

## Isoparaffin-Olefin Alkylations with Crystalline Aluminosilicates

I. Early Studies—C<sub>4</sub>-Olefins

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Rare-earth exchanged crystalline aluminosilicates, conventionally designated as Type Y, have now been found to catalyze isoparaffin-olefin alkylation under suitable conditions. Isoparaffin-olefin alkylation distinctively requires excellent hydride transfer characteristics to produce a highly paraffinic product. Otherwise, the unsaturated nature of the product is more representative of acid-catalyzed polymerization, followed or accompanied by cracking, isomerization, and disproportionation. Successful alkylations have been observed with isobutane and all butene isomers. The products indicate high catalyst activity and selectivity for the principal alkylation, although evidence for so-called self-alkylation of isobutane was also obtained. In particular, controllable amounts of 2,2,4-trimethylpentane relative to the other trimethylpentanes indicate desirable catalyst performance characteristics. Variations in catalyst composition—representing different degrees of cationic exchange—had important effects upon product yield and selectivity.

## INTRODUCTION

Cation-exchanged aluminosilicates catalyze a variety of hydrocarbon reactions generically classified as operating by a carbonium-ion mechanism. Their activity is remarkably high, as Weisz and Miale (1) demonstrated with *n*-hexane cracking at rates up to 10<sup>4</sup> times those produced by amorphous silica-aluminas. Their selectivity is also excellent, whether used to reduce molecular size—as in Plank, Rosinski and Hawthorne's (2) work on gas oil cracking; or to build up molecular size—as Venuto, Hamilton and Landis (3) did in their studies of aromatic-olefin alkylation. When molecular size is preferably unchanged but isomerization is desired, suitably exchanged aluminosilicates have excellent selectivity at good activity, as Rabo *et al.* (4) and Rabo, Schomaker and Pickert (5) have shown.

This paper describes some aluminosilicate-catalyzed alkylations of olefins with isobutane, a reaction better known to occur with concentrated sulfuric acid or hydrogen fluoride as the catalyst. Attempts to achieve

this kind of reaction with solid catalysts other than those of the classical Friedel-Crafts type, have revealed highly unsaturated products (6). Those reports indicate at least as much cracking and disproportionation as true alkylation.

By contrast, the results presented here show highly saturated products with C<sub>5</sub><sup>+</sup> unsaturates being less than 0.1%. Added evidence for alkylation is found in the paraffin distributions and their response to reaction parameters. These results strengthen the view that isoparaffin-olefin alkylation differs sharply from aromatic alkylation in the demands put upon the catalyst.

## METHODS

Reactions were carried out batchwise in a stirred 1-liter autoclave with conventional facilities for charging catalyst and reactants. Pressures were autogenous, ranging from 35 to 400 psig. Isobutane and butenes were proportioned in a Jerguson gauge to achieve predetermined isoparaffin/olefin charge ra-

tios over the range from 5:1 to 22:1. The true ratio in the reactor, which was not measured, depends upon butene conversion rate and is effectively many times the charge ratio. Products and unused reactants were collected at the end of a run. Gases were volumetrically measured by a wet test meter and sampled. Liquid products were weighed and sampled. Some liquids were distilled in a Nester Faust spinning band column (NF-115) and stabilized fractions separated into saturates, olefins, and aromatics by fluorescent indicator adsorption (ASTM No. D-1319). Other liquids were stabilized at 90°F. The overhead from the stabilized liquid was collected and sampled, and the stabilized residue was used directly for capillary gas chromatographic analysis.

Gases were analyzed by two chromatographic columns in series: a 50-ft column with 20% DMS on 60-80 mesh Chromosorb W and a 15-ft column with 5% TCP and 20% DC-500 on the same packing. The chromatograph was a Perkin-Elmer 154D operated at 34°C and 40 psig helium pressure and using a thermistor type of detector. Liquids were analyzed on a Perkin-Elmer 226 capillary gas chromatograph with a 150 ft, 0.01 in. stainless steel column coated with squalene. It was programmed from 25 to 120°C. and operated at 20 psig helium pressure. A flame ionization detector was employed.

Isobutane and butenes were Matheson CP Grade. 2,4,4-Trimethylpentene-1 was Phillips Technical Grade, used after a negative test for peroxide contamination and without further purification or treatment.

