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Etherification of ethylene glycol with methanol provides a sustainable technology for producing widely used dimethoxyethane, which was green solvent and reagent applied in batteries and as potential diesel fuel additives. SAPO-34 zeolite was found to be an efficient and highly selective catalyst for such etherification by continuous flow experiment. It can reach the selectivity of dimethoxyethane up to 79.4% with around 96.7% of conversion. The relationship of the catalysts structure and the dimethoxyethane selectivity was established by control experiments. The results indicated that the pore structure of SAPO-34 effectively limited the formation of 1,4-dioxane from activated ethylene glycol and ehanced the reaction of the activated methanol with ethylene glycol in priority, which results high selectivity of desired products. The continuous flow technology used in the study could efficiently promoted the deeply etherification of EG with methanol to maintain high selectivity of dimethoxyethane.

Introduction

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Ethers, such as dimethyl ether and methyl tert-butyl ether, are known as attractive candidates for fuel additives because of their ability to reduce soot formation during the combustion process¹⁻⁴. Dimethoxyethane, known as ethylene glycol dimethyl ether, attracts increasing interest in recent years because of its advantageous properties (high energy density and cetane number)⁵. It also shows excellent solubility, widely used as green solvent and good etherification agent in cosmetics, perfumes, pharmaceuticals and especially applied in batteries and electrolyte⁷⁻

Industrial preparation of dimethoxyethane was via the reaction of 2-methoxyethanol with CH₃Cl in the existence of sodium or NaOH by Williamson method¹². However, amount of halon and base used in this process brought the issues of separation and environment pollution. Another common used method for the production of dimethoxyethane is by the cleavage of ethylene oxide in presence of dimethyl ether over Lewis acids¹³. While, ethylene oxide is extremely flammable and explosive, and derived from the unsustainable petroleum resources. Catalytic etherification of ethylene glycol (EG) with methanol could be a potential green method for producing dimethoxyethane. The feedstock could be generated from biomass source. For example, the feedstock of EG could be derived from the renewable cellulose^{14, 15}, or biomass-derived polyols (sorbitol, xylitol, glycerol, etc.)^{16, 17} Their availability and non-petroleum route source could meet the rule of green

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chemistry and could be sustainably developed for industrial application.

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The catalytic etherification of EG with methanol was limited reported in literatures. Scheffel et. al. used H₂SO₄ as the catalyst, the conversion of EG was 61.2% and the concentration of dimethoxyethane was only 9.9% in the mixture solutions less than that of 2-methoxyethanol (23.5%)¹⁸. Due to the environmental impact by liquid acid, solid acid was reported to be applied in the etherification. Baimbridge et. al. used Nafion 15 as catalyst for etherification of EG with methanol, and selectivity of 2methoxyethanol and dimethoxyethane was respectively 67% and 28% with 75.7% of EG conversion¹⁹. Ikariya et. al. used Cs-Si-P (1:5:0.8) oxide catalyst to give 2-methoxyethanol with 76% selectivity at 23% conversion under 300 °C and 12 MPa. Sadly, there is no dimethoxyethane detected in the products under such harsh conditions^{20, 21}. From the above reports, we found that 2methoxyethanol was the main product during the etherification of EG with methanol, and it could not be efficiently converted to dimethoxyethane in further which resulted low yield. Another finding for the above reports was that the by-product of 1,4dioxane was detected. EG was easily activated in the existence of acid catalyst, and self-etherification would be finally formed the 1,4-dioxane ^{22, 23}. Besides the formation of by-product 1,4-dioxane, etherification of EG with methanol is an equilibrium reaction²⁴⁻²⁶. The generated water or the existence of water in solvent may affect the reaction equilibrium, which inhibited the further formation of dimethoxyethane. Traditionally, etherification reaction was inclined to be conducted under a water-free environment. However, separation of water from industrial EG and methanol feedstock is an energy-consuming process. The direct using crude feedstock will largely improve the economics of the etherification process, and will exhibit great prospect for industrialization. Therefore, the main challenge for high yield production of dimethoxyethane using crude

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Scheme 1 Catalytic etherification of EG with methanol using fixed-bed reactor

feedstock (aqueous solution) is how to efficient shift the reaction equilibrium and avoid the formation of by-product 1, 4-dioxane.

