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Reaction Mechanism of 2-Propanol Dehydrogenation with a Carbon-Supported Ru–Pt Composite Catalyst in the Liquid Phase

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The liquid-phase dehydrogenation of $(CH_3)_2CHOH$, $(CH_3)_2CHOD$, and $(CH_3)_2CDOH$ to yield acetone and molecular hydrogen was performed selectively under boiling and refluxing conditions by heating a suspended solution of a carbon-supported ruthenium and platinum composite catalyst. The Ru–Pt/carbon composite catalyst gave kinetic isotope effects of 1.54 and 1.96 for dehydrogenation at 82.4 °C from $(CH_3)_2CHOD$ and $(CH_3)_2CDOH$, respectively, which were contrasted to the corresponding magnitudes of 1.69 and 1.57 with a Ru/carbon catalyst and those of 1.13 and 1.81 with a Pt/carbon catalyst. The rate constants of dehydrogenation as a function of the H/D ratio in molecular hydrogen suggest that the step to form molecular hydrogen from surface hydrogen species was slow on the Ru catalyst, whereas the step to split the methine C–H bond was rather difficult for the Pt and Ru–Pt catalysts. Reflecting the facile dissociation at the hydroxy group on the catalyst surface, deuterium transfer from the hydroxy to the methyl groups of both acetone and 2-propanol proceeded tremendously for $(CH_3)_2CHOD$.

A large number of studies about fuel cells has been conducted. With regard to direct methanol fuel cells (DMFCs), decrements of a large overpotential for methanol oxidation and of methanol crossover from the anode side to the cathode seem to be inevitable for its practical use. Recently, Qi et al. have studied the electrochemical performance of direct 2-propanol fuel cells (D2PFCs) using Ru–Pt and Pt blacks as the anode and cathode, respectively, and reported that D2PFCs exhibit a higher cell voltage at a current density of less than about 100 mA/cm^2 at 61 °C and a much smaller crossover rate than those of DMFCs.[1] Umeda et al. have reported that acetone is the only oxidation product of 2-propanol around the anode surface of D2PFCs.[2]

Catalytic 2-propanol dehydrogenation, shown in Eq. 1, proceeds selectively under boiling and refluxing conditions, as proved with suspended copper chromite,[3] Raney nickel,[4] nickel boride,[5] nickel fine particles prepared with a gas-evaporation technique,[6] carbon-supported ruthenium,[7] and ruthenium–platinum composite metal (Ru–Pt/carbon).[8] The Ru–Pt/carbon catalyst gave higher activity and selectivity for 2-propanol dehydrogenation than the other, where the activity became the largest at the atomic ratio of ruthenium/platinum = 1/1.[8]

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

The substrate 2-propanol and the reaction products of both acetone and hydrogen are removed from the liquid-phase reactor and separated by fractional distillation, which is the basis of a catalyst-assisted chemical heat pump system.[9]

In this paper, the reaction mechanism of 2-propanol dehydrogenation with the Ru–Pt/carbon catalyst is elucidated in order to obtain strategies for catalyst designing suitable to D2PFCs and the catalyst-assisted chemical heat pump system.

Experimental

Catalyst Preparation for 2-Propanol Dehydrogenation with Composite Metals. We prepared Ru–Pt/carbon catalysts by reducing an aqueous solution of mixed metal chlorides after adsorption onto active carbon powders. Commercially available powders of highly-porous active carbon (1.9 g, Kansai Netsukagaku Co.), derived from coconut shell and activated with KOH, were used for overnight impregnation at room temperature with an aqueous solution (100 mL) of $RuCl_3 \cdot 3H_2O$ (N. E. Chemcat Co.) and K_2PtCl_4 (Kojima Chemical Co.) mixed in atomic ratio of Ru/Pt = 1/1. An aqueous solution of $NaBH_4$ (900 mg/20 mL) was added dropwise (2 mL/min) at room temperature to the adsorbed metal salts (5 wt % as metal) for reduction in a suspended state. After standing for about 15 min, the carbon-supported catalysts were filtered and washed with a large amount of water (1000 mL). The catalysts were evacuated at 50 °C overnight and kept under nitrogen.

