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SYNTHESIS OF DME BY CO_2 HYDROGENATION OVER La_2O_3-MODIFIED CuO-ZnO-ZrO_2/HZSM-5 CATALYSTS

Article Highlights

- La-modified CuO-ZnO-ZrO2/HZSM-5 catalysts were prepared by an oxalate co-precipitation method
- La-modified CuO-ZnO-ZrO2/HZSM-5 catalysts show higher catalytic performances
- The catalytic performances of the catalysts are strongly dependent on the La content

Abstract

A series of La_2O_3-modified CuO-ZnO-ZrO_2/HZSM-5 catalysts were prepared by an oxalate co-precipitation method. The catalysts were fully characterized by X-ray diffraction (XRD), N_2 adsorption-desorption, hydrogen temperature programmed reduction (H_2-TPR), ammonia temperature programmed desorption (NH_3-TPD), and X-ray photoelectron spectroscopy (XPS) techniques. The effect of the La_2O_3 content on the structure and performance of the catalysts was thoroughly investigated. The catalysts were evaluated for the direct synthesis of dimethyl ether (DME) from CO_2 hydrogenation. The results displayed that La_2O_3 addition enhanced catalytic performance, and the maximal CO_2 conversion (34.3%) and DME selectivity (57.3%) were obtained over the catalyst with 1% La_2O_3, which due to the smaller size of Cu species and a larger ratio of Cu^+/Cu.

Keywords: CO_2 hydrogenation; dimethyl ether; La_2O_3 promoter.

Carbon dioxide emission has caused irreversible climate changes due to its greenhouse effect [1]. CO_2 capture and storage is one of efficient method for reducing the CO_2 emissions. However, this technology requires high cost [2]. Chemical recycling of CO_2 is another main option, which is presented as an economically attractive and sustainable method. CO_2 can be converted into methanol, dimethyl ether (DME), methane and syngas ($CO+H_2$) [3], carboxylic acids, etc. Among them, synthesis of DME has been paid special attention since DME can be applied as a clean fuel, coolant, propellant, and is an important chemical intermediate [4]. The chemical reactions occurring in direct conversion of CO_2 to DME can be described by the following equations [5]:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O, \Delta H^\circ = -49.4\,kJ/mol \quad (1)$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O, \Delta H^\circ = -23.4\,kJ/mol \quad (2)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O, \Delta H^\circ = 41.2\,kJ/mol \quad (3)$$

For the methanol synthesis (reaction (1)), CuO-ZnO-ZrO_2 catalytic system is considered as more favorable than the traditional CuO-ZnO-Al_2O_3, because the interaction of Cu metal particles with ZnO and ZrO_2 lead to the stabilization of a "mix" of Cu and $Cu^{\delta+}$ (not Cu^{2+}, Cu^{1+} and Cu) [6]. For the methanol dehydration process (reaction (3)), solid-acid catalysts (HZSM-5, γ-Al_2O_3 and sulfated zirconia) are employed [7]. HZSM-5 is widely applied for methanol dehydration because: 1) it has very high catalytic activity at the optimum reaction temperature; 2) it is more resistant toward poisoning of acid sites by the water due to more hydrophobic character; 3) predominance of Brønsted-type acidity, which can promote the DME yield [8]. However, H-ZSM-5 presents the disadvantages of narrow pore size and strong acid sites, which

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will limit reactant molecules diffusion and lead to formation of secondary products, respectively. Witoon *et al.* developed sulfated zirconia catalyst with 20% sulfur-loaded on ZrO_2 as methanol dehydration catalyst, the yield of methanol and DME over CuO-ZnO--ZrO_2/20S-ZrO_2 both higher than those over CuO--ZnO-ZrO_2/H-ZSM-5, but the stability of the former catalyst is a little poor [9].

