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Role of CO/CO_2 co-feeding in the dehydrogenation of cyclohexanol to cyclohexanone over Cu–ZnO based catalysts

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Abstract

The present work highlights the role of CO/CO_2 co-feeding in the dehydrogenation of cyclohexanol to cyclohexanone over Cu–ZnO–Cr_2O_3 and Cu–ZnO–Cr_2O_3–La_2O_3 catalysts in the temperature range of 448–523 K at atmospheric pressure under vapor phase conditions. Both the catalysts are prepared by coprecipitation technique and are characterized by BET surface area, XRD, TPR and N_2O pulse chemisorption under dynamic conditions. The co-feeding of CO/CO_2 along with cyclohexanol results in enhanced conversion of cyclohexanol and additional formation of methanol. The hydrogen generated in the dehydrogenation of cyclohexanol to cyclohexanone promotes the methanol formation from CO/CO_2. This is the first report where in methanol formation is observed at atmospheric pressure from CO/CO_2 co-feeding in cyclohexanol dehydrogenation.

Keywords: Dehydrogenation; Cyclohexanol; Cyclohexanone; CO_x; Cu–ZnO; Methanol

1. Introduction

Catalytic dehydrogenation of cyclohexanol to cyclohexanone is an important industrial reaction particularly in the manufacture of Nylon 6 because the two major raw materials in producing polyamide fiber are caprolactam and adipic acid both of which can be obtained from cyclohexanone [1,2]. Copper-containing catalysts have been used in the process for dehydrogenation of cyclohexanol to cyclohexanone for many years [3,4]. From the industrial point of view the production of cyclohexanone is quite limited, since (i) the reaction is highly endothermic ($\Delta H = 15$ kcal/mol) and the conversion is limited by thermodynamic equilibrium; (ii) the selectivity and stability are drastically affected by increasing the reaction temperature and must be limited to below 553 K in order to prevent sintering of the copper catalysts [5,6]. Due to the endothermic nature of the reaction, the increase of the liquid hourly space velocity (LHSV) of cyclohexanol is relatively limited by low external heat supply in a practical reactor. In addition, the released hydrogen cannot be used effectively. Alternatively, oxidative cyclohexanol dehydrogenation has been proposed in order to circumvent some of the cited difficulties [7]. However, in the oxidative dehydrogenation of ethylbenzene to styrene process, the usage of O_2 (strong oxidant) produces unwanted by-products (oxygenates) resulting in low selectivity and has been pointed out that the oxidative dehydrogenation process has its own disadvantages that it consumes large amount of energy [8,9]. For the last two decades CO_2 has received much attention as oxidant as well as diluent instead of super heated steam in reactions like oxidative ethylbenzene dehydrogenation because it is always gaseous throughout the dehydrogenation process [9,10]. This has been attributed to the enhancement in the oxidative conversion as well as catalytic life by suppressing the coke deposition in presence of CO_2. In the present investigation, effect of CO/CO_2 in

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the dehydrogenation of cyclohexanol has been studied for the first time over Cu–ZnO based catalysts promoted with Cr_2O_3 and La_2O_3–Cr_2O_3. The metal dispersion and particle size are measured through N_2O titration method and are correlated with activity results.

2. Experimental

2.1. Preparation of Catalysts

a. Catalyst-A (Composition by weight = 45% CuO–45% ZnO–10% Cr_2O_3): Requisite amounts of $Cu(NO_3)_2$. $3H_2O$ (M/S. Loba Chemie Ltd; India), $Zn(NO_3)_2 \cdot 6H_2O$ (M/S. Loba Chemie Ltd; India) and Cr $(NO_3)_3 \cdot 9H_2O$ (M/S. Loba Chemie Ltd; India) were dissolved in distilled water to get 10 wt% with respect to each salt and were co-precipitated with 10 wt% aqueous solution of Na_2CO_3 at a temperature of 343 K and at pH of 7.

b. Catalyst-B (Composition by weight = 42.5% CuO–42.5% ZnO–10% Cr_2O_3–5% La_2O_3): Requisite amounts of Cu $(NO_3)_2 \cdot 3H_2O$ (M/S. Loba Chemie Ltd; India), Zn $(NO_3)_2 \cdot 6H_2O$ (M/S. Loba Chemie Ltd; India), Cr $(NO_3)_3$ (M/S. Loba Chemie Ltd; India) and $La(NO_3)_3 \cdot 6H_2O$ (M/S. Loba Chemie Ltd; India) were dissolved in distilled water to get 10 wt% with respect to each salt and were co-precipitated with 10 wt% aqueous solution of Na_2CO_3 at a temperature of 343 K and at pH of 7.

