

# Cyclodehydration of diethylene glycol (DEG) catalyzed by clay mineral sepiolite

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## Abstract

Clay mineral sepiolite exhibited high selectivity for the catalytic conversion of diethylene glycol (DEG) into 1,4-dioxane. The selectivity for the 1,4-dioxane formation depended on weight hourly space velocity (WHSV) and the tunnel structure of sepiolite. When an excess DEG was supplied over the adsorption capacity of the tunnels in sepiolite, the selectivity for 1,4-dioxane formation from DEG decreased and by-products formation increased. These results indicate that cyclodehydration of DEG takes place in the internal space of the intracrystalline tunnels of sepiolite and by-products formation occurs on the outer surface of sepiolite. The Mg(II) ion along the tunnel wall of sepiolite acts as an active site for the cyclodehydration. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Sepiolite is a fibrous clay mineral of magnesium silicate and its ideal formula is  $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4 \cdot 4\text{H}_2\text{O} \cdot n\text{H}_2\text{O}$  ( $\text{Sep}4\text{H}_2\text{O}n\text{H}_2\text{O}$ ) where  $4\text{H}_2\text{O}$  and  $n\text{H}_2\text{O}$  represent the coordinated water molecules and zeolitic water molecules, respectively [1]. Sepiolite is composed of lath-like crystallites with long double silica chains running parallel to the fiber axis (*c*-axis). The upper and lower parts of each double chain are joined together by a layer of  $\text{MgO}_6$  octahedra, and to other chains by shared

oxygen atoms along each edge as shown in Fig. 1. Accordingly, the parallel-piped intracrystalline tunnels, of which the effective cross section is  $1.1 \times 0.4 \text{ nm}^2$ , exist along the fiber axis (*c*-axis) in sepiolite. The octahedral coordination of the Mg(II) ions along the tunnel wall is completed by a coordination of two water molecules. A half of the coordinated water molecules in sepiolite dehydrates reversibly at about 513 K [2] and transformed to sepiolite dihydrate ( $\text{Sep}2\text{H}_2\text{O}$ ). The octahedral coordination of Mg(II) ion along the tunnel wall in  $\text{Sep}4\text{H}_2\text{O}$  would be distorted by a transition of  $\text{Sep}4\text{H}_2\text{O}$  to  $\text{Sep}2\text{H}_2\text{O}$  via an unstable five coordination [3]. Therefore, the tunnels of sepiolite can provide both dehydration active site and

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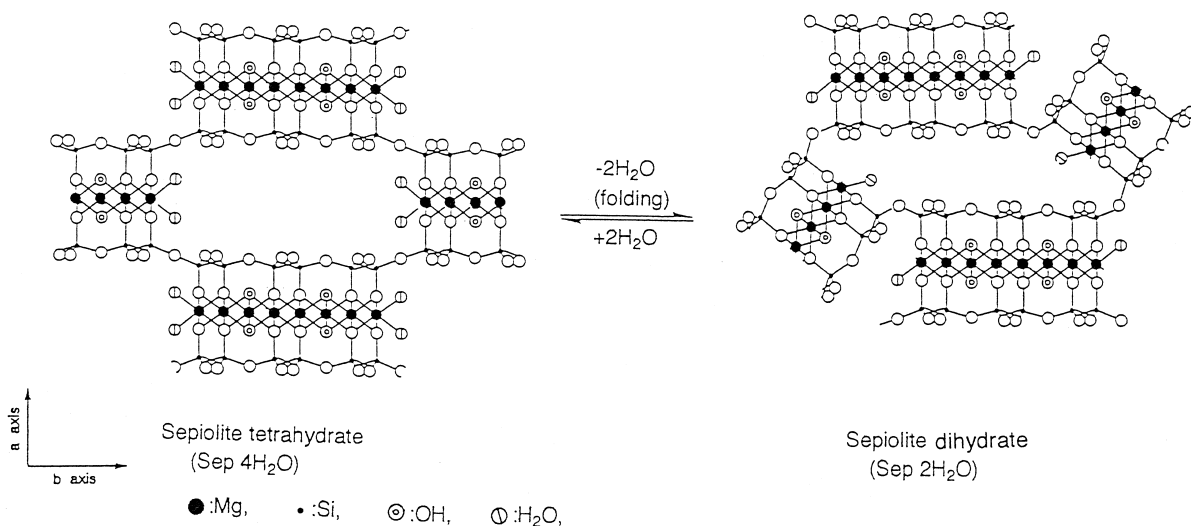


Fig. 1. Structures of sepiolite tetrahydrate (Sep4H<sub>2</sub>O) and sepiolite dihydrate (Sep2H<sub>2</sub>O).

the restricted space for shape selective reactions due to the unstable coordination of the Mg(II) ion along the tunnel wall. Sepiolite have a possibility to use as a shape selective dehydration catalyst.

