Competitive mechanisms of *n*-butane isomerization on sulfated zirconia catalysts

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Isotopic analysis of *n*-butane isomerization over sulfated zirconium oxide, using double ^{13}C-labelled *n*-butane, shows that at low temperature this isomerization is an inter-molecular process. Probably, a C_8 surface intermediate is formed which isomerizes and undergoes β-fission; the iso-C_4 fragments are desorbed as *i*-butane. Previously, the same mechanism was indicated for Fe, Mn promoted catalysts. The isomerization rate at 130°C is drastically lowered by gaseous H_2, because the concentration of the unsaturated species, required for the formation of the C_8 intermediate, is low under such conditions. Whereas ^{13}C-scrambled *i*-butane is a true primary product, isotopic scrambling of *n*-butane continues after chemical equilibrium between *n*-butane and *i*-butane has almost been reached; i.e. ^{13}C scrambled *n*-butane is a secondary product. Intra-molecular rearrangement of carbon atoms in *n*-butane precedes inter-molecular scrambling. The similarity of the isomerization mechanism over unpromoted sulfated zirconia and Fe, Mn promoted sulfated zirconia is paralleled by an equal strength of the acid sites in both catalysts. The shift in the FTIR band of CO adsorbed on the Lewis sites indicates that these sites, presumably surface Zr^{4+} ions, are weaker acids than Al^{3+} in dehydrated alumina.

Keywords: sulfated zirconia; butane isomerization; ^{13}C labelled butane; intermolecular mechanism of isomerization; bimolecular mechanism of isomerization

1. Introduction

Sulfated zirconia (SZ) catalysts are known to catalyze the skeletal isomerization of hydrocarbons [1–3]. Hsu et al. [4] reported and subsequent investigators confirmed [5] that the catalytic activity of SZ for the isomerization of butane to *i*-butane is significantly enhanced by "promoting" the catalyst with the oxides of iron and/or manganese. Over some of these FMSZ catalysts butane isomerization is observed below 100°C, though only for a short time. However, for the activation energy the same value is reported over SZ and FMSZ [4].

Results by Kustov et al. [6] show that the acid strength of Brønsted sites in SZ is lower than in HZSM-5. The same conclusion was obtained by Adeeva et al. [7]

who also found no significant difference in acid strength between SZ and FMSZ by spectroscopic interrogation of the Brønsted acid sites with the bases CH_3CN, CD_3CN, or CCl_3CN. In that work the *change* in IR O–H frequency and the *change* in the chemical shift in proton NMR are used as criteria of the acid strength, as required by theory [8,9]. The strength of Lewis sites, determined by the IR band shift of adsorbed CO, was found equal for SZ and FMSZ [7].

A possible clue for the function of the Fe and Mn promoters is obtained from the isomerization studies with double ^{13}C labelled butanes. A *bi*-molecular mechanism, which probably proceeds through an adsorbed C_8 intermediate, was identified by Adeeva et al. [10] for *n*-butane isomerization over FMSZ at 80°C. A bimolecular mechanism was also proposed by Zarkalis et al. based on studies of *n*-butane and *i*-butane isomerization kinetics over FMSZ [11]. This mechanism requires intermediate formation of an unsaturated compound, possibly butene. As oxidative dehydrogenation of alkanes is known to occur over iron oxide [12], it is conceivable that a small fraction of butane is dehydrogenated to butene on Fe oxide patches at the surface of FMSZ. This leads to the question: is the bimolecular reaction path restricted to the FMSZ catalyst or is it also valid for SZ catalysts where formation of unsaturated intermediates might appear less obvious? This issue is addressed in the present study.

Garin et al. reported that butane isomerization over unmodified SZ and platinum modified SZ (= PtSZ) at 250°C and in the presence of a large excess of H_2 proceeds predominantly via an intra-molecular mechanism [13]. They did detect a small contribution of the inter-molecular mechanism over SZ but none over PtSZ. These data indicate that two competitive mechanisms might occur. The intermolecular mechanism with low activation energy and proceeding via a C_8 intermediate requires formation of an unsaturated molecule or its presence in the feed as an impurity. If the concentration of such unsaturated molecules will be extremely low, e.g. in the presence of a high pressure of H_2, especially over PtSZ, the intramolecular mechanism with higher activation energy might prevail.

