JOURNAL OF CATALYSIS **161,** 194–197 (1996)
ARTICLE NO. 0176

Hydrogen Effects on Cumene Cracking over Zirconium Oxide Promoted by Sulfate Ion and Platinum

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Received June 5, 1995; revised December 18, 1995; accepted January 29, 1996

The effects of hydrogen on the catalytic activity of zirconium oxide modified with sulfate ion and platinum (Pt/SO_4^{2-}–ZrO_2) for cumene cracking were studied with a pulse reactor to examine if the catalytically active protonic acid sites are generated from hydrogen molecules present in the gas phase. In a hydrogen stream, a high conversion was obtained and the deactivation with pulse number was not appreciable. In a helium stream, the activity quickly decreased with pulse number, and the activity gradually recovered when the carrier gas of helium was switched into hydrogen. The formation of carbonaceous residue was extended in the absence of hydrogen, but suppressed in the presence of hydrogen. The effects of hydrogen were examined for other catalysts such as zirconium oxide modified with sulfate ion (SO_4^{2-}–ZrO_2) and zirconium oxide modified with platinum (Pt/ZrO_2), but no promotion effects of hydrogen on the catalytic activity were observed. The promotion effects of hydrogen for Pt/SO_4^{2-}–ZrO_2 are rationalized by the formation of protonic acid sites from hydrogen molecules. The suppression of the carbonaceous residue formation in the presence of hydrogen is also discussed.

INTRODUCTION

Zirconium oxide modified with platinum and sulfate ion (Pt/SO_4^{2-}–ZrO_2) was first introduced by Hosoi *et al.* as an efficient catalyst for skeletal isomerization of alkanes (1). The catalytic activity of Pt/SO_4^{2-}–ZrO_2 is markedly affected by the presence of hydrogen. In the presence of hydrogen, the Pt/SO_4^{2-}–ZrO_2 catalyst exhibited a high catalytic activity for more than 1000 h. Hosoi *et al.* explained the hydrogen effect as removal of carbonaceous residue formed during the reaction by hydrogenation.

In our previous papers, we proposed that the enhancement of the catalytic activity for skeletal isomerization of alkanes in the presence of hydrogen over Pt/SO_4^{2-}–ZrO_2 is due to the generation of protonic acid sites from hydrogen molecules (2, 3). The generation of the protonic acid sites from hydrogen molecules, which is proposed on the basis of IR study of adsorbed pyridine, is suggested to occur as follows (2, 3). Hydrogen molecules are dissociatively adsorbed on the platinum species to form hydrogen atoms which undergo spillover onto the support. The hydrogen atom migrates over the surface of SO_4^{2-}–ZrO_2 to Lewis acid site where the hydrogen atom loses an electron to form a proton. The Lewis acid site that traps an electron reacts with a second hydrogen atom to adsorb hydrogen in the form of a hydride. Since the generation of protonic acid sites from hydrogen molecule is reversible, a high catalytic activity is observed in the presence of hydrogen.

Skeletal isomerization of alkanes is known to proceed by both acid-catalyzed monofunctional mechanism and metal–acid bifunctional mechanism. In the former, only acid sites on the catalyst are involved in the reaction. In the latter, metallic sites and acid sites are involved in the mechanism; dehydrogenation on metallic sites, alkene skeletal isomerization on acid sites, and hydrogenation on metallic sites successively occur (4).

Although we proposed that the alkane skeletal isomerization on Pt/SO_4^{2-}–ZrO_2 proceeds by the acid-catalyzed mechanism, the possibility that the reaction proceeds by the metal–acid bifunctional mechanism still remains. The marked promoting effect of hydrogen on the skeletal isomerization of alkanes might be related to the dehydrogenation and hydrogenation steps which occur on metallic sites. If the hydrogen effects are examined on the reaction which is established to be catalyzed only by protonic acid sites, it will be more clarified as to whether the protonic acid sites generated from hydrogen molecules act as catalytically active sites. One such reaction is cumene cracking. In the present work, hydrogen effects on cumene cracking are studied over Pt/SO_4^{2-}–ZrO_2 to clarify if the protonic acid sites generated from hydrogen molecules participate in the acid-catalyzed reactions.

