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Liquid-Phase Dehydrogenation of 2-Propanol by Suspended Nickel Fine-Particle Catalyst

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Nickel fine particles that were prepared by a gas evaporation method were used to catalyze the liquid-phase dehydrogenation of 2-propanol efficiently in the suspended state. Rate retardation due to the product acetone without catalytic-site deactivation was confirmed kinetically. High reaction rates were attained under the boiling conditions and a reasonable activation energy as well as adsorption heat of acetone was obtained. A useful application of the present catalytic process is proposed.

Dehydrogenation of 2-propanol in gas phase

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CO + H_2 \qquad (1)$$

is unfavored thermodynamically below 202 °C, at which $\Delta G°$(gas) becomes zero.[1] Reactions over zinc oxide or other heterogeneous catalysts that yielded acetone and hydrogen required a rather high temperature (e.g., 350 °C for ZnO).[2]

When homogeneous[3—7] or heterogeneous[8—14] catalysts were used in the liquid phase, however, Reaction 1 proceeded at a moderate temperature (e.g., 82.4 °C for Raney Ni),[8,10] since hydrogen dissolved slightly in the solvent[15] and was easily separated as a gaseous substance.

Among solid catalysts active in the suspended state, nickel fine particles prepared by a gas evaporation method[16,17] have attracted our attention[14] on account of the following characteristics:[18,19]

1) Highly-crystallized spherical particles.
2) Sharp particle-size distribution.
3) Large specific surface area without pores.
4) High chemical purity except for surface oxide.
5) Stability of the suspended state in some polar solvents.

In the present study, the dehydrogenation of 2-propanol with a suspended nickel fine-particle catalyst was investigated from a kinetical viewpoint in order to explore useful applications.

Experimental

Catalyst. Fine particles of nickel were obtained as a soot-like product by evaporating molten nickel metal (99.99% pure) in an argon atmosphere.[16] They were slowly oxidized with nitrogen-diluted air to form thin surface oxide layers. These layers prevent the particles from deep oxidation at room temperature in air. According to electron micrographic measurements, nonporous highly-crystallized spherical particles with a sharp size distribution (average diameter: 19.7 nm) were prepared.[16] The surface-oxidized particles (oxygen content: 10 wt%) gave a BET specific surface area of 43.8 $m^2\,g^{-1}$.[20]

Apparatus. Prior to the reaction, a heating treatment under a hydrogen atmosphere was required in order to disclose active sites by reducing the surface oxide.[21] A closed system consisting of a round-bottom three-neck flask (300 ml) and a gas buret (500 ml) was adopted for measuring hydrogen consumption. A flask containing the reduced catalyst and the reactant 2-propanol inside was connected to another set of gas burets (500 ml and 1 l) through a water-cooled condenser. In this closed system the gaseous product was pursued volumetrically.

An open-ended system was used for a long-period run, in which a round-bottom three-neck flask was connected to a gas-flow meter (STEC Inc., SEF series) and a gas sampler (Gasukuro Kogyo Inc., GS-5000 A). A data processor (Eto Denki Co., Thermodac 32) recorded time-sequentially such reaction data as the flow rate of the gaseous product and the temperature, either inside or outside the flask. The gaseous components were monitored by a gas chromatograph (Shimadzu Co., GC-8APT) with a peak integrator (Shimadzu Co., CR-2A) assisted.

Procedure. A prescribed amount (200 mg) of the nickel fine particles in the flask was heated under hydrogen up to 160 °C in 15 min, held at 160 °C for 1 min and rapidly cooled.[22]

After reduction and evacuation of the nickel fine particles, the flask was filled with the degassed 2-propanol reactant (200 ml) under an argon or nitrogen atmosphere and treated for dispersion with an ultrasonic vibration cleaner (Sharp Co., UTB-152) at room temperature for 1 min.

The reaction proceeded by heating the suspension under boiling conditions. The rate of hydrogen evolution was determined from the volumetric accumulation of hydrogen in the closed apparatus or pursued with a flow meter in the open-ended system. The temperature dependence of the reaction rate was examined by the addition of hexane to 2-propanol in order to decrease the boiling point.[11]

Products were analyzed by gas chromatography using active carbon (gas phase) and PEG 1000 (liquid phase) columns.

