HZSM-5 catalyzed cyclodehydration of diethylene glycol and its derivatives [1]

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Abstract

Diethylene glycol (DEG) is converted into 1,4-dioxane using HZSM-5 as a catalyst at 205–225°C in the liquid phase. Triethylene glycol, diethylene glycol ethers and PEG gave relatively lower yields of 1,4-dioxane. NH_3 adsorption followed by TPD suggests that acidic sites with NH_3 desorbing above 350°C are responsible for the cyclodehydration of DEG and its derivatives. Correlation of activity and efficiency of the catalyst with density of strongly acidic sites suggests that both cyclodehydration and deactivation of the catalysts take place simultaneously.

Keywords: Glycols; Cyclodehydration; 1,4-dioxane; Solid acid; Zeolites; Catalyst

1. Introduction

Zeolites are being increasingly used as solid acid catalysts in organic reactions [1–3]. These aluminosilicate materials exhibit unique selectivity and reactivity in these reactions due to their channel dimensions and stable structures. Such systems further lead to minimum pollution and waste and are thus environmentally benign [4]. Catalytic dehydration of monoalcohol to ether and olefins are known on zeolites [5,6], alumina [7,8] and montmorillonite [9] clay. Cyclodehydration of diols is an important reaction to synthesize heterocycles. There are reports on dehydration of 1,4-butanediol and its homologues using Al_2O_3, SiO_2–Al_2O_3 [10], CuO–ZnO–Cr_2O_3 [11], X and Y zeolites [12–15],

ZSM-5 [16], Nafion-H [17] and montmorillonite clay [18] catalysts. Such heterogeneous reactions often have advantages of ease of setup, product separation, increased yields and higher selectivity [19,20]. We have earlier reported cyclodehydration of 1,n-diols catalyzed by Cp_xMCl_{4-x} [21]. These systems have poor activity for cyclodehydration of diethylene glycol and its derivatives. We explored the utility of zeolites in this reaction and the corresponding results are described herein.

2. Results and discussion

2.1. Cyclodehydration of diethylene glycol

Cyclodehydration of diethylene glycol (DEG) can theoretically give rise to 1,4-dioxane, 2-methyl-1,3-dioxolane [13] and water.

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2.1.1. Evaluation of catalysts

Several heterogeneous catalysts have been examined for the cyclodehydration of DEG. The results are summarised in Table 1. In this reaction only 1,4-dioxane and H_2O are formed as products. There was no reaction with $AlPO_4$ and B_2O_3–Al_2O_3. Cu–NaY, HY zeolites and $ZrOCl_2 \cdot 8H_2O$ gave modest yields of 1,4-dioxane. Montmorillonite K10 was fairly active but in all these systems the selectivity to 1,4-dioxane was low. HZSM-5 exhibits high activity at a faster rate with 73% selectivity to the cyclic ether. So this catalyst was chosen for further studies.

2.1.2. Effect of temperature

The conversion of DEG to 1,4-dioxane was carried out over HZSM-5 in the temperature range 175–225°C. The formation of this cyclic ether is quite high at 205°C and above. From the plot of log rate of formation of dioxane vs. $1/T$ (Fig. 1) the apparent energy of activation (E_a) and enthalpy of activation ($H_{300}^{\#}$) were calculated to be 19 and 18.35 kcal/mol respectively. With increasing time on stream the activity of the zeolite decreases. This decrease is faster with corresponding increase in the reaction temperature. It is observed during the period that the catalyst surface gradually becomes dark. At 205°C the efficiency of the catalyst (moles of dioxane formed per active site/g) is
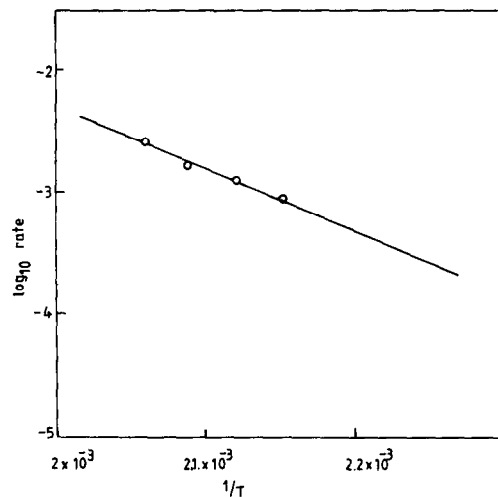

Fig. 1. Plot of logarithm of initial rates vs. $1/T$ in the cyclodehydration of DEG catalyzed by I-HZSM-5.

