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Catalytic Dehydration of 1,2-Propanediol into Propanal over Ag-Modified Silica–Alumina

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Vapor-phase catalytic dehydration of 1,2-propanediol was investigated over several solid acid catalysts, such as alumina, silica–alumina, HY zeolite, and β-zeolite. These acids catalyzed the dehydration of 1,2-propanediol to produce propanal (Figure 1), while zeolites were particularly deactivated because of deposition of carbonaceous species. An amorphous silica–alumina was modified with metals such as Ag and Cu to stabilize the catalytic activity under hydrogen flow conditions. Ag-modified silica–alumina is a promising catalyst for the production of propanal from 1,2-propanediol.

In order to reduce damage to the environment, renewable biomass must be used as an alternative to fossil resources. Glycerol has been a well-known renewable chemical resource, and its practical application has increased considerably in the last decade because of its inevitable formation as a by-product of biodiesel production.[1] Catalytic conversion of renewable biomass into valuable chemicals is expected to reduce damage to the environment. Glycerol can be selectively dehydrated to produce hydroxyacetone over copper[2,3] and silver metals,[4] and hydroxyacetone can be readily hydrogenated into 1,2-propanediol (PDO) in a hydrogen flow.[5,6] On the other hand, over acidic catalysts, glycerol is dehydrated to produce dominantly acrolein.[7]

Silica-supported heteropolyacids such as silicotungstic acid ($H_4SiW_{12}O_{40}$) show excellent catalytic activity for the dehydration of glycerol to produce acrolein.[8] Since the acidic catalysts can preferentially remove a secondary OH group of glycerol, it is expected that propanal can be formed from PDO over acidic catalysts. Actually, a silica-supported phosphotungstic acid ($H_3PW_{12}O_{40}$) shows catalytic activity for the dehydration of PDO into propanal, together with the formation of the corresponding dioxolanes.[9] Unfortunately, only a few examples have been presented for the production of propanal from PDO.[9–12]

We have found that silicotungstic acid ($H_4SiW_{12}O_{40}$) is an active catalyst for the formation of propanal from PDO.[11] In particular, silica-supported silicotungstic acid showed the highest catalytic activity in the formation of propanal. At low conversions, however, the produced propanal reacted with another PDO to produce cyclic acetal (2-ethyl-4-methyl-1,3-dioxolane, DOXL). Such acetal formation reduced the selectivity to propanal. Although the propanal selectivity higher than 93 mol % was attained at PDO conversion of 100% at 200 °C under optimum reaction conditions, the catalytic conversion was gradually deactivated with time on stream. In a similar way, higher than 90 mol % of selectivity to propanal with a complete conversion was also obtained over zeolite catalysts, such as ZSM-23, at 300 °C, whereas all of the catalysts was deactivated in an initial stage of the reaction.[12]

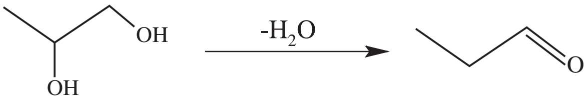

Figure 1. Dehydration of 1,2-propanediol to propanal.

An important issue in catalytic conversion under flow conditions is deterioration of acidic catalysts. The stability of catalyst is highly necessary in an industrial process. In our group, an effective operation on the stabilization of catalytic activity of acidic catalysts was reported.[13,14] Vapor-phase dehydration of tetrahydrofurfuryl alcohol (THFA) into 3,4-2*H*-dihydropyran (DHP) can be catalyzed by acidic alumina:[13] the conversion of THFA over alumina is seriously deteriorated in nitrogen at 300 °C irrespective of its high initial activity. Alumina modified with Cu exhibits stable catalytic activity with high selectivity to DHP under hydrogen flow conditions. Prior to the reaction, CuO was reduced to metallic Cu, which works as a product remover together with hydrogen to prevent coke formation. In the vapor-phase dehydration of pinacolone to 2,3-dimethyl-1,3-butadiene over modified alumina catalysts at 425 °C, Co/Al_2O_3 was also found to stabilize the conversion of pinacolone to produce 2,3-dimethyl-1,3-butadiene selectively under hydrogen flow conditions.[14] In this paper, we investigated the catalytic behavior of commercial solid acids modified by several metals in the dehydration of PDO. We also demonstrated efficient stabilization of the catalytic activity of amorphous silica–alumina by the modification of silver metal.

