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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	38
number	1
page range	76-87
year	1993-03-29
URL	http://hdl.handle.net/10097/28426

CO₂ Methanation Catalysts Prepared from Amorphous Ni-Valve Metal Alloys Containing Platinum Group Elements*

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(Received January 6, 1993)

Synopsis

The amorphous Ni-valve metal (Ti, Zr, Nb and Ta) alloys containing a few at% of platinum group elements were activated by immersion into hydrofluoric acid and used for hydrogenation of carbon dioxide at 100–300°C. This surface activation led to formation of nanocrystalline surface alloys with high surface area, and to surface enrichment of platinum group elements on the titanium-, niobium- and tantalum-containing alloys, but not on the zirconium-containing alloys. The surface of the latter alloys was mainly composed of nickel. The activity and selectivity for methane formation on the titanium-, niobium- and tantalum-containing alloys were significantly affected by the difference in the platinum group elements; the ruthenium- and rhodium-containing alloys showed higher activity and selectivity for methane formation while the platinum-containing alloys exhibited the lowest activity for methane formation and produced mainly carbon monoxide. The zirconium-containing alloys showed the one order of magnitude higher activity for methanation of carbon dioxide in comparison with the titanium-, niobium- and tantalum-containing alloys and produced exclusively methane independent of platinum group elements contained. The alloying with zirconium seems very important to prepare the alloy catalysts having the extremely high activity.

I. Introduction

Amorphous alloys are interesting materials for novel catalysts or catalyst precursors, since it is possible to improve the electronic states of active elements as well as synergistic effects by alloying with various elements. One of the advantages of amorphous alloys is that these alloys are capable of forming single solid solution far exceeding the solubility limits in the equilibrium state. In fact, there are several reports to show that amorphous alloys have extremely high catalytic activity and unique selectivity for some reactions. For instance, amorphous iron- and nickel-

* The 1911th report of Institute for Materials Research.

base alloys have been reported to show about 200 times higher catalytic activity for the Fischer-Tropsch hydrogenation of carbon monoxide than the corresponding crystalline counterparts and to form C_2 and C_3 hydrocarbons especially in good yields[1-4]. Yamashita et al. have reported that the catalytic activities of amorphous Cu-Zr[5], Ni-B[6,7] and Ni-P[6,8] alloys for hydrogenation of olefines are higher than those of the crystalline alloys with the same composition. Furthermore, it has been reported that the surface-activated amorphous Ni-valve metal alloys containing a few atomic percent of platinum group elements are highly active as electrocatalysts for chlorine evolution[9], methanol[10,11] and hydrogen[12] oxidation as well as oxygen reduction[12].

Recently, global warming induced by enormous evolution of carbon dioxide, which has a large green-house effect, resulted from energy conversion becomes a serious problem. Our proposal to solve this problem is to recycle recovered carbon dioxide by its catalytic hydrogenation to useful carbon-containing fuels and organic materials by using hydrogen produced by solar energy. Up to now, extensive investigations concerning the hydrogenation of carbon dioxide on various catalysts have been carried out. In particular, groups 8, 9 and 10 metal catalysts supported on metal oxides[13-18] have been used in most of the investigations. It has been reported[13] that the hydrogenation product of carbon dioxide at atmospheric pressure is almost exclusively methane, and that nickel, ruthenium and rhodium have high activity for methane formation. The catalytic activity was, however, significantly affected by changing the supports[15,18]. The alloying of active elements is also expected to be effective to improve the catalytic activity. This work aims to prepare new alloy catalysts having high activity for CO_2 methanation. Particular attention has been paid for the effects of valve metal elements and platinum group elements for activity and selectivity of methane formation.

II. Experimental Procedures

Crystalline alloy ingots were prepared by argon arc melting of 99.95% pure nickel, 99% pure titanium, zirconium, niobium or tantalum and 99% pure ruthenium, rhodium, palladium, iridium or platinum. Amorphous alloy ribbons of ca. 1 mm width and 20-30 μm thickness were formed by a melt-spinning method under an argon atmosphere and the amorphous structure was confirmed by X-ray diffraction using $Cu K_{\alpha}$ radiation. The amorphous alloys used in this work were shown in Table 1.