Linde sodium Type Y crystalline aluminosilicate in which about 70% of the sodium had been replaced by ammonium was further cation-exchanged with a variety of rare-earth salt solutions, dried, and activated before use. With typical  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 4.3 to 4.8, a rare-earth cation such as lanthanum would then be present at levels sufficient to satisfy the stoichiometric requirements imposed by the alumina tetrahedra in the low-sodium zeolite crystal lattice. Calculation of these levels shows a range of lanthanum from 0.6 to 13.5 wt % for a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 4.6.

## RESULTS

Describing an application of cation-exchanged aluminosilicate catalysts to hydrocarbon reactions not previously reported in the scientific literature is the chief purpose of this paper. Another paper (7) deals with isobutane and olefins other than butenes. These papers will hopefully lead to a better understanding of the catalytic functions involved and of alkylation itself.

### 1. Product Composition and Identification of the Reaction

Products of isobutane-butene-2 reactions have many characteristics of alkylates derived via sulfuric acid (Table 1). The prominence of  $\text{C}_8$  in a spectrum of  $\text{C}_5\text{-C}_9^+$  paraffins, the absence of *n*-paraffins except occasional *n*-pentane, the presence of isopentane, the negligible unsaturate content, and the evident selectivity for trimethylpentanes are all typical of alkylation (8, 9, 10).

Further comparison with conventional alkylates reveals a difference consistently found between those materials and products of aluminosilicate catalysis. Among the trimethylpentanes from conventional acids, the 2,2,4-isomer constitutes more than 40% of the total. Zeolite catalysts show about 10-30% concentrations of 2,2,4-TMP rela-

TABLE 1  
ISOBUTANE-BUTENE-2 PRODUCT COMPOSITIONS

Compound	Al-Si <sup>a</sup> (wt %)	H <sub>2</sub> SO <sub>4</sub> <sup>b</sup> (vol %)	
i-P	3.40	5.78	4.16
2,3-DMB + MP	3.59	3.46	4.58
2,4-DMP	4.14	3.58	2.37
2,2,3-TMB	0.21	0.10	
All MH <sub>x</sub>	0.35	0.32	
2,3-DMP	1.67	1.26	1.38
2,2,4-TMP	16.22	17.70	30.64
All DMH <sub>x</sub>	8.59	8.89	9.02
2,2,3-TMP	3.51	3.97	
2,3,4-TMP	47.34	48.16	41.55
2,3,3-TMP			
2,2,5-TMH <sub>x</sub>	0.78	0.71	1.88
Other C <sub>8</sub> <sup>+</sup>	9.21	6.06	4.41

<sup>a</sup> Different catalysts and conditions used.

<sup>b</sup> From Cupit, Gwyn and Jernigan (8).

tive to its isomers. This difference is not too surprising when the physical and chemical behavior of a liquid-liquid and a solid-liquid system are considered. Neither of these factors can be overlooked in assigning origins of the difference.

### 2. Mode of Alkylate Formation

Isoparaffin-olefin alkylations were carried out in liquid phase under autogenous pressure. By analogy with sulfuric acid, the reactant-catalyst complex could possibly be formed over a period of time and could function as the true catalytic species. Hofmann and Schriesheim (11) have called this acid complex an "isobutane activator" and supported their classification with alkylate yield data taken while this activator was being formed and a steady state was being reached. Alkylation with aluminosilicate catalysts revealed a somewhat similar but far from identical behavior.

When olefin was charged to an exchanged Type Y solid catalyst suspended in isobutane, a kind of induction period was indicated (Fig. 1). Until an optimum yield was reached, the alkylate yield per olefin charged increased profoundly with time, and the product distribution was also modified (Fig. 2). If left in the reactor for a longer time, product began to degrade and the yield per olefin decreased. Attaining the

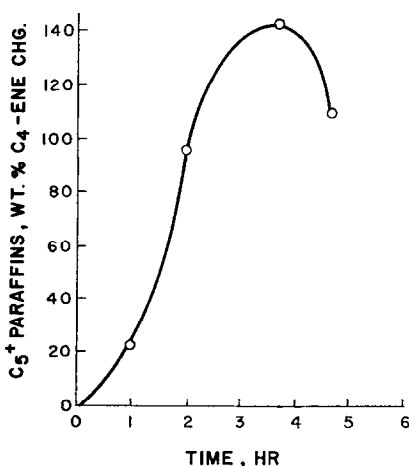


FIG. 1. Effect of reaction time on C<sub>5</sub><sup>+</sup> paraffin yield.

