

New method of production of vinyl ether by vapor phase intramolecular dehydration of glycol ether over solid catalysts

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Abstract

We found that the intramolecular dehydration of glycol ether (2-alkoxyethanol or 2-aryloxyethanol) to vinyl ether (alkyl vinyl ether or aryl vinyl ether) occurs when glycol ether is made contacted with metal oxide catalysts in the vapor phase. The catalytic performance of SiO₂ catalyst alone was very low. Both the conversion of 2-alkoxyethanol and the selectivity for alkyl vinyl ether was markedly increased by the addition of cesium oxide to SiO₂.

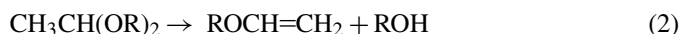
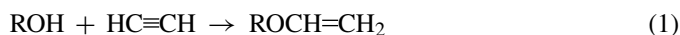
The high activity and selectivity are considered to be due to the presence of both weak acid sites and weak base sites on the modified SiO₂.
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Keywords: Alkyl vinyl ether; 2-alkoxyethanol; Dehydration; SiO₂; Alkali metal oxide-added SiO₂

1. Introduction

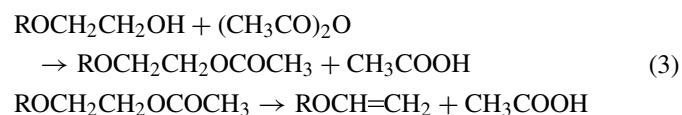
Alkyl vinyl ether is a useful reactive monomer, which is used principally for the production of polymers in the adhesives, paints, cosmetic chemicals and many other chemical products. Various kinds of alkyl vinyl ethers, such as methyl-, ethyl-, propyl-, butyl- and cyclohexyl-vinyl ether are industrially manufactured.

Two types of commercial processes of the alkyl vinyl ether production are well known. The first one is the reaction of alcohol with acetylene in the presence of strong alkali. This method is well known as a commercial process of alkyl vinyl ether production Eq. (1) [1]. The second one is the cleavage of acetal at high temperature in the presence of solid catalysts Eq. (2) [2].

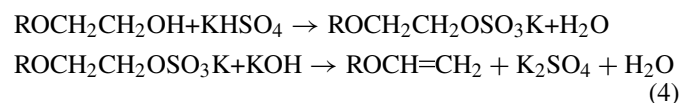


The synthesis methods of alkyl vinyl ether from 2-alkoxyethanol as the raw materials are also known. These methods include the

cleavage of acetate, which is prepared from 2-alkoxyethanol and acetic anhydride Eq. (3) [3].



The other method is the indirect dehydration of 2-alkoxyethanol in the presence of KHSO₄ and KOH in an aqueous solution. It can be understood that the 2-alkoxyethanol reacts with KHSO₄ to form its sulfuric acid ester and that then the ester is decomposed into the alkyl vinyl ether and K₂SO₄ by the action of KOH Eq. (4) [4].



We have reported the vapor phase intramolecular dehydration of *N*-(2-hydroxyethyl)-2-pyrrolidone to *N*-vinyl-2-pyrrolidone in the presence of alkali metal oxide-added SiO₂ catalyst [5,6].

We have also found a new useful method of the direct dehydration of glycol ethers (2-alkoxyethanol or 2-aryloxyethanol) to vinyl ethers (alkyl vinyl ether or aryl vinyl ether) by use of

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the alkali/SiO₂ catalyst Eq. (5) [7]. This report shows that the Cs₂O-added SiO₂ is an excellent catalyst for this dehydration, and describes the features of the catalyst.

We constructed the pilot plant and demonstrated this new production process in 1998.



2. Experimental

2.1. Preparation of catalysts

Metal oxides (SiO₂, ZrO₂, Al₂O₃, Nb₂O₅), SiO₂-containing mixed oxides (SiO₂-Al₂O₃, SiO₂-ZrO₂, SiO₂-Y₂O₃) and alkali (or alkaline earth) metal oxide-added SiO₂ were studied as the catalysts in this work.

