

FTIR AND TPD STUDIES OF ACID PROPERTIES OF $\text{Pt}/\text{SO}_4^{2-} - \text{ZrO}_2$

**Sugeng T.^{1*}, Zalizawati A.², M. Faizal R.², Aishah A.J.², Hadi Nur¹,
M. Nazlan M.M.¹, Mustaffa S.¹, Halimatun H.¹,**

¹Ibnu Sina Institute for Fundamental Science Studies-UTM, 81310 UTM Skudai, Johor, Malaysia.

²Fac. of Chemical & Natural Resources Eng.-UTM, 81310 UTM Skudai, Johor, Malaysia.

Tel: 07-5536071 Fax: 07-5536080 E-mail: sugeng@mail.goo.ne.jp

Abstract

The acidic properties of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ have been characterized by a combined study using temperature-programed desorption (TPD) of ammonia and infrared (IR) spectroscopy. $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ samples were prepared by impregnation of $\text{Zr}(\text{OH})_4$ with 0.5-4.0N of sulfate ion and calcined at 600 °C, followed by addition of 0.5wt% Pt. The ammonia TPD spectra confirmed the existence of peaks at about 200 °C and 400 °C corresponding to the weak and medium acid sites in the addition of sulfate ion up to 1.0N. The further addition of sulfate ion caused the reducing of the intensity of peaks assigned to weak and medium acid sites and developed a new peak at 700-750 °C corresponding to the strong acid site. IR analysis showed that the addition of sulfate ion led to the growth of the OH group bonded to sulfate species as evidenced by the bands at 3585 and 3548 cm^{-1} and diminishing of both the terminal and tri-bridged OH groups as evidenced by the bands at 3757 and 3652 cm^{-1} . This was accompanied by decreasing of the intensity of peak at 1600 cm^{-1} which has been ascribed to the adsorbed molecular water. The results indicated that the acid sites of catalyst were generated by addition of sulfate ion. The excessive amount of sulfate ion converted weak and medium acid sites to strong acid site.

Keywords: $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$; Ammonia TPD; FTIR

Introduction

The study of sulfated metal oxide has become an active area of research because of the high catalytic activity and efficiency of catalyst for carbocationic reactions such as hydrocracking and hydroisomerization of alkanes [1,2]. Several authors pointed out that the catalytic activity of $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst for various acid-catalyzed reactions are enhanced in the present of hydrogen and metal ion. Based on the pyridine preadsorbed FTIR studies, we clarified the role plays of hydrogen and metal ion added over the $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst [3-5].

In the present study, $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst has been characterized by ammonia TPD and FTIR in order to elucidate the effects of sulfate ion concentration to the acidity and activity of catalyst.

Experimental

The PSZ samples were 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 110 °C 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. The concentration of H_2SO_4 aqueous solution was varied from 0.5 N to 4.0 N. The $\text{SO}_4^{2-}\text{-ZrO}_2$ (SZ) was obtained by calcination of the sulfate ion-treated $\text{Zr}(\text{OH})_4$ at 600 °C in air. The PSZ was prepared by impregnation of the SZ with H_2PtCl_6 aqueous solution. The content of Pt was adjusted to be 0.5 wt %.

Temperature-programmed desorption (TPD) of ammonia was carried out with Bell Multitask TPD as follows. The sample was pretreated with hydrogen flow at 400 °C followed by purging with He flow. Then, the pretreated sample was exposed to dehydrated-ammonia (10 Torr) at 100 °C followed by purging with He flow. The TPD was run at a heating rate of 10 C/min from room temperature to 900 °C, and the

