Characteristics of Suspended Ru/Carbon Catalyst for 2-Propanol Dehydrogenation Applicable to Chemical Heat Pump

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Liquid-phase dehydrogenation of $(CH_3)_2CHOH$, $(CH_3)_2CHOD$ and $(CH_3)_2CDOH$ was performed at 82.4 °C with high activity and selectivity under refluxing conditions by heating the suspended solution at 100 °C with a carbon-supported ruthenium catalyst. Since the mixture of $(CH_3)_2CHOH$ and $(CD_3)_2CO$(10 vol%) gave 2-propan-1,1,1,3,3,3-d_6-ol at a rate 7.15-times higher than that of hydrogen evolution, hydrogen transfer from 2-propanol to acetone ought to proceed simultaneously with dehydrogenation. Relatively small kinetic isotope effects of 1.69 and 1.57, obtained from $(CH_3)_2CHOD$ and $(CH_3)_2CDOH$, respectively, on the Ru/carbon catalyst for dehydrogenation, suggests that the slowest step is not a splitting of the methine C–H bond but, rather, the formation of molecular hydrogen from surface hydrogen species. Further improvements regarding easy desorption of both acetone and hydrogen are necessary for the catalyst most suitable for 2-propanol dehydrogenation in a chemical heat pump system.

The utilization of solar and geothermal heat as well as waste heat in factories has recently attracted considerable attention. Chemical heat pumps are important from this viewpoint.[1] Aiming at large temperature rises, high thermal efficiencies and the functions of energy storage and transport, a new chemical heat pump system has been proposed in which an endothermic reaction at low temperature was coupled with its exothermic reverse reaction at high temperature.[2,3] Among the three processes shown in Eqs. 1—3, 2-propanol dehydrogenation in the liquid phase is the most difficult, but essential, reaction, since the endothermic reaction at low temperature converts thermal energy of low quality into chemical energy.

$$(CH_3)_2CHOH(l) \longrightarrow (CH_3)_2CO(g) + H_2(g), \tag{1}$$

$$(CH_3)_2CO(g) + H_2(g) \longrightarrow (CH_3)_2CHOH(g), \tag{2}$$

$$(CH_3)_2CHOH(g) \longrightarrow (CH_3)_2CHOH(l). \tag{3}$$

In spite of the thermodynamic disadvantage, the liquid-phase dehydrogenation of 2-propanol takes place catalytically under boiling conditions, where the product hydrogen is expelled from the reaction medium immediately. On the other hand, acetone hydrogenation is favorable below 202 °C at atmospheric pressure,[4] which is much higher than the boiling temperature of the 2-propanol/acetone mixed solution(82.4—56.3 °C). The role of a coolant at ambient temperature is also to be noted, because the separation of 2-propanol from the gaseous mixture makes it possible to raise the temperature from 80 °C to 200 °C in one effort.

As for the present chemical heat pump system, the development of excellent catalysts is indispensable for both gaseous hydrogenation of acetone and 2-propanol dehydrogenation in the liquid phase.

Hydrogenation of geseous acetone was widely investigated using various metal catalysts,[5] whereas Raney nickel,[6] nickel boride,[7] and fine-particle nickel,[8,9] prepared by a gas-evaporation technique,[10] were both active and selective for 2-propanol dehydrogenation. Homogeneous catalysts comprising rhodium,[11] ruthenium,[12] and iridium complexes[13] were useful for this reaction as well.

High thermal efficiency in the present heat pump system is attainable with high endothermic reaction rates in low temperature regions. A ruthenium catalyst supported on carbon (abbreviated hereafter as Ru/carbon) was recently found to be superior for 2-propanol dehydrogenation in a well-dispersed state.[14]

In the present paper, an elucidation of the characteristics has been attempted for a suspended Ru/carbon catalyst with deuterium-substituted 2-propanol and acetone for the purpose of designing the most suitable catalyst for a chemical heat pump system.

