

# The Hydrogenation of Carbon Monoxide by Amorphous Ribbons

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Fifteen amorphous Fe-Ni base alloys containing P and/or B as additives were studied to determine their catalytic activity for the hydrogenation of CO to produce mainly C<sub>1</sub> to C<sub>3</sub> hydrocarbons. The amorphous state is catalytically stable, if the reaction temperature is maintained considerably below the crystallization point of the amorphous alloy. With the exception of only one composition, the stable activity of the amorphous state is from several to several hundred times higher than the thermodynamically stable crystalline state of the same composition. Both the amorphous and the crystalline catalysts exhibit an activation energy of  $100 \pm 4$  kJ/mol and a rate law  $-dP_{CO}/dt = kP_{H_2}^{1.0}P_{CO}^0$ . These results suggest that the active sites are of similar nature but different in number for the different structures and compositions of the catalysts.

## INTRODUCTION

Several techniques to produce amorphous metallic materials have been developed (1). These techniques include rapid quenching of the melt to prevent nucleation and crystallization. Of these, the disk methods developed in this decade made possible the mass production of amorphous alloys and stimulated the practical application of these new materials.

While considerable effort has been devoted to elucidating the mechanical, electrical, magnetic, and corrosional properties of the amorphous alloys (2), it was only recently that the Fe<sub>0.2</sub>Ni<sub>0.6</sub>P<sub>0.2</sub> amorphous ribbons were first studied as catalysts for the hydrogenation reaction of carbon monoxide (3). The amorphous state was catalytically more active than either the stable crystalline state or the metastable states which were produced in the course of the crystallization process of the amorphous alloy.

In addition to the possibilities of the

amorphous state as a catalytically active material, amorphous ribbons which are made by the disk method are attractive from the practical point of view for their large surface area and homogeneous composition. This study was undertaken as an extension of our previous work (3).

The catalytic properties of various Fe-Ni base amorphous alloys in the hydrogenation of carbon monoxide are studied and compared to catalysis by the thermodynamically stable crystalline alloys of the same chemical compositions.

## EXPERIMENTAL

### *Catalysts*

Amorphous Fe-Ni base alloys were prepared by rapid quenching from liquids containing boron and phosphorus. The addition of metalloid elements is usually required to obtain amorphous structures with relatively high crystallization temperatures. FeP (Fe, 74.9%), NiP (Ni, 85.9%), Fe (99.9%), Ni (99.97%), B (99%) were used to prepare

any desired composition with respect to Fe, Ni, P, and B. These materials were placed into a quartz tube of 5-mm $\phi$ . After the sample had been melted by a high-frequency induction heating coil, the liquid was ejected from the quartz capillary tube by argon and impinged onto the outer surface of a rotating steel roll (Fig. 1). With this method, amorphous alloys were prepared in the shape of ribbons from 0.5 to 1.5 mm wide and 3 to 20  $\mu$ m thick.

An X-ray analysis was made to follow the structure of the amorphous and crystal ribbons before and after each reacting operation. The specific surface area of the ribbons was determined by the BET method using nitrogen at its boiling point.

#### Apparatus and Procedure

A flow-type reaction system was employed. The reactor was a stainless-steel tube of 13-mm i.d. maintained at a constant temperature in a fluidized sand bath. The amorphous ribbons were cut into strips about 1 cm long and packed in the reactor as uniformly as possible, avoiding maldistribution of the reacting gas streams. The streams from cylinders of hydrogen and mixed carbon monoxide/nitrogen (2.01 or 10.3% CO nitrogen balance) were mixed to give the desired composition. Standard operating conditions for the activity tests were: a total flow rate of 30 ml/min, a gaseous composition of 1.26% CO and 36.9% H<sub>2</sub>, and 1 g of the catalyst packed in the reactor. Since the density of the

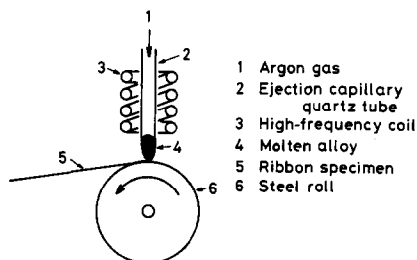


FIG. 1. Schematic illustration of the rapid quenching apparatus for the disk method of preparing amorphous ribbons.

amorphous alloys used in this work is around 7.7 g/ml, the real catalyst volume was around 0.13 ml. Depending on the compression in packing the ribbons, the corresponding reactor volume packed with the catalyst ranged from 1 to 2 ml.