The co-precipitated mass in *a* and *b* was thoroughly washed, filtered and dried at 393 K for 12 h in air followed by calcination in air at 723 K for 5 h to get the catalysts, A and B respectively.

2.2. Catalyst characterization

The catalysts were characterized by BET surface area using N_2 adsorption method at liquid nitrogen temperature (77 K) on an all glass high vacuum unit after attaining a vacuum of 10^{-6} Torr. Powder X-ray diffraction patterns of calcined and reduced catalysts (reduced at 523 K in H_2 flow for 3 h and passivated in N_2 atmosphere) were recorded on a Rigaku Miniflex X-ray diffractometer (M/s. RIGAKU corporation, Japan) using Ni filtered Cu Kα radiation. These samples were scanned in the 2θ range of 2 to 80° at a scan speed of 2°/min. Temperature programmed reduction profiles of the calcined samples were generated on a home made on-line quartz micro reactor interfaced to a thermal conductivity detector (TCD) equipped gas chromatograph (M/S. Shimadzu, model: GC-17A, Japan) and the profiles were recorded on a GC workstation using a GC software Class-GC10. H_2/Ar (11% of H_2 and balance Ar) mixture was used as the reducing gas while the catalyst was heated linearly at a heating ramp of 5 K/min from 303 K to 873 K where the isothermal conditions were maintained for 30 min. N_2O pulse chemisorption experiments using 6% N_2O–He mixture were performed under flow conditions to find out Cu dispersion. The experimental procedure for N_2O pulse chemisorption and calculation procedure for the number of Cu active sites, dispersion and crystallite size has been described in our previous report [11].

2.3. Activity studies

Three different reactions in vapour phase were carried out on the catalysts in the temperature range of 448 K to 523 K in a fixed bed micro reactor made of quartz (8 mm i.d. and 200 mm long) packed with 1 g catalyst. Prior to the activity test the catalyst was reduced in H_2 at 523 K for 3 h and then passivated under commercial N_2 flow at 523 K for 1 h and then temperature was brought down to reaction temperature. All the reactions were conducted at atmospheric pressure. The following reactions were done:

1. Dehydrogenation of cyclohexanol was done at cyclohexanol feed rate of 1 ml h^{-1} in nitrogen flow of 600 cc h^{-1}.
2. Dehydrogenation of cyclohexanol in presence of CO, the cyclohexanol was fed at a rate of 1 ml h^{-1} and 10% CO in He at a flow rate of 600 cc h^{-1} was maintained.
3. Dehydrogenation of cyclohexanol in presence of CO_2, the cyclohexanol was fed at a rate of 1 ml h^{-1} and 10% CO_2 in He at a flow rate of 400 cc h^{-1} was maintained.

The products, both the liquid as well as the gaseous have been collected at regular intervals (for every 1 h) after the steady state is reached. The analysis of the products has been carried out on a GC-MS (QP-5050A, M/S. Shimadzu Instruments, Japan) with EI-mass detector. The gas samples have been analyzed using GS-Q capillary column (M/S. J & W Scientifics, USA), having dimensions of 0.32 mm i.d. × 0.25μm × 30 m long and the liquid samples using ZB-5 capillary column (M/S. Zebron), having dimensions of 0.32 mm i.d. × 0.25μm × 30 m long. The conversions and selectivities of the products have been calculated by comparing their areas with that of the pure reactant samples.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the physical characteristics of the two catalysts under study. The surface area of catalyst A is (72 m^2 g^{-1}) nearly 1.7 times that of catalyst B (42 m^2 g^{-1}). But the Cu metal area of catalyst B (5.6 m^2 g^{-1}) is nearly 4 times that of catalyst A (1.5 m^2 g^{-1}). This is a clear indication that double promotion by Cr_2O_3 and La_2O_3 increased the Cu metal area. This is possible by the formation of smaller crystallites of Cu and thereby in the increased Cu dispersion. The lower BET surface area associated with double promoted catalyst may be due to lower surface area contribution from La_2O_3 crystallites. Liaw and Chen reported

