Modification of the catalytic properties of sulfated zirconia by addition of metal promoters

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We have studied the effects of promoting sulfated zirconia catalysts by addition of transition metals. We have found that the addition of Ni causes an activity enhancement comparable to that caused by the addition of Fe and Mn. The TPD/DRIFTS results show that the catalytic activity does not correlate with either Brønsted or Lewis acidity. The high isomerization activity of these catalysts is explained in terms of a bifunctional mechanism in which the metal promoters are responsible for an enhancement in the surface concentration of olefins rather than an enhanced acidity.

Keywords: alkane isomerization; sulfated zirconia; strong acid catalysts; solid acids; Fe–Mn–SO_4/ZrO_2; Ni–SO_4/ZrO_2

1. Introduction

In recent years, strong solid acid catalysts have received renewed attention. Among these catalysts, sulfated zirconias appear as some of the most promising materials for commercial processes, such as alkane isomerization and alkane–alkene alkylation [1]. Hsu et al. [2] were the first to observe that the activity of sulfated zirconia for the isomerization of *n*-butane could be greatly enhanced by the addition of Fe and Mn. They postulated that this enhancement was due to the generation of additional sites, with higher acid strength than those on plain sulfated zirconia [3]. By contrast, in more recent work, Adeeva et al. [4] have proposed that the rate enhancement is not caused by an increase in acid strength but rather by an increased production of alkenes which may participate in the reaction. These authors have presented convincing arguments in favor of a mechanism previously proposed by Guisnet [5]. This mechanism involves the formation of intermediate C_8 carbenium ions by oligomerization of C_4 carbenium ions and butenes. Subsequently, the C_8 carbenium ion would undergo skeletal rearrangement, and finally a

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β-scission step would produce an isobutane molecule and regenerate the active C_4 carbenium ion. This hypothesis has been demonstrated for the case of *n*-butane isomerization on H-mordenites and is consistent with the observed equimolar formation of C_3 and C_5 hydrocarbons as well as a reaction order of 2. Using isotopically labeled *n*-butane, Adeeva et al. [4] concluded that such a mechanism would also be operative on sulfated zirconia promoted with transition metal oxides. The high dehydrogenation activity normally exhibited by transition metals, would be responsible for the enhanced isomerization activity of the Fe–Mn-promoted catalysts.

In their original patent, Hsu et al. [2] have claimed that not only Fe and Mn, but also other transition metals are effective for the promotion of sulfated zirconia catalysts. However, only the Fe–Mn system has attracted the attention of most researchers. In this contribution, we report a study of the *n*-butane isomerization reaction on a series of sulfated zirconia catalysts promoted with Fe, Fe–Mn, and Ni. Our results support the idea of a bifunctional mechanism in which the role of the transition metals would be to increase the rate of oligomerization rather than the generation of stronger acid sites.

2. Experimental

Table 1 summarizes the main characteristics of the catalysts reported in this work. The samples were labelled according to their ingredients. ZS indicates sulfated zirconia, F iron, M manganese and N nickel. The catalysts were prepared by standard techniques [6]. The zirconium hydroxide, $Zr(OH)_4$ precursor (BET area 180 m^2/g) was precipitated from a 0.5 M zirconium tetrachloride solution by drop-

Table 1
Nominal composition of the samples investigated

Sample	Fe (wt%)	Mn (wt%)	Ni (wt%)	Sulfate (wt%)
ZS	0	0	0	8.0
ZSF-1	0.2	0	0	8.0
ZSF-2	0.3	0	0	8.0
ZSF-3	0.5	0	0	8.0
ZSF-4	1.0	0	0	8.0
ZSF-5	1.5	0	0	8.0
ZSFM-A	1.0 (co) [a]	0.5 (co) [a]	0	8.0
ZSFM-B	1.0 (first) [a]	0.5 (last) [a]	0	8.0
ZSFM-C	1.0 (last) [a]	0.5 (first) [a]	0	8.0
ZSN-1	0	0	0.25	8.0
ZSN-2	0	0	0.50	8.0
ZSN-3	0	0	0.75	8.0
ZSN-4	0	0	1.00	8.0

[a] (co) indicates co-impregnated Fe and Mn precursors. (first) and (last) indicate the order in which the Fe and Mn precursors were sequentially impregnated.