2.1.1. Metal oxide catalysts

Metal oxides in the powder form were first kneaded with water to form slurries. The slurries were dried at 120 °C for 20 h to form solids. The obtained solids were crushed into particles of 9–16 mesh and calcined at 500 °C for 2 h in air. SiO₂ used was the SYLYSIA 350 (Fuji Silysia Chemical Ltd.) and the other oxides (ZrO₂, Nb₂O₅, Al₂O₃, WO₃, CeO₂, TiO₂, Bi₂O₃ and Sb₂O₃) were purchased from Tokyo Chemical Industry Co., Ltd. H-mordenite was a commercially available one.

2.1.2. SiO₂-containing mixed oxide catalysts

SiO₂ and hydroxides (or nitrates) of the pair elements were kneaded with water. Then, the catalysts were prepared in a similar manner to the metal oxide catalysts described above except that the calcination was conducted at a selected temperature in the range of 500–1000 °C.

2.1.3. Alkali metal or alkaline earth metal oxide-added SiO₂ catalysts

SiO₂ and hydroxides (or carbonates) of alkali or alkaline earth metals were kneaded with water. Then, the catalysts were prepared in a similar manner to the metal oxide catalysts described above.

2.2. Reaction procedures

The vapor phase dehydration was carried out in a fixed bed flow type reactor under atmospheric pressure. Pulverized catalysts (9–16 mesh, 5 cm³) were placed in a stainless steel reaction tube having an inside diameter of 10 mm, and heated to the reaction temperature in a molten salt bath. The reactant gas of five volume percent 2-alkoxyethanol in nitrogen was passed through the catalyst bed at gas hourly space velocity (GHSV) of 500–1500 h⁻¹. Reaction was carried out in the temperature range of 380–430 °C. After the reactant gas was fed for 1 h, the products were analyzed by gas chromatography.

2.3. Measurement of acid and base strengths of catalysts

Acid and base strengths of the catalysts were measured by the indicator method [8]. Indicators used were *p*-dimethylaminoazobenzene (p*K*_a = +3.3), 4-phenylazo-1-naphthylamine (p*K*_a = +4.0), neutral red (p*K*_a = +6.8), phenolphthalein (*K*_{BH} = +9.4) and 2,4,6-trinitroaniline (*K*_{BH} = +12.2).

2.4. Adsorption and desorption behavior of reactants on catalyst

The catalyst (50 mg) was fixed by quartz wool in the center of a stainless steel-made reaction tube having an inside diameter of 4 mm and a length of 10 cm. The nitrogen gas was passed through the catalyst kept at 200 °C. A constant quantity (0.3 μl) of the reagent was injected successively into the nitrogen stream ahead of the catalyst. The outlet gases were monitored by mass spectrometry.

3. Results and discussion

3.1. Catalytic performance of various metal oxides

Table 1 shows the conversions of 2-ethoxyethanol (ethyl glycol ether; EGE) and the selectivities for ethyl vinyl ether (EVE) over the metal oxides, SiO₂-containing mixed oxides and alkali or alkaline earth oxide-added SiO₂ in the vapor phase dehydration of EGE.

Table 1
Conversion and selectivity for EGE dehydration on various metal oxides

Catalyst (molar ratio)	Calcination temperature (°C)	Reaction temperature (°C)	EGE conversion (mol.%)	EVE selectivity (mol.%)	AcH + EtOH selectivity (mol.%)
SiO ₂	500	400	10.2	4.6	95.4
ZrO ₂	500	300	81.9	1.0	11.3
Nb ₂ O ₅	400	400	40.4	13.3	86.4
Al ₂ O ₃	400	280	52.1	4.5	74.3
H-mordenite	500	300	79.4	7.2	77.9
MgO/SiO ₂ (10/1)	500	380	56.8	2.5	70.3
Y ₂ O ₃ /SiO ₂ (1/20)	1000	400	53.6	3.0	88.7
ZrO ₂ /SiO ₂ (5/1)	400	380	93.0	3.9	85.6
BaO/SiO ₂ (1/10)	600	420	29.7	7.8	92.1
Cs ₂ O/SiO ₂ (1/20)	500	420	72.5	84.4	15.6

Reaction conditions: EGE gas concentration: 5 vol.% (balanced by N₂), GHSV: 1500 h⁻¹.

The conversion of EGE and the selectivity for EVE is defined as follows in the present report.

Conversion (mol.%) = $100 \times (\text{mol of consumed EGE}) / (\text{mol of fed EGE})$.

