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Isomerization of *n*-Butane over Deuterated Sulfated Zirconia

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Isotopic labeling with deuterium of the surface of a sulfated zirconia catalyst that was precalcined at 650°C and evacuated at 450°C, shows that this surface contains a small number of Brønsted sites; the number ratio of sulfate ions to Brønsted sites is 12.5/1. Isomerization of *n*-butane to *iso*-butane over this catalyst with a C_4 feed from which olefins and dienes were rigorously removed (estimated olefin/paraffin ratio, 10^{-15}) is slow and so is the rate of catalyst deactivation. After 25 min reaction the turnover frequency, based on the number of surface protons detected by exchange against deuterium, is $\sim 10^{-4}$ s^{-1}. At a conversion of 6.6% *n*-butane to *iso*-butane, each surface site has turned over one molecule; all D atoms have been exchanged against H atoms from the butane. The *iso*-C_4 product initially contains roughly 20% *iso*-C_4-d_1. At the same stage, the *n*-C_4 contains 4% *n*-C_4-d_1. In view of the large *n*-C_4/*iso*-C_4 ratio at this stage, this means that more D atoms have moved into *n*-C_4 molecules than into *iso*-C_4 molecules. This indicates the participation of surface Brønsted sites in exchange reactions and events such as the previously detected (V. Adeeva *et al. Catal. Lett.* 33, 135 (1995)) intramolecular rearrangement of C atoms in *n*-butane via a protonated cyclopropane intermediate. The absence of any molecules with more than one D atom indicates that all olefin molecules at the surface of this catalyst are tied up as "carbenium ions" or as surface alkoxy groups.

I. INTRODUCTION

Sulfated zirconia, abbreviated as SZ, is a solid acid catalyst of remarkable performance. It is known that *n*-butane isomerization to *iso*-butane in liquid strong acids is much slower than the isomerization rate of *n*-pentane or higher *n*-alkanes because rearrangement of a *sec*-butyl ion to a *tert*-butyl ion would be roughly 10^{10} times slower than the rearrangement of a *sec*-pentyl ion to a *tert*-pentyl ion. The cause for the striking difference between the isomerization kinetics of C_4 and all C_{5+} alkanes in liquid acids was identified by Brouwer and Hoogeveen (1). Hydrocarbon isomerization mechanisms at low and moderate temperatures generally avoid primary carbenium ions because of their very high energy; instead, they proceed via protonated cyclopropane intermediates. For the butanes, unlike all higher alkanes, opening of the three-membered ring would still lead to a primary carbenium ion; therefore this rate is very low. Likewise, with Pt/H-Mor, *n*-butane isomerization is undetectable under conditions where *n*-pentane isomerization is fast. The different nature of isomerization catalysis over SZ, in comparison to liquid acids or Pt/H-Mor, is illustrated by the fact that over this catalyst the isomerization rates of *n*-pentane and *n*-butane differ only by a factor of seven (at 200°C in the presence of H_2 and a small amount of platinum, required to prevent appreciably catalyst deactivation) (2, 3). The cause for this unusual propensity of SZ is that on catalysts of this class the adsorbed *sec*-C_4^+ ion reacts with butene, C_4H_8, to form a $C_8H_{17}^+$ ion, which subsequently isomerizes and undergoes β-fission. An energetically preferred path makes use of the 2,4,4-trimethyl (tertiary)pentyl cation (TMP$^+$), which is, therefore, the most interesting isomer among the $C_8H_{17}^+$ ions; its preferred β-fission results in two *iso*-C_4 entities. The predominance of this bimolecular mechanism for butane isomerization over SZ follows from work of Adeeva *et al.* with the double-labeled butane, $^{13}CH_3$–CH_2–CH_2–$^{13}CH_3$, which was isomerized over Fe,Mn promoted (4) and unpromoted SZ (5). The bimolecular mechanism is in conformity with the observed kinetics and also with observations by Cheung *et al.* that C_3 and C_5 alkanes are formed from the common C_8 precursor (6). The same by-products are found with Pt containing SZ catalysts: in the presence of H_2 a strongly negative reaction order in H_2 confirms the vital role of the olefin in the formation of the C_8 intermediate (7, 8). In this paper we will be using the conventional terminology, using the term "adsorbed carbenium ion" for the complex of a surface Brønsted site and an olefin, although quantum chemical calculations and spectroscopic evidence by Kazansky show that in reality the adcomplexes are surface alkoxy species; i.e., one carbon atom of the adsorbate forms a chemical bond with a surface "proton," while an adjacent carbon atom forms a bond with an oxygen atom of the catalyst surface (9). Only the transition state resembles a real carbenium ion.

The nature of the acid sites in SZ catalysts has been the subject of intensive research. Early measurements using Hammett indicators suggested that SZ exhibits "superacid

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sites." This was, however, found incompatible with spectroscopic data using FTIR and NMR. These methods revealed that all detectable acid sites are of a strength similar to or lower than the Brønsted sites in ordinary zeolite catalysts or the Lewis sites in alumina (10). This conclusion agrees with calorimetric data by Dumesic *et al.* (11), who showed that their sulfated zirconia catalysts contain 50–70 μmol/g of strong acid sites, characterized by heats of ammonia adsorption from 125 to 165 kJ/mol. Only a small fraction (8–25 μmol/g) of the acid sites displays heats of NH_3 adsorption from 145 to 165 kJ/mol, but these sites deactivate rapidly under reaction conditions. Sites with heats of ammonia adsorption from 125 to 145 kJ/mol deactivate more slowly and are therefore more likely to be responsible for the steady-state activity of the catalyst. These authors also showed that Brønsted acidity is necessary for extended catalytic activity. A crucial role of Brønsted sites has likewise been reported by Lunsford *et al.* (12) for the alkylation of isobutane with 2-butenes. They suggest that Brønsted sites adjacent to Lewis sites are responsible for the activity. The importance of coexisting Brønsted and Lewis acid sites for the isomerization of butane has also been discussed by Nascimento *et al.* (13).

