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The Role of Transition Metal Promoters on Sulfated Zirconia Catalysts for Low-Temperature Butane Isomerization

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The low temperature isomerization of butane to isobutane was catalyzed by sulfated zirconia promoted with transition metals like Fe, Mn, and Pt. At 323 K, the Fe,Mn-promoted sample exhibited the usual induction period to a highly active state, followed by rapid deactivation. At the same conditions, a Pt-promoted catalyst also showed an induction period but was followed by a period of unusually stable activity, even in the absence of dihydrogen. The mechanism of the isomerization reaction, evaluated by using ^{13}C-labeled butane over Fe,Mn-promoted at 323 K and unpromoted sulfated zirconia at 473 K, was found to be intermolecular. Because the formation of a C_8 intermediate in a bimolecular pathway most likely involves the reaction of olefins, the effect of adding *trans*-2-butene to the butane feed was investigated. The increase in isomerization activity that accompanied butene addition was consistent with a mechanism in which butene is protonated by acid sites of the catalyst to initiate a chain reaction that eventually produces isobutane. Since the calculated chain length (moles isobutane formed/moles butene added) was similar for all of the materials studied, the acidities of the catalysts appear to be unaffected by the presence of transition metals. Therefore, the role of transition metal promoters in sulfated zirconia is to increase the surface concentration of intermediate butenes that subsequently react to form isobutane. Due to the very different stabilities of the promoted catalysts at low temperatures, we speculate that the Fe,Mn-promoted sample forms butene non-catalytically whereas the Pt-promoted sample forms butene catalytically.

INTRODUCTION

The reported superacidity of sulfated metal oxides of Fe, Zr, Sn, and Ti [1–4], has attracted considerable attention to these materials as potential replacements for liquid acids. In particular, sulfated zirconia possesses superacid sites with $H_o < -16$ [5] and catalyzes reactions such as cracking, isomerization, alkylation, acylation, esterification, and oligomerization [6]. However, the previously reported superacid strength of surface sites on sulfated zirconia has been questioned [7, 8].

Hsu *et al.* [9] discovered that promoting sulfated zirconia with 1.5 wt% iron and 0.5 wt% manganese increased the rate of *n*-butane isomerization at low temperature by several orders of magnitude. Various attempts have been made to elucidate the nature of the active site responsible for butane isomerization. For example, the acidity (site density and strength) of sulfated zirconia is apparently similar to the acidity of the iron and manganese promoted sulfated zironcia [7, 10, 11]. In an earlier work, we showed by Fe and Zr K-edge EXAFS that iron is not incorporated isomorphously into the tetragonal zirconium oxide but is located on the surface or at defects [10], which suggests that the promoter does not modify the zirconia phase but may play a separate role in the reaction scheme. Indeed, Adeeva *et al.* [7] speculated that promoter metal oxides dehydrogenate butane to butene, a possible intermediate in the isomerization of butane. In addition, Wan *et al.* [11] provided strong experimental evidence of redox active sites on iron and manganese promoted sulfated zirconia. They proposed that the promoter transition metal oxides form an oxy species capable of low temperature dehydrogenation of butane by a “bifunctional/spillover” mechanism. Even though a consensus appears to be emerging regarding the importance of butenes in the isomerization reaction, the specific nature of the Fe,Mn promotion remains elusive.

The role of added Pt on the reactivity of sulfated zirconia is even less clear. Platinum promotion of sulfated zirconia is suggested to occur by increasing the acidity of sulfated zirconia [12–16], increasing hydride transfer to reaction intermediates [17], or reducing deactivation of the catalyst by preventing coke formation [18, 19]. For example, Ebitani *et al.* [13, 14] observed an increase in activity for butane isomerization at 523 K upon addition of Pt to sulfated zirconia in the presence of dihydrogen. The platinum was reported to be in a cationic form that is incapable of hydrogenation/dehydrogenation catalysis but may be active for the dissociation of dihydrogen. The resulting hydrogen adatoms possibly form Bronsted sites active for acid-catalyzed isomerization reactions and reduce coke deposition by decreasing the activity of strong Lewis sites. However, Zhang *et al.* [20] reported that the presence of Pt did not affect the distribution of acid sites. Iglesia *et al.* [17] found that the activity of sulfated zirconia for heptane

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isomerization increased considerably after platinum addition and that the rate was proportional to the dihydrogen partial pressure. They suggested that the metal component participates in rate-determining hydride transfer reactions that convert adsorbed carbocations into products. Liu *et al.* [21] carried out the isomerization of butane over platinum promoted sulfated zirconia at various dihydrogen partial pressures and concluded that Pt prevents coking of the catalyst surface and dehydrogenates butane to the reaction intermediate butene in a mechanism similar to that proposed to occur on sulfated zirconia promoted with iron and manganese.