Four commercially available catalysts, alumina (AL), amorphous silica–alumina (SA), HY, and β (BEA)-zeolites, were used. All the metal catalysts supported on SA are prepared by incipient wetness impregnation using a solution with a prescribed amount of aquous metal nitrate solution. After impregnation, samples were calcined at 500 °C. The name of supported metal catalyst is abbreviated as follows: "SA"-"loaded metal or metal oxide"-"metal loading [wt %]." The experimental details are described in Supporting Information.[15]

Procedures for the catalytic reaction are briefly explained as follows: the catalytic reaction was performed in a fixed-bed down-flow glass reactor at 300 °C and ambient pressure. After the catalyst bed had been preheated in either H_2 or N_2 flow at 300 °C for 1 h, PDO was fed into the reactor at a feed rate of $3.9\ cm^3\ h^{-1}$. The reaction effluent collected every hour was analyzed on a gas chromatograph connected to a hydrogen flame ionization detector (FID-GC, Shimadzu GC-8A) using a 30-m capillary column of TC-WAX (GL Science).

Table 1 shows the reaction results over AL, SA, HY, and BEA catalysts, and the changes in conversion and selectivity over the catalysts with time on stream are shown in Figure S1.[15] Propanal was the main product and the main by-products were DOXL, 2,5-dimethyl-1,4-dioxane (DMDO), and acetol. Other by-products such as 2-propen-1-ol, propionic acid, and 2-ethyl-2-butenal were also detected. AL showed stable conversion of

Table 1. Dehydration of PDO over various solid acid catalysts[a]

Catalyst	Conversion[b] /%	Selectivity/mol %[b]			
		Propanal	DOXL	DMDO	Acetol
AL	95.2	38.0	22.1	21.3	4.7
SA	96.0	53.1	17.8	5.9	4.4
SA[c]	96.0	54.9	18.0	6.2	5.3
HY	58.9	32.1	51.5	5.1	5.7
BEA	83.6	53.7	33.9	3.7	2.5

[a] Reaction conditions: reaction temperature, 300 °C; flow rate of H_2, 90 $cm^3 min^{-1}$; feed rate of PDO, 3.9 $cm^3 h^{-1}$; catalyst weight, 0.3 g. [b] Average activity in the initial 5 h. [c] N_2 was used as the carrier gas, the flow rate of N_2 is 30 $cm^3 min^{-1}$.

Table 2. Dehydration of PDO over metal-loaded SA catalysts[a]

Catalyst	Conversion[b] /%	Selectivity/%[b]			
		Propanal	DOXL	DMDO	Acetol
SA	96.0	53.1	17.8	21.3	4.7
SA-CuO-2	98.4	52.1	16.9	6.5	9.0
SA-Ag-2	99.1	63.0	10.6	4.8	4.8
SA-CoO-2	96.7	52.7	19.6	6.7	10.0

[a] Reaction conditions: reaction temperature, 300 °C; flow rate of H_2, 90 $cm^3 min^{-1}$; feed rate of PDO, 3.9 $cm^3 h^{-1}$; catalyst weight, 0.3 g. [b] Average activity in the initial 5 h.

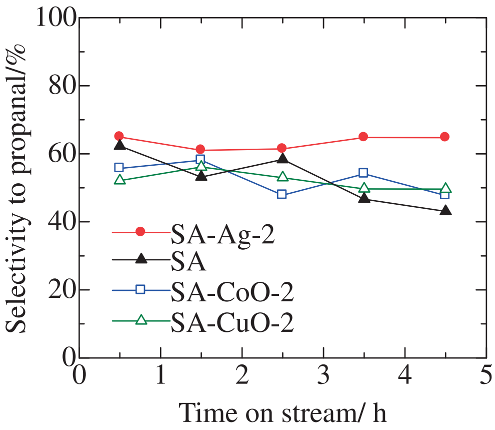

Figure 2. Changes in the selectivity to propanal with time on stream over metal-loaded SA.

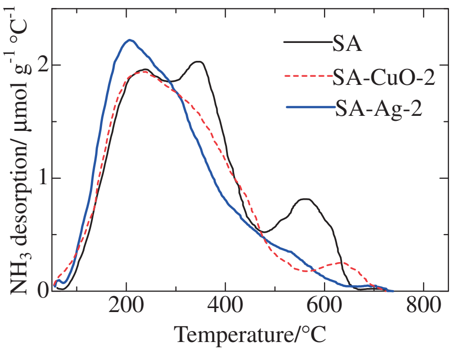

Figure 3. NH_3-TPD profiles of metal-loaded SA catalysts.

