

# Mg/Al complex oxides-A new type of solid basic catalyst for epoxidation

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## ABSTRACT

Hydrotalcites known as anionic clays are found in nature. Hydrotalcites, hydrotalcite-like compounds, and calcined hydrotalcites (as mixed or complex oxides) as highly active, selective catalysts play an important role in many base/catalyzed reactions. Mg/Al hydrotalcite (MAH) as precursor was used to prepare Mg/Al metal complex oxides (MAO), used as epoxidation catalysts in the current research. In this paper, some primary physical and catalytic properties of MAH and MAO were investigated. The results indicated that the qualified MAH (Mg/Al mol ratio of 3) can be achieved when the suspension was crystallized under 80°C for 16h, and after being filtered, dried at 100 °C for 5h in a oven. MAO was prepared by calcining MAH for 4h in a muffle furnace, and calcination temperature was determined to be 500 °C by a differential scanning calorimeter (DSC). Crystal structure and parameters of MAH and MAO were characterized by X/ray diffraction (XRD), good crystal structure was observed and typical peaks of MAH were detected when 2θ was at 11.5 (003), 23.0 (006), 35.0 (009), and 61.0 (110), respectively. The morphology of calcined precursor, i.e. MAO, was investigated with scanning electron microscopy (SEM); the finer lamellar structure and smaller average size of 3μm was observed. Molding research was performed and confirmed by SEM, the results indicated that the surface bulge and cavity with size of several micrometers were increased, which simultaneously suggested the increasing of specific surface area. The catalytic activity of molding MAO was finally examined by using octanol as starting reagent and ethylene oxide as reactant, and narrower molecular distribution was observed comparing with the traditional catalyst-KOH.

**Keywords:** Mg/Al Hydrotalcites; Mg/Al Metal Complex Oxides; Molding, Epoxidation

## 1. INTRODUCTION

Recently Widely used in the varies fields, narrow distribution polyether shows advantages [1,2,3] consisting of low pour point, less pollution, and good compatibility. It has a relatively deep theoretical research and catalytic properties study at the laboratory stage at home and abroad in recent years. Currently, the study on hydrotalcites, as a kind of catalyst for synthesizing narrow distribution polyether, mainly deals with two aspects: one is the pure theoretical study, such as the characterization of hydrotalcites and surface property, etc; the other is water gas shift, nitrobenzene reduction, methane oxidation, and so on. However there is less report about the catalytic activity for ring-opening ethylene oxide [4,5] forming polyether. Although I. Hama [6,7,8] has made an initial attempt in this aspect, the effect of narrow distribution was not ideal and it had a certain distance applied in industrialization.

With its fast reaction rate and narrow molecular weight distribution, Mg/Al metal complex oxides (MAO), as one kind of narrow distribution catalyst, obtained extremely potential development. Based on the previous research, the preparation conditions of MAO which showed greater maneuverability and repeatability, is further improved in this paper. The precursor of Mg/Al hydrotalcites (MAH) was synthesized by the precipitation method, and the MAO power was formed after HT being calcined at high temperature, showing high catalytic activity and selectivity. Furthermore, drawing lessons from the technology [9] of preparing the porous ceramic materials, the molding MAO presenting great activity and selectivity was obtained through studying the molding and granulating of HT. The catalyst separated easily from the product can be used repeatedly, so

it can reduce production cost and improves the production of polyether quality.

## 2. EXPERIMENTAL

The precursor [10] hydrotalcite (HT) was synthesized by co-deposition method described as follows.

A homogeneous solution was formed after mixing the solution of magnesium and aluminium nitrates (solution A) (keeping the Mg:Al molar ratio to a value of 3:1, note: According to similar procedures reported previously, this proportion can get a better ethoxylation performance of the MAO catalyst [6]). The second solution (solution B) was obtained by adding sodium carbonate to sodium hydroxide. Then under intensely stirring, solution A and B was dipped into distilled water in parallel flow way and pH was adjusted to 9.0, controlling the drip speed at a certain amount. A precipitate was formed, and the suspension was crystallized at 80°C, filtered and dried at 100°C for 5h. Finally the resulting paste was transferred into a 30 ml crucible which was introduced into a muffle furnace and was calcined for 4h at 500 °C.

