Study on Catalytic Synthesis of Low Molecular Weight Polyether Polyol by Composite Alkaline Earth Metal

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Abstract: Polyether Polyol is one of the main intermediates in the synthesis of polyurethane. This research work investigated the optimization of polyether polyol from propylene oxide using Single Factor Experiments and Response Surface Methodology (RSM) through composite alkaline earth metal catalyst (BaO/MgO/γ-Al2O3). The BaO/MgO/γ-Al2O3 catalyst was prepared with alkaline earth metal oxide immobilized on γ-Al2O3 by co-precipitation method. The preparation conditions of the catalysts is calcination temperature=600 °C, n(Ba):n(Al)=0.1:1, n(Mg):n(Al)=0.3:1. Represented with XRD, SEM, BET, CO2-TPD, etc. Characterization results showed that the catalysts indicated strong basic site, perfect particle surface area, pore volume, pore size and relatively uniform particle size distribution. Batch analyses demonstrated that the polyether molecular weight and the epoxide conversion was highly influenced by different process factors which include reaction temperature, pressure, time and the amount of catalyst. The conversion of propylene oxide and molecular weight to target product reached almost 63.5% and 600, respectively under the conditions of reaction temperature 190 °C, pressure 2 MPa, time 6 h and catalyst dosage 6%.

Keywords: Low molecular weight; Polypropylene glycol; Alkoxylation; BaO/MgO/γ-Al2O3; Solid base; Single factor experiments; Response surface methodology.

1. Introduction
Polyether polyols are the main raw material for the production of soft, hard, semi-rigid foams and polyurethane adhesives. Polyether polyols are widely used in paper, textile, coatings, adhesives, elastomers, foams, sealants, petroleum development and other industries, and also in high-tech aerospace applications (such as missile propellants) are applied. It is an important chemical raw material with a wide range of applications [1][2].

Polyether polyols are a series of polymer compounds prepared by ring-opening polymerization of epoxides [3], and can be classified into three types according to the polymerizable monomer: polypropylene glycol, Polyether polyol, polytetrahydrofuran glycol. Among them, polypropylene glycol is a polymer starting with polyol or organic amine, and it is the main raw material for synthesizing the sixth largest synthetic polyurethane composite material (PU) [4].

At present, the preparation methods of polypropylene glycol are generally divided into two categories according to the catalysts used in the industry: The first major category is the catalytic synthesis of polypropylene glycol by homogeneous catalysts, which mainly include metal hydroxides catalyst [5][6], double metal cyanide catalyst [7][8][9], phosphazenium salts catalyst [10][11], the advantage of this
method is that the technology is mature and the catalyst is inexpensive; but there are also many disadvantages, all of which are homogeneous catalysts. It is difficult to separate from the product after the reaction, and the post-treatment will produce a large amount of salt. And the liquid alkali catalyst corrodes the equipment seriously, pollutes the environment, etc. [12]. The second major category is the catalytic synthesis of polypropylene glycol by heterogeneous catalysts[13][14], which mainly includes γ-Al2O3[15][16] and ZrO2 as carriers to support the active components alkali metal hydroxides KOH, NaOH, etc.[17][18], such as Wang M W, Wang R L, etc. catalyzed synthesis of polyglycerol by NaOH/Al2O3, NaOH/ZrO2 supported catalyst [19]. The method has the advantages that the pH of the reaction can be lowered, and the reaction is more milder; but at the same time, there are disadvantages that the active component is easy to fall off and the metal hydroxide is not easily decomposed. Yu J K etc. introduced the development of synthetic polyether polyol catalysts in recent years [3], which mentions that Conoco and UCC in the United States replace alkali with alkaline earth metal compounds. The metal compound is used for the alkoxylation polymerization catalyst[20][21] of a fatty alcohol or an alkylphenol, and the obtained product has a narrow relative molecular mass distribution and a low small molecule free alcohol content [22][23]. The basic of alkaline earth metal oxides[24][25] such as MgO, CaO, BaO etc. is weaker than the corresponding alkali metal compounds, therefore reducing the degree of isomerization of PO, thereby reducing the terminal unsaturation of the polyether polyol and increasing the polymerization rate. The production cycle is shortened and the production process is simple and suitable for industrialization [26].