Selectivity (mol.%) = $100 \times (\text{mol of produced EVE}) / (\text{mol of consumed EGE})$.

As shown in Table 1, all of the catalysts studied yielded EVE though the conversion and selectivity depended on the types of catalyst. Among them, Cs₂O/SiO₂ (molar ratio 1/20) showed the best catalytic performance. Other dehydration catalysts, such as Nb₂O₅, Al₂O₃ and H-mordenite promoted the decomposition of EGE to the by-products. The principal by-products observed were acetaldehyde (AcH), ethanol (EtOH) and ethylene. It seems that the acid catalyst cleaves the ether bond of EGE. The formation of ethylene markedly increased on the strong acid catalysts, such as Al₂O₃ and H-mordenite. Ethylene is probably produced by the consecutive dehydration of EtOH on the acid catalysts. SiO₂ catalyst containing a small amount of Cs₂O, Cs₂O/SiO₂ (molar ratio 1/20), showed an extremely high performance of the EVE formation. The amounts of two by-products, AcH and EtOH, were almost the same on this catalyst.

3.2. Catalytic performance of Cs₂O-added metal oxides

Table 2 shows the catalytic performance of Cs₂O-added metal oxides for the dehydration of EGE to EVE. There were no high performance catalysts except Cs₂O-added SiO₂.

3.3. Effect of alkali metal addition to SiO₂

The relationship between the catalytic performance and the ionization potential of the added alkali elements is shown in Fig. 1. Both the catalytic activity and the selectivity for the EVE formation decreased with the increase in the ionization potential of alkali elements. The EGE conversion markedly changed in the lower region of the ionization potential, showing a concave upward curve. On the other hand, the EVE selectivity markedly changed in the higher region of the ionization potential, showing a convex upward curve. The effect of Cs on the conversion was dramatic. The basicity of metal oxide becomes stronger as the ionization potential of the metal is lower. The strength of basicity of alkali metal oxides is estimated to be in the order:

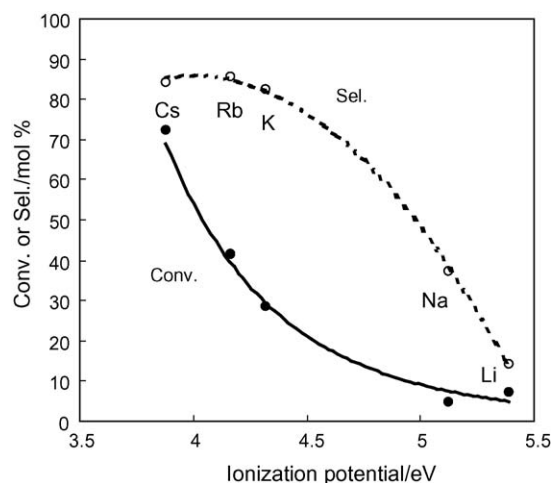


Fig. 1. Effect of alkali metal addition to SiO₂. Reaction conditions: EGE gas concentration: 5 vol.% (balanced by N₂), GHSV: 1500 h⁻¹, catalyst: alkali metal oxides/SiO₂ = 1/20 (molar ratio), calcined at 500 °C for 2 h, reaction temperature: 420 °C ionization potential: 5.39 eV/Li, 5.12 eV/Na, 4.32 eV/K, 4.16 eV/Rb and 3.88 eV/Cs [9].

Cs₂O > Rb₂O > K₂O > Na₂O > Li₂O. The order may hold when they are supported on SiO₂. The highest activity of Cs₂O/SiO₂ is suggested to be due to the strongest basicity among alkali metal oxide-added SiO₂. However, the base strength of Cs₂O/SiO₂ catalyst, which is measured by indicator method, is very weak as described later in Section 3.5.

3.4. Effect of the amount of Cs in Cs₂O/SiO₂ catalysts

The effects of the amount of Cs in Cs₂O/SiO₂ catalyst on the conversion of EGE and the selectivity for EVE are shown in Fig. 2. The conversion increased and attained to a maximum (95.2%) at a Si/Cs molar ratio of 30 and then decreased with the decrease in the Cs amount. The selectivity for EVE slightly increased up to a maximum (84.2%) at a Si/Cs molar ratio of 200 and then decreased with the decrease in the Cs amount.