EXPERIMENTAL METHODS

Catalyst Preparation

The sulfate ion-treated $Zr(OH)_4$ (SO_4^{2-}–$Zr(OH)_4$) 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 hydrolysis of $ZrOCl_2$ $8H_2O$ (Wako Pure Chemicals Industries) with 25% NH_4OH aqueous solution. The final value of pH was about 8.0. The

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precipitate was filtered and washed with distilled water until no Cl^- ions could be detected with $AgNO_3$ aqueous solution. The SO_4^{2-}–ZrO_2 sample was obtained by calcination of SO_4^{2-}–$Zr(OH)_4$ at 873 K. The Pt/SO_4^{2-}–ZrO_2 sample (0.5 wt% Pt) was prepared by impregnation of SO_4^{2-}–$Zr(OH)_4$ with H_2PtCl_6 aqueous solution followed by drying at 383 K and calcination at 873 K in air.

The surface areas of samples were measured from the adsorption isotherms of N_2 at 77 K using the BET method. Surface areas of SO_4^{2-}–ZrO_2 and Pt/SO_4^{2-}–ZrO_2 were 85 and 125 $m^2\ g^{-1}$, respectively.

Cumene Cracking

A microcatalytic pulse reactor was used for the reaction. A catalyst (0.15 g) was pretreated in a hydrogen stream (50 ml/min) at 623 K for 2 h and cooled down to the reaction temperature in the hydrogen stream. When cumene was reacted in a helium carrier, the hydrogen stream was switched helium at the end of pretreatment and the catalyst was cooled down to the reaction temperature in a helium stream. The reaction was carried out at 423 and 473 K.

A dose of cumene, 0.5 μl (0.036 μmol), was passed over the catalyst in a carrier flowing at 50 ml/min, and the products were trapped at 77 K before being flash evaporated into a gas chromatographic column (PEG-20M and/or VZ-7 column). The intervals between doses were kept constant, 25 min.

Amount of Carbonaceous Residue

The amount of carbonaceous residue deposited on the catalyst during reaction was measured as follows. After use for the reaction, the catalyst was evacuated at room temperature for 2 h in a closed circulation reactor and exposed to a recirculating oxygen of 200 Torr at 773 K. Carbon dioxide and water were produced. The amount of produced carbon dioxide was determined by on-line gas chromatography. The amount of the produced carbon which is included in carbonaceous residue was estimated from the amount of carbon dioxide.

RESULTS

Figure 1 shows the catalytic activity of Pt/SO_4^{2-}–ZrO_2 for cumene cracking at 423 K in hydrogen or helium. The products were composed of benzene, propylene, propane, and trace amounts of toluene and xylene. The percentage conversion data can be converted to the rate data by multiplying by 1.81×10^{-8} mol s^{-1} m^{-2} $\%^{-1}$. This conversion value is calculated on the assumption that the retention time for cumene passing through the catalyst bed is negligibly small. In a hydrogen carrier, the activity for cumene cracking was high and deactivation was not appreciable. In a helium carrier (in the absence of hydrogen), a considerable conversion was obtained only at the first dose, but drastic deactivation was observed. The conversion was close to nil at the second and later doses. When the carrier was switched to hydrogen after the 10th dose, the activity gradually increased. The conversion at the first dose was higher for the reaction with hydrogen carrier than in the reaction with helium carrier.

