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Microcalorimetric and infrared spectroscopic studies of γ-Al_2O_3 modified by zinc oxide

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Abstract

The number and strength of surface acid and base sites on the ZnO/γ-Al_2O_3 catalysts were quantitatively measured by the technique of microcalorimetric adsorption (MA) while the nature of the acid and base sites were identified by Fourier transform infrared spectroscopy (FTIR), by using ammonia and carbon dioxide as the probe molecules. Specifically, the effects of ZnO loading and calcination temperature on the structure and surface acid/base properties were studied. It was found that the acidity was not significantly affected by the ZnO loading for the ZnO/γ-Al_2O_3 samples calcined at 673 K. However, the basicity as measured by the coverage of CO_2 increased substantially with the ZnO loading although the initial heats were almost not changed. X-ray diffraction (XRD) showed that the 10% ZnO/γ-Al_2O_3 sample calcined at 673 K exhibited only the phase of γ-Al_2O_3, indicating the well dispersion of ZnO on the surface. ZnO/γ-Al_2O_3 samples with higher loadings showed the phase of ZnO when they were calcined at 673 and 873 K, respectively. The spinel structure $ZnAl_2O_4$ was formed when the 42% ZnO/γ-Al_2O_3 sample was calcined at 1073 K. Accordingly, the surface acidity and basicity were significantly changed. The surface of the 42% ZnO/γ-Al_2O_3 sample calcined at 673 K was mainly covered by Zn^{2+} cations, as evidenced by the FTIR results which showed that this sample exhibited mainly Lewis acid sites associated with Zn^{2+} and Lewis base sites associated with O^{2-} anions adjacent to Zn^{2+} cations. When the spinel structure $ZnAl_2O_4$ was formed upon the calcination at 1073 K, the surface was mainly covered by Al^{3+} again, exhibiting acidity and basicity with both Lewis and Brönsted features associated with Al^{3+} cations. In addition, the number and strength of both acid and base sites on the surface of the spinel were significantly decreased. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Microcalorimetric adsorption; FTIR; ZnO/γ-Al_2O_3 catalyst; $ZnAl_2O_4$ spinel; Surface acidity and basicity

1. Introduction

The acid/base properties of metal oxides are important for determining the catalytic and adsorptive properties of these materials [1–5]. For example, γ-Al_2O_3 has been widely used as acidic catalyst and support. The acidity and basicity of γ-Al_2O_3 can be modified by adding metal oxides onto its surface [6,7]. The γ-Al_2O_3 supported zinc oxide catalysts have been widely studied [8–12]. For example, Vinek, et al. [13] studied the ZnO–Al_2O_3 system by XPS. More detailed characterizations of ZnO/Al_2O_3 catalysts as a function of ZnO loading and calcination temperature were carried out by Strohmeier and Hercules [14]. They found that an 'aluminate-type' phase (surface spinel) was formed preferentially at low ZnO loadings and bulk-like ZnO segregated on the surface at higher

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Table 1
BET surface areas of γ-Al_2O_3, ZnO and ZnO/γ-Al_2O_3 samples calcined at different temperatures

Catalyst sample	Calcination temperature (K)	Surface area (m^2/g)
γ-Al_2O_3	As-received	159
ZnO	673	9
10 wt.% ZnO/γ-Al_2O_3	673	145
21 wt.% ZnO/γ-Al_2O_3	673	138
42 wt.% ZnO/γ-Al_2O_3	673	117
42 wt.% ZnO/γ-Al_2O_3	873	106
42 wt.% ZnO/γ-Al_2O_3	1073	80

loadings. In addition, the decomposition of H_2O_2 was found to depend on the acid strength of the catalyst [15].

In this work, we studied the acid/base properties of γ-Al_2O_3 modified with various amounts of zinc oxide and calcined at different temperatures (Table 1). The technique of microcalorimetric adsorption was employed to measure the number and strength of surface acid and base sites using ammonia and carbon dioxide as the probe molecules, respectively. In addition, in situ infrared (IR) spectroscopy was used to identify the nature of acid/base sites. Specifically, IR spectra of adsorbed ammonia was used to identify the Lewis and Brönsted acid sites, while adsorbed carbon dioxide was used to determine the basic oxygen anions and hydroxyl groups, on the surfaces.