Experimental

Dehydrogenation of unlabled 2-propanol(hereinafter described as propanol-d_0) and its deuterio-isomers, i.e., $(CH_3)_2CHOD$ and $(CH_3)_2CDOH$ (Division of Merck, Frost, Inc.), as well as $(CH_3)_2CHOH$ including 10 vol% $(CH_3)_2CO$ or $(CD_3)_2CO$ were performed under boiling and refluxing conditions at atmospheric pressure. An appropriate amount (200 mg) of a Ru(5 wt%)/carbon powder catalyst (supplied by N. E. Chemcat Co.) and 5 ml of reactant 2-propanol were placed at room temperature in a Schlenk flask(20 ml), through which nitrogen was passed in order to remove both water and oxygen in sufficient amounts.

After the Ru/carbon catalyst was dispersed ultrasonically (Kaijyo Denki Co., Sona 50a) in 2-propanol, the suspension was agitated vigorously by a magnetic stirrer (500 rpm) and heated with an oil bath kept at 100 °C. The product gas was collected in a gas burette (250 ml) through a refluxing condenser cooled to 20 °C.

A gas-chromatographic analysis for gaseous and liquid-phase products was performed with active carbon and PEG

20M columns, respectively. The deuterium distribution in product dihydrogen was determined every fifteen or thirty minutes using a quadrupole-type mass spectrometer(NEC Anelva Co., AQA 360), whereas the ^2H NMR spectra of the solution were taken after appropriate reaction periods in order analyze how the substituted deuterium atoms were transferred among the liquid-phase components using an FT-NMR spectrometer(JEOL Co, GX-400).

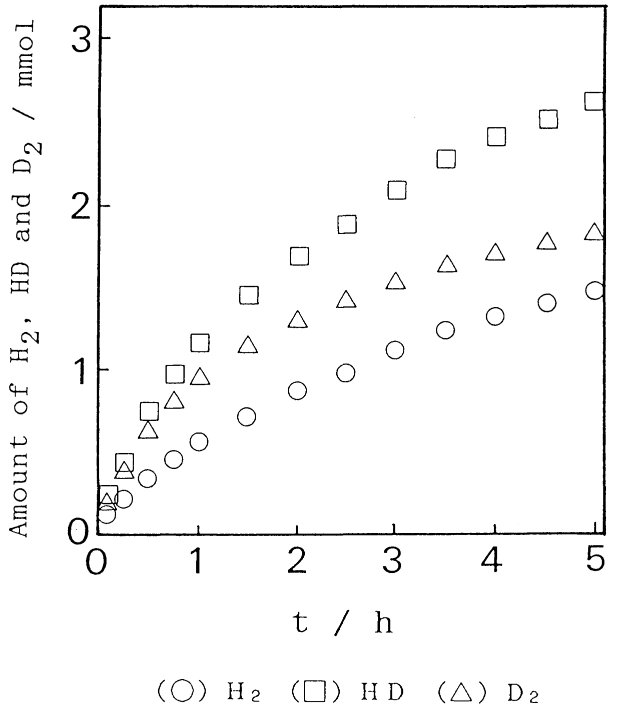

Fig. 1. Accumulation of H_2, HD, and D_2 evolved at 82.4°C from $(CH_3)_2CHOD$ under refluxing conditions (heat at 100°C) with Ru(5 wt%)/carbon catalyst.

Results

Dehydrogenation of 2-Propanol-*d*. The Ru/carbon catalyst suspended in $(CH_3)_2CHOD$ under boiling and refluxing conditions gave acetone and gaseous hydrogen as a mixture of H_2, HD, and D_2:

$$(CH_3)_2CHOD(l) \longrightarrow (CH_3)_2CO(l) + H_2, HD, D_2. \tag{4}$$

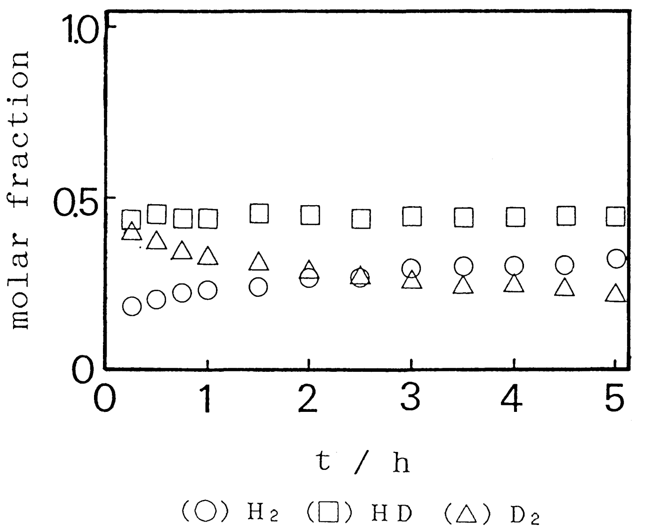

Fig. 2. Deuterium distribution among gaseous hydrogen at the time of evolution from $(CH_3)_2CHOD$ at 82.4°C under refluxing conditions (heat at 100°C) with Ru(5 wt%)/carbon catalyst.

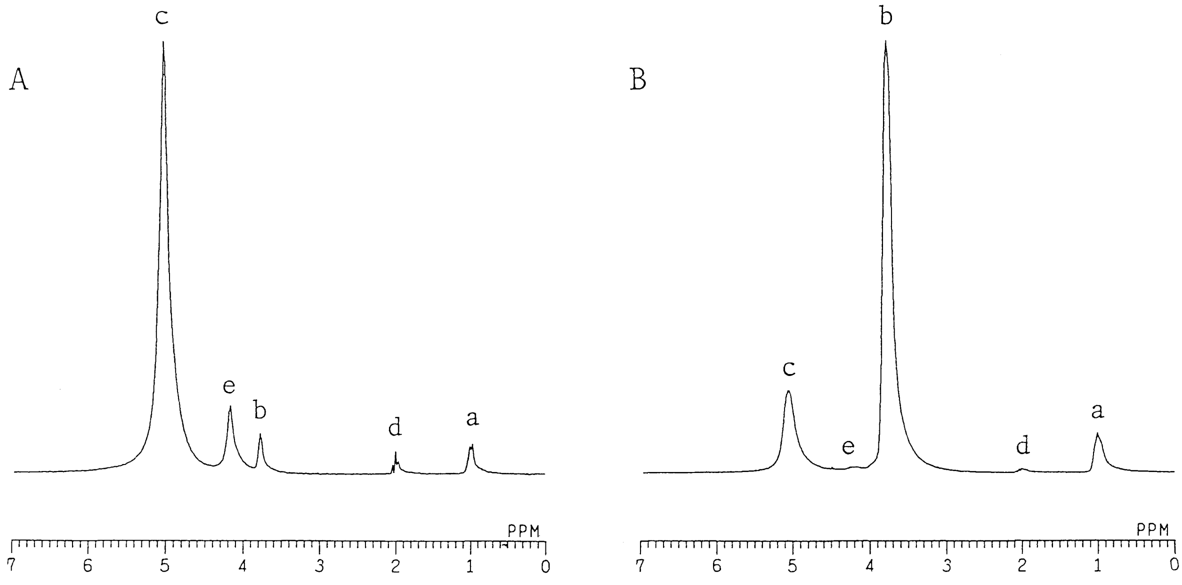

Fig. 3. ^2H NMR spectra of $(CH_3)_2CHOD$ (A) and $(CH_3)_2CDOH$ (B) solutions after 5-h reaction at 82.4°C under refluxing conditions (heat at 100°C) with Ru(5 wt%)/carbon catalyst. Peaks identified as 2-propanol methyl (a), methine (b) and hydroxyl (c) groups, acetone (d), and water (e).

A kinetic isotope effect of 1.69 was obtained from the initial dehydrogenation rates of $(CH_3)_2CHOH$ and $(CH_3)_2CHOD$. The amounts of H_2, HD, and D_2 produced from $(CH_3)_2CHOD$ are shown in Fig. 1 as a function of time.

The H/D ratio of gaseous hydrogen was smaller than unity (0.65) during the initial stage (15 min). The constitution of evolving hydrogen, however, changed with time, as represented in the variation of H_2, HD, and D_2 (Fig. 2). After 5 h from the start of the reaction, the H/D ratio of hydrogen newly-evolved increased to 1.22 at a conversion of 8.5%.

