Journal of Catalysis **181,** 294–298 (1999)
Article ID jcat.1998.2362, available online at http://www.idealibrary.com on IDEAL®

LETTER TO THE EDITOR

Comments on “Effects of Isobutylene on Isobutane Isomerization over H-Mordenite” by K. B. Fogash, Z. Hong, and J. A. Dumesic

Due to the relatively simple product distribution, the conversion of isobutane has been extensively studied to gain more insight into the mechanistic details of acid-catalyzed hydrocarbon reactions (1–15). In general, the number of cracking products is restricted, as pointed out by McVicker and co-workers (4–6), since the *t*-butyl cation can not undergo β-scission. Hall and co-workers (8–15) suggested that, on solid acid catalysts, the reaction is initiated by the protonation of C–H or C–C bonds of the isobutane. Fogash *et al.* (16) reported recently that the isomerization (and disproportionation) of isobutane over H-mordenite did not commence without the presence of traces of isobutene in the feed. They inferred from this that initiation involves the protonation of isobutene rather than isobutane. These results conflict with those reported recently by Engelhardt (17), namely, that isomerization and disproportionation proceed on H-mordenites at a definite rate, even if pure isobutane is used. Nonetheless, conversion and selectivity of isobutane were found to be significantly influenced by the addition of lower alkenes, in accordance with the findings of Fogash *et al.* (16).

In our opinion, more than one initiation mechanism may be effective in generating the intermediate of alkane conversion. It is conceivable that the prevailing reaction route depends on the catalyst and on the reaction conditions. To support this assumption, the catalysts, the reaction conditions, and the results reported in Refs. (16) and (17) are compared and discussed in this letter.

Fogash *et al.* (16) established a kinetic model for catalytic isobutane isomerization in the presence of isobutene based on the data obtained with a single H-mordenite catalyst at atmospheric pressure and 473 K. Engelhardt (17) used a variety of H-form zeolite catalysts in a broader temperature range; different alkene additives were tested. A kinetic analysis of the data was not provided, but rather the issue of the initiation mechanism was addressed. Since the appearance of H_2 and/or CH_4 as product was considered diagnostic regarding the initiation mechanism (10), pure N_2 was used as carrier gas. In contrast, the feed used by Fogash *et al.* (16) contained 10% H_2. The presence of H_2 was found to have almost no effect on isobutane conversion but enabled the preadjustment of different isobutene levels using a separate hydrogenation–dehydrogenation reactor.

Table 1 shows data for the conversion of isobutane that were obtained using an H-mordenite (LZ-M8 from UOP) under conditions comparable to those applied in the work commented on here. In contrast with the H-mordenite used by Fogash *et al.* (16) the LZ-M8 catalyst was active even without adding alkene to the feed. The obvious difference of the conversions suggests that the acidity of the catalysts must be significantly different. This must be due primarily to the difference in the residual sodium content of the H-mordenite preparations. The Na content of the preparation used by Fogash *et al.* (16) was 0.58 wt% while that of the active mordenite catalysts was <0.1 wt%.

It is not surprising that a pronounced drop in catalytic activity can be effected by poisoning a small fraction of the acid sites. For instance, when ammonia was added to H-Y in an amount about 5% that of the aluminum in the framework, the conversion of isobutane at 673 K decreased by more than one order of magnitude (11). Similarly, the H-Y that contained 0.35 wt% Na was five times less active than the sodium-free sample, and the sample with a Na content of 1.5 wt% was inactive at the same temperature (17).

The chemistry of carbonium ion generation through protonation of an alkane C–H or C–C bond requires very strong Brønsted acid, often referred to as superacid. Using the H_0 indicator method, Umansky *et al.* (13) qualified the strongest acid sites of the LZ-M8 mordenite as superacid. Recent results of Valyon *et al.* (18) support this characterization. It was found that adamantane can be converted (most probably dimerized) on the acid sites of LZ-M8 even at room temperature. Adamantane is a thermodynamically very stable rigid cyclic molecule. It contains tertiary carbon atoms at bridgehead positions where the formation of an alkene bond is virtually impossible (19). Although adamantene was substantiated as a short-lived intermediate in some reactions (20) it seems unlikely that the transformation of adamantane over H-mordenite would be introduced by a dehydrogenation step. Olah *et al.* (21) substantiated that three-center, two-electron-bonded pentacoordinated carbonium ions, which can be generated in superacidic media, are involved in the reaction pathway of the adamantane reactions. A similar pathway was suggested for the acid-catalyzed transformation of other alkanes. The initiation

