

A highly active Cu-MgO-Cr₂O₃ catalyst for simultaneous synthesis of furfuryl alcohol and cyclohexanone by a novel coupling route—Combination of furfural hydrogenation and cyclohexanol dehydrogenation

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Abstract

A novel coupling route highlighting the combination of hydrogenation of furfural and dehydrogenation of cyclohexanol in vapor phase conditions over Cu-MgO-Cr₂O₃ catalyst is highly advantageous in terms of avoiding external pumping of H₂ and maintaining the formation of furfuryl alcohol and cyclohexanone, the desired products, respectively, in good amounts at atmospheric pressure. The catalytic activity of this catalyst is compared with a Cu-MgO coprecipitated catalyst and a copper chromite (commercial Cu-1800P supplied by M/s. Engelhard Corp., USA) catalyst. Cu-MgO-Cr₂O₃ catalyst is prepared by coprecipitation method using tetraethyl ammonium hydroxide as precipitating agent. All the catalysts are characterized by BET surface area, temperature programmed reduction, XRD and XPS. The BET surface area of Cu-MgO-Cr₂O₃ catalyst is higher indicating the presence of smaller Cu particles. XRD results also indicate the presence of smaller particles of Cu in Cu-MgO-Cr₂O₃ catalyst. XPS results indicate the presence of Cu species (Cu⁰/Cu⁺) at the surface of Cu-MgO-Cr₂O₃ catalyst. The higher yields of the products over the Cu-MgO-Cr₂O₃ catalyst in independent and combined reactions compared to the other two catalysts may be attributed to the promotional effect of Cr₂O₃, smaller Cu particle size and more number of Cu⁰/Cu⁺ species at the surface.

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Keywords: Combination; Cu-MgO-Cr₂O₃ catalyst; Hydrogenation of furfural; Dehydrogenation of cyclohexanol

1. Introduction

Catalytic hydrogenation and dehydrogenation reactions play a key role in the chemical industry particularly in the synthesis of various pharmaceuticals and fine chemicals apart from bulk chemicals. Furfuryl alcohol (FOL) and cyclohexanone (Cyone) are the typical examples produced by the hydrogenation of furfural (FAL) and dehydrogenation of cyclohexanol (CyOH), respectively, over Cu-based catalysts. FOL is an important chemical, mainly used for the production of resins for bonding foundry sand to produce cores and molds for metal casting, corrosion-resistant mortar for installing acid proof brick, laminating resins for corrosion resistant fiberglass-reinforced

equipment, resins for corrosion resistant furan polymer concrete, impregnating solutions and carbon binders. It is also used as non-reactive diluent for epoxy resins, modifier for phenolic and urea resins, oil-well sand consolidation, solvent, production of tetrahydro furfuryl alcohol and other chemical synthesis. It is also an important chemical intermediate for the manufacture of lysine, vitamin C, lubricant, dispersing agent and plastisizer. Cyone is an industrially important chemical for the manufacture of caprolactum and adipic acid, which are used in producing polyamide fiber in nylon-textiles.

Industrially, FOL is produced by hydrogenation of FAL either in liquid phase or in vapor phase. On the other hand, Cyone is produced in vapor phase by dehydrogenation of CyOH. Both the processes employ copper based catalysts. Hitherto, a number of methods have been reported in patent literature on the preparation of catalysts useful for the hydrogenation of FAL and dehydrogenation of CyOH separately. Various copper chromite

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based catalysts are reported for the hydrogenation of FAL in both liquid as well as vapor phase at high pressures [1–5]. Certain other reports on the non-chromium catalysts for hydrogenation of FAL include Cu/C catalysts [1], Raney Ni and Ni amorphous alloys [6–8], mixed Cu–Zn oxides doped with Al, Mn and Fe [9], and homogeneous complexes of Rh, Ru and Pt [10]. We have reported high yields of FOL by the hydrogenation of FAL & CyOH dehydrogenation over Cu–MgO catalysts at atmospheric pressure [11,12]. Copper chromate catalysts have been patented for dehydrogenation of CyOH in vapor phase and some other copper based catalysts, viz., Cu–MgO, Cu–ZnO, Cu–Al₂O₃ and CuO–ZnO–Al₂O₃ are also reported extensively for the dehydrogenation of CyOH either in liquid or vapor phase [13,14].

The main drawbacks of the FAL hydrogenation processes mentioned above are either to be operated under pressure or use large amounts of hydrogen along with FAL. Since both FAL hydrogenation and CyOH dehydrogenation processes employ mostly Cu based catalysts, the combination of these two processes over a single catalyst system seems to be economical. Thus, the present work highlights a catalytic process for the combination of FAL hydrogenation (without H₂ pumping) and CyOH dehydrogenation in vapor phase conditions. Hydrogen is the latest successor of energy providers, with many social, economic, and environmental benefits to its credit. H₂ is a clean and green fuel producing highly safe by-products, viz., H₂O and thus is focused as the high potential fuel of the future world. Hydrogen consumption in the chemical industries alone for various synthetic processes account for >40% of the total H₂ produced every year. This implicates the preciousness of H₂ and its high demand to the world today and tomorrow. Thus, the present process, which applies in situ generation and application of H₂ in the reaction, i.e., without using any external H₂ source, can be seen as a novel and an economically viable process. Although there are certain reports [15–17] on this type of coupling reactions which involve a catalytic hydrogen transfer, the present report is an attempt in combining two industrially important reactions, viz., an exothermic furfural hydrogenation and endothermic equilibrium constrained cyclohexanol dehydrogenation with good amounts of desired products. Our earlier reports over Cu–MgO coprecipitated catalyst showed high activities towards both hydrogenation of furfural and dehydrogenation of cyclohexanol. The commercial catalyst used in the hydrogenation of furfural is a copper chromite catalyst. Hence, Cr₂O₃ promoted Cu–MgO catalyst has been chosen in the present study.

