

The Effect of Sulfate Ion on the Hydrogen Adsorption over $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ Catalyst

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Abstract

The influence of sulfate ion on the hydrogen adsorption over $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ has been studied. $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ samples were prepared by impregnation of $\text{Zr}(\text{OH})_4$ with 0.5N, 1.0N, 2.0N and 4.0N of sulfate ion and calcined at 873 K, followed by addition of 0.5wt% Pt. XRD, nitrogen physisorption and ammonia TPD have been used to monitor the physical structure of catalyst. Adsorption of hydrogen was carried out at 523 K for 8 h. The increase of sulfate ion up to 4.0N increased the hydrogen uptake markedly. The presence of sulfate ion on catalysts exerts a promotive effect on the hydrogen uptake rate due to the development of medium and strong acid sites.

Keywords: $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$, Adsorption of Hydrogen, Strong Acid

Introduction

Hybrid catalysts such as sulfate and tungsten promoted zirconia exhibit a stable, regenerable and highly active for hydrocracking and hydroisomerization processes at a wide range of reaction temperature which have been investigated extensively in the recent years [1]. The presence of metal-ion and hydrogen enhanced the activity and stability of catalysts due to the removal of coke and generation of active sites from hydrogen molecule [2]. Our research group named the active sites generated from hydrogen as "molecular hydrogen-originated protonic acid sites". We proposed that the hydrogen molecule is adsorbed on the platinum particle and dissociates into two H atoms. The H atom adsorbed on the platinum particle spills over the support and migrates to Lewis acid site where the H atom releases an electron and becomes an H^+ . The H^+ is stabilized at the oxygen atom nearby the Lewis acid site, and acts as an active site for acid-catalyzed reactions [3,4]. The rates of the spillover and the surface diffusion vary with the type of catalyst and the state of the surface where hydrogen atoms undergo surface diffusion. The amount of protons formed from hydrogen molecules and the rate of hydrogen adsorption should affect the

catalytic activities for acid-catalyzed reactions in the presence of hydrogen. However, there have been no reports describing the relation of the surface state with the hydrogen adsorption properties for $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$. In the present study, the effects of acidity on the capacity and rate of hydrogen adsorption of are examined.

Experimental

Synthesis of Catalyst

The $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst was prepared as follows. Zirconium hydroxide was prepared from aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ by hydrolysis with 2.5 wt% NH_4OH aqueous solution. The precipitate was filtered and washed with deionized water. The obtained gel was dried at 383 K to form $\text{Zr}(\text{OH})_4$. The sulfate ion-treated $\text{Zr}(\text{OH})_4$ was prepared by impregnation of the $\text{Zr}(\text{OH})_4$ with H_2SO_4 aqueous solution followed by filtration and drying at 383 K. The concentration of H_2SO_4 aqueous solution was varied: 0.5 N, 1.0N, 2.0N and 4.0N. The $\text{SO}_4^{2-}\text{-ZrO}_2$ was obtained by calcination of the $\text{SO}_4^{2-}\text{-Zr}(\text{OH})_4$ at 600°C in air. Catalyst will denote as xNS where x is a number of concentration and NS is a normality of sulfate ion loaded. The $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst was prepared by impregnation of the $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst with H_2PtCl_6 aqueous solution followed by drying and calcination as in the case of $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst.

Characterization

The surface area and pore distribution of catalyst were determined using a COULTER 5A3100 apparatus. X-Ray powder diffraction pattern of the sample was recorded on a JEOL X-Ray Diffractometer JDX-3500 with a $\text{Cu-K}\alpha$ radiation sources.

The ammonia TPD test was carried out on JEOL Multitask TPD-MS. The pretreated sample was exposed to dehydrated ammonia at 100°C for 30 min (30 torr) followed by purging with He flow. TPD was run from room temperature to 900°C with heating rate 10°C/min.

Hydrogen adsorption

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

Results and Discussion

The textural properties of catalysts with different sulfate ion loading are summarized in Table 1. The sample with 1.0N sulfate ion catalyst obtained the largest surface area and pore volume. This catalyst has a surface area of $118\text{m}^2/\text{g}$ and pore volume 0.127ml/g . For all samples, both of the surface area and pore volume decreased in the increasing of sulfate ion content. The surface area and pore volume for 2.0N and 4.0N sulfate ion decrease to a great extent lower than sample with 1.0N sulfate ion due to the alteration of crystal structure (Figure 1).