Reaction Procedure for 2-Propanol Dehydrogenation in the Liquid Phase. A prescribed amount (200 mg) of the Ru–Pt/carbon catalyst was dispersed in 5 mL of unlabeled 2-propanol (hereinafter described as 2-propnaol-d_0) ultrasonically (Kaijo Denki Co., Sona 50a) for 10 min in a Schlenk flask (20 mL). After substituting the atmosphere with flowing nitrogen gas, the reactor was heated by an oil bath (100 °C) and agitated by a magnetic stirrer (500 rpm) in order to boil the suspended solution vigorously at 82.4 °C. The product gas was collected in a gas burette (250 mL) through a refluxing condenser for 1.5 h. The reaction products were identified by gas chromatography using an active carbon

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column for gases intermittently and a PEG 20M column for the liquid-phase component after the reaction.

Deuterium Analyses on Gaseous and Liquid Phase Components. The dehydrogenation of deuterium-substituted 2-propanol, i.e., $(CH_3)_2CHOD$ (2-propanol-*O*-*d*) and $(CH_3)_2$-CDOH (2-propanol-2-*d*) was also performed for 1.5 h in the same Schlenk flask (20 mL) and 5 mL of the reactant 2-propanol. The deuterium distribution in the product dihydrogen was determined every fifteen minutes using a quadrupole-type mass spectrometer (NEC Anelva Co., AQA 360), whereas the ^{2}H NMR spectra of the solution were taken after appropriate reaction periods in order to analyze how the substituted deuterium atoms were transferred from the deuterium-substituted substrate to other liquid-phase components by using an FT-NMR spetrometer (JEOL Co., GX-400).

Results and Discussion

Dehydrogenation of Deuterium-Substituted 2-Propanol. 2-Propanol substrates with and without deuterium-substitution were dehydrogenated with the suspended Ru–Pt/carbon catalyst under boiling and refluxing conditions. It was found that the hydrogen evolution rate of 2-propanol-d_0 was apparently higher than that of 2-propanol-*O*-*d*, which was followed by 2-propanol-2-*d*, as shown in Fig. 1.

The hydrogen evolution rates were well analyzed for an appropriate amount (200 mg) of the Ru–Pt/carbon powder catalyst suspended in 100 mL of boiling 2-propanol with use of the following Langmuir-type equation:[8]

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

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

Within a limited conversion range of 2-propanol dehydrogenation, the Ru–Pt/carbon catalyst (200 mg) suspended in a small amount of 2-propanol (5 mL) was well analyzed using the same equation as shown in Fig. 2.

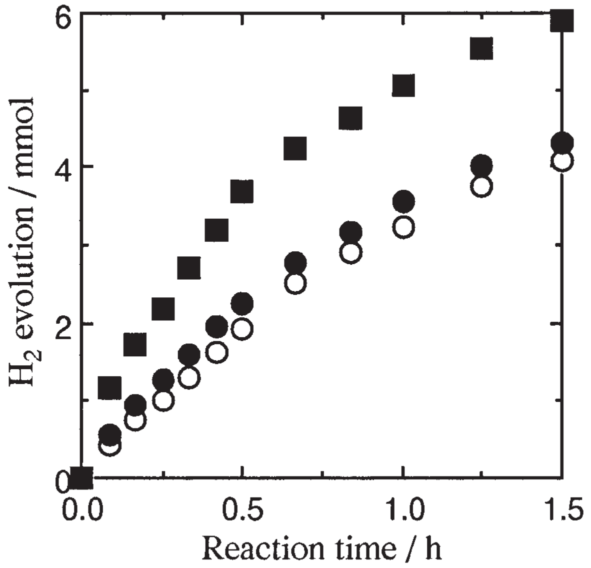

Fig. 1. Time course for the dehydrogenation of 2-propanol-d_0 (■), 2-propanol-*O*-*d* (●), and 2-propanol-2-*d* (○) with Ru–Pt/carbon catalyst under boiling and refluxing conditions (82.4 °C).

