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Concentration Dependence of Ketone Hydrogenation Catalyzed by Ru, Pd, and Pt. Evidence for Weak Ketone Adsorption on Pd Surface

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Synopsis. As the ketone (cyclohexanone, 4-heptanone) concentration in cyclohexane was increased, the hydrogenation rate saturated even below 0.05 mol dm^{-3} on Ru and Pt, but at a much higher concentration of around 0.5 mol dm^{-3} on Pd. This result suggests that ketone adsorption on Pd is weak in comparison with other platinum group metals.

Although palladium is an excellent catalyst for olefin hydrogenation, its activity for ketone (aliphatic and alicyclic) hydrogenation is notoriously low.(1) Breither *et al.*(2) regarded this poor activity as due to the unusual strength of ketone adsorption on Pd. On the contrary, Nishimura *et al.*(3) suggested that the attractive interaction of carbonyl with Pd surface is rather weak compared with other platinum group metals. Preliminary experiments in our laboratory(4) support Nishimura's view. To obtain further evidence for this view, we have carefully studied the concentration dependencies of ketone hydrogenation on Pd, and also on Pt and Ru for comparison. The substrate ketones chosen were cyclohexanone and 4-heptanone.

Experimental

Apparatus. The gas chromatograph was a Shimadzu GC-3BT instrument equipped with a thermocouple detector and a 10%-diglycerol column (3 mm i.d.×3 m, 60—80 mesh supported on C-22 SK). The stainless steel autoclave used for catalyst pretreatment had a capacity of 100 ml. The glass reaction vessel used for kinetic studies has been described before.(5)

Materials. All chemicals were obtained commercially, and used without further purification: cyclohexane (Wako, guaranteed, stated purity 99.99%), cyclohexanone (Wako, guaranteed, 99.93%), 4-heptanone (Tokyo Kasei, extra pure, 99.83%). H_2 (in cylinder). Catalysts (Ru/SiO_2, Pd/Al_2O_3, Pd/SiO_2, Pt/Al_2O_3, Pt/SiO_2) were in the form of cylindrical pellets (Nippon Engelhard, 0.5-wt% metal loaded, 3.9 mmϕ×4.0 mm long for the SiO_2-supported, 3.2 mmϕ×3.7 mm long for the Al_2O_3-supported).

Kinetic Procedure. All catalyst samples were subjected immediately before use to a standard hydrogen-pretreatment procedure as follows. A small glass test tube, after being loaded with an appropriate number (1—10) of catalyst pellets and 10 ml of cyclohexane, was placed in the autoclave. The autoclave was charged with hydrogen, heated to 80 °C, and kept at that temperature for 30 min without stirring. During this 30-min pretreatment no significant decrease in hydrogen pressure (*ca.* 80 atm, 1 atm=101.325 kPa) was observed.

Immediately after pretreatment, while still hot, the catalyst pellets were taken out of the autoclave and transferred to the glass reaction vessel pre-charged with the 5-ml cyclohexane solution of cyclohexanone or 4-heptanone that had already been flushed with hydrogen. Care was taken to minimize the air exposure time for the catalyst. The reaction vessel was connected to a hydrogen reservoir, and flushed with hydrogen one more time. The hydrogenation was started by shaking the reaction vessel vigorously at 30 °C in hydrogen at atmospheric pressure. During reaction the reaction mixture was sampled (usually 5 μl) at intervals, and analyzed by gas chromatography using helium as the carrier gas. The column temperature was set to 115 °C for the cyclohexanone systems and to 80 °C for the 4-heptanone systems.

Results

Preliminary. The hydrogenation rate (V) increased in proportion to the catalyst weight, suggesting that it is not controlled by hydrogen dissolution into the bulk solution. The observed V values were reproducible to within 5%.

In the hydrogenation of 4-heptanone, no product peaks other than the corresponding alcohol were observed by gas chromatography. Also for the cyclohexanone system, hydrogenation to the corresponding alcohol was clean on all of the catalysts but Pd/Al_2O_3. On Pd/Al_2O_3 an unidentified side-product peak (retention time 23.5 min against 6.5 min for cyclohexanol) was detected, but its amount was always 0.1% or less in comparison with cyclohexanol.

Concentration Dependence. Figure 1 shows typical reaction profiles observed in Pd- and Pt-catalyzed hydrogenation. At the initial period of reaction, the ketone concentration (C_K) decreases linearly with time on Pt although on Pd a brief induction period precedes the linear region. The higher the initial C_K, the shorter was this induction period, with its complete disappearance for the 1 mol/dm^3 C_K. The reaction profile for Ru resembled that for Pt, with no induction period.

The values for V at various C_K levels were estimated from the initial linear region of the appropriate reaction profile, and are shown in Fig. 2. Most of the data points are the averages of duplicate experiments. Evidently, Pd-catalysis is distinguished from Pt- and

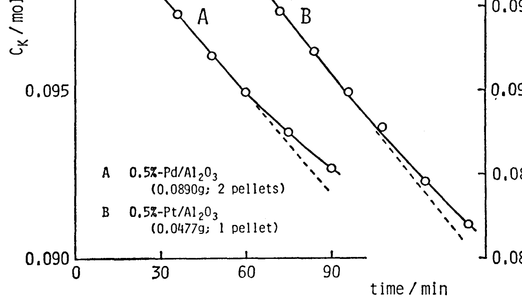

Fig. 1. Typical reaction profiles on Pd and Pt: plot of cyclohexanone concentration *vs.* time.