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TABLE 1

The Rate of Isobutane Conversion on LZ-M8 Mordenite at 473 K

Time (min):	10	40	70	100	130	160
Rate[a]:	0.5	2.2	2.3	2.4	2.3	2.2
Product (mol%)						
Hydrogen:	1.5	0.2	0.3	0.3	0.3	0.3
Methane:	1.9	0.5	0.5	0.5	0.5	0.4
n-Butane:	59.1	54.0	53.8	54.6	54.6	54.6
Propane:	25.2	21.8	21.0	20.6	20.8	21.3
Pentane:	12.3	23.5	24.4	24.1	23.8	23.3

[a] Total rate of product formation × 10^7 mol g^{-1} s^{-1}; 400 mg of catalyst was used; $F/W = 1.1 \times 10^{-5}$ mol g^{-1} s^{-1}.

step in this pathway is the protonation of alkane at the C–H or C–C bonds, forming a carbonium ion, which decomposes to carbenium ions and to the products of monomolecular cracking, viz., hydrogen and methane from isobutane.

The difference in the product distribution suggests that the initiation step of the reaction can be different for the isobutane/H-mordenite systems of Refs. (16) and (17). In both cases the main products were *n*-butane, propane, and pentanes. In addition, Engelhardt (17) detected H_2 and CH_4. Using the LZ-M8 catalyst, an induction period was observed, and deactivation was negligible during about 3 h on stream. The apparent initial increase in conversion can occur because the catalyst retains the product pentane in an amount that decreases over time. Breakthrough time of isobutane, which shows even weaker adsorption, was more than 30 min below 383 K (14). After the reaction had reached its steady state, propane and pentanes were formed at the same rates (Table 1). The latter results are similar to those obtained by Fogash *et al.* (16) at low isobutene concentration in the feed, even though Engelhardt (17) used a reactant in which no traces of alkene impurities were detected by GC. When alkene was added to the isobutane, the results of the two laboratories showed the same general trend: the rate of total hydrocarbon production was higher when the alkene concentration increased and, at the same time, deactivation was faster.

The isomerization of *n*-butane was studied by Tran *et al.* (22, 23). H-mordenites (Si/Al = 7.5 and above) were shown to be acids strong enough to activate *n*-butane by generating butyl carbenium ions that have been proposed as intermediates of mono- and bimolecular butane conversions at temperatures as low as 523 K. Furthermore, it was reported that hydrogen inhibits the reactions. This inhibiting effect was attributed to a process which is the reverse of the protolytic dehydrogenation of *n*-butane, i.e., to a process by which carbenium ions are eliminated. In contrast, Fogash *et al.* (16) did not find an H_2 effect, suggesting that isobutane conversion in their reaction system was initiated by the protonation of the isobutene additive and that dehydrogenation was not involved.

If hydrogen and methane were generated as products of the initiation step, then alkenes must also have been formed from the carbenium ions in an amount equivalent to the total amount of H_2 and CH_4 when the reaction chain was terminated. As shown in Table 1, the concentration of hydrogen and methane is very low relative to that of the main products. Presumably the alkene concentration is also too low to effect significant deactivation of the catalyst. At higher temperatures, the isobutane conversion was higher, and more alkene was produced. Under such conditions, rapid deactivation occurred due to surface deposition of hydrogen-deficient hydrocarbons (coke) formed essentially from the alkenes. Thus, the formation of H_2 and CH_4 may well occur parallel to a coking process. If this is the case, then the H_2 and CH_4 yields should increase similar to coke formation with increasing conversion. Figure 1 demonstrates that the opposite is true, substantiating that H_2 and CH_4 are primary products of the initiation. Similar conversion dependence was found for the yield of hydrogen, methane, ethylene, and ethane from the reaction of *n*-butane, suggesting that each product was formed during monomolecular cracking of a *n*-butonium ion (17). The corresponding yields of the main alkane products increase almost linearly over the whole conversion range studied.

As was mentioned above, the H_2, CH_4, and alkene yields decline with respect to the conversion curves with increasing conversion (Fig. 1). This may indicate that the contribution of the initiation and termination products to the

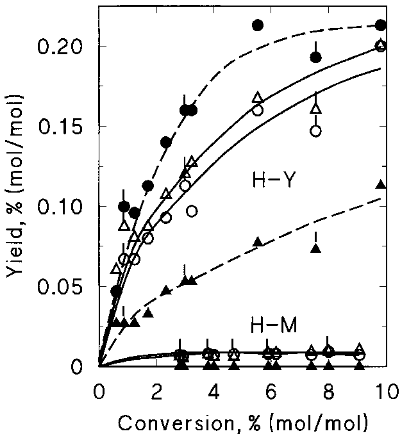

FIG. 1. The yield of hydrogen (○), methane (△), propene (▲), and isobutene (●) as a function of the total isobutane conversion on H-Y zeolites at 643 K [LZ-210(6) and LZ-Y82 (flagged symbols)] and H-mordenites at 523 K [JRC-Z-HM20 and LZ-M8 (flagged symbols)]; the F/W was varied from 1.1×10^{-5} to 1.8×10^{-6} mol g^{-1} s^{-1}. See Ref. (17) for details.

