

The Impact of Pt and H₂ on *n*-Butane Isomerization over Sulfated Zirconia: Changes in Intermediates Coverage and Reactivity

Soo Y. Kim,* James G. Goodwin, Jr.,^{†,1} Sonia Hammache,[‡] Aline Auroux,[‡] and Douglas Galloway[§]

*Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261; [†]Department of Chemical Engineering, Clemson University, Clemson, South Carolina 29634; [‡]French Institute of Catalysis, 69626 Villeurbanne Cedex France; and [§]UOP LLC, Des Plaines, Illinois 60017

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Previous steady-state isotopic transient kinetic analysis (SSITKA) studies in our laboratory showed that the deactivation of an unpromoted sulfated zirconia (SZ) catalyst during *n*-butane isomerization at 150°C is due to a loss of active sites as well as a small decrease in the average site activity (Kim, S. Y., Goodwin, Jr., J. G., and Galloway, D., *Catal. Today* 63, 21 (2000)). The mechanism by which SZ deactivates is linked to coke/oligomer formation and, possibly, surface sulfur reduction. The use of Pt promotion of SZ and H₂ addition to the reaction mixture has been shown to greatly decrease deactivation during *n*-butane isomerization. In this study, the mechanisms by which H₂ addition and Pt promotion affect *n*-butane isomerization over SZ were studied using SSITKA. H₂ probably inhibits *n*-butane isomerization activity of the unpromoted SZ catalyst through inhibition of butene formation. Little effect on the average residence time for reaction was observed. An improvement in catalyst stability was linked to a reduction in coke/oligomer formation. In the absence of H₂ in the feed stream, the presence of Pt did not improve the activity or the stability of the catalyst. An enhanced catalytic activity and stability, however, was evident when both H₂ addition and Pt promotion were used, but only at the higher reaction temperature of 250°C. This enhanced catalytic activity at 250°C upon both Pt promotion and H₂ addition was a result of an increase in the concentration of active surface intermediates leading to isobutane. This concentration did not change greatly during reaction, thus showing the improvement also in catalyst stability. Although the concentration of active intermediates increased significantly, the average reaction rate (inverse seconds) of an intermediate actually decreased, but not enough to prevent an increase in overall activity. Only 4% (SZ)–16% (PtSZ) of the intermediate to strong acid sites appeared to be involved in the reaction after 5 min time-on-stream, suggesting a reason why NH₃ adsorption characterization results do not correlate well with catalyst activity for SZ-based catalysts. The implications of the obtained results on the roles of Pt and H₂ on SZ in enhanced catalyst activity and decreased deactivation are discussed. © 2001 Academic Press

Key Words: *n*-butane isomerization; sulfated zirconia; Pt-promotion; effect of H₂; steady-state isotopic transient kinetic analysis, SSITKA; isotopic transient kinetic analysis.

INTRODUCTION

With the strict environmental regulations imposed on the chemical processing industry (CPI), development of new processes as well as redesign of old ones has focused on eliminating strong liquid acid catalysts such as H₂SO₄ and HF. Use of solid acid catalysts, such as metal oxides and zeolites, in place of these strong liquid acids not only eliminates the problem of processing unit corrosion but also eases catalyst separation and reduces the cost of catalyst disposal. However, the acid sites on these solid acids are often not strong enough to carry out reactions that require liquid strong acids or superacids. For this reason, discovery of the enhancement in acidity of metal oxides upon sulfation has drawn a lot of attention. The nature of the acid sites on these sulfated metal oxides can be probed using alkane isomerization, specifically *n*-butane isomerization (2, 3).

Sulfated zirconia (SZ), which possesses exceptionally high activity and selectivity for *n*-butane (*n*-C₄) isomerization (4–6), appears as the strongest candidate for use in commercial isomerization and alkylation processes. However, the fast deactivation of SZ has limited its use in commercial *n*-butane isomerization units. The deactivation of this catalyst is likely due to oligomer formation, and addition of H₂ to the reactant stream has been found to prolong the lifetime of the catalyst at high reaction temperatures. However, the presence of H₂ also decreases the rate of isomerization (7–10).

It has been determined that a small amount of Pt (<5 wt%) added to SZ reduces the rate at which a SZ catalyst deactivates and enhances the isomerization activity in the presence of H₂ (11–16). Tabora and Davis (16) reported that the optimum Pt content was approximately 1 wt% for low-temperature isomerization. However, results in the literature are ambiguous. For instance, Signoretto *et al.* (12) concluded that Pt content had no significant effect on the catalytic activity.

It has been suggested (17–23) that a Pt-promoted SZ (PtSZ) catalyst does not function as a traditional bifunctional catalyst similar to the commercial *n*-butane

¹ To whom correspondence should be addressed. Fax: (864) 656-0784. E-mail: james.goodwin@ces.clemson.edu.

isomerization catalyst, Pt/chlorinated Al_2O_3 . On the commercial Al_2O_3 -based catalysts and acidic zeolites, Pt is present as Pt° and dehydrogenates *n*-butane to form *n*-butene, which interacts with a C_4 carbenium ion to produce a C_8 active surface intermediate. Following isomerization and β -scission of the surface C_8 species, the isomerized C_4 carbenium ion is desorbed via hydride transfer with a gas-phase *n*-butane molecule (24, 25). At the same time, Pt can reduce oligomer formation on the catalyst surface by hydrogenating surface olefin species in the presence of H_2 , thus enhancing catalyst stability. Therefore, Pt provides hydrogenation/dehydrogenation ability to these catalysts. However, typical PtSZ catalysts have been reported to be inactive for cyclohexane dehydrogenation (26) and benzene hydrogenation (27). Low H_2 and CO chemisorption abilities of the catalyst, even after H_2 treatment (reduction) at well above typical Pt reduction temperatures, have been reported (14, 20, 26). Pt was first suggested to be in the unreduced Pt oxide form following H_2 treatment (reduction) at 300°C (20). However, EXAFS (28) and XPS (17, 26) studies have indicated that metallic Pt is present on the catalyst even following high-temperature calcination ($T_{\text{cal}} \geq 600^\circ\text{C}$). Reduction of Pt is proposed to take place by decomposition of PtO_2 to Pt° during calcination using decomposing sulfate species (SO_2) as the reducing agent (18, 26, 29, 30).

The cause of the enhancement in isomerization activity of SZ in the presence of H_2 upon Pt promotion is still unclear and only speculations have been offered. Pt is suggested (a) to supply hydrogen to surface olefins to reduce coke/oligomer formation (14, 28, 31), (b) to enhance acidity of the catalyst by supplying dissociated H^+ to Lewis acid sites converting the inactive sites into active protonic acid sites (19, 20, 32), and/or (c) to increase the hydride transfer ability of SZ (21, 33, 34) in the presence of H_2 . However, the presence of Pt and H_2 can also contribute to the reduction of sulfur from S^{6+} to a lower valence state, which would result in a decrease in site acidity or loss of active sites (7, 12).

Thus, even with the vast amount of research reported to date, a clear understanding of the Pt promotion mechanism during *n*-butane isomerization is still not available. Utilizing steady-state isotopic transient kinetic analysis (SSITKA), one is able to measure *in situ* surface kinetic parameters, namely the average surface residence time and the concentration of the active surface intermediates leading to products. In recent publications (1, 35), we have reported on the changes in average surface residence time and concentration of the active surface intermediates leading to isobutane (iso- C_4) on unpromoted SZ during *n*-butane isomerization at 150°C . This present study extends the earlier findings, focusing on the effects of H_2 addition and Pt promotion on the surface kinetic parameters of SZ during *n*-butane isomerization.

