Bull. Chem. Soc. Jpn., ***64***, *2619—2623 (1991)*

Reforming of Ethanol —Dehydrogenation to Ethyl Acetate and Steam Reforming to Acetic Acid over Copper-Based Catalysts—

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(Received February 12, 1991)

The title reactions, $2CH_3CH_2OH \rightarrow CH_3COOC_2H_5+2H_2$ and $CH_3CH_2OH+H_2O \rightarrow CH_3COOH+2H_2$, were carried out over copper-based catalysts (Cu, Cu/SiO_2, Cu/ZrO_2, Cu/Al_2O_3, Cu/MgO, and Cu/ZnO). The selectivities to ethyl acetate and acetic acid markedly depended upon the supports used. Acetaldehyde was formed by the dehydrogenation of ethanol and transformed to either ethyl acetate or acetic acid through steps in which a nucleophilic addition of ethanol (or ethoxide ions) or water (or hydroxide ions) to acetaldehyde occurred. The rates of the transformation steps to ethyl acetate and acetic acid were appreciably affected by the kinds of supports used. The transformation steps proceeded slowly, compared with the dehydrogenation step.

Although alcohols are rapidly dehydrogenated to aldehydes or ketones over copper-based catalysts,[1)] the dehydrogenation of higher alcohols is poorly selective. The aldehydes and ketones formed partly undergo an aldol condensation and/or transformation to esters.[2,3)] In the dehydrogenation of methanol, methyl formate is produced in high selectivity over copper-based catalysts.[4—6)] We have shown that this reaction proceeds consecutively through the dehydrogenation of methanol to formaldehyde and the reaction between the formaldehyde and methanol (or methoxide ions).[7)] When water was present along with methanol, steam reforming of methanol ($CH_3OH+H_2O \rightarrow CO_2+3H_2$) occurs selectively.[8,9)] The formaldehyde produced reacted rapidly with water to form carbon dioxide and hydrogen via surface formate or formic acid.[10)]

Although Kawamoto et al. previously studied the dehydrogenation of various higher alcohols over unsupported copper,[2,3)] their experiments were conducted within a restricted range of operating conditions. Regarding the steam reforming of higher alcohols over copper-based catalysts, no paper has been published according to our knowledge.

In the present study, the title reactions were carried out over various copper-based catalysts under a wider range of operating conditions, and differences in the mechanisms of the reactions involving methanol and ethanol were elucidated.

Experimental

The catalysts used in the present experiments were unsupported Cu, Cu/SiO_2 (0.5—90 wt% Cu), Cu/ZrO_2 (0.5—30 wt% Cu). $CuAl_2O_3$ (6.3 and 30 wt% Cu), Cu/MgO (6.2 and 30 wt% Cu), and Cu/ZnO (30 wt% Cu). Support-free Cu was prepared by the decomposition of copper(II) nitrate at 773 K in air for 3 h. The supported catalysts were prepared by impregnation of metal oxides with a solution of copper(II) nitrate and calcined at 773 K in air for 3 h. Prior to the reaction, the catalysts, thus prepared, were reduced in a hydrogen stream of 12 $cm^3\ min^{-1}$ at 523 K for 18 h. Experiments were carried out in a manner similar to those in a previous study.[7)] A conventional flow reactor was used; the concentrations of the reactants and the products in the effluent were determined by gas chromatography. The selectivities to carbon-containing products were evaluated on the carbon basis.

The valence states of copper were determined by diffuse reflectance UV-vis spectroscopy. The amount of metallic copper exposed on the surface was determined by a reaction with dinitrogen monoxide.[11)]

Results and Discussion

Dehydrogenation of Ethanol. 1) Reaction Pathway to Ethyl Acetate: The dehydrogenation of ethanol occurred above 380—420 K, giving acetaldehyde, ethyl acetate and C_4-species (butyraldehyde, 1-butanol, and methyl ethyl ketone). The selectivities to these products depended upon the reaction conditions and the catalysts used. Figure 1 shows the mole fraction of the products against space time over 30 wt% Cu/SiO_2. Both ethyl acetate and butyraldehyde increase with space time. Acetaldehyde increases with an increase in space time,