The surface of amorphous alloy ribbons was activated by immersion in a 47% hydrofluoric acid solution or in diluted ones for several tens of seconds to several tens of minutes[9]. It has been known that this activation treatment of amorphous Ni-Nb- and Ni-Ta-platinum group element alloys led to the selective dissolution of valve metals and nickel and hence to the significant enrichment of platinum group elements in the surface in addition to surface roughening[10]. The specimens were immersed in hydrofluoric acid solutions up to surface blackening owing to surface

Table 1 BET surface area and surface composition of amorphous Ni-valve metal-platinum group metal alloys activated by immersion in hydrofluoric acid.

Alloys(at%)	BET surface area (m ² g ⁻¹)	Surface composition(at%)		
		Ni	Valve metal	Platinum group metal
Ni-40Ti-2Ru	0.7	77.7	13.4	8.8
Ni-40Ti-2Rh	1.1	57.2	20.9	21.9
Ni-40Ti-2Pd	0.9	47.0	10.2	42.8
Ni-40Ti-2Ir	0.8	71.6	10.7	17.7
Ni-40Ti-2Pt	0.4	49.9	11.9	38.4
Ni-40Zr-2Ru	0.4	94.9	5.1	0.0
Ni-40Zr-2Rh	0.6	85.0	15.1	0.0
Ni-40Zr-2Pd	0.7	81.9	5.2	12.9
Ni-40Zr-2Ir	0.6	84.2	12.4	3.4
Ni-40Zr-2Pt	0.9	90.3	3.1	6.6
Ni-40Nb-2Ru	3.0	55.8	7.1	37.0
Ni-40Nb-2Rh	1.4	50.9	7.2	42.0
Ni-40Nb-2Pd	1.4	39.8	9.7	50.5
Ni-40Nb-2Ir	2.7	60.5	7.5	32.0
Ni-40Nb-2Pt	3.8	47.1	9.0	44.0
Ni-30Ta-1Ru	0.7	-	-	-
Ni-30Ta-2Ru	1.4	49.8	8.5	41.8
Ni-30Ta-3Ru	2.9	-	-	-
Ni-30Ta-1Rh	1.6	34.9	15.6	49.5
Ni-30Ta-2Rh	3.0	33.0	16.0	51.0
Ni-30Ta-3Rh	2.2	32.2	17.0	50.9
Ni-30Ta-1Pd	1.5	29.8	7.7	62.5
Ni-30Ta-2Pd	2.8	31.3	5.8	62.9
Ni-30Ta-3Pd	2.2	25.0	8.1	66.9
Ni-30Ta-1Ir	1.5	-	-	-
Ni-30Ta-2Ir	1.6	41.4	7.8	50.8
Ni-30Ta-3Ir	0.8	-	-	-
Ni-30Ta-1Pt	1.5	-	-	-
Ni-30Ta-2Pt	2.1	45.6	8.8	45.6
Ni-30Ta-3Pt	2.1	-	-	-

roughening, and then washed in distilled water and dried in air. As a result of this activation treatment, the amorphous alloy surfaces were covered by very fine micro-crystalline single phase alloy layers, the particle size of which was about 3 nm[11].

The surface areas of the activated alloy specimens were measured by a BET method using nitrogen physisorption at 77 K[19]. The catalytic reaction was carried out in a normal tubular glass reactor of 8 mm inner diameter and 500 mm length, the 50 mm length of which was filled with 0.25-0.55 g of the specimens. The

dead volume of the reaction tube was filled with glass beads. The reaction gas composed of 20 mol% of carbon dioxide and 80 mol% of hydrogen was passed through the reaction tube with a flow rate of 15 ml/min. The reactants and products were quantitatively analyzed by Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector.

The composition of the specimen surfaces was quantitatively analyzed by X-ray photoelectron spectroscopy (XPS)[20,21]. X-ray photoelectron spectra were measured by SSI SSX-100 electron spectrometer with monochromatized Al K_{α} excitation. Binding energies of electrons were calibrated by a method described elsewhere[22,23]. In these calibrations the binding energies of Au $4f_{7/2}$ and $4f_{5/2}$ electrons of gold metal, and Cu $2p_{3/2}$ and $2p_{1/2}$ electrons of copper metal were taken as 87.07, 87.74, 932.53 and 952.35 eV, respectively, and the kinetic energy of Cu $L_{3}M_{4,5}M_{4,5}$ Auger electrons of copper metal was taken as 918.65 eV.

