm^{-1} was attributed to Si–OH stretching vibration. The intensity of this peak decreased in the metal ion incorporated RHA silica (Fig. 2) and completely diminished for samples with higher percentages of In^{3+} metal ions (Fig. 3). This might indicate that some metal ions are attached on the surface of the silica as non-framework metal species, i.e. ≡Si–O–M. The band around 1099 cm^{-1} was shifted to lower wave number for metal incorporated RHA. Since this band is due to the vibration of Si–O–Si bond,

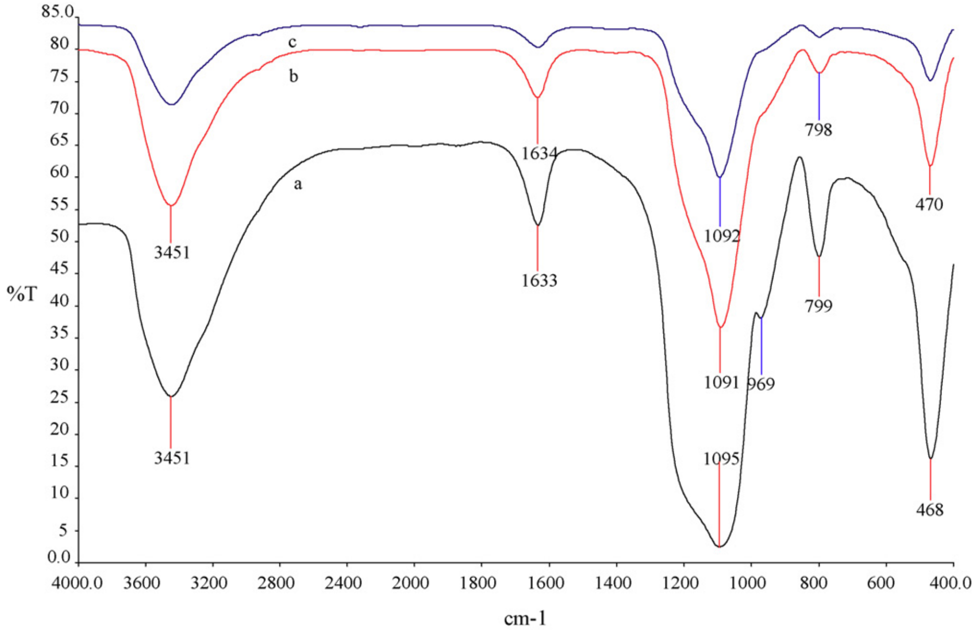

Fig. 3. The FT-IR spectra of modified silica by loading different amounts of In^{3+} ions (a) RHA-5%In, (b) RHA-10%In and (c) RHA-15%In.

