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NOTES

Distribution of Isomers in the Alkylation of Benzene with Long-Chain Olefins over Solid Acid Catalysts

Linear alkyl benzenes (LAB) are used in the manufacture of detergents. These are usually mixtures of C_9–C_{14} alkyl benzenes obtained by the alkylation of benzene with mixed olefins using anhydrous HF as catalyst (*1*). Irrespective of the double bond position in the parent olefin, a mixture of alkyl benzenes with the phenyl group attached to different C-atoms in the chain is obtained. Of the different isomers, the most preferred one is the 2-phenyl isomer, which possesses better emulsibility characteristics than the others (*2*). Due to the hazardous nature of anhydrous HF, efforts to find safer catalysts have begun. UOP has recently announced a new process that uses a solid acid (*2*). The alkylation of benzene with long-chain olefins has been reported over heteropolyacids (*3*), clays (*4*), pillared clays (*5*), and ZSM-12 (*6*). We report a comparative study of the alkylation of benzene with 1-dodecene and a commercial olefin mixture over a number of amorphous and zeolite catalysts. We have examined the factors affecting the distribution of phenyl alkanes in the product.

Amorphous silica–alumina was prepared by the coprecipitation of aluminum sulfate and sodium silicate with sulfuric acid. The gel was washed with water and dil ammonium hydroxide to a Na level of 0.4 wt% (dry basis). It was then dried at 383 K (24 h) and calcined (see below for conditions). Commercial Na–Y (Linde) was converted into the rare earth (RE) form by repeated exchanges with solutions of ammonium acetate (1 *M* solution; 10 ml/g zeolite; temp = 353 K; duration = 6 h; three exchanges) and RE–chloride (obtained from Indian Rare Earths Ltd., Udyogmandal, Kerala; 5 wt% solution, conditions same as ammonium acetate exchanges). The RE–Y was washed free of chloride ions and dried at 383 K for 6 h. H–Y zeolite used was a dealuminated form (US–Y) obtained from Union Carbide in the form of extrudates ($\frac{1}{16}$ in.). A commercial sample of mordenite (Norton, USA; SiO_2/Al_2O_3 = 17.7) was dealuminated by steaming at 923 K for 4 h and extracting with 6 *M* HCl for 1 h (*7*) to give a product with a SiO_2/Al_2O_3 ratio of 43.9. The washed zeolite was dried at 383 K (6 h) and calcined. Zeolite H–β (SiO_2/Al_2O_3 = 39) was prepared from a commercial Na–β (PQ Zeolites, The Netherlands) by repeated exchanges with ammonium acetate (see procedure adopted for Na–Y). The washed zeolite was next dried at 383 K (6 h) and calcined. The zeolite powders were mixed with alumina hydrate (Catapal-B, Vista Chemicals, USA) and blended with 2 wt% acetic acid in water. The hard dough was extruded in a hand press, dried at room temperature (12 h) and at 383 K (12 h), and calcined at 773 K for 6 h as before. The extrudates contained 80 wt% zeolite on dry basis. Montmorillonite (Univ. of Missouri) was extracted three times with 0.1 *N* HCl (10 ml solution/g; 333 K for 3 h) and washed to obtain the H-form. It was then dried at 383 K (6 h), calcined, and pelleted. All the calcinations reported so far were carried out under the same conditions (773 K for 6 h). The furnace temperature was usually increased continuously from room temperature to 773 K at a uniform rate of 60 K/h. Amberlyst-15 was obtained from Aldrich Chemical Co. (Milwaukee, WI).

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The reaction was carried out in a vertical, isothermal reactor (19 mm i.d.; Catatest Model BL-2 supplied by M/s Geomecanique, France). A 50-g charge of catalyst in the form of granules (14–18 mesh) was used in these studies. The length of the catalyst bed was between 30 and 40 cm. The catalyst (except Amberlyst-15) was dried (*in situ*) for 6 h in dry N_2 prior to use. The Amberlyst was dried at 408 K (6 h). Also, to keep the system at the required pressure (0.7 MPa), a small flow of N_2 (10 ml/min) was maintained from the reactor head. The liquid feed entered from the top of the reactor and flowed past the catalyst. With the vapour pressure of benzene at 0.43 Mpa at 408 K (*8*), it is believed that the reactants and product, passed through the catalyst bed in the liquid state (at about 0.7 MPa). The general reaction conditions were: Temp = 408 K; WHSV (h^{-1}) = 0.8; pressure = 0.7 MPa; benzene: olefin mol ratio = 10. These reaction conditions were chosen to keep the reactant benzene in the liquid state and to achieve 100% conversion of the olefins on most of the catalysts. Under the conditions of the reaction, marginal heat effects due to the exothermicity of the reaction were noted. A temperature rise of 5–6 K was observed in the case of dodecene and 1–2 K in the case of the olefin mixture. A steady state was reached in 1–2 h, the activity of the catalyst remaining constant for different durations for the different catalysts. The products were analyzed using a capillary column (HP 1, cross-linked methyl silicone gum, 50 m × 0.5 mm). The repeatability of the analyses was better than ±0.2 wt% for any component.