III. Results

Characterization of catalysts

The surface area and surface composition of the specimens were measured by BET method and X-ray photoelectron spectroscopy, respectively. The results were summarized in Table 1. The activation of the niobium- and tantalum-containing alloys was carried out by immersion in 47% HF solution, while the titanium- and zirconium-containing alloys were activated by immersion in diluted 4.7% and 1.2-0.26% HF solutions, respectively, due to extremely high dissolution rates of the alloys in 47% HF solution. The BET surface areas of the niobium- and tantalum-containing alloys are about 1-3 m^2/g and is twice or three times larger than those of the titanium- and zirconium-containing alloys. The high surface area of the niobium- and tantalum-containing alloys results from selective dissolution of nickel and niobium or tantalum and reconstruction of platinum group element-enriched phases. The dissolution rates of titanium and zirconium were extremely high even in diluted HF solution[24], while the dissolution rate of nickel was relatively low as compared with those of titanium and zirconium in diluted HF solution. Hence, relatively high nickel contents are responsible for lower concentration of platinum group elements in the surface of the titanium- and zirconium-containing alloys in comparison with those in the niobium- and tantalum-containing alloys, as shown in Table 1. In particular, the zirconium-containing alloy has quite low concentration of platinum group elements in the surface. The surface compositions of Ni-30Ta-Rh and Ni-30Ta-Pd alloys containing the different contents of platinum group elements are also shown in Table 1. It is clear that the surface composition after activation is almost independent of the content of platinum group element in the alloys.

The XPS analysis of the surface-activated alloys also revealed that the binding energies of electrons of metallic nickel and metallic platinum group elements were independent of the valve metal elements and those of metallic valve metal elements were not affected by the difference in platinum group elements, although it has been known[24] that the binding energy of metallic platinum in Ni-Ti-Pt and Ni-Nb-Pt alloys is higher than that in platinum metal.

Catalytic behavior

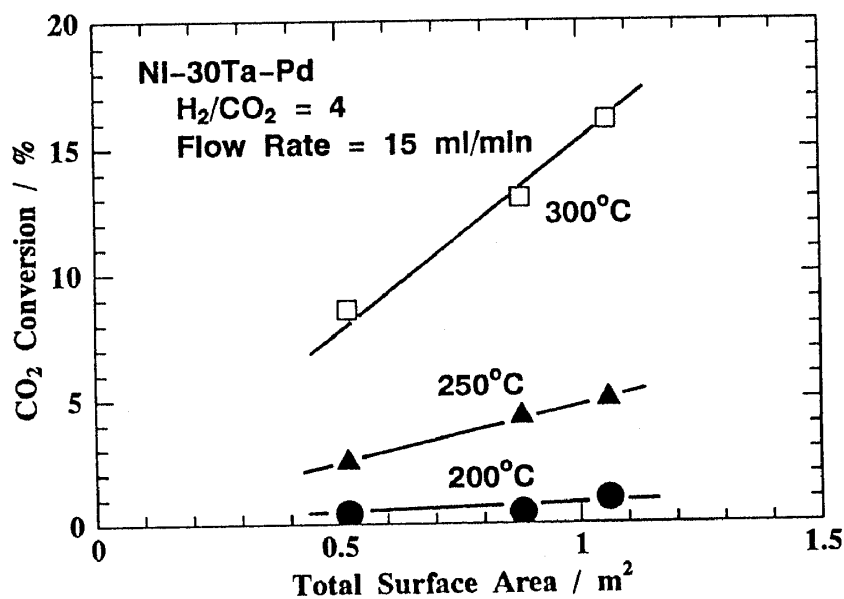


Fig. 1 Conversion of CO_2 on the Ni-30Ta-Pd alloys activated by HF immersion as a function of BET surface area.

