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SHORT COMMUNICATION

ACTIVE AND SELECTIVE COPPER CATALYSTS SUPPORTED ON ALKALI-DOPED SILICA FOR THE DEHYDROGENATION OF CYCLOHEXANOL TO CYCLOHEXANONE

Gyung Soo Jeon and Jong Shik Chung†

Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH),
P.O. Box 125, Pohang 790-600, South Korea

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Abstract—Copper supported on alkali-doped silica was found to be the most effective among various types of copper-containing catalysts tested for the dehydrogenation of cyclohexanol to cyclohexanone. This catalyst could be used with lower copper content than others, and showed the highest conversion and selectivity and good resistance against thermal sintering.

Key words: Cu/SiO_2, Cyclohexanol Dehydrogenation, Cyclohexanone, Support

INTRODUCTION

Cyclohexanone, an important intermediate for the manufacture of nylon-6, is produced mainly by non-oxidative dehydrogenation of cyclohexanol. Since the reaction is endothermic and thermodynamically reversible, catalyst for commercial application must have a high selectivity and a high resistance against sintering at high temperatures. Various types of copper catalysts have been reported to be good commercial candidates for the reaction. Examples are CuO-MgO [1], Cu-ZnO [2], Cu-ZnO-Al_2O_3 [3], CuO-CoO [4], CuO-CrO [5] and CuO-FeO [6]. Nickel-Tin-Silica [7] and Ni supported on activated carbon [8] were also reported to be active for the reaction, but they were less selective than copper-containing catalysts.

We report here that copper supported on alkali-treated silica exhibited an excellent performance concerning activity and selectivity and a good resistance against sintering at rather high temperatures for the dehydrogenation of cyclohexanol to cyclohexanone.

EXPERIMENTAL

Copper-containing binary oxides were prepared by mixing an appropriate portion of copper (II) nitrate (Aldrich Co., 99.9%) solution with nitrate solution of second component metal (Aldrich Co., 99.9%) according to ref. 6. The copper content was kept at 40 wt% for all the binary oxides. Supported copper catalysts were prepared by precipitating copper nitrate solution (0.4 N) with dropping solution of Na_2CO_3 (0.4 N) in a constant stirring vessel containing support material. The precipitation lasted for about 4 hr at 90℃. The final pH was kept at 7 for support materials such as alumina, carbon and zirconia (Aldrich Co., 174, 800, 120 m^2/g, respectively), and that for silica (aero-silica, Alfa Co., 400 m^2/g) was varied from 7 to 10. Filtered slurry was dried at 110℃ followed by calcination in air at 300℃ for 12 hr. The copper loading of the supported catalysts was 20 wt%.

Table 1. Activities and selectivities on various silica-supported copper catalysts at 300°C

Cu/SiO_2/ Mg (wt%)	Precipitation pH	Conversion (%)	Yield (%)	Selectivity (%)			
				Anone[1]	Hexene[2]	Phenol	Others
5/95/0	7	88.7	9.9	11.2	86.2	1.1	1.5
25/75/0	7	89.5	12.7	14.2	83.3	1.3	1.2
5/95/0	9	85.7	62.6	73.1	25.4	0.45	1.1
5/94/1*	9	80.1	78.5	98.0	1.0	0.25	0.75
12/88/0	9	78.2	77.8	99.0	0.10	0.10	0.80
25/75/0	9	80.5	79.9	99.3	0.14	0.06	0.51
50/50/0	10	79.0	74.7	99.6	0.13	0.12	0.35
50/50/0	10**	90.0	54.5	60.5	37.2	1.1	1.2

*Magnesium was doped on silica by impregnation followed by calcination at 300℃ for 12 hr before the precipitation of copper.

**Ammonium hydroxide was used as a precipitating agent.

1: cyclohexanone, 2: cyclohexene

Catalytic activities were tested at 250-390℃ using a fixed-bed flow reactor made of 1/2″ glass tubing. Pure cyclohexanol (Aldrich Co., 99%) was fed to the reactor without carrier gas. Evaporator and feed lines were heated at 180℃ to prevent condensation. LWHSV (liquid weight hourly space velocity) was kept at 10 hr^{-1}. Products were analyzed by gas chromatography using flame ionization detector equipped with a capillary column packed with Carbowax 20 M.

RESULTS AND DISCUSSION

Table 1 lists the conversion of cyclohexanol and the selectivities of various products over several silica-supported catalysts. The three numbers in each catalyst represent wt% of Cu, SiO_2, Mg, respectively. From the results, it is found that a high selectivity (higher than 98%) of cyclohexanone can be achieved when catalyst is precipitated at high pH's (higher than 9) with sodium carbonate solution and the copper content is higher than 12 wt%. Keeping pH high during the preparation probably makes it possible to neutralize acidic sites of the silica surface with sodium. It is well

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†To whom all correspondences should be addressed.

