Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 441-446

MICROCALORIMETRIC STUDIES OF Zn–Al MIXED OXIDES OBTAINED FROM HYDROTALCITE-TYPE PRECURSORS

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Abstract

A series of Zn–Al hydrotalcites with Zn/Al molar ratios of 1, 2, 3 and 6 were prepared by coprecipitation method. TG-DTG results showed that the hydrotalcites decompose in two stages, corresponding to the two endothermic peaks around 180 and 220°C. After calcination at 400°C, the samples were converted into Zn–Al mixed oxides with the only XRD pattern of ZnO, except for the sample with the ratio of 6. The Zn–Al mixed oxides possess similar surface acidity revealed by microcalorimetric adsorption of NH_3. The basicity of the samples increases with the order: ZnO>6Zn/Al>1Zn/Al>Al_2O_3.

Keywords: microcalorimetric adsorption, surface acidity, surface basicity, Zn–Al hydrotalcite, Zn–Al mixed oxide

Introduction

Hydrotalcite and many related compounds have recently attracted attention as the promising precursors of catalysts and catalyst supports [1–9]. For example, calcined hydrotalcites containing Zn and Al have been tested as the catalysts for synthesis of methanol and water-gas shift reaction [1, 6]. In addition, calcined Zn–Al hydrotalcites have been studied as the support for heteropolyacids [1, 4]. For these applications, the surface acidity and basicity of the calcined Zn–Al hydrotalcites should play the important roles [10]. As development of the technique of microcalorimetric adsorption, it has been used to determine the surface acidity and basicity of catalysts [11–15]. This technique has advantages compared with the Hammet indicator and temperature-programmed desorption as it provides the more accurate values of strength and number of acid/base sites on surfaces [10, 11].

In this work, a series of Zn–Al hydrotalcites with Zn/Al molar ratios of 1, 2, 3 and 6 were synthesized by coprecipitation method and then were decomposed into Zn–Al mixed oxides. The Zn–Al hydrotalcites and/or their decomposition were characterized by X-ray diffraction (XRD), thermogravimetric-differential thermal analysis (TG-DTA), and microcalorimetric adsorption of NH_3 and CO_3.

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

All the starting materials were AR chemicals. Hydrotalcite samples with Zn/Al molar ratios of 1, 2, 3, and 6 were prepared by the coprecipitation method [1, 9]. In each batch, $Zn(NO_3)_2$ and $Al(NO_3)_3$ were dissolved to obtain a solution of 250 mL with total cation concentrations of 1 M. NaOH and Na_2CO_3 were dissolved to obtain another solution of 250 mL with appropriate amount: $[OH]=2[Zn^{2+}]+2[Al^{3+}]$ and $[CO_3^{2-}]=0.5[Al^{3+}]$. Then, the two solutions were added dropwise and alternately into 300 mL distilled water at 60°C. Aged for 30 min, the coprecipitate was filtered and washed until pH of the filtered water was near to 7. The resulting materials were then dried at 80°C overnight. The hydrotalcite precursors were calcined in air for 6 h at 400°C to obtain the Zn–Al mixed oxides, denoted as *n*Zn/Al according to the molar ratio. $Zn(OH)_2$ was prepared and treated in the same way to obtain ZnO. Commercial γ-Al_2O_3 (Taiyuan) was used for comparison in this work.

XRD was performed on a Shimadzu XD-3A X-ray diffractometer using FeK_α radiation. TG-DTA experiments were carried out in 60 ml min^{-1} air with heating rate of 20°C min^{-1} up to 630°C on a Rigaku thermoanalyzer (Simultaneous TG-DTA High Temp. Type Cat. No. 8076E1). α-Al_2O_3 was used as the DTA standard. Surface areas were measured by N_2 adsorption at –195.8°C using the BET method. Before the measurements, the samples were evacuated to 0.7 Pa at 400°C. The BET areas of the ZnO, Al_2O_3, and the calcined hydrotalcites 1Zn/Al, 3Zn/Al, and 6Zn/Al were found to be 9, 168, 154, 70 and 65 m^2 g^{-1}, respectively.

Microcalorimetric adsorptions of NH_3 and CO_2 were carried out at 150°C by using a Tian-Calvet heat-flow microcalorimeter [15, 16]. The apparatus was linked to a gas-handling and volumetric adsorption system, equipped with a Baratron capacitance manometer for precision pressure measurement. Heat-flow signal was detected by a transducer assembly manufactured by the ITI Inc. The differential heat of adsorption *vs.* adsorbate coverage was determined by measuring the heats evolved when doses of gas (1–3 μmol) were introduced sequentially onto the sample until a final equilibrium pressure of 700 Pa was available. Before measurements, the samples were calcined on O_2 at 400°C and then evacuated at 400°C for 2 h. The NH_3 and CO_2 ($\geq$99.995%) were purified by successive freeze-pump-thaw cycles.

