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Organic Reactions Catalyzed by Crystalline Aluminosilicates

I. Alkylation Reactions

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A number of crystalline aluminosilicates have been shown to be versatile catalysts for the alkylation of aromatics and for related reactions. Highly acidic faujasites, including rare-earth–exchanged X and Y, and hydrogen Y from thermal decomposition of ammonium Y showed broadest application, although calcium and sodium X faujasites showed activity under certain conditions. Simple monocyclic aromatic nuclei such as benzene, phenol, and thiophene, with a wide variety of alkylating agents, were used, for the most part, in this study.

For the strongly acidic faujasites, operation in the liquid phase at temperatures of 150–230°C was generally required for efficient alkylation of simple aromatics with a variety of olefins, alcohols, and haloalkanes, and for transethylation. For dealkylation reactions, alkylations with paraffins, and toluene disproportionation, higher temperatures were required. With low molecular weight alkylating agents such as ethylene, high molar ratios of aromatic to olefin were necessary to prevent catalyst aging. In typical alkylations of substituted benzenes, *ortho:para* orientation of substituents was observed. With alkylating agents of three or more carbon atoms, the monoalkylate generally consisted of a mixture of isomeric arylalkanes. Similarly, 2-substitution predominated in the alkylation of thiophene.

Under comparable conditions, highly acidic faujasites catalyzed alkylation at lower temperatures than silica-alumina catalysts, but at higher temperatures than Lewis acids such as aluminum chloride and boron trifluoride, or protonic acids such as sulfuric or hydrofluoric acids.

INTRODUCTION

The Friedel-Crafts alkylation has long been of great chemical interest, and has recently been reviewed comprehensively by Olah (*1*). The literature is replete with examples of the use of protonic acids such as sulfuric, phosphoric, or hydrofluoric acids, and proton-donor–promoted Lewis acid combinations such as aluminum chloride-hydrogen chloride and boron trifluoride-water, under a wide variety of conditions, as alkylation catalysts. Many acidic oxides and mixed oxides have been used as alkylation catalysts, notably silica-alumina. Typically, alkylations of aromatic hydrocarbons (*2*, *3*, *4*), phenols (*5*), and heterocyclics (*6*) have been reported with a variety of alkylating agents using this acidic (*7*) catalyst. The reactions have generally been conceded to proceed via carbonium ion mechanisms (*8*, *9*).

Alkylation by acidic organic cation-exchange resins is now well known (*1*), and a recent patent (*10*) discloses the use of a crystalline sodium aluminosilicate (zeolite) for the alkylation of benzene with propylene. Zeolites have long been known as adsorbents and ion exchangers (*11*, *12*), but their catalytic application has only recently come into prominence. Weisz and co-workers reported the use of small-pore zeolites in molecular-shape-selective cracking, alcohol dehydration and hydrogenation reactions (*13*), and a comparison of sodium and calcium X zeolites in cracking of paraffins, olefins, and alkylaromatics (*14*). Rare earth and rare earth-acid faujasites with great activity for cracking were reported subsequently by Plank, Rosinski, and Hawthorne (*15*).

Zeolites of the faujasite family possess an extraordinarily open structure, great rigidity, and a crystallographically well defined surface. Unusual opportunities for catalysis were found to exist when base exchange to substantially eliminate their alkali metal content was practiced. We wish to report data on the facile alkylation of aromatics using crystalline aluminosilicate catalysts, with emphasis on the use of highly acidic faujasite-type catalysts, including rare-earth–exchanged X and Y faujasites and hydrogen Y from thermal decomposition of ammonium Y. The reactants consisted largely of simple, monocyclic aromatic nuclei, and a wide variety of alkylating agents. Synthetic aspects are stressed in this paper.

EXPERIMENTAL

Materials

Catalysts. The rare earth X catalyst (REX) was prepared from Linde 13X by the methods of ref. (*15*). A sodium level of 0.58% by weight was obtained. The rare earth Y catalyst (REY) was prepared similarly by exchanging a synthetic sodium Y aluminosilicate (NaY) with 5% $RECl_3 \cdot 6H_2O$ solution until a sodium level of 0.99% wt was obtained. The ammonium Y catalyst (NH_4Y) was obtained from a synthetic NaY zeolite by repeated exchange with warm 10% aqueous ammonium chloride solution until a sodium level of 1.05% wt was achieved. All three catalysts were crystalline (X-ray) and were dried at 120–130°C before activation. Unit cell compositions and analytical data for REX, NH_4Y, and REY are given in Tables 1 and 2.

TABLE 1
UNIT CELL[a] COMPOSITIONS FOR MAJOR CATALYSTS

	REX	NH_4Y	REY
AlO_2 units[b]	86	51	49
SiO_2 units	106	141	143
$RE^{3+} \times 3$[c]	80.7	Nil	44.2
NH_4^+[d]	Nil	45.9	Nil
$Ca^{2+} \times 2$	2.15	Nil	1.09
Na^+	3.91	5.1	5.88

[a] Values for supercage = unit cell values /8.

[b] Analytical values for Al_2O_3, SiO_2, Ca, Na in catalyst are on ignited basis (1000°C).

[c] Calculated on basis of 140 for average atomic weight of rare earth (RE) cation.

[d] Calculated value; experimental % nitrogen determined by Kjeldahl analysis.

TABLE 2
ANALYTICAL DATA FOR MAJOR CATALYSTS

	REX	NH_4Y[a]	REY
AlO_2 units/g[b]	3.32×10^{21}	2.73×10^{21}	2.16×10^{21}
S.A. (m^2/g, BET)[c]	478	676	568
AlO_2 sites/cm^2 (Calc'd)	6.95×10^{14}	4.04×10^{14}	3.80×10^{14}
Cyclohexane adsorption (g/100 g catalyst)[d]	14.7	20.5	16.7
Water adsorption (g/100 g catalyst)[c]	23.2	31.9	27.7

[a] Also contains Fe (0.019%), Ti (0.03%), Mn (0.001%), Cu (14.7–16.3 ppm), and traces of V, Ca, Mg (all on ignited basis).

[b] On ignited (1000°C) basis.

[c] Dried $\frac{1}{2}$ hr/538°C then heated 400°C/1 hr/1 $\times 10^{-5}$mm Hg before analysis.

[d] Ignited 3 hr/O_2 at 400°C (REX) or 550°C (NH_4Y) or 250°C (REY).

Binder-free Linde sodium 13X (NaX) and calcium 10X (CaX) were calcined 1–3 hr at 343°C in air before use. Norton Hydrogen Zeolon (H-Mordenite) was calcined 3 hr in air at 400°C. The silica-alumina catalysts were Socony Mobil Oil Co. 46 AI bead cracking catalyst (420 m^2/g surface area, 10% wt Al_2O_3) and Houdry S-46 cracking catalyst (290–315 m^2/g surface area, 12.4% wt Al_2O_3). These were crushed and sized to 8/14 mesh, and calcined 3 hr at 500°C in air before use. All zeolite catalysts were pelleted, crushed, and sized to 8/14 mesh before activation. The Amberlyst 15 (Rohm and Haas, Co.) was washed with benzene, then methanol, and dried *in vacuo* with mild heat before use.

Organic reactants. These were obtained from standard commercial sources, and distilled or recrystallized to a purity of better than 99% in most cases. Aromatic hydrocarbons were dried and stored over Linde 5A molecular sieves.

