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Journal of Molecular Catalysis A: Chemical 223 (2004) 339–345

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Effect of method of preparation of copper – magnesium oxide catalyst on the dehydrogenation of cyclohexanol

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Received 10 February 2003; received in revised form 12 November 2003; accepted 21 November 2003

Abstract

The superior catalytic activity in the dehydrogenation of cyclohexanol to cyclohexanone of Cu/MgO coprecipitated catalyst over corresponding impregnated and solid–solid wetting catalysts is ascribed to the higher Cu metal area and interaction between the microcrystals of CuO and MgO associated with coprecipitated catalyst. Further, the effect of Cu loading on the activity of Cu/MgO coprecipitated catalysts indicates that the catalyst comprising of ∼16 wt.% Cu exhibits higher activity. The catalysts have been characterized by different techniques, viz. X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), temperature programmed reduction (TPR), BET-surface area measurements and N_2O decomposition for measuring Cu metal surface areas and the results have been correlated with the activities of catalysts where ever possible.

Keywords: Dehydrogenation; Cyclohexanol; Cyclohexanone; N_2O decomposition; Co precipitation; Impregnation; Solid–solid wetting

1. Introduction

Catalytic dehydrogenation of cyclohexanol to cyclohexanone is an industrially important reaction in the manufacture of nylon because the two major raw materials in producing polyamide fiber are caprolactum and adipic acid, both of which can be obtained from cyclohexanone [1,2]. However, the conventional dehydrogenation process is severely constrained by thermodynamic equilibrium apart from sintering of Cu metal beyond 280 °C [3,4]. The commercial catalysts for the dehydrogenation of cyclohexanol are either Cu-Zn-Al or Cu-Mg catalysts, for which the method of preparation is very crucial to obtain the equilibrium conversions of cyclohexanol, which are in the range of 50–60% in the temperature range of 220–260 °C. Modification of Cu–Al_2O_3 interaction by carbon coverage of Al_2O_3 and its influence on the cyclohexanol dehydrogenation activity has been reported [5]. In the catalytic dehydrogenation of cyclohexanol, the dependence of Cu oxidation state on the catalytic properties of Cu/MgO catalysts has been reported [6]. In the present investigation, we are reporting the influence of method of preparation of Cu/MgO catalysts and the loading of Cu metal on the characteristics and the cyclohexanol dehydrogenation activity.

2. Experimental

2.1. Preparation of Cu/MgO catalysts

Three Cu/MgO catalysts with 16 wt.% of Cu have been prepared by coprecipitation, impregnation and solid–solid wetting methods. An aqueous solution containing requisite amounts of Cu $(NO_3)_2\cdot 3H_2O$ (M/S. Loba Chemie Ltd., India), Mg $(NO_3)_2\cdot 6H_2O$ (M/S. Loba Chemie Ltd., India) with their concentration of 1 M each, have been simultane-

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doi:10.1016/j.molcata.2003.11.046

ously precipitated using an aqueous solution containing 1 M K_2CO_3 (M/S Loba Chemie Ltd., India) at a pH of 9. The coprecipitated mass has been thoroughly washed, filtered and dried at 120 °C for 12 h in air followed by calcination in air at 450 °C for 4 h. This coprecipitated catalyst has been designated as Cu/MgO-CM. In the similar manner, individual oxides of Cu and Mg have been prepared. The MgO, thus, prepared has been impregnated with CuO using requisite amounts of aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$. Excess water has been evaporated and the resulting mass has been dried at 120 °C in air for 12 h followed by calcination in air at 450 °C for 4 h to get Cu/MgO-IM, an impregnated catalyst. The requisite amounts of individual oxides of Cu and Mg have been thoroughly mixed and ground followed by calcination at 450 °C in air for 4 h to get the solid–solid wetting catalyst, called Cu/MgO-SSW.

Cu-MgO catalysts with Cu loadings of 5.2, 10.1, 13.5, 16, 37.3, 42.9, 51.6 and 79.8% (in wt.%) are prepared by coprecipitation method (similar to the preparation of Cu/MgO-CM) and designated as Cu1–Cu8. All the catalysts are reduced in H_2 flow at 250 °C for 4 h prior to the reaction run. The bulk CuO catalyst is also prepared in a similar way using K_2CO_3 as the precipitating agent.

