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Selectivities of Acid-Catalyzed Reactions Over Silica–Alumina and Molecular Sieve Catalysts

SIGMUND M. CSICSERY AND DONALD A. HICKSON
Chevron Research Company, Richmond, California 94802

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1-Methyl-2-ethylbenzene was contacted between 200 and 400°C with a series of Y-type faujasite molecular sieves exchanged with various cations. The most important reactions are isomerization to 1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene, and transethylation forming toluene and methyldiethylbenzenes. The two reactions occur in parallel and are independent of each other. Isomerization has a significantly higher activation energy than transethylation. Relative rates of the two reactions depend on temperature, on the cationic form of the molecular sieve, and on the water content of the reactant mixture. For a given catalyst, the isomerization/transethylation ratio increases with increasing water content of the reactant mixture. These results suggest either that isomerization is primarily catalyzed by Brønsted acid sites, while transethylation is primarily a Lewis acid catalyzed reaction, or, that transethylation is catalyzed by a Brønsted and Lewis site pair, while isomerization by a single-type Brønsted site.

INTRODUCTION

Solid acid catalysts, such as amorphous silica–aluminas or decationized molecular sieves catalyze various reactions of the polyalkylbenzenes. The two most important reactions are isomerization and transalkylation. An example of isomerization is the interconversion of the *ortho-*, *meta-*, and *para*-dialkylbenzenes. Transalkylation forms mono- and trialkylbenzenes from dialkylbenzenes.

At lower temperatures (i.e., below 200°C), isomerization proceeds through transalkylated intermediates (*1*, *2*). Above 300°C, isomerization primarily occurs by intramolecular 1, 2 shifts (*3*). Under these conditions, isomerization and transalkylation occur in parallel and are independent of each other. This paper explores selectivity differences (expressed as isomerization/transalkylation ratios) between molecular sieve and amorphous silica–alumina catalysts. Results are discussed in terms of Brønsted–Lewis theory of acidities for solid acid catalysts.

EXPERIMENTAL METHODS

1-Methyl-2-ethylbenzene was obtained from Columbia Organic Chemicals Company, Columbia, South Carolina. It was dried over sodium wire and purified chromatographically by passing it through activated silica gel under nitrogen. The purified material contained 99.77% 1-methyl-2-ethylbenzene; 0.15% 1-methyl-3-, and 4-ethylbenzenes; and 0.08% xylenes and other hydrocarbons.

Silica–alumina was a commercial cracking catalyst containing 10 wt % alumina, 90 wt % silica, and 0.1 wt % Na_2O. The BET surface area of the catalyst was 340 m^2/g. We pretreated the catalyst at 530°C for 2 hr in helium and 1 hr in hydrogen before the experiments.

The other catalysts were prepared from sodium Y-type molecular sieve (SK-40), manufactured by the Linde Division of Union Carbide Corporation. NH_4 Y-sieve containing 1% Na was prepared by direct exchange with NH_4NO_3 solutions. NH_4 Y-sieve with only 0.007% Na was prepared by first exchanging SK-40 with $AgNO_3$ and then removing Ag by NH_4SCN treatment. The NH_4 Y-sieve thus produced contained 6.75 wt % NH_4^+ ions (Dumas N analysis). Mg, Ca, Zn, and Ba sieves were made by exchanging either the Na Y-sieve or the NH_4 Y-sieve (with 0.007% Na) with the corresponding nitrates. Catalysts were pretreated before each experiment at 540°C in dry H_2.

The experiments were carried out in a continuous flow-type reactor, consisting of a 50-cm long and 0.635-cm o.d. stainless steel tube. The tube held 0.5 ml of catalyst. Experimental conditions were atmospheric pressure and hydrogen diluent, which was dried by passing through 4A molecular sieve. In certain experiments we added 650 ppm water to the H_2 by bubbling it through a phosphoric acid solution at 0°C. Reaction products were collected in an acetone–Dry Ice-cooled condenser. Reaction periods were 65 min long. Catalysts were regenerated after each experiment at 480°C with a 1:1 mixture of air and nitrogen. A 300-ft long, 0.02-in. i.d. capillary column was used for the gas chromatographic analysis of the liquid products. The column was packed with Ucon LB-550-X polypropylene glycol. The analytical procedure is described in detail by Csicsery and Baumann (*4*).

Transalkylation conversions are shown as "moles per 100 moles of feed." The same procedure is followed for isomerization conversions over silica–alumina, where transalkylation does not exceed 2%. Transalkylation is considerably more extensive over molecular sieves. Here we prefer to report isomerization conversions as "percentage of the total methylethylbenzene content of the product." Isomerization/transalkylation ratios are always calculated from conversions expressed as "moles per 100 moles of feed."