The effect of Brønsted site density on catalytic activity of SZ was addressed by Comelli *et al.* (14), who report that the activity of SZ is highest after calcination between 873 and 893 K, where the density of Brønsted acid sites should be quite low. A systematic study of a possible transformation of Lewis sites into Brønsted sites was reported by Keogh *et al.* (15). They reject such a transformation because they found that water acts as a poison which completely deactivates the catalyst at a H_2O/SO_4 ratio of 1/3. Most of the water is released from the catalyst below 150°C. Recently, they reported that desorption of pyridine from SZ during TPD is not a simple decomposition of a Brønsted acid salt but that oxidation/reduction reactions take place (16). Their catalytic data suggest that Brønsted sites are not responsible for the conversion of *n*-hexadecane.

Pinna *et al.* (17) question the key role of Brønsted sites in the conversion of alkanes after they observed that admission of CO, which is assumed to poison Lewis acid sites, results in a total suppression of the catalytic activity for *n*-butane conversion. A similar observation was reported by Mastikhin *et al.* (18) for *n*-pentane conversion; they showed that the activity of SZ is proportional to the density of the strongest Lewis sites detected by ^{15}N NMR of adsorbed N_2. They claim that no relation exists between catalyst activity and the number or type of surface OH groups, though their observations do not exclude that some Brønsted sites may actually play a role in the catalysis (16–18).

Apparently, the surface density of Brønsted sites and their role in this catalysis deserve further study. In the present work, we "count" the number of surface protons that participate in the catalysis of *n*-butane isomerization in order to gain insight into the mechanism of the interaction between surface protons, olefins, alkanes, and carbenium ions. To this end, a carefully degassed SZ catalyst is subjected to D_2O vapor and the H/D ratio in the gas phase is followed mass spectrometrically. After replacing the majority of the surface H atoms with D atoms, *n*-butane is introduced into the catalytic recirculation system. While simultaneously monitoring the extent of isomerization, the concentration of C_4 molecules containing D atoms is analyzed versus time for both *n*-butane and *iso*-butane.

II. EXPERIMENTAL

1. Catalyst Preparation

Sulfated zirconia was prepared by calcination of a sulfated zirconium hydroxide, kindly provided by Magnesium Electron Inc. (MEI lot 93/222/01), in a flow of dry air (100 ml/min) at 650°C for 3 h. ICP analysis showed that this SZ catalyst contains 1.04 wt% of sulfur.

2. Deuteration of SZ and Counting of the Surface Protons

The deuteration of SZ was performed in a greaseless recirculation system (135 ml) with a mixture of D_2O (Cambridge Isotope, DLM-6 (99.96D%)) and He (Matheson, UHP) at a total pressure of 30 Torr (7 Torr $D_2O + 23$ Torr He; 1 Torr = 133 Pa). Prior to the introduction of D_2O, which was purified by freeze–thaw cycles under vacuum before use, 200 mg SZ was treated with O_2 at 450°C to eliminate hydrocarbon contamination. This was followed by evacuation at 450°C for 1 h and cooling to 150°C for the exchange with D_2O. During the exchange the composition of the isotopic water was monitored by an on-line mass analyzer (Dycor M100) with a variable leak valve from the reaction system (5). After the exchange equilibrium had been reached, the catalyst was heated again to 450°C and maintained at this temperature for 20 min to desorb any adsorded water. The material balance in the exchange system after the desorption of water at 450°C has been found to be correct with an error of less than 4%. Calculation of the exchanged D atoms was based on the ideal gas law with a correction for temperature effect on the volume of the reactor.

A blank experiment with no catalyst was carried out under the same conditions as with SZ, in order to measure the amount of deuterium exchanged to the glass/quartz reactor. This exchanged deuterium was then subtracted from that in the system containing the SZ catalyst. The number of proton sites on the surface of SZ was taken as the number of exchanged D atoms. This number was reproduced in repeated experiments within an experimental error of <10%.

3. Isomerization of n-Butane

Isomerization of *n*-butane was carried out at 150°C in the same recirculation system used for the deuterium exchange, with 32 Torr *n*-butane and 700 mg deuterated SZ catalyst. To eliminate traces of butadiene (a known precursor for carbonaceous deposits) and other unsaturated impurities from the reactant, the *n*-butane feed (Matheson, instrument purity >99.5%) was mixed with hydrogen ($P_{\text{butane}} = 50$ Torr, $P_{\text{hydrogen}} = 150$ Torr) and circulated over a 2% Pt/SiO_2 (200 mg) catalyst at 35°C for 1 h. After this treatment the *n*-butane was condensed in a trap cooled with liquid nitrogen and the H_2 was pumped off. This procedure is assumed to establish a *n*-butene/*n*-butane ratio of 10^{-15}.

While the on-line mass analyzer permitted a rough estimate of the isomerization of *n*-butane, a more reliable product analysis was accomplished by trapping the reaction mixture at the end of a catalytic run with liquid nitrogen and analyzing the condensate with a separate GC-MS (HP 1800A GCD system). The conversion and the selectivities were obtained from GC analysis, while the MS spectrum of each product was used to analyze the deuterobutanes. Isomerization of *n*-butane was also performed over a nondeuterated SZ under the same conditions as over the deuterated SZ. The fragmentation patterns of *iso*-butane and *n*-butane obtained from the GC-MS data over this nondeuterated catalyst were applied to correct the fragment contribution within any isotopic *iso*-butane and *n*-butane.

TABLE 1

Butane Isomerization over Deuterated Sulfated Zirconia[a]

Catalyst	D-SZ		SZ
Conversion (%)	6.6	15.3	18.5
Selectivity (%)			
Propane	—	7.1	8.3
Isobutane	100	88.2	85.7
Pentanes	—	4.7	5.9

[a] Reaction temperature, 150°C; catalyst mass, 700 mg; reaction times for attainment of 6.6 and 15.3% conversion are 25 and 65 min, respectively.

