

Support effect in Cu-based catalysts for vapor phase dehydrogenation of 1-decanol to decanal using CO₂ as a soft oxidant

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Summary

The present work aims to produce decanal from the dehydrogenation (DH) of 1-decanol with CO₂ as soft oxidant over copper catalysts. The main advantage of Cu catalysts is that they can promote DH and reverse water gas shift reactions, which are part of oxidative DH of 1-decanol in presence of CO₂. For this purpose, various supported Cu catalysts (Cu/MgO, Cu/CeO₂, Cu/ZnO, and Cu/ZrO₂) have been prepared using K₂CO₃ as precipitating agent. The catalysts were characterized by X-ray Diffraction (XRD), brunauer-emmett-teller (BET) surface area, high resolution transmission electron microscopy, X-ray photoelectron spectroscopy, H₂-temperature programmed reduction, UV-vis diffuse reflection spectroscopy (DRS), and CO₂-temperature programmed desorption analysis. Catalytic activity of these catalysts has been evaluated at atmospheric pressure with CO₂ as soft oxidant in a fixed bed flow reactor. The high catalytic activity by Cu/MgO catalyst was mainly attributed to the presence of basic sites and dispersion of Cu metal particles. Catalytic activity was correlated with catalysts characteristics.

Highlights

- CO₂ as a soft oxidant prevents over oxidation
- CO₂ reacts with H₂ produced via reverse water gas shift reaction (RWGSR)
- Copper catalysts are known to be active for both dehydrogenation and RWGSRs
- The basic sites and interactions between Cu and MgO in Cu/MgO catalyst are responsible for high activity
- 10Cu/MgO catalyst can be regenerated with, little activity loss

KEYWORDS

1-decanol, CO₂ utilization, decanal, dehydrogenation

1 | INTRODUCTION

The transformation of long-chain primary aliphatic alcohols to carbonyl compounds has industrial relevance and is broadly performed for production of fine

chemicals, perfumes, and pharmaceutical sectors.¹ Due to producing toxic waste by KMnO₄ and K₂Cr₂O₇ in oxidation of alcohols, this conventional method is not suitable for friendly environment.^{2,3} So, catalytic oxidation of alcohols has been developed by using molecular

oxygen as an environmental benign route. However, the large scale alcohol oxidation using molecular oxygen still suffers from hazardous reaction parameters.^{4,5} Even though supported Pd and Ru catalysts have been reported for the dehydrogenation of primary aliphatic alcohols (DHPA), these catalysts exhibited lower activity.⁶ At present many researchers have focused on the DHPA to generate respective aldehydes. The design of a stable and cost effective supported catalyst for efficient DHPA is a key challenge regarding economic and environmental viability. Catalytic stability and the establishment of synergistic interface among active metal species and support framework are more important for designing exclusive active supported catalyst.^{7,8} Ag/HT and Cu/HT exhibited better catalytic activity in the dehydrogenation (DH) of benzyl and secondary aliphatic alcohols. But still they were not efficient for DHPA.⁹ Shi et al reported 63% yield of 1-octanal from the transfer hydrogenation of 1-octanol in the presence of La₂O₃ supported copper nano particles. The highest activity was obtained by the synergistic consequence among basic sites and the fast hydrogen spillover of Cu nano particles.¹⁰ Nowadays vapor phase DH of alcohols has become much attention due to environmental friendly nature. The oxidative DH reaction with CO₂ as a soft oxidant was studied extensively by our group because of the fact that CO₂ accounts for 77% of greenhouse gases and thus has a huge impact on environment.^{11,12} The advantage of CO₂ as soft oxidant in DH reactions is that CO₂ reacts with H₂ produced in the DH reaction to get CO and water via reverse water gas shift reaction (RWGSR). Utilization of CO₂ in this way is beneficial in reducing the global warming nature of CO₂ to some extent.^{13–16} The idea of CO₂ utilization fascinates much more due to the green technology, inexpensive, readily available, nonflammable, and nontoxic nature of CO₂.^{17,18} Recently the DH of benzyl alcohol is reported as an efficient and green process by using CO₂ as a soft oxidant as an alternative to molecular O₂ applied as H₂ acceptor. The conversion of benzyl alcohol increased due to RWGSR.¹⁹ Cu-based catalysts are active for

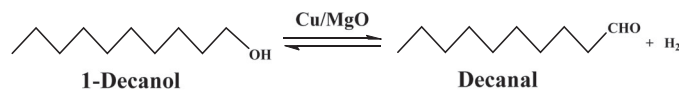
RWGSR.^{20–23} Daolai et al reported that silica supported Cu-displayed better catalytic activity in dehydrogenation of 1-decanol to decanal (DHDD).²⁴ In addition, it was found that the hydrogenation of hydrocarbons accumulates on the catalyst as coke, which causes the catalytic deactivation. This challenging task can be accomplished by in-situ usage of processed H₂ throughout the reaction with CO₂.²⁵ In this study, we try to see the effect of CO₂ as soft oxidant over different supported Cu catalysts such as Cu/ZrO₂, Cu/CeO₂, Cu/ZnO, and Cu/MgO for the oxidative DH of 1-decanol (Scheme 1).

2 | EXPERIMENTAL

2.1 | Catalyst preparation

Cu-based catalysts with different supports (Cu/MgO, Cu/ZrO₂, Cu/CeO₂, and Cu/ZnO) were prepared by simple co-precipitation method with metal nitrates as starting materials. The precursor solution was prepared by dissolving 7.6 g of Cu (NO₃)₂·6H₂O and respective amounts of nitrate precursors of support (ZrO₂, CeO₂, MgO, and ZnO) in 100 mL of distilled water. A total of 5% K₂CO₃ base solution was prepared as precipitating agent. Subsequently, the two solutions were slowly added into a 500 mL beaker under vigorous stirring. The pH was maintained at 9.5 and the solution was further stirred for half an hour. The resultant precipitate was filtered and washed many times with distilled water until the pH of the filtrate becomes neutral. The precipitate was dried in oven at 373 K for 12 hours and calcined at 723 K for 4 hours in air.