2.2. *Catalyst characterization*

All the catalysts have been characterized by BET surface area using N_2 adsorption method on an all glass high vacuum unit capable of yielding 10^{-6} Torr, by XRD using a Siemens D-5000 diffractometer with Ni filtered Cu K_α as a radiation source and by N_2O pulse chemisorption using 6% N_2O–He mixture on a home made pulse reactor with a programmable six port valve having 1000 μL loop (M/S. Valco instruments, USA) and a temperature programmer connected to a electrically heated furnace. Typically, about 100 mg of the catalyst sample taken in a S.S reactor (2 mm i.d. and 200 mm long) has been reduced in H_2 flow at 250 °C for 2 h followed by cooling to 90 °C and replacing the H_2 with He at which 6% N_2O balance He mixture is injected in pulses at regular intervals until there is no change in the concentration of N_2O at the outlet. The product analysis is performed on GC-17A equipped with micro TCD (M/S. Shimadzu Instruments, Japan) connected through a Porapak-T packed column (1/8″ diameter and 2 m long ss column) with a work station having GC software, Class-5000 (M/S. Shimadzu Instruments, Japan). It is known that N_2O oxidizes Cu metal to Cu^{1+} oxide [5,7–10].

$$2Cu + N_2O \rightarrow Cu_2O + N_2$$

A stoichiometry of Cu:N_2O = 2:1 has been taken for calculating the number Cu active sites.

Temperature programmed reduction (TPR) studies of the catalysts have been performed on the same pulse reactor with 6% H_2–Ar as reducing gas and carrier gas. The temperature has been increased linearly at a ramp of 5 °C min^{-1} from room temperature to 700 °C where the isothermal conditions are maintained for 30 min. The change in the H_2 concentration has been detected by micro TCD and recorded on GC workstation.

2.3. *Activity measurements*

The catalytic dehydrogenation of cyclohexanol has been carried out in a fixed bed micro reactor made of quartz (6 mm i.d. and 200 mm long) packed with 1 g catalyst using a liquid cyclohexanol feed rate of 1 ml/h. The reaction temperature has been maintained at 250 °C. The products have been collected in cold trap and analyzed at regular intervals by injecting in to a GCMS–QP-5050 (M/S. Shimadzu Instruments, Japan) with DB-5 capillary column (0.32 mm diameter and 25 m long supplied by M/S. J & W Scientific, USA).

3. Results and discussion

3.1. *Physico-chemical characteristics of Cu/MgO catalysts*

Total surface areas, Cu-dispersion, Cu-metal area and Cu-crystallite size of the various Cu/MgO coprecipitated catalysts have been shown in Table 1. It is observed from our earlier work [7] that the total surface area of Cu/MgO coprecipitated catalyst is higher than that of impregnated catalyst which in turn is higher than that of the catalyst prepared by solid–solid wetting method. The higher area associated with coprecipitated catalyst may be due to the extra area generated by CuO species or the interaction between CuO and MgO might have created the extra area. The same reason can be applied to the effect of loading of Cu studied in the present work, where a slight increase in the surface area of the catalyst with loading up to 16 wt.% is seen and thereafter reduced with further increase in the Cu content probably due to the formation of bigger crystallites of CuO. Our report [7] on the effect of method of preparation on the hydrogenation activity of furfural to furfuryl alcohol, the N_2O pulse chemisorption data indicated that the Cu dispersion and Cu metal area are higher in coprecipitated catalyst compared to the other two catalysts [8,10]. This is because of the lower Cu crystallite size in coprecipitated catalyst. It was reported that the interaction between the Cu particles and the oxygen vacancies on MgO may be another reason for enhanced surface area of CM catalyst [7]. In this report [7] the surface composition of Cu/MgO catalysts obtained from the ESCA results clearly reveals the presence of more amount of Cu^0 species at the surface in CM catalyst than on IM catalyst and SSW catalyst. Thus, both N_2O pulse chemisorption and ESCA results are in agreement, indicating the presence of large number of Cu^0 species at the surface in CM catalyst. The binding energy value of Cu $2p_{3/2}$ in metallic copper and in CuO are reported to be 932.7 and 933.6 eV, respectively [11]. ESCA results of CM, IM and SSW catalysts indicate the presence of Cu^0 (binding energy of Cu $2p_{3/2}$ = 933 eV for Cu^0) in all the catalysts [7]. The shift in the binding energy in IM and

