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Mechanism of 2-Propanol Dehydrogenation with Suspended Nikel Fine-Particle Catalyst

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Selective dehydrogenation of 2-propanol was performed with a suspended nickel fine-particle catalyst at high activity under refluxing conditions. The isotope effects, k_H/k_D, for $(CH_3)_2CDOH$ and $(CD_3)_2CDOD$ were found to be 2.56 and 2.69, respectively, in contrast to 1.68 for $(CH_3)_2CHOD$, suggesting that the C–H bond dissociation at the methine position is rate-determining. With regard to $(CH_3)_2CHOD$ and $(CH_3)_2CDOH$, a distinct difference was observed for the deuterium distributions among the liquid-phase components after the reaction, since deuterium transfer from the hydroxyl to the methyl and other groups proceeded tremendously for $(CH_3)_2CHOD$, whereas the methine group of $(CH_3)_2CDOH$ changed little, even after a 5-h reaction under refluxing conditions. This contrast was well accounted for by the difficult splitting of the methine C–H bond and the facile dissociation of the hydroxyl group, in addition to a gradual H–D exchange due to the keto-enol equilibriation of the adsorbed acetone and the hydrogen transfer from 2-propanol to acetone. Distributions of H_2, HD, and D_2 were interpreted as well, which varied with the reaction periods and the kinds of substrates. Based on the proposed mechanism, strategies for a catalyst improvement suitable for a newly-proposed chemical heat pump system are discussed.

Industrial processes concerning 2-propanol dehydrogenation are carried out on heterogeneous catalysts above 300 °C,[1] since the change in the standard Gibbs free energy becomes negative at high temperature.[2]

2-Propanol dehydrogenation over zinc oxide was investigated by Teichner et al., who concluded that the dissociation of the methine C–H bond is rate-determining.[3] The reaction mechanism was discussed later by Krylov regarding various solid catalysts; the importance of the enol-type adsorption of acetone was pointed out.[4] The dissociation of 2-propanol into isopropoxide and hydrogen surface species on zinc oxide, followed by enforced desorption of acetone with the adsorbed isoproxide species, was revealed by Tamaru et al.[5] The desorption process of 2-propanol from the zinc oxide surface, itself, was studied by Kemball et al. up to a temperature of 300 °C.[6]

Even at a temperature as low as 82.4 °C, however, the reaction can proceed under boiling conditions, since the produced hydrogen is removed from the reaction medium immediately after its formation (Eq. 1).

$$(CH_3)_2CHOH(l) \rightarrow (CH_3)_2CO(l) + H_2(g). \qquad (1)$$

Actually, suspended copper chromite and Raney nickel catalysts proved to be active for 2-propanol dehydrogenation under refluxing conditions.[7,8]

Boudart et al. analyzed the reaction using a suspended nickel boride catalyst using the following equation, in which the rate retardation caused by acetone adsorption was taken into account:[9]

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

where v is the reaction rate, k the rate constant and K the equilibrium constant of acetone adsorption, respectively.

Recently, highly active nickel fine-particle catalysts (116 $\text{mmol h}^{-1}\text{g}^{-1}$), prepared by a gas-evaporation method,[10] were reported by Saito et al., where the same rate equation (2) was ascertained to hold for 2-propanol dehydrogenation.[11] Efficient catalysts for reaction (1) are indispensable to a newly-proposed chemical heat pump system,[12] which raises the temperature of low-quality heat from 80 °C to a more valuable temperature of 200 °C.

In the present paper, the mechanism of the nickel fine-particle catalyst is elucidated in order to obtain strategies for catalyst improvement suitable for 2-propanol dehydrogenation in the newly-proposed chemical heat-pump system.

Experimental

A prescribed amount (200 mg) of the nickel fine-particle catalyst (supplied by Vacuum Metallurgical Co. with an average particle diameter of 20 nm and a specific surface area (BET) of 43.7 $m^2 g^{-1}$, Lot. No. 2180) was laid in a Schlenk flask (20 ml). The catalyst was preheated at 160 °C for 1 min under a hydrogen atmosphere, by which a part of the surface oxide was removed from the nickel fine particles. The catalyst was well suspended in 2-propanol by an ultrasonic treatment (Kaijyo Denki Co., Sona 50a) at room temperature for 1 min under an argon atmosphere.

