Hydrogen Redistribution of Acetone on ZnO Catalysts

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The hydrogen redistribution reaction between d_0-acetone and d_6-acetone was carried out at −10—60 °C over ZnO catalysts subjected to various modes of pretreatment. The activity of ZnO was several times larger than that of Zn metal, being hardly affected by the conditions of pretreatment below 350 °C and illumination with a mercury lamp. The rate of hydrogen redistribution was proportional to the amount of chemisorbed acetone which obeys the Langmuir adsorption isotherm. The activation heat of redistribution and the heat of acetone chemisorption were estimated to be 14 ± 2 and 10 ± 1 kcal/mol, respectively. The time course of the relative amounts of d_n-acetones, independent of the catalyst or its activity, was reproducible by a calculation based on the stepwise exchange model for the hydrogen exchange of acetone. About half of the chemisorbed acetone was found to be active for the redistribution or exchange of hydrogen. From the results and IR spectrometric study of acetone adsorbed on ZnO, the hydrogen redistribution of acetone was concluded to proceed *via* a chemisorbed acetone with an enol type configuration on a pair of sites, Zn^{2+}–O^{2-}, of ZnO surface.

It is well-known that ZnO catalyzes the dehydrogenation of isopropyl alcohol selectively. The hydrogenation of acetone has been found[1] to proceed on ZnO catalyst in the presence of a large excess of hydrogen at temperatures above *ca.* 100 °C, accompanied by a rapid redistribution of hydrogen in methyl groups of acetone. With regard to this hydrogen redistribution reaction, Hine *et al.*[2] reported that d_6-acetone was dedeuterated in acidic or alkaline aqueous solution, being catalyzed by hydrogen or hydroxyl ion, respectively. It is thus of interest to study the mechanism and nature of the active sites on ZnO surface of the present reaction. The reaction was investigated with a mixture of 85% of d_0-acetone ($(CH_3)_2CO$) and 15% of d_6-acetone ($(CD_3)_2CO$), ZnO and Zn metal subjected to various modes of pretreatment being used as catalyst.

Experimental

Powdered ZnO (Kadox-25 from New Jersey Zinc Co.) or Zn metal, first pressed into a wafer *ca.* 0.2 mm thick, was crushed into few mm wide. A known amount of catalyst was mounted in the bottom of a U-tube reactor of a conventional, closed circulating system, volume *ca.* 250 ml, and was activated by varied pretreatment (Table 1). In order to minimize contamination of the catalyst without cold traps, Apiezon grease of the stop cocks was well degassed prior to the experiment.

Chemically pure d_0-acetone from Wako Chem. Co. and d_6-acetone of 99D% from Merck Co. were dried by passing through a $CaCl_2$-tube and then repeatedly distilled in a vacuum. The sample of d_6-acetone contained d_5- and d_4-acetone in a few percent. Reactions were carried out at −10—60 °C under pressures of 0.5—80 mmHg of acetone. In order to estimate the ratio of the amount of adsorbed acetone active for redistribution to the total acetone adsorbed on ZnO, measurements were made of the adsorption isotherm of acetone, the hydrogen exchange between gaseous d_0-acetone and preadsorbed d_6-acetone and the hydrogen redistribution between d_0- and d_6-acetone over ZnO preliminarily saturated with adsorbed d_6-acetone. During some runs of the reaction of the d_0- and d_6-acetone mixture, the catalyst was illuminated with a mercury lamp of medium pressure (Toshiba H-400-P).

TABLE 1. PRETREATMENT OF THE CATALYSTS

Original form	No. of catalysts	Pretreatment	Visible change
ZnO powder,[a] 0.334 g	I	Evacuated at 300 °C for 1 hr	None
	II	Evacuated at 350 °C for 3 hr	Colored with dark green
	III	Evacuated at 450 °C for 3 hr	Zn deposited on the upper part of the reactor
	IV	Heated at 450 °C for 3 hr in 200 mmHg H_2 and then evacuated at 300 °C for 1 hr	Similar as above
Zn powder,[b] 0.380 g	V	None	None
	VI	Heated at 200 °C for 0.5 hr in 5 mmHg O_2 and then evacuated at 200 °C for 1 hr	None
	VII	Heated at 350 °C for 0.5 hr in 5 mmHg O_2 and then evacuated at 300 °C for 1 hr	None
	VIII	Heated at 400 °C for 0.5 hr in 5 mmHg O_2 and then evacuated at 300 °C for 1 hr	ZnO deposited on the upper part of the reactor

a) Prior to pretreatment, pressed Kadox-25 was heated at 450 °C in few cmHg O_2 for 14 hr, evacuated for 3 hr at 350 °C, heated again in O_2 for 0.5 hr and then cooled to the temperature of pretreatment. b) Prior to pretreatment, pressed Zn powder was heated at 350 °C for 14 hr and then evacuated for 1 hr at 350 °C.