Table 1
Physico-chemical characteristics of Cu/MgO coprecipitated catalysts

Catalyst	BET surface area ($m^2 g^{-1}$)	Cu[a] (wt.%)	Cu dispersion[b] (%)	Cu metal area[b] ($m^2 g^{-1}$)	Cu crystalline size[b] (nm)	No. of surface Cu-sites[b] (μmol g.cat^{-1})
Cu1	19	5.23	7.19	2.43	14.50	59.21
Cu2	25	10.08	17.20	11.18	6.06	272.88
Cu3	34	13.52	19.74	17.21	5.28	420.06
Cu4	46	16.04	35.41	36.62	2.95	893.80
Cu5	38	37.29	11.14	26.78	9.36	653.72
Cu6	28	42.93	6.87	19.02	15.18	464.15
Cu7	25	51.62	4.97	16.55	20.98	403.86
Cu8	20	79.78	1.61	8.27	64.91	201.78

[a] Obtained from AAS analysis.

[b] From N_2O decomposition.

SSW catalysts (~934 eV) is a clear indication of presence of CuO species (the binding energy of Cu $2p_{3/2}$ for CuO is 934 eV) in addition to the Cu^0 species. Fridman and Davydov [6] reported the presence of Cu^0 state in the reduced catalysts. Boyce et al. [12] reported that reduction of CuO at 150 °C has resulted in the formation of Cu^0 species. The more number of Cu^0 sites in the surface of the CM catalyst help in yielding high catalytic activity in the dehydrogenation of cyclohexanol. Even though, the dispersion of Cu metal in coprecipitated catalyst is higher than that in impregnated or solid–solid wetting catalysts, this value is not very high [7]. It was reported [13,14] that brucite-periclase transformation is possible with MgO in presence of Cl^- ion. Most probably, the presence of Cl^- ion present in the distilled water (used during the preparation of catalysts) might have helped for such transformation. Because of this, one can expect an over layer of MgO on the surface of CuO and therefore, there is every possibility of decrease in the dispersion of Cu. This may be one of the reason why coprecipitated catalyst also possesses low dispersion of Cu.

3.2. X-ray diffraction results

XRD results (reduced catalysts) of Cu/MgO catalysts prepared by different methods revealed the presence of Cu metallic particles to be either in amorphous or in microcrystalline form (Fig. 1). In addition, poorly crystalline nature of MgO can be observed in coprecipitated catalyst. Thus, the higher surface area of coprecipitated catalyst may be due to either the interacted species formed between Cu and MgO or due to the poorly crystalline nature of MgO [7]. In other two catalysts, bigger crystallites of MgO are present. Even in the used catalysts from their XRD patterns in Fig. 2, poorly crystalline nature of Cu has been observed. Only in Cu/MgO-coprecipitated catalyst, MgO particles are in microcrystalline form indicating a possible interaction of MgO with Cu species. It was reported that MgO has the ability to stabilize the metal particles and to prevent sintering and volatilization [15,16].

Figs. 3–5 show the XRD patterns of different loadings of Cu-MgO catalyst prepared by coprecipitation method in calcined, reduced and used forms respectively, studied for the

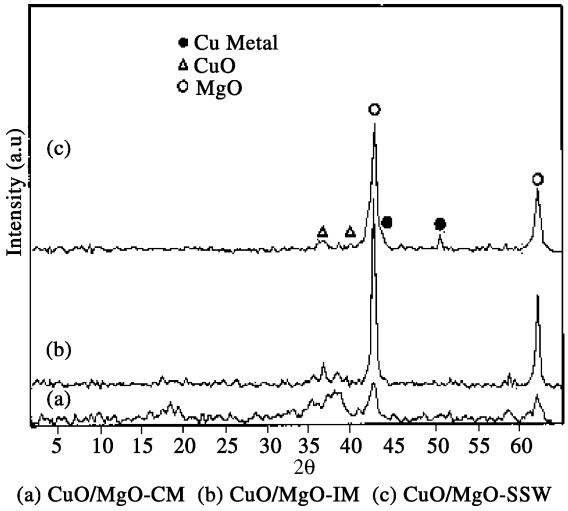

Fig. 1. XRD patterns of reduced Cu/MgO-CM, Cu/MgO-IM and Cu/MgO-SSW catalysts.

