Effect of support modification by carbon coverage in the dehydrogenation activity of Cu/Al_2O_3 catalyst *

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Received 3 September 1998; accepted 8 April 1999

Gamma alumina and carbon covered gamma alumina supported Cu catalysts were prepared and characterized by adsorptive decomposition of N_2O, NH_3 chemisorption and temperature-programmed reduction. The decrease in interaction of copper species with alumina of carbon covered alumina has influence on the conversion and selectivity of the reaction of cyclohexanol to cyclohexanone.

Keywords: carbon covered alumina, dehydrogenation, TPR, N_2O

1. Introduction

Cu-based catalysts are of immense industrial importance such as in the synthesis of methanol [1], steam reforming of methanol to produce hydrogen useful for fuel cells [2,3], CO oxidation and synthesis of glyoxal from glycol [4], oxychlorination of ethylene [5], in the synthesis of cyclohexanone from cyclohexanol [6] and, more recently, the applicability of these catalysts in CO hydrogenation [7–10].

The nature of active sites of these catalysts is still the subject of much research [11]. For example in methanol synthesis, it is suggested that the active component is not only Cu^+ but also Cu^0 and that the support may play the role to control the Cu^+/Cu^0 ratio on which the catalytic activity depends. The catalytic process for cyclohexanol dehydrogenation suffers from low conversion as the reaction is equilibrium controlled [12,13]. The reaction is endothermic, but increase in reaction temperature beyond 280 °C accelerates the sintering of copper as the commercial catalyst contains large amounts of copper [14]. To overcome this, low amounts of Cu-containing catalysts have been developed which yield high cyclohexanone below a reaction temperature of 280 °C. It was reported that addition of Zn as a promoter to Cu/Al_2O_3 catalysts causes increase in the Cu dispersion and thereby higher conversions in the methanol [15].

In the earlier publication, we have reported the influence of support material on the dispersion and dehydrogenation activity of cyclohexanol in correlation with the active metal area of Cu [16]. The present article deals with the effect of support modification with carbon coverage by studying the catalysts for TPR, N_2O adsorptive decomposition and dehydrogenation activity of cyclohexanol instead of adding promoters to Cu/Al_2O_3 catalyst.

* IICT communication No. 4078.

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2. Experimental

Commercial γ-alumina (Harshaw, Al-3996 R, 18–25 mesh, BET surface area 172 $m^2\,g^{-1}$) was used for the preparation of carbon covered alumina (CCA) and supported copper catalysts. CCA is prepared by the pyrolysis of ethylene gas (Matheson, USA) following the method proposed by Vissers et al. [17]. The thus deposited amount of carbon was estimated by a CHN analyzer model CHN-600 (Leco Corp., USA) and found to be 20% by weight. Cu/Al_2O_3 and Cu/CCA were prepared through wet impregnation of γ-Al_2O_3 and CCA, respectively, using an aqueous solution containing the requisite amount of copper nitrate, followed by drying at 120 °C overnight and calcination in N_2 at 400 °C for 6 h. The surface areas of the catalysts were determined by the BET multilayer N_2 adsorption technique at 77 K using an all glass high vacuum (10^{-6} Torr) unit. The same unit was used to measure the amount of NH_3 chemisorbed at room temperature by a double-isotherm method.

A microprocessor-controlled temperature programmable micropulse reactor (Datacat, Vadodara, India) interfaced with a gas chromatograph (Sigma Instruments, Baroda, India) equipped with TCD has been used for nitrous oxide decomposition reaction dynamically and to carry out TPR experiments. About 100 mg catalyst sample is reduced in H_2 flow (40 $ml\,min^{-1}$) for 5 h at 250 °C which was attained at a ramp of 6 °C/min. The gas line is switched to carrier gas (He, flow rate 30 ml/min) which is passed to the GC through the catalyst sample. Then the temperature is brought down to 45 °C, where the N_2O pulse adsorption was carried out and the N_2O and N_2 generated during N_2O pulse adsorptive decomposition were analyzed using a poropak Q column. The Cu surface area has been calculated according to the method described by Evans et al. [20].

For TPR experiments, about 100 mg catalyst sample is pretreated at 400 °C in He (flow rate, 50 ml/min) for 4 h. Then the temperature is brought down to room temperature

and 8% H_2 in He gas mixture is passed over the catalyst and then the temperature is raised at a rate of 11 °C/min up to 600 °C.

