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Reactions in the Adsorbed Layer: Hydrogenation of Acetone on Nickel Catalysts

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The hydrogenation of acetone adsorbed and the dehydrogenation of isopropanol adsorbed on silica-supported nickel catalyst have been studied by following the changes of hydrogen pressure and the reaction products as well as the IR spectra of adsorbed species. It was found that the formation of isopropanol proceeds *via* a precursor composed of acetone and hydrogen. The activation energies of hydrogenation of acetone adsorbed and of dehydrogenation of isopropanol adsorbed were 11—13 and 4—8 kcal/mol, respectively. The activation energy of the desorption was 13 kcal/mol for isopropanol and 19 kcal/mol for acetone. From the results the potential energy change during the hydrogenation of acetone was determined.

Although a number of investigations have been made on the hydrogenation of acetone on nickel catalysts, in most cases the nature of the adsorbed species on the catalysts as well as the energy relation for the reaction was deduced on the basis of the kinetics of the reaction. They can be elucidated more precisely by measurements of the hydrogenation of adsorbed acetone. Work along this line was carried out[1—3] with some decomposition reactions. As an extension of this work, hydrogenation of acetone adsorbed on nickel catalyst has been investigated by an infrared technique as well as by the analysis of reaction products.

Experimental

Materials. The 15 wt% Ni–SiO_2 catalyst was prepared by impregnation of silica gel (30—50 mesh) with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. The supported salt was dried at 100 °C and heated at 400 °C in the air. The catalyst samples were reduced in 100 Torr hydrogen at 400 °C for 60 hr and degassed at the same temperature for 3 hr. The equilibrium amount of hydrogen adsorbed after the reduction was 1.8 cm^3/g at 0 °C and 20 Torr hydrogen. For spectroscopic experiments, Aerosil (Degussa) supporting 6.5 wt% nickel was prepared by impregnation with a nickel nitrate solution. The slurry was dried at 100 °C in the air and heated in a vacuum at 300 °C. The silica-salt mixture was pressed into a disk of 20 mm diameter. Before adsorption of acetone, the disk was heated in hydrogen at 350 °C for 6 hr and degassed at the same temperature.

Acetone and isopropanol (Tokyo Chemical Industry) were dried in a vacuum over a degassed molecular sieve, degassed by freeze-pump-thaw cycles and stored over the molecular sieve. Cylinder hydrogen was purified by diffusing through an electrically heated palladium thimble.

Apparatus and Procedures. A closed circulation system, equipped with Töpler pump and a mercury diffusion pump, was used for desorption experiments. The rate of hydrogen uptake by the catalyst adsorbed acetone was determined manometrically. The experiments of dehydrogenation of isopropanol adsorbed were carried out as follows: Using either liquid N_2 traps or a Töpler pump and a diffusion pump, the desorbed amounts of hydrogen as well as of condensable gases such as acetone, isopropanol, and propane were determined as a function of time, the rate of desorption being obtained. Details were described previously.[1—4] During the rate measurements the temperature of the catalyst was lowered abruptly and the temperature dependence of the rates at the same amount adsorbed was obtained. The desorption products were analyzed by gas-chromatography with the use of a column with 3 m silica gel or 2 m molecular sieve for methane and hydrogen and with a 2 m PEG 1500 column for the other products. Similar desorption experiments were carried out under circulation of hydrogen over the catalyst. In this case the desorption system was kept shut and only the condensable desorption products were analyzed.

The IR cell was the same as that used previously.[5] All the spectra were recorded at room temperature with a Hitachi EPI-G2 grating infrared spectrophotometer with a spectral slit width 2.8 cm^{-1} at 1000 cm^{-1}.