Apparatus and Procedures

For continuous-flow alkylations at atmospheric pressure, the basic apparatus shown in Fig. 1, with occasional variations, was used. Conditions for catalyst activation and subsequent alkylation of benzene with ethylene over REX catalyst are typical: Uncalcined catalyst (1.25 g, 2.5 ml) was diluted with quartz chips to a volume of 5 ml and placed in the electrically heated, tubular Vycor glass reactor. Calcinations were effected with Linde 5A sieve-dried oxygen (2 ml/min) for 3 hr. The reactor was purged with dried Seaford Grade nitrogen and brought to the desired temperature (i.e., 177°C) without transfer of catalyst or exposure to atmosphere. Benzene and ethylene in the desired molar ratio were then admitted to the catalyst bed, and samples of products collected periodically for analysis. In the case of the activation temperature studies (see Fig. 2), the composite product after 135 min on stream at the prescribed conditions was analyzed, and the total per cent conversion of ethylene to ethylbenzene calculated. Each point in Fig. 2, representing a conversion after calcination at a given temperature, is the average of values for three identical runs.

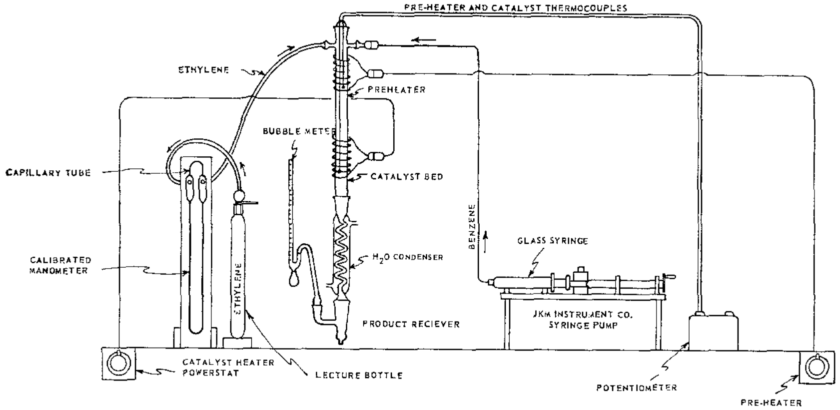


FIG. 1. Vapor-phase continuous-flow glass reactor.

Reactions under 100–500 psig pressure were run in a laboratory-size, stainless-steel continuous-flow analog of the glass reactor shown in Fig. 1. Alkylation procedures were essentially identical to those described above, except on a larger scale (reactor volume of 225 ml). The autogenous pressure of the gas cylinder was often sufficient to maintain liquid-phase conditions, although occasionally the use of additional nitrogen pressure was necessary.

Other reactants with higher boiling points were stirred in the liquid phase at atmospheric pressure in a glass reactor. In a typical example, equimolar amounts of phenol and decyl alcohol were stirred with finely powdered, freshly activated catalyst (1/10–1/16 the weight of reactants) at 180–210°C for a few hours. After reaction, the products were cleanly separated from catalyst by filtration, and analyzed.

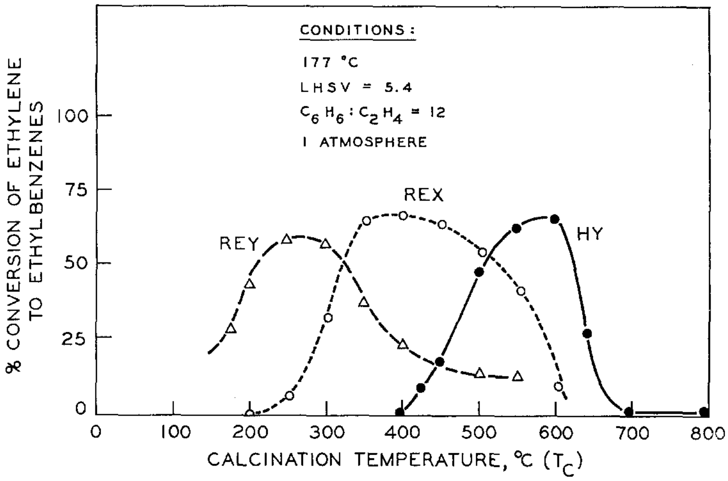


FIG. 2. Ethylene-benzene alkylation activity of acidic faujasite catalysts calcined at different temperatures in oxygen.

Analyses

Reaction mixtures were analyzed by gas-liquid chromatography (GLC) using an F&M model 720 dual-column chromatograph. Products were identified by comparison of peak retention times with those of known standards. In some cases, products were identified by physical separation and comparison; in other cases, selected products were separated by micropreparative GLC and analyzed by the appropriate spectroscopic technique. Ultraviolet spectra were recorded on the Cary 14 spectrophotometer; nuclear magnetic resonance spectra were run at 60 Mc/sec on a Varian A-60 spectrometer using carbon tetrachloride solutions; mass spectra were recorded at 7 and 70 eV on a Consolidated Electrodynamics Corporation Model 21-103 spectrometer with an inlet temperature of 350°C. Parent peaks (molecular weights) and the appropriate fragmentation pattern and isotopic ratios were generally obtained.

Qualitative infrared (IR) analyses were run neat (sodium chloride plate), as potassium bromide pellets, or as solutions on the Perkin-Elmer 421 or Infracord spectrophotometers. Quantitative IR analyses for *o*-, *p*-, and *m*-alkylphenols were run on solutions (10 g/liter) in carbon disulfide using the baseline technique. Calibration spectra were prepared using pure *o*-, *p*-, and *m*-ethylphenols, and it was assumed from Tanaka's work (*16*) that the same extinction coefficients (k), 0.071, 0.049, and 0.025 liter/g, respectively, could be used for the other alkylphenols. Specific identification of *p*-*n*-hexadecylphenol was afforded by its spectra, elemental analysis, and melting point of 78–78.5°C [lit. (*17*) m.p. 78–79°C]. Assignment of orientation in the C-alkylthiophenol system was based on the close correlation of our observed IR bonds with literature values for the corresponding thiocresols (*18*). Spectra and details of analyses for all organic compounds are available from the authors.

RESULTS AND DISCUSSION

Catalyst Activation

To observe reproducible catalytic activity with acidic faujasites, it is apparent that catalysts with similar methods of preparation, and similar analyses and physical properties must be compared. It is equally critical, however, even for samples of the same original batch of catalyst, that identical methods of activation (temperature, time, atmosphere, pressure, and sample geometry) be employed prior to use. This is demonstrated in Fig. 2, where ethylene-benzene alkylation activity at 177°C is plotted vs. temperatures of calcination (T_c) for REX, HY, and REY catalysts. Although the maximum alkylation activities for these three catalyst samples are relatively close, the activation temperatures required to attain these maxima—400°C (REX), 550–600°C (HY), 250°C (REY)—differ strikingly.

When calcined at 400–450°C, REX and REY catalysts change from pale yellow and white, respectively, to deep yellow. This change probably represents oxidation of Ce^{3+} to Ce^{4+} (no color change observed when calcined in nitrogen), and does not appear to significantly affect alkylation activity. The lower activation temperature for REY may be a reflection of the easier removal of sorbed water due to its high silica-alumina ratio and consequent lower charge density.