Three kinds of deuterium-substituted 2-propanol, i.e., $(CH_3)_2CHOD$, $(CH_3)_2CDOH$, and $(CD_3)_2CDOD$, in addition to $(CD_3)_2CO$ (all supplied by the Division of Merck, Frost Inc.) were used without further purification. After the catalyst suspension was heated at the boiling temperature with an oil bath kept at 100 °C, the amount of evolved gas was determined time-sequentially with a gas burette (250 ml) through a refluxing condenser. Gaseous products were collected at the exit of the reaction vessel.

Both gaseous and liquid-phase products were analyzed by gas chromatography with MS-5A and PEG 1000 columns, respectively.

The deuterium distribution of molecular hydrogen was monitored by a quadrupole-type mass spectrometer (NEC Anerva Co., AQA 360), whereas an FT-NMR spectrometer (JEOL Co., GX-270) was used for analyzing the liquid-phase components both before and after the reaction.

Results

Dehydrogenation of Deuterium-Substituted 2-Propanol. The nickel fine-particle catalyst was dispersed in 2-propanol at a concentration ten-times larger than that examined previously.[11] 2-Propanol dehydrogenation proceeded at 82.4 °C under boiling conditions (heat at 100 °C) at high activity and selectivity in a densely suspended solution as well (Fig. 1). The exclusive formation of hydrogen and acetone was confirmed in the gaseous- and liquid-phase components, respectively. The reaction rates and the deuterium distributions were reproducible satisfactorily.

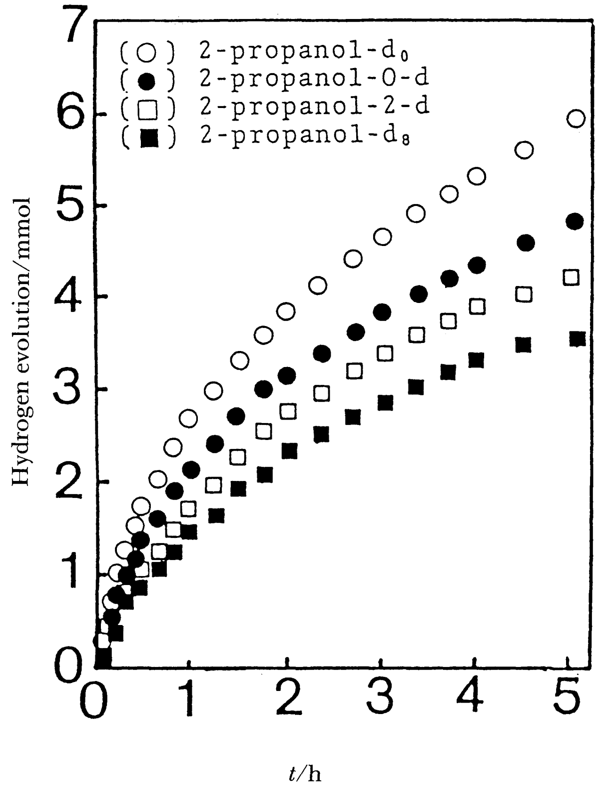

Fig. 1. Dehydrogenation of deuterium-substituted 2-propanol with the suspended nickel fine-particle catalyst (200 mg) at 82.4 °C under refluxing conditions (heat at 100 °C).

A preheat treatment of the nickel fine-particle catalyst under a hydrogen atmosphere was necessary in order to exhibit the dehydrogenation activity.[13] It was revealed that the reaction rates were substantially indifferent to the conditions of a reduction performed with either H_2 or D_2.

The initial rates of hydrogen evolution from 2-propanol-d_0, -O-d, -2-d and -d_8 are summarized in Table 1. Since the gradual decrease of the reaction rates was ascribed to retardation due to the product acetone (Eq. 2),[11] the rate constant k [mmol h^{-1} g^{-1}] was given by the observed initial reaction rate.

