© 1999 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 72, 669—672 (1999)

A Deuterium-Labeling Study on the Dehydrogenation of 2-Propanol with Ru–Pt/Carbon Catalyst in the Liquid-Film State Effective for the 2-Propanol/Acetone/Hydrogen Chemical Heat-Pump System

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(Received October 5, 1998)

A unique feature of the dehydrogenation of 2-propanol with Ru–Pt/carbon catalyst in the liquid-film state has been elucidated by means of various kinds of deuterium labeling. A quite large kinetic isotope effect for 2-propanol-d_8 (k_H/k_D = 14.6) suggests that fission of the methine C–H bond in the isopropoxy intermediate is rate-determining in the overall process. The dominant formation of H_2 for 2-propanol-O-d_1 is explained in terms of rapid scrambling of deuterium together with a large kinetic isotope effect for fission of the methine C–D bond. This picture is supported by both the absence of an appreciable kinetic isotope effect for 2-propanol-O-d_1 and the deuterium distribution among the liquid-phase components. The extent of hydrogen transfer from 2-propanol to acetone-d_6 during the dehydrogenation reaction suggests suppression of the inhibitive adsorption of acetone, leading to a high catalytic activity in the region of high acetone concentration, which is essential for a 2-propanol/acetone/hydrogen chemical heat-pump system with high thermal efficiency.

A catalyst-assisted 2-propanol/acetone/hydrogen chemical heat-pump system has been proposed for the up-grading of low-quality heat (ca. 80 °C) into more valuable heat (ca. 200 °C) with the aid of cooling at ambient temperature (ca. 25 °C).[1)] In this system, the role of a catalyst for 2-propanol dehydrogenation (Eq. 1) is most important, because it should be active and selective under boiling conditions.

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

A ruthenium catalyst supported on carbon (Ru/carbon) is a promising candidate for this reaction, and was characterized using a deuterium-labeling technique.[2)] However, a retardation effect caused by the product acetone was so serious that the reaction in a suspension state scarcely proceeded for a solution containing ca. 40 mol% of acetone or more. Later, the reaction with such a high acetone concentration was found to be possible at the same temperature of external heating (ca. 100 °C), if the reaction was conducted in the manner of liquid-film state with Ru/carbon or more preferably Ru–Pt/carbon catalyst.[3)]

In the present study, a unique feature of the reaction with Ru–Pt/carbon catalyst in the liquid-film state was elucidated by means of various kinds of deuterium labeling.

Experimental

All chemicals were of reagent grade. $(CD_3)_2CDOD$ (>99 atom% D), $(CH_3)_2CHOD$ (> 99 atom% D), and $(CD_3)_2CO$ (>99.9 atom% D) were purchased from Merck Frosst Canada Inc. Ru/carbon catalyst (5 wt% Ru) was supplied by N.E. Chemcat Co. Ru–Pt/carbon catalyst (5 wt% total metal with 1 : 1 atomic ratio) was prepared and characterized as reported previously.[4)] The catalysts were evacuated at 50 °C for 24 h before use.

Batch-wise catalytic dehydrogenation of 2-propanol (with or without added acetone) was performed with external heating at 100 °C and cooling by a reflux condenser under a dinitrogen atmosphere (1 atm). The reaction was conducted in two ways with respect to the catalyst/solution ratio. In one case, the ratio was taken as 0.2 g/5 cm^3 in a Schlenk flask (20 cm^3) to keep the catalyst in a suspension state with magnetic stirring (at least 500 rpm to avoid external diffusional limitations).[3)] In the other, the catalyst was only wetted in a liquid-film state in a round-bottomed flask (300 cm^3) without stirring, where the ratio was taken to be sufficiently large (1.0 g/5 cm^3).[5)] The rate of gas evolution was monitored volumetrically with a gas buret, where the effect of thermal expansion on the initial stage of reaction was corrected precedently.

A gas-chromatographic analysis of gaseous products was made intermittently (MS-5A and Porapak Q columns), while the liquid-phase components were analyzed after the reaction (PEG-20M column). The deuterium distribution in the product dihydrogen was determined every fifteen or thirty minutes using a quadrupole-type mass spectrometer (NEC Anelva Co., AQA 360). The deuterium NMR spectra of the solution were taken after appropriate reaction periods with an FT-NMR spectrometer (JEOL Co., GX-400) in order to analyze the deuterium distribution among the liquid-phase components.

Results and Discussion

The reaction rates of 2-propanol dehydrogenation by suspended catalysts have been well described by the following equation[4,6)] with zero-order kinetics with respect to 2-propanol existing in excess as a dispersing agent as well.

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

Thus, in the present analysis, the rate constant was taken to be equal to the initial rate, where the concentration of acetone was negligible.

