Preparation of 2-Propanol Dehydrogenation Catalysts for Chemical Heat Pump System

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2-Propanol dehydrogenation catalysts were prepared using three types of preparation methods. The catalytic activities of these catalysts were compared through reaction experiments. A Ru catalyst, prepared by an incipient-wetness method followed by $NaBH_4$ reduction, had the predominant reaction rate, and a Pt catalyst, prepared by an incipient-wetness method with H_2 reduction at 400 °C, showed high activity. The Ru catalysts with high temperature reduction and Pt catalysts with $NaBH_4$ reduction showed negligible reaction rates; Also, a catalyst supported on activated carbon had a better activity than that on alumina. The Ru on activated carbon was proper for a chemical heat-pump system because of higher activity and a lower reduction temperature than the Pt catalyst.

The recovery and reuse of waste heat is a very important issue for the efficient use of energy. For this purpose, heat pumps have been used in industry. Traditional forms of heat pumps are mechanical and absorption types. However, they have not been used as widely as expected, because of their limited capacity and operating condition. The chemical heat pump is based on the heat of chemical reactions, and has advantages over the traditional forms of heat pumps, because the magnitude of the chemical reaction heat is usually much larger than those of the latent heat and absorption heat. The chemical reactions also occur in a much higher and broader range of temperatures than the boiling and absorption operations.[1]

The conceptual basis of the chemical heat-pump system involves an endothermic reaction at low temperature and an exothermic reaction at high temperature. Through a continuous process of this pair of reversible reactions, low-temperature heat can be upgraded to high-temperature heat.[1,2]

A 2-propanol/acetone/hydrogen reaction system has been reported as being one of the most suitable reactions for the chemical heat-pump system. It is presumed that the temperature of the heat source in 80 to 100 °C, and that the heat sink is 150 to 200 °C. The chemical reaction in this system[3] is

$$(CH_3)_2CHOH \rightleftarrows (CH_3)_2CO + H_2.$$

The forward reaction, 2-propanol is decomposed into acetone and hydrogen while absorbing heat at low temperature. Products of the forward reaction, acetone and hydrogen, are combined to produce 2-propanol while releasing heat at high temperature.

Various kinds of metal catalysts, such as Ru, Pt, Raney nickel, nickel, Rh, Ir, and Pd have been studied concerning the dehydrogenation of 2-propanol.[4—13] For the hydrogenation of acetone, Cu, Ni, Co, Zn, and Cu–Cr catalysts have studied.[14—16] Mears et al. investigated a Ni catalyst prepared by a sodium borohydride (sodium tetrahydroborate) reduction method for the liquid-phase dehydrogenation of 2-propanol.[5] Saito et al. reported that the Ru/Pt (1 : 1) catalyst reduced with sodium borohydride showed good dehydrogenation reaction rate at low temperature.[6,17—19]

This study covered only the dehydrogenation of 2-propanol. This reaction is thermodynamically disadvantageous because of low equilibrium conversion at low temperature. Therefore, good catalysts are very important for this reaction and chemical heat-pump systems. The purpose of this study was to find a new preparation method of catalysts for the dehydrogenation of 2-propanol and to investigate the effects of the preparation variables.

Experimental

The catalysts were prepared by three different methods for the 2-propanol dehydrogenation reaction. In the first method the catalyst was prepared by a precipitation method. Support of 30—60 mesh was dipped into a solution of a metal compound. The metal was precipitated and reduced by slowly adding an aqueous solution of 0.1 M sodium borohydride (1 M = 1 mol dm^{-3}) ($NaBH_4$, Junsei Chem. Co.) at room temperature. After this step, it was washed and dried (method 1). In the second method the catalyst was prepared by an incipient-wetness method. The catalyst was prepared by adding a precursor solution drop by drop to the support until it became wet. It was then dried at 120 °C for 18 h in a drying oven, and calcined at 250—400 °C for 2 h. The catalyst was reduced by 10% hydrogen diluted with nitrogen at 200—400 °C before the reaction (method 2). In the third method the catalyst was prepared by an incipient-wetness method, as in method 2, and then reduced by a sodium borohydride solution, as in method 1 (method 3). The metal compounds were Ru($RuCl_3 \cdot 3H_2O$, Engelhard Co.) and Pt-($H_2PtCl_6 \cdot 6H_2O$, Engelhard Co.), and the supports were activated

carbon (Samchully Co.) and alumina (γ-Al_2O_3, Kanto Chem. Co.) for all the preparation methods.