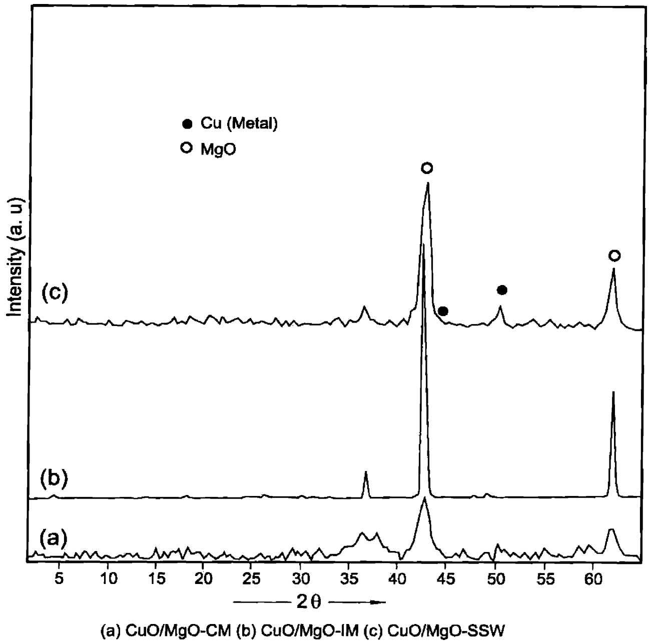

Fig. 2. XRD patterns of used Cu/MgO-CM, Cu/MgO-IM and Cu/MgO-SSW catalysts.

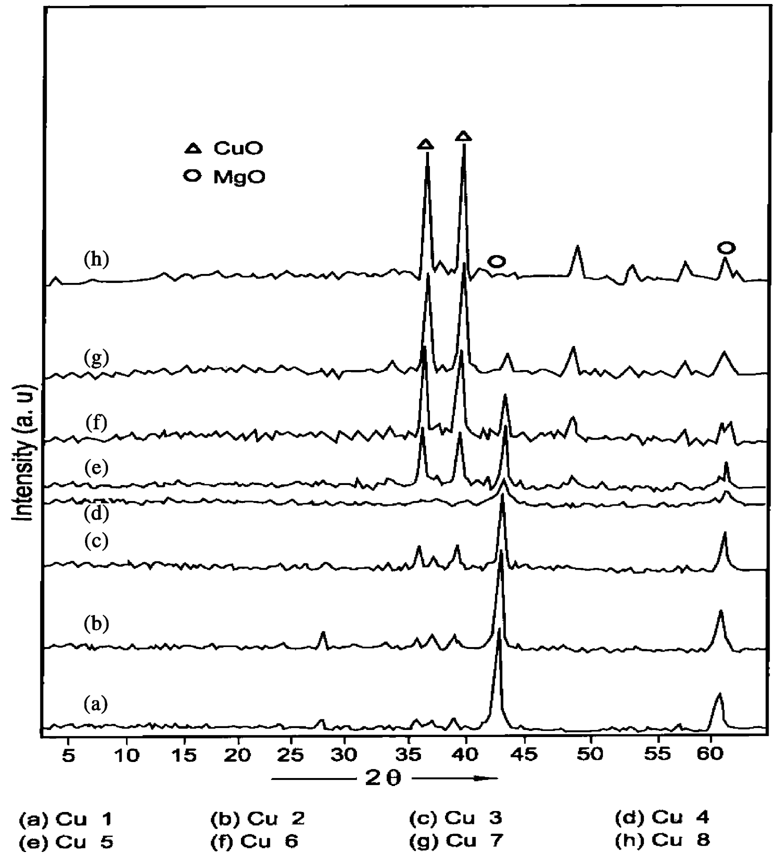

Fig. 3. XRD patterns of calcined coprecipitated catalysts with different Cu loadings.