RESULTS

Silica–Alumina

In order to explore the nature of the isomerization and transalkylation of dialkylbenzenes a number of variables were examined. The effects of space velocity, temperature, and hydrocarbon partial pressure were studied using a silica–alumina cracking catalyst. Experimental results are summarized in Table 1. Isomerization and transethylation at 400°C as functions of space velocity are shown in Fig. 1. At low conversion levels, both types of conversions increase linearly with increasing residence time. Therefore, the isomerization/transethylation ratio (*I/T*) is not dependent on the space velocity or the conversion level. This behavior of *I/T* is important and very useful because it permits comparison between experiments made at different conversions. However, at very high conversion levels, i.e., above 30% isomerization or above 20% transethylation, the reverse reaction and side reactions become significant, and *I/T* ceases to be independent of the conversion level.

Isomerization and transethylation follow Arrhenius' law between 204 and 426°C (*3*). Isomerization has significantly higher activation energy than transethylation. The *I/T* ratio, therefore, increases steeply with increasing temperature (Fig. 2).

Hydrocarbon partial pressure effects were studied at constant residence time by

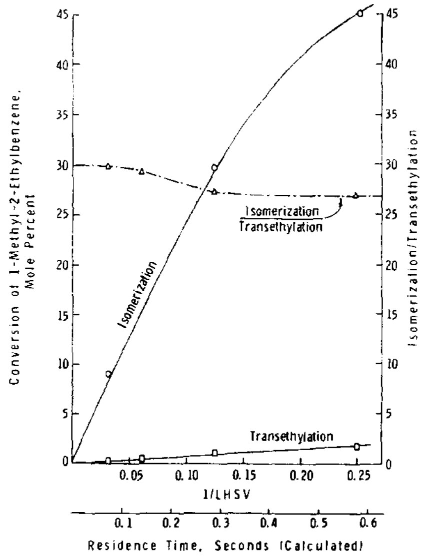


FIG. 1. Effects of residence time on the reactions of 1-methyl-2-ethylbenzene over silica–alumina at 400°C, 1 atm total pressure, and with a H_2:hydrocarbon mole ratio of 3:1.

TABLE I

THE REACTIONS OF 1-METHYL-2-ETHYLBENZENE OVER SILICA–ALUMINA AT 1 atm TOTAL PRESSURE

Reaction temp. (°C):	204	315	371	400	426	400	400	400	400	400	400
Liquid hourly space velocity (hr^{-1}):	8	8	8	8	8	4	16	32	3.2	16	32
Calc residence time (sec):	0.40	0.33	0.30	0.29	0.27	0.57	0.14	0.07	0.29	0.29	0.29
Feed partial pressure (atm):	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.1	0.5	1
Initial H_2:hydrocarbon mole ratio:	3	3	3	3	3	3	3	3	10	1	0
Conversions (moles/100 moles of feed)											
Isomerization	0.24	4.37	18.9	29.4	53.8	45.6	14.9	9.3	22.8	24.0	26.0
Transethylation	0.40	0.72	0.96	1.09	1.19	1.7	0.5	0.3	0.56	0.95	1.3
Transmethylation	0.01	0.07	0.13	0.15	0.2	0.26	0.07	0.04	0.16	0.13	0.18
Isomerization/Transethylation	0.6	5.8	19.4	27.3	44	27	29.4	30	41	25.2	20

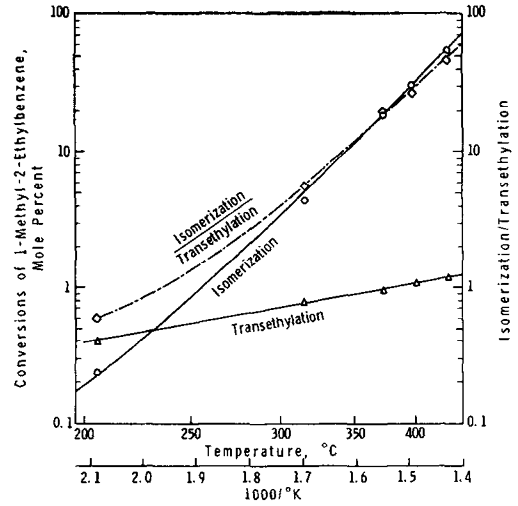


FIG. 2. Effects of temperature on the reactions of 1-methyl-2-ethylbenzene over silica–alumina at 1 atm total pressure, with an LHSV of 8 and with a H_2:hydrocarbon mole ratio of 3:1