The reaction system, as shown in Fig. 1, comprised a feed pump, preheater, reactor, and condenser. The reaction was carried out with less than 1.0 g of the catalyst in a fixed-bed flow reactor (6 mm i.d. SUS tube). Quartz wool was used to support the catalysts. The preheater was used to vaporize the 2-propanol. A gas-phase reaction was performed by controlling the reaction temperature at 90 °C (the boiling point of 2-propanol is 82.5 °C). The condensed liquid components and the gas product were analyzed by gas chromatography (Shimadzu, GC-14A) using a thermal-conductivity detector. The catalysts were analyzed by XRD (Rigaku, D/MAX 2-BKRD) and BET (Micrometrics, ASAP2000).

Results and Discussion

Effect of Preparation Methods. Because the dehydrogenation reaction of 2-propanol is endothermic, thermodynamically this reaction favors high temperature.[1] The idea of carrying out this reaction at low temperature has its own thermodynamic limitation. Because the purpose of this study was to apply a dehydrogenation reaction to a chemical heat-pump system, we had to carry out the dehydrogenation reaction at low temperature. Considering the boiling point of 2-propanol (82.5 °C), the reaction temperature was fixed at 90 °C, which is almost the minimum temperature for the gas-phase reaction of 2-propanol.

The reaction rates along with the catalysts prepared by method 1 are listed Table 1. It shows that AC is an activated carbon and AL is an alumina, respectively. The catalysts were precipitated and reduced spontaneously by hydrogen evolved from a $NaBH_4$ solution.

$NaBH_4$ is dissociated in aqueous solution as follows;[5]

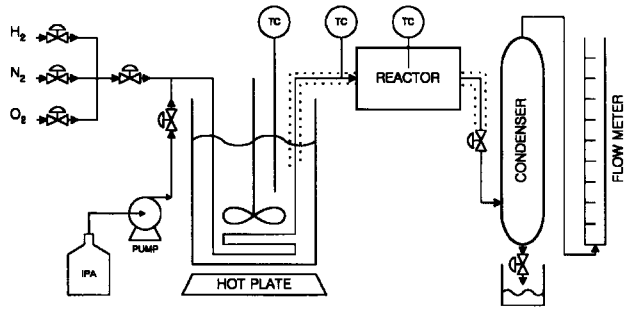

Fig. 1. Schematic drawing of experimental apparatus.

Table 1. Reaction Rates of 2-Propanol Dehydrogenation with Catalysts Prepared by Method 1

Catalysts	Reaction rate / mmol h^{-1} g^{-1}
5wt% Ru/AC	16.4
5wt% Ru/AL	9.2
5wt% Pt/AC	—[a)]
5wt% Pt/AL	—
5wt% Ru–Pt[1 : 1]/AC	38.2[b)]

a) Negligible reaction rate, b) Side reaction was observed (propene).

$$NaBH_4 + 2H_2O \longrightarrow Na^+ + BO_2^- + 4H_2.$$

This reaction is exothermic and its heat of reaction is 63.9 kcal mol^{-1}. Ru^{3+} ions in an aqueous precursor solution were deposited on the support and reduced into Ru by hydrogen evolved from the $NaBH_4$ solution. The ions, such as Na^+ and BO_2^- were removed by washing and drying procedures. The advantage of preparing catalysts by this method is that the oxidation rate of the metal is very slow in the atmosphere.

As shown in Table 1, the Ru catalysts had activity on the 2-propanol dehydrogenation reaction, but the Pt catalysts showed no reaction. The highest conversion was achieved using a 5wt% Ru/AC catalyst. This implies that metal particles were dispersed differently on the support according to the preparation methods. The reason for this is described in detail in the following section. Those catalysts with the same metal precursor showed different reaction rates depending on the support. It might be caused by the difference between the surface area of the activated carbon and the alumina. Table 2 gives the BET surface area and the pore volume of the two supports.

