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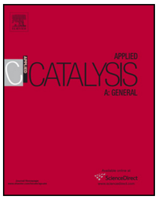

Cyclodehydration of diethylene glycol over Ag-modified Al_2O_3 catalyst

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ABSTRACT

Vapor-phase cyclodehydration of diethylene glycol (DEG) into 1,4-dioxane (DOX) were performed over several solid acid catalysts, such as Al_2O_3, $SiO_2—Al_2O_3$, Beta and MFI zeolites. All the catalytic activity gradually decreased with time on stream, especially Beta and MFI zeolites with strong acidic property. The catalysts were modified with silver metal for stabilizing the catalytic activity: Al_2O_3 modified with 1 wt.% Ag_2O showed the best catalytic performance. Characterizations such as XRD, TPD and FTIR were performed for analyzing the carbonaceous compound deposited on the catalysts after reaction and investigating the effect of the addition of Ag_2O onto Al_2O_3. Polyethylene glycol was proposed as the carbonaceous compound by FTIR analysis. The modification of Ag was found to decrease the averaged acid strength of Al_2O_3, which is supposed to be effective for inhibiting carbon deposition and stabilizing the catalytic activity. It was also found that H_2, as a carrier gas, was indispensable for stabilizing the conversion of DEG into DOX. Silver metal would work as a remover of the product on the catalyst surface together with H_2 to prevent carbon deposition. Over Al_2O_3 modified with 1 wt.% Ag_2O, a stable DOX selectivity of 90% with a complete conversion was achieved at 250 °C and a contact time of 156.8 g h mol^{-1}.

1. Introduction

Cyclodehydration of terminal diols, such as 1,4-butanediol (BDO), 1,5-pentanediol (PDO) and diethylene glycol (DEG), is a useful method to obtain oxygen heterocycles, such as tetrahydrofuran (THF), tetrahydropyran (THP), and 1,4-dioxane (DOX), which are widely used as the solvents in chemical industry [1]. Many researches dealing with the dehydration of BDO, PDO, and DEG to useful chemicals have been reported and it is found that acidic catalysts are generally effective for producing the cyclodehydration products. In particular, acidic solids such as TiO_2-supported silicotungstic acid [2,3], diatomite-supported phosphotungstic acid [4], and ion exchange resin (Indion-130) [5] are efficient for THF formation from BDO in a liquid phase, while 3-buten-1-ol is mainly produced in a vapor phase over base-modified ZrO_2 [6,7], In_2O_3 [8,9], and rare earth oxides with base property, such as CeO_2 and Er_2O_3 [10,11]. Such solid catalysts as sulfated zirconia [1], H-ZSM-5 zeolite [12], tin(IV) phosphate [13], and alumina [14] have been reported to be effective for the liquid-phase formation of THP from PDO, while Na-modified monoclinic ZrO_2 [15] and rare earth oxides such as Yb_2O_3 and Sc_2O_3 [10,16] prefer the formation of 4-buten-1-ol in a vapor phase.

In the cyclodehydration of DEG, DOX can be selectively obtained by liquid-phase catalytic reaction in the presence of sulfated zirconia [1], alumina [14], H-ZSM-5 [17] or Brønsted acidic ionic liquid (1-butyl-3-methylimidazolium hydrogen sulfate) [18] catalysts (Scheme 1). A maximum DOX yield of 87% is obtained in the reaction using Brønsted acidic ionic liquid as a catalyst at 170 °C [18]. Although vapor-phase reactions are widely used in chemical industry, there are a few reports dealing with the cyclodehydration of terminal diols in a vapor phase. Kitayama et al. performed the cyclodehydration of DEG into DOX over clay mineral sepiolite, and a maximum DOX yield of 98% was obtained at 260 °C in the initial period of several hours [19]. However, the catalytic activity decreased with time on stream rapidly. Gradual deterioration of acidic catalysts is an important issue in the catalytic conversion under flow conditions.

The stability of catalyst is highly required in an industrial process. In our group, an effective operation on the stabilization of catalytic activity of solid acids has been reported [20–22]. For example, the vapor-phase dehydration of 1,2-propanediol to propanal can be catalyzed by acidic $SiO_2—Al_2O_3$, whereas both the conversion of 1,2-propanediol and the selectivity to propanal over $SiO_2—Al_2O_3$ are deteriorated at 300 °C. Ag-modified $SiO_2—Al_2O_3$

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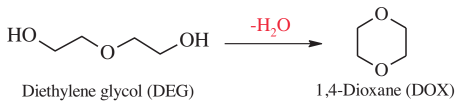

Scheme 1. Cyclodehydration of diethylene glycol to 1,4-dioxane.

catalyst exhibits stable catalytic activity with high selectivity to propanal under hydrogen flow conditions. Prior to the reaction, Ag_2O is reduced to metallic Ag, which prevents carbon deposition together with hydrogen [22].

In this paper, we investigated the vapor-phase cyclodehydration of DEG into DOX (Scheme 1) over several commercial solid acids with modification of Ag. The suitable reaction conditions for the DOX formation and the behavior of the Ag-modified catalysts were also studied.

2. Experimental

2.1. Samples

DEG and polyethylene glycol (PEG) with a molar weight of 4000 were purchased from Wako Pure Chemical Industries Co., Ltd., Japan, and were used for the catalytic reaction without further purification. Al_2O_3 (N611N) and SiO_2—Al_2O_3 (N631L) were purchased from Nikki Chemical. Beta (Si/Al = 31.9) and MFI (Si/Al = 90.2) zeolites were supplied by Clariant Catalysts Industries Co., Ltd. The specific surface areas of Al_2O_3, SiO_2—Al_2O_3, Beta and MFI zeolite are 210, 440, 586 and 431 $m^2 g^{-1}$, respectively. Silica (CARiACT Q-10 with a mean pore diameter of 10 nm) was supplied by Fuji Silycia Chemical Ltd. $AgNO_3$, which was used as the precursor of the additive Ag, was purchased from Wako Pure Chemical Industries Co., Ltd., Japan.