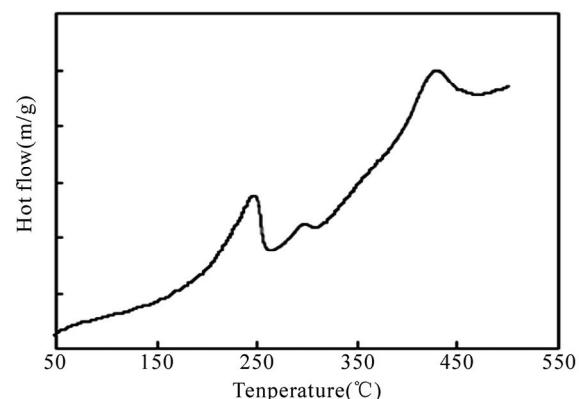
The calcination temperature of Mg-Al hydrotalcite was determined by differential scanning calorimeter (DSC-7, American PE company) at the heating rate of 20 °C/min under nitrogen protection. The structure of MAH and MAO were studied by the D/max-IIA powder X-ray diffractometer (RIGAKU, JAPAN), with mono-chromatized Cu K radiation (= 0.154 nm) at 40kV and 100mA. The spectra were collected on an angle 2θ domain ranging from 4 to 65° with a step of 0.06 and an acquisition time of 2 s on each step. Scanning electron micrographs (SEM) were obtained over on the FEI Q200 SEM under the 20KV. Thin layer chromatography (TLC) was used to analyze the qualitative and quantitative of MAO. Camag III TLC scanner was selected with the steam as the coloration and the detective wavelength at 430nm, baked 5min at 110°C.

## 3. RESULTS AND DISCUSSION

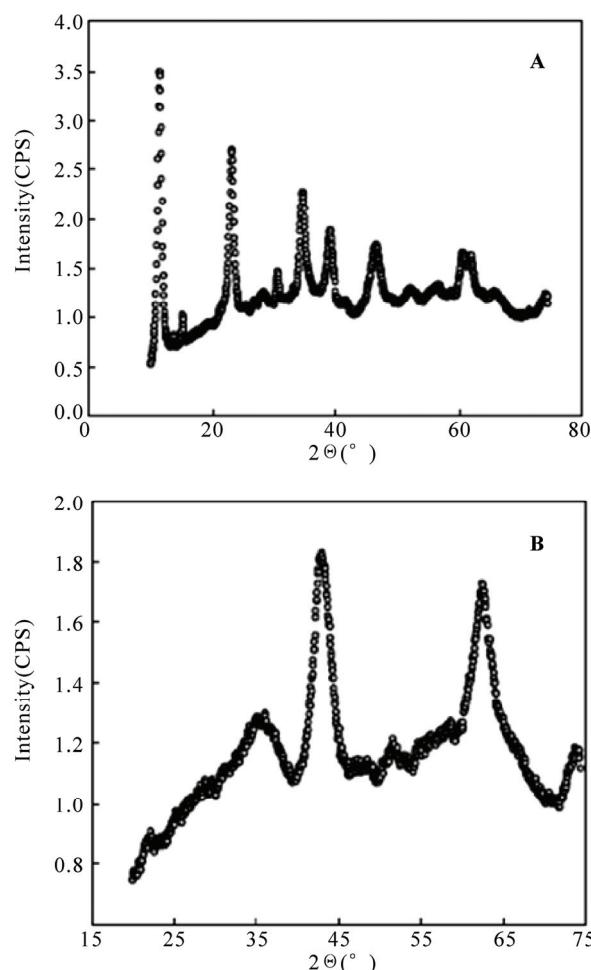
The endothermic and exothermic process of MAH which determines the calcination temperature of MAH was studied by DSC shown in **Figure 1**. There was an endothermic peak between 200~270°C, indicating that it lost the water within the structure of MAH which was the first stage weightlessness. The other peak which was the second stage weightlessness was between 370~470°C and the structure of MAH was destroyed at this stage, CO<sub>32</sub>-at layer space and OH- on the layer were resolved CO<sub>2</sub> and H<sub>2</sub>O. To get the stable structure of catalyst and better alkalescence catalyst effect, 500°C was selected as calcination temperature.

XRD patterns of the MAH and MAO samples were shown in **Figure 2**. It revealed that there were four diffraction maximums at 2θ=11.5°, 23.0°, 35.0°, 61.0° in

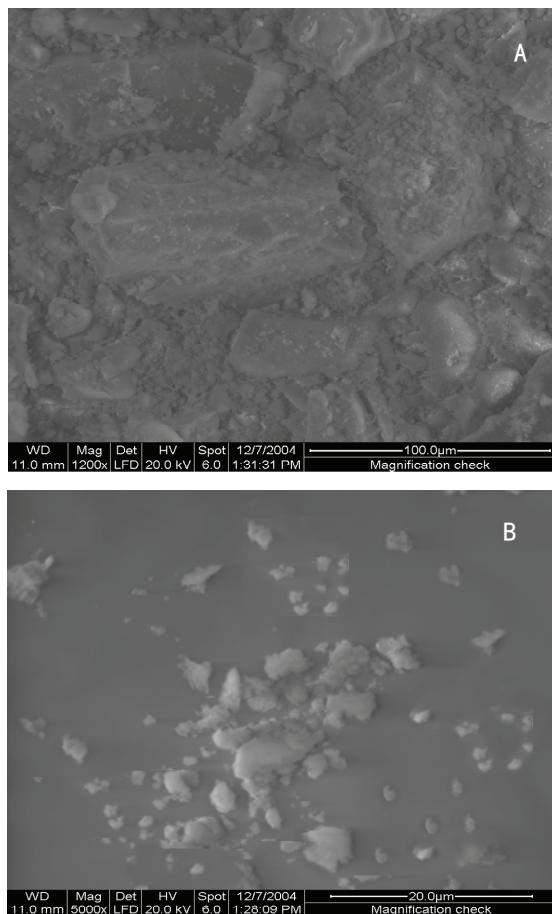
**Figure 2(A)**, indicating that crystalline structure of MAH is regular. The pattern of MAO prepared by calcining MAH at 500°C was recorded in **Figure 2(B)**, showing that the four diffraction maximums were weaken or disappeared obviously with the calcination temperature