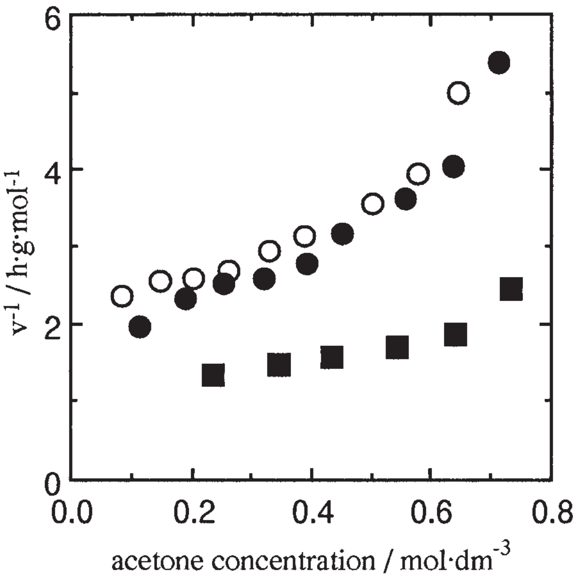

Fig. 2. Langmuir-type analysis for the dehydrogenation of 2-propanol-d_0 (■), 2-propanol-*O*-*d* (●), and 2-propanol-2-*d* (○) with Ru–Pt/carbon catalyst (data taken from Fig. 1).

Deuterium Distributions among the Product Hydrogen. The deuterium distributions of newly-evolved hydrogen from 2-propanol-*O*-*d* and -2-*d* were shown to be a function of the reaction time, Figs. 3a and 3b. At the beginning of the reaction, 2-propanol-*O*-*d* and -2-*d* gave deuterium distributions widely different from each other. Relatively large amounts of deuterium atoms were evolved from 2-propanol-*O*-*d* as HD (40%) and D_2 (10%). On the contrary, the product hydrogen from 2-propanol-2-*d* was mostly H_2, accompanying HD (5%) and D_2 (less than 1%).

The molar fractions of H_2, HD, and D_2 from 2-propanol-*O*-*d* and -2-*d* were found to vary as the reaction time elapsed. With regard to the H/D ratio in the product hydrogen, defined as

$$\text{H/D} = (2 \times [H_2] + [\text{HD}])/(2 \times [D_2] + [\text{HD}]), \tag{3}$$

a gradual increase in the H/D ratio was observed from 2.4 at the beginning of the reaction to 6.6 during the reaction period of 1.5 h for 2-propanol-*O*-*d*, whereas the H/D magnitudes decreased from 30.6 to 7.5 for 2-propanol-2-*d*. It is to be noted that the molar fractions of H_2, HD, and D_2 after the reaction period of 1.5 h reached 80%, 20%, and a trace amount, respectively, regardless of the reactant 2-propanol.

The dissociative adsorption of 2-propanol at its hydroxy group would proceed facile over the catalyst surface. The surface hydrogen atoms from 2-propanol-*O*-*d* ought to contain more D than from -2-*d* besides 2-propoxide. The methine C–H bond of adsorbed 2-propoxide must dissociate as a prerequisite step for hydrogen evolution, since molecular hydrogen is formed from methine and hydroxy hydrogen atoms. Provided that molecular hydrogen is formed from methine and hydroxy hydrogen atoms, the H/D ratio should be unity for 2-propanol-*O*-*d* and -2-*d*. However, the H/D ratios observed for these substrates were much larger than unity. It is therefore reasonable that the H or D atoms of newly-evolved