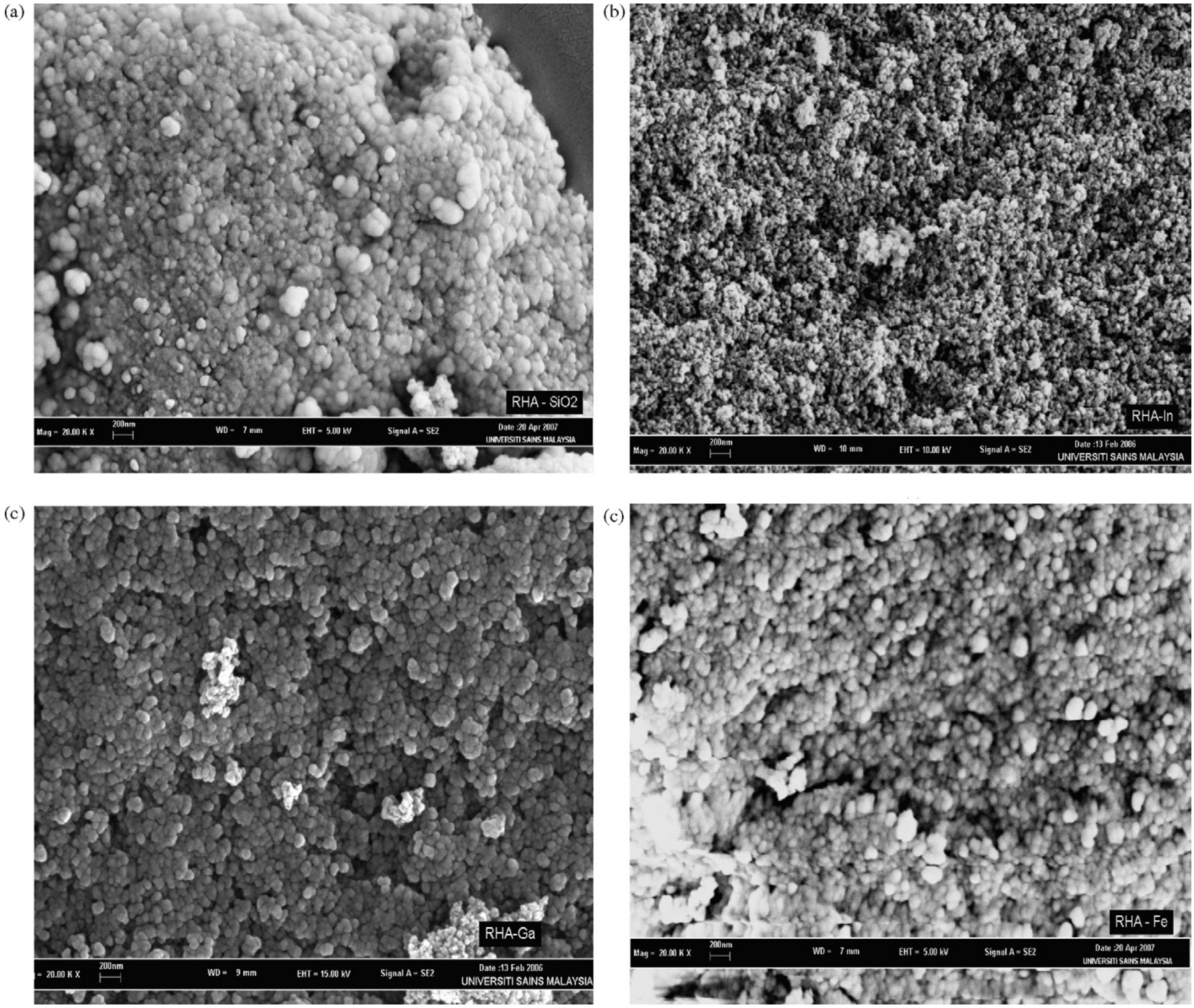

Fig. 4. The SEM micrographs of (a) RHA-SiO_2, (b) RHA-In, (c) RHA-Ga and (d) RHA-Fe.

the red shift observed is consistent with the increasing presence of network metallic species as the metal ion content was increased. Fig. 3 shows that when the metal ion content was increased (i.e. RHA-10%In and RHA-15%In) the red shift also increased for this vibration band.

The SEM micrographs of the catalysts are shown in Fig. 4. These micrographs together with the TEM images (not shown) and N_2 sorption isotherms [18] clearly illustrate the porous structure of RHA-SiO_2 and the metal ion modified catalysts. The surface morphology and spherical structure of the particles were retained even when the silica was modified with In^{3+}, Ga^{3+} or Fe^{3+} ions.

EDX elemental analysis for the metal ion modified silica samples showed the presence of In, Ga and Fe ions on the silica surface (Table 1). However, an irregular distribution of In^{3+} ions were detected for the catalysts prepared by introducing higher amounts of the metal ions, i.e. RHA-10% In (9.9–12.7%) and RHA-15% In (11.3–19%). This showed that the metal was not homogeneously distributed on the surface. Unlike the In and Fe supported catalysts, the amount of Ga species detected on the surface of RHA-Ga (by EDX) were much lower than the actual metal ions which was determined by ICP-MS. This could be explained because most of the gallium ions are accommodating the framework positions of the silica-metal complex of RHA-Ga. The result of ^{71}Ga MAS NMR for RHA-Ga (not shown) supports this hypothesis. Therefore, this maybe one of the reasons why RHA-Ga was found to be less active than RHA-In, although In and Ga have similar redox properties and will be discussed latter.