In this paper, the cyclodehydration of diethylene glycol (DEG) was carried out by using sepiolite as a shape selective catalyst.

## 2. Experimental

Natural sepiolite (Vallecas, Spain) was used for the catalytic cyclodehydration of DEG. The chemical composition of the catalyst is SiO<sub>2</sub> = 62.05, Al<sub>2</sub>O<sub>3</sub> = 1.15, TiO<sub>2</sub> = 0.11, CaO = 0.51, MgO = 23.80, Na<sub>2</sub>O = 0.30, K<sub>2</sub>O = 0.65 and H<sub>2</sub>O = 10.90%. The reactions were carried out in a fixed-bed continuous flow reactor at designated temperature. The granular sepiolite catalyst of 32–60 mesh (1 g) was packed into a Pyrex glass tube (i.d. = 8 mm). As the tunnel size of sepiolite changed with calcining temperature, the catalyst was preheated at the reaction temperature for 2 h in a nitrogen stream prior to the use. Dithylene glycol was kept in an evaporator maintained at constant temperature and introduced into the catalyst bed with nitrogen

gas as the carrier at the designated weight hourly space velocity (WHSV). The reaction products were analyzed by an FID gas–liquid chromatograph (Shimazu-4A) equipped with Porapack Q. Acidities of sepiolite samples were measured by *n*-butylamine titration method using Hammett indicator [4]. Adsorption of N<sub>2</sub> at 77 K was carried out using a conventional BET apparatus.

## 3. Results and discussion

### 3.1. Reaction path

The catalytic conversion of DEG was studied by using sepiolite as a catalyst. Fig. 2 shows a typical example for the time course of the DEG conversion at 533 K and WHSV 0.2 h<sup>-1</sup>. The main product in the reaction was 1,4-dioxane. Acetaldehyde, crotonaldehyde, ethylene glycol and ethanol were produced as by-products. In the initial stage of the reaction, the yield of dioxane was 100%. Increasing of the time on stream, by-products such as acetaldehyde, crotonaldehyde, ethylene glycol and ethanol were produced with a decrease of dioxane formation. After 150 min on stream, a decrease of a selectivity for dioxane formation were observed with a significant deactivation of the catalyst. After

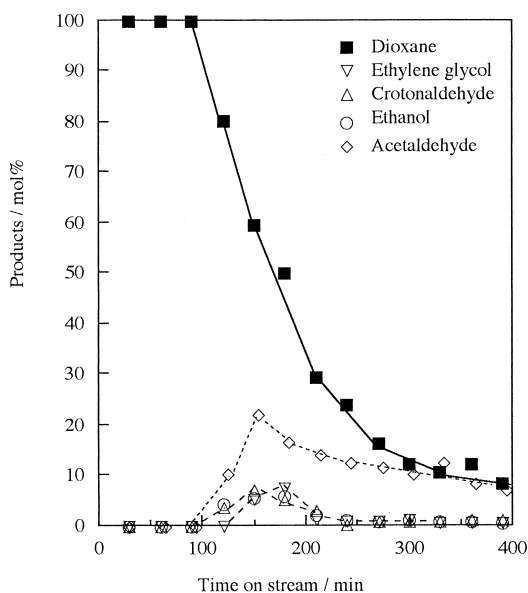


Fig. 2. Reaction path. The reaction was carried out in a fixed bed continuous-flow reactor using 1 g of sepiolite at WHSV  $0.1 \text{ h}^{-1}$  and 553 K.

performing the run, the catalyst was heated in an oxygen stream at 673 K to calculate amount of the carbon deposition on the catalyst. The  $\text{CO}_2$  gas was trapped and was followed a quantitative analysis. The deposited carbon calculated from the carbon dioxide evolution was at most 3% in each run.

