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Promoter Effect of Platinum on Liquid-Phase Dehydrogenation of 2-Propanol by a Nickel Fine-Particle Catalyst

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(Received November 2, 1987)

A platinum-deposited nickel fine-particle catalyst was shown to be more active than a nickel-alone catalyst. A study of the temperature dependence of a rate constant revealed that platinum increased the frequency factor of the rate constant. An experiment regarding poisoning showed that the number of active sites was the same for the two catalysts. Thus the promoter effect was ascribed to an increase in the frequency factor per active site.

Liquid-phase dehydrogenation of 2-propanol proceeded by means of a metallic catalyst[1-4] or a complex catalyst in solution[5-9] or on a support.[10,11]

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CO + H_2$$

Nickel fine particles that were prepared by a gas-evaporation method[12,13] were also a suitable catalyst for the reaction.[14,15]

The surface modification of a metallic catalyst with a platinum-group metal has long been applied in order to increase the reaction rate. For example, platinum salts promoted hydrogenation activity of the Raney nickel catalyst.[16,17] In the present work, the promoter effect was studied through catalysis using nickel fine particles, since their shape and components are sufficiently simple to provide a clear explanation.

Experimental

1. Materials. Nickel fine particles were prepared by means of a gas-evaporation method of Vacuum Metallurgical Co., Ltd. (Chiba Pref., Japan). They comprised black, light powder. Their average diameter and BET surface area were 19.7 nm and 43.8 $m^2\,g^{-1}$. Their surfaces were covered with oxide layers in order to prevent the particles from burning in air. Partial reduction of the surface oxide by heating nickel fine particles under hydrogen was necessary in order to reveal catalytic activity.[18]

Bis(acetylacetonato)platinum(II) (Pt(acac)$_2$) was purchased from Nippon Engelhard Ltd..

2. Pretreatment. Nickel fine particles were pretreated and a reaction rate was measured using the technique described in a previous paper.[15] A prescribed amount (200 mg) of nickel fine particles was put into a round-bottom three-neck flask. After evacuation, the nickel fine particles were heated under hydrogen up to 160 °C in 15 min, held at 160 °C for 1 min and rapidly cooled. The amount of consumed hydrogen was measured with a gas buret. After evacuation, a prescribed amount (200 ml) of 2-propanol was added under nitrogen or argon. The nickel fine-particle catalyst was suspended in 2-propanol by means of vibration with a supersonic cleaner.

Platinum was deposited on the catalyst as follows: A prescribed amount (9 mg) of Pt(acac)$_2$ was dissolved in 2-propanol beforehand. After a nickel fine-particle catalyst was suspended in the solvent, hydrogen was blown into the stirred suspension through a glass straw for 30 min at room temperature. Hydrogen reduced any divalent platinum in the complex. If part of a catalyst suspension was placed on a magnet, the nickel fine particles contained in it precipitated during a day. The visible and ultraviolet spectra of a supernatant were recorded with a Shimadzu UV-365 spectrometer. An XRD pattern of the catalyst was recorded with a Rigaku-Denki Geigerflex D-9C X-ray diffractometer.

3. Measurement. A catalyst suspension was heated under boiling conditions with stirring. The height of the level of the suspension equaled that of an oil bath in which the reactor was soaked. A gas buret was connected to the reactor through a water-cooled condenser. The reaction rate was determined by the volume of gas that accumulated in the gas buret. Products in a gas phase and in the liquid phase were analyzed by gas chromatography using an active carbon column and a PEG-1000 column, respectively.

The temperature dependence of the reaction rate was investigated by addition of hexane to a catalyst suspension, since hexane reduces the boiling point of a solvent. The frequency factor and the coefficient of exponential T^{-1} were determined for the rate constant k and the equilibrium constant of acetone adsorption K.[4]

The number of active sites of a nickel fine-particle catalyst was estimated by means of poisoning. The reaction rate was plotted against an amount of a poison such as water, triethylamine, pyridine, thiophene, or triphenylphosphine. Each poison was easily dissolved in 2-propanol and was added to a catalyst suspension.

