



## Modifying Mg/Al Composite Catalyst for Preparing Narrow-range Distribution Polyether

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*The research is financed by the science and technology development foundational project of Tianjin higher institute. (Grant number: 20050702).*

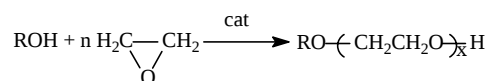
### Abstract

The modifying Mg/Al composite catalyst was prepared by co-precipitation method and it was characterized by FTIR and BET. It was used in the ethoxylation between ethanols and EO, and the narrow-range distribution polyethers which have steady properties were prepared. The product was characterized by FTIR and GC/MS. The molecular weight distribution of the product can arrive to 83.28%.

**Keywords:** Narrow-range distribution, Ethoxylation, Polyether

### 1. Introduction

The ethoxylation of aliphatic alcohol depicted in Scheme 1 has been utilized for the commercial production of non-ionic surfactants. Similar types of ethoxylations for other organic compounds having active hydrogens have been also applied in the production of various wetting and emulsifying agents (Daehwan Kima, Chengzhe Huang, & Hongsun Lee, 2003:229).



Scheme 1. ethoxylation of aliphatic alcohol. R: long-chain alkyl group, n: mole ratio of EO/ROH, x: number of ethoxylene units in product mixture.

It is well known that polyether has the superior properties of nontoxicity, flexibility, hydrophilicity, and biocompatibility. These properties are very useful for a polymer used as a drug delivery system (Shaobing Zhou, Xianmo Deng, & Hua Yang, 2003:3566). In recent years, the synthesis of polyester-polyether type block copolymer has attracted much attention, because they can be used in future medical applications in implantation and wound treatment, and as controlled-release drug carriers (Suh H, Jeong BM, & Rath R, 1998:336; Jeong BM, Bae YH, & Lee DS, 1997:860; Choi SW, Choi SY, & Jeong BM, 1999:2305).

A great number of patents have recently been published dealing with catalytic systems promoting narrow-range ethoxylation (NRE), i.e. ethoxylation of fatty alcohols with a narrow distribution of the molecular weights of the ethoxylated oligomers and containing a very low concentration of the residual unreacted alcohol. Products of this type have better properties than those produced with the traditional alkaline catalyst KOH and for low ethylene oxide/substrate molar ratio, can be sulphonated without forming undesired dioxane (M. Di Serio, P. Iengo, & R. Gobetto 1996:240). In the ethoxylations of aliphatic alcohols, homogeneous basic catalysts, such as NaOH, KOH or NaOCH<sub>3</sub>, are generally used to facilitate EO insertion to the alcohols at relatively low temperature and pressure. In this homogeneous type of alcohol ethoxylation, distributions of oxyethylene units in the ethoxylated product mixture are much broader than the statistical Poisson-type distribution. R. Improta had used Aluminium alkoxide sulphate catalysts to promote ethoxylation of fatty alcohols with a narrow distribution of the molecular weights (R. Improta, M. Di Serio and E. Santacesaria, 1999:170).

Hydrotalcite-type solids have been investigated as one group of catalytic materials for the narrow-range oxyethylation of aliphatic alcohols and esters (Mckenzie A L, Fishel C T, & Davis R J, 1992:548; Rao K K, Gravelle M, 1998:115).

Hydrotalcite-type materials are a class of synthetic mixed metal layered hydroxides, generally described by the formula  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2][A_{x/m}^{m-} \cdot n\text{H}_2\text{O}]$ , where  $x$  may vary from 0.17 to 0.33 depending on the particular combination of divalent  $M^{2+}$  and trivalent  $M^{3+}$  ions.  $A^{m-}$  represents the  $m$ -valent anion necessary to compensate the positive charge of brucite-like hydroxide layer and locates between mixed metal hydroxide layers (Daehwan Kima, Chengzhe Huang, & Hongsun Lee, 2003:231).

In this paper, we prepared the modified hydrotalcite-type catalysts and report its catalytic properties in ethanol ethoxylation. Otherwise, we characterized the catalyst and product.

## 2. Experimental

### 2.1 Materials

Ethanol,  $\text{Na}_2\text{CO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , were of reagent grade and were purchased from Tianjin Chemistry reagent Co. (China). EO of 99.9% was supplied from China Petroleum Chem. Co.

### 2.2 the preparation of Mg/Al composite catalyst

Hydrotalcite-type material was prepared by co-precipitation method at 60°C with water-heating method.  $\text{Na}_2\text{CO}_3$  solution in 500 ml beaker was added mixed solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  which with 15:5:1 ratio of Mg/Al/Co components with strong mixing and stirring for 1h; pH 8-9 was maintained during the co-precipitation reaction. The white cake was isolated by filtration of the suspension and washed five times with distilled water. The cake was dried for 12 h in air circulating oven at 100°C to give white powder and then heated in the tubular stove at 500°C for 5h, at last the catalyst was got.

### 2.3 ethoxylation

Ethoxylation was performed in membrane reactor. The reactor was equipped with a tubular  $\text{Al}_2\text{O}_3$  ceramic membrane which length is 120mm and diameter is 12mm. The catalyst was 1g which was put in the reactor. Ethanol is 1ml/h which was supplied by a piston pump. EO was supplied to the reactor by opening the needle valve of the EO storage chamber and its velocity was controlled by a rotameter. The reaction was processed at 110°C.