EXPERIMENTAL

Catalyst Preparation

Sulfate-doped zirconium hydroxide ($\text{Zr}(\text{OH})_4$) was obtained from Magnesium Elektron, Inc. (XZ0682/01). Sulfated zirconia (SZ) was prepared by calcination at 600°C for 2 h in a high-temperature oven.

For the Pt-promoted SZ catalyst, Pt was incorporated into the sulfate-doped $\text{Zr}(\text{OH})_4$ via the incipient wetness technique using a H_2PtCl_6 solution (5 wt% Pt, Strem Chemical). Sulfate-doped $\text{Zr}(\text{OH})_4$ was dried in an oven at 120°C overnight prior to impregnation with the dilute H_2PtCl_6 solution. Following impregnation, the catalyst precursor was dried in an oven at 120°C overnight before being calcined in air at 600°C for 2 h in a high-temperature oven to produce the Pt-promoted catalyst (PtSZ).

Catalyst Characterization

The sulfur, Pt, and carbon contents of the fresh and used catalysts were determined by Galbraith Laboratories. The total surface areas of the fresh catalysts were determined by Micromeritics using N_2 adsorption. A Philips X'pert X-ray diffractometer with monochromatized $\text{CuK}\alpha$ radiation and a Ni filter was utilized in studying the crystallinity of the SZ-based catalysts. The diffractometer was operated at 40 kV and 30 mA with a scanning rate of $0.5^\circ/\text{min}$ (2θ).

NH_3 Microcalorimetry

Microcalorimetry of NH_3 adsorption was performed using a heat flow microcalorimeter (Setaram C80) at 250°C . A detailed description of the technique has been reported elsewhere (36) and the measurement procedures were based on Ref. (37). The microcalorimeter was linked to a volumetric adsorption line equipped with a barocell capacitance manometer for pressure measurements. The fresh calcined catalyst samples were outgassed at 315°C overnight prior to microcalorimetric measurements. The differential heats of adsorption were measured as a function of coverage by sending repeated doses ($1\text{--}3\ \mu\text{mol}$ for 100 mg of sample) until an equilibrium pressure of about 133 Pa was reached. After the total number of acid sites was measured at the equilibrium pressure of 133 Pa, the sample was evacuated for 1 h (at 250°C) and a second adsorption was performed. The difference between the uptake from the first adsorption and that from the second adsorption was used to determine the amount of irreversibly adsorbed NH_3 .

n-Butane Isomerization

n-Butane isomerization was studied using a quartz microreactor. A fresh calcined catalyst was pretreated *in situ* at 315°C for 4 h in flowing air ($30\ \text{cm}^3/\text{min}$, Praxair, UHP). The catalyst was cooled to the desired reaction

temperature (150 or 250°C) and the reactant mixture then introduced. The reaction was carried out *with* and *without* H₂ addition. The pretreated catalyst was flushed with 30 cm³/min of He for 30 min at the reaction temperature prior to introduction of the reactant mixture. In the absence of H₂, the reactant mixture consisted of 2.5 mol% *n*-C₄ in He with a total feed flow rate of 30 cm³/min. For H₂ addition, a portion of He was replaced with H₂ to provide a specific H₂-to-*n*-C₄ ratio (H₂/HC). Olefin impurities in the reactant streams were removed with the use of a H-mordenite bed held at room temperature (5). The total pressure was kept at 1.5 atm during the study. The effluent was analyzed using a Varian 3700 gas chromatograph (GC) equipped with a 6-ft 80/100 mesh Porapak Q column and an FID.

For SSITKA, a step change between *n*-¹²C₄ (*n*-C₄) and 1,4-¹³C-labeled *n*-C₄ (*n*-[#]C₄) was made without disturbing the other reaction conditions. Samples of the effluent from the reactor were collected during the resulting isotopic transient using a VICI 34-port valve autosampler. After the isotopic transient was completed, the collected samples were separated in an 18-ft 80/100 mesh Porapak Q column at 130°C using a H₂-containing carrier gas. The separated effluent was converted to methane in a hydrogenolysis unit (Pt/SiO₂ held at 250°C) using the carrier gas as a source of H₂. Following hydrogenolysis, the effluent was introduced into a Balzers-Pfeiffer Prisma 200-amu mass spectrometer for isotope analysis. More detailed descriptions of the reaction system and SSITKA can be found in Refs. (38–40).

RESULTS

Catalyst Characteristics: Composition and Crystallinity

The catalyst surface areas and compositions are listed in Table 1. The small difference in the BET surface areas can be considered to be negligible. The measured sulfur contents of the catalysts were the same.

Figure 1 shows the XRD spectra of the parent sulfate-doped Zr(OH)₄ [uncalcined SZ] and of the freshly calcined SZ-based catalysts [SZ and PtSZ]. The uncalcined sulfate-doped Zr(OH)₄ was X-ray amorphous, as indicated by a very broad, low peak. Following calcination at 600°C,

TABLE 1
Catalyst Characteristics

Catalyst	Fresh catalyst		
	BET SA ^a (m ² /g)	Sulfur ^b (wt%)	Pt ^b (wt%)
SZ	94.2	1.6	0
PtSZ	98.7	1.6	0.5

^aError = ±5%.

^bError = ±0.1 wt%.

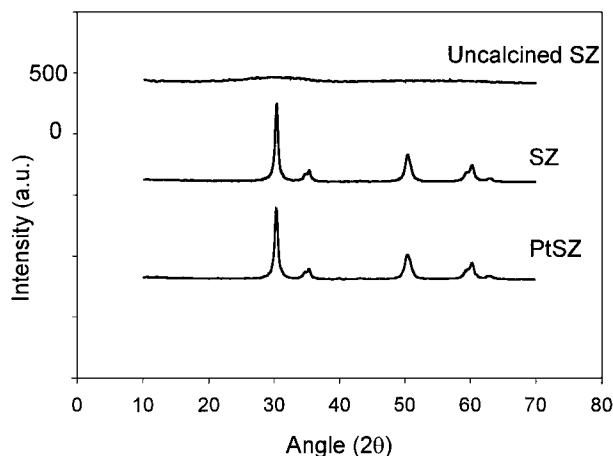


FIG. 1. XRD spectra of the fresh catalysts.

ZrO₂ was found to be in the tetragonal phase for the catalysts. Sulfur-containing species and Pt were not detected, probably due to their small concentrations. Reaction (both in the presence and in the absence of H₂) did not affect the crystallinity of the catalysts (not shown).

Acidity Characteristics: NH₃ Microcalorimetry

The acid sites with $\Delta H_{\text{ads},\text{NH}_3} > 150$ kJ/mol are considered to be the strongest acid sites, while sites with $125 < \Delta H_{\text{ads},\text{NH}_3} < 150$ kJ/mol are designated as intermediate strength acid sites (37, 41, 42). The weak sites with $\Delta H_{\text{ads},\text{NH}_3} < 125$ kJ/mol are considered to be most likely too weak to actively participate in alkane isomerization catalysis (37, 41, 42). Acidity characteristics of SZ and PtSZ, determined by NH₃ microcalorimetry, are shown in Fig. 2 and Table 2. At the adsorption/desorption temperature of 250°C, the catalysts contained approximately 160 to 195 μmol of acid sites per gram of catalyst sample.

