Preparation of isobutylcumenes by liquid-phase isopropylation of isobutylbenzene with 2-propanol using zeolite H-beta

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The liquid-phase isopropylation of isobutylbenzene (IBB) with 2-propanol to 3-isobutylcumene (3-IBC) and 4-isobutylcumene (4-IBC) using zeolite H-beta as a catalyst is reported. The zeolite H-beta-catalyzed isopropylation of isobutylbenzene is found to be more selective for 4-isobutylcumene (52 wt%) than using the conventional catalyst, $AlCl_3$ (19 wt%).

KEY WORDS: isopropylation; isobutylbenzene; H-beta; 4-isobutylcumene; 3-isobutylcumene.

1. Introduction

The alkylation of aromatics through the Friedel–Crafts reaction is of substantial industrial and pharmaceutical significance [1]. Alkylation of the aromatic nucleus has been traditionally carried out with well-known Lewis acids or organometallic reagents using alkyl halides as the alkylating agents. Isopropylation of benzene and toluene with isopropylbromide as alkylating agent and $AlCl_3$ as catalyst has been studied in detail by Olah *et al.* [2]. Alkylation with various alkylating agents and Friedel–Crafts catalysts has provided insight into the trends in which activity and selectivity are mostly considered. Alcohols and alkenes can also serve as sources of electrophiles in Friedel–Crafts reactions in the presence of strong acids. Until recently, solid phosphoric acid and Friedel–Crafts catalysts like $AlCl_3$ and BF_3 were used in the synthesis of many fine chemicals and pharmaceutical intermediates [3]. In many cases, a more than stoichiometric amount of $AlCl_3$ is used for the reaction, giving poor selectivity because of degradation, polymerization and isomerization. Solid acid catalysis is one of the most important areas of research as various industrially important reactions are carried out using solid acids [3–6]. The use of solid acids like zeolitic materials is well defined in the production of aromatics and petrochemicals such as xylene, ethylbenzene, cumene and linear alkylbenzenes [7–10]. A recent Mobil patent claimed cumene production over MCM-56 and MCM-22 [11]. Acidic zeolites, having Brønsted or Lewis acid centers uniformly distributed throughout the micropores, have substantial acid strengths and are capable of replacing homogenous bulk Lewis acids. Here we study liquid-phase isopropylation of isobutylbenzene (IBB) to 3-isobutylcumene (3-IBC) and 4-isobutylcumene (4-IBC) (scheme 1) using 2-propanol as alkylating agent (in the presence of nitrobenzene as solvent) over zeolites and H-Al-MCM-41. The products 3-IBC and 4-IBC serve as precursors for making 3- and 4-hydroxybenzylalcohol, respectively, which are the intermediates for making bisphenol-F. The results concerning the optimization of the reaction conditions with zeolite H-beta are presented here.

2. Experimental

Zeolite H-beta, H-mordenite and ZSM-5 were prepared according to the procedure reported in the literature [12–14]. Zeolite Na-Y was obtained from Laborte Inorganics, Cheshire, UK. The synthesized zeolites were characterized and ion exchanged (H^+ or RE^+) according to procedures described elsewhere [15]. The NH_4^+-exchanged samples were again calcined at 823 K for 8 h to obtain their protonic forms. The mesoporous Na-Al-MCM-41 was synthesized according to the method reported in the literature [16]. H-Al-MCM-41 was obtained by ion exchange (NH_4^+) and subsequent calcination.

The SiO_2/Al_2O_3 ratio of various zeolites and H-Al-MCM-41 was estimated by energy dispersive X-ray (EDX) analysis. X-ray powder diffraction (XRD) was carried out using a Rigaku (D MAX III VC, Ni-filtered CuKα radiation, $\lambda = 1.5404$ Å) instrument. The surface area of the samples was measured by the nitrogen adsorption (BET) method. The size and morphology of the catalysts were measured using scanning electron microscopy (SEM; Cambridge Stereo scan 400). The acidity of the catalysts was measured by the temperature-programmed desorption of ammonia [17]. The alkyaltion of isobutylbenzene with 2-propanol was carried out in a 250 ml stainless steel Parr autoclave