Ag-modified catalysts were prepared by an incipient wetness impregnation method using a solution with a prescribed amount of $AgNO_3$ dissolved in distilled water. The weight percentages of Ag in the support were calculated using the weight of Ag_2O in the calcined catalysts. An appropriate amount of the $AgNO_3$ solution was added to a support, and water was evaporated at ambient pressure and 70 °C by illuminating samples using a 350-W electric light bulb. After the impregnation process, the samples were dried at 110 °C for 12 h, and then calcined for 3 h. The calcination temperature of Ag-modified catalysts was 450 °C. Hereafter, the supported catalysts are expressed as X-Ag-*Y*, where X means the support; *Y* means the weight percentage of Ag_2O. For example, Al_2O_3-Ag-1 means 1 wt.% Ag_2O loaded on Al_2O_3.

2.2. Catalytic reaction

The cyclodehydration of DEG was performed in a fixed-bed down-flow glass reactor with an inner diameter of 17 mm at an ambient pressure of either H_2 or N_2. Prior to the reaction, the catalyst was placed in the catalyst bed and heated at a prescribed temperature for 1 h to stabilize the temperature of the catalyst bed. After the preheating, DEG was fed through the top of the reactor at a liquid feed rate of 2.0 g h^{-1} together with either an H_2 or N_2 flow of 20 $cm^3 min^{-1}$. The reactions were performed at a W/F from 26.1 to 261.4 g h mol^{-1}, where W and F are the catalyst weight and the feed rate of DEG, respectively. The liquid effluents collected

Table 1
Dehydration of DEG over several metal oxide catalysts at 250 °C.[a]

Catalyst	Conversion/%[b]	Selectivity/%[b]						
		DOX	MeOH	EtOH	AA	MDO	EG	TEG
Al_2O_3	58.4	67.5	0.0	1.0	1.0	1.5	15.1	1.6
MFI	86.7	54.0	0.1	0.4	6.5	6.6	14.4	0.4
Beta	91.9	74.6	0.1	1.0	4.2	2.5	8.1	0.2
SiO_2—Al_2O_3	27.1	30.5	0.0	2.2	5.1	7.7	19.5	4.4
SiO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

DOX, 1,4-dioxane; MeOH, methanol; EtOH, ethanol; AA, acetaldehyde; MDO, 2-methyl-1,3-dioxolane; EG, ethylene glycol; TEG, triethylene glycol.

[a] Reaction conditions: W/F = 26.1 g h mol^{-1}; H_2 flow rate, 20 $cm^3 min^{-1}$.

[b] Average activity in the initial 5 h.

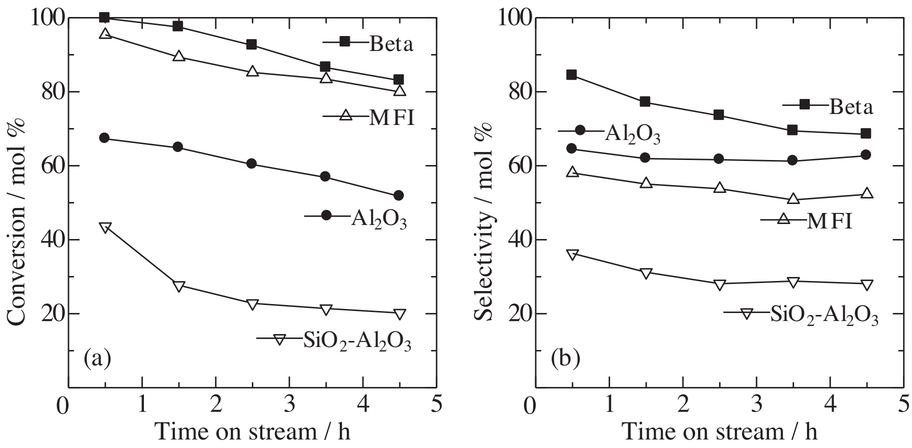

Fig. 1. Changes in conversion and selectivity with time on stream over several solid acid catalyst. Reaction conditions: W/F = 26.1 g h mol^{-1}; H_2 flow rate, 20 $cm^3 min^{-1}$; reaction temperature, 250 °C.

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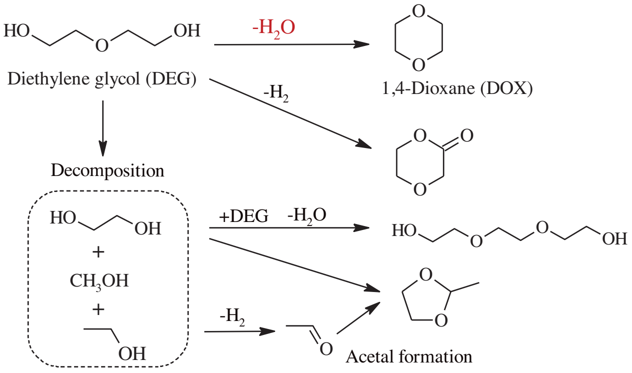

Scheme 2. Probable formation route of the detected products.

in an ice water trap at 0 °C every hour were analyzed by a FID-GC (GC-8A, Shimadzu) with a 30-m capillary column of TC-WAX (GL-Science, Japan). A GC–MS (QP5050A, Shimadzu) was used for identification of the products in the effluent. 1,2-Propanediol was used as an internal standard substance.