3.2. *Catalytic reactions*

The Friedel-Crafts benzylation of *p*-Xyl with BC was carried out using different experimental conditions, namely varying molar ratios of reactants, reaction temperature, reaction time, catalyst type, metal ion loading, recyclability, and leaching. In addition, a comparison of the catalytic behavior with other xylene isomers, i.e. *o*- and *m*-Xyl was also carried out at the optimum condition.

3.2.1. *Influence of reactant molar ratio*

Fig. 5 shows the percentage conversion and selectivity of RHA-In. The rate of reaction was found to decrease as the *p*-Xyl/BC ratio

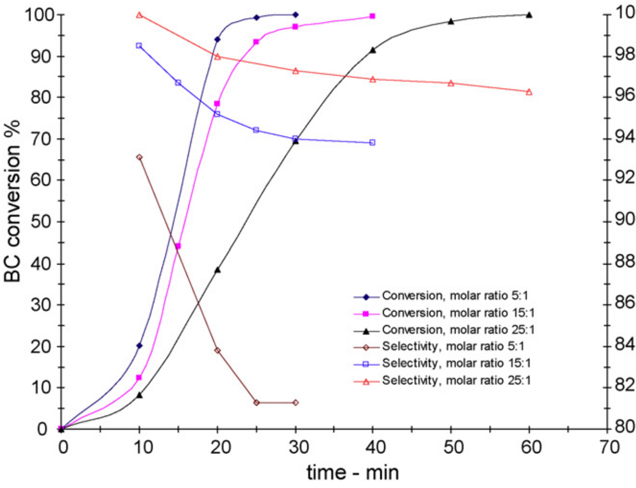

Fig. 5. The reaction profile for the reaction between *p*-Xyl and BC at 80 °C using different molar ratios of *p*-Xyl/BC and over the catalytic activity of RHA-In.

was increased. The reaction time required for complete conversion of BC for the 5:1, 15:1 and 25:1 molar ratios were found to be 25, 40 and 60 min respectively.

Whereas, the selectivity to mono-benzylated product, i.e. 2,5-DMDPM increased from 81 to 96% when the molar ratio was varied from 5 to 25 respectively. This showed that a decrease in BC concentration increased the selectivity for 2,5-DMDPM while taking a longer time to reach complete conversion.

3.2.2. Influence of reaction temperature

As shown in Fig. 6, the catalytic performances were strongly affected by temperature. The conversion rate of BC increased with increasing reaction temperature. However, the selectivity for the mono-substituted product (2,5-DMDPM) decreased. However, this decrease was very small. It was clear that the conversion and the selectivity could be easily controlled by simply adjusting the reaction temperature.

3.2.3. Metal ion loading

The effect of metal ion loading was tested for the benzylation of *p*-Xyl at the optimum conditions using 0.1 g of the catalyst with different loading of indium ions, i.e. RHA-In, RHA-10%In or RHA-15%In. Fig. 7 shows the percentage conversion of BC increased drastically when the percentage of loaded metal ion (indium) was increased from 5 to 10%. Higher metal loading (15%In) did not show further enhancement in the percentage conversion.