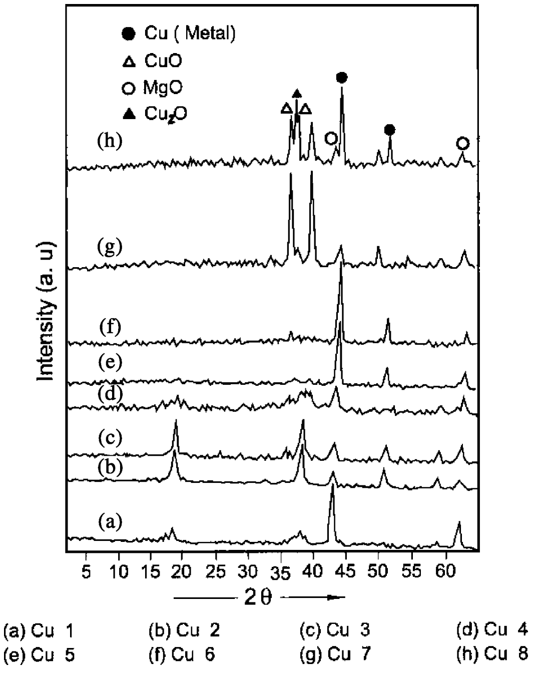

Fig. 4. XRD patterns of reduced coprecipitated catalysts with different Cu loadings.

dehydrogenation of cyclohexanol to cyclohexanone. The patterns in Fig. 3 clearly suggest the growth in the intensity of CuO (diffraction lines with d values of 2.52_x at $2\theta = 35.6°$; 2.32_x at $2\theta=38.78°$ and 2.53_5 at $2\theta=35.45°$; ASTM Card No. 5-661) upon increasing Cu loading from 5.2 to 79.8%. The catalyst comprising of lower loadings of Cu (from 5.2 to 13.5 wt.%) showed the presence of only poorly crystalline MgO phase (d values of 2.11_x at $2\theta = 42.82°$; 1.49_5 at $2\theta = 62.25°$ and 1.22_1 at $2\theta = 78.30°$; ASTM Card No. 4-829) and very poorly marked d lines of CuO. The increase in the intensity of CuO diffraction lines is noticed markedly from Cu4 onwards to Cu8. The patterns of reduced catalysts (Fig. 4) have shown the formation of Cu^0 phase (d values of 2.09_x at $2\theta = 43.25°$; 1.81_5 at $2\theta = 50.37°$ and 1.28_2 at $2\theta = 73.99°$; ASTM Card No. 4-836), but since the d values of Cu^0 and MgO are closer, the diffraction lines are not separated properly in the patterns. At lower loadings, only MgO phase is seen and with the increase in Cu loadings, a shoulder start appearing besides the peak corresponding to MgO whose intensity increased with Cu loading. However, at higher loadings, i.e., in Cu7 and Cu8, the intensity of d lines of Cu^0 phase reduces at the expense of CuO and Cu_2O (d values at 2.47_x at $2\theta = 36.34°$; 2.14_4 at $2\theta = 42.19°$ and 1.51_3 at $2\theta = 61.34°$; ASTM Card No. 5-667) phases. This may be due to incomplete reduction of the bulk CuO or due to reoxidation of the Cu^0 species to Cu^+ and Cu^{2+} formed at these higher

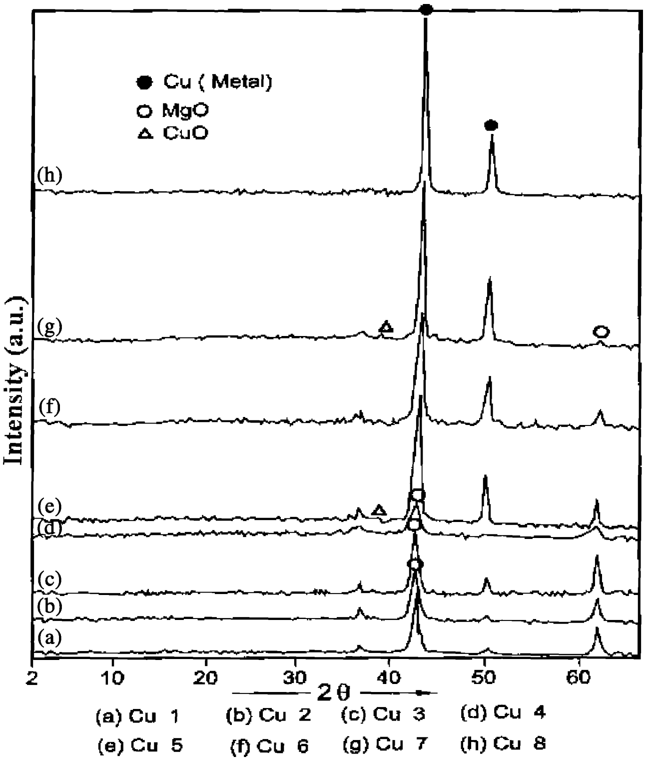

Fig. 5. XRD patterns of used coprecipitated catalysts with different Cu loadings.

loadings of Cu. Fig. 5 depicts the patterns of catalysts after the reaction indicates the intensity increase of CuO phase with increase in Cu loading and the presence of Cu^0 phase is much clear in the patterns of all these catalysts.

