Vapor-phase alkylation of toluene with isopropanol over Mg/Al, Ni/Al and Cu/Al hydrotalcites (layered double hydroxide)

R. Manivannan and A. Pandurangan *

Department of Chemistry, Anna University, Chennai 600025, India

Received 24 September 2001; accepted 11 January 2002

Vapor-phase isopropylation of toluene has been carried out over Mg/Al, Ni/Al and Cu/Al calcined hydrotalcites (CHTs). Reaction conditions were optimized for alkylation by varying temperature, weight hourly space velocity and reactant mole ratio. Side-chain alkylation is found to be more predominant than ring alkylation over Mg/Al CHT, while Ni/Al and Cu/Al CHTs favored ring alkylation. The main products were isobutylbenzene and cymene. The combined participation of acidic and basic sites of the materials is found to be crucial for both side-chain and ring alkylation of toluene with isopropanol. An X-ray diffraction pattern of the resulting oxide indicates a diffuse MgO structure. The incorporation of small amounts of Al^{3+} to MgO generates new surface Lewis acid–base pair sites.

KEY WORDS: isopropylation; Mg/Al; Ni/Al; Cu/Al; hydrotalcites.

1. Introduction

Alkylation of aromatic hydrocarbons with various alkylating agents has a history as long as that of Friedel–Crafts catalysts. The importance of this reaction was realized only when solid acid catalysts were introduced for alkylation of benzene and toluene [1]. But only scant attention has been paid to their use as basic catalysts [2,3]. It is now known that alkylation of aromatic hydrocarbons over acidic zeolite leads to alkylation on the ring, while basic zeolites are known to catalyze side-chain alkylation. Base catalysts applicable for this reaction are not only limited to basic zeolite, but also basic substances like MgO and CaO [4]. Giordano *et al.* [5] have considered the role of the overall acid–base properties of zeolite catalysts for the selective alkylation of aromatic molecules. By using quantum chemical calculation, Itoh *et al.* [6] suggested that the cooperative action of acid and base sites is very important in the side-chain alkylation, where the base site activates the carbon atom of the side chain of toluene and the acid site activates the benzene nucleus.

Hydrotalcites (HT) are composed of charged brucite-like layers of divalent and trivalent metal hydroxides, whose excess positive charge is compensated by anions, present in the interlayer [7]. The most interesting properties of the oxides obtained by calcination are high surface area [8] with very small and thermally stable metal oxide crystallites, which are mainly used as base catalysts. The metallic oxide so obtained is found to be an efficient solid base catalyst for aldol condensation, polymerization of β-propiolactone, alkene isomerization and condensation of aldehydes or ketones with active methylene group [9–12]. Recently, many authors have reported acid–base properties of these catalysts. The nature of the divalent cation present in these compounds controls the acid–base properties of the resulting system. Mg/Al mixed oxides acted as efficient catalysts for the addition of CO_2 with various epoxides due to the co-operative action of acid–base sites derived from the formation of M–O–A1 bonds [13]. Alkylation of phenol with methanol resulted in anisole selectivity over Mg-containing hydrotalcites due to their higher basicity, while Cu-containing hydrotalcite gives rise to direct C-alkylation which can be attributed to the higher acidic nature of these catalysts [14]. Isomorphous substitution of the trivalent Al ions by Fe^{3+} or Cr^{3+} in the framework of hydrotalcites resulted in a decrease in the catalytic activity for phenol conversion, while the selectivity for *ortho*-cresol increased [15]. Hydrotalcites, especially used for alkylation reaction, do not undergo deactivation significantly as alumina and other zeolite systems do with time-on-stream in the alkylation reaction [14]. The aim of the present study is to investigate the activity and selectivity of various calcined hydrotalcites for alkylation of toluene with isopropanol under various reaction conditions.