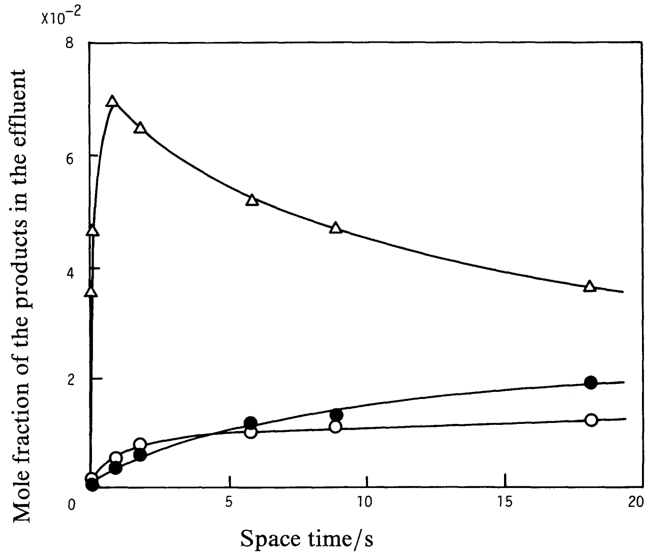

Fig. 1. Mole fraction of the products in the effluent against space time in dehydrogenation of C_2H_5OH over 30 wt% Cu/SiO_2. Temperature: 493 K. Inlet partial pressure $P^0_{C_2H_5OH}$: 20.5 kPa. (△) CH_3CHO, (●) $CH_3COOC_2H_5$, (○) C_3H_7CHO.

passes through a maximum and then decreases. These results strongly suggest that ethyl acetate and butyraldehyde are formed via acetaldehyde. The values of a parameter, $K=P_{CH_3CHO}P_{H_2}/P_{C_2H_5OH}$, which was estimated from the partial pressures of acetaldehyde, hydrogen and ethanol in the effluent, were found to be close to that of the equilibrium constant, K_p,[12,13] of the dehydrogenation of ethanol $C_2H_5OH \rightarrow CH_3CHO+H_2$ at 493 K. Hence, under the reaction conditions the formation of acetaldehyde was much more rapid than those of ethyl acetate and butyraldehyde.

Figure 2 illustrates the selectivity for ethyl acetate formation against conversion of ethanol over 30 wt% Cu/SiO_2 at different temperatures. The selectivity increases considerably with an increase in the conversion of ethanol. At 493 K and an ethanol conversion of 76%, a 56% selectivity was attained. At a given conversion of ethanol, the selectivity increases appreciably with a decrease in the temperature.

To examine the pathway to ethyl acetate, reactions involving acetaldehyde were carried out. In Figs. 3(I) and (II), the mole fraction of various carbon-containing products in the effluent is plotted against time at 433 K. When only acetaldehyde was fed over 30 wt% Cu/SiO_2, crotonaldehyde was exclusively produced. No ethyl acetate was detected in the effluent. However, upon switching acetaldehyde to ethanol, ethyl acetate was formed rapidly, and decreased to a steady value. Crotonaldehyde diminished rapidly. Acetaldehyde in the effluent initially decreased, but then increased with time as the dehydrogenation of ethanol proceeded. When ethanol was fed over the acetaldehyde-free catalyst, ethyl acetate was formed together with acetaldehyde. Since these products increased with time in a monotonic manner, reaching steady values, it was strongly suggested that ester formation occurred appreciably in the presence of adsorbed acetaldehyde. Since methanol was dehydrogenated to methyl formate via reaction between formaldehyde and methanol (or methoxide),[7] we concluded that the acetaldehyde formed by the dehydrogenation of ethanol was subjected to a nucleophilic addition of ethanol (or ethoxide) and transformed to ethyl acetate.