Table 1
Physico-chemical characteristics of catalysts

Catalyst	BET surface Area ($m^2\,g^{-1}$)	Cu dispersion (%)	Cu metal area ($m^2\,g^{-1}$)	Cu crystallite size, (nm)
Catalyst A	72	0.7	1.5	156.0
Catalyst B	42	2.5	5.6	41.2

that dispersion and stability of Cu could be enhanced by doping Cr, Zr and Th to Cu-based catalysts [12]. Martin et al. summarized that chromia acts as a structural promoter because it increases the BET surface area and also inhibits the sintering of copper particles [13]. The other groups have confirmed that doping the trivalent metal ions

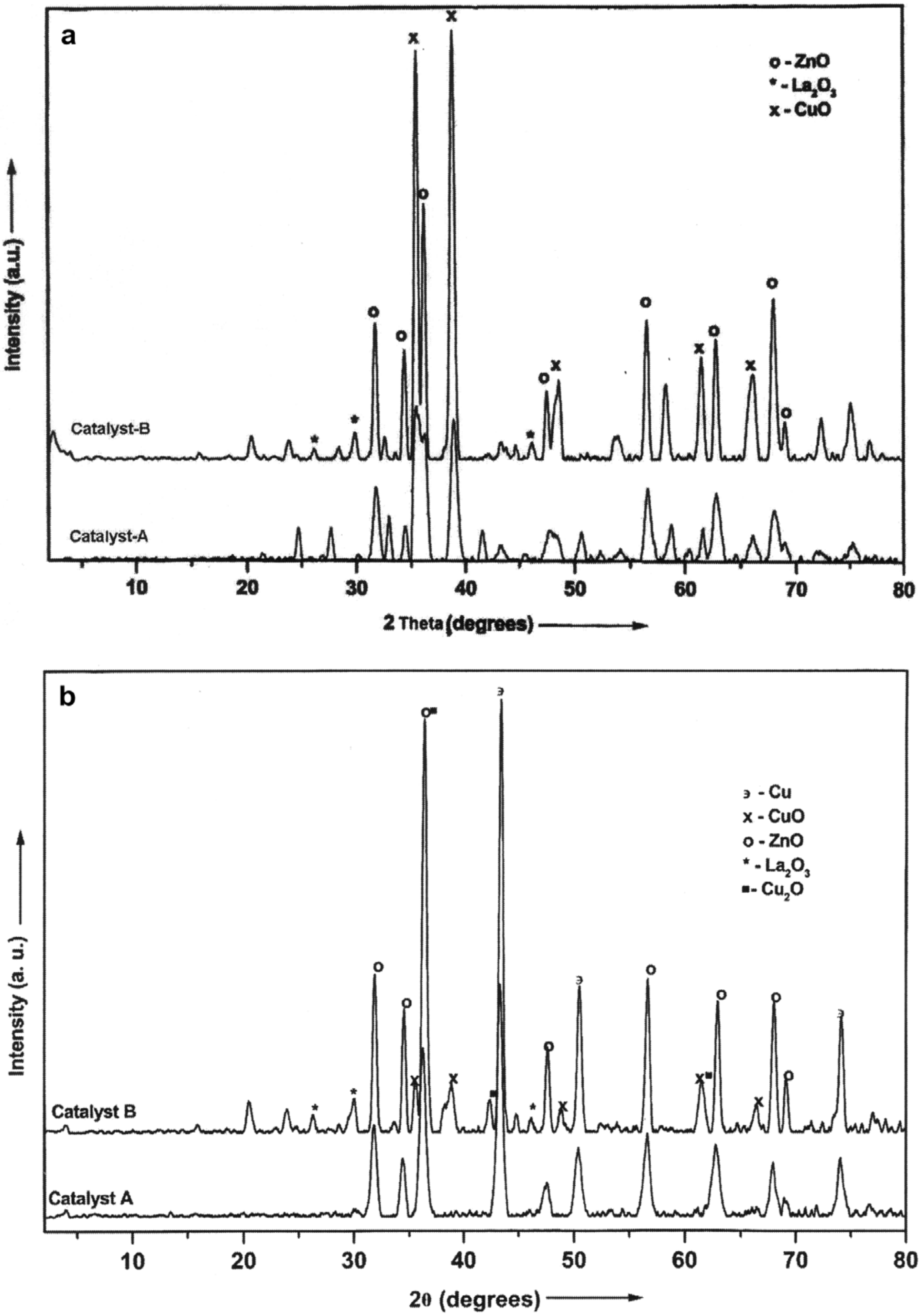

Fig. 1. Powder XRD patterns of catalysts A and B (a) calcined (b) reduced and passivated.

or rare earth elements such as La and Y on to the catalysts could improve its performance [14,15]. The relatively lower Cu dispersion values in both the catalysts are due to the presence of large amount of Cu (more than 40% by weight in the form of CuO).