Despite numerous studies performed on Pt-promoted sulfated zirconia, the chemical state of the Pt is a still source of debate. From XPS studies, Ebitani *et al.* [22, 23] concluded that Pt on sulfated zirconia exists in the cationic state, possibly as platinum oxide. However, these results have been reinterpreted by Paal *et al.* [24], who suggested that the platinum in sulfated zirconia is present as bulk metallic platinum covered by a layer of platinum sulfide. Sayari *et al.* [25, 26] reached a similar conclusion from TPR, XRD, and XPS experiments. Zhao *et al.* [27] found from X-ray absorption spectroscopy that platinum supported on sulfated zirconia is present in a metallic state after calcination in air at 1000 K.

In this paper, we complement our earlier characterization studies of Fe,Mn-promoted sulfated zirconia with mechanistic studies of the butane isomerization reaction utilizing ^{13}C-labeled butane. Since earlier reports strongly suggest a role of intermediate butene in the isomerization reaction mechanism, the effects of adding butene to the feed were investigated. Finally, promotion of sulfated zirconia with Pt is shown for the first time to result in a stable catalyst for butane isomerization at low temperature *in the absence of dihydrogen.*

EXPERIMENTAL METHODS

Materials Synthesis

Zirconium hydroxide (XZ0631/01) and sulfate-doped zirconium hydroxide (XZ0682/01) were kindly donated by Magnesium Elektron Inc. The iron and manganese promoted samples were prepared by incipient wetness impregnation of zirconium hydroxide with a solution of iron nitrate (Aldrich, 99.99%) and manganese nitrate (Aldrich, 99.99%), followed by drying at 373 K in air, and subsequent impregnation with 2 N sulfuric acid. The platinum was added to the catalysts by incipient wetness impregnation of MEI sulfate-doped zirconium hydroxide with a solution of hexachloroplatinic acid (Aldrich ACS Reagent). The sulfate-doped zirconium hydroxide and the platinum-impregnated sample were calcined in flowing air (Airco) at 873 K for 2 h to obtain active sulfated zirconia (ZS) and platinum-promoted sulfated zirconia (ZS-Pt). The iron and manganese promoted sample was calcined at 1020 K for 1 h in flowing air to yield the active material (ZFMS). Following calcination, all the materials were stored in glass vials without particular care.

The BET surface areas of the calcined materials were measured on a Coulter Omnisorb 100CX adsorption instrument and elemental analyses were determined by Galbraith Laboratories, Inc. (Knoxville, TN).

Isomerization of n-Butane

The catalytic activity of the samples for *n*-butane isomerization was evaluated in a single-pass fixed bed reactor loaded with about 0.2−0.3 g of catalyst. Catalysts were reactivated *in situ* in flowing air at 723 K for 1.5 h before reaction. Typically, the feed mixture of *n*-butane (Aldrich 99%) diluted to 10% in helium (Airco, 99.99%) flowed at 5 $\text{cm}^3\ \text{min}^{-1}$. An adsorption bed prior to the reactor contained 0.7 g of sulfated zirconia maintained at room temperature in order to adsorb the trace amounts of butenes present in the butane feed. The adsorption bed reduced the butene concentration in the feed from 0.04% to less than 0.0001%. A six-way valve equipped with a 10 μL sample loop was used to admit small amounts of *trans*-2-butene (Aldrich 99%) into the feed stream. To ensure good mixing with the butane/helium feed, each butene admission actually consisted of a series of 10 pulses (10 μL) separated by intervals of 1 min. This procedure produced a 50-ml "pulse" of feed gas with 0.2% *trans*-2-butene. High concentrations of butene lead to undesirable side reactions like butene oligomerization and coke formation. Products were analyzed with an on-line capillary gas chromatograph.

Reactions with ^{13}C-Labeled Butane

Butane-1-^{13}C (Isotec 99 at.%) was diluted to 25% in He (Roberts Oxygen 99.999%) or H_2 (Roberts Oxygen 99.999%) before reacting over 0.2–0.5 g of catalyst. The products were analyzed with an on-line quadrupole mass spectrometer. Determination of reaction rates from mass spectrometry is complicated by overlapping cracking patterns of the labeled and unlabeled butane and isobutane. Therefore, the conversion rates were calculated from the ratios of the parent peak (P) to the parent peak minus one ($P-1$), which correspond to 1 and 5 for isobutane and *n*-butane, respectively, in our spectrometer. The $P/(P-1)$ ratio was calculated from the signals at $m/e = 59$ and 58. The $m/e = 60$ signal was attributed exclusively to doubly-labeled isobutane product even though a small contribution from doubly-labeled butane is likely to be present.

Pt-L_{III} XANES

The X-ray absorption spectrum associated with the Pt L_{III}-edge of ZS-Pt-3 was recorded in the transmission mode on beam line X18B at the National Synchrotron

Light Source, Brookhaven National Laboratory, Upton, New York. The storage ring operated with an electron energy of about 2.5 GeV with beam currents ranging from 100 to 200 mA. Higher harmonics in the beam were rejected by detuning the Si(111) channel cut monochromator crystal to 80% of the maximum beam intensity. The ion chamber detectors contained appropriate N_2 and Ar mixtures in order to optimize sensitivity. The monochromator slit width was set to 1 mm. As an energy calibration standard, a Pt foil (Goodfellow) was placed between the second and third ion chambers. The zero energy point was defined as the first inflection point in the X ray absorption spectra of the foil.

