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Production of Higher Alcohols from Synthesis Gas over Coprecipitated Nickel Catalysts

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Coprecipitated Ni-TiO_2 and Ni-MnO catalysts efficiently produced higher alcohols such as ethanol, propanol and butanol from synthesis gas. These catalysts showed lower activities for ethane hydrogenolysis but much higher activities for ethylene hydroformylation than conventional supported nickel catalysts.

The reactions of CO and H_2 (synthesis gas) on various catalysts have extensively been studied from chemical interests as well as industrial viewpoints. Nickel-based catalysts are well known as typical methanation (methane formation) catalysts, while only a limited number of reports [1-3] concerning the synthesis of oxygenated compounds on nickel catalysts have been published. In the present paper we report new coprecipitated nickel-containing catalysts which can efficiently produce higher(C_{2+}) alcohols from synthesis gas.

The coprecipitated Ni catalysts (denoted as Ni-TiO_2, Ni-Al_2O_3, etc.) were prepared by coprecipitation from aqueous solutions of metal nitrates, except for titanium sulfate, with sodium carbonate. A supported Ni/TiO_2 catalyst was prepared by impregnation of TiO_2 with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. Reactions were carried out at 6.0 MPa of synthesis gas ($CO/H_2/Ar=32/64/4$) in a fixed-bed stainless-steel microreactor. The effluent gas was analyzed by gas chromatography using a spherocarbo column(TCD) for CH_4, CO_2, CO and Ar, and a series column (FID) of Porapak Q and Porapak R for alcohols, esters and hydrocarbons. Table 1 shows the activities and selectivities of various nickel catalysts in CO hydrogenation. It was found that higher alcohols were produced over the coprecipitated Ni-TiO_2 and Ni-MnO catalysts. In contrast, methane was the main product over the Ni-Al_2O_3, Ni-SiO_2, and Ni/TiO_2 catalysts. It is to be noted that the selectivity to C_{2+}-alcohols was about one order of magnitude higher on the Ni-TiO_2 catalyst than on the Ni/TiO_2 catalyst.

In order to know the catalytic properties of these nickel catalysts, ethane hydrogenolysis and ethene hydroformylation in relation to CO hydrogenation were investigated. The results of these reactions are given in Table 2. The Ni-Al_2O_3 and Ni/TiO_2 catalysts showed high activities for ethane hydrogenolysis but low or negligible activities for ethene hydroformylation. It was found that the hydrogenolysis was drastically suppressed,. while the oxo-reaction of ethene was greatly (10^2-10^4 times) enhanced by the Ni-TiO_2 catalyst as compared with the Ni-Al_2O_3 and Ni/TiO_2 catalysts. The ethane hydrogenolysis is well-known as a structure-sensitive reaction.[4)] Thus, the structures of the used catalysts were studied by means of a transmission electron microscopy. It was found that the Ni particles of the Ni-TiO_2 catalyst were comparatively small and uniform (5-20 nm in diameter) in spite of a rather high content of nickel (ca. 50 wt% as NiO). For the Ni-Al_2O_3 catalyst, on the other hand, nickel particles were very large in size and broad in distribution (0.1-5 µm in diameter). Thus, the Ni-TiO_2 catalyst is considered to be less active for ethane hydrogenolysis than the Ni-Al_2O_3 catalysts. Ichikawa et al.[6)] reported that the C_{2+}-oxygenates forming activity of a rhodium catalyst had an intimate relation with its CO insertion activity. Similarly, the coprecipitated Ni-TiO_2 catalyst with a high ability of

Table 1. Production of higher alcohols from synthesis gas[a)]

Catalysts	Ni:M (M=Ti,Mn,etc.) (atomic ratio)	CO Conv.[b)] %	Selectivity / % [c)] CH_4	C_{2+}	MeOH	EtOH	C_{3+}-OH[d)]
Ni-TiO_2	1:1	19.7	51.4	8.3	17.9	15.1	7.3
Ni-MnO	1:1	20.4	50.4	10.4	15.7	16.9	6.6
Ni-Al_2O_3	1:1	20.5	71.1	22.0	4.2	0.8	1.9
Ni-SiO_2	1:1	20.3	73.4	21.4	4.9	0.2	0.1
Ni/TiO_2[e)]	1:6	25.0	79.0	13.5	5.0	1.0	1.5

a) Reaction conditions: 573 K, 6.0 MPa ,GHSV=4000 h^{-1}, H_2/CO=2.
b) CO converted into CO_2 is excluded. c) on CO base. d) Sum of C_{3+}-oxygenated compounds and ethers. e) This catalyst with 10 wt% NiO deactivated after 40 h on stream.