### 3.2. Effect of the space velocity

The reaction was carried out at various space velocities. The selectivity for 1,4-dioxane formation is plotted against WHSV in Fig. 3. The selectivity for 1,4-dioxane formation and the yield of 1,4-dioxane decreased with an increase of WHSV. A steep drop of the selectivity occurred above  $\text{WHSV } 0.32 \text{ h}^{-1}$ .

After 0.3 g or 0.4 g DEG was flowed at various WHSV values, the product was collected and analyzed. The results are summarized in Table 1. Both yield and selectivity were lower at  $\text{WHSV } 0.1 \text{ h}^{-1}$  than  $0.2 \text{ h}^{-1}$ . The activity and selectivity for 1,4-dioxane formation fell again when the WHSV exceeds  $0.2 \text{ h}^{-1}$ . In both cases, the optimum WHSV for

1,4-dioxane formation was  $0.2 \text{ h}^{-1}$ . When the WHSV is too small, the reactant contacts with the catalyst for a long time. As shown in Table 1, the selectivity for 1,4-dioxane formation was higher at  $\text{WHSV } 0.2 \text{ h}^{-1}$  than  $0.1 \text{ h}^{-1}$ . The results mean that the by-products are produced by decomposition of 1,4-dioxane for too long contact with the catalyst.

When the excess DEG for the adsorption capacity of the tunnels of sepiolite is supplied to the reactor, the reaction should occur not only in the inner space of the tunnel but also on the outer surface of the tunnels of sepiolite. Increases of the by-products with an increase of WHSV depend on an increase in the outer surface reaction on the catalyst. The decreases of the yield and the selectivity at higher WHSV provide an evidence that the cyclodehydration of DEG takes place in the inner space of the tunnels of sepiolite and the by-products formation occurs on the outer surface of sepiolite at the high WHSV.

To investigate the contribution of the diffusion process, experiments were carried out in reaction tubes of various diameters packed with 1 g of sepiolite and the reactant was supplied at  $\text{WHSV } 0.20 \text{ h}^{-1}$ .

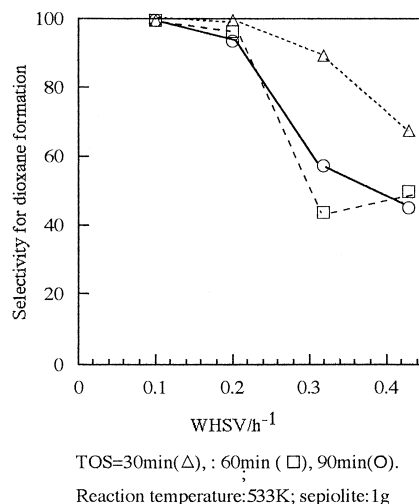


Fig. 3. Relation between WHSV and selectivity for 1,4-dioxane formation.

Table 1

The effect of WHSV on the yield and the selectivity of dioxane (DO) at different amounts of the reacted DEG

WHSV (h <sup>-1</sup> )	Added DEG 0.3 g		Added DEG 0.4 g		Selectivity of dioxane (percent) Added DEG	
	DO yield (g)	TOS (min)	DO yield (g)	TOS (min)	0.3 g	0.4 g
0.10	0.26	180	0.28	240	86	70
0.20	0.29	100	0.38	130	98	94
0.32	0.23	43	0.26	60	77	66
0.43	0.24	30	0.25	40	81	63

The reactions were carried out on 1 g of sepiolite at 533 K.

