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NOTES

Paraffin–Olefin Alkylation over a Crystalline Aluminosilicate

Rare-earth-containing crystalline aluminosilicates have shown versatile catalytic activity in catalytic cracking (*1, 2*) and a wide range of "classical" acid-catalyzed organic reactions (*3*). This communication reports on the use of rare earth–hydrogen X-type faujasite (REHX) as catalyst for alkylation of isobutane with ethylene.

The catalyst was prepared from Linde 13X by the ion-exchange method of Plank *et al.* (*1*); using a solution containing both 5% mixed rare earth chloride ($RECl_3 \cdot 6H_2O$) and 2% NH_4Cl. The final sodium level was 0.31 wt %, and the unit cell calculated from elemental analyses was $(NA)_{0.02} \cdot (RE^{3+} \times 3)_{0.88} \cdot (NH_4^+)_{0.19} \cdot (SiO_2)_{1.24} \cdot (AlO_2)_{1.00}$. The analysis of the rare earth (RE) mixture has been reported earlier (*4*). Reactants (Matheson C. P. grade) were used without further purification.

The catalyst was calcined at 540°C in air for 16 hr (to convert the rare earth–ammonium form to the rare earth–hydrogen form) and charged to a 1-liter stainless steel rocking autoclave. After evacuation at 482°C for 1–2 hr at 2 mm, the autoclave was cooled to Dry Ice temperature (while under vacuum) and a weighed amount of isobutane admitted. The mixture was heated to reaction temperature and ethylene was pressured in. The final ratios of reactants to catalyst (wt/wt) and isobutane to ethylene (mole/mole) were 4 and 3–4, respectively. At the end of the reaction period (under autogenous pressure, at 700 psig), gaseous products were vented through cold traps into a gas collection system. Final desorption of product from catalyst was effected by heating at 121°C. Organic material remaining on the catalyst after this treatment was termed "catalyst adsorbate." After equilibration to 25°C, quantities of total gaseous, liquid, and adsorbed (on catalyst) products were measured. Products were analyzed by gas-liquid chromatography and mass spectroscopy (70 eV).

Yield data for the reaction of isobutane and ethylene over REHX catalyst are shown in Table 1. Moderate conversions to liquid products were obtained at 121–149°C. Alkylation even occurred at room temperature with prolonged contact times. In all runs, significant quantities of catalyst

TABLE 1
ISOBUTANE–ETHYLENE ALKYLATION OVER REHX[a] CATALYST

Temp. (°C)	Time (hr)	% Conversion[b] to alkylate	
		Liquid products	Catalyst adsorbate
27°	169	8	15
121° [c]	3	28	17
	6	46	19
	26	86	24
149°	21	80	22

[a] Under similar conditions at 121°C, CaX, NaX, and amorphous silica-alumina were virtually inactive.

[b] Defined as g alkylate product/g C_2H_4 charged × 100.

[c] In continuous-flow experiments (121°C, *iso*-C_4H_{10}/C_2H_4(molar) = 4, LHSV = 0.7, 700 psig), a 13-hr cumulative conversion to alkylate of only 9% was obtained.

adsorbate, usually dark brown in color, were observed. Alkylation with the same reactants is catalyzed by hydrogen-chloride-promoted aluminum chloride at 25–35°C, but not by 96–100% sulfuric acid or liquid hydrogen fluoride (*5*). We have confirmed earlier reports (*6*) that amorphous silica-alumina cracking catalyst is not effective in paraffin alkylation.

Typical product distributions for these runs are shown in Table 2. At 25°C, the major products are hexanes; at 121–149°C, pentanes are dominant, with increasing amounts of C_7-, C_8-, and higher paraffins. Hexane and octane isomer distributions are shown in Tables 3 and 4, respectively. Over 99% of the pentane fraction was 2-methylbutane. At 27°C, 2,3-dimethylbutane was the major product, with appreciable amounts of methylpentanes appearing at the higher temperatures. 2,2,4-Trimethylpentane was the major octane isomer at 121°C, but all other trimethyloctane isomers were present. At longer contact times, dimethylhexanes and methylheptanes appeared in larger quantities. The proportions of trimethylpentanes far exceed equilibrium values (*7*) for this temperature.

