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Insight into the synergism between copper species and surface defects influenced by copper content over Cu/CeO₂ catalysts for the hydrogenation of carbonate

Huabo Li, Yuanyuan Cui, Qianqian Liu and Wei-Lin Dai *[a]

Abstract: Various Cu/CeO₂ nanorod catalysts with different copper content were synthesized through a facile coprecipitation method for the hydrogenation of diethyl carbonate to methanol in a fixed-bed reactor. The methanol yield enhanced with increasing of copper loading, but excessive amount of copper would lead to the deactivation of catalyst at higher liquid hourly space velocity because of the active metal aggregation. The 20Cu/CeO₂ and 30Cu/CeO₂ catalyst displayed superior catalytic performance with the methanol space-time yield of 8.4 and 8.1 mmol·g_{cat}⁻¹·h⁻¹, respectively. The remarkably enhanced catalytic performance was mainly ascribed to higher Cu⁰ surface area, appropriate ratio of Cu⁺/Cu⁰ and more surface oxygen vacancies associated with Ce³⁺, which stemmed from the strong interaction between Cu and the CeO₂ support.

Introduction

The transformation of chemically stable CO₂ to methanol, which is an important intermediate for present fuels and chemical feedstock, has been intensively studied. While the direct conversion of carbon dioxide to methanol remains a grand challenge if considering the harsh reaction conditions, low CO₂ conversion and methanol yield.^[11] The hydrogenation of CO₂ derivatives (carbonates, formates, carbamates, urea derivatives and so on) compensates the high activation energy barrier for the cleavage of the C=O bond in the conventional hydrogenation process of CO₂.^[2] Recently, designing heterogeneous catalysts for the hydrogenation of carbonates has been an important topic in green and sustainable chemistry.^[3] However, there are still few investigations on continuous fixed-bed reactions being reported in comparison with batch reactions about the hydrogenation of carbonates.

Ceria (CeO₂), as one of important rare-earth oxides, has aroused widespread concern because of its specific physicochemical properties such as the outstanding redox ability, oxygen storage/release capacity (OSC) associated with the formation of oxygen vacancies, and low cost compared with noble metals.^[4] It

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is extensively studied as support or catalyst for many reactions in heterogeneous catalysis. Ceria has been investigated for structure-sensitive reactions with different morphologies, which can be directly catalyzed or assisted by active sites located at a specific facet or edge.^[5] Both theoretical and experimental researches illustrated that CeO₂ nano-structures with well-defined {100} and {110} reactive planes exhibited enhanced catalytic activity than CeO₂ nanoparticles.^[6] Tana et al. demonstrated that the CeO₂ nanorods with highly energetic {100} and {110} facets showed excellent oxygen storage capacity and activity for CO oxidation. Wang et al. reported the outstanding performance of CeO₂ nanorods for selective oxidation of o-xylene and clarified the key role of surface concentration of oxygen vacancy clusters.^[5a]

As well known, the migration of metal cations into the ceria lattice will promote the redox behavior and catalytic activity significantly owing to the formation of more oxygen vacancies. [7] Furthermore, the shape dependence of ceria support for the catalytic properties has been widely studied.[5b] Catalysts with Cu loaded on CeO₂ nanorods were more active and selective in N₂O decomposition reaction^[8] and NO reduction by CO^[6a]. Apparently this depended on the dispersion of the active copper species and the interaction with ceria. Our previous work also indicated the correlation between the enhancement of catalytic performance of diethyl carbonate (DEC) hydrogenation to methanol and the structural characteristics of CeO₂ with different morphologies and we found that the catalyst using CeO₂ nanorods as support got much higher intrinsic hydrogenation catalytic activity.^[3a] However, there is no comprehensive investigation about the role of copper concentration in DEC hydrogenation to methanol, which should never be neglected, as it significantly influences the interaction between active Cu and CeO₂ support, the molar ratio of surface Cu⁺/Cu⁰ and surface defects concentration.^[9] Hence, investigation showing the influence of metal concentration is urgently hankered for a better understanding of CeO₂ supported system. We herein synthesized a series of Cu/CeO₂ nanorods catalysts and explored the role of copper content in the selective hydrogenation of DEC, reaching a conclusion that well-dispersed copper species and certain amount of surface Ce3+-Ov-Ce3+ defects are beneficial for the production of methanol. Moreover, this type of copper-based ceria catalysts revealed an extended application potential for the hydrogenation of carbonates.