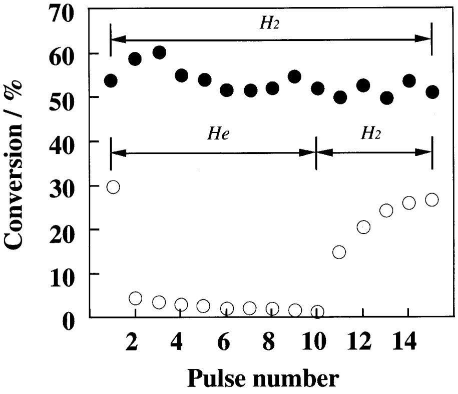

FIG. 1. Effects of hydrogen on the catalytic activity of Pt/SO_4^{2-}–ZrO_2 for cumene cracking at 423 K (●) in a hydrogen stream and (○) in a helium stream (in the absence of hydrogen) followed by switching into hydrogen at 10 doses.

Figure 2 shows the changes in the activity of Pt/SO_4^{2-}–ZrO_2 for cumene cracking at 423 and 473 K as the carrier was sequentially switched. In the presence of hydrogen, the activity was high and stable regardless of the reaction temperature. However, the activity quickly decreased as the carrier was switched to helium. As the carrier was switched back to hydrogen the activity gradually recovered. The promoting effect of hydrogen was reversible. The change in the activity with the kind of carrier was essentially the same regardless of the reaction temperature.

Figure 3 shows the change in the activity of SO_4^{2-}–ZrO_2 for cumene cracking as the carrier was sequentially switched. The products were composed exclusively of benzene and propylene; no propane was formed. The initial activity of SO_4^{2-}–ZrO_2 was lower than that of Pt/SO_4^{2-}–

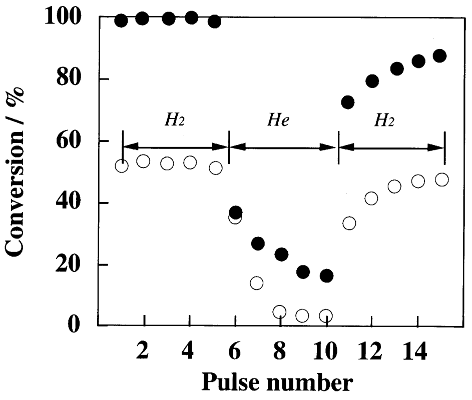

FIG. 2. Reversibility of the promotion effects of hydrogen on the catalytic activity of Pt/SO_4^{2-}–ZrO_2 for cumene cracking at 423 K (○) and 473 K (●).

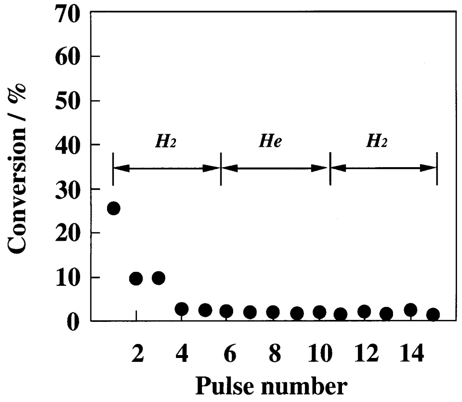

FIG. 3. Effects of hydrogen on the catalytic activity of SO_4^{2-}–ZrO_2 for cumene cracking at 423 K.

ZrO_2 in a hydrogen stream, and comparable with that in a helium stream. The activity markedly decreased with the pulse number in both hydrogen and helium streams. The activity did not recover as the carrier was switched from helium to hydrogen.

Over Pt/ZrO_2, cumene cracking was not appreciable. Only hydrogenation of cumene to *i*-propyl-cyclohexane occurred in a hydrogen stream. In a helium stream (in the absence of hydrogen), no reaction occurred.

The amounts of carbonaceous residue deposited on the catalysts during reaction are summarized in Table 1. When cumene cracking was carried out at 423 K over Pt/SO_4^{2-}–ZrO_2 in the presence of hydrogen (after 15 doses), a small amount of carbonaceous residue was observed (a). The amount of carbonaceous residue was larger for the reaction in a helium carrier than in a hydrogen carrier. When the carrier was switched to hydrogen after the 10th dose, the amount of carbonaceous residue decreased (see (b) and (c)). On SO_4^{2-}–ZrO_2, the amount of carbonaceous residue was much larger than that observed for Pt/SO_4^{2-}–ZrO_2 (see (d) and (f)).