2. Experimental

2.1. Preparation of sample

γ-Al_2O_3-supported ZnO catalysts were prepared by incipient wetness impregnation method. The support was impregnated into solutions containing various amounts of zinc nitrate calculated according to the desired loadings. After impregnation, the samples were dried at 373 K overnight. Then the samples were calcined for 6 h at 673, 873, and 1073 K, respectively. A bulk ZnO was also prepared as the reference by adding the solution of sodium carbonate to the solution of zinc nitrate. The precipitate formed was washed, dried at 373 K and calcined at 673 K for 6 h.

2.2. Microcalorimetric adsorption measurement

Microcalorimetric studies of the adsorption of NH_3 and CO_2 were carried out using a Tian-Calvet heat-flux apparatus, which has been described elsewhere [16]. The microcalorimeter was connected to a gas-handling and volumetric adsorption system, equipped with a Baratron capacitance manometer for precision pressure measurement. The differential heat of adsorption versus adsorbate coverage was obtained by measuring the heats evolved when doses of a gas (2–5 μmol) were admitted sequentially onto the catalyst until the surface was saturated by the adsorbate.

Ammonia and carbon dioxide with a purity of 99.99% were used. Before microcalorimetric measurements, the samples were typically dried under vacuum at 573 K for 1 h, calcined in 500 Torr O_2 at 723 K for 2 h, and evacuated at 723 K for 2 h. Microcalorimetric adsorption of ammonia and carbon dioxide were performed at 423 K.

2.3. FT-IR

Infrared spectra were collected with an IFS66V Vacuum-type FT-IR Spectrophotometer. Each spectrum was recorded at 2 cm^{-1} resolution with 32 co-added scans. Sample pellets were formed with a thickness of 20–30 mg/cm^2. The samples were loaded into a quartz cell equipped with CaF_2 windows. The treatment procedure of the samples for IR was the same as for microcalorimetric adsorption studies. Ammonia and carbon dioxide were then dosed onto the sample at 423 K for 0.5 h. The cell was then isolated, cooled to room temperature and evacuated. Infrared spectra were then collected. Each reported spectrum is the difference between the spectrum of the clean sample and the spectrum after adsorbate dosing.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of ZnO/γ-Al_2O_3 with various ZnO loadings and calcined at different temperatures. Only broad diffraction peaks due to γ-Al_2O_3 phase could be observed for the 10% ZnO/γ-Al_2O_3 sample. As the loading of ZnO increased to 21%, new peaks due to ZnO were observed and the intensities of these peaks increased

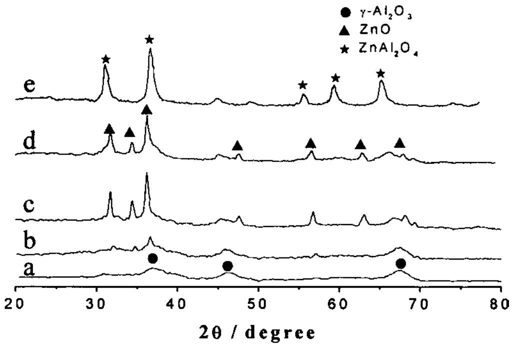

Fig. 1. X-ray diffraction patterns for 10% ZnO/γ-Al_2O_3 (a) and 21% ZnO/γ-Al_2O_3 (b) calcined at 673 K, and for 42% ZnO/γ-Al_2O_3 calcined at 673 K (c), 873 K (d) and 1073 K (e).

with the increase of ZnO loading. After the 42% ZnO/γ-Al_2O_3 sample was calcined at 1073 K, the X-ray diffraction gave the peaks at 31.0, 36.9 and 60.0°, which can be attributed to the $ZnAl_2O_4$ phase. This result is in consistence with that reported by Maezawa et al. [17].

Fig. 2 shows the differential heats of adsorption versus coverage of ammonia on γ-Al_2O_3 and the ZnO/γ-Al_2O_3 samples calcined at 673 K. The initial heat of ammonia adsorption on γ-Al_2O_3 was 150 kJ/mol and the number of acid sites measured was 400 μmol/g. The addition of ZnO did not significantly change the initial heat for ammonia adsorption. The initial heats measured for ammonia adsorption on all the ZnO/γ-Al_2O_3 samples were between 150 and 165 kJ/mol. However, the heats for ammonia adsorption at coverage between 100 and 400 μmol/g seem higher for the ZnO/γ-Al_2O_3 samples than for γ-Al_2O_3. The bulk ZnO has the lowest initial heat (135 kJ/mol) for ammonia adsorption among the samples studied. The coverage of ammonia over the ZnO sample is very low, indicating that the material is not acidic.

