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Isopropylation of Benzene with 2-Propanol over High-Silica Large-Pore Zeolite: NCL-1

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The influence of various reaction parameters such as temperature, WHSV, time on stream, and feed ratio of benzene to 2-propanol, as well as of the Si/Al molar ratio of zeolite NCL-1, on catalytic activity and selectivity was studied in the isopropylation of benzene with 2-propanol. The selectivity towards cumene increases with Al content, contact time, and ratio of benzene to 2-propanol. Among diisopropylbenzenes (DIPBs), the concentration of 1,3-DIPB (vis-à-vis 1,4-DIPB) increases with increases in reaction temperature, Al content of the catalyst, and benzene conversion. The 1,2-DIPB, with relatively high strain energy (4.26 kcal mol^{-1}) compared to that of either 1,3-DIPB (2.02 kcal mol^{-1}) or 1,4-DIPB (2.78 kcal mol^{-1}), was formed in very small quantities (0–2 wt%). © 1995 Academic Press, Inc.

INTRODUCTION

High-silica, large-pore zeolites are very useful materials for catalysis and selective adsorption. Out of many novel zeolites known so far, only a few, such as ZSM-12 and beta, belong to the high-silica large-pore category. Recently, we have synthesized a new high-silica zeolite (Si/Al ≥ 20) designated as NCL-1 (1, 2). The crystallographic structure of NCL-1 is not yet known. The characterization of the pore architecture of NCL-1 through adsorption and catalytic techniques (like *m*-xylene conversion, constraint index (CI), *n*-decane conversion, and spaciousness index (SI)) clearly suggests that NCL-1 possesses 12-membered channels with effective void space comparable to that of zeolite mordenite (MOR) (2–4).

Isopropylbenzene (cumene) is an important intermediate in the production of phenol. The solid phosphoric acid (SPA) and other Friedel Crafts catalysts are commonly used for the isopropylation of benzene to cumene (5, 6). The major drawback of these catalysts is their corrosive and environmentally hazardous nature. To overcome these problems, zeolite ZSM-5 was used as a catalyst for vapor phase isopropylation of benzene by 2-propanol or propene (7, 8). However, over H/ZSM-5-type zeolites, *n*-propylbenzene was coproduced along with isopropylbenzene (7, 8). It was found (7) that very strong acid sites catalyze the isomerization of isopropylbenzene to *n*-propylbenzene, particularly at relatively higher temperatures. Later, isopropylation of benzene by 2-propanol or propene over other zeolites such as H/EU-1 (9), H/ZSM-12 (10), H/beta (11), H/mordenite, and LaH/Y (12) was studied. However, large-pore high-silica zeolites, e.g., ZSM-12 and beta, were found to be quite suitable catalysts for this reaction.

Since NCL-1 also belongs to the rare category of large-pore, high-silica zeolites, we have explored the suitability of NCL-1 catalysts in this reaction. In the present communication, we report the results of studies on the isopropylation of benzene with 2-propanol over zeolite NCL-1. The influence of various reaction parameters on the product selectivities are discussed.

EXPERIMENTAL

The raw materials used in the syntheses were fumed silica (Sigma, USA, S-5005, 99.9%), $Al_2(SO_4)_4 \cdot 16H_2O$ (98%), aluminium triisopropoxide (Aldrich), sodium hydroxide (99% AR), sulfuric acid (96%), and hexamethylene bis(triethylammonium bromide) as an organic additive, which was prepared in our laboratory. The details of the preparation of the template as well as of the zeolite NCL-1 are reported in earlier works (1–3). However, in a typical preparation, the following procedure was used: A solution containing 0.75 g NaOH in 10 g H_2O was added to a slurry of 4.5 g fumed silica in 30 g H_2O. This mixture was stirred for 45 min at 298 K. To the above mixture, a solution containing the required amount of aluminium sulfate in water (0.30, 0.16, or 0.096 g of $Al_2(SO_4)_3 \cdot 16H_2O$ in 10 g of water, to yield Si/Al ratios 80, 150, or 250, respectively) was added. The mixture was stirred for 20 min before a solution of 1.71 g hexamethylene bis(triethylammonium bromide) in 15 g H_2O was added to it. Finally, 0.36, 0.42, or 0.45 g H_2SO_4 in 10 g water was added

