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Skeletal Isomerization of Hydrocarbons over Zirconium Oxide Promoted by Platinum and Sulfate Ion

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The genesis of the high activity of zirconium oxide promoted by platinum and sulfate ion ($Pt/SO_4^{2-}-ZrO_2$) for skeletal isomerization of butane and pentane in the presence of hydrogen is studied in terms of the interaction of the catalyst with molecular hydrogen. For skeletal isomerization of pentane at 523 K, $Pt/SO_4^{2-}-ZrO_2$ showed activity only in the presence of molecular hydrogen, and its activity persisted for a long period. For skeletal isomerization of butane at 523 K, the catalyst showed activity in the absence of hydrogen, but the activity was markedly enhanced in the presence of hydrogen. For pentane and butane skeletal isomerization, the products consisted exclusively of 2-methylbutane and 2-methylpropane, respectively. For a typical acid-catalyzed reaction of cyclopropane ring opening at 373 K, the presence of hydrogen enhanced the activity, but the hydrogen enhancement effect was small. The products consisted exclusively of propene even in the presence of hydrogen; hydrogenation of propene scarcely occurred. Infrared spectroscopic study of adsorbed pyridine showed that by heating the catalyst in the presence of hydrogen in the temperature range 423–623 K, protonic acid sites were formed with concomitant decrease in the number and strength of Lewis acid sites, demonstrating that the protonic acid sites originate from molecular hydrogen. The mechanisms of protonic acid site generation are discussed. It is suggested that molecular hydrogen dissociates on the platinum to hydrogen atoms which undergo spillover on the $SO_4^{2-}-ZrO_2$ and convert to an H^+ and an e^- or H^-. The H^+ acts as catalytic site for acid-catalyzed reactions. © 1991 Academic Press, Inc.

INTRODUCTION

Skeletal isomerization of straight-chain paraffins is of great importance in the petroleum refining industry to increase the octane number of synthetic gasoline (*1*), and to synthesize branched paraffins which react with olefins under mild conditions to give highly branched hydrocarbons (*2*). Recently, Hosoi *et al.* have reported that the loading of certain metals such as Pt, Rh, and Ni on $SO_4^{2-}-ZrO_2$ gave high-performance catalysts for skeletal isomerization of pentane (*3, 4*). Among the series of $SO_4^{2-}-ZrO_2$-supported metals, $Pt/SO_4^{2-}-ZrO_2$ catalyst showed the highest activity. The support, $SO_4^{2-}-ZrO_2$, possesses strong acid sites which catalyze the butane skeletal isomerization at 293 K (*5*) and cyclopropane isomerization at 373 K (*6*).

The $Pt/SO_4^{2-}-ZrO_2$ catalyst is characterized not only by a high activity but also by persistence of the activity for a long period, more than 1000 h, when the reaction is carried out in the presence of hydrogen (*4*). Hosoi *et al.* explained the hydrogen effect as removal of coke formed during the reaction by hydrogenation (*4*).

Hydrogen effects in catalysis are strongly connected with the phenomena referred to "hydrogen spillover" (*7, 8*), and the nature of the spiltover hydrogen has been extensively studied. One of the mechanisms of the hydrogen spillover involves the heterolytic process. A hydrogen molecule dissociates into two H atoms on the metal. The H atom undergoes spillover onto the support where the formation of an H^+ and an H^- or the formation of hydroxyl groups occurs (*9–12*). It seems possible that the formed H^+ acts as a protonic site to catalyze acid-catalyzed reactions. However, there have been no re-

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ports that demonstrate the participation of the spiltover H^+ in an acid-catalyzed reaction.

The effects of hydrogen used as a carrier gas on the activity for the acid-catalyzed reaction have been studied by many researchers (*13–17*). In most cases reported so far, the presence of hydrogen suppressed the activities for the acid-catalyzed reactions. Gnep and Guisnet reported that the activity for disproportionation of toluene over mordenite catalyst decreased in the presence of hydrogen (*13*). They explained the decrease in disproportion activity by a decrease in the concentration of benzylic carbocation intermediates due to the reverse reaction of the carbocation formation on protonic acid sites. Karge *et al.* explained that the decrease in the rate of the ethylbenzene disproportionation on bifunctional Pt/LaNa*X* catalyst was caused by the decrease in the concentration of protonic acid sites (*14*). Matsuda *et al.* (*16*) and Schulz-Ekloff *et al.* (*17*) proposed that the decrease in the disproportionation activity was due to the shielding of Lewis acid sites by hydride ion and hydrogen atom, respectively.

On the other hand, promoting effects of hydrogen on the acid-catalyzed reactions have been reported for the Ag ion exchanged Y zeolite (*18*). In the system of Ag–Y zeolite, a proton is produced by the reaction of Ag^+ with hydrogen molecule accompanied by the formation of Ag^0. The proton acts as the active site for acid-catalyzed reactions.