wise addition of NH_4OH. The Fe, Mn, and Ni promoters were added to the zirconium hydroxide by incipient wetness impregnation with aqueous nitrate solutions. Subsequently, the impregnated materials were heated in air to 473 K. We have observed that the method of sulfate addition, the sulfate loading, and the calcination procedure strongly affect the resulting catalytic activity. The effect of these variables will be discussed in a future paper [7]. In the work reported here, the sulfate addition was accomplished by incipient wetness impregnation with an NH_4SO_4 solution to give a nominal sulfate loading of 8 wt%. After drying, the catalysts were calcined in air at 873 K for 4 h. For comparison, an unpromoted sulfated zirconia catalyst (ZS) was prepared following the same sequence, but without the addition of metals. The surface area of the calcined samples was about 100–120 m^2/g.

The reaction studies were carried out in a microcatalytic flow reactor. Before each run, the catalyst (usually 0.4 g) was pretreated in situ under flow of dry air at 873 K for 4 h and cooled in flow of He to the reaction temperature. Rate measurements were obtained at 373 and 523 K using a space velocity of 3450 h^{-1} with a molar fraction of *n*-butane of 0.25. The gases used in this work were of high purity ($>99.9\%$). Helium was further purified by passing through molecular sieve traps. The reaction products were analyzed by a HP-5890 gas chromatograph, controlled by a ChemStation and equipped with a 50 m KCl/Al_2O_3 capillary column and a flame ionization detector.

The acidity type and distribution of ZS, ZSF, ZSFM, and ZSN catalysts were measured by temperature programmed desorption (TPD) of NH_3. Infrared spectroscopy was employed to measure the amount of NH_3 coordinated to Lewis and Brønsted acid sites as a function of temperature. Diffuse reflectance infrared spectroscopy (DRIFTS) measurements were made for 5–10 mg catalyst samples with a Mattson Instruments, Inc. Sirius 100 FT-IR. This instrument is equipped with a modified Harrick Scientific variable temperature diffuse reflectance vacuum chamber which has been described in detail elsewhere [8]. Samples were pre-treated to remove adsorbates by heating under vacuum ($<1 \times 10^{-6}$ Torr) from ambient temperature to 873 K at a rate of 30 K/min. After a 5 min isothermal period at 873 K, samples were cooled to 673 K under vacuum. Enough NH_3 was added to the vacuum chamber to achieve a pressure of about 100 Torr and the sample was allowed to cool to 373 K. Infrared spectra were acquired at a rate of 1/min at 8 cm^{-1} resolution during TPD of NH_3 under flowing N_2 (10 cm^3/min). The TPD heating ramp was 10 K/min up to 873 K. Diffuse reflectance infrared spectra measured during TPD experiments were converted to apparent absorbance ($-\log R_\infty$) [9].

3. Results and discussion

Fig. 1 shows the *n*-butane isomerization rate as a function of time on stream for an $n\text{-}C_4H_{10}$–He (1 : 3) mixture at 373 K over three different sulfated zirconia

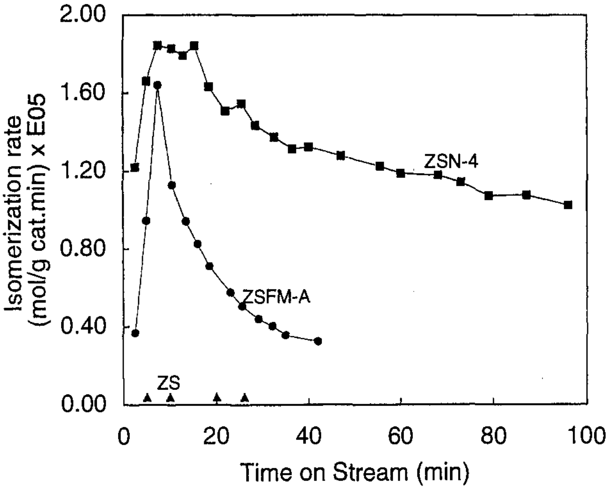

Fig. 1. n-butane isomerization rate as a function of time on stream over various sulfated zirconia catalysts promoted with transition metals. The reaction was conducted at 373 K using a space velocity of 3450 h^{-1} and a molar fraction of n-butane of 0.25 in helium.