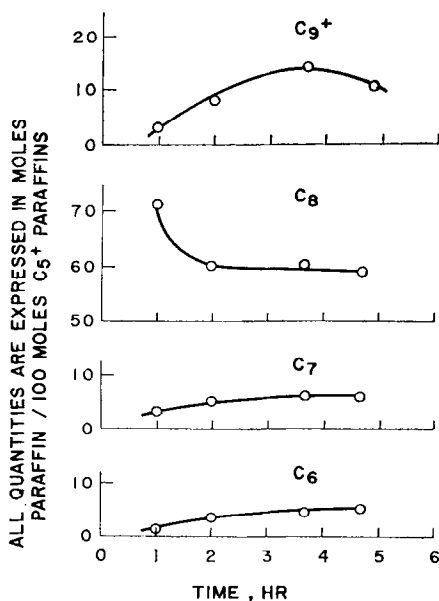


FIG. 2. Effect of reaction time on C<sub>6</sub><sup>+</sup> paraffin distribution.

maximum is analogous to Hofmann's (13) presteady state performance. In that study, however, alkylate was continually removed from the reactor after its steady state had been achieved.

While hydrocarbons in the C<sub>6</sub>, C<sub>7</sub>, and C<sub>9</sub><sup>+</sup> range were increasing slightly at the expense of C<sub>8</sub>, the TMP distribution was virtually unchanged (Fig. 3). It appears, therefore, that C<sub>9</sub><sup>+</sup> paraffins originated from some C<sub>8</sub> precursor carbonium ion by condensation, cracking, and recombination of fragments rather than by degradation of C<sub>8</sub> paraffins once formed. The latter possibility implies equal cracking rates for each of four isomers.

### 3. Alkylation and Reaction Parameters

To explore alkylation with exchanged aluminosilicates, directional effects of reaction parameters are often more illuminating than absolute values. These catalyst and operational parameters can have particular effects on specific product values that could be misleading if compared only on an absolute basis.

Temperature is an example. Two separate exchanged Type Y aluminosilicates were

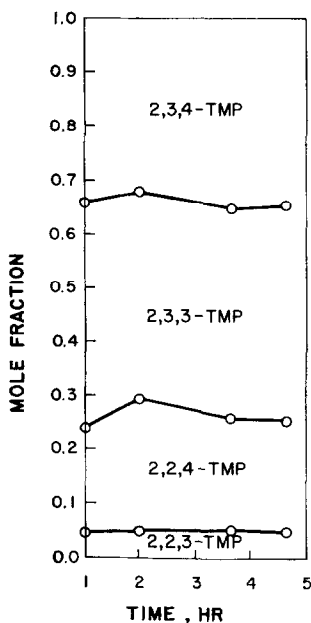


FIG. 3. Effect of reaction time on trimethylpentane distribution.

employed in two series of experiments at temperatures from 25 to 100°C. In each case, maximum alkylate yield occurred at a different temperature, but the steep rise of the yield curves suggests that the same mechanism is operative (Fig. 4). However, as a result of reaction temperatures too high

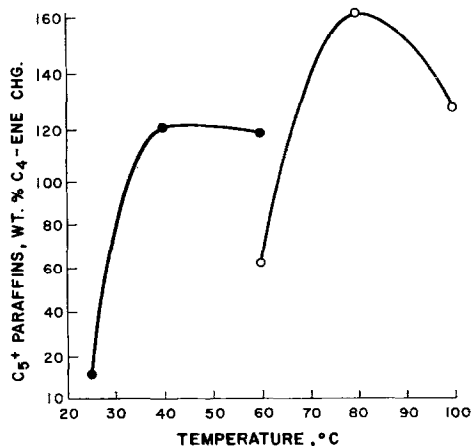


FIG. 4. C<sub>5</sub><sup>+</sup> paraffin yield as a function of temperature for two different rare earth exchanged Type Y aluminosilicates. (●) 0.2 wt % Na; (○) 1.0 wt % Na (ignited basis).