RESULTS

The compositions and surface areas of the catalysts are given in Table 1. The zirconia crystal structure of all samples was found to be exclusively tetragonal by X-ray diffraction, which is consistent with earlier studies [28–30]. The X-ray diffraction patterns of samples with platinum loadings greater than 0.74 wt% exhibited peaks at $2\theta = 40^\circ$ and 46°, corresponding to the (111) and (200) planes of metallic platinum, respectively. The sulfate loading on the platinum-promoted samples was fairly independent of the platinum loading.

Reactions with ^{13}C Labeled Butane

Figure 1a shows the conversion of 25% butane-1-^{13}C in He at 323 K over Fe,Mn-promoted sulfated zirconia. The reaction curve exhibits the induction period that is typically seen for this material. Figure 1b presents the intensity of the $m/e = 60$ signal during the same experiment. This signal corresponds to the formation of a C_4 molecule having two ^{13}C atoms, presumably formed by β-scission of a C_8 intermediate. Although scission of a C_8 intermediate may lead to *n*-butane, isobutane is strongly preferred. Therefore, we assigned the $m/e = 60$ signal exclusively to doubly-labeled isobutane. Adeeva *et al.* [31] have shown that the isomerization of butane at 353 K over Fe,Mn-promoted sulfated zirconia proceeds exclusively via a bimolecular mechanism that involves C_8 intermediates. Since sulfated zirconia was much less active than the Fe,Mn-promoted sample, the isomerization with labeled butane was performed at 473 K in order to obtain measurable conversions. The conversion and the $m/e = 60$ signal for this experiment are shown in Fig. 2. The rapid deactivation in Fig. 2a has been reported previously for reactions over sulfated zirconia at temperatures exceeding 373 K. The high temporal resolution attainable with mass spectrometry allowed us to observe an induction period and a maximum in conversion before the onset of deactivation. Figure 3 shows the corresponding reactivity results for sulfated zirconia in H_2. Sulfated zirconia is very stable under these conditions. The steady state isomerization in Fig. 3b appears to proceed through an intermolecular mechanism.

The results of Figs. 1 to 3 are quantified in Table 2. The tabulated conversion is an average for a period of 5 min during which the activity of each catalyst was fairly stable. The entries in the fifth column correspond to normalized values of the $m/e = 60$ signal intensities for each experiment. Specifically, the signal intensity for $m/e = 60$ is divided by the corresponding conversion reported in the fourth column, and the result is normalized to the $m/e = 59$ signal of

TABLE 1

Compositions and Surface Areas of Catalysts

Sample	Composition/percentage		Surface area/m^2 g^{-1}
ZS	S	1.4	116
ZFMS	S	1.5	92
	Fe	2.1	
	Mn	0.51	
ZS-Pt-1	S	2.0	99
	Pt	0.15	
ZS-Pt-2	S	2.0	124
	Pt	0.27	
ZS-Pt-3	S	2.1	117
	Pt	0.74	
ZS-Pt-4	S	2.0	98
	Pt	1.8	
ZS-Pt-5	S	1.9	94
	Pt	4.1	

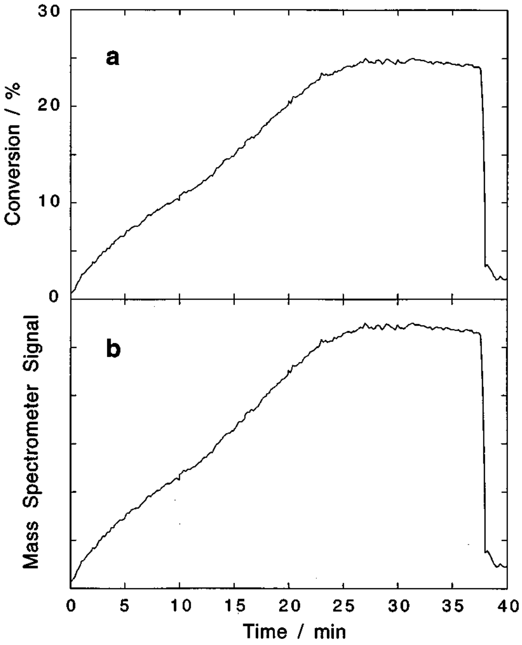


FIG. 1. Conversion (a) and $m/e = 60$ signal (b) corresponding to the isomerization of butane over ZFMS at 323 K in He. Flow was stopped at about 37 min to show the baseline signal.

