

THE FACTORS AFFECTING THE HYDROGEN ADSORPTION ON $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ CATALYST.

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Abstract

Hydrogen adsorption was studied for $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ (PSZ) samples modified with Na addition, pyridine preadsorption, and water preadsorption to elucidate the relation between the rate and capacity of hydrogen adsorption and the surface state. The surface states were monitored by XRD, IR, ammonia TPD, and measurement of catalytic activity for cyclohexane isomerization. All the modifications suppressed the hydrogen uptake. It was suggested that Lewis acid sites promote the hydrogen uptake by stabilizing spillover hydrogen atoms.

Keywords: *protonic acid site, $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$, adsorption of hydrogen*

Introduction

PSZ exhibits high activity and selectivity in alkane skeletal isomerization which is an important reaction for high octane gasoline. The catalytic activity and selectivity of PSZ were enhanced in the presence of hydrogen [1-4]. The role of hydrogen present in the reaction mixture was already studied by kinetic analysis of hydrogen adsorption, IR study of the acid sites, hydrogen pressure dependency on the activity and selectivity in skeletal isomerization of alkanes, and mechanistic study in which deuterium was used as a tracer. We also reported that protonic acid sites are formed on PSZ when hydrogen is adsorbed above 473 K, and that the catalytic activities of PSZ for various acid-catalyzed reactions are enhanced in the presence of hydrogen [5-7]. We named the protonic acid sites formed from hydrogen as "molecular hydrogen-originated protonic acid sites" [6]. The adsorption of hydrogen on PSZ involves four steps; dissociative adsorption of hydrogen molecules on Pt sites, spillover of the hydrogen atoms onto $\text{SO}_4^{2-}\text{-ZrO}_2$ (SZ), diffusion of the spillover hydrogen over the surface of SZ, and the conversion of atomic hydrogen into proton at Lewis acid site. The protons thus formed act as catalytically active sites for acid-catalyzed reactions.

However, there have been no reports describing the relation of the surface state with the hydrogen adsorption properties for PSZ. In the present study, the factors affecting the rate and capacity of hydrogen adsorption are examined for PSZ. We have modified the surface of PSZ with Na, pyridine, and water, and measured the hydrogen adsorption to elucidate the factors affecting hydrogen adsorption.

Experimental Methods

Catalyst preparation: SZ catalyst was obtained by impregnation of $\text{Zr}(\text{OH})_4$ with 1N H_2SO_4 aqueous solution followed by filtration and drying at 383K for 24h and 873K for 12h in air. The PSZ was prepared by impregnation of the SZ with H_2PtCl_6 aqueous solution followed by drying and calcination at 873K for 12h in air. The content of Pt was adjusted to be 0.5wt%. Na-loaded PSZ was prepared by impregnation of PSZ with aqueous NaOH, followed by drying and calcining at 723K in air. The content of Na was adjusted to be 0.1wt% and 0.5wt%. The catalysts obtained will be designated as xNa-PSZ, where x denotes the wt% of Na loaded. Pyridine-preadsorbed PSZ was prepared as follows. The PSZ was pretreated in a hydrogen flow at 573K for 3h followed by outgassing at 573K. The pretreated PSZ was then exposed to 3.5Torr pyridine at 543K for 0.5h followed by outgassing at 543K or 558K. Water-

preadsorbed PSZ was prepared as follows. The PSZ was pretreated in a hydrogen flow at 573K for 3h followed by outgassing at 573K. The pretreated PSZ was then exposed to 4Torr water at 523K for 0.5h followed by outgassing at 523K or 548K.

Characterization: X-Ray powder diffraction pattern of the sample was recorded on a JEOL X-Ray Diffractometer JDX-3500 with a Cu-K α radiation sources. The specific surface area was determined for the samples outgassed at 573K by BET method with Coulter SA-3100. The sulfur content of samples were determined by XRF with JEOL Element Analyzer JSX-3220Z. Temperature-programmed desorption (TPD) of ammonia was carried out with Bell Multitask TPD as follows. The sample was pretreated with hydrogen flow at 673K for 3h followed by purging with He flow for 0.5h. Then, the pretreated sample was exposed to dehydrated-ammonia (10Torr) at 373K followed by purging with He flow at 373K. The TPD was run at a heating rate of 10 K/min from room temperature to 950K, and the desorbed ammonia was detected by mass spectrometry. IR measurement was carried out with a Perkin-Elmer Spectrum One FT-IR Spectrometer equipped with a MCT detector. The sample of self-supported wafer was pretreated in a hydrogen flow at 623K followed by outgassing at 673K. For the measurement of pyridine adsorbed on the sample, the sample was exposed to 2Torr of pyridine at 423K followed by outgassing at 673K for 15min. The spectra was recorded at room temperature with a spectral resolution of 4cm⁻¹ and with 128scans.