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to the gels with Si/Al ratios 80, 150, and 250, respectively. For the preparation of the NCL-1 sample with Si/Al = 20, aluminium isopropoxide (0.78 g) was used as the aluminium source; the amount of sulfuric acid added to the final gel was 0.44 g. The resultant reaction mixture was stirred for 1 h and then autoclaved. The crystallization was conducted in a 100 ml stainless steel autoclave at 443 ± 2 K under agitation (60 rpm). The crystallization times were 4, 7, 10, and 13 days for samples with Si/Al molar ratio (gel) = 250, 150, 80, and 20, respectively. After crystallization, the solid was filtered, washed with water, dried at 393 K, and finally calcined in flowing dry air at 823 K. The yield of crystalline solid (based on SiO_2/Al_2O_3 in gel) ranged between 85 and 90 for all the samples.

Two grams of calcined sample in 50 ml of 1 *M* ammonium acetate solution was subjected to ion exchange at 353 K for 6 h. This procedure was repeated twice. The final sample was washed, dried, and calcined at 753 K for 5 h to give the H form of the sample. The H form of the binder-free zeolites (20–30 mesh size) was used for catalytic studies which were carried out in a fixed-bed downflow silica reactor (1 cm i.d.). The products were analyzed by on-line gas chromatography (HP 5890 equipped with a 50-m capillary column coated with silicone gum) using a flame ionization detector.

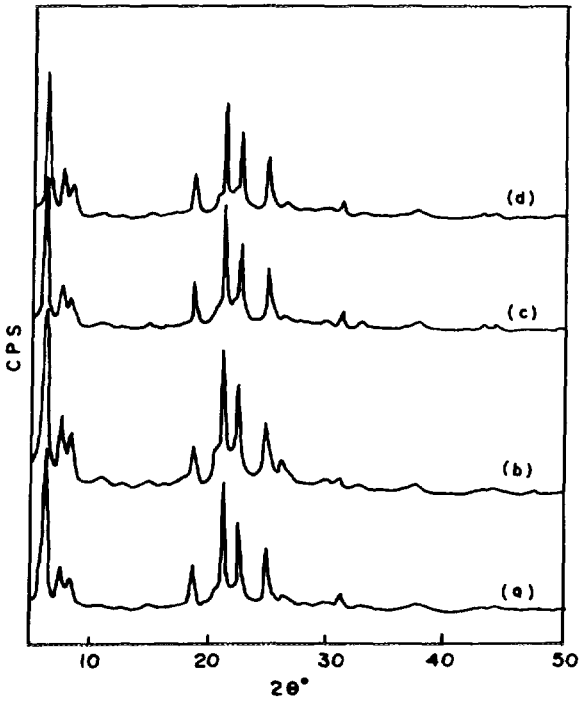

FIG. 1. X-ray powder diffraction patterns of calcined samples of zeolite NCL-1. Curves a–d refer to samples A–D with Si/Al molar ratios of 23, 84, 156, and 257, respectively.

RESULTS AND DISCUSSION

Some physicochemical properties, such as Si/Al molar ratio (gel and product), surface area, and adsorption (*n*-hexane and 1,3,5-trimethylbenzene), exhibited by NCL-1 samples are recorded in Table 1. Figure 1 depicts the X-ray (powder) diffractograms of NCL-1 samples. Curves a–d represent samples A–D with Si/Al molar ratios 23, 84, 156, and 257, respectively. All the samples exhibit the characteristic XRD pattern of NCL-1 (1–3). In Fig. 2, the scanning electron micrographs of these four samples, A–D, are given. All samples exhibited nearly similar morphology and no amorphous material was observed. Generally NCL-1 crystallites are composed of thin long needles or bundles of needles (0.1–0.2 μm thick and 5–8 μm long (Figs. 2A–2D). It was ascertained through XRD (Fig. 1), SEM (Fig. 2), and adsorption and surface area measurements (Table 1) that the samples used in this study are fully crystalline and substantially free from impurities.

Influence of Si/Al Molar Ratio

The influence of the Si/Al molar ratio of NCL-1 samples on activity and product selectivity in the isopropylation of benzene at the same reaction temperature and WHSV is depicted in Fig. 3. As expected, the conversion of benzene

TABLE 1

Physicochemical Properties of NCL-1 Samples

NCL-1 samples	Si/Al molar ratio		Adsorption[a]		Surface area (m^2/g)[b]
	Gel	Solid	*n*-hexane	1,3,5-trimethylbenzene	
A	20	23	6.7	4.7	315
B	80	84	6.8	4.7	318
C	150	156	6.9	4.8	323
D	250	257	6.9	4.7	329

[a] Gravimetric adsorption (wt%) at 298 K and at p/p_0 = 0.5.
[b] From N_2 adsorption (p/p_0 = 0.005–0.01).