2. Experimental

2.1. Preparation of catalysts

Co-precipitation at low supersaturation and constant pH is the method most frequently used in the

---

* To whom correspondence should be addressed.
E-mail: pandurangan_a@yahoo.com

preparation of hydrotalcites [7]. They can be represented by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}_{x/2}]$ mH_2O, where M(II) = Mg, Ni, Cu, Zn, Co and M(III) = Al, Cr, Fe, with M(II)/M(III) atomic ratio of 3, 4 and 5—adding simultaneously a mixture of aqueous solution of metal nitrates (70–100 ml) and a mixture of aqueous solution of NaOH (2–3 M) and Na_2CO_3 (0.2–0.35 M) at room temperature with vigorous stirring at the pH range 7–10. The resulting slurry is aged at 75 °C for 30 min with vigorous stirring. The precipitate has been filtered and washed to eliminate the alkali metal and nitrate ion, then dried in an air oven at 110 °C overnight. Calcination is carried out in the presence of air at 450 °C for 8 h and then cooled to room temperature.

2.2. Characterization

Many techniques have been used to characterize hydrotalcite-like compounds. Chemical composition analysis has been carried out using the ICPES technique (Model 3410 ARL) by dissolving 50 mg of the sample in a minimal amount of dilute hydrochloric acid. X-ray diffractograms of uncalcined and calcined hydrotalcites have been recorded using a Philips X-ray generator (Model PW 1050/81 controlled by a PW 1710) using Ni filtered Cu K_α ($\lambda = 1.5418$ Å) source and using a scan speed of 3°/min. FTIR spectra of these samples from 4000 to 400 cm^{-1} have been recorded in a Shimadzu FTIR spectrometer (Model 983G) using the KBr mull technique. Surface area of the samples is determined by the BET method in a Carlo-Erba (Model 1800) sorptometer at 77 K.

2.3. Catalytic studies

The vapor phase alkylation of toluene with isopropanol has been carried out in a fixed-bed flow-type reactor, consisting of a Pyrex glass tube of 8.0 mm i.d. and 35 mm length, in which a porcelain disc was sintered and sealed in the middle of the reactor to support the catalyst. The catalyst (1.5 g of powdered CHT, 450 °C for 8 h) packed inside the reactor is supported by two glass wool plugs which are surrounded by ceramic beads to fill the space. Before starting the experiment, the catalyst has been activated at 450 °C for 3 h in nitrogen flow (23 cm^3/min) and then brought to the reaction temperature. The alkylation reaction has been carried out using a mixture of toluene and alkylating agent, isopropanol (molar ratio 1 : 1), introduced at the top of the reactor by means of an infusion pump (Electronic Corporation of India) in the absence of carrier gas. The liquid products are collected in cold traps, identified and estimated in a Hewlett-Packard 5890A gas chromatograph with a 2 m 5% bentone column using a flame ionization detector.

3. Results and discussion

3.1. Physicochemical properties

Detailed physicochemical characterization results of the synthetic hydrotalcites are presented in table 1. Chemical composition analysis of LDH systems with different atomic ratios has been subjected to ICPES analysis. The BET surface area of calcined hydrotalcites [16] is more than the uncalcined HT due to dehydration, and decarboxylation leaves more spacing upon decomposition of HT samples. X-ray analysis indicates the hydrotalcites are successfully prepared without the formation of any separate phase. The unit cell parameters (*a* and *c*) for hydrotalcite structures with hexagonal crystal symmetry are calculated in all HT samples from the (110) and (003) X-ray diffraction peaks. In the Mg/Al hydrotalcite system the value of *a* increases with increase of Mg/Al ratio, and the increase in *c* is due to the decrease in the electrostatic attraction between the layers [17]. All the peaks corresponding to HTs are observed up to 400 °C. Calcination at above 450 °C results in loss of all the peaks corresponding to HTs and a phase corresponding to oxides is obtained. After decomposition, Al^{3+} cations remain closely associated with the MgO structure [18] and higher surface area is observed in Al-rich HT, resulting from larger amounts of CO_2 evolved during decomposition.