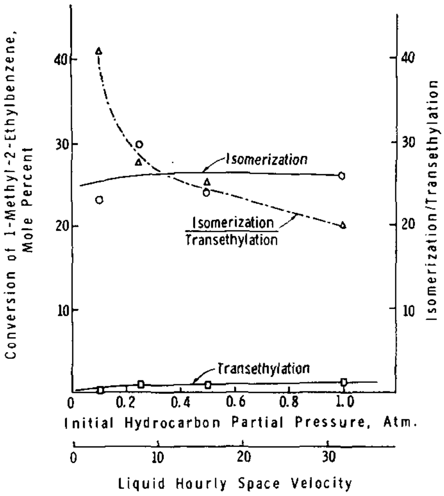


FIG. 3. Effect of the initial hydrocarbon partial pressure on the reactions of 1-methyl-2-ethylbenzene over silica–alumina at 1 atm total pressure. (The residence time was kept constant at 0.3 sec by changing the LHSV and the H_2:hydrocarbon mole ratio.)

varying space velocity and H_2:hydrocarbon mole ratio simultaneously. Isomerization is first order with respect to methylethylbenzene partial pressure. At low hydrocarbon partial pressures, transethylation shows second order kinetics. The resulting relationship between I/T and methylethylbenzene partial pressure is shown in Fig. 3. Experiments were made at a constant hydrocarbon partial pressure of 0.25 atm to simplify interpretation of the results.

Y-Type Faujasite Molecular Sieves

Na Y-type molecular sieve contains approximately 8% Na. About seven-eights of this may be replaced with NH_4^+ by direct cation-exchange with NH_4NO_3. Almost all Na is removed from the Na-sieve in $AgNO_3$ exchange. Further treatment with NH_4SCN replaces Ag^+ with NH_4^+. When heated between about 100 and 400°C, NH_3 evolves, and the H^+ form of Y-sieve is produced. Dehydration at somewhat higher temperature creates the "decationized" form. Table 2 compares acid activities of Y-sieves activated at 540°C with that of the original Na Y-sieve. Although tested at 111°C higher than the decationized sieves, Na Y shows practically no activity. Among the decationized sieves, the one containing only 0.007% Na is significantly more active than the one made by direct NH_4NO_3 exchange.

Exchanging polyvalent cations for Na is another way to generate acid sites in molecular sieves. Two sets of divalent cation-exchanged Y-sieves were prepared. The first set was made from the Na Y-sieve. The second set was made from the NH_4 sieve containing only 0.007% Na. Activities of the resulting sieves varied over more than five orders of magnitude. Therefore, to obtain meaningful conversions, the test temperature was varied. Table 3 summarizes the results. Isomerization and transethylation conversions are shown in Figs. 4 and 5. In general, sieve catalysts prepared from the sodium-free, completely ammonium-exchanged molecular sieves are 10 to 100 times more active than the corresponding ones prepared from the sodium sieve. Acid activities increase with increasing ionic potential (cation charge/ionic radius) of the exchanged cation (Table 4). Figure 6 shows separate curves for the sieves prepared from Na-sieve and from NH_4 sieves. Where experiments were not made at 260°C, conversions in Fig. 6 and Table 4 were determined graphically from data shown in Figs. 4 and 5. Ward (*5*) re-

TABLE 2

EFFECTS OF SODIUM CONTENT ON THE REACTIONS OF 1-METHYL-2-ETHYLBENZENE OVER Y-FAUJASITES AT AN H_2:FEED MOLE RATIO OF 3; ATMOSPHERIC TOTAL PRESSURE; AND A LHSV OF 8

Na^+ Concentration (wt %):	0.007	1	8.1
Cationic sites occupied by Na^+ (% of total cationic sites):	0.1	12	100
Temp (°C):	204	204	315
Isomerization (% of methylethylbenzenes)	42	2.6	0.07
Transethylation (moles/100 moles of feed)	29.5	7.0	0.03
Transmethylation (moles/100 moles of feed)	2.08	0.18	0.002
Isomerization/transethylation	0.9	0.35	2.3

ported a similar relationship between the ionic potential of cation-exchanged sieves and their cumene dealkylation activities.

Figure 7 shows that I/T is significantly higher over amorphous silica–alumina catalyst than over the divalent cation-exchanged sieves. Decationized NH_4 Y-sieve, and the Mg–NH_4 Y-sieve (where more than one-quarter of cationic sites are occupied by NH_4^+) have intermediate I/T ratios.

