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Amorphous SiO_2 catalyst for vapor-phase aldol condensation of butanal

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ABSTRACT

Vapor-phase aldol condensation of butanal to form 2-ethyl-2-hexenal was carried out over several oxide catalysts such as SiO_2-Al_2O_3, Al_2O_3, ZrO_2, and SiO_2. Catalysts with moderate and strong acid sites such as Al_2O_3 and SiO_2-Al_2O_3 were active for the reaction in the initial period, whereas they deactivated rapidly. In contrast, SiO_2 with weak acidity showed a low but a stable catalytic activity for the formation of 2-ethyl-2-hexenal. Thermogravimetric analyses of the samples used after the reactions indicate that SiO_2 has the smallest amount of carbonaceous species that contributed to its stable activity among the tested catalysts. SiO_2 catalysts with different pore sizes and specific surface areas were examined: SiO_2 with a mean pore diameter of 10 nm and a surface area of 295 $m^2\,g^{-1}$ showed the best catalytic performance and gave a 2-ethyl-2-hexenal selectivity of 90% at a conversion of 48% at 240 °C. In the catalytic test using deuterated SiO_2, which was prepared by contacting SiO_2 with deuterated water before the reaction, it was confirmed by a mass spectrometer that the deuterium atom of SiOD was transferred to a 2-ethyl-2-hexenal molecule during the reaction. It is indicated that silanol groups on the SiO_2 surface played a role as an active site.

1. Introduction

In the chemical industry, aldol condensation is an important reaction for the synthesis of long-chain chemicals [1,2], and it has wide applications in the field of biomass conversion to useful chemicals and fuels [3–5] as well as in the field of petrochemistry. Aldol condensation proceeds between aldehydes and/or ketones, and either an acid or a base can catalyze the reaction [1,2]. Industrially, sulfuric acid or sodium hydroxide is generally used as a catalyst in aldol condensation [1,2,6–9], while it is obvious that the utilization of inorganic acid and base is not friendly to the environmental. The development of solid catalysts for aldol condensation has attracted much attention in recent years. Solid acids such as zeolites and heteropolyacids [7,10–14] as well as solid bases such as Na/SiO_2 and MgO [15–18] exhibit catalytic activity for aldol condensation, whereas the catalysts are not stable and they deactivated during the reaction due to a poisoning of the active sites by the deposition of carbonaceous species in most cases.

Self-aldol condensation of butanal to form 2-ethyl-2-hexenal (2E2H) is investigated as a model reaction to study aldol condensation reactions [14,19–25]. In addition, the reaction is attracting great importance because 2E2H has been used as an intermediate for producing perfumes, cosmetics, and plasticizers [19,20,23,24]. A vapor-phase continuous process for 2E2H production is attractive from the viewpoint of industrial application. However, serious deactivation of a catalyst is reported in the previous studies performed in a vapor phase [20–22,25]. For example, the conversion of butanal over Pd/Na/SiO_2 decreased from 81.8 to 49.1% with time on stream from 4 to 8 h at 350 °C [21]. In our recent report, SiO_2-Al_2O_3, Nb_2O_5, and TiO_2 were tested at 200 °C in H_2 flow: all the catalysts gradually deactivated and the conversion of butanal decreased with a range of 10–40% during the initial 5 h of time on stream [25]. In contrast, SiO_2-Al_2O_3 with the strong acidity showed the most serious catalytic deactivation. On the other hand, we found that Ag-modified TiO_2 with hydrogen flow was effective for inhibiting the formation of coke and improving the catalytic stability.

Amorphous SiO_2 is a porous material with weak acidity [26–28], and it is widely used as a catalyst support [29–31]. Recently, we found that SiO_2 can be used as a catalyst for vapor-phase dehydration such as the dehydration of aldoximes to nitriles [26] and the cyclization of levulinic acid to angelica lactones [27]. In the dehydration, the catalysts with strong acidity such as SiO_2-Al_2O_3 exhibited high initial activities, whereas strong acid sites took part in the side reactions to form oligomers, which poisoned the active sites and decreased the stability of catalytic activity. In contrast to the strong acid catalysts, the catalytic activity of SiO_2 was usually low, while it was stable [26,27]. Over the weak acidic SiO_2, also, high conversion levels can be achieved by

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Table 1
Aldol condensation of butanal over various solid acid catalysts. [a]

Catalyst	S_{BET} ($m^2 g^{-1}$)	Conversion[b] (mol%)	Selectivity (mol%)[b] 2E2H[c]	Butanoic acid	1-Butanol	Others
Al_2O_3	198	13.7	87.2	5.6	2.1	5.1
SiO_2-Al_2O_3	397	20.7	77.2	4.0	2.0	16.8
ZrO_2	39	2.5	26.6	62.7	5.6	5.1
10-Li_2O/ZrO_2	–	2.3	10.4	63.4	3.5	22.7
SiO_2 (Q-10)	295	9.4	74.2	21.1	1.5	3.2

[a] Reaction conditions: reaction temperature, 200 °C; catalyst weight, 0.5 g; H_2 flow rate, 5 $cm^3 min^{-1}$.