2. Experimental

2.1. Preparation of catalysts

The catalytic hydrogenation of furfural and dehydrogenation of cyclohexanol both individually and combined were carried out on three catalysts, viz., Cu–MgO (CM), Cu–Cr₂O₃–MgO (CMCr) and Cu-1800P, a Commercial catalyst. All the chemicals used for the preparation of catalysts were of AR grade obtained from M/s. LOBA chemie, India except for tetraethyl ammonium hydroxide that was obtained from M/s. Aldrich Chemicals.

2.1.1. Cu–MgO

CM was prepared by precipitating the mixture of 1 M each of Cu(NO₃)₂·3H₂O and Mg(NO₃)₂·6H₂O aqueous solution with 1 M aqueous solution of K₂CO₃ at a pH of 9 under continuous stirring. The precipitate was washed until pH is 7. The gel was filtered and dried in an oven for 12 h at 383 K. The dried sample was then subjected to calcination in air at 723 K for 4 h to get CM. The final catalyst was found to contain 24 wt.% Cu.

2.1.2. Cu–MgO–Cr₂O₃

CMCr was prepared by coprecipitation of Cu(NO₃)₂·3H₂O, Mg(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O in ethanol solution with 20 wt.% tetra ethyl ammonium hydroxide solution at a pH of 9. The obtained gel was then washed with ethanol, filtered, dried in an oven for 12 h at 383 K and calcined in air at 723 K for 4 h. The final mass contained 22 wt.% Cu–4 wt.% Cr₂O₃–74 wt.% MgO.

2.1.3. Cu-1800P

A commercial copper chromite catalyst obtained from M/s. Engelhard corporations, USA.

2.2. Catalyst characterization

All the catalysts have been characterized for specific surface area by N₂ adsorption at 77 K using a M/s. Micromeritics Pulse Chemisorb 2700 instrument. Before the measurement, the samples were oven-dried at 393 K for 12 h and flushed in-situ with He gas for 2 h. XRD Patterns were recorded on M/s. Rigaku's Miniflex diffractometer with Ni filtered Cu K α as a radiation source at a 2θ scan speed of 2° min⁻¹.

Temperature programmed reduction (TPR) studies of the catalysts were performed on the same pulse reactor used for surface area measurement with 6% H₂–Ar as reducing gas and carrier gas. The temperature was increased linearly at a ramp of 5 K min⁻¹ from room temperature to 973 K where the isothermal conditions were maintained for 30 min. The change in the H₂ concentration was monitored by micro TCD and recorded on GC work-station. The elaborated experimental details of TPR were discussed elsewhere [18].

Kratos Axis 165 XPS Spectrometer, with Mg K α radiation, (1253.6 eV), was used for obtaining XPS data. In the XPS study, C 1s-binding energy value of 285 eV has been taken as a reference level. The relative intensities of the surface composition of different elements were corrected with their corresponding atomic sensitivity factors using the vision two software in unix system. Prior to the XPS studies, all the catalysts were reduced in 6% H₂ balance He flow at 523 K for 4 h, followed by passivation in N₂ atmosphere.

2.3. Activity measurements

The independent hydrogenation, dehydrogenation and simultaneous (hydrogenation and dehydrogenation) reactions were carried out in a fixed bed micro reactor made of quartz (10 mm i.d. and 200 mm long) packed with 1 g catalyst under vapor phase conditions using a liquid cyclohexanol and/or furfural at a feed

Table 1
Structural characteristics of Cu catalysts

S. no.	Catalyst	BET-surface area (m ² g ⁻¹)	Crystallite size of Cu (nm) from XRD	XRD phases	
				Calcined	Reduced
1	CM	42	69	CuO, MgO, Cu ₂ O	Cu, CuO, MgO
2	CMCr	91	42	CuO, MgO, Cu ₂ O	Cu, CuO, MgO
3	Cu-1800P	54	106	CuO	Cu, CuO

rate of 1 ml h⁻¹, at atmospheric pressure and reaction temperature in the range of 453–523 K. In the combination reaction, cyclohexanol:furfural ratio is maintained at 5:1. The products were collected in a 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 dia. and 25 m long, supplied by M/s. J & W Scientific, USA).

3. Results and discussion

3.1. Structural characteristics of the copper catalysts

Table 1 presents the structural characteristics, viz., BET surface area by N₂ adsorption and crystalline phases determined by XRD analysis of the various copper catalysts studied. There is a significant increase in the surface area of Cu-MgO-Cr₂O₃ catalyst (CMCr) prepared by precipitation using tetra ethyl ammonium hydroxide. It is well documented [19–21] that the use of organic precursor and media can change the properties of the resulting materials especially that of mixed metal oxides prepared by co-precipitation method. The surface area of the final solid thus depends mainly on the precursor and the method of preparation adopted. Numerous reports [22,23] reveal the formation of nano-particles of the materials by the use of organic precursor/media. Thus, the enhancement in the surface area of the CMCr may be attributed to the more dispersed Cu-catalyst obtained by precipitation with tetra ethyl ammonium hydroxide. Also, the presence of Cr₂O₃ is reported to have improved both BET surface area as well as the Cu surface area of the catalyst [24]. The purpose of using tetra ethyl ammonium hydroxide as precipitating agent is to prepare a highly active catalyst for the combination of hydrogenation and dehydrogenation reactions.