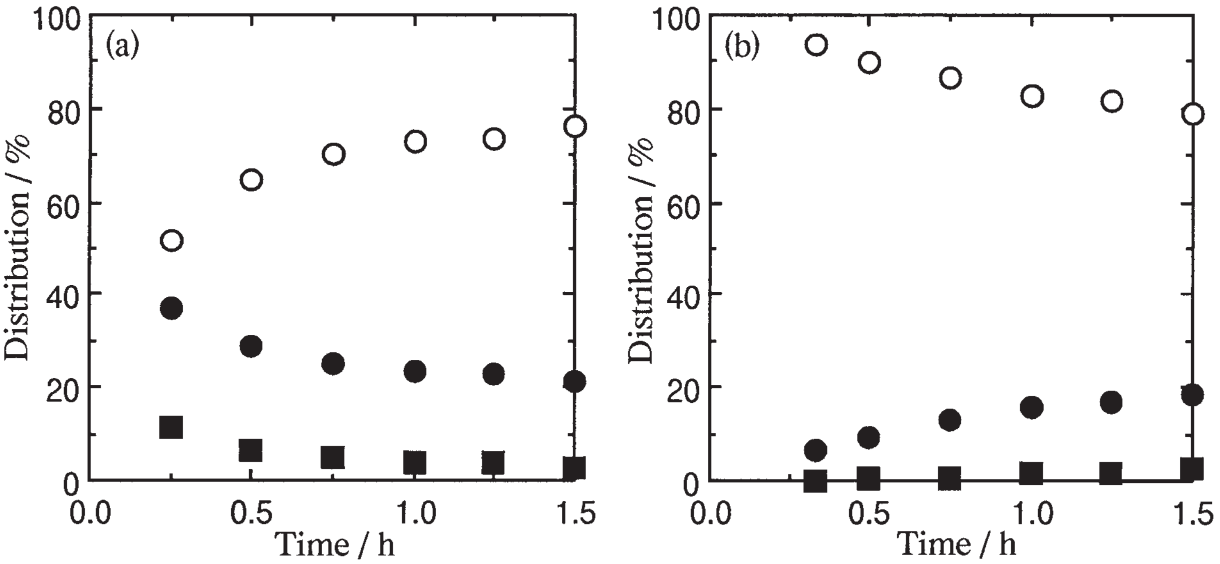

Fig. 3. Time course for the deuterium distribution in molecular hydrogen evolved from 2-propanol-*O-d* (a) and 2-propanol-2-*d* (b) with Ru–Pt/carbon catalyst under boiling and refluxing conditions (82.4 °C). ○: H_2, ●: HD, ■: D_2.

hydrogen are contaminated as a result of time-sequential H–D exchanges among adsorbed organic compounds.

Deuterium Distribution in the Liquid Phase. According to the ^{2}H NMR spectra for the reaction solutions of 2-propanol-*O-d*, the deuterium atoms were transferred from the hydroxy group to the methine and methyl groups of 2-propanol extensively, even after 30 min (Table 1).

The surface deuterium atoms and adsorbed acetone change into 2-propanol-2-*d* as follows:

$$(CH_3)_2CO_{ads} + D_{ads} \rightleftharpoons (CH_3)_2CDO_{ads}, \quad (4)$$

$$(CH_3)_2CDO_{ads} + H_{ads} \rightleftharpoons (CH_3)_2CDOH. \quad (5)$$

During 2-propanol reproduction, many deuterium atoms were thus transferred to the methine group. Moreover, chemical equilibration for adsorbed acetone between its keto and enol forms is rapid on the catalyst surface.[10] During the keto–enol tautomerism, deuterium transfer would also be possible to the methyl group of acetone,

$$(CH_3)_2CO_{ads} \rightleftharpoons CH_2{=}CO{-}CH_{3\,ads} + H_{ads}. \quad (6)$$

The mechanism of this deuterium transfer and the surface hydrogenation of adsorbed acetone would yield methyl-deuterated 2-propanol as one of the solution components from the $(CH_3)_2CHOD$ substrate. Since the H/D ratio of adsorbed hydrogen on the catalyst surface is reflected to that of newly-evolved hydrogen, H–D equilibration on the catalyst surface would result in a gradual increase in the H/D ratio. With regard to 2-propanol-2-*d*, the catalyst surface would be covered mostly with H and 2-propoxide at the beginning stage of the reaction. As the reaction time elapses, deuterium atoms afforded from C–D dissociation of this 2-propoxide are distributed to the catalyst surface, with the H/D ratio gradually decreasing. Deuterium atoms of the substrate are included finally in either gaseous hydrogen or transferred to some other groups of acetone and 2-propanol as a consequence of the keto–enol tautomerism and the surface hydrogenation of the adsorbed acetone. Therefore, it is quite understandable that the H/D ratios of newly-evolved hydrogen from both 2-propanol-*O-d* and 2-propanol-2-*d* were larger than 1, and gradually coincided after the establishment of stationary deuterium distributions.

Reaction Mechanism of 2-Propanol Dehydrogenation on the Ru–Pt/Carbon Catalyst. Based on the experimental results of 2-propanol-*O-d* and -2-*d*, the reaction mechanism of 2-propanol dehydrogenation was reconsidered on the Ru–Pt/carbon catalyst by comparing with the component catalysts of Ru/carbon and Pt/carbon. The kinetic isotope effects for hydrogen evolution from 2-propanol-2-*d* and 2-propanol-*O-d* at the initial stage on a Ru/carbon catalyst were obtained previously as 1.57 and 1.69.[7] Yamashita et al. reported there that the slowest step on the Pt/carbon catalyst was the splitting

Table 1. Deuterium Redistribution during Dehydrogenation of $(CH_3)_2CHOD$

Reactant	Reaction time/h	Deuterium distribution/mmol				
		2-Propanol			Acetone	Water
		Hydroxy	Methine	Methyl	methyl	hydroxy
$(CH_3)_2CHOD$	0	62.2	0.2	0.8	0.0	1.1
	0.5	13.8	20.0	28.3	—*	1.0
	1.5	12.0	18.1	30.8	1.1	0.4

Carbon-supported Ru–Pt (1:1, 5 wt %) 200 mg/5 mL 2-propanol under boiling and refluxing conditions (82.4 °C). *Below the identification limit of ^{2}H NMR.