TABLE 1

Alkylation of Benzene with 1-Dodecene

Catalyst	Product distribution					2-ϕ/6-ϕ ratio
	2-ϕ[h]	3-ϕ	4-ϕ	5-ϕ	6-ϕ	
SiO_2–Al_2O_3	33.4	21.9	14.8	15.6	14.2	2.4
H-Montmorillonite[a]	26.0	19.1	16.7	19.1	19.1	1.4
Amberlyst-15	34.5	20.2	14.3	15.9	15.1	2.3
H–Y	29.5	20.2	17.1	16.9	16.3	1.8
RE–Y	17.6	19.1	19.8	22.0	21.5	0.8
H–β	39.1	26.4	18.9	10.8	4.8	8.2
H–M[b]	63.7	35.4	0.9	Tr	—	70.7[i]
HF[c]	16.7	16.4	17.5	24.1	25.3	0.7
HF[d]	20	17	16	23	24	0.8
HF[e]	13.7	15.1	16.8	54.4		—
$AlCl_3$[f]	32	22	16	15	15	2.1
$AlCl_3$[g]	31.8	20.8	17.2	30.2		—

Note. Conditions: Temperature = 408 K; pressure = 0.7 MPa; WHSV = 0.8 h^{-1}; benzene : olefin (mol) ratio = 10; conversion of olefin 100%; data at 10 h on stream.

[a] WHSV set to 0.5 to obtain 100% conversion.

[b] Conversion incomplete.

[c] C_{12}-alkyl benzene fraction from commercial LAB: liquid phase reaction; WHSV indeterminate.

[d] Data of Olson (*11*); Temp = 289 ± 3 K.

[e] Data of Alul (*12*); Temp = 328 K.

[f] Data of Olson (*11*); Temp = 303–326 K.

[g] Data of Alul (*12*); Temp = 309 ± 1 K.

[h] ϕ = phenyl.

[i] 2-ϕ/4-ϕ ratio: 6-ϕ not detected.

1-Dodecene (95% purity) was obtained from Aldrich. A mixture of C_{10}–C_{13} olefins (10% + 90% C_{10}–C_{13} paraffins) was obtained from a commercial source.

The results of the alkylation of benzene with 1-dodecene over the different catalysts are presented in Table 1. The isomer distribution in the dodecyl benzene fraction of a commercial sample of LAB manufactured using anhydrous HF as the catalyst is also included for comparison. The alkylation of benzene with olefins goes through a carbonium ion mechanism (*9, 10*). In the case of dodecene, six carbonium ions are possible. The relative stabilities of these increase as the C-number increases, the least stable being the primary ion (1-position). In fact, due to its very low stability, the 1-phenyl isomer is not detected in the product. On the basis of the relative stabilities of the other carbonium ions (all secondary), one would expect the isomer content to increase with the carbon number (toward the center of the chain). This is found to be so in the cases of HF and RE–Y, in which thermodynamic equilibrium is probably reached. In the cases of SiO_2–Al_2O_3, Amberlyst-15, H-montmorillonite, and H–Y, the 2-phenyl content is greater, suggesting the nonattainment of thermodynamic equilibrium. The alkylation of benzene with 1-dodecene has been studied by Olson (*11*) and others (*12, 13, 14*), over anhydrous HF and $AlCl_3$, while Venuto *et al.* (*9*) have studied the reaction over the solid acids, X, Y, and mordenite in the liquid phase. The results of Alul (*12*) and Olson (*11*) obtained over HF and $AlCl_3$ are also presented in Table 1. Venuto *et al.* (*9*) did not give any detailed breakup of the isomers in the product. The distribution of products obtained by Olson over HF (Table 1) is similar to those observed by us over RE–Y. A similar distribution is also observed in the commercial (HF-catalyzed) product. Again, the distributions obtained by Olson and Alul on $AlCl_3$ are similar to those observed over SiO_2–Al_2O_3, Amberlyst-15, and H–Y (US–Y). Two main reasons attributed by Alul (*12*) for the differences in product distribution are: (1) the existence of two equilibration steps, one for the olefin (1-dodecene) and another for the phenyl dodecanes, and (2) the differences in the rates of the two reactions (olefin isomerization and alkyl benzene isomerization) over the catalysts. HF catalyzes the isomerization of 1-dodecene into an equilibrium mixture of olefins (1- to 6-dodecenes), but does not "equilibrate" the alkyl benzenes even at 328 K. $AlCl_3$, on the other hand, does not equilibrate the olefins well, but isomerizes the alkyl benzenes into an equilibrium mixture at 308 K (and not at 273 K) (*12*). In addition, in the case of HF, other effects like concentration of HF and the presence of two phases and diluents like *n*-hexane also affect the distribution of isomers. This explains the differences in the product distributions of the three HF data reported (Table 1). The reason for the larger amount of 1-phenyl isomer in the case of $AlCl_3$ even at "equilibrium" has been attributed to steric and solvation effects stabilizing the 2-phenylarenonium ions (*12*).