Fig. 1a,b show the XRD patterns of calcined and reduced catalysts respectively. The presence of crystalline phases of CuO with *d* values [2.32, 2.52, 1.87; ICDD No. 72-0629] and ZnO with d values [2.82, 2.61, 2.48; ICDD No. 89-1397] in calcined catalysts A and B (Fig. 1) are clearly visible. Presence of La_2O_3 crystallites with d values [2.98, 3.41, 1.97; ICDD No. 73-2141] in catalyst B can also be seen. The reduced catalysts (Fig. 1b) indicate the presence of Cu crystallites with d values [2.09, 1.81, 1.28; ICDD No. 85-1326] in both catalysts A and B. An XRD signal due to Cr_2O_3 has not been observed in both calcined and reduced catalysts that may be due to the presence of chromium oxide in amorphous phase. Wang et al. observed that when the chromium content is below 40%, Cu species in the catalysts mainly exist as Cu_2O and Cu^0, and no XRD signal of species containing chromium appears, which suggests that the species containing chromium is highly dispersed and exists in amorphous phase [16]. In addition to metallic Cu, signals due to CuO and Cu_2O with d values [2.46 2.13 1.51 ICDD No: 75-1531] have been observed in reduced catalyst B. Since the d lines of Cu_2O and ZnO overlap or are in close proximity and hence clear separation of two phases couldn't be identified. However, such d lines are not observed in reduced catalyst A. Chen et al. reported that doping trivalent metal ions such as Cr^{3+} could also enhance the formation of monovalent cationic defects on the crystal surface of ZnO, which might accelerate both enrichment and stabilization of Cu^+ on the surface during the reduction and reaction process [16]. This clearly shows that in double promoted catalyst, the addition of La_2O_3 stabilizes a part of the copper in ionic (Cu^+) state.

From Fig. 2, it is clear that Cr_2O_3 promoted Cu–ZnO catalyst gets reduced at a T_{max} of 523 K. The TPR pattern of La_2O_3 and Cr_2O_3 double promoted Cu–ZnO catalyst has shown two reduction maxima, very low intense one at a T_{max} of 420 K corresponding to the reduction of Cu^{2+} to $Cu^+$and a high intense one at a T_{max} of 553 K to the reduction of Cu^{2+} to Cu^0. Addition of Cr_2O_3 to Cu–ZnO permits easy reduction of CuO phase and its role is highly remarkable in increasing the intrinsic activity i.e. specific activity per site [17,18]. Lin et al. have studied La–Cu catalysts and found that the addition of La_2O_3 stabilizes catalyst surface CuO and makes Cu^{2+} ion formation easier. Cu^{2+}–O bond energy is lowered, and meanwhile Cu^{2+} ions also quickly reduce into active Cu^+ ions, thus easily making a redox cycle of Cu^+ to Cu^{2+} ions [19]. A broad peak with low intense signal at high temperature in both the catalysts may be due to the reduction of Cu_2O or partial reduction of ZnO phase. Literature studies reveal the reduction of Cu_2O and ZnO at high temperatures [17].

