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Isopropylation of Benzene over Large-Pore Zeolites: Activity and Deactivation Studies

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Both La–H–Y and H–mordenite catalysts show good initial activity for isopropylation of benzene, but deactivate within a span of 8–10 h. The product distribution and deactivation pattern were observed to be different. Coking induces shape-selective phenomenon in mordenite. The amount of coke, loss in acidity, and void volume of coked samples suggest that deactivation of faujasite is due to acid-site poisoning while deactivation of mordenite is caused by pore blocking.

INTRODUCTION

Acid zeolites are used more and more in industrial processes due to their high thermal stability, greater activity and peculiar shape-selective properties (*1*). But a major limitation in the use of zeolite catalysts is fast aging of the catalysts (*2*). In most of these processes, heavy by-products formed during the course of the reaction remain either in the pores or get deposited on the outer surface leading to zeolite deactivation (*3*). The coke deposited can lower the catalytic activity by site coverage (poisoning) and/or by pore blocking, which prevents the access of the reactants to the active sites (*4*). The literature on deactivation of zeolites has been reviewed recently by M. Guisnet and P. Magnoux (*5*) and S. Bhatia *et al.* (*6*). Excellent reports have been made correlating coking and deactivation with acidic structural and other properties of the zeolites (*7–9*). But no effort has been made to study the deactivation mechanism of industrially important alkylation reactions, especially isopropylation of benzene during the course of the reaction.

Isopropylbenzene or cumene is an important industrial intermediate for the production of phenol. The present industrial processes are based on the use of Friedel–Crafts catalyst (*10*) or solid phosphoric acid (*11*) catalyst. These processes suffer substantially from the drawbacks deriving from corrosion and environmental problems. Although several zeolites are reported to be active for this reaction (*12–15*), no commercial process using zeolite catalyst is in operation. This is mainly due to deactivation of zeolite catalysts. Two large-pore (12-membered ring) zeolites, namely mordenite and faujasite, having characteristic structural differences are selected for this work. A study on the activity and deactivation of these two acid zeolites is reported in this article.

EXPERIMENTAL

Materials

Benzene (>99.98% pure) and propylene (having 4% propane) were used for catalytic studies.

Catalysts

Catalytic studies were carried out using Zeolon mordenite (protonic form supplied by m/s Norton Inc.) and La–H–Y (sodium form supplied by m/s Union Carbide). The faujasite in sodium form was first converted into ammonium form and exchanged with

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TABLE 1

Structural and Physicochemical Properties of Catalysts

Catalyst	La–H–Y	H–mordenite
Channel structure	Three dimensional with interconnecting channels	Unidirectional with 8 MR interconnecting channels
Pore opening	7.2 Å (12 MR)	5.7 × 7.1 Å (12 MR) 2.9 × 5.7 Å (8 MR)
Unit cell crystal symmetry	Cubic	Orthorhombic
Si/Al mole ratio	2.3	6.4
Crystal size (μm)	2.0 ± 0.2	2.0 ± 0.2
Acidity mmole of NH_3/g	1.338	0.535
Equilibrium sorption capacity for benzene (wt%)	20.3	9.8

lanthanum nitrate by the procedure reported elsewhere (*16*).

Characterization

Crystalline phase purity and the state of aluminum in the framework were characterized by techniques like XRD, IR, and MASNMR spectroscopy. Composition of these samples was established by wet chemical methods using atomic absorption (Hitachi, Japan) and inductively coupled plasma spectroscopy (Jubin Yuan, France). Adsorption studies were carried out at 25°C and $P/P_0 = 0.5$ using a McBain balance with a silica spring having a sensitivity of ≈50 cm g^{-1}. Acidity measurements as irreversibly retained ammonia were carried out using an Omnisorp sorption unit (Model 100 CX, Omnicron).

Catalytic studies at atmospheric pressure were carried out using a downflow silica reactor. Benzene was fed from the top using a syringe pump (Sage Instrument) while propylene was metered with a massflow controller (Matheson).

