Rebuttal to the Comments of Lyle F. Albright on “Kinetic Analysis of Isobutane/Butene Alkylation over Ultrastable H-Y Zeolite”

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Sir: We appreciate Professor Albright’s interest in our work (Simpson et al., 1996). His letter makes one valid criticism of our analysis of the product distribution and raises many insupportable concerns which can be traced to his assumption that the product distribution and dominant pathways in zeolite-catalyzed alkylation should be the same as those for the sulfuric acid-catalyzed reaction. We disagree with Professor Albright on his claim that our kinetic analysis is flawed. We respond below to each of the points raised by him.

Choice of Catalyst

Professor Albright states that there exist solid acid catalysts which can be used for several hours before reactivation is needed and raises surprise that we used USHY which deactivated rapidly. The catalyst life depends strongly on the WHSV (based on the feed rate of the butenes and the catalyst mass). Previous work on solid acid-catalyzed alkylation, which, at first sight, gives the impression of a long life, has been carried out at very low WHSV, typically in the range of 0.1–1.0. Whenever a fixed-bed reactor is used in such a study, most of the reactions tend to occur in a rather narrow reaction zone. As the catalyst deactivates, this reaction zone moves down through the reactor, and when it reaches the end of the reactor, the olefin conversion and alkylation quality drop precipitously. It is difficult to carry out a quantitative kinetic analysis of the data from such experiments, and therefore we performed experiments at high WHSVs, in the range of 5–60. The USHY is not much worse than any of the other solid acid catalysts for isobutane/butene reaction.

The extrapolation to time zero performed in our study helped us to ascertain the pronounced effect of intrapellet diffusional resistance. Furthermore, it allowed us to decouple some of the kinetic steps, thereby making the task of parameter estimation easier. If it had turned out that the values of the parameters estimated via extrapolation to time zero had to be adjusted by an appreciable amount in order to fit the transient data, then there is a basis for arguing that the extrapolation method is unreliable. Comparisons such as those shown in Figure 6 reveal that this was not the case.

The data shown in Figure 2 and Table 1 were obtained through the manual sampling procedure described in our paper. In this procedure, each product sample represents an average of the effluent stream collected for about 5–10 s. We have tested the reproducibility of such experiments (see Figure 2 in our paper). As illustrated in Table 1 of our paper, the product composition varied with time, but only gradually. The on-line sampling data obtained using a multiposition valve (reported in Figure 6) are very similar to those obtained by manual sampling, so there is no basis for questioning the reliability of the manual sampling scheme.

Yields Based on Olefins Reacted

We had reported in Table 1 of our paper the yield of alkylation products per unit amount of butene reacted. Professor Albright points out that we should have equated the number of moles of isoparaffins formed to the number of moles of isobutane reacted. His point is valid. He has calculated the yields and found that the product distributions observed in the effluent stream reported in Table 1 for time-on-stream (TOS) of 0.1, 1.0, and 1.6 min correspond to 0.89, 0.93, and 0.92 mol of butene/mol of isobutane reacted, respectively. This is a nice observation, and we are grateful to him for bringing this point to our attention. However, we disagree with his assertion that these numbers negate the discussion in p 3863 of our paper (immediately below Table 1) about isoparaffin accumulation inside the pores. Some accumulation of products inside the pores of the catalyst at early TOS is inevitable. Our finding that the reaction is severely limited by diffusion, coupled with the fact that the diffusivities of the various reaction products are different, makes it tenuous to equate the effluent product distribution at a particular TOS to the intrinsic product distribution at that time. This is the reason why we had restricted our quantitative analysis to kinetics of butene conversion and did not attempt to analyze the time evolution of the product distribution.

Returning to Table 1, at TOS = 0.1 min, we detected 0.76 mol of products in the effluent stream for every 1 mol of butene consumed (or retained) in the reactor. Then, as per the calculation procedure noted in Professor Albright’s paper, the number of moles of butene used to make these products is equal to (0.76)(0.89) = 0.6764. This represents a butene deficit of 32.36%. Repeating this for the other two columns of data in Table 1 of our paper, we find a butene surplus at TOS = 1.0 min and a butene deficit of 8% at TOS = 1.6 min. It is conceivable that the deficit seen at large TOS is a measure of the rate of production of carbonaceous deposit, but there is no basis for assuming that the large deficit seen at early TOS is only due to the formation of carbonaceous deposit. A more logical argument would be that a significant fraction of this deficit at early TOS is due to the accumulation of alkylates inside the pores, as we had suggested in our paper. Because of the diffusional limitation, severe intrapellet gradients will be present for the limiting reactant, butene, and the reaction products. In the case of butene, the concentration will drop off rapidly as one moves inward toward the center of the pellet from the external surface (see Figure 7 of our paper). By the same token, significant accumulation of products must occur in the interior of the pellet, thereby setting up pronounced concentration gradients in the opposite direction, to cause outward diffusion of the products. This does not contradict the observation of Professor Albright that the yield of the carbonaceous deposit may be about 8–12%.