DISCUSSION

Under conditions in which isomerization and transalkylation of dialkylbenzenes occur simultaneously, isomerization is the preferred reaction over silica–alumina and alkaline earth exchanged Y-type molecular sieve catalysts. The latter are more active toward transalkylation, however. Decationized NH_4 and Mg–NH_4 Y-type molecular sieves catalyze both reactions to about the same extent. The selectivity of these reactions can be varied by choice of catalyst. There seems to be general agreement that the majority of the active sites on amorphous silica–alumina catalysts are of the Brønsted type (*6, 7*). Both Brønsted and Lewis sites have been observed for decationized NH_4 Y-sieve by Hughes and White

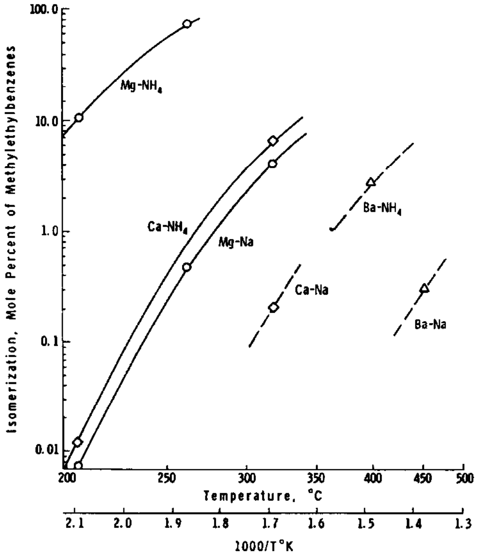


FIG. 4. Isomerization of 1-methyl-2-ethylbenzene over Y-type faujasites exchanged with divalent cations.

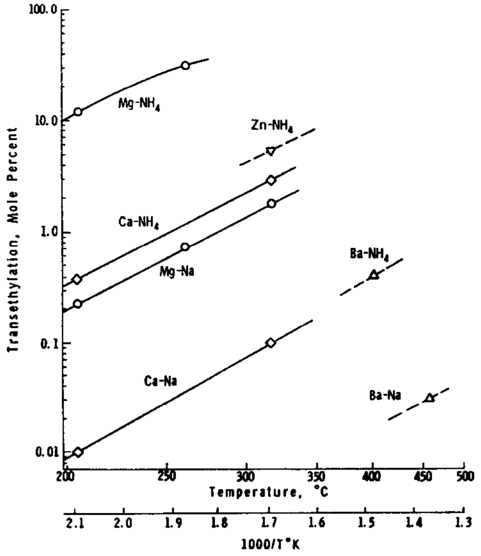


FIG. 5. Transethylation of 1-methyl-2-ethylbenzene over Y-type faujasites exchanged with divalent cations.

TABLE 3

Reactions of 1-Methyl-2-ethylbenzene over Molecular Sieves Exchanged with Divalent Cations[a]

Monovalent cation:		Na				Na		Na	Mg			Ca			Ba	Zn
Polyvalent cation:		Mg				Ca		Ba	NH_4			NH_4			NH_4	NH_4
Polyvalent:monovalent ion equivalent ratio:		73:27				92:8		79:21	84:16			98:2			95:5	93:7
Reaction temp (°C):	204	204	260	315	204	315	454	204	260	204	315	315	400	400	315
Water added to H_2 during pretreatment and experiment (ppm):	0	650[b]	0	0	0	0	0	0	0	0	0	650[c]	0	650[c]	0
Isomerization (mole % of methylethylbenzenes)	0.007	0.03	0.49	4.2	0	0.22	0.32	10.8	73.0	0.012	6.75	3.0	2.7	2.9	6.86
Transethylation (mole %)	0.23	0.38	0.74	1.72	0.01	0.10	0.03	12.0	32.4	0.38	2.94	0.87	0.40	0.40	5.3
Transmethylation (mole %)	0.005	0.01	0.04	0.12	0	0.007	0	0.47	7.45		0.21	0.06	0.04	0.04	0.34
Isomerization/transethylation	0.03	0.08	0.66	2.3		2.2	10	0.75	1.24	0.03	2.2	3.4	6.7	7.2	1.3

[a] Reaction conditions: Atmospheric total pressure, a H_2:feed mole ratio of 3, and a LHSV of 8. Experiments were 85 min long. Catalysts were pretreated before each experiment at 540°C in dry H_2. Catalysts were regenerated at 480°C between experiments in dry air.

[b] The catalyst was pretreated for 16 hr at 204°C in H_2 containing 650 ppm H_2O.

[c] The catalyst was pretreated for 16 hr at 480°C in H_2 containing 650 ppm H_2O.

