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POROUS AND AMORPHOUS $Ni_{67}Zr_{33}$ CATALYST PREPARED BY HYDROGENATION OF CARBON MONOXIDE

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Porous structure of ample specific surface area as catalyst, of 5.3 m^2/g, has been successfully developed in the amorphous $Ni_{67}Zr_{33}$ ribbon of 0.05 m^2/g by the hydrogenation of carbon monoxide at 538 K. The porous and amorphous catalyst shows stable catalysis for the hydrogenation reaction below 493 K.

It has been recently found that some alloys can be solidified from the melts into the amorphous state by rapid quenching technique.[1] Some attempts have been made to investigate the catalysis of this attractive new material.[2-12] Unique activities[2-8] and selectivities[9,10] of amorphous catalysts, derived from their surface topography, were reported. Amorphous NiZr alloys are known to have hydrogen absorption capability and thermal resistivity due to their high crystallization temperatures.[13,14] Activity and stability as hydrogenation catalyst is anticipated. In our previous study[11] of the hydrogenation of carbon monoxide on an amorphous $Ni_{63}Zr_{37}$ ribbon catalyst, spontaneous activation process during the reaction was found to take place. The final structure of the catalyst was a porous Ni/ZrO_2. Here we studied the structural change of the amorphous catalyst during the reaction and found that the activation process proceeds through an intermediate stage where the catalyst is porous as well as amorphous. The small surface area of the amorphous ribbon has been pointed out to be disadvantageous from the practical viewpoint. The present results provide a solution to this problem.

Amorphous $Ni_{67}Zr_{33}$ alloys were made by the disk method[1] in the atmosphere of argon. The amorphous alloy in the shape of 10 to 20 μm thick, 1 to 2 mm wide, and about 2 m long was put into a tubular reactor. The reaction temperature was mea-

sured by a thermocouple which was directly inserted into the center of the catalyst bed. An X-ray diffraction (XRD) analysis was made to follow the structure of the amorphous catalysts before and after each reaction. The specific surface area of the catalyst was determined by the BET method, using flowing nitrogen at its boiling point. In advance of a run, the amorphous catalyst was polished by a sand paper and reduced by flowing hydrogen at 523 K for 2 h to remove surface contaminated layer mostly composed of zirconium oxide. The standard reaction conditions employed were: the total flow rate; 50 ml/min, the hydrogen to carbon monoxide ratio; 4, the total pressure; 1 atm (=0.105 MPa), and the reaction temperature; 538 K. Under the standard conditions, the fractional conversion of carbon monoxide was no more than 10% so that a differential reactor condition was satisfied.

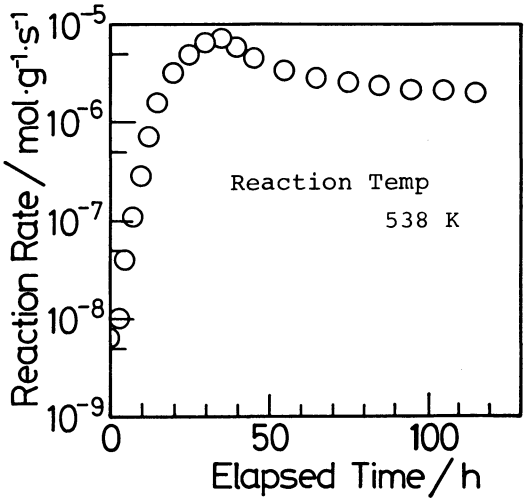

Fig. 1. The activity change of amorphous $Ni_{67}Zr_{33}$ catalyst.

Figure 1 shows the reaction rate based on a unit catalyst weight as a function of the elapsed time from the start of a run. The activity increased with time, but through a maximum at 30 to 40 h decreased gradually to approach a constant value. The structure of the catalyst, analyzed by XRD, also changed with time as are shown in Fig.2 a-c. The amorphous structure was maintained for around 10 h, when the surface area was 7.8 m^2/g, gradually crystallizing to yield Ni and ZrO_2. After 115 h, it finally changed into crystalline Ni/ZrO_2, whose specific surface area was 70 m^2/g. Figure 3 shows the change of the BET surface area and the specific reaction rate divided by the surface area at each time. The specific surface

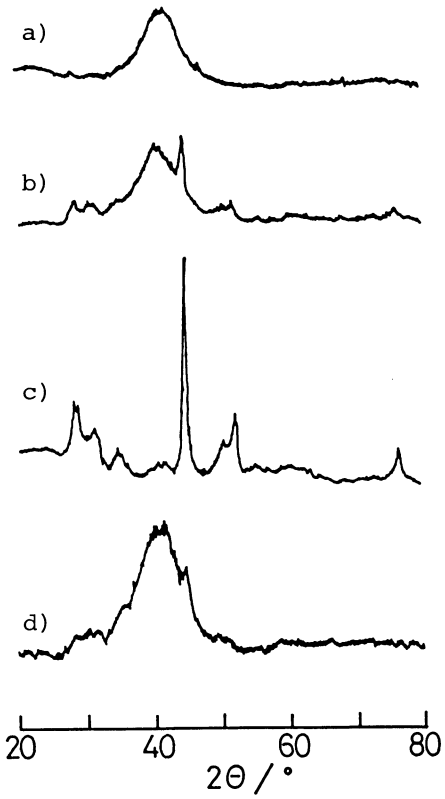

Fig. 2. The XRD charts of amorphous catalyst (Rad. Cu-kα).
a) as quenched (0.05m^2/g)
b) 10 h spent (7.8 m^2/g)
c) 115 h spent (70 m^2/g)
d) pretreated by CO/H_2 reaction (5.3 m^2/g)