A total of 7.6 g of Cu (NO₃)₂·6H₂O, and requisite amount of support nitrate precursor, MgNO₃, and formic acid (with HCOOH/Cu²⁺ molar ratio of 12/1) were physically mixed in a mortar and ground for 5 minutes. In this process, brownish-yellow fumes, probably NO_x gases due to decomposition of nitrate precursors were released. After that homogeneous metal-formic acid precursors were formed. The grubby state



Dehydrogenation



RWGSR

SCHEME 1

Dehydrogenation of 1-decanol to decanal with CO₂ as soft oxidant



Dehydrogenation + RWGSR



Side Reaction

metal-formic acid material was dried at 373 K for 12 hours. Then, the material was changed to bubbly bluish metal-formic acid precursors. The obtained solid was calcined at 723 K for 3 hours in N_2 atmosphere. It was reported that formic acid decomposes to release H_2 on PdAg-CeO₂ catalyst.²⁶ Hence, it can be thought that H_2 released from formic acid might be helpful to reduce CuO species into Cu⁰ species.

2.2 | Catalyst characterization

The complete catalyst characterization procedures are introduced in supplementary information.

2.3 | Catalytic activity

Catalytic activity tests were conducted in a fixed bed reactor made up of quartz at atmospheric pressure. One gram of catalyst with the equal quantity of quartz beads (18 mesh sieved particles) was loaded into the middle of the reactor (14 mm id and 300 mm length) by sandwiching between two plugs of quartz wool. Quartz glass chips were positioned on top of the catalyst bed to perform as a preheating zone. Before the catalytic reaction, the catalyst was reduced at 553 K for 3 hours with H_2 gas flow at a rate of 40 mL/min. Then the reaction temperature was set to 523 K and liquid 1-decanol was passing with a feed rate of 1 mL/h along with CO₂ flow at a rate of 40 mL/min. The outcome mixture was collected at regular intervals in an ice cold trap and analyzed by GC-17A (M/s. Shimadzu Instruments, Japan), which was equipped with flame ionization detector and verified by GCMS, QP-2010 (M/s. Shimadzu Instruments, Japan).

3 | RESULTS AND DISCUSSIONS

3.1 | Characterization results

3.1.1 | X-ray diffraction

Figure 1 shows the X-ray Diffraction (XRD) patterns of reduced samples of supported Cu catalysts. The characteristic peaks of CeO₂ were detected at 2θ values of 28.5, 33.1, 47.4, and 56.4°. The diffraction peak position at $2\theta = 30.3^\circ$ indicates the existence of tetragonal ZrO₂ phase. The sharp intense peaks were observed at 2θ values of 31.8, 34.5, 36.3, and 56.8° related to ZnO crystalline phase. The XRD patterns of MgO showed diffraction peaks at $2\theta = 36.7$ and 62.1° assigned to a cubic

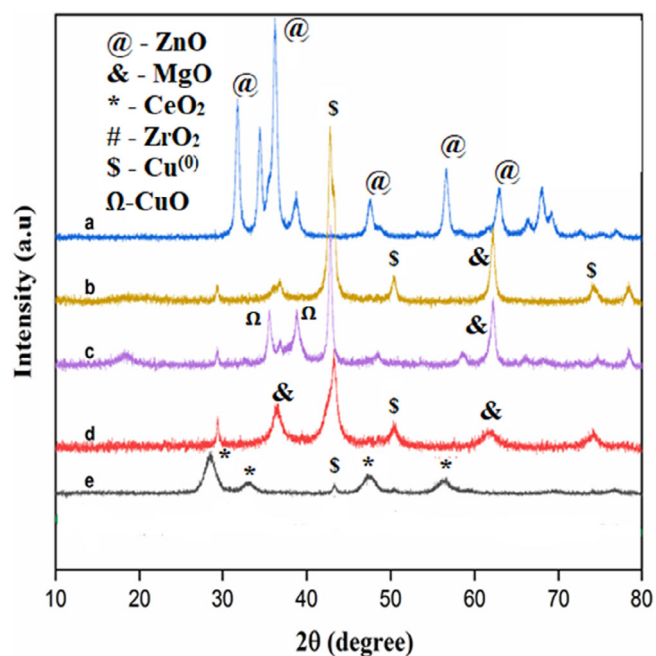


FIGURE 1 XRD patterns of reduced supported Cu catalysts A, Cu/ZnO; B, spent Cu/MgO; C, formic acid-assisted Cu/MgO; D, fresh Cu/MgO; (E), Cu/CeO₂; and (F), Cu/ZrO₂

MgO phase. The additional peaks indicating CuO are at 2θ values of 35.6, 38.8, and 48.5°. Here the high intense peaks observed for CuO at $2\theta = 35.6$ and 38.8 corresponding to (111) and low intense diffraction peak is obtained at $2\theta = 48.5^\circ$ corresponding to (202) plane. The diffraction peaks at 2θ values of 43.3, 50.5, and 74.1° are assigned to metallic copper. In Cu/MgO catalyst, the high intense peaks are observed at $2\theta = 42.9$ and 62.1°, which are corresponding to (200) and (220) planes. No significant phase changes were observed in spent catalyst (collected after 24 hours time-on-stream study [TOS] in DHDD), which is correlated with XRD patterns of fresh catalyst. The high dispersion of Cu and good metal support interactions were reported by previous studies. The crystallite sizes of metallic copper in all supported catalysts were calculated by using Scherrer equation.²⁷⁻²⁹

3.1.2 | BET Surface analysis

The brunauer-emmett-teller (BET) surface area and pore size distribution analysis of Cu/CeO₂, Cu/ZnO, Cu/MgO, and Cu/ZrO₂ catalysts and of supports CeO₂, ZnO, MgO, and ZrO₂ are listed in Table S1. N_2 adsorption-desorption isotherms of the catalysts and their supports were exhibited in Figure 2. The isotherm curves of all catalysts and supports are showed as type IV with large type H3 hysteresis loops as per

