Preparation and characterization of ternary cation hydrotalcite-like compounds and their adsorption of NO$_x$

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Hydrotalcite-like compounds with different molar ratios of Mg:Cu:Al have been prepared by co-precipitation method and characterized by XRD, IR, TG-DTA. The results show that the sample possess feitknecht structure when Mg:Cu:Al molar ratios are 2.5:0.5:1, 2:1:1 and 1:2:1. W-Si-heteropolyacid pillared hydrotalcite-like compounds have been obtained by ion exchange method. The heteropolyacid pillared hydrotalcite is a crystallloid with highly regular layers. The maximum spacing of interlayer is 1.4786 nm. The adsorption capacity of these materials for nitric oxides has also been measured.

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Hydrotalcite-like compounds are anionic clays, with generic formula [M$_{2}$+$_{1}$M$^{n+}$(OH)$_{2}$][A$^{m-}$]$_{x/n}$·mH$_2$O, where M$^{2+}$ and M$^{3+}$ are the bivalent and trivalent metal cations, and A$^{m-}$ is an exchangeable interlayer anion$^1$. These materials have a special anion pillared structure and exhibit memory effect, interlayer anionic exchangeability and adjustability in the cation layer. Under specific conditions, some functional species (e.g. atom, molecule, ion) can be introduced in the interlayer of layered compounds to change the properties of the layers by ion exchange. The hydrotalcites are used widely in catalysis, adsorption, medicine, and as organic polymer materials due to their special properties$^2$-$^6$. In this note, MgCuAl-HTlcs and MgAlCu-WSi-HTlcs were prepared, and their adsorption capacities for NO$_x$, measured.

**Experimental**

**Preparation and characterization of HTlcs**

Aqueous solutions of the nitrates of Mg (II), Cu (II), and Al (III) were added slowly, at the rate of 1 droplet/s with vigorous stirring into a mixture of NaOH and Na$_2$CO$_3$ at 303 K, and the pH was kept between 9 and 10. The mixture was continuously stirred for about 30 min, then heated to 338 K, and kept at this temperature for 18 h. The precipitate was washed with deionized water until pH = 7, dried at 353 K for 12 h, calcined at 773 K for 5 h, and then cooled to room temperature.

MgAlCu-WSi-HTlc was prepared as follows: the W-Si-heteropolyacid was prepared with sodium tungstate and sodium silicate, then W-Si-heteropolyacid was added slowly at a rate of 1 droplet/s with vigorous stirring to MgCuAl-HTlcs which scattered completely in deionized water with nitric acid. The pH was adjusted and keeping 338 K. The mixture was stirred for 10 h. The HTlc was washed with deionized water until pH = 7, dried at 353 K for 12 h, calcined at 773 K for 5 h, and then cooled to room temperature.

The HTlcs were characterized by FT-IR, XRD, and TG-DTA analyses. FT-IR analyses were carried out by using German Buluke Vector 22 infrared Spectrometer. X-ray diffraction patterns were obtained on a Rigaku D/Max-3B diffractometer with Cu-K$^a$ radiation. TG-DTA were measured on a Peking PCT-1A differential thermal balance.

**Adsorption of the HTlcs on NO$_x$**

The HTlcs were loaded in a vacuum container (0.29 L). Nitric oxides were injected into the container and shaken at the room temperature. The concentration of NO$_x$ was measured by N-(1-naphthyl) ethylenediamine hydrochloric acid spectrophotometer. After adsorption of NO$_x$, the hydrotalcite was recycled by washing, drying at 353 K, and calcination at 773 K for 5 h.

**Results and discussion**

FT-IR spectrum of the HTlcs (Fig.1) show peaks at around 3400-3490 cm$^{-1}$ which may be assigned to the expanding vibrations of water, which is comparable to the adsorption peak of the free –OH (3600 cm$^{-1}$). In this case, the peaks shift to lower values, due to hydrogen bond between H$_2$O of interlayer and carbonate anion of interlayer or –OH of layer sheet. There being some water on the surface of the particles or in the interlayer of crystal lattice, the bending vibration peaks of crystal water were observed at 1500-1650 cm$^{-1}$. The peaks at 1370-1400 cm$^{-1}$ may be
Fig. 1—IR spectrum of MgCuAl-HTlcs before and after calcinations. (a) n (Mg):n (Cu):n (Al)=2.5:0.5:1; (b) n (Mg):n (Cu):n (Al)=2:1:1, before calcinations; 2, after calcinations.

Fig. 2—XRD patterns of MgAlCu-HTlcs before calcinations. (a) n (Mg):n (Cu):n (Al)=2.5:0.5:1; (b) n (Mg):n (Cu):n (Al)=2:1:1.

assigned to C-O expanding vibration of CO$_3^{2-}$, which is comparable to the adsorption peak of CO$_3^{2-}$ (1430 cm$^{-1}$). The peak of C-O shift to lower wave number, indicating that CO$_3^{2-}$ is not really free in the interlayer and hydrogen bonds must exist between CO$_3^{2-}$ and H$_2$O. After the HTlcs were calcined at 773 K, the peak intensities of stretching and bending vibration of H$_2$O and vibration peaks of CO$_3^{2-}$ were weakened.