The higher temperatures necessary to obtain maximum catalytic activity in HY reflect the increased energy requirements for decomposition of the zeolitic ammonium groups. Analyses showed that only traces of nitrogen remained in the catalyst after calcination at 450–500°C, and that all nitrogen was removed upon activation at 500°C and higher. While the over-all activation process may be visualized as

$$NH_4^{\oplus}\ \text{Zeolite}^{\ominus} \xrightarrow{O_2} H^{\oplus}\ \text{Zeolite}^{\ominus} + NH_3$$

the presence of large amounts of nitrogen gas, in addition to ammonia, in the effluent of the oxygen calcination suggests the operation of an oxidative process similar to those mentioned earlier by Barrer for ammonium mordenite and chabazite (*19*). Alkylation activity for samples calcined in nitrogen at a given temperature paralleled that for samples calcined in O_2 at about 50°C lower temperature. This parallel appears to reflect the residual nitrogen content in the sample, the presence of oxygen carrier being associated with the removal of more zeolitic nitrogen at a given temperature than was removed in the presence of nitrogen gas.

Locus of Catalysis

Faujasite-type zeolites (*20, 21*) have a structure composed of sodalite cages in such arrangement that a series of wide, roughly spherical cavities (supercages) exists, each opening by common windows (8–9 Å diameter) into four, identical, tetrahedrally distributed cavities. The capacity of the approximately 12-Å diameter supercage is such that it can contain about 2.8 isooctanes or 5.4 benzene molecules at 25°C (*20*). This constitutes the large-pore system of the zeolite. Faujasites also have a small-pore system, consisting of the interiors of the sodalite cages and the hexagonal prisms, but this is inaccessible to most organic molecules. Neglecting the extremely small contribution by external crystal surface, the adsorptive surface, and hence, locus of catalytically effective sites, is *within* the internal large-pore system. Sorptive capacities, differential thermal analysis, and thermogravimetric studies on the activated REX, HY, and REY catalysts show conclusively that all physically adsorbed and loosely held water has been removed. Thus the intrazeolitic volume is open for the entrance of organic reactants.

Alkylation of Benzene with Ethylene

Optimum conditions. Optimized reaction conditions for continuous-flow alkylation of benzene with ethylene over REX catalyst are given in Table 3. At benzene: ethylene molar ratio of 5, 500 psig, and 204°C, initial single-pass conversion of ethylene to ethylbenzene of 80%, declining to 50% after 33 days, for a total of 2200 g of ethylbenzene/g of catalyst, was observed. If the benzene:ethylene ratio was decreased, in addition to increased polyethylation, shorter catalyst life was observed due to ethylene poisoning. In starting the reaction, it was necessary to contact the catalyst first with benzene to protect it from direct interaction with ethylene alone. For long catalyst life, it was necessary to operate under sufficient pressure to maintain liquid-phase conditions, and no differences were noted when the pressure was increased from 400 to 800 psig. The aged REX catalyst could be regenerated with very little loss of activity by heating in a stream of air at 510°C.

At optimum conditions, the mono-/polyethylbenzene molar ratio was 4.65. The polyalkylate consisted of about 80% dieth-

TABLE 3

ALKYLATION OF AROMATIC HYDROCARBONS OVER ACID ZEOLITE CATALYSTS

Aromatic	Alkylating agent	Molar ratio, aromatic/alkylating agent	Catalyst	LHSV[a]	Total reactant/[b] catalyst (wt/wt) ratio (time, hrs)	Pressure	Highest alkylation activity[c]		
							Temp (°C)	% Conversion of alkylating agent to alkylaromatic	Molar ratio, mono-/poly-alkylate
C_6H_6	CH_3OH	3.0	REX	2.0	—	Atm	200	17.3	5.2
C_6H_6	$CH_2{=}CH_2$	5.0	REX	4.0	—	500 psig	204	100.0	4.65
C_6H_6	C_2H_5Cl	12.0	REX	12.0	—	Atm	218	80.5	16.9
C_6H_6	C_2H_5OH	5.0	REX	14.0	—	Atm	204	74.0	5.05
C_6H_6	iso-C_3H_7OH	5.0	REX	6.2	—	Atm	150	92.7	1.63
C_6H_6	*n*-C_4H_9OH	5.0	REX	4.2	—	Atm	200	97.5	22.4
C_6H_6	iso-C_4H_{10}	0.5	REX	1.2	—	Atm	371	8.3[d]	>100
C_6H_6	1-C_6H_{12}[e]	1.0	REX	—	0.72 (1.0)	Atm	80	33.2	1.52
C_6H_6	1-$C_{10}H_{20}$	5.0	REX	3.7	—	400 psig	160	96.0	13.3
C_6H_6	$C_6H_4(C_2H_5)_2$	8.7	REX	2.0	—	800 psig	232	100.0[f]	—
$C_6H_5CH_3$	$C_6H_5CH_3$	—	REX	0.25	—	400 psig	264	21.0[g]	—
m-$C_6H_4(CH_3)_2$	1-$C_{10}H_{20}$	1.0	HY	—	22 (6.0)	Atm	150	78.0	>100
m-$C_6H_4(CH_3)_2$	1-$C_{10}H_{21}Cl$	1.0	HY	—	26 (7.0)	Atm	150	72.0	>1000
$C_{10}H_8$	C_3H_6	3.0	REX	2.0[h]	—	Atm	205	87.0	18.0
tert-$C_4H_9C_6H_5$[i]	—	—	REX	1.4	—	Atm	260	86.2	—

[a] Liquid hourly space velocity (continuous flow system).

[b] Stirred reactor, liquid phase.

[c] Highest alkylation activity usually occurred within 1 or 2 hr on stream at a given temperature in flow system.

[d] % Conversion of aromatic to alkylated products.

[e] Reaction in sealed tube; 22.2% of 1-hexene also converted to polymer.

[f] Transalkylation reaction: optimum conditions; $C_6H_4(C_2H_5)_2 + C_6H_6 = 2C_6H_5C_2H_5$.

[g] Transalkylation reaction: 21% of toluene converted to mixture of C_6H_6 and $C_6H_4(CH_3)_2$ isomers.

[h] Wt of $C_{10}H_8$ vaporized/g catalyst/hr.

[i] Dealkylation reaction; 86% conversion occurred on fresh catalyst.

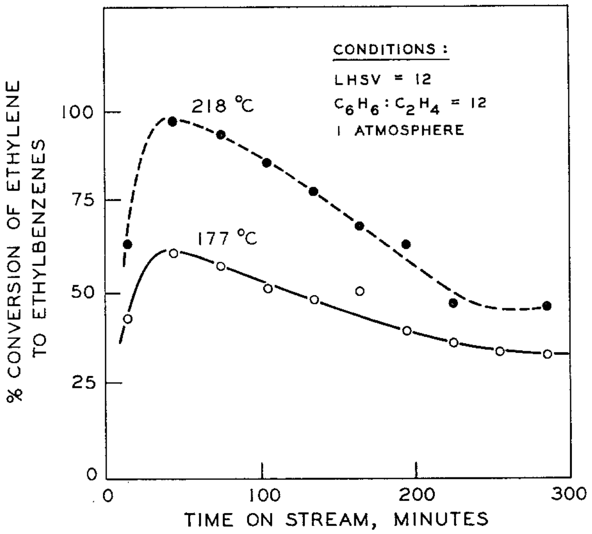


FIG. 3. Vapor-phase ethylene-benzene alkylation activity versus time for REX catalyst.

ylbenzenes (largely *ortho* and *para* isomers) and 20% triethylbenzenes (largely 1,2,4-orientation). As has been observed earlier in this reaction with silica-alumina catalyst (*22*), small amounts of *sec*-butylbenzenes were noted, with traces of other alkylaromatics.