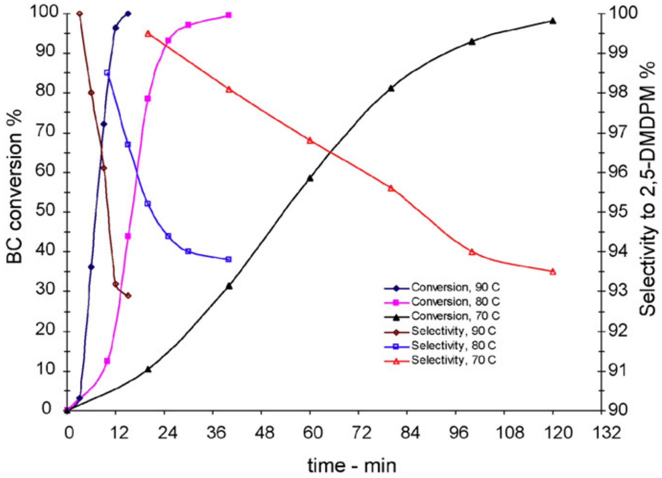

Fig. 6. The reaction profile of *p*-Xyl and BC for the 15:1 *p*-Xyl/BC molar ratio and over the catalytic activity of RHA-In at different temperatures.

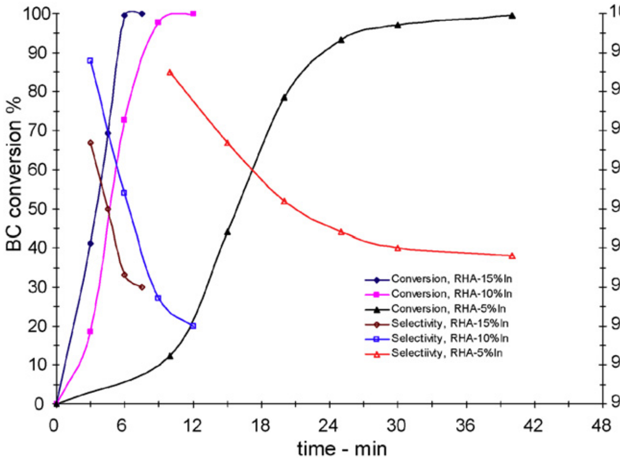

Fig. 7. The reaction profile between *p*-Xyl and BC at 80 °C using 15:1 *p*-Xyl/BC molar ratio and over the catalytic activity of RHA-In with different loading of indium ions.

Although higher conversion was registered in a shorter time with the catalysts of 10 and 15% In loading, there was a slight decrease in the selectivity for 2,5-DMDPM. Nevertheless, the selectivity remained above 90% for all the three indium composition in the catalysts.

3.2.4. Influence of catalyst type

In order to study the effect of the incorporated metal, the *p*-Xyl benzylation reaction was studied further over RHA-Ga and RHA-Fe catalysts. The reactions were carried out at the optimum conditions (i.e. at 80 °C and *p*-Xyl/ BC molar ratio of 15:1) using 0.1 g of the catalyst. The results were compared with that of RHA-In.

No reaction was seen over RHA-SiO_2 (blank). However, the type of supported metal ions on the RHA silica was found to influence the catalytic activity significantly. Fig. 8 shows the reaction profiles of the catalysts studied. The rate of the benzylation reaction decreased in the following order of the catalysts:

RHA-Fe > RHA-In > RHA-Ga

Although there were clear changes in the rate of the reaction, the variation in the selectivity at the time of complete conversion

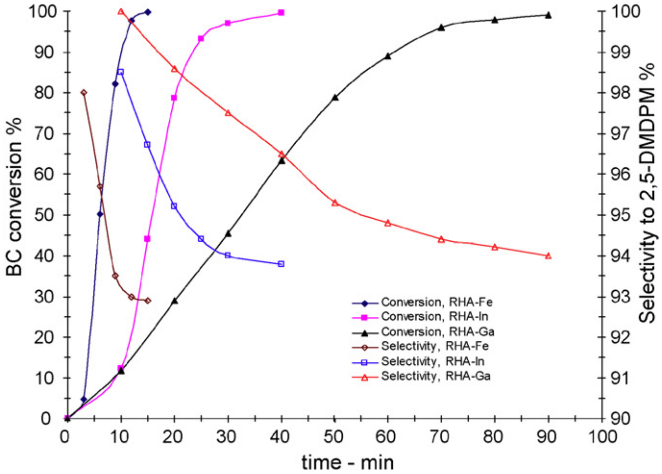

Fig. 8. The reaction profile between *p*-Xyl and BC at 80 °C using 15:1 *p*-Xyl/BC molar ratio and over the catalytic activity of different catalysts.