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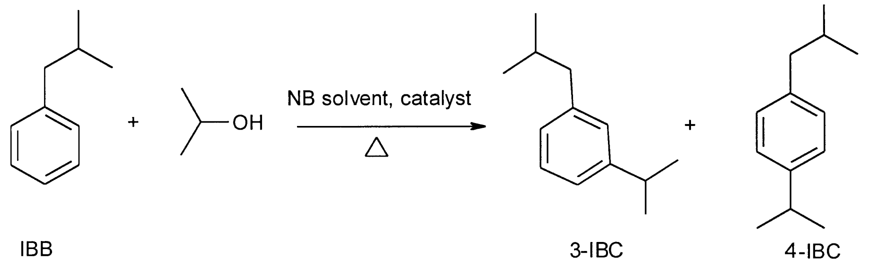

Scheme 1.

equipped with a stirrer and a temperature controller. In a typical run freshly activated catalyst (0.5 g) was added to the isobutylbenzene (25 mmol), 2-propanol (25 mmol) and nitrobenzene (20 ml) mixture in the stainless steel autoclave and flushed with nitrogen before heating to the required temperature. The products were analyzed using a gas chromatograph (HP 6890) equipped with a FID detector and capillary column (50 m × 0.2 mm) of methyl silicone gum. The products were confirmed using GC–MS and GC–IR.

3. Results and discussion

All the synthesized samples were characterized by XRD for phase purity, SEM for morphology, EDX analysis for Si/Al ratio and N_2 adsorption (NOVA) techniques for surface area. The catalytic activities for the isopropylation of IBB with 2-propanol and the physical characteristics of the different catalysts are given in table 1.

3.1. *Influence of various catalysts*

Zeolite H-beta was found to be the active catalyst in the isopropylation of IBB to 3- and 4-isobutylcumene with 2-propanol. Among the three isomers, the *meta*-isomer was found to form in a significant amount followed by the *para*-isomer due to its lower strain energy compared with the *ortho*-isomer. The strain energies for the *ortho*-, *meta*- and *para*-isomers were calculated to be −312470.0835, −312474.1799 and −312474.2110 kcal mol^{-1}, respectively. The calculated strain energy differences of the *ortho*-isomer with respect to the *meta*- and *para*-isomers were 4.0964 and 4.1275 kcal mol^{-1}, respectively. The mesoporous H-Al-MCM-41 catalyst having a SiO_2/Al_2O_3 ratio of 50 showed higher TOF ($10^{-2}\,h^{-1}\,mol^{-1}$ Al) for isobutylbenzene conversion than the other zeolites except H-beta. Medium pore size and strong acid sites promote the catalytic activity of isopropylation of IBB to *para*- and *meta*-alkylated products, and hence H-beta is found to be the active catalyst in the isopropylation of IBB while H-Y and RE-Y showed lower activities due to their weaker acid sites. H-mordenite, having unidimensional pores, showed lower activity than H-Y, RE-Y and H-beta. The small pore openings of zeolite H-ZSM-5 (5.4 × 5.6 and 5.1 × 5.5 Å) made this catalyst inactive for the reaction (<1 wt% conversion of IBB). The conventional homogeneous catalyst $AlCl_3$ showed higher activity but poor selectivity for 3-IBC or 4-IBC. The conversion of IBB and 4-IBC/3-IBC ratios over $AlCl_3$ were 79 wt% and 0.45, respectively.

Table 1
Isopropylation of isobutylbenzene

Catalyst[a]	SiO_2/Al_2O_3	NH_3 chemisorbed at 303 K ($mmol\,g^{-1}$)[b]	Conversion of IBB (wt%)[c]	TOF ($10^{-2}\,h^{-1}\,mol^{-1}$ Al)[d]	Product distribution (wt%)[e]			4-IBC/3-IBC ratio
					3-IBC	4-IBC	Others	
H-beta	26.0	0.75	17	59.0	44	52	4	1.18
H-Y	4.1	0.74	3.4	2.5	43	51	6	1.19
RE-Y	4.1	1.21	4.6	3.3	41	47	12	1.15
H-mordenite	22.0	0.71	1.8	5.4	40	60	0	1.5
H-ZSM-5	41.0	1.45	0.8	5.2	42	53	5	1.26
H-Al-MCM-41	50	0.35	2.0	14.4	60	40	0	0.67
$AlCl_3$[f]	–	–	79	22.0	42	19	39	0.45

[a] Surface area ($m^2\,g^{-1}$), degree of ion exchange (%) and crystal size (μm): H-beta = 745, 98, 0.5; H-Y = 615, 98, 1.0; RE-Y = 659, 70.6, 1.0; H-mordenite = 552, 98, 1.0; H-ZSM-5 = 413, 98, 0.4, respectively.

