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Remarkable Activities of Ni-Cu/SiO_2 Catalysts for the Decomposition of Methanol to Syngas

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The activities and selectivities of Ni-Cu/SiO_2 catalysts for the titled reaction were investigated. The binary metal catalysts exhibited much higher performances than Ni/SiO_2 and Cu/SiO_2. In particular, 100% conversion and 100% CO selectivity were obtained over $Ni_{0.1}Cu_{0.9}/SiO_2$ at a reaction temperature as low as 280 °C during the process time of 96 h.

Recently, the decomposition of methanol to syngas(a mixture of H_2 and CO) has been focussed as a reaction for an on-board reforming of methanol in the automotive engine system and as a reaction which can readily produce syngas for a C_1 chemical industry. Several types of transition metal catalysts have been investigated so far.[1-8] Niiyama et al.[3] reported that $ZnCu_{0.16}Cr_{0.49}$ catalyst was effective for the selective decomposition of methanol to syngas (react. temp:300 °C; conv.:100%; selec.:CO 95%, CO_2 5%). According to Inui et al.,[4] nickel was found to be a favorable main catalyst component for the same reaction, and syngas was selectively produced on Ni/SiO_2 and Ni/Al_2O_3 catalysts at 320 °C, corresponding to ca.87% methanol conversion.[5] Very recently, we found that Ni/$AlPO_4$ catalyst was a promising catalyst for the selective decomposition of methanol to syngas in the reaction temperature range of 300-400 °C(react. temp:300 °C; conv.:99.4%, selec.:CO 97.6%, CH_4 2.4%).[9] Therefore, the complete decomposition of methanol to syngas alone (conv. :100%; selec. of CO:100%) has not been accomplished in spite of much effort: the higher the conversion of methanol, the lower the selectivity of syngas because of the formation of by-products such as methane, carbon dioxide, etc. which were produced by the secondary reactions of the resulting syngas.

The present paper describes remarkable catalytic features of Ni-Cu/SiO_2 catalysts which enabled the decomposition of methanol to syngas exclusively proceed. This catalyst system exhibited a satisfactory activity at such a low temperature as 280 °C throughout the process time of 240 h.

All catalysts used in this investigation were prepared by impregnating the corresponding supports with solutions of nickel and/or copper nitrates in the usual way. After impregnation, the resulting slurries were dried at 110 °C for 20 h, followed by calcining at 500 °C in air for 2 h. Then the catalyst samples were pressed at 200 kg/cm^2 into tablets, followed by crushing and sieving (16-32 mesh). A magnesia support was prepared by calcining magnesium hydroxide (Kanto Chemical

Co.) at 750 °C in air for 2 h. Zirconia (surface area:0.6 m^2 g^{-1}) was obtained from High Purity Chemicals Co. The reaction was carried out using a flow type reactor. A catalyst sample was packed with quartz wool plugs in quartz tube reactor, and reduced in situ with a hydrogen stream at 500 °C for 2 h, followed by a helium flush at the same temperature for 30 min prior to reaction. The feed rate was 43 cm^3 min^{-1} for helium saturated with the vapor of methanol maintained at 10 °C. An effluent gas was analyzed chromatographically using thermal conductivity detector with active carbon and triacetine columns.

Table 1 shows the effects of the metallic composition in Ni-Cu/SiO_2 catalysts on their catalytic activities and selectivities. In general, much high selectivities of CO were observed on the Ni-Cu/SiO_2 catalysts, while the substantial formation of by-products were found on Ni/SiO_2 catalyst or Cu/SiO_2 catalyst. The methane selectivities on the Ni-Cu/SiO_2 catalysts decreased sharply with increasing content of copper. The catalytic activity passed through a minimum at 30% copper content. The Cu/SiO_2 catalyst yielded methyl formate which was not formed on the Ni-Cu/SiO_2 catalysts at all. Table 2 lists the results of methanol decomposition over the Ni-Cu/SiO_2 catalysts with different metal loading. The catalytic activities increased with increasing metal loading, while the selectivity of CO was kept at 100% regardless of the metal loading. Table 3 summarizes the effects of supports of nickel-copper catalysts on their catalytic activities and selectivities. Four kinds of catalysts were subjected to similar

Table 1. Effects of the Metallic Composition of Silica-supported Ni-Cu Catalysts on Catalytic Activities and Selectivities[a)]

Metallic composition[b)]	Conversion %	Composition /%				
		CO	CH_4	CO_2	CH_3OCH_3	$HCOOCH_3$
0	100.0	87.2	12.8	0.0	0.0	0.0
10	96.7	98.3	1.7	0.0	0.0	0.0
30	90.6	99.9	0.1	0.0	0.0	0.0
50	95.8	100.0	0.0	0.0	0.0	0.0
70	98.1	99.9	0.1	0.0	0.0	0.0
90	100.0	100.0	0.0	0.0	0.0	0.0
100	86.6	54.3	1.1	1.5	0.3	42.8

a) Catalyst: metal loading 30 wt%; pretreatment 500 °C, H_2 flow, 2 h. Reaction conditions: react. temp 280 °C; catal. 0.1 g.

b) Atomic % Cu/(Cu+Ni).

