MOLECULAR HYDROGEN-ORIGINATED PROTONIC ACID SITE ON Pt/WO$_3$-ZrO$_2$

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Abstract

Pt/WO$_3$-ZrO$_2$ catalyst exhibits high activity and selectivity in alkane skeletal isomerization which is an important reaction for a gasoline of high quality. The catalytic activity and selectivity were enhanced in the presence of hydrogen. The roles of hydrogen present in the reaction mixture was studied by kinetic analysis of hydrogen adsorption and IR study of the acid sites. The active sites on Pt/WO$_3$-ZrO$_2$ are interpreted in terms of a concept of acid site generation "molecular hydrogen-originated protonic acid site". The catalytic features of Pt/WO$_3$-ZrO$_2$ in comparison to those of Pt/SO$_4$-ZrO$_2$ are high selectivity for isomerization against cracking. The features arise from a fast surface diffusion of spiltover hydrogen atoms which convert into protons and hydrides at Lewis acid sites. A high availability of protons and hydrides causes high activity and selectivity for alkane isomerization.

Introduction

Skeletal isomerization of light naphtha becomes an important process in modern refining processes for a gasoline of high quality. Three types of catalyst employed in the isomerization process are Pt/Al$_2$O$_3$-Cl, Pt/zeolite, and Pt/SO$_4$-ZrO$_2$. Pt/Al$_2$O$_3$-Cl is highly active but suffered from extreme sensitivity to all kinds of feed contaminants. Pt/zeolite needs high temperature to operate satisfactorily. Pt/SO$_4$-ZrO$_2$ catalyst was recently developed for isomerization process (UOP & COSMO, Parlsom process) [1, 2] and as HYSOPAR-SA catalyst for isomerization process (SUED-CHEMIE) [3].

Recently, Pt/WO$_3$-ZrO$_2$ was explored widely because it has a similar of catalytic activities with those of Pt/SO$_4^{2-}$-ZrO$_2$ for isomerization of alkanes, though the selectivities to isomerization against cracking of alkanes are higher for Pt/WO$_3$-ZrO$_2$ than for Pt/SO$_4^{2-}$-ZrO$_2$. Hydrogen effects were also observed for Pt/WO$_3$-ZrO$_2$. Barton *et al.* [4] suggested on the basis of the hydrogen effects on the catalytic activity that protonic acid sites are formed on Pt/WO$_3$-ZrO$_2$ in the presence of hydrogen by a mechanism similar to that found in the case of Pt/SO$_4^{2-}$-ZrO$_2$. The protonic acid sites formed from molecular hydrogen act as active sites for isomerization of alkanes and other acid-catalyzed reactions such as o-xylene isomerization. The objectives of the present paper are (1) to confirm the concept "molecular hydrogen-originated protonic acid site" [5-7] be applicable to Pt/WO$_3$-ZrO$_2$- and (2) to elucidate the structure of acid site of Pt/WO$_3$-ZrO$_2$.

Experimental Methods

Catalyst preparation: The WO$_3$-ZrO$_2$ was prepared by impregnation of Zr(OH)$_4$ with aqueous (NH$_4$)$_6$[H$_2$W$_{12}$O$_{40}$], followed by calcination at 1093 K in air. The Pt/WO$_3$-ZrO$_2$ was prepared by impregnation of the WO$_3$-ZrO$_2$ with aqueous H$_2$PtCl$_6$ followed by calcination at 723 K in air.

IR study: A self-supported wafer placed in an *in-situ* IR cell was pretreated with a hydrogen

stream at 673 K, followed by out gassing at 673 K. For the measurement of IR spectra of adsorbed pyridine affected by the presence of H_2, the sample was exposed to 1 Torr of pyridine at 423 K for 15 min, followed by outgassing at 673 K for 15 min. Then the sample was exposed to 150 Torr of H_2 at room temperature, and heated stepwise from room temperature in 25 K increments. After the sample was heated up to a certain temperature, the sample was cooled to room temperature and gaseous hydrogen was outgassed. Then the sample was heated in a vacuum stepwise from room temperature in 50 K increments.

Hydrogen adsorption: Hydrogen uptake was measured by an automatic gas adsorption apparatus Belsorp 28SA. Catalyst sample placed in an adsorption vessel was pretreated with a flowing hydrogen at 673 K, followed by outgassing at 673 K. Then, the sample was cooled to an adsorption temperature and held at the temperature for 3 h.