[b] Total ammonia desorbed at different temperature range.

[c] Reaction conditions: catalyst (g) = 0.5; IBB (mol) = 0.025; IPA (mol) = 0.025; nitrobenzene (ml) = 25; reaction temperature (K) = 453; reaction time (h) = 12.

[d] Turnover rates are expressed as turnover frequency (TOF, moles of IBB converted per mole of aluminum per hour).

[e] 3-IBC = 3-isobutylcumene; 4-IBC = 4-isobutylcumene; others = disubstituted and higher molecular weight products.

[f] Reaction temperature (K) = 323.

3.2. *Influence of H-beta/IBB ratio*

Figure 1 shows the conversion of IBB, rate of IBB conversion (TOF) and product distribution as a function of catalyst loading. The different H-beta/IBB (wt/wt) ratios were obtained by varying the amount of catalyst loading corresponding to IBB. Without catalyst the conversion of IBB was less than 0.5 wt%. Addition of a small amount of catalyst (H-beta/IBB = 0.06) causes the reaction to proceed with higher rate than before. Conversion of IBB increases from 0.5 to 4.6 wt% when the H-beta/IBB ratio is increased from 0 to 0.06. A sharp increase in conversion and rate of IBB conversion, 17.0 wt% and $59.0 \times 10^{-2}\,h^{-1}\,mol^{-1}$ Al, respectively, were observed when an H-beta/IBB ratio of 0.15 is used. Further increase in the ratio did not affect the conversion of IBB significantly whereas selectivity to 3-IBC and 4-IBC was found to be nearly similar in all cases. Increase in the catalyst loading provides higher surface area with higher acid site concentration for reactant molecules to adsorb.

3.3. *Influence of IBB/i-PrOH molar ratio*

The effect of molar ratios of reactants on the conversion of IBB, rate of IBB conversion and selectivity to 4-IBC and 3-IBC was studied by changing the alkylating agent (*i*-PrOH) concentration and keeping the IBB concentration constant. Four different combinations of molar ratio of IBB/*i*-PrOH (1, 2, 3 and 5) were studied (figure 2). As the molar ratio of IBB/*i*-PrOH increases, the *i*-PrOH concentration decreases and hence the competitive adsorption of *i*-PrOH on the surface of the catalytic sites increases to react with the substrate molecule. Almost 95.0% of *i*-PrOH was consumed at the molar ratio (IBB/*i*-PrOH) of 5, but only 17% of *i*-PrOH was consumed when an equimolar ratio of IBB and *i*-PrOH was used. The 4-IBC/3-IBC ratio remains the same in all the cases.

3.4. *Influence of reaction temperature*

The influence of temperature on the isopropylation of IBB with H-beta at constant catalyst/IBB ratio, 0.15, was studied over a range of temperatures. The variation of conversion of IBB, rate of IBB conversion and product distribution as a function of reaction temperature is shown in figure 3. An increase in the conversion of IBB is achieved with an increase in reaction temperature. The conversion of IBB, TOF and 4-IBC/3-IBC ratio increased from 9.0 to 16.1 wt%, 31.3 to $55.9 \times 10^{-2}\,h^{-1}\,mol^{-1}$ Al and 1.00 to 1.08, respectively, when the temperature increased from 413 to 433 K. A further increase in the reaction temperature, >433 K, gave a marginal increase in the IBB conversion, rate of IBB conversion (TOF) and 4-IBC/3-IBC ratio. The apparent activation energy calculated for the isopropylation of IBB is $18.5\,kJ\,mol^{-1}$.