The superficial gas velocity ( $v$ ) was calculated by the following equation:

$$v = \frac{\text{flow rate of DEG}}{\text{cross section of the reaction tube}}$$

Results are shown in Fig. 4. In each reaction, no DEG was detected in the initial stage of the reaction. The selectivity for 1,4-dioxane formation showed a maximum at 0.03 m/min of superficial velocity. In lower superficial velocity (the gas was contacted with short length and large cross section of the catalyst), the selectivity for 1,4-dioxane was low and six components of by-products were contained in the product. A small amount of acetic acid and crotonaldehyde were produced in the product at only the initial

stage of the reaction. Crotonaldehyde and acetic acid were contrarily not observed on the reaction of higher superficial velocity. The production of acetic acid may be attributed to the reaction between adsorbed oxygen and acetaldehyde produced on the outer surface of the tunnels. When the reaction carried out at WHSV 0.74 h<sup>-1</sup>, acetic acid was observed though it was not observed in the reaction of WHSV 0.21 h<sup>-1</sup>. The results also indicate that the formation of acetic acid occurred on the outer surface of the tunnels of sepiolite. In higher superficial velocity, the selectivity for 1,4-dioxane formation decreased. The result means that a diffusion of DEG on the inner surface of the tunnels of sepiolite is an important process for the 1,4-dioxane formation. The rate determining step of the 1,4-dioxane formation from DEG should be a diffusion process of DEG into the tunnels of sepiolite.

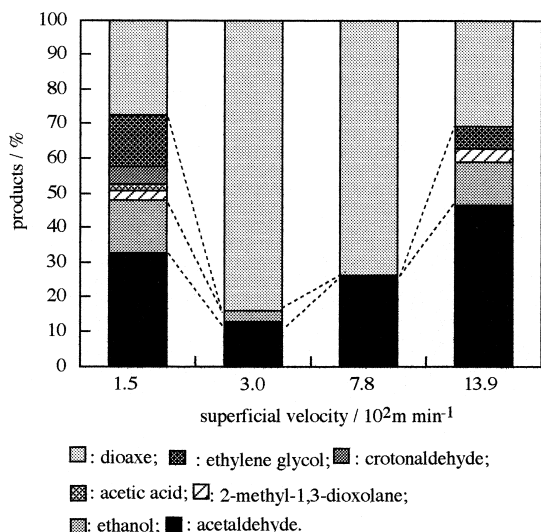
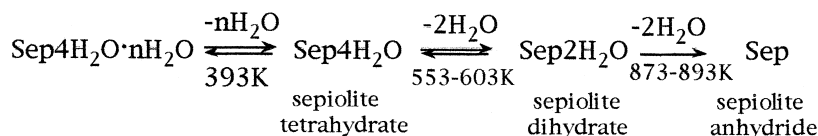


Fig. 4. Effect of the superficial velocity on the distribution of products. Catalyst: 1 g; reaction temperature: 573 K; TOS: 30 min; WHSV: 0.2 h<sup>-1</sup>.

### 3.3. Temperature dependency of the reaction

Sepiolite calcined at different temperatures has a possibility to exhibit the different activity and selectivity for the cyclodehydration of DEG, because the cross section of the tunnels and the coordination state of the Mg(II) ion along the lattice of the tunnel wall in sepiolite are changed by calcining temperature. To investigate a relation between the catalytic properties and hydration state of sepiolite, a thermal behavior of the sepiolite was measured. It has been reported that the dehydration of water molecules con-



Scheme 1.

tained in sepiolite takes place stepwise [2,3]. The TG-DTA profile of the sepiolite used in our experiments showed that dehydration of water molecules in sepiolite occurred stepwise. Zeolitic water was dehydrated near 373 K. The transition of sepiolite tetrahydrate (Sep4H<sub>2</sub>O) to dihydrate (Sep2H<sub>2</sub>O) took place in the temperature range from 553 K to 603 K in our sample. The dehydration of Sep2H<sub>2</sub>O took place in the range from 873 K to 893 K and sepiolite anhydride (Sep) was produced. The result can be represented by Scheme 1.

Detail investigation on porosity and surface area of sepiolite from Spain has been reported by Rodoriguez-Reinoso et al. [5]. Similar results were obtained in our sample from Spain. Drastic decrease of the surface area was observed on the transition temperature of Sep4H<sub>2</sub>O to Sep2H<sub>2</sub>O as shown in Fig. 5. Surface area of the sepiolite in this study was slightly smaller

than that of their sample (the surface area of the sample heating at 383 K was 321 m<sup>2</sup>/g). This difference results from the difference in particle size. Rodoriguez-Reinoso et al. reported that a sharp maximum peak of pore distribution existed around 1.5 nm diameter, whereas higher temperatures led to a broad distribution of pore diameter around 2, 2.8 and 4.5 nm. In this study, the pore volume up to 1.5 nm diameter of the sepiolite evacuating at 393 K was 70 ml/g. Calcining the sample at 473 K, 533 K and 583 K, the pore volume of sepiolite decreased to 62 ml/g, 50 ml/g and 25 ml/g, respectively.