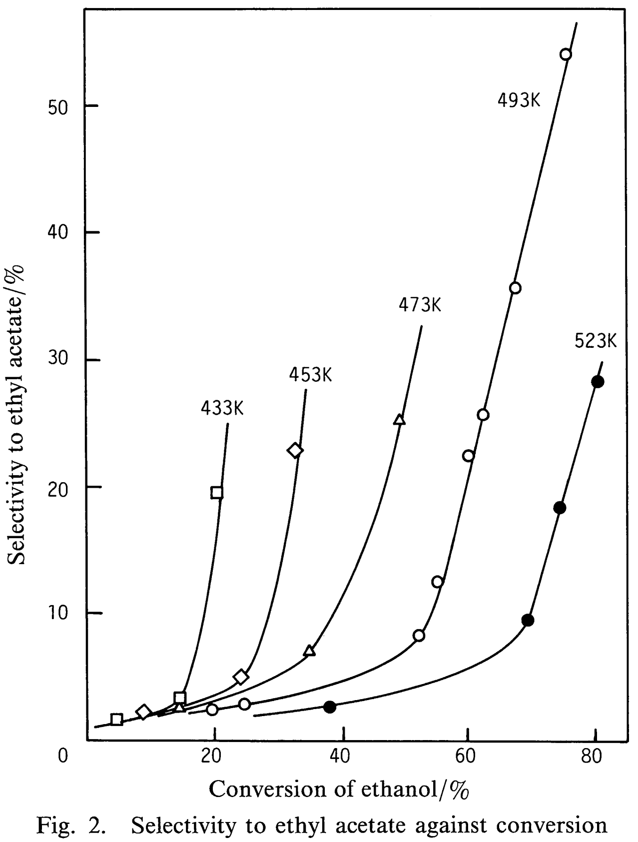

Fig. 2. Selectivity to ethyl acetate against conversion of ethanol over 30 wt% Cu/SiO_2. Inlet partial pressure $P^0_{C_2H_5OH}$: 20.5 kPa.

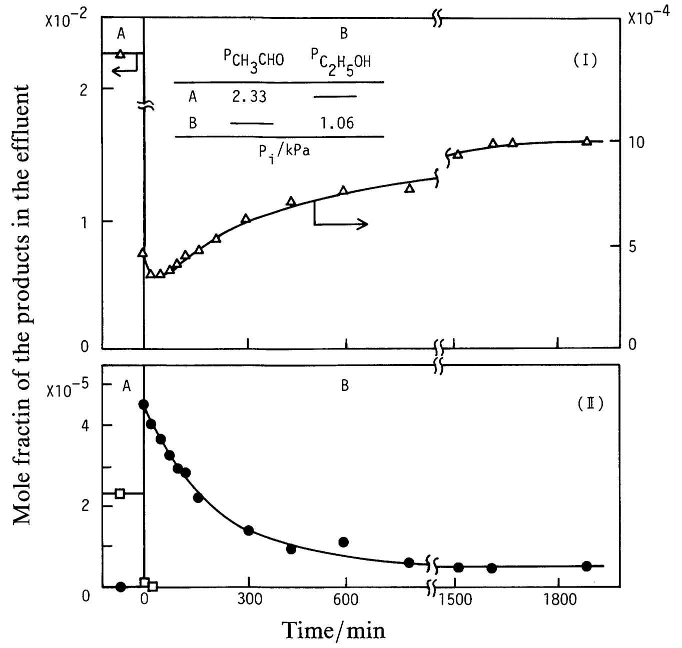

Fig. 3. Carbon-containing products formed in the reactions involving CH_3CHO over 30 wt% Cu/SiO_2: (A) in the absence of C_2H_5OH, (B) in the presence of C_2H_5OH. Temperature: 433 K. (△) CH_3CHO, (●) $CH_3COOC_2H_5$, (□) $CH_3CH=CHCHO$.

2) Effect of the Supports upon the Reaction: Table 1 lists the selectivity to the carbon-containng products and the product ratio, (C_4/Ester), of C_4-species to ethyl acetate at an ethanol conversion of 50% over various copper-based catalysts. These parameters are greatly affected by the kinds of supports. Cu/ZrO_2 and Cu/ZnO are highly selective for ethyl acetate formation. The C_4-species and diethyl ether are produced appreciably over Cu/Al_2O_3. However, when KOH (1 wt% K) was doped on Cu/Al_2O_3 (not listed in Table 1), the product ratio decreased from 4.3 to 0.4, and the formation of diethyl ether was completely suppressed. These results strongly suggested that C_4-species such as butyraldehyde, methyl ethyl ketone and 1-butanol were

Table 1. Dehydrogenation of Ethanol — Selectivity to Carbon-Containing Products and Product Ratio (C_4/Ester) at 493 K and $P^0_{C_2H_5OH}$=20.5 kPa —