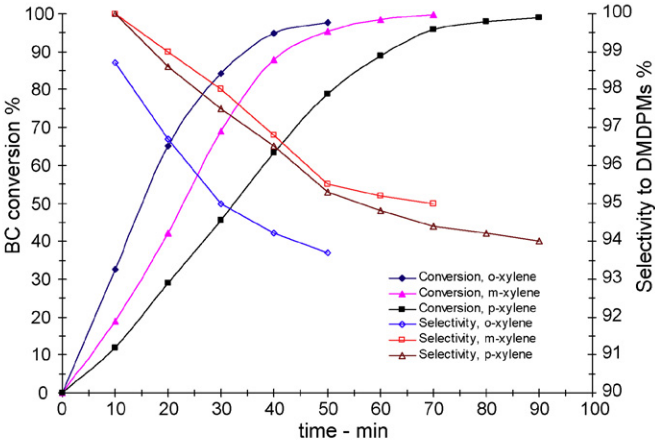

Fig. 9. The reaction profile of xylene isomers on BC conversion over the catalytic activity of RHA-In at 80 °C using 15:1 Xyl/BC ratio.

was considered not significant as it was between a narrow range of 93–94%.

The activity of RHA-M (M = In, Ga or Fe) catalysts can be attributed to the presence of In^{3+}, Ga^{3+} or Fe^{3+} ions on the catalyst surface and/or matrix. This is true as there was no reaction with RHA-SiO_2. The catalytic activity correlated well with the redox properties of the metal ions, since the variation in the activities seems to follow the change in their redox potentials. This redox property was expected to play an important role for initiating the BC carbocation for the benzylation reaction [8,23,24]. The iron, having the highest redox potential value (+0.77 V), showed superior activity over the rest. However, the higher activity of RHA-In over RHA-Ga catalyst could be due to the lower amount of non-framework Ga species present on the surface of RHA-Ga. Since the two supported metals ions (In and Ga) have equivalent redox potentials (−0.44 V). Similar explanation was given by Choudhary and Jana [21].

3.2.5. *Effect of different isomers*

The reaction of *o*- and *m*-Xyl isomers was also investigated at the optimum condition using RHA catalysts. A reaction profile of the catalyst (RHA-Ga as example) over different xylene isomers is shown in Fig. 9. It is obvious that higher percentage of BC conversion was observed with *o*-Xyl, while *p*-Xyl showed the lowest activity. However, the selectivity for DMDPM decreased in the following order of xylene isomers:

$$m\text{-Xyl} > p\text{-Xyl} > o\text{-Xyl}$$

Nevertheless, the variation of the selectivity can be considered not very significant. The same trend of activity and selectivity with respect to the xylene isomers was also observed for RHA-In and RHA-Fe as shown in Table 2.

Fig. 10 shows the positions which are expected to be attacked by the benzyl carbocations. The differences in reactivity and selectivity between these isomers (Table 2) might be assigned to the steric and field effects, i.e. the directing ability of the methyl substituents.

In *p*-Xyl, each substitutable carbon centre on the benzene ring experience a positive *ortho* directing effect by the adjacent methyl group, while the other methyl substituent decreases this enhancement for substitution because it is in a *meta* position. All four substitutable carbons are chemically equivalent, and therefore, only one mono-substituted product was observed, i.e. 2,5-DMDPM.

However, the advantage of the field effect together with the slightly lower steric effect allowed *m*-Xyl to produce relatively higher percentage of mono-benzylated products compared to other xylene isomers.