3.2. X-ray diffraction results

The results of XRD analysis of both the calcined and reduced samples of copper catalysts are presented in Table 1. The predominant phases observed in the calcined and reduced CMCr and Cu-1800P catalysts are shown in Fig. 1. In CMCr calcined catalyst phases due to CuO (diffraction lines with *d* values of 2.52_x, 2.32_x and 2.53₅; ICDD file No. 5-661) and MgO (*d*-values of 2.11_x, 1.49₅ and 1.22₁; ICDD file No. 4-829) are visible. Same observation is made in case of Cu-MgO catalyst [12]. However, the commercial Cu-1800P showed only CuO phase. Cu₂O phase (*d*-values at 2.47_x, 2.14₄ and 1.51₃; ICDD file No. 5-667) is observed as a minor phase in both the catalysts. No

d-lines corresponding to Cr₂O₃ are observed in any of the catalysts which may be due to the low amount of Cr₂O₃ (4 wt.%) in CMCr and Cr₂O₃ may be present either in X-ray amorphous form or as fine particles below X-ray detection levels in Cu-1800P. The XRD patterns of reduced catalysts presented in Fig. 1 have shown the metallic Cu⁰-phase (*d*-values of 2.09_x, 1.81₅ and 1.28₂; ICDD file No. 4-836) in the catalysts along with CuO and MgO phase. The crystallite size of Cu⁰ has been calculated by X-ray line broadening technique using Debye-Scherrer equation, $D = k\lambda/\beta \cos \theta$ where $k = 0.9$ and D corresponds to Cu-Crystallite size. It is observed that the Cu-crystallite size in the CMCr catalyst is lower compared to that in CM and Cu-1800P catalysts. This information clearly demonstrates the advantage of using tetra ethyl ammonium hydroxide to obtain more dispersed Cu or smaller particles of Cu.

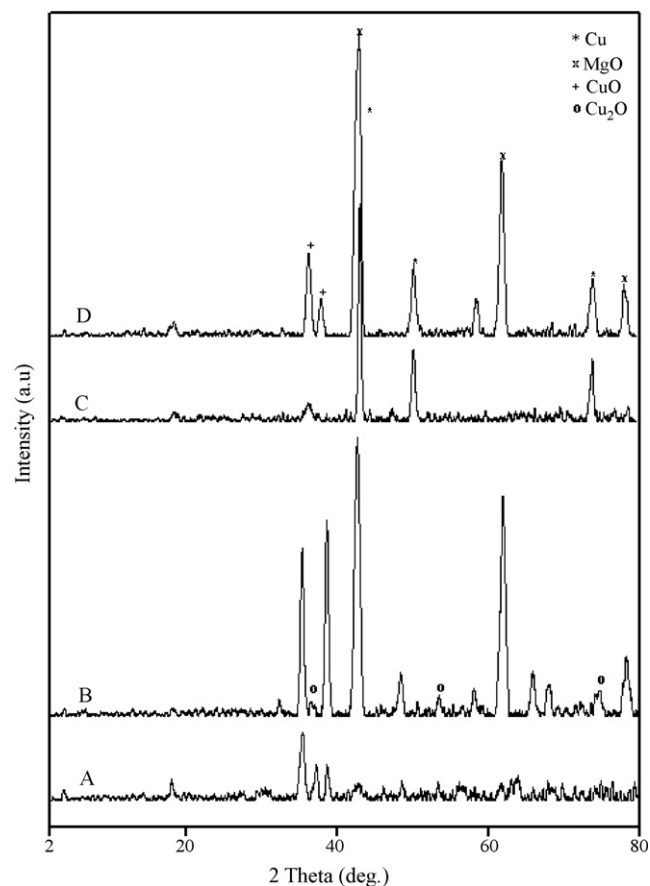


Fig. 1. X-ray diffraction patterns of calcined and reduced Cu-catalysts. (A) Cu-1800P (calcined), (B) CMCr (calcined), (C) Cu-1800P (reduced) and (D) CMCr (reduced).

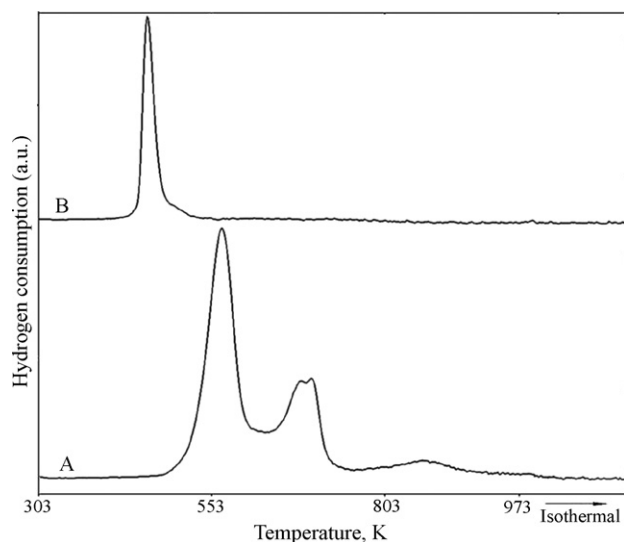


Fig. 2. TPR profiles of calcined Cu-catalysts. (A) CMCr and (B) Cu-1800P.