Kinetic Isotope Effect in the Dehydrogenation of 2-Propanol-d_8 in the Liquid-Film State. When the dehydrogenation of 2-propanol-d_8 was conducted in the liquid-film state, a quite large kinetic isotope effect was observed. Figure 1 shows the time sequences for the dehydrogenation of $(CD_3)_2CDOD$ and $(CH_3)_2CHOH$. From the initial slopes of the respective plots, the value of k_H/k_D was determined to be 14.6. This value is too large as secondary deuterium isotope effects, and should reflect a primary deuterium isotope effect associated with fission of the bond including deuterium.

Usually the dehydrogenation of alcohols is considered to proceed through C–H bond fission at the β-position in the alkoxy intermediate.[7)] The magnitude of k_H/k_D, therefore, suggests that this step (fission of methine C–H bond) is rate-determining in the overall process.

Deuterium Distribution in Dihydrogen Evolved by the Dehydrogenation of 2-Propanol-O-d_1. When 2-propanol-O-d_1 was used as a reactant in the liquid-film state, H_2 was mainly formed and its content was almost constant from the early stage of the reaction (Fig. 2a). This result is somewhat surprising, because HD would be formed if the dehydrogenation occurs for the hydroxy and methine hydrogens intact. The quite high H/D ratio (calculated as 23.5) in the evolved dihydrogen suggests that deuterium initially charged as O–D is scrambled.

The observed ratio (23.5) is, however, too high if only the statistical distribution of deuterium due to scrambling (H/D = 7) is taken into account. We consider that it is reconciled if the large kinetic isotope effect in the fission of methine C–D bond is incorporated. Under the condition of rapid scrambling of deuterium, fission of the corresponding C–H bond would occur more frequently than that of the C–D bond ($k_H/k_D \approx 14.6$) to form dihydrogen, and hence protium would be concentrated in the evolved dihydrogen. Another fact of virtual invariance of the rate for 2-propanol and 2-propanol-O-d_1 supports this view.

If the reaction of 2-propanol-O-d_1 was conducted in the suspension state, the deuterium distribution in dihydrogen was dependent on time (Fig. 2b); the fraction of H_2 as well

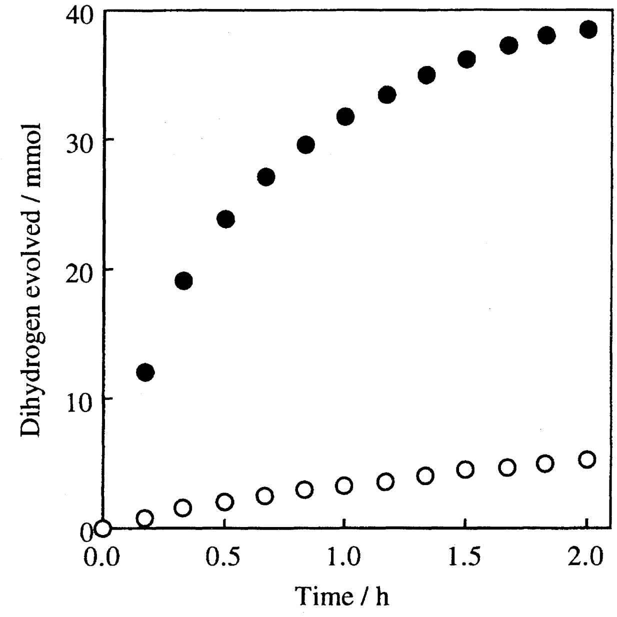

Fig. 1. Time course for the dehydrogenation of 2-propanol (●) and 2-propanol-d_8 (○) with Ru–Pt/carbon catalyst in the liquid-film state.