The catalysts were characterized by XRD (Philips PW 1051 using Ni-filtered Cu K_α and Mo K_α radiation). Differential thermal analysis (DTA) of the samples was carried out at a heating rate of 12.5 °C/min (using Leeds and Northup DTA instruments, USA).

A fixed bed micro-catalytic reactor was employed to carry out the cyclohexanol reaction. Prior to the activity test, the catalyst sample was reduced in H_2 flow for 5 h at 400 °C followed by cooling to reaction temperature. A microprocessor-controlled (Secura, B. Braun, Germany) syringe pump has been used to feed the reactant into the reactor. The products, collected every 1 h, were analyzed by GC (Sigma Instruments, Baroda) equipped with FID using a 10% carbowax 20 m column.

3. Results and discussion

The TPR patterns of Cu/Al_2O_3 and Cu/CCA (figure 1) show thermoreduction peaks at 243 and 238 °C with major intensities. These peaks in Cu/Al_2O_3 and Cu/CCA were ascribed to the CuO/Al_2O_3 interacted species which resembles surface spinel $CuAl_2O_4$ [18]. It was reported that this surface aluminate phase was detected even on materials calcined at as low as 300 °C [19]. Depending upon the method of preparation, the thermoreduction peak due to surface $CuAl_2O_4$ may appear at different temperatures. Dumas et al. [20] have reported that as the Cu loading increases in Cu/Al_2O_3 catalysts prepared in acid medium the intensity due to surface $CuAl_2O_4$ species centered in a temperature range of 240–250 °C decreases at the expense of crystallites of CuO appeared at around 320 °C in their TPR patterns.

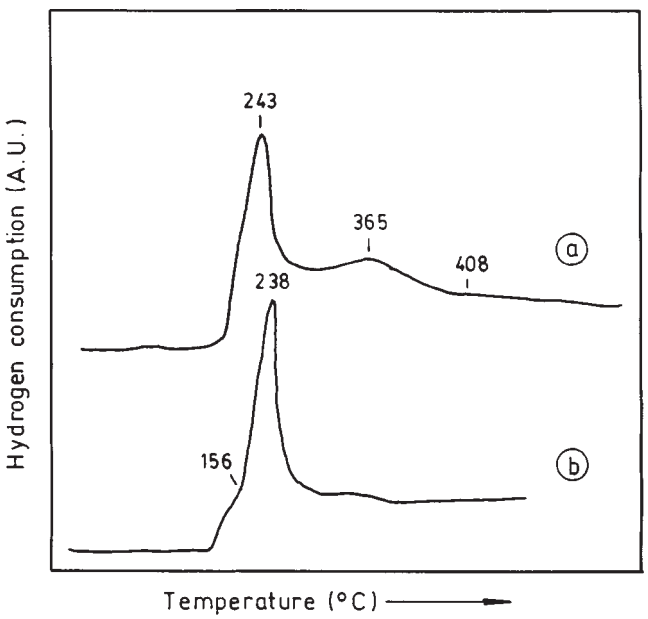

Figure 1. TPR profiles of (a) Cu/γ-Al_2O_3 and (b) Cu/CCA catalysts.

Thus in the present investigation, the TPR patterns of Cu/Al_2O_3 and Cu/CCA (figure 1) clearly indicate the formation of surface $CuAl_2O_4$ species. It has also been reported that in the $CuAl_2O_4$ surface spinel, the Cu^{2+} ions are predominantly (∼90%) in a tetragonally distorted octahedral environment with some (∼10%) tetrahedrally coordinated ions present [19]. In contrast, the Cu^{2+} distribution in bulk $CuAl_2O_4$ is 60% in tetrahedral environment and the remaining 40% is in octahedral environment [19,21].

CuO is exclusively square planar [19,22]. Even though it was reported [22,23] that among the first row transition metal aluminates, formation of $CuAl_2O_4$ is least favourable, Lo Jacono and Schiavello [26] have reported that the surface spinel $CuAl_2O_4$ is the most readily formed compared to the surface aluminates of Co and Ni. It was also reported that among the divalent metal aluminates, H_2 reduction of $CuAl_2O_4$ to Cu metal occurs readily, even at 250–350 °C [22,23,25]. γ-Al_2O_3 being a defect spinel yields a well dispersed interacted phase at low loadings of Cu, i.e., approximately upto Cu loadings of 10 wt% and above this loading, segregation of CuO occurs [25]. The thermoreduction peak centered at 365 °C in both Cu/Al_2O_3 and Cu/CCA catalysts appears to be due to the reduction of CuO leading to metallic copper of lower dispersion [20].