Sampled gases were analyzed with a mass spectrometer (Hitachi RMU-6); ionization voltage 70 V. Relative peak heights of *m/e* 58—65 give relative amounts of d_n-acetones $n=0, 1, —, 6$ since no fragments of acetone were present in this region of the spectra.

Results and Discussion

The initial activity of ZnO catalysts was fairly high but decreased to a steady value after several runs of reaction were repeated followed by evacuation at room temperature (Table 1). Figure 1 shows a typical time course of the reaction with a mixture of 85% d_0- and 15% d_6-acetone carried out on the stabilized catalyst II, with surface area *ca.* 4 m²/g Cat.

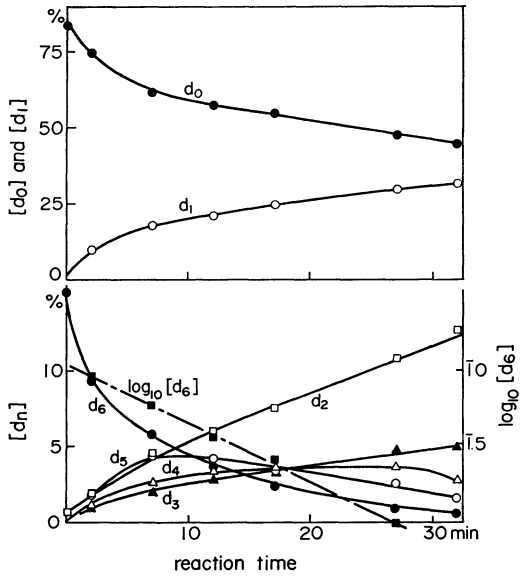


Fig. 1. Time courses of the relative amounts of d_n-acetones formed by the hydrogen redistribution with a 20 mmHg mixture of 85% d_0- and 15% d_6-acetone on ZnO (the catalyst II) at 0 °C.

The relative amounts of respective d_n-acetones depend solely upon the relative amount of d_6-acetone (Fig. 2). This suggests that the hydrogen redistribution reaction obeys the same rate equation, irrespective of the pretreatment of the catalyst. The presence of maxima of d_4- and d_5-acetone in the time courses (Fig. 1) suggests a stepwise hydrogen exchange mechanism, *i.e.*, not more than one hydrogen atom undergoes exchange before desorption of adsorbed acetone molecule. The full curves in Fig. 2 represent the results of simulation by the stepwise mechanism,

$$d_n\text{-acetone} \rightleftarrows a_m + h, \qquad (1)$$

where h is an adsorbed H or D atom and a_m ($m=n$ or $n-1$) is the adsorbed species of acetone loosing h. Provided that the kinetic hydrogen isotope effect on the rate of reaction (1) is negligible and the steady state condition is established for respective a_m's, we can derive the following equations which give the relative amounts of d_n-acetones, $[d_n]$, as a function of $[d_6]$.

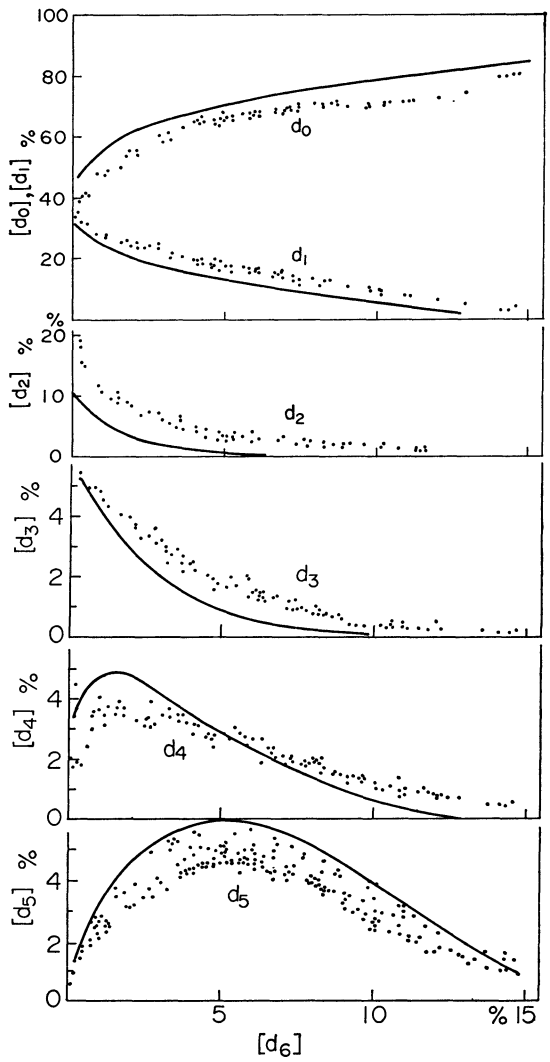


Fig. 2. The relations among the relative amounts of d_n-acetones formed by the hydrogen redistribution with a mixture of 85% d_0- and 15% d_6-acetone. Plots are the experimental results obtained by the use of all the catalysts listed on Table 1 and the full curves are those calculated by Eqs. (2).