Vapor-Phase Alkylation and Catalyst Comparisons

Figure 3 shows typical reaction profiles for benzene–ethylene reaction at atmospheric pressure. Brief induction periods and rapid catalyst aging occur at both 218° and 177°C in these vapor-phase runs, even at high benzene:ethylene ratios. Aging is more rapid at the higher temperature. Low activity for alkylation was observed at 121°C.

The standard REX, HY, and REY catalysts showed maximum conversions of ethylene to ethylbenzenes of 67%, 65%, and 58% at 177°C (Fig. 2). Low sodium levels were critical for high alkylation activity with REX catalyst. A REX catalyst containing 0.79% wt sodium had only 55% the activity of a similar catalyst containing 0.22% wt sodium. Extrapolating to the extreme case, with NaX no benzene–ethylene alkylation was observed, even at 316°C. With CaX, no reaction was observed at or below 218°C. The somewhat lower alkylation activity of the REY catalyst reflects its slightly higher sodium level (Table 2). Under identical conditions, H-mordenite showed about 20% of the activity of the standard REX; its reaction profile was characterized by high initial activity followed by strikingly rapid aging, possibly associated with its narrower pore size.

Silica-alumina (46 AI) showed only 5% the activity of standard REX at 177°C, although appreciable reaction of benzene with ethylene has been reported at 496°C and 50 psig (*2*), and at temperatures as low as 270°C employing higher pressures (*23*). Sulfuric acid (*24*) and sulfonic-acid–type ion-exchange resins (*25*) have generally been ineffective for benzene–ethylene alkylation, but phosphoric acid affords good yields at 325°C and 600 psig (*26*). Lewis acids such as aluminum chloride and boron trifluoride, on the other hand, show significant conversions at temperatures as low as 75°C and 25°C, respectively (*27*).

Alkylation of Benzene with Other Olefins, Alcohols, and Alkyl Halides

Gas-phase alkylations. As shown in Table 3, REX catalyzes the atmospheric pressure alkylation of benzene with low molecular weight primary alcohols and halides at 200–218°C, and with isopropanol at 150°C. Yields of the expected alkylbenzenes were good with the exception of methanol, where a competing coke-forming reaction was prominent. With *n*-butanol, the ratio of *sec*- to *n*-butylbenzene in the alkylate was 49.4. Catalyst aging was severe in all cases except with isopropanol, where an apparent "steady state" formation of isopropylbenzene was observed for the duration of the 3-hr run. Generally, at temperatures higher than those indicated, only slightly higher conversion, at the expense of more severe catalyst aging, was observed.

While methanol reaction with benzene was negligible at 150°C, about 21% conversion of *n*-butanol occurred at this temperature. With isopropanol, low yields of isopropylbenzenes were observed at temperatures as low as 100–113°C. Much higher temperatures of 400–500°C have been reported necessary for low conversions of methanol and benzene to toluene using a silica-alumina catalyst (*28*). Conversion of propylene and benzene to isopropylbenzene has been reported at 204°C with NaX (*10*) and at 382°C and 75 psig with silica-alumina (*2*).

Liquid-phase alkylations. Side reactions of the alkylating agents and only traces of decylbenzenes were observed in benzene alkylation attempts with 1-decene and 1-decanol over REX at atmospheric pressure. At 400 psig pressure in the liquid phase, however, 90% conversion of 1-decene to a mixture of decylbenzenes occurred with REX catalyst at 160°C and 3 hr on stream. As seen in Fig. 4, fairly good catalyst life was observed at 160°C, and some alkylation activity was even observed at 100°C. Side-chain cracking, such as observed in the alkylation of benzene with higher olefins at 450°C and 100 atm over silica-alumina (*29*) was not observed under these relatively mild conditions.

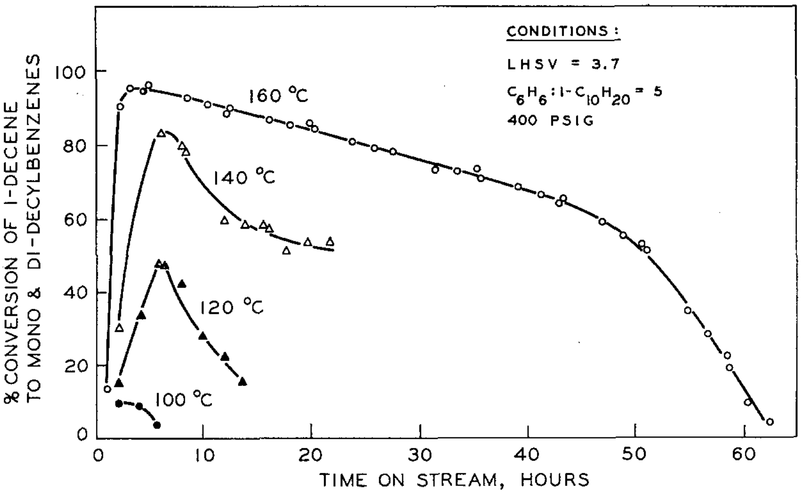
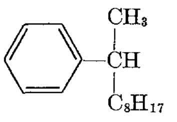
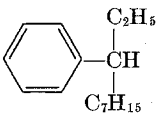


FIG. 4. Liquid-phase 1-decene-benzene alkylation activity versus time for REX catalyst.

GLC and spectroscopic analysis showed that there were at least three major monoalkylation products, which can probably be represented by structures (I–III). Likewise,



(I)



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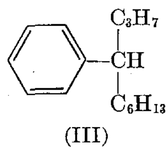


(III)

in the sealed-tube reaction of 1-hexene and benzene at 80°C, the monoalkylate consisted almost exclusively of 2- and 3-phenylhexane. Such mixtures of arylalkanes are also typical of benzene alkylation with terminal olefins using protonic and Lewis acids. With 1-dodecene and benzene, Olson has shown that hydrogen fluoride (at 16°C), aluminum chloride (at 30–53°C), and sulfuric acid (at 0–10°C) all form mixtures, in similar proportions, of 2-, 3-, 4-, 5-, and 6-phenyldodecanes.

Alkylation of Benzene with Alkylaromatics (Transalkylation) and Paraffins

A useful corollary to the ethylbenzene synthesis described earlier is the smooth, liquid-phase transalkylation reaction of polyethylbenzene fractions with benzene to form ethylbenzene. For REX catalyst, optimum conditions of 232°C, 800 psig, LHSV 2, and benzene:diethylbenzene molar ratio of 9 afforded 100% conversion of diethylbenzene, viz.,

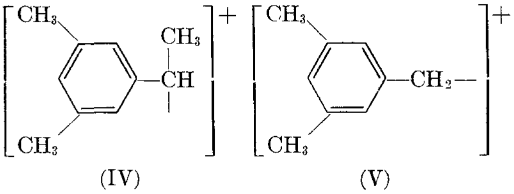
$$C_6H_4(C_2H_5)_2 + C_6H_6 \rightarrow 2C_6H_5C_2H_5$$

Under these conditions, little or no decline in activity was observed in 776 continuous hours on stream. At atmospheric pressure, however, there was much lower conversion and more rapid catalyst aging. The facility of the zeolite-catalyzed reaction stands in marked contrast to the high temperatures (450–500°C) required for such reactions with silica-alumina (*31*) and to the general inability of sulfuric acid to transalkylate under alkylation conditions (*32*).