In this paper, we study the hydrogen effect on the catalytic activity of Pt/SO_4^{2-}–ZrO_2 and report that the spiltover hydrogen forms protonic acid sites and enhances the catalytic activities for acid-catalyzed reactions. The mechanisms of the formation of the protonic acid site from molecular hydrogen are discussed.

EXPERIMENT

Catalyst preparation. The sulfate ion-treated $Zr(OH)_4$ was prepared by the impregnation of $Zr(OH)_4$ with 1 *N* H_2SO_4 aqueous solution followed by filtration and drying at 383 K. The $Zr(OH)_4$ was obtained by the hydrolysis of $ZrOCl_2$ $8H_2O$ with 25% NH_4OH aqueous solution followed by filtration. The obtained gel was washed with distilled water until no Cl^- ions could be detected. The Pt/SO_4^{2-}–ZrO_2 sample (0.5 wt% Pt) was prepared by impregnation of SO_4^{2-}–$Zr(OH)_4$ with 1% H_2PtCl_6 aqueous solution followed by drying at 383 K and calcination at 873 K in air. The amount of S remained in the resulting catalyst was 1.5 wt%, determined by XRF technique. The Pt/ZrO_2 (0.5 wt% Pt) was prepared by the impregnation of $Zr(OH)_4$ with 1% H_2PtCl_6 aqueous solution followed by drying at 383 K and calcination at 873 K. The SO_4^{2-}–ZrO_2 was obtained by calcination of SO_4^{2-}–$Zr(OH)_4$ at 873 K. The surface areas of the Pt/SO_4^{2-}–ZrO_2 and Pt/ZrO_2 after successive reduction with hydrogen at 623 K were 114.0 and 56.6 m^2 g^{-1}, respectively.

Reaction procedures. The catalyst was treated in a hydrogen stream at 623 K for 2 h prior to the reaction. The products were analyzed by a gas chromatograph (GC) equipped with VZ-7 column. Reaction of pentane was performed in a flow reactor with fixed bed at 523 K. The WHSV to pentane was 17.3 h^{-1} with 30 cc/min carrier gas of nitrogen; partial pressure of pentane was 253 Torr.

For carrying out the reaction of butane at 523 K (70 Torr, 1 Torr = 133.3 Nm^{-2}), a closed recirculation reactor was used because butane is easily handled in a vacuum system. In this reaction, the prereduction temperature of catalyst was varied from 523 to 693 K.

Cyclopropane ring opening to propene was also carried out in a closed recirculation reactor at 373 K with a mixture of 30 Torr cyclopropane and 100 Torr D_2. After separation by GC, each hydrocarbon was separately collected and subjected to the mass spectrometric analysis to determine the number of D atoms incorporated into the products.

To examine the catalytic property of supported Pt, propene hydrogenation was carried out at various temperatures in a closed recirculation reactor with a mixture of 20 Torr propene and 40 Torr H_2.

Infrared spectroscopy. All IR spectra were recorded on FT/IR-7000 infrared spectrometer (Japan Spectroscopic Co., Ltd.) at room temperature. Pyridine used for probe molecule to determine the type of acid sites was purified by repeated freeze–pump–thaw degassing cycles. A self-supported wafer placed in an *in situ* IR cell with CaF_2 windows was pretreated at desired temperatures in a hydrogen flow for 1.5 h. To determine the effect of prereduction temperature of catalyst on the fractions of protonic acid sites and Lewis acid sites, the prereduced sample was exposed to 2 Torr of pyridine at 423 K for 15 min and, then, evacuated at the same temperature for 15 min.

To examine the conversion of Lewis acid sites to protonic acid sites by heating in the presence of hydrogen, IR was measured as follows. The sample was prereduced by hydrogen flow at 623 k for 1.5 h, and evacuated at room temperature for 30 min. Then, the sample was exposed to 2 Torr of pyridine at 423 K for 15 min, evacuated at 673 K for 15 min and exposed to 600 Torr of hydrogen at room temperature. After heating the sample at 423, 473, 523, 573, and 623 K in the presence of hydrogen, IR spectra were measured.

For the determination of the fractions of protonic acid sites and Lewis acid sites on the surface, the integrated absorbances of the bands at 1450 cm^{-1} (due to pyridine chemisorbed on Lewis acid sites: L–Py) and 1490 cm^{-1} (due to both the L–Py and pyridine chemisorbed on protonic acid sites: B–Py) (*19*) were used with the tangent background, employing the apparent integrated absorption proposed by Hughes and White (*20*) (3.26 cm/μmol for L–Py at 1450 cm^{-1}, 3.4 cm/μmol for B–Py at 1490 cm^{-1}, 0.56 cm/mol for L–Py at 1490 cm^{-1}). The determination of the fraction of protonic acid sites and Lewis acid sites by the bands at 1450 and 1540 cm^{-1} gave essentially the same results. However, the calculation was done on the absorbances of the bands at 1450 and 1490 cm^{-1} because of ambiguous background for the band at 1540 cm^{-1}.