3.3. Results of TPR analysis

Fig. 2 shows the TPR profiles of calcined catalysts of CMCr and Cu-1800P. A two stage reduction of CuO to Cu⁰ is observed in the CMCr catalyst and the Cu-1800P commercial catalyst seem to reduce in a single step at a T_{\max} of 459 K which is lower compared to CMCr and Cu-MgO catalysts [12]. The standard CuO is found to reduce at a T_{\max} of 606 K (profile not shown in the figure) in single stage attributed to the reduction of CuO to Cu⁰. Most of the oxidic copper in the CMCr catalyst is found to reduce at T_{\max} in the range of 523–563 K. But, a complete reduction seems to occur at ~673–713 K. Thus, it appears that the reduction of CMCr sample takes place in two stages with the first peak corresponding to the transformation of CuO to Cu₂O and the second H₂ consumption peak corresponding to the reduction of Cu₂O to Cu⁰. Our earlier [12] studies on TPR of the co-precipitated Cu-MgO catalyst have shown similar results. However, a shift in the T_{\max} of these two H₂ consumption peaks to the higher temperature region can be seen from Cu-MgO to CMCr catalysts. This indicates that the incorporation of Cr₂O₃ enhances the dispersion and interaction of CuO with the support MgO. Agrell et al. [25] attributed the shifting in the reduction temperature in the TPR patterns of CuO-ZnO-Al₂O₃ catalysts to the formation of larger CuO crystallites and/or possibly to a strong interaction between copper and support. The reduction of commercial catalyst at lower temperatures compared to Cu-MgO can be explained on the same basis of strong interaction between CuO and Cr₂O₃. On the other hand the interaction of CuO with the support MgO in Cu-MgO catalyst & CMCr catalyst makes the reduction of CuO phase difficult. The low intense & broad signals centered at ~855 K can be ascribed to the reduction process of Cr₂O₃ [26]. Thus, it seems that though the ease of reducibility is higher in case of commercial catalyst, the higher dispersion of Cu in CM and CMCr as observed from the formation of smaller crystallites (XLB analysis) and a stronger synergistic interaction between Cu and MgO in these catalysts are probable reasons for their superior activity over Cu-

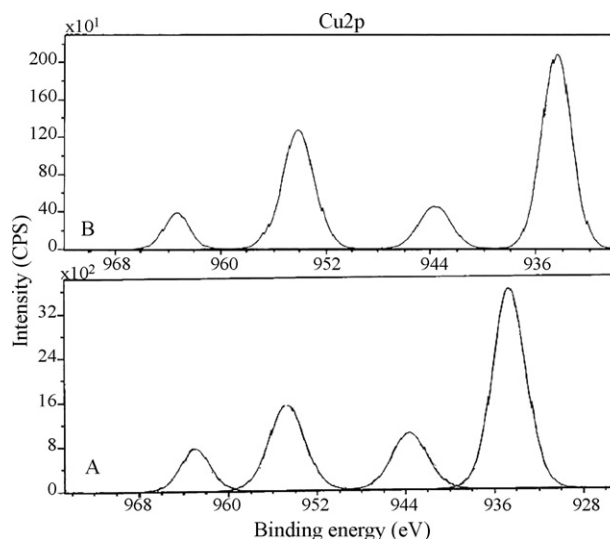


Fig. 3. Cu 2p XPS spectra of reduced Cu catalysts. (A) CMCr and (B) Cu-1800P.

1800P towards hydrogenation–dehydrogenation reactions in the present study. Chang et al attributed the copper species reducing at higher temperatures to smaller CuO particles with a certain degree of interaction with the chromium species used as the promoter in the copper supported on rice husk ash catalyst [27]. They further opined that the shift in the reduction peak to higher temperatures implying the existence of a phase composed of well-dispersed CuO particles surrounded by fine chromia particles with a certain degree of interaction thus interrupting the formation of large bulk CuO crystallites [27].

3.4. XPS results

The XPS patterns of reduced catalysts for Cu 2p and Cr 2p are shown in Figs. 3 and 4, respectively. The corresponding characteristics of binding energy values of Cu 2p_{3/2}, Mg 2p, O 1s, Cr 2p_{3/2} along with the Cu/Mg (in CM catalyst), Cu/(Mg + Cr) (in CMCr catalyst) and Cu/Cr (in Cu-1800P) atomic ratios and Cu_s/Cu_p (intensity ratio of the Cu 2p satellite peak to Cu 2p parent peak) are given in Table 2. The higher Cu_s/Cu_p observed in case of CuO and CM samples probably indicate the presence of more Cu²⁺ or CuO species. The satellite peaks observed in case of Cu²⁺ compounds are due to the shake up transitions by

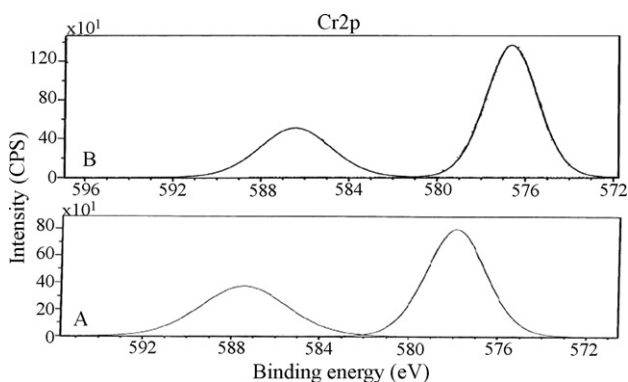


Fig. 4. Cr 2p XPS spectra of reduced Cu catalysts. (A) CMCr and (B) Cu-1800P.