[b] Conversion and selectivity were averaged between 1–5 h of time on stream, TOS.

[c] 2E2H, 2-ethyl-2-hexenal.

increasing the contact time. It should be emphasized that the selectivity to the dehydration products over SiO_2 can be maintained since no side reactions proceed even at high conversions. For example, in the cyclization of levulinic acid to angelica lactones performed at 250 °C [27], the selectivity to angelica lactones over SiO_2 was ca. 90% at a conversion of ca. 50%, whereas that was only ca. 80% over SiO_2-Al_2O_3 at the same conversion level due to the further oligomerization of angelica lactones.

In the present study, several solid catalysts including different kinds of SiO_2 were investigated in the vapor-phase aldol condensation of butanal. This study aims to achieve a high selectivity to 2E2H with stable and high conversions using appropriate solid catalysts. Furthermore, the active sites on the SiO_2 surface were investigated and discussed.

2. Experimental

2.1. Samples

Four kinds of SiO_2 (CARiACT Q-3, Q-6, Q-10, and Q-15 with mean pore diameters of 3, 6, 10 and 15 nm, respectively) samples were supplied by Fuji Silycia, Ltd., Japan. γ-Al_2O_3 (DC-2282) was supplied by Dia Catalyst & Chemicals Ltd., Japan. SiO_2-Al_2O_3 (N631HN) was purchased from Nikki Chemical Co. Ltd., Japan. Monoclinic ZrO_2 (RSC-HP) was supplied by Daiichi Kigenso Kagaku Kogyo Co. Ltd., Japan. 10 mol % Li_2O-modified monoclinic ZrO_2, denoted as 10-Li_2O/ZrO_2, was prepared by an impregnation followed by calcination at 600 °C for 3 h, and the details are described in our previous report [32]. Butanal, which was purchased from Wako Pure Chemical Industries, Japan, was utilized for the catalytic reaction without further purification.

2.2. Catalytic reaction

Vapor-phase aldol condensation of butanal to 2E2H was performed in a fixed-bed glass tube reactor in a similar way to the previous report [25]. The details were described in the supplementary information, and the typical reaction conditions were as follows: butanal was fed into the reactor at 200 °C and a feed rate of 1.3 g h^{-1} together with an H_2 flow at a flow rate of 5 $cm^3 min^{-1}$ and an ambient pressure.

A pretreatment of SiO_2 (Q-10) with D_2O was performed in the fixed-bed down-flow reactor. Before the pretreatment of D_2O, 4.0 g of silica placed on the catalyst bed was heated at 250 °C for 1 h. D_2O was fed at 250 °C and a feed rate of 1.8 g h^{-1} for 1 h, and then the silica sample was heated at 250 °C for 1 h to remove the residual D_2O. After the pretreatment, the temperature was decreased to 200 °C, and the reaction was started by feeding butanal under the same conditions as mentioned above. A mass spectrometer in a gas chromatograph system (GC–MS, QP5050, Shimadzu, Japan) was used for the mass analysis of 2E2H in the reaction effluent collected during an appropriate period of the reaction.

2.3. Characterization of catalysts

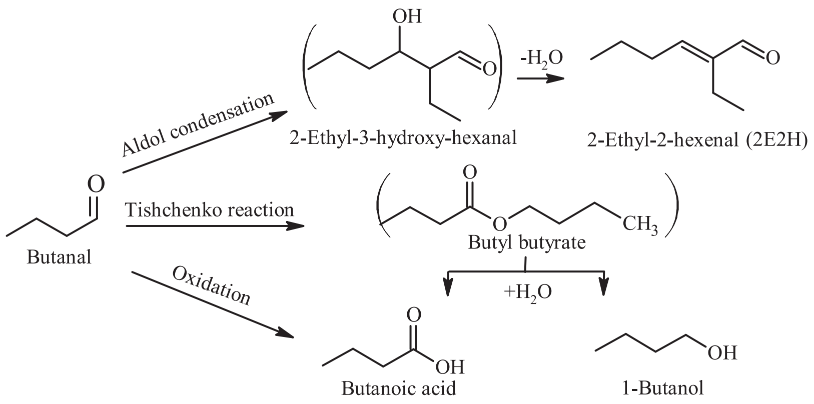
The specific surface area (S_{BET}) of catalysts was calculated by the Brunauer-Emmett-Teller (BET) method in the N_2 adsorption-desorption isotherm at −196 °C. The thermogravimetry (TG) analysis was performed using Thermoplus 8120E2 (Rigaku). The TG analysis conditions were as follows: sample weight, ca. 10 mg; the rate of temperature increment, 5 °C min^{-1}; the range of heating temperature, between room temperature and 900 °C. The temperature-programmed desorption of adsorbed NH_3 (NH_3-TPD) measured by neutralization titration was the method introduced elsewhere [33,34], and the details were described in the supplementary information. The diffuse reflectance infrared Fourier transform (DRIFT) spectra of catalysts were recorded on spectroscopy using FT/IR-4200 (JASCO Corp., Japan) under vacuum conditions. Before the DRIFT measurement, a sample was pretreated in vacuum at 150 °C for 1 h to remove the H_2O adsorbed on the catalyst surface.