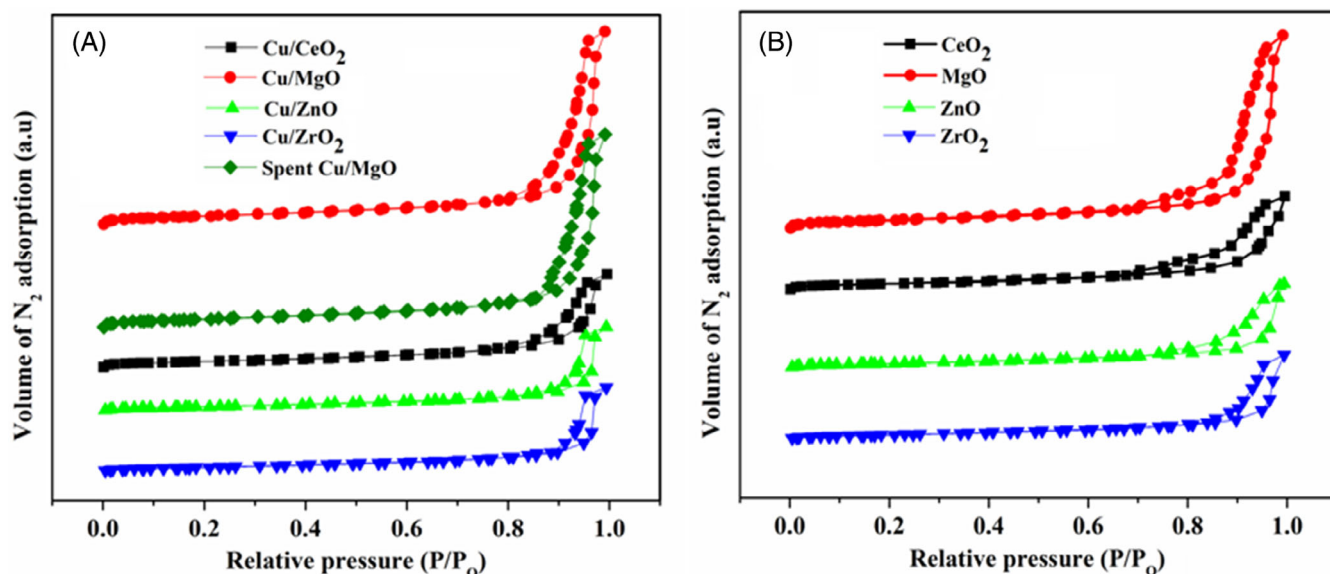


FIGURE 2 N_2 adsorption-desorption isotherms of A, supported Cu catalysts; B, pure supports

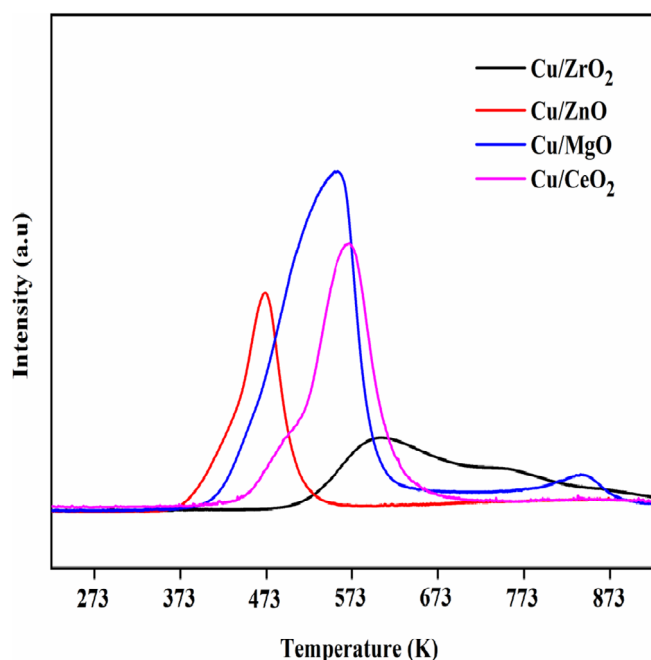


FIGURE 3 H_2 -TPR patterns of supported Cu catalysts

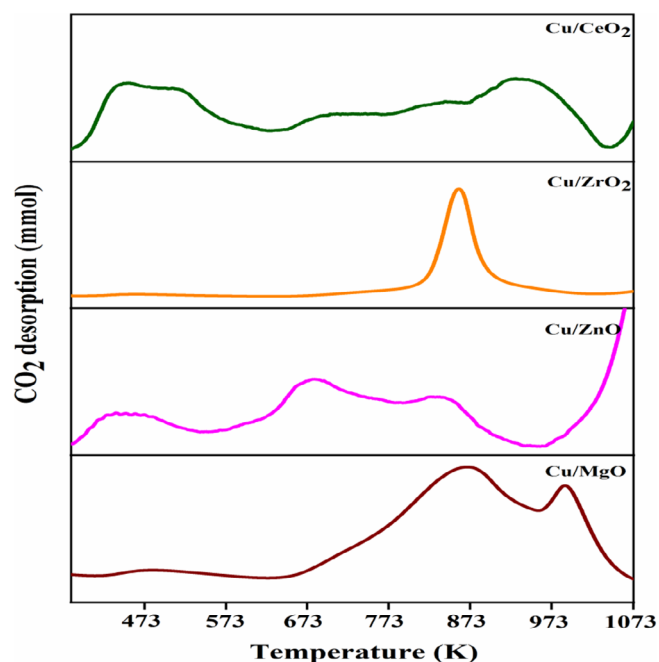


FIGURE 4 CO_2 -TPD profiles of supported Cu catalysts

International Union of Pure and Applied Chemistry (IUPAC) classifications. This type of hysteresis loops is usually found on solids consisting of aggregates or agglomerates of particles forming slit shaped pores, with a non-uniform size.³⁰ Such types of isotherms are mostly characteristic to regular mesoporous materials.^{31,32} From textural properties, among all the prepared catalysts, Cu/MgO has possessed the highest BET surface area of $51.5 \text{ m}^2/\text{g}$ and pore size compare to Cu/CeO₂, Cu/ZnO, and Cu/ZrO₂ catalysts may be due

to consistently dispersed Cu particles on the surface of MgO support, which are in good agreement with transmission electron microscope (TEM) results of Cu/MgO catalyst. However, the MgO support showed more surface area than Cu/MgO catalyst, due to loading of 10% Cu on MgO collapsed the pores present in their catalyst and the Cu nanoparticles agglomerate, which decrease the specific surface area and pore volume.³³ Similar trend was observed in CeO₂, ZnO, and ZrO₂ supports and their Cu/CeO₂, Cu/ZnO, and Cu/ZrO₂ catalysts.