2.3. *Characterization of catalysts*

The specific surface area of a catalyst sample was calculated with the Brunauer–Emmett–Teller (BET) method using N_2 adsorption isotherm at −196 °C. The thermo gravimetry-differential thermal analysis (TG-DTA) was performed using Thermoplus 8120E2 (Rigaku, Japan) under the conditions: sample weight, *ca.* 10 mg; the heating rate, 5 °C min^{-1}; heating range, from the room temperature to 900 °C. In the TG plots, profiles were located to be contacted each other at around 150–200 °C. The temperature-programmed desorption (TPD) of adsorbed NH_3 was measured by neutralization titration using an electric conductivity cell immersed in an aqueous solution of H_2SO_4 to estimate acidity of the catalysts, as has been described in the TPD experiment of adsorbed NH_3 [22,23]. The X-ray diffraction (XRD) patterns of powder samples were recorded on a D8 ADVANCE (Bruker, Germany) using Cu Kα radiation. The

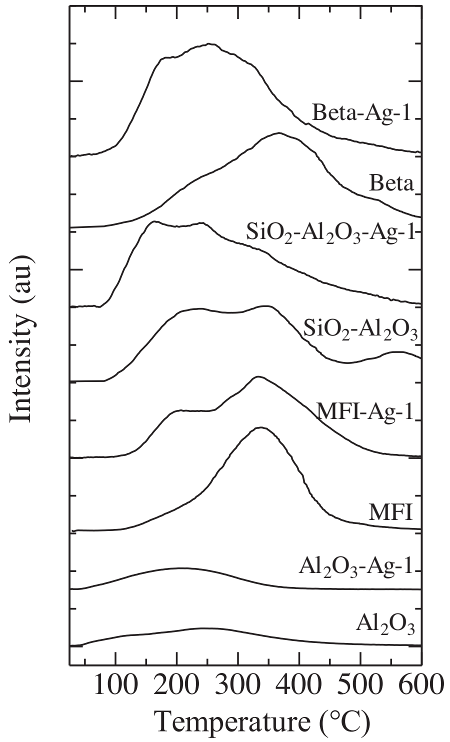

Fig. 2. NH_3-TPD profiles of Ag-modified solid acid catalysts.

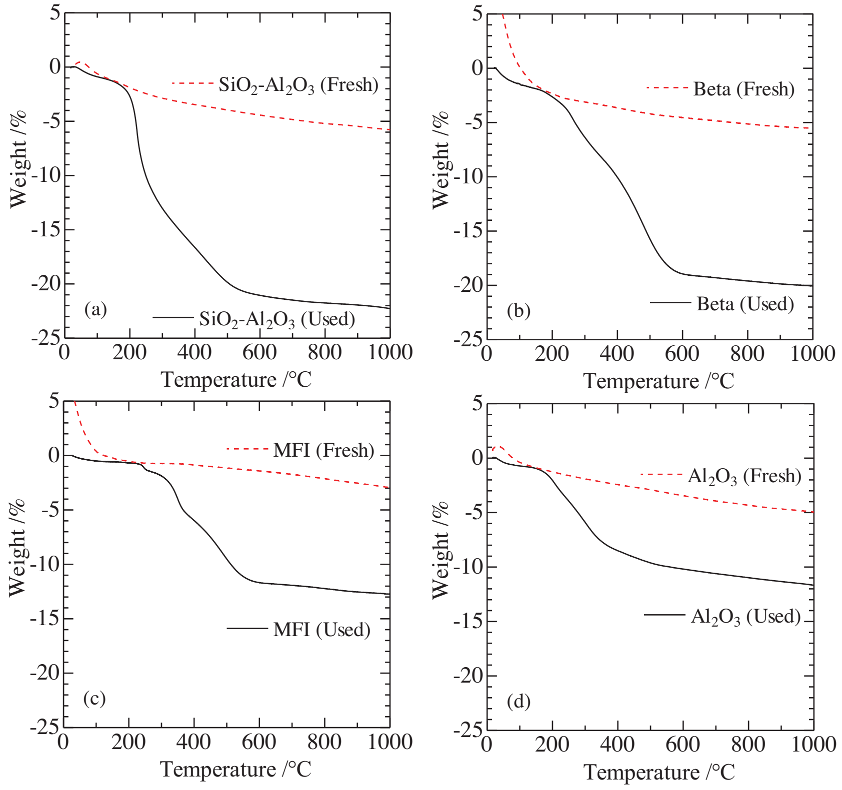

Fig. 3. TG profiles of solid acid catalysts before and after the reaction. Reaction conditions: H_2 flow rate, 20 cm^3 min^{-1}; reaction temperature, 250 °C; W/F = 26.1 g h mol^{-1}.

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diffuse reflectance infrared Fourier-transform (DRIFT) spectra of catalyst samples were recorded on a spectroscope using FT/IR-4200 (JASCO, Japan).

3. Results and discussion

3.1. Cyclodehydration of DEG over solid acid catalysts

Table 1 summarizes results of the cyclodehydration of DEG over several solid acid catalysts, and Fig. 1 shows the changes in conversion and selectivity with time on stream in each reaction. The reactions were performed at a *W*/*F* of 26.1 g h mol^{-1} at 250 °C. H_2 was used as a carrier gas and the flow rate of H_2 was 20 cm^3 min^{-1}. DOX was the main product in all the reactions, while methanol, ethanol, acetaldehyde, ethylene glycol, 2-methyl-1,3-dioxolane (MDO), and triethylene glycol were generated as the by-products. The carbon balance was higher than 90% in all the reactions. The probable formation routes of DOX and the by-products are shown in Scheme 2. Methanol, ethanol, acetaldehyde, and ethylene glycol are the decomposition products of DEG. MDO is proposed to be generated from acetaldehyde and ethylene glycol through acetal formation, and triethylene glycol must be produced by the etherification of DEG with by-produced ethylene glycol. Beta zeolite gave the highest averaged DEG conversion of 91.9% and the highest DOX selectivity of 74.6% (Table 1), whereas both of them decreased steeply with time on stream (Fig. 1). The averaged DEG conversion and selectivity to DOX was 58.4% and 62.5% over Al_2O_3, respectively. Although the conversion of DEG decreased with time on stream over Al_2O_3, the selectivity to DOX was stable comparing with those over the other catalysts. Although MFI zeolite gave a high averaged DEG conversion of 86.7% and 54.0% selectivity to DOX, the decrease of DEG conversion was rapid. $SiO_2—Al_2O_3$ showed poor catalytic activity on DEG conversion into DOX, and also deactivated with time on stream. The reaction did not proceed over SiO_2 catalyst at 250 °C.

