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PROPYLENE OXIDE POLYMERIZATION IN THE PRESENCE OF LAYERED DOUBLE HYDROXIDES

POLIMERYZACJA TLENKU PROPYLENU W OBECNOŚCI WARSTWOWYCH WODOROTLENKÓW PODWÓJNYCH

Abstract: Propylene oxide polymerization in the presence of layered double hydroxides with different concentration of basic sites on their surface has been studied. It is shown that the polymerization can be catalyzed by both basic and acidic sites. On the basis of kinetic experiments the mechanisms of reaction undergoing were proposed.

Keywords: propylene oxide, layered double hydroxides, polymerization, catalytic activity

Introduction

Propylene oxide is an organic compound with the molecular formula of $\text{CH}_3\text{CHCH}_2\text{O}$. Primarily, propylene oxide is used to produce polyurethane plastics and propylene glycol. In addition, it is the feedstock for the production of propylene carbonate, isopropanolamines, polyoxypropylene polyols, polypropylene oxide, propylene oxide cancers, propylene sulphide and some surfactants. Worth noting, it is a probable human carcinogen, which may cause hemodynamic disorders, possibly due to increased concentration of histamine and other biological active substances. It is included into the List of IARC Group 2B carcinogens [1, 2].

Propylene oxide polymerization is one of the most widely practiced operations in the chemical industry [3, 4]. Reports on the catalytic activity of basic heterogeneous catalysts such as calcined synthetic hydrotalcite in this reaction have been published [5-8].

Layered double hydroxides (LDHs) is a class of inorganic compounds consisting of positively charged layers of metal hydroxides, and anions in the inner space. Their general formula is $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}[\text{A}_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$. The structure of LDHs is based on brucite-like layers. There is a fraction of divalent metal cations (e.g., Mg^{2+} , Fe^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} or Zn^{2+}) coordinated octahedrally by hydroxyl groups. They can be replaced

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isomorphously with trivalent metal cations (e.g., Al^{3+} , Cr^{3+} , Ga^{3+} , In^{3+} , Mn^{3+} or Fe^{3+}), resulting in positively charged layers [9-14].

Mg/Al LDHs can be obtained from chemical production waste containing magnesium and aluminum salts. Thus, on the one hand, a rational solution for waste disposal has been found, and on the other hand, the obtained substances are of low cost [10].

For these reasons, LDHs are potential candidates for industrial applications in various fields, such as medicine, separation technology, polymer reinforcement, electrochemistry, etc. Calcined LDHs can also find the wide application as sorbents and catalysts (Fig. 1) [15].

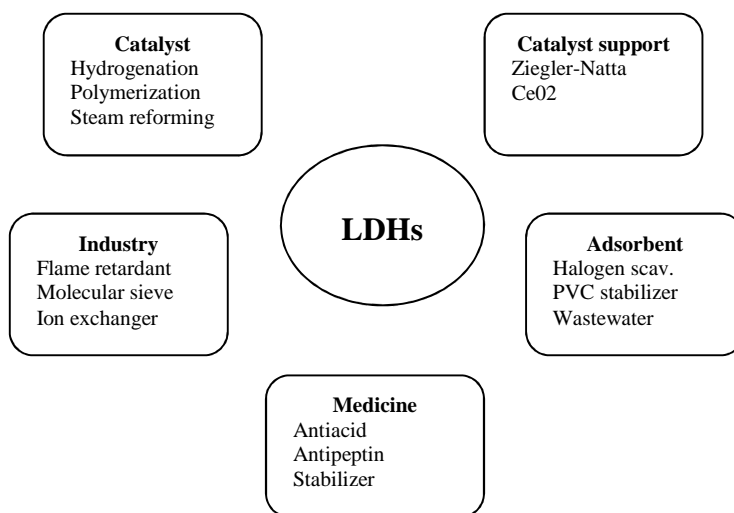


Fig. 1. Layered double hydroxides applications [15]

However, the non-calcined LDHs can be used not only as sorbents and precursors, but also as acid-base catalysts directly. Their catalytic activity is a result of the presence of different basic sites on the surface. Additional thermal and oxidizing treatment causes the change of basic and acid sites number on the surface, and hence results in the change of catalytic activity.

