CHEMISTRY LETTERS, pp. 967-970, 1976. Published by the Chemical Society of Japan

ACTIVITY OF Ni-P CATALYST FOR THE DEHYDROGENATION OF METHYLCYCLOHEXANE

Fumio NOZAKI, Takashi SEKURA, and Masaji KAWAI
Department of Industrial Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 280

The Ni-P catalyst prepared by reduction of $Ni_3(PO_4)_2$ in hydrogen promoted selectively the dehydrogenation of methylcyclohexane to toluene. The repeated reoxidation-reduction of the catalyst resulted in an increase in dehydrogenation activity.

The Ni-P binary catalyst is known to have a characteristic selectivity for the hydrogenation of various organic compounds.[1-3] In the previous paper,[4] we have reported about the activity of Ni-P catalyst for the hydrogenation of butadiene. However, the study on the dehydrogenation has not been reported. The present report describes the activity of the Ni-P catalyst for the dehydrogenation of methylcyclohexane(MCH).

The Ni-P catalyst was prepared by the same method described in the previous paper.[4] That is, the alumina-supported sample containing about 20 wt% $Ni_3(PO_4)_2$ was prepared by the wet mixing method, which entailed the respective slurries of powdered $Ni_3(PO_4)_2$ and alumina sol(Nissan Kagaku Inc.,Alumina Sol Type 200). The sample dried at 110 °C was sieved to collect a 20–30 mesh fraction that was calcined in air at 600 °C for 2 hr. The resultant sample was reduced to obtain the Ni-P catalyst with hydrogen at the spcified temperatures. In order to characterize the Ni-P catalyst, three kinds of catalysts were used: the Ni(10 wt%) on SiO_2, Ni(15 wt%) on Al_2O_3 and the Pt(0.5 wt%) on Al_2O_3. The silica- or alumina-supported Ni catalyst was prepared by the same method described in the previous paper.[5] in which $Ni(OH)_2$ was precipitated from a solution of $Ni(NO_3)_2$ with an aqueous solution of ammonia in the presence of a suspension of carrier hydogel. The Pt on Al_2O_3 catalyst was supplied from Nippon-Engelhard Inc.These three catalysts were calcined in air at 500 °C for 2 hr and were reduced before use with hydrogen at 500 °C for 4 hr. The catalytic tests were carried out with a conventional pulse-reaction apparatus by use of hydrogen as a carrier gas. The procedures for the catalytic activity measurements and for the analysis of the reaction products were practically the same as those described in the previous paper.[6]

In Table 1, the activity and the selectivity of the Ni-P catalyst are compared with those of Ni and Pt catalysts. Both the activity and the selectivity were almost constant during the repeated sample injections for all the catalysts. Besides the dehydrogenation, metallic Ni promotes the dehydro-demethylation and the hydrocracking reactions leading to a considerable formation of benzene and methane. There was no appreciable difference in the selectivity between the Ni on SiO_2 catalyst and the Ni on Al_2O_3 catalyst, although the activity of the former was somewhat higher than that

Table 1. Comparison of Ni-P catalyst with Ni and Pt catalysts for the reaction of MCH

Catalyst weight(W): 0.21 g, Flow rate of H_2 carrier gas(F): 30 ml(NTP)/min= 0.083 mol/hr, Sample size in liquid of MCH injected(S_1): 2 µl/injection.

Catalyst	Reaction temperature (°C)	Fractional coversion of MCH	Selectivity for thr reaction		
			Dehydrogenation[b]	Dehydro-demethylation[c]	Hydrocracking[d]
Ni-P on Al_2O_3[a]	300	0.21	1.00	——	——
	400	0.85	1.00	——	——
Ni on SiO_2	250	0.48	0.75	0.23	0.02
	300	0.94	0.17	0.47	0.36
Ni on Al_2O_3	250	0.27	0.82	0.15	0.03
	350	0.87	0.24	0.39	0.37
Pt on Al_2O_3	250	0.35	1.00	——	——
	300	0.97	1.00	——	——

a) the catalyst was reduced with hydrogen at 600 °C. b) toluene formation. c) benzene formation. d) methane formation by hydrocracking of MCH.

