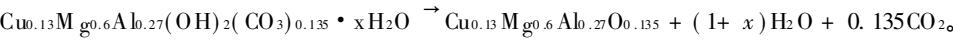


含铜类水滑石催化材料热分解过程的研究

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共沉淀法合成了 $\text{Cu}_{0.13}\text{Mg}_{0.6}\text{Al}_{0.27}(\text{OH})_2(\text{CO}_3)_{0.135} \cdot x\text{H}_2\text{O}$ 类水滑石物质 (CuHTlc), 采用 XRD、DTA-TG、BET、TEM 和 ^{27}Al MAS NMR 技术对其热分解过程进行了表征。结果表明, 在较低焙烧温度时(低于 300℃), 氢氧根和层间水部分脱除, 但水滑石仍保持其层状结构; 500℃时, 其层状结构被完全破坏, 出现氧化镁晶相结构, 随着焙烧温度的进一步升高, 尖晶石晶相生成。500℃时的焙烧产物具有最大比表面 ($193\text{m}^2 \cdot \text{g}^{-1}$)。当温度高于 500℃, 焙烧产物组成可表示为 $\text{Cu}_{0.13}\text{Mg}_{0.6}\text{Al}_{0.27}\text{O}_{0.135}$, CuHTlc 的热分解过程可表示为:

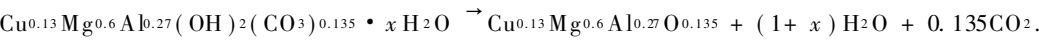


关键词: 类水滑石物质 热分解 焙烧温度
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Study on the Thermal Decomposition of a Copper-Containing Hydrotalcite-like Catalytic Material

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The hydrotalcite like compound $\text{Cu}_{0.13}\text{Mg}_{0.6}\text{Al}_{0.27}(\text{OH})_2(\text{CO}_3)_{0.135} \cdot x\text{H}_2\text{O}$ (CuHTlc) are synthesized by coprecipitation method and are characterized by XRD, DTA-TG, BET, TEM and ^{27}Al MAS NMR. The results show that at relatively low calcination temperatures (below 300℃), the layer structure of CuHTlc is retained, although partial dehydroxylation in addition to dehydration occurs. At 500℃, the hydrotalcite structure is destroyed and MgO phase appears, the spinel phase forms with the further increase of calcination temperature. CuHTlc calcined at 500℃has the highest surface area ($193\text{m}^2 \cdot \text{g}^{-1}$). When CuHTlc are calcined above 500℃, the composition of resusting products is $\text{Cu}_{0.13}\text{Mg}_{0.6}\text{Al}_{0.27}\text{O}_{0.135}$, the equation of thermal decoposition of CuHTlc can be expressed as following:



Keyword: hydrotalcite like compound thermal decomposition calcination temperature

0 Introduction

Recently, it has been found that Cu-Mg-Al-HT (CuHTlc), a synthetic hydrotalcite-like anionic

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layered clay mineral (HTlc), after a heat activation at 750 °C, gives rise to special catalytic activation for the reduction of NO and the removal of SO_x from the exhaust gas of FCC units^[1~3]. During the experiment, we learnt that the catalytic properties of the calcined CuHTlc are greatly influenced by the activation (calcination) temperature, but this process has not yet received any attention in the literature^[1~3]. In this article, The various changes which occurred when the CuHTlc was heated in order to render it catalytically active have been studied by means of XRD, TG/DTA, N₂ adsorption-desorption, TEM and ²⁷Al MAS NMR. Many novel and interesting results are obtained.

1 Experimental

1.1 Preparation

The CuHTlc was prepared by coprecipitation of an aqueous solution of Cu(NO₃)₂ · 9H₂O, Mg(NO₃)₂ · 6H₂O and Al(NO₃)₃ · 9H₂O (total cation concentration of 1 mol · L⁻¹) with an aqueous solution of NaOH and Na₂CO₃ (CO₃²⁻-to-Al molar ratio of 0.5). Other procedures followed those described by Valenzuela^[4]. The slurry thus obtained was stirred for additional 15min and aged quiescently at 65 °C for 4h, then filtered and washed with a large amount of water to eliminate the alkali metal and the nitrate ions. The filter cake was dried at 120 °C in a forced air oven overnight and CuHTlc was obtained. CuHTlc was calcined in air at the required temperatures (300 °C, 500 °C, 750 °C, and 1050 °C respectively) for 3h in a small muffle furnace and the corresponding products were designated CuHT300, CuHT500, CuHT750 and CuHT1050.

1.2 Characterization

X-Ray powder diffraction patterns were obtained on D5005 diffractometer with a solid detector and Cu Kα radiation (40kV, 40mA).

The contents of Cu, Mg, Al and Na of samples were determined using X-ray fluorescence spectroscopy by a Rigaku Model 3271E spectrometer (XRFS).