The deuterium distribution among the liquid-phase components after the 5-h reaction can be seen in the ^2H NMR spectrum (Fig. 3A). A part of the hydrogen atoms in the methine and methyl groups of $(CH_3)_2CHOD$, as well as in the methyl group of $(CH_3)_2CO$, was exchanged with the deuterium supplied from the OD group of the reactant. In addition, a new peak due to HDO appeared, since water exuded from the carbon support was contaminated with deuterium.

The total amount of deuterium remaining in the solution was 58.27 mg-atom, as calculated from the $(CH_3)_2CHOD$ charged (64.51 mmol) and gaseous deuterium evolved (6.24 mg-atom). The deuterium distribution among the liquid-phase components is summarized in Table 1.

Dehydrogenation of 2-Propan-2-*d*-ol. The dehydrogenation products of $(CH_3)_2CDOH$ were acetone and the mixture of H_2, HD, and D_2:

$$(CH_3)_2CDOH(l) \longrightarrow (CH_3)_2CO(l) + H_2, HD, D_2. \quad (5)$$

The amounts of H_2, HD, and D_2 produced from $(CH_3)_2CDOH$ are shown in Fig. 4 as a function of time. Figure 5 depicts the variation in the molar fractions of H_2, HD, and D_2 produced at the reaction time concerned. As for $(CH_3)_2CDOH$, the H/D ratio of newly-evolved hydrogen changed from 1.7 to 6.9 during a 5-h reaction. In contrast to slight deuterium transfer to the methyl groups of 2-propanol and acetone, an H–D exchange at the hydroxyl group

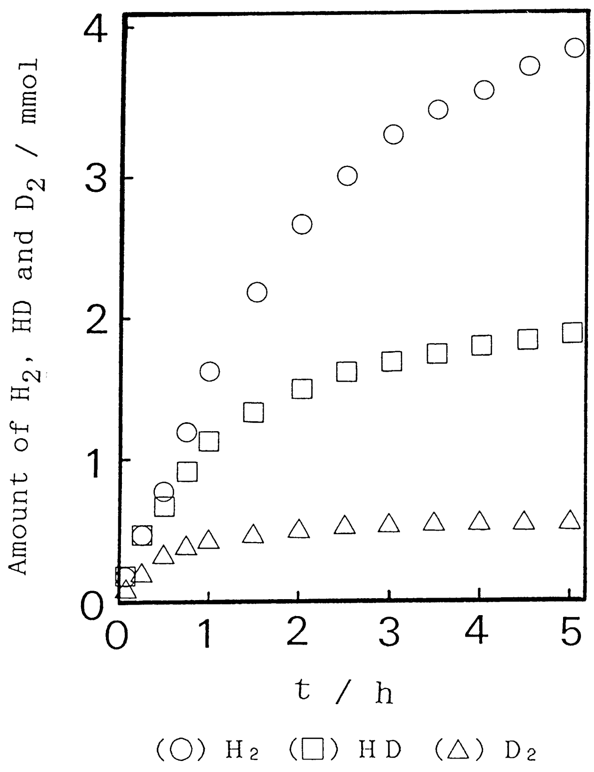

Fig. 4. Accumulation of H_2, HD, and D_2 evolved at 82.4 °C from $(CH_3)_2CDOH$ under refluxing conditions (heat at 100 °C) with Ru(5 wt%)/carbon catalyst.