Catalyst[a]	Selectivity[b]/%					C_4/Ester[d]
	Acetaldehyde	Acetone	Diethyl ether	C_4-species[c]	Ethyl acetate	
Cu/Al_2O_3	54.1	Trace	19.3	21.6	5.0	4.3
Cu/SiO_2	77.9	0.4	0.3	13.9	7.5	1.9
Cu/MgO	74.2	4.0	0	8.0	13.8	0.6
Cu/ZrO_2	57.3	0.5	0	14.6	27.6	0.5
Cu/ZnO	67.3	0.7	0	3.9	28.1	0.1
Cu[e]	70.6	1.7	0	7.4	20.3	0.4

a) Supported Cu catalyst: 30 wt% Cu. b) Selectivity to carbon-containing products at ethanol conversion of 50%. c) Including butyraldehyde, methyl ethyl ketone, and 1-butanol. d) Ratio of mole fraction of C_4-species to ethyl acetate in the effluent at ethanol conversion of 50%. e) Obtained at ethanol conversion of 45%.

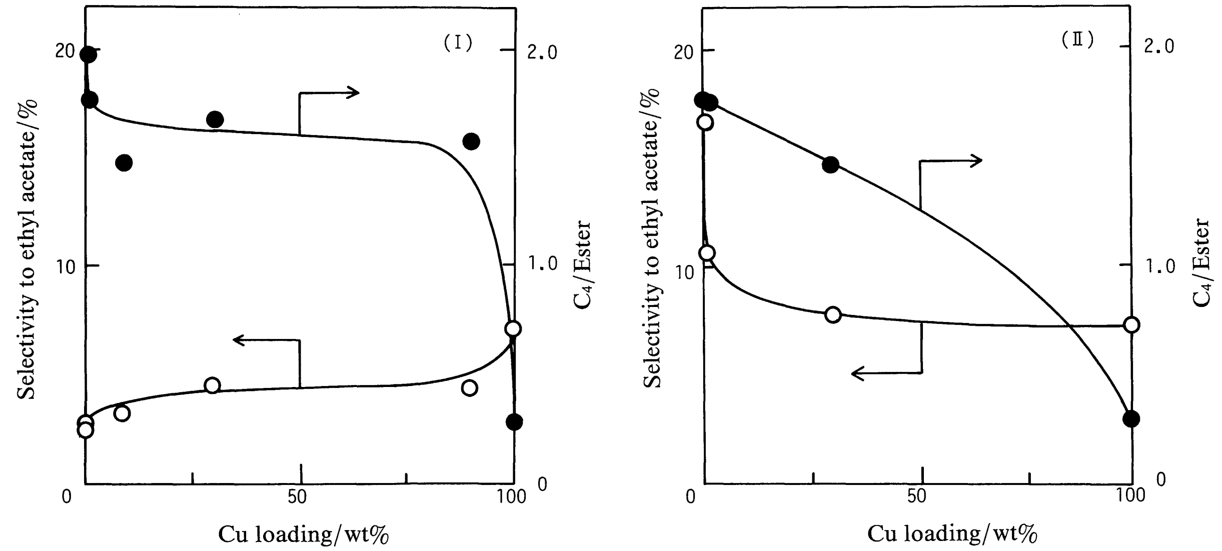

Fig. 4. Selectivity to ethyl acetate and product ratio C_4/Ester obtained at C_2H_5OH conversion of 35%: over Cu/SiO_2, (II) over Cu/ZrO_2. Temperature: 493 K. Inlet partial pressure $P^0_{C_2H_5OH}$: 20.5 kPa.

produced by acid-catalyzed reactions.

Figures 4(I) and (II) illustrate the selectivity to ethyl acetate and the product ratio obtained at an ethanol conversion of 35% over Cu/SiO_2 and Cu/ZrO_2 with various copper loadings. These parameters depend upon the copper loading as well as the kinds of supports. Over Cu/SiO_2, the selectivity for ethyl acetate formation gradually decreases with a decrease in copper loading. On the other hand, the product ratio increases considerably when the copper loading changes from 100 wt% to 90 wt% Cu. This ratio gradually increases with decreasing loading from 90 wt% to 1 wt% Cu; at 0.5 wt% Cu increases considerably. At low copper loadings an appreciable amount of diethyl ether was detected in the effluent. This again suggested that the formation of C_4-species was enhanced in the presence of an acid. Over Cu/ZrO_2 ester formation slowly increases slowly with a decrease in copper loading to 1 wt% Cu. At 0.5 wt% Cu the selectivity to ester increases to a great extent. The product ratio increases with decreases in copper loading.