From Fig. 10, it can be seen that there are three possible positions for substitution on *m*-Xyl. However, only positions 1 and 2 had been substituted yielding 2,4-DMDPM and 2,6-DMDPM in a percentage ratio of about 79:21. No product was observed for substitution at position 3 due to the field effect, considering the fact that methyl groups are poor *meta* directors. The percentage of 2,6-DMDPM was much lower because position 2 is much more sterically hindered than position 1. Furthermore, there are two possible position 1 sites

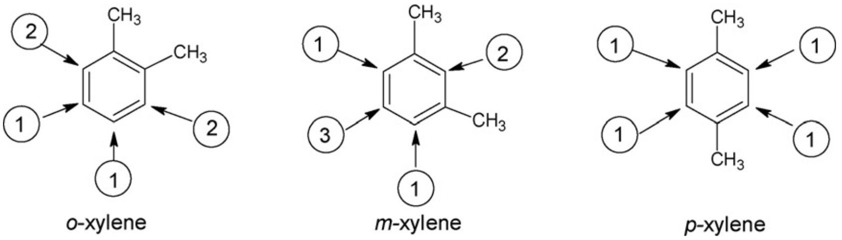

Fig. 10. The expected positions targeted for the BC carbocations to react with the *o*-, *m*- and *p*-Xyl isomers. Similar numbers on each molecule indicate chemically equivalent carbon atoms.

Table 2
The effect of different xylene isomers on the percentage conversion and product distribution at 80 °C and Xyl/BC molar ratios of 15:1

Catalyst	Xylene	50% BC conversion		90% BC conversion		TOR[a]
		Time (min)	Selectivity (%)	Time (min)	Selectivity (%)	
RHA-Ga	*o*-Xylene	15	97.7	35	94.6	71.7
	m-Xylene	23	98.7[b]	42	96.5[b]	46.8
	p-Xylene	32.3	97.3	61	94.8	33.3
RHA-In	*o*-Xylene	10.4	97.1	23.8	94.2	103.4
	m-Xylene	13.5	98.3[b]	24.5	96.4[b]	79.7
	p-Xylene	15.9	96.4	23.5	94.6	67.6
RHA-Fe	*o*-Xylene	2.3	93.5	4.0	92.7	467.4
	m-Xylene	3.4	97.8[b]	5.5	96.3[b]	316.2
	p-Xylene	6.0	95.7	10.2	93.3	179.2

[a] Turn over rate for 50% conversion in $\mu mol\,g^{-1}\,s^{-1}$.

[b] Two mono-substituents 2,4-DMDPM and 2,6-DMDPM in a percentage ratio of about 79:21.

Table 3
The effect of RHA-In reuse on the percentage conversion and product distribution at 80 °C and *p*-Xyl/BC molar ratio of 15:1

Catalyst	BC conversion (%)	2,5-DMDPM (%)
Fresh	100	93.6
1st	100	91.6
2nd	100	93.8

Table 4
Leaching effect for RHA-In at 80 °C and *p*-Xyl/BC reactant molar ratio of 15:1 during the benzylation of *p*-Xyl with BC

Reaction time (min)	BC conversion (%)	2,5-DMDPM (%)
15	44.6	96.7
60[a]	50.7	96.7

[a] Duration of reaction after catalyst had been removed.

as compared to only one position 2 site. The observed product distribution for *m*-Xyl conforms to the statistical availability of the substitution sites.

For *o*-Xyl, the possible products are 2,3-DMDPM (substitution at position 2) and 3,4-DMDPM (substitution at position 1). However, the only mono-substituted product observed was 3,4-DMDPM. While 1% of 2,3-DMDPM was observed by Singh et al. [20], this product was not observed in this study. This could be due to the steric hindrance of position 2 by the adjacent methyl group. However, the percentage reported by Singh et al. is very low and can be considered insignificant.

In all three cases the di-substituted products were also observed, making the total product composition 100% (not shown in Table 2).