H–M, H–β, and H–Y are classified as wide-pore zeolites. H–M has unidirectional pores (0.67 × 0.70 nm), H–β has a complicated 3-D pore system (0.73 and 0.55 nm), while the faujasites (Y-type) have large cavities (1.3 nm diam) along with a 3-D pore system (0.73 nm). H–M and H–β produce much more 2-phenyl isomer than H–Y or RE–Y. In H–M and H–β, shape selectivity appears to play a role, with the relatively thinner 2-phenyl product being favored. H–M is so shape selective that the 5- and 6-phenyl isomers are not formed at all (or are present in negligible amounts). The similarities in the product distribution between RE–Y and HF suggests the absence of shape selectivity in the Y (faujasite)-system.

The results of alkylation with a commercial mixed olefin feed (C_{10}–C_{13}) are presented in Table 2. The composition of the feed according to the C-fractions is also presented in the table. The results are found to be similar to those reported earlier (Table

TABLE 2

Alkylation of Benzene with a Mixture of (C_{10}–C_{13}) Olefins

Product (C_n)	n-ϕ[b]	Catalyst					HF[d]
		H–M[c]	H–β	H–Y	RE–Y	SiO_2–Al_2O_3	
		Product distribution (wt%)[a]					
C_{10}	2	16.2	8.0	4.7	2.9	4.9	5.0
	3	5.2	3.5	2.8	2.8	3.4	3.5
	4	4.5	2.9	2.6	3.5	2.5	3.0
	5	9.4	2.5	2.6	5.0	3.0	3.1
C_{11}	2	27.7	16.1	11.4	7.9	12.5	5.9
	3	6.3	10.1	7.3	7.4	8.4	5.9
	4	Tr	7.8	6.4	7.9	5.7	6.4
	5	—	2.1	6.2	8.8	5.9	8.4
	6	—	3.1	3.1	3.9	2.7	4.3
C_{12}	2	2.6	10.5	10.9	6.1	12.2	5.8
	3	Tr	7.1	7.3	6.6	8.0	5.7
	4	—	5.2	6.2	7.0	5.4	6.1
	5	—	2.9	6.4	8.4	5.7	8.4
	6	—	1.3	6.4	7.0	5.2	8.8
C_{13}	2	—	6.7	4.0	2.3	4.5	2.9
	3	—	4.3	2.8	2.3	3.2	2.6
	4	—	2.2	2.4	2.8	2.0	3.2
	5	—	1.9	2.6	3.2	2.0	4.3
	6	—	0.8	2.6	3.2	2.0	4.7
	7	—	1.0	1.3	1.2	0.8	2.0
2-ϕ		69.0	41.3	31.0	19.2	34.1	19.6

Note. Conditions: Temperature = 408 K; pressure = 0.7 MPa; WHSV = 0.8 h^{-1}; benzene : olefin (mol) ratio = 10; conversion of olefin 100%; data at 10 h time on stream.

[a] Composition of feed (wt%) : olefins (total), 9.7; C_{10} = 1.9, C_{11} = 3.1; C_{12} = 2.9; C_{13} = 1.8. Paraffins (C_{10}, C_{11}, C_{12}, and C_{13}) constitute the rest; the breakup of the olefin isomers is not known.

[b] ϕ = phenyl.

[c] Conversion incomplete.

[d] Composition of parent olefin mixture not known. LAB obtained from commercial sources; liquid phase reaction; WHSV indeterminate. The larger amount of the 2-ϕ and 3-ϕ decanes is probably due to their carry over from the fractionater.

1). SiO_2–Al_2O_3, H–β, and H–M produce more 2-phenyl isomers than RE–Y and HF. As expected, shape selectivity in the case of H–M and H–β increases with increase in the C-number of the fraction.

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