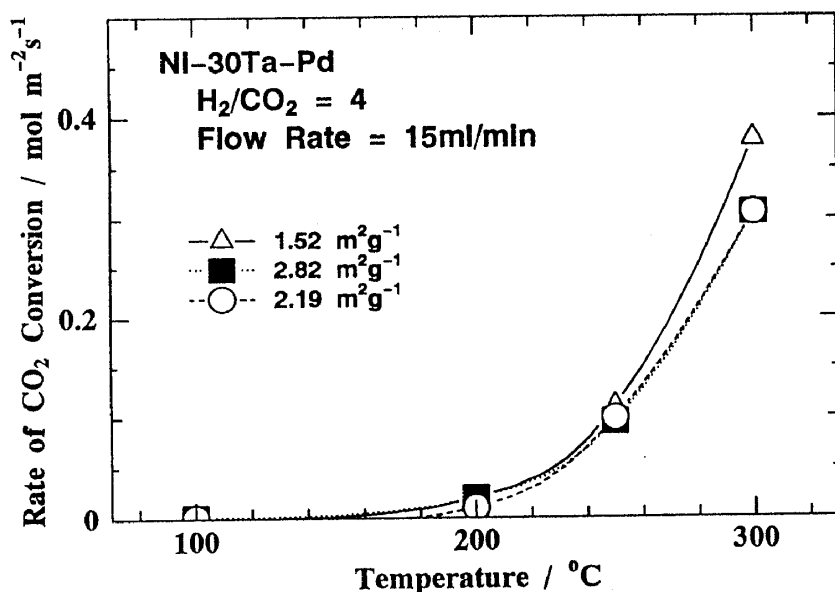


Fig. 2 The rate of CO_2 conversion on the HF-treated Ni-30Ta-Pd alloys with different BET surface areas as a function of reaction temperature.

The hydrogenation of carbon dioxide on various alloy catalysts used in this work resulted in the exclusive formation of methane as hydrocarbons, although a trace amount of ethane was detected when the catalysts had quite high activity for methane formation. Carbon monoxide was also formed on some alloy catalysts. Figure 1 shows the relationship between the CO_2 conversion on the Ni-30Ta-Pd

alloys and the total surface area of these alloy specimens. These alloys with different BET surface areas have almost the same surface composition as shown in Table 1. The catalytic conversion of CO_2 increases linearly with total surface area at each temperature. Hence, the rate of CO_2 conversion per a unit surface area for Ni-30Ta-Pd alloys with different BET surface areas is almost the same as each other as shown in Figure 2. The same results were obtained for the alloy catalysts containing other platinum group elements. It can, therefore, be said that the rate of CO_2 conversion per a unit surface area is better than the rate of conversion per a

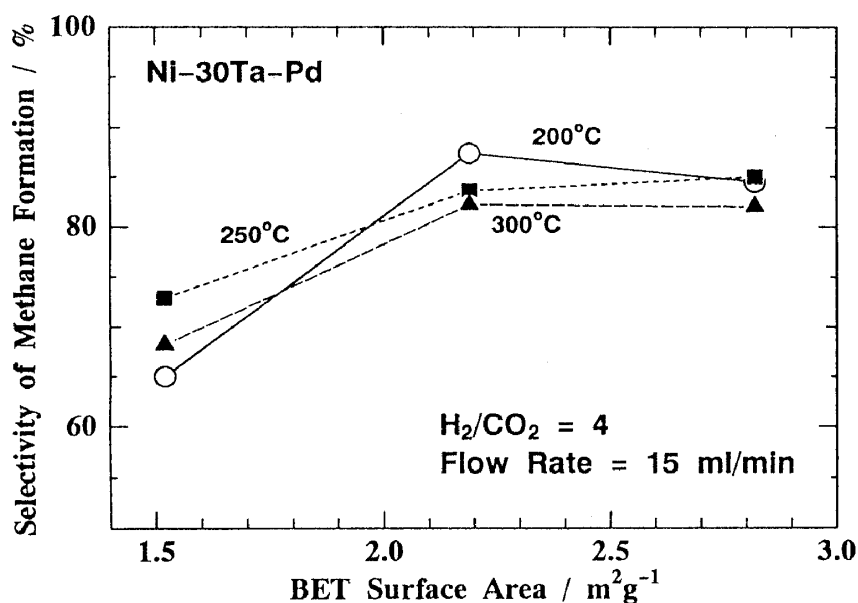


Fig. 3 Selectivity of methane formation on the HF-treated Ni-30Ta-Pd alloys at 200, 250 and 300°C as a function of BET surface area.