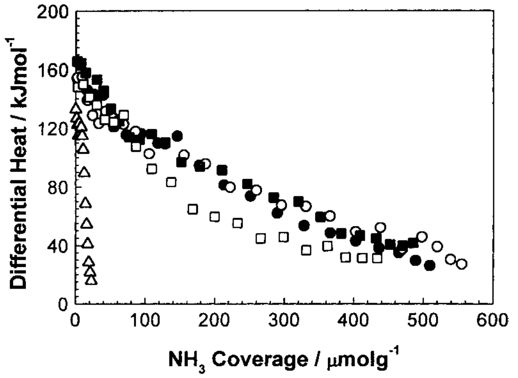

Fig. 2. Differential heat versus adsorbate coverage for adsorption of NH_3 at 423 K on γ-Al_2O_3 (□), 10% ZnO/γ-Al_2O_3 (■), 21% ZnO/γ-Al_2O_3 (○), 42% ZnO/γ-Al_2O_3 (●) and bulk ZnO (△). All the samples were calcined at 673 K.

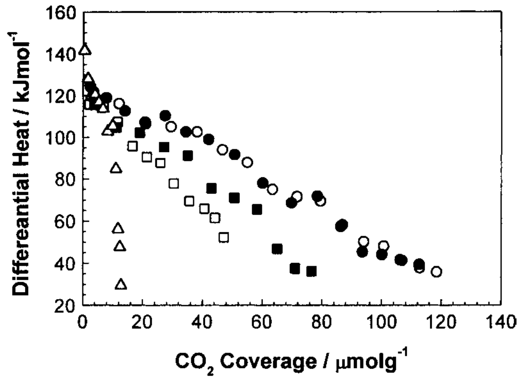

Fig. 3. Differential heat vs. adsorbate coverage for adsorption of CO_2 at 423 K on γ-Al_2O_3 (□), 10% ZnO/γ-Al_2O_3 (■), 21% ZnO/γ-Al_2O_3 (○), 42% ZnO/γ-Al_2O_3 (●) and bulk ZnO (△). All the samples were calcined at 673 K.

Fig. 3 shows the plots of differential heat versus coverage for CO_2 adsorption on the γ-Al_2O_3 and ZnO/γ-Al_2O_3 samples calcined at 673 K. The γ-Al_2O_3 exhibited the initial heat of 115 kJ/mol and saturation coverage of 46 μmol/g for CO_2 adsorption. This initial heat is lower than the value reported by Shen et al. [18] for CO_2 adsorption on γ-Al_2O_3. One reason may be that we used the dose size that was too large to determine the initial heat. In fact, the differential heats for CO_2 adsorption on the γ-Al_2O_3 measured by Shen et al. decreased sharply and reached 120 kJ/mol at the third dose. Then, the heat continued to decrease with the smaller slope [18]. Thus, our result for CO_2 adsorption on γ-Al_2O_3 agrees well with the heats as measured by Shen et al. after the third dose. The initial heats for CO_2 adsorption on the ZnO/γ-Al_2O_3 were around 120 kJ/mol, which were not significantly higher than the heat for CO_2 adsorption on γ-Al_2O_3 although the initial heat for CO_2 adsorption on ZnO was higher (about 140 kJ/mol). However, the coverage of CO_2 was significantly higher on the ZnO/γ-Al_2O_3 samples than on /γ-Al_2O_3, indicating that ZnO exhibits the nature of basicity. The CO_2 coverage reached its maximum value of 120 μmol/g when ZnO loading reached 21%.

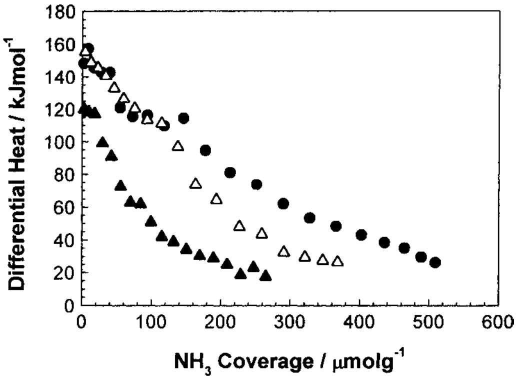

Fig. 4. Differential heat versus adsorbate coverage for adsorption of NH_3 at 423 K on 42% ZnO/γ-Al_2O calcined at the temperature of 673 K (●) 873 K (△) and 1073 K (▲), respectively.