As shown in Table 1, the isotope effects, k_H/k_D, related to the methine hydrogen of 2-propanol were obtained as large as 2.56 and 2.69 from 2-propanol-2-d and d_8 respectively, with reference to 2-propanol-d_0 and the catalyst pre-reduced by H_2.

On the contrary, the isotope effect concerning the hydroxyl hydrogen was rather small (k_H/k_D: 1.68 for 2-propanol-O-d).

Table 2. Deuterium Distribution in the Product Hydrogen Evolved from Deuterium-Substituted 2-Propanol at 82.4 °C under Refluxing Conditions (heat at 100 °C) with Nickel Fine-Particle Catalyst

Deuterium-substituted 2-propanol	Preheated atmosphere	Product hydrogen/%		
		H_2	HD	D_2
d_0	H_2	100	0	0
d_0	D_2	100	0	0
O-d	H_2	42.2	41.2	16.6
2-d	H_2	79.0	19.8	1.2
d_8	H_2	0.73	6.37	92.7

Pretreatment of catalyst: Heated at 160 °C for 1 min under hydrogen atmosphere. Catalyst solution: Suspension of 200 mg in 2-propanol (5 ml). Reaction conditions: Refluxing for 5 h under atmospheric pressure.

Table 1. Dehydrogenation of Deuterium-Substituted 2-Propanol at 82.4 °C under Refluxing Conditions (heat at 100 °C) with Nickel Fine-Particle Catalyst and Kinetical Isotope Effect

Deuterium-substituted 2-propanol	Preheat atmosphere	Conversion	Initial rate	Isotope effect
		%	mmol g^{-1} h^{-1}	k_H/k_D
d_0[a)]	H_2	9.36	81.3	—
d_0	D_2	9.33	78.1	1.04
O-d	H_2	7.68	48.5	1.68
2-d	H_2	6.71	31.8	2.56
d_8	H_2	6.39	30.2	2.69

a) -d_0 stands for undeuterated. Pretreatment of catalyst: Heated at 160 °C for 1 min under hydrogen atmosphere. Catalyst solution: Suspension of 200 mg in 2-propanol (5 ml). Reaction conditions: Refluxing for 5 h under atmospheric pressure.

Deuterium Distribution in the Product Hydrogen. Even when the catalyst was preheated under a D_2 atmosphere, the gaseous product of 2-propanol-d_0 dehydrogenation was found to be H_2 exclusively. The amount of surface deuterium species left after the pretreatment of D_2 reduction is therefore negligible.

As shown in Table 2, the gaseous products of 2-propanol-O-*d* and 2-*d* were found to be the mixture of H_2, HD, and D_2, as shown in the following equations:

$$(CH_3)_2CHOD(l) \rightarrow (CH_3)_2CO(l) + H_2,\ HD,\ D_2(g), \quad (3)$$

and

$$(CH_3)_2CDOH(l) \rightarrow (CH_3)_2CO(l) + H_2,\ HD,\ D_2(g). \quad (4)$$

The product hydrogen was more abundant with H_2 from 2-propanol-2-*d* than from 2-propanol-O-*d*.

Figure 2 shows the deuterium distribution of newly-evolved hydrogen from 2-propanol-O-*d* as a function of time. H_2 gradually increased at the expense of both HD and D_2.

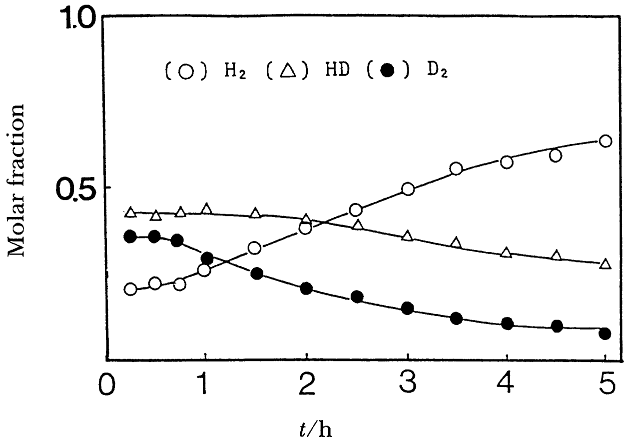

Fig. 2. Variation among the molar fractions of H_2, HD, and D_2 in hydrogen evolved from 2-propanol-O-*d* as a function of time.