3. Results and discussion

3.1. Aldol condensation of butanal over various solid catalysts

Table 1 shows the catalytic reaction results of the aldol condensation of butanal over solid catalysts such as SiO_2-Al_2O_3, Al_2O_3, ZrO_2, 10-LiO/ZrO_2, and SiO_2 (Q-10) where the reaction was performed at 200 °C and a catalyst loading of 0.5 g. 2E2H, butanoic acid, and 1-butanol were detected as the major products in all the reactions. Values of the conversion and the selectivity were averaged between 1–5 h. Scheme 1 shows the proposed formation route of each detected product. Aldol condensation of butanal firstly forms 2-ethyl-3-hydroxy-hexanal, which further dehydrates to form 2E2H. Tsuji et al. reported that Tishchenko esterification of butanal occurred over both acid and base catalysts [15], which means that the reactions, Tishchenko esterification and aldol condensation, require similar active sites. Therefore, Tishchenko esterification usually proceeds as the major side reaction in aldol condensation [15,22,25]. In the present study, the major by-products, butanoic acid and 1-butanol, were probably formed by the hydrolysis of butyl butyrate, which was formed by the Tishchenko esterification of butanal. However, the selectivity to butanoic acid was higher than that to 1-butanol in all the cases. The yield of butanoic acid, which was calculated by the butanal conversion multiplied by the selectivity to butanoic acid, was less than 2.5% and it was almost constant at ca. 2% in the cases at 200 °C. Some undetectable products, summarized as others in Table 1, were formed in the reactions, and they are supposed to be mainly attributed to the oligomers of butanal.

In our recent report, ZrO_2 showed a catalytic activity in the vapor-phase intramolecular aldol condensation of 2,5-hexanedione to form 3-methylcyclopent-2-enone, and 10-Li_2O/ZrO_2 exhibited an enhanced activity, providing 97.9% selectivity to 3-methylcyclopent-2-enone with a conversion of 18.7% at a W/F of 0.29 h and a reaction temperature of 250 °C [32]. In the present study, however, ZrO_2 and 10-



Scheme 1. Proposed formation routes of the detected products. (2Ethyl-3-hydroxy-hexanal and butyl butyrate were not detected in the products).

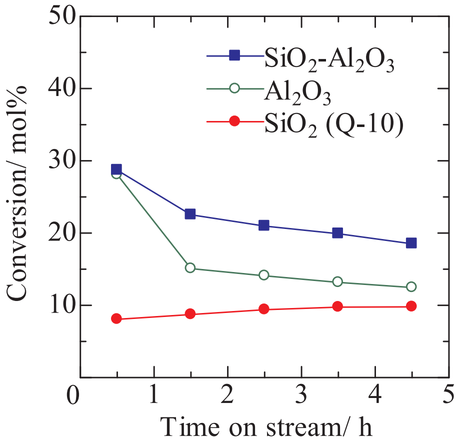


Fig. 1. Changes in catalytic conversion of butanal over SiO_2-Al_2O_3, Al_2O_3, and SiO_2 (Q-10) with time on stream.
Reaction conditions: temperature, 200 °C; catalyst weight, 0.5 g; H_2 flow rate, 5 cm^3 min^{-1}.

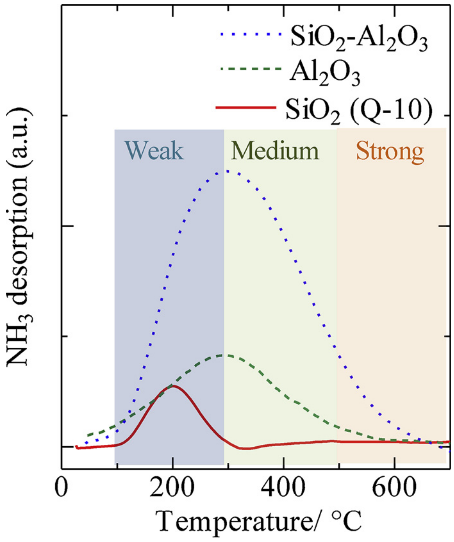


Fig. 2. NH_3-TPD profiles of SiO_2-Al_2O_3, Al_2O_3, and SiO_2 (Q-10).

