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Selective Dehydrogenation of Cyclohexanol to Cyclohexanone on Cu–ZnO–Al_2O_3 Catalysts

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Letter

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Catalytic dehydrogenation of cyclohexanol to cyclohexanone is an industrially important reaction in the manufacture of nylon. Cyclohexanone is also used as a solvent and as a building block in the synthesis of many organic compounds such as pharmaceuticals, insecticides, etc. Industrially, cyclohexanone is manufactured by the dehydrogenation of cyclohexanol [1,2] which is produced either by hydrogenation of phenol [3] or by air-oxidation of cyclohexane [4]. The catalytic dehydrogenation of cyclohexanol has gained much importance in recent years [5–7]. For example, Sideltseva and Erofeev [5] have studied the dependence of metal deposition on the specific surface and catalytic properties of Cu–MgO catalysts. Petrova et al. [6] 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. In this communication we report highly selective ($>$ 99%) dehydrogenation of cyclohexanol to cyclohexanone over Cu–ZnO–Al_2O_3 catalysts prepared by a novel deposition–precipitation method. These catalysts are characterized by means of a reversible carbon monoxide adsorption technique to assess the nature of the active species on the catalyst surface.

The Cu–ZnO–Al_2O_3 catalysts with various compositions of copper, zinc and aluminium were prepared by a deposition–precipitation method using urea as hydrolysing agent. In a typical experiment about 20 g of a fine powder of γ-Al_2O_3 (surface area 205 m^2g^{-1}, pore volume 0.6 ml g^{-1}, particle size 0.1 mm) was suspended in a solution containing the required amount of copper nitrate, zinc nitrate, urea and the resulting mixture was heated to 90–95 °C. The precipitate thus formed (pH = 7–7.5) was filtered and washed thoroughly with deionised water, dried at 110 °C and finally calcined at 400 °C in air for 24 h. The copper and zinc content of the finished catalysts were determined by atomic absorption spectrometry. Activity measurements were conducted on a fixed bed flow micro-reactor operating under normal atmospheric pressure. For each run about 0.5 g (average particle size 0.6 mm) of catalyst was loaded and the

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activities were measured at 250°C and at a cyclohexanol feed rate of 0.25 mol h^{-1}. Products were analysed by gas chromatography using a 10% carbowax 20 M (2 m long) column. The reaction products analysed were mainly cyclohexanone and cyclohexene. The carbon monoxide adsorption measurements were made on a static volumetric high-vacuum system incorporating an in situ reduction facility. Catalysts were prereduced in a flow of purified hydrogen (35 ml min^{-1}) at 250°C for 5 h followed by evacuation (10^{-6} Torr, 1 Torr = 133.3 Pa) for 2 h at the same temperature prior to carbon monoxide adsorption measurements. Before the introduction of carbon monoxide (Matheson, 99.9% purity), the system was further evacuated at room temperature. Carbon monoxide from a storage bulb was then allowed to enter the catalyst chamber with known dead space. An initial quick fall in the pressure was followed by a levelling off within about 15 min and the equilibrium pressure was noted. This process was repeated with different initial pressures and the first adsorption isotherm, representing both the irreversible and reversible carbon monoxide, was generated. Then the catalyst was evacuated at 25°C for 1 h to remove the reversibly adsorbed carbon monoxide. After this a fresh second isotherm, representing only the reversible carbon monoxide was generated in an identical manner. From this second isotherm reversibly adsorbed carbon monoxide was determined [8].

Composition, activity and selectivities of various catalysts are given in Table 1. Activity of the catalyst increased linearly with increase in copper loading upto about 15.9 wt.-% and then declined with further copper loading. The cyclohexanone selectivity also increased linearly with copper loading again upto 15.9 wt.-%, but remained constant beyond this loading. The selectivity to cyclohexanone formation varied between 60 and 99% depending on the copper content in the catalyst. However, at a copper loading of 15.9 wt.-%, the selectivity to cyclohexanone formation was more than 99%. Reversible carbon mon-

TABLE 1

Catalyst composition, reversible carbon monoxide adsorption, BET surface area, activity and selectivity of various catalysts