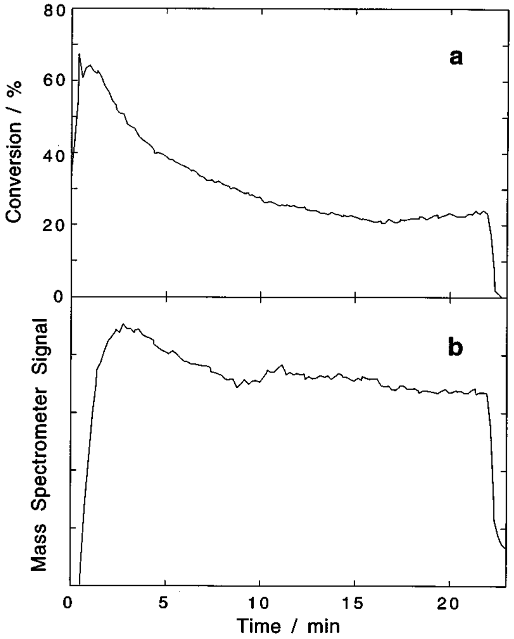


FIG. 2. Conversion (a) and $m/e = 60$ signal (b) corresponding to the isomerization of butane over ZS at 473 K in He. Flow was stopped at about 22 min to show the baseline signal.

the butane in the feed prior to reaction. This normalized ratio indicates the level of isotopic scrambling independent of the conversion level. The level of isotopic scrambling was fairly independent of the catalyst for all of the conditions used in this study.

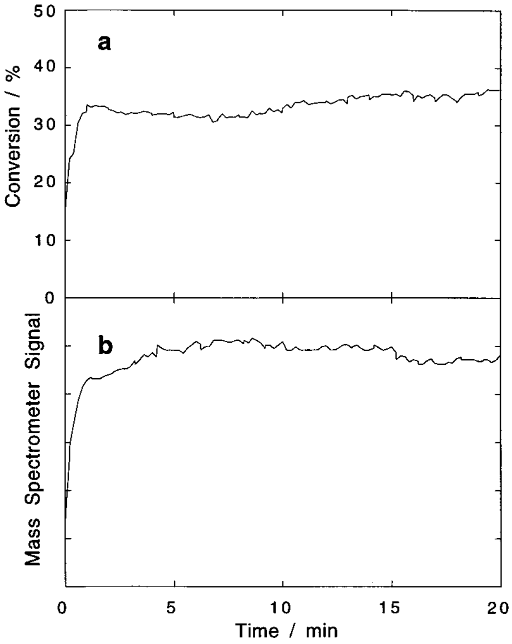


FIG. 3. Conversion (a) and $m/e = 60$ signal (b) corresponding to the isomerization of butane over ZS at 473 K in H_2.

TABLE 2

Isotopic Scrambling for the Catalysts during Butane Isomerization

Sample	Carrier gas	T/K	Conversion	I_{60}/Conv[a]
ZFMS	He	323	0.20	0.13
ZS	He	473	0.22	0.13
ZS	H_2	473	0.32	0.10

[a] Ratio of intensity of $m/e = 60$ signal to conversion of butane.

Isomerization of n-Butane

Figure 4 shows the rates for butane isomerization over sulfated zirconias, with and without transition metal promoters, at 323 K in He. The activity of ZS was an order of magnitude lower than any of the metal promoted samples. Similar to the results shown in Fig. 1, the ZFMS sample exhibited a characteristic induction period followed by a maximum and subsequent rapid deactivation. Likewise, the Pt-promoted sample exhibited an induction period followed by a weak maximum. Even though the maximum activity of ZFMS was greater than the maximum activity of ZS-Pt-3 by a factor of three, the Pt-containing catalyst was far more stable. The selectivity for isobutane was above 97% in the regions of stable activity for all the materials studied, and the main side products observed were propane and iso and *n*-pentane.

Figure 5 illustrates the effect of platinum loading on the rate of butane isomerization. All the samples were remarkably stable, which is surprising given that no dihydrogen is fed to the reactor. Indeed, the rate measured after 500 min on stream diminished only by about 5% after 2 days of continuous reaction. The maximum rate and the rate after 500 min on stream are tabulated for ZS-Pt series in Table 3. The isomerization rate increases with increasing platinum content to about 1 wt% Pt (sample ZS-Pt-3), above which the activity of the samples decreases.

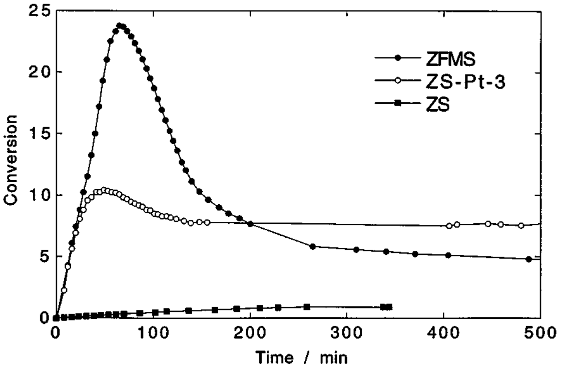


FIG. 4. Isomerization of butane over sulfated zirconia, ZS, sulfated zirconia promoted with iron and manganese, ZFMS, and a representative sample of the sulfated zirconia promoted with platinum, ZS-Pt-3. Reaction conditions: 323 K, 10% butane in He; WHSV $= 6 \times 10^{-5}$ h^{-1}; feed flowrate $= 5.0$ cm^3 (STP)/min.