3.2.6. *Reusability*

The recyclability of the catalyst was studied by running the benzylation reaction successively (under the optimum conditions) with *p*-Xyl and RHA-In as described earlier. The results are shown in Table 3. In three successive trials the percent conversion and selectivity did not show any significant change. These results indicate the catalyst could be reused several times.

3.2.7. *Leaching effect*

In order to study the heterogeneous nature of the reaction, a test reaction using RHA-In was conducted according to published method [25]. Table 4 shows the results of this study. No significant increase in the BC conversion was observed after the removal of the catalyst. This indicated that the heterogeneous RHA-In catalyst was necessary for the reaction to proceed. It was therefore safe to conclude that a purely heterogeneous catalytic reaction was taking place when RHA-In was used as the catalyst.

4. Conclusion

The catalytic activity of RHA-In, RHA-Ga and RHA-Fe were tested in the benzylation of *p*-Xyl employing BC as the alkylating agent. RHA-Fe showed the highest catalytic activity whereas RHA-In and RHA-Ga gave higher selectivity to 2,5-DMDPM. The catalytic activity followed the order: RHA-Fe > RHA-In > RHA-Ga. The catalysts also showed good activity for the benzylation of *o*- and *m*-Xyl. The activity of the catalyst towards xylene isomers followed the order: *o*-Xyl > *m*-Xyl > *p*-Xyl whereas the selectivity for DMDPM products decreased as follows: *m*-Xyl > *p*-Xyl > *o*-Xyl. Increasing the In^{3+} ion loading from 5 to 10% was found to accelerate the catalytic activity drastically whereas further increase in In^{3+} ion loading did not show significant changes in activity or in the selectivity. The catalysts could be reused for the benzylation reaction several times without significant change in their activity and selectivity. These catalysts showed superior catalytic activity compared to other catalysts reported in the literature.

Acknowledgements

The authors would like to express their thanks to Leong Guan Rice Mill Sdn. Bhd, Penang for providing the rice husk. We would also like to thank the Ministry of Education, Malaysia, for the FRGS grant (Ac. No.: 203/PKIMIA/671021) which partly supported this work. We thank the Sudan University of Science & Technology for a scholarship to Adil Elhag Ahmed.