$$\left.\begin{aligned} \frac{d[d_n]}{d[d_6]} &= \frac{[a_n](1-x)+[a_{n-1}]x-[d_n]}{[a_5](1-x)-[d_6]} \\ \frac{d[a_n]}{dt} &= \frac{(6-n)[d_n]}{6} + \frac{n[d_{n+1}]}{6} - [a_n] = 0, \end{aligned}\right\} \qquad (2)$$

where x is the D atomic fraction of h, being equal to 0.15 in the present reaction. In spite of the crude approximation in the simulation and no correction being made as regards ^{13}C and H contained in the d_6-acetone sample, observations for all the catalysts were well reproduced.

A linear relation of $\log_{10}[d_6]$ *vs.* time indicates that the rate of $[d_6]$ decrease obeys the first-order rate equation (Fig. 1(b)).

$$-d[d_6]/dt = (v_{ex}M/P_AV)[d_6], \qquad (3)$$

where P_A is the total pressure of acetone, V the volume of reaction system and M the weight of catalyst used. Constant v_{ex} is the exchange rate (ml·mmHg/min·g Cat.) and a measure of catalytic activity. The values

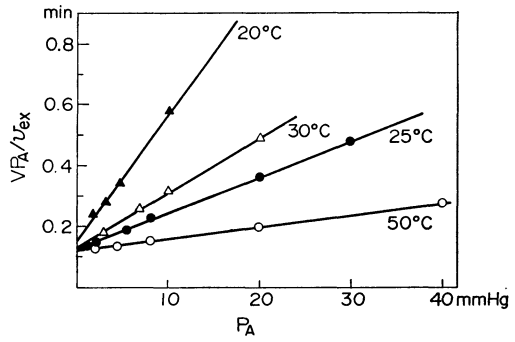


Fig. 3. Dependence of the exchange rate, v_{ex}, on acetone pressure. The experimental condition is similar to the case of Fig. 1.

of v_{ex} obtained for the catalyst II at various acetone pressure and temperatures establish the following relation (Fig. 3).

$$v_{ex} = k_{ex}K_A P_A/(1+K_A P_A), \quad (4)$$

where k_{ex} and K_A are the apparent rate constant of the exchange and the apparent equilibrium constant of acetone adsorption on ZnO catalyst, respectively. The activation heat of the exchange and the heat of acetone adsorption were evaluated to be 14 ± 2 and 10 ± 1 kcal/mol, respectively, from the results given in Fig. 4. The activation heats are nearly the same for all the catalysts. This indicates the same mechanism for all the reactions.

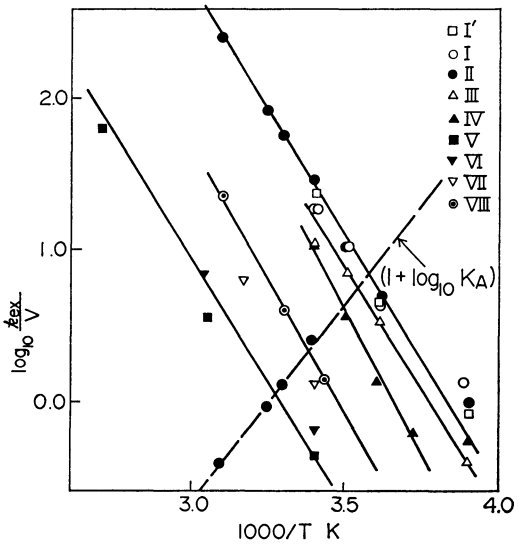


Fig. 4. Temperature dependences of the exchange rate constant, k_{ex}, and the adsorption constant, K_A (mmHg). Annexed figures are the number of the catalyst used.

The ZnO catalyst evacuated at a temperature below 350 °C gives a catalytic activity (Fig. 4), several tens times larger than that of the Zn metal. The activity of ZnO which decreased with evacuation at 450 °C is probably due to the deposition of Zn metal on ZnO surface (Table 1). In contrast, Zn metal became active with preliminary heating in oxygen. The high activity of ZnO as compared with Zn was further proved by use of catalyst VIII consisting of ZnO deposition on the upper part of the U-tube reactor and Zn metal at the bottom. The exchange reaction rate did not change by cooling the bottom of the reactor to −10 °C, where Zn metal was mounted, indicating that the reaction mainly takes place on ZnO deposited on upper part of the reactor wall.

