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LETTER TO THE EDITOR

Reply to Comments on “Effects of Isobutylene on Isobutane Isomerization over H-Mordenite” by J. Engelhardt and J. Valyon

In the preceding Letter to the Editor, Engelhardt and Valyon (1) supplied previously unpublished kinetic data for the reactivity of isobutane over an H-mordenite catalyst at 473 K, and they compared these results with our recently published kinetic data for another H-mordenite catalyst at 473 K (2). The major difference between these two sets of kinetic data is that Engelhardt and Valyon (1) observed conversion of isobutane at 473 K in the absence of feed olefins, whereas no measurable isobutane conversion was detected over our H-mordenite catalyst in the absence of feed olefins. Engelhardt and Valyon (1) also showed that dihydrogen and methane were formed from isobutane over H-mordenite at 473 K, suggesting the importance of initiation reactions that form reactive hydrocarbon intermediates, e.g., adsorbed olefinic species in the form of “carbenium-ion like” species or alkoxy species (depending on the extent of charge transfer from the hydrocarbon fragment). The results presented in the preceding letter, as well as results in a recent paper by Engelhardt (3), are in agreement with our results that the addition of feed olefins enhances the reactivity of isobutane over solid acid materials (2). As noted by Engelhardt and Valyon in their letter (1), the difference observed by these two research groups in the reactivity of isobutane in the absence of feed olefins may be caused by differences in the H-mordenite used in these studies, for example, different sodium contents, different Si/Al ratios, and different suppliers.

It is important to stress that there is general agreement that the isomerization and cracking of isobutane over solid acid materials can be viewed as being a surface chain reaction, involving the formation of surface intermediates which undergo propagation steps such as oligomerization, β-scission, olefin desorption, isomerization, and hydride ion transfer reactions. Termination steps involve coke formation, as well as hydride transfer between isobutane and higher molecular weight reactive intermediates to form heavier alkanes. It was the intent of our recent paper to describe the observed reaction kinetics using a reaction scheme that employed catalytic cycles involving the above initiation, propagation, and termination steps.

In our previous work, we have utilized a set of catalytic cycles to describe the acid-cracking of isobutane over Y-zeolites at temperatures from 733 to 773 K (4–6), the isomerization of isobutane over H-mordenite at 473 K (2), and the isomerization of isobutane over sulfated-zirconia catalysts at 423 K (7). Although the fundamental chemistry involved in acid-catalyzed reactions of isobutane remains unchanged, different experimental conditions or changes in catalyst properties may change the relative rates of these cycles and thus alter catalytic activity and selectivity. Importantly, the rates of various initiation steps to form the necessary reactive intermediates on the surface appear to be particularly dependent on reaction conditions and the nature of the catalyst.

We are in agreement with Engelhardt and Valyon that initiation of acid-catalyzed reactions of isobutane can proceed through more than one type of mechanism, as determined by the nature of the solid acid catalyst and the reaction conditions (8–11). For example, production of reactive intermediates from paraffins may take place via protolysis (9, 12), via hydride abstraction by a Lewis acid site (13), and via the protonation of alkenes formed by the decomposition of surface-assisted isoalkyl radical cations generated on electron acceptor sites (8, 14). Finally, the quasi-equilibrated adsorption of olefins is another important possible pathway to form reactive intermediates on solid acid catalysts.

In our investigations of the acid-catalyzed cracking of isobutane over Y-zeolites at temperatures from 733 to 773 K, significant amounts of dihydrogen and methane were produced (4–6). Initiation processes involving protolysis and radical cation mechanisms are kinetically equivalent and cannot be distinguished by kinetic analysis, since both processes are first order with respect to hydrocarbon pressure. For simplicity, protolysis was chosen as the initiation process for forming these gaseous products from isobutane in our analysis of the kinetic data. This analysis combined these protolysis initiation steps with propagation steps involving oligomerization/β-scissions, isomerization, and hydride ion transfer. Importantly, a catalytic cycle involving oligomerization to form C_8 intermediates followed by isomerization and β-scission was found to be important in describing the observed product distribution for the cracking of isobutane.

In our recent analysis of the reactions of isobutane over an H-mordenite catalyst (2), an oligomerization/β-scission catalytic cycle was employed which is similar to that

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proposed for the cracking of isobutane over Y-zeolite (4–6). As already discussed, the H-mordenite sample of this investigation showed measurable activity for the conversion of isobutane only when olefins were added to reactor inlet. Therefore, for our catalyst under our reaction conditions, the adsorption of olefins appears to be the predominant pathway for the formation of the necessary reactive intermediates which participate in the subsequent propagation and termination steps.

We have recently employed the same catalytic cycles to describe the conversion of isobutane over sulfated-zirconia catalysts (15). Importantly, we have recently reported evidence for the production of dihydrogen during butane isomerization over sulfated zirconia (7). This production of dihydrogen may occur via protolysis of isobutane over the strongest acid sites (16); however, dihydrogen production was still observed after the strongest acid sites of sulfated zirconia had been poisoned by pre-adsorbed ammonia (7). Accordingly, we suggested that the primary initiation step in the absence of feed olefins over sulfated-zirconia catalysts is the dehydrogenation of isobutane, generating butenes which adsorb onto acid sites to form reactive intermediates. The conclusion is supported by quantum-chemical calculations which suggest that the dissociative adsorption of dihydrogen, isobutylene hydrogenation, and dissociative adsorption of isobutane are feasible over sulfated zirconia (7).

