Direct Synthesis of Glycol Ethyl Ethers from Glycol with Modified HZSM-5 as Catalyst

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Abstract. Glycol ethyl ethers possess many excellent properties and are widely used in paint industry, chemical industry and so on. In this paper, glycol ethyl ethers were synthesized from glycol with the modified HZSM-5 as catalyst. The modified HZSM-5 was characterized by XRD, SEM, EDS, BET and NH₃-TPD. The results showed that the modification did not change the structure and morphology of HZSM-5, sulfur was adsorbed on the surface of catalyst and strong acid sites appeared. The influence of ratio of the reactants, reaction temperature, reaction pressure, and time on the yield and selectivity was studied. The optimal reaction condition was performed with the molar ratio of glycol and ethanol 1:4 under 7MPa pressure at 453K for 4 h. Under these conditions, the conversion of glycol was 68.12%, and the selectivity of glycol ethers could be up to 98.61%.

1. Introduction
Glycol ethyl ethers, including glycol monooethyl ether and glycol diethyl ether, were important chemical material. It can be used as solvent, jet fuel, deicing agent and chemical intermediate etc. [1, 2] Traditionally, glycol ethers were synthesized through addition reaction of epoxy ethane [3-10]. There are limitations to this method owing to flammability and explosibility of epoxy ethane. Syngas method was also not ideal for the high reaction pressure, low yield and low selectivity of glycol ethers [11, 12]. Although ethylene glycol (EG) is a safe raw material for synthesis of glycol ethyl ethers, it is also derived from petroleum in traditional method. With the industrialization of preparation of EG from coal [13-17], production of EG will increase a lot in the future and synthesis of glycol ethers from EG will have advantages in price [18] and more safety than epoxy ethane method. However there are few literatures about synthesized of glycol ethers from EG. Tomoharu Oku synthesized glycol monomethyl ether from glycol with Cs-P-Si mixed oxide as catalyst, but the conversion of glycol and selectivity of glycol monomethyl ether were low [19]. Yadong Zhang also prepared glycol ether from EG which was catalyzed by aluminum chloride and diammonium hydrogenphosphate, but it is also less desirable for the short life and difficult recovery of the catalysts [20]. Junfeng Liu synthesized diethylene glycol ethyl ether from diethylene glycol and ethanol catalyzed by heteropoly acid, the conversion of diethylene glycol was 92% and the selectivity for diethylene glycol ethyl ether was 73.5% [21]. Owing to unique pore structure controlled acidity and high hydrothermal stability, ZSM-5 has became one of the most widely studied and used catalysts. Furthermore, the intrinsic micropore size of ZSM-5 is similar to that of small organic molecules, which offer the benefits shape to selectivity of glycol ethers in the micropore space. Those characters make ZSM-5 become one of the most important
shape-selective catalysts, which are widely used in alkylation, isomerization, cracking, disproportionation and other processes [22]. In this paper, modified HZSM-5 catalysts were firstly prepared, characterized and then employed for the direct synthesis of glycol monoethyl ether from EG and ethanol. In order to obtain optimal reaction conditions, single factor experiment was conducted. Finally the reusability of the modified catalyst was tested.

2. Results and discussion

2.1 Optimization of reaction conditions

With the desired catalysts in hand, the effects of reaction temperature, feed ratio, pressure, time and the concentration of modification were investigated respectively by means of single factor experiment method. The results were shown in Table 1-5.

2.1.1 Effect of concentration of modification on the performance of catalysts. In order to explore the influence of concentration of modification on the performance of catalysts, HZSM-5 was firstly modified by ammonium sulfate aqueous solution from 0.1 mol•L\(^{-1}\) to 0.7 mol•L\(^{-1}\). The catalytic performances were measured under the following reaction conditions: reaction pressure was 7 MPa, reaction temperature was 473K, reaction time was 4 hours and the molar ratio of EG to ethanol was 1:3. The result was shown in Table 1.

| Concentration of modifier /mol·L\(^{-1}\) | Conv\(_1\)/% | Sel\(_2\)/% | Sel\(_3\)/% | Sel\(_{(2+3)}\)/% |
|------------------------------------------|-------------|-------------|-------------|------------------|
| 0.1                                      | 47.2        | 69.0        | 10.4        | 79.4             |
| 0.3                                      | 53.8        | 71.5        | 17.5        | 89.0             |
| 0.5                                      | 69.1        | 61.5        | 26.6        | 88.1             |
| 0.7                                      | 66.5        | 62.2        | 24.9        | 87.1             |

Reaction conditions, n (EG): n (ETOH)=1:3, 473K, 4h, 7MPa, the loading of catalyst 0.6%.