Results and discussions

Figure 1 shows XRD patterns of the hydrotalcite samples with Zn/Al molar ratios of 1, 2, 3 and 6. The samples exhibit the typical hydrotalcite structure, in which the main peak with d value of 7.6 is due to the diffraction for the space between the adjacent layers in the hydrotalcites [1]. The Zn–Al hydrotalcites have a rhombohedral R-3m symmetry, in which the Zn^{2+} and Al^{2+} cations are incorporated in brucite-type layers and the excessive positive charges on the layers are compensated by carbonate anions in the interlayers. No other separate phases were detected for the samples prepared with the ratios of 1, 2 and 3 while the additional ZnO phase was found in the sample with the ratio of 6.

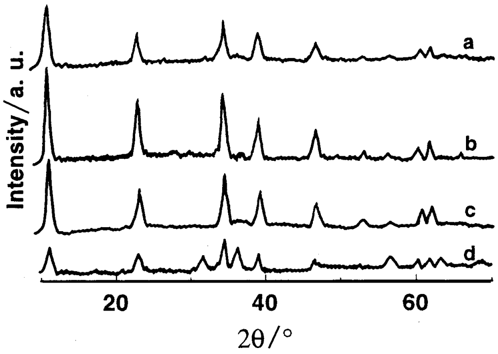

Fig. 1 XRD patterns of the Zn–Al hydrotalcite samples with Zn/Al molar ratios of 1a, 2b, 3c and 6d

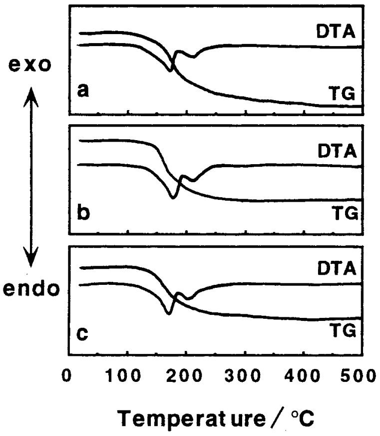

Fig. 2 TG-DTA profiles of the Zn–Al hydrotalcite samples with Zn/Al molar ratios of 1a, 2b and 3c

Figure 2 shows the TG-DTA profiles of the hydrotalcite samples with Zn/Al molar ratios of 1a, 2b and 3c. These samples display two similar mass loss stages, in agreement with the observations of other [1]. The first endothermic peak at about 180°C corresponds to the loss of interlayer water without collapse of hydrotalcite structure. The second endothermic peak at about 220°C is due to the loss of hydroxyl groups from the brucite-like layer and the interlayer CO_3^{2-} anions.

XRD patterns of the calcined Zn–Al hydrotalcite samples are shown in Fig. 3. The samples exhibit the only phase of ZnO and the intensity of the diffraction lines increases as increase of the Zn content [1]. The absence of any detectable aluminum phases suggests that the Al^{3+} cations be highly dispersed in the lattice of ZnO when calcined at 400°C. This property is similar to that of the calcined Mg–Al and Mg–Fe hydrotalcites which showed the only phase of MgO [5, 9].

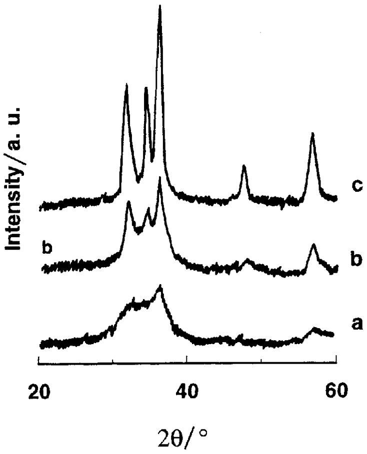

Fig. 3 XRD patterns of the Zn–Al mixed oxides with Zn/Al molar ratios of 1a, 3b and 6c

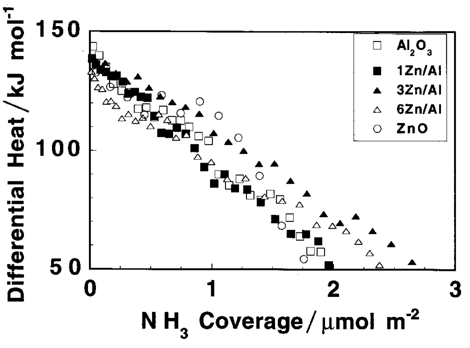

Fig. 4 Differential heat *vs.* NH_3 coverage at 150°C on the Zn–Al mixed oxides, Al_2O_3 and ZnO

The catalytic properties of solid acid/base are usually determined by the number and strength of acid/base sites on surfaces [10, 12]. In our previous paper, we defined the specific strength distribution of the acid/base sites, which can be obtained by normalizing the site strength distribution to surface area [15]. Figure 4 shows the results of microcalorimetric adsorption of NH_3 on ZnO, Al_2O_3, and calcined Zn–Al hydrotalcites. The plots of the differential heat for all the samples show the similar trend: the differential heat decreased from ca 140 to about ca 50 kJ mol^{-1} with the increase of NH_3 coverage to about 2 μmol m^{-2}. This suggests that the samples studied possess similar surface acidity in density and strength.