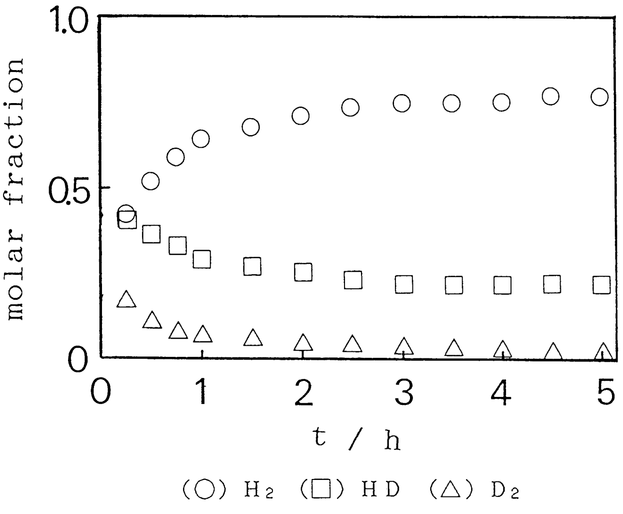

Fig. 5. Deuterium distribution among gaseous hydrogen at the time of evolution at 82.4 °C from $(CH_3)_2CDOH$ under refluxing conditions (heat at 100 °C) with Ru(5 wt%)/carbon catalyst.

Table 1. Deuterium Distribution in Liquid-Phase Components Obtained from $(CH_3)_2CHOD$ or $(CH_3)_2CDOH$ after 5-h Reaction under Refluxing Conditions (100 °C) with Ru(5 wt%)/Carbon Catalyst

Reactant	Deuterium amount in solution	Deuterium distribution/%				
		2-Propanol			Acetone	Water
	mmol	Methyl	Methine	Hydroxyl		
$(CH_3)_2CHOD$	58.27	2.97	3.17	83.54	1.19	9.12
$(CH_3)_2CDOH$	61.61	6.16	74.48	17.62	1.17	0.47

amounted to an extent as large as 17.6% (Fig. 3B and Table 1).

The initial dehydrogenation rates of $(CH_3)_2CHOH$ and $(CH_3)_2CDOH$ gave a k_H/k_D of 1.57.

Dehydrogenation of the Mixture of 2-Propanol-d_0 and Acetone-d_6. As previously reported for a nickel fine-particle catalyst,[8] the initial rate of 2-propanol dehydrogenation on the Ru/carbon catalyst was suppressed 1/2.95 times by adding acetone (10 vol%). A mixture of $(CH_3)_2CHOH$ and $(CD_3)_2CO$ (10 vol%) gave gaseous hydrogen as mainly H_2, the molar ratios of HD/H_2 and D_2/H_2 being 0.03 and 0.02, respectively.

Most of the hydroxyl and methine groups of 2-propanol remained intact after the 1-h reaction, since the extents of deuterium exchange shown in the ^2H NMR spectrum (Fig. 6A) were only 0.78 and 0.49% of all the deuterium species in the solution, respectively. On the contrary, 75.2% of the deuterium atoms in acetone-d_6 changed to the methyl group of 2-propanol within 1 h.

The extent of hydrogen transfer from 2-propanol-d_0 to acetone-d_6, yielding 2-propan-1,1,1,3,3,3-d_6-ol within 1 h, was estimated to be 4.65 mmol from the deuterium peaks due to the two kinds of methyl groups, which was 7.15-times larger than that of hydrogen evolution (0.65 mmol).

After a reaction for 5 h, 88% of the added acetone-d_6 changed into 2-propanol (Fig. 6B and Table 2).

Effects of Gaseous Hydrogen and Hydrogen Surface Species on Deuterium Distribution. In order to ascertain the possibility of a reverse reaction between gaseous hydrogen and acetone under the dehydrogenation conditions of 2-propanol, a suspended Ru/carbon catalyst was heated in $(CH_3)_2CHOH$ as well as in $(CH_3)_2CHOH$ including $(CH_3)_2CO$ (10 vol%) under a deuterium atmosphere. After the solution was boiled for 5 h, a ^2H NMR analysis was performed at room temperature.

The amount of hydrogen evolved from the mixture of 2-propanol and acetone (10 vol%) under refluxing conditions for 5 h (2.33 mmol) was much larger than that of deuterium incorporated from the gas phase to the liquid components (0.17 mmol). The extents of H–D exchange between gaseous deuterium and the