Results and Discussion

1. Promoter Effect of Pt(acac)$_2$. Platinum chloride promoted catalytic activity of the Raney nickel in various hydrogenation reactions.[16,17] Nevertheless, a slight amount of PtCl$_2$ extremely retarded any liquid-phase dehydrogenation of 2-propanol that was catalyzed by nickel fine particles. Instead of PtCl$_2$, Pt(acac)$_2$ was selected as a supply source of platinum. Platinum was deposited on a nickel fine-particle catalyst by means of reducing the complex with hydrogen. The disappearance of a characterestic peak of Pt(acac)$_2$ at 344 nm in visible and ultraviolet spectra

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of a supernatant indicated that the platinum in the complex was reduced. No platinum peak was observed in the XRD pattern of the catalyst after a reaction. This showed that the reduced platinum did not form a particle.

A platinum-deposited nickel fine-particle catalyst was more active than a nickel-alone catalyst, as shown in Fig. 1. Both catalysts exclusively produced hydrogen and acetone.

2. Retardation Effect of Acetone. A gradual decrease in the reaction rate was observed for various nickel catalysts in liquid-phase dehydrogenation of 2-propanol. The decrease in activity was ascribed to an adsorptive retardation of the produced acetone. Reaction rates are well expressed by

$$v = k/(1 + K[\text{acetone}]), \qquad (1)$$

where k is a rate constant and K is an equilibrium constant of acetone adsorption.[1–4,15] Symbol [acetone] refers to the amount of acetone, expressed in units of mmol.

Equation 1 also expressed the reaction rate provided by a platinum-deposited nickel fine-particle catalyst. Though the boiling point of the solvent decreased from 82.4 to 80.7 °C after a 5-h reaction, this change hardly affected the constants k and K. Figure 2 illustrates a linear relation between v^{-1} and the amount of acetone, into which data of Fig. 1 were converted. Values of k and K were determined from the section and the slope of Fig. 2; k was 330 mmol h^{-1} g^{-1} and K was 0.0403 mmol^{-1}. As for a nickel-alone catalyst, k was 116 mmol h^{-1} g^{-1} and K was 0.0301 mmol^{-1}.[15]

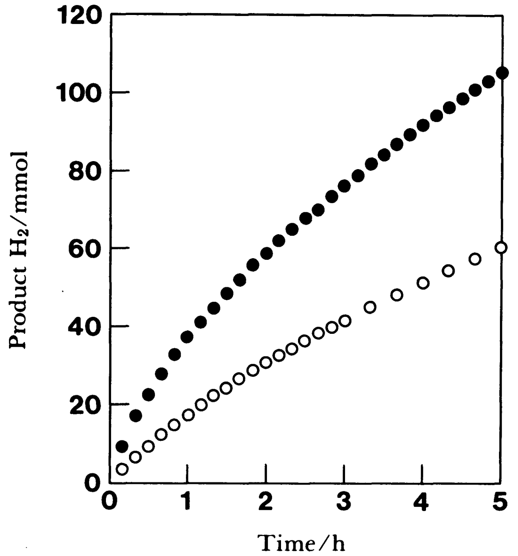

Fig. 1. The time course of H_2 evolution in the liquid-phase dehydrogenation of 2-propanol by a nickel fine-particle catalyst. Nickel alone (○) or platinum-deposited nickel (●) in 2-propanol (200 mg/200 ml).

3. Temperature Dependence of the Reaction Rate. It is already known that a normal alkane does not adsorb on nickel near the boiling point of 2-propanol and does not affect the reaction rate.[3] Mears and Boudart have reported that the addition of hexane (48 vol%) to 2-propanol reduces the boiling point to 62 °C and that Eq. 1 holds for the reaction of a suspended nickel boride catalyst in the solvent.[4] The method of adding hexane was followed in the present study.