Infrared spectra have been used for the characterization of intercalated anions. Figure 1 shows the FTIR spectrum of the uncalcined samples. In all the cases the absorption around 3000–3600 cm^{-1} present in all HTs indicates the H-bonding stretching vibration of the −OH group in the brucite layer [19], bonded to M(II) or M(III) and hydroxyl groups from interlayer water molecules. A broad shoulder around 3000 cm^{-1} is attributed to hydrogen bonding between H_2O and the

Table 1
Chemical composition and lattice parameters of M(II)/M(III) CO_3HT

Catalysts	M(II)/M(III) [a]	Lattice parameters (Å)		Surface area (m^2/g)	
		a	*c*	Uncalcined	Calcined [b]
Mg/Al 3.0	2.71	3.049	23.301	99.5	168.0
Mg/Al 4.0	3.74	3.061	23.609	103.8	172.6
Mg/Al 5.0	4.69	3.092	23.801	88.7	154.8
Ni/Al 3.0	2.78	3.082	22.969	110.0	189.3
Cu/Al 3.0	2.72	3.058	22.867	119.6	206.4

[a] ICPES result.

[b] BET method at 450 °C.

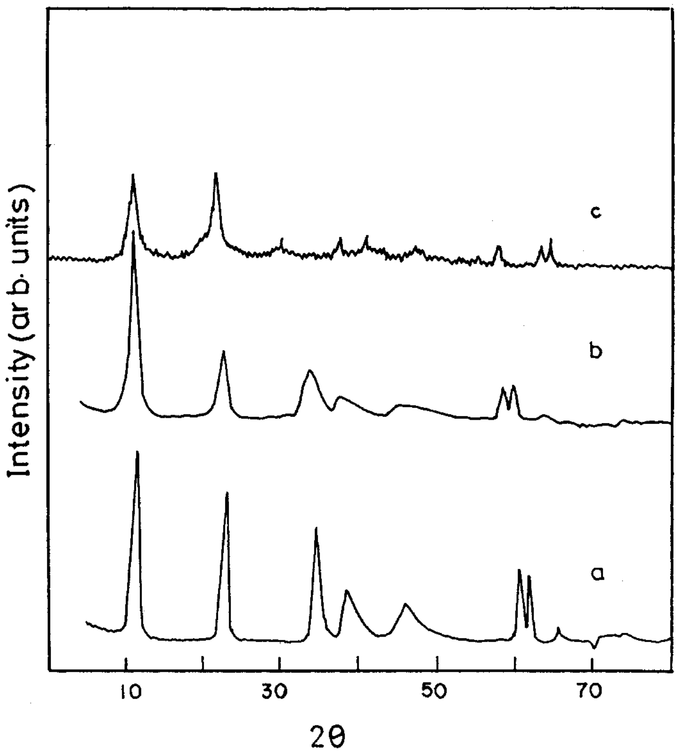

Figure 1. Powder X-ray diffraction patterns of hydrotalcites. (a) Mg/Al$_3$, (b) Ni/Al$_3$, (c) Cu/Al$_3$.

interlayer [20,21] carbonate anions. The band around 1600 cm^{-1} represents the bending vibration of H_2O in the interlayer space, which is also related to the presence of bicarbonate species [22]. The sharp absorption band close to 1365 cm^{-1} can be attributed to interlayer CO_3^{2-} (ν_3) absorption and also some trace impurities like NO_3^- that would have formed during the synthesis. Absorption bands shown at lower wave number are associated with metal oxygen vibration. The intense absorption bands of H_2O and CO_2 are immensely reduced in calcined samples. The weak band close to 1400 cm^{-1} should be due to the adsorbed carbonate species, and the band formed around 900–400 cm^{-1} should be due to M–O, M–O–M and O–M–O related modes.