Results and Discussion

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Table 1. Physicochemical properties of various xCu/CeO2 catalysts with different copper content.												
Catalyst	S _{вет} (m²⋅g⁻¹)	V _{pore} (cm ³ ⋅g ⁻¹)	D _{pore} (nm)	D _{Cu} ^[a] (%)	S _{Cu^{0[a]} (m²⋅g_{cat}-1)}	d _{Cu^[b] (nm)}	STY _{MeOH} ^[c] (mmol·g _{cat} -1·h ⁻¹)	TOF _{MeoH} ^[d] (h ⁻¹)				
CeO ₂	86.3	0.55	25.2	-	-	-	-					
2Cu/CeO ₂	72.0	0.18	9.8	80.7	10.5	-	6.2	0.68				
5Cu/CeO ₂	76.7	0.23	11.8	71.2	23.1		7.7	0.74				
10Cu/CeO ₂	69.4	0.16	9.1	54.0	35.0	30.8	7.8	0.78				
20Cu/CeO ₂	69.4	0.23	15.1	36.9	47.9	39.3	8.4	1.04				
30Cu/CeO ₂	57.6	0.21	14.4	17.4	33.9	45.9	8.1	0.83				

[a] Cu dispersion and surface area of Cu⁰ determined by N₂O titration. [b] Cu crystallite size calculated by the Scherrer formula. [c] Space-time yield (STY). Reaction conditions: $P(H_2) = 2.5 \text{ MPa}$, $H_2/DEC = 190 \text{ mol/mol}$, Liquid hour space velocity (LHSV) of DEC = 1.3 h⁻¹, T = 503 K. [d] TOF: calculated as moles of MeOH formed in the initial 1 h per mole of surface copper calculated from a copper dispersion.

Physicochemical properties of the catalysts

Table 1 lists the chemical compositions and textural properties of xCu/CeO₂ (x denotes the mass content of copper) nanorod catalysts with different copper loading. The N2 adsorptiondesorption isotherms and pore-size distribution curves of samples are illustrated in Figure S1. All the calcined xCu/CeO₂ samples exhibit a typical adsorption curve of Langmuir type IV isotherms with H3-type hysteresis loops. The as-synthesized CeO₂ has the BET specific surface area of 86.3 m²/g, pore volume of 0.55 cm³/g, and pore size at 25.2 nm. After the introduction of copper, the BET surface area and pore volume decrease with copper particles filling into the pores or the surface of the support. The broaden pore size distribution of 30Cu/CeO₂ could stem from the excess amount of copper species, which varied with the porous structure. The molar ratios of surface-to-bulk copper and concentrations of cupreous surface have been treated as key factors affecting the adsorption properties and catalytic performance of copper-based catalysts.^[10,11] The metallic copper dispersions and cupreous surface areas of xCu/CeO2 determined by N2O titration method are also shown in Table 1. The increase of copper content causes the gradually reducing in the copper dispersion, while the exposed copper surface areas reach maximum when the copper content is 20 wt.%.

Figure 1A shows the wide-angle XRD patterns of the calcined catalysts. Distinct diffraction peaks of CuO at 35.5° and 38.7° (PDF No.: 45-0937) are observed when copper content is higher than 5 wt.% and the peaks intensity enhanced with the increasing of copper content. All the patterns showing legible diffraction at the positions of 28.6°, 33.1° , 47.5° , 56.3° , and 59.0° can be ascribed to {111}, {200}, {220}, {311}, and {222} planes of the cubic fluorite structure CeO₂ (PDF No.: 34-0394), respectively. After reduction (Figure 1B), a sharply diffraction peak at 43.3° characteristic of face-centered cubic Cu {111} (PDF No.: 04-0836) is observed while the peaks of CuO disappeared. The Cu crystallite sizes calculated by the Scherrer formula indicates that

the average grain size increases from approximately 30.8 to 45.9 nm with the increasing of copper content from 10 to 30 wt.% (Table 1). Almost no diffraction peak of any other phase of copper species can be observed when the loading mass is lower than 10 wt.%, suggesting that too much copper species in the catalysts will lead to the aggregation of the copper species.