The boiling point of a mixture of 2-propanol (200 ml) and hexane (7, 15, 25, and 40 ml) decreased to

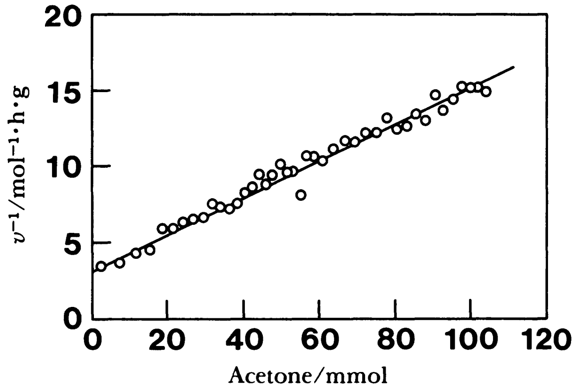

Fig. 2. The analysis of the retardation effect of produced acetone on a platinum-deposited nickel fine-particle catalyst. Data of Fig. 1 were converted into the form of Eq. 1.

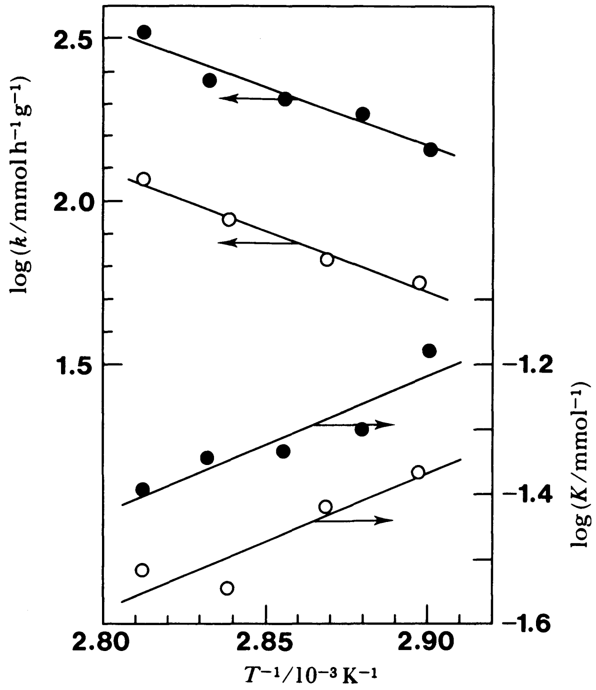

Fig. 3. The temperature dependence of the rate constant k and the equilibrium constant of acetone adsorption K of a nickel fine-particle catalyst. Nickel alone (○) and platinum-deposited nickel (●).

79.9, 77.0, 74.1, and 71.4 °C from the boiling point of 2-propanol (82.4 °C). The reaction rate was measured for 5 h at each temperature. Values of k and K were determined in terms of Eq. 1 and are plotted against T^{-1} in Fig. 3. Data regarding the nickel-alone catalyst are those found in the previous paper.[15)]

Figure 3 shows that a pair of lines were parallel; the correlation coefficients in the least-square method were 0.913—0.981 for plots of v^{-1} against [acetone] and 0.973—0.991 for the Arrhenius plots in Fig. 3. The value of the activation energy or adsorption heat of acetone was much the same between the platinum-deposited nickel and the nickel-alone catalysts. On the other hand, the frequency factor of k of the former catalyst was larger than that of the latter catalyst. Hence, the increase in the activity of the platinum-deposited nickel catalyst could be ascribed to an increase in the frequency factor of the rate constant k.

The accumulated acetone lowered the boiling point of a solvent mixture slightly (0.3—1.7 degrees) in a 5-h run. Values of the frequency factors of k and K, the activation energy and the adsorption heat of acetone were determined in terms of the least-square method while taking account of all the experimental values of the rates and boiling points in the five runs. Consequently, the activation energy was 79.3 kJ mol^{-1} and the adsorption heat of acetone was −24.7 kJ mol^{-1} for a platinum- deposited nickel fine-particle catalyst. These values were similar to those of other metallic catalysts.[1,4,15)] The activation energy slightly surpassed the enthalpy change of this endothermic reaction (69.9 kJ mol^{-1}).