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Table 1. Strength of ketone adsorption

Ketone	Catalyst	K_K / dm³ mol⁻¹	$\Delta G_K^\ominus$ / kcal mol⁻¹	$\Delta G_K^\ominus(M)^{a)} - \Delta G_K^\ominus(Pd)$ / kcal mol⁻¹
4-Heptanone				
	Pt/Al_2O_3	66.9	−2.5	−1.3
	Pd/Al_2O_3	7.2	−1.2	
Cyclohexanone				
	Pt/Al_2O_3	50.5	−2.4	−0.4
	Pd/Al_2O_3	26.1	−2.0	
	Ru/SiO_2	186	−3.1	−1.6
	Pt/SiO_2	73.9	−2.6	−1.1
	Pd/SiO_2	12.2	−1.5	

a) Symbol (M) stands for a metal other than Pd.

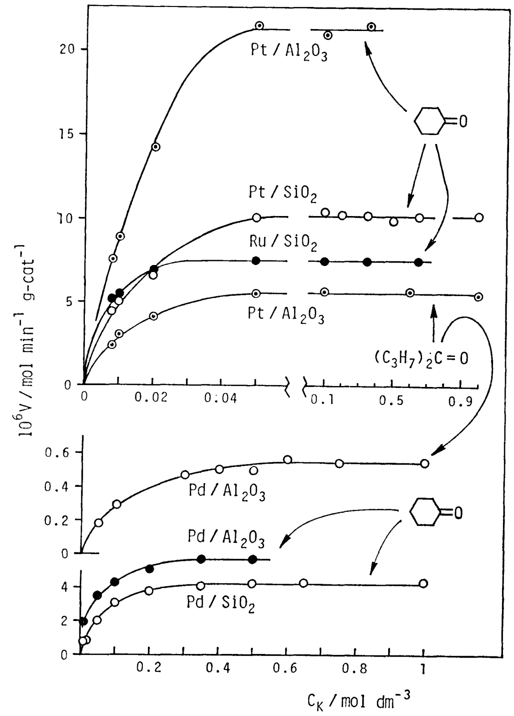

Fig. 2. Concentration dependence of ketone hydrogenation rate.

Ru-catalysis by the much slower increase in V with increasing C_K. This tendency is seen irrespective of the kind of catalyst support and reactant ketone, and therefore might be interpreted as due to the difference in ketone adsorption strength between Pd and the other metals.

Ketone Adsorption. All the plots in Fig. 2 have a long horizontal region, and there is no sign of rate decrease with increasing C_K at the higher C_K region. Rate V is thus given fairly well as a function of C_K:

$$V = kK_KC_K/(1+K_KC_K), \tag{1}$$

where k is the hydrogen pressure-dependent rate constant and K_K is the adsorption equilibrium constant of the substrate ketone. Rate expression (1) can be derived by assuming (a) the Langmuir isotherm for substrate ketone, (b) the neglect of alcohol adsorption, and (c) either the adsorption of hydrogen and ketone without mutual displacement or the hydrogenation of adsorbed ketone by a hydrogen source other than chemisorbed hydrogen. Item (b) is justified as far as the initial stage of reaction is concerned. Among examples of non-displacing hydrogen adsorption, in connection with item (c), might be hydrogen adsorption beneath the hydrocarbon ring or chain of the adsorbed ketone molecule. A small hydrogen atom or molecule might have access to this "shadow of ketone," but not another ketone molecule.

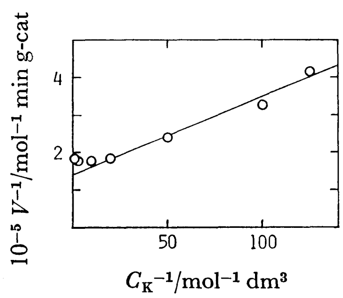

Fig. 3. Typical linear relationship due to Langmuir isotherm. 4-Heptanone on Pt/Al_2O_3.

Taking the reciprocal of both sides of Eq. (1), we have

$$\frac{1}{V} = \frac{1}{k} + \frac{1}{kK_KC_K}. \tag{2}$$

A typical linear relationship between $1/V$ and $1/C_K$ is shown in Fig. 3. The values of K_K were estimated from the slope and the intercept, and are listed in Table 1. Also included in Table 1 are the values for the standard free energy of ketone adsorption ($\Delta G_K^\ominus$), which is calculated using the K_K values from

$$\Delta G_K^\ominus = -RT\ln(K_KC^\ominus) \tag{3}$$

where $C^\ominus$ is a standard concentration. For the calculation of $\Delta G_K^\ominus$, $C^\ominus$ was set equal to 1 mol dm⁻³, and T to 303 K. The $\Delta G_K^\ominus$ data clearly indicate that ketone adsorption on Pd is weaker than on the other metals, as predicted in the Introduction.

There is a general rule proposed by Tanaka and Tamaru of Yokohama National University⁶⁾ for chemisorption of gases on metals. For many gases, according to this rule, the initial heat of chemisorption on various metals increases as the heat of formation of the highest oxide of the metal per metal atom ($-\Delta H_0^\ominus$) is increased. Interestingly, in Table 1 the K_K values for cyclohexanone adsorption on the SiO_2-supported metals are in the sequence, Pd<Pt<Ru, which is parallel to the $-\Delta H_0^\ominus$ sequence.

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