III. RESULTS

1. D_2O Exchange of Protons on SZ

An excess of gaseous D_2O was used for the deuteration of the surface; the ratio of D atoms to surface sulfate groups was ∼1.4. Figure 1 shows the changes of the three isotopic water molecules, H_2O, HDO, and D_2O, during the exchange reaction in the recirculation system. Because of a simultaneous exchange of D_2O with residual OH groups at the reactor glass/quartz walls (Fig. 1a), these curves (Fig. 1b) do not present the true kinetics of the exchange with the protons in the SZ catalyst. To determine the number of exchanged D atoms, the peak intensity of H_2O ($m/e = 18$) was calculated from the equilibrium constant at 150°C (19) $K = P_{\text{HDO}} \times P_{\text{HDO}}/(P_{H_2O} \times P_{D_2O}) = I_{19} \times I_{19}/(I_{18} \times I_{20}) = 3.90$, because the directly measured MS intensity I_{18} is mainly due to fragmentation of D_2O and HDO.

The number of protons on SZ obtained from the exchange reaction is 25 ± 3 μmol/g, which corresponds to 8% of the sulfate ions in the SZ sample; i.e., the SO_4/H ratio is 12.5. The original excess of D atoms in the gas phase (as D_2O) to exchangeable surface H atoms thus amounts to 17.5. The number of exchangeable protons found in this study, is slightly lower than the number of 33–66 μmol/g ((0.2–0.4) × 10^{20}/g after evacuation at 400–600°C) measured by Mastikhin *et al.* (18), who used ^{1}H NMR of an SZ sample (1.7 wt% S or 4.2 wt% SO_3) that had been calcined at 600°C. As the SZ sample of the present study has been pretreated at more severe conditions and contains less sulfur (1.04 wt%), the count of protons by D_2O exchange ($SO_4/H = 12.5$) appears to be in good agreement with these ^{1}H NMR data ($SO_4/H = 8$–16). Not surprisingly, these numbers are significantly lower than those measured by ^{31}P NMR of adsorbed trimethylphosphine (12) on SZ samples after a much milder pretreatment and with much higher sulfur content (3.9 wt%).

2. Butane Isomerization over Deuterated SZ

Table 1 shows the conversion and product selectivity of *n*-butane over deuterated SZ. Results over the nondeuterated

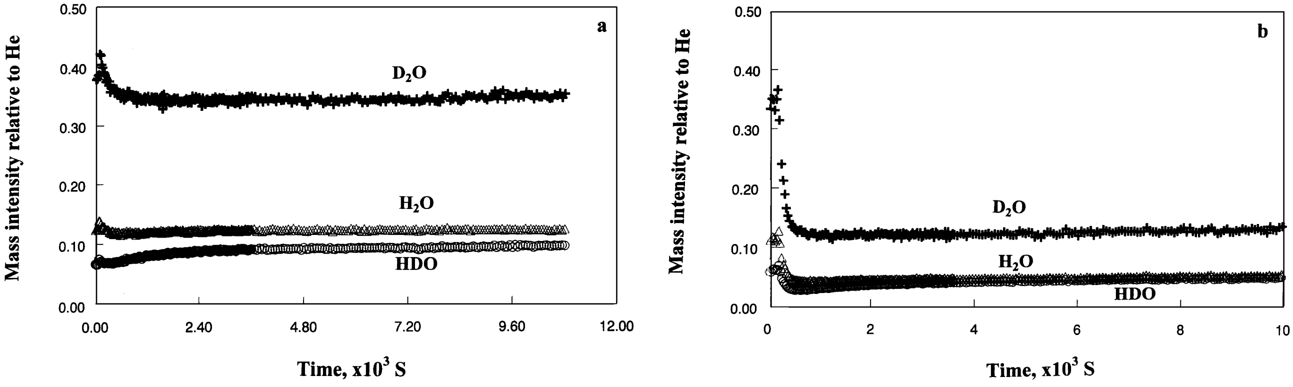

FIG. 1. Change of mass intensity of water components during D_2O exchange in the recirculation system. (a) Blank experiment; (b) with SZ catalyst.