3100 after 12 h at 98% conversion of DEG with a selectivity of 75% for 1,4-dioxane. The same efficiency was achieved at 225°C in 10 h. The conversion of diethylene glycol was 87.7% and the selectivity to 1,4-dioxane remained at 73%. GC–MS analysis of undistilled residue in flask showed up a peak corresponding to $m/z = 195$ besides unreacted DEG. Fragmentation pattern of this compound corresponds to tetraethylene glycol formed by intermolecular dehydration of DEG.

2.2. Cyclodehydration of other glycols

In this study HZSM-5 was used for cyclodehydration of ethylene glycol and other higher homologues and the results are summarized in Table 2. 1,4-Dioxane is not formed from ethylene glycol whereas the cyclic ether is formed from DEG and its higher homologues. This suggests that 1,4-dioxane is formed only through intramolecular cyclization. It is generally observed that as the molecular weight of the glycol increases there is proportional decrease in the yield of 1,4-dioxane. In all the cases the cyclodehydration reaction was stopped after HZSM-5 catalyst exhibited appreciable fall in activity.

Table 1
Cyclodehydration of DEG catalyzed by solid acid catalysts [a]

Entry	Catalysts	Time(h)	Conversion of DEG [b]	Selectivity to dioxane
1	B_2O_3–Al_2O_3	3.0	–	–
2	$AlPO_4$	3.0	–	–
3	Cu–NaY	2.0	8.1	27.0
4	HY	3.0	16.3	13.0
5	$ZrOCl_2 \cdot 8H_2O$	2.5	22.0	19.7
6	Montmorillonite K10	2.5	46.5 [c]	38.6
7	I-HZSM-5	1.5	100	73

[a] Reaction conditions: DEG (0.1 mol), 500 mg catalyst, 225°C.
[b] Determined from GC analysis.
[c] At 180°C.

Table 2
Cyclodehydration of ethylene glycol and higher homologues by I-HZSM-5 [a]

Entry	Glycol	Time (h)	Turnover [b]
8	Ethylene glycol	2	–
9	Diethylene glycol	2	561
10	Triethylene glycol	4.25	224.5
11	Polyethylene glycol 200	3	235.6
12	Polyethylene glycol 300	3	178.1
13	Polyethylene glycol 400	2	165.5
14	Polyethylene glycol 600	3	71.1
15	Diethylene glycol monomethyl ether	2.5 [c]	231
16	Diethylene glycol dimethyl ether	2 [d]	53.1

[a] 200°C; 0.5 g I-HZSM-5; 10 g DEG.
[b] Turnover = moles of 1,4-dioxane/g-cat·h.
[c] 180°C.
[d] 150°C.

2.3. Cyclization of diethylene glycol ethers

When diethylene glycol monomethyl ether and diethylene glycol dimethyl ether were allowed to react with HZSM-5 catalyst at 180°C and 150°C respectively in liquid phase 1,4-dioxane was formed (Table 2). With diethylene glycol monomethyl ether at 92.2% conversion the selectivity to 1,4-dioxane and diglyme was 78% and 4.3% respectively. The total efficiency for formation of 1,4-dioxane after 9 h was 1880. In this reaction methanol was formed as a by product. As in the case of diethylene glycol the rate of formation of 1,4-dioxane decreases with time from cyclization of diethylene glycol monomethyl ether. However the reaction of diethylene glycol dimethyl ether on HZSM-5 is sluggish. After 2 h the efficiency for formation of 1,4-dioxane is only 106.2.