The reactions have been carried out at different temperatures using the catalyst calcined at the reaction temperature to study the effects of the reaction temperature and the results are shown in Fig. 6. The 1,4-dioxane yield was nearly equal to 100% up to 543 K. On the other hand, a drastic decrease of the 1,4-dioxane yield was observed above 553 K. The selectivity for 1,4-dioxane formation also decreased above 553 K. After 30 min on stream at 553 K, DEG

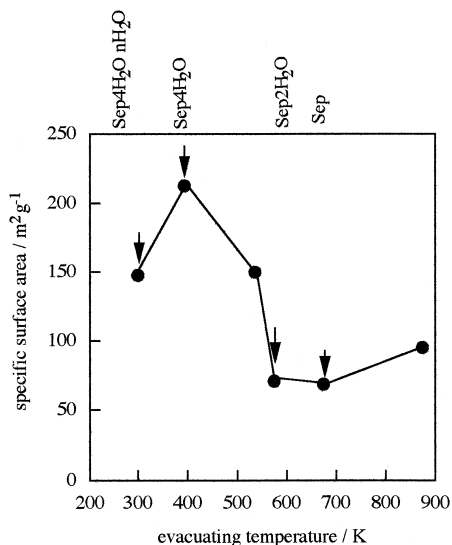


Fig. 5. Relation between the surface area of sepiolite and its calcining temperature.

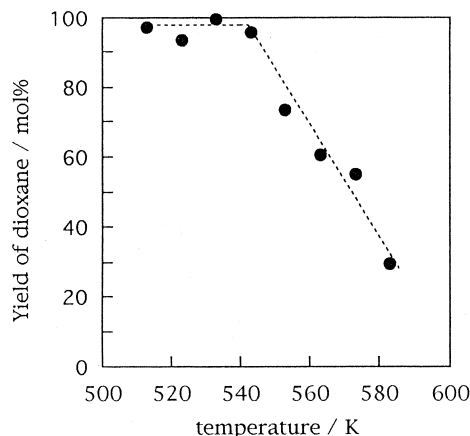


Fig. 6. Temperature dependency of 1,4-dioxane yield. Catalyst: 1 g; TOS: 30 min; WHSV: 0.2 h<sup>-1</sup>; reaction temperature: 553 K.

converted to 72.7 mol% of 1,4-dioxane and 27.3 mol% of acetaldehyde, although no DEG was contained in the product. In the higher temperature, a very small amount of 2-methyl-1,3-dioxolane was contained in the product in addition to the product produced at lower temperature. The result indicates that the isomerization of 1,4-dioxane takes place at high temperature. As shown in Fig. 1, the structural change of the tunnels in sepiolite occurs with dehydration of Sep4H<sub>2</sub>O to Sep2H<sub>2</sub>O. The first step is the dehydration of the zeolitic water without the structural change of the tunnels in sepiolite (Scheme 1). The second step is a reversible transition from/to sepiolite tetrahydrate (Sep4H<sub>2</sub>O) to/from sepiolite dihydrate (Sep2H<sub>2</sub>O) by the dehydration/hydration of two coordinated water molecules. Nagata et al. [2] and Serna et al. [3] reported that the crystals folded in the second step by the change of the coordination state of Mg(II) ion along the tunnel wall with the dehydration of the water coordinated to the Mg(II) ion (Fig. 1). Since the tunnel size of Sep2H<sub>2</sub>O is smaller than that of Sep4H<sub>2</sub>O, DEG would be difficult to enter into the tunnel of Sep2H<sub>2</sub>O. Therefore, the drastic decreases of the activity and selectivity for 1,4-dioxane formation from DEG above 553 K should be attributed to the structural change of sepiolite with the dehydration of the coordinated water. From these results, the drastic decreases of the catalytic activity and selectivity for the reaction above 553 K are closely related to the dehydration of the coordinated water molecule in sepiolite.