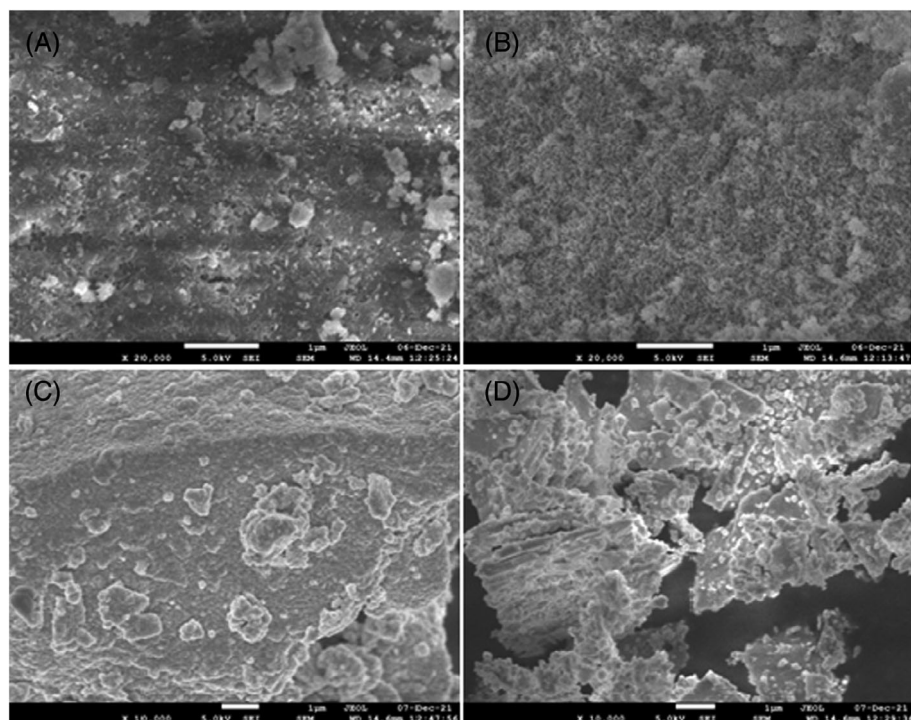


FIGURE 5 FESEM images of catalysts A, Cu/MgO; B, Cu/ZnO; C, Cu/ZrO₂; and D, Cu/CeO₂