Results and Discussion

Hydrogenation of Acetone Adsorbed. The IR spectra of acetone adsorbed on the nickel catalyst at 25 °C showed bands at 1700 cm^{-1} (ν(C=O)), 1420, 1370 ($\delta(CH_3)$), and also around 3000 cm^{-1} (ν(CH)).[6] When hydrogen was admitted into the catalyst with adsorbed acetone at room temperature, the spectra changed gradually, hydrogen uptake occurring simultaneously. With increasing time of contact with hydrogen, the band due to the carbonyl group became

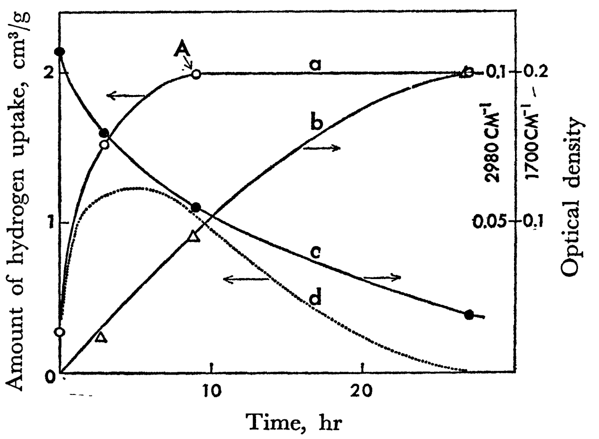

Fig. 1. Changes in the intensities of the bands and in the amount of hydrogen uptake: (a) amount of hydrogen uptake; (b) band intensity at 2980 cm^{-1}; (c) band intensity at 1700 cm^{-1}; (d) amount of the precursor. The amount of acetone adsorbed at 25 °C and hydrogen pressure were 1.75 cm^3/g and 20 Torr, respectively.

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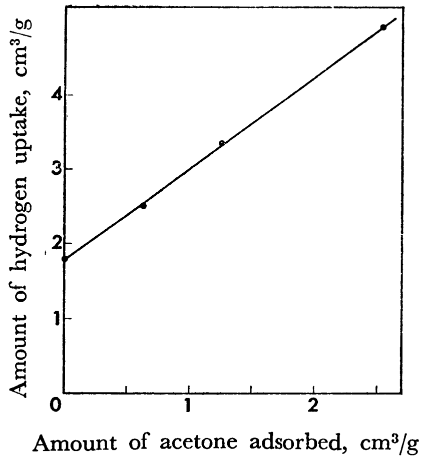

Fig. 2. Hydrogen uptake by the acetone-covered surface. Temp, 20 °C. The amount of catalyst and the equilibrium pressure of hydrogen were 6.67 g and 20 Torr, respectively.

weak, while a new band at 2980 cm^{-1} was intensified. The new band is attributable to ν(CH) of isopropanol.[7] The results are shown in Fig. 1. After 8 hr the amount of hydrogen uptake appears to attain a saturation value, while the intensities of the bands at 1700 and 2980 cm^{-1} still change. Such a phenomenon suggests that during the hydrogenation of acetone adsorbed, hydrogen adsorption of a certain type takes place to form an intermediate. In other words, the formation of isopropanol proceeds *via* a precursor composed of acetone and hydrogen. The amount of hydrogen uptake at the saturation (point A, Fig. 1) increased with increasing amount of acetone adsorbed. The increase in the amount of hydrogen uptake is 1.2 times as much as the amount of acetone adsorbed (Fig. 2).[8] Such a constant ratio suggests the formation of the precursor. A similar phenomenon was reported by Akhtar and Tompkins[9] who suggested that on the Pt surface containing adradicals such as $-NH_2$, $-OH$, and $-CH_3$, hydrogen is molecularly adsorbed on the adradicals (possibly by H-bonding). It was found that the intensity of the band at 2980 cm^{-1} was proportional to the amount of adsorbed isopropanol in the range 0.6—1.5 cm^3/g.[10] Assuming that the amount of hydrogen uptake at the saturation corresponds to the intensity of the band observed at 2980 cm^{-1} after 25 hr, it is possible to estimate the amount of the precursor which has a maximum (curve d, in Fig. 1).