Alkylation of benzene with isobutane over REX catalyst occurred in very low yield at 371°C and atmospheric pressure. Catalyst aging was very rapid. The major products were toluene and ethylbenzene in 3:1 molar ratio, and light paraffin gas from the cracking and isomerization of isobutane. Small amounts of alkylation occurred at 316°C. The corresponding reaction over silica-alumina occurs at 550–660°C (*33*). The fact that the alkyl residue placed on the aromatic ring contains fewer carbon atoms than the original paraffin suggests alkylation by a carbonium-ion–type intermediate generated by cleavage of the original paraffin.

Alkylation of Other Aromatic Hydrocarbons

Reaction of *m*-xylene with 1-decene or 1-chlorodecane in the liquid phase using HY catalyst proceeded smoothly at 150°C to form mixtures of decylxylenes, $C_{18}H_{30}$, in good yields. Selectivity for monoalkylation was virtually 100%. $C_{18}H_{30}$ isomer distributions in the alkylates derived from the two C_{10} alkylating agents were markedly different as shown by GLC and IR analysis. Mass spectroscopic base peaks were observed at *m/e* 133 [possibly fragment (IV)]



in the 1-decene alkylate and at *m/e* 119 [possibly (V)] in the 1-chlorodecane alkylate. This suggests predominance of 2-xylyldecanes with the former, and the possibility of large amounts of 1-xylyldecanes (terminal substitution on chlorodecane) with the latter alkylating agent.

Alkylation of naphthalene with propylene on REX did not occur at 100°C, but went easily in the vapor phase at 205°C. Isopropylnaphthalenes were the major products, with small amounts of binaphthyls and other higher molecular weight species. Catalyst aging was rapid.

In a reaction analogous to the transalkylation discussed earlier, but at a higher temperature (264°C), toluene was disproportionated over REX catalyst at 400 psig in the liquid phase. Only 21% of toluene was converted to a mixture of benzene and xylene isomers, with smaller amounts of tri- and tetramethylbenzenes. Aging was very severe in this reaction, even under hydrogen pressure.

Dealkylation

High initial activity for *tert*-butylbenzene dealkylation was observed with REX catalyst at 260°C and atmospheric pres-

TABLE 5
ALKYLATION OF PHENOL OVER ACID ZEOLITE CATALYSTS

						Highest alkylation activity		
Alkylating agent	Molar ratio, aromatic/ alkylating agent	Catalyst	LHSV[a]	Total reactant[b] catalyst (wt/wt) ratio (time, hr)	Pressure	Temp (°C)	% Conversion of alkylating agent to alkylaromatic	Molar ratio, mono-/poly-alkylate
CH_3OH	0.085	H-Mordenite	0.33	—	Atm	400	91.2[c]	11.9
$CH_2{=}CH_2$[d]	3.13	REX	6.8	—	Atm	316	14.1	>100
$CH_2{=}CH_2$[d]	3.13	REX	4.0	—	400 psig	218	59.1	8.6
C_2H_5Cl[d]	3.13	REX	6.8	—	Atm	260	63.0	13.0
C_2H_5OH	5.0	REX	6.8	—	Atm	204	75.0	13.2
C_2H_5OH[d]	4.0	REX	4.0	—	400 psig	316	72.0	12.5
1-C_6H_{12}	1.0	HY	—	10.4 (1)	Atm	182	100.0	15.7
n-$C_6H_{13}OH$	1.0	REX	—	8.9 (6.75)	Atm	182	100.0	24.0
1-$C_6H_{13}Cl$	1.0	REX	—	9.8 (5.5)	Atm	182	100.0	19.0
Cyclo-$C_6H_{11}Cl$	1.0	REX	—	9.8 (1.0)	Atm	182	100.0	4.3
1-$C_{10}H_{20}$	1.0	HY	—	10.4 (1.0)	Atm	182	100.0	5.3
1-$C_{10}H_{20}$	1.0	REX	—	10.4 (1.0)	Atm	182	100.0	13.3
1-$C_{10}H_{20}$	1.0	REY	—	10.5 (15)	Atm	182	13.4	>100
1-$C_{10}H_{20}$[d]	3.0	REX	4.0	—	400 psig	200	100.0	>100
1-$C_{10}H_{20}$[d]	3.0	HY	2.3	—	400 psig	200	100.0	>100
n-$C_{10}H_{21}OH$	1.0	REX	—	11.3 (3)	Atm	182	96.5	>100
n-$C_{10}H_{21}OH$	1.0	HY[e]	—	11.3 (3)	Atm	182	98.5	>100
n-$C_{10}H_{21}OH$	3.0	REX	6.8	—	Atm	204	98.2	13.6
1-$C_{10}H_{21}Cl$	1.0	REX	—	12.1 (2)	Atm	182	62.9	>100
1-$C_{16}H_{32}$	1.0	REX	—	14.2 (2)	Atm	210	92.5	>100
1-$C_{16}H_{33}Cl$	1.0	REX	—	15.9 (6.75)	Atm	210	53.0	>100

[a] Liquid hourly space velocity.

[b] Stirred reaction, liquid phase.

[c] % Conversion of phenol to methylphenols.

[d] Solvent benzene.

[e] Reaction was completely inhibited with nitrobenzene as solvent.

TABLE 4
CUMENE DEALKYLATION ACTIVITY OF SYNTHETIC ALUMINOSILICATES

Catalyst	Temperature (°C) of significant dealkylation activity	Reference
NaX	510°[a]	*14*
NaY	550°	*34*
CaX	470°	*14*
BeY	400°	*34*
Decationized Y	325–350°	*35*
Silica-alumina	450–550°	*31*

[a] Only 6% conversion.

sure. The liquid product was mainly benzene, with small amounts of toluene, ethylbenzene, and cumene. Isobutane was the major gaseous product, and no olefins were observed. Other related catalysts (Table 4) show significant cumene dealkylation activity at appreciably higher temperatures.

Phenol Ethylation

General conditions. Relative to the temperatures required for benzene ethylation with REX catalyst, phenol ethylation occurred at somewhat higher temperatures than might be expected, considering its greater nucleophilicity. As seen in Table 5, REX catalyst effected ethylation of phenol at temperatures of 204–316°C and pressures ranging from atmospheric to 400 psig. High selectivity for monoalkylation was favored by phenol:ethylating agent molar ratios of 3–5. The most efficient ethylation conditions utilized ethanol at atmospheric pressure, although catalyst aging was severe in all runs. Phenol alkylation with ethylene has been reported with aluminum halides at 60°C and phosphoric acid at 225°C, but not with silica-alumina (*36*). The use of benzene as solvent in these studies was feasible since at no temperature did benzene ethylation, relative to phenol ethylation, become appreciable. Significantly, benzene, in the presence of phenol, was alkylated at a much higher temperature than in the absence of phenol.