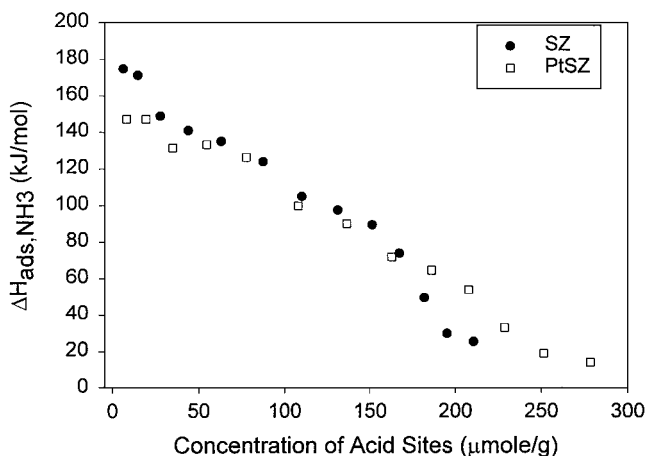


FIG. 2. Acidity characterization using NH₃ microcalorimetry ($T_{\text{ads}} = 250^\circ\text{C}$).

TABLE 2
NH₃ Microcalorimetry Results^a

Catalyst	Total ^b (μmol/g)	Irreversible adsorption (μmol/g) ^b	Concentration of acid sites (μmol/g) ^b		
			50 < Δ <i>H</i> _{ads} < 125 kJ/mol	125 < Δ <i>H</i> _{ads} < 150 kJ/mol	Δ <i>H</i> _{ads} > 150 kJ/mol
SZ	163	72	59	85	20
PtSZ	195	94	116	79	0

^a Adsorption temperature = 250°C.

^b Maximum error = ±10%.

As can be seen in Fig. 2, the amounts of strong and intermediate strength acid sites for the catalysts were not greatly different considering experimental error. The apparent absence of strong acid sites (Δ*H*_{ads,NH₃} > 150 kJ/mol) for PtSZ was probably just due to the greater experimental error involved in measuring the initial heat of adsorption.

Activity in the Absence of H₂

The isomerization activities of the fresh catalysts at 150°C in the absence of H₂ with time-on-stream (TOS) are shown in Fig. 3. The observed decrease in the rate of iso-C₄ formation on SZ with TOS followed the same trend as that observed for other typical SZ catalysts (5, 6). In the absence of H₂ in the feed stream, Pt did not have a promoting effect on the *n*-C₄ isomerization ability of SZ. The initial (5 min TOS) isomerization activity of PtSZ was ca. 30% lower than that of SZ. With TOS, the observed difference in activity for the catalysts remained. The lowest selectivity toward iso-C₄ was at 5 min TOS for the catalysts: 85% for SZ and 90% for PtSZ. The selectivity, however, increased to and remained above 95% after 45 min TOS for both catalysts. Following reaction, the carbon content of SZ was

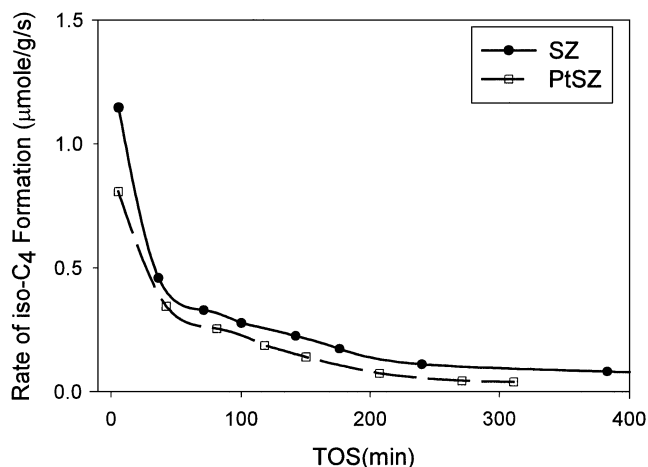


FIG. 3. *n*-Butane isomerization activities of the catalysts in the absence of H₂ (*T* = 150°C).

TABLE 3
Catalyst Deactivation and Composition during Reaction at 150°C with H₂/*n*-C₄ = 0

Catalyst	<i>k</i> _d (min ⁻¹)		300 min TOS (wt%)	
	Initial ^a	Steady-state ^b	Sulfur ^c	Carbon ^c
SZ	0.03	0.005	1.5	0.7
PtSZ	0.01	0.006	1.8	0.3

^a Maximum error = ±0.002.

^b Error = ±0.001.

^c Error = ±0.1 wt%.

double that of PtSZ (Table 3). Reaction did not appear to affect the sulfur content of the SZ-based catalysts (Table 3).

Deactivation of a SZ catalyst is often characterized using a pseudo-first-order deactivation constant, *k*_d (5):

$$\text{rate} = \text{rate}_0 \exp(-k_d t). \quad [1]$$

Table 3 lists the initial (TOS < 45 min) and pseudo-steady-state (TOS > 45 min) *k*_d values for the catalysts. As the reaction proceeded, *k*_d decreased significantly for the SZ-based catalysts. The rates of catalyst deactivation for the catalysts were not significantly different.

Similar catalytic behavior was observed at the higher reaction temperature of 250°C in the absence of H₂ (H₂/HC = 0) (Fig. 4, Table 4). At 250°C, PtSZ also exhibited a lower activity than the unpromoted SZ. Compared to the reaction at 150°C, the lower initial activities at 250°C are probably due to the detrimental effect of the increased reaction temperature on catalyst deactivation via coke/oligomer formation prior to the initial rate measurement. As shown in Table 4, following reaction (300 min TOS) at 250°C in the absence of H₂, the catalysts

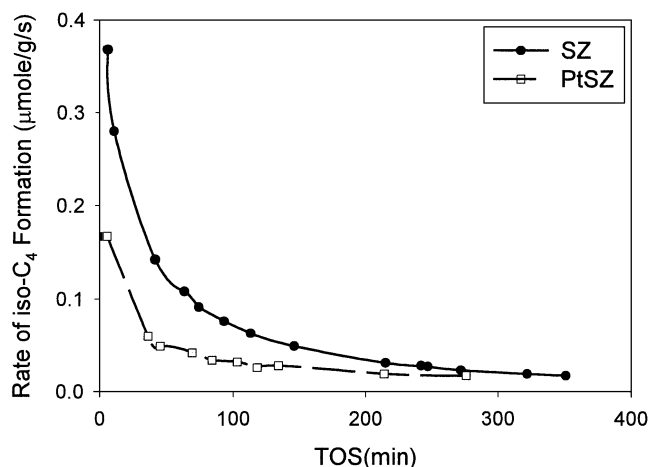


FIG. 4. *n*-Butane isomerization activities of the catalysts in the absence of H₂ (*T* = 250°C).

TABLE 4

Catalyst Deactivation and Composition during Reaction at 250°C

Catalyst	Without H ₂ addition (H ₂ /HC = 0)				With H ₂ addition (H ₂ /n-C ₄ = 4)	
	k _d (min ⁻¹)		300 min TOS (wt%)		300 min TOS (wt%)	
	Initial ^a	Steady-state ^b	Sulfur ^c	Carbon ^c	Sulfur ^c	Carbon ^c
SZ	0.02	0.006	1.5	1.2	1.7	0.1
PtSZ	0.03	0.005	1.6	0.9	1.5	0.2

^aError = ±0.002.^bError = ±0.001.^cError = ±0.01 wt%.

had higher carbon contents than after reaction at 150°C (Table 3). The insignificant difference in the calculated values of k_d at 150°C and 250°C between the catalysts (Tables 3 and 4) suggests that, at the reaction temperatures studied, addition of Pt did not have a significant impact on the catalyst stability in the *absence* of H₂.