TABLE 4
ACTIVITIES OF Y-TYPE MOLECULAR SIEVES EXCHANGED WITH DIVALENT CATIONS

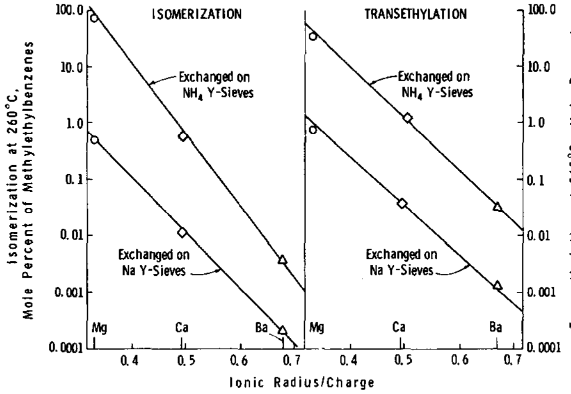
Sieve	Ionic potential[b]	Conversions at 260°C[a]	
		Isomerization (% of methylethylbenzenes)	Transethylation (mole %)
A. Exchanged on Na Y-sieve			
Mg	3.04	0.49	0.74
Ca	2.02	0.011	0.036
Ba	1.49	0.0002	0.0014
B. Exchanged on NH_4 Y-sieve			
Mg	3.04	73	32
Ca	2.02	0.62	1.2
Ba	1.49	0.004	0.03

[a] Determined graphically from experiments at other temperatures where experiments were not made at 260°C.

[b] Cation charge/ionic radius; ionic radii taken from Ref. (*13*).

(*8*) in infrared studies of chemisorbed organic nitrogen bases. Using the same method, Ward (*5*) observed both Brønsted and Lewis sites on alkali earth exchanged Y-sieves heated above 500°C.

Comparing our experimental results with the observation of Hughes and White (*8*) suggests either that isomerization is catalyzed primarily by Brønsted acid sites and transalkylation is primarily a Lewis acid catalyzed reaction,* or, that one of these reactions, most probably transethylation, is catalyzed by a Brønsted and Lewis site pair, while the other (isomerization) by a single–type Brønsted site. Alkane cracking results of Hopkins (*9*) over acidic molecular sieves support this latter assumption. Hopkins concluded that the strongest Brønsted sites contribute most or all of the activity for alkane cracking and that Lewis sites might have a synergestic effect on the activity. In either case, the *I/T* ratio is proportional to the Brønsted/Lewis site ratio.



Conversions were determined graphically from experiments at other temperatures where experiments were not made at 260°C.

FIG. 6. Effects of divalent cations on acid catalyzed reactions of 1-methyl-2-ethylbenzene.

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* However, by assigning isomerization to Brønsted acidity (or transethylation to Lewis acidity), we do not exclude overlap. In other words, isomerization occurs predominantly by Brønsted sites; whereas, transethylation is catalyzed predominantly by Lewis sites.

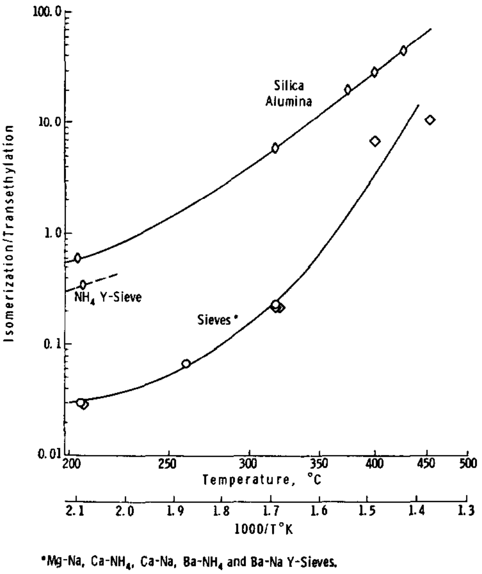

FIG. 7. The isomerization/transethylation ratio in the reactions of 1-methyl-2-ethylbenzene over Y-type molecular sieves and silica–alumina.

Finally, inspection of the possible reaction intermediate gives additional support to our hypothesis that the isomerization of methylethylbenzenes is catalyzed by Brønsted acidity, while transalkylation occurs over Lewis sites. Isomerization of methylethylbenzenes probably involves protonated ring intermediates (*10*, *11*). Protonation can be accomplished by Brønsted sites. Pines and Arrigo, and Streitwieser and Reif suggested benzyl carbonium ion intermediates for transethylation (*12*). These intermediates could occur via hydride transfer to Lewis acid sites.

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