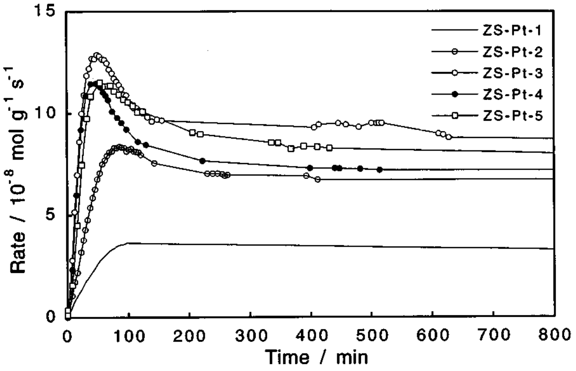


FIG. 5. Isomerization of butane over different platinum-containing sulfated zirconias. Reaction conditions: 323 K, 10% butane in He.

The effect of dihydrogen partial pressure on the isomerization reaction catalyzed by ZS-Pt-3 at 573 K is presented in Fig. 6a. At 323 K and in dihydrogen, ZS-Pt-3 was not even as active as unpromoted ZS. Therefore, we increased the temperature to 573 K in order to observe the same level of isomerization activity in dihydrogen that was measured in He at 323 K at the same partial pressure of butane. The inhibitory effect of dihydrogen is in agreement with the observations of Liu *et al.* [21]. Figure 6b shows the effect of halving the dihydrogen partial pressure at the same butane partial pressures. Clearly, the activity of ZS-Pt-3 increases with a decrease in dihydrogen partial pressure indicating a negative reaction order in H_2. This contradicts some earlier studies that report a positive order in dihydrogen for butane reaction on Pt-promoted sulfated zirconias [12–14, 18, 32].

Effect of Butenes

Recent studies suggest that the high activity exhibited by Fe,Mn-promoted sulfated zirconia is associated with the formation of butene intermediates [7, 11]. These butenes are subsequently used in the catalytic cycle to form isobutane from butane through a classical bimolecular mechanism involving surface acid sites. To test this hypothesis, we injected small amounts of *trans*-2-butene into the butane/helium feed mixture while monitoring the production of isobutane.

TABLE 3

Effect of Platinum Content on the Activity of Sulfated Zirconia

Sample	Platinum loading wt%	Maximum rate/ 10^{-8} mol g^{-1} s^{-1}	Steady state rate/ 10^{-8} mol g^{-1} s^{-1}
ZS-Pt-1	0.15	3.6	3.5
ZS-Pt-2	0.27	8.3	6.7
ZS-Pt-3	0.74	12.9	9.4
ZS-Pt-4	1.8	11.4	8.2
ZS-Pt-5	4.1	11.4	6.7

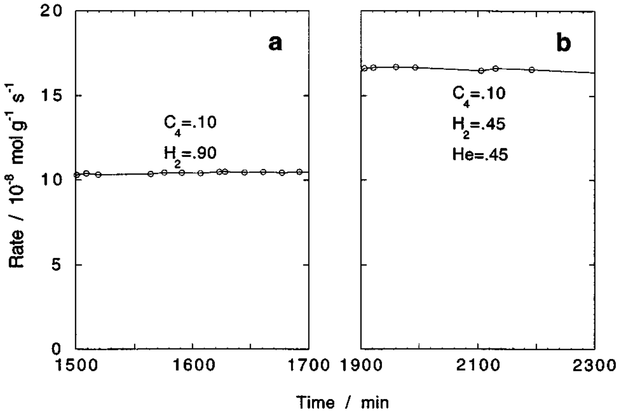


FIG. 6. Isomerization of butane over ZS-Pt-3 in dihydrogen (a) and a mixture of dihydrogen and helium (b) with the same mole fraction of butane (10%) at 473 K.

Figure 7a shows the results of admitting 100 μL of *trans*-2-butene over active ZS and ZFMS catalysts after about 350 min on stream. Figure 7b shows the effect of a similar addition of butene over ZS-Pt-2 after 270 min. For each run, the isobutane production increases immediately after butene injection, then slowly returns to the steady state. The increase in activity over the steady state prior to injection is sustained for period of time much longer than the residence time in the reactor. In addition, the increase in isobutane molecules produced exceeded the number of butene

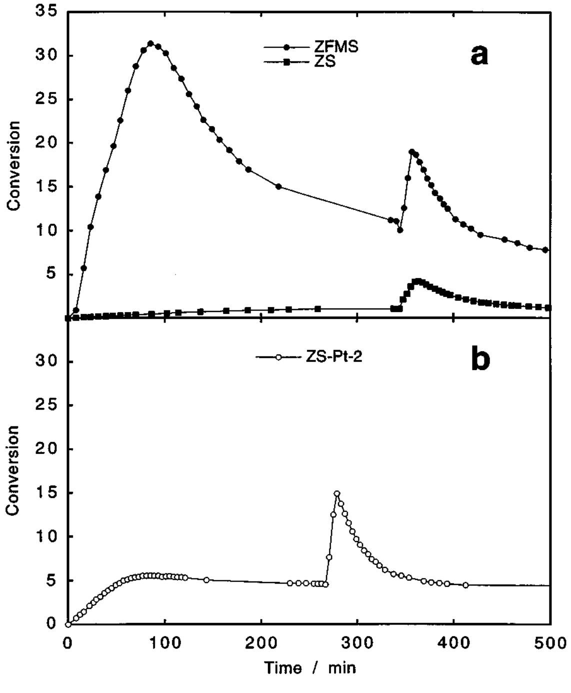


FIG. 7. Effect of admitting 100 μL of *trans*-2-butene during the isomerization of butane catalyzed by ZS and ZFMS (a) and ZS-Pt-2 (b). Reaction conditions: 323 K; 10% butane in He; WHSV = 6×10^{-5} h^{-1}; feed flowrate = 5.0 cm^3 (STP)/min.