Thus, the aim of this study is to develop efficient solid catalyst systems associated with continuous flow strategy for highly selective etherification of crude EG with methanol to dimethoxyethane (Scheme 1). Microporous zeolites were selected as solid acid catalyst to perform the etherification reaction. Fixed bed was used as the reactor to reduce the contact time between water and the catalyst bed. The relationship between the catalysts structure and the dimethoxyethane selectivity was also established.

Experimental

Catalysts

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The following catalysts were used in the present work. HY (ratio of SiO_2/Al_2O_3 was 7, 11 and 14), H-beta (ratio of SiO_2/Al_2O_3 was 25 and 40), HZSM-5(ratio of SiO_2/Al_2O_3 was 25,100 and 300), HZSM-35 (ratio of SiO_2/Al_2O_3 was 30), SAPO-11 (ratio of SiO_2/Al_2O_3 was 0.5) SAPO-34(ratio of SiO_2/Al_2O_3 was 1) and Mordenite (ratio of SiO_2/Al_2O_3 was 25) were purchased from the Catalyst Plant of Nankai University. Al_2O_3 , Ca(OH)₂ and Mg(OH)₂ were derived from Tianjin Kemiou Chemical Reagent Co., Ltd. All the catalysts were calcined at 550°C for 5h under air conditions, and then pressed into pellets, crushed and sieved to 20-40 mesh.

Characterizations of catalyst

NH₃-temperature-programmed desorption (NH₃-TPD) were used to study catalyst acidity on a Micromeritics AutoChem II 2920 instrument. All the samples (0.1 g) were pre-treated at 473 K for 30 min in flowing Ar (25 ml/min) in order to remove the surface impurities. Then, samples were saturated with NH₃ at 323 K for 15 min by flowing 5% NH₃-He (25 ml/min). After saturation, the temperature was increased from 323 to 873 K at 10 °C min⁻¹ in flowing helium (25 ml/min). Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC instrument with mass spectrometry (MS) detector. Samples were heated at a rate of 10 °C min⁻¹ from 100 °C to 800 °C in an N₂ flow of 30 mL min⁻¹.

Catalytic reaction and analysis

The etherification of EG with methanol was performed in a continuous flow fixed bed made of a 1/2 inch stainless steel reactor (length: 300 mm, Swagelok Company) mounted inside a tubular furnace (1000 W/12 V). Two thermocouples (K-Type) were used, one of which was for controlling the furnace's temperature and

another one was monitoring the reaction temperature. The catalyst (1 g) with a diameter of 20-40 mesh was placed between two layers of quartz sands for each test. N₂ was passed through the catalyst bed at a total flow rate of 40ml/min with pressure of 0.3-0.4 MPa. Liquid reactants were continuously pumped into the fixed-bed reactor with a high-pressure pump (Agilent 1100 Pump). For example, 85 w.t. % ethylene glycol aqueous solution mixed with 90 w.t. % methanol (molar ratio was around 1:3.5) was used to test the etherification performance over SAPO-34 catalyst. N₂ and solution flows were mixed at the inlet of the reactor. All the effluent flowed from the reactor were maintained at high temperature (eg. 215 °C) and then partial were directly introduced into the chromatography and online analysed automatically (GC-7890 gas chromatograph equipped with 10-way valve, a FID conductivity detector and a HP-5 column). Products identification was performed by GC-MS. The products of EG reacted with ethanol was collected in a separator at room temperature and analysed using GC auto injector. Conversion and selectivity were calculated by peak area normalization method.