Mg/Al LDHs catalytic activity in the reaction of propylene oxide polymerization has been studied in this paper, and it was shown, that activity is determined by concentration of basic and acid sites of definite strength, which was determined by Hammett indicators titration.

The purpose of this work was to study the processes of polymerization of propylene oxide with heterogeneous catalysis, which does not require complex post-reaction separation of the catalyst. The novelty of the work lies in the fact that layered double hydroxides were used for the first time as a heterogeneous catalyst for the polymerization process of propylene oxide.

Experimental

Catalysts preparation

LDHs consist of carbonate as interlayer anions with Mg and Al as octahedral cations (designed MgAl-CO₃).

Salt solutions with different molar ratios were prepared by adding Mg (NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O in de-ionized water. After complete dissolution, the above solution was added drop-wise to a vigorously stirred Na₂CO₃ solution in de-ionized water. Then freshly prepared 1 M NaOH solution was added drop-wise to the above solution to maintain constant pH = 11. The resultant gel was aged by stirring at 85 °C for 24 h. The precipitate was separated from the solution by centrifugation, washed several times with de-ionized water and dried in vacuum. All these reactions were carried out in an inert atmosphere.

Characterization of catalysts

X-ray diffraction patterns show that well-crystallized hydrotalcite like compounds are obtained and no other phase is identified. The X-ray diffraction of these samples typically indicate the presence of anionic clay with molecular formula Mg₆Al₂(OH)₁₆CO₃·4H₂O possessing carbonates in the interlayer space.

Basic properties of LDHs catalysts were determined by Hammett indicator titration method in the presence of Bromothymol Blue (pK_a = 7.2). The special appliance was used in order to investigate acid and basic properties by means of titration with Hammett indicators [16].

A sample of LDH and a magnetic stirrer were inserted into a small glass, the glass was put on a magnetic stirring device and it was filled with benzene. After that a glass cylinder divided by porous separator, with a standard sample, was inserted into the small glass. After the Hammett indicator was added into benzene the changes in color could be seen on the surface of the standard sample.

The following indicators were used: Bromothymol Blue (pK_a = 7.2), 4-Chloro-2-Nitroaniline (pK_a = 17.2), 4-Chloroaniline (pK_a = 26.5), purchased from Aldrich and 2,4,6-Trinitroaniline (pK_a = 12.2), 2,4-Dinitroaniline (pK_a = 15.0), 4-Nitroaniline (pK_a = 18.4), purchased from Fluka.

Catalytic tests

Catalytic activity was studied in the reaction of propylene oxide polymerization.

0.001 kg of LDHs was placed into a 0.005 dm³ glass ampoule under a nitrogen stream, and 0.01 dm³ of propylene oxide was introduced. The ampoule was frozen by liquid nitrogen, sealed after the degassing and kept into a bath with the device for shaking. The product was washed with acetone and subjected to evaporation of the residual propylene oxide and acetone. The final product was carbon-containing polypropylene oxide.

Benzene was used as a solvent in order to separate the polymer from carbon.

Viscosity was measured using the Ubbelohde viscometer.

Results and discussion

Over the past decade, layered double hydroxides named otherwise as hydrotalcites have attracted attention of the researchers due to their layered structure and high anion exchange capacity. The structure of LDHs can be described from brucite-type $Mg(OH)_2$, where metal ions are located in the center of the octahedron and the vertices are occupied by hydroxide ions. The positive charge is generated by partial substitution of divalent metal cations by trivalent ones within the brucite-like layers and is balanced by an equally negative charge from the inter layer solvated anions.

Samples properties of Mg/Al LDHs with the content of Mg and Al - 0.27, 0.72, 0.80 and 0.86 mol/mol - used in researches are shown in Table 1.

Description of studied LDHs

Table 1

MgO [mol/mol]	MgO [%] mass	V [dm ³ /kg]	S·10 ³ [m ² /kg]
0.27	30	0.5	250
0.72	50	0.2	200
0.80	63	0.2	160
0.86	70	0.2	180

There is a reverse dependence which cannot be explained only the numbers of basic sites change. With the correlation increase of MgO/Al₂O₃ the number of high basicity sites is increased, thus this dependence has extremely character as well (Table 2). For sample with 0.72 mol part MgO the concentration of acid sites is calculated through examples:

$$H_0 = 4.8 - E = 0.4 \cdot 10^3 \text{ meq/kg};$$

$$H_0 = 1.5 - E = 0.3 \cdot 10^3 \text{ meq/kg}.$$

The concentration of different strength basic sites in the LDHs with different composition