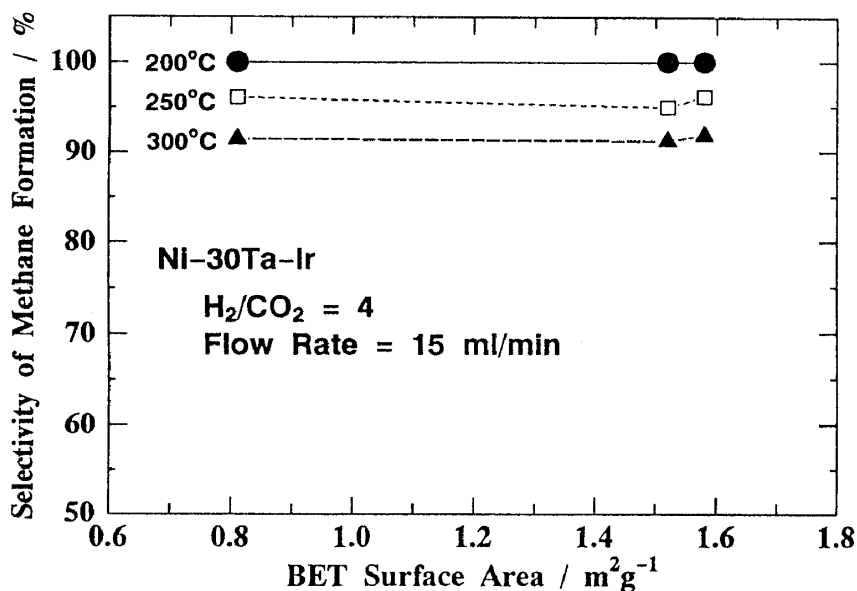


Fig. 4 Selectivity of methane formation on the HF-treated Ni-30Ta-Ir alloys at 200, 250 and 300°C as a function of BET surface area.

unit weight of the specimens for the evaluation of the catalytic activity of alloy catalysts used in this work.

Figure 3 shows the selectivity of methane formation on the Ni-30Ta-Pd alloys as a function of BET surface area. Another carbon-containing product is carbon monoxide. When the BET surface area is small, the selectivity of methane formation is slightly lower at each reaction temperature. However, the BET surface area of the specimens containing other platinum group metals did not affect the selectivity of methane formation at each reaction temperature. The typical example is shown for the Ni-30Ta-Ir alloys in Figure 4.

Figure 5 shows the rate of methane formation on the Ni-30Ta alloys containing different platinum group elements as a function of temperature. The methanation rate on each alloy catalyst increases with reaction temperature. The rate is greatly dependent on the platinum group elements. The rhodium- and ruthenium-containing alloys have quite higher activity at each temperature and the decreasing order of methanation activity is Ru, Rh, Ir, Pd, Pt-containing alloys. Similar trend was observed for the alloy catalysts containing niobium and titanium, as shown in figures 6 and 7, respectively, although in the niobium alloys the rhodium-containing alloy exhibits the higher activity for methanation than the ruthenium-containing alloy. The niobium- and titanium-containing alloys with platinum group elements also show the same order of the methanation rate as that for the tantalum-containing alloys with the same platinum group metals. Figure 8 shows the rate of methanation on the Ni-40Zr alloys with different platinum group elements as a function of temperature. In comparison with the tantalum-, niobium- and titanium-containing alloys, the zirconium-containing alloys have about one order of magnitude higher activity for methanation and show the lower dependence of the activity on the platinum group elements. The lower dependence on the platinum group elements

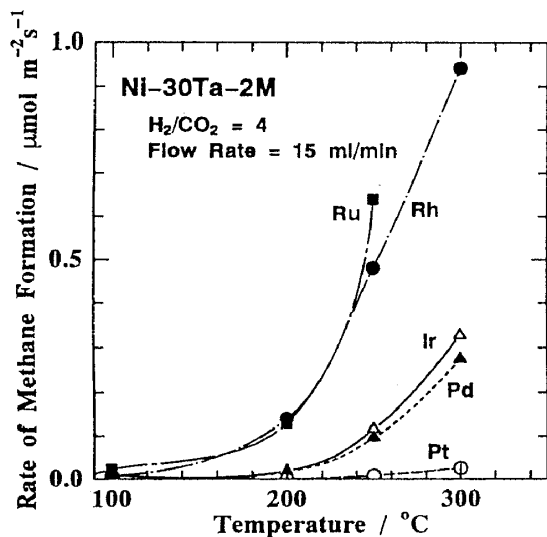


Fig. 5 The rate of methane formation on the HF-treated Ni-30Ta alloys containing 2at% of platinum group elements as a function of reaction temperature.

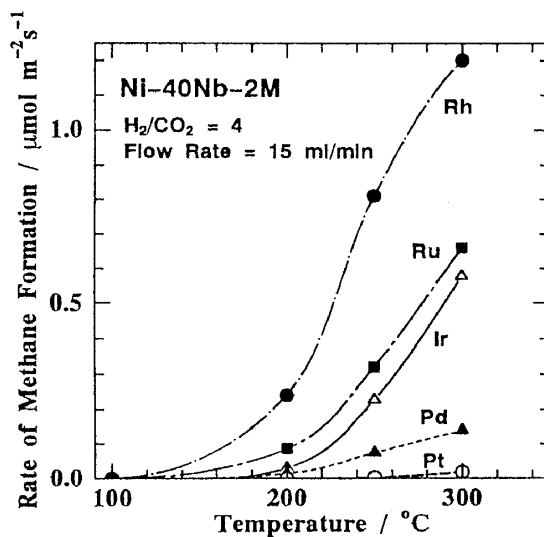


Fig. 6 The rate of methane formation on the HF-treated Ni-40Nb alloys containing 2at% of platinum group elements as a function of reaction temperature.