Table 2
XPS characteristics of Cu catalysts

Catalyst	Cu 2p _{3/2} (parent) B.E. (eV)	Cu 2p _{3/2} (satellite) B.E. (eV)	Cu _s /Cu _p	Mg 2p B.E. (eV)	O 1s B.E. (eV)	Cr 2p B.E. (eV)	Cu/M* (atomic ratio)
CMCr	934.655	943.676	0.2979	50.783	531.380, 533.415	577.924, 587.476	0.1339
Cu-1800P	934.491	943.755	0.2363	–	531.037, 532.583	576.617, 586.433	1.0215

M* = (Mg + Cr) for CMCr & Cr for Cu-1800P.

ligand to metal 3d charge transfer [28]. These satellite peaks are not seen in Cu⁺ compounds or in metallic Cu because of completely filled 3d shells. In fact, transition metal ions with unfilled 3d orbital are well reported to show satellite peaks in the core level XP spectra due to electron shake-up and the structure of satellite, i.e., the peak number, intensity and splitting which reflect the nature of chemical bondings of the transition metal ions [29,30]. The concentration of Cu with respect to Mg (Cu/Mg) in CM catalyst is almost same as that with respect to (Mg + Cr) in CMCr catalysts. However, the intensity ratios of Cu_s/Cu_p indicate that CM catalyst contain more amount of Cu²⁺ than in CMCr catalyst. Thus, the role of Cr₂O₃ seems to stabilize the Cu⁰ species, which are responsible for the higher activity and selectivity towards furfuryl alcohol formation [1]. The Cu/Cr atomic ratio in Cu-1800P is much higher compared to the Cu surface contribution in other two catalysts.

The XPS spectra of Cr 2p_{3/2} and Cr 2p_{1/2} are found to be in the range of 576.6–577.9 eV and 586.4–587.5 eV, respectively, indicating the presence of Cr³⁺ species status as Cr₂O₃ [24,31].

The O 1s spectra show the binding energy values in the range of 529.6–533.4 eV for all the catalysts in the study that is characteristic of metal oxides and closer to O 1s binding energy in MgO. The Mg 2p binding energy values are almost the same in all the MgO containing samples.

3.5. Activity studies

The combination of furfural hydrogenation and cyclohexanol dehydrogenation has been carried out in vapor phase at atmospheric pressure. In order to understand the results of this

combination reaction, the individual reactions of furfural hydrogenation and cyclohexanol dehydrogenation are also studied under similar conditions on the same three copper catalysts, viz., CM, CMCr and Cu-1800P in the temperature range of 453–523 K. The steady state conversion value at a reaction run time of 6 h has been taken for the sake of comparison in these reactions.

3.5.1. Hydrogenation of furfural

Fig. 5 shows the activities of the copper catalysts studied for the hydrogenation of furfural in the temperature range of 453–523 K. The figure clearly shows a steady increase in the conversion levels of furfural over all the catalysts with temperature. The selectivity towards the alcohol (furfuryl alcohol) however is getting reduced with increase in the reaction temperature on account of formation of the other side-products. The formation of side-products may be expected with the ring hydrogenation (C=C hydrogenation) taking place at these temperatures [32]. Our previous results on the hydrogenation of FAL over Cu-MgO catalysts showed a similar trend [11]. Thus, 473 K seems to be an optimum temperature yielding higher amounts of FOL over all the catalysts of the present study. Among all these catalysts, CMCr showed higher ability in yielding the desired product, FOL.

Our previous study of hydrogenation of furfural over Cu-MgO catalysts clearly demonstrated the advantage of Cu-MgO co-precipitated catalyst, which has been found to possess more number of Cu⁰ species at the surface [12]. The presence of more Cu⁰ species has been attributed to the presence of defect sites of MgO which are reported to be more reactive and that

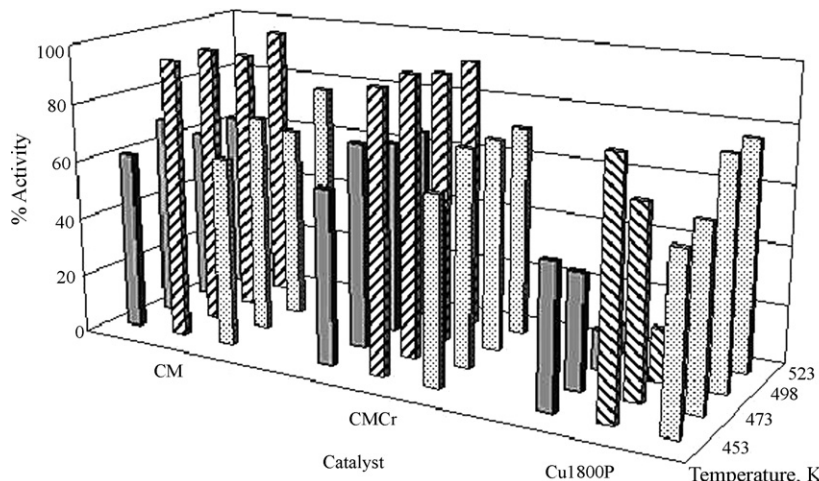


Fig. 5. Hydrogenation of FAL over the Cu-catalysts. ▨ %FAL conversion, ▩ %FOL selectivity and ■ %FOL yield.