Thermal analyses (DTA/ TGA) were performed on TA 2100 thermal analysis system in a highly pure N₂ (50mL · min⁻¹), the heating rate is 10 °C · min⁻¹.

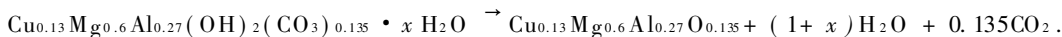
Surface area and pore distribution measurements were conducted by N₂ adsorption-desorption in a Micromeritics ASAP 2405 instrument, using the BET equation for surface area and BJH method for pore-distribution calculations.

TEM micrographs were taken on a JEOL JEM-2000FXII electron microscope operated at 120kV.

²⁷Al MAS NMR spectra were recorded with a Bruker AM 300 spectrometer operating at 78.171 MHz with sample spinning rates of 9~12 kHz.

2 Results and discussion

The composition of CuHTlc is determined by element analysis method as Cu_{0.13}Mg_{0.60}Al_{0.27}(OH)₂(CO₃)_{0.135} · xH₂O. When CuHTlc are calcined above 500 °C, the composition of resulting products is Cu_{0.13}Mg_{0.6}Al_{0.27}O_{0.135}, the equation of thermal decomposition of CuHTlc can be expressed as following:



2.1 XRD analysis

The XRD pattern of the CuHTlc (Fig. 1) illustrates the formation of the desired HTlc, taking on the general features that are typical of hydrotalcite. Fig. 2 shows the X-ray diffraction patterns of CuHTlc calcined in a temperature-programmed mode. From 120 °C to 300 °C, the (003) reflection, giving the basal spacing $d(003)$, decreases in intensity and shifts towards higher 2θ value accompanied by the disappearance of (006) and (113) reflections, suggesting disorder in the stacking of the layers. After calcination at 500 °C, the (003) reflection becomes very weak and the broad, diffuse, and weak diffraction pattern corresponding to MgO is detected. Up to 750 °C, the diffraction pattern of MgO is more intense and the spinel pattern begins to appear. However, the diffraction pattern of MgO shifts to higher positions of 2θ compared to that of pure MgO. This fact, combined with no aluminium oxide pattern in the X-ray diffraction patterns, indicates that substitution of Al for Mg (the Al^{3+} ion is smaller than Mg^{2+}) into MgO lattice occurred. After calcination at 1050 °C, the diffraction lines of both MgO and spinel phases are sharp and intense; the diffraction pattern of the MgO in the diffractogram is in good agreement with that of pure MgO. This means that calcination at 1050 °C led to sintering of the mixed oxides (MgO phase doped with aluminium), with phase segregation and formation of pure MgO and of spinel.

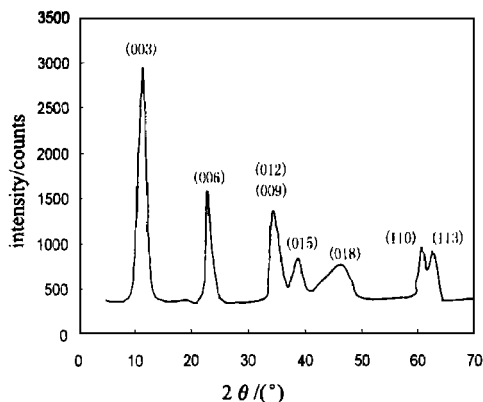


Fig. 1 XRD pattern of CuHTlc

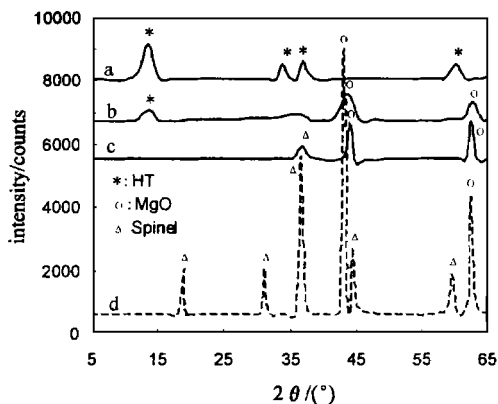


Fig. 2 XRD pattern for CuHTlc after calcination at different temperatures
a: 300 °C b: 500 °C c: 750 °C d: 1050 °C

CuO is not observed by XRD even after calcination at high temperature. This means that CuO is either amorphous, or present in the form of very small crystallites, or dissolved within magnesium oxide.