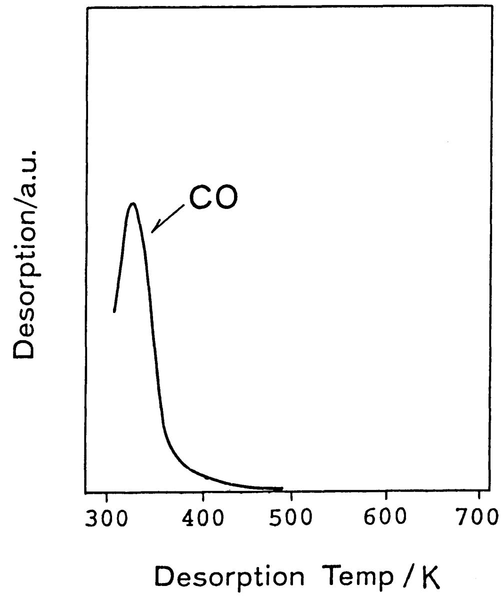

Fig. 1. TPRE spectrum of adsorbed CO on the Ni-TiO_2 catalyst ; heating rate : 3.0 K min^{-1}, H_2 flow rate : 40 cm^3 min^{-1}.

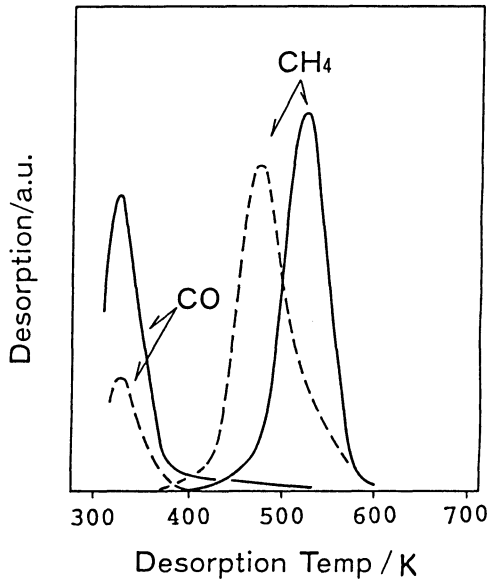

Fig. 2. TPRE spectra of adsorbed CO on the Ni-Al_2O_3 (——) and Ni/TiO_2 (---) catalysts ; heating rate : 3.0 K min^{-1}, H_2 flow rate : 40 cm^3 min^{-1}.

Table 2. Activities of three catalysts for ethane hydrogenolysis and oxo-reaction

Catalysts[a)]	Ethane hydrogenolysis[b)] Yield / %	Oxo-reaction[c)] Yield / %
NiO-TiO_2	0.2	9.6
NiO-Al_2O_3	73.4	0.14
NiO/TiO_2	83.7	0.001

a) Catalysts, which CO hydrogenation was performed over, were treated with hydrogen at 573 K for 2 h. b) 573 K, $C_2H_6/H_2/Ar(47/47/6)$, SV=6000 h^{-1} at atmospheric pressure. c) 523 K, $C_2H_4/CO/H_2/Ar(31/31/31/7)$, SV=4000 h^{-1} at atomospheric pressure.

CO insertion showed a high activity for the formation of C_{2+}-alcohols.

Furthermore, we carried out the temperature-programmed reaction (TPRE) of CO adsorbed on nickel catalysts. CO adsorbed on nickel catalysts (at 298 K) was allowed to react with flowing hydrogen while increasing the temperature and the desorbed compounds were simultaneously measured by gas chromatograghy. The results are shown in Figs. 1 and 2. The Ni-TiO_2 catalyst gave a CO desorption peak at 327 K. On the other hand, each of the Ni-Al_2O_3 and Ni/TiO_2 catalysts gave a CH_4 desorption peak at 423-473 K above the CO desorption temperature. These results suggest that CO is weakly adsorbed by the Ni-TiO_2 catalyst as compared with other catalysts. The preferential non-dissociative CO adsorption suggested by Fig. 1 is compatible with the formation of relatively large amounts of methanol and may bring about an easy formation of oxygenated intermediate species indispensable for the higher alcohols formation owing to non-dissociative CO insertion into a alkyl species. On the contrary conventional nickel catalysts predominantly produce methane owing to dissociative adsorption of carbon monoxide.[7-10]

The details of the characterization of nickel and the characteristic feature of the interaction between nickel and titanium in the coprecipitated Ni-TiO_2 catalyst which produces higher alcohols from synthesis gas will be reported in the following paper.

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References

1) JP59-170023.
2) JP56-169634.
3) JP58-42998.
4) J.L.Carter, J.A.Cusumano, and J.H.Sinfelt, J. Phys. Chem., 70,2257(1966).
5) S. Uchiyama et al., to be published.
6) M. Ichikawa, Chemtech, 12, 674 (1982).
7) M. A. Vannice, J. Catal., 37, 449, 462 (1975).
8) G. A. Somorjai, Catal. Rev., 18, 173 (1978).
9) I. Toyoshima and G. A. Somorjai, Catal. Rev., 19, 105 (1979).
10) G. Broden, T. N. Rhodin, and C. Brucker, Surf. Sci., 59, 593 (1976).

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