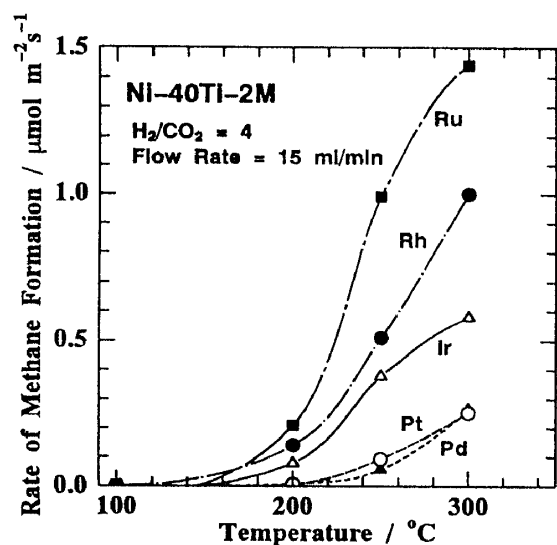


Fig. 7 The rate of methane formation on the HF-treated Ni-40Ti alloys containing 2at% of platinum group elements as a function of reaction temperature.

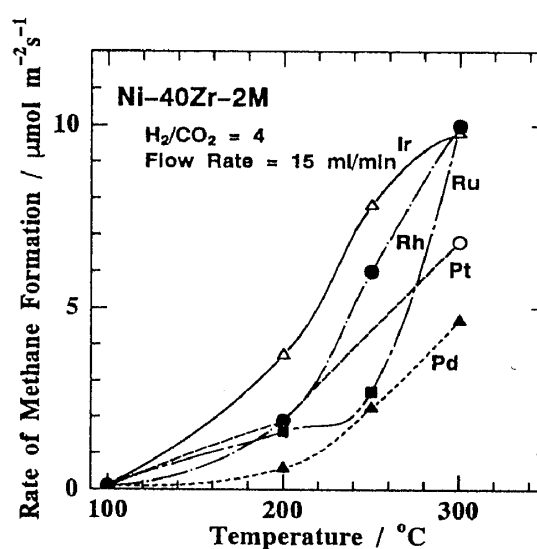


Fig. 8 The rate of methane formation on the HF-treated Ni-40Zr alloys containing 2at% of platinum group elements as a function of reaction temperature.

possibly results from the low concentration of platinum group metals in the surface. Accordingly, the extremely high activity of the Ni-Zr-platinum group element alloys seems to be brought about by nickel. The lower activity of the Ni-40Zr-2Pd alloy than that of the other alloys containing zirconium is attributable to the slight enrichment of palladium, which may be less active than nickel, in the surface, as can be seen in Table 1.

The selectivity of methane formation was dependent on platinum group elements and valve metal elements. However, the temperature dependence of the selectivity was not high for all the alloy catalysts used. The examples of the Ni-30Ta-Pd and Ni-30Ta-Ir alloys are shown in Figs. 3 and 4. Figure 9 shows the selectivity of methane and carbon monoxide formations at 250 $^{\circ}\text{C}$ for the Ni-valve metal-platinum group element alloy catalysts. The ruthenium- and rhodium-containing alloys, which have the high methanation rate, form exclusively methane despite the difference of valve metal elements. The iridium-containing alloys also show the high selectivity for methane formation, although the small amount of carbon monoxide is produced when titanium, niobium or tantalum are contained in the iridium-containing alloys. By contrast, the platinum-containing alloys show the low selectivity for methane formation and form mainly carbon monoxide except for the Ni-40Zr-2Pt alloy which forms only methane. The decreasing order of the selectivity of methane formation on the platinum-containing alloys is zirconium, titanium, niobium and tantalum alloys. This order is in agreement with the increasing order of the surface platinum content. Hence, it is clear that platinum element is active for carbon monoxide formation but not for methanation. The largest dependence of the selectivity on the valve metal elements is seen for the palladium-containing alloys. The selectivity of methane formation is more than 95% on the Ni-Zr-Pd alloy but