Figure 1. XRD patterns of xCu/CeO₂ catalysts with different copper content after calcination (A) and reduction (B).

Representative micrographs of the as-synthesized $5Cu/CeO_2$, $20Cu/CeO_2$ and $30Cu/CeO_2$ sample after reduction are illustrated in Figure 2 (A, B and C) to demonstrate their morphology and crystallite growth. For the Cu/CeO₂ catalysts with low copper content, Cu also exists as well-dispersed and permeated into the CeO₂ lattice forms which could not be distinguished due to the poor contrast.^[6a] The particles size significantly enlarges with the increasing of copper loading, and aggregation of the species can be clearly observed in the $30Cu/CeO_2$, which is agreement with N₂O titration and XRD results. The HRTEM image (inset of Fig. 2B) of the $20Cu/CeO_2$ catalyst illustrates the lattice fringe of 0.31 nm, which fit well with the {111} planes of cerianite,^[3b] confirming the maintenance of the crystalline CeO₂ structure after the

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Figure 2. TEM images of the reduced catalysts: 5Cu/CeO₂ (A), 20Cu/CeO₂ (B), 30Cu/CeO₂ (C).

incorporation of Cu. Meanwhile Cu {111} plane can be identified with lattice fringe of 0.21 nm distinctly.^[12] For the 30Cu/CeO₂ catalysts, the morphology here seems reversed, the CeO₂ nanorods are sheathed in the copper species, which is similar with the results reported by Skårman.^[12b]

The real redox property of xCu/CeO₂ catalysts was investigated by temperature programmed reduction (TPR) method to reveal the metal-support interaction and the results were shown in Figure 3. Generally, there is no H₂ consumption for pure CeO₂ phase under the temperature lower than 500 K.[6a] Two obvious reduction peaks at ~450 and ~470 K correspond to the welldispersed copper and the species interacting with CeO₂ support strongly (Cu-O-Ce), respectively. And the higher H₂ consumption around 470 K may contribute to large numbers of Cu2+ ions incorporated into the lattice of CeO₂ during calcination and some of Ce⁴⁺ ions reduced at low temperature which agree with the XPS results as discussed below.^[12c] Shoulder peak at 505 K, which is observed from the 20Cu/CeO₂ and 30Cu/CeO₂, is due to larger and aggregated copper oxide that weakly interacts with ceria. Hence, it can be deduced that the copper species are mostly welldispersed on the supports or in easily reduced bulk state with lower copper content.



Figure 3. H2-TPR patterns of xCu/CeO2 catalysts with different copper content.

To better understand the surface elemental composition and chemical state, X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) tests were conducted. Figure 4A shows the Ce 3d, O 1s and Cu LMM spectra of reduced catalysts. The peaks *u*1 and *v*1 correspond to the $3d^{10}4f^1$ electronic state of Ce³⁺ ions, while the peaks *u*, *u2*, *u3*, *v*, *v2* and *v3* are the main representative of the $3d^{10}4f^0$ state corresponding to Ce⁴⁺.^[13] The amount of Ce³⁺ increases gradually from 12.7%, maximum at 18.4% then decreases to 17.8% (Table 2). The oxygen vacancies are generated to maintain the electrostatic balance of Ce³⁺-containing fluorite ceria. To further investigate the chemical state of O, O 1s spectra of different catalysts are shown in Figure 4B. Three types of surface oxygen species are identified by performing a peak-fitting deconvolution. The peaks at 529.5, 531.7 and 533.6 eV can be ascribed to lattice



Figure 4. Ce 3d, O 1s XPS spectra and Cu LMM XAES spectra of the reduced xCu/CeO_2 catalysts with different copper content.