TABLE 4

Results from Injections of *Trans*-2-Butene

Sample	Activity[a]/ 10^{-8} mol g^{-1} s^{-1}	Additional i-C_4H_{10}[b]/ μmol g^{-1}	Chain length[c]
ZS	1.3	130	10
ZFMS	11.9	200	15
ZS-Pt-2	7.2	290	18

[a] Activity at the time of injection.

[b] Amount of isobutane formed from added butene.

[c] Ratio of additional isobutane formed to added butene.

molecules injected. Both the long time of reaction and the high level of isobutane produced are consistent with a chain reaction in which butene participates. The chain length was estimated by integrating the area of the burst in activity and then calculating the ratio of isobutane produced to the amount of butene admitted with the feed. Table 4 shows the steady state rate at the moment of injection, the area of the isobutane production peak, and the chain length, for sulfated zirconia and the transition metal-promoted systems.

Although the activities of the catalysts are very different at the moment of butene admission, the burst in activity is similar for all three cases. The chain lengths associated with the promoted catalysts are within a factor of 2 of that for sulfated zirconia, even though the steady state activities at the time of injection are nearly an order of magnitude higher. The similarity of the chain lengths for these catalysts confirms results from earlier spectroscopic studies that indicate promoters do not significantly affect the surface acidity of sulfated zirconia [7, 10, 11, 33].

Near Edge XAS of the Pt-L_{III} Edge

Figures 8a and 8b show the near edge region for the platinum present in the sample ZS-Pt-3 and a standard platinum foil, respectively. The spectrum for the platinum in the sample has a considerably large white line than the metallic platinum indicating that platinum is present in a oxidized state. In fact, the near edge structure of the sample is very similar to the spectrum corresponding to PtO_2 reported earlier [27].

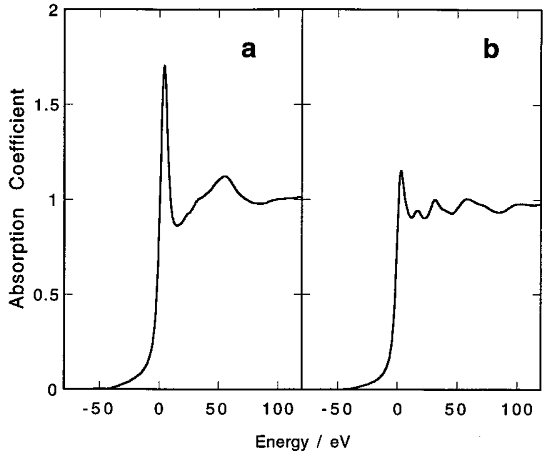
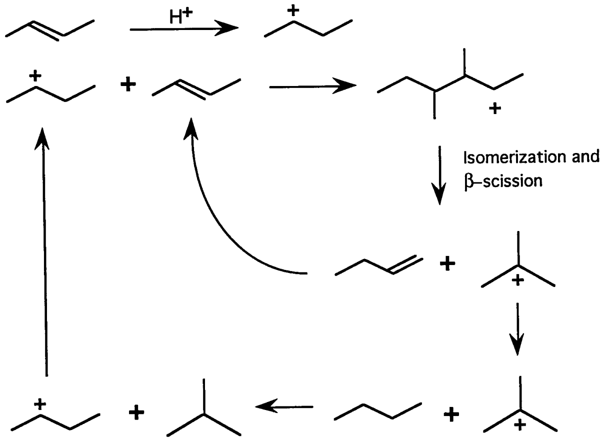


FIG. 8. Near Edge XAS of the Pt-L_{III} edge of ZS-Pt-3 (a) and a platinum metal foil (b).

DISCUSSION

Both the reaction kinetics and the distribution of side products during butane isomerization over Fe,Mn-promoted sulfated zirconia are consistent with an intermolecular, or bimolecular, reaction mechanism involving C_8 intermediates [34, 35]. However, Adeeva *et al.* used isotopic labeling to show conclusively that isomerization proceeds exclusively by an intermolecular mechanism at 353 K on Fe,Mn-promoted catalysts [31]. A simplified version of the classical bimolecular reaction sequence is given in



