CORRESPONDENCE

Comments on "Supercritical-Phase Alkylation Reaction on Solid Acid Catalysts: Mechanistic Study and Catalyst Development"

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Sir: This paper (Fan et al., 1997) is reportedly an investigation of supercritical-phase alkylation of isopentane and isobutane with isobutene using solid catalysts. The major reactions investigated, however, in many, if not most, experimental runs were not alkylations but were instead oligomerizations. Although some experiments were made using supercritical fluids and although the claim was made, or at least implied, that improved transfer of the product mixture from the catalyst pores occurred with supercritical liquids, the highest yield of alkylate product apparently occurred when a regular liquid was used.

Two light isoparaffins (isopentane or isobutane) were mixed with isobutene in this investigation, and the mixture was reacted. Insufficient details relative to experimental and analytical results or procedures were reported as next indicated in order for the reader to interpret the results.

(1) The surface areas and the pore sizes of the zeolite catalyst used were not reported. Pore size and particle size would appear to be important variables when mass transfer in the catalyst particles is apparently a rate-controlling step. In addition, what are the sizes of the catalyst particles?

(2) The fixed-bed reactor was not described. The reactions investigated are exothermic, and temperature variations may have occurred in the bed. Furthermore, the catalyst deactivated within a few hours as the experimental run proceeded. Probably the inlet portion of the fixed bed deactivated initially. The dimensions of the bed and the method of temperature control may be important. Will the investigators please provide details on the reactor?

(3) More details on the analytical results are needed in order to determine the type of reactions that occurred in this investigation. The authors used GC−MS analytical equipment for analysis of their product mixtures. They reported these hydrocarbons as alkylate, C_8 paraffin, C_9 alkylate, C_9 paraffin, C_9 olefin, C_{12} olefin, C_1−C_3, C_5−C_7, and C_{13}^+. This description of products is not clear. The products from refinery alkylation units are generally referred to as alkylates, and they contain 18−20 C_5−C_9 isoparaffins plus many more C_{10} and heavier isoparaffins. *With liquid acids, oligomerization and subsequent decomposition reactions result in numerous isomers with carbon numbers varying from perhaps 4 to 16.* The investigators presumably employed mass spectrometric results to differentiate between olefins and saturated hydrocarbons. In this investigation, the ratio of isobutane (or isopentane) to isobutene was 50:1. As a result the product mixture from the fixed bed presumably contained about 96% isobutane (or isopentane) and at most 4% of mixtures of oligomers and alkylate. Hence, numerous isoparaffins and heavy olefins were probably never detected by their analytical procedure.

(4) Yields. How are the yields for alkylate, oligomers, byproducts, etc., defined and how were they calculated? Yields may not be easy to calculate since part of the olefins may form conjunct polymers, other deactiviting hydrocarbons, etc., or be trapped in the catalyst pores.

For the experiments using isopentane and isobutene as feeds, the following results seem to indicate oligomerizations were the main reactions.

(a) In Figure 3, 85.3−92.6% yields were reported for C_8 olefins and C_{12} olefins. Only 1.4−4.1% yields were reported for C_9 alkylate. Will the authors please give more details relative to the compositions of the alkylate, C_8 olefins, C_{12} olefins, and the unreported hydrocarbons that were produced. Were any C_4−C_8 isoparaffins, any C_{10} and heavier isoparaffins, and any C_{16} olefins produced? It should be recognized that heavier hydrocarbons may never diffuse out of the catalyst pores.

(b) Figure 2 apparently gives more details on the products obtained. In one case, the yield of C_9 paraffin was reported as 33.9%. The composition of the C_9 paraffin is not reported. Since C_8 and C_{12} olefins were produced, the question is raised as to whether part of the C_9 paraffin is not C_9 olefins. In Figure 2, 26.9−81.2% is reported to be C_5−C_7. What is the composition of this fraction? Olefins, isoparaffins, or *n*-paraffins? Since isopentane was in the feedstream, presumably a C_5 hydrocarbon(s) was being produced, but which one? Which hydrocarbons are the authors considering to be part of the alkylate in Figure 2?