Deterioration of acidic catalysts in a vapor-phase is a serious issue in many cases. For example, in the dehydration of 1,2-propanediol into propanal, the propanal selectivity exceeds 90% with a completed conversion over strong acidic catalysts such as silica-supported silicotungstic acid [24] and ZSM-23 [25], whereas they are rapidly deactivated with time on stream. In the dehydration of 1,2-propanediol into propanal, silica-supported WO_3 catalyst, which has weak acidic property, shows a stable propanal selectivity of 93.5% at 250 °C when 1,2-propanediol is diluted by 80 wt.% water, but it is also deactivated gradually when pure 1,2-propanediol is used as the reactant [26]. It is generally recognized that the carbon accumulation proceeds fast over strong acid catalysts, which always results a rapid catalyst deactivation [22]. Fig. 2 shows the acidic property of catalysts evaluated by NH_3-TPD measurement. Al_2O_3 showed a weak acidic property, whereas $SiO_2—Al_2O_3$, Beta and MFI zeolites had much larger number of medium and strong acid sites than Al_2O_3. Thus, the weak acidity of Al_2O_3 would cause a stable selectivity to DOX compared to those of $SiO_2—Al_2O_3$, Beta and MFI zeolites (Fig. 1b).

Fig. 3 shows the difference in TG profiles between fresh and used catalysts. The used samples were prepared by being recovered after the reaction at 250 °C for 5 h. In contrast to the fresh catalyst with a gradual weight decrease, all the used catalysts had a steep decrease in weight at temperatures higher than 200 °C. The difference in the weight loss between fresh and used catalysts must attribute to the carbon deposition [20–22]. The carbon content, which was calculated by the difference in the TG curves between fresh and used catalysts, was 16.5, 14.6, 9.8, and 6.8 wt.% in the used $SiO_2—Al_2O_3$, Beta, MFI, and Al_2O_3, respectively. The amount of accumulated carbon on Al_2O_3 was the smallest among all the tested catalysts. Thus, it is assumed that carbon is relatively difficult to be accumulated on Al_2O_3 because of the weak acidic property of Al_2O_3. The deterioration behaviors are quite similar to those observed in the dehydration of 1,2-propanediol [22]. The commercial Al_2O_3, $SiO_2—Al_2O_3$ and Beta zeolite are also applied for the dehydration of 1,2-propanediol: $SiO_2—Al_2O_3$ and Beta zeolite with a large number of medium and strong acid sites give initial propanal selectivities higher than 60%, which decreases to *ca.* 40% after 5 h of the reaction; Al_2O_3 with a small number of weak and medium acid sites shows stable catalytic activity, whereas the selectivity to propanal is low at *ca.* 40%.

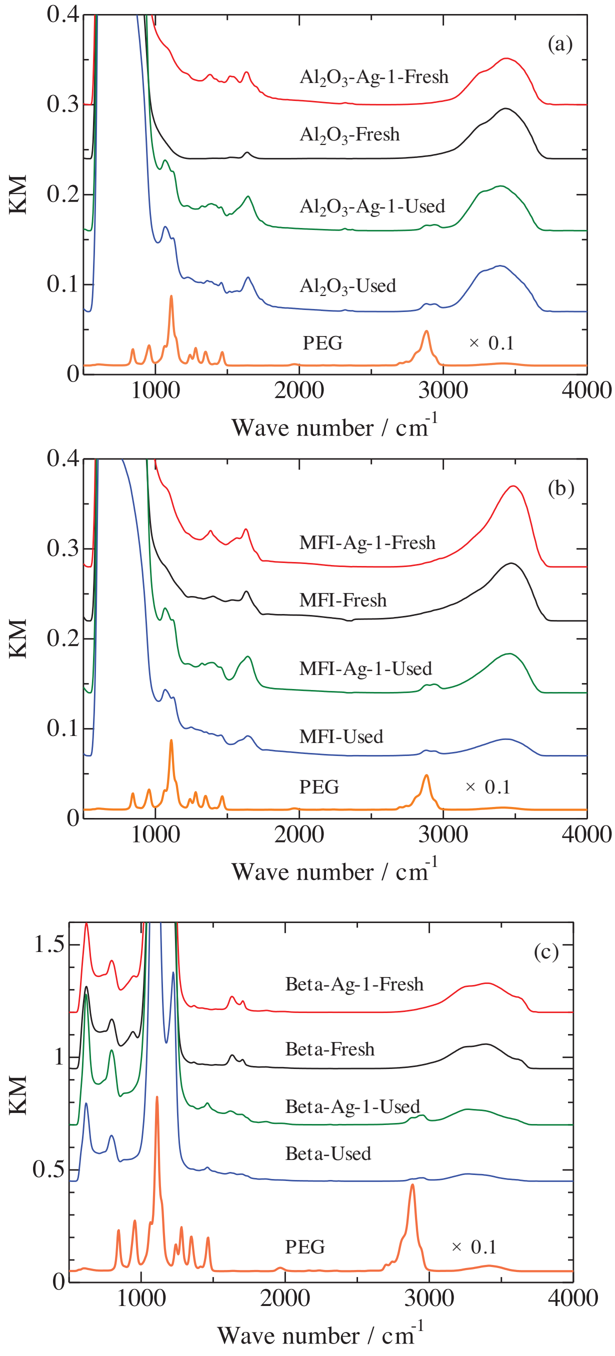

Fig. 4. FTIR spectra of (a) Al_2O_3 series, (b) MFI series, (c) Beta series. The used catalysts were prepared under the following reaction conditions: H_2 flow rate, 20 cm^3 min^{-1}; reaction temperature, 250 °C; *W*/*F* = 26.1 g h mol^{-1}.

Table 2
Dehydration of DEG over Ag-modified solid acid catalysts at 250 °C.[a]

Catalyst	Conversion/%[b]	Selectivity/%[b]						
		DOX	MeOH	EtOH	AA	MDO	EG	TEG
Al_2O_3-Ag-1	72.6	71.5	0.1	0.8	1.5	1.4	12.7	1.3
MFI-Ag-1	67.3	52.3	0.1	0.4	3.6	5.5	17.4	1.2
Beta-Ag-1	91.9	83.7	0.1	1.0	3.9	2.4	8.1	0.3
SiO_2—Al_2O_3-Ag-1	34.9	30.8	0.1	2.2	7.0	7.1	18.9	4.5

The abbreviations of the products are the same as those shown in Table 1.