Table 1: Surface area and pore volume of catalysts

Catalysts	Surface Area (m^2/g)	Pore Volume (ml/g)
0.5NS	116	0.116
1.0NS	118	0.127
2.0NS	38	0.049
4.0NS	10	0.016

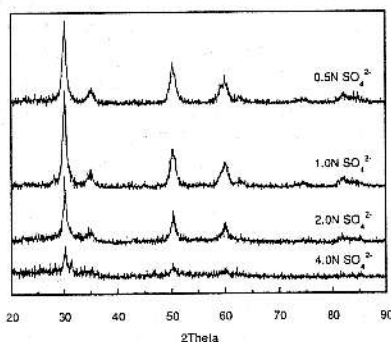


Figure 1. XRD pattern of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts.

Figure 2 shows ammonia TPD plots for $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ with different amount of sulfate ion loaded. At low temperature, the TPD plots consisted of two peaks of ammonia adsorptions. The first peak at about 200°C can be attributed to ammonia adsorb over weak acid site. While the second peak at about 400°C is due to adsorption of ammonia over medium acid site. $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ with

1.0N sulfate ion obtained the highest intensity for weak acid site and medium acid site followed by 0.5N, 2.0N and 4.0N sulfate ion. The further addition of sulfate ion caused the reducing of the intensity of peaks assigned to weak and medium acid sites. At high temperature, the peak appeared at about $700\text{--}750^\circ\text{C}$ is due to adsorption of ammonia over strong acid site. At this region, catalyst with 4.0N sulfate ion obtained the highest amount adsorbed followed by catalyst with 2.0N sulfate ion. But, there is no ammonia adsorption for catalysts with 0.5N and 1.0N sulfate ion. This phenomenon can be interpreted that the excessive amount of sulfate ion converted weak and medium acid sites to strong acid site.

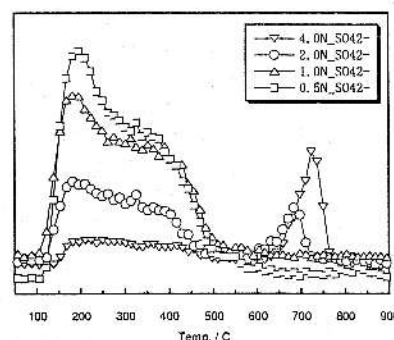


Figure 2. Ammonia TPD plots for $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$

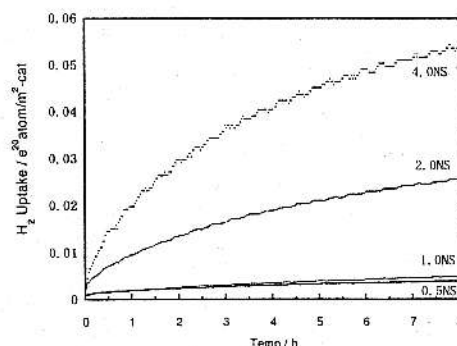


Figure 3. Time course of hydrogen adsorption over $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts.

The variations of hydrogen uptake as a function of time for different amount of sulfate ion loaded at 523K are shown in Figure 1. Hydrogen uptake increased for at least 8 h for catalyst with 2.0N and 4.0N sulfate ion loaded and only a small amount of hydrogen uptake was observable for catalyst with 0.5N and 1.0N sulfate ion loaded. We also observed that in the absence of Pt and/or sulfate ion, the rate of hydrogen uptake decreased to some extent [5].

It is obvious that the presence of Pt and sulfate ion is essential for hydrogen uptake. Pt will facilitate the dissociative adsorption of hydrogen molecules and sulfate ion exerts a promotive effect on the hydrogen uptake rate.

Conclusion

The increase of sulfate ion up to 4.0N increased the hydrogen uptake markedly. The presence of sulfate ion on catalysts exerts a promotive effect on the hydrogen uptake rate due to the development of medium and strong acid sites.

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