In this study, γ-Al2O3 was used as carrier to synthesize environmentally friendly BaO/MgO/γ-Al2O3 ternary composite alkaline earth metal catalyst, and its structure, morphology and alkali strength were characterized and applied to the synthesis of polypropylene glycol. The effects of reaction temperature, time, pressure and catalyst dosage on the reaction of propylene oxide and glycerol to polypropylene glycol were investigated.

2. Experiment

2.1. Materials
Glycerol (AR), 1,2-Epoxypropane (AR), γ-Al2O3, Mg(NO3)2·6H2O (AR), BaCO3 (AR), NH3·H2O (AR), N2 (99.99% AR).

2.2. Preparation of Catalysts
According to the ratio of $n_{(Ba)}: n_{(Mg)}: n_{(Al)} = 0.1: 0.3: 1$ in the ternary composite catalyst and weighting a certain amount of γ-Al2O3, Mg(NO3)2·6H2O, BaCO3. Immersion in 90 mL of deionized water at 30 °C for 2 h; then add 30 mL of concentrated NH3·H2O (25 wt%) to the above solution with a constant pressure dropping funnel until the pH reaches 9-11 and with vigorous stirring. Continue to stir at 30 °C for 12 h, after ultrasonic for 3 h, transfer to hydrothermal synthesis reactor and aged at 120 °C for 24 h; After cooling, The precipitate was dried at 120 °C for 20 h, and the excess water was evaporated. At last the solid was calcined at 600 °C for 5 h to obtain a solid base catalyst BaO/MgO/γ-Al2O3.

2.3. Catalytic Synthesis of Polypropylene Glycol
The initiator glycerin and a certain amount (6%) of BaO/MgO/γ-Al2O3 solid base catalyst were added to the autoclave, and replaced with high-purity nitrogen three times. According to the experimentally set raw material ratio, quantitative epoxypropane was added. Passing a protective gas nitrogen into the autoclave to a certain initial reaction pressure, and react at 190 °C for 6 h. After the reaction is stopped, it is cooled to room temperature under nitrogen protection, and diluted with methanol. The catalyst is filtered off and then rotary evaporated to remove the methanol to obtain a polypropylene glycol product. The principle of synthesis[27][28] is shown in Figure 1.
2.4. Detection of Polypropylene Glycol
The hydroxyl value was determined by phthalic anhydride esterification method according to GB/T12008.3-2009 standard; The molecular weight and degree of polymerization of the synthesized polypropylene glycol were determined by Shimadzu Prominence GPC; The ¹HNMR qualitative of the synthesized polypropylene glycol was tested by German AVANCE 400 NMR, using deuterated DMSO as solvent; The structure was characterized by German Tensor 27 Fourier transform infrared spectroscopy.

2.5. Characterization of Catalysts
The qualitative and external shape of samples were characterized by Japanese D/max-r CX-ray diffractometer and JSM-5610LV scanning electron microscope. The metal ion content, basic, specific surface area and pore size of samples were analyzed by ICP-OES-Optima 8300, AutoChem 2920 (CO₂-TPD) and Micromeritics ASAP. The thermogravimetric analysis was performed by a Perkin-Elmer type thermogravimetry/differential heat combination instrument.

3. Results and Discussion
3.1. Catalyst Characterization Analysis
3.1.1. Structure and Morphology. The XRD comparison of the three catalysts BaO/MgO/γ-Al₂O₃, MgO/γ-Al₂O₃ and γ-Al₂O₃ is shown in Figure 2[29]. The sample A showed that the characteristic diffraction peaks to (311), (400), (440) crystal planes of Al₂O₃ are observed at $2\theta = 37.3^\circ$, 46.01°, 66.8°. With the addition of Mg²⁺, the characteristic diffraction peaks corresponding to the (200), (220), (311), (400), (440), (511) crystal planes of MgAlO are observed at $2\theta = 19.60^\circ$, 31.27°, 37.3°, 46.01°, 66.8°, 59.32°. The characteristic diffraction peaks to the (202), (220) crystal planes of BaO are observed at $2\theta = 28.28^\circ$, 40.12°, as shown by C in Figure 2. The diffraction peak has a slight shift difference with the introduction of Ba, but the overall crystallinity is higher and the crystal form is intact, which proves the existence of the composite oxide solid base catalyst.
Figure 2. The XRD profiles of the BaO/MgO/γ-Al₂O₃, MgO/γ-Al₂O₃ and γ-Al₂O₃.