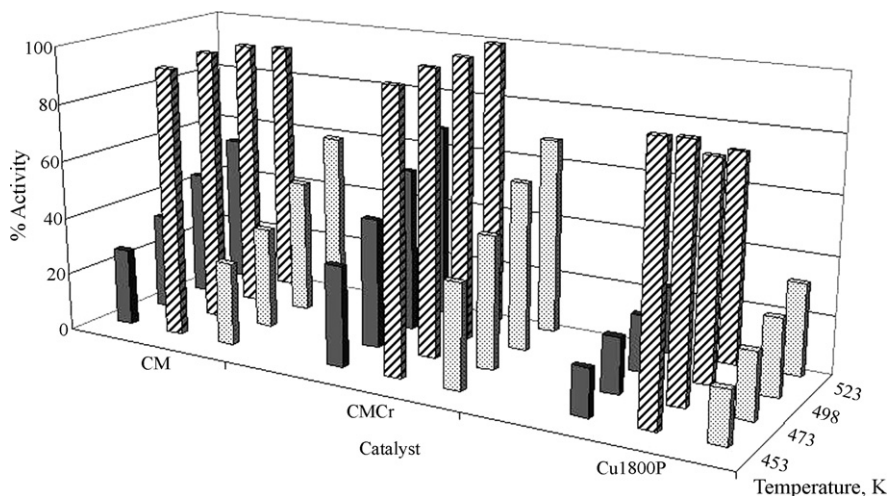


Fig. 6. Dehydrogenation of CyOH over the Cu-catalysts. ■ %CyOH, conversion, ▨ %Cyone selectivity and ■ %Cyone yield.

the adsorption properties for metal species can be qualitatively different from those of regular surface sites [33–37]. It is also reported that the defect sites at the metal support interfacial region in case of Pt-TiO₂ system are helpful to coordinate the oxygen atom of the C=O group via lone pair of electrons and thus activate the hydrogenation of C=O group [38]. However, in the present study we observed the presence of Cu²⁺ species along with Cu⁰ species in Cu-MgO catalyst at the surface as well as in the bulk. The different methodology adopted in CMCr catalyst preparation compared to CM catalyst preparation is to get highly dispersed smaller crystallites of more number of Cu⁰ rather than Cu²⁺ sites at the surface.

3.5.2. Dehydrogenation of cyclohexanol

Dehydrogenation of cyclohexanol is known to be an equilibrium-controlled reaction [39]. Fig. 6 shows an increase in cyclohexanol dehydrogenation with rise in temperature over all the catalysts. The catalyst, CMCr exhibited highest yield of cyclohexanone, i.e., 67.3% at 523 K. Cu-1800P, the commercial Cu catalyst however showed a decrease in the percentage selectivity to cyclohexanone with rise in temperature (>473 K) because of formation of other products, viz., cyclohexene, phenol, etc., through the side-reactions such as dehydration taking place at the elevated temperatures over this catalyst. However, the selectivity towards cyclohexanone increases with reaction temperature over CM and CMCr catalysts. The large amount of Cr component in Cu-1800P might have induced acidity in the catalyst because of which dehydration of cyclohexanol finds its way in the reaction.

3.5.3. Coupling reaction

Since above 473 K the dehydration of cyclohexanol is significant in Cu-1800P, a reaction temperature of 473 K has been chosen as optimum temperature for the comparison of activities of these catalysts in the coupling process.

Fig. 7 shows the hydrogenation and dehydrogenation abilities in the coupling process of these catalysts against time on stream at 473 K. CMCr catalyst exhibits a steady conversion

(≥40% conversion of cyclohexanol and ~85% conversion of furfural). On CM catalyst the dehydrogenation activity drops against time on stream and maintains a steady activity after 2 h. This is reflected in the furfural hydrogenation. However, it is interesting to see that the initial conversion of cyclohexanol over Cu-1800P catalyst is very high (>50%). However, it dropped to half within 4 h after which a steady activity is maintained. A similar trend is observed in furfural hydrogenation on this catalyst. The interesting observations one can draw from the coupling process are:

- On Cu-1800P, the initial cyclohexanol conversion of >50% at 473 K is clear above the equilibrium value.
- The conversions (for both dehydrogenation and hydrogenation reactions) on all the catalysts in the coupling process are well above those in the independent reactions.

It seems both furfural and cyclohexanol are competing each other to adsorb on the active sites. In the initial stages over CM

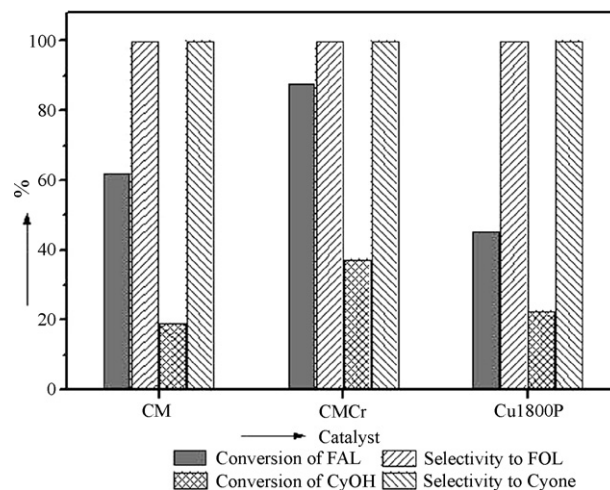


Fig. 7. The activities of Cu catalysts towards the combination reaction of FAL hydrogenation and CyOH dehydrogenation at 473 K. ■ Conversion of FAL, ▨ selectivity to FOL, ▩ conversion of CyOH, and ▧ selectivity to Cyone.