TABLE 1

Catalyst	Reaction temp. (K)	Reaction[a]	Carbon amount (mmol g^{-1})
(a) Pt/SO_4^{2-}–ZrO_2	423	H_2 15 pulse	0.10
(b)	423	He 10 pulse	0.31
(c)	423	He 10 pulse H_2 5 pulse	0.23
(d)	423	H_2 5 pulse He 5 pulse H_2 5 pulse	0.16
(e)	473	H_2 5 pulse He 5 pulse H_2 5 pulse	0.45
(f) SO_4^{2-}–ZrO_2	423	H_2 5 pulse He 5 pulse H_2 5 pulse	0.89

[a] 5 μl/pulse.

DISCUSSION

Among the catalysts examined, a high and stable activity for cumene cracking was observed only for Pt/SO_4^{2-}–ZrO_2 catalyst in the presence of hydrogen. It was evidenced that protonic acid sites are generated from hydrogen molecules on Pt/SO_4^{2-}–ZrO_2 by IR spectroscopy of the adsorbed pyridine (2, 3). It is also accepted that cumene cracking is catalyzed by protonic acid sites (5–8). The high activity in the presence of hydrogen is considered to be due to the fact that the protonic acid sites generated from hydrogen molecules act as the catalytically active sites for cumene cracking over Pt/SO_4^{2-}–ZrO_2 in the presence of hydrogen.

Hosoi *et al.* suggested that a stable activity of Pt/SO_4^{2-}–ZrO_2 for pentane skeletal isomerization in the presence of hydrogen is due to the removal of carbonaceous residue deposited on the catalyst surface by hydrogenation (1). They did not mention about the high activity observed in the presence of hydrogen in the initial stage of the reaction when carbonaceous residue is considered to be small. For cumene cracking examined in the present study, the conversion at the first dose was about 55% in the presence of hydrogen, while the conversion at the first dose in the absence of hydrogen was about 30% (see Fig. 1). The conversion at the first dose was considerably higher for the reaction in the presence of hydrogen. The high conversion at the initial stage of the reaction is due to the increase in the concentration of the protonic acid sites in the presence of hydrogen.

As Hosoi *et al.* suggested, the carbonaceous residue was less when the reaction was carried out in the presence of hydrogen. The carbonaceous residue accumulated during reaction in a helium stream decreased when the helium stream was switched to a hydrogen stream. Removal of carbonaceous residue by hydrogenation does occur. In our previous papers, we proposed that hydrogen atoms spill over the surface of SO_4^{2-}–ZrO_2 (2, 3). The spiltover hydrogen atoms are most likely to take part of hydrogenation of the carbonaceous residue to remove off the surface.

Carbonaceous residue accumulated on the Pt/SO_4^{2-}–ZrO_2 catalyst both with and without hydrogen. The amount of the residue was much larger when reacted without hydrogen. The smaller amount of the carbonaceous residue in the presence of hydrogen is considered to be caused by the following two reasons. One is the removal of the residue by hydrogenation as mentioned above, and the other is the elimination of the sites responsible for the formation of the carbonaceous residue.

The elimination of the sites for carbonaceous residue may be interpreted as follows. Although the sites responsible to form carbonaceous residue are not definite, the strong Lewis acid site is one of the candidates for causing carbonaceous residue formation because hydrocarbons are possibly dehydrogenated on the Lewis acid sites to form precursors of carbonaceous residue. In the presence of hydrogen, the spiltover hydrogen atom releases an electron at the Lewis acid site to form an H^+ nearby the Lewis acid site. The electron trapped by the Lewis acid site reacts with a second spiltover hydrogen atom to form an H^- adsorbed on the Lewis acid site. The Lewis acid site becomes weakened and loses an ability to dehydrogenate hydrocarbons.