The morphology of the sample BaO/MgO/γ-Al₂O₃ is shown in Figure 3. It can be seen that the prepared composite catalyst is a coarse spherical structure, and the spherical structure of γ-Al₂O₃ remains intact in the catalyst. The Ba and Mg oxides are well deposited on the surface of the γ-Al₂O₃ spheres to form a ternary composite metal oxide solid base catalyst.

Figure 3. The SEM pictures of the BaO/MgO/γ-Al₂O₃.

3.1.2. The Analysis of Component Content of Catalysts. The inductively coupled plasma characterization data of the sample BaO/MgO/γ-Al₂O₃ is shown in Table 1. As shown in table 1, the BaO/MgO/γ-Al₂O₃ sample metal ion content were determined by ICP. The molar ratios of Ba/Al and Mg/Al in sample are 0.093 and 0.259. The contents of Ba, Mg and Al are basically the same as the addition amount, which is close to the theoretical value (Ba/Mg/Al=0.1:0.3:1).

Table 1. The determination of the BaO/MgO/γ-Al₂O₃ metal elements content.

| Catalyst                     | W(Ba)/% | W(Mg)/% | W(Al)/% |
|------------------------------|---------|---------|---------|
| BaO/MgO/γ-Al₂O₃             | 14.53   | 7.08    | 30.72   |

3.1.3. The Investigation of Alkaline Sites of Catalysts. The alkaline test results and the CO₂ temperature programmed desorption curve of the sample BaO/MgO/γ-Al₂O₃ are shown in Table 2 and Figure 4. It can be seen from the graph that compared with the γ-Al₂O₃ and MgO/γ-Al₂O₃ composite oxides. The
ternary composite metal oxide solid base catalyst BaO/MgO/γ-Al2O3 exhibits a peak of adsorption at a high desorption temperature of 530 °C-700 °C. There is a strong basic site exists and the total alkali amount increases.

Table 2. The alkaline test results of the BaO/MgO/γ-Al2O3.

| Catalysts                  | Weak base center | Medium strong base site | Strong base site |
|----------------------------|------------------|-------------------------|------------------|
|                            | $T$ (°C)         | adsorption quantity (mmol/g) | $T$ (°C)         | adsorption quantity (mmol/g) | $T$ (°C)         | adsorption quantity (mmol/g) |
| γ-Al2O3                    | 87.00            | 0.249                   | 278.00           | 0.261                     | /                 | /                  |
| MgO/γ-Al2O3                | 83.00            | 0.277                   | 340.00           | 0.257                     | /                 | /                  |
| BaO/MgO/γ-Al2O3            | 86.00            | 0.221                   | 269.00           | 0.101                     | 558.00           | 0.232               |

Figure 4. The CO2-TPD pictures of the BaO/MgO/γ-Al2O3, MgO/γ-Al2O3 and γ-Al2O3.

3.1.4. The Study on Specific Surface Areas and Pore Diameter of Catalysts. The BET test results and the adsorption (desorption) isotherms of the sample BaO/MgO/γ-Al2O3 are shown in Table 3 and Figure 5. It can be seen from Table 3 that the specific surface area and pore volume of the solid base catalyst after loading are decreased, the main reason is that some of the pores on the γ-Al2O3 are blocked by the metal oxide with the loading of the metal oxide. In addition, a small amount of BaO diffuses into the surface of MgO to form a MgO-based BaO-MgO solid solution, causing a change in the bulk structure of the catalyst, so that the specific surface area and pore volume of the catalyst are both reduced. As can be seen from figure 5, the synthesized solid base catalyst adsorption (desorption) isotherm is close to the "S" type, and the type II has mesopores, and there is a significant jump at a relative pressure of about 0.75.