[a] Reaction conditions: W/F = 26.1 g h mol^{-1}; H_2 flow rate, 20 cm^3 min^{-1}.

[b] Average activity in the initial 5 h.

Fig. 4 shows the DRIFT spectra of original and Ag-modified Al_2O_3, Beta, and MFI catalysts before and after the reaction. Because polyethylene glycol (PEG) is considered as the possible component of the accumulated carbon, the DRIFT spectra of PEG was measured. PEG showed a clear peak at 1076 cm^{-1}, which was originated from the vibration of stretching C—O [27–29]. A clear peak at 2881 cm^{-1}, which was assigned to the stretching vibration of CH_2 [29,30], was also observed in PEG. The peaks at 1076 and 2881 cm^{-1} were observed in the used catalysts such as original and Ag-modified Al_2O_3, Beta, and MFI, whereas they were observed in the fresh catalysts. Thus, it is reasonable that the etherification of DEG proceeded over the catalyst surface, and PEG is a possible component of the accumulated carbon.

3.2. Effect of Ag loading on Al_2O_3

We have reported several papers dealing with the catalyst deactivation [20–22]. It is found that the modification of acid catalysts by loading some metal contents is effective for inhibiting the catalyst deactivation: Cu-modified Al_2O_3 exhibits stable catalytic activity with high selectivity to DHP in THFA dehydration [20]; Co-modified Al_2O_3 stabilizes the conversion of pinacolone to produce 2,3-dimethyl-1,3-butadiene [21]; Ag-modified SiO_2—Al_2O_3 gives stable and increased selectivity to propanal in 1,2-propanediol dehydration [22]. The metal modifiers work effectively for the stabilization in the reactions only in H_2 flow. In this work, Ag-modified catalysts are estimated to inhibit catalyst deactivation under H_2 flow conditions.

Table 2 shows the averaged reaction data of Ag-modified catalysts, and Fig. 5 depicts the changes in conversion and selectivity to DOX with time on stream. The loading of Ag_2O onto Beta, Al_2O_3 and SiO_2—Al_2O_3 was found to be efficient for increasing both the conversion of DEG and the selectivity to DOX, whereas MFI-Ag-1 gave a lower conversion and a lower selectivity to DOX comparing with those over MFI without the loading of Ag_2O. Ag-modified Beta zeolite and SiO_2—Al_2O_3 were still deactivated rapidly with time on steam (Fig. 5), while the catalytic activity of Al_2O_3-Ag-1 was stable. A stable DOX selectivity of 71.5% with a DEG conversion of 72.6% was achieved over Al_2O_3-Ag-1. Fig. 6a shows the TG profiles of Al_2O_3-Ag-1 before and after the reaction for 5 h, and the carbon content in the used Al_2O_3-Ag-1 was 5.9%, which is lower than that of 6.8% in the used Al_2O_3 without modification of Ag (Fig. 3d).

Fig. 2 compares the acidic property of Ag-modified catalysts with non-modified ones. The NH_3 desorption peak of Al_2O_3 was observed at 251 °C, which shifted to 210 °C at Ag_2O loading of 1 wt.%. The loading of Ag_2O into SiO_2—Al_2O_3, Beta and MFI zeolites also decreased their averaged acid strength, respectively. A similar result is observed in Ag-modified SiO_2—Al_2O_3 in our previous research dealing with 1,2-propanediol dehydration into propanal [22]: the loading of Ag_2O onto SiO_2—Al_2O_3 decreases the number of strong and medium acid sites, whereas increases the number of weak acid sites. As a result, the catalyst deactivation is inhibited and a stable propanal selectivity of 68.5% is achieved. In this study, it is proposed that the additive Ag_2O associates with the strong acid sites of each catalyst, and it decreases the number of the strong acid sites and forms new weak acid sites. Although the averaged acid strengths of SiO_2—Al_2O_3, Beta and MFI zeolites are decreased by the loading of Ag_2O, the numbers of medium and strong acid sites are still much larger than that of Al_2O_3-Ag-1. Thus, it can be concluded that the weak acid property of Ag-modified Al_2O_3 is effective for inhibiting carbon formation and stabilizing the catalytic activity.

Table 3 summarizes the DEG cyclodehydration over Ag-modified Al_2O_3 catalysts at different Ag_2O loadings. Fig. 7 shows the changes of DEG conversion and DOX selectivity with time on stream. The selectivity to EG and TEG decreased by Ag modification and the selectivity to DOX increased over the Ag-modified

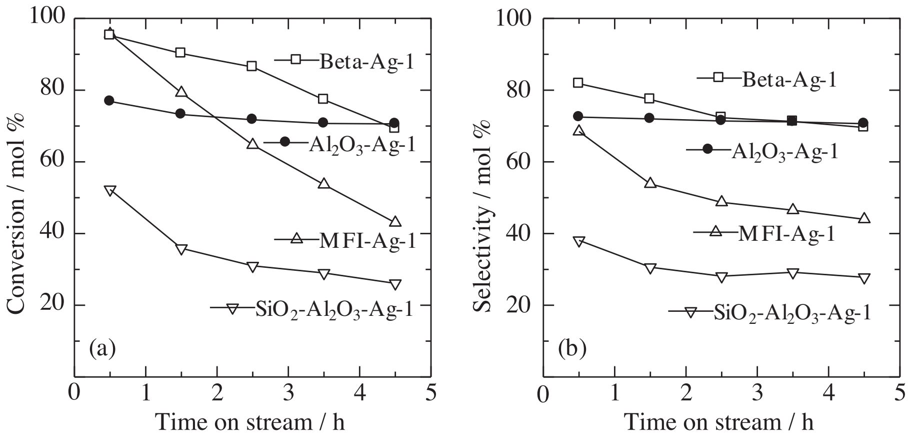

Fig. 5. Changes in conversion and selectivity with time on stream over Ag-modified solid acid catalysts. Reaction conditions: W/F = 26.1 g h mol^{-1}; H_2 flow rate, 20 cm^3 min^{-1}, reaction temperature, 250 °C.