3.5. Acid and base strengths of catalysts

The maximum acid strength of SiO₂ itself was $H_0 = +3.3$. On the other hand, the alkali metal oxide-added SiO₂ catalysts did

Table 2
Catalytic performance of Cs₂O added metal oxides

Catalyst (molar ratio)	Temperature (°C)	EGE conversion (mol.%)	EVE selectivity (mol.%)	AcH + EtOH selectivity (mol.%)
Cs ₂ O/SiO ₂ (1/20)	420	72.5	84.4	15.6
Cs ₂ O/TiO ₂ (1/20)	430	15.7	15.3	63.1
Cs ₂ O/ZrO ₂ (1/20)	380	21.0	12.6	68.1
Cs ₂ O/Nb ₂ O ₅ (1/10)	430	17.0	10.3	76.8
Cs ₂ O/CeO ₂ (1/20)	430	45.5	7.9	55.2
Cs ₂ O/La ₂ O ₃ (1/10)	430	11.2	–	79.2
Cs ₂ O/MoO ₃ (1/20)	430	44.3	11.3	75.3
Cs ₂ O/WO ₃ (1/20)	430	12.9	38.1	52.0
Cs ₂ O/Bi ₂ O ₃ (1/10)	430	31.4	–	90.4
Cs ₂ O/Sb ₂ O ₃ (1/10)	430	37.2	20.8	70.9

Reaction conditions: EGE gas concentration: 5 vol.% (balanced by N₂), GHSV: 1500 h⁻¹, catalyst: calcined at 500 °C for 2 h.

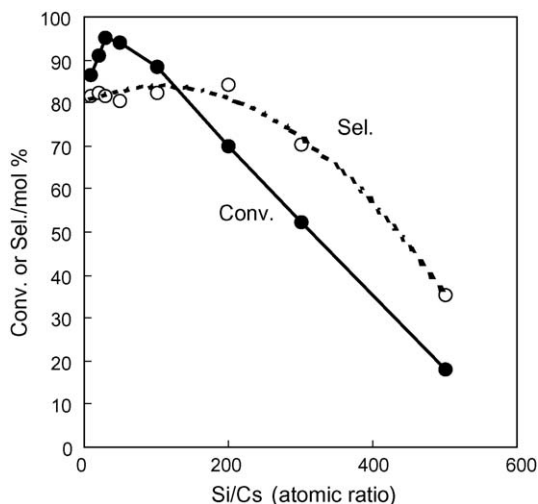


Fig. 2. Effect of the amount of Cs in $\text{Cs}_2\text{O}/\text{SiO}_2$ catalyst on the conversion and selectivity. Reaction conditions: EGE gas concentration: 5 vol.% (balanced by N_2), GHSV: 1500 h^{-1} , catalyst: calcined at 500°C for 2 h, reaction temperature: 420°C .

not change the colors of all the indicators used; namely, the acid strength is lower than $H_0 = +6.8$ and the base strength is lower than $H^- = +9.4$.

3.6. Effect of reaction conditions

3.6.1. Effect of GHSV

Fig. 3 shows the effects of GHSV on the conversion of EGE and the selectivity for EVE under the following reaction conditions; catalyst: $\text{Cs}_2\text{O}/\text{SiO}_2$ (molar ratio 1/20), temperature: 380°C , EGE concentration: 5 vol.% in N_2 .

The EGE conversion linearly decreased with the increase in GHSV; however, the selectivity for EVE remained almost constant (89–90 mol.%). This result suggests that the by-products (EtOH, AcH) are produced by the parallel decomposition of EGE, not by the consecutive hydrolysis of EVE.

3.6.2. Effect of raw material concentration

Fig. 4 shows the effect of the EGE concentration under the following reaction conditions; catalyst: $\text{Cs}_2\text{O}/\text{SiO}_2$ (molar ratio 1/20), temperature: 380°C , GHSV: 1000 h^{-1} .