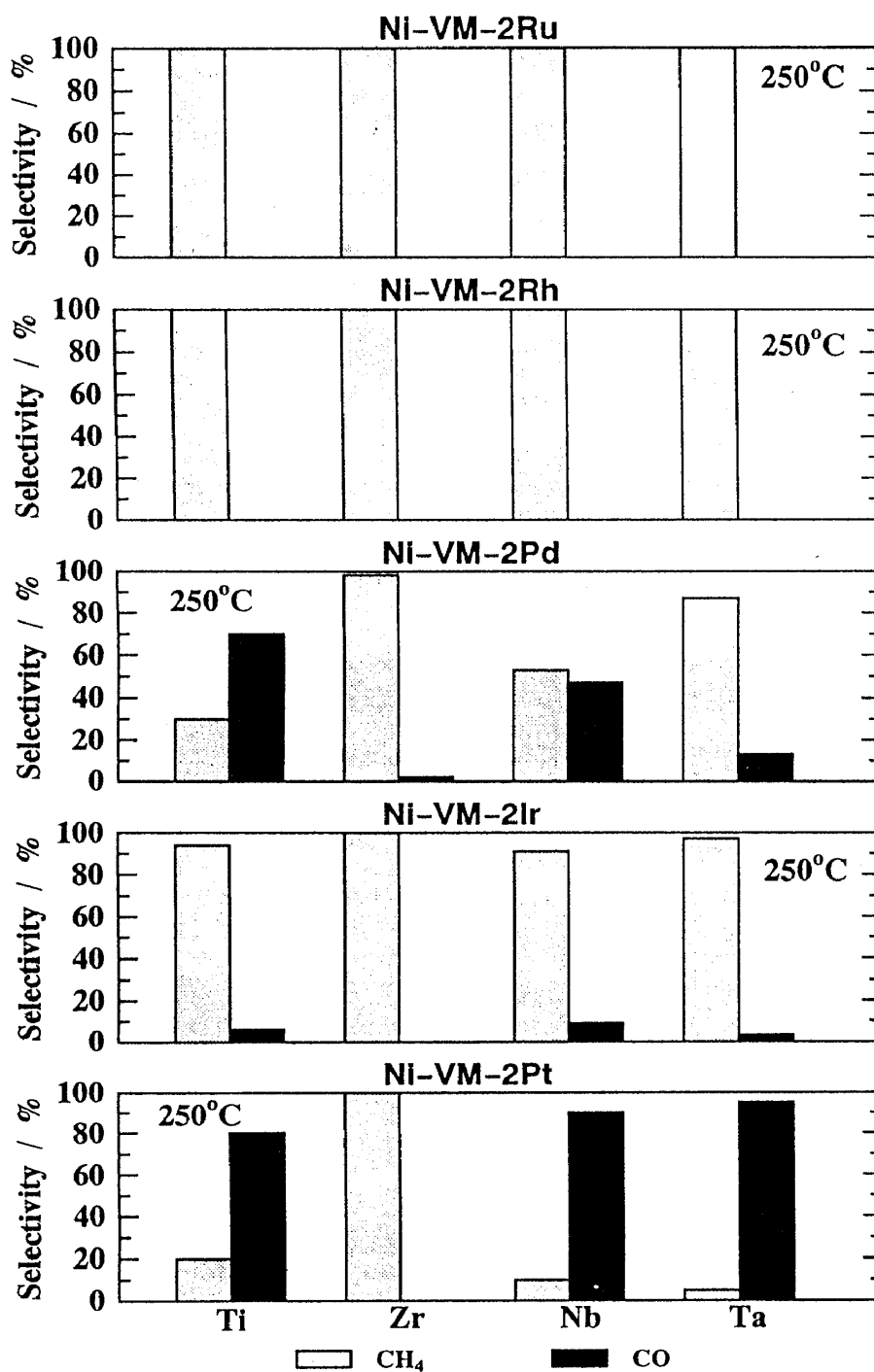


Fig. 9 Selectivity of methane and CO formation at 250°C on the HF-treated Ni-valve metal alloys containing 2at% of platinum group elements.

only 30% on the Ni-Ti-Pd alloy. This selectivity does not depend on the surface palladium content. It is, therefore, clear that the difference of valve metal elements affects the selectivity of products for hydrogenation of carbon dioxide on the Ni-valve metal-Pd alloys.