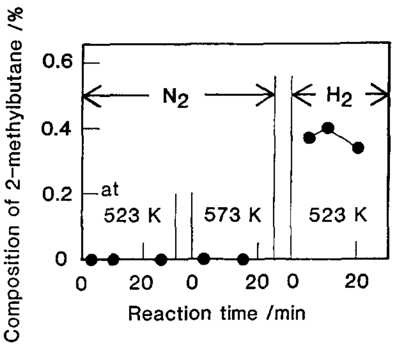

FIG. 1. The effect of hydrogen on the catalytic activity of Pt/SO_4^{2-}-ZrO_2 for pentane skeletal isomerization.

RESULTS

Catalytic performance. The effect of hydrogen on the catalytic activity of Pt/SO_4^{2-}-ZrO_2 for pentane skeletal isomerization is shown in Fig. 1. Under a nitrogen stream, no isomerization occurred even when the reaction temperature was raised to 573 K. On switching the nitrogen to hydrogen, the catalytic activity appeared. The products consisted exclusively of 2-methylbutane. Although the catalytic activity appeared, the activity was about one order of magnitude smaller than that observed when the reaction was carried out in the hydrogen stream from the beginning of the reaction, as described below.

The changes in the activities of Pt/SO_4^{2-}-ZrO_2 and SO_4^{2-}-ZrO_2 with reaction time in a hydrogen stream are shown in Fig. 2. Over Pt/SO_4^{2-}-ZrO_2, neither deactivation nor the hydrogenolysis of pentane occurred for at least 2 h. The hydrocarbons containing carbon numbers smaller than five were not produced at all. Over the SO_4^{2-}-ZrO_2 catalyst drastic deactivation was observed in the initial period of time on stream. In the case of Pt/ZrO_2 (without sulfate ion), no pentane

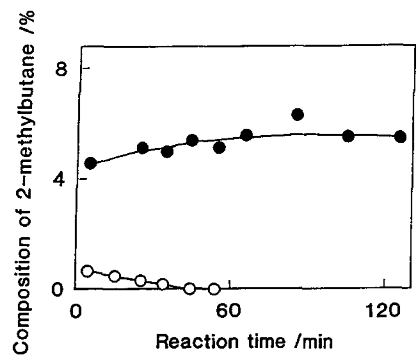

FIG. 2. The changes in the activities of Pt/SO_4^{2-}–ZrO_2 (●) and SO_4^{2-}–ZrO_2 (○) for pentane skeletal isomerization in a hydrogen stream.

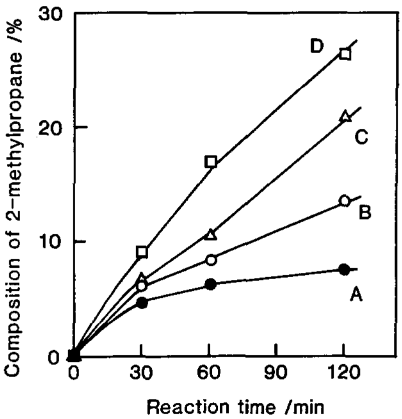

FIG. 3. The time dependence of the composition in butane skeletal isomerization over Pt/SO_4^{2-}–ZrO_2 in the presence of different hydrogen pressures. Hydrogen pressure: (A) 0, (B) 40, (C) 150, (D) 450 Torr.

skeletal isomerization occurred, and only a small amount of products resulting from pentane hydrogenolyis were observed. It should be noted that the alkane hydrogenolysis ability of Pt is completely suppressed when supported on SO_4^{2-}–ZrO_2. As mentioned above, the activity observed in Fig. 2, where the reaction was carried out in a hydrogen stream, was much higher than the activity that appeared by switching the nitrogen stream to hydrogen.

The time dependence of the composition in the reaction of butane over Pt/SO_4^{2-}–ZrO_2 in the presence of different hydrogen pressures in a closed recirculation reactor is shown in Fig. 3. Skeletal isomerization of butane over Pt/SO_4^{2-}–ZrO_2 proceeded to some extent in the absence of hydrogen. However, the rate of the reaction quickly decreased after 10 min, indicating considerable deactivation. In the presence of hydrogen, the reaction was accelerated to a great extent and deactivation became smaller with further increases in the hydrogen partial pressure.