3. Mechanism

3.1. Possible reactions

In order to establish the mechanism involved in the cyclodehydration of DEG and derivatives few pilot experiments were carried out. When DEG was reacted with water in equimolar ratio at 180°C over HZSM-5 in an autoclave, it gave a low conversion (31.6%) of the diol with poor selectivity (16%) to 1,4-dioxane. This suggests that water which is normally formed in dehydration of DEG inhibits the reaction. In another reaction DEG and ethylene glycol were reacted over HZSM-5 at 200°C for 2 h. This run gave better (43%) DEG conversion and selectivity (26.3%) to 1,4-dioxane. Interestingly peaks due to ethylene glycol did not show up during GC analysis of the reaction mixture. This suggests a possible reaction of ethylene glycol with DEG to furnish PEG. In the cyclodehydration of TEG GC analysis of the product and residue did not show up peaks due to ethylene glycol and only 1,4-dioxane was observed. Based on these observations it can be assumed that conversion of TEG to 1,4-dioxane may involve the scission of TEG to 1,4-dioxane and ethylene glycol and the ethylene glycol thus formed would react with another molecule of TEG to give higher oligomers. In the case of PEG, dehydration reaction leads to modest to poor yield of 1,4-dioxane suggesting a poor interaction with the actual catalyst sites.

3.2. Temperature programmed desorption of ammonia(TPD) over HZSM-5 catalysts

Fig. 2 shows TPD profiles of HZSM-5 catalysts with NH_3 adsorbed at 100°C, 200°C and 350°C. For HZSM-5 with NH_3 adsorbed at 100°C the low temperature peak was observed at 218°C whereas the high temperature peak was observed at 440°C. The low temperature peak indicates weak acidic sites where ammonia molecules are weakly adsorbed. On the other hand the high temperature peak corresponds to strong acid sites present on the catalyst. The entire amount of ammonia which was desorbed between 100°C and 550°C was 0.39 mmol of NH_3/g catalyst (I-HZSM-5). The HZSM-5 catalysts with NH_3 adsorbed both at 200°C and 350°C predominantly show up peak with strong acidic sites only in the TPD profiles.

Fig. 3 depicts the TPD profile of HZSM-5 having varying amounts of acid sites per gram
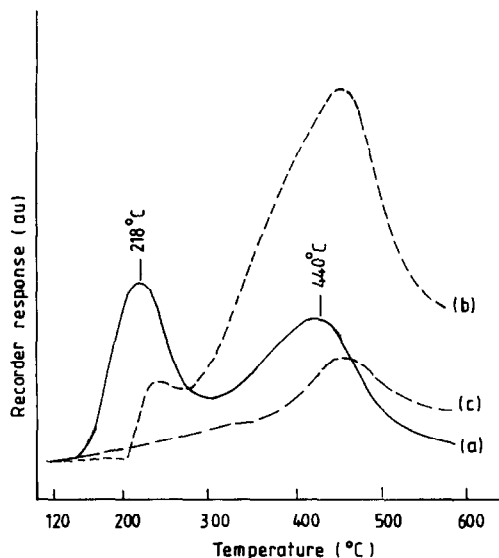
Fig. 2. Temperature programmed desorption profiles of I-HZSM-5 and NH$_3$ adsorbed I-HZSM-5. (a) I-HZSM-5 with NH$_3$ adsorbed at 100°C, (b) I-HZSM-5 with NH$_3$ adsorbed at 200°C, (c) I-HZSM-5 with NH$_3$ adsorbed at 350°C.

of catalyst (density of acid sites). All the HZSM-5 catalysts have similar TPD profiles except in the case of III-HZSM-5 which does not show any strong acid sites. The concentration of NH$_3$ desorbed up to 310°C was considered as amount of weak acid sites and NH$_3$ coming out above 310°C was taken as strong acid sites. The values thus estimated are given in Table 3.
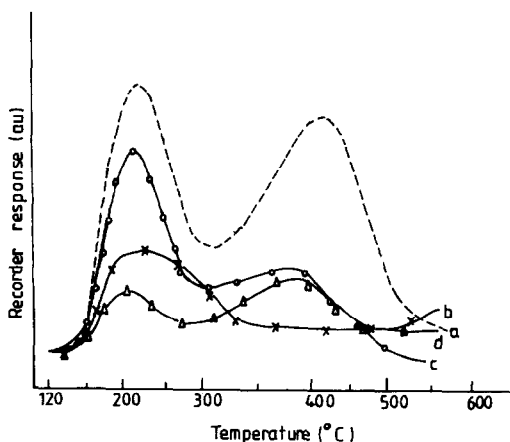

Fig. 3. Temperature programmed desorption profiles of (a) II-HZSM-5, (b) III-HZSM-5, (c) IV-HZSM-5, (d) V-HZSM-5.