Table 3. The BET test results of catalysts.

| Catalyst                  | BET surfaces area (cm²·g⁻¹) | Average pore volume (cm³·g⁻¹) | Average pore diameter (nm) |
|---------------------------|-----------------------------|-------------------------------|---------------------------|
| γ-Al2O3                   | 170.537                     | 1.015                         | 9.794                     |
| MgO/γ-Al2O3               | 166.823                     | 0.966                         | 10.162                    |
| BaO/MgO/γ-Al2O3           | 156.167                     | 0.413                         | 10.583                    |
Figure 5. Low-temperature N\textsubscript{2} adsorption-desorption isotherms of the BaO/MgO/\textgreek{g}-Al\textsubscript{2}O\textsubscript{3}.

3.1.5. Thermal Stability Analysis. The thermogravimetric analysis of the sample BaO/MgO/\textgreek{g}-Al\textsubscript{2}O\textsubscript{3} is shown in Figure 6. It can be seen from the TG curve of the catalyst that during continuous heating from 25 °C to 800 °C, the catalyst mainly has three weight loss stages: The first stage is below 180 °C, which is the weight loss caused by the volatilization of free water on the catalyst surface; The second stage is between 180 °C and 360 °C, this stage has a large weight loss peak, which is the removal of part of the crystal water in the catalyst and the decomposition of Mg(NO\textsubscript{3})\textsubscript{2} into MgO in the catalyst; The third stage is between 360 °C and 560 °C, which is caused by the further removal of the remaining part of the crystal water and the decomposition of BaCO\textsubscript{3} into BaO in the catalyst; After 560 °C, the TG curve of the catalyst tends to balance, the sample composition and structure tend to be stable.

Figure 6. TG-DTA diagrams of the BaO/MgO/\textgreek{g}-Al\textsubscript{2}O\textsubscript{3}.

3.2. Single Factor Experiment
The effects of reaction temperature, pressure, time and amount of catalyst on the molecular weight of synthetic polypropylene glycol were investigated by using glycerol, propylene oxide as raw materials and ternary composite solid base BaO/MgO/\textgreek{g}-Al\textsubscript{2}O\textsubscript{3} as catalyst. The initial conditions of the synthesis experiment are: the mass ratio \(m_{(PO)}: m_{(GI)} = 1: 10\), the amount of catalyst is 6% of the total amount of propylene oxide and glycerol, the reaction temperature is 190 °C, the reaction time is 6 h, the pressure is 2 MPa.
3.2.1. **The Effect of the Reaction Temperature.** The effect of reaction temperature on the performance of synthetic polypropylene glycol is studied under initial synthesis conditions. The changes trend about hydroxyl value and molecular weight of polypropylene glycol at different reaction temperatures (150 °C, 170 °C, 190 °C, 210 °C, 230 °C) were investigated. The influence of reaction temperature on the conversion of propylene oxide and the hydroxyl value of polypropylene glycol, molecular weight were obtained. The result is shown in Figure 7.

![Figure 7](image_url)

*Figure 7. The influence of reaction temperature on the properties of polypropylene glycol.*

It can be seen from Figure 7: When the temperature is lower than 190 °C, the catalytic activity of the catalyst increases with the increase of the reaction temperature, increasing the collision chance of the reactants, speeding up the polymerization reaction, thereby increasing the molecular weight of the polypropylene glycol. When the temperature is higher than 190 °C, the excessive reaction temperature leads to coking of the solid base catalyst, decreased catalytic activity. The polyether polyol side reaction increases, resulting in gradually increase in the hydroxyl value of the polypropylene glycol and gradually decrease in the molecular weight. Therefore, the optimum reaction temperature for the synthesis of PPG was 190 °C.

3.2.2. **The Effect of the Reaction Pressure.** The other conditions were unchanged: the mass ratio $m_{(PO)}: m_{(GI)} = 1:10$, the amount of catalyst is 6% of the total amount of propylene oxide and glycerol, the reaction time was 6 h, and the reaction temperature was 190 °C. Investigating the influence of different reaction pressures (1.5 MPa, 2.0 MPa, 2.5 MPa, 3.0 MPa, 3.5 MPa) on the conversion of propylene oxide and the hydroxyl value of polypropylene glycol, molecular weight. The results are shown in Figure 8.