activity showed a maximum at the initial stage of a run and remained almost constant untill 20 h. During this period, the catalyst remained amorphous as proved by XRD. The decreased surface activity at 40 h suggests that the segregation of amorphous NiZr to crystalline Ni/ZrO_2 made rapid progress during 20 to 40 h.

An attempt was made to create a porous as well as amorphous catalyst by controlling the spontaneous proceeding of the surface area enlargement. Namely, amorphous $Ni_{67}Zr_{33}$ catalyst was pretreated by the above mentioned procedures and used for the hydrogenation of carbon monoxide for a few hours. Then, the reaction temperature was suddenly decreased to prevent further structural change of the catalyst. Figure 4 shows the results. After a three hour standard reaction, the activity increased about 100 times. The reaction temperature was suddenly decreased from 538 K to 493 K at this point. The reaction temperature was decreased stepwisely by 20 K, and kept constant for 3 h at each temperature. No activation or deactivation was observed. An Arrhenius plot of Fig.4 almost exactly fits to a straight line, showing an activation energy of 100.6 kJ/mol which is often reported on the other traditional supported Ni catalysts.[15)]

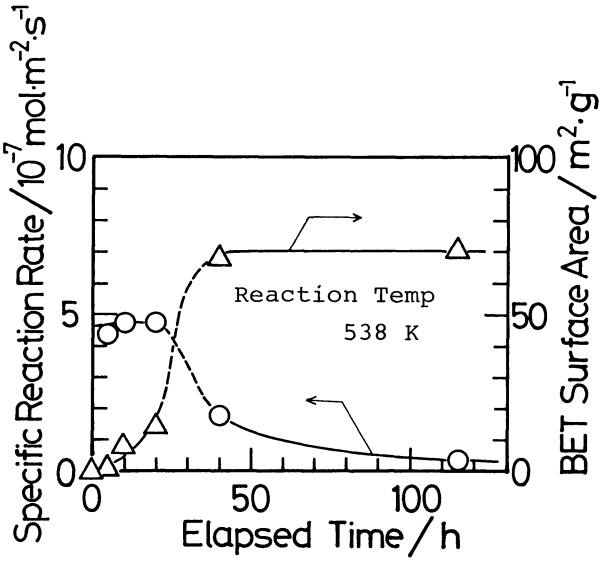

Fig. 3. The change of surface activity and BET surface area with amorphous $Ni_{67}Zr_{33}$ catalyst.

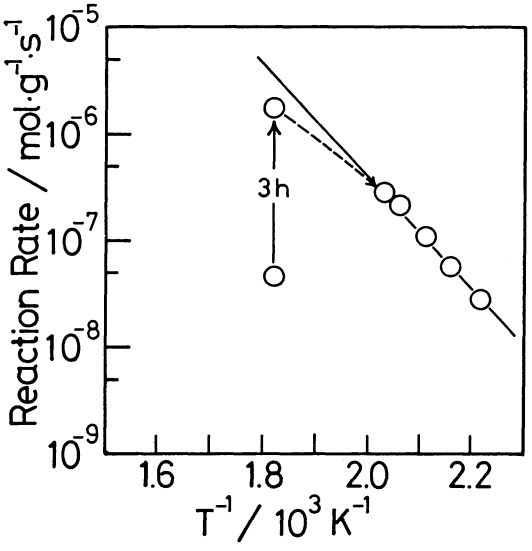

Fig. 4. The temperature dependence of catalytic activity with amorphous $Ni_{67}Zr_{33}$ catalyst after CO/H_2 reaction treatment.

Figure 2d shows the structure of this catalyst after this experimental run. The amorphous structure was well maintained. The BET surface area of this catalyst after the reaction was 5.3 m^2/g, and its initial ribbon shape was kept. The specific activity calculated from this surface area was $3.9\times10^{-7}mol\cdot m^{-2}\cdot s^{-1}$ at 538 K. This value is as much as the maximum value shown in Fig.3. Thus this porous cata-

lyst was proved to maintain its high specific activity derived from amorphous surface. Therefore it is demonstrated that a porous and amorphous catalyst can be prepared by the above mentioned procedures, including the CO/H_2 reaction as one of the indispensable steps.

In conclusion, highly active and porous catalysts can be prepared from amorphous $Ni_{67}Zr_{33}$ ribbons as precursors by the CO/H_2 reaction treatment. The outer surface of the original amorphous ribbons is often affected by contamination and deviation from the bulk composition. This treatment is quite effective for investigating the true catalysis of amorphous alloys, since "well-defined surface" of amorphous alloy is obtained. The catalysis for the other reactions on the genuine surface of amorphous alloy, exposed by this technique, is now under investigation.

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