Table 3
Estimation of acid sites by TPD measurement

No.	ZSM-5 catalyst	Si/Al	Total NH$_3$ desorbed/ g-cat (mmol)	Weak acid [a] sites/g (mmol)	Strong acid [b] sites/g (mmol)
1	I-HZSM-5	40	0.39	0.195	0.195
2	II-ZSM-5	22	0.63	0.28	0.35
3	III-HZSM-5	280	0.011	0.011	–
4	IV-HZSM-5	30	1.340	0.390	0.950
5	V-HZSM-5	100	0.194	0.087	0.107

[a] Weak acid sites/g = amount of NH$_3$ desorbing up to 310°C in TPD.

[b] Strong acid sites/g = amount of NH$_3$ desorbing from 310°C to 550°C in TPD.

3.3. Role of acidic sites

In order to identify the type of sites that are responsible for cyclodehydration of DEG and derivatives the following experiments have been carried out. NH$_3$ was adsorbed on two I-HZSM-5 catalyst samples one at 200°C and another at 350°C. These samples were used as catalyst at 205°C. The TPD profiles of these catalysts are given in Fig. 2. In the case of I-HZSM-5 with NH$_3$ adsorbed at 200°C (Fig. 2b) the conversion of DEG was only 8.5% with 89% selectivity to 1,4-dioxane in a 2 h run. Here all the strong acidic sites are blocked by NH$_3$ as NH$_4^+$ ions whereas in the case of zeolite with NH$_3$ adsorbed at 350°C (Fig. 2c) a fraction of strongly acidic sites are available. On these sites the cyclodehydration takes place. It is observed that III-HZSM-5 catalyst, which does not have any strong acidic sites, does not give any dioxane when reacted with DEG. This clearly proves that the weakly acidic sites have no activity while the strongly acidic sites are mainly responsible for cyclodehydration of DEG. Similar observation is noticed with diethylene glycol monomethyl ether. It is also important to note that selectivity to 1,4-dioxane is higher in the case of I-HZSM-5 with NH$_3$ adsorbed at 350°C compared to I-HZSM-5 catalyst. This suggests that in the presence of strongly acidic sites with NH$_3$ desorbing above 350°C both cyclodehydration to 1,4-dioxane and further cleavage of ether

is most probable. It is known that in presence of acidic sites cleavage of cyclic ethers to aldehydes and olefins [22,23] and ring opening of epoxides [24–26] takes place.

Cyclodehydration of DEG was carried out with HZSM-5 having different density of acid sites. Both activity and efficiency of the zeolites at 2 h reaction are plotted against the density of strongly acidic sites (Table 3) of the zeolites (Fig. 4). It is clear from the plot that as the density of strongly acidic sites increases the activity of zeolite for formation of 1,4-dioxane increases. On the other hand the efficiency vs. density of the strongly acidic sites plot shows the opposite behaviour. It is apparent from this study that the strongly acidic sites are responsible for the cyclodehydration of DEG and the population of the strongly acidic sites per gram of the zeolite is a critical factor. At lower density of the sites cyclodehydration is the dominant factor. It is observed that II-HZSM-5 and IV-HZSM-5 catalysts do not give any 1,4-dioxane after 4 h and 3 h reaction, respectively, due to deactivation whereas I-HZSM-5 gives 1,4-dioxane even after 12 h reaction. This suggests that both cyclodehydration of DEG and deactivation of zeolite catalysts take place on strongly acidic sites simultaneously. Two likely explanations for deactivation of catalysts are structural changes with time and build-up of coke deposit on the catalyst active sites [27].

Fig. 5. Possible reaction scheme for the cyclodehydration of DEG.

Temperature programmed oxidation of used I-HZSM-5 shows that CO_2 is formed suggesting there is coke on the catalyst. Most of this coke is oxidised in the region 200–450°C. It is estimated that 5.2% coke is deposited on the I-HZSM-5 catalyst after 12 h reaction.

Cyclodehydration of DEG on HZSM-5 leads to 1,4-dioxane and not 2-methyl 1,3-dioxolane. The most probable mechanism involves the protonation of OH group of DEG by the strongly acidic Brønsted site, elimination of water to give a highly reactive surface alkoxide species [28], followed by cyclization and elimination of product as depicted in Fig. 5.