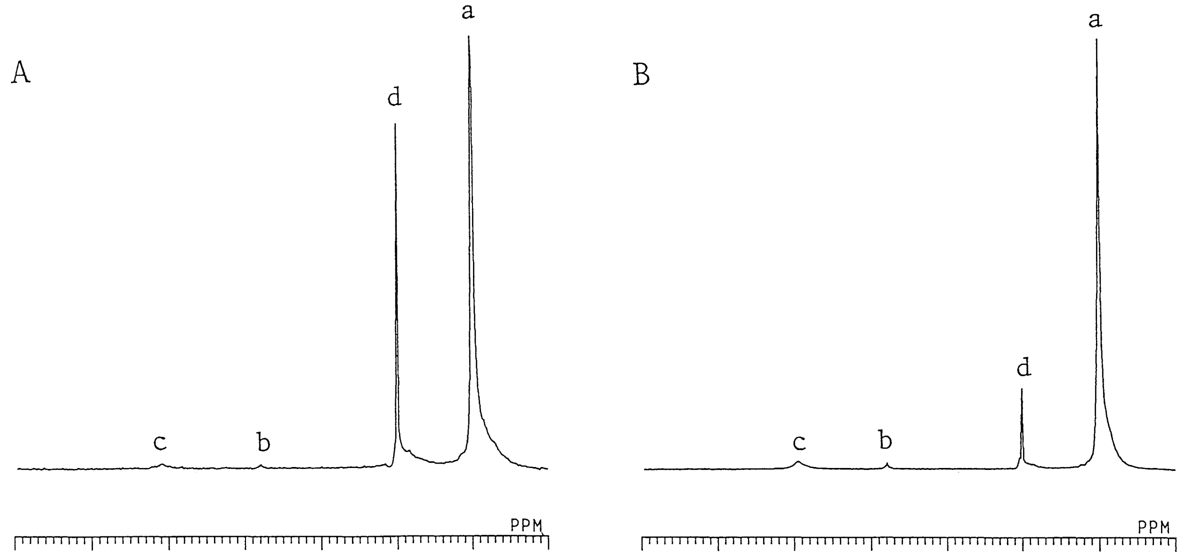

Fig. 6. ^2H NMR spectra of the mixed solution of $(CH_3)_2CHOH$ and $(CD_3)_2CO$ (10 vol%) after 1-h (A) or 5-h (B) reaction at 77.0 °C under refluxing conditions (heat at 100 °C) with Ru(5 wt%)/carbon catalyst. Peaks identified as 2-propanol methyl (a), methine (b) and hydroxyl (c) groups, and acetone (d).

Table 2. Deuterium Distribution in Liquid-Phase Components Obtained from the Mixture of $(CH_3)_2CHOH$ and $(CD_3)_2CO$ (10 vol%) after 1-h or 5-h Reaction at 77 °C under Refluxing Conditions (100 °C) with Ru(5wt%)/Carbon Catalyst

Reaction time/h	Deuterium distribution/%			
	2-Propanol			Acetone
	Methyl	Methine	Hydroxyl	
0	0.00	0.00	0.00	100.00
1	75.24	0.49	0.78	23.50
5	88.07	0.76	1.22	9.94

Table 3. Incorporation and Distribution of Deuterium from Gaseous Phase or Pre-Adsorbed State into Liquid-Phase Components as the Mixture of $(CH_3)_2CHOH$ and $(CH_3)_2CO$ (10 vol%) during the Reaction at 77.0 °C for 5 h under Refluxing Conditions (100 °C) with Ru(5 wt%)/Carbon Catalyst

Deuterium origin	Deuterium incorporated into solution	Deuterium distribution/mmol			
		2-Propanol			Acetone
	ppt	Methyl	Methine	Hydroxyl	
Gas phase	33.0	94.1	34.4	39.8	1.3
Pre-adsorbed at 130 °C	32.7	94.1	26.1	47.0	1.7

hydrogen atoms in 2-propanol or acetone were extremely small with no predominance to the methine and hydroxyl groups of 2-propanol (Table 3). The distribution and extent of deuterium incorporation in the solution of 2-propanol alone were similar to those obtained in a mixed solution of 2-propanol and acetone.

The effect of deuterium pre-adsorption on the catalyst was examined for a mixture of 2-propanol and acetone (10 vol%) at either 80 °C or 130 °C (Table 3). An extremely small amount of deuterium (0.17 mmol) was incorporated into the liquid components, irrespective of the pre-adsorption temperatures (80 °C and 130 °C) of gaseous deuterium.