![Figure 8](image_url)

*Figure 8. The influence of reaction pressure on the properties of polypropylene glycol.*
It can be seen from Figure 8: When the pressure is less than 2.0 MPa, since the monomer propylene oxide is a gas at a certain temperature, the product polypropylene glycol is a viscous liquid. According to the principle of chemical equilibrium, as the reaction pressure increases, accelerate the reaction rate, increase the conversion of propylene oxide, thereby increasing the molecular weight of polypropylene glycol and reducing the hydroxyl value; When the pressure is higher than 2.0 MPa, the molecular weight of the product polypropylene glycol does not change significantly, but due to the ring-opening polymerization of propylene oxide It is an exothermic reaction, the pressure is too high, and a large amount of reaction heat cannot be removed in time, which will cause the temperature to rise rapidly, thus affecting product quality (dark color, high unsaturation). Therefore, the optimal reaction pressure for synthetic PPG experiments is 2.0 MPa.

3.2.3. The Effect of the Reaction Time. Other conditions are the same: The mass ratio \( m_{(PO)}: m_{(GI)} = 1:10 \), the amount of catalyst is 6% of the total amount of propylene oxide and glycerol, the reaction temperature is 190 °C, and the reaction pressure is 2.0 MPa. The relationship between the hydroxyl value and molecular weight of polypropylene glycol with different reaction time (4 h, 5 h, 6 h, 7 h, 8 h) was investigated. The relationship between the conversion of propylene oxide and hydroxyl value, molecular weight of polypropylene glycol and reaction time was obtained. Shown as Figure 9.

![Figure 9](image)

**Figure 9.** The influence of reaction time on the properties of polypropylene glycol.

It can be seen from Figure 9: When the reaction time is less than 6 h, too low reaction time is not conducive to the reaction, a large amount of intermediate product is generated, and the reaction efficiency is lowered. As the reaction time increases, the conversion of propylene oxide gradually increased, the molecular weight of the product polypropylene glycol increased and the hydroxyl value decreased. However, when the reaction exceeded 6 h, the conversion of propylene oxide, the molecular weight and the hydroxyl value of the product did not increase significantly, and the energy consumption increased. Therefore, the optimal reaction time for the synthesis of PPG was 6 h.

3.2.4. The Effect of the Catalyst Amount. Other conditions are the same: The mass ratio \( m_{(PO)}: m_{(GI)} = 1:10 \), the reaction temperature is 190 °C, the reaction pressure is 2 MPa, the reaction time is 6 h. Investigating the influence of different amount of catalysts (2%, 4%, 6%, 8%, 10%) on the conversion of propylene oxide and the hydroxyl value of polypropylene glycol, molecular weight. The results are shown in Figure 10.
Figure 10. The influence of catalyst amount on the properties of polypropylene glycol.
It can be seen from Figure 10: When the amount of the catalyst is less than 6%, the number of active sites of the catalyst and activated reactive monomers per unit time increase with the increase of the amount of the catalyst, the molecular weight of the product polypropylene glycol gradually increases and the hydroxyl value increases. When the amount of catalyst is higher than 6%, as the amount of catalyst increases, the active center of the catalyst increases, the polymerization rate increases, and the side reaction is intensified simultaneously, resulting in gradually decrease in the molecular weight of the product polypropylene glycol and increase in the hydroxyl value. Therefore, the optimum catalyst dosage for the synthesis of PPG is 6%.