Up to now, the conversion of CO_2 and the selectivity of DME are still not high. To enhance the catalytic activity, efforts have been addressed by adding promoters for methanol synthesis catalyst, besides developing new preparation methods [10-14]. Our previous results showed that V and Mn oxides modified CuO-ZnO-ZrO_2/HZSM-5 exhibited higher catalytic performance [15-16]. La_2O_3, as a rare earth metal oxide, is considered as owing some basic character [17], and it can promote many metal oxide catalytic reactions. Guo *et al.* [18] investigated catalysis performance of La doping Cu/ZrO_2 for CO_2 hydrogenation to methanol, and they found the amount of basic site increases with La loading and the presence of La enhance the selectivity of methanol. Gao *et al.* reported appropriate amount of La can decrease the crystallite size of CuO and enhance the dispersion of Cu [19]. Sun's group has investigated the effect of La on the performance of Cu/Zn/Al catalysts via hydrotalcite-like precursors for CO_2 hydrogenation to methanol, and the results showed La addition not only led to higher BET specific surface area and Cu dispersion, but also increased the total number of basic sites and proportion of strongly basic sites [20]. Furthermore, Sun's group also reported that addition of Zr to La-Cu-Zn-O with perovskite structure catalyst, for synthesis of methanol from CO_2 hydrogenation, will lead to smaller particles, lower reduction temperature, higher Cu dispersion, larger amount of hydrogen desorption at low temperature as well as higher concentration of basic sites are obtained [21]. However, the introduction of La_2O_3 into the CuO-ZnO--ZrO_2/HZSM-5 catalyst for CO_2 to DME has not been reported.

Herein, La_2O_3-modified CuO-ZnO-ZrO_2/HZSM-5 catalysts with a different La_2O_3 content were prepared, aiming at investigating the effect of La_2O_3 modification on the structure and performance the catalysts.

EXPERIMENTAL

Catalyst preparation

The La_2O_3 modified CuO-ZnO-ZrO_2/HZSM-5 (CuO:ZnO:ZrO_2 mass ratio: 5:4:0.2) catalysts, abbreviated as CZZL*x*H where *x* stands for theoretical La_2O_3/CZZ wt.%, were prepared by an oxalate co-precipitation method (CZZL*x*/HZSM-5 mass ratio: 2:1), HZSM-5 (SiO_2/Al_2O_3 mole ratio: 50) was purchased from Catalyst Plant of Nankai University (China). The preparation method is same as described in other work [15]. In brief, first, metal nitrates were dissolved into a certain amount of ethanol (denoted as solution A); $H_2C_2O_4{\cdot}2H_2O$ (200 mol.% of metal nitrate) was also dissolved into ethanol (solution B). Then, solutions A and B were slowly dropped into a beaker containing a HZSM-5 suspension in ethanol suspension kept under stirring at 333 K. The suspension was sealed and aged for 2 h and then the ethanol was evaporated at 353 K to get a precipitate. Finally, the precipitate was dried at 393 K for 12 h and calcined in air at 673 K for 4 h.

Catalyst testing

Catalytic performance was evaluated in a continuous-flow fixed-bed reactor made of stainless steel with inside diameter of 0.01 m. First, the catalyst was reduced with 10% H_2/N_2 at 573 K for 3 h under atmospheric pressure. Then it was cooled to 653 K and reactant gas flow was introduced, raising the pressure to 3.0 MPa, the reaction temperature was 543 K. The exit line was heated to prevent condensation. The products were analyzed on line with a gas chromatograph (SP2100A) equipped with both a TCD (for CO and CO_2, GDX-101 connected with Porapak T column) and a FID (for CH_4, CH_3OH and CH_3OCH_3, Porapak Q column). Conversion and selectivity values were calculated by internal standard method [22]. X_{CO2}, S_{pi} and Y_{DME} represent the conversion of CO_2, the selectivity of the product (DME, MeOH and CO) and the yield of DME, respectively. Each experimental data was corresponds to an average of three independent measurements, with error of ±2%.