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oxygen (O_{α}), oxygen vacancies (O_{β}), and other weakly bound and chemisorbed oxygen species (O_v). The ratio of O_β to O_T ($O_T = O_\alpha +$ $O_{B}+O_{v}$) can be used to roughly estimate the concentration of surface oxygen vacancies.^[14] Notably, for 20Cu/CeO₂ and 30Cu/CeO₂, the y-peak nearly disappeared, which shows that 20Cu/CeO₂ and 30Cu/CeO₂ own little amount of surface weakly bound oxygen species. Further evidence is provided by FT-IR characterization (Figure S2), and the peak between 3300 and 3600 cm⁻¹ is attributed to stretching vibration of surface hydroxyl (-OH).^[15] The peaks are stronger for catalysts with lower copper content, especially for 2Cu/CeO₂ and 5Cu/CeO₂. Generally, the ratio of band intensity in LMM XAES can be representative for the reduced copper species analysis on the catalyst surface due to almost the same binding energy for Cu⁰ and Cu⁺ species. The Cu LMM XAES spectra of working catalysts of xCu/CeO2 are illustrated in Figure 4C, and peaks observed are deconvoluted into two symmetrical peaks located at around ~916 and ~919 eV, corresponding to Cu⁺ and Cu⁰ species, respectively. It can be concluded from the deconvolution results that copper loading amounts could significantly affect the distributions of surface Cu+ and Cu⁰, and the molar ratio of surface Cu⁺/Cu⁰ is gradually enhanced with an increase of the copper loading and peaks at 20 wt.% (Table 2).

Catalytic activity

The gas-phase hydrogenation of DEC as a probe reaction is conducted to investigate the relevance between catalytic performance and intrinsic structure of xCu/CeO_2 catalysts. Methanol and ethanol are formed in the hydrogenation process



Figure 5. The conversion of DEC (A), selectivity to MeOH (B) and yield of MeOH (C) over xCu/CeO₂ catalysts with different copper content. Reaction condition: $P(H_2) = 2.5 \text{ MPa}$, $H_2/DEC = 190 \text{ (mol/mol)}$, T = 503 K.

of DEC as main products, and the tail gas mainly consisting of CO₂ and CO which means the occurrence of side-reactions such as methanation, decarbonylation and decomposition under the reaction conditions. The carbon balance calculated maintained at >97%. Figure 5 presents the DEC conversion, MeOH selectivity and MeOH yield based on LHSV. The $20Cu/CeO_2$ catalyst displays the highest conversion in higher LHSV range compared with other samples, indicating its superb catalytic activity, and the 2Cu/CeO₂ exhibits the poorest catalytic activity. When we consider MeOH selectivity carefully, the differences could also be distinguished obviously. Although the DEC conversion on the 5Cu/CeO₂ and 10Cu/CeO₂ catalysts are close to 30Cu/CeO₂, the selectivity on the latter is higher and further resulting in superior yield to MeOH. The sample of 20Cu/CeO₂ show a superior yield to MeOH of >75% even at a high LHSV of 1.2 h⁻¹ compared to other samples and it is quite stable during long-term stability test. To gain further insight into the action mechanism of the copper content, the STY and TOF values are estimated to acquire the catalytic properties of the xCu/CeO₂ catalysts. The 20Cu/CeO₂ displays the highest STY (8.4 mmol·g_{cat}-1·h⁻¹) for MeOH at 503 K and DEC LHSV of 1.3 h⁻¹ (see Table 1) and TOF value, which confirms the superior properties of 20Cu/CeO2. As shown in Table S1, the severe reaction conditions of CO₂ direct hydrogenation reaction can be avoided to some extent by substitution of the carbonates hydrogenation. Methanol formation rate of 20Cu/CeO₂ catalyst is the highest among the reported Cu-based catalysts for the hydrogenation of carbonates (Table S1).