3.3. Response Surface Methodology Optimization and Statistical Analysis
According to the 29 sets of experiments, the central composite design (BBD) model[30][31] was used to perform regression fitting analysis on the response propylene oxide conversion rate $X_{(PO)/%}$ and various factors, the regression as in Equation (1) and the correlation coefficient $R^2 = 0.9995$ were obtained. It can be seen that the change in response value (propylene oxide conversion rate $X_{(PO)/%}$) is almost derived from the selected variable.

$$
X = +65.24 + .42A + .50B - 37C + .58D - 1.54AB + 3.44AC + 3.11AD
-2.98BC + 7.08BD - 1.32CD - 8.04A^2 - 3.31B^2 - 1.52C^2 - 0.84D^2
$$

(1)

Where in $X$ is the conversion of propylene oxide ($X_{(PO)/%}$); $A$, $B$, $C$ and $D$ are the reaction temperature ($T$), the amount of the catalyst ($W$), the reaction pressure ($P$) and the reaction time ($t$). In order to more intuitively observe the influence of the interaction between polymerization temperature, catalyst dosage, reaction pressure and reaction time on the conversion of propylene oxide $X_{(PO)/%}$, the 3D response surface analysis diagrams of the interaction between the two factors was drawn. As shown in Figure 11.
Figure 11. The 3D response surface plots of interaction effects between factors on $X_{(PO)}/\%$.

It can be seen from Figure 11(a, b, c) that the 3D response surface of the influence between the reaction temperature and the amount of the catalyst, the reaction pressure, the reaction time on the conversion of the propylene oxide $X_{(PO)}/\%$ is approximately elliptical. indicating that the three factors are between the reaction temperature and the reaction temperature. it can be seen that the interaction between the three factors and the reaction temperature has a greatest significant effect on the conversion of propylene oxide $X_{(PO)}/\%$. From the slope of the 3-D response surface analysis, the reaction temperature has the greatest influence. Similarly, As shown in Figure 11(e, f), the interaction of catalyst dosage with reaction pressure, reaction time has a significant effect on the conversion of propylene oxide $X_{(PO)}/\%$, and the amount of catalyst has the great influence; The effect of The interaction between reaction pressure and reaction time on the conversion of propylene oxide $X_{(PO)}/\%$ is not significant, and the effect of reaction pressure is slightly greater than the reaction time, as shown in Figure 11(d). Through the response surface analysis of the surface map in Figure 11, it is more intuitive to show that the propylene oxide conversion rate $X_{(PO)}/\%$ response surface optimization test, the significance of each factor from strong to weak performance: reaction temperature > catalyst dosage > reaction pressure > reaction time.
3.4. Structural Characterization of Polypropylene Glycol Products

3.4.1. Infrared Spectroscopy. Fourier infrared analysis was performed on the existing polypropylene glycol standards and the polypropylene glycol samples prepared under the optimal experimental conditions. The results are shown in Figure 12.

![FTIR spectrum of Polyether Polyol product.](image)

As can be seen from Figure 12, the broad and strong absorption peak appearing at about 3400 cm\(^{-1}\) in the figure is the stretching vibration characteristic absorption peak of the polyether polyol terminal hydroxyl group (-OH). The strong absorption peak appearing at around 1100 cm\(^{-1}\) is the ether bond (C-O-C) in the polyether polyol. When the C-O bond vibrates, the dipole moment changes more than the C-C bond, so the FTIR absorption intensity of the ether bond is stronger, which is also the characteristic absorption band for identifying the polyether compound. The absorption peak appearing at 900 cm\(^{-1}\) to 1000 cm\(^{-1}\) can be attributed to the symmetric stretching vibration absorption of the ether bond. The antisymmetric stretching vibration absorption peak of methyl (-CH\(_3\)) is about 2970 cm\(^{-1}\), and the symmetric stretching vibration absorption peak of methyl (-CH\(_3\)) is about 2875 cm\(^{-1}\). The absorption peaks of the methylene (-CH\(_2\)) and methine (-CH) on the propylene oxide segment and the glycerin initiator should appear near 2930 cm\(^{-1}\), and overlap with the absorption peak of the methyl group. The asymmetric deformation vibration and the symmetric deformation vibration absorption peak of the methyl group at about 1454 cm\(^{-1}\) and 1375 cm\(^{-1}\). The above analysis can prove that the target product polypropylene glycol was obtained experimentally.