of the latter. In contrast to metallic Ni, Ni-P selectively dehydrogenates without any other reaction, similarly to the Pt catalyst commercially used in the platforming process. This platinum-like selectivity of the Ni-P catalyst was quite similar to the partially sulfurated nickel catalyst reported in the previous paper.[6]

Influence of the temperature of catalyst preparation on the activity of Ni-P catalyst is shown by the curve 1 in Fig. 1. The activity is beginning to emerge when $Ni_3(PO_4)_2$ is reduced with hydrogen at temperatures near 350 °C, and increases with rise of temperature, passes through a maximum at about 600 °C, and then slightly decreases at 700 °C. These results were obtained when the time interval of catalyst reduction was kept constant for 4 hr. But, the catalyst activity was scarcely affected by changes in the time interval of catalyst reduction ranging from 1 to 5 hr. The selectivity of the Ni-P catalyst was entirely independent on the temperature of catalyst preparation, giving toluene alone.

The kinetic measurements were carried out with the Ni-P catalyst prepared at 600 °C. The conversion data were approximately expressed by the first order kinetics. The rate constants, k(mol/g-cat hr) were calculated by Eq.(1).

$$k = \frac{1}{(W/F)} \ln \frac{1}{1 - x} \qquad \ldots\ldots(1)$$

where W/F is the time factor used as an indication of contact time in the pulse reactor and where x is the fractional conversion of MCH. Arrhenius plot for the rate constants was shown by the straight line 2 in Fig.1. The apparent activation energy was found to be 15 kcal/mol.

A characteristics of the Ni-P catalyst was that the dehydrogenation activity

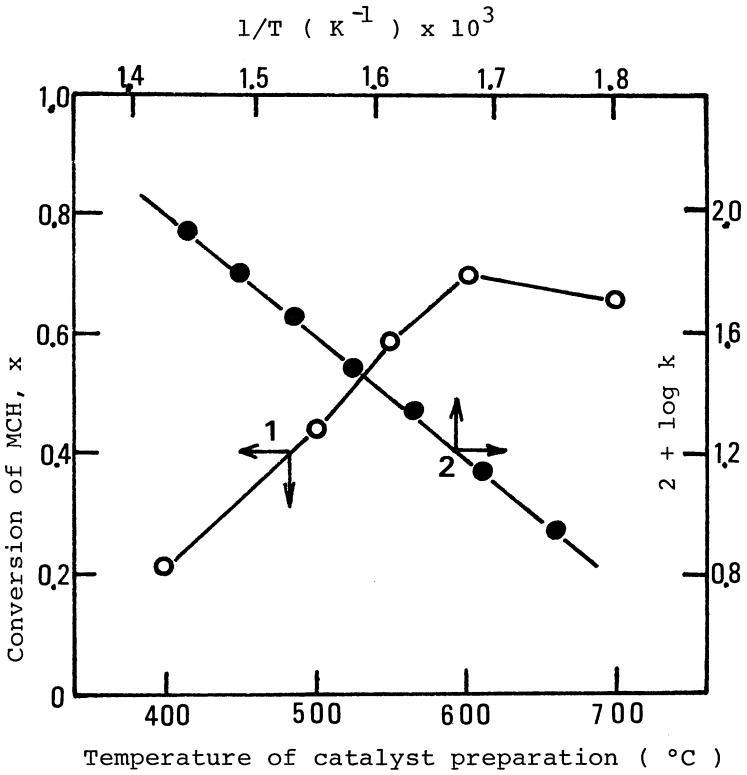

Fig.1. Influence of the temperature of catalyst preparation on the activity of Ni-P catalyst and Arrhenius plot for the rate constants.