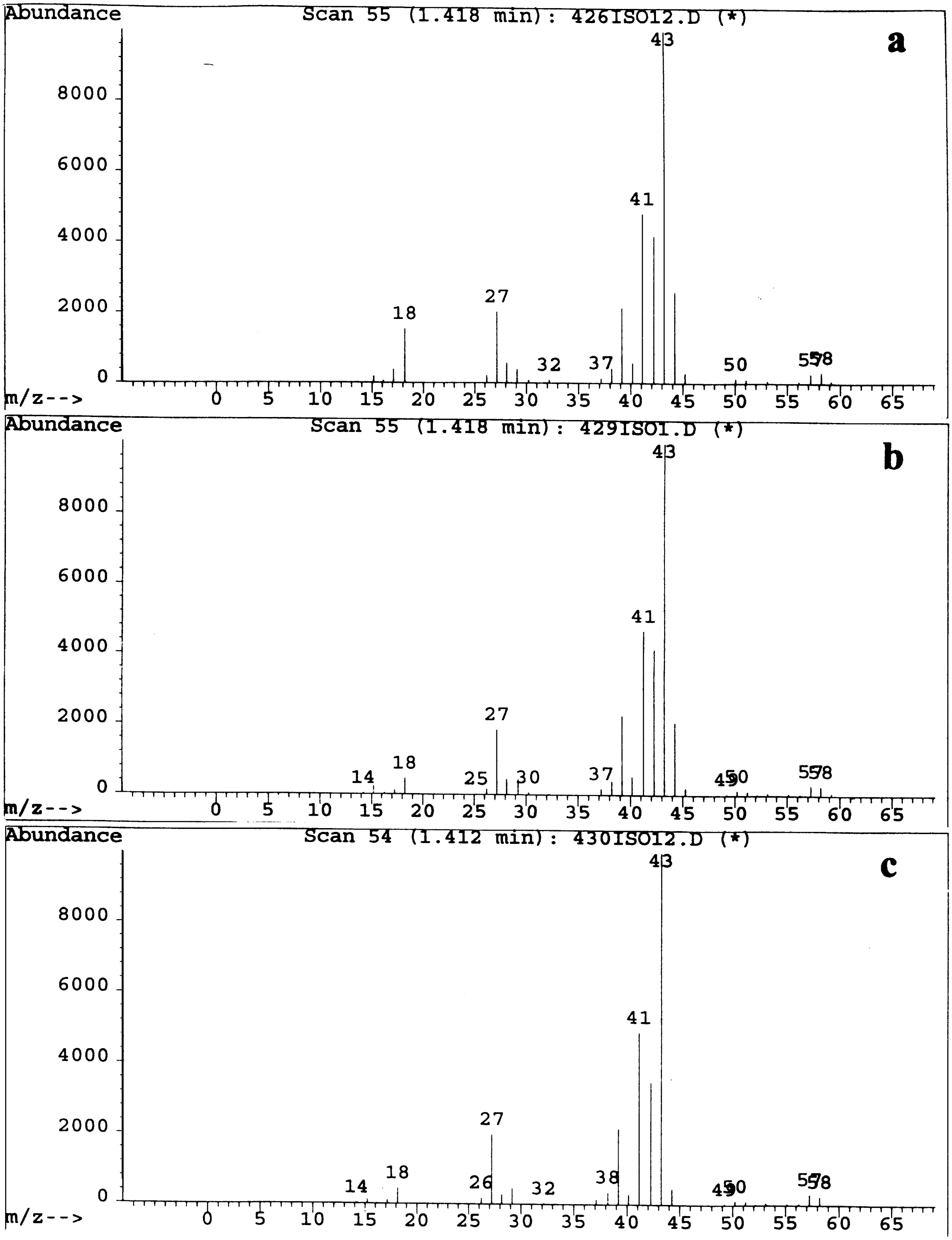

FIG. 2. Mass spectra of *iso*-butane. (a) Product over D-SZ at 6.6% conversion; (b) product over D-SZ at 15.3% conversion; (c) product over H-SZ at 18.5% conversion.

catalyst are also shown as a reference. The product selectivity is similar to that obtained in a conventional flow system at comparable conversion levels (2, 6, 20). In Figs. 2–5 the mass spectra of the molecules in the reaction system with deuterated SZ (D-SZ) are compared with those of their partners in the system with nondeuterated SZ. Judging from the most abundant fragments of each component, it appears that every molecular species in the D-SZ containing system contains some d_1 component; i.e., deuterium is incorporated into each hydrocarbon species that was in con-

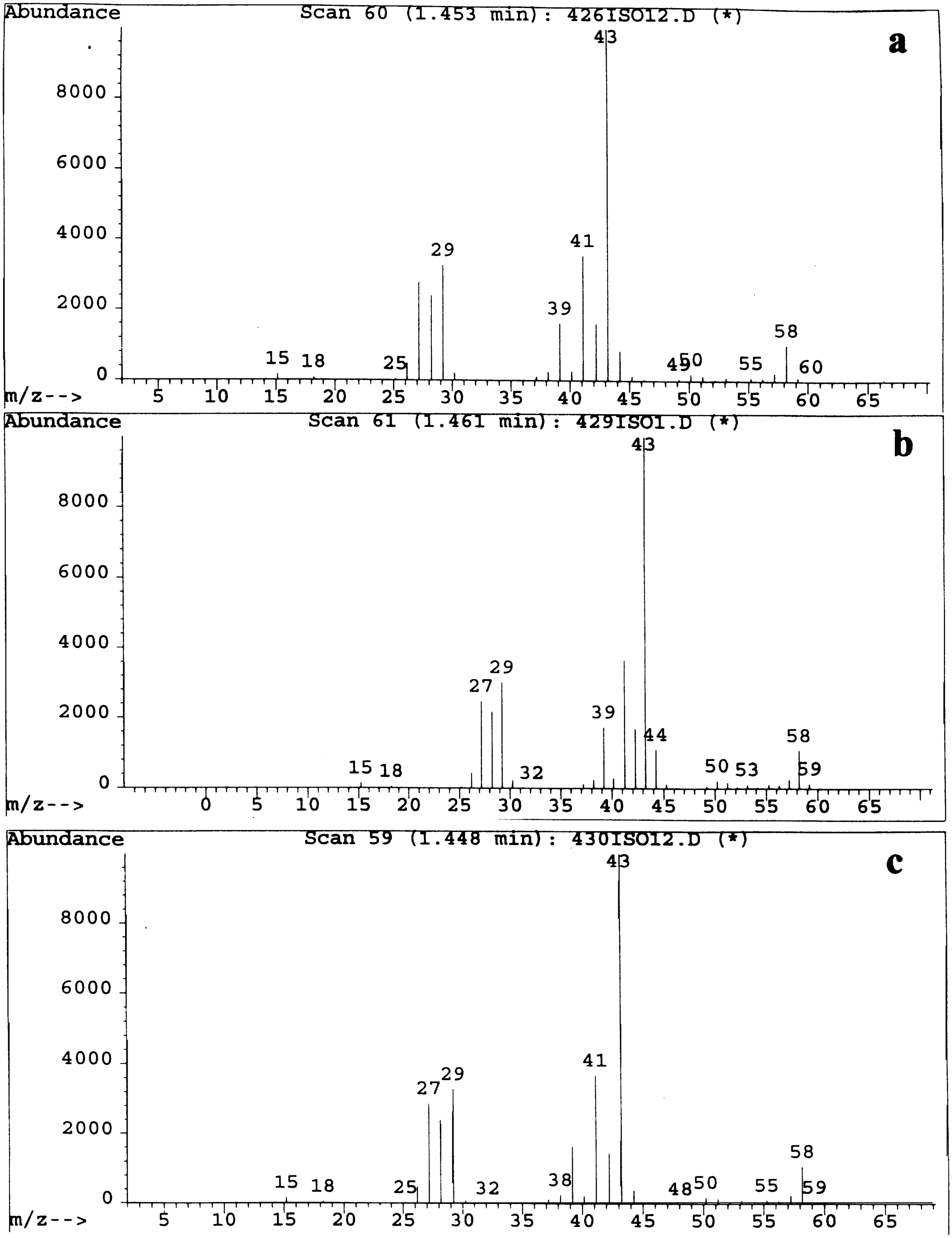

FIG. 3. Mass spectra of *n*-butane. (a) Over D-SZ at 6.6% conversion; (b) over D-SZ at 15.3% conversion; (c) over H-SZ at 18.5% conversion.

tact with the D-SZ catalyst. No formation of d_2 molecules is observed.