With SO_4^{2-}–ZrO_2 catalyst, a promoting effect of hydrogen on the catalytic activity was not observed, and the amount of carbonaceous residue was much larger than that observed for Pt/SO_4^{2-}–ZrO_2. On the SO_4^{2-}–ZrO_2 catalyst, adsorption of hydrogen was not appreciable (9). Without platinum species, spiltover hydrogen atoms do not exist on the surface of SO_4^{2-}–ZrO_2. In addition, generation of protonic acid sites was not observed by IR study of the adsorbed pyridine (3). Therefore, neither the removal of carbonaceous residue by hydrogenation nor adsorption of an H^- to weaken the strength of Lewis acid site occurs even in the presence of hydrogen. To enhance the catalytic activity and to suppress the carbonaceous residue, the formation of spiltover hydrogen which occurs on platinum species is required.

With Pt/ZrO_2, cumene cracking did not occur at all at a reaction temperature of 423 K, but hydrogenation of cumene occurred to form *i*-propyl-cyclohexane. The lack of cracking activity for Pt/ZrO_2 is easily understood by the absence of acid sites on ZrO_2. The strong acid sites are generated by the addition of sulfate ions to ZrO_2 (10, 11).

Occurrence of cumene hydrogenation on Pt/ZrO_2 is in contrast to the catalytic activity of Pt/SO_4^{2-}–ZrO_2. Over Pt/SO_4^{2-}–ZrO_2, hydrogenation of cumene and benzene was not appreciable, but hydrogenation of propylene was observed at a reaction temperature of 423 K. The products consisted more of propane than of propylene. Propylene is much more easily hydrogenated than cumene. Pt/SO_4^{2-}–ZrO_2 is able to hydrogenate propylene but not cumene. Pt/ZrO_2 is, however, able to hydrogenate cumene. The hydrogenation ability of the platinum species is much lower for Pt/SO_4^{2-}–ZrO_2 than for Pt/ZrO_2. The states of the platinum in Pt/SO_4^{2-}–ZrO_2 should be different from those in Pt/ZrO_2 and were reported to be in the form of cationic platinum, though it is not certain whether the counteranion is a sulfur or an oxygen anion.

Ebitani *et al.* reported, based on the characterization by XPS, XAFS, IR, and TPR techniques that the states of platinum in Pt/SO_4^{2-}–ZrO_2 are mostly cationic, at least on the surface of the platinum species (12–15). Sayari *et al.* on the other hand, reported that the platinum species in Pt/SO_4^{2-}–ZrO_2 are reduced much more easily than those in Pt/ZrO_2, and that the state of platinum in Pt/SO_4^{2-}–ZrO_2 is exclusively metallic even after calcination in air at 823 K (16, 17). If the platinum species in Pt/SO_4^{2-}–ZrO_2 were mostly in the metallic state, Pt/SO_4^{2-}–ZrO_2 would have exhibited a high hydrogenation activity. This was not observed. The low hydrogenation ability of Pt/SO_4^{2-}–ZrO_2 as compared to Pt/ZrO_2 is consistent with the proposal that the state of platinum is cationic, at least at the surface of the platinum species, for Pt/SO_4^{2-}–ZrO_2.

CONCLUSION

In the presence of hydrogen, the activity of cumene cracking is high and deactivation is small over Pt/SO_4^{2-}–ZrO_2, since the protonic acid sites from hydrogen molecule act as the active site for this reaction. Platinum and sulfate ions are essential for promotion effects of hydrogen for cumene cracking. It is suggested that not only active sites for dissociation of hydrogen molecule (Pt) but also superacidic sites formed by adsorption of sulfate ions on zirconium oxide are necessary for generation of protonic acid sites from hydrogen molecules.

ACKNOWLEDGMENTS

This work has been carried out as a research project of the Japan Petroleum Institute commissioned by the Petroleum Energy Center with the subsidy of the Ministry of International Trade and Industry.

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