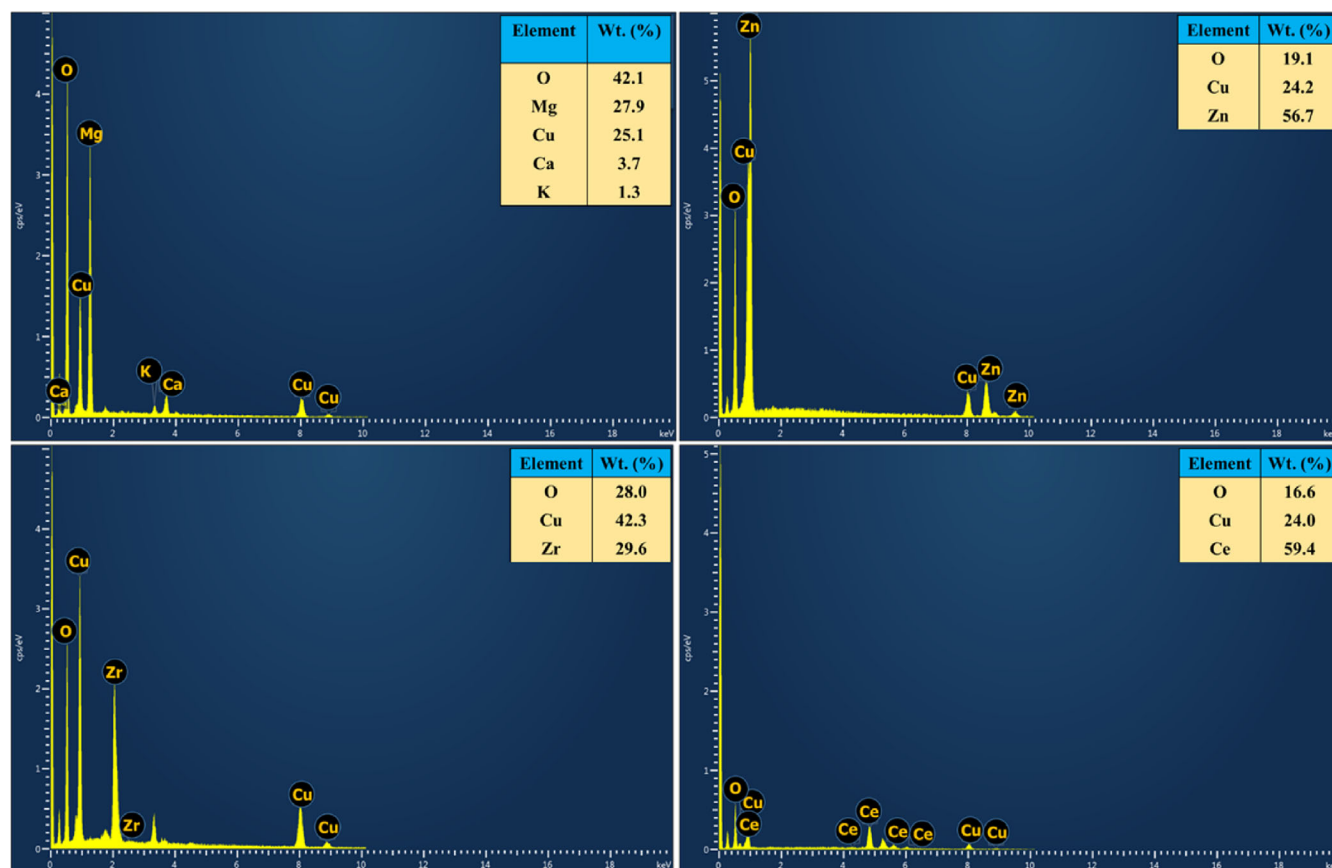


FIGURE 6 EDS analysis of supported Cu catalysts

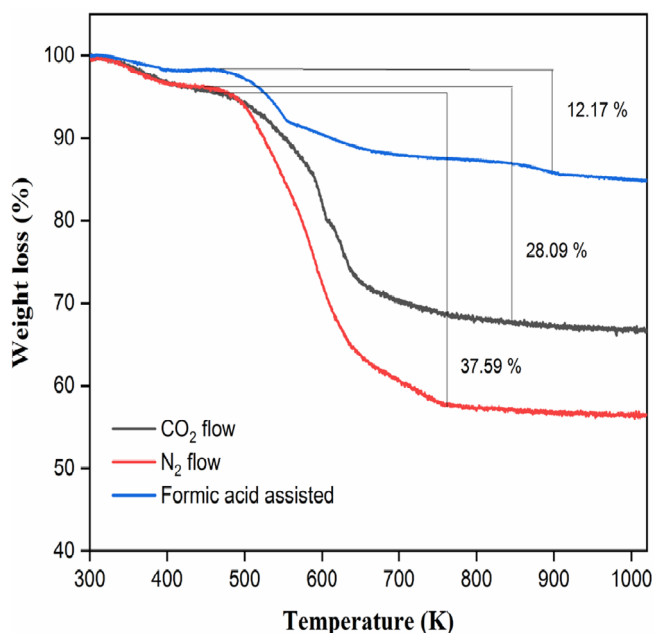
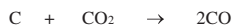


FIGURE 7 TGA profiles of spent 10Cu/MgO catalyst (CO₂ flow), spent 10Cu/MgO catalyst (N₂ flow), and spent 10Cu/MgO catalyst-formic acid-assisted (CO₂ flow)



SCHEME 2 Reducing coke formation through Boudouart reaction

3.1.3 | H₂-Temperature programmed reduction

The reducibility supported copper catalysts were examined by H₂-temperature programmed reduction (TPR) (Figure 3). Cu/CeO₂, Cu/ZnO, Cu/MgO, and Cu/ZrO₂ catalysts showed reduction of CuO species at T_{max} in between 470 and 590 K. When compared to other catalysts, Cu/MgO has the change in T_{max} to higher value (553 K), which can be attributed to the interaction between copper oxide and MgO support. H₂-TPR profile of Cu/ZnO showed a low intense, low temperature peak at around 470 K corresponding to reduction of fewer number of CuO species interacted with ZnO support. The tetragonal Cu/ZrO₂ shows at 590 K, which is ascribed to the reduction of CuO species present on the surface of the support ZrO₂. The reduction peak at 753 K represents either the reduction of CuO bulk species or CuO species strongly interacted with ZrO₂ support. Even though Cu/ZrO₂ catalyst has better metal support interactions, bulk formation of some CuO species with ZrO₂ support and more acidic nature of ZrO₂ inhibit the catalytic activity in the DH of 1-decanol. The low intense reduction peak of CuO/CeO₂ located at around 492 K

corresponding to highly dispersed CuO species and the peak at 557 K was described to the reduction of bulk CuO species. So, the presence of fewer number of interacted species between CuO and CeO₂ in Cu/CeO₂ catalyst is also not much active when compared to Cu/MgO catalyst.³⁴⁻³⁹

3.1.4 | Temperature programmed desorption of CO₂

The basicity of supported copper catalysts was determined by CO₂-temperature programmed desorption (TPD) analysis. Figure 4 shows CO₂-desorption patterns of Cu/CeO₂, Cu/ZrO₂, Cu/ZnO, and Cu/MgO catalysts. The total basicity of the catalyst was estimated with the amount of CO₂ desorbed at weak (353-573 K), moderate (573-823 K), and strong (>823 K) basic sites present on the catalyst. The basic sites would have significant role in the DHDD and were major responsible for better catalytic activity. From CO₂-TPD profiles, it is possible to observe that the huge amount of medium and strong basic sites present on the surface of MgO leads to be most basic. Therefore, it is possible to think that decanal formation could be in proportion to the number of basic sites of Cu/MgO catalyst. For the Cu/ZrO₂ catalyst, the total basicity was found to be lower as shown in Figure 4. This indicates the order of basicity as follows Cu/MgO > Cu/CeO₂ > Cu/ZnO > Cu/ZrO₂. Here Cu/ZnO possessed weak and moderate basic sites whereas Cu/ZrO₂ has only moderate basic sites. Although Cu/CeO₂ possessed weak, moderate, and strong basic sites, the lower number of moderate and strong basicity gives second priority to Cu/CeO₂ catalyst.⁴⁰⁻⁴² In case of Cu/ZnO catalyst CO₂ adsorbs on the surface of the ZnO species and formed ZnCO₃ species. This was observed beyond the temperature 1073 K. So, the peak at the end of TPD belongs to ZnCO₃ species.⁴³

3.1.5 | Field emission scanning electron microscopy

Field emission scanning electron microscopy (FESEM) images were used in order to observe the morphology of prepared catalysts. The surface morphology of supported Cu catalysts is analyzed by FESEM and is shown in Figure 5. The figure represents FESEM images of Cu catalysts supported on MgO, ZnO, ZrO₂, and CeO₂. The morphology of MgO support showed the flakes like shaped structure and the top-view FESEM images for Cu/ZnO are like nanorods shown in Figure 5.^{44,45} It is noted that the synthesized Cu/ZrO₂ catalyst is in nano