SSITKA was carried out for reaction in the absence of H₂ at 250°C for both SZ and PtSZ. Our previous study (35) showed the effect of iso-C₄ readsorption on the kinetic parameters measured utilizing SSITKA. Failing to correct for this effect of product readsorption can lead to misinterpretation of the results based on isotopic tracing (35, 43). To correct for these effects $\tau_{\text{iso-C}_4}$, the average residence time for carbon in the isobutane intermediates, was measured at various space times. By extrapolating to zero space time, a corrected value for $\tau_{\text{iso-C}_4}$, $\tau_{\text{iso-C}_4}^*$, was determined (35). The average reaction rate of surface intermediates (TOF_{ITK}^{*}) was determined as $1/\tau_{\text{iso-C}_4}^*$ (40). The corresponding concentration of active surface intermediates leading to iso-C₄, $N_{\text{iso-C}_4}^*$, was calculated by multiplying $\tau_{\text{iso-C}_4}^*$ with the rate of isobutane formation (40). Readsorption of n-C₄ in the catalyst bed did not appear to be significant and was not corrected (thus $N_{n\text{-C}_4}$ is not denoted with an *). More detailed descriptions of the correction of τ and N values can be found in Refs. (35) and (43).

Table 5 lists the initial (5 min TOS) surface kinetic parameters measured at 250°C in the absence of H₂. Due to the fast deactivation of the catalysts during the period of the isotopic switch (approximately 6 min) for the initial measurement, the surface kinetic parameters obtained contain larger than normal error (ca. ±1.5 s for τ vs a normal error of ±0.2 s). $\tau_{\text{iso-C}_4}^*$ was very similar for the two catalysts; however, the concentration of the active surface intermediates leading to iso-C₄ ($N_{\text{iso-C}_4}^*$, which is related to the concentration of active sites) on PtSZ was significantly lower than that on SZ. The concentration of reversibly adsorbed n-C₄, $N_{n\text{-C}_4}$, was approximately an order of magnitude higher than $N_{\text{iso-C}_4}^*$ for both SZ and PtSZ.

The estimated surface coverages of the reversibly adsorbed n-C₄ and of the active surface intermediates leading to iso-C₄ (in the absence of H₂ addition) with respect to the total sulfur content ($\theta_{\text{i,sulfur}}$) and with respect to the total concentration of strong and intermediate strength acid sites measured by NH₃ microcalorimetry ($\theta_{\text{i,acid}}$) are reported in Table 6. Pt promotion did not appear to have a significant effect (within experimental error) in the absence of H₂ on the fraction of sulfate species/acid sites utilized in formation of the active surface intermediates leading to iso-C₄ or the amount of n-butane reversibly adsorbed. The calculated values of $\theta_{\text{iso-C}_4,\text{acid}}$ and $\theta_{n\text{-C}_4,\text{acid}}$ suggest that only approximately 2.5% and 20% of the strong and intermediate strength acid sites were utilized for reaction and the reversible adsorption of n-C₄, respectively.

Activity in the Presence of H₂

The inhibiting effect of H₂ on n-butane isomerization activity at 150°C is clearly seen by comparing the results shown in Figs. 3 and 5. The initial activities for both the catalysts were ca. 2 orders of magnitude lower in the presence of H₂ (Fig. 5) than in the absence (Fig. 3) at this temperature. SZ still exhibited fast initial deactivation. The initial activity on PtSZ was also still lower than that on SZ, but there was a lack of significant initial deactivation of the Pt-promoted catalyst. Upon an increase in reaction temperature from 150°C to 250°C, however, the promoting effect of Pt in the

TABLE 5

Initial (5 min) Surface Kinetic Parameters in the Absence of H₂ at 250°C^a

Catalyst	TOS (min)	H ₂ /HC	Rate _{iso-C₄} (μmol/g/s)	$\tau_{\text{iso-C}_4}^*$ ^b (s)	TOF _{ITK} ^c (10 ⁻³ s ⁻¹)	$N_{\text{iso-C}_4}^*$ ^d (μmol/g)	$N_{n\text{-C}_4}$ ^e (μmol/g)
SZ	5 (initial)	0	0.37	8.2	122	3.0	19.6
PtSZ	5 (initial)	0	0.17	10.3	97	1.8	19.8

^a Reaction conditions: 250°C, 1.5 atm, n-C₄ = 2.5 mol%, space time = 0.02–0.06 s.^b Asterisk indicates values obtained following correction for product readsorption. Maximum error = ±15%.^c TOF_{ITK}^{*} = $1/\tau_{\text{iso-C}_4}^*$. Maximum error = ±15%.^d $N_{\text{iso-C}_4}^*$ = $R_{\text{iso-C}_4} \tau_{\text{iso-C}_4}^*$. Maximum error = ±15%.^e No significant readsorption in catalyst bed, $N_{n\text{-C}_4} = F_{n\text{-C}_4} \tau_{n\text{-C}_4} = (2.55 \mu\text{mol/g/s}) \tau_{n\text{-C}_4}$. Maximum error = 15%.

TABLE 6

Estimated Initial (5 min) Surface Coverages in the Absence of H₂ at 250°C with Respect to the Total Sulfur Content (θ_{sulfur}) and to the Strong and Intermediate Strength Acid Site Concentration (θ_{acid})

Catalyst	TOS (min)	H ₂ /HC	Surface coverage based on total sulfur content		Surface coverage based on acid sites (strong + intermediate)	
			$\theta_{\text{iso-C}_4,\text{sulfur}}^c$	$\theta_{n\text{-C}_4,\text{sulfur}}^d$	$\theta_{\text{iso-C}_4,\text{acid}}^c$	$\theta_{n\text{-C}_4,\text{acid}}^d$
SZ ^a	5 (initial)	0	0.006	0.040	0.03	0.19
PtSZ ^b	5 (initial)	0	0.004	0.040	0.02	0.25

^aTotal sulfur content (N_{sulfur}) = 493.7 μmol of S/ g_{cat} , concentration of acid sites ($N_{\text{acid}} > 125$ kJ/mol) = 104.4 μmol of acid sites/ g_{cat} .

^bTotal sulfur content (N_{sulfur}) = 496.9 μmol of S/ g_{cat} , concentration of acid sites ($N_{\text{acid}} > 125$ kJ/mol) = 78.6 μmol of acid sites/ g_{cat} .

^cMaximum error = $\pm 15\%$.

^dMaximum error = $\pm 15\%$.

presence of H₂ was clearly observed (Fig. 6 vs Fig. 4). The initial activity on PtSZ was ca. 26% higher than that on the unpromoted SZ catalyst. With the increase in reaction temperature, a slight decrease in the pseudo-steady-state selectivity toward isobutane (from 98% to 94%) was observed for both catalysts. Another obvious change in the activity profile with the addition of H₂ was the reduction in catalyst deactivation seen for both catalysts, but, especially, for the Pt-promoted catalyst. At 250°C, the catalytic activity on PtSZ remained essentially constant for TOS ≥ 50 min, while a steady decrease in the activity with TOS was observed for SZ.

Tables 1 and 4 show that the sulfur contents of the catalysts were constant within experimental error following reaction in the presence of H₂ at 250°C. The carbon contents of the catalysts were similar for SZ and PtSZ but were much lower than when the reaction was carried out in the absence of H₂ at 250°C (Table 4) or at 150°C (Table 3).

