

AN ACTIVE METHANATION CATALYST PREPARED FROM AN AMORPHOUS Pd₃₅Zr₆₅ ALLOYAkinori YOKOYAMA^{*}, Hiroshi KOMIYAMA, Hakuai INOUE,Tsuyoshi MASUMOTO⁺, and Hisamichi KIMURA⁺Department of Chemical Engineering, Faculty of Engineering,
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Highly active methanation catalyst was prepared in situ from an amorphous Pd₃₅Zr₆₅ alloy. In the reaction at 260°C, 1 atm, the catalytic activity remarkably increased with time, showing about hundred fold enhancement, compared with the initial value, at the steady state attained in 60 h. The turnover frequency was greater than or comparable to those for the most active methanation catalysts as ever known.

In the preceding papers,^{1,2)} we reported the interesting catalysis by amorphous alloys which are composed of the metal element(s) and the metalloid element(s). Recent development in the manufacturing technique provides a lot of new amorphous alloys of miscellaneous compositions. Among them, the combination of the VIII group metal(s) and the element(s) of the IVa group is attractive as a hydrogenation catalyst, because of their hydrogen absorbing capability and thermal stability.³⁾ We previously reported the methane synthesis from CO and H₂ by amorphous Ni₆₃Zr₃₇ catalyst.²⁾ In this paper, we will describe the preparation of quite active methanation catalyst, by using an amorphous Pd₃₅Zr₆₅ alloy as a precursor.

The amorphous alloy was prepared by the disk method,⁴⁾ the important feature of which is the impinging of the molten alloy onto the cold surface of a rotating metallic disk to freeze the amorphous structure of the melt. The details were described elsewhere.⁴⁾ The amorphous alloy, in the shape of a ribbon 10 to 20 thick, 1 to 2 mm wide, and about 2 m long, was put into a tubular reactor. The temperature of the catalysts was measured by a thermocouple which was directly inserted in the center of the catalysts bed layer. The difference of the temperature

between the reacting fluid and the catalyst was negligibly small under the reacting condition. The surface area of the ribbon was $0.1 \text{ m}^2/\text{g}$ (N_2 -BET at 77 K). The reaction was carried out at an atmospheric pressure, using a flow reactor which was described in detail elsewhere. ²⁾ Carbon monoxide (99.95%) and hydrogen (99.9%) was used without further purification. The gaseous composition at the reactor outlet was determined by a gaschromatograph and the catalyst structure and composition were analyzed by X-ray diffraction spectra.

Figure 1 shows the change of the catalytic activity, represented by the conversion of CO, as a function of the time elapsed from the start of experimental runs. The space velocity as shown in Figure 1 was defined at the gaseous flow rate at the standard condition divided by the volume of the amorphous alloy. The catalytic activity monotonously increases and, after 60 h to 70 h, reaches a constant value which is about two orders of magnitude greater than the initial activity. During this transient period, the selectivity of methane, the predominant product, decreased from 92% to 86%. Ethane and propane were the products other than methane. CO_2 was not detected gaschromatographically and H_2O was the only oxygen containing product. In the hydrogenation of CO, Pd catalysts produce exclusively methane. ⁵⁾ Hence, the product distribution of the present catalyst shows that the active site is different from the pure Pd.

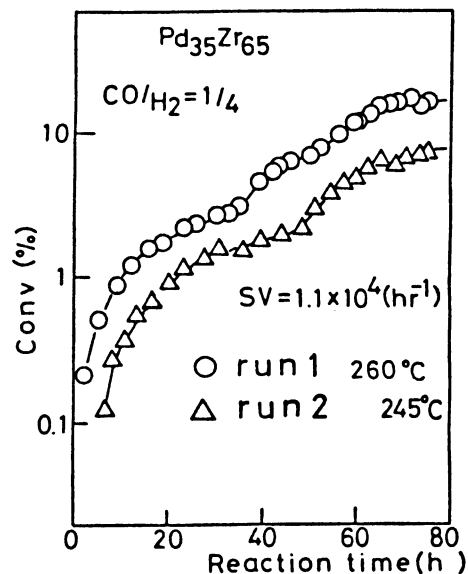


Fig.1 The activity change of $\text{Pd}_{35}\text{Zr}_{65}$ amorphous catalyst

Table 1 TF values for methanation catalysts.