### 3.4. XRD

XRD patterns of sepiolite were measured at different temperature using a high temperature XRD measurement apparatus. The results are shown in Fig. 7. A large peak at  $d = 1.20$  nm due to  $d_{110}$  of Sep4H<sub>2</sub>O was observed. Peaks  $d = 0.45$  and  $0.43$  nm were also assigned to the peaks of Sep4H<sub>2</sub>O (Fig. 7a). After heating the sample at 553 K, an intensity of the peak at

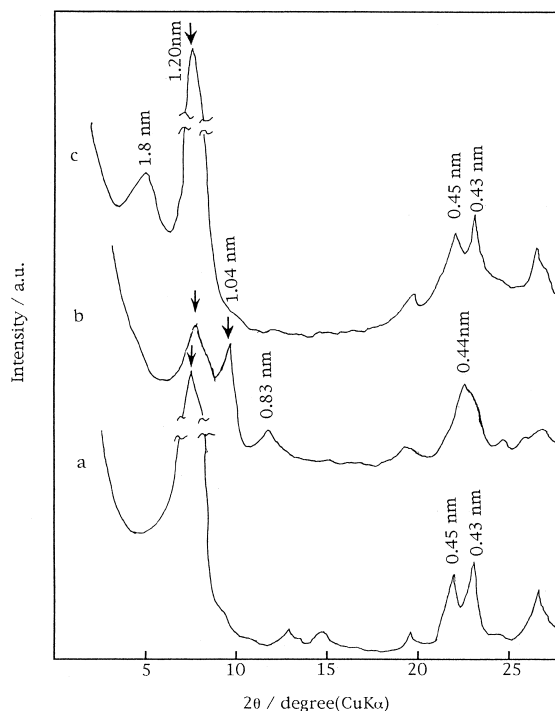


Fig. 7. XRD patterns of sepiolite before and after use as the catalyst for cyclodehydration of DEG. (a) Sep4H<sub>2</sub>O, (b) Sep2H<sub>2</sub>O obtained by evacuating Sep4H<sub>2</sub>O at 553 K for 1 h. (c) Sep2H<sub>2</sub>O used to cyclodehydration of DEG at 553 K for 30 min.

$d = 1.20$  nm decreased and new peaks at  $d = 1.04$ ,  $0.83$  and  $0.44$  nm due to Sep2H<sub>2</sub>O appeared (Fig. 7b) [2]. After the catalytic reaction was carried out 553 K for 30 min, the XRD peak due to Sep2H<sub>2</sub>O was disappeared and the XRD pattern of Sep4H<sub>2</sub>O with a new peak at  $d = 1.8$  nm were reproduced (Fig. 7c). These results indicate that Sep2H<sub>2</sub>O is rehydrated with the water molecule produced by cyclodehydration of DEG and is transformed to Sep4H<sub>2</sub>O. A new peak at  $d = 1.8$  nm may be assigned to a peak due to intercalation of DEG or 1,4-dioxane into the inter-layer of sepiolite. Although it was reported that the space of the tunnels in sepiolite does not expand by the intercalation of ethylene glycol [6], the sample used in this study showed a small peak at  $1.4$  nm by ethyleneglycol intercalation. Since the crystallinity of the sepiolite used in our experiment is not so complete, the sepiolite contains partly layered phase as like as

