CHEMISTRY LETTERS, pp. 777-780, 1989.

Dehydrogenation of Cyclohexanol to Cyclohexanone on Supported Nickel Catalysts

Yoshio UEMICHI,* Takeshi SAKAI, and Takaji KANAZUKA
Department of Industrial Chemistry, Muroran Institute of Technology, Mizumoto, Muroran 050

Nickel supported on activated carbon was highly active as a catalyst for the dehydrogenation of cyclohexanol to cyclohexanone. The activity of nickel catalysts strongly depended on the support; activated carbon was most efficient, while silica, alumina and magnesia were much less effective.

Industrially, cyclohexanone produced by the dehydrogenation of cyclohexanol is an important intermediate in the manufacture of nylon. Many copper-based catalysts such as CuO-ZnO,[1] Cu-ZnO-Al_2O_3,[2] CuO-CoO,[3] and Cu-MgO[4] have been reported to be effective for the dehydrogenation of cyclohexanol to cyclohexanone. The reaction was also catalyzed by unsupported group VIII metals[5] and nickel-tin-silica,[6] but they were not sufficiently selective.

We report here that a nickel catalyst supported on activated carbon exhibited an excellent activity at rather low temperatures for the dehydrogenation of cyclohexanol to cyclohexanone.

Catalytic activities were measured by the use of a conventional flow reactor at 170-350 °C and 1 atm. Cyclohexanol was supplied into the reactor at a flow rate of 1.0×10^{-2} mol·h^{-1} by using a microfeeder. The feed was diluted with a carrier gas (N_2) to 20 mol%. Products were analyzed by gas chromatography using an OV-101 capillary column (40-240 °C) for cyclohexanol, cyclohexanone, phenol, cyclohexane, cyclohexene, benzene and a few unknown components.

Supported nickel catalysts were prepared by impregnating supports with an aqueous solution of nickel nitrate, followed by drying at 110 °C and calcining in a stream of nitrogen at 500 °C for 2 h. The supports were activated carbon (AC)

(Mitsubishi Chem. Ind. Ltd., Diasorb-G, 1060 $m^2 \cdot g^{-1}$), γ-alumina (Nishio Ind. Co., 167 $m^2 \cdot g^{-1}$), silica (Merck Co., SiO_2-100) and magnesia (Merck Co.). Two copper catalysts, Cu/AC prepared in a similar manner to that described above and CuO-CoO (9:1 mol ratio) prepared according to Ref. 3, were also employed for comparison.

Results on the catalytic conversion of cyclohexanol are shown in Table 1. In some cases, material balance based on carbon atom at the initial stage of the reaction was low, but the value of 93% or more was obtained after 60 min of reaction for all catalysts. Therefore, the activity and selectivity were estimated from the data at 75 min. The catalytic properties of supported nickel were remarkably dependent on the support. A highly active nickel catalyst for the dehydrogenation to cyclohexanone was obtained when activated carbon was used as support. Its catalytic activity was somewhat higher than that of CuO-CoO which is known as a good catalyst. The cyclohexanone selectivity of the carbon-supported catalyst, on the other hand, was slightly lower, but increased gradually with reaction time and exceeded 98% after 5 h. Furthermore, when the carbon support was used, nickel was more excellent as supporting metal than copper.

Al_2O_3 and Ni/Al_2O_3 catalysts exhibited almost the same activity and produced

Table 1. Activities and Selectivities of Catalysts[a)]

Catalyst	Conversion/%	Selectivity/%					
		Cyclo-hexanone	Phenol	Cyclo-hexene	Cyclo-hexane	Benzene	Others
AC	1.1	85.4	0	0	0	0	14.6
4%-Ni/AC	50.6	95.5	0.6	0.3	0.9	2.7	0
Al_2O_3	5.6	23.9	0	76.1	0	0	0
4%-Ni/Al_2O_3	9.7	7.7	0	92.3	0	0	0
4%-Ni/MgO	1.4	100	0	0	0	0	0
4%-Ni/SiO_2	0.9	87.9	0	0	0	0	12.1
4%-Cu/AC	6.8	55.9	0	39.7	2.4	0	2.0
20%-Cu/AC	35.7	82.1	0	15.7	2.2	0	0
CuO-CoO	43.5	99.7	0	0	0	0	0.3

a) Reaction temperature: 200 °C, contact time: 30 g-cat·h·mol^{-1} and reaction time: 75 min.