Results and Discussion

Catalytic performance of different catalysts

We initiated the investigations for the etherification EG with methanol over different kinds of catalysts. The reaction was stable in 100-120 min after the liquid reactants pumped into the fixed-bed reactor under the desired conditions, therefore samples was analysed in this time period and the results are shown in Table 1. The products included 2-methoxyethanol, dimethoxyethane, and 1, 4-dioxane identified by GC online analysis. According to the results, it could be seen that no etherification product listed above were detected using alkaline, like Ca(OH)₂ and Mg(OH)₂ as catalyst (Table 1, entry 1-2). When γ -Al₂O₃ was used as catalyst, 2-methoxyethanol

Table 1 Performance of different catalysts in catalyticetherification of EG with methanol. ^[a]

Ent ry	Catalysts	EG Conv. (%)	Distribution of Products (%)			
			MME	DME	1,4- dioxane	Others
1	Ca(OH) ₂	-	n.d.	n.d.	n.d.	n.d.
2	Mg(OH) ₂	-	n.d.	n.d.	n.d.	n.d.
3	γ -Al ₂ O ₃	3.6	52.6	32.4	n.d.	15.0
4	HY(7)	67.5	14.5	23.0	43.9	18.6
5	HZSM-5(25)	64.5	48.4	25.1	26.6	n.d.
6	H-beta(25)	88.4	5.0	26.4	66.2	2.3
7	SAPO-11	73.0	26.1	25.9	44.6	3.4
8	SAPO-34	96.7	17.3	79.4	n.d.	3.4

^[a] Reaction conditions: 483 K (entry3, 473K; entry 4 and 6, 488K), 0.3 MPa N₂, LHSV = $1.5 h^{-1}$ (entry 4-7, $3 h^{-1}$). DME, MME were represented dimethoxyethane and 2-methoxyethanol.

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and dimethoxyethane were detected (Table 1, entry 3). The EG conversion was only 3.6%. When introduced microporous zeolites (HY, HZSM-5, H-Beta and SAPO-11) in the etherification, the conversion of EG were increased dramatically (Table 1, entry 4-7). However, the selectivity of desired product of dimethoxyethane was low over above catalysts, in the range of 20%-30%. The by-products of 1, 4-dioxane were also detected in these zeolites, the selectivity was even higher than dimethoxyethane. SAPO-34 exhibited best catalytic performance in the etherification of EG with methanol, with 96.7% conversion of EG and 79.4% selectivity of dimethoxyethane (Table 1, entry 8). The results showed that SAPO-34 can efficiently catalyse the etherification of EG with methanol and provide the high selectivity to dimethoxyethane.

Effect of acidity of microporous zeolites on its catalytic performance in etherification

The surface acid sites played crucial roles for catalytic etherification, which provided the catalytically active centres for reaction of EG with methanol. To verify the above information, we did series of experiments to understand it. As well-known, the ratio of SiO₂/Al₂O₃ in zeolites could influence the acidity. Therefore, different SiO₂/Al₂O₃ ratio of zeolites was studied. Fig.1 showed the catalytic performance of HZSM-5, HY and H-Beta in the etherification of EG and methanol with different SiO₂/Al₂O₃ ratio. For HZM-5, the EG conversion was promoted with ratio of SiO_2/Al_2O_3 increased from 25 to 300. As shown, HZSM-5 with intermediate acidic content (SiO₂/Al₂O₃=25) gives the EG conversion of 64.5% and that with strong acidic content ($SiO_2/Al_2O_3=300$) gives the conversion close to 100%. HY (SiO₂/Al₂O₃=7, 11, 14) and H-beta $(SiO_2/Al_2O_3=25, 40)$ were also conducted the similar etherification reactions. As seen from the Fig. 1, EG conversion was promoted from 67.5% to 89.0% for HY zeolites with the increased ratio of SiO₂/Al₂O₃. Same trend was also found for H-beta zeolites and EG was almost completely converted with SiO₂/Al₂O₃=40. It was indicated that the increasing of SiO_2/Al_2O_3 ratio improve the acid



Fig.1 Different ratio of SiO_2/Al_2O_3 of zeolites for the etherification of EG with methanol. Reaction conditions: 488 K, 0.3 MPa N₂, LHSV=3 h^{-1. [a]} 483K. DME, MME represent dimethoxyethane and 2-methoxyethanol.