Li_2O/ZrO_2 showed poor selectivity for the formation of 2E2H while they had a high selectivity to butanoic acid. This indicates that the reactions, the intramolecular aldol condensation of 2,5-hexanedione and the self-aldol condensation of butanal, would require different active sites with different reaction mechanisms. In contrast to the ZrO_2-based catalysts, SiO_2-Al_2O_3, Al_2O_3, and SiO_2 (Q-10) exhibited high activities, and the selectivity to 2E2H was higher than 70%. Among the tested catalysts, SiO_2-Al_2O_3 showed the highest conversion of 20.7% with a 2E2H selectivity of 77.2%, while Al_2O_3 showed the highest 2E2H selectivity of 87.2% with a conversion of 13.7%. Fig. 1 shows the changes in the activity of SiO_2-Al_2O_3, Al_2O_3, and SiO_2 (Q-10) with time on stream. It is obvious that the conversion of butanal gradually decreased with time of stream in the case of SiO_2-Al_2O_3 and Al_2O_3, indicating the deactivation of catalysts occurs during the reaction. However, SiO_2 (Q-10) was stable during the reaction, and no decrease in conversion was observed irrespective of a low conversion. These results show that SiO_2 (Q-10) is the most stable catalyst although the intrinsic activity is low.

Fig. 2 shows the NH_3-TPD profiles of SiO_2-Al_2O_3, Al_2O_3, and SiO_2 (Q-10). SiO_2-Al_2O_3 shows a broad desorption peak located from ca. 100 to 700 °C with a peak temperature at 293 °C. This indicates that SiO_2-Al_2O_3 includes weak, medium, and strong acid sites, which were defined by NH_3 desorption peaks at 100–300, 300–500, and 500–700 °C, respectively, and the amount of medium acid sites is the largest. Al_2O_3 shows a desorption peak appeared at temperatures from ca. 100 to 600 °C with a peak temperature at 296 °C, which is similar to that of SiO_2-Al_2O_3. However, the total acid amount of Al_2O_3 is much smaller than that of SiO_2-Al_2O_3. SiO_2 shows a desorption peak appeared from ca. 100 to 300 °C with a peak temperature of 201 °C, meaning that SiO_2 has the weakest acidity.

Meanwhile, SiO_2 has the smallest amount of acid sites. The order of the number of acid sites, SiO_2-Al_2O_3 > Al_2O_3 > SiO_2, agrees with the order of their catalytic activity, indicating that the aldol condensation of butanal is catalyzed by the acid sites on the catalysts. In general, the catalyst with strong acidity is easy to be deactivated, which has been demonstrated in our previous studies dealing with dehydration processes such as the cyclodehydration of diethylene glycol to 1,4-dioxane [35] and the dehydration of 1,2-propanediol to propanal [29,30]. In the present study, the deactivation of SiO_2-Al_2O_3 and Al_2O_3 is supposed to be attributed to their relatively strong acidity because polymerizable compounds such as the oligomers of butanal would be easily formed over strong acid sites. In another word, SiO_2 is stable without side reactions because of its weak acidity.

Fig. 3 depicts the TG profiles of SiO_2-Al_2O_3, Al_2O_3, and SiO_2 (Q-10) samples used after the reactions shown in Fig. 1. All the used samples show a weight loss between ca. 200 and 500 °C, which is attributed to the coke decomposition [25,35]. The order of the amount of deposited carbon is SiO_2-Al_2O_3 > Al_2O_3 > SiO_2, which agrees with the order of the amount of their medium and strong acid sites, demonstrating that carbon is readily formed and deposited on the surface of a strong acid catalyst. The used SiO_2 sample shows the smallest amount of accumulated carbonaceous species, which agrees with the stable activity of SiO_2, demonstrating that the accumulation of carbonaceous species primarily causes the catalytic deactivation.

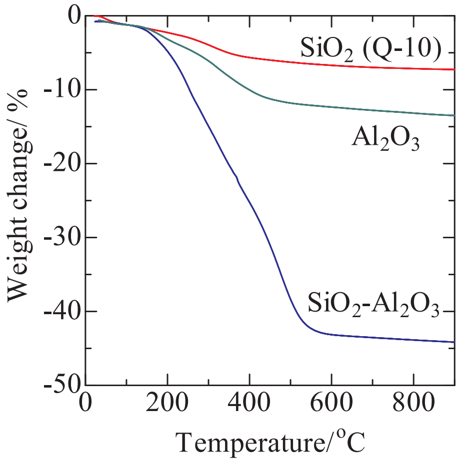


Fig. 3. TG profiles of SiO_2-Al_2O_3, Al_2O_3, and SiO_2 (Q-10) used after the reaction.