The surface area of activated carbon is about 6-times larger than the alumina, and the pore volume of activated carbon is about twice as large as that of alumina. For that reason, a catalyst supported on activated carbon showed a high reaction rate. While preparing the catalyst by the adding a $NaBH_4$ solution, the solution was dropped very slowly. If the addition rate was too fast, the activated carbon became broken into small particles, probably due to the high heat of reaction.

A catalyst prepared by method 1 with Ru (2.5% by weight) and Pt (2.5% by weight) showed a higher activity than others, and the reaction rate was about twice as high as that with the Ru/AC catalyst. However, in this case, the formation of propene was observed as a by-product. This suggests that 2-propanol is decomposed into propene and water because of its high activity. The side reaction is very undesirable during the operation of a chemical heat pump because any accumulation of a by-product decreases the efficiency of the system.

Table 3 gives the reaction rate of 2-propanol dehydrogenation using the catalysts prepared by method 2. The catalysts prepared by method 2 are importantly affected in their characteristics by the calcination and reduction temperatures, which were controlled to be between 200 to 400 °C. The catalysts supported on activated carbon were calcined at 250 °C, and those supported on alumina were calcined at 400 °C, respectively. In the case of alumina, the catalysts calcined and reduced at high temperature showed better activity. In the case of activated carbon, the catalysts reduced at 200 °C

Table 2. Surface Area and Pore Volume of the Supports

Supports	BET surface area / m^2 g^{-1}	Pore volume / mL g^{-1}
Activated carbon	1400	0.71
Alumina	240	0.38

Table 3. Reaction Rates of 2-Propanol Dehydrogenation with Catalysts Prepared by Method 2

Catalysts	Calcination temperature	Reduction temperature	Reaction rate
	°C	°C	mmol h^{-1} g^{-1}
5wt% Ru/AC	250	200	—[a]
5wt% Ru/AL	400	400	1.1
5wt% Pt/AC	250	200	20.1
		250	6.8
5wt% Pt/AL	400	200	7.8
		400	25.8
5wt% Ru–Pt[1 : 1]/AL	250	400	6.4

a) Negligible reaction rate.

showed better activity than those at 250 °C. This different catalytic activity can be interpreted by different thermostable characteristics of the supports. Activated carbon burns up completely at 300 °C. The catalytic activity might have be reduced because a part of the activated carbon was burned at 250 °C.

The activities of catalysts prepared by this method were opposite to that of method 1. Pt catalysts showed high activity and Ru catalysts showed negligible reaction rates. The Pt catalysts supported on alumina showed better catalytic activity than those supported on activated carbon. The catalysts supported on activated carbon could not increase the reduction temperature too much, while catalysts with an alumina support could be reduced at high temperature. This means that the reduction temperature has a more important effect on the catalytic activity than the surface area of the support in this preparation method. These different catalytic behaviors were caused by the different characteristics of the metals, themselves. Generally, the catalytic activity depends on the size of the dispersed metal particles. In this study, it was shown that Pt particles on a catalyst prepared by method 2 and Ru particles on catalysts prepared by method 1 are well dispersed on the support. Therefore, in order to obtain good catalytic activity, the Pt catalyst requires calcination and reduction at high temperature and the Ru catalyst requires reduction at room temperature. This is also described in detail in the following section concerning XRD analysis.

A Ru–Pt[1 : 1]/Al_2O_3 catalyst prepared by method 2 showed a slower reaction rate than that by method 1. Therefore, a side reaction was not observed because of the low activity.

To find the effect of the metal contents in catalysts, reactions were performed by varying the Pt contents in the range of 1—5 wt%. The other variables, such as preparation method, reaction temperature, and amount of catalyst, were kept constant. The result are shown in Fig. 2. The reaction rate increases with the metal contents, as expect, and the reaction rate increases at high temperature.