mainly cyclohexene. These results indicate that nickel species on alumina were inactive for the dehydrogenation reaction and the dehydration of cyclohexanol to produce cyclohexene occurred by catalysis of acidic sites on the alumina support. On the use of magnesia support which is a typical solid base, a complete cyclohexanone selectivity was obtained in the temperature range of 200-350 °C (Fig.1). Since the magnesia itself had very little activity even at 350 °C, nickel species appear to be active sites for the dehydrogenation activity of the Ni/MgO catalyst. However, the activity was much lower than the case of activated carbon support. Further, silica-supported nickel catalyst also showed insufficient activity and selectivity. It is suggested from these results that an acidic support was unfavorable for producing cyclohexanone selectively.

The effect of reaction temperature on the activity and the cyclohexanone selectivity of the carbon-supported nickel catalyst is shown in Fig. 1. The activity increased with increasing reaction temperature, while the selectivity decreased, mainly due to a higher formation of phenol. Therefore, it is found that the carbon-supported nickel catalyst exhibits a prominent performance at lower temperatures for the selective dehydrogenation to cyclohexanone.

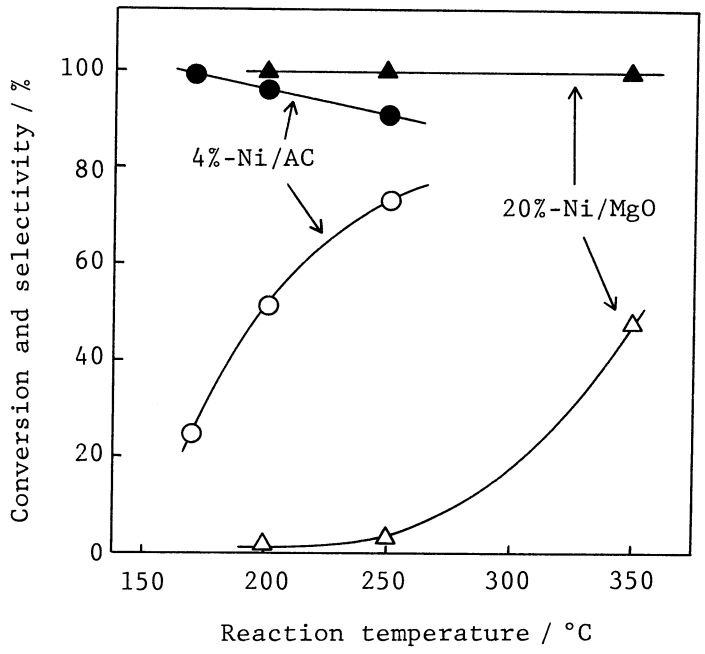

Fig. 1. Effect of reaction temperature on the catalytic activity (○, △) and selectivity to cyclohexanone (●, ▲).

The role that the carbon support or nickel plays in the catalyst system is not yet clear. Electron transfer between activated carbon and nickel has been pointed out to be essential for the catalysis of the metal in the methanol carbonylation reaction.[7] A similar interaction between support and metal seems to be responsible for the formation of highly active nickel species on the carbon surface in this study. Another explanation based on a reverse-spillover mechanism[8] may be also possible: that is, the step of hydrogen desorption involved in the dehydrogenation of cyclohexanol was very slow on activated carbon, but was greatly accelerated by the added nickel, resulting in an enhancement of the overall dehydrogenation rate. Further investigations on the catalytic properties of the carbon-supported nickel are now in progress.

This work was supported in part by funds from Saneyoshi Scholarship Fundation.

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(Received February 16, 1989)