It can be seen that an instantaneous hydrogen uptake is followed by a slow uptake. Taking account of the practical absence of hydrogen uptake without adsorbed acetone, it is concluded that the instantaneous uptake is due to the hydrogen adsorption between acetone molecules[12] and the slow uptake to the formation of isopropanol as well as of the precursor. The activation energy of the slow hydrogen uptake increased from 11 to 13 kcal/mol with the progress of uptake in the range 0.3—0.8 of the fraction of hydrogenated acetone. The rate of hydrogen uptake varied in proportion to the square root of hydrogen pressure in the range 20—100 Torr.

Dehydrogenation of Isopropanol Adsorbed. In order to obtain information on the energy changes for the dehydrogenation of isopropanol, the following experiments were carried out. After the hydrogenation of adsorbed acetone at 0 °C was completed, hydrogen was removed from the reaction vessel. The temperature of the catalyst was then raised stepwise to 20, 50, and 100 °C. The products are shown in Table 1. In the temperature range below 50 °C the hydrogen evolved amounted to 80% of the total hydrogen uptake, while a negligible evolution was observed for acetone as well as isopropanol. This suggests that acetone as well as isopropanol is adsorbed more strongly than hydrogen.

The rates of evolution of hydrogen were measured at 20 and 0 °C with various amounts of isopropanol adsorbed. The value of E for the hydrogen evolution ($\text{Rate}\propto\exp(-E/RT)$) increased from 4 to 8 kcal/mol with increasing fraction of dehydrogenated isopropanol from 0.1 to 0.3. It appears that the rate of dehydrogenation of isopropanol adsorbed is equal to the evolution rate of hydrogen, since the observed rate of hydrogen evolution was much larger than that for the catalyst with only adsorbed hydrogen.

In order to obtain energetic information on the hydrogenation of acetone, the dehydrogenation of isopropanol adsorbed was carried out in the presence of hydrogen circulating over the catalyst. The results of experiments in which the temperature of the catalyst was raised stepwise are shown in Fig. 3. Evolution of acetone as well as isopropanol began at 50 °C, showing a maximum at 100 °C and then decreased. Figure 4 shows the results of experiments at a constant temperature. The evolution rate of the products decreased with a decrease in the amount of isopropanol adsorbed. Dependence of the rate of evolution of the products upon hydrogen pressure was determined by abruptly changing the pressure during the course

TABLE 1. DEHYDROGENATION OF ISOPROPANOL ADSORBED

Temp range °C	Products,[a] cm^3/g × 10^2						Remaining amount,[b] cm^3/g	
	A	IPA	C_3H_8	CH_4	H_2O	H_2	A	H_2
0	—	0.09	—	—	0.11	57.3	2.51	3.96
0— 20	0.45	1.17	—	—	0.27	121.2	2.50	2.73
20— 50	18.4	3.87	0.30	4.68	1.89	190.2	2.25	0.748
50—100	86.2	0.35	1.39	33.6	7.32	158.8	1.26	—

a) A, Acetone; IPA, isopropanol. The temperature of the catalyst was kept constant for 2 hr at each step of temperature rise. b) The remaining amount is expressed as acetone+H_2, *e.g.*, at 0 °C isopropanol remained 2.51 and hydrogen 1.45 cm^3/g. Above 50 °C most of the hydrogen formed arises from the decomposition of acetone adsorbed.

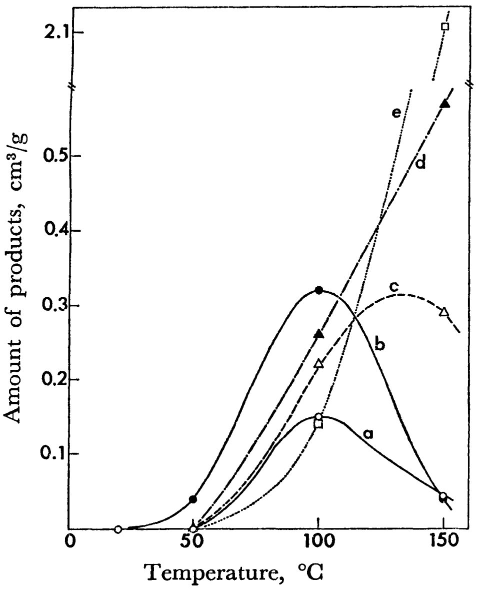

Fig. 3. Dehydrogenation of isopropanol adsorbed: (a) acetone; (b) isopropanol; (c) propane; (d) water; (e) methane. The amount of acetone adsorbed at 0 °C and hydrogen pressure were 2.51 cm³/g and 20 Torr, respectively.