2.2 TG-DTA study

A TG-DTA curve of the CuHTlc is shown in Fig. 3. The three endothermic peaks detected in DTA curve are ascribed to losses of interlayer water, OH groups, and carbonate ions (as CO_2) from the brucite-like layer respectively. The exothermic peak at 825.8 °C is speculated to be attributed to the transformation of $\text{Cu}_{0.13}\text{Mg}_{0.6}\text{Al}_{0.27}\text{O}_{0.135}$ to MgO and spinel. Surprisingly, the TG curve shows a slow weight loss accompanied by a wide endothermic peaks (not measured above 1150 °C) above

850 ℃, presumably assigned to the formation of eutectic mixture of MgO and spinel.

2.3 Relationship between surface area and calcination temperature

Fig. 4 illustrates the values of surface areas as a function of the calcination temperature. Between 120 ℃ and 300 ℃, surface area has apparent changes (from 23 to 119 m² · g⁻¹) which is due to the dehydration and dehydroxylation during calcination at this temperature range. After calcination at 500 ℃, the surface area increases up to 193 m² · g⁻¹. The reason is that H₂O and CO₂, resulted from the elimination of hydroxylation and carbonate ions, escape through holes in the crystal surface which then appear as small, fairly regularly spaced craters perpendicular to the crystal surface, as is shown in the TEM (not given in this paper). Compared to that of CuHT 500, the surface area of CuHT 750 slightly decreases to 161 m² · g⁻¹, resulting from the partial collapse of the layered structure of CuHTlc. A sharp decrease of surface area occurs upon calcination at 1050 ℃, in correspondence with the appearance of more intense X-ray diffraction lines typical of the spinel phase, indicating that calcination at 1050 ℃ leads to sintering of the mixed oxides, which is not consistent with the behavior of Mg-Al-HT^[5]. Data about the porosity distributions of samples show that the pore radius mainly concentrate at 60~ 200 Å for CuHTlc and CuHT 300, at 100~ 400 Å for CuHT 500 and CuHT 750, and almost no pores exist for the CuHT 1050.

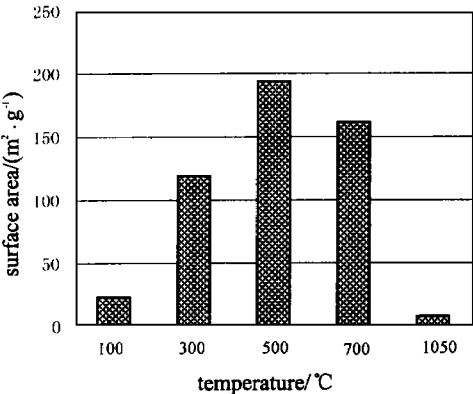


Fig. 4 Surface area as a function of calcination temperature

2.4 ²⁷Al MAS NMR analysis

The ²⁷Al MAS NMR spectra of CuHTlc, CuHT 300, CuHT 750 and CuHT 1050 are shown in Fig. 5. Two phenomena can be observed with the increment of calcination temperature: (1) a change in the aluminum environment from octahedral to tetrahedral, and (2) a deformation in the coordi-

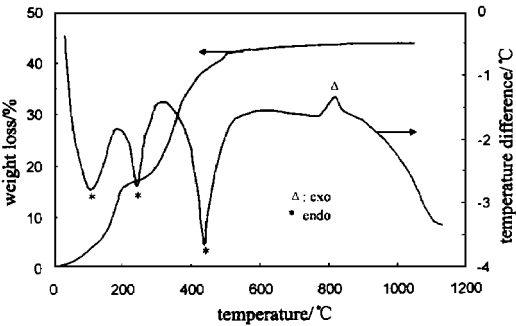


Fig. 3 Decomposition DTA- TG curve of CuHTlc in N₂

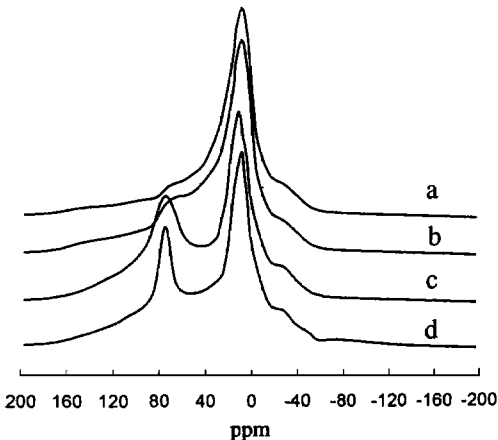


Fig. 5 ²⁷Al MAS NMR spectra of a: CuHTlc b: CuHT 300 c: CuHT 750 d: CuHT 1050

nation sphere of the remaining octahedral aluminum, as deduced from variation of chemical shift of the NMR resonance line from 7.8 to 9.4 and then to 8.0ppm. These phenomena are consistent with the XRD(phase transformations) and N₂ adsorption-desorption(changes of BET surface area) results.

A detailed study about the relationship between calcination temperature of CuHTlc and corresponding catalytic activity for NO + CO reaction is on the way and results will be reported in forthcoming paper.

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