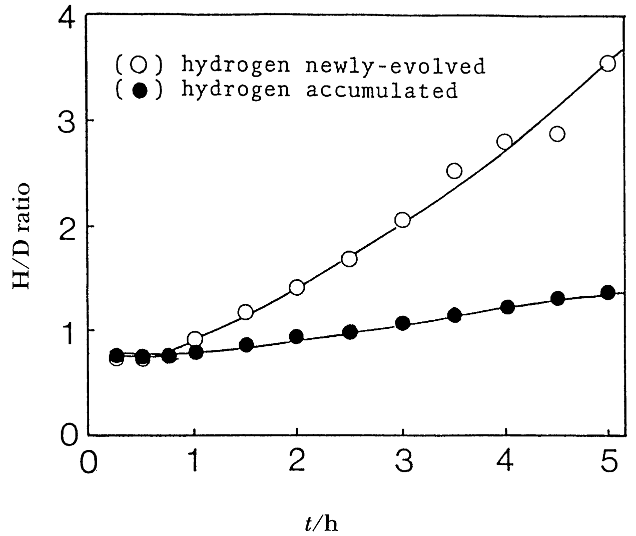

Fig. 3. H/D ratio in newly-evolved hydrogen and the one accumulated till the time concerned.

The time dependence of the deuterium distribution, represented as the H/D ratio in the product hydrogen, was more sensitive to newly-evolved hydrogen than to that accumulated in the gas burette (Fig. 3). The latter was obtained by combining the composition with the amount of hydrogen. Since the reaction rate gradually decreased, the variation of the deuterium distribution in the newly-evolved hydrogen was smoothed out in the accumulated hydrogen during the reaction period from the beginning until the time concerned.

As for 2-propanol-O-*d*, the H/D ratio of the newly-evolved hydrogen gradually increased from 0.82 at the intitial stage to 3.55 after 5 h along with the reaction progress.

Deuterium Distribution Among the Liquid-Phase Components. The ^{2}H NMR spectra for the solutions of 2-propanol-O-*d*, 2-*d* and d_8 after a dehydrogenation reaction for 5 h are shown in Fig. 4.

The deuterium spectral peaks changed variously. Many deuterium atoms were transferred from the hydroxyl group to the methyl and methine groups of 2-propanol-O-*d*. The strongest peak was not observed at the hydroxyl position but, rather, at the methyl position of 2-propanol (Fig. 4A). On the contrary, most of the deuterium atoms in the methine group of

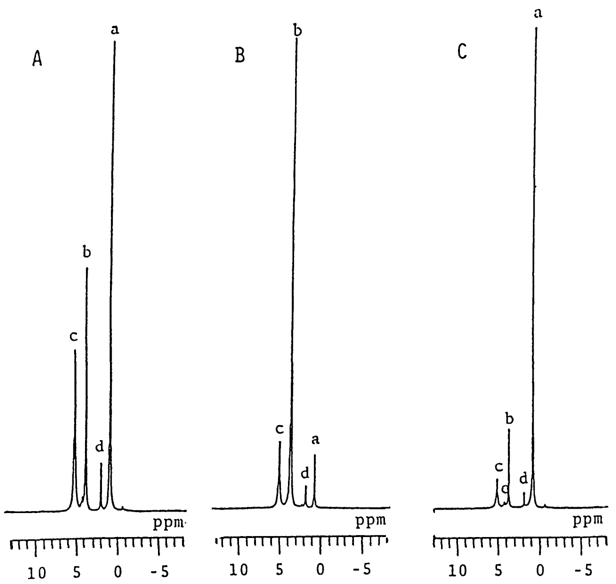

Fig. 4. ^{2}H NMR spectra of $(CH_3)_2CHOD$ (A), $(CH_3)_2CDOH$ (B), and $(CD_3)_2CDOD$ (C) solutions after 5-h reaction with the suspended nickel fine-particle catalyst (200 mg) at 82.4 °C under refluxing conditions (heat at 100 °C).