The effects of calcination temperature on the adsorption of ammonia and carbon dioxide on the 42% ZnO/γ-Al_2O_3 sample are shown in Figs. 4 and 5. The heats for ammonia adsorption on the samples calcined at 673 and 873 K are the same at the coverage lower than 120 μmol/g. These two samples exhibited the same XRD pattern as shown in Fig. 1, which indicated the presence of ZnO phase beside that of γ-Al_2O_3. This may explain why the two samples displayed the same heats initially. The lower coverage of ammonia on the sample calcined at 873 K than on the sample calcined at 673 K may be due to the decrease of surface area of the sample upon calcination at the higher temperature. The same trend can be observed for the adsorption of CO_2 as shown in Fig. 5. However, when the sample was calcined at 1073 K, the initial heat and coverage for the adsorption of both ammonia and CO_2 are greatly decreased. In fact, XRD showed that the only phase present in this sample was of the spinel structure of $ZnAl_2O_4$. Thus, Figs. 4 and 5 showed that the spinel $ZnAl_2O_4$ exhibited weak acidity and basicity. The basicity was so low that the coverage of CO_2 on this sample was less than 20 μmol/g. If we divide the surface coverage of CO_2 by the corresponding surface areas of these samples, we obtain the surface densities of basic sites as titrated by CO_2. It is easily found that the surface densities of basic sites are 1, 0.6 and 0.2 μmol/m^2 for the samples calcined at 673, 873 and 1073 K, respectively. The decrease of the basic site density upon increase of calcination temperature indicated the fact that Zn^{2+} cations migrated into the bulk from the surface upon the calcination for the formation of the spinel structure, as has been evidenced by the above XRD results.

Fig. 6 shows the IR spectra collected after exposure of the samples to ammonia at 423 K. The bands at 1619 and 1246 cm^{-1} originate from the asymmetric and symmetric deformation vibrations, respectively, of NH_3 molecules coordinated to aluminum cations, revealing Lewis acid sites on γ-Al_2O_3 [19,20]. The bands at 1686, 1478, and 1393 cm^{-1} are due to deformation modes of NH_4^+ formed by the interaction of NH_3 with Brönsted acid sites on γ-Al_2O_3 [19,20].

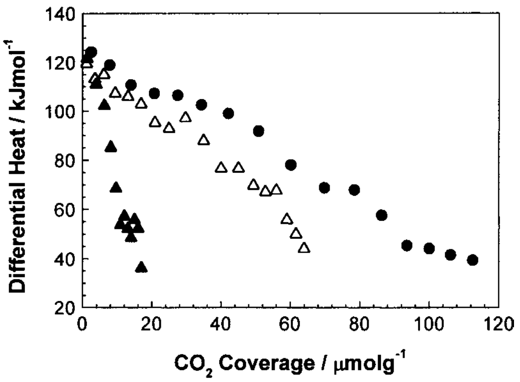

Fig. 5. Differential heat versus adsorbate coverage for adsorption of CO_2 at 423 K on 42% ZnO/γ-Al_2O calcined at the temperature of 673 K (●) 873 K (△) and 1073 K (▲), respectively.

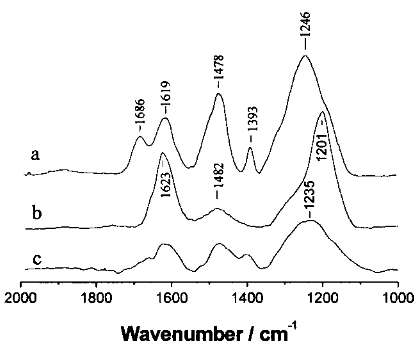

Fig. 6. FT-IR spectra collected after ammonia adsorption at 423 K followed by evacuation at room temperature on γ-Al_2O_3 (a), and on the 42% ZnO/γ-Al_2O_3 sample calcined at 673 K (b) and 1073 K (c), respectively.