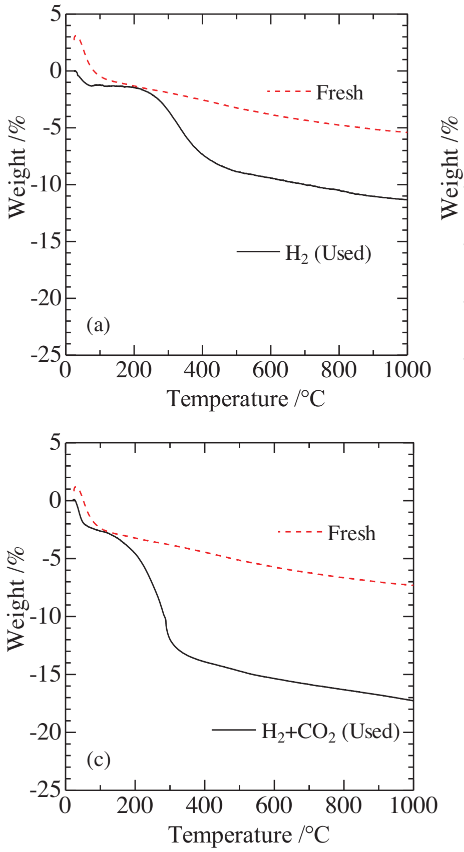

Fig. 6. TG profiles of Al_2O_3-Ag-1 before and after the reaction under different carrier gases. Reaction conditions: flow rate, 20 cm^3 min^{-1}; reaction temperature, 250 °C; W/F = 26.1 g h mol^{-1}.

Al_2O_3 catalysts. Because Al_2O_3-Ag-1 shows the highest averaged DEG conversion of 97.2% and a relatively stable DOX selectivity of 82.5%, 1 wt.% loading of Ag_2O is considered to be suitable. Although the initial conversion and the initial selectivity to DOX were high over Ag-modified Al_2O_3 at Ag_2O loadings of higher than 3 wt.%, they decreased with time on stream.

Fig. 8 shows XRD patterns of Ag-modified Al_2O_3 at different Ag_2O loadings. No peak attributed to Ag is observed at Ag_2O loadings lower than 3 wt.%. A diffraction peak of Ag_2O at $2\theta = 33.9°$ [JCPDS file 12-793] and a diffraction peak of Ag at 38.4° [JCPDS file 4-0783] are observed at Ag_2O loadings of 5 wt.% or higher. This indicates Ag and Ag_2O are highly dispersed on catalyst surface at small Ag_2O loadings. The used Al_2O_3-Ag-10 shows a diffraction peak of Ag, whereas no peak attributed to Ag_2O is observed. It is suggested that the additive Ag_2O in the metallic form works to inhibit carbon accumulation during the reaction.

3.3. Cyclodehydration of DEG over Al_2O_3-Ag-1 at different reaction conditions

Table 4 shows the cyclodehydration of DEG over Al_2O_3-Ag-1 at different contact times, W/F. The conversion of DEG increased with increasing the W/F, and a complete conversion was obtained at a W/F of 156.8 g h mol^{-1} or higher than. The selectivity to methanol

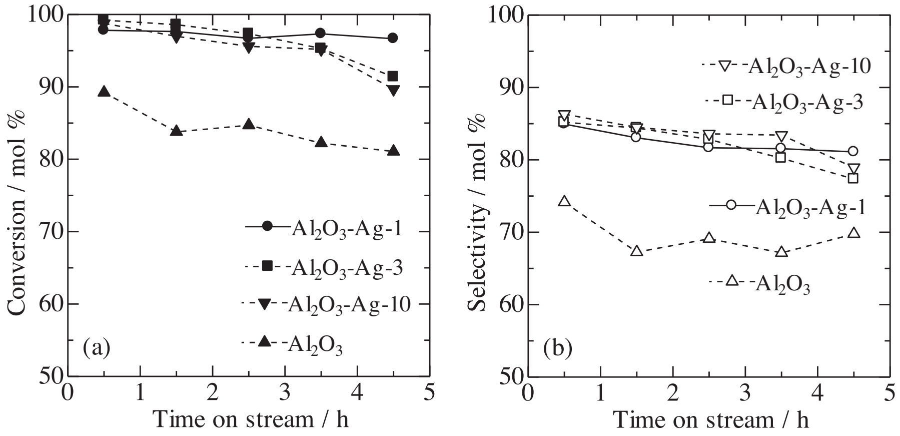

Fig. 7. Changes in conversion and selectivity with time on stream over Ag-modified Al_2O_3 at different Ag loadings. Reaction conditions: W/F = 52.3 g h mol^{-1}; H_2 flow rate, 20 cm^3 min^{-1}; reaction temperature, 250 °C.

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Table 3
Dehydration of DEG over Ag-modified Al_2O_3 at different Ag_2O loadings at 250 °C.[a]

Catalyst	Conversion/%[b]	Selectivity/%[b]						
		DOX	MeOH	EtOH	AA	MDO	EG	TEG
Al_2O_3	84.2	69.5	0.1	1.8	1.8	1.6	12.4	1.2
Al_2O_3-Ag-0.5	96.0	81.2	0.1	1.7	1.5	1.3	7.4	0.1
Al_2O_3-Ag-1	97.2	82.5	0.2	1.8	1.7	1.1	5.6	0.1
Al_2O_3-Ag-3	96.4	82.0	0.1	1.1	1.8	1.1	6.2	0.1
Al_2O_3-Ag-5	93.2	82.7	0.1	0.9	1.7	0.9	5.5	0.3
Al_2O_3-Ag-10	95.2	83.3	0.3	0.9	1.9	0.7	4.1	0.3

The abbreviations of the products are the same as those shown in Table 1.