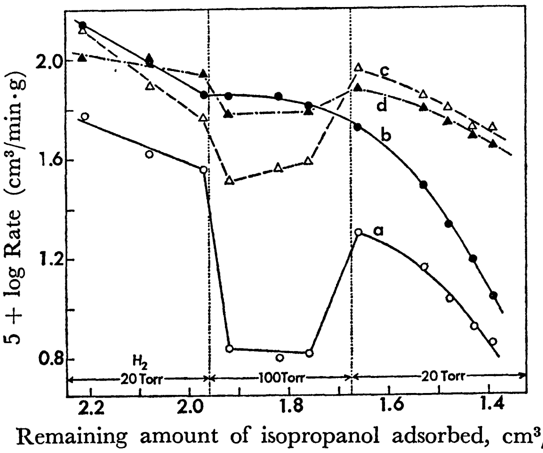

Fig. 4. Dehydrogenation of isopropanol adsorbed at 100 °C. Symbols are the same as for Fig. 3.

of dehydrogenation. The rate of evolution of acetone changes inversely proportional to P_H, while that of isopropanol is independent of P_H (Fig. 4).

The temperature dependence of the rate of evolution for isopropanol and for acetone was determined from the results shown in Fig. 5. The values of E at 1.95 cm³/g of the amount of isopropanol adsorbed are calculated to be 26.8 for acetone and 13.3 kcal/mol for isopropanol. Another experiment at 4.2 cm³/g of the amount of isopropanol adsorbed gave the activation energies 22.5 and 13.3 kcal/mol, respectively. It is seen that the value of E for acetone evolution changes with the remaining amount of isopropanol but that for isopropanol is nearly constant.

Dependence of the rates of evolution of the products upon the amount of isopropanol adsorbed was examined over a wide range of adsorbed amounts. The rate of evolution of propane changes slightly with increasing amount adsorbed, while that of isopropanol markedly increases (Fig. 6). Such a behavior suggests that propane is formed from a strongly adsorbed species.

Potential Energy Change During the Hydrogenation of Acetone. Taking into account the results given in Table 1 and Fig. 1, it seems that the hydrogen uptake by the catalyst with adsorbed acetone and its reverse reaction, *i.e.*, hydrogenation of acetone adsorbed and dehydrogenation of isopropanol adsorbed[13] are much faster than the desorption of acetone as well as isopropanol at around 100 °C, where the dehydrogenation experiments were carried out. It appears that the equilibrium is established for the dehydrogenation and its reverse reaction. Since hydrogen is adsorbed between the acetone molecules, it would be expected that the acetone adsorption is independent of hydrogen adsorption. Hence

$$k_4\theta_A\theta_H'^2 = k_{-4}\theta_{IPA}(1-\theta_H')^2, \qquad (1)$$

where $\theta_H'=1$ corresponds to a saturated amount of hydrogen adsorbed between acetone molecules; the rate constants refer to the following steps:

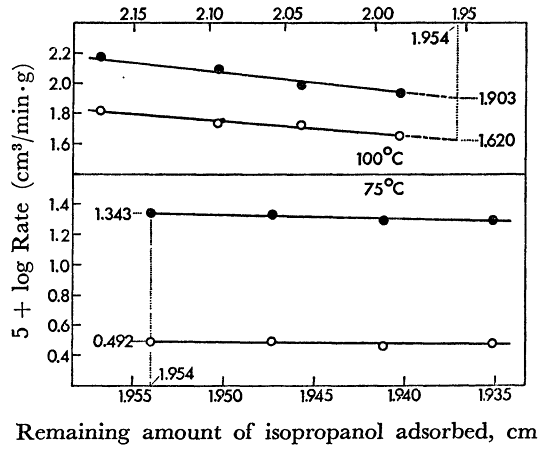

Fig. 5. Change in the rates of evolution of the products with temperature. During the measurements the temperature was changed abruptly from 100 to 75 °C, the rates at 1.954 cm³/g being compared. Hydrogen pressure, 20 Torr. Symbols are the same as for Fig. 3.