In summary, at the lower reaction temperature of 150°C, even with H₂ addition, the presence of Pt actually decreased the activity of the SZ catalyst. Only at the higher reaction temperature of 250°C was a promoting effect of Pt observed in the presence of H₂. This promoting effect of Pt as a function of reaction temperature is in agreement with the results of Alvarez *et al.* (11).

H₂ appeared to have both positive and negative effects on the SZ-based catalysts. Figure 7 shows the rate of iso-C₄ formation with TOS as the H₂/HC ratio was varied from 4 to 9 and then returned to 4 (*n*-C₄ concentration kept constant). With the increase in H₂ partial pressure, decreases in the catalytic activities of both catalysts were observed, in agreement with the literature (9, 23, 44). A higher H₂ partial pressure enhanced the catalyst stability, as catalyst deactivation was not observed for SZ during reaction at H₂/HC = 9. This is evident in the catalytic activities of the catalysts upon returning to H₂/HC = 4. The catalytic activity

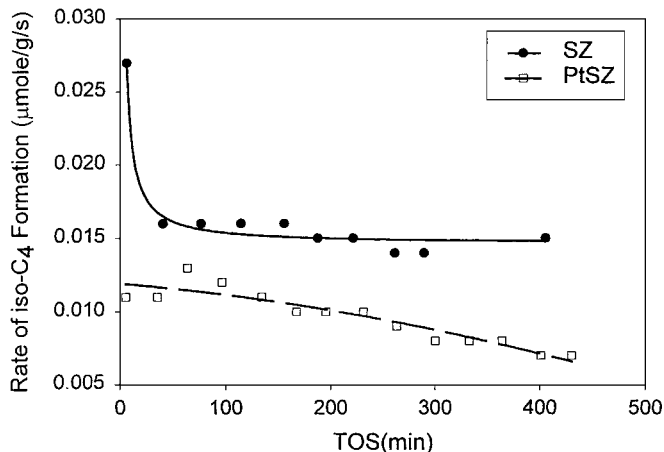


FIG. 5. *n*-Butane isomerization activities of the catalysts in the presence of H₂ ($T = 150^\circ\text{C}$).

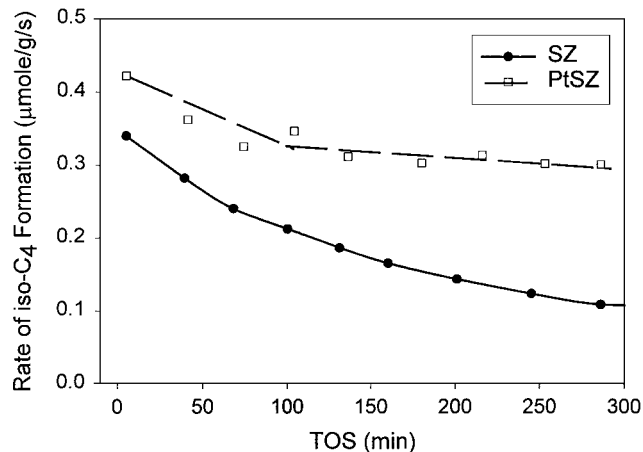


FIG. 6. *n*-Butane isomerization activities of the catalysts in the presence of H₂ ($T = 250^\circ\text{C}$).

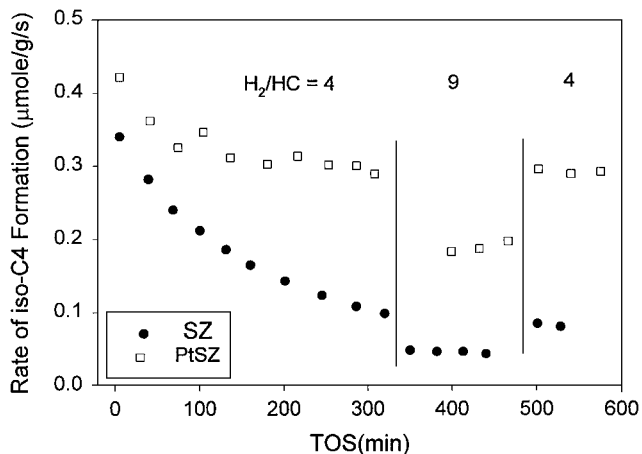


FIG. 7. *n*-Butane isomerization activities of SZ and PtSZ: effect of changes in H₂ partial pressure (*T* = 250°C).

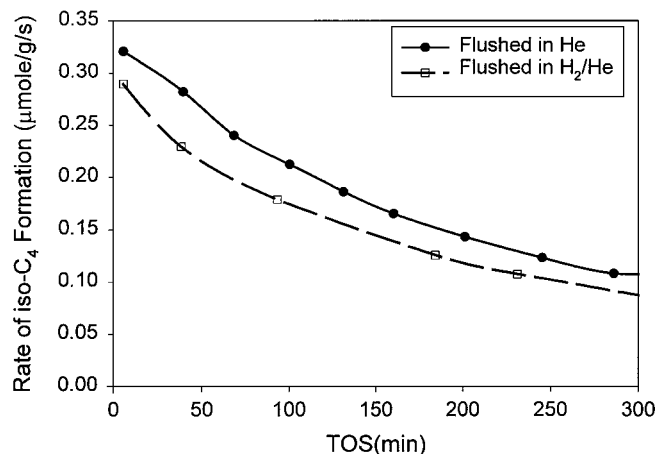


FIG. 8. Effect of flushing gas on the *n*-butane isomerization activity of SZ in the presence of H₂ (*T* = 250°C).

of PtSZ returned to its earlier steady-state value and that of SZ was only slightly lower than the earlier pseudo-steady-state value even after 120 min of reaction at the higher H₂ partial pressure.

The effect of using a H₂/He mixture rather than pure He to flush the pretreated catalysts prior to reaction at 250°C was also studied. The H₂/He mixture flush did not affect the catalytic activity of PtSZ. However, a small decrease in the catalytic activity was observed when the pretreated SZ was flushed with the H₂/He mixture rather than with pure He (Fig. 8). This decrease in activity of SZ upon H₂ treatment has been reported in the literature previously and is suggested to be related to the reduction of surface sulfate species by H₂ (12, 45). The presence of Pt has been shown to enhance the reduction of surface sulfate species in the presence of H₂, especially at a higher treatment/flush temperature (350°C) (45). As to why the catalytic activity of PtSZ was not affected by the H₂/He flush, no explanation can be given at this time.