4. Effect of Poisons. The effects of five kinds of poisons were studied. Water of 1.0 mmol or triethylamine of 1.4 mmol did not change the reaction rate, but the other three poisons affected the activity of a nickel fine-particle catalyst. A prescribed amount of a poison such as pyridine, thiophene, or triphenylphosphine was continually added to a catalyst suspension, and the reaction rate was plotted against the amount of accumulated poison. Table 1 shows the amount of a poison that made a rate half per 200 mg of a nickel fine-particle catalyst.

A plot of v^{-1} against the amount of a poison resembled Fig. 2 for a small amount of poison. Thus the reaction rate could be expressed by

$$v = k/(1 + K'[\text{poison}]). \qquad (2)$$

The initial rate was substituted for the rate constant k, because the two values were approximately the same under conditions of no poison and little acetone in the initial state. Table 1 shows the inhibition constant of a poison K'. This table also contains the equilibrium constant of acetone adsorption K and the amount of acetone producing half the rate, for the purpose of comparison.

The retardation effect of triphenylphosphine and thiophene was strong and the effect of pyridine was intermediate. Equation 2 fitted experimental data up to 0.05 mmol of pyridine, but it did not fit the data for more than 0.01 mmol of triphenylphosphine and thiophene. According to the principle of hard and soft acids and bases, soft bases adsorb on metal surfaces which are a soft acid.[19)] The order of the effect of the poisons, that is,

triphenylphosphine, thiophene>pyridine>acetone, triethylamine, water

corresponded to the order of softness as a base and was explained in terms of the principle. This fact showed that the properties of active sites of this catalyst could be explained by concepts of usual metallic catalysts.[20)]

The value of the inhibition constant of every poison in Table 1 or its amount which produced half the rate was almost the same between the platinum-deposited nickel and the nickel-alone catalysts. This fact showed that the number of active sites was almost the same for the two catalysts. Therefore, the increase in the frequency factor of the rate constant k of a platinum-deposited nickel fine-particle catalyst was ascribed to a change of the frequency factor per active site. Probably the change also caused a slight difference in the frequency factor of an equilibrium constant of acetone adsorption K between the two catalysts.

5. Properties of Active Sites. As shown in studies of bonding orbitals of a metal-hydrogen cluster, the 5d orbitals chiefly work in a platinum cluster, though the 4s orbital of nickel works more than its 3d orbitals.[21—23)] The difference in the frequency factor or reaction probability per active site can be ascribed to a

Table 1. Effect of Poisons on the Reaction Rate

Poison	Half-rate amount[a)]/mmol		K'[b)]/mmol^{-1}	
	Ni	Pt/Ni	Ni	Pt/Ni
Acetone[c)]	33	25	0.0301	0.0403
Pyridine	0.014	0.011	57	76
Thiophene	0.006	0.009	169	113
Triphenylphosphine	0.006	0.006	178	191

a) The amount of a poison producing half the rate per 200 mg of a platinum-deposited nickel or a nickel-alone fine-particle catalyst. b) The inhibition constant of Eq. 2. c) The value of a half-rate amount was calculated from the constant K of Eq. 1.

difference in a valence orbital working in the rate-determining step.

The platinum-deposited nickel and nickel-alone fine-particle catalysts were similar to other metallic catalysts, because the values of activation energy and adsorption heat of acetone resembled the reported ones, in addition to the fact that the time course of the reaction rate fitted Eq. 1. The cleavage of a methine C–H bond was regarded as the rate-determining step of liquid-phase dehydrogenation of 2-propanol by means of a nickel boride catalyst.4) We also think that the cleavage of a methine C–H bond is the most important among the elementary steps.

Appendix

1. Effect of Experimental Conditions. The rate constant k and the equilibrium constant of acetone adsorption K depended on the reducing conditions and on the amount of a catalyst or a solvent, as summarized in Table 2.

The usual pretreatment under hydrogen removed about 10% of the oxygen from surface-oxide layers of nickel fine particles. When a pretreatment under hydrogen was continued for 30 min at 160 °C, about 50% of the oxygen was removed. This severe reducing condition made values of k and K large.