Figure 5 shows the results of microcalorimetric adsorption of CO_2 on ZnO, Al_2O_3, and calcined Zn–Al hydrotalcites. All the samples display the similar initial differential heats of CO_2 adsorption around 140 kJ mol^{-1}. However, the number of base sites on these samples decreases with the order: ZnO (1.3 μmol m^{-2})>6Zn/Al (1.0 μmol m^{-2})>1Zn/Al (0.5 μmol m^{-2})>Al_2O_3 (0.3 μmol m^{-2}). Apparently, the basicity increases with the increase of the Zn content in the samples.

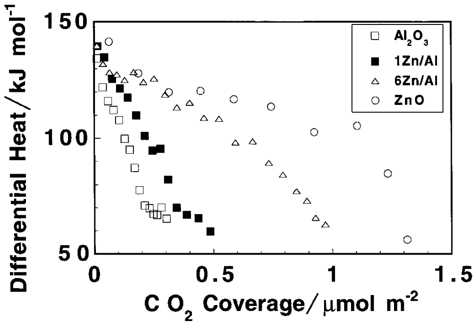

Fig. 5 Differential heat *vs.* CO_2 coverage at 150°C on the Zn–Al mixed oxides, Al_2O_3 and ZnO

A better view of the acid-base site energy distributions are shown in Fig. 6. The histograms were plotted by fitting the curves of differential heat *vs.* coverage by polynomials and then using the fitted polynomials to determine the number of adsorbates that interact with the differential heat within a given range of coverage. It is seen from Fig. 6(a), the acid sites on the Zn–Al mixed oxides as determined by microcalorimetric adsorption of NH_3 are mainly distributed in the range of 50 to 140 kJ mol^{-1}. There are about 0.07 mmol m^{-2} acid sites stronger than 140 kJ mol^{-1} on the Al_2O_3. However, these sites are not available on the Zn–Al samples. The most populated acid sites on the ZnO are between 110 and 130 kJ mol^{-1}. Figure 6(b)

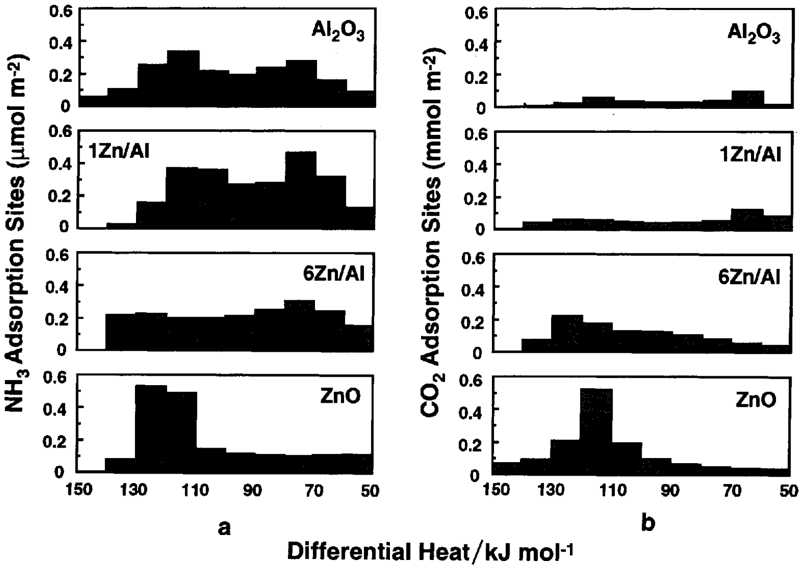

Fig. 6 Distribution of interaction strengths for NH_3 (a) and CO_2 (b) adsorption on the Zn–Al mixed oxides, Al_2O_3 and ZnO

clearly shows that the basicity in terms of CO_2 adsorption increases with the Zn content in the samples. The Zn–Al samples possess the base sites with heats in the region of 50 to 140 kJ mol^{-1}. The ZnO is the only sample with base sites stronger than 140 kJ mol^{-1} (~0.07 mmol m^{-2}). The most populated base sites on the ZnO are around 120 kJ mol^{-1}.

Conclusions

Zn–Al hydrotalcites with Zn/Al molar ratios of 1, 2, 3 and 6 were prepared and decomposed into Zn–Al mixed oxides. Microcalorimetric adsorption of NH_3 and CO_2 reveal that the mixed oxides have similar surface acidity to that of the ZnO and Al_2O_3 samples, while the basicity increases with the order: ZnO>6Zn/Al>1Zn/Al>Al_2O_3. Thus, the acidity/basicity of the Zn–Al mixed oxides can be controlled by adjusting the Zn/Al ratios according to different demands.

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We acknowledge the financial supports from the Trans-Century Training Program Foundation for Talents by the State Education Commission of China and the National Natural Science Foundation of China No. 29673021.

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