Differences with ethylating agent. The three two-carbon alkylating agents showed marked differences in efficiency of ethylation. At atmospheric pressure, the temperature of highest alkylation activity decreased in the order $CH_2{=}CH_2 > C_2H_5Cl > C_2H_5OH$ and yields decreased in the order $C_2H_5OH > C_2H_5Cl > CH_2{=}CH_2$. These differences with ethylating agent are also reflected in their relative initial temperatures of alkylation (Table 6).

TABLE 6
INITIAL PHENOL ETHYLATION ACTIVITY OVER REX CATALYST

Alkylating agent	Pressure	Lowest temperature of ethylation (°C)
$CH_2{=}CH_2$	Atm	204°
$CH_2{=}CH_2$	400 psig	93°
C_2H_5Cl	Atm	204°
C_2H_5OH	Atm	149°
C_2H_5OH	400 psig	204°

Effect of pressure. Marked differences in the effects of a moderate pressure increase upon alkylation activity with ethylene and ethanol were observed (Tables 5 and 6). Phenol alkylation with ethylene occurred at a much lower temperature and with

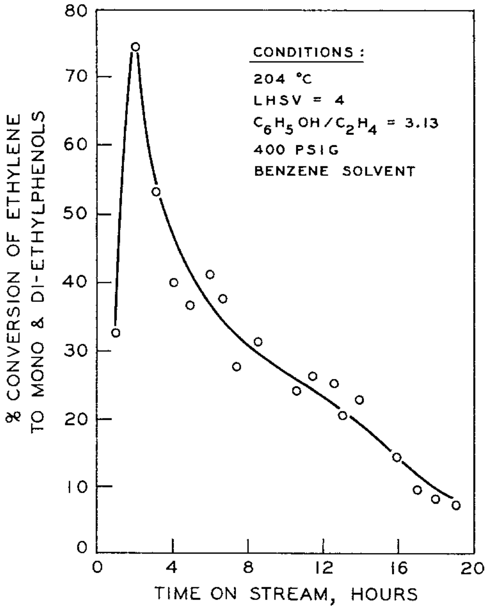


FIG. 5. Liquid-phase ethylene-phenol alkylation activity versus time for REX catalyst.

higher conversions at 400 psig than at atmospheric pressure. With ethanol, on the other hand, increasing the pressure to 400 psig inhibited alkylation, with significant conversions occurring at much higher temperatures than at atmospheric pressure. The behavior of ethyl chloride at 400 psig would be expected to resemble that of ethanol.

Catalyst aging. Figure 5 shows the severe catalyst aging encountered in these runs for the specific case of ethylene at 200°C under pressure. The decrease in conversion from 75% to 6% after only 19 hr is typical. In all runs, the rate of aging, as well as polyalkylation, increased as the temperature was raised.

Phenol Alkylation with C_6–C_{16} Olefins, Alcohols, and Haloalkanes

General conditions. Generally, high, often quantitative, conversion of C_6–C_{16} alkylating agents to alkylphenols could be obtained by stirring the liquid reactants for a few hours at 180–210°C in the presence of HY or REX catalyst (Table 5). Even with equimolar amounts of reactants, very high selectivity for monoalkylation could be obtained under these mild conditions. As contrasted to benzene, the high boiling point of phenol allowed liquid-phase conditions to be maintained at atmospheric pressure at high enough temperatures for rapid reaction rates.

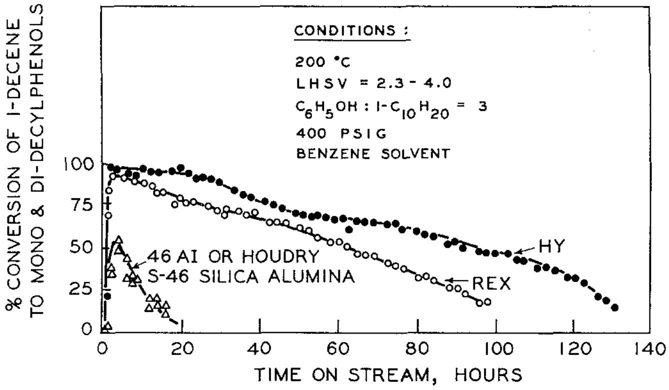


FIG. 6. Liquid-phase 1-decene-phenol alkylation activity versus time for HY, REX, and silica-alumina catalysts.

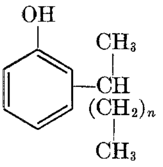
Differences with alkylating agents. With C_6 and C_{10} olefins and alcohols, phenol alkylation occurred at temperatures as low as 144°C, but longer stirring times were needed for higher conversion. Secondary halides and 1-olefins generally reacted much faster with phenol than primary alcohols and halides. For example, using REX catalyst at 182°C, chlorocyclohexane was converted to alkylphenol five times as fast as 1-hexyl chloride. Dialkyl ethers were formed in small yield from C_6 and C_{10} alcohols, but selectivity for alkylation appeared to increase with stirring time. With 1-hexadecene, the unreacted olefin had isomerized to a mixture of isomers, and with 1-chlorohexadecane, the presence of hexadecene isomers indicated the occurrence of dehydrohalogenation. Under conditions identical to those of the C_{16} olefin and chloride reaction, 1-hexadecanol gave no reaction when stirred with phenol and REX catalyst for 22 hr at 180–210°C.

Catalyst comparisons. The high activity of REX and HY in 1-decanol alkylation of phenol at 180°C (Table 5) contrasts with the complete inactivity of NaX, CaX, ZnX, CuX, and H-Mordenite in this reaction. H-Mordenite, however, was used successfully in phenol methylation. REX and HY both afforded 100% conversion of 1-decene to decylphenol in 1 hr, while REY, perhaps again reflecting its higher sodium level, showed only 13.4% conversion in 15 hr.

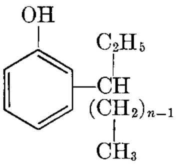
By comparison, the sulfonic acid cation-exchange resin Amberlyst 15 afforded almost 100% conversion of 1-decanol to decylphenol when stirred at 144°C for 20 hr.

However, when REX and HY catalysts were subjected to long-term, continuous-flow runs, significant differences became apparent. Figure 6 compares the activity of the two acid faujasites to that of silica-alumina catalysts for the alkylation of phenol with 1-decene (benzene solvent) at 200°C and 400 psig. HY showed greater activity (173 g decylphenol/g catalyst over 130 hr) than REX (113 g decylphenol/g catalyst over 99 hr). Both acid faujasites showed vastly greater activity and slower aging than either silica-alumina catalyst in this reaction.

Product distributions. In all cases, for a given carbon number, the alkylphenol isomer distribution varied according to whether the 1-olefins, 1-alcohol, or 1-chloride was used, all other conditions remaining constant. As in the case of benzene, the alkyl side chains in the monoalkyl aromatics consisted largely of straight chains attached at the second or third carbon atoms (VI, VII) to the phenol nucleus.



(VI)



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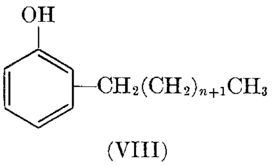


(VIII)

However, with 1-alcohols and chlorides, spectroscopic evidence showed the presence of some *n*-alkyl isomers (VIII). Direct evidence for *n*-alkyl isomers was provided by the isolation of a small amount of *p*-*n*-hexadecylphenol (VIII, $n = 13$), the structure of which was rigorously proven, from the reaction of 1-chlorohexadecane and phenol over REX (Table 5).