Table 7 contains the surface kinetic parameters, at 250°C and in the presence of H₂, obtained utilizing SSITKA. Compared to the initial surface kinetic parameters obtained in the absence of H₂ (Table 5), addition of H₂ resulted in significantly increased values of $\tau_{\text{iso-C}_4}^*$ and $N_{\text{iso-C}_4}^*$ for PtSZ, while values for SZ remained essentially constant. For H₂/HC = 4, at 5 min TOS, $\tau_{\text{iso-C}_4}^*$ for PtSZ was approximately 3 times that of SZ. The concentration of the active surface intermediates leading to iso-C₄ was also significantly higher for PtSZ (ca. 3–4 times), but no significant difference in the concentrations of reversibly adsorbed *n*-C₄ was observed between SZ and PtSZ in the presence (H₂/HC = 4) or absence (Table 5) of H₂ at 250°C. When the steady state was reached for PtSZ (at 150 min), $\tau_{\text{iso-C}_4}^*$ had increased slightly from 28 to 36 s, while $N_{\text{iso-C}_4}^*$ remained relatively constant. Apparent decreases in $\text{TOF}_{\text{ITK}}^*$ ($1/\tau_{\text{iso-C}_4}^*$), $N_{\text{iso-C}_4}^*$, and $N_{n\text{-C}_4}$ were observed with an increase in H₂ partial pressure (H₂/HC = 4–9) during *n*-C₄ isomerization on PtSZ at steady state. In the presence of H₂, the Pt-promoted

TABLE 7

Surface Kinetic Parameters in the Presence of H₂ at 250°C^a

Catalyst	TOS (min)	H ₂ /HC	Rate _{iso-C₄} (μmol/g/s)	$\tau_{\text{iso-C}_4}^*$ ^b (s)	$\text{TOF}_{\text{ITK}}^*$ ^c (10 ⁻³ s ⁻¹)	$N_{\text{iso-C}_4}^*$ ^d (μmol/g)	$N_{n\text{-C}_4}$ ^e (μmol/g)
SZ	5 (initial)	4	0.35	10.9	92	3.8	19.1
	5 (initial)	4	0.44	28.3	35	12.5	18.4
PtSZ	150 (ss)	4	0.34	35.8	28	12.2	18.9
	480 (ss)	9	0.19	40.1	25	7.6	10.0

^a Reaction conditions: 250°C, 1.5 atm, *n*-C₄ = 2.5 mol%, space time = 0.02–0.06 s.

^b Asterisk indicates values obtained following correction for product readsorption. Maximum error = ±10%.

^c $\text{TOF}_{\text{ITK}}^* = 1/\tau_{\text{iso-C}_4}^*$. Maximum error = ±10%.

^d $N_{\text{iso-C}_4}^* = R_{\text{iso-C}_4} \tau_{\text{iso-C}_4}^*$. Maximum error = ±10%.

^e No significant readsorption in catalyst bed, $N_{n\text{-C}_4} = F_{n\text{-C}_4} \tau_{n\text{-C}_4} = (2.55 \mu\text{mol/g/s}) \tau_{n\text{-C}_4}$. Maximum error = ±15%.

TABLE 8
Estimated Surface Coverages in the Presence of H₂ at 250°C

Catalyst	TOS (min)	H ₂ /HC	Surface coverage based on total sulfur content		Surface coverage based on acid sites (strong + intermediate)	
			$\theta_{\text{iso-C}_4, \text{sulfur}}^c$	$\theta_{n\text{-C}_4, \text{sulfur}}^d$	$\theta_{\text{iso-C}_4, \text{acid}}^c$	$\theta_{n\text{-C}_4}^d$
SZ ^a	5 (initial)	4	0.008	0.039	0.04	0.18
	5 (initial)	4	0.0025	0.037	0.16	0.23
PtSZ ^b	150 (ss)	4	0.025	0.038	0.16	0.24
	480 (ss)	9	0.015	0.020	0.10	0.13

^aTotal sulfur content (N_{sulfur}) = 493.7 μmol of S/g_{cat}, concentration of acid sites ($N_{\text{acid}} > 125$ kJ/mol) = 104.4 μmol of acid sites/g_{cat}.

^bTotal sulfur content (N_{sulfur}) = 496.9 μmol of S/g_{cat}, concentration of acid sites ($N_{\text{acid}} > 125$ kJ/mol) = 78.6 μmol of acid sites/g_{cat}.

^cMaximum error = $\pm 10\%$.

^dMaximum error = $\pm 15\%$.

catalyst appeared to utilize a significantly larger fraction of sulfate species/acid sites in forming active surface intermediates leading to iso-C₄ than the unpromoted SZ catalyst (Table 8). The results suggest that 16% of the strong and intermediate strength acid sites were utilized initially in the formation of the active surface intermediates on the Pt-promoted SZ in the presence of H₂ at 250°C, compared to only 2% in the absence of H₂. Only 4% appeared to be utilized on the unpromoted SZ initially at 250°C, as was also approximately the case in the absence of H₂.

DISCUSSION

Fundamental Facts

A discussion of results for butane isomerization is best understood by keeping several important facts in mind. First, the initial step in butane isomerization has been hypothesized to be butene formation according to the well-accepted bimolecular mechanism (46). This has been shown to be the case for this reaction on SZ under the reaction conditions utilized in this study (50). For this study, butene impurities were removed from the *n*-butane reactant stream before introduction into the reactor so that only butene formed from *n*-butane on the catalyst would participate in the reaction.

Second, the most active sites of a catalyst are usually the first to deactivate. Also, a more active catalyst can hypothetically deactivate to an activity lower than that of a less active catalyst during an initial reaction period.

Third, there can be competing effects from the change in a particular parameter (such as the concentration of H₂ added). For example, something may decrease activity but increase catalyst stability. Because of the large impact on the rate of deactivation during the initial reaction period, the initial activity may actually appear to be increased at lower values of the parameter and decreased at higher values. This

can lead to a philosophical discussion as to whether low values of the parameter lead to an “increase” in activity. It would in an effective way, but only by decreasing rapid initial deactivation more than any concomitant decrease in absolute activity.

It is helpful to remember these facts and complexities as one considers the various results from this study.

Effect of H₂ on SZ

Regardless of the reaction temperature used in this study, addition of H₂ to the feed stream reduced the measured initial catalytic activity of the unpromoted SZ catalyst. At 150°C, the detrimental impact of H₂ on *n*-C₄ isomerization was more clearly shown. The initial catalytic activity decreased by approximately 2 orders of magnitude at this temperature upon the addition of H₂ (Figs. 3 and 5). The smaller difference in activity seen at 250°C upon addition of H₂ (Figs. 4 and 6) was probably simply due to an enhanced catalyst deactivation at the higher reaction temperature in the *absence* of H₂ which compensated for a higher initial activity at TOS = 0 min. The enhanced catalyst deactivation in the *absence* of H₂ at 250°C as opposed to that at 150°C is clearly indicated in the higher carbon content of the catalyst following reaction at the higher temperature (Tables 3 and 4).

The results from SSITKA (Tables 5 and 7) indicate that introduction of H₂ (at H₂/HC = 4) had little impact on the average reaction rate of surface intermediates ($\text{TOF}_{\text{ITK}}^* = 1/\tau_{\text{iso-C}_4}^*$ for SZ at 250°C). It can be seen in Tables 5 and 7 that the values of $N_{\text{iso-C}_4}^*$ were also initially very similar (3 vs 3.8). Considering that catalyst deactivation was more severe during the initial 5 min TOS when H₂ was not present in the feed stream, one might conclude that these values reflect a similar number of intermediates initially with or without H₂ present. However, it is likely that the concentration of active surface intermediates at TOS = 0 min upon H₂ addition

was actually somewhat lower due to a suppression effect of H₂ on butene formation. A more rapid decrease in the number of intermediates in the absence of H₂ due to site deactivation during the first 5 min of reaction would be consistent with the activity results at 150 and 250°C (Figs. 3 and 5 and Figs. 4 and 6, respectively).

