Highly Effective Dehydrogenation of Cyclohexanol to Cyclohexanone over Carbon-Supported Cobalt Catalyst

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The dehydrogenation of cyclohexanol to cyclohexanone has been studied over activated carbon-supported transition metals as catalysts. The Co/carbon catalyst was found to be highly effective for the reaction. Its catalytic behaviors strongly depended on the temperature of hydrogen reduction. Highly dispersed and well-reduced cobalt catalyst showed pronounced activity and stability.

The dehydrogenation of cyclohexanol to cyclohexanone is an industrially important reaction in the manufacture of nylon. Copper-based catalysts have been extensively used in the reaction: CuO–ZnO,[1,2] CuO–CoO,[3] Cu–ZnO–Al_2O_3,[4] Cu/Al_2O_3,[5] and Cu–Fe_3O_4.[6] The dehydrogenation of cyclohexanol is an endothermic reaction, which favors a higher reaction temperature. However, since the copper catalysts seriously sinter at high temperature, they are mostly employed below 280 °C.

Novel catalysts such as Ni/carbon[7] and sulfated tin oxide,[8] which are free from copper element, have been recently reported to be more effective than the conventional copper catalysts for the dehydrogenation of cyclohexanol to cyclohexanone. The authors have attempted to develop highly active and thermostable cyclohexanol dehydrogenation catalysts. In the previous study,[7] it was shown that the use of carbon support was essential for the excellent activity of the Ni/carbon in the dehydrogenation of cyclohexanol. More recently, carbon-supported active catalysts have been developed for alcohol dehydrogenation reactions, MoO_3/carbon for oxidative dehydrogenation of various alcohols[9] and Ru–Pt/carbon for 2-propanol dehydrogenation.[10] Thus, there has been growing evidence on the usefulness of carbon as a catalyst support. We therefore expect that carbon supports of high surface area will be appropriate to prepare highly dispersed metal catalysts with excellent performance for cyclohexanol dehydrogenation.

In the present study, various transition metals supported on activated carbon were examined as catalysts for the dehydrogenation of cyclohexanol to cyclohexanone.

Experimental

The catalysts used in this study were prepared by impregnation of activated carbon (C; Mitsubishi Chem. Ind. Ltd., Diasorb G, specific surface area 1240 $m^2\,g^{-1}$, particle size 32—42 mesh) with aqueous solutions of transition metal salts, nitrates of Co, Ni, Fe, Cr, Cu, and Ag, chlorides of noble metals, ammonium molybdate, and manganese acetate. After impregnation, the catalyst precursors were dried at 110 °C for 12 h, followed by calcination at 500 °C for 2 h in a stream of nitrogen (30 $ml\,min^{-1}$). They were finally reduced in 50% H_2/He (30 $ml\,min^{-1}$) at 400 °C for 2 h before catalytic activity measurements. The Co/C was also reduced at various temperatures without calcination to investigate the effect of cobalt reduction degree on the activity of the catalyst. The metal loading was 3 wt% for the noble metal catalysts, 4 wt% for the other catalysts. A commercially available CuO–ZnO catalyst (Nikki Chemical Co., Ltd.) was also employed for comparison. It was reduced with hydrogen at 200 °C for 2 h prior to use, according to the procedure noted in the catalogue. The dehydrogenation of cyclohexanol was carried out at 200 °C using a conventional fixed-bed flow reactor system operating under normal atmospheric pressure. For each run, 0.1 g of catalyst was loaded into a glass reactor of 8 mm i.d. Cyclohexanol was introduced into the reactor by a microsyringe pump at a flow rate of 1.0×10^{-2} mol h^{-1}. Helium (16 $ml\,min^{-1}$) was used as carrier gas. The reaction products were collected at 30 min intervals and were analyzed by a Shimadzu 9A gas chromatograph equipped with a flame ionization detector and an OV-1701 capillary column.