As he notes at the end of this paper, it would be desirable to perform a quantitative analysis of the yield
of the carbonaceous deposit to get a complete closure on material balance.

Analytical Results for Alkylation Products

Professor Albright questions the reliability and completeness of our analytical results, citing as a reason for his suspicion the fact that commercial alkylates produced using liquid acid catalysts contain as many as 140–160 chromatographic peaks. For very specific reasons stated in our paper, we performed experiments using very high isobutane-to-butene (I/O) ratios. In these experiments, we detected only the products listed in Tables 1 and 3 of our paper. There may have been small amounts of other products which are below the detection limit of our analytical system (which is better than 0.1 ppm). Even if there were 150 products at this concentration level, all of which escaped detection, they would add up to only about 15 ppm, which is about 1.5% of the total concentration of the butenes and reaction products. Therefore, there is simply no basis for claiming that the compounds which were not detected individually will add up to a substantial total. We have detected most of the compounds that are generally reported in the literature as the dominant alkylation products for zeolite-catalyzed alkylation (for example, see Kirsch et al., 1972; Weitkamp, 1980; Corma and Martinez, 1993).

2,2,3-Trimethylpentane is simply not the most abundant TMP isomer in alkylation catalyzed by Y zeolite (for example, see Kirsch et al., 1972; Weitkamp, 1980; Corma and Martinez, 1993), and this has been a subject of much intrigue. We looked for it carefully by first using a calibration sample to ascertain when it elutes from the GC column and then by using different feed split ratios to see if this peak can be amplified. We simply did not find it. We are puzzled that Professor Albright thinks that we failed to detect 2-methylpentane and 2,3-dimethylbutane—they were indeed detected, and we have reported their percentages in Tables 1 and 3 of our paper. 2-Methylhexane and 3-methylhexane are also not observed in large amounts in alkylation catalyzed by Y-zeolite (Kirsch et al., 1972; Weitkamp, 1980; Corma and Martinez, 1993).

C\textsubscript{12} and bigger products generally do not come out of the zeolite pores under alkylation reaction conditions. C\textsubscript{12} compounds have indeed been extracted from spent catalyst by contacting the catalyst with supercritical isobutane (Nakamura et al., 1995). Our analytical system is capable of detecting C\textsubscript{12} compounds. We simply cannot see how the effluent product samples in our experiments could have contained as much as 12–15 wt % of heavy isoparaffins and we could have missed every one of them. It appears that Professor Albright expects the product distribution obtained in our study to match that obtained with sulfuric acid catalyst. There is no basis for this expectation. Indeed, Chu and Chester (1986) have stated, “The observed product selectivity over Y zeolite is dramatically different from that catalyzed by HF and H\textsubscript{2}SO\textsubscript{4}...”.

Chemistry of Alkylation

The intent of Table 4 in the paper was to list only those reaction steps for which we could obtain direct evidence or expect to remain important even in the limit of very high I/O ratios. It was not claimed that this table represents the complete set of all possible reactions. The section of our paper on alkylation mechanism begins with an observation that the initiation occurs through a step involving an olefin. It was our intention to communicate to the reader that this is also the case in liquid-acid-catalyzed alkylation. The fact that there are substantial differences in alkylation characteristics manifested by HF and H\textsubscript{2}SO\textsubscript{4} has been established by Professor Albright and co-workers, and we hardly dispute that. We are puzzled that Professor Albright asserts that we do not provide any experimental answers for the chemical steps.

(1) We had noted in the paper that the production of n-butane could not be verified with confidence in our experiments because of the presence of large amounts of butane impurity in the feed. n-Butane has indeed been observed by other researchers in the products during alkylation of isobutane with butenes over zeolites. We had cited the review by Corma and Martinez (1993) as a concise reference for the various studies in the literature that have reported the presence of n-butane in the reaction products.