## REACTION PATH

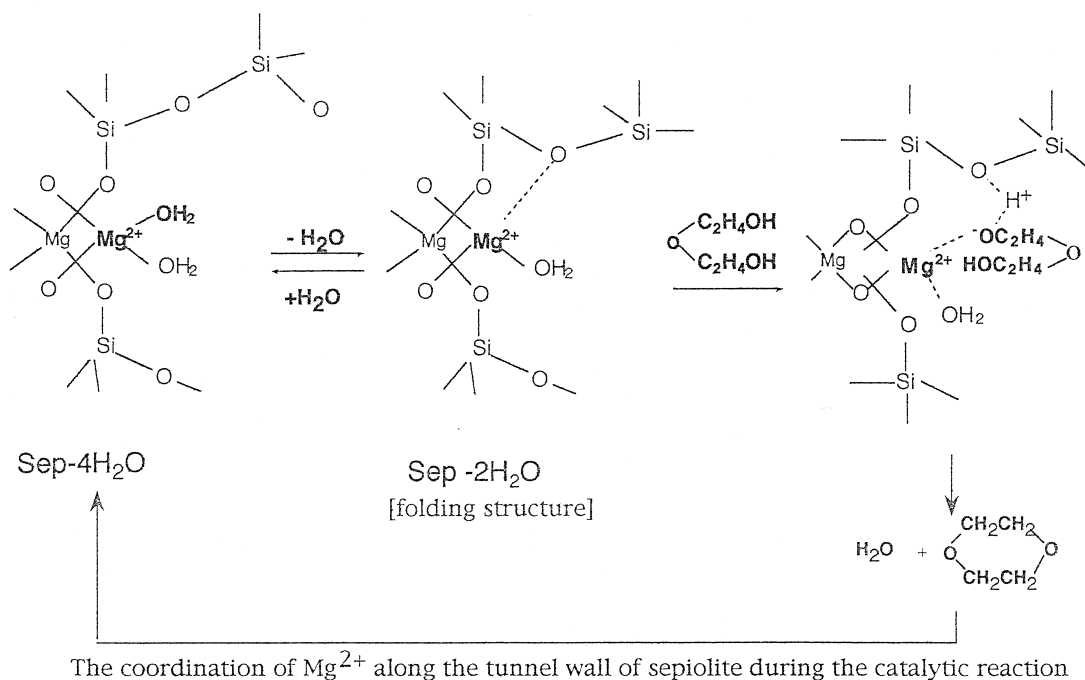


Fig. 8. Reaction path.

a clay mineral aquacryptite [7,8]. Therefore the new peak may be attributed to the intercalation of DEG into the defective lattice in the sepiolite. Similar result was obtained in catalytic conversion of 1,4-butandiol to tetrahydrofuran in our unpublished data. A reaction process is shown in Fig. 8. When the  $\text{Mg}(\text{II})$  ion along the tunnel wall of sepiolite is used as an active site for the reaction, DEG coordinates to  $\text{Mg}(\text{II})$  ion along the tunnel wall to complete six coordina-

tion and then cyclodehydration occurs. The catalyst is changed from  $\text{Sep}2\text{H}_2\text{O}$  to  $\text{Sep}4\text{H}_2\text{O}$  with the hydration of the water molecule produced by the cyclodehydration of DEG as shown in Fig. 8. Supposing that one water molecule coordinated to the  $\text{Mg}(\text{II})$  ion along the tunnel wall in  $\text{Sep}4\text{H}_2\text{O}$  substitutes with DEG as shown in Fig. 8, a peak at  $d = 1.80$  nm may be assigned to an intermediate formed by the substitution of the coordinated water molecule with

Table 2

Distributions of the products of the catalytic conversion of DEG over sepiolite and magnesium silicate

Catalyst	Product (%)					
	DEG	1,4-Dioxane	$\text{CH}_3\text{CHO}$	Ethanol	Crotonaldehyde	Ethylene glycol
Sepiolite <sup>a</sup>	44.9	22.4	16.4	3.0	10.2	3.9
Sepiolite <sup>b</sup>	49.5	20.3	14.8	2.4	11	3.0
$\text{MgO-SiO}_2$ (1:2) <sup>c</sup>	47.0	5.9	14.5	11.7	10.5	10.1

Reaction temperature, 573 K.

WHSV,  $0.20 \text{ h}^{-1}$ .TOS: <sup>a</sup> = 150 min; <sup>b</sup> = 180 min; <sup>c</sup> = 30 min.

Table 3  
Acidity of sepiolite

Sample	Acidity (mmol/g)				
	$pK_a = +6.8$	$pK_a = +3.3$	$pK_a = +2.0$	$pK_a = +1.5$	$pK_a = -1.5$
Sep4H <sub>2</sub> O · nH <sub>2</sub> O	0.47	0.10	0.02	0	0
Sep4H <sub>2</sub> O	0.71	0.33	0.12	0.06	0.02
Sep2H <sub>2</sub> O	1.57	0.24	0.22	0.11	0.09
Sep	0.22	0.07	0.03	0.02	0