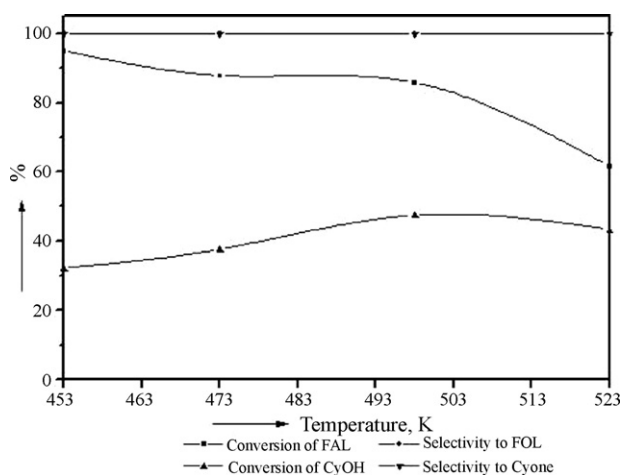


Fig. 8. Activity of CMCr catalyst towards combination reaction vs. reaction temperature. (■) %Conversion of FAL, (●) %selectivity of FOL, (▲) %conversion of CyOH and (▼) %selectivity of Cyone.

and Cu-1800P catalysts, large number of both cyclohexanol and furfural might have adsorbed on the active sites. However, during the course of the reaction there may be a change in the active sites (may be a change in the oxidation state of Cu or agglomeration of Cu sites) on CM and Cu-1800P catalysts. After restructuring of active sites, stable activity in both dehydrogenation and hydrogenation reactions were observed. On the other hand a stable activity in both dehydrogenation and hydrogenation reactions were observed on CMCr catalyst. This is a clear indication that during the pretreatment of CMCr catalyst (reduction) active sites were developed, which is not the case with other two catalysts. Thus, the role of small amount of Cr species in CMCr catalyst is to get the required active sites during the reduction and to maintain the Cu particle size during the reaction.

The catalytic activity of the CMCr catalyst towards the combination reaction of furfural hydrogenation and cyclohexanol dehydrogenation in the temperature range of 453–523 K has been presented in Fig. 8. A fall in conversion of furfural from 99.5% to 61% takes place with the increase in temperature from 453 to 523 K whereas the conversion of cyclohexanol increased from 22% to 43%. The increase in the conversion of cyclohexanol with temperature can be expected since dehydrogenation of cyclohexanol is an endothermic reaction and rise in temperature shifts the equilibrium to the right favoring the forward reaction (dehydrogenation of cyclohexanol to cyclohexanone) [39]. Even though the increased conversion levels of cyclohexanol against temperature generates more amount of H₂, furfural hydrogenation could not be proceeded as expected probably because most of the active Cu sites might have participated in the cyclohexanol dehydrogenation. However, it is interesting to observe that the selectivity to both FOL & cyclohexanone maintained a maximum (100%) at all the reaction temperatures although there is a fall in the conversion of FAL. Apparently the yields of FOL are also very high at all these temperatures with an optimum yield of 88% observed at 473 K. This temperature is regarded as the optimum with high yields towards both FOL and cyclohexanone. The combination reaction is advantageous in producing enhanced yields of the desired products,

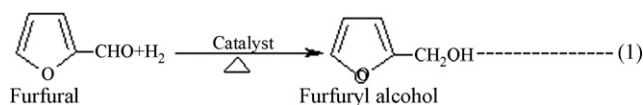
viz., FOL and cyclohexanone when compared to the individual reactions.

The results clearly indicate the advantageous role played by chromia in showing high activity towards FOL formation with 88% of FAL conversion. The activities of the catalysts are found to be in the order CMCr > CM > Cu-1800P. The chromia promoted Cu-MgO catalyst has shown higher activity compared to the unpromoted Cu-MgO and the commercial Cu-1800P catalysts. The reason may be attributed to the stabilization of surface Cu⁰ or Cu⁺ species by chromia as observed from the XPS results and the presence of smaller Cu particle size.

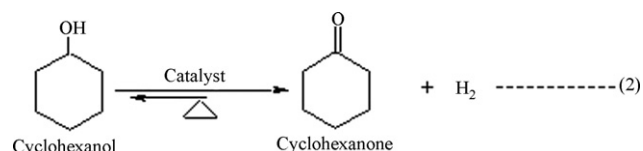
Various reports [1,32,40,41] reveal the selective nature of Cu-based catalysts in the hydrogenation of C=O bond in the side group leaving C=C bonds intact in the furan ring. Rao et al. [42] made an extensive study and proposed a surface mechanism explaining the hydrogenation of furfural over copper chromite catalyst by a Langmuir-Hinshelwood model with a competitive adsorption between furfural and hydrogen either on one type of site or two different sites with each reactant on one site. They opine that Cu⁺ species are involved in the catalytic process and the presence of Cu⁰ sites is also required for activation of H₂.

