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ELECTRONIC EFFECTS OF ADDITIVES ON THE SELECTIVITY IN CO/H_2 REACTION OVER NICKEL CATALYSTS

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It was found with CO/H_2 reaction over unsupported Ni catalysts that the C_{2+}/CH_4 selectivity decreased in the order; Ni-boride > Raney-Ni > Decomposed-Ni ∿ Ni-phosphide. This suggests that both the activity and selectivity increase as the electron density on Ni metal increases. The H/C atomic ratio of the surface carbon species deposited during the reaction was also dependent on the catalyst.

Ni metal is a typical catalyst for the methane formation from CO and H_2.[1,2) Although a major product is CH_4 in the reaction, higher hydrocarbons (C_{2+}) are also produced, the C_{2+}/CH_4 ratio depending on the catalyst, particularly, on the catalyst support. According to Vannice,3) Al_2O_3-supported Ni catalysts formed more C_{2+} hydrocarbons than SiO_2-supported and bulk Ni catalysts. Of Particular interest is that when reduced at high temperature, TiO_2-supported catalysts show higher activity for CO hydrogenation and produce considerably greater amounts of C_{2+} hydrocarbons than Al_2O_3-supported catalysts.4) Analogous observations were noted with Ni catalyst deposited over TiO_2(100) surface in a vacuum.5) These facts are referred to strong metal-support interactions (SMSI).6) Kao et al.5,7) showed by using XPS and UPS that Ni metal is negatively charged by electron transfers from TiO_2. Charge transfers from TiO_2 (reduced) to supported metals are confirmed with other metal/TiO_2 systems8) and consistent with the results of SCF-Xα calculations made by Horsley.9) However, it is open to question as to whether characteristic behavior of Ni metal supported on TiO_2 for CO/H_2 reaction is caused by enhanced electron density on Ni metal. In this study, the selectivity in the CO/H_2 reaction was studied with Ni-boride and Raney-nickel catalysts, which were found to possess enhanced electron density on Ni metal compared with that in pure Ni,10) in order to examine the dependency of the selectivity on the electron density on Ni metal.

The catalysts studied here were Ni-boride (Ni-B(P-1)), Raney-Ni (R-Ni), and decomposed-Ni (D-Ni). Ni-phosphide (Ni-P-1) catalyst was examined in brief. Their detailed preparation methods have been described elsewhere.10) Ni-B(P-1) was prepared by reducing Ni acetate with $NaBH_4$ in water and R-Ni by activating a 42 wt% Ni-Al alloy with NaOH. Ni formate was decomposed in a vacuum at 573 K to prepare D-Ni. Ni-P-1 was prepared by reducing Ni hydroxide by NaH_2PO_2 in water. After preparation, the catalyst was sufficiently washed with distilled water, followed by replacement of water with acetone. The wet catalyst was charged into a reactor connected with a conventional closed-circulation system. After evacuating the acetone at 373 K, the catalyst was treated with H_2 at a reaction temperature to remove carbon deposits.[11)] The total pressure of the reaction gas with various CO/H_2 ratios was 2.13×10^4 Pa. The detailed procedures have been shown elsewhere.[11)]

The H/C atomic ratio in carbon residues deposited during the reaction was obtained by treating the catalyst with D_2 (ca. 1.2×10^4 Pa) at the reaction temperature for 20 min after 20-min reaction and successive evacuation for 10 min. In these experiments, only methane was detected. The amount of methane produced could not be accurately measured (1-3 μmol m^{-2}). The methane produced was analyzed by a mass spectrometer (Hitachi RMS-4, ionization voltage; 80 V) to obtain isotopic distributions in CH_xD_{4-x}. The mass pattern coefficients for the isotopic methane were assumed to be identical with those for CH_4. The fragments of isotopic species were subtracted from the mass spectrum in the sequence of heavy to light. The reproducibility of the isotopic distributions was ± 3 % for CD_4 and CHD_3 and slightly worse for CH_2D_2. CH_3D was not detected within the accuracy of the measurements. No significant isotopic redistributions were observed.

The catalytic activities of the catalysts for the CO conversion decreased in the order; Ni-B(P-1) > R-Ni > D-Ni > Ni-P-1, being consistent with that found previously.[11)] The product distributions of the catalysts are shown in Table 1. It is evident that the C_{2+} formation increases for all the catalyst systems with decreasing the reaction temperature and H_2/CO ratio. It is noteworthy that the C_{2+}/CH_4 ratio decreases in the order; Ni-B(P-1) > R-Ni > D-Ni $\sim$ Ni-P-1. Uken and Bartholomew[12)] also observed high C_{2+}/CH_4 ratios for Ni-boride catalysts in steady states. It is interesting to note that Ni-B(P-1) shows, to some extents, characteristics of the Ni catalysts modified by SMSI (high activity and high C_{2+}/CH_4), although no significant suppression of H_2 adsorption was observed.