Results and Discussion

The carbon support used in this study showed no significant catalytic activity for the reaction of cyclohexanol under operating conditions. The initial activities and selectivities of activated carbon-supported transition metal catalysts in the dehydrogenation of cy-

Table 1. Activities and Selectivities of Carbon-Supported Transition Metal Catalysts in Cyclohexanol Dehydrogenation

Catalyst	Conversion	Selectivity/%					
	%	Cyclohexanone	Phenol	Benzene	Cyclohexane	Cyclohexene	Others[a)]
Ag	0.8	81.5	0	0	0	11.9	6.7
Cu	1.5	83.5	0	0	0	16.5	0
Cr	2.0	62.4	0	0	0	22.3	15.3
Mn	1.6	77.7	0	0	1.3	15.5	5.5
Mo	3.9	43.5	0	0	2.5	51.2	2.8
Fe	1.7	90.4	0	0	0	8.4	1.2
Co	57.4	93.0	0.6	0.2	1.0	4.4	0.8
Ni	55.3	90.0	4.8	3.0	0.8	0.3	1.1
Pt	42.2	75.8	5.4	4.7	1.6	0.1	12.4
Pd	1.2	45.5	6.2	18.8	0	4.8	24.7
Rh	11.5	62.1	4.4	5.7	1.6	0	26.2
Ir	34.6	76.9	1.0	1.6	3.0	1.1	16.4
Ru	9.6	77.8	0	2.1	1.9	15.4	2.8
CuO–ZnO	49.1	98.0	0.1	0	0	0	1.9

a) Mostly high-boiling products.

clohexanol are summarized in Table 1. Here the catalysts reduced at 400 °C after calcination were employed. Among the catalysts tested, Co catalyst was most active for the dehydrogenation of cyclohexanol, followed by Ni, Pt, Ir, Rh, and Ru catalysts in that order, but the other catalysts exhibited very low activities. Table 1 also shows the results of the reaction over CuO–ZnO catalyst. The Co/C catalyst was more active than the conventional copper catalyst. Furthermore, the Co catalyst showed a very high selectivity to cyclohexanone. The dehydrogenation to phenol occurred to only a small extent. A major by-product was cyclohexene, which was probably formed through the dehydration of cyclohexanol on acidic sites.[3,11)] A preferential formation of cyclohexanone was also observed over Ni/C catalyst, but its selectivity to cyclohexanone was slightly lower than that of Co/C. On the other hand, the noble metal catalysts were rather less selective because more phenol and high-boiling-products were formed. These results indicate that the activated carbon-supported cobalt is highly promising as a new cyclohexanol dehydrogenation catalyst, and hence its catalytic behaviors were further investigated.

A series of experiments were conducted to observe the effect of hydrogen reduction on the activity, selectivity and stability of the Co/C catalyst. In these runs, uncalcined catalyst was used, because during calcination at 500 °C the reduction of cobalt species to metallic form was produced by the carbon support, which made it difficult to control the extent of cobalt reduction by hydrogen treatment. The reduced Co catalyst without calcination was slightly more active and selective than the catalyst reduced after calcination. Figure 1 shows the effect of reduction temperature on the activity and selectivity of the Co/C catalyst in the dehydrogenation of cyclohexanol. Its catalytic activity strongly depended on the temperature of hydrogen reduction. A maximum conversion was obtained upon the reduction at around 450 °C. On the other hand, the selectivity to cyclohexanone was little changed up to 400 °C, but it increased gradually with further increase in reduction temperature.

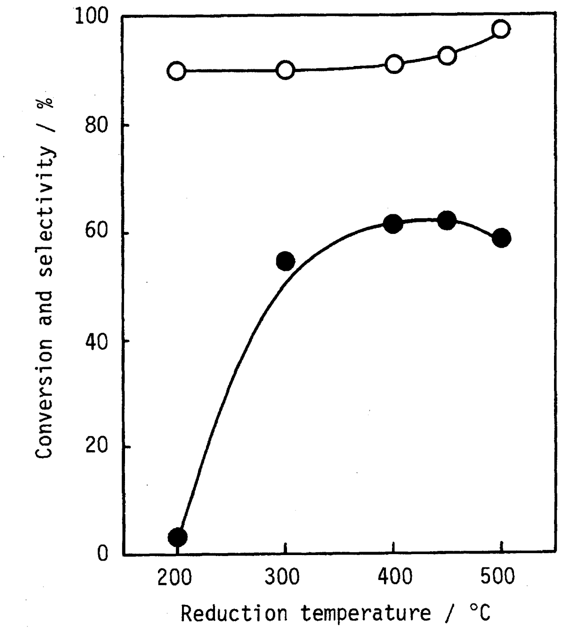

Fig. 1. Effect of reduction temperature on the activity (●) and cyclohexanone selectivity (○) of Co/C catalyst.