Hydrogen Adsorption: The hydrogen uptake was measured by automatic gas adsorption apparatus Belsorp 28SA. The sample was pretreated in hydrogen flow at 573K for 3h, followed by outgassing at 573K for 2h, and cool to an adsorption temperature of 523K. Hydrogen (100Torr) was then introduced to the system, and hydrogen pressure change with time was monitored. The hydrogen uptake was calculated from a pressure change.

Reaction Procedures: Isomerization of cyclohexane was carried out in a closed recirculation reactor. The catalyst (0.4gr) was pretreated with circulating hydrogen (100Torr) at 573K followed by outgassing at 573K. A mixture containing cyclohexane (25Torr) and hydrogen (150Torr) was allowed to react at 473K. The products were analyzed by on-line gas chromatography, a VZ-7 column being used.

Results And Discussion

Surface Structure: The content of sulfur species, surface area and ratio of crystal phase M/T (monoclinic/tetragonal) for the prepared samples are summarized in Table 1. The surface area and content of sulfur species did not change much by addition of Na to PSZ. However, the XRD peaks ascribed to monoclinic ZrO₂ become apparent with the Na loaded which increased the fraction of monoclinic ZrO₂ markedly.

Table 1. Physical properties of prepared samples

	Na wt%	S wt%	SA m ² /g	M/T ^[8]
PSZ	-	1.69	119	9/91
0.1Na-PSZ	0.1	1.64	117	19/81
0.5Na-PSZ	0.5	1.61	116	36/64

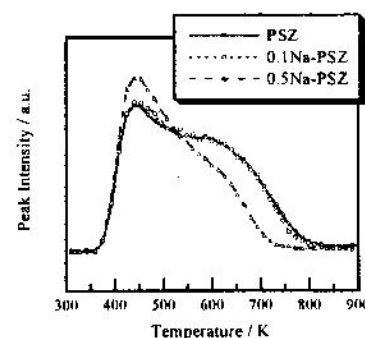


Fig. 1 Ammonia TPD plots for prepared samples

Acidity: Figure 1 shows ammonia TPD plots for prepared samples. The TPD plots consisted of two TPD peaks; one peak appearing at about 443K (weak acid) and the other about 623K (strong acid). The TPD plot did not change much by addition of 0.1wt% Na, but changed considerably by addition of 0.5wt% Na. By addition of 0.5wt% Na, strong acid sites were converted into weak acid sites, though the conversion was too small to be detected when 0.1wt% Na was added.

Figure 2 shows IR spectra of pyridine adsorbed on prepared samples. Since the samples were outgassed at 673K after exposure to pyridine vapor, the peaks in the spectra should be due to the pyridine adsorbed only on the strong acid sites. The PSZ sample showed all three bands, indicating both Lewis acid sites and protonic acid sites were present. On addition of Na, the intensities of all the bands decreased. In particular, the band at 1540cm^{-1} decreased to a great extent. The addition of Na causes decrease more extensively in the number of strong protonic acid sites than in the number of strong Lewis acid sites.

Hydrogen Uptake: Figure 3 shows the variations of hydrogen uptake as a function of time at an adsorption temperature of 523 K for PSZ, 0.1Na-PSZ and 0.5Na-PSZ. The variations of hydrogen uptake as a function of time for PSZ samples which adsorbed pyridine and water at different amounts are shown in Figures 4 and 5.

From the Figures 3, 4 and 5, the hydrogen adsorption on PSZ was suppressed by the addition of Na, preadsorption of pyridine, and preadsorption of water. Although the quantities of pyridine and water adsorbed on PSZ were unknown, it would be helpful for imagination of the state of the surface to compare the surface concentrations of Na, SO_4^{2-} , and hydrogen uptake on unit surface area basis. Decrease in the hydrogen uptake caused by addition of Na to PSZ is interpreted by a decrease in the Lewis acid sites on PSZ. As shown in Figure 2, both protonic acid sites and Lewis acid sites decreased on addition of Na to PSZ.

Preadsorption of pyridine also suppressed hydrogen uptake. The PSZ that adsorbed pyridine followed by outgassing at 558K adsorbed 5.8×10^{19} hydrogen atom/g, while the 0.1Na-PSZ adsorbed 4.2×10^{19} hydrogen atom/g.