[a] Reaction conditions: H_2 flow rate, 20 cm^3 min^{-1}; $W/F = 52.3$ g h mol^{-1}.

[b] Average activity in the initial 5 h.

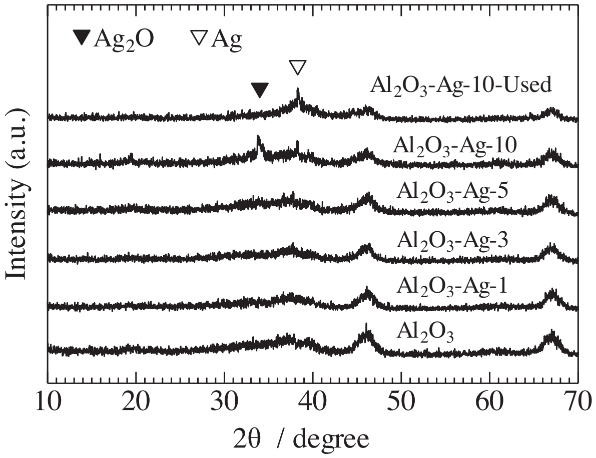

Fig. 8. XRD patterns of Ag-modified Al_2O_3 at different Ag loadings. Used Al_2O_3-Ag-10 was tested under the following reaction conditions: H_2 flow rate, 20 cm^3 min^{-1}; reaction temperature, 250 °C; $W/F = 26.1$ g h mol^{-1}.

and ethanol increased with increasing the *W*/*F*, whereas the selectivity to EG, TEG and MDO decreased. Thus, the changes in the selectivity indicate that EG and TEG are difficult to form at a high contact time. However, EG and TEG could be firstly produced and then decompose to methanol and ethanol at a high contact time. The highest selectivity to DOX was obtained at a *W*/*F* of 156.8 g h mol^{-1}. Table 4 also shows the averaged reaction results in the initial 10 h over Al_2O_3-Ag-1 and Al_2O_3 at a *W*/*F* of 156.8 g h mol^{-1}, Fig. 9 shows the changes of DEG conversion and DOX selectivity with time on stream. It is obvious that a change in the selectivity to DOX with time on steam is more stable over Al_2O_3-Ag-1 than that over Al_2O_3.

Table 5 shows the effect of reaction temperature over Al_2O_3-Ag-1 at a *W*/*F* of 26.1 and 52.3 g h mol^{-1}. High reaction temperatures increase the selectivity to the decomposition products such as methanol, ethanol and acetaldehyde. However, a low reaction temperature increases the formation of EG and TEG, as the etherification of alcohols prefers low reaction temperatures [31,32]. Since the contact time also affects the selectivity to the products (Table 4), the appropriate temperatures for DOX formation are different at different contact times. The highest selectivity to DOX is 79.7% at a *W*/*F* of 26.1 g h mol^{-1}, and 82.5% at a *W*/*F* of 52.3 g h mol^{-1}.

Since H_2 carrier gas is indispensable for inhibiting the catalyst deactivation in our precious research [20–22], the effect of the carrier gas was studied at 250 °C (Table 6). The reactions were performed in N_2, $H_2 + N_2$, $H_2 + CO_2$, $H_2 + NH_3$ and H_2 flow over Al_2O_3-Ag-1 at a *W*/*F* of 26.1 g h mol^{-1} and a flow rate of 20 cm^3 min^{-1} individually. $H_2 + NH_3$ and $H_2 + CO_2$ mixed gases, which are helpful to know the effect of acidic and basis sites on the reaction, respectively, were used to block the sites of catalyst surface. A high averaged DEG conversion of 72.6% and DOX selectivity of 71.5% were obtained in H_2 flow, and they were relatively stable, as shown in Fig. 5. A significant decrease of DEG conversion and DOX selectivity was observed when the reaction was performed in $H_2 + NH_3$ flow (Table 6). This indicates that acid sites on Al_2O_3-Ag-1 are the active sites for DEG conversion into DOX. There were no significant differences on the averaged conversion and the selectivity to DOX in N_2, H_2, $H_2 + N_2$, and $H_2 + CO_2$ flow, whereas the catalyst deactivation in N_2, $H_2 + N_2$ and $H_2 + CO_2$ flow proceeded faster than that in H_2 flow. The decreases in DEG conversion from 1 h to 5 h were 16.3, 15.7, 22.8 and 6.3% in N_2, $H_2 + N_2$, $H_2 + CO_2$ and H_2 flow, respectively. The decreases in the selectivity to DOX from 1 h to 5 h were 5.3, 4.7, 10.3 and 1.9% in N_2, $H_2 + N_2$, $H_2 + CO_2$ and H_2 flow, respectively. The carbon content was calculated to be 9.8 and 11.9% in Al_2O_3-Ag-1 used in $H_2 + N_2$ and $H_2 + CO_2$ flow, respectively (Fig. 6b and c). Those carbon contents are much higher than 5.9% observed over Al_2O_3-Ag-1 in H_2 flow (Fig. 6a).

In our previous researches dealing with catalyst deactivation, the metal-loaded solid acid catalysts show stable catalytic activity

Table 4
Effect of *W*/*F* on dehydration of DEG over Al_2O_3-Ag-1 at 250 °C.[a]

W/*F*/g h mol^{-1}	Conversion/%[b]	Selectivity/%[b]						
		DOX	MeOH	EtOH	AA	MDO	EG	TEG
26.1	72.6	71.5	0.1	0.8	1.5	1.4	12.7	1.3
52.3	97.2	82.5	0.2	1.8	1.7	1.1	5.6	0.1
156.8	100	90.0	0.7	3.5	2.0	0.2	0.5	0.0
261.4	100	87.7	1.5	4.2	1.7	0.3	0.2	0.0
156.8[c]	100	90.0	0.5	3.2	2.3	0.2	0.7	0.0
156.8[d]	100	87.1	0.4	3.6	2.0	0.7	2.8	0.0

The abbreviations of the products are the same as those shown in Table 1.