Catalyst	Composition, wt.-%			Reversible CO uptake (μ mol g^{-1} cat.)	BET surface area (m^2g^{-1} cat.)	% Conversion of cyclohexanol	% Selectivity to cyclohexanone
	Cu	Zn	Al				
CZA-3	3.7	38.2	25.3	11.2	130	19	60.8
CZA-4	11.0	37.6	20.9	42.8	124	35	85.9
CZA-5	15.9	37.5	17.7	53.5	96	42	99.0
CZA-6	20.6	37.3	14.7	45.5	88	38	99.2
CZA-7	25.5	36.0	12.3	35.6	80	36	99.3
CZA-8	28.5	35.3	10.8	33.5	73	35	99.4
CZA-9	32.7	34.7	8.4	26.8	53	31	99.4

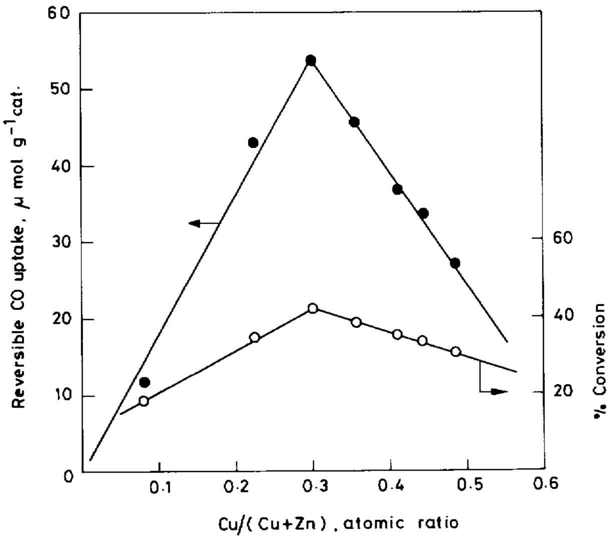

Fig. 1. Reversible carbon monoxide uptake at 25°C and cyclohexanol conversion at 250°C as a function of Cu/(Cu+Zn) atomic ratio.

oxide uptake capacity and the activities of various catalysts as a function of Cu/(Cu+Zn) atomic ratios are shown in Fig. 1. As can be seen in Fig. 1, the activity of the catalyst increases with increase in Cu/(Cu+Zn) ratio and reaches a maximum at a ratio of 0.3, after which it decreases sharply with further copper loading. A maximum in reversible carbon monoxide uptake at this particular Cu/(Cu+Zn) atomic ratio can also be seen in Fig. 1. A closer look at Fig. 1 also reveals that a good correlation exists between cyclohexanol dehydrogenation activity and reversible carbon monoxide uptake.

It was well established that the surface Cu° and Cu^+ species can be estimated quantitatively with carbon monoxide adsorption measurements [9]. As demonstrated by Klier [9], reversibly adsorbed or physisorbed carbon monoxide is a measure of the metallic copper species and Cu^+ species corresponds to the irreversible carbon monoxide uptake, whereas Cu^{2+} is totally inactive for both. In the present study a large reversible carbon monoxide adsorption with some irreversible uptake was observed on the reduced catalysts. Furthermore, no adsorption, either reversible or irreversible, was observed on the unreduced samples as well as on pure ZnO. These observations clearly show that the reduced Cu–ZnO–Al_2O_3 catalyst consists of copper essentially as Cu° with a lesser amount Cu^+ species and in the unreduced sample the copper oxidation state is invariably +2. The direct correlation as observed in Fig. 1 also clearly demonstrates that the metallic copper species is the probable active site for dehydrogenation activity of the catalyst. From these results it appears that the maximum activity and a maximum reversible carbon monoxide uptake at a

Cu/(Cu+Zn) ratio of 0.3 may be due to the availability of a maximum of Cu° species on the surface of the catalyst. A similar correlation was also reported earlier with Cu° species on Cu/Al_2O_3 catalyst for isopropanol dehydrogenation activity [10]. However, the selectivity of the catalyst appears to be not so sensitive as compared to the activity with respect to catalyst composition.

Thus, from the present study, this Cu–ZnO–Al_2O_3 catalyst prepared via a novel deposition–precipitation method appears to be most efficient for selective dehydrogenation of cyclohexanol to cyclohexanone. Reversible carbon monoxide adsorption appears to be a promising technique for rapidly assessing the activity of these catalysts.

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