The reaction was carried out at atmospheric pressure. Under the standard condition, the fractional conversion of carbon monoxide was no more than 5% so that a differential condition was satisfied. The exit gas stream from the reactor was introduced into a gas chromatograph (Shimadzu GC-6A) equipped with a Porapak N column and a combination of FID and TCD to determine the concentrations of the reaction products.

The major reaction products were methane, ethylene, ethane, propylene, and propane along with a trace of carbon dioxide and longer-chain hydrocarbons. The distribution of the major products depended considerably on the catalysts.

## RESULTS

#### Catalyst Pretreatment

The effects of pretreating the amorphous Fe<sub>0.4</sub>Ni<sub>0.4</sub>P<sub>0.16</sub>B<sub>0.04</sub> ribbons are shown in Fig. 2, in terms of percentage

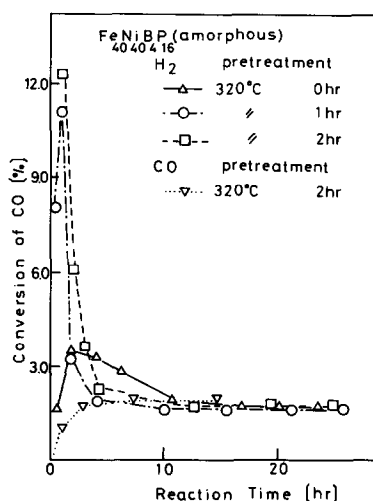


FIG. 2. The activity of amorphous catalyst as a function of time following various pretreatment procedures.

conversion of carbon monoxide (under the standard operating condition) vs time. Pretreatment with a stream of hydrogen at the same temperature as the reacting condition (320°C) increased the activity during the initial period of operation, but the activity rapidly decreased and approached a constant value about 10 hr after the start of a run.

Pretreatment with a stream of helium containing 1.26% CO decreased the initial activity but the same activity was reached after about 10 hr. The catalyst without any pretreatment exhibited a change in activity intermediate between the H<sub>2</sub> and the CO pretreatments, reaching the same constant activity. These results indicate the pretreatment procedures affect the initial surface conditions related presumably to the reduction state, but regardless of the pretreatment similar surface conditions are reached under the reacting gas stream.

The X-ray diffraction analysis (Fig. 3)

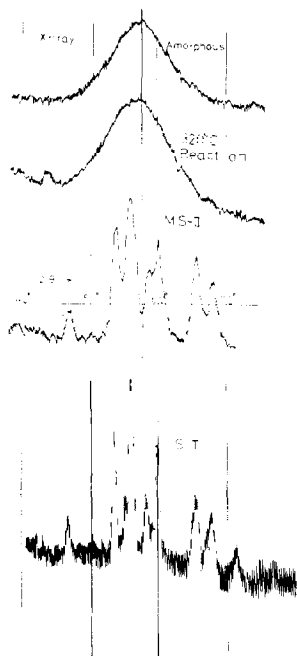


FIG. 3. X-Ray diffraction patterns: fresh amorphous ribbon; amorphous ribbon following a reaction at 320°C; metastable crystalline phase II following heat treatment at 400°C; and thermodynamically stable crystalline ribbon.

TABLE I

Representative Thicknesses and BET Surface Areas of Catalysts

Catalysts	Thickness (μm)	BET surface area (m <sup>2</sup> /g)	
		Amorphous	Stable crystalline
Fe <sub>0.8</sub> B <sub>0.2</sub>	13	0.32	0.25
Fe <sub>0.2</sub> Ni <sub>0.6</sub> P <sub>0.2</sub>	12	0.37	0.33
Ni <sub>0.66</sub> B <sub>0.34</sub>	14	0.27	0.30

made after each run confirmed the retention of an amorphous structure during the pretreatment and reaction experiments.

The effects of the pretreatment procedures were also examined for the crystalline catalysts. The amorphous strips were heated in the reactor under a stream of helium in advance of a reaction experiment. The heating temperature was set between 500 and 600°C and the formation of the thermodynamically stable crystalline phase (ST) was confirmed by XDA (Fig. 3) after the reaction experiment. As shown in Fig. 4, a constant activity was obtained for the catalysts both with and without the pretreatment.