Table 2. Methanol Decomposition over Silica-supported Ni-Cu Catalysts with Different Metal Loading[a)]

	Metal loading /%			
	10	20	30	50
Conversion /%	77.3	98.6	100.0	100.0

a) Catalyst: metallic composition Ni:Cu=1:9; pretreatment 500 °C, H_2 flow 2 h. Reaction conditions: react. temp 280 °C; catal. 0.1 g.

Table 3. Methanol Decomposition over Ni-Cu Supported on Various Metal Oxides[a)]

Support	Conversion %	Composition /%				
		CO	CH_4	CO_2	CH_3OCH_3	$HCOOCH_3$
Al_2O_3	96.6	87.0	0.0	3.1	9.9	0.0
ZrO_2	48.4	100.0	0.0	0.0	0.0	0.0
MgO	91.7	100.0	0.0	0.0	0.0	0.0
SiO_2	100.0	100.0	0.0	0.0	0.0	0.0

a) Catalyst: metallic composition Ni:Cu=1:9, metal loading 50 wt%; pretreatment 500 °C, H_2 flow, 2 h. Reaction conditions: react. temp 280 °C; catal. 0.1 g.

measurements. The catalytic activities decreased in the following order: silica> alumina> magnesia> zirconia. This order was essentially the same as that of surface areas of these supports. Only when alumina was employed as a support, considerable amounts of by-products were observed. The formation of dimethyl ether will be ascribed to an acidic property of the alumina support, considering the fact that the other supports are known to be less acidic than alumina.

As shown in Fig. 1, the catalytic activity of the Ni/SiO_2 catalyst decreased rapidly with the process time. On the other hand, over $Ni_{0.1}Cu_{0.9}/SiO_2$ catalyst, no change in activity was observed within 96 h, its selectivity being held at 100%.

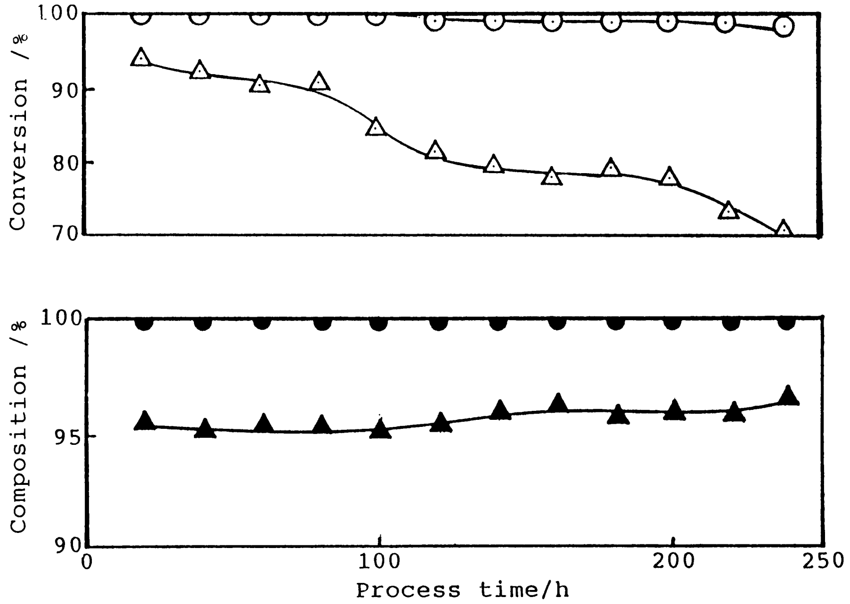

Fig. 1. The decomposition of methanol over $Ni_{0.1}Cu_{0.9}/SiO_2$ (○, ●) and Ni/SiO_2 (△, ▲) catalysts.[a)]

a) Catalyst: metal loading 30 wt%; pretreatment 500 °C, H_2 flow, 2 h. Reaction conditions: react. temp 280 °C; catal. 0.1 g. Open and closed symbols denote conversion and selectivity.

A marked difference in catalytic properties between the Cu/SiO_2 and $Ni_{0.1}Cu_{0.9}/SiO_2$ catalysts suggests that there should be essencial interaction between nickel and copper. As an attempt to characterize the $Ni\text{-}Cu/SiO_2$ catalysts, X-ray diffraction (abbreviated as XRD) studies were carried out. It was confirmed that no metal oxides remained in the Cu/SiO_2 and $Ni\text{-}Cu/SiO_2$ (Ni:Cu=1:9 and 3:7) catalysts after reduction at 500 °C. However, the XRD pattern of the $Ni_{0.1}Cu_{0.9}/SiO_2$ catalyst was not apparently different from that of the Cu/SiO_2 catalyst, that is, no XRD lines due to a nickel-copper alloy were observed. Since it is known that the surface composition of a bimetallic catalyst is considerably different from its bulk composition, a prominent analytical technique including Auger electron spectroscopy will be applied to the $Ni\text{-}Cu/SiO_2$ catalysts in the near future to examine their surface layers which are responsible for the titled reaction.

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