3.3. TPR analysis

The TPR patterns of Cu/MgO catalysts prepared by different methods are shown in Fig. 6. Broad reduction peaks centered at ∼295, 393 and 410 °C with a shoulder at ∼300 °C are observed with the catalysts made by coprecipitated, impregnated and solid–solid wetting methods, respectively. Coprecipitated sample seems to have reduced in two stages at 405 °C ($CuO \rightarrow Cu_2O$) and 460 °C ($Cu_2O \rightarrow Cu^0$) (The profile is not shown in the figure) whereas a commercial CuO sample (M/S. Loba Chemie India Ltd.) showed a reduction peak centered at ∼385 °C, $CuO \rightarrow Cu^0$ (not shown in figure). Many a literature reports suggest this reduction peak of unsupported CuO to correspond to the reduction of bulk CuO to Cu^0 [17–23]. However, the reported temperatures varied from 187 to 352 °C. The absence of any great difference in reduction temperature between the Cu/MgO-IM and SSW samples and the unsupported CuO implies the existence of weak metal support interaction [22]. The reduction pattern of Cu/MgO coprecipitated sample has peak maximum at ∼295 °C indicating the presence of easily reducible Cu^{2+} species. A similar behaviour is reported to have observed with Cu/Al_2O_3 [5] where the lowering of the t_{max} is attributed to the formation of a surface aluminate ($CuAl_2O_4$) species, which readily reduces to Cu^o even at 250–350 °C and the defect spinel structure of γ-Al_2O_3 is reported to [5] have yielded a well dispersed interacted phase. The defect sites known to be present in MgO probably contribute to the formation of surface interacted species of copper in the Cu-MgO catalysts that reduce at lower temperatures compared to the reduction of bulk CuO. Since the crystallite size of the supported CuO determines the effect on reduction behavior of the catalyst with highly dispersed CuO (smaller crystallites) showing low temperature reduction peak while the bulk CuO (larger crystallites) showing a peak centered at a higher reduction temperature [22,24,25]. The XRD patterns also confirm that the Cu/MgO coprecipitated catalyst show poorly crystalline CuO phase in contrast to Cu/MgO-IM and SSW catalysts. The higher dispersion provides larger reactive surface area and a higher concentration of defects where the reduction can start at a lower reduction temperature [26]. Contributing to the higher activity of the Cu/MgO coprecipitated catalyst compared to the other catalysts in the dehydrogenation of cyclohexanol to cyclohexanone. The small shoulder at ∼400 °C besides the peak at ∼410 °C observed in the TPR profile of Cu/MgO–SSW may be ascribed to the reduction of surface CuO particles and the peak at ∼410 °C to the reduction of bulk CuO [27]. Wang et al. [21] reported to have observed three different TPR peaks in the impregnated Cu/SiO_2 catalysts. The major one corresponding to the reduction of larger CuO clusters and the minor ones to the reduction of small CuO clusters and highly dispersed Cu (II) species, respectively.

TPR results of the calcined Cu-MgO coprecipitated catalysts with different loadings of Cu ranging from 5.23 to 79.78 wt.% indicate that the samples with lower loadings of Cu show a similar reduction temperature maxima to that of the bulk CuO and a low temperature peak observed with the sample Cu1 probably corresponds to the presence of smaller clusters of CuO. The reduction peak shifted to lower temperature with increase in Cu content up to ∼37 wt.%. The higher reduction temperature at lower loadings may be attributed

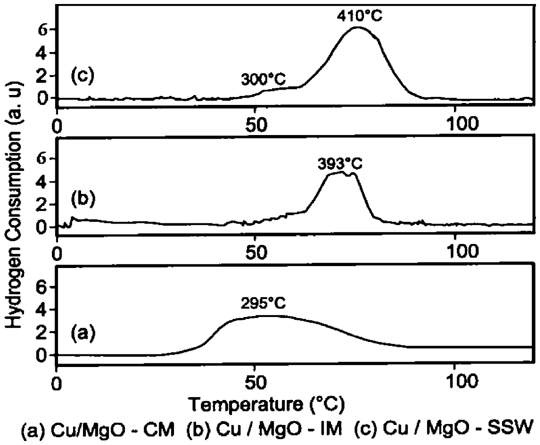

Fig. 6. TPR patterns of calcined Cu/MgO-CM, Cu/MgO-IM and Cu/MgO-SSW catalysts.