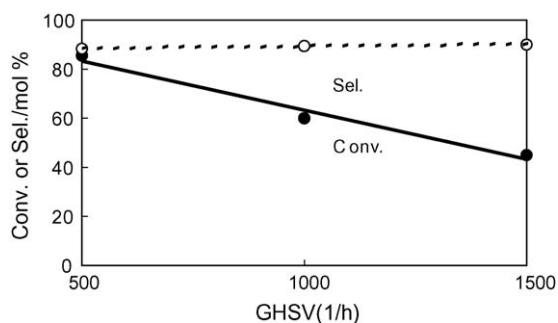


Fig. 3. Effect of GHSV. Reaction conditions: EGE gas concentration: 5 vol.% (balanced by N_2), GHSV: 1500 h^{-1} , catalyst: $\text{Cs}_2\text{O}/\text{SiO}_2$ (molar ratio 1/20), calcined at 500°C for 2 h, reaction temperature: 380°C .

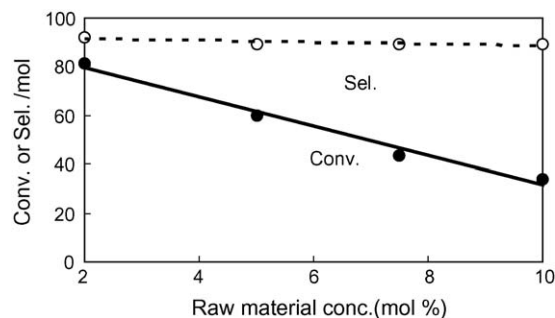


Fig. 4. Effect of the EGE concentration. Reaction catalyst: $\text{Cs}_2\text{O}/\text{SiO}_2$ (molar ratio 1/20), calcined at 500°C for 2 h, reaction temperature: 380°C .

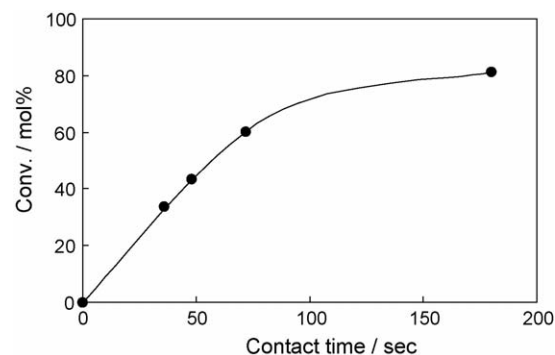


Fig. 5. Effect of contact time. Reaction conditions: GHSV: 1000 h^{-1} , catalyst: $\text{Cs}_2\text{O}/\text{SiO}_2$ (molar ratio 1/20), calcined at 500°C for 2 h, reaction temperature: 380°C .

The EGE conversion decreased with the increase in the EGE concentration. The EVE selectivity was independent of the EGE concentration and almost constant.

The plot of the EGE conversion versus the EGE contact time, which is calculated from the EGE concentration and the GHSV, is shown in Fig. 5. In the region of the short contact times (below 72 s), the conversion linearly increased with the contact time, indicating that the reaction rate followed a zero order with respect to the EGE concentration. However, at longer contact times, the relationship was not linear, indicating that the rate obeyed a positive order with respect to the EGE concentration.

3.6.3. Effect of reaction temperature

Fig. 6 shows the effect of reaction temperature under the following reaction conditions; catalyst: $\text{Cs}_2\text{O}/\text{SiO}_2$ (molar

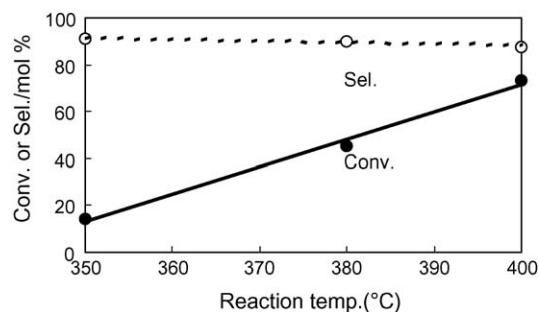


Fig. 6. Effect of reaction temperature. Reaction conditions: EGE gas concentration: 5 vol.% (balanced by N_2), GHSV: 1500 h^{-1} , catalyst: $\text{Cs}_2\text{O}/\text{SiO}_2$ (molar ratio 1/20), calcined at 500°C for 2 h.