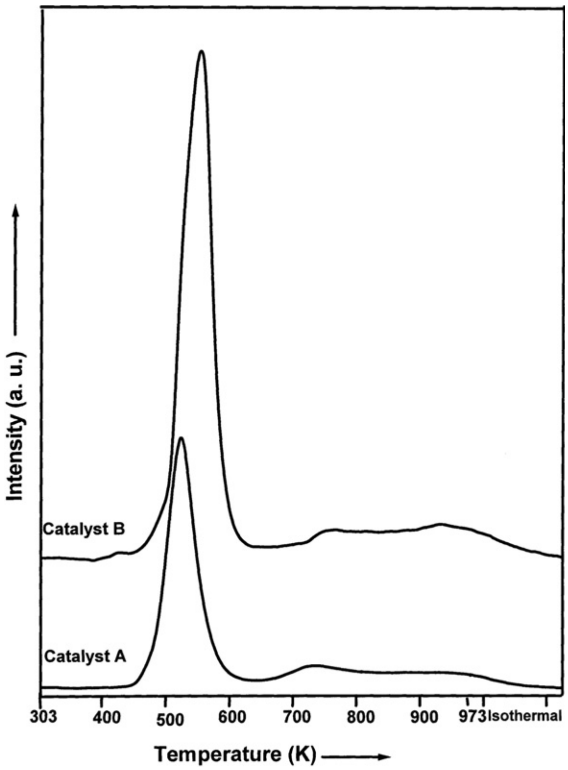

Fig. 2. TPR profiles of catalysts A and B.

3.2. Activity results

Cyclohexanol dehydrogenation activity data in presence of N_2 over catalysts A and B is shown in Fig. 3a. Cyclohexanone is the major product in the cyclohexanol dehydrogenation. The conversion of cyclohexanol is slightly higher at all temperatures on double promoted catalyst than on single promoted catalyst and shows higher yield of cyclohexanone on catalyst B (60%) compared to that of single promoted catalyst A (48%) at 523 K. Cyclohexene (~27.5% at 523 K) is also formed via dehydration, which takes place particularly at higher temperatures. Phenol and cyclohex-2-ene-1-one are formed as the other minor by-products over both the catalysts studied which accounted for a yield of ~3.5%. The pathway for the formation of byproducts in cyclohexanol dehydrogenation has been reported elsewhere [20]. Cyclohexanol dehydrogenation is an equilibrium-controlled reaction and it is reported that the equilibrium value of the cyclohexanone is 68.69% at 513 K and 45.22% at 473 K [6,21]. In the present investigation the cyclohexanone yields on the catalysts A and B are below the equilibrium values.

The activity data for cyclohexanol dehydrogenation in presence of 10% CO and balance helium is shown in Fig. 3b and rate of conversion of CO is shown in Fig. 4a. The conversion of cyclohexanol and selectivity towards the formation of cyclohexanone are more on double promoted catalyst than on single promoted catalyst. Rate of conversion of CO to methanol formation is also more on