The reason why butane reacted and pentane did not in the absence of hydrogen is not certain. The different reactor types employed for the reactions might have caused the different reactivities of pentane and butane. In the flow reactor employed for the reaction of pentane, the conversion during the initial period of time on stream might have been overlooked.

The activity of the catalyst varied with the prereduction temperature of the catalyst as well as with the hydrogen pressure during the reaction. The variations of the activity, which were obtained by excluding the conversion in the initial 10 min, in both the absence and presence of hydrogen as a function of the prereduction temperature are shown in Fig. 4. The activities decreased with increase in the prereduction temperature, and disappeared at the prereduction temperature at 693 K.

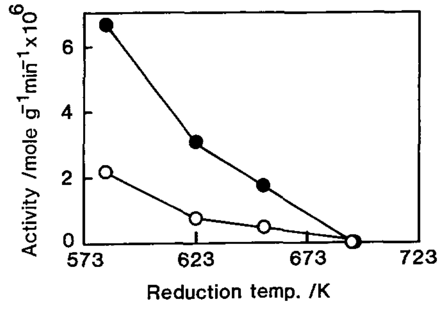

FIG. 4. The variations of the activity of Pt/SO_4^{2-}–ZrO_2 for butane skeletal isomerization as a function of the prereduction temperature. (○) without hydrogen, (●) with hydrogen (40 Torr).

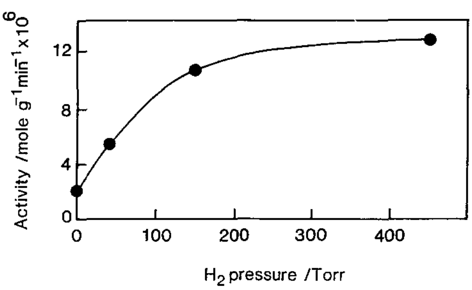

FIG. 5. The effect of the hydrogen pressure on the catalytic activity of Pt/SO_4^{2-}-ZrO_2 for butane skeletal isomerization. The catalyst was prereduced at 583 K.

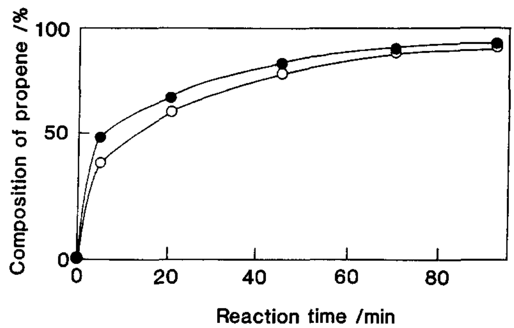

FIG. 7. The time dependence of propene composition for cyclopropane ring opening at 373 K over Pt/SO_4^{2-}-ZrO_2 in both the presence of D_2 (●) and absence of D_2 (○).

The effect of the hydrogen pressure on the catalytic activity of Pt/SO_4^{2-}-ZrO_2 for butane skeletal isomerization is shown in Fig. 5. The rate of butane skeletal isomerization increased with increasing hydrogen pressure.

The responses of the activity to the reaction temperature and to introduction and removal of hydrogen in the reaction mixture are shown in Fig. 6. As hydrogen was removed from the reaction mixture, the reaction rate decreased. It should be noted that the activity was not restored when hydrogen was reintroduced to the reaction mixture. The activity after reintroduction of hydrogen (D) was about one order of magnitude smaller than the initial activity (B). During the reaction without hydrogen, the catalyst deactivation proceeded.

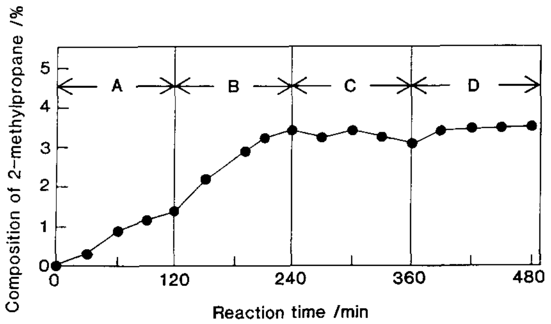

FIG. 6. The responses of activity to the reaction temperature and to introduction and removal of hydrogen in the reaction mixture. (A) with hydrogen at 523 K, (B) with hydrogen at 573 K, (C) without hydrogen at 573 K, (D) with hydrogen at 573 K.

In Fig. 7 are shown the time dependences in cyclopropane ring opening at 373 K in both the presence and absence of D_2. In this reaction, too, positive hydrogen effect was observed. However, the effect was not large as compared to those in the skeletal isomerization of butane and pentane. The products consisted mainly of propene even in the presence of D_2 over Pt/SO_4^{2-}-ZrO_2. All cyclopropane converts into propane in 5 min over Pt/ZrO_2 at the same reaction conditions.