Results and Discussion

1. Dispersion Stability of the Nickel Fine Particles in 2-Propanol.

The nickel fine particles were easily suspended in 2-propanol through an ultrasonic treatment. The suspension was sufficiently stable.

As shown in Fig. 1a, sedimentation of the nickel

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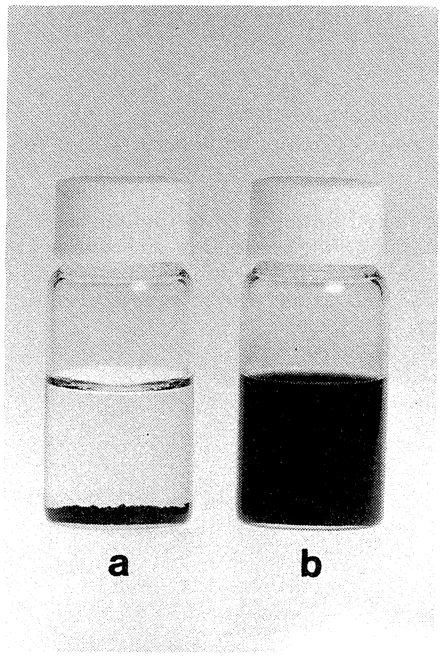

Fig. 1. Effect of the ultrasonic treatment on dispersion of nickel fine particles in 2-propanol.
(a) Effect of vigorous hand-shaking on the nickel fine particles (5 mg) in 2-propanol (5 ml). (b) Effect of the ultrasonic treatment on the same materials.

fine particles took place rapidly, when both materials (nickel 5 mg/2-propanol 5 ml) were hand-shaked vigorously. On the other hand, an ultrasonic treatment at a room temperature for 1 min resulted in a well-dispersed state (Fig. 1b). Without stirring, partial sedimentation was observed after 24 h. Continuous stirring with a conventional magnetic stirrer (1500 rpm) was sufficient for retaining the suspended state for a long period. The adopted stirring conditions were ascertained to sufficiently agitate the suspension, since the total time courses of hydrogen evolution were well-reproduced at different stirring rates.[23]

The ultrasonic treatment gave a stable suspension that could be maintained for 24 h or more by using the following solvents: dimethyl sulfoxide, *N*,*N*-dimethylformamide, bis(2-methoxyethyl) ether, methanol and cyclohexanol. On the contrary, sedimentation started within 1 h in suspensions of hexane, cyclohexane, toluene, ethylbenzene, triethylamine, diethyl ether, ethyl acetate, chloroform, carbon tetrachloride, nitromethane, tetrahydrofuran, acetone, and ethanol. Ethylene glycol, acetonitrile, 2-butanone, cyclohexanone, acetic acid, formic acid, and water gave an intermediately-stable suspension.

Since a well-dispersed state is important in liquid-phase reactions, nickel fine particles suspended in 2-propanol are of interest as a catalyst for Reaction 1.

2. Effect of Acetone on the Rate of 2-Propanol Dehydrogenation.

The dehydrogenation of 2-propanol with suspended nickel fine particles gave no other reaction product than hydrogen and acetone gas-chromatographically.[14] Since only hydrogen passed the condenser, acetone gradually accumulated during the reaction. The concentration of 2-propanol remained almost constant, since it was used both as the solvent and as the reactant.

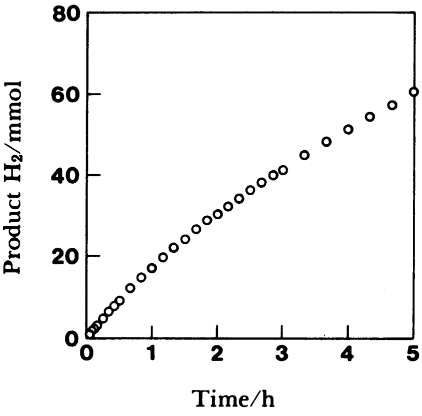

Fig. 2. Time course of H_2 evolution by liquid-phase dehydrogenation of 2-propanol with the nickel fine-particle catalyst under boiling conditions.
Nickel fine-particle catalyst (200 mg) suspended in 2-propanol (200 ml).