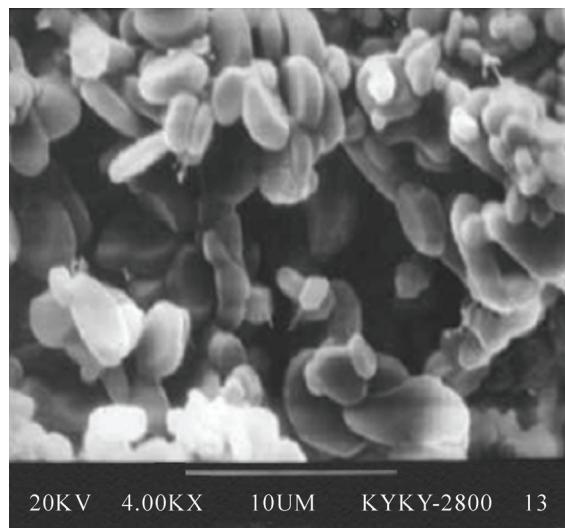
**Figure 1.** DSC analysis of MAH.



**Figure 2.** XRD patterns of MAH (A) and MAO (B). (Room temperature, 40kv, copper target, 10°/min).



**Figure 3.** SEM image of MAH (A) and MAO (B).



**Figure 4.** SEM image of molding MAO.

increasing. It indicated that the characteristic structure of HT was destroyed.

The structure of MAH and MAO were characterized [11,12] by SEM, as shown in **Figure 3**. It presented that

the form of MAH (**Figure 3(A)**) about 30μm in diameter was not regular. From **Figure 3(B)**, it can be clearly observed that the shape of MAO which was about 3μm in diameter, smaller than the MAH was oval. From the result of SEM images, it can be confirmed that the particle size was decreased significantly after calcination.

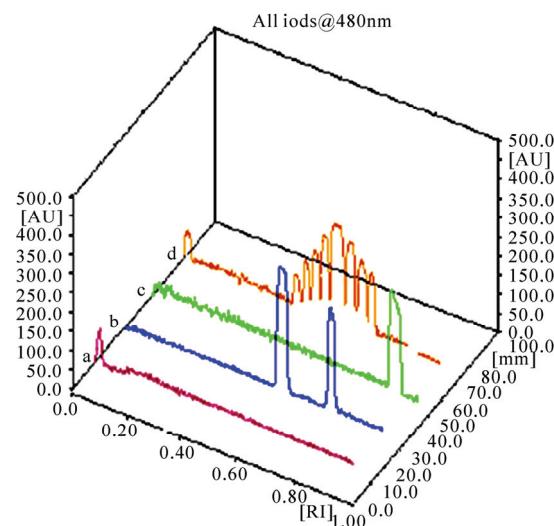
The structure of molding MAO was also detected by SEM which was shown in **Figure 4**. There were higher pore-forming rate of molding MAO whose internal arrangement was regular.

The qualitative and quantitative of MAO was analyzed by thin layer chromatography. The orbit of molding MAO catalyzed products (d) had a series of peaks compared with other three orbits, shown in **Figure 5**. It presented that molding MAO had PEG, standard samples but did not have octanol, indicating that MAH had reacted completely, and the products didn't contain the unreacted raw material. It showed that the molding MAO possessed the better catalysis selectivity compared with MAO.

#### 4. CONCLUSION

We systematically investigated the optimum synthesis conditions of MAH and MAO, and the results of SEM and TLC confirm the formation of molding MAO. Conclusions were shown as follows:

MAH can be successfully synthesized by the codeposition method when the mole ratio of the raw materials was Mg/Al=3, NaOH/(Mg+Al)=2.5, NaOH/Na<sub>2</sub>CO<sub>3</sub>=4. The crystallizing time was 20h and the titration speed was less than 20ml/l. The process showed good stability and reproducibility. MAO was obtained after calcining MAH which presented best ethoxylation catalytic activity and selectivity.



**Figure 5.** Thin layer scanning of molding MAO catalyzed product (a, PEG; b, control; c, octanol; d, molding MAO catalyzed product).

The size of MAH and MAO calculated from SEM data was about 30 and 3 $\mu$ m respectively, indicating that the particle size was decreased significantly after calcining. The structure of molding MAO was also confirmed by the results of SEM and TLC. There were higher pore-forming rate of molding MAO whose internal arrangement was regular.

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