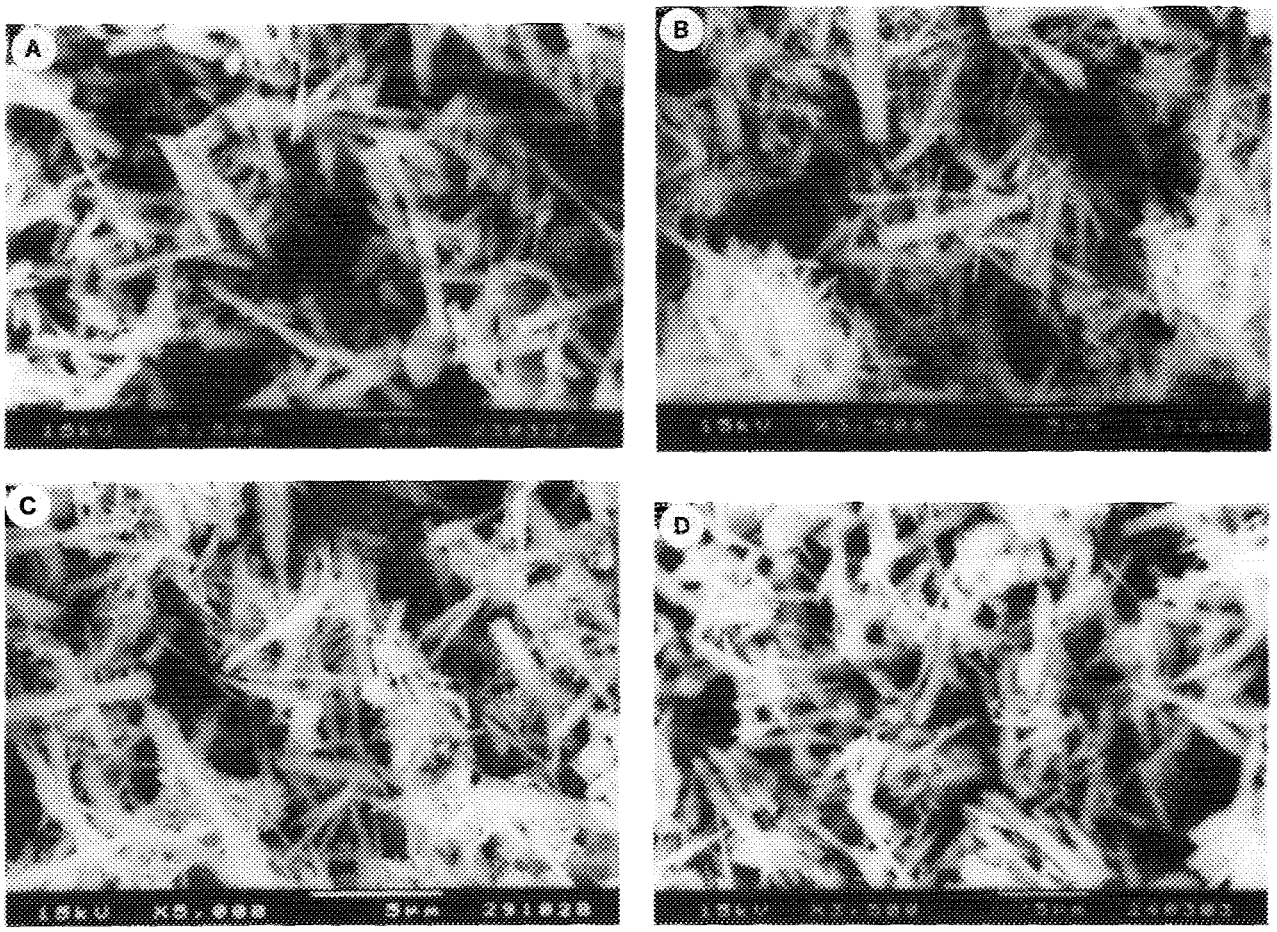

FIG. 2. Scanning electron micrographs a–d of samples A–D, respectively.