catalysts. The selectivity to isobutane was initially above 85% and increased to about 95% with time on stream. The main by-products were C_3 and C_5. It can be observed that the catalyst promoted with Fe and Mn (ZSFM-A) was much more active than the unpromoted sulfated zirconia (ZS), which was essentially inactive under these conditions. A catalyst promoted with Mn but without Fe was even less active than the unpromoted sulfated zirconia. The synergistic promoting effect of Fe and Mn has been previously reported [2] and confirmed by several authors [6]. It is then interesting to note that, as can be observed in fig. 1, the Ni-promoted catalyst (ZSN-4) was even more active than the one promoted with Fe and Mn. We do not imply that Ni is necessarily a better promoter than Fe and Mn. In fact, we have observed that the activity of the metal-promoted sulfated zirconia catalysts can be greatly affected by other preparation variables such as sulfate content and calcination time. In some cases, the catalyst promoted with Fe–Mn was more active than that promoted with Ni [7]. What we want to emphasize here is that the promoting effect is not a unique characteristic of Fe and Mn.

When H_2 was used as a diluent instead of He, a much lower reaction rate was observed for the same catalyst series. In fact, the n-C_4 conversion at 373 K was essentially zero on all of the catalysts. The activity of these catalysts at 523 K is compared in fig. 2. Again, the Ni-promoted catalyst exhibited an activity significantly higher than those promoted with Fe and Mn. The runs under hydrogen not only show a great difference in catalytic activity but also in the time dependence of the rate. Under He, the activity exhibited an initial induction period, reached a maximum and finally started to decrease. By contrast, no induction period was observed under H_2 for any of the catalysts investigated.

We have studied the effect of varying the transition metal loading on the isomer-

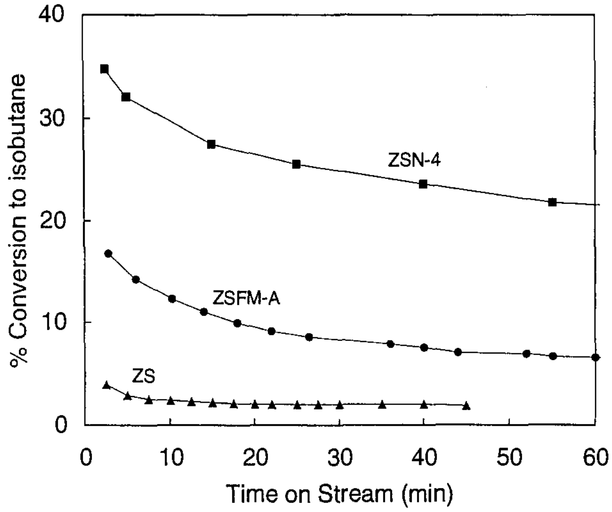

Fig. 2. *n*-butane conversion to isobutane as a function of time on stream over various sulfated zirconia catalysts promoted with transition metals. The reaction was conducted at 523 K using a space velocity of 3450 h^{-1} and a molar fraction of *n*-butane of 0.25 in hydrogen.

ization activity of the catalysts under *n*-C_4H_{10}–H_2 (1 : 3) mixtures at 523 K. As shown in fig. 3, both the Ni-promoted and the Fe-promoted catalysts were more active than the unpromoted sulfated zirconia (0% metal). Different trends were observed for Fe and Ni as the amount of each metal was increased. Whereas the activity of the Ni-promoted catalysts increased with Ni loadings up to 1.0 wt% Ni,

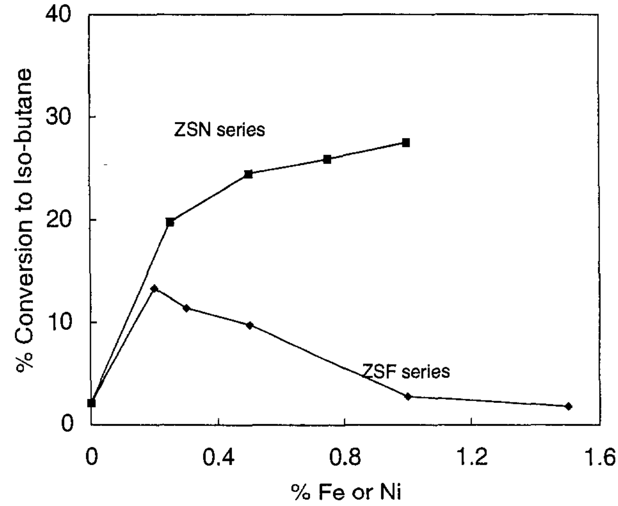

Fig. 3. *n*-butane conversion to isobutane after 20 min on stream as a function of metal (Fe or Ni) content, expressed in wt%. The reaction was conducted at 523 K using a space velocity of 3450 h^{-1} and a molar fraction of *n*-butane of 0.25 in hydrogen.

the activity for the Fe-promoted catalysts exhibited a maximum at very low loadings (about 0.2 wt% Fe) and then decreased as the amount of Fe was increased.