PDO and selectivity to propanal, whereas the selectivity to propanal was low. The conversion of PDO was stable over SA, and the initial selectivity to propanal, which decreases with time on stream, was high in an atmosphere of both H_2 and N_2. Both the conversion of PDO and the selectivity to propanal decreased steeply with time on stream over HY and BEA. Figure S2[15] shows the NH_3-TPD profiles of the solid acid catalysts, and Table S1[15] shows the numbers of weak, medium, and strong acid sites, and the surface areas of the catalysts. HY and BEA show strong acid sites more than those of AL and SA. It has been known that silicotungstic acid[11] and zeolite,[12] which have strong acid sites, are deactivated in the PDO dehydration to propanal. Thus, the deactivation of HY and BEA must be affected by their strong acidity.

For stabilizing the catalytic activity of SA, SA-supported metal catalysts were examined for the PDO dehydration. Table 2 shows the average conversion in the initial 5 h. The conversion of PDO slightly increased over supported metal catalysts. SA-CuO-2 and SA-CoO-2 show almost no change in the selectivity to propanal, whereas SA-Ag-2 gave a higher propanal selectivity of 63.0% comparing with 53.1% over SA. Figure 2 shows the changes in the selectivity to propanal. The addition of Cu or Co into SA showed little effect in the PDO dehydration into propanal, whereas Cu and Co are effective metals for the modification of alumina to stabilize the catalytic activity in the THFA dehydration to DHP[13] and the pinacolone conversion to 2,3-dimethyl-1,3-butadiene,[14] respectively. On the other hand, supported Ag catalyst (SA-Ag-2) was effective for stabilizing the selectivity to propanal.

Figure 3 shows the NH_3-TPD profiles of metal-loaded SA catalysts. Table 3 lists the number of weak, medium, and strong acid sites as well as the specific surface area of the catalysts, S_{BET}. The loading of metal affects the acidity of SA. The number of weak acid sites increased, whereas the number of medium and strong acid sites decreased over SA-Ag-2 comparing with those of SA and SA-CuO-2. A similar result is also reported: the loading of Cu–Ni onto alumina decreases the acid strength.[16] It has been known that strong acid sites lead to catalytic deactivation in PDO dehydration to propanal.[11,12] SA-Ag-2 shows a large number of weak acid sites and small numbers of medium and strong acid sites, compared with SA and SA-CuO-2. Thus, the weakness of the acid sites on SA-Ag-2 could stabilize the catalytic activity and give a high selectivity to propanal.

Table 4 shows the effect of the loading of CuO and Ag on the catalytic activity of SA. The selectivity to propanal decreased with increasing the loading of CuO. SA-CuO-1 showed the highest propanal selectivity of 57.9% in the supported Cu catalysts, whereas the catalytic activity was not stable: the selectivity to propanal decreased with time on stream at PDO conversion of ca. 100% (Figure S3[15]). The selectivity to acetol increased with increasing the Cu loading because of the dehydrogenation ability of Cu. However, no significant change of the selectivity to acetol was observed over Ag-loaded SA catalysts. The suitable Ag loading onto SA is 3 wt % (Table 4). SA-Ag-3 showed the highest propanal selectivity of 68.5%, and the selectivity to propanal was stable with the PDO conversion of ca. 100% (Figure 4). The average selectivity to propanal over SA-Ag-3 was even higher than the initial propanal selectivity of 62.3% over SA. The selectivity to DOXL over SA-Ag-3 was

Table 3. Properties of metal-loaded SA catalysts

Catalyst	S_{BET} /$m^2 g^{-1}$	Number of acid sites/μmol g^{-1}		
		Weak[a]	Medium[b]	Strong[c]
SA	425	141	122	42
SA-CuO-2	342	144	107	19
SA-Ag-2	398	168	88	17

[a]Defined as the desorption of NH_3 from 80 to 300 °C; [b]from 300 to 500 °C; [c]from 500 to 730 °C.