The numbers of D atoms incorporated into propene and cyclopropane were small; in 20 min at 70% conversion, isotopic distribution of propene was d_0, 97.1; d_1, 2.4; d_2, 0.5%; and that of cyclopropane was d_0, 97.4; d_1, 2.2; d_2, 0.4%. These numbers were the same level of those incorporated into propene in the exchange reaction of propene-d_0 with D_2 over Pt/SO_4^{2-}-ZrO_2 under the same reaction conditions. Therefore, it was not clear from the isotopic distribution whether D_2 is involved in the cyclopropane ring opening or not. Over Pt/ZrO_2, the formed propane contained four to eight deuterium atoms in a molecule at 98% cyclopropane conversion.

The results of propene hydrogenation over Pt/SO_4^{2-}-ZrO_2 and Pt/ZrO_2 at different

TABLE 1

The Activities of Propene Hydrogenation over $Pt/SO_4^{2-}-ZrO_2$ and Pt/ZrO_2

Catalyst	Reaction temp. (K)	Activity (min^{-1})[a]
$Pt/SO_4^{2-}-ZrO_2$	323	0.16
Pt/ZrO_2	273	18.46

[a] Number of formed propane molecules per total number of platinum atoms per minute in the initial 5 min at the conversions 1.8% for $Pt/SO_4^{2-}-ZrO_2$ and 6.6% for Pt/ZrO_2.

temperatures are summarized in Table 1. At the reaction temperature of 273 K, hydrogenation proceeded rapidly over Pt/ZrO_2 while hydrogenation was not appreciable over $Pt/SO_4^{2-}-ZrO_2$. Hydrogenation became appreciable over $Pt/SO_4^{2-}-ZrO_2$ when the reaction temperature was raised to 323 K. The hydrogenation activity was much higher for Pt/ZrO_2 than for $Pt/SO_4^{2-}-ZrO_2$. The hydrogenation activity of Pt is greatly suppressed when supported on $SO_4^{2-}-ZrO_2$.

Poisoning experiments with pyridine were carried out for butane skeletal isomerization. The catalyst used was $Pt/SO_4^{2-}-ZrO_2$ which had been pretreated at 623 K in a hydrogen stream followed by evacuation at room temperature. The catalyst was exposed to 2 Torr of pyridine at 423 K for 15 min and then evacuated at 643 K for 15 min. Then butane was exposed to the catalyst at 523 K. No reaction occurred. The catalyst was completely poisoned by the adsorbed pyridine that remained on the sample after evacuation at 643 K.

IR spectroscopy. The acid-site types on the $Pt/SO_4^{2-}-ZrO_2$ catalyst were examined by IR spectroscopy of adsorbed pyridine. The IR spectra of adsorbed pyridine on the catalysts prereduced at different temperatures are shown in Fig. 8. As the pyridine-covered samples were outgassed at 643 K prior to IR measurement, the spectra represent the pyridine adsorbed on strong acid sites. The absorption bands at 1448 and 1540 cm^{-1} are ascribed to the pyridine adsorbed on a Lewis acid site and protonic acid site, respectively.

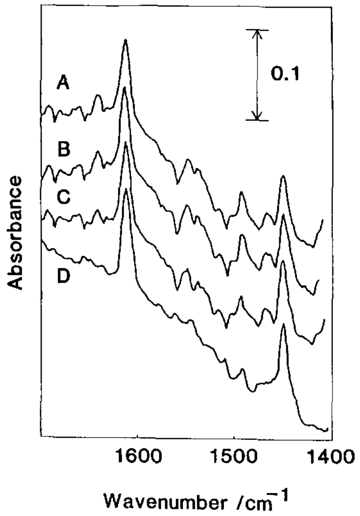

FIG. 8. The IR spectra of pyridine adsorbed on the $Pt/SO_4^{2-}-ZrO_2$ prereduced at different temperatures. Prereduced at (A) 583 K, (B) 623 K, (C) 653 K, (D) 693 K. Pyridine was adsorbed on the prereduced sample at 423 K and then evacuated at the same temperature for 15 min.

The variations of the amount of protonic acid sites and Lewis acid sites as a function of the prereduction temperatures are shown in Fig. 9. With increasing prereduction temperature, Lewis acid sites increased, while protonic acid sites decreased and diminished at the prereduction temperature of 698 K.