4. Experimental procedure

4.1. Materials

Ethylene glycol and DEG were obtained from Gloxo, India. TEG and diethylene glycol dimethyl ether were supplied by BDH, England. PEG 200, 300, 400 and 600 were used as received from E. Merck, India. Diethylene glycol monomethyl ether and Montmorillonite K10 were purchased from Fluka, Switzerland and used without further purification.

All the samples of ZSM-5 were synthesised by the hydrothermal crystallization of an alkaline gel system comprising of Na_2O–SiO_2–
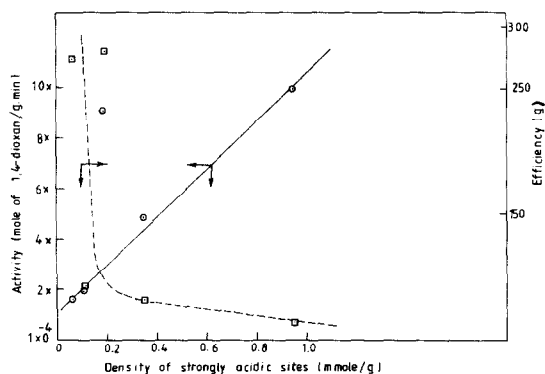

Fig. 4. Effect of the density of strongly acidic sites on activity and efficiency of zeolites on formation of 1,4-dioxane. (○) activity, (□) efficiency.
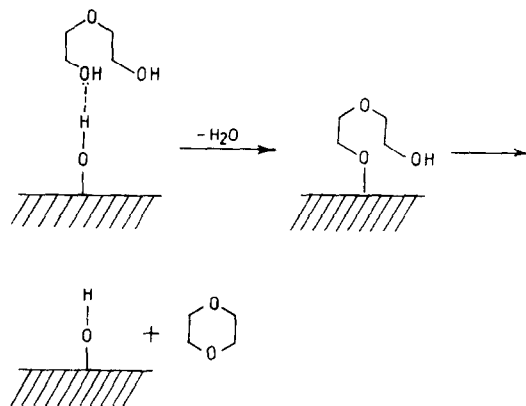
Al_2O_3–TEBA–H_2O (TEBA = triethyl n-butyl ammonium hydroxide) system under autogenous pressure as per standard synthetic procedure [29]. The samples were converted into the acid (H^+) form via NH_4^+ ion exchange and calcination at 550°C. SiO_2/Al_2O_3 ratio was varied by varying appropriate quantity of Al_2O_3 in the synthesis gel. All HZSM-5 zeolites are > 95% crystalline in nature. $AlPO_4$, HY and Cu–NaY [30] zeolites were all synthesized as per the literature methods.

4.2. TPD study

The NH_3 temperature programmed desorption (TPD) study was carried out using a heating rate of 10°C/min. Prior to TPD, 50 mg of the sample was placed in a pulse micro reactor and calcined at 540°C. Then a series of 0.5 ml NH_3 pulses were given at 100°C. These pulses were continued until no more uptake of NH_3 was observed. Helium was then flown over the sample at a flow rate of 30 ml/min followed by the start of temperature programming. The desorbed NH_3 was detected by a thermal conductivity detector and the TPD profile was drawn.

4.3. Reaction procedure

The cyclodehydration of DEG and its derivatives was carried out using a microdistillation unit in an oil bath. In a typical run 0.5 g HZSM-5 catalyst was taken in a 25 ml round bottom flask and 10 ml of DEG was added. The mini distillation unit was assembled and the oil bath was heated to 205°C. The temperature of the condenser was kept at 10°C by passing ice cold water through its jacket. The 1,4-dioxane and water formed in the reaction distilled over and collected in the receiver.

4.4. Analytical methods

The yield of 1,4-dioxane was followed by analyses of the products and residue in the flask by a Shimadzu 7AG gas chromatograph fitted with a flame ionization detector. The samples were analysed on a 2 metre column having 1.5% OV-17 on Chromosorb W at 50–200°C under a temperature programme of 2–8–4 (min –°C– min). Quantification was done by internal standard method. Formation of 1,4-dioxane was further confirmed by mass, ^1H and ^{13}C NMR spectroscopic analyses.

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