3.2. Acid–base properties

The acid–base properties of calcined hydrotalcites are very important in determining the catalytic activity and product selectivity for a catalyzed reaction. Methods such as non-aqueous titration using benzoic acid as titrant are used to determine the acid–base properties of hydrotalcites [11]. The basicity range (pK_a) of MgO is 16.5–26.5, while that of Al_2O_3 is 7–14.7. The basicity of calcined Mg/Al hydrotalcites is also in the range 13–26. Cheng and Lin [23] have reported that Lewis acid sites are introduced in MgO with the incorporation of Al^{3+}. The dehydration of ethanol to ethylene and the coupling and dehydration to diethyl ether increased with Al^{3+} content has been reported by Apesteguia *et al.* [18], as a result of increase in the density of both Al^{3+}–O^{2-} pairs and low- and medium-strength basic sites. The results of the condensation reaction reveal that the selectivity to acrolin decreases with an increase in acidity. Hence Ni/Al catalyst exhibits lower selectivity to acrolin [24]. Jyothi *et al.* [25] reported the acid–base properties of hydrotalcite-like materials, using cyclohexanol test reaction where the selectivity of cyclohexene formed is a measure of the acidity of the catalysts and the selectivity of cyclohexanone formed is a measure of their basicity. We have studied these test reactions under the same condition and derived similar results. Based on this result, Mg^{2+} is found to be more basic, while Ni^{2+} and Cu^{2+} substitution are more acidic in nature.

3.3. Isopropylation of toluene

The alkylation of toluene with isopropanol over Mg/Al, Ni/Al and Cu/Al calcined hydrotalcites has been carried out at 375 °C with toluene to isopropanol feed ratio 1 : 1 and weight hourly space velocity (WHSV) 1.33 h^{-1}. Toluene conversion and selectivity towards isobutylbenzene and *ortho*-, *para*- and *meta*-cymene are shown in table 2. Vasanthi *et al.* [26] reported the isopropylation of toluene over alkali-exchanged Naβ, NaY and NaZSM-5. Exchange of Naβ with K and Cs shows an increase in the selectivity of isobutylbenzene,

Table 2
Effect of variation of catalyst on toluene isopropylation

Catalysts	Toluene conversion (wt%)	Product selectivity (wt%)				
		IB[a]	Cymene			Benzene and other products
			para	*meta*	*ortho*	
Mg/Al 3.0	46.2	85.7	2.1	1.6	1.5	9.1
Mg/Al 4.0	44.8	83.3	3.5	3.0	2.2	7.5
Mg/Al 5.0	44.0	82.9	4.0	3.7	2.9	6.5
Ni/Al 3.0	54.6	21.1	34.5	29.6	6.5	11.2
Cu/Al 3.0	57.5	17.8	33.3	31.9	8.5	9.3

Reaction temperature: 375 °C; feed molar ratio: 1.1; WHSV: 1.33 h^{-1}.
[a] IB: isobutylbenzene.

while with Li-exchanged zeolite the reaction occurs exclusively at the nucleus. Among the catalysts studied, Mg/Al CHT showed exclusive side-chain alkylation at lower temperature. Substitution of Mg^{2+} by Ni^{2+} and Cu^{2+} resulted in higher cymene selectivity compared with isobutylbenzene. This is due to the formation of strong acid sites, as is suggested and proved by different authors [27,29]. Dumitriu *et al.* [24] reported, from the TPD data, that Mg/Al CHT was the most basic catalyst while Ni/Al CHT was the most acidic catalyst, and noted basicity decreases in the order Mg/Al > Ni/Al > Cu/Al CHTs. In general, it is found that ring alkylation requires acidic sites and side-chain alkylation requires both acidic and basic sites. By quantum chemical calculation [6], the base sites make the carbon atom of the side-chain more active than that of the benzene ring. The role of acid sites is attributed to the adsorption and stabilization of toluene. The methyl group condenses with the carbonyl group adsorbed in acidic sites.