Since the most abundant mass signal for butanes appears at $m/e = 43$ for butane-d_0 but at $m/e = 44$ for butane-d_1, the intensity of these two signals (I_{43} and I_{44}) was used, after correction for the fragmentation of both d_1 and d_0 butanes, to evaluate the relative contents of butanes-d_1 to butanes-d_0. The deuterated components of *iso*-butane and *n*-butane are calculated according to the following equations:

$$\textit{iso}\text{-butane-}d_1/\textit{iso}\text{-butane-}d_0 = (I_{44} - 0.05 \times I_{43})/(I_{43} - 0.35 \times I_{44})$$

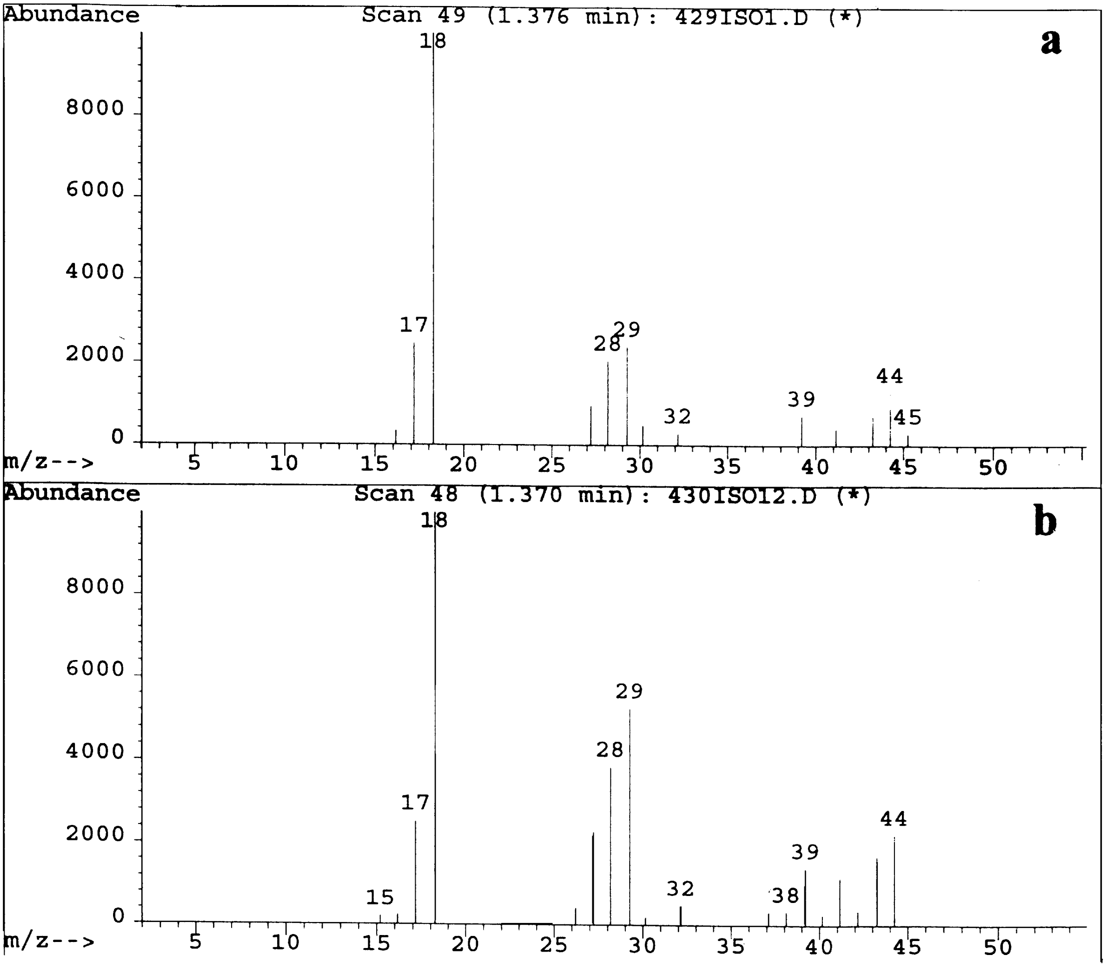

FIG. 4. Mass spectra of propane. (a) Product over D-SZ at 15.3% conversion; (b) product over H-SZ at 18.5% conversion.

$$n\text{-butane-}d_1/n\text{-butane-}d_0 = (I_{44} - 0.04 \times I_{43})/(I_{43} - 0.15 \times I_{44}).$$

In these equations, the subtracted terms represent the fragment contributions of d_1 or d_0 butanes to the signals of the d_0 or d_1 butanes. These equations assume that the deuterium atoms in d_1-butanes appear in the C_3 ($m/e = 44$) fragments, not in the C_1 ($m/e = 16$) fragment. This is confirmed for *n*-butane-d_1, because no signal at $m/e = 16$ could be observed in the mass spectra of *n*-butane (Figs. 3a and 3b). For *iso*-butane-d_1 an estimate based on the intensities of the C_1 fragments at $m/e = 15$ and $m/e = 16$ suggests that the assumption is correct for >85%. The results at two different conversion levels of *n*-butane are presented in Table 2. Assuming that protons (deuterons) are the active sites for the isomerization reaction, the magnitude (10^{-4}) of TOF to *iso*-butane is rather low in comparison to those of other reactions over heterogeneous catalysts. If the sulfate ions are used as a basis for calculating the TOF, the resulting value is 10^{-5}, because the number of protons is 12 times lower than the number of sulfate ions. This demonstrates the difficulty of catalyzing the butane isomerization reaction in a feed rigorously purified of unsaturated impurities.