Aromatic Orientation in Alkylphenols

Representative aromatic isomer distributions for the alkylphenol mixtures obtained in these studies are shown in Table 7. The *ortho*:*para* ratios observed varied between 0.50 and 2.16. Between temperatures of 204° and 316°C, *ortho*:*para* ratios of 1.3–1.5 were typical for the C_2 alkylating agents, while with the C_6 through C_{16} alkylating agents, a broader range (0.5–1.6) was observed. This general range of *ortho*:*para* ratios shows a slight preference for *para* substitution, but does not suggest the operation of any general orienting effects in the intrazeolitic environment, at least under these conditions. A single exception to this generality was the reaction of phenol and ethylene under pressure at low temperatures (93–149°C). Here, a distinct *ortho*-directing tendency (more than twice as much *ortho*-isomer as *para*-isomer) was observed. With all alkylating agents, the *ortho*:*para* ratio tended to decrease with increasing temperature.

With the C_2-alkylating agents, the amount of *meta* isomer formed between 204° and 260°C was negligible. At 316°C, however, significant amounts of *meta* isomer appeared. No *meta* isomers were detectable by infrared with the C_{16} alkylating agents. On the other hand, with C_6 and C_{10} alkylating agents, *meta* isomers appeared at 155–204°C, with the largest amounts occurring at the higher temperature. As a general rule, the amounts of *meta* isomer in the reaction mixtures increased with length of stirring time, with *meta* isomers appearing even at 144°C with prolonged stirring in some cases.

While moderate differences in isomer ratios were observed between the 1-olefin, 1-chloride, and 1-alcohol of the same carbon number with a given catalyst, and between different catalysts with a given alkylating agent, more data would be required for interpretation. The data in Table 7, however, do confirm a general *ortho*:*para*-directing tendency in these acid-zeolite–catalyzed phenol alkylations. The identification of 2,4-dialkylphenols as

TABLE 7
REPRESENTATIVE AROMATIC ORIENTATION DATA IN ALKYLPHENOLS

Alkylating agent	Catalyst	Temp. (°C)	Pressure	Stirring[a] time (hr)	Mole %			Ratio
					o-	p- + m-		o-/p- + m-
$CH_2{=}CH_2$	REX	204°	Atm	—	66	34		1.94
$CH_2{=}CH_2$	REX	260	Atm	—	54	46		1.17
$CH_2{=}CH_2$	REX	316°	Atm	—	38	62		0.61
$CH_2{=}CH_2$	REX	93°	400 psig	—	100	0		∞
$CH_2{=}CH_2$	REX	121°	400 psig	—	84	16		5.25
$CH_2{=}CH_2$	REX	149°	400 psig	—	75	25		3.00
$CH_2{=}CH_2$	REX	177°	400 psig	—	63	37		1.70
$CH_2{=}CH_2$	REX	204°	400 psig	—	57	43		1.33
$CH_2{=}CH_2$	REX	232°	400 psig	—	54	46		1.17
					o-	p-	m-	o-/p-
C_2H_5Cl	REX	204°	Atm	—	57	38	5	1.50
C_2H_5Cl	REX	260°	Atm	—	58	40	2	1.45
C_2H_5OH	REX	204°	Atm	—	52	40	2	1.30
C_2H_5OH	REX	260°	Atm	—	49	48	3	1.02
C_2H_5OH	REX	316°	400 psig	—	46	34	20	1.35
1-C_6H_{12}	REX	144°	Atm	2.25	60	40	0	1.50
1-C_6H_{12}	HY	144°	Atm	2.25	61	39	1	1.56
1-C_6H_{12}	HY	155°	Atm	4.83	59	41	0	1.44
1-C_6H_{12}	HY	169°	Atm	4.73	45	45	10	1.00
1-C_6H_{12}	HY	182°	Atm	1.43	27	44	29	0.61
1-$C_6H_{13}OH$	REX	182°	Atm	6.75	54	32	14	1.69
1-$C_6H_{13}Cl$	REX	182°	Atm	5.50	20	40	40	0.50
1-$C_{10}H_{20}$	REX	182°	Atm	1.50	45	46	9	0.98
1-$C_{10}H_{20}$	HY	182°	Atm	1.66	37	51	12	0.73
1-$C_{10}H_{21}Cl$	REX	182°	Atm	2.00	49	43	8	1.14
1-$C_{10}H_{21}OH$	REX	155°	Atm	23.00	54	25	21	2.16
1-$C_{10}H_{21}OH$	HY	182°	Atm	5.00	40	50	10	0.80
1-$C_{10}H_{21}OH$	REX	204°	Atm	—	41	45	14	0.91
1-$C_{16}H_{32}$	REX	210°	Atm	2.00	66	34	0	1.94
1-$CH_{16}H_{33}Cl$	REX	210°	Atm	6.75	57	43	0	1.32
Statistical Distribution					40	20	40	2.00

[a] Data without stirring time are for continuous-flow systems.

the major polyalkylation products is consistent with this observation.

Alkylation of Other Aromatic Nuclei

Thiophene and other heterocyclics. Table 8 shows data for the alkylation of thiophene and several other heterocyclic and substituted benzene nuclei. Alkylations of thiophene with *tert*-butanol or isobutylene were catalyzed by six different crystalline aluminosilicates at atmospheric pressure and temperatures of 204–288°C. Under roughly comparable conditions, with *tert*-butanol as alkylating agent at 204°C, the yields of alkylthiophenes decreased in the order CaX > REY > HY > REX. At 288°C, NaX showed about the same activity as HY at 204°C. Using silica-alumina, thiophene has been alkylated with propylene, isopropanol, *tert*-butanol, amylene, and cyclohexene at 200°C and 12–24 psig, and with isobutylene at 60° and atmospheric pressure (*6*). With phosphoric acid–kieselguhr, alkylation with propylene and isobutylene occurred at 270–288°C (*37*). The monoisopropyl and mono-*tert*-butyl derivatives obtained were mixtures of 2- and 3-substituted thiophenes in a ratio of about 1.5.

In the thiophene–*tert*-butanol reactions

TABLE 8

ALKYLATION OF OTHER AROMATICS OVER ACID ZEOLITE CATALYSTS

							Highest alkylation activity		
Aromatic	Alkylating agent	Molar ratio, aromatic/alkylating agent	Catalyst	LHSV[a]	Total reactant[b] catalyst (wt/wt) ratio (time, hr)	Pressure	Temp (°C)	% Conversion of alkylating agent to alkylaromatic	Molar ratio, mono-/poly-alkylate
C_4H_4S	*tert*-C_4H_9OH	1.0	REY	4.52	—	Atm	204°	12.6	1.6
C_4H_4S	*tert*-C_4H_9OH	1.0	HY	4.52	—	Atm	204°	7.7	3.1
C_4H_4S	*tert*-C_4H_9OH	1.0	CaX	6.8	—	Atm	204°	21.8	1.5
C_4H_4S	*tert*-C_4H_9OH	1.0	NaX	6.8	—	Atm	288°	6.9	7.6
C_4H_4S	*tert*-C_4H_9OH	4.0	REX	5.5	—	Atm	204°	3.8	—
C_4H_4S	iso-C_4H_8	2.54	H-Mordenite	1.0	—	Atm	250°	27.7	7.2
C_4H_4S	iso-C_4H_8	2.54	HY	1.0	—	Atm	200°	33.0	4.7
C_4H_5N	CH_3OH	0.05	H-Mordenite	—	5.95 (2)	Atm	200°	100.0[c]	0.11
C_4H_4O	C_2H_5OH	0.10	NaX	0.8	—	Atm	150°	100.0[c]	11.8
C_6H_5SH	1-$C_{10}H_{20}$	1.0	HY	—	8 (2.0)	Atm	182°	8.2[d]	>100
$C_6H_5NH_2$	CH_3-$CH{=}CH_2$	0.38	NaX	0.55	—	100 psig	330°	26.7[c]	2.16
$C_6H_5NH_2$	$CH_2{=}CH_2$	0.89	NaX	0.49	—	100 psig	340°	52.0[c]	—
$(C_6H_5)_2NH$	Cyclo-C_6H_{10}	0.39	REX	—	7.62 (5)	Atm	300°	11.0[c]	—
$C_6H_5OCH_3$	$C_6H_5OCH_3$	—	NaX[e]	5.0	—	Atm	371°	19.0[f]	5.5

[a] Liquid hourly space velocity.