Peaks identified as 2-propanol methyl (a), methine (b), and hydroxyl (c) groups, acetone (d) and deuterium oxide (e).

$Si(CD_3)_4$ was used as the standard reference (0.0 ppm).

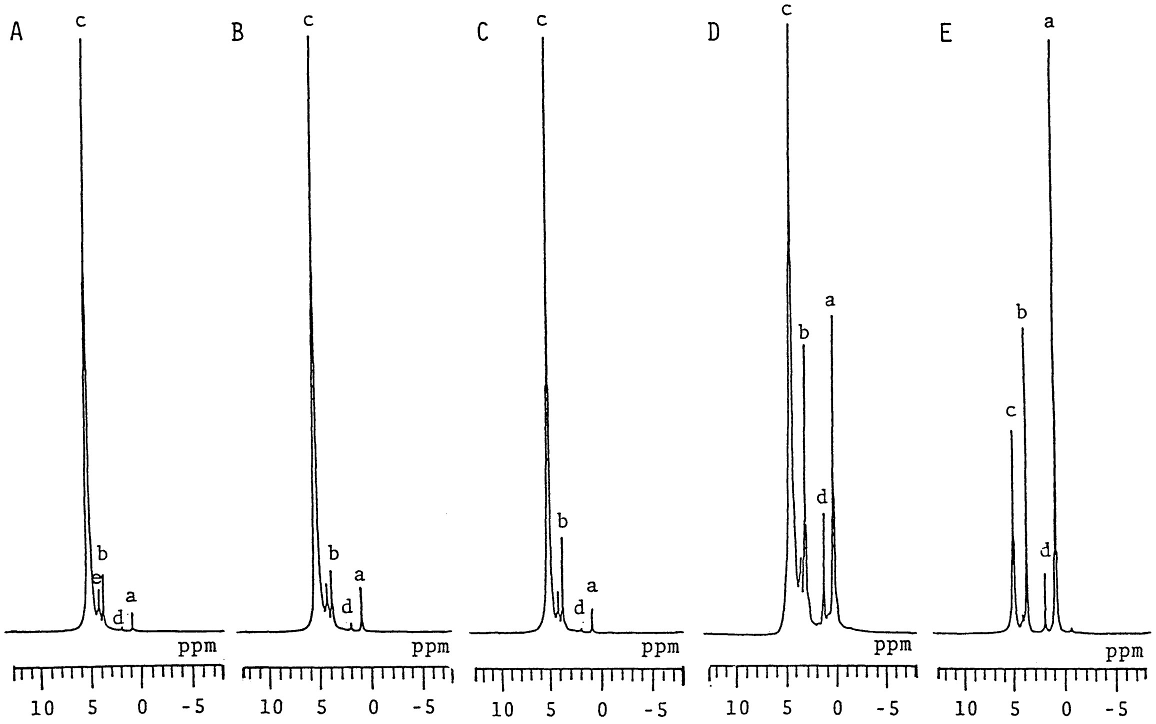

Fig. 5. ^{2}H NMR spectra of 2-propanol-O-*d* after 1/4 h (A), 1 h (B), 2 h (C), and 3 h (D) and 5 h (E) reactions with the suspended nickel fine-particle catalyst (200 mg) at 82.4 °C under refluxing conditions (heat at 100 °C).
Peaks idenified as 2-propanol methyl (a), methine (b), and hydroxyl (c) groups, acetone (d), and deuterium oxide (e) and set as 95% height for the strongest one in each chart.
$Si(CD_3)_4$ was used as the standard reference (0.0 ppm).

2-propanol-2-*d* remained unchanged, though a small amount of deuterium was found at the methyl and hydroxyl groups of 2-propanol (Fig. 4B). The deuterium transfer to acetone was clearly larger from the hydroxyl group than from the methine group of 2-propanol, corresponding to the extents of transfer to the other groups of 2-propanol. As for 2-propanol-d_8, the deuterium peak at the hydroxyl position changed rather extensively, while the other peaks exhibited the smallest variations (Fig. 4C).