At an *n*-butane conversion level of 6.6%, which requires 25 min at 150°C, just one isomerization event of *n*-butane to *iso*-butane occurs over each proton (D) site ($\text{TON} = 0.96$). The count of deuterium in butane molecules at this $\text{TON} = 0.96$ amounts to 95% of the number of D atoms on the catalyst, thus suggesting that one "turnover" suffices to incorporate all the surface deuterons into butane molecules. At this point, 20% of the *iso*-butane product molecules contains one deuterium (*iso*-butane-d_1/*iso*-butanes $= 0.19$) and 4% of the *n*-butane molecules contain one D atom. However, the absolute number of *n*-butane-d_1 molecules exceeds the number of *iso*-butane-d_1 by a factor of three. In other words, of four D atoms transported from the catalyst surface to a C_4 molecule, three appear in the *n*-butane and one in the *iso*-butane product. During the same period, four to five *iso*-butane molecules are formed with no incorporation of D atoms.

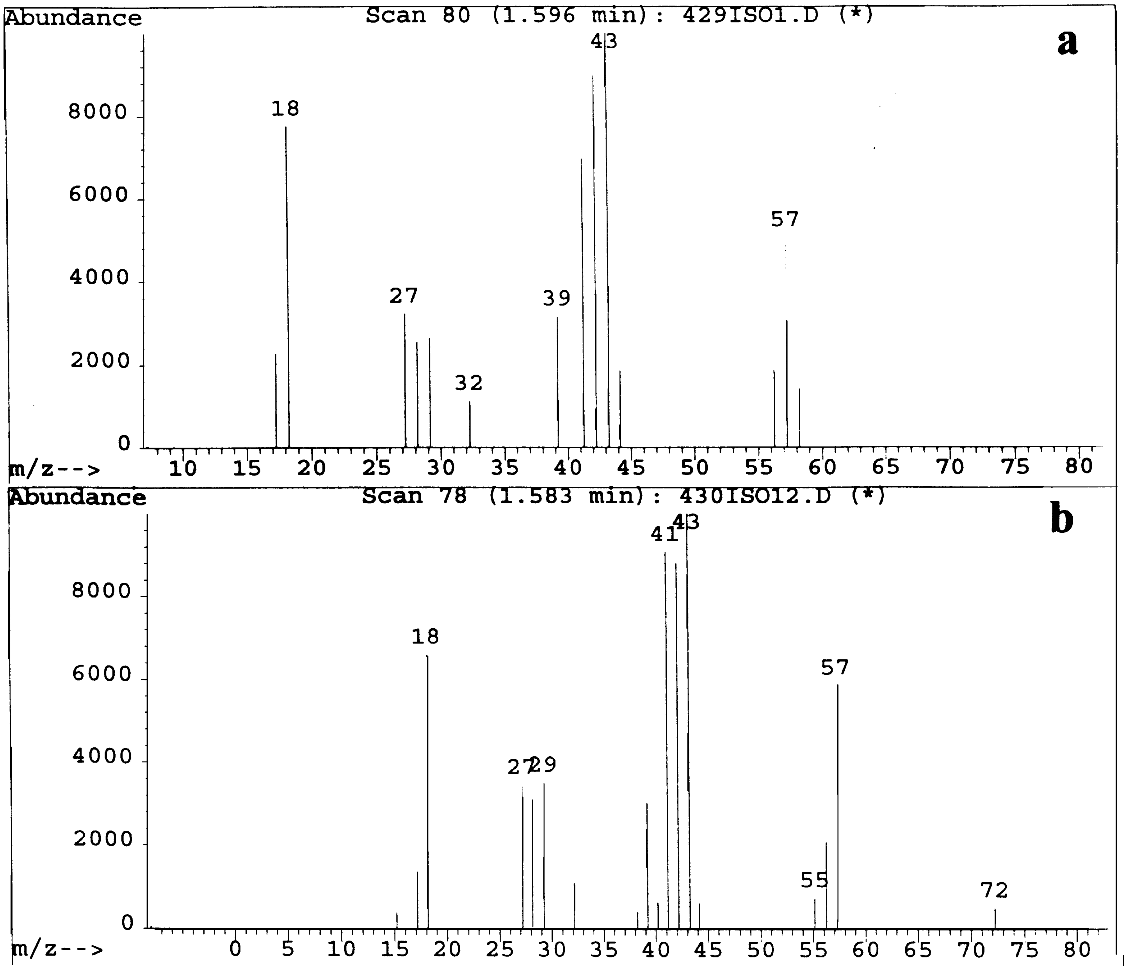

FIG. 5. Mass spectra of 2-methylbutane. (a) Product over D-SZ at 15.3% conversion; (b) product over H-SZ at 18.5% conversion.

We note that the TOF numbers at these two conversion levels differ only by 15%, which does not agree with the known rapid deactivation feature of SZ catalyst. In a flow type reaction, Adeeva *et al.* (10) showed that the same catalyst lost 50% of its activity during the first 1 h of reaction. The lower deaction rate shown in the present work is considered to be a consequence of the elimination of diene and olefin impurities from the *n*-butane reactant by the pretreatment with H_2 over Pt/SiO_2 catalyst. As will be mentioned below, we have been able to obtain conversion up to equilibrium with this "olefin-free" feed.

As expected, the percentage of deuterated *iso*-butane (d_1) decreases and that of deuterated *n*-butane (d_1) increases with increasing conversion of *n*-butane. When the composition of the butane isomers approaches equilibrium (61.5% *iso*-C_4; 38.5% *n*-C_4, i.e., a ratio of *iso*-C_4/*n*$C_4 = 1.5$), the percentage of *n*-butane-d_1 in *n*-butane becomes comparable to that of *iso*-butane-d_1 in *iso*-butane. Using the data in Ref. (21), the C_4 isomer composition in thermodynamic equilibrium is calculated to be 63% *iso*-C_4 and 37% *n*-C_4.