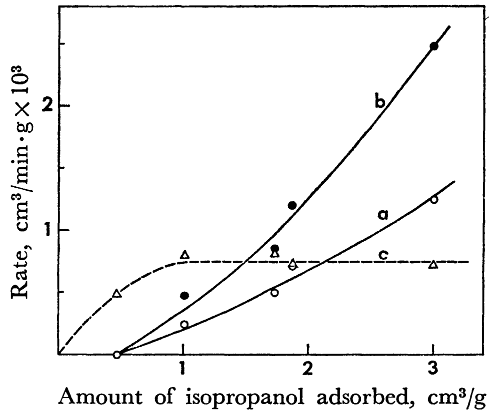

Fig. 6. Change in the rates of evolution of the products with the amount of isopropanol adsorbed. Symbols are the same as for Fig. 3. The temperature and hydrogen pressure were 100 °C and 20 Torr, respectively.

$$\begin{tikzcd}
A(g) & H_2(g) & & IPA(g) \\
A(a) \arrow[u, "k_1"] & + \; 2H(a) \arrow[u, shift left, "k_2"] \arrow[from=u, shift left, "k_{-2}"'] \arrow[rr, shift left, "k_4"] & & IPA(a) \arrow[u, "k_3"] \arrow[ll, shift left, "k_{-4}"]
\end{tikzcd}$$

where A, H_2, and IPA represent acetone, hydrogen, and isopropanol, respectively. Since adsorption equilibrium is established for hydrogen, we have

$$k_{-2}P_{\mathrm{H}}(1-\theta_{\mathrm{H}}')^2 = k_2\theta_{\mathrm{H}}'^2, \;\; K = k_{-2}/k_2 \qquad (2)$$

Substitution of equation (2) into equation (1) gives

$$\theta_{\mathrm{A}} = k_{-4}\theta_{\mathrm{IPA}}/k_4KP_{\mathrm{H}}\,. \qquad (3)$$

Hence, the evolution rates of isopropanol and acetone, R_{IPA} and R_{A}, are given by

$$R_{\mathrm{IPA}} = k_3\theta_{\mathrm{IPA}} \qquad (4)$$

$$R_{\mathrm{A}} = k_1\theta_{\mathrm{A}} = k_1k_{-4}\theta_{\mathrm{IPA}}/k_4KP_{\mathrm{H}}\,. \qquad (5)$$

In the case where θ_{IPA} is independent of hydrogen pressure, R_{IPA} becomes independent of P_{H} and R_{A} inversely proportional to P_{H}, in agreement with the results described above. Such a pressure independence of θ_{IPA} suggests that during the experiments such as shown in Fig. 6 the values of $\theta_{\mathrm{IPA}}/(\theta_{\mathrm{A}}+\theta_{\mathrm{IPA}})$ are always close to unity, although θ_{IPA} as well as θ_{A} decrease with progress of the reaction. The pressure dependence of R_{A} as well as R_{IPA} would support the assumption that equilibrium is established for the hydrogenation and dehydrogenation reaction.