In the present work the double labelled *n*-C_4 molecule $^{13}CH_3$–CH_2–CH_2–$^{13}CH_3$ has been used to discriminate between these mechanisms over SZ in the absence of hydrogen. In addition, the effect of hydrogen on the isomerization rate has been studied. Whereas the present paper mainly focuses on *inter*-molecular scrambling, i.e. formation of *i*-butane molecules containing zero, one, three or four ^{13}C atoms from *n*-butane molecules containing two ^{13}C atoms, the phenomenon of *intra*-molecular rearrangement of carbon atoms in *n*-butane is also observed. In liquid superacids this internal rearrangement of C atoms is a well-known feature of C_4 isomerization, resulting from the formation of protonated methylcyclopropane intermediates, as reported by Brouwer and Hoogeveen [14].

The results are compared with previous data obtained with FMSZ catalysts. A second comparison is based on the IR band position of adsorbed CO, which is symptomatic for the acid strength of surface exposed Lewis sites.

2. Experimental

SZ was prepared by calcination of sulfated zirconium hydroxide, kindly provided by Magnesium Electron Inc., in a flow of dry air (30 ml/min) at 650°C for 1 h. ICP analysis showed that catalyst contained 2.2 wt% of sulfur.

Reaction studies with 1,4-^{13}C-butane (ISOTEC Inc.) were carried out in a recirculation system, as described in ref. [10]. 1.5 g of catalyst was pretreated in dry air (30 ml/min) at 450°C for 2 h. After evacuation of the reactor and the circulation system, and heating of the catalyst to reaction temperature, 30 Torr of 1,4-^{13}C-butane were introduced into the system. The reaction products were monitored by an on-line mass-spectrometer (Dycor M100) connected with the reaction system by a leak valve. At the end of a catalytic run, the content of the recirculation system was condensed in a liquid nitrogen cooled trap, and analyzed by GC-MS in the Analytical Laboratory of the Chemistry Department of Northwestern University.

For studies in an atmospheric micro-flow reactor as described in ref. [7], 1.5 g catalyst was pretreated in dry air at 450°C for 2 h and cooled to 180°C flowing dry air. The feed consisted of 1 vol% of *n*-butane in nitrogen, 33 ppm of butene was present as an impurity (75 ml/min, Linde, CG) and He (45 ml/min, Linde, UHP). In some runs the He was replaced by H_2 (Linde, UHP).

3. Results

GC-MS analysis of the mixture after 1 h reaction of 1,4-^{13}C-butane over SZ at 130°C showed that 40% of the reactant was converted to *i*-butane; in addition, minor amounts of propane and *i*-pentane were observed. At this temperature, equilibrium corresponds to 68% *i*-butane and 32% *n*-butane. The butane isomers were analyzed separately for their ^{13}C content. The resulting mass-spectra of *i*-butane and *n*-butane are shown in figs. 1a and 1b. Two groups of peaks are of relevance. The parent peaks of the five isotopic C_4 molecules are located in the region around m/e 60; C_3 fragments formed by the loss of a methyl group from the molecular ion are located in the region of m/e 44. As the peak at $M-1$, with M = mass of the molecule, is caused by a carbenium ion, the ratio of this peak to the parent peak is much higher for *i*-butane than for *n*-butane, reflecting the higher stability of tertiary versus secondary carbenium ions.

Comparison of the peak distribution near mass 60 in figs. 1a and 1b clearly shows that after 1 h of reaction at 130°C the concentration of molecules with three or four ^{13}C atoms is significant for *i*-butane, but in the *n*-butane fraction mass 60 predominates while the contribution of mass 61 is very small. In other words: the *i*-butane is isotopically scrambled, but the reactant *n*-butane is mainly present as the original compound. It is clear from this qualitative inspection that an important isomerization path is *inter*-molecular, leading to isotopic scrambling. This result,