Ammonia adsorption on the 42% ZnO/γ-Al_2O_3 calcined at 673 K produced three bands around 1623, 1482 and 1201 cm^{-1}. The bands at 1623 and 1201 cm^{-1} can be assigned to ammonia coordinately adsorbed on Lewis sites of ZnO [20]. No NH_4^+ groups can be detected on ZnO [20], indicating that no Brönsted acid sites can be formed on the surface of ZnO. The lower wavenumber of the peak at 1201 cm^{-1} for Zn^{2+} as compared to that of the peak at 1246 cm^{-1} for Al^{3+} indicates that Zn^{2+} is a weaker Lewis acid than Al^{3+}. In fact, this symmetric deformation band of NH_3 is sensitive to the electronic environment so that it is usually used to obtain the information about the relative charge densities related to the Lewis sites that the molecules are adsorbed. The peak at 1482 cm^{-1} belongs to the Brönsted acid sites associated with Al^{3+}. These results clearly demonstrated that the surface of the 42% ZnO/γ-Al_2O_3 sample after calcination at 673 K composed of mainly Lewis acid sites associated with Zn^{2+} with little Brönsted acid sites associated with Al^{3+}. The calcination at 1073 K for the 42% ZnO/γ-Al_2O_3 sample brought the wave number of the symmetric deformation band of NH_3 back to 1235 cm^{-1}, revealing that the surface Zn^{2+} cations have been replaced by Al^{3+} cations owing to the penetration of Zn^{2+} into the bulk. The two bands around 1686 and 1393 cm^{-1} that were not present for the sample calcined at 673 K appeared again. Thus, the sample calcined at 1073 K possessed both Brönsted and Lewis acid sites associated with only Al^{3+} cations. In addition, the peak at 1235 cm^{-1} has lower wave number, broadened width and lower intensity as compared to the peak at 1246 cm^{-1} for γ-Al_2O_3, indicating the weaker acidity, wider acidity strength distribution and less acidic sites on the ZnO/γ-Al_2O_3 sample calcined at 1073 K as compared to γ-Al_2O_3.

Fig. 7 shows the IR spectra collected after exposure of the samples to CO_2 at 423 K. The bands around 1645, 1442, and 1229 cm^{-1} can be assigned to the features normally seen for bicarbonate species formed by adsorption of CO_2 on surface hydroxyl groups of γ-Al_2O_3 [21,22]. The intensities of these bands were significantly lowered for the ZnO/γ-Al_2O_3 sample calcined at 673 K. In addition, two new bands at 1536 and 1402 cm^{-1} appeared on this sample, which can be assigned to bidentate carbonate adsorbed on Zn^{2+} cations [23]. Calcination at 1073 K restored the IR feature similar to that for CO_2 adsorption on γ-Al_2O_3, confirming again that the surface of the spinel $ZnAl_2O_4$ composed of mainly Al^{3+} cations.

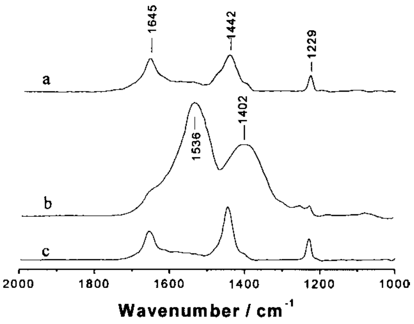

Fig. 7. FT-IR spectra collected after CO_2 adsorption at 423 K followed by evacuation at room temperature on γ-Al_2O_3 (a), and on the 42% ZnO/γ-Al_2O_3 sample calcined at 673 K (b) and 1073 K (c), respectively.

4. Conclusion

The addition of ZnO onto γ-Al_2O_3 does not seem to affect significantly the surface acidity. However, the surface basicity increased substantially with the ZnO loading. The surface structures of ZnO/γ-Al_2O_3 are greatly influenced by the loading and calcination temperature. ZnO can be highly dispersed on γ-Al_2O_3 when the loading is lower than 10%. Crystal ZnO appears when the loading is higher. The spinel structure $ZnAl_2O_4$ can be formed when the samples are calcined at 1073 K. Accordingly, the surface acidity and basicity are significantly altered. For example, it was found that the surface of the 42% ZnO/γ-Al_2O_3 sample calcined at 673 K was mainly covered by Zn^{2+} cations. When the sample was calcined at 1073 K, the spinel structure $ZnAl_2O_4$ began to form with the migration of Al^{3+} cations onto the surface. Accordingly, the number and strength of both acid and base sites on the surface of the spinel were significantly decreased.

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