Table 2. Activities and selectivities on various copper-containing catalysts at 300°C

Catalyst	Conversion (%)	Yield (%)	Selectivity (%)							
			Anone[1]	Hexene[2]	Phenol	CHA[3]	CHIA[4]	DCHE[5]	BCHO[6]	Unknown
40%Cu-CoO	74.3	64.5	86.8	0.55	11.6	0.26	0.42	–	0.05	0.35
40%Cu-Mn_2O_2	51.7	41.4	80.1	0.12	4.2	6.7	8.7	0.14	–	0.05
40%Cu-Fe_2O_3	70.6	62.8	89.0	3.1	5.8	1.2	0.42	0.11	0.07	0.30
40%Cu-ZnO	75.2	72.6	96.6	0.05	2.6	0.11	0.32	0.03	–	0.27
40%Cu-MgO	77.8	77.1	99.1	0.02	0.26	0.30	0.12	0.08	0.03	0.10
20%Cu-ZrO_2	71.8	64.1	89.3	0.04	3.2	13.7	5.4	0.02	0.88	0.07
20%Cu-Al_2O_3	78.5	68.6	87.4	10.1	0.75	1.21	0.15	0.08	0.08	0.26
20%Cu-Carbon	33.2	32.6	98.3	0.05	0.56	0.14	0.71	0.05	–	0.19
20%Cu-SiO_2	81.8	81.4	99.2	0.04	0.40	0.07	0.05	0.12	0.07	0.05

The final precipitation pH was kept at 9 for silica and 7 for the other supports.

1: cyclohexanone, 2: cyclohexene, 3: cyclohexene cyclohexanone, 4: cyclohexylidene cyclohexanone, 5: dicyclohexylether, 6: 1-1'bicyclohexyl 2-one.

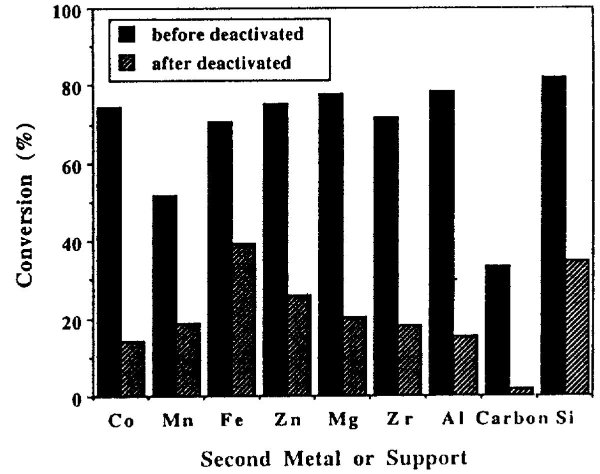

Fig. 1. Effect of the support and second metal in the copper-loaded catalysts on the conversion of cyclohexanol before and after deactivation.

known that cyclohexene is produced on the acidic sites of the support [2, 3, 8]. This is also supported by the fact that catalyst prepared using ammonium hydroxide does not show a good selectivity as shown in Table 1. The silica surface must remain acidic even after the precipitation in the solution of pH 10 owing to the evaporation of ammonia during the calcination of the catalyst. Even for the catalysts having low copper content (5 wt% Cu), additional doping of 1.0 wt% of basic magnesium (by impregnation method) was sufficient to keep the catalyst to be selective for cyclohexanone.

Table 2 shows the reaction tests with other catalysts in comparison with Cu-SiO_2. As expected, the commercial type catalysts, Cu-MgO and Cu-ZnO, exhibited good performance. However, the best performance is observed for the copper catalyst precipitated on silica at pH 9. Besides its superior activity and selectivity, cheaper material cost of silica and lower copper content than the other supported catalysts make it be a potential candidate for the commercial application. The alkali-treated carbon support also showed a good selectivity, but the activity was considerably low. The alumina support produced an appreciable amount of cyclohexene even after the alkali treatment. All amphoteric oxides like CoO, MnO_2, and Fe_2O_3 exhibited low selectivities of cyclohexanone. Main by-products on these catalysts were phenol produced by a deep dehydrogenation products and CHA (cyclohexenyl cyclohexanone) and CHIA (cyclohexylidene cyclohexanone) produced by dehydrogenation-dimerization. It was reported that the magnetite formed on Cu-Fe oxide was responsible for the formation of phenol [6]. The dimerized by-products may be produced by coexistence of acidic and basic sites on the amphoteric oxides.

Another important factor governing catalyst selection is deactivation resistance during a long run test. Results on accelerated deactivation tests for various catalysts were shown in Fig. 1. After reaction test with fresh catalyst at 300℃ for 8 hr, the temperature increased to 390℃ and the reaction continued for another 8 hr to accelerate deactivation. The temperature was decreased back to 300℃ to measure the conversion of the deactivated catalyst. Cu-Fe_2O_3 binary oxide exhibited the lowest deactivation tendency among catalysts tested. However, the low selectivity of cyclohexanone limits the practical application of the catalyst. The second best one concerning the deactivation resistance is copper supported on silica. Formation of copper silicate at high pHs might be responsible for the high sintering resistance. Further investigation on the catalytic properties of copper precipitated on silica at high pHs is now in progress.

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