IV. DISCUSSION

The present data indicate that all protons that could be exchanged against deuterons participate in the catalyzed reactions and are replaced by H atoms from butane. The D atom numbers at the surface of SZ after the exchange with D_2O agree with those in the butanes at a conversion level of 6.6% (Table 2, last row). At this stage, virtually all D atoms have been transferred from the surface to either *n*-butane or *iso*-butane molecules. The surface concentration of the protons is low; for the pretreatment conditions chosen in the present work the H(D)/S ratio is roughly 1/12. Knowledge of the number of Brønsted sites permits expression of the kinetic data in terms of true turnover frequencies (TOFs). It is also useful to consider that, in the experiments described in this study, the molar ratio of butane molecules to surface H(D) sites is 14/1, which corresponds to an overall atomic isotope ratio in the reaction system of $H/D = 140$. The absence of butane molecules with more than one D atom is thus in agreement with statistics: it shows that no multiple exchange events have to be considered.

TABLE 2

Distribution of Deuterated Butanes in Butane Isomerization over Deuterated Sulfated Zirconia

Conversion (%)	6.6	15.3
TOF to isobutane ($\times 10^4$/sec)	6.4 (1.2)[a]	5.5 (0.82)[a]
TOF to *n*-butane-d_1 ($\times 10^4$/sec)	3.6	2.1
TON to isobutane[b]	0.96 (0.15)[a]	2.2 (0.32)[a]
TON to *n*-butane-d_1[b]	0.54	0.80
Isobutane-d_1/isobutanes	0.19	0.15
N-butane-d_1/*n*-butanes	0.039	0.066
Isobutane-d_1/*n*-butane-d_1	0.34	0.40
Deuterium in butanes/deuteron on SZ	0.95	1.02

[a] Numbers in parentheses refer to isobutane-d_1 related ones.

[b] Assuming that exchangeable protons are the active site for butane isomerization, TON is defined as the number of molecules converted per proton (deuteron) during the period until the mentioned conversion levels are reached.

On the basis of the known number of surface protons, a turnover frequency of 10^{-4} molecules (sites)$^{-1}$ s^{-1} is calculated for the isomerization to isobutane. This value does not include the simultaneous isomerization of $n\text{-}^{13}CH_3–CH_2–CH_2–^{13}CH_3$ to $n\text{-}CH_3–^{13}CH_2–CH_2–^{13}CH_3$ detected by Adeeva *et al.* (5) on the same SZ catalyst; this "internal rearrangement" reaction is, of course, observable only with carbon-labeled molecules. For the isomerization of *iso*-butane under flow conditions at 370°C, Umansky *et al.* (22) reported TOF values of $(3.1 \pm 2.1) \times 10^{-5}$ s^{-1} for HY, $(1.3 \pm 0.9) \times 10^{-5}$ s^{-1} for HZSM-5, and $(2.1 \pm 1.5) \times 10^{-2}$ s^{-1} for H-mordenite.

The measured TOF value for *n*-butane isomerization to *iso*-butane permits us to calculate the Gibbs free energy of activation from the absolute rate theory:

$$k = (\mathbf{k}T/h)\exp(-\Delta G^{\#}/RT).$$

From the measured values we calculate $\Delta G^{\#} = 69$ kJ/mol. This is very similar to the values (70.3–76.6 kJ/mol) reported by Brouwer for the carbenium ion isomerization of C_{5+} alkanes with change in branching, i.e., via a protonated cyclopropane ring intermediate (23). It is also close to the value of 75 kJ/mol reported by Bittner *et al.* (24) for the rearrangement of the *sec*-butyl carbenium ion to the *tert*-butyl carbenium ion, but is significantly higher than the apparent activation energy $\Delta H^{\#} = 45$ kJ/mol reported by Hsu *et al.* (25) for butane isomerization over SZ. The activation energy for the reverse reaction, reported by Umansky *et al.* (20), is in the range of 100–200 kJ/mol. As the energy of the tertiary carbenium ion is 67 kJ/mol lower than that of the secondary ion, it is to be expected that the activation energy of the reverse reaction exceeds that of the forward reaction by this amount.

In view of the evidence obtained with double ^{13}C-labeled butane (4, 5), it follows that the prevailing mechanism of C_4 skeletal isomerization over SZ involves formation of a C_8 intermediate. The negative reaction order in H_2 for *n*-butane isomerization over PtSZ catalysts reported by Liu *et al.* (2, 7) shows that the low concentration of butene, present in equilibrium with butane and H_2, will be absolutely vital for this reaction mechanism.

Initially the olefin concentration must have been very low in the present study. If equilibrium was established between butane, butene, and hydrogen over Pt/SiO$_2$ at 35°C a ratio of $P_{C_4H_8}/P_{C_4H_{10}} = 1.5 \times 10^{-15}$ is calculated. Previous work by Liu *et al.* has shown that the reaction order in butene is $+1$. It is therefore in agreement with expectations that the isomerization rate of a rigorously purified butane must be rather low. As olefins are necessary in the bimolecular mechanism, it seems possible that olefin molecules are formed via carbonium ions over the sites of high acidity with heats of ammonia adsorption >150 kJ/mol, as detected by Dumesic *et al.* (11). Olefin formation via hydride abstraction on Lewis sites has also been considered in the literature (26, 27) but was dismissed by Engelhardt and Hall (28), who studied the reaction of perdeutero-*iso*-butane over zeolite catalysts and concluded that protonation of *iso*-butane on Brønsted acid sites was most likely.