The negative effect of H₂ on catalytic activity was accompanied by a positive impact on catalyst stability, as evidenced by a much slower decline in activity. The reduced carbon content following reaction at 250°C (in the presence of H₂) (Table 4) suggests that deactivation via coke/oligomer formation on SZ was inhibited by the presence of H₂. Two experiments provided more insight into the potential role of sulfur reduction on catalyst deactivation. Flushing of the catalyst surface with a H₂-containing mixture prior to the reaction should promote sulfur reduction (45). A loss of activity following the H₂/He flush was observed, but the impact of the H₂/He flush was not significant compared to that of a flush by He alone (Figure 8). A higher H₂ partial pressure in the feed stream should also lead to greater reduction of surface sulfate species. As shown in Fig. 7, the catalytic activity of SZ was not significantly reduced upon return to a lower H₂ partial pressure following reaction at a higher H₂ partial pressure. The results from these two experiments and from reaction with and without H₂ strongly support a conclusion that deactivation of SZ is mainly due to coke/oligomer formation rather than sulfur reduction.

Effect of Pt Addition on SZ in the Absence of H₂

It was found that promotion of SZ with 0.5 wt% Pt did not enhance the initial isomerization activity nor the stability of the catalyst in the *absence* of H₂ (Figs. 3 and 4, Tables 3 and 4). In fact, a decrease in the initial isomerization rate upon Pt addition was observed relative to that of SZ at reaction temperatures of 150 and 250°C in the absence of H₂ addition. Deactivation rates for PtSZ were similar to those for SZ.

The SSITKA results at 250°C showed a simultaneous decrease in the surface intermediates' concentration ($N_{\text{iso-C}_4}^*$) upon addition of Pt (Table 5). It has been reported that Pt supported on SZ has poor hydrogenation-dehydrogenation ability (26, 27). However, the lack of a Pt metallic function would not explain a decrease in the concentration of the active acid sites. In fact, as shown in Table 2, the strong and intermediate strength acid site concentrations on SZ and PtSZ were quite similar.

Butene formation appears to be critical for isobutene formation. Less formation of butene could lead to active site coverages significantly less than 1. However, it is not clear why, in the absence of H₂, butene formation would be lower on PtSZ than on SZ. In addition, the carbon contents were similar for both SZ and PtSZ (Table 4), permitting us to conclude that the lower number of active sites on PtSZ was

not due to excess carbon deposition. It cannot be ruled out, however, that the presence of Pt may have caused a rapid deactivation of the available catalyst sites during initial reaction, resulting in a lower activity than SZ during most of the TOS (13). A rapid decrease in the concentration of surface intermediates during the initial period of reaction could have been the result of butene generation by Pt, initially resulting in rapid deactivation of the catalyst sites due to formation of coke/oligomers (5).

In any case, Pt promotion of SZ does not result in any obvious enhancement of desirable catalyst properties in the absence of H₂.

Synergistic Effects of H₂ and Pt

In this study, the promoting effect of Pt was *only observed* in the *presence* of H₂ at the higher reaction temperature of 250°C, but not at 150°C. Alvarez *et al.* (11) reported similar results during temperature-programmed reaction (TPRx) where a significant promoting effect of Pt was apparent only when the reaction temperature was higher than 200°C in the presence of H₂.

Comparing the initial (5 min TOS) surface kinetic parameters of SZ and PtSZ (Table 7), the promoting ability of Pt on SZ in the *presence* of H₂ appears to be related to a significant increase in the concentration of active surface intermediates, leading to iso-C₄ for TOS ≥ 5 min. The higher concentration of active surface intermediates may have been due to (a) a proposed formation of active protonic sites (18–20, 32) and/or (b) a role of Pt and H₂ in enhancing formation of the C₈ intermediates without causing as much site deactivation. On the other hand, the average surface residence time of the active reaction intermediates on PtSZ was more than double that on the unpromoted SZ (TOF_{TK}^{*} thus lower). The apparent increase in the average residence time of the most active surface intermediates may have been simply due to an averaging effect. Newly formed or additionally utilized active sites could have possessed lower activities than the relatively smaller concentration of "original" very active sites, thereby causing the average residence time of the reaction intermediates measured to increase. In any case, the more than 6 times higher concentration of intermediates resulted in a higher initial activity for PtSZ.

Two observations can be made about the change in catalytic activity with TOS for PtSZ. First, an increase in the average residence time of the surface intermediates ($\tau_{\text{iso-C}_4}^*$), from 28.3 to 35.8 s, was found. This apparent increase was probably due to the loss of a few highly active sites during the initial deactivation of PtSZ, resulting in a decrease in the average site activity and an increase in average surface residence time, similar to the case for unpromoted SZ (1). The second observation is that the concentration of the active surface intermediates remained relatively constant with TOS for PtSZ. This result clearly indicates that H₂ and

Pt acted together to maintain the active sites, most likely by preventing coke/oligomer formation.

Interestingly, the observed increase in $\tau_{\text{iso-C}_4}^*$ (decrease in $\text{TOF}_{\text{ITK}}^*$) following Pt addition does not agree with the proposed enhancement of the catalytic activity via increased hydride transfer ability of SZ (21). However, Iglesia *et al.* (21) studied *n*-hexane isomerization and observed a positive effect of H₂ on the isomerization rate. For *n*-hexane isomerization, the reaction proceeds via a monomolecular mechanism (which involves one hydrocarbon molecule), and desorption of the isomerized carbenium ions is the rate-determining step (21, 34, 47, 48). Therefore, an increase in hydride transfer ability would be reflected in an increase in isomerization rate. It is well known that the reaction mechanism of *n*-butane isomerization is somewhat different from that of larger alkane isomerization (such as *n*-pentane and *n*-hexane) (9, 23, 49). Under the reaction conditions utilized in this study, *n*-butane isomerization on PtSZ appears to occur via a bimolecular mechanism (7, 23, 46, 49, 50). Therefore, differences in the hydrocarbon reactant, the reaction mechanism, and, most importantly, the rate-determining step may have contributed to the differences seen in the role of H₂ and Pt on the average site activity in the present study and that reported by Iglesia *et al.* (21). The increase in the average residence time of the active surface intermediates observed upon both Pt promotion and H₂ addition in this study suggests that, for *n*-C₄ isomerization on SZ, the rate-determining step is not related to an enhanced hydride transfer ability of the catalyst.

With an increase in H₂ partial pressure (H₂/HC = 4 → 9; $p_{\text{H}_2} = 0.15 \rightarrow 0.34$ atm), a decrease in $N_{\text{iso-C}_4}^*$ was observed on PtSZ. This decrease may have been due to an increased concentration of surface hydrogen. Garin *et al.* (31) have speculated that, at higher H₂ partial pressures, some active sites may be occupied by surface hydrogen, thereby decreasing the amount of active sites available for reaction. Another possibility, as has also been previously suggested, is that H₂ spillover to the surface of SZ could have disturbed the balance between the Brønsted and Lewis acid sites (51, 52), known to be of critical importance, rather than simply blocking the active acid sites. A third and even more likely possibility is that H₂ inhibited the dehydrogenation of *n*-C₄ (31). As H₂ surface coverage on Pt increases with H₂ partial pressure, the dehydrogenation reaction becomes less favored. This inhibition of butene formation would result in a decrease in the concentration of active surface intermediates. It is important to note that H₂ addition to *n*-butane isomerization on PtSZ probably has both positive and negative effects—possibly decreasing deactivation but also decreasing butene formation. Thus, one might expect there to be an optimum for H₂ addition: a lower concentration improving the deactivation characteristics but a higher one causing a lower activity.