Reaction conditions: temperature, 200 °C; catalyst weight, 0.5 g; H_2 flow rate, 5 $cm^3 min^{-1}$; time on stream, 5 h.

3.2. Aldol condensation of butanal over SiO_2 catalysts

From the viewpoint of industrial production, catalytic stability is highly required. Although SiO_2 (Q-10) showed the lowest activity for 2E2H formation among the three acid catalysts (Table 1), it showed the highest stability among the tested catalysts. Therefore, various SiO_2 catalysts with different properties were tested and investigated in the following studies. Table 2 shows the catalytic activity of various SiO_2 for aldol condensation of butanal at 200 °C. Four types of SiO_2, Q-3, Q-6, Q-10, and Q-15, with different pore sizes and surface areas, exhibited different catalytic activities. Among the tested SiO_2 samples, Q-10 showed both the highest conversion of butanal and the highest selectivity to 2E2H. Q-3 and Q-6 had larger surface areas and larger acid amount than Q-10 [27], whereas they showed lower catalytic activities. It is supposed that the small mesopores of Q-3 and Q-6 would disturb the diffusion of the dimers and oligomers of butanal in the pores, which leads to their poor activity. On the other hand, Q-15 with the largest pore size but the smallest surface area showed the lowest activity, indicating that the surface area is an important factor for the aldol condensation over SiO_2. These results demonstrate that both large pore sizes and sufficient surface areas of SiO_2 are required for the efficient aldol condensation of butanal to form 2E2H.

Because of the high catalytic activity of Q-10 among SiO_2, it was selected for investigating the effect of the catalyst loading, i.e., contact time. As shown in Table 2, both the conversion and the selectivity to 2E2H increased with increasing the loading of Q-10, indicating that large contact time was effective for achieving a high yield of 2E2H from butanal. The formation of butanoic acid was inhibited at large contact time. A high 2E2H selectivity of 88.6% with a conversion of 38.6% was achieved over Q-10 at 200 °C and a catalyst loading of 4.0 g.

Table 2

Aldol condensation of butanal over various SiO_2 catalysts.[a]

Catalyst	S_{BET} ($m^2 g^{-1}$)	Conversion[b] (mol%)	Selectivity (mol%)[b]			
			2E2H[c]	Butanoic acid	1-Butanol	Others
Q-3	705	4.0	42.7	45.0	0.0	12.3
Q-6	401	8.1	65.2	28.9	1.0	4.9
Q-10	295	9.4	74.2	21.1	1.5	3.2
Q-10[d]	295	20.5	86.0	10.0	1.9	2.1
Q-10[e]	295	38.6	88.6	4.4	2.1	4.9
Q-15	226	1.9	40.7	59.3	0.0	0.0

[a] Reaction conditions: reaction temperature, 200 °C; catalyst weight, 0.5 g; H_2 flow rate, 5 $cm^3 min^{-1}$.

[b] Conversion and selectivity were averaged between 1–5 h of TOS.

[c] 2E2H, 2-ethyl-2-hexenal.

[d] Catalyst weight, 2.0 g.

[e] Catalyst weight, 4.0 g.

Table 3

Aldol condensation of butanal over SiO_2 (Q-10) at different reaction temperatures.[a]

Temperature (°C)	Conversion[b] (mol%)	Selectivity (mol%)[b]			
		2E2H[c]	Butanoic acid	1-Butanol	Others
180	27.3	92.2	4.3	1.6	1.9
200	38.6	88.6	4.4	2.1	4.9
220	43.9	89.1	2.7	2.8	5.4
240	48.3	90.0	4.0	2.8	4.2
260	51.6	87.9	4.0	4.1	4.0

[a] Reaction conditions: catalyst weight, 4.0 g; H_2 flow rate, 5 $cm^3 min^{-1}$.

[b] Conversion and selectivity were averaged between 1–5 h of TOS.

[c] 2E2H, 2-ethyl-2-hexenal.

The effect of reaction temperature on the catalytic activity of Q-10 was investigated at temperatures from 180 to 260 °C with a catalyst loading of 4.0 g (Table 3). The conversion of butanal increased with increasing the reaction temperature, while the selectivity to 2E2H was kept at 88–92% in the reactions irrespective of reaction temperature. This indicates that the reaction temperatures did not significantly affect the selectivity to 2E2H over Q-10. In the previous study, however, high temperatures such as 220 and 240 °C decreased the selectivity to 2E2H over TiO_2 with a relatively strong acidity [25]. In addition, high reaction temperatures decreased the selectivity to 2E2H in the case of over basic Na/SiO_2 [21] and MgO/SiO_2 with acid/base properties [22]. In the present study, the high selectivity to 2E2H over Q-10 can be maintained at such a high temperature of 260 °C at high conversion levels. This could be attributed to the weak acidity of Q-10 which would be less active for catalyzing the side reactions such as the oligomerization of butanal.