(curve a, wt% of theoretical maximum based on benzene/2-propanol molar ratio) decreases with the Si/Al molar ratio of the sample. Further, with the increased Al content, the cumene selectivity (curve b) increases whereas the selectivity towards diisopropylbenzene (DIPB) (curve c) decreases. The isopropylation of benzene with 2-propanol is a multistep and sequential reaction. The main reaction scheme can be represented as follows:

1. 2-propanol → propene + H_2O
2. benzene + propene → cumene
3. cumene + propene → diisopropylbenzene (DIPB)
4. DIPB + benzene → 2 cumene
5. 2 cumene → DIPB + benzene.

A decrease in cumene selectivity accompanied by an increase in DIPB selectivity with increasing Si/Al ratio (decreasing Al content and lower acid site density) may be due to the following reasons: (a) the alkylation of cumene (reaction 3) is faster than the alkylation of benzene (reaction 2) (13), and (b) the transalkylation of DIPB with benzene to cumene (reaction 4), as well as the cracking of DIPB (reaction 3, reverse), need a higher density of acid sites (14). Further, the cracking/dealkylation of the main product of cumene (reaction 2 reverse) into benzene and propene (15–17) may also contribute to the decrease in cumene selectivity. Since no or negligible propene or other gaseous products are obtained, it is also possible that the propene formed due to cumene cracking (reverse of reaction 2) alkylates another molecule of cumene to form DIPB, resulting in a consequent increase in the selectivity towards DIPB. Corma *et al.* (15) have already shown that very small densities of acid sites are needed for cumene cracking. This may also be a possible reason for the decrease in benzene conversion and cumene selectivity accompanied by increase in DIPB selectivity with increased Si/Al ratio (Fig. 3) and time on stream (discussed later, Fig. 5). However, the total selectivity of cumene + DIPB remained almost constant at about 94 ± 3%.

Among the diisopropylbenzene isomers the 1,3-DIPB isomer is always predominant over the 1,4 isomer (Fig. 3, upper) the 1,2 isomer being absent or formed in small quantities (<2%). However, 1,3-DIPB decreases sharply with a decrease in Al content (increasing Si/Al ratio) of

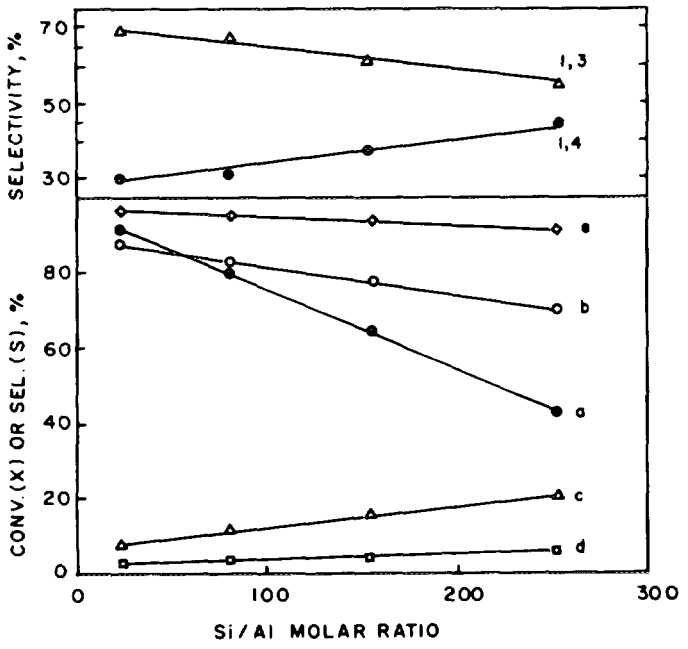

FIG. 3. Isopropylation of benzene over zeolite NCL-1. Influence of Si/Al ratio on conversion or product selectivity (lower) and selectivity for 1,3 and 1,4 isomers of diisopropylbenzene (DIPB) (upper). Temperature, 503 K; Benzene/2-propanol ratio, 6; WHSV, 3.5 h^{-1}. Curve a, conversion; curve b, cumene; curve c, DIPB; curve d, others (aliphatics, *n*-propylbenzene C_6–C_8 aromatics, and C_{10} aromatics); curve e, cumene + DIPB.