total conversion of *i*- or *n*-butane gradually decreases as the secondary carbenium ion chain process becomes dominant. Thus, at high conversions, a significant number of primary products and alkenes were produced on H-Y zeolite, while at comparable conversions, much less H_2 and CH_4 and only traces of alkenes were present in the product mixture formed in long reaction chains over the stronger acid mordenites.

It is important to understand that, in addition to *n*-butane, the main products formed from isobutane, with (16) or without (17) cofed isobutene, are propane and pentanes. Products suggest that octyl carbocation is a possible intermediate of the reaction.

An octyl carbenium ion is generated during the reaction of a butyl carbenium ion with a butene, as suggested by Fogash *et al.* (16). The carbenium ion is then fragmented by β-scission to a new ion and an alkene. Protonation of the alkene and hydride transfer reactions bring forth the alkane products. In principle, the alkene concentration does not increase as a result of these processes. Instead, a steady-state alkene concentration was established in the reactor effluent, even though the rate of product formation decreased with time on stream.

If the butyl carbenium ion reacts with a butane molecule, then an octyl carbonium ion is generated, breaking to give a carbenium ion and an alkane molecule in a process similar to that described previously as a possible way in which alkane is activated (17). Hydride transfer chain processes allow the carbenium ions to be replaced and released as alkanes. Again, no alkene is produced during these processes. The maximum amount of alkene which can be present is equivalent to the number of Brønsted acid sites which activated the alkane reactant in the first place.

Figure 2 shows the dependence of the catalytic activity as a function of time on stream for LZ-M8 with and without cofeeding alkene at 573 K. It is remarkable that, when alkene is not added, the rate of product formation increases continuously during 200 min of the experiment (Fig. 2a). This finding cannot be explained by delayed product release, since steady-state activities were reached in about 40 min at a much lower temperature (Table 1 and Fig. 3 in Ref. (16)). As demonstrated by Fogash *et al.* (16) and shown in Figs. 2b–2d, an increase in activity can be effected by increasing the alkene concentration in the feed. Thus, a continuous increase in alkene concentration could bring about the observed rate increase. It is suggested that alkene is produced from the reactant isobutane, also in reaction(s) independent of those induced by the strong Brønsted acid sites. The alkene can be readily protonated and, by launching additional reaction chains, increases the rate of product formation. Data suggest that there is more than one way to initiate the conversion of isobutane on mordenite. A number of possible initiation mechanisms were suggested in the earlier literature:

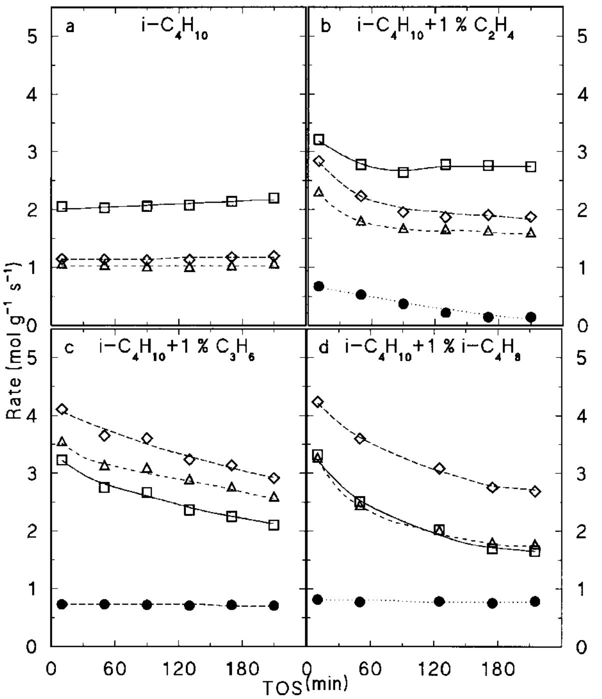

FIG. 2. The rate of propane (△), *n*-butane (□), and pentane (◇) formation from isobutane on LZ-M8 at 573 K without (a) and with (b–d) alkene in the feed as well as the rate of alkene consumption (●) as a function of TOS; the *F*/*W* was 1.1×10^{-5} mol g^{-1} s^{-1} for isobutane and 1.1×10^{-7} mol g^{-1} s^{-1} for the alkene. See Ref. (17) for details.