The time course of hydrogen evolution is shown in Fig. 2. A gradual decrease of the reaction rate observed regarding the nickel catalysts was similarly ascribed to a product retardation. The reaction rates were well-expressed by

$$v = k/(1 + K[\text{acetone}]), \qquad (2)$$

where k was a rate constant and K was an equilibrium constant of acetone adsorption.[8–11] A linear correlation of the inverse rate with the product acetone can be derived from Eq. 2:[11]

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

which was verified to hold for a nickel fine-particle catalyst. The time course of Fig. 2 was converted into Fig. 3 as a function of the acetone. The retardation effect of acetone was ascertained by the following experimental approaches.

In the first place, the effect of acetone on a fresh catalyst was examined. In a reference experiment (Fig. 4a) the reaction started with neat 2-propanol and the product acetone accumulated up to 5.0% after 6 h. The 2-propanol/acetone premixed solvent prepared to be 5.0% of acetone was then used for the reaction (Fig. 4b). The initial rate of the latter was almost the same as the final rate of the former. Acetone was thus responsible for the rate decrease.

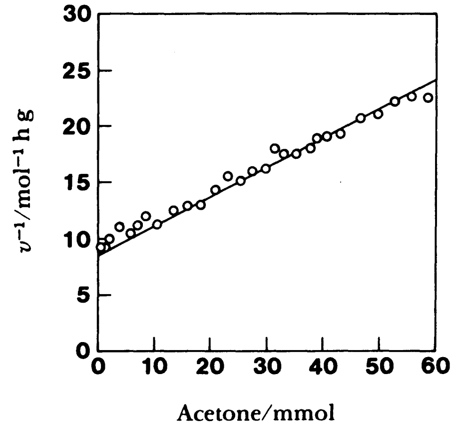

Fig. 3. Rate analysis of Fig. 2 on the postulate of acetone retardation.

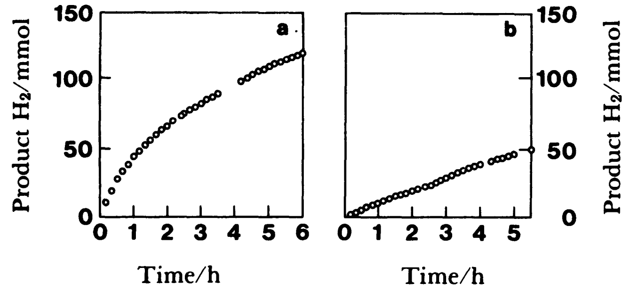

Fig. 4. Effect of initial addition of acetone on the liquid-phase dehydrogenation of 2-propanol with the nickel fine-particle catalyst.

Nickel fine particle catalyst (1.00 g) reduced on the severe conditions and suspended in (a) 2-propanol (200 ml) or (b) 2-propanol containing acetone (200 ml in total) prepared by initial addition of acetone upto the same concentration (5.0%) as in suspension a after the 6-h reaction.

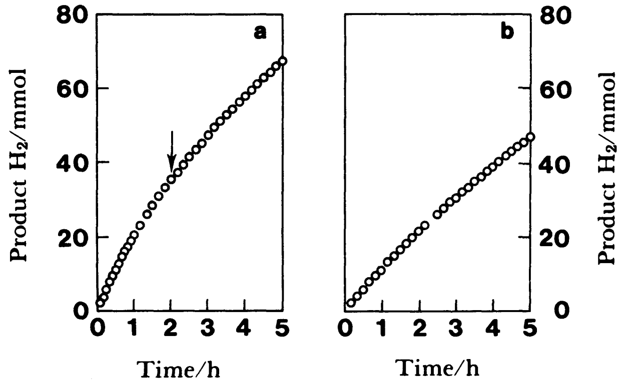

Fig. 5. Effect of partial removal of acetone on the liquid-phase dehydrogenation of 2-propanol with the nickel fine-particle catalyst.

(a) Nickel fine-particle catalyst (200 mg) suspended in 2-propanol (200 ml). (b) Partial solvent removal from suspension a after the 5-h reaction and the replenishment with neat 2-propanol to the same acetone concentration as the arrow-indicated level (1.2%).