as to a weak metal support interaction and the shift in this reduction temperature to lower values with increase in Cu concentration may be due to the increased contribution of uniformly dispersed CuO crystallites as ascribed by Chang et al. [22]. Further increase in Cu loadings above 37 wt.% leads to the shift in the reduction peak back to higher temperature (∼380 °C) with the apparent formation of poorly dispersed CuO species [22].

3.4. Dehydrogenation of cyclohexanol to cyclohexanone

Fig. 7 shows the activity data, i.e., cyclohexanol conversion towards cyclohexanone against time on stream over the catalysts prepared by different methods. On Cu/MgO-CM catalyst, the activity slowly increases with time on stream and beyond 240 min, the conversion of cyclohexanol is steady at 64.3%. It is reported that at 240 °C, the equilibrium conversion of direct dehydrogenation of cyclohexanol is 68.89% [28]. The selectivity towards cyclohexanone on Cu/MgO-CM is 100%. On Cu/MgO-IM catalyst, initially the conversion of cyclohexanol is as high as 50.0% but gradually with time it came down to 2.3%. However, the selectivity towards cyclohexanone is again 100%. Cu/MgO-SSW catalyst exhibits very poor activity. The initial conversion of cyclohexanol is 2.3% which remains steady during the duration of the run.

The large number of Cu^0 species at the surface in Cu/MgO-CM catalyst might be in interaction with the defect sites of MgO which helped in yielding superior activity for cyclohexanol conversion. It is reported that various kinds of defects like steps, kinks, edges, etc., impurities and vacancies at the surface of supports can interact with metal species [29,30]. There are reports with experimental evidence that the growth of metal clusters and films is initiated at the defect sites, in particular on surface vacancies. The adsorption of Cu [31–34] and Pd [35] moities on MgO support with exposed (0 0 1) planes has been reported. The defect sites of MgO are assumed to be more reactive and the adsorption properties for metal species interacted with these sites can be qualitatively different from those of regular surface sites. Studies of adsorption of Cu, Ni, Ag and Pd atoms on F_s and $F_s{}^+$, oxygen vacancy sites as well as regular O^{2-} centers of MgO (0 0 1) surface by gradient-corrected density functional calculations using cluster models embedded in a matrix of model potentials and point charges indicate that the adsorption is stronger on F_s sites rather than on regular O^{2-} sites by 1–2.4 eV [36]. On the $F_s{}^+$ site of MgO, the single valance electron of Cu and Ag atom couples with an unpaired electron of the vacancy forming a covalent bond [36]. MgO is known to posses defect sites and these defect sites or oxygen vacancies at the Cu–MgO interface may be responsible for the selective dehydrogenation of cyclohexanol to cyclohexanone.

In the present investigation, even though the coprecipitation method yielded relatively smaller Cu particles compared to those prepared by impregnation and solid–solid wetting methods, the particle size of Cu is not so small. The defective sites at Cu and MgO interfacial region and suitable particle size of Cu appear to be the key factors in governing the selectivity towards cyclohexanone.

Fig. 8 indicates the effect of Cu loading on the cyclohexanol conversion over coprecipitated catalysts. With Cu loading, the conversion of cyclohexanol gradually increases, reaching a maximum of 64.3% at a Cu loading of 16.04% and thereafter, the conversion of cyclohexanol decreased with further increase in Cu loading. The high activity by the catalyst with 16.04% Cu loading is due to the large number of smaller Cu crystallites at the surface as evidenced by N_2O pulse chemisorption and XRD data. Fig. 9 is the effect of reaction temperature on the conversion of cyclohexanol over Cu4. From this figure, it is clear that a reaction temperature of 250 °C is optimum for getting good conversion of cyclohexanol. It is worthwhile to mention that at a reaction temperature