DEG. It has been reported that the dehydrated Mg(II) ion acts as an active site by the coordination of the reactant instead of the coordinated water in the catalytic conversion of ethanol to 1,3-butadiene [9–11]. The cross section of tunnel in sepiolite is sufficient to admit DEG into the tunnel. The relation between WHSV and the selectivity for 1,4-dioxane formation suggests that cyclodehydration of DEG takes place in the inner space of the tunnels of sepiolite. Therefore, we propose a reaction mechanism as shown in Fig. 8. DEG coordinates to the Mg(II) along the tunnel wall by a substitution of the coordinated H<sub>2</sub>O, the cyclodehydration of DEG takes place. Then the coordination of Mg(II) is returned to octahedral by the water molecule which is produced by the cyclodehydration of DEG.

### 3.5. Roles of tunnels

To investigate the contribution of the tunnels of sepiolite, the reaction carried out on magnesium silicate. Magnesium silicate was prepared by calcining the mixture of SiO<sub>2</sub> and Mg(OH)<sub>2</sub> in air at 673 K for 2 h. The molar ratio of SiO<sub>2</sub>/Mg(OH)<sub>2</sub> has been adjusted to 2 which is equal to the Si/Mg molar ratio of sepiolite. As the catalytic activity of magnesium silicate was lower than that of sepiolite, the distribution of the product produced on sepiolite was compared with that on magnesium silicate at similar extent of DEG conversion. As shown in Table 2, the selectivity for 1,4-dioxane formation was significantly larger on sepiolite than on magnesium silicate. The result indicates that the tunnel of

sepiolite plays an important role for 1,4-dioxane formation from DEG.

### 3.6. Role of acid site

Acidic sites are responsible for the cyclodehydration of DEG [12–14]. The weakly acidic sites have no activity while the strongly acidic sites are mainly responsible for cyclodehydration of DEG [13]. Acidities of various sepiolite hydrates were measured by Benesi's method [4]. The results are shown in Table 3. Acid strength of sepiolite samples distributed in the range from  $pK_a = -1.5$  to  $+6.8$ . The acidity of the Sep2H<sub>2</sub>O was larger than that of Sep4H<sub>2</sub>O in the all acid strength ranges. However, the catalytic selectivity and activity for 1,4-dioxane formation from DEG was larger Sep4H<sub>2</sub>O than Sep2H<sub>2</sub>O. Therefore, in this case, the structure of sepiolite rather than the acidic property contributes to the catalytic property.

## References

- [1] K. Brauner, A. Preiginger, *Tcherm. Miner. Petro. Mittlgn.* 6 (1956) 120.
- [2] M. Nagata, S. Shimoda, T. Sudo, *Clays Clay Miner.* 22 (1974) 285–293.
- [3] C. Serna, J.L. Ahlriches, J.M. Seratosa, *Clays Clay Miner.* 23 (1975) 452.
- [4] H.A. Benesi, *J. Am. Chem. Soc.* 78 (1956) 5490.
- [5] F. Rodoriguez-Reinoso, A. Ramirez-Saenz, J.D.C. De Lopez-Gonzalez, C. Valenzuela-Calahorro, L. Zurita-Herrera, *Clay Miner.* 16 (1981) 315.
- [6] R. Otsuka, S. Shimoda, K. Shimosaka, H. Nagata, Y. Shinohara, M. Shimizu, T. Sakamoto, *J. Clay Sci. Soc., Japan* 32 (1992) 154.



- [7] S. Shimoda, Clay Sci. 2 (1964) 8.
- [8] S. Shimoda, Clay Sci. 2 (1965) 138.
- [9] Y. Kitayama, A. Michishita, J. Chem. Soc. Chem Commun. (1981) 401.
- [10] Y. Kitayama, T. Hoshina, K. Kimura, T. Asakawa, Proc. 8th Intern. Cong. Catal., Vol. 5, 1984, 647.
- [11] Y. Kitayama, A. Abe, J. Chem. Soc. Jpn. (1989) 1824.
- [12] D. Kotkar, P.K. Ghosh, J. Chem. Soc. Chem. Commun. (1986) 650.
- [13] A. Wali, S.M. Pillai, S. Unnikishnan, S. Satish, J. Mol. Catal. A 109 (1996) 149.
- [14] D.A. Olah, A.P. Fung, R. Malhotra, Synthesis (1981) 474.