3.4. *Effect of temperature on product selectivity*

Isopropylation of toluene has been carried out in the temperature range 300–400 °C. The effect of reaction temperature on toluene conversion is shown in figure 2. The general trend for the alkylation is that conversion usually increases with the increase of temperature and reaches a steady state at high temperature [30,31], which is also observed in this study. From figure 3 it can be seen that the selectivity of isobutylbenzene decreases with an increase in temperature over all the catalysts due to the increase in cymene selectivity. From the cyclohexanol test reaction, Dumitriu *et al.* [24] have pointed out that the selectivity to cyclohexene increases with a higher conversion of cyclohexanol and with an increase in reaction temperature. It may be explained that the Al^{3+} cations remain closely associated with the MgO structure after decomposition of HT samples [18]. At low temperature, isobutylbenzene alone is formed as a result of side-chain alkylation in the Mg/Al–CHT system, which may be due to an increase in the surface density of active acid–strong base pairs. In the case of Ni^{2+} and Cu^{2+} ion substitution, both isobutylbenzene and cymene are formed and the cymene selectivity is found to increase with an increase in temperature due to the higher acidic nature of these catalysts.

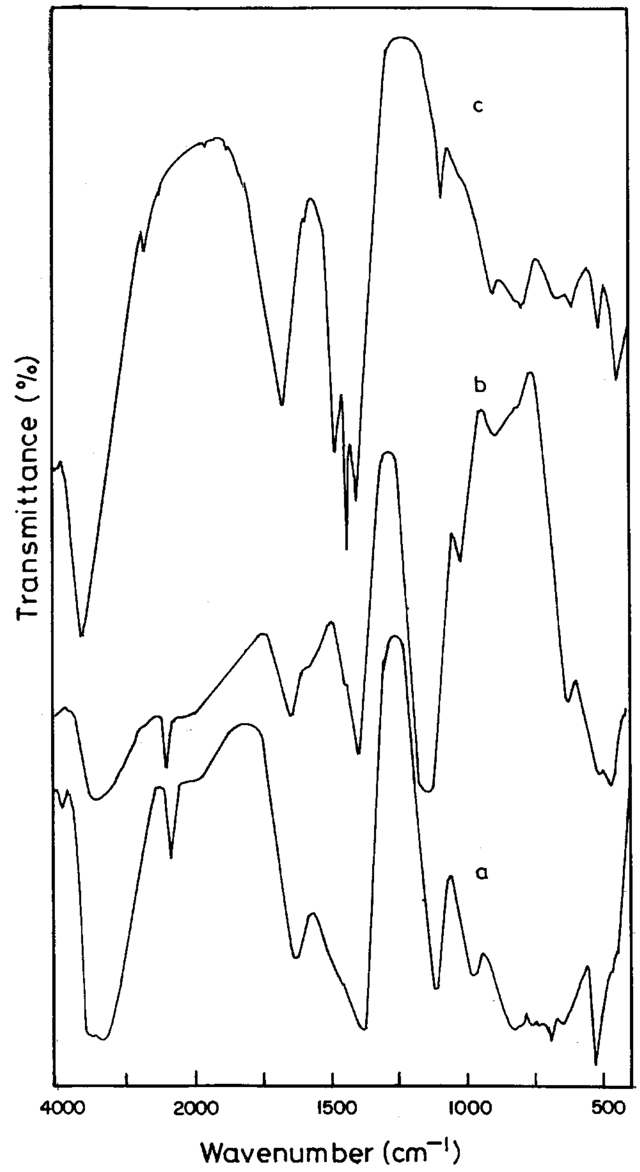

Figure 2. FTIR spectra of hydrotalcites. (a) Mg/Al_3, (b) Ni/Al_3, (c) Cu/Al_3.