To study the combined effect of Fe and Mn, we investigated a series of catalysts containing the same amount of Fe and Mn (1.0 wt% Fe and 0.5 wt% Mn) but prepared following different impregnation procedures. As illustrated in table 2, the catalyst prepared by co-impregnation (ZSFM-A) showed the highest activity. On the other hand, for the sequentially impregnated catalysts, the Mn-first catalyst (ZSFM-B) was significantly more active than the Fe-first catalyst (ZSFM-C). To explain these results, we propose that the observed decrease in conversion as the amount of Fe increases from 0.2 to 1.5% is due to the agglomeration of Fe species. As shown above, the addition of Mn alone does not improve the catalytic activity of ZS [6]. Therefore, our results would indicate that the main role of Mn would be to increase (or stabilize) the dispersion of Fe. Likewise, it is noteworthy that when Ni was used as a promoter, the activity continuously increased with the Ni loading up to 1 wt% Ni. On the basis of the previous discussion, this trend would indicate that Ni is better dispersed than Fe on the surface of zirconia. This may be the reason for the high activity of the Ni-promoted catalysts reported in this contribution. We are currently conducting characterization studies to test this hypothesis and to determine the oxidation state of these promoters, which under reaction conditions are certainly not in the metallic form. Iglesia et al. [10] have recently shown that, when sulfated zirconia catalysts were promoted with Pt an increase in activity was observed in the presence of hydrogen. They explained this promotion in terms of an enhanced hydride transfer promoted by Pt. This mechanism may not be operative in our case since the activity *decreases* with the addition of hydrogen. As discussed below, it is possible that the bimolecular mechanism only operates over the promoted ZS catalysts under He at low temperatures, while over the unpromoted ZS catalysts under H_2 at higher temperatures the classical monomolecular mechanism is still valid.

To compare the catalytic behavior with the density of acid sites we conducted NH_3 TPD-DRIFTS studies on the same samples used in the catalytic activity measurements. It has been previously proposed [11] that the number of Lewis and Brønsted acid sites occupied by NH_3 is proportional to the absorbances measured

Table 2
Conversion of *n*-butane to isobutane after 5 min on stream in (1 : 3) *n*-butane/hydrogen reaction mixture at 523 K and at a space velocity of 3450 h^{-1} over various sulfated zirconia catalysts promoted with Fe and Mn

Sample	Description	Conversion (%)
ZSFM-A	Fe–Mn co-impregnated	11.0
ZSFM-B	Mn (first) Fe (last)	8.2
ZSFM-C	Fe (first) Mn (last)	5.0
ZSF-4	Fe	3.2
ZS	unpromoted	2.5

at 1610 and 1450 cm^{-1}, respectively. In order to compare absorbance temperature profiles for different catalyst samples, absorbance values were normalized by dividing by the absorbance of the 1390 cm^{-1} band measured at 873 K, which represents the S=O stretching vibration and is indicative of the total amount of surface sulfate, which was similar for the four samples. The variations in the intensities of the absorbance bands at 1610 and 1450 cm^{-1} as a function of sample temperature are shown in fig. 4 for samples ZSFM-A, ZSF-3, ZS, and ZSN-4. The corresponding Brønsted/Lewis ratios are plotted in fig. 5 as a function of temperature.

Some differences were observed in both, the acidity densities and the Brønsted/Lewis ratios among the four catalysts investigated, but no correlation with catalytic activity was apparent. For example, despite their significant differences in activity, the two Fe-containing samples (ZSF-1 and ZSFM-6) exhibited about the same level of Brønsted and Lewis acidity. At the same time, both exhibited less Brønsted acidity than the unpromoted sulfated zirconia sample. Finally, the sample containing Ni, which is the most active in our catalyst series, showed almost identical profiles for both types of acidities as those of the unpromoted sulfated zirconia, which was the least active sample.