Table 2 Acidity of HZSM-5, HY and SAPO-34

Catalusta	Total acid	Desorption in LT ^a		Desorption in HT ^a				
Catalysts	sites (mmol/g)	Temp. (°C)	Acid sites ^b (mmol/g)	Temp. (°C)	Acid sites ^b (mmol/g)			
HZSM-5(25)	1.0	151	0.8	435	0.2			
HY(7)	1.6	165	1.5	425	0.1			
SAPO-34	1.7	130	1.2	421	0.5			
^a IT. Jaw to managentures, UT, high to managenture								

^a LT: low temperature; HT: high temperature.

^b Determined by NH₃-TPD.

strength for the zeolites, which generated the influences on the conversion. These experiments were evidences for revealing that the strong acid sites in the zeolites was contributed to the EG conversion.

The acidity of the catalysts was further studied via NH₃-TPD technology. HZSM-5, HY and SAPO-34 were characterized and the results were shown in Fig.2. There were two kinds of NH₃ desorption peak in the studied three zeolites according to the NH₃-TPD curves. Desorption peak in the temperature range of 100-300°C (defined as LT) were attributed to the weak acid sites and in the range of 400-500 °C (defined as HT) were attributed to the strong acid sites. The total acid amount of the acid sites is calculated from the TPD curves, and the results were shown in Table 2. It can be seen that the total acid amount varied in the following order: HZSM-5 (1.0mmol/g) < HY (1.6 mmol/g) < SAPO-34 (1.7mmol/g). The EG conversion was compatible with the acidity order, indicated that acidity of zeolites effected the EG conversion. An interesting phenomenon was found that the acidity of HY and SAPO-34 was close, but the EG conversion have big difference. Therefore, the strength distribution of the acid sites is also calculated in Table 2. The amount of strong acid sites in the SAPO-34 was 0.5mmol/g, higher than that of HZSM-5 and HY. The results indicated that the strong acid sites in zeolites were probably contributed to the EG conversion.

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Pore structure of microporous zeolites for catalytic etherification

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Above results described that the surface acid sites of zeolites were beneficial for the conversion, but there is no big difference for the selectivity when the ratio of Si/Al was changed using same zeolite. The pore structure of zeolites could be another important aspect for the etherification reaction. The different pore window size of zeolites would give the influence on the distribution of the final products. We firstly analyse the structure of the used zeolites. HY and H-beta have 12-membered rings (12R) in their structures, attributed to the large pore zeolites^{27, 28}. HZSM-5 and SAPO-11 frameworks can be accessed via a 10R window, and attributed to medium pore zeolites. SAPO-34 has CHA topology, the framework can be accessed via an eight-membered ring (8R) window SAPO-34^{29,30}, attributed to the small pore zeolites. From the analysis and association with the reaction results, it could be indicated that the smaller pore size of zeolites was effective for promoting the selectivity of dimethoxyethane in the etherification of EG with methanol. In order to study such effect, zeolites that framework contains 8R window were used in the reaction, including ZSM-35³¹ and mordenite³², and their catalytic performance were tested. The results were shown in Fig.3. From the results, it can be seen that mordenite and HZSM-35 gave 76.5% and 47.3% selectivity of dimethoxyethane respectively. They exhibited same phenomenon in promoting the selectivity of dimethoxyethane as the SAPO-34. By-product of 1, 4-dioxane was also detected over both of the two zeolites. In fact, these two zeolites have not only one kind of pore window size, but also have bigger pore size than 8R. The existence of bigger pores takes the similar effect as HY, H-beta and H-ZSM-5. These results suggested that the structure of zeolites having 8R windows was essential for promoting the selectivity of dimethoxyethane and zeolites structures having >8R windows would resulted the generation of by-product of 1,4-dioxane which decreased the selectivity of dimethoxyethane.



Fig.3 8R-containing zeolites for catalytic etherification of EG with methanol. Reaction conditions: 483 K, 0.3 MPa N₂, LHSV = $1.5 h^{-1}$. DME, MME were represented dimethoxyethane and 2-methoxyethanol.



