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NOTES

Surface State and Catalytic Activity and Selectivity of Nickel Catalysts in Hydrogenation Reactions

V. Electronic Effects on Methanation of CO and CO_2

Methanation reactions of CO and CO_2 have been extensively studied by many workers (*1*, *2*). Of particular interest are the support effects on the reactions (*3*–*6*), including strong metal–support interactions (*7*). Metal species are affected by supports in the electronic state (*8*) as well as in dispersion, although they are closely connected. It is very informative to separate the electronic and geometric effects of supports in order to understand the support effects on the reactions as well as the reaction mechanism. In the previous studies on a series of unsupported nickel catalysts (*9*–*12*)(nickel-boride, nickel-phosphide, Raney-nickel, and decomposed-nickel), it has been demonstrated that the electron density of Ni metal is modified by the additives (B, P, and Al) and that the change in the electron density of Ni metal alters remarkably the specific activity and selectivity of the hydrogenation reactions in a liquid or gas phase. A parameter Δq was proposed on the basis of the XPS characterization of the Ni catalysts to designate the electron density of Ni metal (*11*). It is a main purpose in this study to examine the electronic effects on the methanation of CO and CO_2 over Ni catalysts.

The catalysts employed here were: nickel-boride catalysts (Ni-B(P-1) and Ni-B(P-2) prepared by the reduction of Ni acetate with $NaBH_4$ in an aqueous or 95% ethanol solution, respectively), Raney-nickel catalyst (R-Ni; Al-Ni alloy with 42 wt% Ni was activated by NaOH at 70°C for 30 min), decomposed-nickel catalyst (D-Ni; Ni formate was decomposed under vacuum at 300°C), and nickel-phosphide catalysts (Ni-P-1 and Ni-P-2 prepared by the reduction of $Ni(OH)_2$ obtained from $NiCl_2$ with NaH_2PO_2 in an aqueous or 50% ethanol solution, respectively). The detailed procedures and surface properties of the catalysts were described elsewhere (*9*, *10*). After preparation, the catalyst was washed with distilled water, followed by replacement of the water with acetone. The wet catalyst was charged into a reactor connected with a conventional closed-circulation system. The acetone was evacuated at 100°C for 1 h, followed by evacuation at 300°C for 1 h and by a H_2 treatment (H_2; 90 Torr, 1 Torr = 133 Pa) at the reaction temperature before the reaction. The total volume of the circulation system was 350 ml, including the reactor. The water produced was trapped at 201 K during the reaction. The reaction gas was analyzed by gas chromatography. The X-ray photoelectron spectra of the catalyst treated in the circulation system were measured after the catalyst was immersed in degassed ethyl alcohol to avoid contact with air during the mounting of the catalyst sample on a stainless-steel holder. The detailed procedures were given elsewhere (*9*, *12*).

Shown in Fig. 1 is the catalyst behavior of Ni-B(P-1) catalyst for the methanation of CO in comparison with that of R-Ni catalyst. The catalysts were evacuated at 250°C for 30 min between the treatments or reactions. After evacuation at 300°C, the catalyst was exposed to H_2. A small amount of CH_4 was produced by the hydrogenation of carbon deposited during the catalyst preparation and pretreatments. A subsequent introduction of the reaction gas (CO/H_2) pro-

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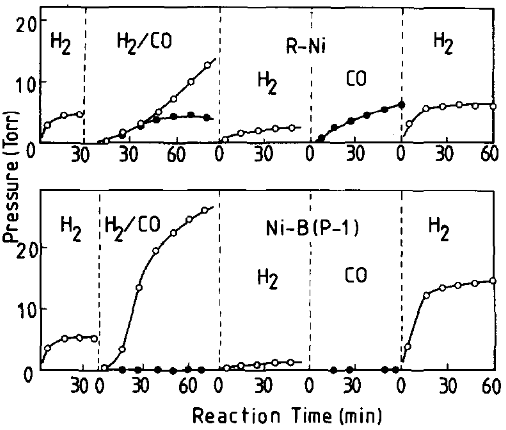

FIG. 1. Catalytic behavior of Ni-B(P-1) and R-Ni catalysts in a sequence of treatments and reactions at 250°C after evacuation at 350°C for 1 h: H_2 treatments (90 Torr), CO methanation ($H_2/CO = 3.7$, 115 Torr), and CO disproportionation (55 Torr). ○, CH_4 pressure and ●, CO_2 pressure. The catalysts were evacuated at 250°C for 30 min between the treatments or reactions.