3) Active Site: When the catalyst was previously reduced to metallic copper, the dehydrogenation of ethanol took place rapidly. No reactions occurred over unreduced catalysts or the supports. The catalysts used for the reaction gave a typical color due to metallic copper. The UV/VIS spectra of the catalysts only exhibited the absorption edge at 560 nm ascribed to metallic copper.[14] This strongly suggested that the dehydrogenation occurred over the metalic copper surface.

Table 2 illustrates the results for the reaction between ethanol and adsorbed acetaldehyde over Cu/SiO_2, Cu/ZrO_2, SiO_2, and ZrO_2. The ethyl acetate formation over 30 wt% Cu/ZrO_2 is about 30 times as fast as that over 30 wt% Cu/SiO_2. The selectivity to this species is 70% over Cu/ZrO_2, whereas that over Cu/SiO_2 is 18%. Over SiO_2 and ZrO_2 supports, no reactions occurred with ethanol alone. However, when acetaldehyde was preadsorbed over the supports, ethyl acetate was produced. Over ZrO_2, ester formation is highly selective and rapid. This reaction proceeds at a rate comparable to that obtained over 30 wt% Cu/ZrO_2. On the other hand,

Table 2. Ethyl Acetate Formation from Adsorbed Acetaldehyde and Ethanol at 433 K

Catalyst[a]	Ethyl acetate formation[b]	
	Rate/cm^3 min^{-1} g-cat^{-1}	Selectivity/%
Cu/ZrO$_2$	8.4 $\times 10^{-2}$	70
Cu/SiO$_2$	0.29$\times 10^{-2}$	18
ZrO$_2$	8.3 $\times 10^{-2}$	100
SiO$_2$	0.03$\times 10^{-2}$	0.18

a) Cu/ZrO$_2$, Cu/SiO$_2$: 30 wt% Cu. b) Obtained at $P^0_{C_2H_5OH}$=1.3 kPa. Acetaldehyde was preadsorbed at P_{CH_3CHO}=2.0 kPa and at 433 K.

over SiO$_2$ ethyl acetate is produced sluggishly. The selectivity to this species is extremely low compared with that over ZrO$_2$. The rate of ethyl acetate formation over SiO$_2$ alone is one-tenth that over 30 wt% Cu/SiO$_2$. These results strongly suggests that over Cu/SiO$_2$ this step proceeded practically over copper surface, whereas over Cu/ZrO$_2$ the support played a role in the formation of ethyl acetate.

Steam Reforming of Ethanol. 1) Reaction Pathway to Acetic Acid: When the mixture of ethanol and water was fed over copper-based catalysts, acetic acid was formed together with products of the dehydrogenation of ethanol. The formation of ethyl acetate and the C$_4$-species was appreciably retarded by the presence of water. In Fig. 5, the mole fraction of the ethyl acetate and the C$_4$-species in the effluent is plotted against space time over 30 wt% Cu/SiO$_2$. Acetaldehyde increases with an increase in space time, and then decreases through a maximum. By contrast, both acetic acid and ethyl acetate increase steadily with increasing space time, suggesting that both of these species are produced through parallel pathways via acetaldehyde. The selectivity to acetic acid increased with an increase in the conversion level of ethanol. At an ethanol conversion of 88%, the selectivity was found to be 43%. At high conversion levels, the dehydrogenation of ethanol to acetaldehyde was found to be practically in equilibrium, suggesting that this step proceeded rapidly, compared with the step for acetic acid formation.

When the mixture of acetaldehyde and water was fed over 30 wt% Cu/SiO$_2$, acetic acid was formed at a rate comparable to that in the steam reforming of ethanol. No ethyl acetate was detected in the effluent. These findings were quite similar to those in the reaction between formaldehyde and water.[10] This suggested that adsorbed acetaldehyde underwent a nucleophilic addition of water (or hydroxide ions), giving acetic acid.

