Synergetic effect of nickel and platinum supported on silica in catalytic methanol decomposition

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Alloy formation of nickel and platinum leads to a synergetic effect in the decomposition of methanol to carbon monoxide and hydrogen over silica supported metal catalysts.

Methanol is recognized as an alternative energy carrier as well as an important chemical feedstock. Methanol decomposition to hydrogen and carbon monoxide is very beneficial in saving energy because the industrially produced waste heat can be utilized to increase the heating value of a fuel. Methanol decomposition is also applicable in vehicles (on-board reforming) to increase the fuel efficiency and reduce the amount of formaldehyde by-product.[1] Catalysts containing nickel have been reported to be active for this reaction,[2–6] however, further improvement is still necessary especially for the application to the recovery of waste heat. Studies on the surface science of the nickel–platinum single-crystal alloy suggest a synergetic effect of the alloy towards some catalytic reactions such as hydrogenation,[7–9] although the effect was not evident on a nickel–platinum alloy supported on alumina.[10] Here, we show the coexistence of nickel and platinum on silica results in a significant improvement in the catalytic activity of methanol decomposition.

Catalysts were prepared by the impregnation technique from an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (Mitsuwa Chemical, GR grade) and/or H_2PtCl_6 (Kanto Chemical, GR grade) using silica (Fuji Silicia, ID G) as a support. The resulting solids were calcined in air at 500 °C for 5 h after being vacuum-dried for 1 day. The samples were further washed five times in boiling water for 1 h to remove chloride ion, and dried at 300 °C for 5 h. The residual chlorine content in the catalysts was found to be < 40 ppm (emission spectral analysis). The prepared catalysts listed in Table 1 all contain 10% Ni by mass.

Catalytic experiments were performed in a fixed-bed continuous flow reactor operated under atmospheric pressure at 250 °C. The catalyst was sandwiched with quartz wool plugs in a quartz tube reactor (i.d., 10 mm) whose contribution to the reaction was negligible. After reducing the sample (0.50 g) in a flow of 10 vol.% hydrogen in argon at 500 °C for 1 h, methanol was fed in an argon carrier stream at a concentration of 20 vol.% with a total flow rate of 2.5 $dm^3\ h^{-1}$. The reactant and products were analysed with two on-stream Ohkura 802T gas chromatographs equipped with TC detectors. An activated carbon (2 m, Ar carrier) column and a Porapak T (2 m, He carrier) column were employed in the analyses.

The surface areas of the catalysts were measured by the conventional BET nitrogen adsorption method. Powder X-ray diffraction (XRD) patterns of the catalysts removed from the reactor after reaction were recorded on a Rigaku Rotaflex 20 diffractometer using nickel-filtered Cu-Kα radiation. X-Ray photoelectron spectra (XPS) of the catalysts after reaction were recorded on a Shimadzu ESCA 750 instrument. The samples were sputtered with argon ions (2 kV, 0.5 min) prior to measurement to eliminate surface contaminants. Charge correction of the XPS data was accomplished by assuming that the binding energy of the C 1s peak is 284.6 eV.

Methanol was decomposed mainly to carbon monoxide and hydrogen with methane detected as a by-product over the catalysts containing nickel and/or platinum at 250 °C (Table 1). The specific surface areas of the catalysts were in the range 172–191 $m^2\ g^{-1}$. The catalysts containing both nickel and platinum were more active than those containing only one of the metals revealing a significant synergetic effect between nickel and platinum. The catalytic activity was 95.3% at 3 mass% loading of Pt.

XRD peaks attributed to metallic nickel were recorded in the pattern of Ni/SiO_2 at $2\theta = 44.1°$ [Ni(111)] and 51.4° [Ni(200)].[11] The lattice parameter, *a* of 0.355 nm (*Fm*3*m*) is slightly larger than that for nickel metal (0.352–0.354 nm).[12] In the case of Pt/SiO_2 XRD peaks at $2\theta = 39.7$ and 46.2° were observed.[11] Although 1- and 2-$PtNi/SiO_2$ contained platinum, no peaks attributable to platinum could be been in the patterns which were very similar to that of Ni/SiO_2. However, the patterns for 3- and 4-$PtNi/SiO_2$ were significantly different from the samples containing lower amounts of platinum. Peaks for nickel were shifted to lower values at $2\theta = 43.5 \pm 0.3°$ and $50.8 \pm 0.3°$ with considerably lower intensities and with broad and asymmetric shapes. The stronger peak at $2\theta = 43.5°$ can be deconvoluted into two peaks at 43.2 and 43.7°, showing that