Table 2. Isotope Effects for Catalytic 2-Propanol Dehydrogenation

Metal catalyst	k_H/k_D		Ref.
	O-d	2-*d*	
Ru	1.69	1.57	7
Pt	1.13	1.81	11

Carbon-supported metal (5 wt %) 200 mg/5 mL 2-propanol under boiling and refluxing conditions (82.4 °C).

process of the methine C–H bond, because the magnitude of the k_H/k_D obtained from 2-propanol-2-*d* was much larger than that obtained from 2-propanol-*O-d*.[11] These isotope effects are summarized in Table 2.

The rate constant of 2-propanol dehydrogenation was derived from the observed reaction rate (v), acetone concentration, and the equilibrium constant of the acetone adsorption (K), to which the magnitude observed for 2-propanol-d_0 was adopted commonly. The rate constants observed on the Ru–Pt/carbon catalyst, together with those on Ru/carbon,[7] were given as a function of the H/D ratio in molecular hydrogen (Figs. 4 and 5). The rate constant derived from the two kinds of deuterium-substituted 2-propanol on the Ru/carbon catalyst was not constant, but increased remarkably, and finally coincided with the rate constant of the d_0 substrate, the H/D ratio of which should be infinity. From the sensitive dependence of the rate constant on the H/D ratio in molecular hydrogen for the Ru/carbon catalyst and the small kinetic isotope effects for hydrogen evolution from 2-propanol-2-*d* and 2-propanol-*O-d*, the slowest step is now concluded to be hydrogen evolution from the catalyst surface. On the contrary, the rate constant over the Ru–Pt/carbon catalyst is almost constant regardless of the H/D ratio or the 2-propanol substrate. The slowest step on the Ru–Pt/carbon catalyst should not be considered to be the formation of molecular hydrogen from the catalyst surface.

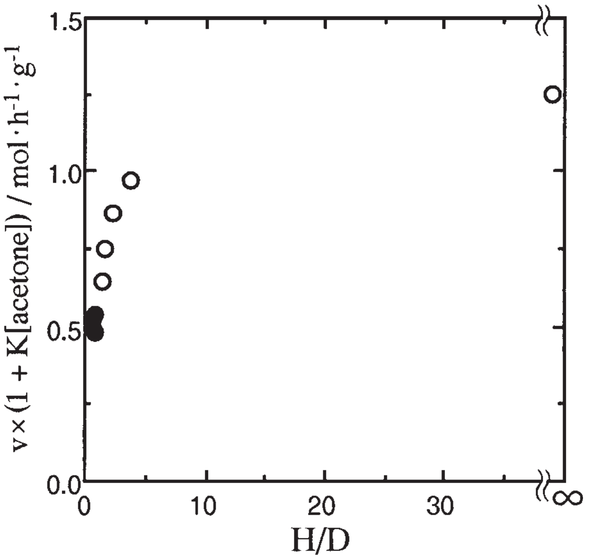

Fig. 4. Rate constant of 2-propanol dehydrogenation as a function of H/D ratio in molecular hydrogen obtained for Ru/carbon catalyst under boiling and refluxing conditions (82.4 °C). ●: $(CH_3)_2CHOD$, ○: $(CH_3)_2CDOH$.