As shown in Table 1, when the concentration less than 0.5 mol•L\(^{-1}\), the conversion of EG and the yield of glycol ethyl ethers increased with the increasing of modification concentration, but the selectivity of ethylene glycol monoethyl ether slightly decreased. The total selectivity of ethylene glycol ethers almost kept unchanged when the concentration is larger than 0.3 mol•L\(^{-1}\). When the modification concentration reached 0.5 mol•L\(^{-1}\), the yield of glycol ethyl ethers reached the top. Based on these results, the optimum concentration of ammonium sulfate was 0.5 mol•L\(^{-1}\).

2.1.2 Effect of reaction temperature on the reaction results. The effect of reaction temperature on the conversion of EG, selectivity and yield of product 2 and 3 were investigated and the results were summarized in Table 2.

| Reaction temperature/ K | Conv\(_1\)/% | Sel\(_2\)/% | Sel\(_3\)/% | Y\(_{(2+3)}\)/% |
|-------------------------|-------------|-------------|-------------|----------------|
| 473                     | 75.74       | 55.16       | 35.54       | 68.70          |
| 453                     | 68.77       | 64.20       | 28.24       | 63.57          |
| 433                     | 59.91       | 67.63       | 27.84       | 57.20          |
| 413                     | 53.39       | 72.43       | 20.17       | 49.44          |
| 393                     | 6.45        | 92.17       | 0.00        | 5.94           |

Reaction conditions: n (EG): n (ETOH) =1:3, 3h, 7MPa, the loading of catalyst 0.6%.

Table 2 showed that the conversion of EG and the yield of glycol ethyl ethers increased with the increasing of reaction temperature, but the selectivity of glycol ethyl ethers decreased. Although the yield of glycol ethyl ethers could reach the highest value (68.70%) at 473 K, the selectivity of glycol
ethyl ethers was the lowest, which means the appearance of more byproducts. It also could be seen that the yield of glycol ethyl ethers was 63.57% at 453 K, which was only lower than at 473 K, but the conversion of EG was much higher than at 433 K, so that 453 K was the optimum reaction temperature.

2.1.3 Effect of reaction time on the reaction results. The dependence of EG conversion, products selectivity and yield on reaction time were investigated, the results were shown in Table 3.

| Reaction time/h | Conv₁/% | Sel₂/% | Sel₃/% | Y(2+3)/% |
|----------------|---------|--------|--------|----------|
| 8              | 75.63   | 48.57  | 38.12  | 65.56    |
| 6              | 75.66   | 49.26  | 39.29  | 66.99    |
| 4              | 74.92   | 55.43  | 37.50  | 69.62    |
| 2              | 66.72   | 67.19  | 29.05  | 64.21    |
| 1              | 67.63   | 64.64  | 29.35  | 63.56    |

Reaction conditions: n (EG): n (ETOH)=1:4, 473K, 7MPa, the loading of catalyst 0.6%.

It could be seen from Table 3 that reaction time had great influence on the conversion of glycol and selectivity of glycol monoethyl ether and glycol diethyl ether. When the reaction time was 4 h, the conversion of glycol reached the peak value. Meanwhile, the selectivity of glycol ethyl ethers increased firstly, but then decreased with the reaction time prolonged. The optimum reaction time was 4 h.

2.1.4 Effect of reaction pressure on the reaction results. The effect of reaction pressure was also studied by single factor experiment method, and the results were listed in Table 4.

| Reaction pressure (MPa) | Conv₁/% | Sel₂/% | Sel₃/% | Y(2+3)/% |
|------------------------|---------|--------|--------|----------|
| 2                      | 20.29   | 90.92  | 2.49   | 18.95    |
| 3                      | 39.57   | 65.41  | 30.54  | 37.97    |
| 4                      | 46.38   | 64.92  | 32.65  | 45.26    |
| 5                      | 51.07   | 65.81  | 31.96  | 49.93    |
| 6                      | 54.82   | 64.39  | 31.57  | 52.6     |
| 7                      | 60.37   | 63.99  | 32.59  | 58.31    |

Reaction conditions: n (EG): n (ETOH)=1:3, 413 K, the loading of catalyst 0.6%.

It was evident from Table 4, better conversion of EG and higher yield of glycol ethyl ethers could be obtained with the increasing of reaction pressure, but selectivity of glycol monoethyl ether and glycol diethyl ether almost kept unchanged when the reaction pressure was higher than 3 MPa. At the same reaction temperature, the lower pressure and the less liquid ethanol in the autoclave, there were not enough effective contact of ethanol with the catalyst. Less contact will lead to less collisions of activated ethanol molecule with glycol, resulting in low conversion of EG. For the same reason, less collisions of activated ethanol molecule with glycol monoethyl ether, less glycol monoethyl ether converted to glycol diethyl ether, resulting in lower glycol diethyl ether yield and higher selectivity of glycol monoethyl ether. On the contrary, the higher pressure the more liquid ethanol in the autoclave, the conversion of EG and yield of glycol diethyl ether increased with the increasing of reaction pressure. The pressure of 7 MPa was suitable for this transformation.