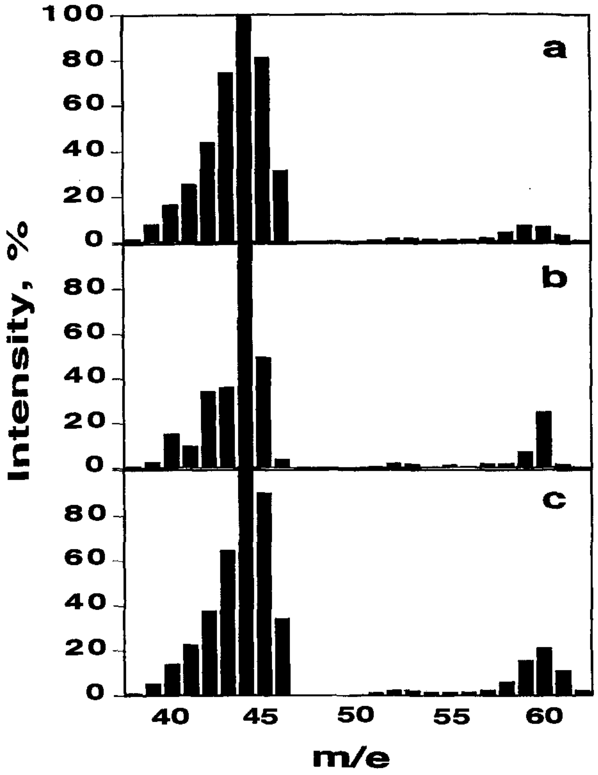

Fig. 1. Mass-spectra, obtained from GC-MS analysis of the reaction mixture of 1,4-^{13}C-butane over SZ; (a) *i*-butane, 130°C 1 h; (b) *n*-butane, 130°C 1 h; (c) *n*-butane 150°C 2 h.

previously found with FMSZ catalysts at 80°C, thus, also holds for SZ catalysts at 130°C.

A quantitative evaluation, taking into account fragmentation and corrections for natural abundance, was performed by means of a computer program to analyze the concentrations of all five isotopic *i*-butane molecules. The same was done with the five isotopic *n*-butane molecules. The results are compiled in table 1, which also lists the calculated values of the binomial distribution coefficients. It is obvious, that the observed distribution of the *i*-butanes is indistinguishable, within experimental error, from the binomial distribution. In contrast, the distribution of the *n*-butanes after 1 h at 130°C is far from isotopic equilibrium, the molecule with two ^{13}C atoms still predominates. In this case the error in the mass spectra is highest for the lighter butanes, to which fragmentation of the abundant $^{13}C_2$ butane ions strongly contributes. The apparent skewing of the distribution in favor of lower masses in table 1, clearly, is an artifact; there is absolutely no reason to assume that the $^{13}C/^{12}C$ ratio for the total population of C_4 molecules or the sub-population of *n*-butane molecules would differ from that of the feed.

Table 1
Isotopic distributions for C_4 molecules with overall ratio of $^{13}C/^{12}C = 1$

Molecule	$^{12}C_4$	$^{13}C_1{}^{12}C_3$	$^{13}C_2{}^{12}C_2$	$^{13}C_3{}^{12}C_1$	$^{13}C_4$
equilibrium					
binom. coeff.	1	4	6	4	1
percentage	6.25	25.0	37.5	25.0	6.25
observed (%)					
i-butane (1 h, 130°C)	3.9	24.2	39.9	25.5	6.5
n-butane[a] (1 h, 130°C)	3.4	6.1	85.9	3.5	1.0
n-butane (2 h, 150°C)	6.7	25.1	39.5	23.6	5.0

[a] Higher abundance of $^{12}C_4$ and $^{13}C_1{}^{12}C_3$ over $^{13}C_3{}^{12}C_1$ and $^{13}C_4$ is experimental artefact; see text.

Fig. 1c shows the distribution of the isotopic *n*-butane molecules after 2 h at 150°C; the mathematical evaluation of the mass spectrum is given in the fourth row of table 1. In this stage, 58% of *n*-butane was converted to *i*-butane; i.e. chemical equilibrium with 65% *i*-butane has been approached. Whereas, the mass spectrum of *i*-butane is indistinguishable from that after 1 h at 130°C, the isotopic distribution within the *n*-butane fraction differs significantly from that after 1 h reaction at 130°C. An increase in peaks with m/e 61 and 62 in fig. 1c indicates that *n*-butane underwent significant isotopic scrambling; accordingly the data in table 1 show that *n*-butane has virtually reached isotopic equilibrium, i.e. binomial distribution.