[a] Reaction conditions: H_2 flow rate, 20 cm^3 min^{-1}.

[b] Average activity in the initial 5 h.

[c] Average activity in the initial 10 h.

[d] The reaction was performed over pure Al_2O_3 and the data was averaged in the initial 10 h.

Table 5
Dehydration of DEG over Al_2O_3-Ag-1 at different reaction temperatures.[a]

W/F/g h mol^{-1}	Temperature/°C	Conversion/%[b]	Selectivity/%[b]						
			DOX	MeOH	EtOH	AA	MDO	EG	TEG
26.1	250	72.6	71.5	0.1	0.8	1.5	1.4	12.7	1.3
	275	98.1	79.7	0.3	3.9	3.4	1.2	5.5	0.0
	300	97.8	71.4	1.0	5.8	8.6	1.3	4.2	0.0
52.3	250	97.2	82.5	0.2	1.8	1.7	1.1	5.6	0.1
	275	97.9	76.7	0.8	4.6	4.2	0.7	3.3	0.0
	300	100	74.0	1.7	6.7	8.0	0.4	0.7	0.0

The abbreviations of the products are the same as those shown in Table 1.
[a] Reaction conditions: H_2 flow rate, 20 cm^3 min^{-1}.
[b] Average activity in the initial 5 h.

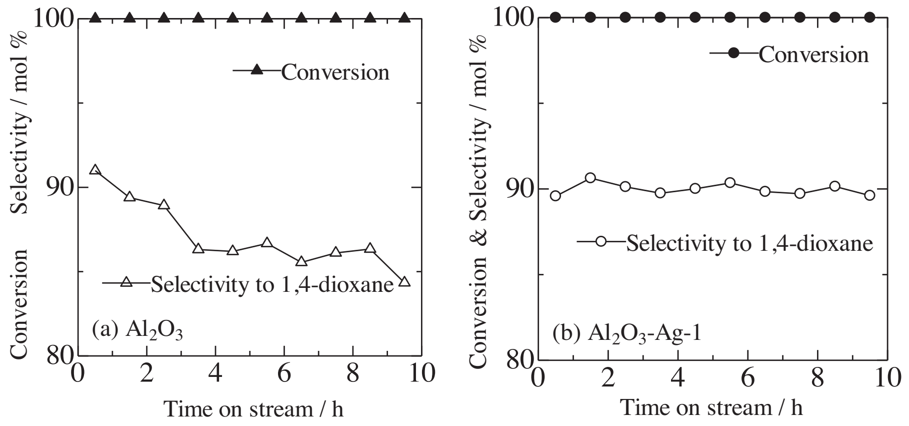

Fig. 9. Changes in conversion and selectivity with time on stream over Al_2O_3 and Al_2O_3-Ag-1 at a W/F of 156.8 g h mol^{-1}. Reaction conditions: H_2 flow rate, 20 cm^3 min^{-1}; reaction temperature, 250 °C.

Table 6
Dehydration of DEG over Al_2O_3-Ag-1 at different carrier gas flows at 250 °C.[a]

Carrier gas	Conversion/%[b]	Selectivity/%[b]						
		DOX	MeOH	EtOH	AA	MDO	EG	TEG
N_2	68.8	73.8	0.0	0.5	1.7	1.2	10.5	1.5
$H_2 + N_2$	70.0	73.7	0.0	0.6	1.8	1.3	10.4	1.6
$H_2 + CO_2$	68.0	74.4	0.1	0.4	2.1	0.9	9.3	1.3
$H_2 + NH_3$	13.8	33.0	0.3	0.6	4.0	0.1	19.9	4.4
H_2	72.6	71.5	0.1	0.8	1.5	1.4	12.7	1.3

The abbreviations of the products are the same as those shown in Table 1.
[a] Reaction conditions: W/F = 26.1 g h mol^{-1}, total carrier gas flow rate, 20 cm^3 min^{-1}; the flow rate of each gas in the mixed gas flow was 10 cm^3 min^{-1}.
[b] Average activity in the initial 5 h.

only in H_2 flow [20–22]. In this study, the reaction performed in H_2 flow gives the highest DEG conversion, the most stable selectivity to DOX and the smallest amount of accumulated carbon. This agrees with the results of our previous researches [20–22], in which we have concluded that the added metals work as a remover of product from the catalyst surface together with H_2 to prevent carbon deposition. It is assumed that Ag also plays the same role of the added metal: Ag metals would dissociate H_2 into hydrogen atoms, which move to the surface of Al_2O_3, which can be explained as spillover effect. In other words, Ag together with H_2 absorbed on the support would assist desorption of the products before the polymerization of the products and/or carbonization of the polymer proceeds.

4. Conclusions

Vapor-phase cyclodehydration of DEG into DOX was firstly performed over several solid acid catalysts such as Al_2O_3, SiO_2—Al_2O_3, Beta and MFI zeolites. Strong acidic catalysts such as Beta zeolite showed high catalytic activity, whereas deactivated rapidly with time on stream. Al_2O_3 gave a relatively stable selectivity to DOX, but the conversion of DEG gradually decreased with time on stream. Metal-modified catalysts were prepared for inhibiting the catalyst deactivation and Al_2O_3 modified with 1 wt.% Ag_2O showed the best catalytic performance. High and stable DEG conversion and DOX selectivity can be achieved over the Ag-modified Al_2O_3 under H_2 flow. The addition of Ag_2O onto Al_2O_3 decreased the averaged acid strength of Al_2O_3, which is proposed to be effective for inhibiting carbon deposition. The catalytic activity of the Ag-modified Al_2O_3 under H_2 flow is more stable than that in the other gas flow, so that H_2 carrier was indispensable for stabilizing the conversion of DEG into DOX. It is proposed that Ag works as a remover of the product adsorbed on the catalyst surface together with H_2 to prevent carbon deposition. A stable DOX selectivity of 90% with a complete conversion was achieved over the Ag-modified Al_2O_3 at 250 °C and a W/F of 156.8 g h mol^{-1} under H_2 flow.

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