the zeolite and thus in benzene conversion. Vapor phase alkylation of aromatics over the acid form of the zeolites is an electrophilic reaction. Hence, among DIPBs, 1,4 and 1,2 isomers can be formed via isopropylation of cumene as the primary product. However, during the present studies, the 1,2 isomer was formed only in small quantities (<2%), the 1,4 and 1,3 isomers being predominant, in accordance with earlier studies of other zeolites (9–11). It seems that the direct formation of 1,2-DIPB is hindered either sterically or due to overcrowding at the 1,2 positions, the later reason being more probable because even in zeolite beta with a 3-dimensional open structure, no or trace amounts of 1,2-DIPB were observed (11). This argument is further supported by the total strain energy (18, 19) of 4.26, 2.02, and 2.78 kcal mol^{-1} observed for the final energy minimized molecules of 1,2-, 1,3-, and 1,4-DIPB, respectively. The equilibrium geometry of the molecules was obtained by the molecular mechanics method developed by Gelin and Karplus (18) and adapted as detailed in (19). The total strain energy of the molecules is expressed by the equation $E_{\text{total strain}} = E_{\text{bond length}} + E_{\text{dihedral angle}} + E_{\text{improper torsion}} + E_{\text{electrostatic}} + E_{\text{van der Waals}}$. Since 1,2-DIPB has a very high strain energy compared to the 1,3 and 1,4 isomers, the formation of 1,4-DIPB is highly favored initially, followed by further isomerization to the 1,3 isomer. Since the alkylation of aromatic compounds over acid catalysts is an electrophilic (and hence *ortho–para* directing) reaction, 1,3-DIPB is not expected to be formed as a primary product in the alkylation of cumene, in spite of the low strain energy of the 1,3 isomer. Hence, 1,3-DIPB can be formed either through isomerization of the 1,4 and 1,2 isomers, or via cumene disproportionation into benzene and DIPB (reaction 5). Since 1,3-DIPB decreases with increasing Si/Al ratio and decreasing conversion, and the 1,2-isomer is either not observed or formed in small quantities (Fig. 3), it can be argued that the 1,3 isomer is mainly formed through isomerization of the 1,4 isomer.

Influence of Temperature

The influence of temperature on activity and product distribution is presented in Fig. 4. The temperature has a marked effect on the conversion of benzene and the product distribution. As expected, the benzene conversion increases with temperature. With increased reaction temperature, the selectivity towards: (a) aliphatics decreases very sharply, (b) cumene increases, and (c) DIPB increases initially and then decreases after passing through a maximum. This is probably due to the fact that initially at lower temperatures the alkylation of cumene (reaction 3) competes favorably with the transalkylation of DIPB with benzene to cumene (reaction 4). However, at higher temperatures the transalkylation of DIPB with benzene (reaction 4) predominates over the alkylation of

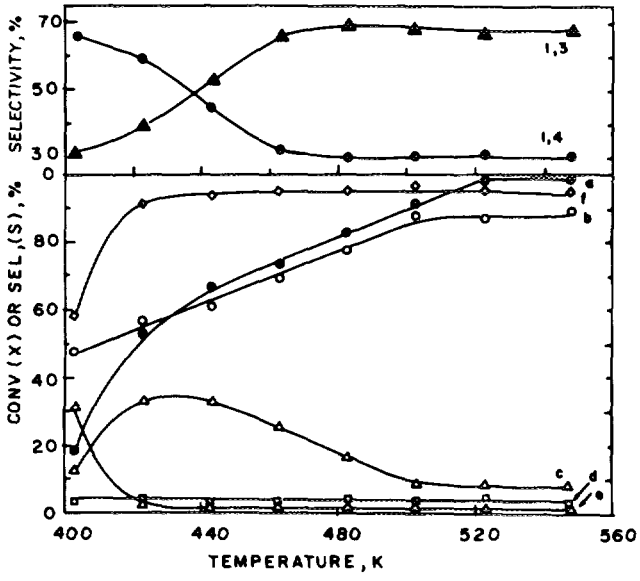

FIG. 4. Isopropylation of benzene with 2-propanol over NCL-1 (sample A). Influence of temperature on conversion or product selectivity (lower) and selectivity for 1,3 and 1,4 isomers of DIPB (upper). WHSV, 3.5; benzene/2-propanol ratio, 6; WHSV, 3.5 h^{-1}. Curve a, conversion; curve b, cumene; curve c, DIPB: curve d, others (*n*-propylbenzene, C_6–C_8 aromatics, and C_{10} aromatics); curve e, aliphatics; curve f, cumene + DIPB.

