MONOLAYER COVERAGE AND ACIDITY STUDY OF BIFUNCTIONAL OXIDATIVE ACIDIC CATALYST BY INFRARED SPECTROSCOPY: ZIRCONIA SULFATE LOADED TITANIUM SILICALITE

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Introduction

Bifunctional oxidative and acid catalysts have been prepared by incorporation of trivalent metal ions (Al\(^{3+}\), B\(^{3+}\), Fe\(^{3+}\), Ga\(^{3+}\)) and titanium ion (Ti\(^{4+}\)) together in the framework of zeolites [1]. The catalysts are active both in the oxidation reactions and in acid catalyzed reactions. Our group is developing the bifunctional oxidative-acidic catalysts using zeolite titanium silicalite, (TS-1) having Ti\(^{4+}\) as oxidative site and introducing metal oxides having acidity properties to the TS-1 framework. Sulfated zirconia has been paid much attention due to its significant catalytic activity in many hydrocarbon conversions [2]. The activity is mainly related to its acid properties. Some research groups have studied the structure and reactivity of zirconia-loaded on silica or alumina [3,4]. This work concentrates on the influence of the zirconium content to the acidity properties of the zirconium sulfate loaded TS-1.

Methodology

The support, TS-1 (1%mol of Ti) was prepared according to a procedure described earlier [5]. The white powder of zirconium sulfate (ZS500) was prepared by drying off zirconium sulfate hydrate [Zr(SO\(_4\)]\(_2\) 4H\(_2\)O] at 110°C for 24 h. The material was ground and calcined at 500°C for 6 h. TS-1 containing zirconium sulfate (ZS) at different %w/w zirconium was prepared by impregnating ZS (solution in water) on the TS-1 powder using sufficient amounts of ZS hydrate as precursor. The mixture was stirred at room temperature for 3 hrs, followed by evaporation of the water at 60°C. Finally, the solid was dried at 110°C for 24 hrs and calcined at 500°C for 5 hrs. The resulting sample was denoted as XSZ/TS-1, in which X is the percentage of zirconium in the sample.

Samples were characterized by powder x-ray diffraction (XRD) using a Bruker Advance D8 diffractometer with the Cu K\(\alpha\) (\(\lambda=1.5405\) Å) radiation at 40 kV and 40 mA. The pattern was scanned in the 2\(\theta\) ranges of 20° to 40° at a step 0.020° and step time 1s. The hydroxyl groups, pyridine, and sulfate vibration on the samples were collected on a Shimadzu Fourier Transformed Infrared (FTIR) spectrometer with a spectral resolution of 2 cm\(^{-1}\), scans 10 s, at room temperature. For acidity study, the sample in the form of wafer disc(10-12 mg) was locked in the cell equipped with CaF\(_2\) windows, and evacuated at 400°C under vacuum for 4 hrs. Pyridine was introduced into cell followed by evacuation under vacuum at 150 °C for 1 hrs. Infrared spectra of the samples were recorded at room temperature.

Results and Discussions

Dispersion of zirconium sulfate on the TS-1

Zirconium sulfate (ZS) in the various content were dispersed on TS-1. Samples were characterized by XRD and FTIR techniques. Figure 1 shows the XRD pattern of the ZS500 and ZS/TS-1 samples and the graph of diffraction line intensity of TS-1 at 20=23° versus loading amount of zirconium on the samples. The XRD pattern of all ZS/TS-1 samples show that diffraction line for tetrahedral or monoclinic phases of zirconia are not observed, indicates that the ZS is highly dispersed on the surface of TS-1. It is found that the structure
of TS-1 having MFI structure, still maintained after the ZS loading. However, the XRD peaks intensity of TS-1 decreased as the loading amount of the ZS increase. It might due to the decrease in the concentration of the TS-1 in the samples as the amount loading of ZS increased. The monolayer coverage of ZrO\text{2} can be determined from the graph of peak intensity at \(\theta = 23^\circ\) vs loading amount of zirconium on the samples as is shown in Fig 1b. A horizontal line is found for low ZS loading and another straight line can be drawn for higher ZS loading. The interception of these two lines occurs at the value 6 wt\% zirconium, which is equal to the monolayer coverage of 0.65 Zr\text{4+}/nm\text{2} TS-1.