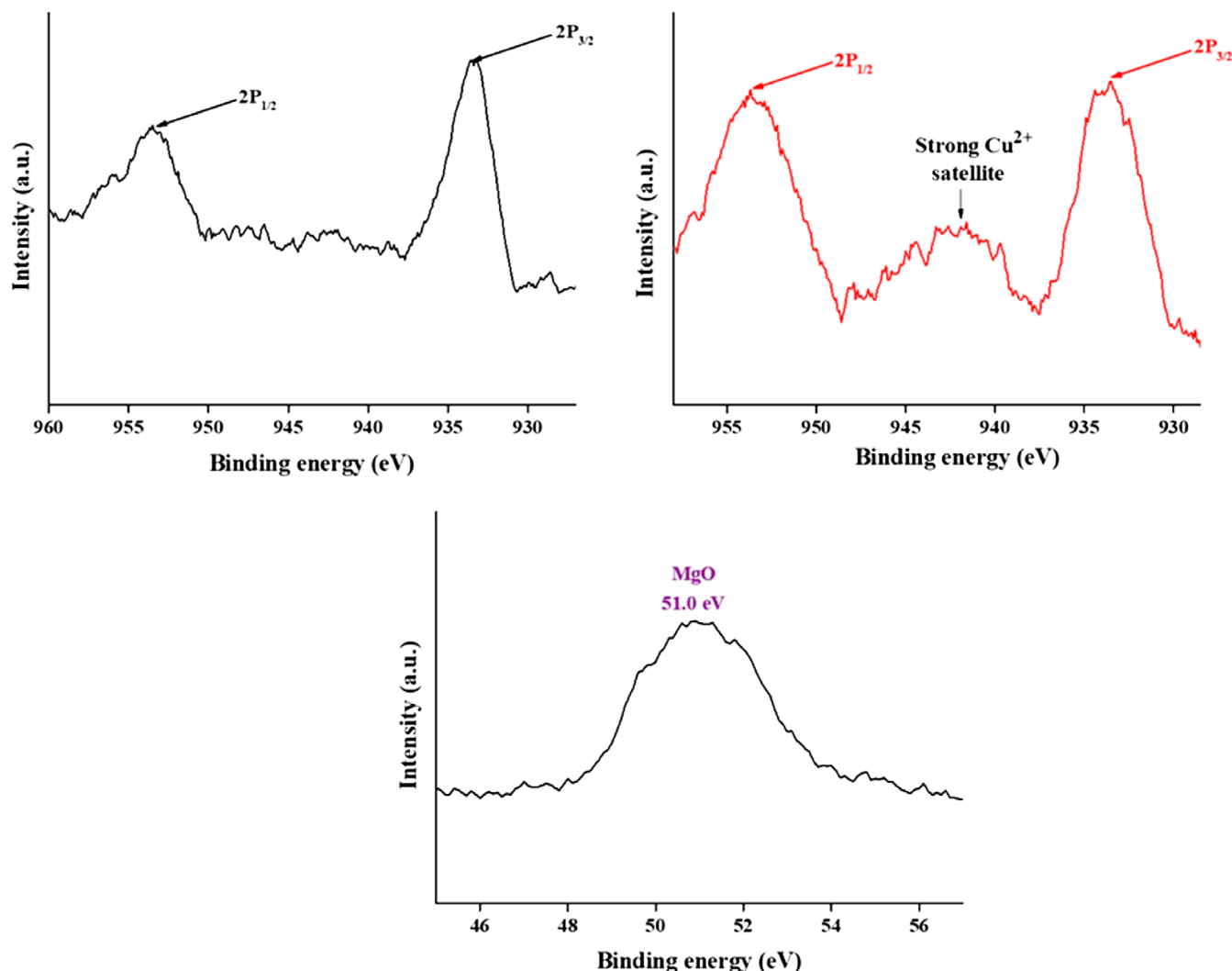


FIGURE 8 XPS spectra of Cu 2P and Mg 2P of the reduced Cu/MgO catalyst (Red: formic acid-assisted catalyst)

Catalyst	Conversion of		Selectivity (%)		
	1-decanol (%)	Decanal	Decanoic acid	Decyl decanoate	Decene
10Cu/CeO ₂	73.0	95.2	2.9	1.9	-
10Cu/MgO	87.0	98.7	0.8	0.5	-
10Cu/ZnO	56.8	92.0	5.2	1.5	1.3
10Cu/ZrO ₂	32.3	88.4	6.4	2.9	2.3

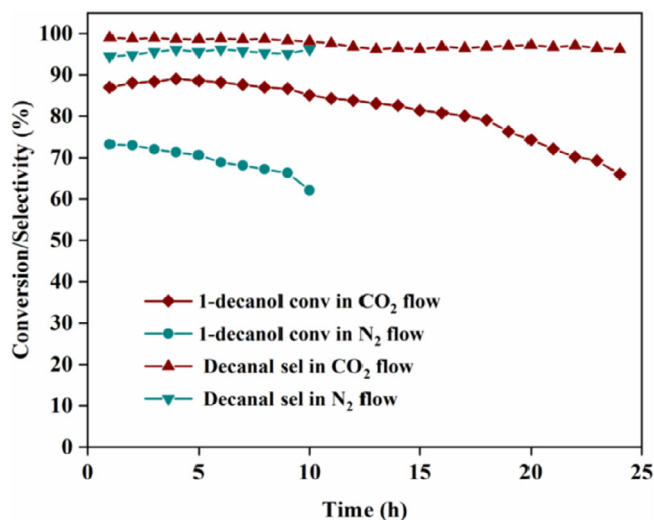
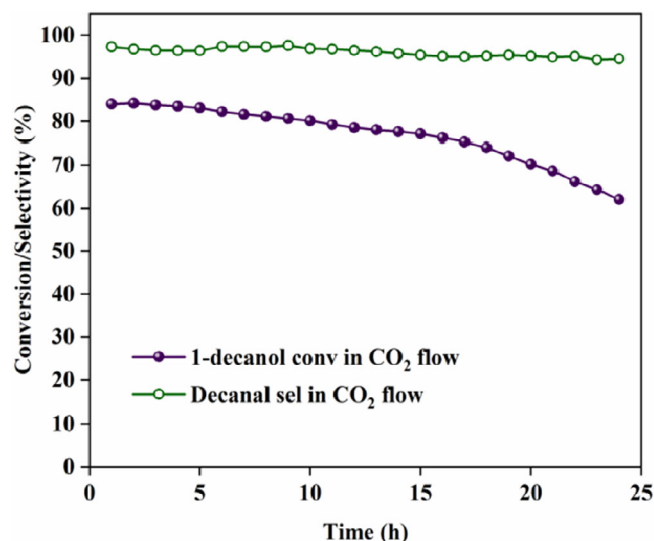
Note: Reaction conditions: catalyst amount: 0.5 g, temperature: 523 K, WHSV: 0.5 hour⁻¹, time: 8 hours, CO₂ flow rate: 30 mL/min.