Fig. 4 shows the changes in the activity of Q-10 with time on stream at different reaction temperatures. In the reactions especially at high temperatures such as 240 and 260 °C, the catalytic activity was stable, and a significant decrease in either the conversion or the selectivity to 2E2H was not observed. In contrast, both the conversion and the selectivity to 2E2H decreased with time on stream in the case of Pd/Na/SiO_2 at 350 °C [21], MgO/SiO_2 at 300 °C and 350 °C [22], Pd/KX zeolite at 150 °C [20], and TiO_2 at 240 °C [25]. Fig. 5 shows the TG profiles of Q-10 used after the reactions at 200 and 260 °C. Compared with the TG profile of fresh Q-10, the weight loss of the samples used after the

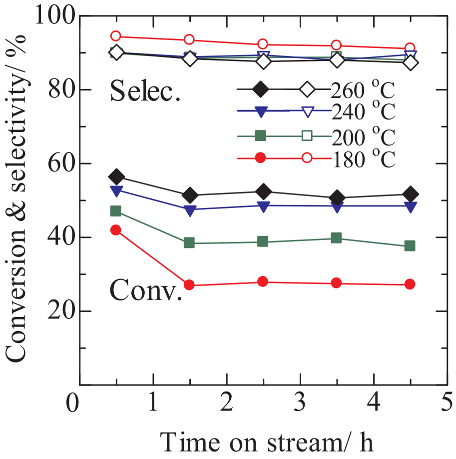


Fig. 4. Changes in the catalytic activity over SiO_2 (Q-10) with time on stream at different reaction temperatures.

Reaction conditions: catalyst weight, 4.0 g; H_2 flow rate, 5 $cm^3 min^{-1}$.

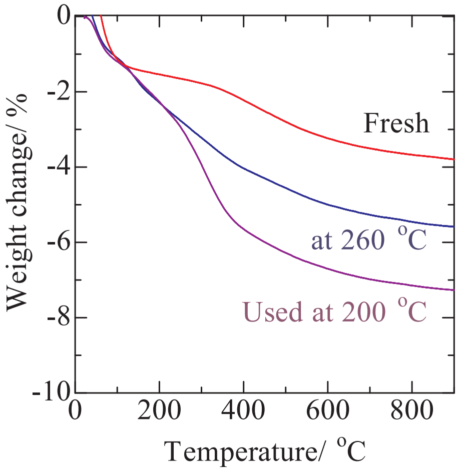


Fig. 5. TG profiles of SiO_2 (Q-10) used at different reaction temperatures. Reaction conditions: catalyst weight, 4.0 g; H_2 flow rate, 5 cm^3 min^{-1}; time on stream, 5 h.

reaction was large, indicating that carbonaceous species was accumulated on the surface of Q-10 during the reaction. On the other hand, the weight loss of the sample used at 260 °C was smaller than that of the sample used at 200 °C. This indicates that the carbonaceous species deposited on the samples are not a heavy coke because of the ready desorption at low temperatures. We have studied the dehydration of 1,2-alkanediols to aldehydes over WO_3/SiO_2 with a moderate acidity: high temperatures promoted the formation of coke in that case [30]. In contrast to the present SiO_2, it is probable that a high temperature promotes the formation of coke through dehydrogenation over WO_3/SiO_2 with stronger acidity. This difference in temperature dependence on carbon formation between the two studies is considered to be attributed to the different acid strength of the catalysts as well as the different type of reactions. In the present study, a low temperature of 200 °C could not promote the desorption of residual product on the catalyst surface that increases the amount of carbonaceous species, which is a precursor of coke.

Fig. 6 shows the effects of carrier gas on the catalytic activity of SiO_2 (Q-10) at 250 °C. The reaction was performed in either N_2 or H_2 atmosphere with different flow rate. In our previous report dealing with the dehydration of 1,2-propanediol to propanal over WO_3/SiO_2, H_2 showed a better performance than N_2 for keeping the catalytic activity [29]. Also, H_2 carrier gas effectively works as an inhibitor of deactivation over Ag/TiO_2 for the aldol condensation of butanal [25]. Therefore, H_2 was mainly used as the carrier gas in the present study. However, we found no significant difference between H_2 and N_2, as shown in Fig. 6. It is evident that the conversion of butanal decreased with increasing the flow rate of gas, either N_2 or H_2. Because the aldol condensation of butanal is a dimerization process, it can be expected that the high concentration of butanal would promote the contact of butanal molecules with each other and accelerate the reaction. In this study, the flow rate of carrier gas significantly affects the partial pressure of butanal and thus changes the conversion of butanal. Although the selectivity to 2E2H was not influenced by the flow rate of N_2, the selectivity to 2E2H significantly decreased with increasing the flow rate of H_2. It is an important finding that carrier gases are not necessary for the vapor-phase aldol condensation. Since the aldol addition is an equilibrium reaction, the high partial pressure of butanal without carrier gas would be the best reaction conditions to shift the equilibrium to the right. In other words, usage of carrier gas at high partial pressure would shift the equilibrium to the left.