Liquid product was analyzed using a Shimdzu gas chromatograph (Model GC 15A) fitted with Apiezone L column and FID detector, while gaseous product was analyzed using Porapak Q column.

RESULTS

The unit cell composition of H-mordenite, estimated by chemical analysis on the dry basis, is

$$H_{6.8}Na_{0.4}Al_{7.2}Si_{42.6}O_{96},$$

while that of La–H–Y is

$$La_{17.7}H_{4.5}Na_{0.5}Al_{58}Si_{134}O_{384}.$$

Both samples were highly crystalline as revealed by XRD pattern. Physicochemical and structural features of these samples are presented in Table 1. Both zeolites

TABLE 2

Isopropylation of Benzene over Zeolite Catalysts[a]

Catalyst	H–mordenite	La–H–Y
Product distribution (wt%)		
Aliphatics	0.53	1.06
Benzene	78.19	77.58
toluene	0.01	0.02
Ethylbenzene	0.26	1.02
Cumene	18.01	18.06
n-Propylbenzene	0.74	0.44
C_{10}–C_{11} Aromatics	0.12	0.34
1,3-DIPB	1.14	0.71
1,2-DIPB	—	0.03
1,4-DIPB	0.64	0.31
Σ-DIPB	1.78	1.05
H.B.F.	0.36	0.43
C_3 = Conversion	99.55	99.05
Cumene selectivity (%)	82.6	80.6
Selectivity (Cum + DIPB)	9.7	85.3

[a] Reaction temperature, 230 ± 2°C; pressure, atmospheric; benzene to propylene molar ratio, 7 ± 0.2; WHSV, 2.5 ± 0.05 h^{-1}; TOS, 2 h.

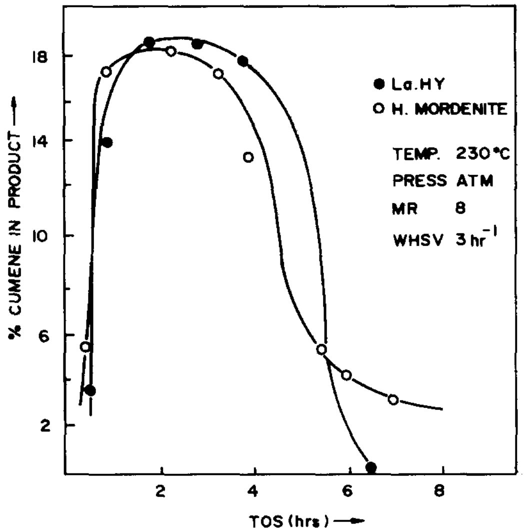

FIG. 1. Effect of time on stream on catalytic activity. Reaction temperature, 230°C; pressure, atmospheric; benzene to propylene molar ratio, 7; WHSV, 2.5 h^{-1}.

have a 12-membered channel system with characteristic structural differences. The acidity revealed by irreversibly retained ammonia in the case of faujasite La–H–Y is almost twice that of H–mordenite. The equilibrium sorption capacities for benzene and diisopropylbenzene (DIPB) for La–H–Y are greater than those for H–mordenite.

These samples in self-supported pellet form (10–20 mesh) were tested for alkylation of benzene to cumene using propylene as an alkylating agent at atmospheric pressure. Comparison of activity of these two zeolites is shown in Table 2. Both catalysts show high initial conversion (Fig. 1) followed by gradual deactivation. From the product distribution it is apparent that formation of ethylbenzene and C_{10}–C_{11} aromatics (which mainly contain butylbenzenes) occurs to a greater extent over the faujasite catalyst.

Due to dissimilarities in the product distribution and fast deactivation at atmospheric pressure, efforts were made to study the deactivation mechanism of these two catalysts. The study was carried out using simple techniques and deactivation phenomenon were correlated with acidic and structural properties of these samples.