Fig. 4 The continuous production dimethoxyethane via etherification over SAPO-34. Reaction conditions: 483 K, 0.3 MPa N_2 , LHSV=1.5 h^{-1} .

Continuous producing dimethoxyethane via etherification over SAPO-34

SAPO-34 exhibited a good catalytic performance in etherification of EG with methanol. To study the long-term behaviour of the tested catalysts and understand the deactivation mechanism, the continuously producing dimethoxyethane was performed over SAPO-34 catalyst in a flow-type reactor. Fig.4 shows a plot of catalytic activity of SAPO-34 for etherification of EG with menthol as a function of time. It reveals the change of conversion of EG and selectivity of 2-methoxyethanol and dimethoxyethane over the course of the reaction. As noted, the selectivity of dimethoxyethane was decreased slowly in 150 min, and then keeps stable in subsequent 150 min, maintained by ca. 70%. 2-methoxyethanol was gradually climbing in the 150mins and then keept stable by ca. 20% in the last 150 min. 2-methoxymethanol was the precursor of



dimethoxyethane, so the total selectivity of ethers was always keep at around 90%, which indicated that the as-used SAPO-34 was highly selective catalyst for the etherification of EG with methanol. For the EG conversion, it was ca. 95% at the beginning and decreased with the time prolonging to 300 min, which indicated that the catalyst was deactivated in the long-term run.

Such deactivation may be due to the deposition of organic compounds, which formed in the cavities of SAPO-34 and trapped inside³³. Therefore, the used SAPO-34 was subsequently characterized by TPR technology and mass spectrometry (MS) as the detector. The results were seen in Fig.5. The colour of the used SAPO -34 was turned to yellow, indicating that the coke was formed in the SAPO-34. From the TG curves, it can be seen that the catalyst weight were decreased by 10% when temperature was elevated to 800°C. Mass frag of m/z=16, 28 and 44 was detected, which represented that the compounds of CH₄, CO and CO₂ were released during the test course. These organic carbon-containing compounds were probably derived from the decomposition of the coke formed in the SAPO-34 in high temperature under air atmosphere. Because of catalyst deactivation with the long-term run, regeneration or catalyst pre-treatment was conducted (Results was listed in Fig S18 and Fig.19). Sadly, the catalyst activity has not been fully recovered after regeneration. New catalyst modification method and regeneration method would be studied in the further work.

Although the SAPO-34 faced the issues of deactivation, the continuous flow strategy was effective keeping the selectivity of desired products. As known, the existence of water and newly formed water in the etherification would take great influence on the reaction equilibrium. Amount of water stayed could inhibit the reaction progressed, and probably made the reaction kept in the 2-methoxyethanol stage and was not continuously formed the final dimethoxyethane. Fixed bed was used as the reactor to reduce the contact time between water and the catalyst bed³⁴ and increase the process efficiency³⁵⁻³⁷.

Insights of dimethoxyethane production by the etherification of EG with methanol overs SAPO-34

Base on above results, it can be seen that SAPO-34 provides very high selectivity to dimethoxyethane, whereas HY with larger pore size gives different results with amount of 1, 4-dioxane. The comparison results encouraged us to further understand the mechanism of the reaction. As for the etherification, the hydroxyl in the alcohol was first activated by the hydrogen proton over zeolite catalyst $^{\scriptscriptstyle 38}$, and then the activated species attacked another alcohol molecular. The reactant used in this work was methanol and EG, and generally EG was more easily to be activated than methanol over acid catalyst and resulted the increasing of 1,4-dioxane. Therefore, it was important to understand the mechanism of products generation in the studied zeolites catalyst and find effective method to enhance the selectivity of dimethoxyethane. Control experiments were conducted using candidate etherification agent reacted with EG for the comparison study. As methanol homologues, ethanol was selected as the etherification agent to react with EG over SAPO-34 and HY catalysts. The results were shown in Fig.6. It can be found that when ethanol was involved in the etherification over SAPO-34, EG conversion was detected as



Fig.6 Etherification of EG with ethanol over SAPO-34 and HY(7). Reaction conditions: 483 K, 0.3 MPa N₂, LHSV = $1.5 h^{-1}$, 4 h.