Table 2

MgO [mol]	H ₀ [meq/kg]	26.5	18.4	17.2	15.0	12.2	7.2
	0.27	–	0.14	0.32	0.82	1.40	1.52
0.72	0.01	0.09	0.40	1.11	1.21	1.22	
0.80	0.01	0.21	0.40	1.33	1.42	1.40	
0.86	0.02	0.32	0.68	1.41	1.55	1.58	

The reaction of the opening and polymerization of cyclic oxides can occur both in acidic and basic catalysis, as described in [3-9]. The greater the acidity or basicity of the catalyst, the higher the reaction rate. Layered double hydroxides possess both basic and acidic active sites. The presence of two types of sites leads to a synergistic process. The rate of polymerization with binary catalysis is significantly higher than with acid or basic catalysis.

It is interesting to compare this information to the number of basic sites change based on the degree of isomorphous substitution [17, 18].

To elucidate the catalytic activity of LDHs in the polymerization, the following compounds were mixed with catalysts (10:1) and allowed to react 3 h at 50 °C: styrene,

methylmethacrylate, tetrahydrofuran, epichlorohydrin. For all catalysts, the full conversion was observed. For catalyst with the 0.27 MgO, only epichlorohydrin produced a small amount of the polymer.

The presence of both acid and basic sites on LDHs surface results into the cation and anion opening of the ring. The reaction in the presence of acid catalysis has high rate.

To elucidate the catalytic activity of different LDHs the reaction of propylene oxide polymerization was carried out. The catalytic activity of the explored catalytic systems in the given reaction was determined by the polymerization degree, η , of propylene oxide. The dependence of reaction activity on the catalyst composition is shown in Figure 2.

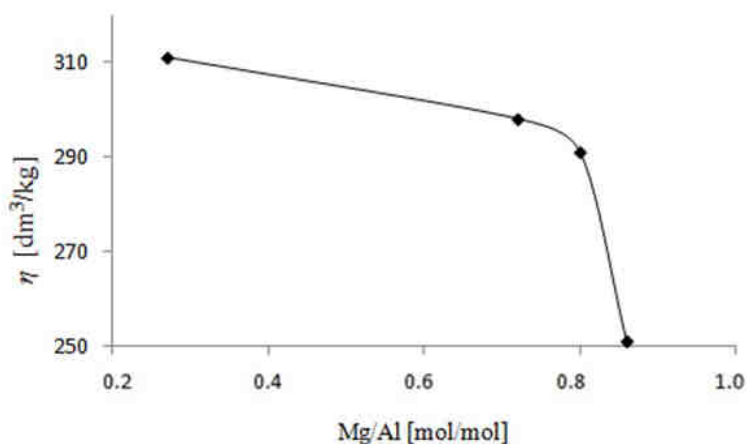


Fig. 2. Dependence of polymerization degree on the composition of the catalyst

The mechanism of anionic polymerization is corresponded to formation of intermediate anion and undergoing on the mechanism, closed to S_N2 (Fig. 3).

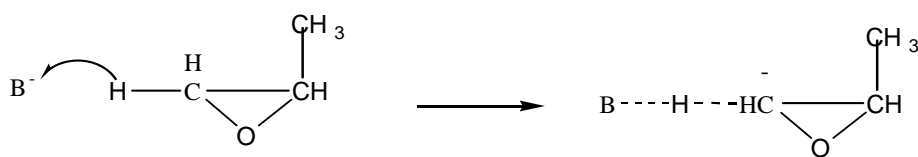


Fig. 3. Anionic polymerization mechanism

In case of base heterogeneous catalysis the product appears with the large molecular weight. In the case of homogeneous catalysts the value of η is about 250 dm³/kg [19].

Conclusions

1. The process of heterogeneously catalyzed polymerization of propylene oxide have been studied; for the first time, layered double hydroxides were used as a heterogeneous catalyst for the polymerization process of propylene oxide.
2. The main features of the catalytic process have been studied, and the reaction mechanism has been proposed.

3. The dependence of activity on the acidity of the active sites has been shown.
4. It has been shown that the catalytic process proceeds involving both the basic and acidic sites.