$$X_{CO_2} = \frac{CO_{2,in}/N_{2,in} - CO_{2,out}/N_{2,out}}{CO_{2,in}/N_{2,in}} \quad (4)$$

$$S_{Pi} = \frac{P_i}{1 - CO_{2,out}} \quad (5)$$

where P_i stands for the concentration of a specific i product (DME, MeOH orCO):

$$Y_{DME} = S_{DME} X_{CO_2} \quad (6)$$

Catalyst characterization

XRD measurements were performed on a Rigaku D/max 2500pc X-ray diffractometer with Cu-Kα

radiation (λ = 1.54156 Å) at a scan rate of 4° min^{-1} at 50 kV and 250 mA. For the reduced catalysts were first reduced with 10% H_2/N_2 at 573 K for 3 h, and cooled to room temperature under the N_2 flow, and then keep it into a bottle full of N_2 and send it to XRD chamber immediately. The crystallite size was calculated using the Scherrer equation. BET surface areas were measured by N_2 adsorption at 77 K using a Quantachrome Autosorb 1-C. Before measurements, samples were degassed under vacuum at 573 K for 4 h. H_2-TPR was carried out in 10% H_2/Ar flowing at 50 mL min^{-1}, using a ramp rate of 10 K min^{-1} to 773 K. NH_3-TPD was conducted on a Chemisorb from 373 to 873 K. XPS measurements were performed on an ESCALAB-250. The catalysts were first reduced with 10% H_2/N_2 at 573 K for 3 h, and cooled to room temperature under the N_2 flow, then put into the chamber of X-ray photoelectron spectrometer immediately for measurement. The exact composition of the surface of the catalyst was determined by XPS. Acidity on the catalyst was measured on a NICOLET 500 FT-IR through pyridine adsorption. The sample was prepared to the load slice, which was subject to purification under vacuum pressure 0.0133 Pa at 673 K, after cooling down to the room temperature, pyridine was adsorbed for 0.5 h. Desorption was carried out by programming temperature to 423 K. The infrared spectrum was generated within the scope of 1400–1700 cm^{-1} at room temperature.

RESULTS AND DISCUSSION

Catalytic performance of catalysts

The catalytic performances of CZZL*x*H catalysts with varying La_2O_3 content are summarized in Table 1. The major product was DME, and the side products were methanol, CO and trace hydrocarbons. The amount of hydrocarbons was less than 1% and therefore they were neglected. The CO_2 conversions and DME selectivities over the La_2O_3-modified catalysts are higher than those over unmodified one ($CZZL_0H$), indicating that La_2O_3-modification can efficiently enhance the catalytic performances. The $CZZL_1H$ exhibited the maximum CO_2 conversion and DME selectivity of 34.3 and 57.3%, respectively. CO_2 conversion over $CZZL_1H$ increases 18.6%, compared with $CZZL_0H$. The influence of the catalyst composition on the performance does not seem distinct, which is due to the thermodynamic regime of reaction test because of combination of high temperature and long contact time. If the temperature is decreased to 533 K, the differences of conversion and DME selectivity between $CZZL_1H$ and $CZZL_0H$ become much larger (Table 2). It is also noted that the selectivity of CO is high (about 30%), which may due to the higher reaction temperature of 543 K. CO was produced by reverse water-gas reaction, the reaction has endothermic character, as shown in reaction (2). Meanwhile, compared to methanol synthesis, the RWGS reaction has a higher apparent activation energy [23], indicating that the increase in CO production is faster than that of methanol with higher reaction temperature. The selectivity of CO over $CZZL_1H$ exhibited the minimal value, indicating that a certain amount of La_2O_3 can inhibit the RWGS reaction. However, as Gao *et al.* pointed out, further work needs to be carried out to investigate how La_2O_3 changes the RWGS reaction [19].