In the mass spectra of completely scrambled *i*-butane and *n*-butane the region near m/e 44 is complicated by overlapping spectra of C_3 fragments, containing one, two or three ^{13}C atoms. This complication is, however, minimal in the mass spectrum of *n*-butane after 1 h at 130°C, i.e. in the absence of large isotopic scrambling. This feature has been exploited to gain evidence for internal rearrangement of carbon atoms in *n*-butane molecules. In the spectrum of the original $^{13}CH_3$–CH_2–CH_2–$^{13}CH_3$ (not shown) the peak with $m/e = 44$ is predominant; it is formed by loss of a $^{13}CH_3$ group from the parent ion with $m/e = 60$. Remarkably, a peak with $m/e = 45$ that is negligible in the original spectrum becomes prominent in the mass spectrum of *n*-butane after 1 h of reaction at 130°C (fig. 1b). Only a small part of this peak can be contributed by $^{13}CH_3$–CH_2–$^{13}CH_2$–$^{13}CH_3{}^+$ ions that have lost a heavy $^{13}CH_3$ group. Obviously, parent ions containing two ^{13}C atoms have lost a *light* methyl group $^{12}CH_3$. This observation indicates that internal rearrangement of $^{13}CH_3$–CH_2–CH_2–$^{13}CH_3$ to $^{13}CH_3$–CH_2–$^{13}CH_2$–CH_3 has taken place over the SZ catalyst, in close analogy to previous findings by Brouwer et al. in liquid superacids. These authors had found that at low temperature *intra*-molecular rearrangement of *n*-butane via a protonated cyclopropane intermediate does not lead to isobutane (which would require a primary carbenium ion intermediate) but to inverted *n*-butane [13].

The effect of hydrogen on the rate of *n*-butane isomerization is shown in fig. 2. Fig. 2a is the trace of *n*-butane conversion over SZ at 180°C in He, in the absence of

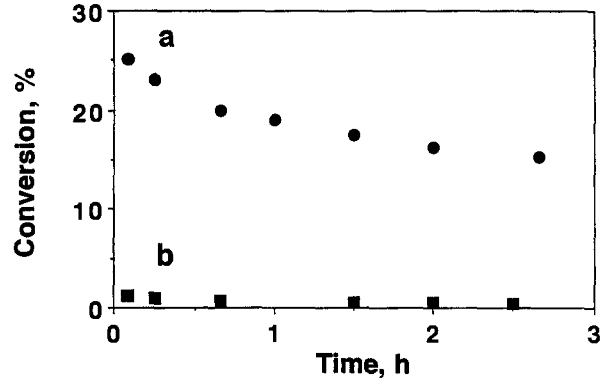

Fig. 2. Isomerization of *n*-butane over SZ at 180°C (a) in the absence and (b) in the presence of H_2 ($C_4 : H_2 = 1 : 60$).

H_2. Although the catalyst deactivates at this temperature, an appreciable activity was observed even after 3 h. In fig. 2b the conversion is shown vs. time on stream under identical conditions except for the replacement of He by H_2. Clearly, the conversion is more than one order of magnitude lower in H_2 than in He. Again, the activity continued to decrease. Preliminary TPR data exclude sulfate reduction by H_2 as a plausible cause of catalyst deactivation at 180°C.

4. Discussion

The results with double labelled *n*-butane indicate that at 130°C and in absence of hydrogen, the predominant mechanism for *n*-butane isomerization over the SZ catalyst is an *inter-molecular mechanism*, leading to complete isotopic scrambling in the reaction product. This is identical to the result reported earlier and measured in the same equipment with an FMSZ catalyst [4]. It can thus be concluded that promoting with Fe and Mn does not create a totally different reaction pathway. Apparently, the presence of these oxides merely facilitates the reaction path that is used also on the unpromoted SZ.

Formation of an adsorbed C_8 intermediate can be visualized, at least formally, by interaction of an "adsorbed carbenium ion" (more probably: a surface butoxy group) with a butene molecule. The negative effect of hydrogen on the rate of isomerization indicates that in hydrogen the concentration of unsaturated intermediates – butene or carbenium ions – is much lower. Previously it was shown that alkane dehydrogenation is possible over Brønsted/Lewis combinations [15,16]. It is, therefore of interest to also characterize the Lewis sites in the SZ catalyst. It has been shown before that the strength of the Brønsted and Lewis acid sites is equal for SZ and FMSZ [7]; the FTIR band of adsorbed CO was observed at 2200 cm^{-1} on both catalysts [7]. This suggests that surface exposed Zr^{4+} ions are the predominant Lewis acid sites and that their acidity is little affected by the presence of Fe^{3+} or Mn^{2+} ions. As Knözinger et al. have shown that the strength of surface Lewis acid sites can be derived from a graph of the CO band position vs. the effective charge density [17,18], we have included the point for SZ and FMSZ in the graph displayed by Beutel [19] which comprises all data known at present. The result is shown in fig. 3. The charge density was calculated as in refs. [16,17], assuming that the coordination number of Zr^{4+} with O^{2-} ions is four. The position of the shifted CO band indicates that the acid strength of the Lewis sites on SZ and FMSZ is lower than that of Al^{3+} ions in the surface of dehydrated γ-Al_2O_3; i.e. they should not be called superacids, as we stated before in ref. [7].