3.4.2. Nuclear Magnetic Resonance Spectroscopy. Nuclear magnetic resonance analysis was performed on the existing polypropylene glycol standards and the polypropylene glycol samples prepared under the optimal experimental conditions. The results are shown in Figure 13.
Nuclear magnetic resonance spectroscopy analysis of polyether polyol synthesized from glycerol as starting agent in Figure 13: The peaks in the graph can be divided into two regions, and the first region (I) is δ 1.1. The second area (II) is δ 3.0–4.0. According to the structural analysis of polypropylene glycol, the germanium region should be the absorption peak of the methyl proton on the propylene oxide segment of the polypropylene glycol molecule; and the sputum region is the absorption peak of the remaining protons in the polypropylene glycol molecule, including methylene oxide on the propylene oxide segment, the hydrogen nuclei in methine, the hydrogen nuclei in methylene and methine groups on the terminal glycerol starter segment, and the hydrogen nuclei in terminal hydroxyl groups. The above analysis can prove that the target product polypropylene glycol was obtained experimentally.

4. Conclusions
(1) BaO/MgO/γ-Al₂O₃ solid base catalyst replaces KOH and is used in catalytic synthesis of polypropylene glycol. It has high catalytic activity, can be reused, requires no post-treatment, and is convenient for continuous production. It is a stable and environmentally friendly catalyst.
(2) Using BaO/MgO/γ-Al₂O₃ as catalyst, the polymerization was optimized by single factor and response surface experiments. Polypropylene glycol was prepared from glycerol and propylene oxide, and the optimal synthesis conditions were reaction temperature 190 °C, reaction time 6 h, reaction pressure 2 MPa and catalyst dosage 6%. Under optimal conditions the molecular weight of polypropylene glycol was 600-650 and the conversion of propylene oxide was 63.5%.

References
[1] Yan Z R, Yang S Y, Yu A F and Cheng L B. 2001. Research progress in synthesis of polyether using bimetallic catalysts Polym. Bull. (5) 1-6
[2] Qin Z Y, Ba Q Y. 1996. New high molecular weight polyether Polyurethane Industry 11(4) 7-11
[3] Yu J K, Zhao W, Yuan Z 2017 Progress in the synthesis of polyether polyols Chemical Propellants & Polymeric Materials 5(3) 19-37
[4] Yang B 2009 Progress of the polyether polyols synthesis Guangdong Chemical Industry 36(12) 78-80
[5] Zhang M Q 2000 Study on glycerol ethylene oxide propylene oxide block copolyether Chemical Propellants & Polymeric Materials (3) 24-25
[6] Tian C Y 2000 Highly efficient alkoxylation catalyst Detergent & Cosmetics 23(S1) 164-166
[7] Yao L N, Sun L Y, Zhao R C and Gu R 2015 Synthesis of polyether polyol Shanghai Plastics (4) 34-37
[8] Yan Z R, Wu L C, Yang S Y, Yu A F and Chen L B 2004 Synthesis of DMC polyether polyols with small molecular regulators *Polymeric Materials Science & Engineering* **20**(3) 57-58

[9] Gonzalez M D B 2014 Process for preparing highly active double metal cyanide catalysts and their use in the synthesis of polyether polyols US **0243497A**

[10] Yu J K, Zhang J L, Lu G H 2016 Novel phosphazenium type catalysts and their applications in synthesis of polyether polyols *Chemical Propellants & Polymeric Materials* **14**(4) 12-18

[11] Shinji K, Masahiro K, Kazumi M, Sonobe Y and Suzuki T 1997 Phosphazenium salt and preparation process thereof, and process for producing poly (alkylene oxide) EP **0791600**

[12] Yao L N, Sun L Y, Zhao R C and Gu R 2016. Research progress on catalysts for synthesis of polyether polyol *Shanghai Plastics* (1) 16-25

[13] Park Y M, Lee D W, Kim D K, Lee J S and Lee K Y 2008 The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel *Catalysis Today* **131**(1-4) 238-243

[14] Dou Z Y, Xu L, Zhi Y F, Zhang Y W and Xia H 2016 Metalloporphyrin-Based Hypercrosslinked Polymers Catalyze Hetero-Diels-Alder Reactions of Unactivated Aldehydes with Simple Dienes: A Fascinating Strategy for the Construction of Heterogeneous Catalysts *Chemistry - A European Journal* **22**(29) 9919-9922

[15] Yin N, Kang M Q, Liu Z M, Li Q F and Feng Y L 2014 KOH/γ-Al2O3 catalytic synthesis of Poly (Triethylene Glycol Carbonate) Ester Glycol *Chemical Propellants & Polymeric Materials* **12**(2) 71-75.

