CHEMISTRY LETTERS, pp. 511-514, 1972. Published by the Chemical Society of Japan

STUDY OF RANEY NICKEL CATALYSTS BY ELECTRON MICROPROBE X-RAY ANALYZER

Jiro YASUMURA and Ichiro NAKABAYASHI
Department of Chemical Engineering, Faculty of Engineering,
Tokushima University, Minami-josanjima, Tokushima, Japan

On the basis of several observations of laminated Raney nickel catalysts with an electron microprobe X-ray analyzer, it is concluded that the activity of the catalysts is seemingly correlated to the composition of Raney nickel alloys, and that the active centers are distributed probably at random on the surface of the catalysts.

In our previous paper,[1)] a method for preparing laminated Raney nickel catalysts and the formation of Raney nickel alloys at the phase boundary of nickel and aluminum are described. The alloys are formed when aluminum is sprayed onto the surface of a nickel plate, and then the plate is heated to an appropriate temperature in the air. The laminated Raney nickel catalyst is prepared by treating this plate with a caustic alkali solution. In this letter, we deal with mainly the dependence of the activity of the catalyst upon the composition of the alloys formed at the interphase. In addition, the distribution of the active centers on the catalyst surface is refered to.

Aluminum-coated nickel plates were kept at various temperatures up to 800°C in the air for 2 hrs. At any temperature below 600°C, the alloy formation at the boundary was not detected by X-ray diffraction method. The alloy phase formed was composed of $NiAl_3$ or Ni_2Al_3 , which was the same as was reported in the previous papers.[2,3)]

Fig. 1 shows a back scattered electron image of the phase boundary, and the results of line analysis with electron scanning along the straight line (Z) across the boundary. As the lines (a) and (b) indicate the amounts of nickel and aluminum respectively, it is clear that the part (A) in the figure is an aluminum phase, (B) an alloy phase, and (C) a nickel phase. This conclusion is also supported by Fig. 2 and 3, which are Ni-K_α and Al-K_α radiation profiles, respectively, showing the distribution of nickel and aluminum atoms in the same cross section of the sample for Fig. 1. From such a pattern as Fig. 1 the thickness of the alloy phase is to be easily estimated.

Some of the observed values of the heat treatment temperature, the alloy phase thickness, and the activities of the catalysts for hydrogenation of acetone are listed in Table 1. The Raney nickel catalyst that was prepared from an original sample, heat-treated at 700°C, was the most active.

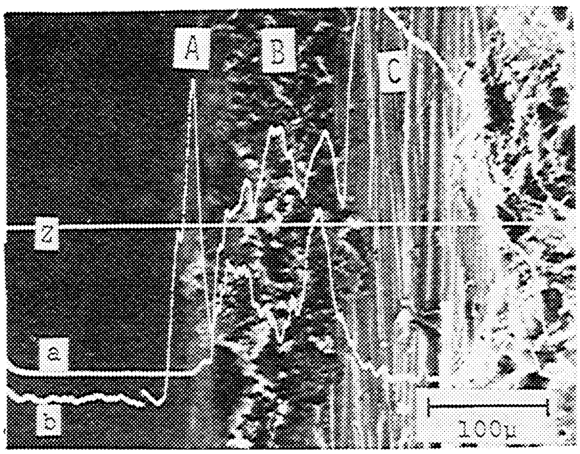

Fig. 1

Cross section of Raney nickel alloy boundary (700 °C, 2 hrs.).

line a : Ni-K_α radiation

line b : Al-K_α radiation

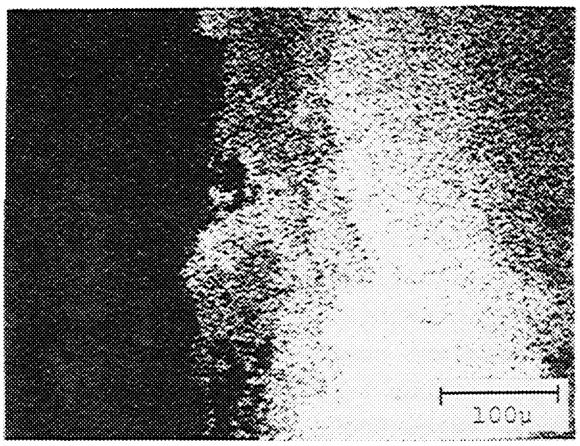

Fig. 2

Ni-K_α radiation profile of the same cross section.