Medvedeva et al. [43,44] have reported the presence of only Cu⁰ as the active sites in the dehydrogenation of cyclohexanol. However, in the kinetic studies reported by Fridman et al. [45] they suggested two different mechanisms, viz., one on Cu⁺ species over Cu-ZnO-Al₂O₃ catalysts and the other on Cu⁰ species over Cu-MgO catalysts. They suggested that cyclohexanol adsorption on zero valent copper sites is dissociative and proceeds by the rupture of the O–H bond. The formation of adsorbed species of cyclohexanol alcoholate which acts, as an intermediate for the formation of cyclohexanone by the abstraction of the nonhydroxylic hydrogen is further found by them to be the rate determining step.

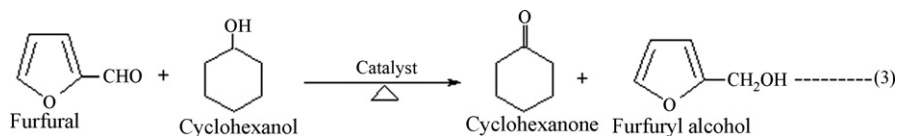
Considering these mechanisms in the major reports and our observations in the present study of the combination of FAL hydrogenation and the cyclohexanol dehydrogenation, the following possible surface mechanism with these steps may be proposed. The first step (1) is a dissociative adsorption of cyclohexanol on metallic copper forming an alcoholate and hydrogen atom abstracted from the O–H group maintains adsorbed state. The next step (2) is the removal of the α-hydrogen, which has been reported as the rate-determining step by Fridman et al. [45]. The successive step (4) and (5) are the interaction of furfural



Scheme 1. Reaction scheme for furfural hydrogenation.

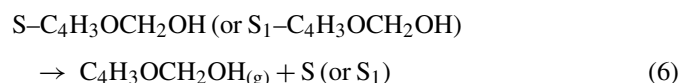
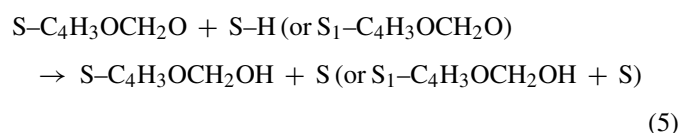
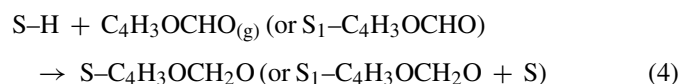
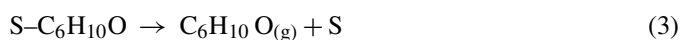
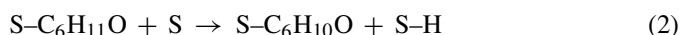
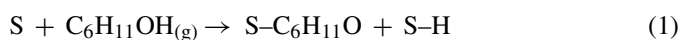


Scheme 2. Reaction scheme for cyclohexanol dehydrogenation.



Scheme 3. Reaction scheme for coupling route—combination of furfural hydrogenation and cyclohexanol dehydrogenation.

either in gas phase or in the adsorbed form on yet another active site (either Cu^0 or Cu^+). The formation of furfuryl alcohol and cyclohexanone then take place in independent steps (3) and (6). The adsorbed hydrogen (S-H) in step (1) and step (2) may get desorbed to give gas phase H_2 that may then combine with the adsorbed furfural molecule to yield furfuryl alcohol.



where $\text{S} = \text{Cu}^0$; $\text{S}_1 = \text{Cu}^0/\text{Cu}^+$

However, further study is required in order to confirm the above mechanism.

Thus, the advantages of the coupling process are mainly:

- (i) External hydrogen pumping can be avoided as in-situ generation of hydrogen from the dehydrogenation of cyclohexanol is utilized and thus seems to be an economical route in the synthesis of furfuryl alcohol from furfural.
- (ii) Furfural hydrogenation is an exothermic reaction with a $\Delta H = -52.32$ kcal/mol (Scheme 1).

Whereas cyclohexanol dehydrogenation is an endothermic ($\Delta H = +15$ kcal/mol) and equilibrium constrained process (Scheme 2).

Thus, apart from the effective utilization of the hydrogen evolved in the reaction (2), the combination of reactions (1)–(2) as reaction (3) gives a better thermal balance ($\Delta H = -37.32$ kcal/mol) through hydrogen transfer between the two reactants (Scheme 3).

- (iii) The foremost of all advantages is the achievement of enhanced yields of furfuryl alcohol and considerably good yields of cyclohexanone by employing the combination reaction.
- (iv) In contrast to the large amount of Cr-oxide in commercial catalyst, the lab made catalyst contains small amount of Cr-oxide.
- (v) A simple chromia promoted Cu-MgO catalyst prepared by coprecipitation method using tetra ethyl ammonium

hydroxide as a precipitating agent, yields FOL in good amounts.

- (vi) The coupling route provides in-situ generation of H_2 which helps in preventing the by-products, viz., tetrahydrofurfuryl alcohol, furan, methyl furan, etc., in the hydrogenation of FAL and thus high yields to FOL are maintained.

4. Conclusions

A combination reaction of FAL hydrogenation and CyOH dehydrogenation over CMCr-P catalyst is found to be advantageous in eliminating the use of any external source of H_2 and in enhancing the yields to desired products, viz., FOL and Cyone. The presence of Cr_2O_3 is responsible in stabilizing Cu^0/Cu^+ species required for both the hydrogenation/dehydrogenation reactions as evidenced from XPS analysis & XRD results. Further, smaller crystallite size (XLB analysis) of Cu and stronger synergism between Cu and MgO (TPR) seem to be responsible for the higher activity of this catalyst.

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