In order to further increase the DME yield, the catalytic performance of the $CZZL_1H$ catalyst was also investigated at lower gas hourly space velocity. As shown in Table 2, when the GHSV was as low as 1800 h^{-1}, the CO_2 conversion and DME selectivity increase to 36.4 and 58.2%, respectively. The increase of the conversion can be attributed to the longer contact time of CO_2 and H_2 over the catalyst at lower GHSV. Similarly, methanol dehydration can proceed to a higher degree with increasing contact time, leading to higher DME selectivity. In addition, a contrast experiment was carried out at a reaction pressure of 5 MPa while keeping other conditions constant. DME selectivity increased by approximately 7.3% and CO selectivity decreased by 24.6% compared with those obtained at 3 MPa. This result suggests that an increase of reaction pressure can improve the catalytic performance.

The structure of catalyst

Figure 1A shows the XRD patterns of CZZL*x*H catalysts. The peaks appearing at 35.5, 38.7, 48.7,

Table 1. Catalytic performances of the catalysts; reaction conditions: T = 543 K; p = 3.0 MPa; CO_2:H_2 = 1:3; GHSV = 4200·h^{-1}

Catalyst	Conversion of CO_2, %	Selectivity, %			DME Yield, %	DME Productivity, g g cat^{-1} h^{-1}
		DME	CH_3OH	CO		
$CZZL_0H$	28.9	55.1	12.9	32.0	15.9	0.171
$CZZL_{0.5}H$	30.4	55.2	12.4	31.7	16.8	0.181
$CZZL_1H$	34.3	57.3	13.3	29.4	19.6	0.212
$CZZL_2H$	31.1	53.6	12.7	33.7	16.7	0.180

Table 2. Catalytic performances of the catalysts at different reaction conditions; reaction conditions: CO_2:H_2 = 1:3

Catalyst	*T*	Conversion of CO_2	*p*	*GHSV*	Selectivity, %			DME Yield	DME Productivity
	K	%	MPa	h^{-1}	DME	CH_3OH	CO	%	g g cat^{-1} h^{-1}
$CZZL_1H$	543	34.3	3	4200	57.3	13.3	29.4	19.6	0.212
$CZZL_1H$	543	36.4	3	1800	58.2	14.2	27.6	21.1	0.098
$CZZL_1H$	543	38.5	5	1800	62.5	16.7	20.8	24.0	0.111
$CZZL_0H$	533	24.2	3	4200	57.1	13.7	29.2	13.8	0.148
$CZZL_1H$	533	30.4	3	4200	61.8	14.2	24.0	18.8	0.203

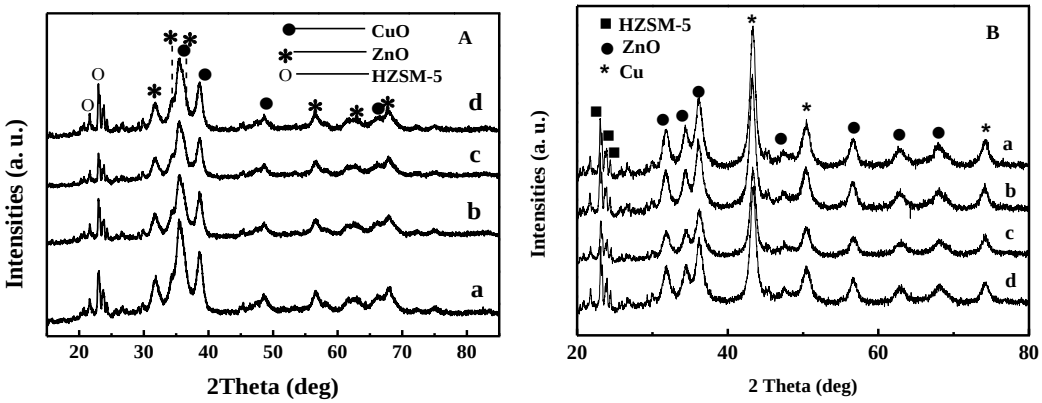

Figure 1. A) XRD patterns of La_2O_3-modified CuO-ZnO-ZrO_2/HZSM-5 and B) reduced catalysts: a) $CZZL_0H$; b) $CZZL_{0.5}H$; c) $CZZL_1H$; d) $CZZL_2H$.