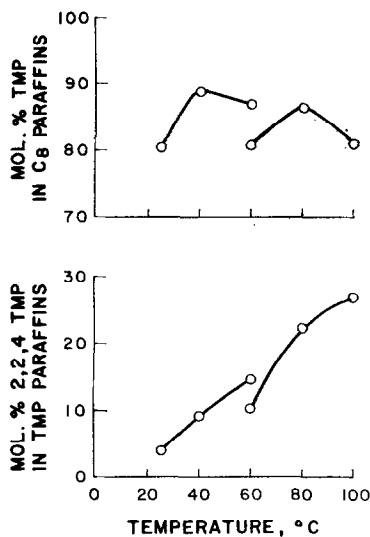


FIG. 5. TMP in C<sub>8</sub> paraffins and 2,2,4-TMP in TMP paraffins as functions of temperature for two different rare-earth exchanged Type Y aluminosilicates.

or too low, yield can decrease, and the preferred value for one catalyst is not necessarily the same for another. Similarly, a TMP optimum occurred at a different temperature for each catalyst (Fig. 5), but the 2,2,4-isomer content of the TMP fraction showed a steady increase with rising temperature. Merely comparing single product values at the same conditions could have been misleading.

#### 4. Effects of Olefin upon Alkylation

All of the results discussed thus far were obtained with butene-2, but other olefins can be alkylated satisfactorily with aluminosilicate catalysts.

Butene-1 and isobutylene were readily alkylated by isobutane with catalysts and conditions similar to those used with butene-2. In particular, butene-1 exhibited product distributions distinguishable from those of butene-2 only by a slightly altered C<sub>8</sub> distribution, in favor of dimethylhexanes:

	Butene-1	Butene-2
TMP	85.4	87.2
DMHx	14.6	12.8
MHp	0.0	0.0



### 5. Importance of Rare-Earth Exchange

Although a formulation of catalyst structure and function is not the purpose of this paper, the importance of rare-earth exchange was recognized.

A series of similar catalysts with increasing proportions of rare earth were evaluated with isobutane and butene-2. As the amount of rare earth increased, appreciable gains were realized in  $C_5^+$  paraffin yield,  $C_8$  content of the alkylate, and TMP/DMHx ratio (Fig. 6). At the same time, desirable decreases were realized in  $C_5^+$  unsaturate yield and  $C_9^+$  content of the alkylate (Fig. 7).

### DISCUSSION

Although specific product components differ for these alkylates relative to conventional ones ( $H_2SO_4$  or HF), the resemblances between compound types and their mutual departure from equilibrium indicates basic similarities that are mechanistically significant.

It is important to recall that  $H_2SO_4$  and HF alkylations admittedly represent a selective competition among reactions which depart drastically from thermodynamic con-

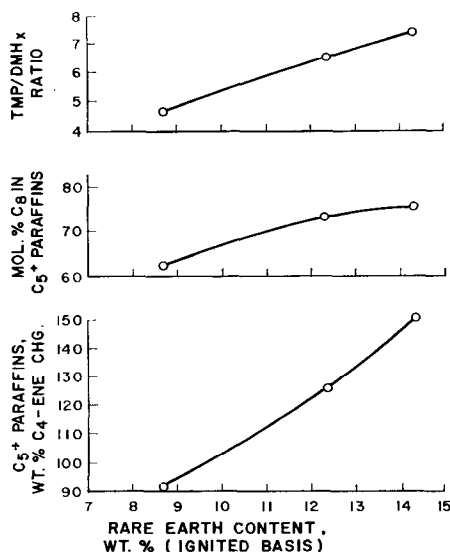


FIG. 6.  $C_5^+$  paraffin yield, mole %  $C_8$  in  $C_5^+$  paraffin, TMP/DMHx ratio as functions of rare-earth content.

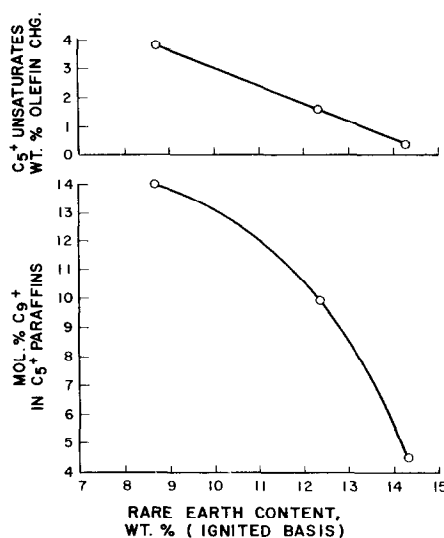


FIG. 7.  $C_5^+$  unsaturates and mole %  $C_9^+$  in  $C_5^+$  paraffin as functions of rare-earth content.

trol. Calculated equilibrium amounts of trimethylpentanes are only 10–12% of the  $C_8$  paraffins, instead of the 70% found experimentally (8). Among the TMP, the 40% concentration of 2,2,4-isomer in conventional alkylates is significantly less than thermodynamic predictions of more than 70% at temperatures below 30°C (12). The still lower amount of 2,2,4-TMP from these solid catalysts may be a kinetic effect of physical factors in addition to the chemical differences between an aluminosilicate and  $H_2SO_4$  or HF. Cupit, Gwyn and Jernigan (8) and others have written about the role of physical factors in plant scale operation.