Table 1 Catalytic activity and surface properties of catalysts containing nickel and/or platinum

Catalyst	Content (mass%) Ni	Pt	MeOH Conv. (%)	Selectivity (%) CO	CH_4	S_{BET}[a]/ $m^2\ g^{-1}$	E_b[b]/eV Pt $4f_{7/2}$	Ni $2p_{3/2}$	Pt/Ni : surface atomic ratio[c]
Ni/SiO_2	10	0	56.8	96.6	3.4	180	—	852.8	
1-$PtNi/SiO_2$	10	1	79.3	94.4	5.6	174	71.1	853.0	0.05 (0.06)
2-$PtNi/SiO_2$	10	2	78.1	94.6	5.4	178	71.1	852.9	0.09 (0.11)
3-$PtNi/SiO_2$	10	3	95.3	92.1	7.9	172	71.4	852.7	0.11 (0.17)
4-$PtNi/SiO_2$	10	4	78.9	95.0	5.0	177	71.3	853.5	0.11 (0.22)
Pt/SiO_2	0	2	5.2	100.0	0.0	191	70.7	—	

[a] BET surface area. [b] Binding energy. [c] Atomic ratio calculated from the XPS peak areas using atomic sensitivity factors of 3.0 for Ni $2p_{3/2}$ and 4.4 for Pt 4f.[14] Atomic ratios calculated from the chemical composition are given in parentheses.

there are two crystalline phases in the metal. The lattice parameters (*a*) are tentatively calculated as 0.362 and 0.358 nm, respectively. Deconvolution of the peak at 50.5° was impossible because of its weak intensity. The *a* parameter for $Ni_{23}Pt_2$ is 0.3564 nm (*Fm*3*m*) which is discernibly smaller than the above values,[12] and the change in the XRD pattern suggests that a phase transition of a Ni–Pt alloy such as $Ni_{23}Pt_2$ to new phases such as Ni_3Pt (space group *Pm*3*m*) occurs at high platinum content.[12,13] It should be noted that the surface atomic ratio of Pt/Ni for 3- or 4-PtNi/SiO_2 obtained by XPS analyses was considerably lower than the ratio calculated from the chemical composition while the value for 1- or 2-PtNi/SiO_2 was close to that expected from the composition (Table 1). This implies that the concentration of platinum in the bulk of 3- or 4-PtNi/SiO_2 is higher than the chemical composition (Pt/Ni ratio = 0.17 and 0.22, respectively) and formation of $PtNi_3$ may well be possible in the bulk.

The binding energy of Pt $4f_{7/2}$ in the XPS of Pt/SiO_2 was 70.7 eV, but PtNi/SiO_2 were appreciably higher in energy (Table 1). This shows that platinum in PtNi/SiO_2 is not present as a separate single phase on the surface of silica but rather interacts with nickel. The difference in the binding energies of Pt $4f_{7/2}$ between 1- and 2-PtNi/SiO_2 and those for 3- and 4-PtNi/SiO_2 reflect more clearly on the difference in the catalytic activity than does the change in the XRD patterns. Hence, it is strongly indicated that platinum and nickel form an alloy on the surface of silica and this is the active phase for methanol decomposition. The binding energy of Ni $2p_{3/2}$ for all the samples was at 852.8 ± 0.2 eV except for 4-PtNi/SiO_2 for which it was at 853.5 eV. This higher binding energy may account for the lower catalytic activity of 4-PtNi/SiO_2 relative to 3-PtNi/SiO_2. Binding energies for Si 1s and O 1s were 103 ± 0.2 and 532.8 ± 0.2 eV, respectively, for all the samples.

K. K., Y. U. and M. K. gratefully acknowledge financial support from the New Energy and Technology Development Organization.

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Received, 28th October 1996; Com. 6/07301H