3.5. *Recycling*

In order to check the stability and catalytic activity of zeolite H-beta in the isopropylation of IBB, three cycles (fresh and two cycles) were carried out using the same catalyst. The results are presented in table 2. After workup of the reaction mixture, the zeolite H-beta was separated by filtration, washed with acetone and calcined for 16 h at 773 K in the presence of air. The recovered zeolite after each reaction was characterized for its chemical composition by EDX analysis and crystallinity by XRD. It was found that there is a slight decrease in the content of aluminum and the crystallinity of H-beta

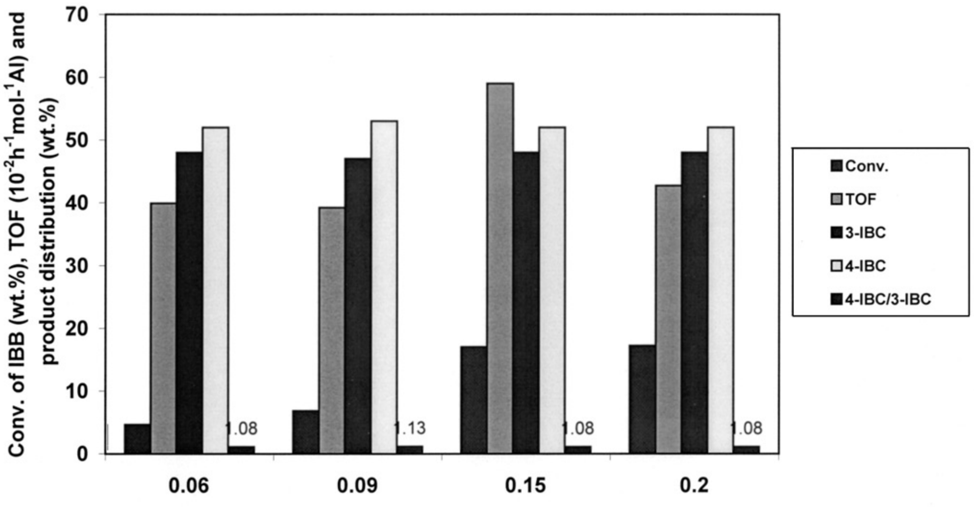

Figure 1. Effect of H-beta/IBB ratio on the conversion of IBB, TOF ($10^{-2}\,h^{-1}\,mol^{-1}$ Al) and product distribution (wt%). Reaction conditions: see footnotes to table 1, except H-beta/IBB ratio.

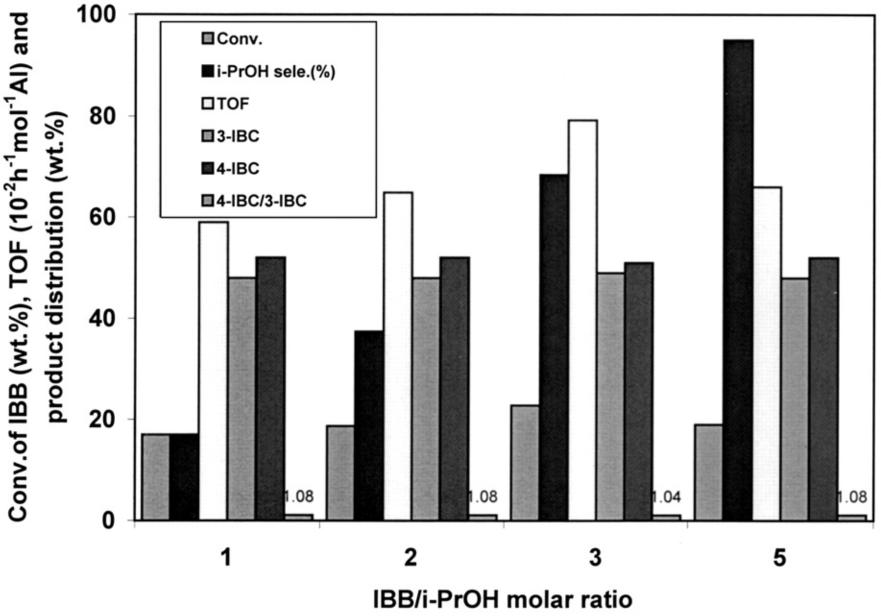

Figure 2. Effect of IBB/*i*-PrOH molar ratio on the conversion of IBB, TOF (10^{-2} h^{-1} mol^{-1} Al) and product distribution (wt%). Reaction conditions: see footnotes to table 1, except IBB/*i*-PrOH molar ratio.