A remarkable change which took place in the liquid-phase deuterium distribution of 2-propanol-O-*d* was demonstrated in the ^{2}H NMR spectra after reactions for 1/4, 1, 2, 3, and 5 h time-sequentially (Fig. 5). It should be noted that the deuterium peak at the methine position of 2-propanol increased more rapidly than did the other peaks until 2 h, whereas an extensive change of the hydroxyl peak and a simultaneous increase in the methyl deuterium of 2-propanol became apparent only after 2 h.

Rate Retardation in 2-Propanol Dehydrogenation Due to Acetone. In order to elucidate the retardation effect of acetone on the dehydrogenation rate of 2-propanol, the amounts of hydrogen evolved from solutions of 2-propanol, including acetone-d_6 of 0, 4 and 20 wt%, were pursued as a function of time (Fig. 6). A concentration of 4 wt% corresponded to the

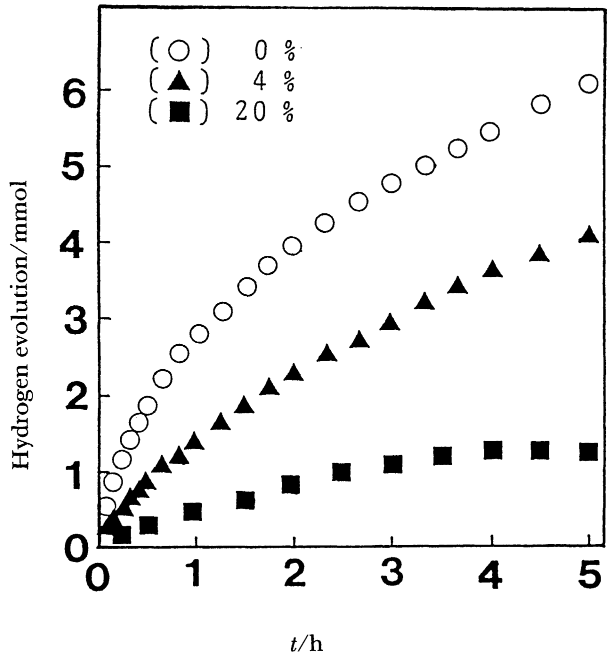

Fig. 6. Dehydrogenation of 2-propanol including acetone-d_6 of 0, 4, and 20 wt% with the suspended nickel fine-particle catalyst (200 mg) at 82.4 °C under refluxing conditions (heat at 100 °C).

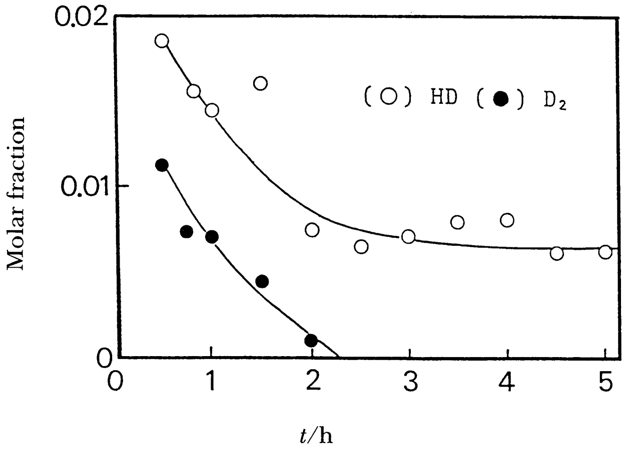

Fig. 7. Variation of HD and D_2 molar fractions in hydrogen evolved from the mixture of 2-propanol-d_0 and acetone-d_6 (4 wt%).

Table 3. Deuterium Distribution among Liquid-Phase Components Yielded from the Mixture of $(CH_3)_2CHOH$ and $(CD_3)_2CO$ (10 vol%) after 1-h or 5-h Reaction with Nickel Fine-Particle Catalyst at 82.4 °C under Refluxing Conditions (heat at 100 °C)

Reaction time/h	Deuterium distribution/% 2-propanol			Acetone
	Methyl	Methine	Hydroxyl	
0	0.00	0.00	0.00	100.00
1	49.5	3.2	19.7	27.7
5	60.1	5.1	17.2	17.7

Catalyst pretreatment: Heated at 160 °C for 1 min under H_2. Catalyst solution: Suspension of 200 mg in the mixed solution (5 ml).

amount of acetone yielded from neat 2-propanol during the 2-h reaction.