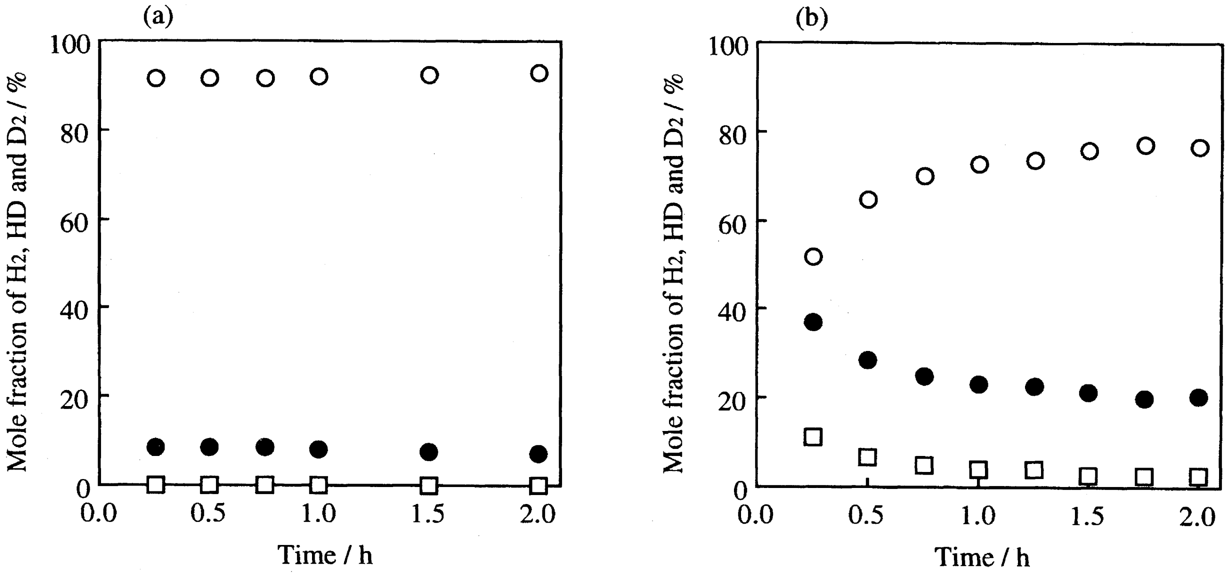

Fig. 2. Time course for the deuterium distribution in dihydrogen evolved by the dehydrogenation of 2-propanol-O-d_1 with Ru–Pt/carbon catalyst in the liquid-film (a) and suspension (b) states. ○: H_2, ●: HD, □: D_2.

as the H/D ratio increased gradually. This feature suggests a relatively slow rate of deuterium scrambling, and is consistent with an appreciable k_H/k_D value (2.0) for 2-propanol-O-d_1 (Fig. 3).

Deuterium Distribution among the Liquid-Phase Components for the Dehydrogenation of 2-Propanol-O-d_1. The situation suggested above is consistent with the deuterium distribution among the liquid-phase components (Table 1). In the liquid-film state with rapid deuterium scrambling, difficulty concerning the fission of the methine C–D bond relative to the methine C–H bond tends to concentrate deuterium at the positions of methine as well as methyl groups of product acetone more than expected from the statistical distribution (15.1>7.7 and 52.5>38.1, respectively). In the suspension state, however, scrambling of deuterium would not be so rapid, although methine C–D is still abundant compared to O–D.

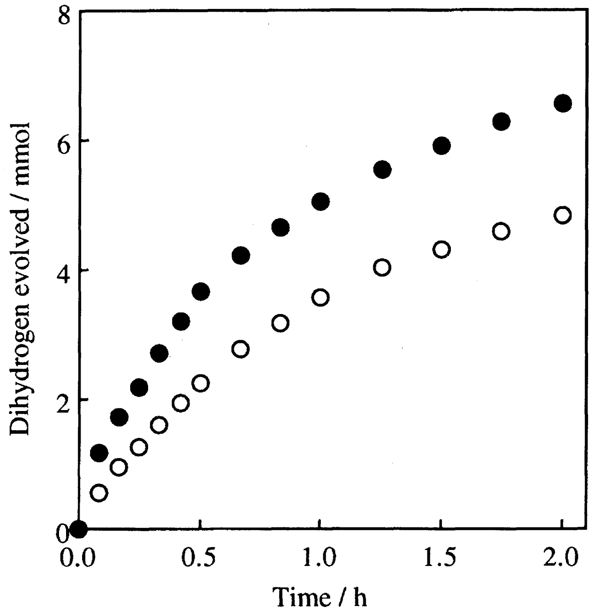

Fig. 3. Time course for the dehydrogenation of 2-propanol (●) and 2-propanol-O-d_1 (○) with Ru–Pt/carbon catalyst in the suspension state.

Table 1. Deuterium Distribution among the Liquid-Phase Components for the Dehydrogenation of 2-Propanol-O-d_1[a)]

State of reaction	Deuterium distribution/%			
	2-Propanol			Acetone
	Hydroxy	Methine	Methyl	
Liquid film	4.4 (7.7)	15.1 (7.7)	28.0 (46.5)	52.5 (38.1)
Suspension	19.4 (11.8)	29.2 (11.8)	49.7 (70.6)	1.7 (5.8)

a) After the reaction of 2 h with Ru–Pt/carbon catalyst. Values in parentheses are calculated on the basis of statistical distribution.