and 66.2° can be ascribed to CuO phase (tenorite, JCPDS 48-1548), the peaks at 31.7, 34.3, 36.6, 56.5, 62.8 and 67.8° can be indexed to ZnO phase (JCPDS 65-3411), and the peaks appearing in the 2θ range of 21-25° belong to HZSM-5 (JCPDS 44-0003). No peaks belonging to ZrO_2 or La_2O_3 are observed, indicating that ZrO_2 and La_2O_3 are amorphous or well dispersed in catalyst body. The intensities of the peaks assigned to CuO and ZnO weakened and the widths of the peaks broadened gradually with increasing La_2O_3 content from 0 to 1%, then they became sharper and narrower again when La_2O_3 content was 2%. This result indicates that the addition of a proper amount of La_2O_3 can enhance the dispersion of CuO and ZnO [24]. This changing trend can be well reflected in the changing trends of Cu and CuO grain size, as shown in Table 3.

Table 3. Physicochemical properties of the catalysts; diffraction peak at 2θ 38.7° for CuO and 43.3° for Cu

Catalyst	S_{BET} / m^2 g^{-1}	D_{XRD} / nm	
		CuO	Cu
$CZZL_0H$	135.4	11.3	13.5
$CZZL_{0.5}H$	136.7	9.6	11.9
$CZZL_1H$	138.2	8.4	10.5
$CZZL_2H$	135.8	9.3	11.4

The XRD patterns of the reduced catalysts are shown in Figure 1B. The diffraction peaks at 2θ values of 43.3, 50.4 and 74.1° can be indexed to the crystal planes of (111), (200) and (220) of metallic copper phase, respectively (JCPDS 04-0836). No diffraction peaks belonging to the CuO phase could be detected, suggesting all CuO species had been reduced to copper. The intensities of the peaks assigned to Cu and ZnO changed in a similar trend as those of CuO and ZnO (Figure 1A).

The specific surface areas and the calculated crystallite sizes of the catalysts using Scherrer's equation are listed in Table 3. The S_{BET} increased from 135.4 of $CZZL_0H$ to 138.2 m^2 g^{-1} of $CZZL_1H$, and then decreased to 135.8 m^2 g^{-1} for $CZZL_2H$. The changing trend of the D_{Cu} is opposite to the trend of the S_{BET}, a minimum of 10.5 nm is obtained over $CZZL_1H$. Although the S_{BET} change is not as significant as D_{Cu}, the trend is in accordance with XRD results. Combining the results in both Tables 1 and 3, it can be observed that $CZZL_1H$ shows the smallest Cu crystallite size and the best catalytic performance, which indicates the activity is closely related to the crystallite size of Cu. Guo *et al.* also reported the catalytic performance of Cu-TiO_2-ZrO_2 related to the crystallite size of CuO [25].

The reducibility of catalyst

H_2-TPR results are depicted in Figure 2. It is obvious that La_2O_3 modification displays a significant effect on the interaction between the metal and the carriers. Each catalyst exhibits a broad peak with peak maximum in 423-563 K, corresponding to the reduction of CuO to Cu [26]. For the catalysts with increasing La_2O_3 content from 0 to 0.5 or 1%, the peaks maxima shift to higher temperature from 529 to 554 or 556 K while no shape changes are observed, which indicates the interaction between ZnO and CuO or La_2O_3 and CuO becomes stronger [19,23,27]. This result seems conflicting with XRD result. According to XRD result, the dispersion of CuO becomes better and the crystalline size becomes gradually smaller with La_2O_3 addition amount from 0 to 1%, suggesting that the reducibility of CuO should become easier. This fact implies La_2O_3 modification still plays another role. For $CZZL_2H$ catalyst, it is evident that the H_2--TPR change tendency becomes more different and the peak maximum shifts towards the lower temperature, indicating the reducibility of CuO becomes easier [28,29]. It is concluded that La_2O_3 modification has at least two roles. On one hand, La modification promotes the dispersion of CuO, leading to easier reduction of CuO; on the other hand, La_2O_3 modification enhances the interaction between CuO and other metal oxides resulting in a more difficult reduction process. The two effects compete with each other and the reduction temperature is dependent on which effect is predominant. Xiong *et al.* also found that the La_2O_3 can increase the dispersion of Co/AC catalysts, whereas the reduction temperature shifted to a higher position due to stronger interaction [30].