(i) Isobutane may contain traces of alkenes. Catalysts with weaker Brønsted acid sites may protonate the alkenes to form carbenium ion-like intermediates. (The term "carbenium ion-like intermediate" is used here in the same sense as it was used by Fogash *et al.* (16); i.e., it refers to a protonated species associated with its conjugated base.)

(ii) Catalysts with strong Brønsted acid sites protonate isobutane and, by dehydrogenation and/or demethanation, carbenium ions are formed.

(iii) At somewhat higher temperatures sites consisting of a Lewis acid and base pair can dehydrogenate and demethanate isobutane (15, 24). The product alkenes can be protonated on neighboring Brønsted acid sites.

It is not possible to differentiate between cases (ii) and (iii) on the basis of catalytic experiments only. However, convincing evidence exists that such pair sites can generate isobutene intermediates from isobutane. Alumina has no Brønsted acidity, but its surface carries acid–base pair sites. H–D exchange was found to proceed between perdeuterioisobutane and the surface of pure aluminum oxide already at 523 K (25). Under the mild reaction conditions, no isobutene appeared as a product. However, since exchange requires isobutene as an intermediate, the data suggest that aluminum oxide has dehydrogenation activity.

A fraction of the negative charges on the framework of LZ-M8 mordenite catalyst are probably balanced by positively charged extraframework alumina species. These sites are Lewis acid–Lewis base pair sites, which can function in a manner similar to the sites of aluminum oxide, generating alkene intermediates from isobutane for the Brønsted acid-catalyzed isobutane conversion. The involvement of dehydrogenation sites in the chemistry of alkane conversion on H-mordenite can explain the finding that the reaction rate increases slightly with time on stream (Fig. 2a).

Figure 2 shows the effect of adding lower alkenes to the isobutane reactant on the rate of product formation over LZ-M8 mordenite. Without alkene addition the rate of propane and pentane formation increased slightly and remained close to equimolar quantity during the experiment. Ethylene, propene, and isobutene additives resulted in a significant initial increase in the rate. However, catalyst activity decreased continuously with time on stream. The individual products were affected differently by the different alkenes. The alkenes are easily protonated and through hydride transfer can also generate *t*-butyl carbenium ions (26). As expected, the effect of different alkenes reflects the stability of the corresponding carbenium ion; i.e., the effect of *i*-butene and propene is more significant than that of ethylene. Note that the consumption of propene and isobutene varied insignificantly, while the rate of alkane formation decreased with time on stream.

A similar increase of reaction rate by addition of isobutene to isobutane was published by Sommer *et al.* (29) in the H/D exchange occuring at low temperature between isobutane and D-exchanged solid acids. An induction period, which was apparent at 373 K and below, was also suppressed when small amounts of isobutene were admixed. From this it follows that carbenium ions may be generated by protonation of alkanes, but more easily from alkenes.

On mordenite, the rate of *n*-butane isomerization relative to cracking and disproportionation was shown to depend on the carbocation concentration (22, 23, 27, 28). According to Rice and Wojciechowski (30), the effective catalytic sites are not sites of the original solid catalyst, but are rather carbenium ions residing on the primary sites. The residence times and the stability of the different surface-bound carbenium ions vary with time on stream, and this way their activity are not identical. Consequently, their contribution to the alkane conversion is different and changes differently with time on stream.

It was observed that, under identical conditions, the *iso*- and the *n*-pentane were formed in different relative amounts from *iso*- and *n*-butane on H-mordenite catalysts (17). The *iso*-pentane to *n*-pentane molar ratio is roughly 16 in the product from *iso*-butane and about 1.6 in the product from *n*-butane. Fogash *et al.* (16) also reported very low rates of *n*-pentane production from isobutane. The pentanes are formed through bimolecular dimerization cracking or disproportionation processes. The pentane isomer predominantly formed seems to be determined by the structure of the carbenium ion, i.e., tertiary or secondary, and not by the way in which it was generated. Obviously not much can be learned about the initiation reaction from the product distribution.

The success of Fogash *et al.* (16) in developing a kinetic model that properly fits the measured kinetics is probably due to the fact that the simplest possible system was selected: an inactive H-mordenite that could be activated for isobutane conversion by the controlled addition of isobutene in cocatalytic amounts. It is easy to demonstrate that diverse factors affect the activity of mordenite and the mechanisms controlling butane transformations.

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Received July 13, 1998; revised September 25, 1998; accepted September 25, 1998