Suppressive effect of preadsorption of pyridine was not so severe on hydrogen uptake as compared to Na addition. Preadsorption of water also suppressed hydrogen uptake, though the suppressive effect was not so extensive. The hydrogen uptake on the water-preadsorbed PSZ followed by outgassing at 523K was 5.6×10^{19} hydrogen atom/g, which is 77% of the hydrogen uptake on the original PSZ. Preadsorption of water on PSZ should convert Lewis acid sites into protonic acid sites. It is not certain as to whether protonic acid sites or acidic OH groups promote hydrogen spillover and hydrogen uptake on PSZ, but the Lewis acid sites

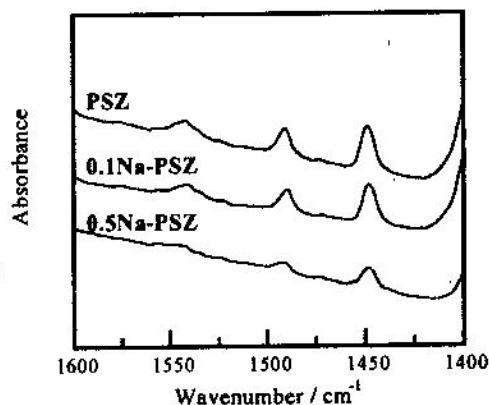


Fig. 2 IR spectra of pyridine adsorbed on samples

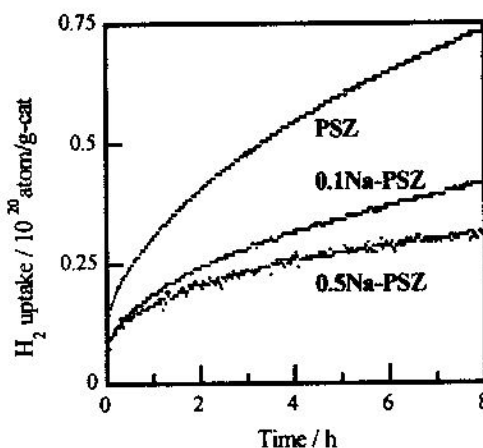


Fig. 3 Variations of hydrogen uptake as a function of time.

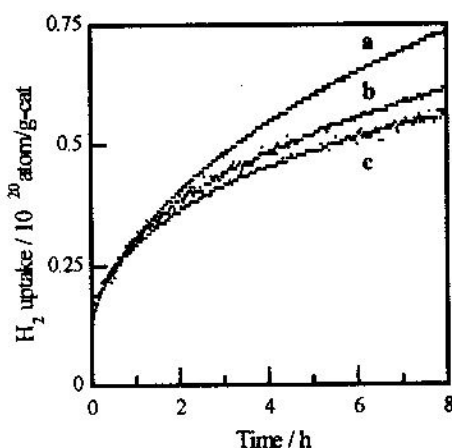


Fig. 5 Variations of hydrogen uptake as a function of time for a) PSZ, b) PSZ (water:523K), and c) PSZ (water:548K).

are possibly decreased by preadsorption of water and lose the ability to stabilize spillover hydrogen. Even if there is a promotive effect of the protonic acid sites, negative effect caused by elimination of Lewis acid sites surpasses the positive effect on hydrogen uptake.

Conclusions

The effects of surface acidity on hydrogen adsorption have been studied in order to elucidate the relation of the rate and capacity of hydrogen adsorption with the surface state. The surface acidity was monitored by IR spectroscopy and ammonia TPD. The hydrogen uptake decreased when the surface Lewis acid sites were weakened and/or blocked by addition of Na and adsorption of pyridine and water. It is suggested that the presence of Lewis acid sites promote the hydrogen uptake by stabilizing spillover hydrogen atoms.

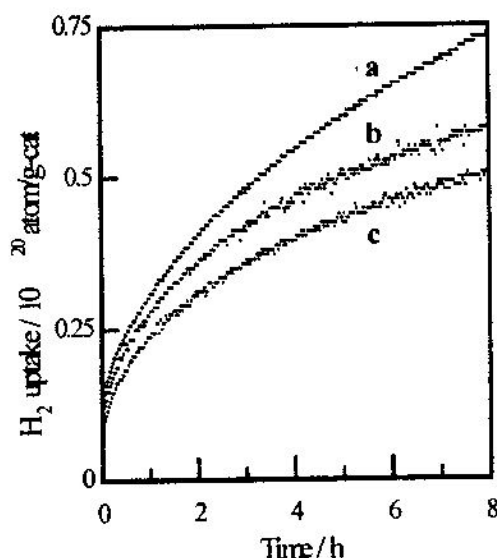


Fig 4 Variations of hydrogen uptake as a function of time for a) PSZ, b) PSZ (pyridine:543K), and c) PSZ (pyridine:558K).

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