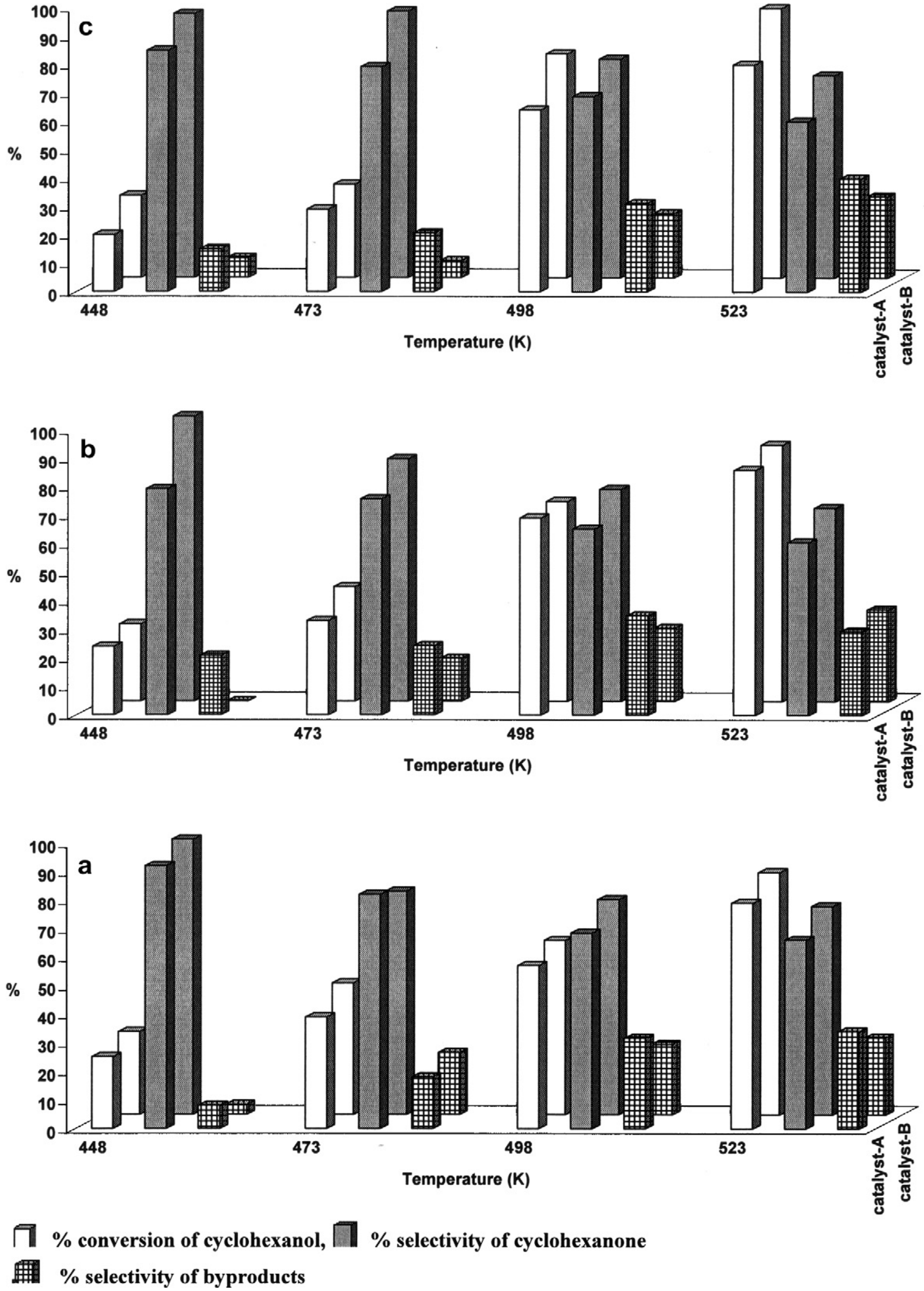

Fig. 3. Cyclohexanol dehydrogenation activity over catalysts A and B (a) in presence of N_2 (b) in presence of CO (c) in presence of CO_2.

the double promoted catalyst in the high temperature region and more or less the same at lower temperatures. Formation of methanol can be explained as a result of reaction between CO and the hydrogen formed from the cyclohexanol dehydrogenation process. Cu–ZnO catalysts are also well known for synthesis of methanol [22,23]. Cyclohexanol dehydrogenation in presence of CO shows a slightly higher conversion of cyclohexanol on both

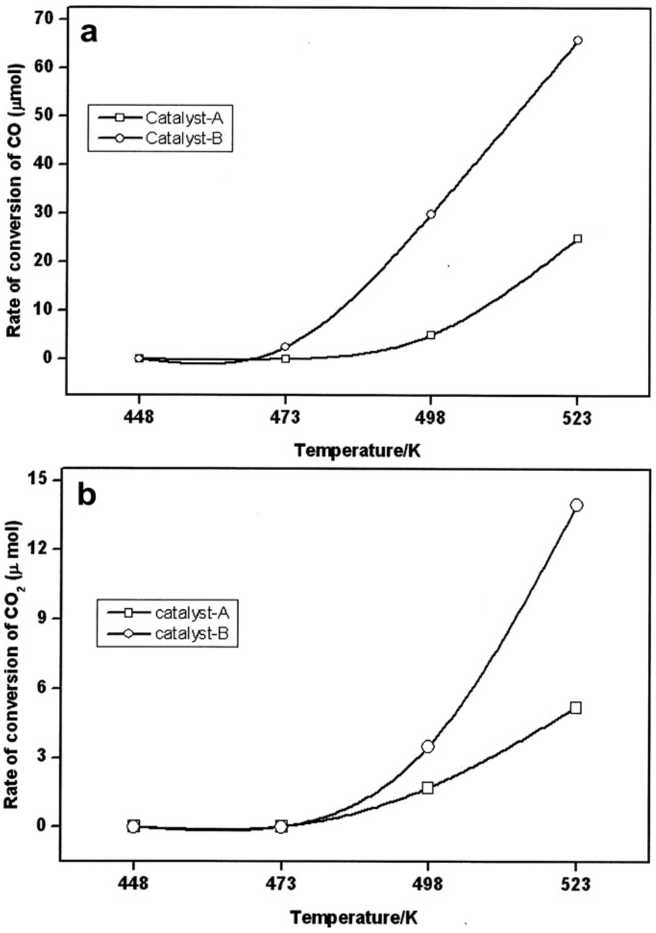

Fig. 4. (a) Rate of conversion of CO and (b) rate of conversion of CO_2 in the cyclohexanol dehydrogenation over catalysts A and B.

catalyst A (84%) and catalyst B (94%) in comparison to cyclohexanol dehydrogenation in presence of N_2 on catalyst A (80%) and on catalyst B (91%) at 523 K. The dehydrogenation process in presence of CO on catalyst B shows cyclohexanone yields of 68% at 523 K, which is very close to the equilibrium value.