TABLE 2

ALKYLATE COMPOSITION VS. TEMPERATURE

	Wt % of liquid[a] product		
Product	27°C (169 hr)	121°C (6 hr)[b]	149°C (21 hr)
C_5H_{12}	6	40	45
C_6H_{14}[c]	76	35	26
C_7H_{16}	tr.	7	9
C_8H_{18}	6	11	14
Other[d]	12	7	6
	100	100	100

[a] Gaseous products were largely isobutane, small amounts of C_2H_6 and unreacted C_2H_4, and traces of CH_4 and C_3H_8.

[b] With increasing contact time at 121°C, the proportions of C_5H_{12} and C_6H_{14} decreased, while those of C_7H_{16} and higher increased.

[c] GLC examination of C_6 fraction showed no olefin or cycloparaffins.

[d] Mainly C_9- and higher paraffins.

TABLE 3

HEXANE ISOMER DISTRIBUTION

	Mole %		
Isomer	27°C (169 hr)	121°C (26 hr)	149°C (21 hr)
2,3-Dimethylbutane	90	44	33
2,2-Dimethylbutane	tr.	1	3
3-Methylpentane	10	27	27
2-Methylpentane	tr.	27	35
n-Hexane	tr.	1	2
	100	100	100

Based upon studies using strong protonic acids and promoted Lewis acids as catalysts, a mechanistic picture involving a carbonium ion chain has emerged for paraffin alkylation (*5*). This scheme explains the appearance—as side products—of paraffins having molecular weights which are not the sum of the molecular weight of one mole of isoparaffin and one or more moles of olefin. Hydrogen-transfer processes and reaction of the primary alkylate or its ionic precursor with isobutane or other product isoparaffins—sometimes followed by β-scission—are specifically involved.

TABLE 4

TYPICAL OCTANE ISOMER DISTRIBUTION[a]

Isomer	Mole %
2,2,4-Trimethylpentane	37
2,2,3-Trimethylpentane	16
2,3,3-Trimethylpentane	20
2,3,4-Trimethylpentane	16
2,4-Dimethylhexane 2,5-Dimethylhexane	10
Other Isomers[b]	1
	100

[a] At 121°C, 6-hr contact time.

[b] Largely dimethylhexanes, methylheptanes.

In the present study over REHX catalyst —(1) formation of 2,3-dimethylbutane (primary C_6 alkylation product), (2) appearance of small quantities of 2,2,4-trimethylpentane and related isomers ("self-alkylation" of isobutane), (3) the formation of large amounts of pentanes and higher odd carbon number paraffins (from β-scission of higher molecular weight carbon chains), (4) detection of ethane in gaseous products (hydrogen-transfer reactions of $C_2H_5^+$)—all point to the operation of a carbonium ion chain mechanism.

Since paraffin alkylation is thermodynamically less favorable than olefin polymerization (*6*), the latter side reaction has frequently been encountered (*5*). Large amounts of brown adsorbate were also observed when ethylene *alone* was reacted over REHX at 121–149°C, but white, essentially organic-free catalysts were obtained after treatment with isobutane alone under similar conditions. These facts suggest ethylene polymerization as a major source of the brown adsorbate formed under alkylation conditions, but with the added complexity of the known (*4*) hydrogen-transfer reactions of rare earth faujasites superimposed.

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Reaction Probabilities for Methane and Oxygen on (111) Silicon Single-Crystal Surfaces

Molecular dynamics of gas–solid reactive collisions is very poorly known. Yet, it is essential to a quantitative understanding of surface catalysis. In this note we report the rates of reaction of cold methane and oxygen molecules with a single-crystal wafer of pure silicon at surface temperatures between 1030° and 1150°K. These data were obtained with a nozzle-produced beam apparatus described in detail elsewhere (*1, 2, 3*).

In the present work, the potential of the beam instrument was not fully used since the number of collisions of background molecules with the target equaled or even exceeded the number of collisions of beam molecules with the surface under study. Yet the results are interesting in that they demonstrate a rather high reactivity of silicon surfaces with methane.

Target wafers were heated by radiation from a projection lamp placed at one focus of an ellipsoidal aluminum reflector, with the target placed at the other focus. Changes in the mass of the target from reaction with the impinging molecules were measured by observing changes in the extension of a quartz spiral spring, following the method of Koros *et al.* (*4*). Hot filament ionization gauges used to measure the beam fluxes and the background pressures were calibrated for methane and oxygen