In the case of preparation method 3, the reaction rates are listed in Table 4. This method involved a combination of methods 1 and 2. The precursor solution was impregnated by the incipient wetness method and a $NaBH_4$ solution was

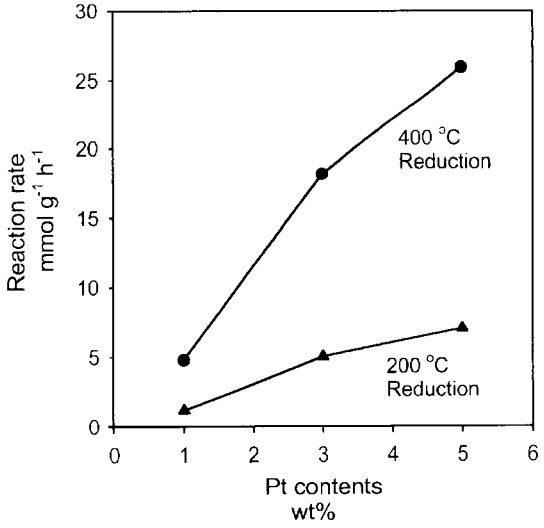

Fig. 2. The changes of 2-propanol dehydrogenation rate according to the changes of Pt contents on alumina support prepared by method 2.

Table 4. Reaction Rates of 2-Propanol Dehydrogenation with Catalysts Prepared by Method 3

Catalysts	Reaction rate
	mmol h^{-1} g^{-1}
5wt% Ru/AC	42.8
5wt% Ru/AL	20.0
5wt% Pt/AC	—[a]
5wt% Pt/AL	—[a]
5wt% Ru–Pt[1 : 1]/AL	11.1[b]

a) Negligible reaction rate. b) Side reaction was observed.

used to reduce the metal at room temperature. Thus, the preparation time was very short and the reproducibility was improved remarkably. Compared to method 1, method 3 had a higher dispersion because the precursor was inside the pores. Metal particles could be kept inside the pores during $NaBH_4$ reduction. As shown in Table 4, the Ru catalysts prepared by this method showed the best catalytic activity, and no side reaction was observed. The Ru/AC catalyst at this method showed a reaction rate of 2,6-times higher than the Ru/AC catalyst prepared by method 1 and 1.7-times higher than the Pt/Al_2O_3 by method 2. The Pt catalyst did not show any activity like method 1. In this method, like method 1, the Ru catalyst on activated carbon had better activity than that on alumina. In the case of the Ru-Pt catalyst, the side reaction was negligible, and the reaction rate was higher than that of method 2. Because of the different characteristics between Ru and Pt, the preparation method combining Ru with Pt is not useful to enhance the reactivity.

XRD Analysis. XRD is one of the most useful techniques in the characterization of layered structure materials. The XRD pattern of the catalysts prepared by methods 2 and 3 is shown in Fig. 3. Curves #1 and #2 represent 5 wt% Pt/Al_2O_3, curves #3 and #4 represent 5 wt% Ru/Al_2O_3, and curves #5 and #6 represent Ru–Pt[1 : 1]/Al_2O_3, respectively. Curves

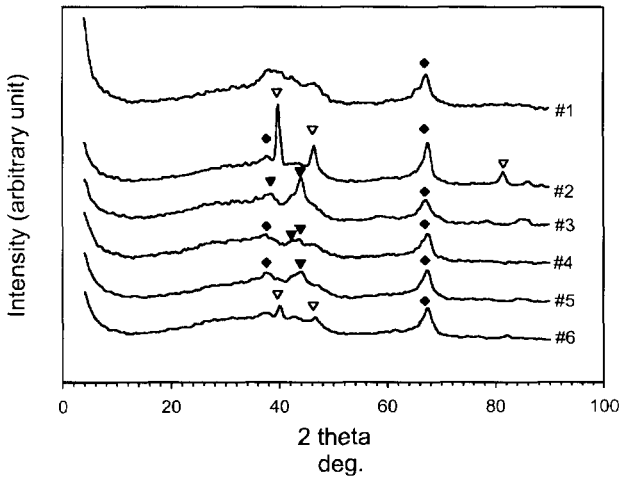

Fig. 3. X-Ray diffraction patterns of various catalysts. #1: 5wt% Pt/Al_2O_3 (method 2); #2: 5wt% Pt/Al_2O_3 (method 3); #3: 5wt% Ru/Al_2O_3 (method 2); #4: 5wt% Ru/Al_2O_3 (method 3); #5: 5wt% Ru–Pt[1 : 1]/Al_2O_3 (method 2); #6: 5wt% Ru–Pt[1 : 1]/Al_2O_3 (method 3); ▽: Platinum; ▼: Ruthenium; ◆: Al_2O_3.