SCHEME I

A bi-labeled C_8 intermediate forms from the reaction of two mono-labeled C_4 species, and methyl shifts on the C_8 intermediate lead to isotopic scrambling. Thus, β scission will produce zero, mono, and bi-labeled isobutane. This mechanism has also been associated with the isomerization of butane over mordenite and chlorinated alumina catalysts [36–38]. In our work, the isomerization of butane over Fe,Mn-promoted sulfated zirconia was studied at 323 K, a temperature slightly lower than the one used previously by Adeeva *et al.* [31]. Regardless of the small temperature difference, the isomerization reaction should also proceed exclusively by an intermolecular mechanism under our conditions. Based on the amount of bi-labeled isobutane produced from mono-labeled butane over the catalysts listed in Table 2, we also conclude that the isomerization reaction mechanism is intermolecular over sulfated zirconia at 473 K in the presence of either helium or dihydrogen. These results are in agreement with the findings of Adeeva *et al.* [39] for the isomerization of butane on sulfated zirconia at 403 K in He, which proceeds predominantly by a intermolecular mechanism. However, Garin *et al.* [40] showed that isomerization on sulfated zirconia under a dihydrogen atmosphere at 623 K proceeds mainly by a monomolecular mechanism via adsorbed protonated cyclopropanes. Adeeva *et al.* [39] rationalized this discrepancy by suggesting that the mono and bimolecular mechanisms are competitive mechanisms for the isomerization of butane on sulfated zirconia. Under helium atmosphere and at low temperature (403 K), the bimolecular mechanism involving olefin intermediates predominates, whereas under dihydrogen the surface concentration of olefin intermediates is reduced. A more recent paper by the same group found that isomerization was bimolecular on Pt-promoted sulfated zirconia at 523 K [21]. It is not clear why our results differ from those of Garin *et al.* One possible reason may be that they stabilized the steady state activity of their catalyst in the presence of unlabeled butane and subsequently injected a pulse of labeled reactant. The contribution of unlabeled surface intermediates to the isotopic distribution in their product may be significant. In our case, we used a steady flow of labeled butane throughout the experiment.

The role of olefins as carbocation initiators in the isomerization of butane is well known in the liquid acid literature. For example, Pines *et al.* [41] demonstrated that trace amounts of olefin are necessary to isomerize butane in $AlCl_3$/HCl. Under certain conditions, olefins can be produced by oxidation reactions of the reactant paraffins [42, 43]. In addition, Sommer *et al.* recently concluded from H/D exchange reactions that alkenes are formed as intermediates on solid acids such as acidic zeolites and sulfated zirconia at low temperature [44, 45]. Although the mechanism for olefin formation on these materials is not clear, the authors argue that protonation of the olefins might form the initial carbocation responsible for the low-temperature activation of paraffins on solid acids. Thus, these solid acids would not be considered strongly superacidic since the paraffin is not directly protonated and there is no evidence of formation of pentacoordinated carbon (carbonium ion) with the subsequent evolution of dihydrogen to form the classical carbenium ion.

Several studies have shown that the acidities of sulfated zirconia and Fe,Mn-promoted sulfated zirconia are the same [7, 10, 11, 33]. The similarity of our results for the chain length (isobutane formed divided by butene admitted) over all catalysts shown in Table 4 is consistent with the surface acidity of sulfated zirconia being little affected by the presence of Fe, Mn, or Pt promoters. Apparently, the great differences in the observed butane isomerization rates over the samples at low temperature are due to differences in the surface butene concentrations.

Adeeva *et al.* [7] suggested that since the iron and manganese promoters did not affect the acidity of sulfated zirconia, they may dehydrogenate butane to butene. These intermediate butenes subsequently react on the acid sites of sulfated zirconia to form carbocation initiators in the chain cycle of butane isomerization given in Scheme I. Wan *et al.* [11] recently demonstrated that the iron in the promoted system has an "oxy-function" capable of low temperature oxidation of CO to CO_2, and they suggest that this site activates butane by a *non-catalytic* (emphasis added) oxidative process that eventually forms butene. The active site was proposed to be an Fe(IV) surface species. Assuming a stoichiometric oxidation of CO to CO_2, they determined the density of oxy species to be 10–15 μmol g^{-1} of catalyst or 5–7% of the iron present in the catalyst.

We can calculate from our work an approximate number of moles of butene required for the high initial activity of ZFMS. The initial production of isobutane estimated by integrating the curve in Fig. 4 from 0 to 350 min corresponds to 4.5 mmol of isobutane g^{-1}. Using the chain length obtained for ZFMS of 15 moles of isobutane per mole of butene, we estimate that at most 300 μmol of butene g^{-1} must be produced to give the initial activity of ZFMS. If the surface site that produces butene contains at least one iron atom, a loading of 0.017 g Fe/g of catalyst is needed to account for the stoichiometric formation of butene. The iron loading of our ZFMS sample, 0.02 g Fe/g catalyst, exceeds the stoichiometric requirement. Since we have likely underestimated the size of the catalytic chain length of butene due to bed effects, it is quite probable that the actual surface density of dehydrogenating species is much lower than the total amount of promoters, which is in agreement with the estimate of Wan *et al.* [11]. Evidently, the initially high activity of ZFMS for low-temperature butane isomerization results from the *non-catalytic formation* of intermediate butenes that subsequently participate in the classical acid-catalyzed intermolecular rearrangement of hydrocarbons. The long term activity of ZFMS is likely due to other sites on the surface [11]. Coelho *et al.* [46] reported that the variation in the rate of butane isomerization with time is consistent with the presence of two types of sites on ZFMS. A very active site that is prominent at short times undergoes rapid deactivation, while a less active, but more stable, site accounts for the long term activity of the system.