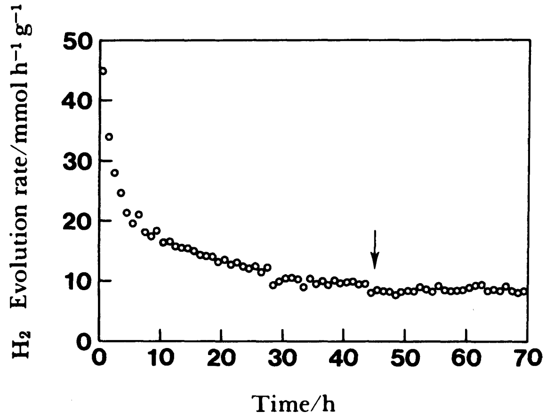

Fig. 6. Effect of accumulation and succeeding stationary removal of acetone on the liquid-phase dehydrogenation of 2-propanol with the nickel fine-particle catalyst.

Nickel fine-particle catalyst (200 mg) suspended in 2-propanol (300 ml) was used in the open-ended apparatus under partial distillation conditions.

The second approach was tried in order to reveal the equilibrium adsorption of acetone. After a 5-h reaction the suspension was rapidly cooled (Fig. 5a), followed by a partial removal of the solvent from the reactor under vacuum. Neat 2-propanol was added to the residual suspension until the liquid was supplemented in amount. Not only the amount of acetone left in the solvent after this transfer procedure but also the initial rate in the 2-propanol/acetone solvent thus prepared (Fig. 5b) was the same as that marked by an arrow. The rate-time correlation was obtained in a duplicated manner thereafter. The catalytically-active sites were occupied with acetone by a reversible adsorption from the bulk solvent.

The third experiment produced a state in which the concentration of acetone in the solvent was constant under partial distillation conditions.[10] Two kinds of condensers were set in series in the open-ended apparatus. The product acetone in excess and a small amount of 2-propanol were evaporated from the reactor and passed through the first condenser (57 °C). They were trapped with the second condenser (−10 °C). As shown in Fig. 6, a gradual rate decrease was observed in the initial reaction stage (0—45 h); then, the rate became constant and did not change thereafter (45—70 h). Except for the initial reaction stage, newly formed acetone was removed stationarily under the adopted distillation conditions.

Therefore, it is concluded that active sites of the nickel fine-particle catalyst are occupied by the product acetone without irreversible deactivation.

The rate constant of Eq. 2 of the nickel fine-particle catalyst (116 mmol h^{-1} g^{-1}) was larger than the values reported previously concerning Raney nickel (55 mmol h^{-1} g^{-1})[8] and nickel boride (60 mmol h^{-1} g^{-1})[11] catalysts. It has been pointed out that the equilibrium constant of acetone adsorption was sensitive to the conditions of acetone diffusion, which was regulated by the stirring rate. Sufficient stirring conditions resulted in an adsorption constant of 8.6 l mol^{-1} to the nickel boride catalyst. However, values as large as 10—16 l mol^{-1} were obtained for the Raney nickel catalyst under diffusion-controlling conditions.[11] A rather small adsorption constant (6.0 l mol^{-1}) was obtained for the well dispersed nickel fine particles (Fig. 3), suggesting that this catalyst was not affected by diffusion-controlling conditions.

3. Effect of Temperature on the Reaction Rate. An efficient removal of the product acetone from the catalyst surface was important to Reaction 1. The temperature effect on the reaction rates was examined with and without adopting the boiling conditions. In one series, an inert and soluble substance, i.e., hexane was added to 2-propanol little by little in order to maintain the boiling conditions at various temperatures.[24] In the other, the suspension was heated without boiling in the temperature region below 82.4 °C.[6]

As shown in Fig. 7, the reaction rates on the boiling conditions in the 2-propanol/hexane solvent prepared by the successive addition of hexane were higher than those in the neat 2-propanol without boiling. The rate difference was large in the low-temperature region. One possible interpretation is as follows: The retardation effect owing to acetone adsorption on the catalyst is large at low temperatures without boiling. Bubbles made under boiling conditions favor the desorption of acetone and result in a relatively high reaction rate.