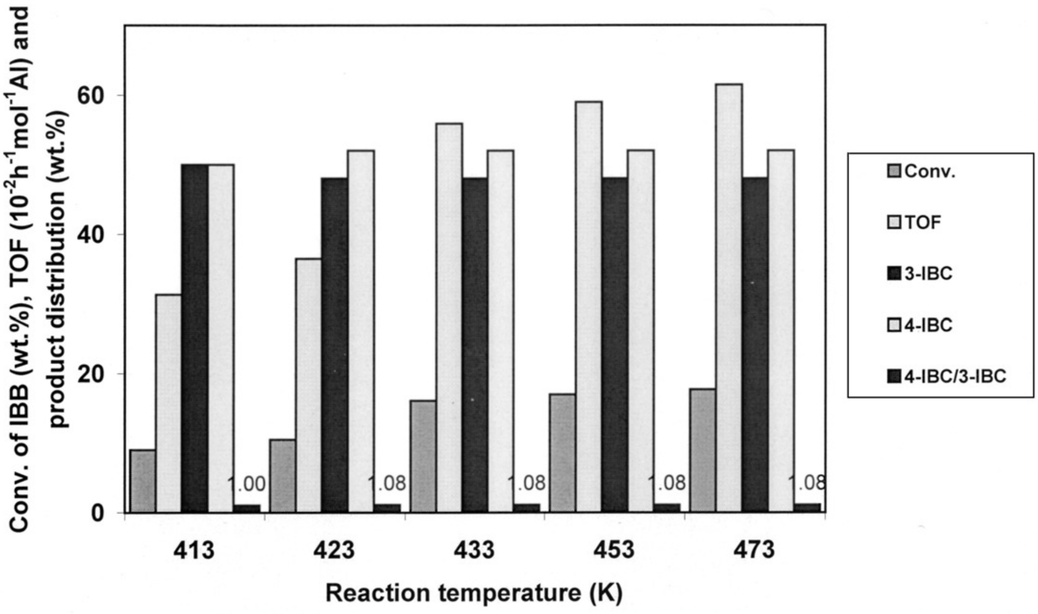

Figure 3. Influence of reaction temperature on the conversion of IBB, TOF (10^{-2} h^{-1} mol^{-1} Al) and product distribution (wt%). Reaction conditions: see footnotes to table 1, except reaction temperature.

Table 2
Effect of recycling of H-beta catalyst in the isopropylation of IBB

Catalyst	SiO_2/Al_2O_3 ratio [a]	Conversion of IBB (wt%) [b]	TOF (10^{-2} h^{-1} mol^{-1} Al) [c]	Product distribution (wt%) [d]			4-IBC/3-IBC ratio	Crystallinity (%) [e]
				3-IBC	4-IBC	Others		
Fresh	26	17.0	59.0	44	52	4	1.18	100
First cycle	26.8	16.7	58.0	47	50	3	1.06	98
Second cycle	27.0	16.1	56.0	46	49	5	1.07	97

[a] Determined by EDX analysis.

[b,c,d] See footnotes c, d, e, respectively, to table 1.

[e] By X-ray diffraction.

after each cycle. The activity of H-beta decreases progressively but marginally on each recycle and the conversion of IBB decreases from 17.0 to 16.1% when H-beta was recycled from fresh to the second cycle, respectively, in the isopropylation of IBB. The loss of aluminum and a small decrease in crystallinity of zeolite H-beta may lead to the decrease in catalytic activity after each cycle.

4. Conclusion

Zeolite H-beta catalyzes the isopropylation of IBB efficiently with 2-propanol as the alkylating agent and is found to be superior to other zeolite catalysts. The conventional homogeneous catalyst, $AlCl_3$, does not possess shape selectivity and favors the formation of a large amount of high molecular weight products. Among the isomers, the *meta*-isomer was found to form in a significant amount followed by the *para*-isomer as the *ortho*-isomer has relatively high strain energy compared to the other two isomers. Selectivity of the order of 52% for 4-IBC and 44% for 3-IBC is achieved at 17.0 wt% conversion of IBB over H-beta, whereas $AlCl_3$ gives 19% 4-IBC and 42% 3-IBC under similar reaction conditions. A higher strength of acid sites of H-beta is responsible for the conversion of IBB. The conversion of IBB increased significantly with increase in catalyst concentration (H-beta), reaction temperature and IBB/*i*-PrOH molar ratio. At higher IBB/*i*-PrOH molar ratio, i.e. 5, the consumption of 2-propanol is comparatively high (95%) compared to that for an equimolar ratio (2-propanol consumption is 17.0%). Recycling of the catalyst does not affect the activity of the catalyst significantly.

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