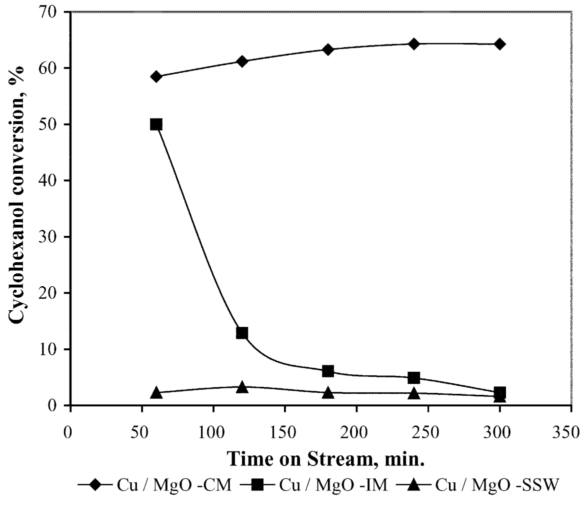

Fig. 7. Time on stream studies of Cu/MgO-CM, Cu/MgO-IM and Cu/MgO-SSW catalysts in the dehydrogenation of cyclohexanol.

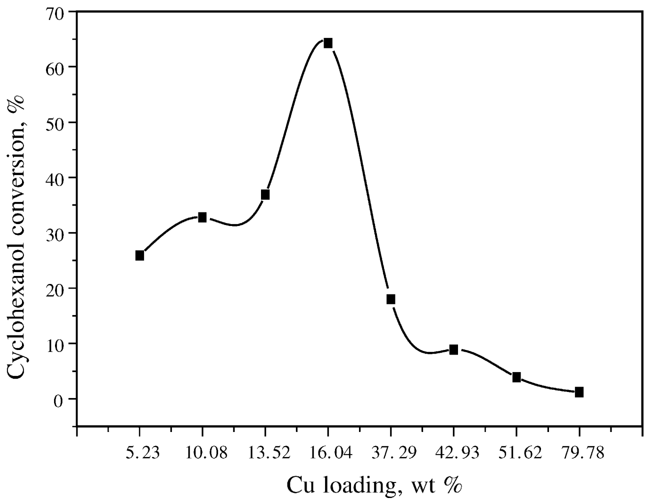

Fig. 8. Effect of Cu loading on the cyclohexanol conversion.

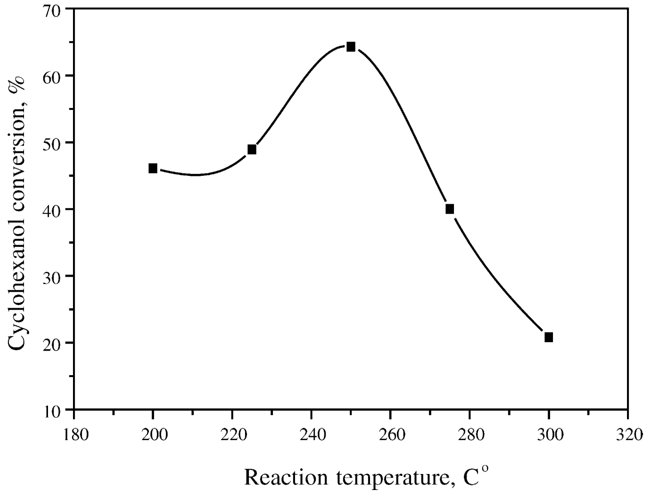

Fig. 9. Effect of reaction temperature on the conversion of cyclohexanol over Cu/ MgO-CM.

of 200 °C, the conversion of cyclohexanol to cyclohexanone matches with those of thermodynamic equilibrium conversion [28].

The advantage of coprecipitation method in yielding a Cu/MgO catalyst with maximum number of Cu metal species is demonstrated. The Cu/MgO-CM catalyst with 16.04 wt.% Cu gave a cyclohexanol conversion of 64.3% with a cyclohexanone selectivity of 100% at a reaction temperature of 250 °C.

4. Conclusion

The maximum number of Cu active species in the Cu-MgO catalyst having ∼16% Cu content prepared by coprecipitation method is responsible for getting higher conversion of cyclohexanol.

Acknowledgements

Authors thank Dr. J.S. Yadav, Director, Indian Institute of Chemical Technology, Hyderabad for his keen interest, and the authors, AHP and VS acknowledge CSIR, New Delhi, India, for the award of fellowship.

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