Despite particular distinctions—such as TMP isomer distribution—the strong qualitative resemblance between alkylate from solid and conventional acid catalysts leaves little doubt about the occurrence of alkylation with these aluminosilicates.

Olefin protonation has been accepted as an initiating step in the complex chain of events leading ultimately to alkylate (10). This concept is supported by the *n*-butane formation which occurred in this study while the reactant-catalyst condition analogous to Hofmann's steady state was being attained (Fig. 8). When alkylate yield was



probable consequence of proton transfer to another base by  $C_5^+$  carbonium ions resulting from slow hydride transfer from *n*-butane relative to isobutane.

Alkylation of *n*-paraffins is considered reasonable and defensible, especially in view of the  $C_5^+$  product distribution and the absence of  $C_5^+$  unsaturates. If *n*-pentane and higher homologs could be alkylated and the products well characterized by CVPC, the alkylation of *n*-pentane would be factually unassailable. Certainly more research on this point is necessary.

Isobutylene, as the alkylating olefin, sheds light on a more subtle aspect of alkylation. One of the obvious product differences between butene-1 and -2 and isobutylene is the much higher (60 to 64%) proportion of the 2,2,4-isomer among the trimethylpentanes from isobutylene. That isomer is expected to be a primary product of isobutane-isobutylene reaction, and its increase is consistent with the expectation. An interesting sidelight is that olefins other than butenes also have produced a high proportion of 2,2,4-TMP in the  $C_8$  fractions of their alkylates. Very probably  $C_8$  formation under those conditions involves proton transfer from *t*-butyl cation followed by alkylation of the resulting isobutylene (13).

Attempts to characterize these catalysts further resulted in a correlation between alkylate yield and the ESR total spin count measured in separate experiments when anthracene was adsorbed on the catalyst (Fig. 9). Catalysts with total spin counts above  $3 \times 10^{19}/g$  with anthracene were found preferable for alkylation of butene-2 with isobutane.

This apparent correlation between alkylate yield—with its essential dependence upon hydride ion transfer—and the electron withdrawal from anthracene is most interesting but not conclusive. It could even be fortuitous when the high degree of complexity in the system is recalled.

Titration acidity measurements and the interdependence of ir spectra for adsorbed bases and catalyst OH have shown that Bronsted acidity and Lewis acidity have different responses to catalyst activation temperature (14 and 15). Reactions more

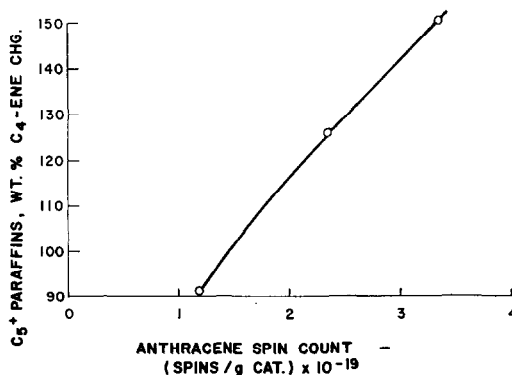


FIG. 9.  $C_5^+$  paraffin yield versus ESR anthracene spin count.

dependent upon Bronsted acidity have generally had a lower optimal temperature than those responsive to Lewis acidity. Several researchers have noted changes in catalyst behavior that could be or were interpreted in this light (16-18). Alkylation performance could be related to one set of phenomena, and ESR spin results to another. The apparent correlation has not been carried far enough to be conclusive.

#### CONCLUSIONS

Alkylation of butenes by isobutane has been demonstrated with exchanged Type Y aluminosilicate catalysts. Reaction parameter effects were studied chiefly with butene-2. Product distributions also revealed interesting differences from conventional  $H_2SO_4$  and HF alkylates. Some alkylation of butenes by *n*-butane was indicated. Catalysts were characterized by ESR measurements of total spin count when anthracene was adsorbed on them, and some apparent correlation with performance was inferred.

How far aluminosilicate catalysts can lead toward a better understanding of alkylation as a hydride transfer reaction will be reported in subsequent papers.

#### ACKNOWLEDGMENTS

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