Figure 2 shows the XRD patterns of Cu/Al_2O_3 and Cu/CCA catalysts. In both the catalysts, formation of CuO (Tenorite Synergism; ASTM card No. 5-0661) due to two major diffraction peaks centered at $2\theta = 35.6°$ and at 38.8° in addition to γ-Al_2O_3 phase is observed. A trace amount of the formation/occurrance of the paramelaconite ($6CuO{\cdot}Cu_2O$) phase could also be identified in the XRD pattern of the Cu/Al_2O_3 catalyst. No such phase is detected in the XRD pattern of the Cu/CCA catalyst. However, formation of $CuAl_2O_4$ may not be ruled out because both $CuAl_2O_4$ and γ-Al_2O_3 are spinel type phases and their diffraction peaks nearly coincide [19]. Another argument is the presence/formation of highly dispersed or amorphous $CuAl_2O_4$ species. This finding is consistent with previously reported results [25].

No crystalline carbon phases are observed, even though the carbon content in CCA support is 20 wt%. This is in agreement with earlier findings on CCA [26,27]. It was observed that there was no appreciable carbon loss in CCA during the calcination step due to oxidation by NO_3^- ions present in the copper nitrate precursor. The carbon content after calcination was found to be 19.4% by weight.

The advantages of CCA over Cu/Al_2O_3 are (i) decrease in the strong acidity of γ-Al_2O_3, (ii) prevention of strong interaction between γ-Al_2O_3 and CuO phase, and (iii) the beneficial role of both γ-Al_2O_3 and carbon like high mechanical strength of γ-Al_2O_3 and the electron withdrawing capacity of carbon [26,27].

DTA patterns of Cu/CCA and Cu/γ-Al_2O_3 (figure 3) show the peak at around 150 °C for the presence of physically adsorbed water in both the catalysts. The endothermic signal at 280 °C in the Cu/Al_2O_3 catalyst indicates the presence of Cu^{2+} species in interacted form with the support.

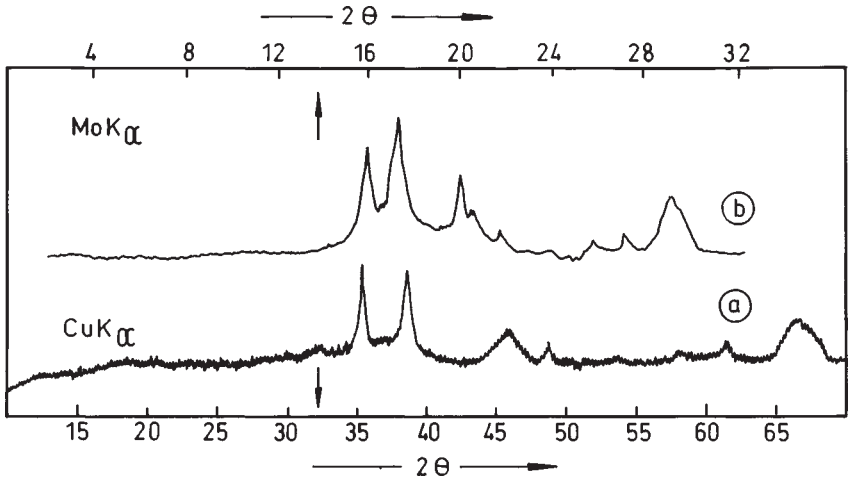

Figure 2. XRD patterns of (a) Cu/γ-Al_2O_3 and (b) Cu/CCA catalysts.