*Specific Surface Area*

Table I shows some examples of BET surface areas and micrometrically determined thicknesses of the ribbons. The BET

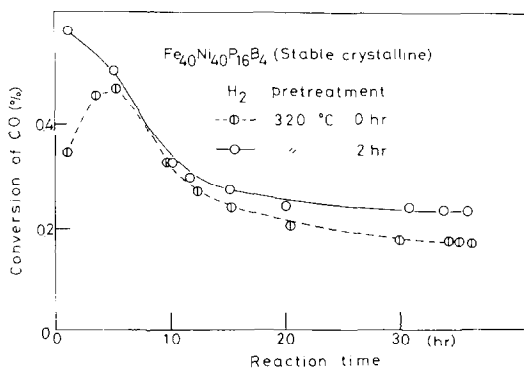


FIG. 4. The activity of crystalline catalyst as a function of time after hydrogen pretreatment.

TABLE 2

The Relationship of the BET Surface Area to the Activity of the  $\text{Fe}_{0.2}\text{Ni}_{0.6}\text{P}_{0.2}$  Amorphous Ribbons

BET surface area ( $\text{m}^2/\text{g}$ )	Activity (%)
0.75	6.9
0.37	2.84

surface area is about 13 to 22 times greater than the geometrical area which is calculated from the thickness and the density of the ribbon. Crystallization due to the thermal treatment does not affect the surface area significantly. As shown in Table 2 the catalytic activity per unit BET surface area is almost constant.

#### Activity and Activation Energy

The stable activities, which are reached after the initial transient period as shown in Fig. 2, were measured for 15 Fe-Ni base alloys. The thickness of the alloys range from 15 to 20  $\mu\text{m}$ . Since the BET surface areas ranged from 0.2 to 0.4  $\text{m}^2/\text{g}$  the activity of the ribbon represents approximately the activity which is characteristic

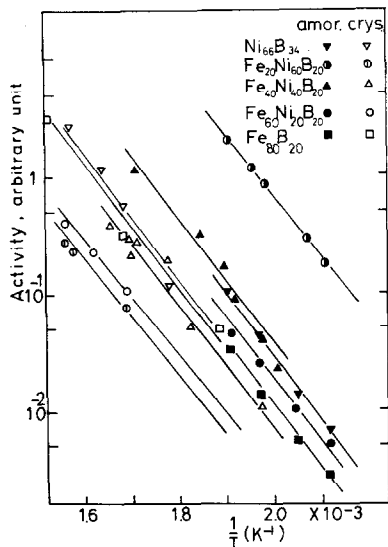


FIG. 5. Temperature dependency of catalytic activity with Fe-Ni-B catalysts.

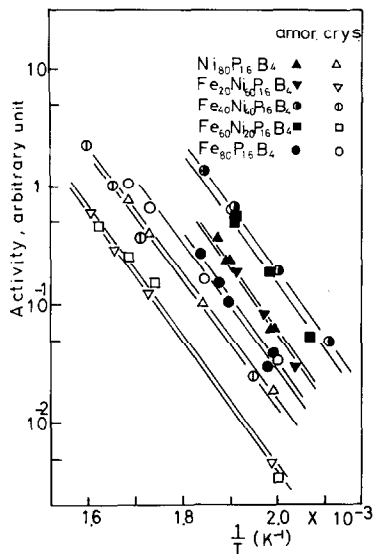


FIG. 6. Temperature dependency of catalytic activity with Fe-Ni-PB catalysts.

of the chemical composition and solid structure of the catalyst.

Figure 5 shows the results with Fe-Ni-B ribbons at various temperatures. The activities of the ST state are compared with the amorphous state of the same composition. The amorphous state is catalytically more active than the corresponding ST

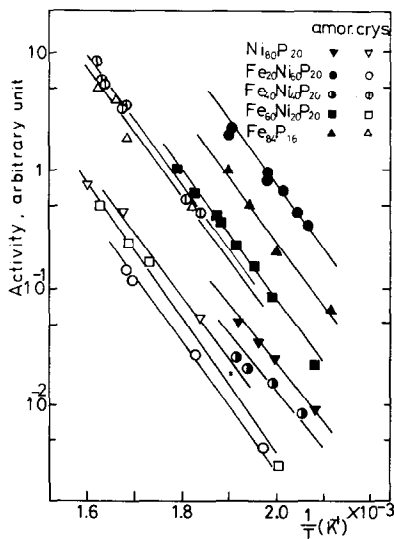


FIG. 7. Temperature dependency of catalytic activity with Fe-Ni-P catalysts.