It is true that hydride ion transfer from isobutane to conjunct polymers can yield t-C\textsubscript{4}H\textsubscript{9} and that it is an important pathway in liquid-acid-catalyzed alkylation. As noted by Professor Albright, the quality of the alkylate improves in these systems when a small amount of conjunct polymer is added to H\textsubscript{2}SO\textsubscript{4}. The occurrence of conjunct polymerization during zeolite catalyst alkylation has been discussed previously (for example, see Chu and Chester, 1986). We have simply not seen any evidence in our experiments to support the notion that this pathway is more significant than the reactions R6, R7, and R10 listed in Table 4 of our paper, particularly when we consider the fact that our experiments have been run at extremely dilute butene concentrations. Furthermore, when we consider the ease with which an isobutane molecule can approach a conjunct polymer coordinated next to one or more acid sites located inside the zeolite cages, we are inclined to suspect that this reaction will be much more hindered than reactions R6, R7, and R10. Reactions R6 and R7 are considered to be important pathways for zeolite-catalyzed alkylation by other researchers as well (for example, see p. 531 in the review by Corma and Martinez, 1993).

(2) Disproportionation is certainly very important as it must be playing a role to account for the roughly 20% yield of the non-C\textsubscript{8} compounds produced under liquid phase reaction conditions (listed in Table 1 of our paper). When the reaction was carried out under vapor phase conditions, disproportionation was found to be even more significant.

(a) The basic chemistry, in which all the isoparaffin products are produced by disproportionation, reported by Hofmann and Schriesheim (1962) and elaborated by Albright et al. (1988a,b), apply to sulfuric acid catalyzed alkylation. To the best of our knowledge, there is no documented evidence to support the notion that this is the dominant route for the USHY catalyst as well. Surely, some TMP and DMH could have been formed through disproportionation in our experiments, but, under conditions of high I/O ratios employed in our experiments, the likelihood that disproportionation is the dominant route for the formation of all isoparaffins is very small.

(b) We had used the results obtained with 2-pentene pulse experiments (reported in Table 5 of our paper) to
argue that disproportionation alone cannot explain the formation of large amounts of C₈ (much higher than the C₆ and C₇) and that self-alkylation must have also occurred.

(c) Professor Albright's argument appears to be based on the assumption that the product distribution and dominant pathways of alkylation of USHY catalyst must be the same as that for H₂SO₄. As noted earlier, this is simply not supported by the data in the literature (for example, see Chu and Chester, 1986). Reactions R₄, R₅, and R₇ are generally considered to be important in the context of zeolite-catalyzed alkylation (for example, see Corma and Martinez, 1993; Corma et al., 1994).

(d) It is true that a number of different disproportionation reactions are possible. R₉ in Table 4 illustrates one possible disproportionation reaction. In the text of our paper, we have noted a broader possibility.

The extrapolation from the 2-pentene pulse data (Table 5) to steady-flow experiments with 2-butene (Table 1) is a plausible speculation and is not concrete evidence. Even if one accepts these estimates, it merely shows that 65–80% (that is, a major part) of the TMP's production comes from a route other than disproportionation, and reaction R₆ is the most logical route. Given the complex interaction between chemistry, diffusional limitation, and catalyst deactivation, we had to limit our kinetic analysis to a highly simplified kinetic scheme. Accordingly, we selected the simplified mechanism based on the steps which must have contributed the most. Professor Albright's arguments support this, rather than disprove it.

(3) We believe that, under the extremely low olefin concentrations employed in our study, R₃, R₄, and R₅ account for the majority of the TMP and DMP produced.

(4) In our experiments we have taken care to trap the peroxide impurities in the feed, pretreat the catalyst to drive off the moisture, and purge the catalyst with ultrahigh purity nitrogen in order to remove as thoroughly as possible oxygen or oxygen-containing molecules. Therefore, the extent of ester formation, even if it had occurred under reaction conditions, must have been very small.

(5) The nature of the carbonaceous deposit on the catalyst was not analyzed in our study. We had simply cited in our paper the study by Weltkamp and Maixner (1987), who have reported that ¹³C-NMR study of the deposit generated by reaction over Y-zeolite at 80 °C failed to detect any unsaturated molecules even though the elemental analysis indicated a H/C ratio of 1.8.