3.5. *Mg/Al molar ratio*

In table 2, the activity of Mg/Al CHTs with different mole ratios is compared. Velu *et al.* [17] reported that Mg/Al 4.0 CHT is the most active due to the large surface area of the sample. Shen *et al.* [32] have reported, from microcalorimetric measurements, that Mg/Al ratios from 3 to 12 exhibited similar surface acid–base properties. However, in this study both the conversion

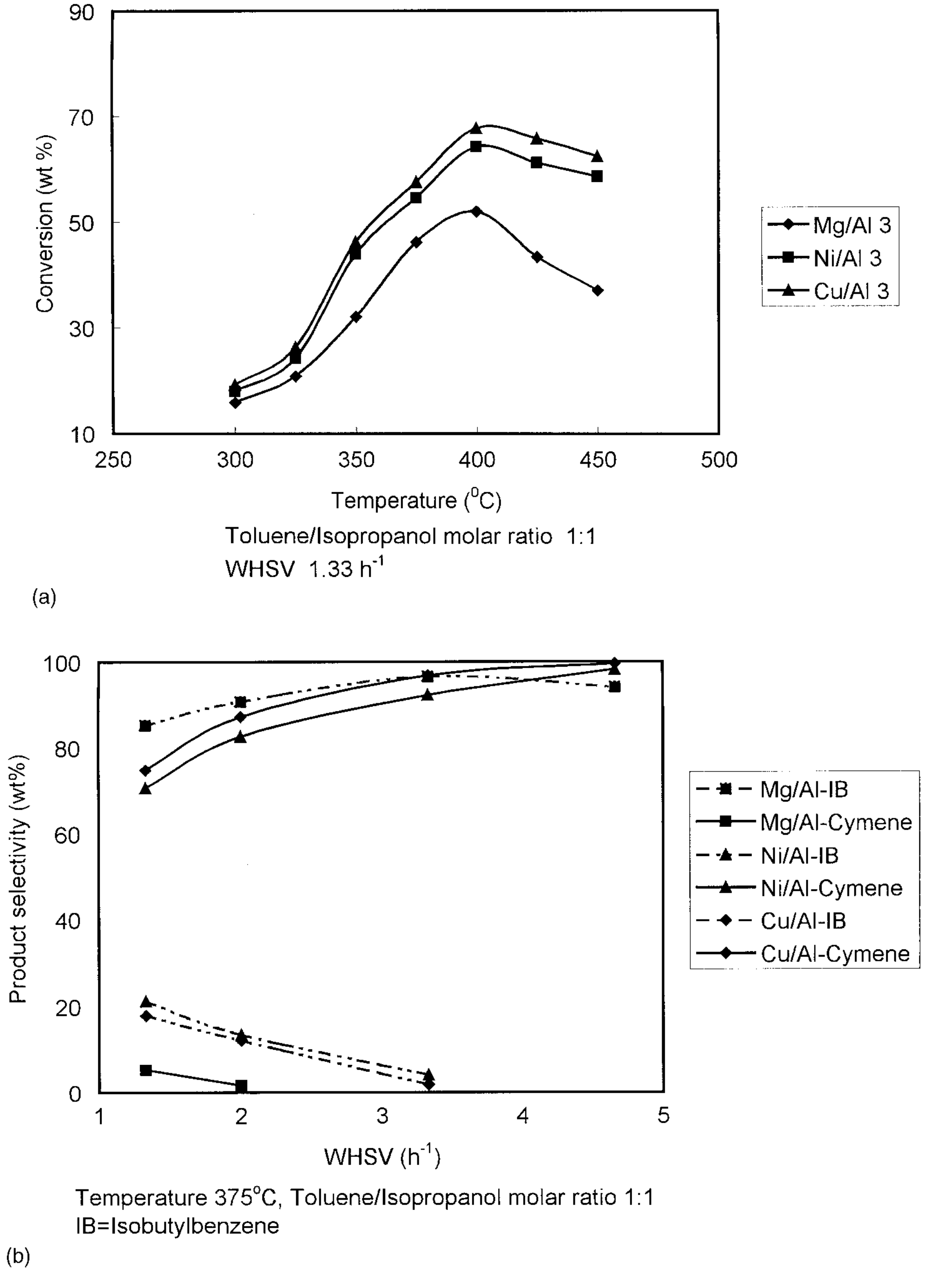

Figure 3. (a) Effect of temperature on the conversion of toluene, (b) effect of variation on WHSV.

and selectivity are not much affected by the change in Mg/Al atomic ratio.