Effect of Coking on Product Distribution

During the course of reaction, the ratio of 1,3- to 1,4-DIPB in the product was monitored (Fig. 2). Over faujasite the ratio was observed to be equal to 2 and remains constant throughout the run, whereas over mordenite catalyst the ratio gradually decreases from a value of 2 to 0.5 with deactivation of the catalyst.

Kinetics of 1,4-DIPB Sorption

The kinetics of 1,4-DIPB sorption were studied over fresh and coked (having ≈10% of initial activity) zeolite samples (Fig. 3). Although the rate of sorption of 1,4-DIPB is the same as that for fresh and coked La–H–Y, the equilibrium sorption capacities are different. The rate of sorption over the fresh H–mordenite sample is very slow and gradually attains the equilibrium value, whereas within a short span of time, coked H–mordenite sample attains equilibrium value.

Acidity Measurements

Acidity measurements as irreversibly retained ammonia were carried out over fresh and deactivated samples (see Table 3). Coked La–H–Y was observed to retain only 20% of its initial acidity, while in the case of H–mordenite, a 50% decrease in acidity was observed with coking.

Amount of Coke

The amount of coke present in the deactivated sample was estimated by thermal analysis. As shown in the Table 3, the amount of coke formed in La–H–Y was observed to be double (14.8 wt%) that of H–mordenite (7.5 wt%).

DISCUSSION

The present studies are aimed at the deactivation mechanism of H–mordenite and La–H–Y zeolites during isopropylation of benzene. Mordenite possesses a unidimensional pore structure having 12-membered

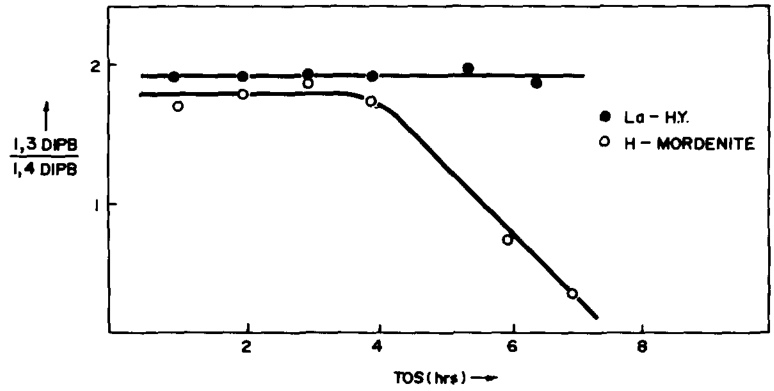

FIG. 2. Ratio of 1,3-DIPB to 1,4-DIPB in the product.

(6.7 × 7.1 Å) parallel channels interconnected by 8-membered (2.9 × 5.7 Å) channels, whereas the three-dimensional framework structure of faujasite consists of interlinking supercages having 12-membered ring channel openings (7.4 Å), which are sufficiently large to allow diffusion of reactant and product molecules. Acidity of these samples is in agreement with the aluminum content of the zeolite. Benzene and 1,4-DIPB sorption capacities are more characteristic of the void volumes than the pore sizes of the zeolites.

The isopropylation reaction of benzene was carried out under identical conditions over these two samples. Although both catalysts were deactivated within the span of 8–10 h, differences in the product distribu-