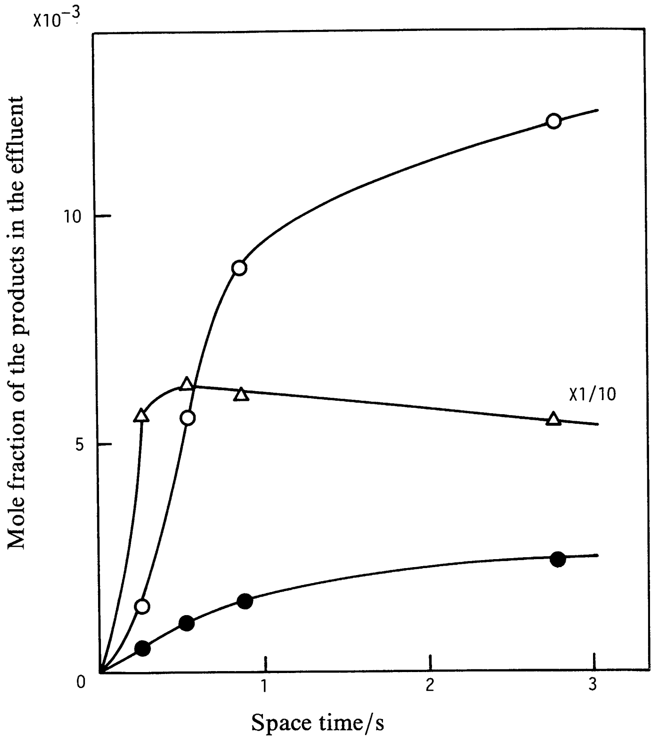

Fig. 5. Mole fraction of carbon-containing products against space time in steam reforming of C$_2$H$_5$OH over 30 wt% Cu/SiO$_2$. Temperature: 523 K. Inlet partial pressure: $P^0_{C_2H_5OH}$: 10.1 kPa, $P^0_{H_2O}$: 20.2 kPa. (○) CH$_3$COOH, (●) CH$_3$COOC$_2$H$_5$, (△) CH$_3$CHO.

Table 3 summarizes the selectivity to the carbon-containing products in the steam reforming over various copper-based catalysts (30 wt% Cu) at an ethanol conversion of 80%. The selectivity to acetic acid is greatly affected by the kinds of supports. Over Cu/ZnO, the selectivity was attained to 38% at this conversion level.

Difference in the Mechanisms of Reforming of Ethanol and Methanol. Reforming of methanol has been studied over various copper-based catalysts.[4-11,15] In

Table 3. Steam Reforming of Ethanol — Selectivity to Carbon-Containing Products at 523 K, $P^0_{C_2H_5OH}$=10.1 kPa and $P^0_{H_2O}$=20.2 kPa —

Catalyst[a]	Selectivity[b]/%					
	Acetaldehyde	Acetone	Diethyl ether	Acetic acid	C$_4$-species[c]	Ethyl acetate
Cu/Al$_2$O$_3$	55.1	0.2	7.0	5.7	16.1	15.9
Cu/SiO$_2$	53.9	0.3	Trace	24.5	5.9	15.4
Cu/ZrO$_2$	56.2	4.7	0	0	8.5	30.7
Cu/ZnO	36.4	8.6	0	38.0	0	17.0
Cu[d]	88.0	0.7	0	5.2	0	6.1

a) Supported Cu catalyst: 30 wt% Cu. b) Selectivity to carbon-containing products at ethanol conversion of 80%. c) Including butyraldehyde, and 1-butanol. d) Obtained at ethanol conversion of 64%.

the absence of water, methyl formate and hydrogen were produced, whereas in the presence of water carbon dioxide and hydrogen were produced. These reactions were highly selective. Formaldehyde was produced in the course of the reactions and subsequently transformed to the final products through a reaction with methanol (or methoxide) or water (or hydroxide ions).[7,10] The dehydrogenation to formaldehyde was concluded to be rate-determining in the reforming of methanol.[4-10]

In the reforming of ethanol, ethyl acetate and acetic acid were produced, respectively, in the absence and presence of water. These reactions proceeded in a similar way to those of methanol. The dehydrogenation step to acetaldehyde occurred much more rapidly than the steps to ethyl acetate and acetic acid. The steps to ethyl acetate and acetic acid were strongly affected by the kinds of supports, compared with that to acetaldehyde. Hence, the selectivities for the reforming of ethanol were considerably lower than those for the reforming of methanol and were strongly affected by the kinds of supports. By contrast, since the dehydrogenation step was rate-determining in the reforming of methanol, the effect of the support upon the reaction was not as appreciable as that upon the reforming of ethanol.

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