The Pt-promoted catalysts in this work behave very differently from ZS and ZFMS, since they are active and stable, even in the absence of dihydrogen. The traditional bifunctional reforming catalyst, Pt supported on chlorinated alumina, contains both metallic and acidic surface sites that act together in a concerted mechanism. For skeletal isomerization reactions, paraffins are dehydrogenated to form intermediate olefins that are subsequently isomerized on acidic sites and hydrogenated on metallic sites to give isoparaffins [43]. Although most researchers find this classical bifunctional mechanism unlikely for butane isomerization on Pt-promoted sulfated zirconia, many studies have been carried out in a dihydrogen atmosphere at relatively high temperatures. For example, Garin *et al.* [18] and Yori *et al.* [19] observed that the initial activity of sulfated zirconia for butane isomerization was not affected by the presence of platinum. Thus, they claimed that the role of platinum in the presence of dihydrogen was to stabilize the catalyst against deactivation by inhibiting coke formation. It is important to note that relatively high temperatures were used in those works compared to ours. Also, since sulfated zirconia deactivates rapidly in the absence of dihydrogen, the initial activities of the catalysts in those studies may have been underestimated.

At our conditions, platinum on sulfated zirconia also enhanced the activity for butane isomerization under a helium atmosphere. In addition, the Pt-containing catalysts exhibited remarkable activity for up to 36 h of continuous operation. To the best of our knowledge, this is the first time that such stability has been reported for this system at low temperature in the absence of dihydrogen. The negative reaction order in dihydrogen is most likely due to a combination of intermediate butene concentration decreasing with increasing H_2 pressure [21] and competitive adsorption on the promoter sites.

We studied the activity of Pt-promoted sulfated zirconia at different loadings of the promoter. Figure 5 and Table 3 suggest that, for our preparation conditions, 0.74 wt% is an optimum loading of Pt on ZS for the isomerization of butane at 323 K. Recently, Hino *et al.* [15, 16] studied the effect of Pt loading on the activity and stability of sulfated zirconia. Samples with Pt contents of 0.5 to 10 wt% Pt were synthesized and calcined at 873 K in air. Butane isomerization was performed in a pulse reactor at 353 K with helium as the carrier gas. Their maximum activity was reported for a catalyst with 7.5 wt% Pt, a full order of magnitude greater than the optimum loading in this work.

The XRD patterns of our Pt-containing materials showed that only the samples with a Pt loading exceeding the optimum exhibited peaks corresponding to metallic platinum. In fact, the *ex-situ* XANES spectrum of our optimum material showed that, on the average, the platinum in the catalyst is present in the oxidized form. Hino *et al.* [15] established by XPS measurements that the Pt is in a cationic Pt^{+4} state. Ebitani *et al.* also reported that the Pt was not metallic [22, 23]. However these results have been contested by Paal *et al.* [24]. Additionally, studies of platinum on sulfated zirconia by XPS, XRD, and TPR suggested that it was present in a metallic state [25, 26]. However, in those studies, the Pt loading was fairly high (4–5 wt%), and calcination at 873 K reduced Pt to form large aggregates. Similarly, our sample containing 4.1 wt% Pt also contained large aggregates of metallic Pt as revealed by XRD. However, we did not observe an increase in the activity with Pt loadings above 0.74%. Evidently, reduced Pt metal that forms aggregates does not contribute significantly to the observed catalysis. This effect may also explain the recent observations of Zhao *et al.* [27], who found by XANES and EXAFS that platinum on sulfated zirconia was metallic. Even though the platinum loading of their sample was only 1%, calcination at 1000 K was sufficient to form large aggregates of Pt of about 10 nm in size. From the results presented here, we cannot confidently assign an oxidation state to the active Pt phase during butane isomerization at 323 K without additional *in situ* characterization.

CONCLUSIONS

The mechanism for butane isomerization over the promoted and unpromoted catalysts in this work is intermolecular and involves the formation of intermediate butene. The butene initiates a chain reaction involving cationic intermediates that produces at least 10 moles of isobutane for every mole of butene added. Thus, the role of the transition metal promoters is to enhance the steady-state concentration of surface olefinic intermediates, which subsequently increases the overall rate of butane isomerization. In addition, the similarity of the chain length for all the catalysts studied indicated that the acidity of the materials was unaffected by the addition of promoters. The Fe,Mn system appears to form butene initially in a single turnover oxidative reaction, which necessarily leads to a decrease in the observed isomerization activity with time. However, the Pt-promoted samples do not deactivate with time, which suggests that olefin formation is catalytic on these materials. Since butane isomerization over Pt-promoted catalysts was studied at low temperature (323 K), dihydrogen was not needed to prevent coke formation and subsequent deactivation. The optimal level of Pt loading on the catalyst was about 1% since higher loadings resulted in metal agglomeration and lower isomerization rates.

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