Nascimento et al. [12] have recently proposed that the low-temperature isomerization activity of sulfated zirconia catalysts is related to the simultaneous presence of Brønsted and Lewis sites. In fact, they have observed that the maximum activity is obtained when the Brønsted/Lewis ratio is about unity. By inspecting fig. 5 it could be argued that the addition of Fe decreases that ratio from about 3 to about 1, and this change would account for the promoting effect of Fe. However, the addition of Ni does not decrease the Brønsted/Lewis ratio but still causes a dramatic enhancement in catalytic activity. Therefore, it appears that the promoting effect of the transition metals is not related to the modification of acidity.

It has been recently suggested that Fe is not incorporated into the zirconium oxide lattice but rather it is dispersed on its surface, mainly in the form of iron oxide [13]. Our results support this view and indicate that the isomerization activity is strongly affected by the dispersion of the transition metal. These results, in combination with the lack of correlation between acidity and catalytic activity displayed by our samples, would favor the idea of a *bifunctional mechanism*. Our TPD-DRIFTS spectra indicate that the acid sites are still provided by the sulfated zirconia since the addition of the transition metal does not result in an increase in the density of acid sites. Yet, these transition metals may perform a secondary but extremely important function in the isomerization reaction. As mentioned above, a possible secondary function of the transition metals has been proposed by Adeeva et al. [4]. On the basis of the idea that isomerization on these catalysts may involve an oligomerization step, these authors have postulated that the role of the transition metals might be to act as dehydrogenation sites. The olefins thus generated would participate in the subsequent oligomerization step. Of course, in order to explain the promoting effect, it would be necessary to assume that the rate limiting step for the *n*-butane isomerization reaction is the dehydrogenation of *n*-butane