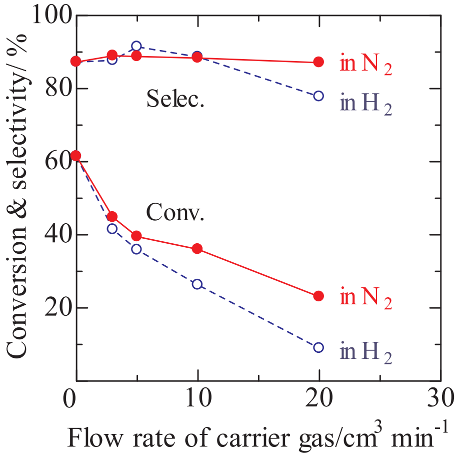


Fig. 6. Effects of carrier gas on the catalytic activity of SiO_2 (Q-10) catalyst at 250 °C.
Reaction conditions: catalyst weight, 4.0 g. The carrier gas was either N_2 or H_2.

3.3. Study of the active sites on SiO_2

In the cyclization of levulinic acid to angelica lactones [27], we have confirmed that the silanol groups on the surface of SiO_2 are the active sites. Also, the cyclization of 5-amino-1-pentanol to piperidine was performed over D_2O-treated SiO_2 [28]: SiOH groups were exchanged to SiOD groups, and it was confirmed that the deuterium atoms in silanol groups shifted to the product piperidine in the initial periods when SiOD remained.

In the present study, to confirm the active sites on Q-10, the aldol condensation of butanal was performed over Q-10 deuterated by D_2O. The pretreatment of D_2O was performed in the fixed-bed down flow reactor under D_2O flow conditions at 250 °C for 1 h. Fig. 7 compares the DRIFT spectra of fresh Q-10 and deuterated Q-10. An absorption peak at 3737 cm^{-1}, which is assigned to the stretching of SiO-H in isolated silanol groups [36], can be observed in the spectra of both fresh Q-10 and deuterated one. In the DRIFT spectra of the deuterated Q-10, an absorption peak attributed to the stretching of SiO-D in isolated silanol groups was observed at 2711 cm^{-1} [36], indicating the partial introduction of SiOD groups on the surface of Q-10.

Fig. 8 shows the mass profiles of 2E2H and butanal collected in the effluents over deuterated Q-10 at 200 °C in different periods of time on stream. In the catalytic reaction of butanal over undeuterated Q-10, 2E2H showed a major molecular peak at *m/z* of 126, which corresponded to the molecular weight of $C_8H_{14}O$, as well as a small isotope peak at *m/z* of 127 (Fig. 8a). In the reaction of butanal over deuterated Q-10, the 2E2H collected in the initial 30 min of time on stream had peaks at *m/z* of 127 and 128 with stronger intensity than that at 126 (Fig. 8b). Therefore, most of the produced 2E2H molecules include

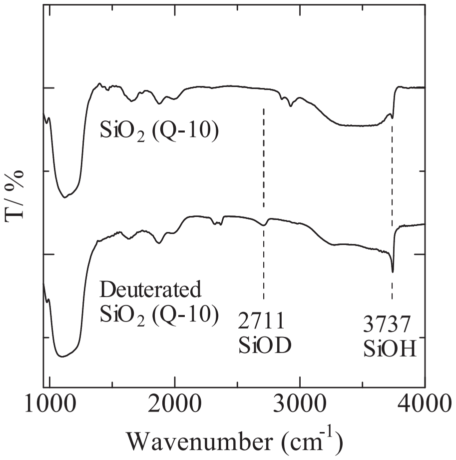


Fig. 7. DRIFT spectra of SiO_2 (Q-10) and deuterated SiO_2 (Q-10).

