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Selectivity Dependence on the Acidity of Copper–Alumina Catalysts in the Dehydrogenation of Cyclohexanol*

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Catalytic dehydrogenation of cyclohexanol to cyclohexanone is an industrially important reaction in the production of caprolactam. Copper-based catalysts are used in the dehydrogenation of cyclohexanol [1], which is produced either by hydrogenation of phenol or by air oxidation of cyclohexane. The catalytic dehydrogenation of cyclohexanol has gained much importance in recent years [2 - 4]. For example, Sideltseva and Erofeev [2] have studied the dependence of the metal deposition procedure on the specific surface and catalytic properties of Cu/MgO catalysts. Petrova *et al.* [3] have examined the promotional role of cadmium in Cu—Al_2O_3 alloy catalysts. They achieved about 87% cyclohexanone selectivity at a reaction temperature of 370 °C. More recently, copper-based catalysts have been studied in the dehydrogenation [5] and oxidative dehydrogenation [6] of cyclohexanol. Cyclohexene is one of the byproducts of the reaction [5, 7]. However, the characteristics of the catalysts that govern the selectivity of the reaction is not known. In the present communication we present results on the dependence of the selectivity to cyclohexanone or cyclohexene in the reaction of cyclohexanol on the acidity and metal area of highly active copper–alumina catalysts prepared by a novel co-precipitation method. The acidity of the catalysts was measured by chemisorption of ammonia at room temperature, and the copper area was determined by adsorptive decomposition of nitrous oxide.

Copper–alumina catalysts of varying composition (12 - 31 wt.% Cu) have been prepared using the urea hydrolysis procedure [8, 9]. In a typical experiment, a solution containing the required amounts of copper(II) nitrate, aluminium(III) nitrate and urea was heated at 90 - 95 °C. After the precipitation was completed (pH 7.5), the solids were filtered, washed with distilled water and dried at 110 °C for 24 h. The oxide catalysts were

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obtained by calcining the catalyst precursors at 400 °C for 24 h. The copper content of the catalysts was determined by atomic absorption spectrometry.

Activity measurements were made in a fixed bed flow microreactor operating under normal atmospheric pressure. For each run about 0.5 g of the catalyst with an average particle size of 0.6 mm was loaded in a borosilicate glass reactor of 10 mm i.d and reduced at 250 °C for 5 h in H_2 flow. The activities were measured at 250 °C on the reduced catalyst, maintaining a cyclohexanol flow rate of 0.25 mol h^{-1}. The products were analyzed by gas chromatography using a S.S. column filled with 10% Carbowax 20M (2 m × 3 mm). The reaction products analysed were mainly cyclohexanone and cyclohexene.

A conventional glass high vacuum system was used to measure the BET surface areas by nitrogen adsorption at −196 °C. The same system, having a stationary background vacuum of 10^{-6} torr (1 torr = 133.3 Pa), was employed to carry out NH_3 chemisorption measurements. In a typical experiment, about 0.5 g of the catalyst sample was placed in a glass adsorption cell and evacuated at 110 °C (10^{-6} torr) for 2 h, and then cooled to room temperature (25 °C) under vacuum prior to NH_3 adsorption measurements. The first adsorption isotherm, representing both reversible and irreversible ammonia adsorption, was generated allowing 20 min equilibration time at each pressure. Then the catalyst was evacuated at 25 °C for 1 h to remove reversibly adsorbed ammonia. After this, a fresh second isotherm, representing only the reversibly adsorbed ammonia, was generated in an identical manner. From the difference between the first and second adsorption isotherms, the irreversibly chemisorbed ammonia was calculated. Helium was used to measure the dead volume. Specific copper area of the catalysts was determined by reaction with nitrous oxide at room temperature using chromatographic pulse technique according to the procedure described by Evans *et al.* [10] and modified by Denise *et al.* [11]. Each catalyst was reduced in a stream of hydrogen at 250 °C for 5 h, followed by cooling to 25 °C in helium flow for 1 h prior to the nitrous oxide decomposition experiment. The number of surface Cu atoms of the catalysts was calculated from N_2O decomposition data.