Results and Discussion

Generation of protonic acid site in the presence of hydrogen: The generation of protonic acid site in the presence of hydrogen was confirmed by IR study of adsorbed pyridine. Figure 1 shows the spectral change when pyridine-preadsorbedPt/WO$_3$-ZrO$_2$ was heated in hydrogen at different temperatures(A), followed by heating in a vacuum (B). Heating in the presence of hydrogen caused increase in the absorption band at 1540 cm^{-1} assigned to pyridine adsorbed on protonic acid site, accompanied by decrease in the absorption band at 1450 cm^{-1} assigned to pyridine coordinated to Lewis acid site. It is demonstrated that the concept of protonic acid generation "molecular hydrogen-originated protonic acid site" is applicable to Pt/WO$_3$-ZrO$_2$. The absorbances at 1540 and 1450 cm^{-1} are plotted against heating and outgassing temperature in Figure 2. The generation of protonic acid sites was observed even at room temperature. Considering that the generation of protonic acid sites is appreciable above 423 K for Pt/SO$_4$-ZrO$_2$ [7], it is obvious that the generation of protonic acid sites originating from molecular hydrogen is much easier for Pt/WO$_3$-ZrO$_2$ than for Pt/SO$_4$-ZrO$_2$.
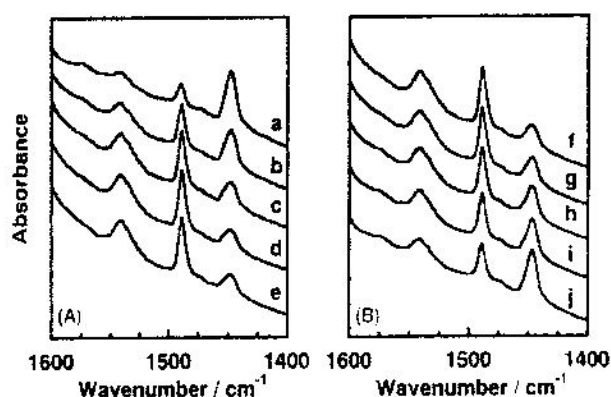

Fig. 1 IR spectra of pyridine adsorbed on Pt/WO$_3$-ZrO$_2$. (A Spectral changes when pyridine-preadsorbed sample wa heated in hydrogen at (b) 298 K, (c) 323 K, (d) 348 K (e) 373 K (a) Before exposure to hydrogen. (B) Spectral changes whe the sample (e) was heated in a vacuum at (f) 323 K, (g) 373 K, (h) 423 K, (i) 423 K, (j) 573 K
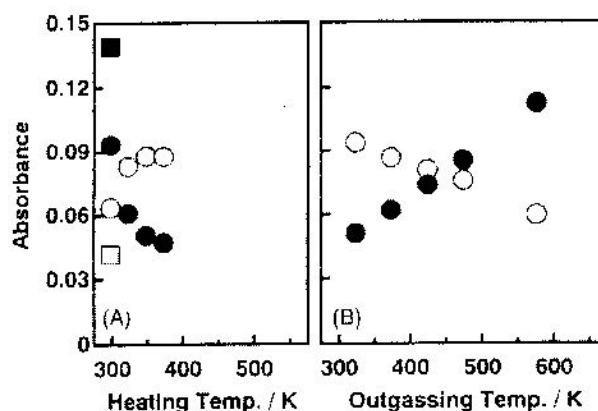

Fig. 2 Variations of the absorbance of IR bands at 1450 an 1540 cm^{-1} with heating in hydrogen (A) and heating in vacuum (B) for Pt/WO$_3$-ZrO$_2$. (●) Absorbance at 1450 cm^{-1} (○)Absorbance at 1540 cm^{-1}; (■,□)Before exposure t hydrogen.

Hydrogen adsorption kinetics: The rate of hydrogen adsorption was measured for Pt/WO$_3$-ZrO$_2$. Figure 3 shows the variations of hydrogen uptake on Pt/WO$_3$-ZrO$_2$ as a function of time at different temperatures. The initial hydrogen pressure was 50 Torr. For the initial few minutes, very fast adsorption occurred at all the temperatures. Above 373 K, hydrogen adsorption reached equilibrium within 6 h. At equilibrated state, the hydrogen uptake was larger for the

adsorption at lower temperature, which is expected because of an exothermic process of general adsorption. Below 373 K, hydrogen adsorption did not reach equilibrium even after 10 h. Hydrogen uptake was still increasing over 10 h at an adsorption temperature of 323 K. It should be noted that hydrogen uptake exceeded the H/Pt ratio of unity which corresponds to 0.15×10^{20} atom/g-cat.

From the kinetic analysis of the rate of hydrogen adsorption, the following conclusions are obtained [8]. For Pt/WO_3-ZrO_2, two routs are operating. One route is the same as that for WO_3-ZrO_2 [8] which each hydrogen molecule is dissociated on a specific site of WO_3-ZrO_2 to form hydrogen atoms, which undergo surface diffusion over the surface of WO_3-ZrO_2. The
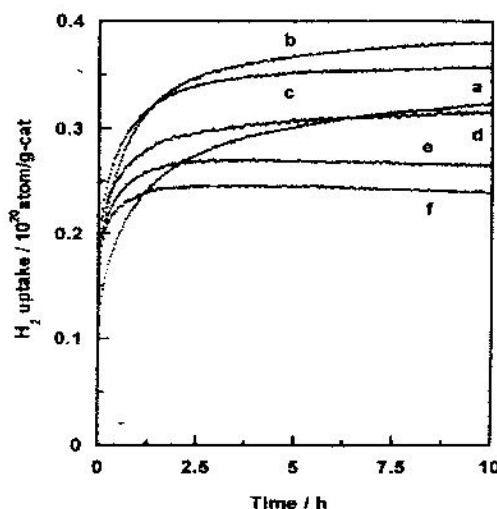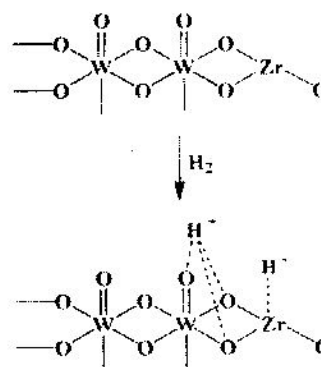
Fig. 3 Variations of hydrogen uptake o Pt/WO_3-ZrO_2 as a function of time at differen temperatures. (a) 323 K;(b) 373 K; (c) 423 K; (d) 47 K; (e) 523 K; (f) 573 K.