Table 4. Effect of metal loading amounts on SA catalyst[a]

Catalyst	Conversion[b] /%	Selectivity/%[b]			
		Propanal	DOXL	DMDO	Acetol
SA-CuO-1	98.9	57.9	14.6	5.7	7.9
SA-CuO-2	98.4	52.1	16.9	6.5	9.0
SA-CuO-5	96.9	49.0	18.6	6.2	10.3
SA-CuO-10	98.0	43.9	17.0	7.2	12.0
SA-Ag-1	99.3	55.8	13.7	5.9	8.0
SA-Ag-2	99.1	63.0	10.6	4.8	4.8
SA-Ag-3	99.1	68.5	9.3	4.3	5.5
SA-Ag-4	99.3	64.4	10.4	5.2	5.9
SA-Ag-10	95.2	32.6	14.5	4.7	6.1

[a]Reaction conditions: reaction temperature, 300 °C; flow rate of H_2, 90 $cm^3 min^{-1}$; feed rate of PDO, 3.9 $cm^3 h^{-1}$; catalyst weight, 0.3 g. [b]Average activity in the initial 5 h.

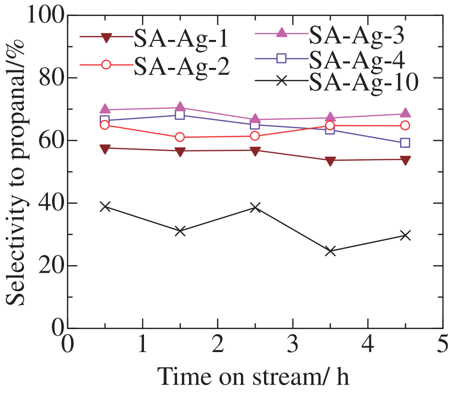

Figure 4. Changes in the selectivity to propanal with time on stream over different Ag loadings on SA.

only 9.3%, which was the lowest in all the reactions. Suitable Ag loading is not only effective for stabilizing the catalytic activity, but also effective for inhibiting DOXL formation and increasing the propanal selectivity. Large Ag loading, however, decreased both the conversion of PDO and the selectivity to propanal: the selectivity was only 32.6% over SA-Ag-10.

The effect of H_2 flow rate over SA-Ag-2 on the catalytic activity is summarized in Table 5. The selectivity to the products were affected by H_2 flow rate, which changes the partial pressure of every composition. The suitable H_2 flow rate for the effective formation of propanal is 90 $cm^3 min^{-1}$. Table 5 also shows the catalytic conversion of PDO in N_2 flow over SA-Ag-2. Because the selectivity to propanal decreased with time on stream in N_2 flow, the average selectivity to propanal was lower than that in H_2 flow.

Table 5. Effect of H_2 flow rate over SA-Ag-2 catalyst on the PDO dehydration[a]

Flow rate /$cm^3 min^{-1}$	Conversion[b] /%	Selectivity/mol %[b]			
		Propanal	DOXL	DMDO	Acetol
30	99.0	57.0	12.7	5.8	5.9
60	98.4	60.4	12.2	5.0	5.5
90	99.1	63.0	10.6	4.8	4.8
120	97.3	51.2	19.1	5.8	10.3
30[c]	98.7	55.3	14.2	6.3	6.3

[a]Reaction conditions: reaction temperature, 300 °C; feed rate of PDO, 3.9 $cm^3 h^{-1}$; catalyst weight, 0.3 g. [b]Average activity in the initial 5 h. [c]Flow rate of N_2, 30 $cm^3 min^{-1}$.

We have reported that alumina modified with Cu and Co are effective for exhibiting stable catalytic activity, and the added metals work as a remover of product from the catalyst surface together with H_2 to prevent coke formation.[13,14] In this study, Ag also plays the same role of Cu and Co in previous reports. In other words, we can say that Ag together with H_2 would assist the desorption of the products before the polymerization of the products, which leads to the coke formation, could proceed.

The vapor-phase dehydration of PDO into propanal was performed over several solid acid catalysts. SA showed a high initial selectivity to propanal, but it was seriously deactivated with time on stream. SA-supported metal catalysts were examined for inhibiting the deactivation of catalytic activity. SA-supported Ag was effective for stabilizing the catalytic activity, a high propanal selectivity of 68.5% was obtained over SA-Ag-3 in H_2 flow. The Ag loading decreased the numbers of medium and strong acid sites, while it increased the number of the weak acid sites, which are effective for inhibiting catalytic deactivation. Since the supported Ag catalysts were effective only in H_2 atmosphere, Ag would play a significant role for removing the product from the catalyst surface together with hydrogen flow.

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