	copper content.										
	Cataluat	C _{Ce} ^{3+[a]}	Ο _β /Ο _Τ –	К. Е. [[]	X _{Cu} +[c]						
	Catalyst	(%)		Cu⁺	Cu ⁰	(%)					
	2Cu/CeO ₂	12.7	0.37	915.8	919.3	43.5					
	5Cu/CeO ₂	13.2	0.37	916.1	918.8	46.7					
	10Cu/CeO ₂	17.1	0.29	916.2	919.0	50.4					
	20Cu/CeO ₂	18.4	0.39	916.0	919.1	66.2					
	30Cu/CeO2	17.8	0.36	916.1	919.2	42.2					

Table 2. XPS parameters of the reduced xCu/CeO2 catalysts with different

[a] $C_{Ce}^{3+}=Ce^{3+}/(Ce^{3+}+Ce^{4+})$. [b] Kinetic Energy. [c] $X_{Cu}^{+}=Cu^{+}/(Cu^{+}+Cu^{0})$.

Discussion

Usually, the catalytic performance of supported metal catalysts is intrinsically associated with the microstructure of active metal and supports, including active metal surface, metal-support interactions and the contribution of support. In this work, Cu/CeO_2 catalysts are prepared with different copper content, various of characterization techniques are employed to obtain structural and surface feature of the samples. As we know, the samples with

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lower copper content cannot supply sufficient active sites, which can give explanation about the poorest activity of 2Cu/CeO2. The 20Cu/CeO₂ catalyst with the maximum Cu⁰ surface shows the best performance and the highest TOF value, while for 30Cu/CeO₂, the MeOH yield is high at low LHSV (h⁻¹) and dramatically decreases with prolonging the reaction time or increasing LHSV, which is mainly because of the weak interaction between active metals and supports, further agglomeration of active species due to the relatively small specific surface area and lager copper particle size observed from the BET and XRD results of previous paper. Similar results can be found in literatures elsewhere.^[16] The mole ratio of Ce³⁺/(Ce³⁺+Ce⁴⁺) and Cu⁺/(Cu⁺+Cu⁰) on the basis of copper loading are shown in Figure 6. It is notable that the 20Cu/CeO₂ catalyst shows the highest C_{Ce}^{3+} and X_{Cu}^{+} value. Thus, the proper copper content in the catalysts could significantly regulate the physicochemical characteristics of the Cu/CeO₂ catalysts.

In order to verify the influence of copper dispersion, $20Cu/CeO_2$ -DM and $20Cu/CeO_2$ -PG catalysts were synthesized and characterized. From Table S2 we can see that the $20Cu/CeO_2$ -DM shows the lowest copper dispersion and methanol yield. The copper dispersion of the $20Cu/CeO_2$ -PG catalyst is 35.4%, which is close to the value of $20Cu/CeO_2$ (36.9%), whereas the catalytic activity of the latter is much higher than that former. Therefore, we can give a preliminary conclusion that copper dispersion plays a certain role in the catalytic performance of catalysts, but is not the critical one. The surface composition and valence state of copper species should be further studied.



Figure 6. The mole ratio of Ce $^{3+}$ and Cu $^+$ over the reduced xCu/CeO_2 catalysts as a function of Cu content.

Previous studies have indicated that the synergy between Cu⁰ and Cu⁺ was also a crucial factor for the hydrogenation of carbonates. It was well documented that the Cu⁰ sites would dissociate adsorb hydrogen molecules, whereas surface Cu⁺ as electrophilic specie may conduct the hydrogenation procedure by cleaving the C=O bond via interaction with the electrons of oxygen atom.^[17] However, an excessive amount of Cu⁰ species might induce the side reactions such as decomposition of the reaction intermediates (ethyl formate, etc.), which probably results in the generation of gas by-products during the hydrogenation of DEC, while the substrate stabilized on the Cu⁺ species is not easy to involve in the dissociative process.^[18] In the case of the xCu/CeO₂ catalysts, the catalytic activities dramatically changed with the number of Cu⁺ sites, which suggests that cuprous species acted as efficient sites to motivate carbonyl group and that the relatively higher amount of Cu⁺ led to the ideal catalytic activities.