14.8%, with 38.6% selectivity of 2-ethoxyethan-1-ol and no 1,4dioxane was detected. As the catalyst changed to HY, the conversion was increased obviously and nearly to 91.5%. The byproduct of 1, 4-dioxane was appeared which selectivity was 26.3%.

From the results, it can be found that EG conversion was lower over SAPO-34 than HY when using ethanol as etherification agent. It was probably ascribed to the relationship of reactant molecular dimensions with zeolites pore size. The detailed relationship between the reactant molecular dimensions and zeolites pore size was studied. SAPO-34 has an eight-membered ring (8R) window with a pore diameter of ~0.43 nm³⁹. The kinetic diameter of methanol is 0.38nm which is smaller than the pore size of SAPO-34 40 . Ethanol, which molecular size is around 0.43 nm (bigger than methanol), is a good candidate as etherification agent for the comparison study. The kinetic diameter data of EG was not found in literature. Because its molecular was bigger than ethanol, kinetic diameter of EG was estimated as exceeded 0.43 nm. From the analysis, low EG conversion generated over SAPO-34 was probably attributed to that the diameter of ethanol and EG were similar or larger than SAPO-34 and decreased its probability accessing into the pores of zeolites. For HY, the pore size was allowed the entrance of ethanol and EG easily, which resulted conversion increased and 1,4dioxane appeared.

Another result in Fig.5 was found that 1, 4-dioxane was not detected using SAPO-34 when ethanol was used as etherification agent. The phenomenon was similar with the methanol reacted with EG. It was speculated that EG was not sufficiently formed 1,4-dioxane due to the structure of SAPO-34, because 1,4-dioxane is the main product of EG self-etherification. As a 6-membered molecular, the kinetic diameter of 1,4-dioxane was estimated similar with benzene, which kinetic diameter was 0.585nm, higher than that of pore size of SAPO-34 pores. However, large pore zeolites of HY allowed the EG into its pores to be activated, generating amount of 1, 4-dioxane and increasing the EG conversion, which give the similar results in the etherification of EG with methanol

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Scheme 2 Proposed mechanism over microporous zeolites

and ethanol.

According to the control experiments, the process of etherification of EG with methanol were proposed as in Scheme 2. It can be found that the kinetic diameter of methanol is smaller and matching with pore structure of SAPO-34, can enter into the pores of SAPO-34 and then activate by the inside acid site of catalyst. The entered EG could not form the 1, 4-dioxane due to the pore size of SAPO-34. The activated methanol molecule attacked the EG molecules via SN₂ substitution to first give 2-methoxyethanol. And such activated methanol attacks another side OH in EG to give the final desired product of dimethoxyethane. For the larger pore size zeolite, such as HY, EG was easily accessed into its pores and rapidly activated to generate 1,4-dioxane, decreased the selectivity of desired product. It can be learned from the discussion that efficiently limiting the formation of 1,4-dioxane by pore size control is an effective method to improve the desired products selectivity.

Conclusions

In summary, an efficient microporous zeolite has been developed to achieve high selectivity of dimethoxyethane via etherification of crude ethylene glycol with methanol, using fixed bed reactor. SAPO-34 was the most appropriate catalyst for such etherification, which could realize the selectivity of dimethoxyethane up to 79.4% with around 96.7% of conversion. To the best of our knowledge, the selectivity of dimethoxyethane in this report is much higher than the data reported in the literature. Further study reveals that the pore structure of SAPO-34 could effectively limit the formation of 1,4-dioxane from ethylene glycol and enhanced the activated methanol reacted with ethylene glycol in priority, resulting the high selectivity of dimethoxyethane. Such technology only uses EG, methanol and water, which provide a green route for dimethoxyethane producing and could expand its application.

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Selective synthesis of dimethoxyethane via directly catalytic etherification of crude ethylene glycol

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Potential diesel fuel additive of dimethoxyethane was highly selective produced by etherification of crude ethylene glycol over SAPO-34.