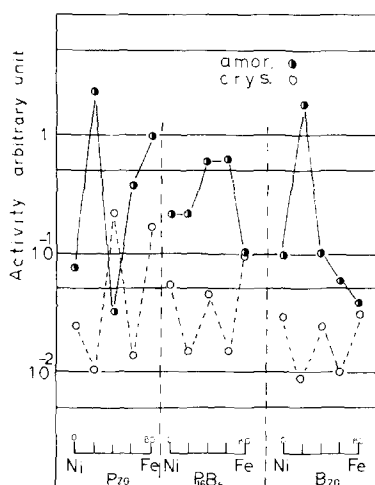


FIG. 8. The variation of activity with the composition of the catalysts.

state. Interestingly, in spite of the different compositions and solid structures, the activation energy for the hydrogenation of carbon monoxide is constant at  $100 \pm 4$  kJ/mol.

Figures 6 and 7 show similar results for experiments in which the metalloid elements are respectively  $P_{0.16}B_{0.04}$  and  $P_{0.2}$ . The activation energy for the depletion of carbon monoxide is  $100 \pm 4$  kJ/mol for all the catalysts tested in this work.

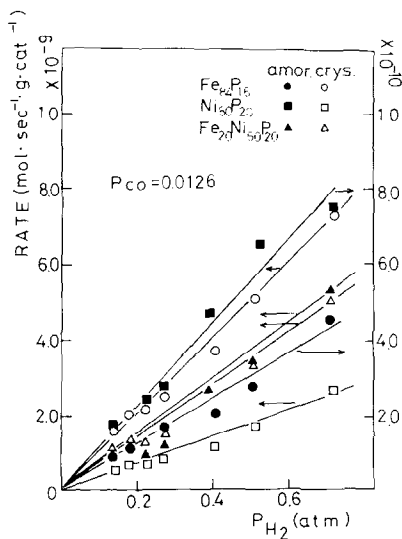


FIG. 9. Rate of hydrogenation of CO vs pressure of hydrogen.

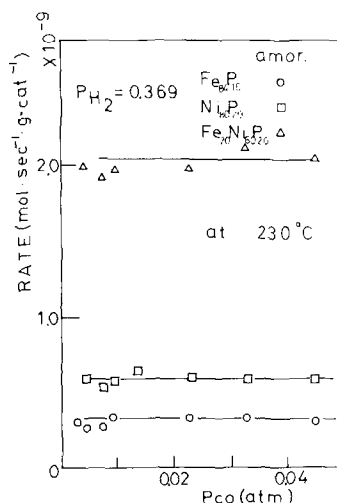


FIG. 10. Rate of hydrogenation of CO vs pressure of CO with amorphous catalysts.

The results as shown in Figs. 5, 6, and 7 were replotted in Fig. 8 in terms of the activity vs catalyst composition. Since the activation energy is constant with these catalysts, the activity at a constant temperature ( $255^\circ\text{C}$ ) represents the activity of each composition. The amorphous states are more active than the corresponding ST states, with the exception of the  $Fe_{0.4}Ni_{0.4}P_{0.2}$  catalyst.

### Kinetics

Kinetic measurements were made to examine the reaction rate dependencies on

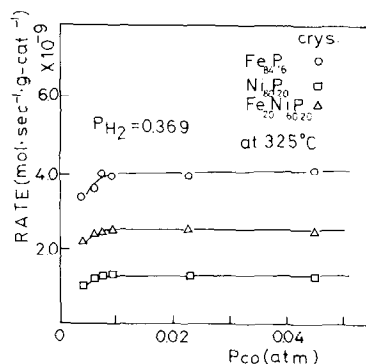


FIG. 11. Rate of hydrogenation of CO vs pressure of CO with crystalline catalysts.

the gas-phase composition. Three alloy compositions of particular interest were selected:  $\text{Fe}_{0.2}\text{Ni}_{0.6}\text{P}_{0.2}$  and  $\text{Fe}_{0.84}\text{P}_{0.16}$  respectively have the largest and medium differences in activity between the amorphous and the ST states; and  $\text{Ni}_{0.8}\text{P}_{0.2}$  has a very different product distribution. Of all the catalysts the crystalline catalyst shows the highest selectivity for methane (99%), while the amorphous catalyst produces about 28%  $\text{C}_2$  and  $\text{C}_3$  hydrocarbons.