duced CH_4 over both catalysts after short induction periods. The CH_4 production rate after the induction period was taken as an initial activity of the catalyst. R-Ni catalyst formed CO_2 together with CH_4. However, no CO_2 formation was observed with Ni-B(P-1) catalyst. A subsequent H_2 treatment produced CH_4 due to the carbon deposited during the reaction. The disproportionation of CO occurred to provide CO_2 over R-Ni catalyst, while no CO_2 formation was detectable over Ni-B(P-1) catalyst, although a considerable amount of CO was adsorbed (15 Torr/0.5 g cat. in Fig. 1). After evacuation for 30 min, the catalyst was subjected to a H_2 treatment. R-Ni catalyst produced the same amount of CH_4 as that of CO_2 produced in the previous CO disproportionation and Ni-B(P-1) catalyst provided exactly the identical amount of CH_4 as that of preadsorbed CO. As for the H_2O formation, R-Ni catalyst produced a comparable amount of H_2O to that of CH_4 in the CO/H_2 reaction. However, neither H_2O nor CO_2 was found with Ni-B(P-1) catalyst. Therefore, Ni-B(P-1) catalyst shows a peculiar behavior in the methanation reaction. This is due to the incorporation of oxygen into the catalyst because of strong interactions between adsorbed O and B;

$$\mathrm{CO} \rightarrow \mathrm{C_{ad}} + \mathrm{O_{ad}},$$
$$x\mathrm{O_{ad}} + \mathrm{B} \rightarrow \mathrm{BO}_x,$$
$$\mathrm{C_{ad}} + 4\mathrm{H_{ad}} \rightarrow \mathrm{CH_4}.$$

The XPS results in Table 1 substantiate the above considerations. The CO or CO/H_2 treatment decreased the surface concentration of the boron which connects with nickel (B-I, B 1*s* binding energy; 188.2 ± 0.3 eV) and increased considerably boron oxide (B 1*s*; 191.7 ± 0.3 eV)/B-I ratio. However, no appreciable oxidation of Ni metal was detected by XPS.

Ni-B(P-1) catalyst showed much higher activity for the methanation of CO than R-Ni catalyst as shown in Fig. 1. Nevertheless, the decrease in the concentration of B-I species in Ni-B(P-1) catalyst with proceeding reaction must cause a deactivation of the catalyst. In Fig. 2, the extent of the deactivation of Ni-B(P-1) catalyst is compared with that of R-Ni catalyst. As expected, Ni-B(P-1) catalyst lost the activ-

TABLE 1

X-Ray Photoelectron Spectroscopic Characterization of Ni-B(P-1) Catalysts Treated with CO/H_2 and CO

Treatment	XPS intensity ratio	
	B 1*s* (B oxide)/ B 1*s* (B-I)[a]	B 1*s* (B-I)/ Ni $2p_{3/2}$
Evacuation at 350°C for 1 h	0.11	0.29
H_2 reduction (10 Torr) at 350°C for 40 min	0.14	0.38
H_2/CO (3.14/1, 200 Torr) at 220°C for 10 h	0.69	0.08
CO (150 Torr) at 250°C for 30 min	1.30	0.07

[a] B oxide: B 1*s* binding energy, 191.7 ± 0.3 eV. B-I (boron which connects with Ni): B 1*s* energy, 188.2 ± 0.3 eV.

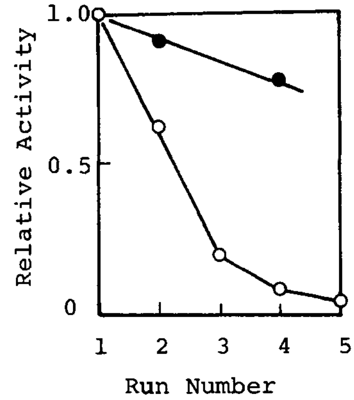

FIG. 2. Deactivations of Ni-B(P-1) and R-Ni catalysts by repeated CO methanation at 250°C (H_2/CO = 3.7; 115 Torr; reaction time, 60 min). The catalysts were evacuated at 250°C for 30 min between the reactions. ○, Ni-B(P-1) and ●, R-Ni.

ity much more rapidly than R-Ni catalyst did. After several runs, Ni-B(P-1) catalyst began to produce CO_2 and H_2O as the other Ni catalysts. Kurita and Tsutsumi (*13*) and Uken and Bartholomew (*14*) reported the CO_2 formation over Ni-boride catalysts in flow systems. The latter authors showed that Ni-boride catalysts were less active than Raney-nickel catalysts but were very effective compared with pure nickel catalysts. This is in good agreement with our observations for the deactivated Ni-B(P-1) catalyst. In this study, the initial properties of Ni-B catalyst were regarded as the true characteristics of the fresh catalyst and compared with the previous XPS results (*9, 10*) and then with Δq for the fresh catalyst (*11*). In the case of CO_2 hydrogenation, Ni-B(P-1) catalyst was highest in the activity among the catalysts employed here. On the other hand, in the initial stage of the reaction neither CO nor H_2O was detected.