It is generally accepted that the defect sites may significantly impact the catalytic hydrogenation performance of catalyst, among which oxygen vacancies are common characteristics.^[19] The surface $Mn^{2+}-O_v-Mn^{2+}$ defect of CuMn-x catalysts can promote the hydrogenation of dimethyl succinate via interacting with the carbonyl group and then weakening the C=O.^[20] Furthermore, Mudiyanselage et al. revealed that the surface Ce³⁺ ions and oxygen vacancies can act in the same way as the Cu⁺ species to stabilize the immediate products.^[21] Herein, a plausible simplified mechanism for DEC hydrogenation over Cu/CeO₂ catalysts is proposed (Scheme 1).

Firstly, the oxygen vacancies neighbor with surface Ce³⁺ ions coordinate with the oxygen atom of carbonyl group. Meanwhile, Ce³⁺ species convert to Ce⁴⁺ via interacting with the C=O group, thus resulting in the formation of C-O σ bond. Correspondingly,



Scheme 1. Synergistic catalytic effect of Cu^0 and CeO_2 support (A), Cu^+ and CeO_2 support (B).

adjacent oxygen vacancy is occupied by the O atom. Simultaneously, the Cu⁺ species also could offer sites for the stabilization of carbonyl group. The H dissociated by Cu⁰ participates in the next step, which plays important role in the cleavage of C-O bond, producing ethanol, and aldehyde group interacted with oxygen vacancy and Cu⁺ is left. And the transformation is finally accomplished by the reduction of aldehyde group to methanol. ^[2,3c,22] In comparison, the significantly improved MeOH yield for 20Cu/CeO₂, with the relatively higher maximum amount number of Cu⁺ and Ce³⁺, is likely due to the stability of DEC and carbonyl group by Cu⁺. Therefore, the efficiently enhanced catalytic performance is attributed mainly to synergism between active copper species and surface defects. In a word, Cu⁰ species are responsible for the dissociation of hydrogen and following activation of carbonyl groups. Briefly, Cu⁺ and surface Ce³⁺-O_v-

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Ce³⁺ defect sites promote the adsorption of the substrates and stabilization of intermediate products.

Conclusions

In summary, a series of Cu/CeO₂ catalysts with different copper content were synthesized by a facile co-precipitation method to achieve the optimized catalytic performance. Among the assynthesized Cu/CeO₂ samples, the 20Cu/CeO₂ catalyst presents superb activity for the vapor phase continuous hydrogenation of DEC to methanol. Catalyst characterization revealed that the efficiently enhanced catalytic performance is attributed mainly to the synergism between active copper species and surface defects. Cu⁰ species can activate hydrogen and carbonyl groups, and Cu⁺ and surface defects promote the adsorption of DEC and stabilization of intermediate products. The loading of copper influences the interaction between Cu and CeO₂ support, further resulting in the structural evolution. This work holds possibilities for the achievement of methanol via indirect chemical utilization of CO₂ with an inexpensive and efficient copper-based catalyst.

Experimental Section

CeO₂ nanorods were synthesized by a hydrothermal method as reported in Ref. [3a]. Then, Cu(NO₃)₂·3H₂O was deposited on the CeO₂ nanorods using the Na₂CO₃ as precipitant to obtain the Cu/CeO₂ catalysts. Analogously, by adjusting the content of copper respectively, the same procedures were carried out to synthesis other catalysts xCu/CeO₂ (x denotes the copper content). More experiments details were further shown in supporting information.

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Synergistic catalysis: Cu/CeO_2 catalysts with proper copper content achieve the superb activity for the vapor phase continuous hydrogenation of DEC to methanol. The enhanced catalytic performance is attributed mainly to the synergism between active copper species and surface defects of CeO_2 support.

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Insight into the synergism between copper species and surface defects influenced by copper content over Cu/CeO₂ catalysts for the hydrogenation of carbonate