Figure 2 shows the FTIR spectra of the ZS/TS-1 samples after evacuation at 400°C for 4 hrs under vacuum condition. In the region of hydroxyl groups (Fig. 2a), it is shown that the peak of silanol groups at 3745 cm\text{1} can still be observed for samples with low loading of ZS (i.e: samples 2ZS/TS-1 and 5ZS/TS-1). This silanol peak disappeared for samples with higher loading (10-20ZS/TS-1). This finding suggests that the monolayer coverage of the ZS on the TS-1 is in the range of 0.57 to 1.12 Zr\text{4+}/nm\text{2} TS-1, in which all silanol groups or the surface of TS-1 is covered with the ZS at the amount of 1.12 Zr\text{4+}/nm\text{2} TS-1. This result supports the XRD finding for determination of monolayer dispersion, 0.65 Zr\text{4+}/nm\text{2} TS-1.

**Acidity study of zirconium sulfate on the TS-1**

The acidity of the samples was monitored by FTIR spectroscopy. Figure 2b shows the FTIR spectra of the ZS/TS-1 samples after evacuation at 400°C for 4 hrs in vacuum condition. No vibration peak of pyridine is observed in all samples. Meanwhile, in the sulfate region, samples with 2-10 wt\% of ZS loading show similar pattern, while samples with 15 and 20 wt\% of ZS loading show additional peak at 1370 cm\text{1}. This peak is assigned to the \(v_{\text{S=O}}\) asymmetric for sulphate[6]. In addition, the intensity of this peak is higher for sample 20ZS/TS-1 as compared to that of sample 15ZS/TS-1, suggesting that the amount of sulfate increased as ZS loading increase. It is interesting to relate this finding with the surface coverage of ZS on TS-1. The XRD data found that the monolayer dispersion is 0.65 Zr\text{4+}/nm\text{2} TS-1, while the FTIR data found that the \(v_{\text{S=O}}\) asymmetric appeared in sample 15ZS/TS-1 (1.76 Zr\text{4+}/nm\text{2} TS-1), but not in sample 10ZS/TS-1 (1.12 Zr\text{4+}/nm\text{2} TS-1). It can be proposed that the \(v_{\text{S=O}}\) asymmetric vibration appeared on the samples containing double layer of ZS which is equal to or more than 1.3 Zr\text{4+}/nm\text{2} TS-1.

The types of acid sites were measured by FTIR using pyridine as probe molecule. The pyridine is adsorbed at room temperature after evacuation at 400°C. The spectra were monitored at room temperature after evacuation at 150°C for 1 h. to eliminate physisorb of pyridine (Fig. 3). In the region of hydroxyl groups (Fig. 3a), the spectra show insignificant
change compare to before pyridine adsorption (Fig. 2a). The presence of the peak of silanol even after pyridine adsorption, indicates that the silanol groups is not an acid sites. In the region of pyridine and sulfate (Fig. 3b), samples 2-10ZS/TS-1 show similar peaks at 1608 and 1444 cm\(^{-1}\). These bands appeared when adsorbed pyridine coordinatively bind to the Lewis acid sites. Meanwhile, samples 15-20ZS/TS-1 show the absorption bands at 1640 and 1545 cm\(^{-1}\) which correspond to pyridine interacting with the Bronsted acid sites, instead of bands at 1608 and 1444 cm\(^{-1}\) characteristic for Lewis acid. In addition, the peak for \(v_{S=O}\) asymmetric disappeared after adsorption of pyridine, suggesting that the S=O also bind with pyridine. This finding indicates that the S=O act as an active acid site. As such, the sulfated zirconia, ZS is an important factor, which contributes to the formation of Bronsted acid site in TS-1 support. The amount of acid sites are calculated based on the area under the peaks at 1545 and 1444 cm\(^{-1}\) for Bronsted and Lewis acid sites, respectively. In general, it is found that the amount of both types of acid sites increased with the increase amount of ZS loading.

Fig. 2 FTIR spectra of the samples after evacuation at 400\(^{\circ}\)C for 4 hrs in vacuum condition.

Fig. 3 FTIR spectra of samples after pyridine adsorption and evacuation at 150\(^{\circ}\)C for 1 h

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References