3.6. Effect of flow rate

The effect of WHSV on toluene was studied in the range 0.66–5.3 h^{-1} over the CHTs at 375 °C. Figure 4 shows the influence of WHSV over Mg/Al, Ni/Al and Cu/Al CHTs at the molar ratio of toluene and isopropanol equal to one. The WHSV 1.3 h^{-1} has recorded maximum yield of required product, while an increase in WHSV to 3.3 h^{-1} decreases the conversion of toluene and higher alkylated products. Among the catalysts studied, Mg/Al CHT shows very high selectivity to isobutylbenzene which has increased with WHSV, while the other catalysts yield exclusively C-alkylation products.

4. Conclusions

The experimental results indicate that side-chain alkylation of toluene with isopropanol is highly favored over Mg/Al CHT with maximum activity. The role of acid–strong base helps the selective side-chain alkylation

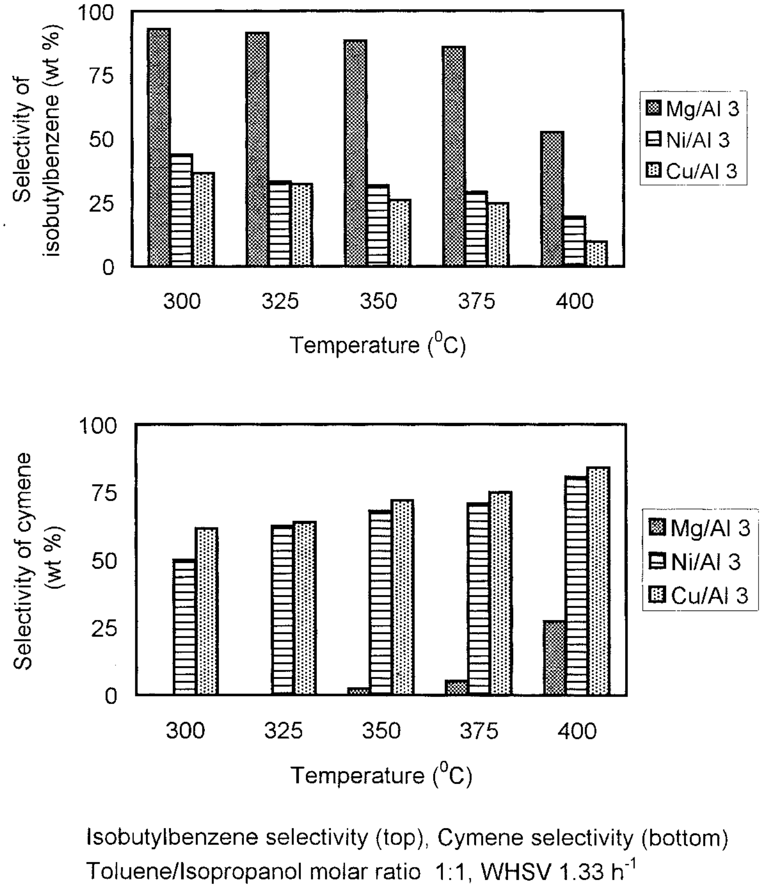

Figure 4. Effect of temperature on product selectivity in isopropylation of toluene.

of toluene by Mg/Al CHT. Upon decreasing the basicity by M(II) ion substitution, side-chain alkylation along with C-alkylation occurs. Ni^{2+} and Cu^{2+} in the hydrotalcite system lowered the selectivity of isobutylbenzene compared with Mg^{2+} ions due to the formation of cymene. This is due to the acid–base properties of the catalysts.