rate-controlling step is the surface diffusion of hydrogen atoms. The activation energy is 25.9 kJ/mol for the surface diffusion. The other route involves dissociation of hydrogen molecules on the Pt sites to form hydrogen atoms that undergo spillover onto the WO_3-ZrO_2 surface, followed by surface diffusion. For the later route, the rate-controlling step is the spillover step; its activation energy is 35.5 kJ/mol. We have reported the kinetic analysis of hydrogen adsorption on Pt/SO_4-ZrO_2 [9]. The rate-controlling step for Pt/SO_4-ZrO_2 is surface diffusion of the spillover hydrogen atoms over SO_4-ZrO_2, and the activation energy of the diffusion is 84 kJ/mol. In the preceding section, we describe that the generation of protonic acid sites from molecular hydrogen is appreciable at lower temperature for Pt/WO_3-ZrO_2 than for Pt/SO_4-ZrO_2. The difference in the temperature required to generate protonic acid sites is suggested to be caused by the easiness of the surface diffusion of hydrogen atoms.

Structure of active site on Pt/WO_3-ZrO_2: The mechanism of the generation of protonic acid sites from molecular hydrogen on WO_3-ZrO_2 was studied by IR spectroscopy [10]. Although it is not shown in the present paper, the spectral changes in the W=O stretching and OH stretching regions were observed in response to the exposure to hydrogen and the removal of hydrogen. By heating in the presence of hydrogen, the W=O stretching bands at 1021 and 1014 cm^{-1} eroded and a broad band around 980 cm^{-1} was developed. The peaks at 1021, 1014 and 980 cm^{-1} restored to their original intensities on heating in a vacuum. A brad OH stretching band around 3600 cm^{-1} was intensified by heating in the presence of hydrogen and restored to its original intensity by removal of the hydrogen from gas phase. Pyridine adsorption caused

Scheme 1 A mechanism proposed for the generation of protonic acid site o WO_3-ZrO_2

essentially the same changes in the W=O stretching region as hydrogen adsorption. Base on the spectral changes, the changes in the structure of acid sites caused by hydrogen adsorption are proposed as illustrated in Scheme 1.

Two types of W=O groups exist: one type is linked to the cus Zr^{4+} through O, and the other type is the same W=O as those in bulk WO_3. Adsorption of hydrogen forms an H^+ and H^-; the H^+ is located on the O nearby the cus Zr^{4+} to form OH which is hydrogen bonded to the other O coordinating to the W, and the H^- is coordinated to the cus Zr^{4+}. When pyridine is adsorbed on

the WO_3-ZrO_2, pyridine is coordinated to the cus Zr^{4+}. When hydrogen is adsorbed on the pyridine-preadsorbed WO_3-ZrO_2, the hydrogen atom donates an electron to the cus Zr^{4+} and becomes the acidic OH. The cus Zr^{4+} becomes Zr^{3+} and weakens Lewis acid site. Pyridine adsorbed on the cus Zr^{3+} becomes easy to be desorbed and migrate to the acidic OH to form pyridinium ion. The cus Zr^{3+} reacts with the other hydrogen atom to form Zr^{4+} bonded to hydride. It is not certain on which O atom the H^+ is located. It is most likely that the H^+ is loosely bounded to three O atoms; two O atoms bridging Zr and W, and one O atom in the W=O of which W is connected to Zr through O. The H^+ may be mobile among the three O atoms.

Conclusions

It is suggested based on the results of IR study of adsorbed pyridine that protonic acid sites acting as active sites for alkane isomerization are generated on Pt/WO_3-ZrO_2 from hydrogen molecules present in the gas phase. The generation of protonic acid sites from hydrogen molecules is accompanied by the formation of hydride ions bounded to Lewis acid sites. The generation of protonic acid sites is much easier for Pt/WO_3-ZrO_2 than for Pt/SO_4-ZrO_2. The structural change of the acid sites on WO_3-ZrO_2 caused by hydrogen adsorption was studied also by IR spectroscopy, and the model of the acid sites is proposed.

Kinetics of hydrogen adsorption reveal that the rate of hydrogen adsorption is faster for Pt/WO_3-ZrO_2 than Pt/SO_4-ZrO_2, which results in a high availability of both H^+ and H^- on the surface of Pt/WO_3-ZrO_2. A fast adsorption is caused by the fast surface diffusion of the spiltover hydrogen atoms over the surface of WO_3-ZrO_2.

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