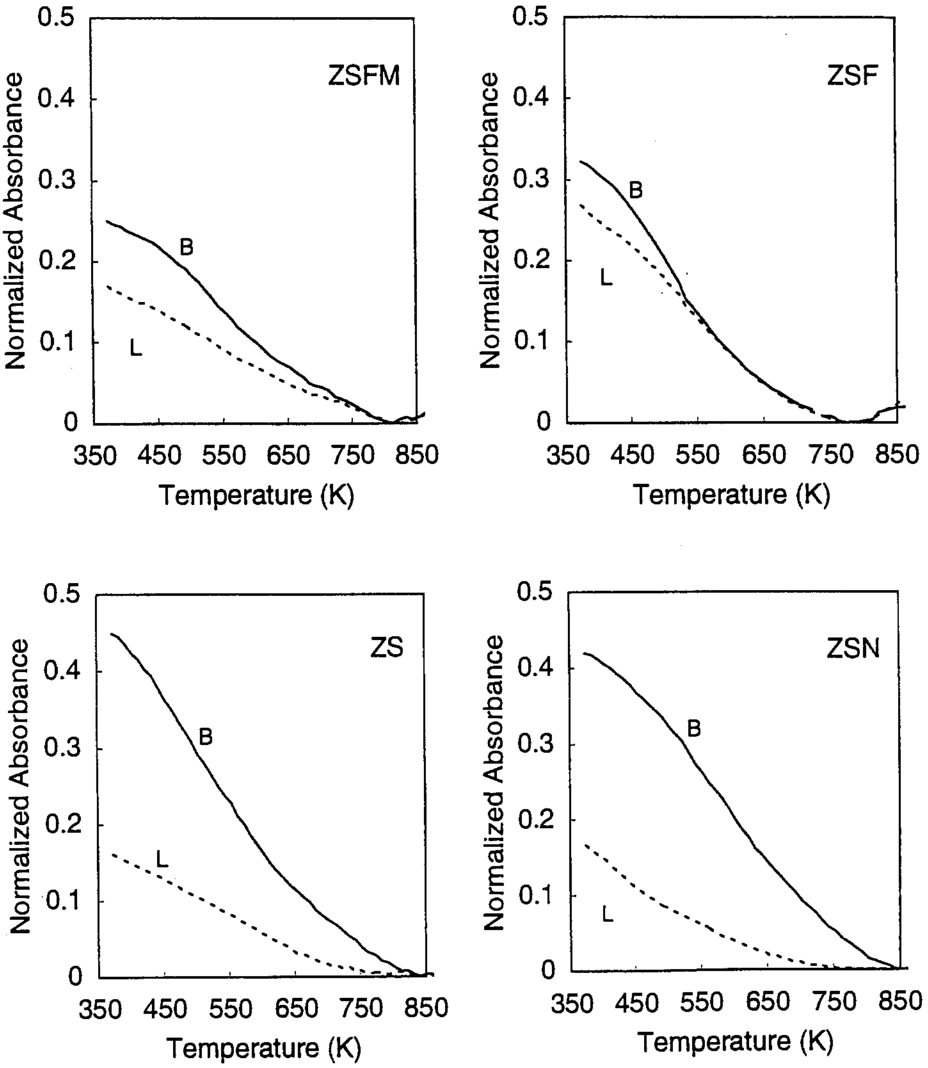

Fig. 4. Intensities of the adsorbed ammonia IR bands at 1450 $\mathrm{cm^{-1}}$ (curve B) and 1610 $\mathrm{cm^{-1}}$ (curve L) as a function of sample temperature normalized by dividing by the absorbance of the 1390 $\mathrm{cm^{-1}}$. The observed decrease in band intensity as a function of temperature is due to the desorption of NH_3. The four samples investigated were ZSFM-A, ZSF-3, ZS, and ZSN-4.

to produce butenes. However, dehydrogenation reactions are generally much faster than the other steps involved in the mechanism and, therefore, dehydrogenation is not likely to be rate determining.

We might propose an alternative hypothesis, which is closely related to that postulated by Adeeva et al. [4], but does not require the dehydrogenation step to be rate limiting. We might speculate that the presence of transition metals may attract olefin molecules which form a butene pool that enhance the local concentration of olefins near the acid sites. Such *enhanced surface concentration* of olefins may not

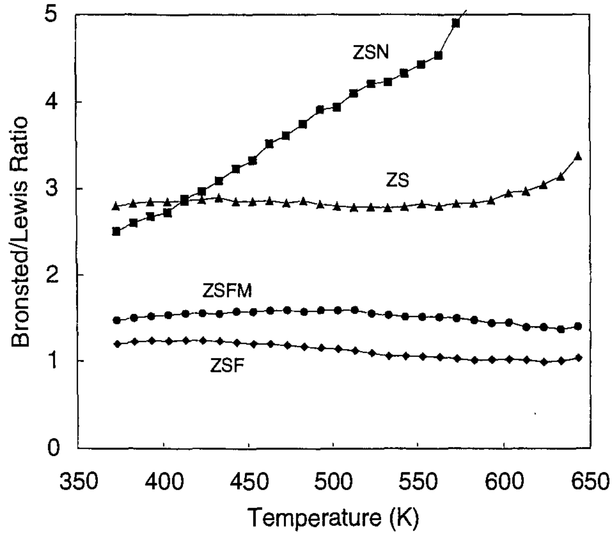

Fig. 5. Variation of the Brønsted to Lewis ratio as a function of sample temperature, as determined from the ratio of curve B to curve L in fig. 4 for each of the four catalysts investigated.

be in equilibrium with the gas phase. Under those conditions, the oligomerization step could still be rate limiting but it would be greatly accelerated by the higher surface concentration of olefins. According to this hypothesis, the initial induction period, observed when the reaction was conducted under He, would be ascribed to the proposed buildup of olefins on the catalyst surface rather than a modification of the catalyst structure [6].

As expected, such a buildup would not occur under H_2, consistent with the lower reaction rate and with the fact that no induction period was observed in this case. Also, since the formation of coke is directly related to the surface concentration of olefins, the lower deactivation rate observed under H_2, despite the higher temperatures and higher conversions involved, would be expected if the surface concentration of olefins was much lower under H_2 than under He. A word of caution is important here since it is possible that the mechanisms that operate under He on sulfated zirconia promoted with Fe–Mn or Ni are very different than those under H_2 on unpromoted sulfated zirconia. For example, Garin et al. [14] have recently reported results that directly oppose those of Adeeva et al. [4]. From the analysis of ^{13}C isotope distribution in the products, they have concluded that the *n*-butane isomerization reaction is intramolecular in the presence of hydrogen at 523 K. The percentage of double labelling was extremely small when SO_4/ZrO_2 catalysts were used and zero when the catalysts were promoted with Pt.

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