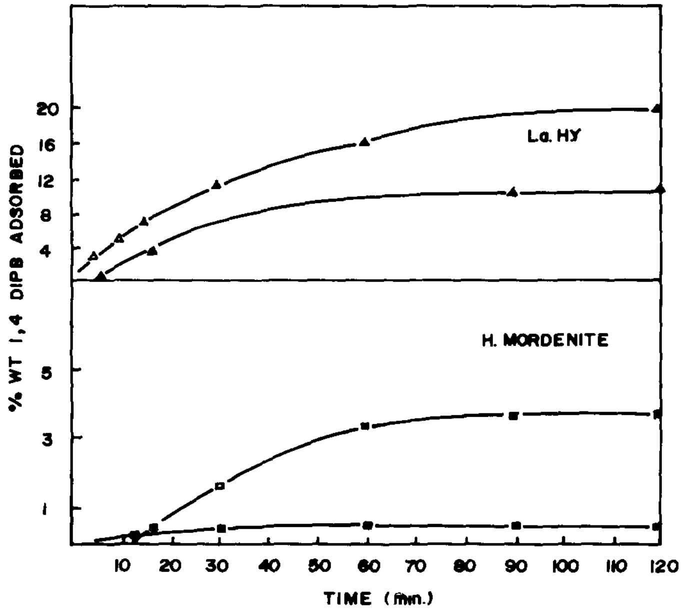

FIG. 3. Kinetics of 1,4-DIPB sorption studied over fresh and deactivated zeolite samples. Temperature, 25°C, $P/P_0 = 0.5$.

TABLE 3

Physicochemical Studies on Fresh and Coked Catalyst[a] Samples

Catalyst	H–mordenite	La–H–Y
Equilibrium sorption capacity of 1,4-DIPB over fresh sample (wt%)	3.64	20.2
Equilibrium sorption capacity of 1,4-DIPB over deactivated sample (wt%)	0.53	10.1
Percentage sorption capacity retained	14.6	50.0
Acidity of fresh sample mmole of NH_3/g	0.535	1.338
Acidity of deactivated sample mmole of NH_3/g	0.265	0.271
Amount of coke formed (wt%)	7.5 ± 0.2	14.8 ± 0.2

[a] Has ≈10% of its initial activity.

tion and deactivation pattern were observed. Formation of ethyl- and butylbenzenes in greater quantities over faujasite catalyst is due to reactions like cracking of cumene formed during the course of the reaction (*17*). This can be explained by higher acidity and higher sorption capacity of the faujasite.

In the alkylation reaction, formation of dialkylated product (5–10 wt%) always accompanies monoalkylated product. In the isopropylation reaction the dialkylated product formed is DIPB having two major isomers. The difference between these two isomers is their size. The critical size of 1,3-DIPB is 9.0 × 7.4 Å, while the critical diameter of 1,4-DIPB is 7.2 Å. Hence, the extent of coking was studied by monitoring the ratio of 1,3- to 1,4-DIPB. Gradual decrease in the ratio in the case of mordenite results from shape-selective phenomena induced by coking (*7*). Partial coking in the channels of mordenite induces shape selectivity by allowing smaller 1,4-DIPB molecules to diffuse out faster than bulky 1,3-DIPB molecules. The bigger supercages fail to induce this phenomenon.

To investigate further, the kinetics of 1,4-DIPB sorption over fresh and coked samples were studied (Fig. 3). The equilibrium sorption capacity of the coked La–H–Y sample indicates that half the void volume (50% of initial sorption capacity) is still available for the sorption of reactant molecules. The deactivation in the unidirectional pore system of mordenite leads to a drastic decrease in the sorption capacity of the coked sample. In fact, the sorption kinetics and equilibrium sorption capacity of the coked mordenite (retained sorption capacity 14.6%) suggests only surface adsorption of solvent, indicating blocking of pores.

As ammonia molecules are small in size, all acid sites of fresh and coked samples are accessible to them even through sodalite cages in faujasite and through 8-membered ring channels of mordenite. In deactivated La–H–Y most of the acid sites (about 80%) were observed to get covered by coke, while in deactivated mordenite almost half the acid sites remained unused. These sites are inaccessible to reactant molecules because of blocking of unidimensional channels of mordenite.

The amount of coke present in the deactivated samples was 14.8 wt% in the case of La–H–Y and 7.5 wt% in the case of H–mordenite. Even though both catalysts were deactivated to the same extent, the amount of coke needed to deactivate mordenite, having a unidirectional pore system is smaller than that needed for the three-dimensional La–H–Y.

CONCLUSIONS

Various techniques suggest that deactivation of faujasite during the isopropylation of benzene is due to blocking (poisoning) of active sites while deactivation of mordenite is due to blocking of the channels by bulkier molecules like DIPB.

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