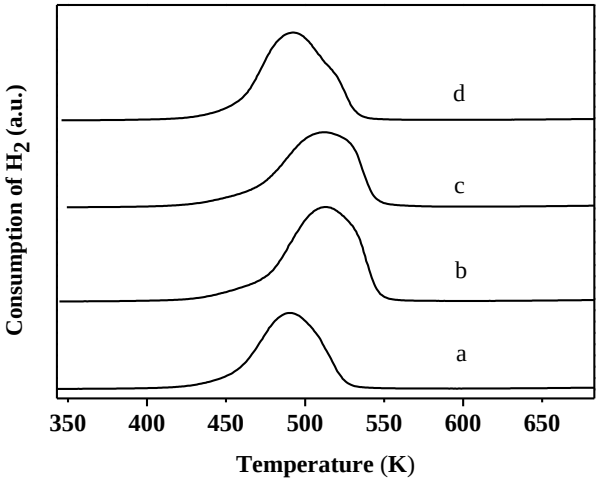

Figure 2. H_2-TPR profiles of catalysts: a) $CZZL_0H$; b) $CZZL_{0.5}H$; c) $CZZL_1H$; d) $CZZL_2H$.

Surface acidity of catalyst

Figure 3 shows the NH_3-TPD results obtained for pure HZSM-5 and CZZL*x*H catalysts. The total acidic amount, the strength and the fraction of various acid sites are summarized (supporting info, available from the authors upon request). On pure HZSM-5 profile, two NH_3 desorption peaks are observed, indicating the existence of at least two different acid strengths. In general, the peak located in 393-523 K and 573-773 K can be attributed to weak and strong acid strengths, respectively [31]. But for all catalysts, three NH_3 desorption peaks, in the temperature regions of 373-473 K, 473-573 K and 573-673 K are observed, denoted as α, β and γ peak, which can be assigned to weak, medium and strong acid strengths of HZSM-5, respectively [32]. This result is similar with that of the reported V-modified catalyst [15]. According to the study, the reason why the catalysts showed another more NH_3 desorption peak than pure HZSM-5 is mainly ascribed to the fact that strong acid strength on pure HZSM-5 are blocked and modified by metal oxides and oxalic acid, respectively. Compared with La_2O_3-free catalyst, peaks α and β on the other curves shift a little to higher temperature with the increasing La_2O_3 content, implying that the weak and medium acid strengths become stronger; on the contrary, the peak γ shifts a little towards lower temperature, indicating strong acid strength becomes weaker. It is also worth noting that the total acid amount decreases with the increasing amount of La_2O_3 from 0.5 to 1%, which can be explained by the basic character of La_2O_3. Sugi *et al.* also observed this effect and suggested that La_2O_3-modification resulted in reducing the support acidity [33]. However, continuous addition of La_2O_3 to 2% increases the total

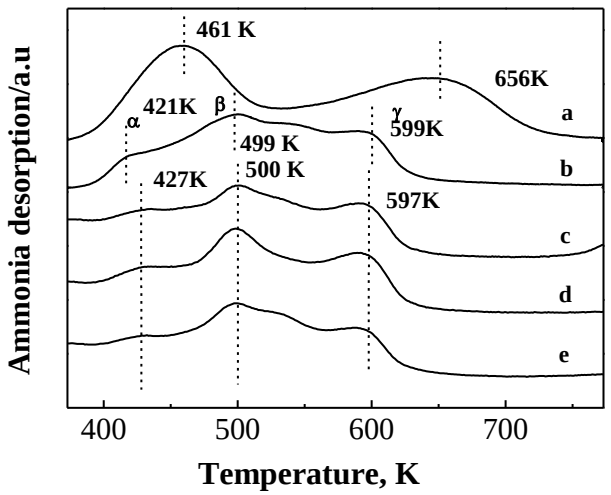

Figure 3. NH_3-TPD profiles of pure HZSM-5 and the catalysts: a) HZSM-5; b) $CZZL_0H$; c) $CZZL_{0.5}H$; d) $CZZL_1H$; e) $CZZL_2H$.