The high rate of butane isomerization shows that the Gibbs free energy of the transition state for butane isomerization is lower on SZ based catalysts than on conventional solid acids. As the acid strength of the surface sites on the SZ family of catalysts is not higher than, for instance, in HZSM-5, it follows that stabilization of adsorbed intermediates is likely to be the crucial cause for the high catalytic activity of these materials. In a related paper a model was presented for the surface groups that might be responsible for this high activity [7].

It is remarkable that intramolecular isotopic scrambling of *n*-butane, as expected on the basis of Brouwer's results, precedes intermolecular isotopic scrambling; the latter process is strong only when the chemical normal/iso equilibrium is virtually attained. In terms of the classical carbenium ion theory, the most favorable path for

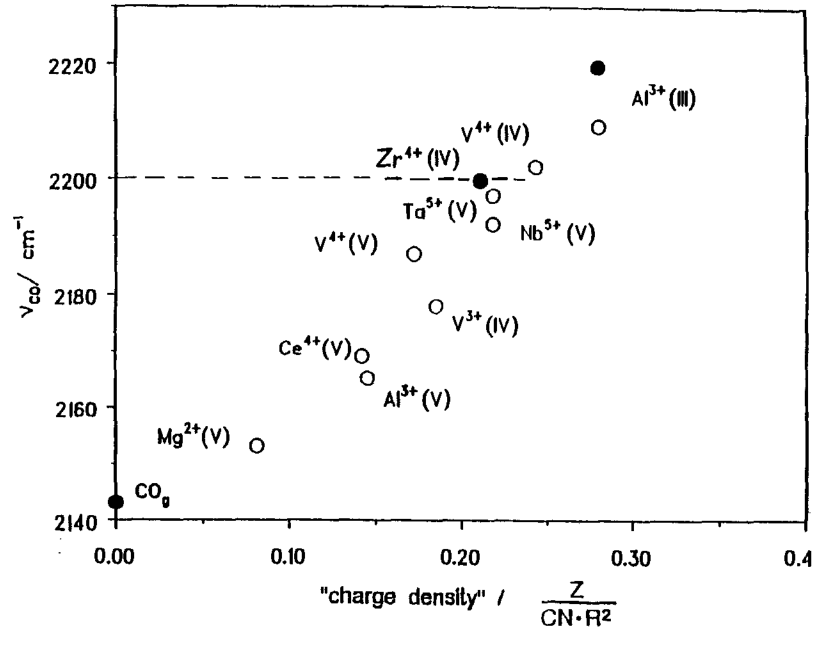

Fig. 3. CO stretching frequency vs. effective charge density on various solid acids; Z: charge, CN: coordination number and R: metal ion radius.

β-fission of the family of tertiary C_8 carbenium ions leads to two iso-C_4 fragments [20]. A second, though energetically less favorable path is rupture of the adsorbed C_8 species into a normal-C_4 + iso-C_4 pair, while formation of C_3 and C_5 fragments is still less favorable. It follows that isotopically scrambled *n*-butane is only a small side product of the isomerization to scrambled *i*-butane. However, *i*-butane molecules will react again, without changing the extent of isotopic scrambling of the population of *i*-butane molecules, but in every step when a C_8 intermediate is formed there is a finite chance of its decomposition to *n*-C_4 + *i*-C_4. Therefore, also *n*-butane must, ultimately, approach isotopic equilibrium. Isotopically scrambled *n*-butane thus is a secondary product of the isomerization reaction.

Previously Chen et al. and Garin et al. studied the effect of hydrogen on *n*-butane isomerization over SZ at 250°C [21,22]. Under these conditions, the catalyst deactivates rapidly in the absence of hydrogen. These authors report that in the presence of hydrogen the initial activity is lower, but the catalyst does not deactivate. The authors ascribed the promoting effect of hydrogen to lowering the deactivation rate by hydrogenation of coke precursors. Garin et al. also reported that at high hydrogen to hydrocarbon ratios this promoting effect is overrated by an opposing effect. They suggested that *n*-butane isomerization can proceed via a bimolecular mechanism, but a large excess of hydrogen inhibits dehydrogenation of *n*-butane. This assumption is confirmed by the present results.

Under the much milder conditions of the present study, 130°C instead of 250°C, catalyst deactivation is very slow, the negative effect of hydrogen on the isomerization rate is therefore not masked by an effect of hydrogen on catalyst deactivation.

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