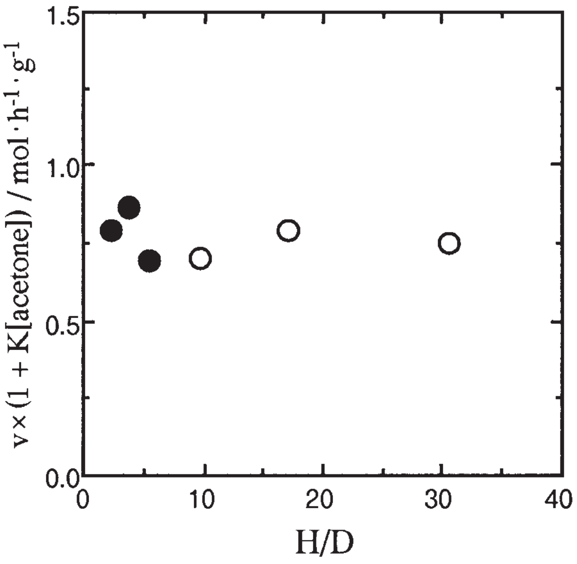

Fig. 5. Rate constant of 2-propanol dehydrogenation as a function of H/D ratio in molecular hydrogen obtained for Ru–Pt/carbon catalyst under boiling and refluxing conditions (82.4 °C). ●: $(CH_3)_2CHOD$, ○: $(CH_3)_2CDOH$.

Table 3. Reaction Parameters for Catalytic 2-Propanol Dehydrogenation

2-Propanol	k/mol h^{-1} g^{-1}	k_H/k_D	K/dm^3 mol^{-1}
d_0	0.927	—	1.05
2-*d*	0.474	1.96	1.18
O-d	0.602	1.54	1.87

Carbon-supported Ru–Pt (1:1, 5 wt %) 200 mg/5 mL 2-propanol under boiling and refluxing conditions (82.4 °C). Rate equation: $v = k/(1 + K[\text{acetone}])$; k: rate constant, K: retardation constant.

The isotope effects, k_H/k_D, obtained on the Ru–Pt/carbon catalyst for 2-propanol-*O-d* and 2-propanol-2-*d* below 5% acetone conversion, are shown in Table 3, together with other reaction parameters. Since the kinetic isotope effect of 2-propanol-*O-d* was relatively smaller than that of 2-propanol-2-*d*, the slowest step on the Ru–Pt/carbon catalyst would be shifted from the desorption process of hydrogen to the splitting process of the methine C–H bond compared with the Ru/carbon catalyst.

Enthalpy profiles of 2-propanol dehydrogenation with the Ru/carbon, Pt/carbon, and Ru–Pt/carbon catalysts are depicted for a comparison in Fig. 6. As far as the Ru/carbon catalyst in concerned, the dissociation process of the methine C–H bond is facile, whereas a large activation energy is required for the formation of molecular hydrogen. On the contrary, the Ru–Pt/carbon catalyst could decrease the activation energy for the formation of molecular hydrogen, being inherited from the hydrogen-releasing character of platinum. Nevertheless, the advantage of the Ru/carbon catalyst with respect to the C–H bond scissoring seems to be taken over to smooth the barriers of elementary steps.

These characteristics of the Ru–Pt/carbon catalyst would be the reason why this bimetallic composition exhibits splendid catalytic activity for 2-propanol dehydrogenation.[8]

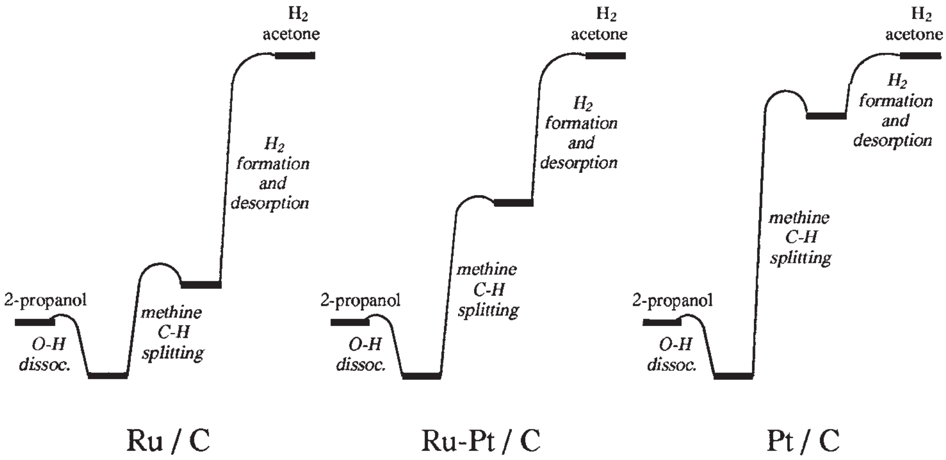

Fig. 6. Enthalpy profile of catalytic 2-propanol dehydrogenation.

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