The spectra of adsorbed pyridine changed much if the pyridine-covered sample was heated in the presence of hydrogen. The changes in IR spectra of pyridine adsorbed on the catalyst prereduced at 623 K caused by heating in the presence of hydrogen (650 Torr) at different temperatures are shown in Fig. 10. On raising the temperature, the intensity of the band at 1448 cm^{-1} decreased and the bands at 1540 and 1490 cm^{-1} developed. This indicates that the pyridine ad-

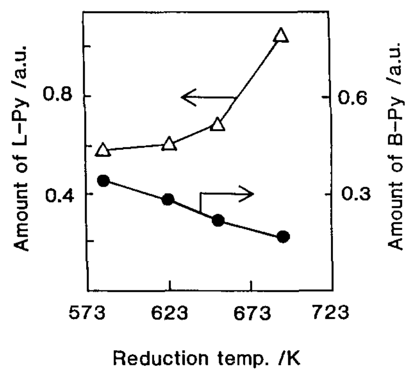

FIG. 9. The variations of the amount of protonic acid sites and Lewis acid sites as a function of the prereduction temperature. Pyridine was adsorbed on the prereduced sample at 423 K and then evacuated at the same temperature for 15 min.

sorbed on the strong Lewis acid site converted to pyridinium ion on heating in the presence of hydrogen. In other words, protonic acid sites were generated from molecular hydrogen, and the pyridine adsorbed on Lewis acid sites moved to the newly formed protonic acid sites.

The change in the amounts of protonic acid sites and Lewis acid sites on heating in the presence of hydrogen in the temperature range 423–623 K is shown in Fig. 11. It is clear that the amount of protonic acid sites increases with the increase in the hydrogen exposure temperature, and the numer of Lewis acid sites decreases with the increase in the number of protonic acid sites. Without platinum or hydrogen, the spectral change was not observed by heating the pyridine-covered sample. The presence of Pt is necessary for generation of protonic acid sites in the presence of hydrogen.

The changes in the IR spectra in the range of S=O stretching frequency of sulfate ion caused by heating in the presence of hydrogen in the temperature range 423–623 K are shown in Fig. 12. The band at 1370 cm^{-1} is attributed to the asymmetric vibration of S=O bond of the bidentate sulfate ion coordinated to the metal cation (*6*). The band position relates to the strength of Lewis acid sites of the metal cations in SO_4^{2-}-promoted metal oxides (*6*). The stronger the Lewis acid site, the higher the frequency of the asymmetric vibration of the S=O band. With increase in the amount of protonic acid sites on heating in the presence of hydrogen, this band subsequently shifted to lower frequencies.

Measurement of the percentage of metal exposed to Pt/SO_4^{2-}-ZrO_2 was attempted with CO adsorption. However, no distinct absorption band of CO stretching vibration was appreciable by IR.

DISCUSSION

The reactions occurring on the Pt/SO_4^{2-}-ZrO_2 catalyst in the presence of hydrogen are characteristics of an acid-catalyzed reaction. The promotion effects of hydrogen on the catalytic activities of the Pt/SO_4^{2-}-ZrO_2 are interpreted as being the re-

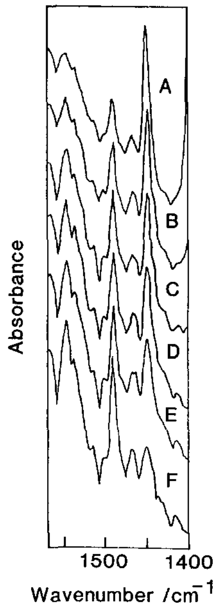

FIG. 10. The changes in IR spectra of pyridine adsorbed on Pt/SO_4^{2-}-ZrO_2 caused by heating in the presence of hydrogen (600 Torr) at different temperatures. (A) Before heating, (B) 423 K, (C) 473 K, (D) 523 K, (E) 573 K, (F) 623 K. Pyridine was adsorbed on the prereduced sample at 423 K and then evacuated at 673 K for 15 min before introduction of hydrogen.

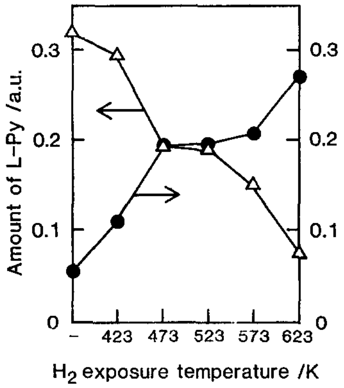

FIG. 11. The change in the amount of protonic acid sites and Lewis acid sites on heating in the presence of hydrogen in the temperature range 423–623 K. Pyridine was adsorbed on the prereduced sample at 423 K and then evacuated at 673 K for 15 min before introduction of hydrogen.

sult of the generation of protonic acid sites originating from molecular hydrogen.