References

- [1] Atta AM, Ismail HS, Elsaeed AM, Fouad RR, Fada AA, Abdel-Rahman AA-H. *J Dispersion Sci Technol*. 2013;34(2):161-172. DOI: 10.1080/01932691.2012.657538.
- [2] Laino T, Tuma C, Moor P, Martin E, Stolz S, Curioni A. *J Phys Chem A*. 2012;116:4602-4609. DOI: 10.1021/jp300997d.
- [3] Herzberger J, Niederer K, Pohlit H, Seiwert J, Worm M, Wurm FR, et al. *Chem Rev*. 2016;116:2170-2243. DOI: 10.1021/acs.chemrev.5b00441.
- [4] Luinstra GA. *Polymer Rev*. 2008;48(1):192-219. DOI: 10.1080/15583720701834240.
- [5] Chakraborty D, Rodriguez A, Chen EY-X. *Macromolecules*. 2003;36(15):5470-5481. DOI: 10.1021/ma034050a.
- [6] Kohjiya S, Sato T, Nakayama T, Yamashita S. *Makromol Chem Rapid Commun*. 1981;2:231-233. DOI: 10.1002/marc.1981.030020306.
- [7] Navajas A, Campo I, Moral A, Echave J, Sanz O, Montes M, et al. *Fuel*. 2018;211:173-181. DOI: 10.1016/j.fuel.2017.09.061.
- [8] Wang L, Ammar M, He P, Li Y, Cao Y, Li F, et al. *Catal Today*. 2017;281:360-370. DOI: 10.1016/j.cattod.2016.02.052.
- [9] Wang Q, O'Hare D. *Chem Rev*. 2012;112(7):4124-4155. DOI: 10.1021/cr200434v.
- [10] Tian R, Liang R, Wei M, Evans DG, Duan X. *Struct Bonding*. 2016;172:65-85. DOI: 10.1007/978-3-319-35138-4.
- [11] Duan X, Evans DG. *Layered Double Hydroxides*. Berlin: Springer-Verlag; 2006. eBook ISBN: 9783540324959.
- [12] Fan G, Li F, Evans DG, Duan X. *Chem Soc Rev*. 2014;43(20):7040-7066. DOI: 10.1039/c4cs00160e.
- [13] Zhao G, Li C, Wu X, Yu J, Jiang X, Hu W, et al. *Appl Surf Sci*. 2018;434:251-259. DOI: 10.1016/j.apsusc.2017.10.181.
- [14] Jiang H, Ken-ichi K, Jeongsoo H, Akira Y, Kazuya N, Chiaki T, et al. *Appl Catal B*. 2018;224:783-790. DOI: 10.1016/j.apcatb.2017.11.011.
- [15] Hoyo CD. *Appl Clay Sci*. 2007;36:103-121. DOI:10.1016/j.clay.2006.06.010.
- [16] Topaloglu Yazıcı D, Bilgic C. *Surf Interface Anal*. 2010;42: 959-962. DOI: 10.1002/sia.3474.
- [17] Parida K, Das J. *J Molecular Catalysis A: Chemical*. 2000;151:185-192. DOI: 10.1016/s1381-1169(99)00240-x.
- [18] Hattori H, Ono Y. Roles of acid sites and base sites in acid-and base-catalyzed reactions. In: Jacques C. Vedrine, editor. *Metal Oxides in Heterogeneous Catalysis*. Cambridge: Elsevier; 2018. eBook ISBN: 9780128116326.
- [19] Van Leeuwen PWNM. *Homogeneous Catalysis*. Amsterdam: Kluwer Academic Publisher; 2004. eBook ISBN: 1402020007.

POLIMERYZACJA TLENKU PROPYLENU W OBECNOŚCI WARSTWOWYCH WODOROTLENKÓW PODWÓJNYCH

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Abstrakt: W artykule badano polimeryzację tlenku propylenu w obecności warstwowych wodorotlenków podwójnych o różnej ilości centrów zasadowych na powierzchni. Wykazano, że kataliza polimeryzacji zachodzi zarówno w centrach zasadowych, jak i kwasowych. Na podstawie doświadczeń kinetycznych zaproponowano mechanizmy reakcji.

Słowa kluczowe: tlenek propylenu, podwójne warstwowe wodorotlenki, polimeryzacja, aktywność katalityczna