Catalyst	N_{CH_4} at 275°C $\text{sec}^{-1} \times 10^3 \text{ a)}$	E_{CH_4} (kJ/mol)	Refs.
$\text{Pd}_{35}\text{Zr}_{65}$	635	100	this work
4.75% Pd/ SiO_2	0.32	112±7.5	5)
1.86% Pd/ TiO_2	27	98.6±2.9	5)
Raney Ni	45	130	6)
5% Ni/ ZrO_2	91	117	7)
5% Ni/ Al_2O_3	37	105	8)
5% Ru/ Al_2O_3	181	101	8)
1.5% Ni/ TiO_2	528 (H_2 chemisorption)		9)
Ni_5Si_2	280		10)

a); $P_{\text{CO}}=0.25 \text{ atm}$ $P_{\text{H}_2}=0.75 \text{ atm}$

Table 1 shows the turnover frequency (TF) at the steady state, based on the CO chemisorption. The TF values from literature are also included in the table. The TF for the present catalyst is one to three orders of magnitude greater than those for the supported Pd catalyst and is about one order of magnitude greater than that of ordinary supported Ni catalysts. Recently, active methanation catalysts have been reported, which include supported Ru and Ni catalysts and the Ni catalysts prepared from the intermetallic compounds. The TF of the present catalyst is still greater than or comparable to those for these active catalysts. The present catalyst increased its surface area during the reaction, but only slightly in contrast with the case of the amorphous $\text{Ni}_{63}\text{Zr}_{37}$ catalyst, where the surface area increased by two orders of magnitude during the same reaction.²⁾ These experimental results and consideration indicates that some catalytically active species was formed on the catalyst surface, in the transient reaction period as shown in Figure 1.

Figure 2 shows X-ray diffraction spectra. The spectrum (B), the catalyst used in the run 1 in Figure 1, shows that the amorphous alloy (the spectrum (A), showing a typical amorphous structure was crystallized during the reaction. The spectrum (B), however, does not coincide with any spectrum of Pd, Zr, and the bimetallic Pd-Zr alloy. Hence, the active species should be entirely different from them, and be produced by a reaction among Pd, Zr, and the reactant molecules.

Because the spectrum (B) is not found in the spectra of the oxides and hydrides of Pd and Zr which have been reported in the literature, an attempt was made to determine the active species experimentally. The spectrum (C) and (D) were those for the specimens which were prepared by heating the amorphous $\text{Pd}_{35}\text{Zr}_{65}$ alloy in a stream of oxygen or hydrogen at the reaction temperature (260°C). The hydrogen treatment at this temperature, which is lower than the crystallization point of

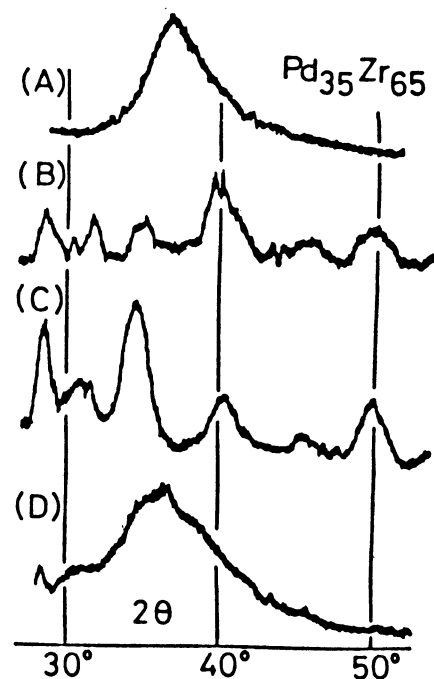


Fig.2 X-ray diffraction pat-

terns

(A); amorphous phase (as quenched)

(B); Pd-Zr-O type compound phase
(reacted at 260°C for 80 h)

(C); Pd-Zr-O type compound phase
(treated at 260°C in O_2 for 50 h)

(D); amorphous phase (treated at
260°C in hydrogen for 50 h)

this amorphous alloy (285°C), does not affect the amorphous structure. The close resemblance of the spectrum (C) with (B) indicates that the amorphous alloy was oxidized during the hydrogenation reaction.

Similar experimental observation of the in situ activation and the formation of oxides such as SiO_2 , CeO_2 , ZrO_2 and ThO_2 ^{10,11)} during the hydrogenation of CO by intermetallic catalysts, have been reported. The characterization of the unknown oxide composed of Pd, Zr and O will be required to elucidate the activity of the present catalyst.

The present results indicates that novel catalysts, which are different from usual metal catalysts supported on the metal oxides in activities and/or selectivities, are prepared by using amorphous alloys as precursors. Applications of the method to preparation of various catalysts is currently under way.

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