Once a small concentration of olefins is built up, a catalytic cycle will be established; in its simplest form the cycle is given by the sequence [A-1] to [A-4]:

A. *Catalytical Cycle*

$$\text{Alkylation}\quad n\text{-}C_4H_9^+ + iso\text{-}C_4H_8 \Rightarrow C_8H_{17}^+ \qquad [\text{A-1}]$$

C_8^+-isomerization to TMP$^+$

$$C_8H_{17}^+ \Rightarrow (CH_3)_3CCH_2C^+(CH_3)_2 \qquad [\text{A-2}]$$

Beta-fission

$$(CH_3)_3CCH_2C^+(CH_3)_2 \Rightarrow iso\text{-}C_4H_9^+ + iso\text{-}C_4H_8 \qquad [\text{A-3}]$$

H$^-$transfer

$$iso\text{-}C_4H_9^+ + n\text{-}C_4H_{10} \Rightarrow iso\text{-}C_4H_{10} + n\text{-}C_4H_9^+. \qquad [\text{A-4}]$$

These reactions add up to

$$n\text{-}C_4H_{10} \Rightarrow iso\text{-}C_4H_{10}. \qquad [\text{A-5}]$$

This scheme assumes that β-fission of the 2,4,4-trimethyl (tertiary)pentyl cation (TMP$^+$) is the predominant process for the formation of *iso*-C$_4$ moieties, as was shown by Brouwer *et al.* (23). It converts a tertiary carbenium ion into another tertiary carbenium ion and an olefin. The surface protons do not show up in the catalytic cycle; equilibrium will be established between olefins, protons, and carbenium ions (or alkoxy groups) at the surface. In this equilibrium, tertiary carbenium ions prevail, as shown by Engelhardt and Hall for proton–mordenite catalysts (28).

Proton transfer processes also lead to formation of n-C_4H_8 from iso-C_4H_8:

$$iso\text{-}C_4H_8 + n\text{-}C_4H_9^+ \Rightarrow iso\text{-}C_4H_9^+ + n\text{-}C_4H_8. \qquad [B\text{-}1]$$

This process is exothermic because a *sec*-carbenium ion is replaced by a *tert*-carbenium ion; therefore, a variant of the catalytic cycle replaces the alkylation step [A-1] with

$$n\text{-}C_4H_9^+ + n\text{-}C_4H_8 \Rightarrow C_8H_{17}^+. \qquad [A\text{-}1a]$$

After including [B-1], this variant of the cycle leads to the same overall reaction [A-5].

Hydride transfer from *n*-butane molecules to *tert*-butyl carbenium ions formed during the β-fission of the C_8 intermediates is endothermic, but may be the most efficient method for forming *iso*-butane. At low conversion, the high concentration of *n*-butane will favor this transfer over that from *iso*-butane. The latter H^- transfer is energetically more favorable, but is not "counted" as a contributing step for the isomerization.

It was shown by Otvos *et al.* (29) that isotope exchange of acid deuterons with the hydrogen atoms in a carbenium ion is fast, which is the result of fast olefin/carbenium ion equilibration. The present results confirm the same type of chemistry between surface Brønsted sites and adsorbed olefins/carbenium ions. Recently, the same chemistry was proven to operate on SZ catalyst by Sommer *et al.* (30) and with the proton form of zeolites at higher temperatures by Engelhardt and Hall (28). The work by Otvos *et al.* in deuterated sulfuric acid and Engelhardt and Hall over deuterated zeolites also shows that in an excess of D^+ the rapid exchange leads to deuterium-rich hydrocarbons. If this were presently the case in the initial state of the reaction, when all Brønsted sites at the surface are deuterons, one would expect the *iso*-butane molecules to contain up to nine D atoms. The absence of any observable hydrocarbon molecules with more than one D atom is additional proof that the equilibrium,

$$D^+ + C_4H_8 \Rightarrow C_4DH_8^+,$$

is far to the right; i.e., no olefin molecules exist on the surface except those attached to a proton (deuteron), i.e., as carbenium ions (or alkoxy groups).

We thus assume that initially the carbocations on the surface will be *sec*-butyl-d_1 carbenium ions formed from the interaction of C_4H_8 with D^+ sites. Hydride abstraction from a n-C_4H_{10} molecule releases a *sec*-butyl-d_1 carbenium ion as a *n*-butane-d_1 molecule. Reaction of the surface *sec*-butyl-d_1 carbenium ions with olefins provides entry into the catalytic cycle. At its exit an *iso*-butane molecule appears which contains either one D atom or none. As a result, the initial *iso*-butane is fairly rich in the d_1 fraction, but does not consist exclusively of *iso*-butane-d_1. While the D content of *iso*-butane is initially fairly high, simultaneous formation of *n*-butane-d_1 takes place by hydride transfer with *sec*-butyl-d_1 carbenium ions, a reaction which is not counted as a catalytic isomerization. In fact, the results show that more deuterium is removed from the surface to *n*-butane than to *iso*-butane because of the much larger number of the *n*-butane molecules in the gas phase.

The fact that the initial *iso*-butane product contains only 20% d_1 molecules at an *n*-butane conversion of 6.6% suggests that not all *sec*-butyl-d_1 carbocations enter the catalytic cycle in C_8 intermediates. The initial ratio of *n*-butane-d_1 to *iso*-butane-d_1 might indicate that the rate of the interchange reaction between *sec*-butyl ions and the *n*-butane reactant is faster than the rate at which the *sec*-butyl ion participates in the catalytic cycle via C_8^+ ions. At higher conversion levels of *n*-butane, secondary reactions of *n*-butane-d_1 and *iso*-butanes become possible and most surface species will have zero D atoms.

V. CONCLUSIONS

This study shows that the number of Brønsted sites at the surface of a sulfated zirconia catalyst precalcined at 650°C is roughly a factor of 12 lower than the number of sulfur atoms at the same surface. These surface protons participate in butane isomerization and hydride transfer from impinging alkane molecules as "carbenium ions" or surface alkoxy groups which are formed by adsorbing intermediate olefin molecules. After a conversion (defined by the isomerization level) of only 6.6%, a virtually total exchange between surface protons and hydrocarbons has taken place. On a surface that initially had a very high D/H ratio, the carbenium ions with only one D atom initially predominate. Once adsorbed carbenium ions are formed, they undergo fast hydride ion transfer with the prevailing *n*-butane molecules; the absolute rate of this process is higher than the rate by which these *sec*-butyl carbenium ions enter the catalytic cycle to form C_8 intermediates which are isomerized and yield iso-C_4^+ ions via β-fission. Still, the d_1 fraction of the initial *iso*-butane product is substantially larger than that of the *n*-butane.

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