[16] Song M L, Yang X G and Wang G Y 2018 Preparation of polycarbonate diols (PCDLs) from dimethyl carbonate (DMC) and diols catalyzed by KNO3/γ-Al2O3 *RSC Advances* 8 35014-35022

[17] João P C E, Gondim A D, Souza L D and Antonio S A 2016 Alumina-supported potassium compounds as heterogeneous catalysts for biodiesel production: A review *Renewable & Sustainable Energy Reviews* **59** 887-894

[18] Huang Z X, Pei X R, Sun H J, Chen L X and Jia Y H 2018 Study on properties of KF/ZrO2 solid alkaline catalysts for transesterification of soybean oil to make biodiesel *Xiandai Huagong/Modern Chemical Industry* 38(2) 95-97 and 99

[19] Wang M W, Wang R L, Qu J W and Zeng Z L 2012 Method for synthesizing polyglycerol by using supported sodium hydroxide solid base catalyst *CN 201210004532.3*

[20] Liao Z, Yi H, Li Z, Fan C, Zhang X, et al 2015 Copper-Catalyzed Radical Carboxygenation: Alkylation and Alkoxylation of Styrenes *Chemistry - An Asian Journal* **10**(1) 96-99

[21] Challioui A, Derouet D, Oulmidi A and Bresse J C 2004 Alkoxylation of epoxidized polyisoprene by opening of oxirane rings with alcohols *Polymer International* **53**(8) 1052-1059

[22] Yu J K 1994 Study on synthesis of polyethylene glycol with alkaline earth metal catalyst *Surfactant Industry* (4) 38-42

[23] Xie W L, Huo G Q 1995 Progress in the narrow ethoxylation of fatty alcohols *Journal of Zhengzhou Grain College* 16(4) 84-91

[24] Li J, Zhang Q, Zhao Y, Qi P and Chao C 2017 Alkaline earth metal oxide modification of Ni/Al2O3 for hydrogen production from the partial oxidation and reforming of dimethyl ether *Reaction Kinetics, Mechanisms and Catalysis* **122**(2) 1193-1202

[25] Elkins T W, Roberts S J, Hagelin-Weaver H E 2016 Effects of alkali and alkaline-earth metal dopants on magnesium oxide supported rare-earth oxide catalysts in the oxidative coupling of methane *Applied Catalysis A General* **528** 175-190

[26] Lambert T L 1996 Process for preparing low unsaturaturation polyether polyols WO **9641829**

[27] Herzberger J, Niederer K, Pohlit H and Swiwert J 2015 Polymerization of Ethylene Oxide, Propylene Oxide, and Other Alkylene Oxides: Synthesis, Novel Polymer Architectures, and Bioconjugation *Chemical Reviews* **116**(4) 2170-2243

[28] Tran C H, Pham L T T, Lee Y, Jang H B, Kim S, et al 2019 Mechanistic insights on Zn(II)−Co(III) double metal cyanide-catalyzed ring-opening polymerization of epoxides *Journal of Catalysis* **372** 86-102

[29] Forutan H R, Karimi E, Hafizzi A, Rahimpour M R and Keshavarz P 2015 Expert representation chemical looping reforming: A comparative study of Fe, Mn, Co and Cu as oxygen carriers
supported on Al₂O₃. *Journal of Industrial and Engineering Chemistry* **21** 900-911

[30] Esonye C, Onukwuli O D, Ofoefule A U 2018 Optimization of Methyl Ester Production from, Prunus Amygdalus, Seed Oil Using Response Surface Methodology and Artificial Neural Networks. *Renewable Energy* **130** 61-72

[31] Almashjary K H, Khalid M, Dharaskar S, Jagadish P, Walvekar R, et al 2018 Optimisation of extractive desulfurization using Choline Chloride-based deep eutectic solvents. *Fuel* **234** 1388–1400