Discussion

Surface Species Formed on the Ru/Carbon Catalyst during 2-Propanol Dehydrogenation. The reaction mechanism previously proposed for 2-propanol dehydrogenation (Eqs. 6—9)[7] seems to be responsible for the Ru/carbon catalyst as well.

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CHO_{ads} + H_{ads}, \tag{6}$$

$$(CH_3)_2CHO_{ads} \longrightarrow (CH_3)_2CO_{ads} + H_{ads}, \tag{7}$$

$$(CH_3)_2CO_{ads} \longrightarrow (CH_3)_2CO, \tag{8}$$

$$H_{ads} + H_{ads} \longrightarrow H_2. \tag{9}$$

As is apparent from the constitutions of the product hydrogen as the mixture of H_2, HD, and D_2, hydrogen molecules are formed irrespective of the groups to which the hydrogen atoms previously belonged.

The H/D ratio of gaseous hydrogen produced from $(CH_3)_2CHOD$ was slightly smaller than unity during the initial stage, whereas the H/D ratio from $(CH_3)_2CDOH$ exceeded unity to some extent. It is therefore conceivable that the hydroxyl group of 2-propanol is dissociated more easily than its methine group, while supplying an excess amount of isopropoxyl and hydrogen species adsorbed on the catalyst surface. A gradual increase in the H/D ratio of gaseous hydrogen indicates that the methyl and methine hydrogen atoms of either $(CH_3)_2CHOD$ or $(CH_3)_2CDOH$ exchange with the surface deuterium species directly, but slowly.

The low extent of H–D exchange between the surface hydrogen species and acetone was also confirmed by the fact that most of the gaseous hydrogen which evolved from the $(CH_3)_2CHOH/(CD_3)_2CO$ (90/10 mixed by volume) solution was H_2. The possibility of acetone adsorption in its enol form[15] is therefore unlikely on a Ru/carbon catalyst.

Hydrogen Transfer from 2-Propanol to Acetone. Acetone hydrogenation is thermodynamically more favorable than 2-propanol dehydrogenation in temperature regions as low as the boiling point of 2-propanol (82.4 °C).[4] Under boiling conditions, however, hydrogen evolution took place catalytically, even at 77.0 °C, from the 2-propanol/acetone (90/10 mixed by volume) solution.

The small extents of deuterium incorporation from pre-adsorbed deuterium or from gaseous deuterium under the reaction conditions indicate that either an intermediation of pre-adsorbed hydrogen or a dissolution and adsorption of gaseous hydrogen are insignificant for the reaction. Once expelled from the reaction medium to the gas phase, the product hydrogen becomes indifferent to the catalysis under refluxing conditions. The observed rate retardation due to acetone (1/2.95 times in the 90/10 mixed solution) would be ascribed to the following two factors: (i) occupation of sites active for 2-propanol dehydrogenation and (ii) consumption of surface hydrogen by adsorbed acetone through hydrogen transfer from 2-propanol.

As for the 2-propanol/acetone-d_6 (90/10) mixed solution, hydrogen transfer from 2-propanol to acetone is described as

$$(CH_3)_2CHOH(l) + (CD_3)_2CO_{ads} \longrightarrow (CD_3)_2CHOH(l) + (CH_3)_2CO_{ads}. \tag{10}$$

The surface hydrogen species supplied from 2-propanol is consumed not only by evolving gaseous hydrogen, but also by converting $(CD_3)_2CO$ into $(CD_3)_2CHOH$ (Eqs. 11—14):

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CO_{ads} + 2H_{ads}, \tag{11}$$

$$(CD_3)_2CO \longrightarrow (CD_3)_2CO_{ads}, \tag{12}$$

$$(CD_3)_2CO_{ads} + 2H_{ads} \longrightarrow (CD_3)_2CHOH, \qquad (13)$$

and

$$(CH_3)_2CO_{ads} \longrightarrow (CH_3)_2CO. \qquad (14)$$

Eq. 13 is eventually the reverse process of 2-propanol dehydrogenation(Eqs. 6 and 7).