cumene (reaction 3). The selectivity towards cumene + DIPB at all temperatures is above 94%, except at very low temperatures (403 K). The distribution of 1,3- and 1,4-DIPB is shown in Fig. 4 (top). At lower temperatures and hence lower benzene conversion, the 1,4 isomer is predominant. 1,3-DIPB increases at the expense of 1,4 with increased temperature. 1,2-DIPB is always less than 2%. This suggests that 1,4-DIPB is the primary product of the alkylation of cumene. With increased temperature, the isomerization of 1,4-DIPB to 1,3-DIPB increases and attains a near-equilibrium value (1,4 = 32.5%, 1.3 = 58.5%, and 1,2 = 9.0% at 100°C (8)).

Influence of Feed Ratio (Benzene to 2-Propanol)

The influence of the benzene to 2-propanol mole ratio in the feed on the conversion and the product selectivity is shown in Table 2. As expected, benzene conversion and TOF h^{-1} (moles of benzene converted per mole of Al atoms present in the catalyst per hour) increased with the benzene/2-propanol ratio. The selectivity towards cumene increases, whereas the selectivity towards DIPB decreases with the increased ratio of benzene to 2-propanol. However, the total selectivity to cumene and DIPB remained almost constant at about 95.0%. At benzene to 2-propanol ratio 4 the selectivity for DIPB is significantly high (mainly at the cost of cumene) due to increased alkylation of cumene to DIPB (reaction 3). At a higher benzene to 2-propanol molar ratio, cumene formation through transalkylation of DIPB with benzene (reaction 4) as well as primary reaction of benzene isopropylation may be envisaged. However, among DIPBs, isomer distribution did not vary significantly with ratio of benzene to 2-propanol.

TABLE 2

Isopropylation of Benzene with 2-Propanol over H-NCL-1 (23): Effect of Benzene on 2-Propanol Ratio

	Benzene to 2-propanol ratio			
	4	6	8	15
Benzene conversion (wt% of theoretical)	80.0	91.1	97.0	100
TOF (h^{-1})[a]	42.5	51.7	56.4	61.0
2-propanol conversion (%)	95.0	100.0	100.0	100.0
Product selectivity (wt%)				
Aliphatics[b]	2.9	0.6	0.3	0.1
Cumene	64.9	88.5	89.6	91.0
DIPB[c]	30.0	8.5	7.8	6.9
n-propylbenzene	0.5	0.2	0.2	0.1
Others[d]	1.7	2.2	1.9	1.8
DIPB distribution (wt%)				
1,2-DIPB	0.9	1.2	1.3	1.3
1,3-DIPB	62.2	67.5	64.5	65.8
1,4-DIPB	36.9	31.3	34.2	32.9

Note. Temperature, 503 K, WHSV, 3.5 h^{-1}; TOS, 1 h.
[a] Moles of benzene converted per mole of Al present in the catalyst.
[b] Mainly propene.
[c] DIPB = diisopropylbenzene.
[d] Others include C_6–C_8 aromatics and C_{10} aromatics.

TABLE 3

Isopropylation of Benzene with 2-Propanol over H-NCL-1 (23): Effect of WHSV

	WHSV			
	1.75	3.5	7.0	15
Benzene conversion (wt% of theoretical)	97.8	91.1	77.4	67.6
TOF (h^{-1})[a]	27.7	51.7	87.8	153.4
2-propanol conversion (%)	100.0	100.0	95.0	90.0
Product selectivity (wt%)				
Aliphatics[b]	0.1	0.6	1.4	2.4
Cumene	90.5	88.5	70.5	66.1
DIPBs[c]	6.0	8.5	25.9	29.4
n-propylbenzene	0.2	0.2	0.1	0.2
Others[d]	3.2	2.2	2.0	1.6
DIPB distribution (wt%)				
1,2-DIPB	1.8	1.2	0.8	0.6
1,3-DIPB	69.0	67.5	61.0	55.4
1,4-DIPB	29.2	31.3	38.2	44.0

Note. Temperature, 503 K; benzene to 2-propanal, 6; TOS, 1 h.
[a] Moles of benzene converted per mole of Al present in the catalyst.
[b] Mainly propene.
[c] DIPB = diisopropylbenzene.
[d] Others include C_6–C_8 aromatics and C_{10} aromatics.