Composition, activity and selectivities along with BET surface area, ammonia uptake, copper area and XRD data of calcined catalysts are given in Table 1. Activity of the catalysts increased with increasing copper loading up to 23.6 wt.%, and then declined with further copper loading. The cyclohexanone selectivity increased with copper loading, while cyclohexane selectivity decreased. The cyclohexanone selectivity varied between 70.2 to 93.8% depending on the copper content in the catalyst, and the cyclohexanone selectivity increased with copper loading, while cyclohexene coprecipitated $Cu—Al_2O_3$ catalysts have shown higher activity in the dehydrogenation of cyclohexanol than the $Cu—ZnO—Al_2O_3$ catalysts prepared by deposition–precipitation [5]. However, the latter catalysts have shown higher selectivities for cyclohexanone. Ammonia uptake and the selectivities

TABLE 1

Catalyst composition, BET surface area, XRD, copper area, ammonia chemisorption, activity and selectivities of copper–alumina catalysts

S.No.	Copper content (wt.%)	BET surface area (m^2 per g cat)	XRD	Copper area (m^2 per g cat)	NH_3 uptake (μmol per m^2 cat)	Reaction rate (mol h^{-1} per g cat) × 10	Selectivity (%)	
							cyclo-hexanone	cyclo-hexene
1	12.0	250	amorphous	3.9	1.06	0.202	70.2	29.8
2	17.0	220	amorphous	7.9	0.79	0.231	75.4	24.6
3	21.2	200	amorphous	10.2	0.57	0.252	80.0	20.0
4	23.6	150	CuO, $CuAl_2O_4$, γ-Al_2O_3	12.0	0.60	0.275	82.5	17.5
5	25.4	128	CuO, $CuAl_2O_4$, γ-Al_2O_3	9.2	0.62	0.260	83.8	16.2
6	30.7	75	CuO, Al_2O_4, γ-Al_2O_3	7.0	0.47	0.207	93.8	6.2

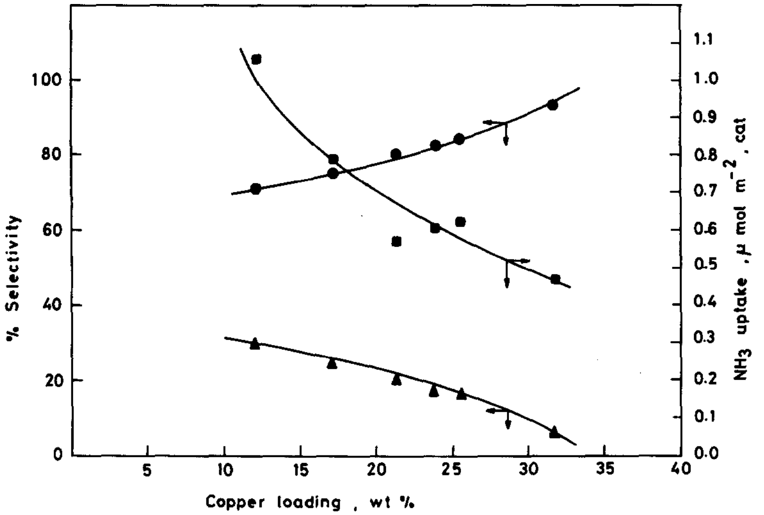

Fig. 1. Effect of copper loading on ammonia uptake and selectivity to cyclohexanone and cyclohexene. (■) Ammonia uptake, (●) selectivity to cyclohexanone and (▲) selectivity to cyclohexene. Reaction temperature = 250 °C, feed rate of cyclohexanol = 0.25 mol h^{-1}.