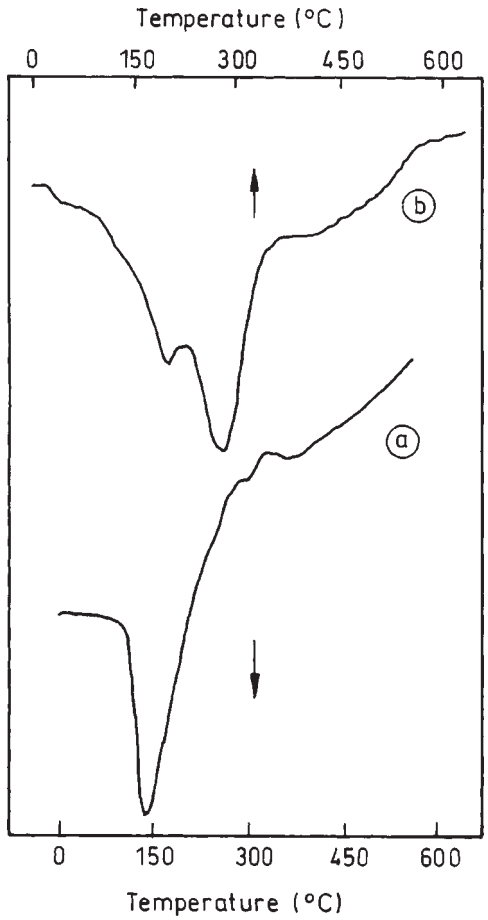

Figure 3. DTA patterns of (a) Cu/γ-Al_2O_3 and (b) Cu/CCA catalysts.

The absence of this signal in Cu/CCA clearly suggests that carbon coverage on γ-Al_2O_3 prevents the interaction between Cu^{2+} species and γ-Al_2O_3.

The higher BET surface area (table 1) of Cu/CCA (166 $m^2\,g^{-1}$) than that of Cu/Al_2O_3 (136 $m^2\,g^{-1}$) clearly indicates the formation of amorphous carbon which might have contributed to the extra area. The decrease in acidity of Cu/Al_2O_3 (434 μmol g^{-1}) due to carbon coverage

Table 1
Characterization of Cu/Al_2O_3 and Cu/CCA catalysts.

S. No.	Characteristic	Cu/Al_2O_3	Cu/CCA
1	Cu content (%)	10.0	11.0
2	BET surface area ($m^2\,g^{-1}$)	136.0	166.0
3	NH_3 uptake (mol g^{-1})	434.0	3890–0
4	N_2O uptake (mol g^{-1})	51.0	49.0
5	Dispersion (%)	6.4	5.6
6	Crystallite size (Å)	16.0	18.3
7	Activity results		
	(a) Conversion (%)	56.0	40.5
	(b) Selectivity (%)		
	(i) Cyclohexanone	68.0	88.0
	(ii) Cyclohexene	32.0	12.0
8	Rate (mol h^{-1} g-cat.$^{-1}$)	5.3×10^{-2}	3.8×10^{-2}
9	Turnover number (No. of cyclohexanol molecules converted s^{-1}(Cu atom)$^{-1}$)	14.6×10^{-2}	11.0×10^{-2}

in Cu/CCA (389 μmol g^{-1}) to a modest extent may be attributed to two facts. Upon calcination of Cu/CCA catalyst in N_2 a catalyst is produced with coverage of carbon on the strong acid sites of Al_2O_3. Secondly, part of the copper may interact with Al_2O_3 and part deposit on carbon on Al_2O_3. The data on N_2O uptake values of both the catalysts indicate that copper dispersion on γ-Al_2O_3 is slightly higher than that on CCA perhaps due to the presence of high amount of interacted Cu on the γ-Al_2O_3 support than on the CCA support. Carbon is known to be a poor interacting support. The dispersion and crystallite size (assuming a cubic crystal) of Cu values in the table, respectively, are those calculated from N_2O uptake data using the equations:

$$2Cu^0 + N_2O \rightarrow Cu_2O + N_2 \quad (1)$$

$$\text{Crystallite size (Å)} = 6000/(\text{Cu metal area per gram Cu} \times \text{Cu density}). \quad (2)$$

The dispersion and crystallite size values of copper strongly support the above discussion.

The results of cyclohexanol dehydrogenation reaction over Cu/Al_2O_3 and Cu/CCA catalysts are also shown in

table 1. The conversion of cyclohexanol over Cu/Al_2O_3 is slightly higher than that of Cu/CCA. It indicates that the turnover number (number of cyclohexanol molecules converted per second per Cu atom) is slightly higher on Cu/Al_2O_3 (TON $= 14.57 \times 10^{-2}$) than on Cu/CCA (10.95×10^{-2}). However, the selectivity towards cyclohexanone over Cu/CCA (88%) is greater than that of Cu/Al_2O_3 (68%). Activity versus time on stream studies reveal that even after 10 h of continuous run there was no appreciable change ($\pm 1\%$) in the conversion and selectivity. The difference in activity behaviour of the two catalysts may be attributed to the differences in acidity and Cu dispersion on the two catalysts. The higher selectivity for cyclohexanone on Cu/CCA than on Cu/Al_2O_3 are in line with the acidity data with probable carbon coverage on stronger acid sites of γ-Al_2O_3.