A catalyst of 100 mg showed large values of k and K, in spite of the usual pretreatment. Nickel fine particles piled on the bottom of a reactor (a flask) through a hydrogen pretreatment. When the amount of particles was 100 mg, the particles were sufficiently exposed to hydrogen. Probably the surface oxide of 100-mg particles was considerably reduced after much exposure to hydrogen.

The amount of 2-propanol was varied from 200 ml to 6.4 ml. A reactor of different size was selected in response to it . The rate constant k decreased with the volume of the solvent, or rather, the reactor. The reaction and boiling essentially required heat, which was transmitted through the wall of the reactor soaked in an oil bath. Probably any decrease in a thermal-conduction area reduced heat supply and, consequently, the rate constant k. The heat supply was so small that the boiling of 2-propanol was suppressed when the thermal-conduction area was 22 or 28 cm^2.

The decrease in the amount of 2-propanol increased the value of K by about two orders of magnitude. However, any comparison should be based on a common measure, namely, molarity. If the amount of acetone is expressed in units of molarity, the units of K become mmol^{-1}·l and the value of K has to be multiplied by the volume of the solvent. In fact, the value of K multiplied by the volume of 2-propanol was almost constant as shown in Table 2, suggesting that the conversion of the value of K was reasonable.

2. Other Attempts for Promoting Catalysis with Pt(acac)$_2$. The divalent platinum in 9 mg of Pt(acac)$_2$ was also reduced, when a catalyst suspension containing the complex was held at about 40 °C for 2 h with stirring. The reductant was 2-propanol at that time. Constants k and K were 325 mmol h^{-1} g^{-1} and 0.0430 mmol^{-1}. This method resulted in much the same promoter effect as that of reducing platinum by means of blowing hydrogen into a catalyst suspension. The two methods seemed to sufficiently draw out a promoter effect from 9 mg of Pt(acac)$_2$.

A mixture of 60 ml of acetone and 140 ml of 2-propanol dissolved 100 mg of Pt(acac)$_2$. After the reduction of platinum, acetone was removed under vacuum and then 2-propanol was added to make up for the lost volume. An observed promoter effect, however, did not surpass that of 9 mg of Pt(acac)$_2$; k was 226 mmol h^{-1} g^{-1} and K was 0.0463 mmol^{-1}. Furthermore, a peak of platinum appeared in the XRD pattern of the catalyst after a reaction. Probably, excessive platinum coagulated and scarcely showed a promoter effect. The promoter effect of platinum reached a limit when the amount of Pt(acac)$_2$ was 9 mg.

Table 3 shows the reaction rate in a high mole fraction of acetone. The value was compared with that calculated from Eq. 1, by taking account the temperature dependence of k and K for a catalyst promoted by 9 mg of Pt(acac)$_2$ or a nickel-alone catalyst. The two values were approximately the same. This is consistent with the fact that coagulated platinum scarcely showed a promoter effect.

Table 2. Effect of Experimental Conditions on the Reaction Rate

Ni/mg	2-Propanol/ml	Thermal-conduction area/cm^2	ka)/mmol h^{-1} g^{-1}	Kb)/mmol^{-1}
100	200	120	180	0.062
200c)	200	120	164	0.089
200	200	120	116	0.030
200	100	94	94	0.046
200	30	28	79	0.268
200	6.4	22	51	1.321

a) The rate constant of Eq. 1. b) The equilibrium constant of acetone adsorption of Eq. 1. c) Surface oxide was severely reduced at 160 °C for 30 min.

Table 3. Reaction Rates in a High Mole Fraction of Acetone

Pt(acac)$_2$/mg	Mole fraction of acetone	Acetone/mmol	Bp/°C	Ratea)/mmol h^{-1} g^{-1} Obsd	Calcdb)
0	0.3	296	70	2.9	3.8
100	0.3	296	70	3.7	8.1
100	0.5	1361	64	0.8	1.0

a) The nickel fine-particle catalyst (200 mg) in an acetone/2-propanol solvent (200 ml). b) Calculation using Eq. 1 and the kinetic data of k and K of a catalyst promoted by 9 mg of Pt(acac)$_2$ or a nickel-alone catalyst.

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