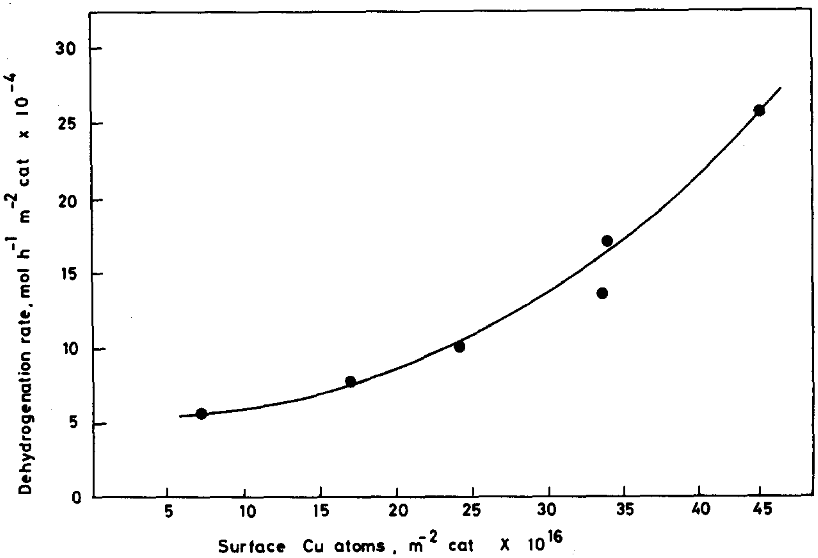

Fig. 2. Dependence of the rate of dehydrogenation of cyclohexanol on the number of surface Cu atoms per unit area of the copper–alumina catalysts.

of cyclohexanone and cyclohexene for various catalysts as a function of copper loading are shown in Fig. 1. As can be seen in Fig. 1, the ammonia uptake decreases with increasing Cu loading. Meanwhile, the selectivity to cyclohexanone increases when increasing the Cu loading, and consequently the selectivity to cyclohexene decreases. The dependence of the dehydrogenation rate of cyclohexanol on the number of surface Cu atoms per unit area is depicted in Fig. 2. It can be observed from Fig. 2 that the dehydrogenation rate increases with increasing numbers of surface Cu atoms.

The dehydrating activity of γ-Al_2O_3 is well known [8, 12]. When copper is added, the dehydrogenation activity rises, which is shown to depend on the copper content. Alumina produces mainly cyclohexene by the dehydration of cyclohexanol on the acidic sites of the catalyst [7]. Recently Corma *et al.* demonstrated that the acidity of aluminas could be measured by ambient-temperature NH_3 chemisorption [13]. Hirschler has demonstrated that adding metal ions to silica–alumina replaced strong acid sites with weak acids sites [14]. It is reported that in the CuO–alumina system copper complexes are formed with Cu^{3+}, Cu^{2+} and Cu^{+} depending on the composition and thermal treatment [15, 16] and Cu^{2+} complexes are grouped into clusters on the support surface [17]. From a FT–IR study, Busca demonstrated that the CuO surface displays a basic character [18], which was deduced from the relevant stability of the surface carbonate species deriving either from the relative adsorption of carbon oxides or being residual from the preparation procedures. In Fig. 1 it can be seen that the large amount of ammonia chemisorbed at the lowest Cu loading studied, decreases with increasing copper loading in the catalysts. The results on ammonia uptake capacities of these catalysts, which is a measure of their acidity, are in agreement with the findings that the CuO surface displays a basic character. As the copper loading in the catalyst increases, the acidic sites of alumina are neutralized by the basicity of CuO, as evidenced by the decrease in ammonia uptake. The correlation observed in Fig. 1 clearly demonstrates that the selectivity to cyclohexene depends on the acidity of the catalyst. Furthermore, the selectivity to cyclohexanone increases with decreasing acidity of the catalyst. However, the activity of the catalysts depends on the Cu loading, exhibiting a maximum at 23.6 wt.% Cu. Interestingly, at this Cu loading CuO, $CuAl_2O_4$ and γ-Al_2O_3 phases have been detected by XRD, while the catalysts with lower copper content do not show the presence of crystalline phases by XRD. According to Wolberg and Roth [20], the direct formation of a $CuAl_2O_4$ surface phase can occur even at 300 °C when there is an appropriate combination of copper concentration and alumina surface area. It was shown that metallic copper species is the probable active site for the dehydrogenation activity of copper-based catalysts [5, 9, 19]. From Fig. 2 it is clear that the activity of Cu—Al_2O_3 catalysts for the dehydrogenation of cyclohexanol to cyclohexanone is dependent on the number of surface Cu atoms per unit BET area.

Thus from the present study, the Cu—Al_2O_3 catalysts prepared by coprecipitation using the urea hydrolysis procedure appear to be highly active for the reaction of cyclohexanol to cyclohexanone and cyclohexene.

Room temperature ammonia chemisorption appears to be a promising technique for rapidly assessing the Cu—Al_2O_3 catalysts for their relative selectivity to cyclohexanone and cyclohexene in the reaction of cyclohexanol.

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