Table 3
Reaction of various 2-alkoxyethanols and aryloxyethanol

R in ROCH ₂ CH ₂ OH	Temperature (°C)	Conversion (mol.%)	Selectivity (mol.%)	Bond cleavage energy (kcal/mol) ^a
Me	380	48.5	91.8	
Et	380	48.9	91.6	80.6
i-Pr	380	50.5	93.0	80.1
n-Pr	380	51.1	93.3	80.4
i-Bu	380	56.7	94.0	79.2
n-Bu	380	56.5	92.7	80.4
t-Bu	380	44.6	70.5	77.6
Ph	350	75.3	41.2	60.8

Reaction conditions: catalyst: Cs₂O/SiO₂ (molar ratio 1/60) (calcined at 500 °C for 2 h), 2-alkoxyethanol concentration: 5 vol.% (balanced N₂), GHSV: 1500 h⁻¹.

^a Calculated value about the R–O bond in ROCH₂CH₂OH.

ratio 1/20), EGE gas concentration: 5 vol.% in N₂, GHSV: 1000 h⁻¹.

The EGE conversion increased and the EVE selectivity slightly decreased with the increase in the temperature. The principal by-products were EtOH and AcH. This result suggests that the decomposition of EGE accelerates with the increase in the temperature. From the initial rates at different temperatures, activation energy was calculated at 110.5 kJ/mol.

3.7. Reaction of various glycol ethers

Table 3 shows the dehydration results of various glycol ethers (2-alkoxyethanol or 2-aryloxyethanol) and the cleavage energies of R–O bond in glycol ethers.

For the aliphatic 2-alkoxyethanol, the selectivity for vinyl ether was very low for 2-tert-butoxyethanol. This result is probably due to the weak bond between a tertiary carbon atom and an oxygen atom compared to the bond between a secondary or a primary carbon atom and an oxygen atom.

For the 2-aryloxyethanol, 2-phenoxyethanol, the conversion was high even if the temperature was 30 °C lower than that for the dehydration of aliphatic 2-alkoxyethanol. However, the selectivity for vinyl ether was very low. This result is considered due to that the weak bond between an aromatic carbon atom and an oxygen atom compared to the bond between an aliphatic carbon atom and an oxygen atom.

3.8. Features of catalysts

Adsorption and desorption behavior of EGE, EtOH and 1,2-diethoxyethane on the Cs₂O/SiO₂ (molar ratio 1/20) catalyst at 200 °C was studied by a pulse method. EtOH was used for investigating the effect of the hydroxyl group alone. 1,2-Diethoxyethane was used for investigating the effect of the ethoxyl group alone.

As shown in Fig. 7, the desorption peak intensity of EGE increased with increasing pulse number for the initial five pulses, and then leveled off after the sixth pulse. Each peak of EGE showed a long tailing, which suggests that EGE is strongly adsorbed on the catalyst. The adsorption behavior of EtOH is quite similar to that of EGE. Therefore, EtOH is also suggested to strongly adsorb on the catalyst. On the other hand, the desorption peaks of 1,2-diethoxyethane showed an intensity corresponding

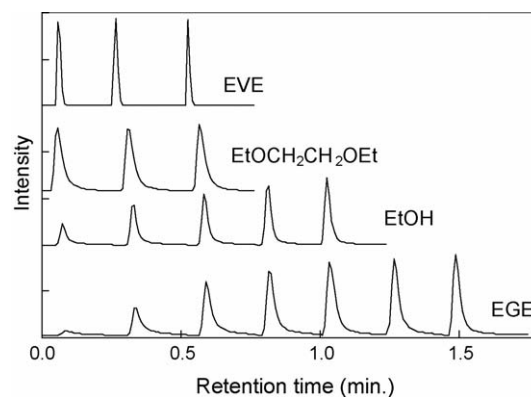


Fig. 7. Desorption peaks of model compounds (pulse method). Reaction conditions: catalyst: Cs₂O/SiO₂ (molar ratio 1/20) (20 mg), temperature: 200 °C.

to the injection amount regardless of the pulse number. This result indicates that 1,2-diethoxyethane is not strongly adsorbed on the catalyst because of its non-affinity to the catalyst. Namely, the hydroxyl group is strongly adsorbed on this catalyst but the ethoxyl group is not adsorbed.

EVE showed a similar behavior to 1,2-diethoxyethane and has no long tailing, indicating that EVE is not adsorbed on the catalyst either. During the reaction of EGE, the surface active sites are fully covered with EGE, and EVE is desorbed immediately after formed by the intramolecular dehydration of EGE. It is consistent with the zero order reaction that the only raw material is adsorbed on the catalyst. This is similar to the result of the dehydration of *N*-(2-hydroxyethyl)-2-pyrrolidone to *N*-vinyl-2-pyrrolidone [6].