Figure 9 shows that the reaction rates obey good first-order kinetics in hydrogen for these three alloys in both their amorphous and crystalline states. Figures 10 and 11 show that the reaction rates are almost independent of the partial pressure of carbon monoxide. Thus, the rate of hydrogenation of carbon monoxide is expressed as

$$r = k P_{\text{H}_2}.$$

#### DISCUSSION

One of the important results of the present work is the demonstration of a stable elevated catalytic activity for 15 amorphous alloys. However, the stable elevated activity is maintained only at temperatures below some critical temperature which is considerably lower than the crystallization point of the amorphous ribbon. At the present stage, it is difficult to predict the critical temperature. For example, amorphous  $\text{Fe}_{0.4}\text{Ni}_{0.4}\text{P}_{0.16}\text{B}_{0.04}$  catalyst exhibited a stable elevated activity at  $320^\circ\text{C}$  which is only  $73^\circ\text{C}$  lower than the crystallization temperature. On the other hand,  $\text{Fe}_{0.8}\text{B}_{0.2}$  catalyst crystallized and lost the high activity at  $255^\circ\text{C}$ ,  $132^\circ\text{C}$  below the crystallization point.

Figure 12 shows a typical example of crystallization during a reaction. In this case the activity of the amorphous  $\text{Fe}_{0.2}\text{Ni}_{0.6}\text{B}_{0.2}$  ribbon suddenly decreased due to a temperature jump from 230 to  $313^\circ\text{C}$ ,  $57^\circ\text{C}$  below the crystallization temperature.

Crystallization of amorphous materials under nonreactive atmosphere has been

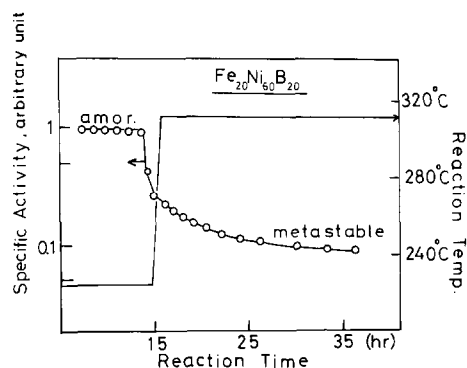


FIG. 12. Activity change with temperature jump during reaction.

studied in terms of a time-temperature-transformation diagram (4). Crystallization during a reaction does not seem to be related directly to the T-T-T diagram and should be studied in the future.

Figures 5, 6, and 7 show that with one exception the amorphous state is more active than the corresponding crystalline state, and that the activation energy for this hydrogenation reaction is constant for all 30 catalysts including both the amorphous and the crystalline states.

Furthermore, Figs. 9, 10, and 11 show that the dependency of the reaction rate on hydrogen and carbon monoxide is the same for both the amorphous and the crystalline states. These results indicate that the active sites of these catalysts are of similar nature but differ in number depending on the catalyst composition and that, in particular, the amorphous state usually has more active sites per unit surface area than the crystalline state.

Since chemisorption measurements to evaluate the number of surface metallic atoms have not been made, the activities measured in the present work cannot be represented in terms of turnover frequency (TF). Possibly minimum TF were calculated by using the  $\text{N}_2$  physisorption BET area. TF for  $\text{Fe}_{0.2}\text{Ni}_{0.6}\text{P}_{0.2}$  at  $275^\circ\text{C}$  and  $P_{\text{H}_2} = 0.75 \text{ atm}$  was  $7.5 \times 10^{-3} \text{ sec}^{-1}$ . While the TF is underestimated, the value might give a limiting value for comparison with other

works. The correct TF will be given on the basis of chemisorption measurements of CO which is planned by the authors.

The product distribution was not significantly affected by the reaction temperature but considerably affected by the gaseous composition. A high partial pressure of carbon monoxide is obviously favorable for C<sub>2</sub> and C<sub>3</sub> hydrocarbon production, with a corresponding decrease in the production of methane. Also, the product distribution strongly depended on the composition and structure of the catalysts. Selectivity to C<sub>2</sub> and C<sub>3</sub> hydrocarbons varied

from zero to 50%, with most of the other product methane. The detailed analysis of the selectivities is now under way.

#### REFERENCES

1. Klement, W., Jr., Willens, R. H., and Duwez, P., *Nature (London)* **187**, 869 (1960).
2. Masumoto, T., and Suzuki, K., "Structure and Properties of Amorphous Metals" (Suppl. to *Sci. Rep. Res. Inst. Tohoku Univ.*, A-27), 1978.
3. Yokoyama, A., Komiyama, H., Inoue, H., Kimura, H. M., and Masumoto, T., submitted for publication.
4. Masumoto, T., and Maddin, R., *Mater. Sci. Eng.* **19**, 1 (1975).