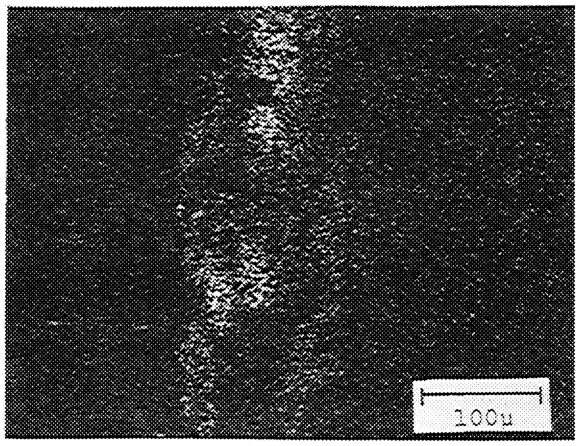

Fig. 3

Al-K_α radiation profile of the same cross section.

Table 1. Heat treatment temperature, Thickness of the alloy phase, and Activity of the catalyst for hydrogenation of acetone.

Heat treatment temp. (°C)	Thickness (μ)	Activity (Yield of 2-propanol) (%)
500	5	10
600	25	32
650	55	38
700	150	48
800	360	9

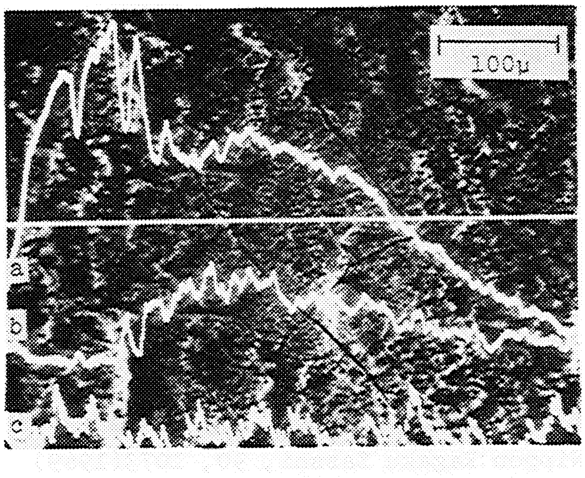

Fig. 4

Surface of poisoned catalyst prepared from the Ni-Al alloy formed at 700 °C.

line a: Ni-K_α radiation
line b: Al-K_α radiation
line c: S-K_α radiation

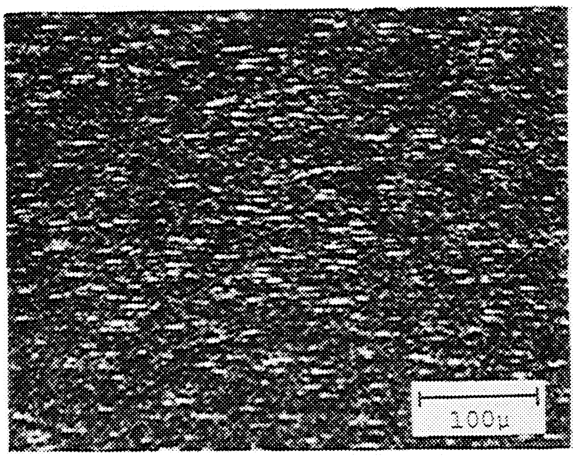

Fig. 5

S-K_α radiation profile of the same surface.

In the case where the temperature of heat treatment was 800°C, the catalyst obtained was very poor in the activity. It was proved that the alloy phase was $NiAl_3$ when formed at 700°C, and was Ni_2Al_3 when formed at 800°C. The aluminum in a Ni_2Al_3 phase, as compared with that in a $NiAl_3$ phase, was difficult to be leached by a 20% sodium hydroxide solution.(1) This is probably a reason for the significant reduction of the catalytic activity shown in the table.

In order to poison the active centers on the surface, the catalyst was immersed in water saturated with H_2S at 20°C for 10 sec. Fig. 4 is a back scattered electron image of the surface of the poisoned catalyst, and Fig. 5 is a radiation profile of the same sample. These figures show that the aluminum remained on the surface is located here and there in groups; the sulfur is, on the contrary, uniformly distributed. For hydrogenation of acetone, an ordinary nickel plate is inactive. After immersion of a nickel plate in a H_2S aqueous solution for 10 min., the amount of sulfur detected by electron beam microprobe analysis was very small. With a poisoned Raney nickel catalyst, on the other hand, a large amount of sulfur was found (Fig. 5). It is a well-known fact that nickel catalysts which are poisoned by sulfur lose their activities for hydrogenation. Consequently, the positions of combined sulfur which appeared in Fig. 5 seem to be the positions of active centers of the catalyst. If it is true, these observations may lead to a conclusion that the active centers on the surface are distributed uniformly, irrespective of the irregular distribution of the aluminum remaining.

References

1) I.Nakabayashi, Kogyo Kagaku Zasshi, 74, 1527(1971)
2) I.Nakabayashi, S.Masuda,and J.Yasumura, Nippon Kagaku Zasshi, 90, 344(1969)
3) I.Nakabayashi, S.Masuda,and J.Yasumura, Nippon Kagaku Zasshi, 90, 1073(1969)

(Received March 30, 1972)