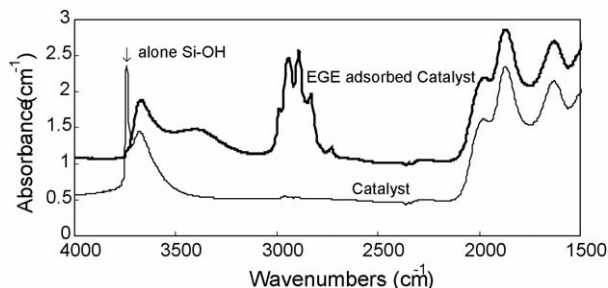


Fig. 8. IR spectrum of the EGE adsorbed catalyst. Catalyst: Cs₂O/SiO₂ (molar ratio 1/20), calcined at 500 °C for 2 h.

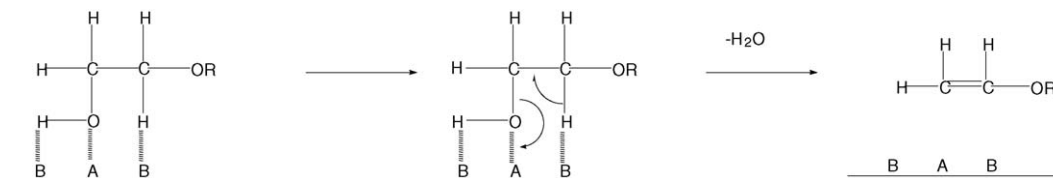


Fig. 9. Reaction mechanism of the intramolecular dehydration of 2-alkoxyethanol to alkyl vinyl ether on the catalyst. A: acid site, H⁺ of silanol and/or Cs⁺. B: base site, O²⁻ bound to Si and/or Cs⁺.

The reaction mechanism including adsorption of 2-alkoxyethanol and the successive reaction is proposed as shown in Fig. 9. 2-Alkoxyethanol is first adsorbed on both base sites, O²⁻ in -OCs and/or -OH, and acid sites (Cs⁺, H⁺) on the catalyst surface of Cs₂O/SiO₂ and then forms alkyl vinyl ether by the intramolecular dehydration. Although, the acidic strength of Cs₂O/SiO₂ catalyst is very weak as measured by the indicator method, the role of the acid sites cannot be excluded. This reaction occurred on SiO₂ alone. The active sites could be acid and base sites of the hydroxyl group on SiO₂. This hydroxyl group can remain on the Cs₂O/SiO₂ catalyst because the amount of Cs₂O is not large enough to cover the SiO₂ surface. The acid sites presumably interact with the O atom of the hydroxyl group in 2-alkoxyethanol.

The IR spectrum of this catalyst shows the absorption peak of single silanol at 3740 cm⁻¹. This peak was absent on the EGE adsorbed catalyst as shown in Fig. 8. This result suggests that EGE is adsorbed on the silanol group on the catalyst.

SiO₂ catalyst containing a very small amount of Cs (Cs/Si molar ratio 1/200) shows considerably high activity (Fig. 2) and SiO₂ itself, which is known to have almost no basic property, shows some catalytic activity. Probably, the acid site of silanol and/or silicate plays an important role in the catalytic performance.

4. Conclusions

- (1) A new route to the synthesis of vinyl ether by the intramolecular dehydration of glycol ether in vapor phase has been developed using the alkali metal added silica catalysts.
- (2) It was found that silica to which a small amount of cesium was added exhibited a pronounced catalytic performance for this dehydration, the conversion and the selectivity being 81% and 96%, respectively.

- (3) The 2-alkoxyethanol conversion decreased and the alkyl vinyl ether selectivity increased with the increase in the ionization potential of the alkali metal added to SiO₂.
- (4) The acid and base strengths of good catalysts were lower than $H_0 = +6.8$ and lower than $H^- = +9.4$, respectively.
- (5) It is presumed that 2-alkoxyethanol is adsorbed on the acid–base pair sites on the catalyst surface through the interaction of the hydroxyl group with those sites and forms alkyl vinyl ether by the intramolecular dehydration.

Acknowledgment

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