1 : conversion of MCH vs. temperature of catalyst preparation.
(Reaction temp.:350 °C, W: 0.21 g, S_1: 2 μl)

2 : log k vs. 1/T plot.
(Temperature of catalyst preparation: 600 °C)

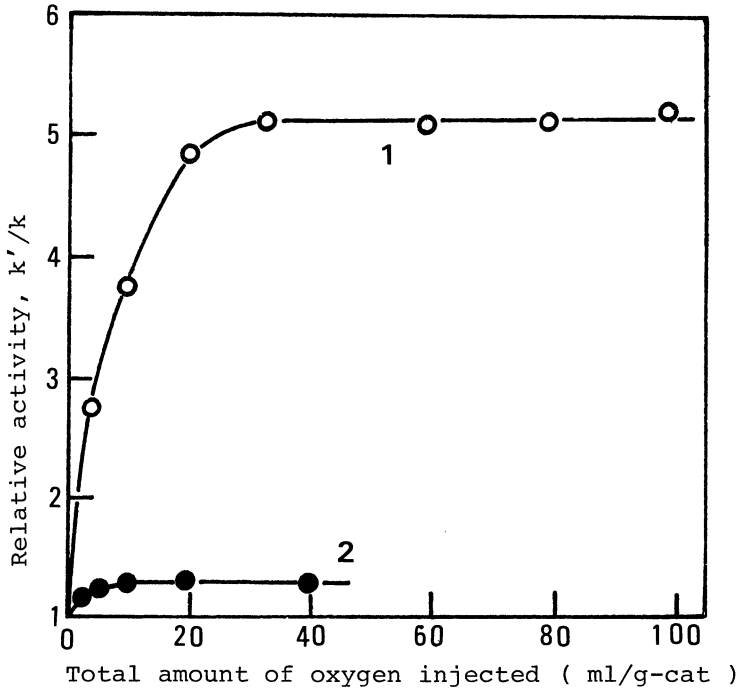

Fig. 2. Effect of the repeated reoxidation-reduction treatments on the activity of Ni-P catalyst.

1 : catalyst prepared at 400 °C.
2 : catalyst prepared at 600 °C.

increased by the repeated reoxidation-reduction treatments of the catalyst. The catalyst was reoxidized with the air pulse and then was reduced with the hydrogen carrier gas (this procedure was subsequently referred as the redox treatment). The experiments of the catalytic reaction of MCH and the following redox treatment of the catalyst were repeated at 350 °C. The increase in the activity is shown in Fig. 2 as a function of the integral amount of oxygen injected, where k'/k indicates the ratio of the rate constants obtained before and after the redox treatment of the catalyst. The catalyst selectivity of the Ni-P catalyst was entirely unchanged even after the redox treatment had been done. Figure 2 shows that the redox treatment of the catalyst is allowed to increase in activity about 5 times for the catalyst prepared at 400 °C and about 1.3 times for the catalyst prepared at 600 °C, respectively. In the cases of Ni and Pt catalysts,there was no such enhancement of the activity observed with the Ni-P catalyst. The increase of activity of the Ni-P catalyst by the redox treatment was irreversible. This enhancement of the dehydrogenation activity may be attributable to new active sites of Ni^0 formed by decomposition of nickel-phosphorus solid-solution or nickel-phosphides in the Ni-P catalyst, as suggested by the fact that the amount of CO uptake on the Ni-P catalyst increased with the redox treatment.

REFERENCES

1) N.P.Sweeny, C.S.Rohrer,and O.W.Brown, J.Am.Chem.Soc., 80, 799(1958).
2) S.Sada, Kogyo Kagaku Zasshi, 71, 957(1968); Nippon Kagaku Kaishi, 1976, 32,37.
3) E.L.Muetterties and J.C.Sauer, J.Am.Chem.Soc., 96, 3410(1974).
4) F.Nozaki and R.Adachi, J.Catal.,40, 166(1975).
5) K.Morikawa and F.Nozaki,Kogyo Kagaku Zasshi, 64, 898(1961).
6) F.Nozaki and V.S.Nguyen, Nippon Kagaku Kaishi, 1975).

(Received July 13, 1976)