References

[1] Y.B. Young, S.A. Butter and W.W. Kaeding, J. Catal. 76 (1982) 418.
[2] P.E. Hathway and M.E. Davis, J. Catal. 119 (1989) 497.
[3] M. Huang, S. Kaliaguine, M. Maura and A. Auroux, J. Catal. 157 (1995) 266.
[4] K. Tanabe, O. Takahashi and H. Hattori, React. Kinet. Catal. Lett. 7 (1977) 347.
[5] N. Giordano, L. Pino, S. Cavallaro, P. Vitarelli and B.S. Rao, Zeolite 7 (1987) 131.
[6] H. Itoh, A. Miyamoto and Y. Murakami, J. Catal. 64 (1980) 284.
[7] F. Cavani, F. Trifiro and A. Vaccari, Catal. Today 11 (1991) 172.
[8] W.T. Reichle, J. Catal. 94 (1985) 547.
[9] A. Corma, V. Fornes, R.M. Martin-Aranda and F. Ray, J. Catal. 34 (1992) 58.
[10] E. Suzuki and Y. Ono, Bull. Chem. Soc. Jpn. 61 (1988) 1008.
[11] H. Schaper, J.J. Berg-Slot and W.H.J. Stork, Appl. Catal. A 54 (1989) 79.
[12] A. Corma and R.M. Martin-Aranda, Appl. Catal. A 105 (1993) 271.
[13] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.
[14] S. Velu and C.S. Swamy, Appl. Catal. A 145 (1996) 141.
[15] S. Velu and C.S. Swamy, Appl. Catal. A 162 (1997) 81.
[16] S. Miyata and A. Okada, Clays and Clay Minerals 25 (1977) 14.
[17] S. Velu and C.S. Swamy, Appl. Catal. A 119 (1994) 241.
[18] J.I. Di Cosimo, V.K. Diez, M. Xu, E. Iglesia and C.R. Apesteguia, J. Catal. 178 (1998) 499.
[19] S. Kannan and C.S. Swamy, J. Mater. Sci. Lett. 11 (1992) 1585.
[20] S. Miyata, Clays and Clay Minerals 23 (1975) 369.
[21] E.C. Kruissink, L.J. Van Reijden and R.H. Ross, J. Chem. Soc. Faraday Trans. 77 (1981) 649.
[22] C.J. Serna, J.L. White and S.L. Hem, Clays and Clay Minerals 25 (1977) 384.
[23] S. Cheng and J.T. Lin, in: *Synthesis of Microporous Materials, Expanded Clays and Other Microporous Solids*, Vol. 2, eds. M.L. Occelli and H.E. Robson (1992) p. 170.
[24] E. Dumitriu, V. Hulea, C. Chelaru, C. Catrinescu, D. Trichit and R. Durand, Appl. Catal. A 178 (1999) 145.
[25] T.M. Jyothi, T. Raja, K. Sreekumar, M.B. Talawar and B.S. Rao, J. Mol. Catal. A 157 (2000) 193.
[26] B.K. Vasanthi, M. Palanichamy and V. Krishnaswamy, Appl. Catal. A 148 (1996) 51.
[27] D. Martin and D. Duprez, J. Mol. Catal. A 118 (1997) 113.
[28] A. Gervasini and A. Auroux, J. Catal. 131 (1991) 190.
[29] S. Velu and C.S. Swamy, Catal. Lett. 40 (1996) 265.
[30] S. Narayanan, V. Durgakumari and S. Rao, Appl. Catal. A 111 (1994) 133.
[31] S. Narayanan and K. Deshpande, J. Mol. Catal. 104 (1995) L109.
[32] J. Shen, J.M. Kobe, Y. Chen and J.A. Dumesic, Langmuir 10 (1994) 3902.