On the basis of the XPS analyses of the Ni catalysts employed here, we have proposed a parameter Δq to describe the electron density on Ni metal in the catalyst surface.[10)] The Δq values are -0.11, -0.07, 0, and +0.36 for Ni-B(P-1), R-Ni, D-Ni, and Ni-P-1, respectively (larger negative value indicates higher electron density on Ni metal and vice versa). With the CO/H_2 reaction over various Ni catalysts including the catalysts used here, it has been shown[11)] that the activation energy and turnover number of CH_4 formation are correlated to Δq. In addition, Kelly et al.[13)] found that CH_4 formation over Ni catalysts was structure insensitive on the basis of the reaction over Ni single crystals with different crystal faces. These findings, therefore, suggest that methanation is significantly affected by the electron density on Ni metal.

The selectivity in Table 1 shows that the C_{2+}/CH_4 ratio increases as Δq decreases. Namely, higher electron-density Ni metal forms higher hydrocarbons. It is unlikely to attribute the high selectivity of Ni-B(P-1) catalyst to its amorphous nature alone, since Ni-P-1 produced only a trace amount of C_2H_6 (< 0.5 mol% compared with 8 mol% for Ni-B at 573 K) inspite of amorphousness. Therefore, it is considered that both the activity and selectivity of the Ni catalysts for the CO hydrogenation increases with increasing the electron density of Ni metal. On the basis of the present results, it is implied that some of remarkable catalytic features induced by SMSI in TiO_2-supported metal catalysts are resulted from enhanced electron densities on the metals.

Table 1 Product Distributions (/mol %) in CO/H_2 Reaction over Nickel Catalysts[a)]

Catalyst	Reaction Temperature /K	$H_2/CO = 0.55$				$H_2/CO = 2.60$			
		CH_4	C_2H_6	C_3H_8	C_3H_6	CH_4	C_2H_6	C_3H_8	C_3H_6
Ni-B(P-1)	473	75	17	8	0	93	5	2	0
	573	92	8	0	0	100	tr.	0	0
R-Ni	473	84	4	4	8	98	2	0	0
	573	100	tr.	tr.	0	100	0	0	0
D-Ni[b)]	573	100	0	0	0				
Ni-P-1	573	100	tr.	0	0				

a) Measured at the CO conversion of 20-50 %, total pressure; 2.13×10^4 Pa, tr.; less than 0.5 mol %.

b) $H_2/CO = 0.90$

Table 2 Isotope Distribution in Methane Produced by D_2 Treatment of Nickel Catalyst after CO Hydrogenation[a)]

Catalyst	Reaction or Treatment Temperature/K	H_2/CO	Methane Distribution/%			Averaged x in CH_x Species
			CD_4	CHD_3	CH_2D_2	
Ni-B(P-1)	473	0.76	88	9	3	0.15
	473	2.93	91	9	0	0.09
	523	0.76	92	8	0	0.08
R-Ni	473	0.76	62	25	13	0.51
	473[b)]	0.76	60	28	12	0.52
	523	0.76	71	23	6	0.35
D-Ni	523[c)]	0.90	68	23	9	0.41
	573[c)]	0.90	71	11	18	0.47

a) Measured after 20-min reaction (total pressure; 2.13×10^4 Pa) at the indicated temperature, followed by evacuation for 10 min and subsequent treatment with D_2 (1.2×10^4 Pa) for 20 min at the same temperature.

b) After 60-min reaction.

c) After 120-min reaction.

The H/C ratio of the carbon species deposited during the CO/H_2 reaction was obtained by D_2 treatment after evacuating a gas phase to provide informations about the distributions of CH_x species which might elucidate the activity and selectivity of the catalysts. The reaction gases with low H_2/CO ratios were used to facilitate the comparison with the results in Table 1. It is obvious from Table 2 that carbon deposits consist mainly of C over Ni-B(P-1) catalyst, whereas considerable amounts of CH and CH_2 species are present over R-Ni and D-Ni catalysts. These features were almost independent of the reaction temperature. The surface carbon species detected by the deuteration are expected to be catalytically active during the CO/H_2 reaction, since the rate of methane formation was much faster than that in the presence of CO. It is considered that the difference in the surface species is coupled with the catalytic activity and selectivity. While reactivities of CH_x species on metal surface and in metal cluster complex are not fully developed,14) it is proposed that the reactivity and surface mobility of CH_x species (x = 1-3) are increased with increasing the electron density on Ni metal. Enhanced mobility induces high probability for coupling reactions between CH_x species, thus resulting in a high C_{2+}/CH_4 ratio. Higher reactivities of CH_x species result in higher catalytic activities and lower concentrations of the CH_x species in the residual carbon deposits formed during the reaction. On the basis of the assumption, the results in Table 2 are compatible with the selectivity data in Table 1. Other models, however, cannot be excluded.15,16) Further developements in the CH_x-metal chemistry are required to establish the precise reaction mechanism.

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