### 2.4 Product analysis

Liquid product was separated by filtration of crude produce and was analyzed using FTIR and GC/MS.

## 3. Results and discussion

### 3.1 Characterization of the catalyst

Adding a third metal ion into the complex was to adjust the pore size of catalysts. There is a three-tier electron out of  $\text{Co}^{2+}$  ions so that its volume is bigger than  $\text{Mg}^{2+}$  ions.  $\text{Co}^{2+}$  ions were embedded into hydrotalcite structure to adjust the pore size and lead to the hydrotalcite surface lattice defects. After calcination its surface would form a large number of nano-pores and huge amounts of alkaline center which are helpful to the latter reaction.

Figure 1 shows power IR patterns of the Mg/Al and Mg/Al/Co composite catalyst. The IR patterns of two samples are almost identical. The position of  $885\text{cm}^{-1}$ ,  $744\text{cm}^{-1}$  is the absorption proportion of metal-oxygen bond. It shows that the entry of  $\text{Co}^{2+}$  has entered into don't change the crystalline structure.

The specific surface area of modification Mg/Al composite catalyst is  $135.8\text{m}^2/\text{g}$ . High specific surface area is useful for the touch between reactants and alkaline center of the catalyst surface so that the ethoxylation is accelerated.

### 3.2 Analysis of polyether

Figure 2 shows the IR curve of the product. From the figure 2 we can see the characteristic absorption band: the position of  $3401\text{cm}^{-1}$  is hydroxyl; the position of  $2925\text{cm}^{-1}$ ,  $2858\text{cm}^{-1}$ ,  $1458\text{cm}^{-1}$  are methyl, the stretching vibration and rocking vibration band of methylene respectively and the position of  $1112\text{cm}^{-1}$  is the C-O-C bond skeleton vibration.

The product has been analyzed by the GC/MS. The results show that the selectivity of object product comes to 83.28% which is high than KOH as the catalyst.

## 4. Conclusions

The modifying Mg/Al composite catalyst was prepared which is very active for narrow-range ethoxylation of ethanol. The products are narrow-range, high purity and light color which have excellent performance in application. From analysis of the product, the selectivity of object product comes to 83.28%.

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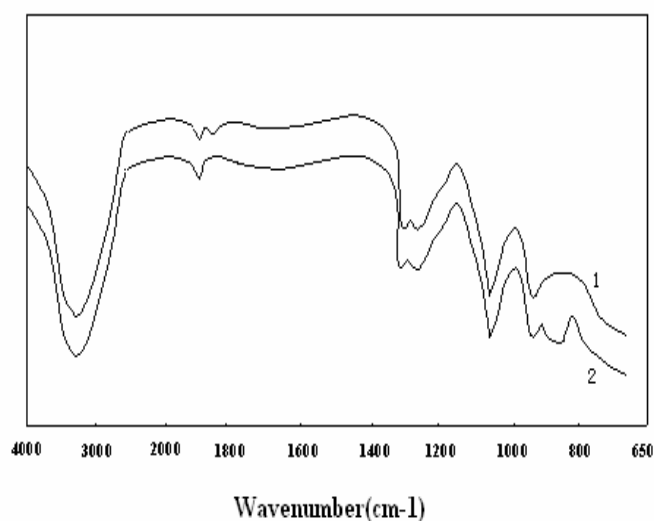


Figure 1. FT-IR adsorption spectra of (1) Mg/Al, (2) Mg/Al/Co

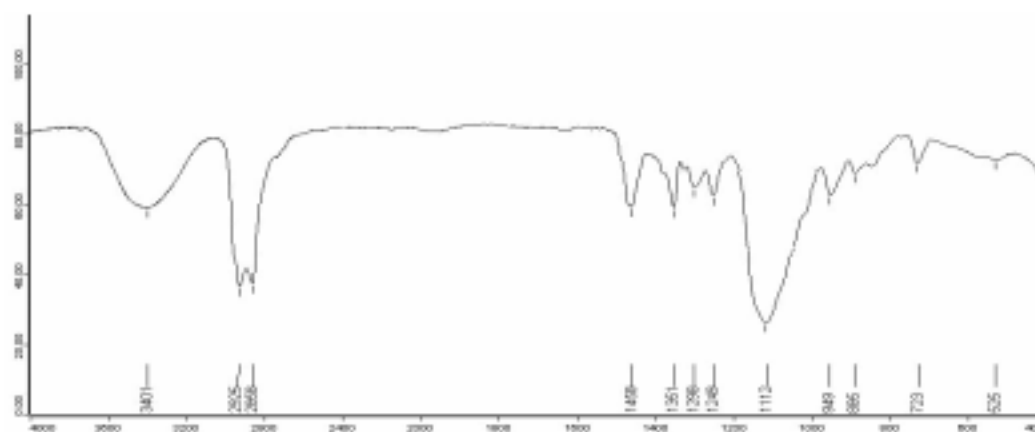


Figure 2. FT-IR spectra of the product