acid amount again. Previously published studies proposed that there are two reasons for the acidity amount increase [34]. One is that the La^{3+} has some Lewis acidic property originated from an empty f orbital; the other reason is that Si-OH and Al-OH in the zeolite framework are polarized by La^{3+}, which result in a stronger acidity. Therefore, the acidity of the CZZL*x*H catalysts is dependent on the La_2O_3 content.

Moreover, La_2O_3 modification can also affect the concentration and distribution of the three acid strengths of HZSM-5 in the catalysts. With the increasing amount of La_2O_3, the concentration and fraction of medium acid strength increase and those of strong acid strength become smaller as compared to those on $CZZL_0H$, but the difference is too small (supporting info). It is generally considered that the strong acidic strength on HZSM-5 zeolite promotes the generation of secondary products like hydrocarbons, resulting in low selectivity to DME [6]. However, here the change of the acidity could not be a factor accounting for the higher DME selectivity because the methanol selectivity of the various catalysts was almost the same, as shown in Table 1. This result suggests that the acidity of the catalysts is strong enough to efficiently convert the produced methanol to DME. In addition, the acidity of Brønsted acid sites and Lewis acid sites for $CZZL_0H$ and $CZZL_1H$ catalysts were determined (supporting info, available from the authors upon request). The results show the acidity of both type acid sites of $CZZL_1H$ decreased compared $CZZL_0H$, thus it can be inferred that there is no direct relationship between the selectivity of DME and the change of acid type of the two catalysts. So, the improvement of DME selectivity is due to the decrease in CO selectivity resulted from the Cu-based catalyst but not from the acid component of the bifunctional catalysts. In addition, according to the literature, it could be speculated that the introduction of La_2O_3 into catalyst will increase the surface basicity of catalyst, which in turn promotes the adsorption of CO_2 and sequence enhances the yield for methanol, finally DME selectivity is increased after methanol dehydration [18].

Results of XPS investigations

The reduced CZZL*x*H catalysts characterized by XPS, the binding energy of $Cu2p_{3/2}$, $Zn2p_{3/2}$, as well as the surface compositions of the catalysts are summarized (supporting info, available from the author upon request). For all the reduced catalysts, binding energies (BE) of $Cu2p_{3/2}$ are located at about 932.3 eV, which are the characteristic peaks of reduced Cu^+/Cu species [35]. The binding energy shifted to higher positions with increasing amounts of La_2O_3, which indicated stronger interaction between CuO and other metal oxides carriers [36]. For the purpose of distinguishing Cu^+ from Cu species, their kinetic energies in the XAES Cu LMM line positions were measured (Figure 4). The Cu LMM spectra show a broad and asymmetrical peak, implying the coexistence of Cu^+ and Cu in the surface of the catalysts. Two symmetrical peaks centered at near 916.6 and 918.7 eV can be obtained by deconvolution, which are corresponding to Cu^+ and Cu species, respectively [37]. Additionally, Cu^+/Cu can be calculated based on the results. Volcanic shape change trends of the Cu^+/Cu *versus* La addition content are observed, the $CZZL_1H$ exhibited the maximum of 0.144, which may consequently lead to higher activity due to the stabilization of Cu^+ favoring the hydrogenation of CO_2 [38]. The binding energies (BE) of $Zn2p_{3/2}$ for all catalysts are located at about 1021.8 eV, which are close to the characteristic peaks of ZnO species [39]. Compared to the nominal surface compositions of the catalysts, it can be seen that the actual surface composition Cu/Zn decreased significantly, implying enrichment of Zn. Similarly, La_2O_3 content is much higher on the surface. It is worth noting that is La_2O_3 is not detectable in $CZZL_{0.5}H$, possibly because the content is too small to give enough signal.