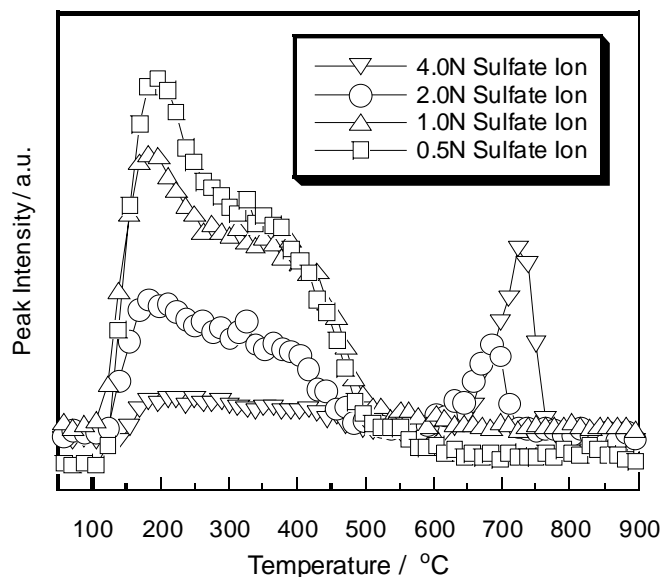


Fig 1 Ammonia TPD plot of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts

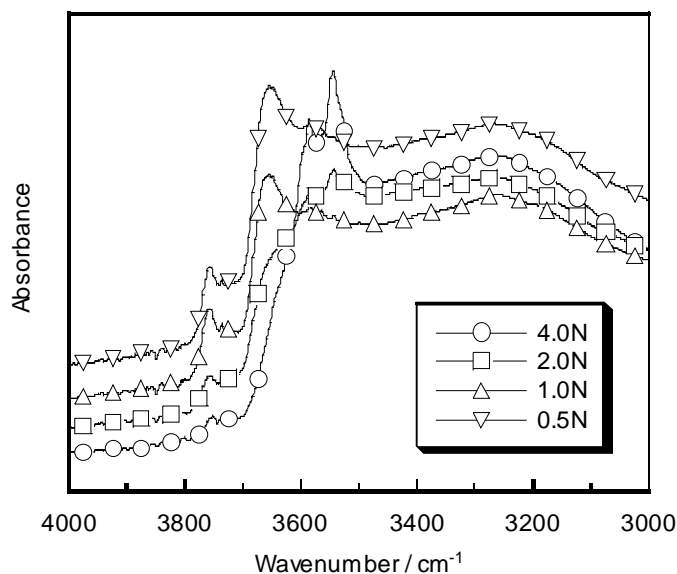


Fig 2 IR spectra of the hydroxyl region of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts with different sulfate ion content.

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 350 °C followed by outgassing at 400 °C. The spectra were recorded at room temperature with a spectral resolution of 4 cm^{-1} and with 128 scans.

Results and Discussion

Fig. 1 shows ammonia TPD plots for $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts at different amount of sulfate ion loaded. The TPD plots consisted of two TPD peaks; one peak appearing at about 200 °C and 400 °C corresponding to the weak and medium acid sites for the addition of sulfate ion up to 1.0N. The further addition of sulfate ion caused the reducing of the intensity of peaks assigned to weak and medium acid sites, and developed a new peak at about 700–750 °C corresponding to the strong acid site. This phenomenon can be interpreted that the excessive amount of sulfate ion converted weak and medium acid sites to strong acid site.

The phenomena of decreasing of weak and medium acid sites and the generation of strong acid site were also strongly evidenced by the results of IR study. Fig. 2 shows plots of IR spectra of the hydroxyl group spectral region. The addition of sulfate ion generated the hydroxyl groups at 3757 cm^{-1} (terminal OH) and 3652 cm^{-1} (tri-bridged OH). The further addition of sulfate ion led to erode the terminal and tri-bridged OH groups and developed new peaks assigned to the OH group bonded to sulfate species OH groups at 3585 cm^{-1} and 3548 cm^{-1}

Based on the ammonia TPD and IR results, we concluded that the addition of sulfate ion on metal oxide generate the weak and medium acid sites. The large excess amount of sulfate ion diminished weak and medium acid sites and developed a strong acid site.

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