The deuterium distribution in hydrogen evolved from a mixed solution of 2-propanol and acetone-d_6 (4 wt%) showed that both HD and D_2 were appreciably formed only during the initial stage (Fig. 7). From the ^{2}H NMR spectra of a solution mixed with 2-propanol and acetone-d_6 (20 wt%) after the 1- and 5 h reactions, it was found that the deuterium atoms of acetone were transferred mainly to the methyl position of 2-propanol. The variations of the deuterium distribution with the reaction time are summarized in Table 3.

Discussion

Adsorbed Species on the Catalyst Surface. The relatively large molar fractions of HD and D_2 evolved from 2-propanol-O-*d* during the initial stage (Figs. 2 and 3) suggest that 2-propanol adsorbs on the catalyst surface by a facile dissociation of its hydroxyl group. The present view of easy O-D splitting is supported by the fact that an extensive HD exchange was observed among the liquid-phase components after a 5 h reaction for 2-propanol-O-*d*, in contrast to 2-*d* (Fig. 4). The methine C-H bond of adsorbed isopropoxide is rather strong and difficult for dissociation.

$$(CH_3)_2CHOD(l) \rightarrow (CH_3)_2CHO_{ads} + D_{ads}. \qquad (5)$$

It is, therefore, deduced that the nickel fine-particle catalyst is covered with the isopropoxide and hydrogen surface species to appreciable extents during the reaction.

The adsorbed acetone is equilibriated rapidly between the keto and enol forms on the catalyst surface,[14] since many deuterium atoms were introduced to acetone during the dehydrogenation of 2-propanol-O-*d* (Figs. 4 and 5).

$$(CH_3)_2CO_{ads} \rightleftarrows CH_2{=}CO{-}CH_{3ads} + H_{ads}. \qquad (6)$$

The appearance of deuterium during the earliest stage of the reaction as a gaseous product from acetone-d_6 confirms the view concerning the rapid keto-enol equilibrium of adsorbed acetone (Fig. 7).

Hydrogen Transfer from 2-Propanol to Acetone during 2-Propanol Dehydrogenation. The rapid conversion of acetone-d_6 (20 wt% in 2-propanol-d_0) into the methyl part of 2-propanol (Table 3) strongly suggests that hydrogen transfer from 2-propanol to acetone proceeds on the catalyst surface (Eq. 7)[15] simultaneously with hydrogen evolution.

$$(CD_3)_2CO + (CH_3)_2CHOH \rightarrow (CD_3)_2CHOH + (CH_3)_2CO. \qquad (7)$$

The rapid deuterium incorporation from OD into the methine group during the early stage of 2-propanol-O-*d* dehydrogenation (<2 h, Fig. 5) supports the mechanism of hydrogen transfer from 2-propanol to acetone.

The extensive substitution of the methyl hydrogen with deuterium observed during the later stage (>2 h, Fig. 5) is well interpreted in terms of both the keto-enol equilibrium occurring in the product acetone (Eq. 6) and the hydrogen transfer from 2-propanol to acetone (Eq. 7).

These two processes (Eqs. 6 and 7) account for the gradual predominance of H to D species on the surface as well, which was demonstrated by the H/D ratio in the product hydrogen (Fig. 3), especially during the later stage of 2-propanol-O-*d* dehydrogenation.

The sharp contrast in deuterium distribution observed for the product hydrogen from 2-propanol-O-*d* and 2-*d* after the 5-h reaction (Table 2) is ascribed not only to the facile dissociation of the hydroxyl group (Eq. 5) but also to the rapid keto-enol equilibrium (Eq. 6) and the easy hydrogen transfer (Eq. 7).

Rate-Determining Step in 2-Propanol Dehydrogenation. The isotope effects, k_H/k_D, for the dehydrogenation of 2-propanol-2-*d* and d_8 were obtained at 82.4 °C as large as 2.56 and 2.69, respectively, in contrast to 2-propanol-O-*d* of 1.68 (Fig. 1 and Table 1).