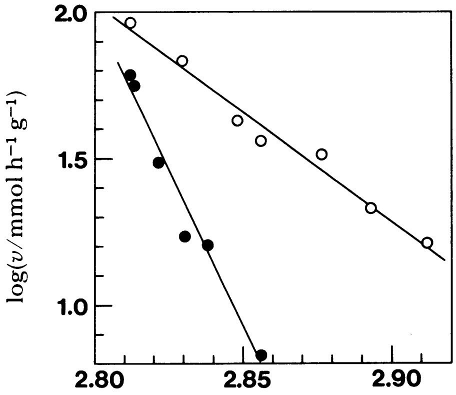

Fig. 7. Temperature dependence of the rate of 2-propanol dehydrogenation with the nickel fine-particle catalyst on boiling or non-boiling conditions. Reaction temperatures were controlled by adding hexane with the boiling conditions kept (○) or by varying the extent of heat supply without boiling (●).

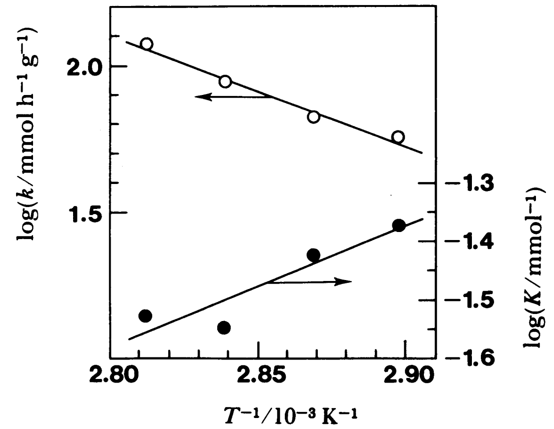

Fig. 8. Temperature dependence of the rate constant of 2-propanol dehydrogenation and the equilibrium constant of acetone adsorption of the nickel fine-particle catalyst under boiling conditions.
Reaction temperatures were controlled by changing the amount of hexane added to the suspension.

An accurate temperature dependence of the kinetical parameters k and K in Eq. 2 was examined by the use of a series of 2-propanol (200 ml)/hexane solvents with 0, 8, 21, and 38 ml of hexane, which exhibited boiling temperatures of 82.4, 79.1, 75.4, and 72.0 °C, respectively. An Arrhenius plot and a similar plot of the constant K are shown in Fig. 8.

During each experiment the boiling point of the solvent was slightly lowered by the accumulated acetone. The frequency factor and the exponential coefficient of k and K were determined by a least-square optimization to all of the experimental values, during which slight changes in the boiling point were taken into account. The activation energy of the nickel fine-particle catalyst (71.4 kJ mol^{-1}), surpassing slightly the enthalpy change of this endothermic reaction (69.9 kJ mol^{-1}), was similar in magnitude to those of the heterogeneous nickel boride (85.8 kJ mol^{-1})[11] and Raney nickel (73.2 kJ mol^{-1})[8] catalysts or of the homogeneous tin(II)-coordinated rhodium(III) complexes (117 kJ mol^{-1}).[6] The adsorption heat of acetone of this catalyst (−33.3 kJ mol^{-1}) was a little larger than that of the nickel boride catalyst (−20.9 kJ mol^{-1}).[11]

4. Application of 2-Propanol Dehydrogenation by Suspended Nickel Fine-Particle Catalyst. The reverse of Reaction 1 is favored below 202 °C.

$$(CH_3)_2CO + H_2 \longrightarrow (CH_3)_2CHOH \qquad (3)$$

An endothermic low-temperature Reaction 1 in the liquid phase can be coupled to exothermic high-temperature Reaction 3 in the gas phase, as long as acetone (bp 56.3 °C) and 2-propanol (bp 82.4 °C) are separated by cooling through distillation. Since these reactions proceed at different temperatures, simultaneously and stationarily, a new heat-pump system will be constituted, with which low-quality heat at 80 °C can be partially upgraded to 200 °C by heat expense at 30 °C.[25] A heat supply is required for both the dehydrogenation reaction and the evaporation of organic compounds.

Appropriate catalysts are indispensable for this chemical heat-pump system. In order to efficiently convert the thermal energy of low-quality heat into chemical energy, 2-propanol dehydrogenation should be catalyzed with high activity and selectivity under boiling conditions.

The nickel fine-particle catalyst is advantageous for this purpose, since it is well-suspended through conventional stirring with an attainable high space-time yield. However, the development of a catalyst that is active in much acetone is desired, since both the low boiling point of the solvent and the large vapor pressure of acetone are favorable for this chemical heat-pump system.

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