Dehydrogenation of 2-Propanol in the Presence of Acetone-d_6. By performing the dehydrogenation of 2-propanol in the presence of an appreciable amount of acetone-d_6, the extent of hydrogen transfer from 2-propanol to acetone (yielding 2-propanol-1,1,1,3,3,3-d_6) can be evaluated).[2)] Table 2 shows that deuterium atoms are distributed predominantly among the methyl groups of acetone and 2-propanol (>90 %), irrespective of the reaction conditions. It can also be seen that the hydrogen transfer occurs quite readily with the Ru/carbon catalyst in the suspension state,[2)] while the reaction with the Ru–Pt/carbon catalyst in the liquid-film state retains deuterium considerably in the original form of acetone-d_6; the reaction with Ru/carbon catalyst in the liquid-film state seems to be in an intermediate situation.

Table 2. Deuterium Distribution among the Liquid-Phase Components for the Dehydrogenation of 2-Propanol in the Presence of Acetone-d_6

Catalyst	State of reaction	Deuterium distribution/%			
		Acetone	2-Propanol		
			Hydroxy	Methine	Methyl
Ru/carbon	Suspension[a)]	23.5	0.78	0.49	75.2
	Liquid film[b)]	39.7	4.1	5.3	50.9
Ru–Pt/carbon	Liquid film[b)]	63.3	2.8	3.5	30.4

a) From Ref. 2. Reaction time 1 h. Acetone-d_6 10 vol% (1.36 mol dm^{-3}). b) Reaction time 2 h. Acetone-d_6 40 vol% (5.44 mol dm^{-3}).

Table 3. Amounts of Hydrogen Evolved and Transferred for the Dehydrogenation of 2-Propanol in the Presence of Acetone-d_6

Catalyst	State of reaction	Dihydrogen evolved	Dihydrogen transferred
		mmol	mmol
Ru/carbon	Suspension[a)]	0.65	4.65
	Liquid film[b)]	9.0	15.6
Ru–Pt/carbon	Liquid film[b)]	12.7	9.5

a) From Ref. 2. Reaction time 1 h. Acetone-d_6 10 vol% (1.36 mol dm^{-3}). b) Reaction time 2 h. Acetone-d_6 40 vol% (5.44 mol dm^{-3}).

The amounts of dihydrogen evolved and transferred to acetone-d_6 are tabulated in Table 3. Whereupon the small amounts of deuterium liberated into the gas phase are taken into account, and the small portions of deuterium atoms present at methine and hydroxy groups are incorporated in the hydrogen transfer, assuming deuterium scrambling in the initially formed 2-propanol-1,1,1,3,3,3-d_6. It is obvious that hydrogen transfer is suppressed relative to dehydrogenation in the case of the Ru–Pt/carbon catalyst in the liquid-film state, as compared with the Ru/carbon catalyst in the suspension state.

Mechanistic Considerations. It is plausible that the dehydrogenation of 2-propanol proceeds by the following scheme.[2,6,7)]

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CHO_{ads} + H_{ads} \qquad (3)$$

$$(CH_3)_2CHO_{ads} \longrightarrow (CH_3)_2CO_{ads} + H_{ads} \qquad (4)$$

$$(CH_3)_2CO_{ads} \longrightarrow (CH_3)_2CO \qquad (5)$$

$$H_{ads} + H_{ads} \longrightarrow H_2 \qquad (6)$$

For the dehydrogenation of 2-propanol with the Ru/carbon catalyst in the suspension state, the kinetic isotope effect (k_H/k_D) of 1.57 was observed for 2-propanol-2-d_1, where scrambling of deuterium was negligible.[2)] On the basis of this small value, it was suggested that the formation of dihydrogen from the surface hydrogen species (Eq. 6) was the slowest step. In contrast, the fission of methine C–H bond (Eq. 4) would be rate-determining for the Ru–Pt/carbon catalyst in the liquid-film state. Since the interaction of the metal center with β-hydrogen in the C–H bond fission is usually electrophilic,[8)] this may give a criterion for choosing a catalyst modifier to promote the catalytic activity.

The remarkable suppression of hydrogen transfer observed for the Ru–Pt/carbon catalyst in the liquid-film state would possibly be derived from a decrease of acetone adsorption,[2)] which is a prerequisite step to the hydrogen-transfer process. On the other hand, the adsorption of acetone retards the dehydrogenation reaction.[4)] Thus, by using the present catalyst system, it would be possible to retain a high catalytic activity in the region of high acetone concentration, which is essential for operation of a chemical heat pump with high thermal efficiency.[3)]

In conclusion, the high catalyst performance of the Ru–Pt/carbon catalyst in the liquid-film state would be associated with (1) rate-determining fission of the methine C–H bond (vs. desorption of H_2), and (2) lowering of inhibitive adsorption of the product acetone, as reflected in the suppression of the relevant hydrogen-transfer process.

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