Influence of Weight Hourly Space Velocity

Table 3 shows the influence of WHSV on product distribution and activity. As expected, with increased WHSV the conversion of benzene decreased, and the selectivity towards DIPB increased mainly at the cost of cumene. This is because of the increased alkylation of cumene (reaction 3) at high WHSV. At higher contact times (lower WHSV) the transalkylation of DIPB with benzene (reaction 4) predominates, causing an increase in cumene selectivity. However, once again the selectivity to cumene and DIPB did not vary significantly with WHSV. Among DIPBs, the 1,3 isomer decreases and consequently the 1,4 isomer increases with increasing feed rate of WHSV. This may be due to the fact that at high feed rate (low contact times), alkylation reactions are favored over the isomerization of primarily formed 1,4-DIPB into 1,3-DIPB.

Influence of Time on Stream (TOS)

Figure 5 exhibits the effect of time on stream (TOS) on conversion and the selectivity of the catalyst. In the

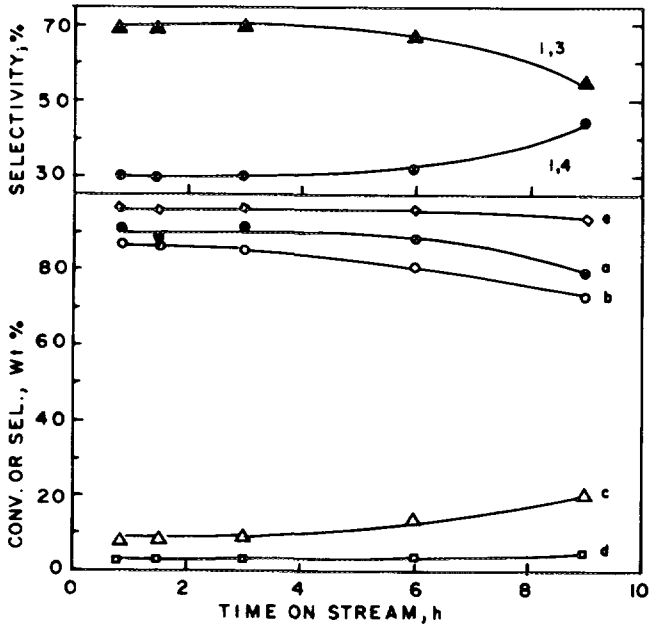

FIG. 5. Isopropylation of benzene with 2-propanol over NCL-1 (sample A). Influence of time on stream on conversion or product selectivity (lower) and selectivity for 1,3 and 1,4 isomers of DIPB (upper). Temperature, 503 K; WHSV, 3.5; benzene/2-propanol ratio, 6. Curve a, conversion; curve b, cumene; curve c, DIPB; curve d, others (aliphatics, *n*-propylbenzene, C_6–C_8 aromatics, and C_{10} aromatics); curve e, cumene + DIPB.

beginning, the conversion of benzene increased slightly then decreased very slowly. With time, the selectivity to cumene decreases whereas that to DIPB increases, but overall selectivity remains constant. Interestingly, 1,3-DIPB initially decreases with conversion due to the deactivation behaviour of the catalyst and consequently 1,4-DIPB increases at the cost of 1,3-DIPB. This effect of deactivation on conversion, DIPB selectivity (vis-à-vis cumene selectivity), and 1,3-DIPB and 1,4-DIPB distribution seems to be quite similar to that of increasing Si/Al ratio (Fig. 3), suggesting that deactivation may be due to the poisoning of active sites.

CONCLUSIONS

Zeolite NCL-1 exhibits high activity and selectivity in the isopropylation of benzene by 2-propanol to form cumene. The cumene selectivity generally ranges between 65 and 90% while cumene + diisopropylbenzene selectivity remains mostly around 94 ± 3%. *n*-Propylbenzene is not formed in significant quantity (~0.5% selectivity). DIPBs are valuable products as they can be recycled and transalkylated with benzene over the same catalyst. Among DIPBs, while the 1,2 isomer was not formed significantly, 1,4-DIPB was formed as a primary product by the isopropylation of benzene. However, 1,4-DIPB isomerized to give 1,3-DIPB in nearly thermodynamic quantity. The selectivities for cumene and cumene + DIPB exhibited by H-NCL-1 are typical of large-pore zeolites.

ACKNOWLEDGMENTS

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Note added in proof. Strong dependence of TOF on space velocity may be due to mass transfer effects instead of or in addition to kinetic effects. More work is needed to unambiguously answer this question.

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