Adsorption isotherms of acetone on the catalyst II were determined at temperatures 0—100 °C and at P_A up to a few mmHg. Saturated adsorption was observed at 0 °C, its amount being estimated to be 1.5 ml/g Cat. The adsorbed amount at 0 °C and 1 mmHg of P_A was 0.93 times this saturated adsorption, whereas it was 0.5 during the course of redistribution reaction according to the value of K_A (Fig. 4) and the adsorption isotherm

$$n = n_\infty K_A P_A/(1+K_A P_A) \quad (5)$$

derived from Eq. (4), where n is the amount of adsorbed acetone active for hydrogen redistribution and n_∞ its saturated value. The difference in the fractions of adsorbed acetone suggests that only a part of adsorbed acetone contributes to the hydrogen redistribution. This result was further supported by the hydrogen exchange reaction between gaseous d_0-acetone and preadsorbed d_6-acetone as follows. The reaction vessel was divided into A and B, the former containing catalyst II. A known amount of d_6-acetone was introduced into A and brought into adsorption equilibrium with the catalyst. d_0-Acetone was then introduced into B at an equal pressure to the residual pressure in A and was mixed with d_6 acetone in A by circulating over the catalyst causing hydrogen redistribution. The deuterium atomic fraction y_∞ in gaseous acetone at exchange equilibrium is given by

$$y_\infty = (N_6+n)/(N_0+N_6+n),$$

where N_0 and N_6 are amounts of gaseous d_0- and d_6-acetone, respectively, and n is the amount of preadsorbed d_6-acetone active for the hydrogen exchange. y_∞ is given by the steady value of y_A (Fig. 5). n was evaluated at 0.62 or 0.56 ml/g Cat. By introducing this value into Eq. (5), n_∞ was evaluated at 0.68 or 0.66 ml/g Cat., which is also *ca.* a half of the amount of saturated adsorption of acetone (1.5 ml/g Cat.). Thus, k_{ex} and K_A are proved to be the rate constant of the hydrogen redistribution and the equilibrium constant of the chemisorption of active acetone for the exchange, respectively.

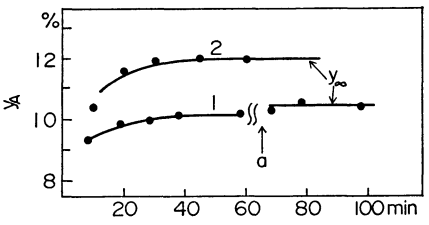
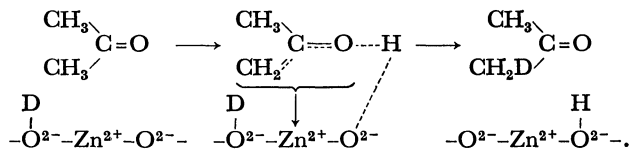


Fig. 5. Hydrogen exchange between d_6-acetone preadsorbed on the catalyst II and gaseous d_0-acetone at 0 °C.
Curve 1: 0.19 g ZnO and 6 mmHg at the adsorption equilibrium, curve 2: 0.5 g ZnO and 10 mmHg. At the time, *a*, of curve 1 the temperature was raised to 40 °C to accelerate the exchange.

The value of n_∞, being *ca.* a half of the monolayer on ZnO surface, indicates that the active sites for the hydrogen redistribution is the normal crystal plane but not the interstitial zinc[3] and/or the anion vacancies,[4] which might be far rarer than the normal lattice points of ZnO surface and have been reported to be active for the oxidation of CO, decomposition of N_2O[5] and so on. For the sake of confirmation catalyst II was illuminated with a mercury lamp of medium pressure in the course of the redistribution reaction. The rate did not change with illumination, indicating that the conduction electrons and/or the interstitial zinc is not responsible for the reaction.

From the above conclusions on the mechanism and the active sites of the exchange reactions and the results of the IR spectrometric study,[1] which established the presence of acetone chemisorbed on ZnO surface dissociatively with an enol-type configuration, the hydrogen redistribution reaction of acetone is supposed to be caused *via* acetone chemisorbed on a pair of sites, Zn^{2+}–O^{2-}, of ZnO surface such as



References

1) K. Nagai, to be published.
2) J. Hine, J. C. Kaufmann, and M. S. Cholod, *J. Amer. Chem. Soc.*, **94**, 4590 (1972).
3) M. N. Danchevskaya, G. P. Panasyuk, and N. I. Kobozev, *Zh. Fiz. Khim.*, **43**, 671 (1961).
4) O. V. Krylov and E. A. Fokina, Proc. IV International Congress on Catalysis, Moscow, 1968, Vol. 2, p. 229, Publ. 1971.
5) K. Tanaka and G. Blyholder, *J. Phys. Chem.*, **76**, 1807 (1972).