The primary isotope effect for eliminating β-hydrogen from the adsorbed propyl species on an aluminium film was reported to be 2.6 at 247 °C.[16] The apparent coincidence in magnitudes suggests that the rate-determining step is the C–H bond dissociation of the methine hydrogen (Eq. 8), which is reconciled with the kinetical conclusion deduced for zinc oxide by Teichner et al.[3]

$$(CH_3)_2CHO_{ads} \rightarrow (CH_3)_2CO_{ads} + H_{ads}. \qquad (8)$$

The rate-determining step of the methine C–H dissociation is succeeded by the formation and desorption step of molecular hydrogen:

$$2H_{ads} \rightarrow H_2. \qquad (9)$$

Recently, the dehydrogenation rates with a ruthenium catalyst supported on carbon were revealed to be in the order $(CH_3)_2CHOH > (CH_3)_2CDOH > (CH_3)_2CHOD$ under boiling and refluxing conditions, for which the rate-determining step was deduced as the process mentioned above (Eq. 9).[17] On the other hand, the amounts of species adsorbed on the surface can affect the availability of sites for splitting the methine C–H bond of the isopropoxyl moiety. Hence, the predissociation process of the hydroxyl group (Eq. 5) would be relevant to the small, but unnegligible, isotope effects observed for $(CH_3)_2CHOD$ vs. $(CH_3)_2CHOH$ or $(CD_3)_2CDOD$ vs. $(CH_3)_2CDOH$ on the nickel fine-particle catalyst.

Strategies of Catalyst Improvement Suitable for the Newly-Proposed Chemical Heat Pump System. The newly-proposed chemical heat pump[12] requires a catalyst with high selectivity, long life and large space-time yield for 2-propanol dehydrogenation in the presence of acetone.

The strategies for catalyst improvement of the rate constant and the retardation constant consist of: (1) facilitating C–H bond splitting at the methine position and (2) obstructing acetone adsorption in order to avoid any undesirable active-site occupation and hydrogen transfer on the surface.

The reaction rate constant of the nickel fine-particle catalyst (96.9 mmol h^{-1} (metal-g)$^{-1}$) was surpassed by the Ru/carbon catalyst (4630 mmol h^{-1} (metal-g)$^{-1}$),[18] for which the formation and desorption step of molecular hydrogen was elucidated to be rate-determining.[17] Consequently, 2-propanol would be dehydrogenated rapidly as long as the methine C–H bond is easily split.

The adsorption strength of acetone seems to be large with regard to the enol-type surface species. In contrast to the nickel fine-particle catalyst, it was observed that the keto-enol isomerization occurred little on the Ru/carbon catalyst.[17] A larger retardation constant due to acetone adsorption obtained for nickel (0.066 mmol dm^{-3}) than for ruthenium (0.017 mmol dm^{-3})[18] is ascribed to the mode of adsorption (at least partly), since no enol-type species was formed for the latter, according to an ^{2}H NMR analysis.[17]

Conclusion

(1) The nickel fine-particle catalyst exhibited high selectivity and activity for 2-propanol dehydrogenation at concentrations ten-times larger than those examined previously, with an accompanying rate retardation due to acetone.

(2) The large isotope effects, k_H/k_D, of 2.56 and 2.69 for $(CH_3)_2CDOH$ and $(CD_3)_2CDOD$, respectively, suggested that the C–H dissociation process at the methine position is rate-determining, whereas the unnegligible magnitude of 1.68 for $(CH_3)_2CHOD$ would be related to the predissociation process of the hydroxyl group.

(3) The keto-enol equilibriation of adsorbed acetone proceeded rapidly on the catalyst surface, which would make a certain unfavorable contribution to rate retardation.

(4) The hydrogen transfer from 2-propanol to acetone proceeded simultaneously with the evolution of molecular hydrogen from 2-propanol.

(5) Catalysts more suitable for the chemical heat pump system would be developed by fascilitating methine C–H dissociation and by avoiding enol-type acetone adsorption.

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