The activation energies for the CH_4 formation in the methanation of CO (H_2/CO = 2.9) and CO_2 (H_2/CO_2 = 3.0) are summarized in Table 2 and illustrated in Fig. 3 as a function of the parameter Δq which has previously been proposed to describe the electron density of Ni metal in the catalysts (*11*) as follows.

$$\Delta q = \frac{-\Delta E}{k}\left(\frac{\mathrm{A}}{\mathrm{Ni}}\right),$$

$$\mathrm{A} = \mathrm{B} \text{ or } \mathrm{P},$$

where k is a proportional constant in the equation; $\Delta E_0 \propto kq_0$ (ΔE_0: XPS chemical shifts of A for standard compounds containing A; q_0: calculated charges on atom A in the compounds). ΔE is the XPS chemical shift for the component element A in the nickel catalyst compared to pure element A. (A/Ni) represents the concentration of

TABLE 2

BET Surface Area, Amount of H_2 Adsorption, Activation Energies for CO and CO_2 Methanation, Turnover Number, and Electron Density of Ni Metal (Δq) for Various Nickel Catalysts Evacuated for 1 h

Catalyst	Evacuation temperature (°C)	Surface area (m^2/g)	Amount of H_2 adsorption[a] (μmole/m^2)	Activation energy[b] (kJ/mole)		N_{CH_4}[c] ($\times 10^3$ sec^{-1})	Δq[d]
				CO	CO_2		
Ni-B(P-1)	300	12	4.8	75 (110–250)	71 (140–225)	69	−0.11
R-Ni	300	65	2.3	146 (130–250)	54 (140–225)	26	−0.07
Ni-B(P-2)	300	59	3.7	126 (175–230)		11	−0.05
D-Ni	350	13	8.3	160 (290–340)	96 (225–290)	0.40	0.00
Ni-P-2	350	30	1.1	176 (300–350)		0.0022	+0.22
Ni-P-1	350	30	1.3	218 (300–350)	138 (300–350)	0.0014	+0.36

[a] Chemisorbed H_2 at 25°C.

[b] The numbers in parentheses are the temperature range (°C) where the activation energies were measured.

[c] Turnover number for CH_4 formation in the CO methanation at 275°C (measured or extrapolated value).

[d] Taken from Ref. (*11*).

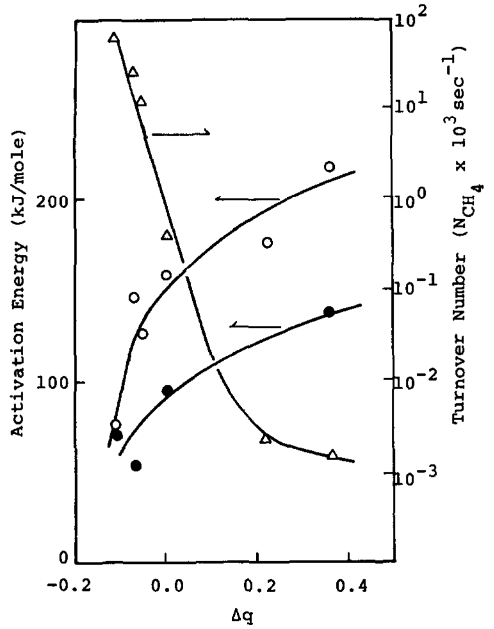

FIG. 3. Activation energies and turnover number for CH_4 formation in the CO and CO_2 methanation over Ni catalysts as a function of the electron density of Ni metal (Δq). ○, activation energy in CO methanation; ●, activation energy in CO_2 methanation; and △, turnover number in CO methanation at 275°C.

A responsible for the electron transfer expressed by the atomic ratio of A to the Ni metal in the catalyst surface. The Δq value for R-Ni catalyst was estimated from the reaction behavior in hydrogenation reactions by comparing with the behaviors of Ni-B and Ni-P catalysts with known Δq values. The Δq values thus obtained are cited in Table 2. The negative Δq implies the increase in the electron density of Ni metal by a charge transfer from B or Al to Ni metal, whereas the positive one means the decrease in the electron density of Ni metal by a charge transfer from Ni to P. The activation energy in CO_2 reaction was lower than that in CO methanation, this being consistent with other workers (*15, 16*). The amount of H_2 adsorption on the catalyst is summarized in Table 2. The turnover number for the production of CH_4 (N_{CH_4}) in the CO hydrogenation at 275°C was calculated on the basis of the initial reaction rate and the number of active sites obtained from the H_2 adsorption. N_{CH_4} is also plotted in Fig. 3 against Δq.

It is evident from Fig. 3 that with decreasing electron density of Ni metal, the activation energies of the reactions increase, while N_{CH_4} decreases. These results would be interpreted by assuming that CO dissociation is a rate-determining step (*17–19*) under the reaction conditions employed in this study. The high electron density of the Ni metal in Ni-B(P-1) or R-Ni catalyst facilitates the dissociation of adsorbed CO by enhanced $d\pi$–$p\pi^*$ back bonding. The high activation energy and low turnover number of the reaction over Ni-P catalysts are due to σ bonding and less back bonding because of low electron density of Ni metal. This is consistent with the UPS observations by Kishi and Roberts (*20*) that sulfur incorporation into Fe catalyst suppresses the dissociation of CO by withdrawing the *d* electrons of Fe. It is demonstrated that the electron density of Ni metal affects remarkably the catalytic properties in the methanation.

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