Even through hydrogen transfer proceeded rapidly from $(CH_3)_2CHOH$ to $(CD_3)_2CO$, deuterium was incorporated into the methine and hydroxyl groups infinitesimally. As is evident from the ^{2}H NMR spectra shown in Fig. 6, $(CH_3)_2CO$ and $(CD_3)_2CHOH$ were yielded predominantly during the dehydrogenation of $(CH_3)_2CHOH$ in the presence of $(CD_3)_2CO$.

After the reaction of 2-propanol-d for 5 h, deuterium in the methine and methyl groups of 2-propanol-*d* amounted to 3.17 and 2.97%, respectively (Table 1). H–D exchange of the methine group proceeded more extensively than that of the methyl group per hydrogen atom (3.17/1 vs. 2.97/6), which strongly suggests that the surface deuterium species is incorporated through a transfer reaction to acetone (Eq. 15) more efficiently than through an exchange reaction with methyl hydrogen (Eq. 16):

$$(CH_3)_2CO_{ads} + 2D_{ads} \longrightarrow (CH_3)_2CDOD, \qquad (15)$$

and

$$(CH_3)_2CHOD + D_{ads} \longrightarrow (CH_3)(CH_2D)CHOD + H_{ads}. \qquad (16)$$

The reactions of hydrogen transfer and hydrogen evolution ought to proceed simultaneously, since the rate of either Eq. 13 or Eq. 15 is large.

Reaction Mechanism of 2-Propanol Dehydrogenation on the Ru/Carbon Catalyst. The isotope effects for hydrogen evolution from 2-propan-2-*d*-ol and 2-propanol-*d* with a suspended Ru/carbon catalyst were obtained during the initial stage as 1.57 and 1.69, respectively.

It should not be assumed that splitting the methine C–H bond is difficult, since the magnitude (1.57) is rather small as a primary isotope effect for the elimination of β-hydrogen[16] and is preceded by the magnitude obtained from 2-propanol-*d*.

Provided that the formation of molecular hydrogen from the surface hydrogen species is the slowest step, these magnitudes and tendency of the isotope effects become conceivable. More abundant deuterium species were supplied from $(CH_3)_2CHOD$ than from $(CH_3)_2CDOH$ on the catalyst surface, as indicated by the difference between 0.65 and 1.7 in the H/D ratios of molecular hydrogen formed during the initial stage. It should also be noted that the magnitudes of the k_H/k_D obtained from $(CH_3)_2CDOH$ and $(CH_3)_2CHOD$ are comparable to those for the formation of molecular hydrogen from metal hydride complexes, i. e., $Co(H)_2$-$P(OCH_3)_3]_4^+$ (k_H/k_D=1.51 at 23 °C)[17] and $[Ir(H)_2(CO)_2(PMePh_2)_2]^+$(2.1 at 20 °C).[18]

As $(CH_3)_2CDOH$ changed appreciably into $(CH_3)_2$-CHOD on the catalyst (Table 1), the dissociation and formation processes of the methine C–H bond were facile. These distinctive characteristics of the Ru/carbon catalyst would be the reason for its superiority regarding the activity of 2-propanol dehydrogenation.[14] The splitting process of the methine C–H bond has been considered to be the most difficult step for catalytic 2-propanol dehydrogenation.[19]

New abilities for easy desorption of both acetone and hydrogen should be added to the Ru/carbon catalyst from the viewpoint of designing a catalyst most suitable for 2-propanol dehydrogenation in a chemical heat pump system.

Conclusive Remarks

The suspended Ru/carbon catalyst exhibited the following characteristics for 2-propanol dehydrogenation: i) highly selective and active performance under boiling conditions, ii) relatively small isotope effects, being larger for $(CH_3)_2CHOD$ than $(CH_3)_2CDOH$, iii) simultaneous occurrence of hydrogen evolution and hydrogen transfer from 2-propanol to acetone on the catalyst surface, and iv) the slowest step presumed not to be the splitting process of the methine C–H bond but to be the formation of molecular hydrogen from the surface hydrogen species.

Further improvements of the Ru/carbon catalyst are necessary, especially regarding easy desorption of both acetone and hydrogen.

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