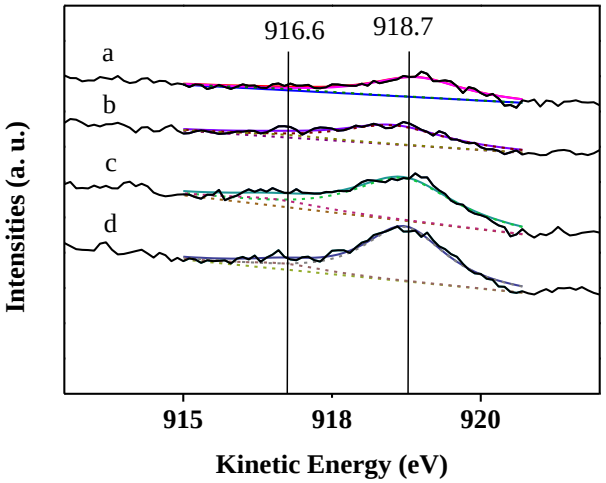

Figure 4. Cu LMM XAES spectra of the reduced catalysts: a) $CZZL_0H$; b) $CZZL_{0.5}H$; c) $CZZL_1H$; d) $CZZL_2H$.

CONCLUSIONS

La_2O_3 modification has great impact on the catalytic performance of CuO-ZnO-ZrO_2/HZSM-5 catalysts for promoting direct CO_2-to-DME. La_2O_3-modification can efficiently enhance the catalytic performance of CuO-ZnO-ZrO_2/HZSM-5 catalysts. The sample containing a nominal amount of 1% La_2O_3

gave the maximum CO_2 conversion and DME selectivity of 34.3 and 57.3%, respectively, benefiting from smaller Cu particles and a larger Cu^+/Cu ratio. When the La_2O_3 content is low (from 0.5 to 1%), it can strengthen the interaction between CuO and other metal oxides and inhibit the reduction of CuO species; meanwhile, the total acid amount decreases slightly but the medium strong acid concentration and strength increase a little. However, excess of La_2O_3 content, *e.g.*, 2%, will lead to an opposite effect. In summary, suitable La_2O_3 addition can improve the catalytic performance of CuO-ZnO-ZrO_2/HZSM-5 for one step CO_2 to DME transformation.

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NAUČNI RAD

SINTEZA DIMETIL ETRA HIDROGENIZACIJOM CO_2 POMOĆU LA_2O_3-MODOFOKIVANIH CuO-ZnO-ZrO_2/HZSM-5 KATALIZATORA

Oksalatnom ko-precipitacionom metodom je pripremljena serija katalizatora CuO-ZnO--ZrO_2/HZSM-5 modifikovanih pomoću La_2O_3. Katalizatori su okarakterisani X-difrakcionom metodom (XRD), N_2 adsorpcijom-desorpcijom, termoprogramiranom redukcijom (H_2-TPR), termoprogramiranom desorpcijom (NH_3-TPD) i fotoelektronskom spektroskopijom X-zraka (XPS). Istražen je i uticaj sadržaja La_2O_3 na strukturu i performanse katalizatora. Katalizatori su testirani u procesu CO_2 hidrogenizacije i direktne sinteze dimetil etra (DME). Rezultati pokazuju da dodatak La_2O_3 poboljšava performanse katalizatora, kao i da su maksimalna konverzija CO_2 (34,3%) i DME selektivnost (57,3%) dobijeni upotrebom katalizatora sa 1% La_2O_3, zbog manjih Cu čestica i većeg odnosa Cu^+/Cu^0.

Ključne reči: hidrogenizacija CO_2, dimetil etar La_2O_3 promoter.