(6) Rapid isomerization of n-butene over Y-zeolite has been known for a long time (for example, see Kirsch et al., 1972).

(7) We disagree with Professor Albright on the issue of kinetic modeling. As already noted above, the rapid deactivation of the catalyst, coupled with the severe diffusional limitation, makes it unrealistic to postulate a large kinetic network involving several pathways and perform parameter estimation. Therefore, we focused our attention on the butene conversion data and further simplified the analysis by considering the simplest possible set of reactions that can capture the butene conversion data obtained under the high H/O ratios employed in our experiments. The rate constants estimated from the liquid-phase reaction data through such an exercise did not reveal any internal inconsistency. We did not claim anywhere in our paper that this simplified kinetic model will hold for very high olefin concentrations or for the liquid acid catalysts. Quite obviously, such a simplified kinetic model is not an adequate framework for analyzing the data on product distribution. We have no reason to believe that any substance other than isobutane is the dominant source of hydride ions. Although there are a number of different isoparaffins in the system, isobutane is available in such a huge excess (by a factor of 1000) that hydride transfer from isobutane will overwhelm the contributions from other sources. Because we felt that no one pathway obviously dominated in the vapor phase experiments, we did not attempt kinetic modeling of the limited set of vapor phase data gathered in our study. The Weisz–Prater analysis of the vapor phase data does not assume any specific reaction mechanism.

(8) Degradation of TMP and DMH can indeed occur over the zeolites. This has been noted by Kirsch et al. (1972), who found that in their batch experiments such degradation occurred after several hours. Our flow-through kinetic experiments were performed with contact times of less than 1 s, so the likelihood of such a degradation is extremely remote.

Transfer Steps in Catalyst Pores and in the Reactor

For the purpose of analyzing the butene conversion data, it suffices to consider only the diffusivities of the reactants as there is no evidence to suggest that the rate of butene conversion is limited by equilibrium or the rate of product desorption. Isobutane is present at a 1000-fold excess and available everywhere inside the pellet. In our analysis, we had lumped all the isomers of butene together. The values of the diffusivities of the various isomers of butene in the intercrystalline voids in the pellet will be similar, at least in an order of magnitude sense. Now, if one tries to analyze quantitatively the product distribution, then one must consider a much more complex kinetic model and the resistance for the diffusive transport of each of the product species in the intercrystalline and intracrystalline voids. We did not undertake such a venture, as the experimental data gathered in our study are not adequate to extract the much larger number of parameters that will be contained in such a more complex kinetic model.

Professor Albright concludes by saying that we recommend a nonporous catalyst. We did not. We had said that it would be desirable to place the active sites near the external surface of the pellet. Placing the active sites near the external surface of a porous pellet is not the same as using a nonporous catalyst.

In summary, Professor Albright's comment about the analysis of data on alkylation yield is valid and insightful. It clearly exposes the need for a more detailed quantitative study of the product distribution and the carbonaceous deposit. However, his assumption that the product distribution and dominant pathways in zeolite-catalyzed alkylation should match those in sulfuric acid catalyzed reaction is simply not borne out by the evidence in the literature and our data.

Literature Cited


Chu, Y. F.; Chester, A. W. Reactions of isobutane with butene over zeolite catalysts. Zeolites 1986, 6, 195.

ADDITIONS AND CORRECTIONS

Some Design Aspects of Reactive Distillation Columns (RDC). Sanjay M. Mahajani* and Aspi K. Kolah

Page 4589. There is a typographical error in eqs 13 and 15. The correct equations are as follows:

Liquid side mass balance in the rectifying section

\[ \frac{dx_i}{dz} = - \frac{\psi_i(RF + 1)}{HTU^\ell \left(\frac{RF}{RF} + 1\right)} - \frac{DaF(RF + 1)}{V} \left(\frac{x_2^2}{x_1x_3K_i} + \frac{x_1x_3}{K_i}\right) \quad i = 1, 3 \quad (13) \]

Liquid side mass balance in the stripping section

\[ \frac{dx_i}{dz} = - \frac{\psi_i(SF)}{HTU^\ell(SF + 1)} - \frac{DaF(SF + 1)}{L + F} \left(\frac{SF}{SF + 1} \left(\frac{x_2^2}{x_1x_3K_i} + \frac{x_1x_3}{K_i}\right) \quad i = 1, 3 \quad (15) \]

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