Rebuttal to the Comments of Lyle F. Albright on "Supercritical-Phase Alkylation on Solid Acid Catalysts: Mechanistic Study and Catalyst Development"

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Sir: It is appreciated that Professor Albright shows interest in our paper (Fan et al., 1997). We noticed that recently a similar rebuttal appeared in *Ind. Eng. Chem. Res.* between Professor Albright at Purdue University and Professor Sankaran Sundaresan at Princeton University (Albright, 1997; Simpson et al., 1997), which focused on the paper published by Professor S. Sundaresan's group (Simpson et al., 1996). As answers to many questions raised by Professor Albright here can be found in the previous rebuttal (Albright, 1997; Simpson et al., 1997), we respond here simply to each of the questions from him.

Experimental and Analytical Part

(1) The surface area of the used H-USY was 390 m^2/g, with a pore size of 0.7 nm. The particle size of the catalyst was 20−40 mesh, as clearly indicated in our paper.

(2) The temperature variation in the fixed bed was not remarkable due to the high heat-exchange efficiency of the coexisting supercritical phase isobutane or isopentane. The fixed reactor was composed of a prefixer and a reactor. The prefixer was 50 cm in length and 0.8 cm in inner diameter. It was full of inert glass beads to improve the mixing efficiency of paraffin and olefin. The reactor was 35 cm in length and 0.7 cm in inner diameter. The upper part of the reactor was full of glass beads, where the catalyst bed was supported by a spacer.

(3) The definition of the alkylate is not fixed in every published paper on alkylation, especially in solid acid-catalyzed alkylation. In our paper, in order to discuss the mechanism of alkylation reaction clearly, we defined C8 or C9 paraffin as alkylate. If other paraffins formed through a lot of secondary reaction calculated as alkylate, the alkylate selectivity in our research would be increased remarkably, different from the conclusion made by Professor Albright that oligomerization dominated our reaction. We used GC−MS to recognize various products only but quantitatively analyzed hydrocarbons by the capillary GC with top-class sensitivity.

(4) The calculation of the yields was based on olefins reacted, as that used in another group (Simpson et al., 1996).

Reaction of Isopentane and Isobutene

(a) It is common to use a high paraffin-to-olefin ratio in this reaction, especially in our case where excessive paraffin acted as the supercritical fluid. C4−C8 isoparaffins formed, but little C10 and heavier isoparaffins were detected. No C16 olefins were found.

(b) Our paper focused on mainly catalyst development and the supercritical fluid effect. A large space to describe in detail the composition of the complicated hydrocarbons, from C1 to C12 including paraffin, olefin, and isomer in nearly unlimited types was not available for us. Our gas chromatograph could discern C9 olefins from C9 paraffin. C5−C7 fractions in Figure 2 contained 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, C6 olefins, 2,4-dimethylpentane, 2,2,3-trimethylbutane, 2-methylhexane, C7 olefins, and so on.

Reaction of Isobutane and Isobutene

(a) It should be noted that the abscissa of Figure 4 was the amount of the charged olefin. A period of response time was necessary for the reactor system to reach the liquid phase or supercritical phase. In the case of supercritical phase reaction, this period was about 2 h. Regarding the hydrocarbon distribution of these reactions, a lot of C12 olefins formed in the liquid phase reaction if the reaction time was extended. Due to the high reaction temperature in the gas phase or supercritical phase reaction, C5−C7 fractions were enhanced in either case.

(b) The definition of alkylate was discussed above.

Supercritical-Type Reaction

(a) As mentioned above, In the case of supercritical phase reaction, the initial period was about 2 h.

(b) Different supercritical fluids have different critical temperatures and critical pressures. These two factors exerted great influence on reaction behavior. Based on this meaning, the selection of a suitable supercritical fluid was not easy.

(c) Dynamic analysis on the mass-transfer process is not the theme of our paper, but we want to simulate it after we collect enough data.

(d) High but short-lasting alkylate yield was found for liquid phase reaction as its reaction temperature was lower than that of gas phase or supercritical phase reaction.

(e) Extraction with a regular liquid could not completely restore the deactivated catalyst. As the formation rate of C12 olefins was highly more than that of other heavy olefins, only C12 olefins were extracted from the deactivated catalysts.

Professor Albright concluded that it was necessary to extract all hydrocarbons from the pores of solid catalysts. It is impossible. It is necessary to extract isobutene, the reactant, from zeolite inner surface? Without the coadsorption of the light olefin and the paraffin-derived carbenium ion onto the zeolite acidic sites, this solid acid-catalyzed alkylation reaction is not available. The catalytical process here was completely different from that in a sulfuric acid catalyzed reaction.

Generally, Professor Albright's comment is experienced. It is necessary here to give a more detailed

quantitative study of the product distribution and carbonaceous deposit. But the reaction performances on solid acid catalyst remarkably differed from those accompanied by liquid acid.

Literature Cited

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