Figure 1 shows the reaction scheme that we used to describe the conversion of isobutane over sulfated zirconia. Isobutylene is formed by the dehydrogenation of isobutane on sulfated zirconia, whereas the propagation and termination steps are the same as proposed for H-mordenite (2). Additionally, this reaction scheme incorporates steps to form reactive intermediates through the adsorption of olefins. In this figure, we have now added for completeness that initiation of the surface chain reaction may take place on strong acid sites via protolysis steps, with the accompanying production, for example, of H_2 and CH_4.

Finally, we have attempted to compare the observed reactivity of isobutane reported in the letter of Engelhardt and Valyon (1) over H-mordenite at 473 K with the rate constants reported in our earlier paper (2). In this exercise, we employed steps for the protolysis of isobutane to form dihydrogen and methane. Similar steps were used in our earlier investigations (4–6) of isobutane cracking over Y-zeolite at elevated temperatures. The rate constants for the protolysis steps were adjusted to predict the rates of production of dihydrogen and methane reported by Engelhardt and Valyon (1). These protolysis steps were then combined with the reaction scheme and rate constants reported in our previous study of H-mordenite at 473 K to predict the rates of production of *n*-butane, propane, and pentane observed by Engelhardt and Valyon. Table 1 presents a comparison of the predicted rates and the observed rates. This table shows that the predicted rates of formations for *n*-butane, propane, and pentanes are only about a factor of 2 to 4 times lower than the rates observed by Engelhardt and Valyon. Thus, the rates of the propagation steps on the two different H-mordenite catalysts used by these two research

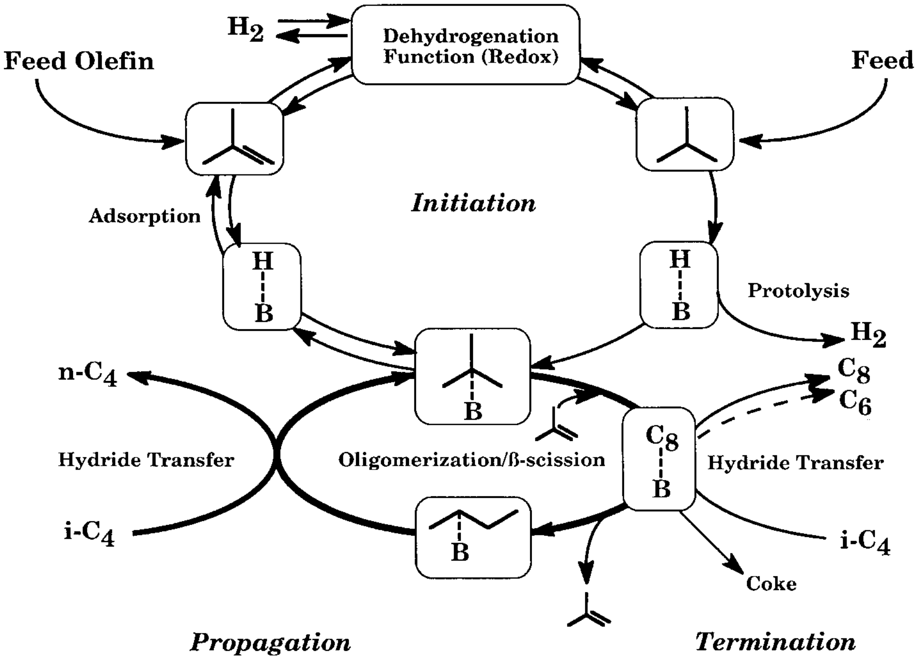

FIG. 1. General reaction scheme for conversion of isobutane over solid acid catalysts.

TABLE 1

Observed versus Predicted Production Rates for the Reaction of Isobutane over LZ-M8

Production rates	Predicted TOF[a]	Observed TOF[a]
Overall rate	8.7×10^{-08}	2.2×10^{-07}
Dihydrogen	4.8×10^{-10}	4.4×10^{-10}
Methane	1.0×10^{-09}	1.1×10^{-09}
n-Butane	5.4×10^{-08}	1.2×10^{-07}
Propane	1.8×10^{-08}	4.8×10^{-08}
Pentanes	1.3×10^{-08}	5.2×10^{-08}

[a] Turnover frequencies in units of molecules produced/molecule of Al_F/s. Molecules of AlF for LZ–M8 = 10.6×10^{20} (3).

groups are similar. It is possible that the higher rates observed by Engelhardt and Valyon may be related to the lower sodium content of their catalyst. In this respect, it is possible that the stronger acidity of H-mordenite caused by the lower sodium content may enhance the rates of propagation steps, as well as enhance the activation of isobutane through protolysis.

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