TABLE 1 CO₂ assisted oxidative DHDD over different supported Cu catalysts

pattern with spherical shaped particles and in some areas, they are agglomerated also.⁴⁶ We found that Cu particles are present on the surface of the CeO₂ in the form of nano bars. The corresponding energy dispersive spectroscopy (EDS) spectra and atomic percentage of prepared catalysts are shown in Figure 6 and confirmed the presence of Cu, Mg, Ce, Zr, Zn, and O elements.

3.1.6 | Thermo gravimetric analysis

The Thermo gravimetric analysis profiles of spent Cu/MgO are showed in Figure 7. The weight loss between 473 and 1073 K is due to the coke formed during the DH of 1-decanol. In the presence of CO₂ flow Cu/MgO surface mostly not blocked by coke through

FIGURE 9 TOS on 10Cu/MgO catalyst in both CO₂FIGURE 10 TOS on formic acid-assisted Cu/MgO catalyst N₂ flow in CO₂ flow

RWGS reaction, which supports higher durability of the catalyst. By contrast, in N₂ flow, high coke deposition was obtained. Here CO₂ molecules could efficiently hinder the progress of carbonaceous species on the surface of the catalyst. The spent formic acid-assisted Cu/MgO catalyst exhibited low amount of coke. After 24 hours of TOS Cu/MgO catalyst accomplished 28.09% carbon weight loss, whereas formic acid-assisted Cu/MgO catalyst possessed 12.17% carbon weight loss both in CO₂ flow. But in N₂ flow, 37.59% carbon weight loss was obtained even after 8 hours of TOS reaction. These results are reliable with activity trend conferred in this paper.⁴⁷ The advantage of CO₂ co-addition is to prevent coke formation via Boudouart reaction (Scheme 2).

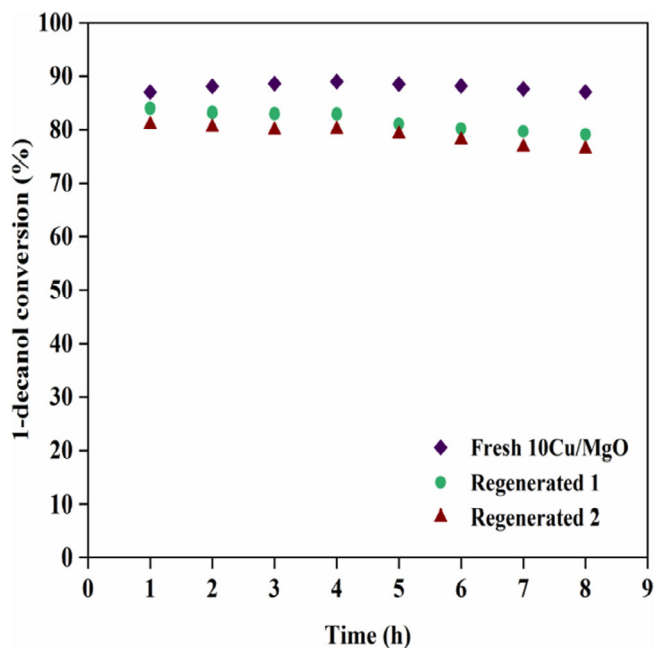


FIGURE 11 Activity comparison between Fresh 10Cu/MgO and its regenerated catalysts

3.1.7 | X-ray photoelectron spectroscopy studies

The representative X-ray photoelectron spectroscopy (XPS) spectrum of reduced Cu/MgO and formic acid assisted synthesized Cu/MgO catalysts are shown in Figure 8. We observed two different peaks corresponding to Cu 2P_{3/2} and Cu 2P_{1/2} at the binding energy (BE) values of 933.3 and 953.6 eV. But in case of formic acid assisted synthesized Cu/MgO catalyst, the strong satellite peak was also observed at a BE value of 941.5 eV corresponding to the presence of Cu⁺² species. This is due to partial reduction of CuO species when formic acid was added to copper nitrate precursor. The XPS spectra for Mg 2p exhibited the presence of MgO support at a binding energy value of 51.0 eV in both type of catalysts.^{48–50} Here red color XPS spectrum indicates the formic acid-assisted Cu/MgO catalyst. The XPS results of the Cu/MgO catalyst are in good agreement with the reported literature.

3.2 | Activity studies

3.2.1 | Support effect

The role of support in supported Cu catalysts influences the catalytic activity. The performance of catalytic activity in DHDD is associated with the surface basicity of catalysts. In the present study, the reaction was carried out at

TABLE 2 Comparison of the catalytic performance of Cu/MgO catalyst in CO₂ assisted conversion of 1-decanol to decanal with reported catalytic processes

Catalyst	Reaction conditions	1-decanol conversion (%)	Decanal selectivity (%)	References
Cu/La ₂ O ₃	Batch, 423 K, 10 hours, 0.2 g catalyst N ₂ atm, solvent: mesitylene	45	100	10
Cu/La-MgAlO	Batch, 423 K, 8 hours, 0.2 g catalyst N ₂ atm solvent: mesitylene	89	100	7
Cu/La ₂ O ₂ CO ₃	Batch, 423 K, 8 hours, 0.2 g catalyst N ₂ atm solvent: mesitylene	85	100	39
Cu/SiO ₂	Vapor phase, 548 K, 5 hours 0.5 g catalyst, N ₂ flow: 30 mL/min	77.4	98.4	24
Cu/MgO	Vapor phase, 523 K, 8 hours 0.5 g catalyst, CO ₂ flow: 30 mL/min	87	98.7	Present
Cu/MgO ^a	Vapor phase, 523 K, 8 hours 0.5 g catalyst, CO ₂ flow: 30 mL/min	81	96	Present