The stability of the Co/C catalyst was also affected by the temperature of hydrogen reduction, as shown in Fig. 2, in which the time courses of cyclohexanol dehydrogenation over Co/C reduced at different temperatures and CuO–ZnO are given. The cobalt catalysts reduced at temperatures higher than 400 °C showed good

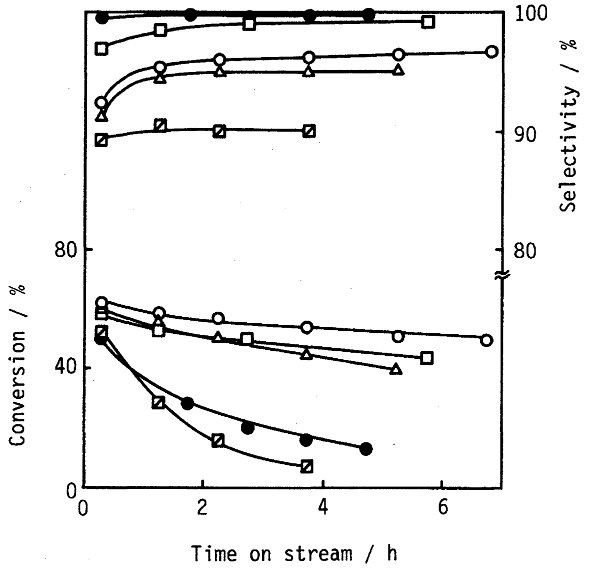

Fig. 2. Time courses of cyclohexanol dehydrogenation over Co/C catalysts reduced at 300(▨), 400 (△), 450 (○), and 500 °C (□), and CuO–ZnO catalyst (●).

stabilities and their selectivities to cyclohexanone were maintained at high levels above 95% in each operating time range except for the initial stage of the reaction. In particular, the activity of the catalyst reduced at 450 °C continued for a long period, while the conventional CuO–ZnO catalyst was rapidly deactivated with time on stream. Lin et al.$^{1)}$ have reported that the deposition of cyclohexanone oligomers on the active sites was the primary cause of the deactivation of the copper catalyst. Such oligomers seems to be also formed on the Co/C catalyst, leading to a slight activity decay with process time. However, the deactivated Co/C catalyst was thoroughly regenerated by the treatment with hydrogen at 400 °C. This finding is of significance to industrial operations.

In Figs. 1 and 2, the optimum results were obtained when Co/C catalyst was reduced with hydrogen at 450 °C. The influence of reduction temperature seemed to be associated with reducibility of cobalt species. The degree of cobalt reduction was determined from the amount of gaseous hydrogen generated by the dissolution of the reduced Co/C catalyst in sulphuric acid. The reducibility of the Co/C catalyst increased with reduction temperature. The degree of reduction was 46, 80, 100, and 100% when reduced at 350, 400, 450, and 500 °C, respectively. Therefore, it seems reasonable to speculate that the dehydrogenation of cyclohexanol to cyclohexanone proceeds on the reduced metallic cobalt sites. This may be supported by the observation that the Co/C catalyst lost its dehydrogenation activity on exposure to air at room temperature after hydrogen reduction, probably due to oxidation of the catalyst, but the activity of the oxidized catalyst was almost completely restored by hydrogen reduction at elevated temperature.

Cobalt dispersion was estimated from the amounts of adsorbed H_2 by assuming an adsorption stoichiometry of one hydrogen atom per surface cobalt atom.$^{12)}$ Percentage dispersion was 21, 13, 13, and 4% for the Co/C catalysts reduced at 350, 400, 450, and 500 °C, respectively. The dispersion of cobalt catalysts supported on oxides is usually rather low, mostly less than 10%.$^{13)}$ In this study, however, a considerably higher cobalt dispersion was obtained by using carbon support. Unsupported cobalt metal with a face centered cubic (fcc) structure has been reported to catalyze effectively the dehydrogenation of cyclohexanol to cyclohexanone.$^{14)}$ The fcc structure is stable when cobalt particle size is small.$^{12)}$ Activated carbon support is presumed to contribute to the formation of such active cobalt species. Further studies are necessary to elucidate the detailed catalysis of Co/C.

The hydrogen reduction at a high temperature such as 500 °C resulted in a low cobalt dispersion by sintering, which would likely be responsible for the slight decline of the high reduction temperature portion of the activity curve shown in Fig. 1. A considerable amount of methane was detected during hydrogen reduction of the Co/C catalyst at 500 °C, indicating hydrogenation of the carbon support. This gasification of the support may also affect cobalt dispersion. On the other hand, methane was formed only in limited amounts when the catalyst was reduced at 450 °C and no detectable amounts were formed at 400 °C or lower.

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