The activity for the cyclohexanol dehydrogenation in presence of 10% CO_2 and balance helium on both the catalysts is shown in Fig. 3c. Fig. 4b represents the rate of conversion of CO_2 in presence of cyclohexanol dehydrogenation. The conversion of cyclohexanol and that of CO_2 are more on double promoted catalyst at all temperatures. The same is true in the case of selectivities towards cyclohexanone and methanol formation. Conversion of cyclohexanol is more in presence of CO/CO_2 compared to N_2, this is because of the fact that the H_2 formed in the dehydrogenation reaction is being continuously consumed for methanol synthesis. Zheng et al. reported that cyclohexanol dehydrogenation activity is more when the reaction is coupled to furfural hydrogenation and they proposed that the activated hydrogen species on the catalyst surface due to cyclohexanol dehydrogenation probably plays an important role in improving the selectivity in the hydrogenation of furfural [24]. The consumption of the activated hydrogen species can break the thermodynamic equilibrium of cyclohexanol dehydrogenation and facilitates the dehydrogenation of cyclohexanol to cyclohexanone. The other byproducts observed in this reaction are cyclohexene and phenol. However in the case of single promoted catalyst, it seems that the H_2 produced is not getting consumed more effectively as on double promoted catalyst since conversion of CO/CO_2 is less on single promoted catalyst. In our earlier publication, the role of CO_2 in the aromatization of isophorone to 3, 5–xylenol, is described as to suppress the strong basic sites of catalyst [25], where as we report for the first time the beneficial role played by CO/CO_2 in the dehydrogenation of cyclohexanol in yielding methanol in the present study. In presence of CO_2, the RWGS reaction and the formation of CO in traces is also observed. The selectivity towards methanol formation is predominant on both the catalysts when compared to RWGS reaction. The double promoted catalyst is again a better catalyst in yielding more amount of methanol. CO_2 hydrogenation is more difficult than CO hydrogenation and is the reason for the higher rate of conversion of CO over CO_2 and the same may be attributed to high conversion of cyclohexanol in presence of CO than in presence of CO_2. The rates of conversions of CO and CO_2 are very low since methanol synthesis is an equilibrium controlled reaction and the methanol formation at atmospheric pressure is very low [26,27]. In all the above-discussed reactions, the double promoted catalyst showed higher conversions of cyclohexanol and CO/CO_2, which could be ascribed to higher Cu dispersion, smaller Cu particle sizes and to the presence of more number of active copper species present as Cu^0/Cu^+ as reported by several authors [28–30].

4. Conclusions

It is concluded that the cyclohexanol dehydrogenation in presence of CO/CO_2 has several advantages in terms of enhanced yields of cyclohexanone and optimal utilization of hydrogen in yielding methanol. The amount of cyclohexanone is higher on the double-promoted catalyst (conversion of cyclohexanol = 90% with a selectivity towards cyclohexanone = 67.8%) than on single promoted Cu–ZnO catalyst (conversion of cyclohexanol = 86% with a selectivity towards cyclohexanone = 60.5%) in presence of CO. Similarly, the double-promoted catalyst exhibited higher conversion of cyclohexanol (95% with a selectivity towards cyclohexanone = 71.5%) than on single promoted Cu–ZnO catalyst (conversion of cyclohexanol = 80% with a selectivity towards cyclohexanone = 60%) in presence of CO_2. The H_2 produced in the dehydrogenation of cyclohexanol is responsible for obtaining significant yields of methanol from CO/CO_2. Addition of La_2O_3 to Cu–ZnO–Cr_2O_3 leads to the formation of more number of stabilized active Cu^0/Cu^+ species, which is responsible for its higher activity compared to catalyst A.

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