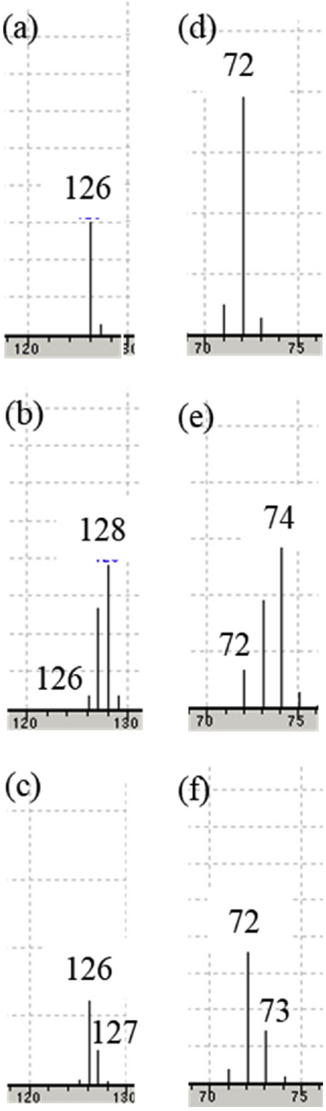


Fig. 8. Mass profiles of 2-ethyl-2-hexenal (a,b,c) and butanal (d,e,f) in the reaction over undeuterated and deuterated SiO_2 (Q-10) with different periods of time on stream.

(a,d), a sample collected between 0–60 min of time on stream in the usual reaction over undeuterated SiO_2 (Q-10); (b,e) collected between 0–30 min of time on stream in the reaction over deuterated SiO_2 (Q-10); (c,f) collected between 70–90 min of time on stream in the reaction over deuterated SiO_2 (Q-10). Reaction conditions: temperature, 200 °C; catalyst weight, 4.0 g; H_2 flow rate, 5 cm^3 min^{-1}. Mass profiles in a full range are presented in the supplementary information (Fig. S1).

either one or two deuterium atoms, which have a molecular formula of $C_8H_{13}DO$ and $C_8H_{12}D_2O$. In the mass profile of 2E2H collected in the reaction over deuterated Q-10 during 70–90 min, the intensity of the peak at *m/z* of 126 becomes stronger again than that of the peak at *m/z* of 127 (Fig. 8c).

In addition, as for the recovered reactant, butanal, had peaks at *m/z* of 73 and 74 as well as 72 in the initial 30 min of time on stream (Fig. 8e), while butanal, C_4H_8O, with a peak of *m/z* of 72 was recovered after 70 min of the reaction (Fig. 8f and d). This indicates that the surface SiOD groups can readily react to the reactant butanal groups to form C_4H_7DO and $C_4H_6D_2O$, which would have a structure of $CH_3CH_2CH_2CDO$ and $CH_3CH_2CHDCDO$, respectively. Thus, SiOD groups are consumed, and SiOH groups are regenerated after an appropriate period of the catalytic reaction while the possible reaction equation is expressed as follows: $C_4H_6D_2O + C_4H_6D_2O$ – > $C_8H_{12}D_2O + D_2O$. These results demonstrate that hydrogen of silanol groups transfers to the product of 2E2H and the reactant butanal during the reaction, and suggest that the silanol groups on the SiO_2 surface are the active sites for the reaction. However, there remains a question about whether SiOH catalyzes the aldol condensation or not. Aldol condensation of butanal has been recently studied over Ti species supported on silica at 80 °C and proposed a reaction mechanism using isolated titanol, TiOH [37]. However, we could not propose a probable mechanism using isolated silanol in this paper. Because the evidence to considering the reaction mechanism is not enough in this experiment (Fig. 7), we need further work on the isotope experiment in detail to clarify the mechanism of the aldol condensation and the role of SiOH groups.

4. Conclusions

In this study, aldol condensation of butanal to form 2E2H was performed over several solid catalysts. Although strong acidic catalysts such as SiO_2-Al_2O_3 and Al_2O_3 were active, they were deactivated rapidly due to the significant accumulation of carbonaceous species on the catalyst surface. In contrast, SiO_2 with a weak acidity showed a low activity, but the activity was the most stable because carbonaceous species was relatively difficult to be accumulated on the surface of SiO_2. Both the pore size and the surface area affected the activity of SiO_2: SiO_2(Q-10) with a mean pore diameter of 10 nm and a surface area of 295 m^2 g^{-1} showed the best catalytic performance. High conversion levels could be obtained by increasing the loading of SiO_2, and the 2E2H selectivity of ca. 90% could be maintained at high conversion levels. To study the active sites on SiO_2, the surface SiOH groups on SiO_2 were exchanged to SiOD groups by contacting SiO_2 with deuterated water at 250 °C. It was confirmed by mass analysis that most of the produced 2E2H molecules contained deuterium atoms, indicating that the deuterium atom transferred from Q-10 to a 2E2H molecule during the reaction. It is demonstrated that the silanol groups on the surface of SiO_2 could be the active sites for the vapor-phase aldol condensation of butanal.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.11.012.

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