We still lack a clear understanding about the nature of the acid sites responsible for *n*-butane isomerization. Fogash *et al.* (37) have suggested that the catalytic activity is carried out by the acid sites with $\Delta H_{\text{ads,NH}_3} > 125$ kJ/mol. The acid sites with $\Delta H_{\text{ads,NH}_3} > 150$ kJ/mol have been proposed to be responsible for the high initial activity, with the sites with $125 < \Delta H_{\text{ads,NH}_3} < 150$ kJ/mol contributing most of the activity after the fast initial deactivation of the sites with $\Delta H_{\text{ads,NH}_3} > 150$ kJ/mol (42). Ardizzone *et al.* (53) and Vartuli *et al.* (54) arrived at similar conclusions for etherification of benzoic acid on SZ catalysts and for *n*-hexane isomerization on tungsten/zirconia catalysts, respectively. Analysis of results from Gao and co-workers (41, 42) for *n*-butane isomerization on SZ-based catalysts, however, does not show a clear relationship between the concentration of the intermediate and strong acid sites and the catalytic activity for a variety of SZ-based catalysts. Our results are in complete agreement. As can be discerned from data for $\theta_{\text{iso-C}_4,\text{acid}}$ and rate in Tables 5–8, the catalytic activity is not a simple function of acid sites of specific strength. Rather, the catalyst composition and reaction conditions have a significant effect on the concentration of active surface species and their relationship to the acid sites of strong and intermediate strengths. Under the reaction conditions studied, only 4–16% of strong and intermediate strength acid sites appeared to participate in formation of active surface intermediates. The small fraction of even the most acidic sites involved in the reaction makes a clear elucidation of the nature of the catalytically active sites on these SZ-based catalysts by any acidity measurement technique very difficult, especially since all active sites may not be utilized due to deactivation and/or low coverage.

CONCLUSIONS

During *n*-butane isomerization, the unpromoted SZ catalyst deactivates quickly. Introduction of H₂ in the feed stream reduces the rate of catalyst deactivation. The enhanced catalyst stability at higher H₂ partial pressure and the negligible effect of pretreating the catalyst in H₂ and He rather than He alone permits us to conclude that catalyst deactivation is mainly due to active site loss by coke/oligomer formation and not surface sulfate reduction. With the enhancement in catalyst stability, however, there is also a decrease in the initial isomerization activity for SZ, especially at 150°C. This is less obvious for reaction at 250°C, probably due to a more rapid initial deactivation at this higher temperature in the absence of H₂. The presence of H₂ probably causes a decrease in the concentration of the active surface intermediates by inhibition of butene formation, which simultaneously decreases deactivation by coke formation.

Promotion of SZ with 0.5 wt% Pt did not improve the activity (Fig. 9) nor the stability of the catalyst in the

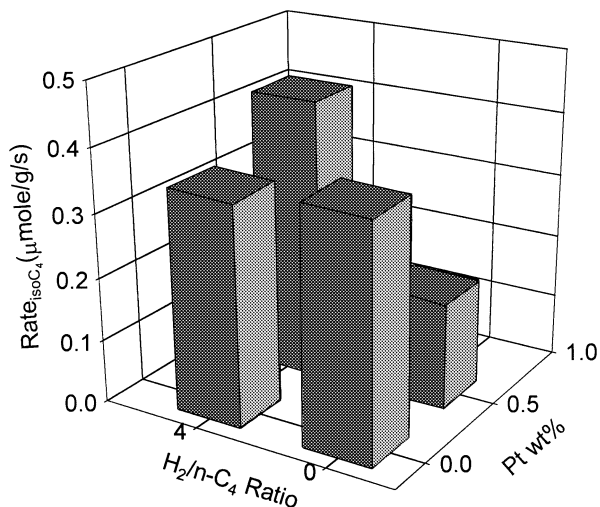


FIG. 9. Effects of Pt and H₂ on initial *n*-butane isomerization activity of SZ-based catalysts ($T = 250^\circ\text{C}$ TOS = 5 min).

absence of H₂. The significant decrease in the measured isomerization activity upon Pt promotion was due to a decrease in the concentration of active surface intermediates and an increase in surface residence time for reaction, $\tau_{\text{iso-C}_4}^*$ (Figs. 10 and 11).

The promoting effect of Pt was only observed for the higher reaction temperature of 250°C and in the presence of H₂. The presence of Pt and H₂ increased the concentration of the most active surface intermediates, leading to isobutane by more than 3-fold (Fig. 11); however, an increase in the average surface residence time of reaction intermediates was also observed (Fig. 10). This increase in the surface residence time suggests that the enhancement

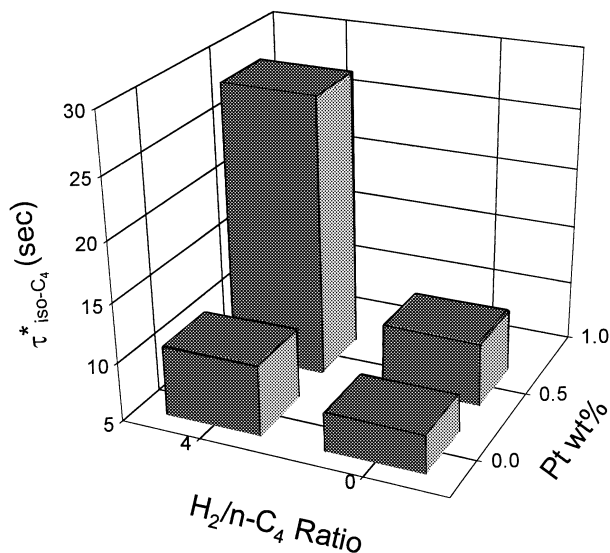


FIG. 10. Effects of Pt and H₂ on the initial average site activity of SZ-based catalysts ($T = 250^\circ\text{C}$, TOS = 5 min).

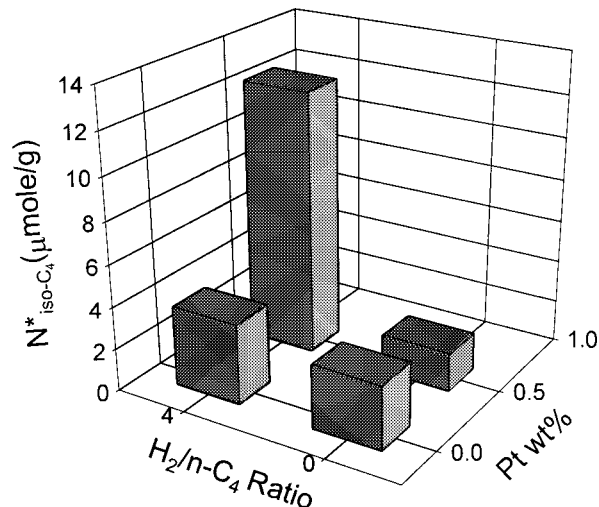


FIG. 11. Effects of Pt and H₂ on the initial concentration of the most active surface intermediates ($T = 250^\circ\text{C}$, TOS = 5 min).

in hydride transfer ability of SZ does not significantly affect *n*-butane isomerization, unlike *n*-hexane isomerization (21). The combined effects of Pt promotion and H₂ addition cause a significant increase in the concentration of active intermediates. Part of this increase must be due to a decrease in coke formation on the active sites. However, it is highly possible that formation of butene with a concomitant decreased chance to form coke could also play a role.

There has been no obvious correlation found between the concentration of acid sites having certain ranges of heats of adsorption for ammonia and rates of reaction seen. Given the relatively low occupancy (4–16%) of the intermediate and strong acid sites by reaction intermediates, this is not surprising. This low occupancy is caused probably by fast deactivation of the most active sites and possibly by the rate of generation of butene from *n*-butane, a likely requirement in the genesis of C₈ intermediates on the active acid sites.

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