2.1.5 Effect of feed ratio on the reaction results. In order to investigate the effect of feed ratio of EG and ETOH, the values of n(EG):n(ETOH) were varied from 1:2 to 1:6 in the following experiments, keeping the other reaction conditions unchanged. The results were summarized in Table 5.
Table 5. Effect of feed ratio on the results

| n(EG):n(ETOH) | Conv₁/% | Sel₂% | Sel₃% | Y(2+3)% |
|---------------|---------|-------|-------|---------|
| 1:2           | 56.42   | 65.77 | 25.69 | 51.60   |
| 1:3           | 61.58   | 64.93 | 30.23 | 58.59   |
| 1:4           | 65.37   | 63.99 | 32.59 | 63.13   |
| 1:5           | 67.89   | 54.53 | 42.32 | 65.75   |
| 1:6           | 68.06   | 56.55 | 40.41 | 65.99   |

Reaction conditions: 433 K, 4 h, 7 MPa, the loading of catalyst 0.6%.

As indicated in Table 5, the higher feed ratio of ethanol to EG could afford better conversion of EG and higher selectivity of glycol diethyl ether, but lower selectivity of glycol monoethyl ether. Increasing the amount of ethanol will bring more activated ethanol, which could react with EG better, resulting in higher EG conversion and more glycol monoethyl ether. Then the glycol monoethyl ether further reacted with activated ethanol to generate more glycol diethyl ether causing higher selectivity of glycol diethyl ether and lower selectivity of glycol monoethyl ether. When the feed ratio of ethanol to EG was higher than 3, the total selectivity of glycol ethyl ethers kept stable. However, too much ethanol would cause extra difficulty in the separation of products. Based on these observation, 1:4 was chosen as the optimum feed ratio of EG to ethanol.

2.1.6 Reusability of the catalyst. The reusability of the catalyst is important for the large scale operation from industrial point of view. The reusability was evaluated by operation under the optimized conditions (1:4, 4 h, 453 K, 7 MPa, the quantity of catalyst 0.6%). After every run, the catalyst was recovered by filtration from crude reaction mixture, and calcined at 773 K for 2 h. The results were shown in Figure 1.

Figure 1 showed that the conversion of glycol and the yield of glycol ethyl ethers decreased slightly with the reused time increasing, but the selectivity of glycol ethyl ethers was almost unchanged. This suggested that the catalyst has high stability and excellent reusability.

2.2 Characterization of catalysts

2.2.1 XRD of catalyst. The XRD patterns of unmodified and modified HZSM-5 were shown in Figure 2. The XRD patterns of unmodified HZSM-5 (a) and modified HZSM-5 (b) showed intense and sharp lines values at 7.9°, 8.8°, 23.1°, 23.3°, 23.9°. These signals are characteristic of ZSM5-type zeolites,
and they are agreement well with the XRD patterns of ZSM-5 in the Ref. [23]. That means the modification does not affect the structure of HZSM-5.

2.2.2 SEM and EDS. It is well known that the size and the relative content of surface elements of the catalyst have strong effect on their catalytic performance. Figure 3 is the image and EDS of the catalyst.

![SEM and EDS of (a) unmodified HZSM-5, and (b) modified HZSM-5](image)

As indicated in Figure 3, the morphology of catalysts had not changed after modification. The particle size was still between 1-5μm. The EDS showed that there were only O, Si, Al elements on the surface of unmodified HZSM-5, and the S element was introduced into the surface of catalyst after modification, which was the reason for the appearance of strong acid sites as shown in Figure 4.

2.2.3 Specific surface area and pore structure. The quantitative comparison of the BET surface area and pore size of catalysts were given in Table 6.

| Catalysts          | \( \text{S}_{\text{BET}} \) m\(^2\) g\(^{-1}\) | Pore volume/cm\(^3\) g\(^{-1}\) | Pore size/nm |
|--------------------|---------------------------------|----------------------------------|--------------|
| Unmodified HZSM-5  | 340.36                          | 0.2705                           | 3.1790       |
| Modified HZSM-5    | 292.87                          | 0.2259                           | 3.0859       |

As shown in Table 6, the BET surface area, the pore volume and the pore size decreased obviously after modification, which means the modification was not only stick to the surface of catalyst but also get into the inner surface of the pores, resulting in the decrease of the above three parameters.