According to Eqs. (4) and (5), the temperature dependence of k_3 and k_1k_{-4}/k_4K is the same as that of R_{IPA} and R_{A}, which are 13.3 (E_3) and 22.5—26.8 kcal/mol (E_{A}), respectively. When Eqs. (4) and (5) hold, the value of $R_{\mathrm{IPA}}/R_{\mathrm{A}}$ should be constant at a constant hydrogen pressure, irrespective of the amount of isopropanol adsorbed. Such a prediction was confirmed by experiments (Fig. 6, $R_{\mathrm{IPA}}/R_{\mathrm{A}}=1.98$ at 20 Torr hydrogen). The activation energy (E_4) of 11—13 kcal/mol for the hydrogen uptake corresponds to the temperature dependence of k_4. The activation energy (E_{-4}) of 4—8 kcal/mol for the evolution of hydrogen from isopropanol adsorbed corresponds to the temperature dependence of k_{-4}. Schuit and Reijen[14] investigated the adsorption isotherms of hydrogen on a silica supported nickel catalyst similar to the one we used. By applying their results to the present system, the coverage of hydrogen during the course of dehydrogenation of isopropanol at 100 °C and 20 Torr hydrogen is estimated at 0.7. Their results show that the heat of adsorption at $\theta=0.7$ is 16 kcal/mol.[15] Thus the temperature dependence (E_2) of K is estimated as -16 kcal/mol. From the relationship $E_{\mathrm{A}}=E_1+E_{-4}-E_4-E_2$, the value of E_1 for k_1 can be calculated. The values of E_4 and E_{-4} vary with the progress of dehydrogenation. $E_4=12$ and $E_{-4}=4$ are obtained from the values at the fraction of hydrogenated acetone of 0.8. Combining these values with $E_{\mathrm{A}}=27$, the value of E_1 for k_1 is obtained as 19 kcal/mol. Figure 7 shows the energy values as the change of potential energy during the course of reaction. The activation energies of adsorption of acetone, hydrogen, and isopropanol are neglected.

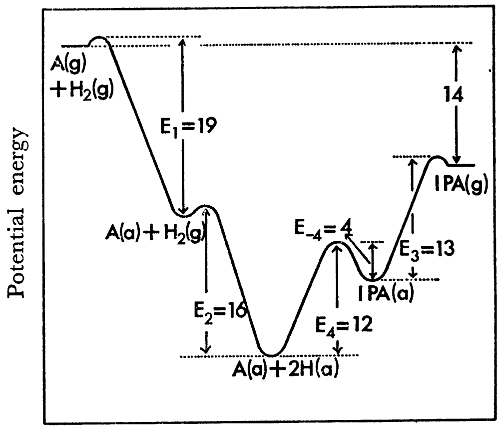

Fig. 7. Potential energy diagram for acetone hydrogenation. Figures indicate the potential energy in kcal/mol. The amount of isopropanol adsorbed and hydrogen pressure were 2.0 cm^3/g and 20 Torr, respectively.

Strictly speaking, Fig. 7 is valid only in the case where the fraction of hydrogenated acetone is 0.8. In the case where the fraction of hydrogenated acetone is small, it is expected that the value of E_{-4} becomes larger than 8, although other quantities such as E_1, E_3, and E_4 do not change a great deal.

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8) The results in Fig. 2 were obtained with a catalyst differing from the one used in IR studies. Similar results were obtained with Aerosil supported nickel catalyst as well as unsupported nickel catalyst.

9) M. Akhtar and F. C. Tompkins, *Trans. Faraday Soc.*, **67**, 2461 (1971).

10) No simple relationship appears between the intensity of the carbonyl band and the surface concentration of acetone, since there are two types of adsorbed species, *i.e.*, associatively and coordinately adsorbed species for acetone adsorption as reported by Young and Sheppard.[11]

11) R. P. Young and N. Sheppard, *J. Catal.*, **20**, 333 (1971).

12) C. L. Herbo, *J. Chim. Phys.*, **47**, 454 (1950).

13) Since only the products appearing in the gas phase have been examined (Fig. 6), it is impossible to distinguish isopropanol from its precursor. Consequently, in the following discussion IPA(a) refers to the state of isopropanol adsorbed as well as of its precursor.

14) G. C. A. Schuit and L. L. van Reijen, *Advan. Catal.*, **10**, 243 (1958).

15) In the presence of acetone adsorbed, θ appears to differ from 0.7. According to Schuit and Reijen,[14] the heat of adsorption does not change markedly with coverage. It seems unlikely, therefore, that the above conclusion is affected seriously by a different θ value.