The figure of peaks became dull, and the stretching and bending vibration of H$_2$O moved towards lower wave number. These features show that there was a part of H$_2$O and -OH in the spacing of the HTlcs after calcination, and CO$_3^{2-}$ was decomposed to CO$_2$ partially, and the double hydroxide anionic structure was broken to produce MgAlCu (O). The adsorption peaks at 420-520 cm$^{-1}$ may be ascribed to the ion (Mg$^{2+}$, Al$^{3+}$, Cu$^{2+}$) vibration of crystal grating.

XRD patterns of MgAlCu-HTlcs dried at 80°C are shown in Fig. 2. The X-ray diffraction patterns show that they were just qualitative hydroxalite$^7$. The typical hydroxalite diffraction peaks were observed at the low diffraction angles for all synthetic samples. Though the crystallities of the samples were not very good, they all possessed "feitknecht" structure$^8$. The d$_{003}$ spacing of Mg$_2$Cu$_{0.5}$Al-HTlcs (0.7879 nm) was bigger than that of Mg$_3$CuAl-HTlcs (0.7761 nm) and MgCu$_2$Al-HTlcs (0.7662 nm). The reason for this is probably that the ionic radius of Cu$^{2+}$ is bigger than that of Mg$^{2+}$. The d$_{003}$ spacing decreases with the increase in copper content and decrease in magnesium content when the content of aluminium is kept constant in the solid solutions. It was seen that the MgAlCu-HTlcs were prepared more easily and the structure was more regular with less content of copper at the same synthetic parameter.

The thermal stabilities of MgAlCu-HTlcs were studied by TG-DTA. These compounds decomposed in two stages. The first stage was the weight loss of physical adsorption water and interlayer water molecules. The second stage was the removal of carbonate anion in the interlayer and hydroxy on the layer. When Mg/Cu/Al was 2.5:0.5:1, 2:1:1 and 1:1:2, respectively, the temperature of the removal of interlayer water molecules was 399, 403 and 421 K, respectively, and the temperature of the removal of interlayer carbonate anion and hydroxy of layer sheet was 675, 662, 607 K, respectively. The thermal stabilities of the hydroxalitecs increased with the increase in copper content and the decrease in magnesium content when the amount of aluminium was kept constant in the solid solutions. The temperature of the removal of interlayer water molecule increased slightly, due to the d$_{003}$ increases with the increase in the copper content, the atom arrangement in the layer sheet became close and the hydrogen bond of interlayer water molecules and the mutual effect between water molecule and interlayer carbonate anion became enhanced.
It was observed that the MgCuAl-HTlc were a suitable adsorbent for NOx, and their adsorption capability was higher than that of the activated carbon (Fig. 3). Perhaps, the sour-alkali reaction took place for strong alkalinity on the surface of the hydrotalcite besides adsorption. Copper had catalytic activity and more active centers, while the aqueous solution was still neutral after the MgAlCu-HTlc with saturation adsorption was washed by deionized water. So, it was supposed that this process should make not only simple surface physics adsorption and sour-alkali reaction but also accompany with the other catalytic reaction in the meantime. It was likely that NO3 entered the interlayer of the hydrotalcite, and reconstitute the original hydrotalcite layered structure. Adsorption capacity of Mg2.5Cu0.5AlWSi-HTlc had maxima 1518.7mg/g and its adsorption rate was very fast in the first 60 min, the efficiency of adsorption had exceeded 77.9%. The adsorption capacity of the MgCuAl-HTlc for NOx had something to do with amount of copper. Adsorption capacity did not isochronously change with the copper content increase. Perhaps, the more copper was added to the HTlc, the smaller surface area was, and catalyst activity of copper did not develop out completely at lower temperature.

The above study shows that MgCuAl-HTlc may be prepared when Mg/Al/Cu molar ratios were 2.5:0.5:1, 2:1:1 and 1:2:1. MgAlCu-HTlc were easily prepared and their structures were more regular with less copper amount. W-Si heteropolyacid were successfully introduced in the Mg2.5Cu0.5Al-HTlc. The compound has Keggin-structure and layer spacing (1.48 nm) was far larger than that of the MgCuAl-HTlc. MgCuAl-HTlc decomposed in two stages and their thermal stabilities increased with the increase in copper content and the decrease in magnesium content when the content of aluminium was kept constant in the solid solutions. MgCuAl-HTlc and MgAlCuWSi-HTlc could adsorb nitric oxides better. Their adsorption capacities were higher than those of activated carbon. Adsorption capacity of Mg2.5Cu0.5AlWSi-HTlc showed maximum value of 1518.7mg/g.

References