2.2.4 NH\(_3\)-TPD. The acid property of unmodified and modified catalysts were measured by NH\(_3\)-TPD experiments, and was shown in Figure 4.

![NH\(_3\)-TPD patterns of unmodified and modified HZSM-5](image)
The NH$_3$-TPD profiles showed that unmodified HZSM-5 had 2 broad desorption feature while the modified had 3 broad desorption feature, it could be assigned to the desorption of physisorbed NH$_3$ from acid sites. After NH$_3$ was adsorbed 1 h on the samples at 353 K, the desorption temperatures of unmodified HZSM-5 at 373 K–573 K and 583 K–853 K, and the modified one were monitored at 373 K–573 K, 573 K–753 K and 753 K–963 K respectively, which means that modified HZSM-5 had higher acidity than the unmodified. According to our previous research [21], higher conversion of EG could be obtained with higher acidic catalyst, which means that the catalytic activity could improve with the enhancement of acidity.

3. Experimental

3.1 Material and reagents
All chemicals used in this study were commercially available. They were used without further purification unless otherwise mentioned. HZSM-5 was obtained from the Catalyst Plant of Nankai University, ammonium sulfate was supplied by Sinopharm Chemical Reagent Co., Ltd., EG and ethanol were purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd.

3.2 Catalysts preparation
The catalysts were prepared by excessive impregnation. Firstly, ammonium sulfate were dissolved in deionized water, and the concentrations were 0.1 to 0.9 mol·L$^{-1}$. HZSM-5 with the mass of 1 g was dipped into different aqueous, then stirred for 8 h at 353 K, filtered the suspension, finally dried for 8 h at 373 K, and calcined at 773 K for 6 h.

3.3 Characterization of the catalysts
X-ray diffraction (XRD) was obtained by using a BDX-3200 with Ni-filtered Cu Kα radiation. The X-ray tube was operated at 40 kV, 20 mA, and 20 was ranged from 5° to 60°. BET surface areas and pore structure were measured by N$_2$ adsorption at the temperature of liquid nitrogen using a Micromeritics Chemisorb 2720 (U.S.A) with 0.10 g catalyst and support sampled respectively. Before measurement, every sample was heated under ultrapure He atmosphere at a flow rate of 30 mL·min$^{-1}$ at 773 k for 1 h to remove surface adsorbate, cooled to 353 K and saturated with 5% NH$_3$-He before flushed with He to remove physisorbed NH$_3$. The effluent of NH$_3$-TPD was quantified by a flame ionization detector (FID) under a heating rate of 10 K·min$^{-1}$. The morphology and size of the samples were identified by scanning electronic microscopy (SEM), which was conducted on a JEM-100CXII instrument combined with energy dispersive spectrometer (EDS).

3.4 General procedure of synthesis of glycol ethyl ethers
Glycol ethyl ethers were synthesized in a 250 mL high-pressure autoclave (made in Weihai, China) equipped with a magnetically driven impeller. In a typical run, the reactor were charged with 100 g mixture of EG and ethanol, 0.5 g catalyst (modified HZSM-5). The reactor was pressurized with N$_2$ to 3 MPa and then was heated to 433 K and stirred for a designated period of time. Then the reactor was cooled quickly to a low temperature by placing in an ice/water bath, and the pressure was released slowly. The reaction mixture was filtered and the catalyst was washed by ethanol for reusing. The remained liquid mixture was weighted and analyzed by gas chromatography (GC). The possible reaction pathways of EG were shown in Scheme 1. The conversion of EG and selectivity of product 2 and 3 were calculated by the Formulas.
H₂O

\[
\begin{align*}
\text{HOC}_2\text{H}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{HOCH}_2\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH} \\
\text{HOCH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} & \rightarrow \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{OH} \\
\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{OH} \\
\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{C}_2\text{H}_5\text{OH}
\end{align*}
\]

\[
\text{Conv}_j = \frac{M_{0\text{EG}} - M_{1\text{EG}}}{M_{0\text{EG}}} \times 100\%
\]

\[
\text{Sel}_2 = \frac{M_2}{M_{0\text{EG}} - M_{1\text{EG}}} \times 100\%
\]

\[
\text{Sel}_3 = \frac{M_3}{M_{0\text{EG}} - M_{1\text{EG}}} \times 100\%
\]

4. Conclusion

It can be seen from the experiment, the optimal reaction condition was performed with the molar ratio of glycol and ethanol 1:4 under 7MPa pressure at 453K for 4 h by modified HZSM-5 as catalyst. Under these conditions, the conversion of glycol was 68.12%, and the selectivity of glycol ethers could be up to 98.61%.

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