IV. Discussion

The most interesting result is that the Ni-Zr-platinum group element alloys show about one order of magnitude higher activity than the other valve metal-containing alloys. The activity and selectivity of methane formation on the zirconium-containing alloys are not greatly affected by platinum group elements. On the other hand, those on the other valve metal-containing alloys reveal the high dependence on the platinum group elements. The platinum group elements are concentrated in the surface of the titanium-, niobium- and tantalum-containing alloys but not in the surface of the zirconium-containing alloys as shown in Table 1. These results suggest that the catalytic activity is caused by nickel on the zirconium-containing alloys while it is caused by platinum group elements on the alloys containing the other valve metal elements. The titanium, niobium and tantalum alloys also contain 25-78at% of nickel in the surface, but the activity for methanation is quite low in comparison with the zirconium alloys which contain 82-95at% of nickel in the surface. It can, therefore, be said that the nickel in the Ni-Zr-platinum group element alloys is more active than that in the alloys containing other valve metal elements.

It has been proposed[14] that carbon dioxide hydrogenation on nickel catalysts proceeds via $\text{Ni}_4(\text{CO})_{\text{ads}}$ and $\text{Ni}_3\text{C}_{\text{surf}}$ intermediates, where $(\text{CO})_{\text{ads}}$ and C_{surf} means the CO adsorbed and carbon deposited on the surface, respectively. If the surface concentration of nickel is decreased by the alloying with platinum group elements, it becomes difficult to form such intermediates. Accordingly, the difficulty of the formation of $\text{Ni}_4(\text{CO})_{\text{ads}}$ and $\text{Ni}_3\text{C}_{\text{surf}}$ intermediates may be responsible for the lower activity of the titanium, niobium and tantalum alloys.

However, it has also been reported[13] that ruthenium and rhodium have higher activity for CO_2 methanation than nickel. In this work, the Ni-Zr alloys, the surface of which is composed mainly of nickel, show the higher methanation rate than the titanium, niobium and tantalum alloys in which ruthenium and rhodium are enriched. Our recent work also showed[25] that the Fe-Zr-Ru alloy activated by the immersion in hydrofluoric acid had the high concentration of ruthenium in the surface and revealed the high activity for methanation of CO_2 comparable with the Ni-Zr alloys containing platinum group elements. Furthermore, the addition of niobium to the Fe-Zr-Ru alloy decreased the rate of methanation. Hence, valve metal elements seem to affect significantly the activity for methane formation. To clarify the role of valve metal elements on the CO_2 hydrogenation, the detailed investigation of catalytic behavior of nickel-valve metal binary alloys is now in progress.

The selectivity of methane formation is largely affected by the difference in platinum group elements in the alloy catalysts when the platinum group elements are enriched in the surface. The higher the rate of methanation, the higher the selectivity of methane formation. When the platinum group elements are enriched in the

surface, the valve metal dependence of the selectivity of products is low except for the palladium-containing alloys. It is not clear why the selectivity of products is largely affected by the valve metal elements only on the palladium-containing alloys. The selectivity of methane formation on the Ni-30Ta-Pd alloys is also slightly affected by the BET surface area, as shown in Figure 3. Erdohelyi et al.[26] reported that highly dispersed palladium catalysts formed mainly methane while poorly dispersed palladium catalysts produced carbon monoxide at the reaction pressure of 1 atm. Hence, the microstructural investigation seems necessary to clarify the effect of valve metal elements in the palladium-containing alloys on the selectivity of products.

V. Conclusions

The amorphous Ni-valve metal-platinum group element alloys were activated by immersion in hydrofluoric acid and their catalytic behavior for hydrogenation of carbon dioxide was investigated by using a flow reactor. The following conclusions are obtained:

- 1 The activation of amorphous Ni-valve metal-platinum group element alloys by immersion in hydrofluoric acid results in the surface roughening. Furthermore, this activation leads to the remarkable enrichment of platinum group elements in the surface when titanium, niobium and tantalum are contained in the alloys. However, the significant enrichment of platinum group element in the surface does not occur and nickel is enriched in the surface when the amorphous Ni-Zr-platinum group element alloys are activated.
- 2 The catalytic activity of Ni-Ti, Ni-Nb and Ni-Ta alloys containing platinum group elements depends on platinum group elements. The ruthenium and rhodium-containing alloys show the higher activity while the platinum-containing alloys exhibits the lowest activity for methanation. The higher the activity of the catalysts for methanation, the higher the selectivity of methane formation.
- 3 By contrast, the activity of Ni-Zr alloys containing platinum group elements is almost one order of magnitude higher and has low dependence on platinum group elements in comparison with the Ni-Ti, Ni-Nb and Ni-Ta alloys containing platinum group elements. The alloying with zirconium is quite important to prepare the catalysts having the extremely high activity for methanation.

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