Skeletal isomerization of alkanes are known to proceed both by the acid-catalyzed reaction and by metal–acid bifunctional mechanisms in which alkane dehydrogenation, alkene skeletal isomerization, and hydrogenation occur successively (*21*). Although the present catalyst consists of a metal component and an acid component, no indication that the Pt/SO_4^{2-}–ZrO_2 acts as a bifunctional catalyst was observed. Bifunctional catalysis normally shows negative order in hydrogen pressure, because the initial dehydrogenation equilibrium is unfavorable in the presence of hydrogen. The positive hydrogen effect observed in the present study suggests that bifunctional catalysis is negligibly small, although the possibility of a small contribution of bifunctional catalysis cannot be excluded. In addition, hydrogenation activity of Pt/SO_4^{2-}–ZrO_2 is greatly suppressed as compared with that of Pt/ZrO_2. This is also unfavorable for bifunctional catalysis involved in the isomerization of alkanes over Pt/SO_4^{2-}–ZrO_2.

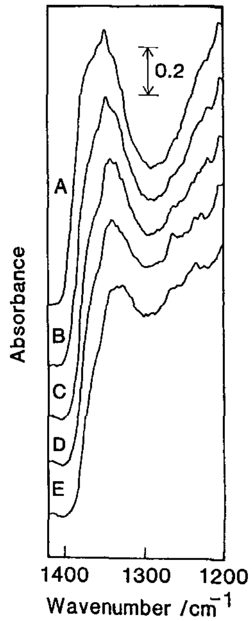

FIG. 12. The changes in the IR spectra due to S=O band of sulfate ion caused by heating in the presence of hydrogen in the temperature range 423–623 K. (A) 423 K, (B) 473 K, (C) 523 K, (D) 573 K, (E) 623 K. Sample was prereduced with hydrogen flow at 623 K followed by evacuation at room temperature for 30 min.

In butane skeletal isomerization in the absence of hydrogen, variations of the activity and the concentration of the protonic acid sites (obtained by the spectra after evacuation at 643 K) with the prereduction temperature are replotted in Fig. 13. The almost linear relation indicates that the protonic acid sites present in the absence of hydrogen

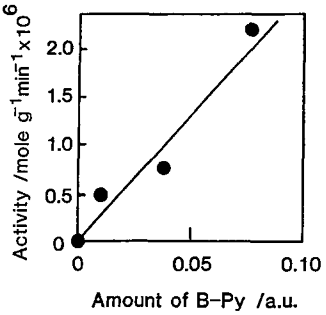

FIG. 13. The relationship between the activity and the concentration of the protonic acid sites for the samples prereduced at different temperatures.

act as active sites for butane skeletal isomerization.

The formation of protonic acid sites from molecular hydrogen on Pt/SO_4^{2-}-ZrO_2 occurs more effectively at higher temperature. This is consistent with the report that the spillover of hydrogen onto a support involves a step with a high-energy barrier (*22*). At a low temperature, the formation of protonic acid sites from molecular hydrogen is difficult. A small promoting effect of hydrogen on the catalytic activity for cyclopropane ring opening is explained by insufficient conversion of H_2 to H^+ at the reaction temperature of 373 K.

Baba *et al.* studied promoting effects of molecular hydrogen on acid-catalyzed reactions over Ag–Y zeolite (*18*). They proposed that the protonic acid sites are generated by the reduction of Ag^+ with hydrogen as expressed by

$$Ag^+ + \tfrac{1}{2}H_2 = Ag^0 + H^+. \qquad (1)$$

In the case of Pt/SO_4^{2-}-ZrO_2, however, it is unlikely that the similar mechanism operates in the formation of protonic acid sites from molecular hydrogen as expressed by

$$Pt^+ + \tfrac{1}{2}H_2 = Pt^0 + H^+. \qquad (2)$$

First, since the catalyst is prereduced at a temperature much higher than the reaction temperature, it seems not plausible that the platinum of a higher oxidation state remaining after prereduction undergoes further reduction at the reaction temperature. Second, if Pt^0 were formed in the presence of hydrogen, the catalyst would have exhibited hydrogenation activity in addition to the activity for acid-catalyzed reaction. This was not observed.

The formation of an H^+ from molecular hydrogen is considered to occur in the following way. At first, the hydrogen molecule is dissociated on the platinum surface to form hydrogen atoms. The hydrogen atoms spill over onto the support (SO_4^{2-}-ZrO_2), where an H atom converts to an H^+ either by donating electron to the H atom or by releasing an electron, as expressed by

$$H_2 \rightarrow 2H \rightarrow H^+ + H^- \qquad (3)$$

$$H_2 \rightarrow 2H \rightarrow 2H^+ + 2e^-. \qquad (4)$$

The formation of an H^+ needs an H^- or e^- acceptor. Considering the shift of the S=O stretching band to a lower frequency, Lewis acid sites were weakened by heating in the presence of hydrogen. In other words, the formation of an H^+ is accompanied by weakening Lewis acid site. Therefore, it is suggested that the Lewis acid site acts as an acceptor of an H^- or e^-. As a result of accepting an H^- or e^-, the Lewis acid site is weakened.