References

[1] R. Commandeur, N. Berger, P. Jay, Dielectrics comprising methyl/benzyl derivatives of diphenylmethane, US Patent No. 5,601,755 (1997).
[2] G.A. Olah, S.J. Kuhn, S. Flood, Aromatic substitution. X^1. The $AlCl_3$–CH_3NO_2-catalyzed benzylation of benzene and *n*-alkylbenzenes with benzyl chloride in nitromethane solution, J. Am. Chem. Soc. 84 (1962) 1688–1695.
[3] P. Ratnasamy, A.P. Singh, S. Sharma, Halogenation over zeolite catalysts, Appl. Catal. A 135 (1996) 25–55.
[4] Y. Sun, S. Walspurger, J.P. Tessonnier, B. Louis, J. Sommer, Highly dispersed iron oxide nanoclusters supported on ordered mesoporous SBA-15: a very active catalyst for Friedel-Crafts alkylations, Appl. Catal. A 300 (2006) 1–7.
[5] K. Bachari, O. Cherifi, Study of the benzylation of benzene and other aromatics by benzyl chloride over transition metal chloride supported mesoporous SBA-15 catalysts, J. Mol. Catal. A 260 (2006) 19–23.
[6] K. Bachari, O. Cherifi, Gallium-containing mesoporous silicas as a catalyst for alkylation of benzene and other aromatics by benzyl chloride, J. Mol. Catal. A 253 (2006) 187–191.
[7] K. Okumura, K. Nishigaki, M. Niwa, Prominent catalytic activity of Ga-containing MCM-41 in the Friedel-Crafts alkylation, Micropor. Mesopor. Mater. 44–45 (2001) 509–516.
[8] M.S. Hamdy, G. Mul, J.C. Jansen, A. Ebaid, Z. Shan, A.R. Overweg, Th. Maschmeyer, Synthesis, characterization, and unique catalytic performance of the mesoporous material Fe-TUD-1 in Friedel-Crafts benzylation of benzene, Catal. Today 100 (2005) 255–260.
[9] E. Diaz, S. Ordonez, A. Vega, A. Auroux, J. Coca, Benzylation of benzene over Fe-modified ZSM-5 zeolites: correlation between activity and adsorption properties, Appl. Catal. A 295 (2005) 106–115.
[10] V.R. Choudhary, S.K. Jana, N.S. Patil, S.K. Bhargava, Friedel-Crafts type benzylation and benzoylation of aromatic compounds over Hβ zeolite modified by oxides or chlorides of gallium and indium, Micropor. Mesopor. Mater. 57 (2003) 21–35.
[11] V.R. Choudhary, R. Jha, V.S. Narkhede, In–Mg-hydrotalcite anionic clay as catalyst or catalyst precursor for Friedel-Crafts type benzylation reactions, J. Mol. Catal. A 239 (2005) 76–81.
[12] V.R. Choudhary, S.K. Jana, Benzylation of benzene and substituted benzenes by benzyl chloride over $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ supported on clays and Si-MCM-41, J. Mol. Catal. A 180 (2002) 267–276.
[13] T. Cseri, S. Békássy, F. Figueras, S. Rizner, Benzylation of aromatics on ion-exchanged clays, J. Mol. Catal. 98 (1995) 101–107.
[14] M.S. Niasari, J. Hasanalian, H. Najafian, Alumina-supported $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ as catalysts for the benzylation of benzene by benzyl chloride, J. Mol. Catal. A 209 (2004) 209–214.
[15] S. Sebti, R. Tahir, R. Nazih, S. Boulaajaj, Comparison of different Lewis acid supported on hydroxyapatite as new catalysts of Friedel-Crafts alkylation, Appl. Catal. A 218 (2001) 25–30.
[16] A. Saber, A. Smahi, A. Solhy, R. Nazih, B. Elaabar, M. Maizi, S. Sebti, Heterogeneous catalysis of Friedel-Crafts alkylation by the fluorapatite alone and doped with metal halides, J. Mol. Catal. A 202 (2003) 229–237.
[17] F. Adam, K. Kandasamy, S. Balakrishnan, Iron incorporated heterogeneous catalyst from rice husk ash, J. Colloid Interface Sci. 304 (2006) 137.
[18] A.E. Ahmed, F. Adam, Indium incorporated silica from rice husk ash and its catalytic activity, Micropor. Mesopor. Mater. 103 (2007) 284–295.
[19] F. Adam, J. Andas, Amino benzoic acid modified silica—an improved catalyst for the mono-substituted product in the benzylation of toluene with benzyl chloride, J. Colloid Interface Sci. 311 (2007) 135–143.
[20] A.P. Singh, B. Jacob, S. Sugunan, Liquid-phase selective benzylation of *o*-xylene using zeolite catalysts, Appl. Catal. A 174 (1998) 51–60.
[21] V.R. Choudhary, S.K. Jana, Benzylation of benzene by benzylchloride over Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts, Appl. Catal. A 224 (2002) 51–62.
[22] M.D. Alba, Z. Luan, J. Klinowski, Titanosilicate mesoporous molecular sieve MCM-41: synthesis and characterization, J. Phys. Chem. 100 (1996) 2178–2182.
[23] K. Bachari, O. Cherifi, Benzylation of aromatics on tin-containing mesoporous materials, Appl. Catal. A 319 (2007) 259–266.
[24] N. He, S. Bao, Q. Xu, Fe-containing mesoporous molecular sieves materials: very active Friedel-Crafts alkylation catalysts, Appl. Catal. A 169 (1998) 29–36.
[25] I.W.C.E. Arends, R.A. Sheldon, Activities and stabilities of heterogeneous catalysts in selective liquid phase oxidations: recent developments, Appl. Catal. A 212 (2001) 175–187.