It would also help significantly if the authors could provide more information when isobutane is reacted with isobutene.

(a) In Figure 4, the highest yield of alkylate reported was about 68%, and not 70% as claimed in the text. This value is for the run with liquid phase (at 50 °C) and not for the run with supercritical phase (at 140 °C). The data point at 68% yield is based on samples obtained after about 15−20 min of the run. It would have been more convincing if a sample had been taken in the 1−3 min period of time. For the liquid phase run, the alkylate yield decreased to perhaps 8% after about 2 h. For the supercritical phase experiments, essentially no quantitative information is supplied on the composition of products formed. How do the product mixtures for supercritical phase and liquid phase experiments compare quantitatively? In addition, no results are reported

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for the first 2 h of the supercritical run. What were the results during this period?

(b) The authors never defined alkylate when isobutane was employed. On p 1459, they seem to imply that alkylate is just 2,2,4-trimethylpentane. In commercial alkylates, this compound always accounts for less than 50% of C_8 isoparaffins. In many alkylates, appreciable amounts of dimethylhexanes are produced when isobutene is used as the feed.

The results for the supercritical-type reactions raise more questions than they answer:

(a) Why did the investigators not measure (or report) yield results for alkylate and C_8 plus C_{12} olefins during the first 1−2 h of each run as reported in Figures 4−6 and 10? (I used information reported on p 1458 to estimate times.) Results during the first portion of a run would be most helpful in evaluating whether supercritical fluids offer advantages. There is also no quantitative evidence reported on how the compositions of the alkylates, C_8 olefins, C_{12} olefins, and other hydrocarbon produced differed as the run progressed.

(b) Figure 6 reports that the sums of yields for alkylate, C_8 olefins, and C_{12} olefins vary from about 30 to 60%. What is the remaining 40−70%? Based on the available information, supercritical fluids do not appear to be very effective for extraction. In one supercritical run (see Figure 5), the highest yield of alkylate was about 20%.

(c) Temperature also affects the mass-transfer steps of all hydrocarbons to and from the catalyst sites. Did the investigators consider this in their study?

(d) How do the authors explain that the highest yields were for regular liquids and not for supercritical liquids? This highest yield was apparently the 68% reported on Figure 4 or a yield of maybe 70% as reported in Figure 1. Why do the authors refer to the catalyst producing such a moderate yield as a catalyst with "very high initial activity"?

(e) The author's investigation in which they partially restored the activity of a used catalyst using a supercritical fluid is important; see Figure 6. *Would a regular liquid also give similar results*? The authors reported that two C_{12} olefins were extracted. How can the authors be certain that these hydrocarbons were really C_{12} olefins? Obviously not all hydrocarbons were extracted. The apparent suggestion that only C_{12} olefins are the sole deactivation species is, in my opinion, incorrect. Maybe the authors can provide more details.

In discussing supercritical alkylations, the authors state that there is a need to "extract" high-molecular-weight hydrocarbons from the catalyst micropores, in order to minimize catalyst deactivation. This statement is not completely correct. There is a need to extract all hydrocarbons from the pores regardless of their molecular weight. There is reason to believe that olefins strongly adsorb or even chemically bond to a significant extent to the catalyst surfaces. As yet, relatively little is known on the composition of the major deactivating species. Possibly, they are conjunct polymers (Miron and Lee, 1963) which probably cannot be easily removed for at least two reasons: high molecular weights (in the 200−400 range), and they are highly unsaturated (and they probably strongly bond to the surface). I question if the deactivating species is coke as postulated on p 1463. This statement seems to be inconsistent with their earlier statement suggesting C_{12} olefins as the deactivating species.

The authors' discussion on "Reaction Mechanics" is of interest, but I fail to see its importance. Until the mass transfer or diffusion steps and until the nature of the species that deactivate the catalyst are better understood, difficulty will likely occur in understanding the chemistry. In my opinion, catalysts such as those employed in this investigation are not promising for commercial applications.

Literature Cited

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