In addition to the high activity, the Pt/SO_4^{2-}-ZrO_2 catalyst is characterized by its long persistence of the catalytic activity in the presence of hydrogen. Hosoi *et al.* reported that the activity persisted more than 1000 h in the reaction of light naphtha (*4*). In the present study, no trend of deactivation was observed for 2 h as shown in Fig. 2. Catalyst deactivation is considered to be due to the coke formation on the surface. Actually it was reported that the amounts of coke deposited during the reaction of pentane on the used Pt/SO_4^{2-}-ZrO_2 catalyst were nearly zero, while the used SO_4^{2-}-ZrO_2 contained 2 wt% coke (*4*).

The differences in the conversion level observed under different reaction procedures as shown in Figs. 1 and 2 are indicative of the cause of catalyst deactivation. When the pentane skeletal isomerization was carried out in a hydrogen stream from the beginning of the reaction, the conversion level was 5%, whereas the conversion decreased to 0.4% when the nitrogen-containing stream was used. Considerable deactivation of Pt/SO_4^{2-}-ZrO_2 seems to proceed during the reaction in the stream of nitrogen. This was more clearly demonstrated in butane skeletal isomerization. Once the reaction was carried out without hydrogen, the activity could not be restored. This demonstrates that, besides creation of the active center for skeletal isomerization, the other role of hydrogen is to prevent the catalyst from coking.

The sites responsible for coke formation are proposed to be strong Lewis acid sites (*23*) and strong protonic acid sites (*24*). In the present catalyst, since the Lewis acid sites are weakened in the presence of hydrogen, the deactivation may be caused by coke formation by strong interaction of Lewis acid sites with pentane and butane. The weakening of the Lewis acid sites in the presence of hydrogen is considered to be a cause of persistence of the activity.

Coke formation on metallic catalysts is known to occur by dehydrogenation and polymerization. It is reported that the sites responsible for the coke formation on Pt are the hydrogenolysis sites of Pt (*25–29*). The lack of hydrogenolysis ability of the Pt in Pt/SO_4^{2-}–ZrO_2 catalyst may be another reason for the persistence of the catalytic activity of Pt/SO_4^{2-}–ZrO_2.

The state of Pt in Pt/SO_4^{2-}–ZrO_2 should be different from the usual supported Pt. The Pt in Pt/SO_4^{2-}–ZrO_2 scarcely exhibited hydrogenation and hydrogenolysis activities, but was still able to dissociate molecular hydrogen. Although the characterization of Pt in Pt/SO_4^{2-}–ZrO_2 has not been made yet, there may be two possibilities which differentiate the Pt in Pt/SO_4^{2-}–ZrO_2 from usual supported Pt. One possible state of the Pt is as follows. Platinum particles on the support are covered with sulfur atoms which originated from H_2S evolving during prereduction of the catalyst. Even when the surface of the Pt particles are covered with S, the surface has a small concentration of exposed Pt where a small molecule of hydrogen can react but a large hydrocarbon molecule cannot.

The other possible state of the Pt is the so-called SMSI state (*30, 31*). The SMSI state of Pt supported on alumina was observed if a small amount of SO_4^{2-} was contained in the case of alumina support (*32, 33*). Although the SMSI state of Pt has not been reported on the support of ZrO_2, sulfate ions present on the ZrO_2 may cause the SMSI state of Pt. In the SMSI state, the metal decreases in adsorption capacity for hydrogen and CO (*30*), and in catalytic activity for hydrogenolysis of butane (*34*), but still reserves the activity for H_2–D_2 exchange reaction (*35*). Platinum in the SMSI state can dissociate molecular hydrogen (*8, 10, 35*).

In summary, the promoting effects of hydrogen on the acid-catalyzed reactions over the Pt/SO_4^{2-}–ZrO_2 catalyst are speculated to be as follows. A hydrogen molecule is adsorbed on the platinum particle to dissociate into two H atoms. The H atom adsorbed on Pt particle spills the support over and migrates to the Lewis acid site, where the H atom releases an e^- to convert into an H^+. The H^+ is localized on an O ion near the Lewis acid site, and acts as an active site for acid-catalyzed reaction. Lewis acid sites accept an e^- to be weakened. The platinum is in such a state as to be able to dissociate the hydrogen molecule but not able to react with hydrocarbons. The formation of coke, resulting from dehydrogenation on exposed platinum metal and due to a strong Lewis acid site, becomes negligibly small, and, therefore, the activity of the Pt/SO_4^{2-}–ZrO_2 catalyst persists for a long period in the presence of hydrogen.

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