^aFormic acid assist synthesized catalyst.

a temperature of 523 K with 30 mL/min of CO₂ flow. Table 1 lists the DHDD over supported metal catalysts. It obviously demonstrates the impact of basic nature on the conversion of 1-decanol. Here MgO supported Cu catalyst with more number of basic sites shows better conversion and selectivity. Along with decanal, the by-products, that is, decene, decanoic acid, and decyl decanoate are also formed. Due to fewer number of basic sites present in Cu/ZrO₂ catalyst supports dehydration of 1-decanol to decene with lower conversion of 1-decanol. Cu/ZnO also showed lower conversion of 1-decanol {56.8%}. 10Cu/CeO₂ offered a relatively high conversion of 1-decanol (73%) with 95.2% selectivity to decanal. But with increasing TOS, conversion of 1-decanol gradually decreases. A sudden decrease of conversion was observed in 10Cu/CeO₂ catalyst. Among the tested catalysts, 10Cu/MgO exhibited better catalytic activity with 87% 1-decanol conversion and with 98.7% selectivity to decanal.

3.2.2 | TOS and reusability of the catalyst

Cu/MgO catalyst was stable upto 24 hours TOS (Figure 9), whereas Cu/CeO₂, Cu/ZnO, and Cu/ZrO₂ catalysts were unstable and within short period of time they lost their stability and catalytic activity. Here, we report 87% conversion of 1-decanol with 98.7% selectivity to decanal and the catalyst Cu/MgO can be regenerated with little activity loss. 10Cu/MgO catalyst executed higher 1-decanol conversion with CO₂ flow by eliminating the produced H₂ via RWGS. Hence, CO₂ can be recognized as a soft oxidant. It can be noted that the rate of formation of decanal over 10Cu/MgO catalyst in CO₂

aided DH is more compared to N₂ assisted DH. The employment of CO₂ as feed gas in DHDD provides consumption of H₂ through RWGS and supports maximum selectivity to decanal. The consumption of H₂ through RWGS plays a vital role in CO₂ aided DH reactions. In this paper, we also synthesized metallic Cu/MgO catalysts by the novel formic acid-assisted solid-state method and employed precisely in DH of 1-decanol without further reduction. The formic acid assists synthesized MgO supported Cu catalyst is also shown better catalytic activity upto 24 hours TOS with the conversion of 1-decanol as 79% and selectivity to decanal as 96% (Figure 10). But the catalytic activity is less when compared to reduced MgO supported Cu catalyst. This is due to partial reduction of Cu particles in formic acid-assisted MgO supported Cu catalyst. We have also conducted reusability comparisons on 10Cu/MgO catalyst up to two repeated cycles. The recycle studies of 10Cu/MgO catalyst are presented in Figure 11. No huge change was observed up to 2 cycles regarding the conversion of 1-decanol. We understood that Cu/MgO catalyst is most stable and a well-established one compared to other supported Cu catalysts for 1-decanol DH.

Nowadays, the increased concentration of CO₂ in the atmosphere results in temperature rise. Hence, there is an urgent necessity to address the CO₂ emission issue with the interest of future generations. CO₂ capture and utilization are the options to mitigate the CO₂ emissions.⁵¹ CO₂ utilization is a well-developing field with considerable interest in research and development.⁵² The utilization of CO₂ is viable due to inexpensive, nonflammable, readily available, and nontoxic nature of CO₂. CO₂ is recognized as a proper oxidant for DH reactions because it can be able to act as a soft

oxidant thus preventing the over oxidation of 1-decanol into other side products like decanoic acid. In the case of CO₂ aided DH of 1-decanol, there is a less chance for produced hydrogen to participate in hydrogenolysis to form hydrocarbons owing to RWGS with CO₂. It enhances the decanal selectivity and reduces the accumulation of carbonaceous species over Cu metal surfaces. While in N₂ flow, the liberated hydrogen has an option to join with another 1-decanol molecule to form hydrocarbon as a by-product over active sites of the catalyst. Therefore, the formed carbonaceous species deactivated the catalyst and also decreased decanal selectivity.

The reaction conditions for different catalysts used for the DHDD are reported in Table 2. Ruijuan et al reported 45% 1-decanol conversion and 100% decanal selectivity over Cu/La₂O₃. Over Cu/La-Mg-Al catalyst, 89% 1-decanol conversion and 100% decanal selectivity were recognized from the report of Zhang et al and Wang et al reported 85% 1-decanol conversion and 100% decanal selectivity over Cu/La₂O₂CO₃ catalyst. All the above mentioned reactions are carried out in batch process. Daolai et al reported 77.4% 1-decanol conversion and 98.4% decanal selectivity in vapor phase over Cu/SiO₂ catalyst. In the present work, we report 87% conversion of 1-decanol and 98.7% selectivity to decanal in vapor phase over Cu/MgO catalyst.

4 | CONCLUSIONS

In conclusion, 10Cu/MgO catalyst exhibited 87% 1-decanol conversion and 98.7% decanal selectivity in CO₂ flow at 523 K with more stability. Due to the present higher number of basic sites and robust interactions between Cu particles and MgO support, it shows high catalytic activity and is stable up to 24 hours TOS. Using CO₂ as a soft oxidant has advantages in terms of higher 1-decanol conversion because the H₂ produced will be continuously removed via RWGS. One more advantage of CO₂ co-addition is it removes coke via Boudouart reaction. While in N₂ flow, the activity declined due to accumulation of coke on the surface of the catalyst. 10Cu/MgO catalyst can be regenerated with little activity loss. Formic acid assists synthesized MgO supported Cu catalyst was also shown better catalytic in CO₂ flow without prereduction of the catalyst.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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