#1, #3, and #5 are for the catalysts prepared by method 2 with calcining and reducing at 400 °C; curves #2, #4, and #6 are for the catalysts produced by method 3, respectively. The reaction rates of these catalysts are summarized in Table 5.

In comparison to Pt catalysts, catalyst #2, prepared by method 3, shows a very sharp Pt peak; catalyst #1, prepared by method 2, shows broad Pt shoulders. This means that Pt crystallites of catalyst #1 are much smaller and have higher dispersion than in the case of #2. In the case of Ru catalysts, on the contrary, catalyst #3 prepared by method 2 shows a larger Ru peak than catalyst #4, and catalyst #4 shows better catalytic activity. Catalysts #5 and #6 with the same amount of Ru with Pt show the same pattern as in the above cases. The catalyst prepared by method 2 has a large Ru peak and that by method 3 has a large Pt peak. This result proves that the catalyst, which has a small crystallite size, has predominant catalytic activity.

From the above results, Ru crystallites have been shown to be well dispersed when the catalyst is reduced by $NaBH_4$ at low temperature, because method 3 and Pt crystallites have good dispersibility when the catalyst is reduced at high temperature, as in method 2. The catalytic activities of Ru with method 2 and Pt with method 3 decrease abruptly because of increasing metal crystallite size on the support. It cannot be explained in this paper why Ru is well dispersed under $NaBH_4$ and Pt is well dispersed under hydrogen. It needs some more theoretical studies.

Table 5. Reaction Rate of 2-Propanol Dehydrogenation for the Catalysts Used in XRD

XRD Curves	Catalysts	Method	Reaction rate / mmol h^{-1} g^{-1}
# 1	5wt% Pt/Al_2O_3	2	25.8
# 2	5wt% Pt/Al_2O_3	3	—[a)]
# 3	5wt% Ru/Al_2O_3	2	1.1
# 4	5wt% Ru/Al_2O_3	3	20.0
# 5	5wt% Ru–Pt[1 : 1]/Al_2O_3	2	6.4
# 6	5wt% Ru–Pt[1 : 1]/Al_2O_3	3	11.1

a) Negligible reaction rate.

Applying to Chemical Heat Pump. Among the catalysts which were prepared in this study, the Ru catalyst prepared by method 3 and Pt by method 2 had predominant reaction rates. Therefore, it is necessary to know which of these two catalysts is better when we apply to chemical heat-pump system. In the 2-propanol/acetone/hydrogen chemical heat-pump system, dehydrogenation of 2-propanol occurs at low temperature (about 100 °C) and hydrogenation of acetone occurs at high temperature (about 200 °C). This means that the maximum temperature of the entire system is 200 °C, which is the temperature we wish to ultimately obtain. Even though the Pt/Al_2O_3 catalyst made by method 2 with reduction at 400 °C showed high catalytic activity, its use for a chemical heat-pump system would be restricted by the fact that it requires an additional heat source for such a high reduction temperature. Furthermore, it brings about an increasing capital investment because of the additional heat source. Although a reduction process is necessary at once before operating, any reduction process by hydrogen (method 2) must be proceeded in the reactor. However, for the catalyst prepared by method 3, no of heating device is necessary because of being reduced before packing. Therefore, this additional expense for reduction only at a time is not desirable because a heater must be installed outside of the reactor. As a consequence, the Ru catalyst prepared by method 3 is more suitable because the catalyst can be reduced at room temperature as well as having good catalytic activity, no side reaction, and a short preparation time.

Conclusions. The Ru catalysts prepared by the incipient-wetness and $NaBH_4$ reduction method (method 3) had the predominant reaction rate, and the Pt catalysts prepared by incipient-wetness with H_2 reduction at 400 °C (method 2) were excellent. However, the Ru catalysts with a high-temperature reduction and Pt catalyst reduced by a $NaBH_4$ solution showed negligible reaction rates. In the case of low-temperature reduction methods (methods 1 and 3), a catalyst supported on activated carbon has better activity than that on alumina; however, in the case of method 2, high-temperature reduction with H_2, the alumina was excellent. The Ru catalyst on activated carbon prepared by the incipient-wetness and $NaBH_4$ reduction method is the best one for a chemical heat-pump system because of the higher activity and lower reduction temperature than for the Pt catalyst.

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