[b] Stirred reactor, liquid phase.

[c] Conversion of aromatic to alkylaromatic.

[d] C-alkylation.

[e] Binder free; pelleted Linde 13X with the clay binder gave almost 36% conversion at 371°C.

[f] To a mixture of phenol, methylphenols and methylanisoles.

catalyzed by CaX, REY, and HY, the ratio of 2-/3-*tert*-butylthiophene was about 2. The monoalkylate in the isobutylene–thiophene reaction also consisted of a mixture of the 2- and 3-isomers. Diisobutylene was observed in small amounts in these runs, and catalyst aging was generally severe, especially at the higher temperatures. Attempts to alkylate thiophene with ethylene, using REX or NiX, were unsuccessful.

The monoalkylate from the H-mordenite-catalyzed reaction of pyrrole and methanol consisted largely of a mixture of 2- and 3-methylpyrrole, together with about 9 mole % of pyridine. Ethylfurans were obtained when furan and ethanol were passed over NaX at 150°C.

Alkylation of aniline. NaX catalyzed the reaction of propylene and aniline at 330°C to form mono- and diisopropylaniline, and the reaction of ethylene and aniline at 340°C to form a mixture of *o*- and *p*-ethylaniline and diethylaniline.

Anisole disproportionation. NaX served as catalyst for a disproportionation reaction of anisole at 371°C. No reaction occurred over tempered quartz chips under identical conditions. In this reaction, which is essentially a Friedel-Crafts reaction using an ether as alkylating agent, 19% of anisole was converted to a mixture of phenol, methylphenols, and methylanisoles. A typical product distribution for this reaction is given in Table 9. The observed preference for *ortho–para* substitution, which is characteristic of selective electrophilic attack on activated aromatic ring, suggests that at the relatively high temperature of 371°C, NaX has distinct acid-catalytic activity for alkylation. This contrasts to a decane cracking pattern over this catalyst at 470–500°C, that is characteristic of pure silica or pyrolytic reaction (*14*).

TABLE 9

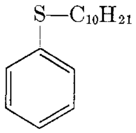
Products from Reaction of Anisole over NaX at 371°C

Product	Mole %
Phenol	58.8
o-Cresol	7.6
m- and *p*-Cresol	1.1
Xylenols	1.8
o-Methylanisole	15.0
m- and *p*-Methylanisole[a]	11.7
Dimethylanisoles	2.0
Other polymethylanisoles[b]	1.0
	99.8

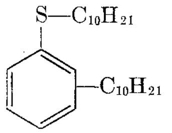
[a] Mostly *p*-methylanisole.

[b] Calculated on basis of trimethylanisole.

Thiophenol alkylation. When thiophenol was treated with 1-decene over HY catalyst at 182°C, 100% conversion of 1-decene was observed. In contrast to phenol, where negligible O-alkylation occurred, S-alkylation accounted for 91.8% of the 1-decene, while C-alkylation (on the benzene nucleus) accounted for only 8.2% of the decene. Thus, the reaction product consisted of a mixture of four isomeric decyl phenyl sulfides (IX) and more than 10 isomeric decyl decylphenyl sulfides (X) in 10.2:1 molar ratio. No decylthiophenols were found. *n*-Decyl phenyl sulfide, probably arising from a competing free radical addition, comprised about 21% of the decyl phenyl sulfide fraction, with the remaining isomers showing attachment of the decyl residue to the sulfur atom at secondary carbon atoms.



(IX)



(X)

In the C-alkylate (X), there were about equal amounts of *ortho*- and *para*-isomers, with only small amounts of *meta*-isomer. Mixtures of S- and C-alkylate, with *ortho*- or *para* nuclear alkylation, also usually resulted when thiophenol was alkylated with simple olefins in the presence of various acid catalysts (*38, 39*).

Conclusions

Reaction Variables

It is apparent that crystalline aluminosilicates actively catalyze a wide variety of alkylation reactions, with considerable variation in conditions. Nevertheless, for efficient use of highly acidic faujasites (REX, HY, REY) some general guidelines have emerged. First, liquid-phase operation is usually essential, since catalyst aging and many side reactions are more rapid in the vapor phase. With materials where a sufficiently rapid reaction rate can be maintained at temperatures near or below their boiling point, a liquid phase is assured. With more volatile reactants, however, the use of pressure is necessary.

With low molecular weight species such as ethylene, high molar ratios of aromatic to alkylating agent are required to minimize unfavorable interaction of the reactive alkylating agent with the catalyst surface, and to favor monoalkylation. With higher molecular weight (C_6–C_{16}) alkylating agents, however, lower ratios may be employed.

Temperatures in the range of 150–230°C are generally required for efficient alkylation of simple aromatics with C_2–C_{16} olefins, alcohols, and haloalkanes, and for transethylation. For dealkylation reactions, alkylation with paraffins, and toluene disproportionation, higher temperatures are required, in accord with the higher energy requirements of these processes.

Product Distributions

In typical alkylations of substituted benzenes, *ortho–para* orientation of substituents was generally observed. The *meta* isomers did not appear in significant quantity except at higher temperatures or upon prolonged exposure of reactants to catalyst. Similarly, 2-substitution was predominant in alkylated thiophenes. With alkylating agents of three or more carbon atoms, the monoalkylate consisted of a mixture of isomeric arylalkanes, with structures analogous to (I–III) and (VI–VIII) above.

Catalyst Comparisons

For the same or similar reactants, the highly acidic faujasites consistently catalyzed alkylation at significantly lower temperatures than silica-alumina-type catalysts, thus eliminating many of the undesirable side reactions encountered at the higher temperatures. Lewis acids such as aluminum chloride or boron trifluoride, and protonic acids such as sulfuric or hydrofluoric acids (but not phosphoric acid), however, generally showed significant activity at much lower temperatures than the acidic faujasites. By comparison, the less acid CaX showed useful thiophene alkylation activity at 204°C, and even NaX, at sufficiently high temperatures (288–371°C) showed acid catalytic activity in some reactions.

Thus, not only do crystalline aluminosilicates show high activity and versatility in alkylation capacity, together with the advantages of ion-exchange resin catalysts, but they also lack many of the undesirable features of sulfuric acid and aluminum chloride catalysts. Mechanistic possibilities and aging pathways will be discussed in a subsequent paper.

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