4. Conclusion

It is concluded that the modification of Al_2O_3 support by carbon coverage has a beneficial role in increasing the selectivity towards cyclohexanone at the expense of dehydration (cyclohexene) product which generally forms over an acidic site in the reaction of cyclohexanol. The decrease in the dehydration product is attributed to the decrease in the acidity of Cu/CCA, due to carbon coverage.

Acknowledgement

GKR thank CSIR for a Research Associateship.

References

[1] P. Mittash and E.P. Winkler, US Patent 571356 (1923) to BASF.
[2] K. Takahashi, H. Kobayashi and N. Takezawa, Chem. Lett. (1985) 759.
[3] M.L. Hair, *Infrared Spectroscopy in Surface Chemistry* (1967).
[4] C.L. Thomas, in: *Catalytic Processes and Proven Catalysts* (Academic Press, New York, 1970).
[5] S.S. Naworski and E.S. Velez, in: *Applied Industrial Catalysis*, Vol. 1 (1983) p. 239.
[6] H.F. Chang and M.A. Slague, J. Mol. Catal. 88 (1994) 223.
[7] T. Inui, H. Hara, T. Takeguchi and H.B. Kim, Catal. Today 36 (1997) 25.
[8] K.W. Jun, K.S. Rama Rao, M.H. Jung and K.W. Lee, Bull. Korean Chem. Soc. 19 (1998) 466.
[9] K.W. Jun, W.J. Shen, K.S. Rama Rao and K.W. Lee, Appl. Catal. 174 (1999) 231.
[10] K.W. Jun, M.H. Jung, K.S. Rama Rao, M.J. Choi and K.W. Lee, Stud. Surf. Sci. Catal. 114 (1998) 447.
[11] J.C.J. Bart and R.P.A. Sneeden, Catal. Today 2 (1987) 1.
[12] H.A. Cubberley and M.B. Muller, J. Am. Chem. Soc. 69 (1947) 1535.
[13] J.B. Conn, G.B. Kistiakowsky and E.A. Smith, J. Am. Chem. Soc. 61 (1939) 1868.
[14] Y. Lin, I. Wang and C. Yeh, Appl. Catal. 41 (1988) 53.
[15] W.R.A.M. Robinson and J.C. Mol, Appl. Catal. 60 (1990) 73.
[16] A. Rachel, Ch. Sivaraj, G. Krishna Reddy, V. Vijay Kumar and P. Kanta Rao, Ind. J. Chem. 32 A (1993) 857.
[17] J.P.R. Vissers, F.P.M. Mercx, S.M.A.M. Bouwens, V.H.J. de Beer and R. Prins, J. Catal. 114 (1988) 291.
[18] J.W. Evans, M.S. Wainwright, A.J. Bridge Water and D.J. Young, Appl. Catal. 7 (1983) 75.
[19] J.M. Dumas, C. Geron, A. Keribii and J. Barbier, Appl. Catal. 47 (1989) L9.
[20] R.M. Freidman, J.J. Freeman and F.W. Lyte, J. Catal. 55 (1978) 10.
[21] G. Ertl, K. Hieri, K. Knojinger, N. Thiele and H.P. Urbach, Appl. Surf. Sci. 5 (1980) 49.
[22] A. Navrotsky and O.J. Kleppa, J. Inorg. Nucl. Chem. 30 (1968) 479.
[23] A. Navrotsky and O.J. Kleppa, J. Inorg. Nucl. Chem. 29 (1967) 2701.
[24] Y. Okamoto, K. Fukino, T. Imanaka and S. Teranishi, J. Phys. Chem. 37 (1983) 3747.
[25] M. Lo Jacono and M. Schiavello, in: *Preparation of Catalysts*, eds. B. Dalmon, P.A. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1976) pp. 474–487.
[26] B.R. Strohmeir, D.E. Leyden, R. Scott Field and D.M. Hercules, J. Catal. 94 (1985) 514.
[27] K.S. Rarna Rao, S.K. Masthan, P.S. Sai Prasad and P. Kanta Rao, Appl. Catal. 73 (1991) L1.