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Influence of rare-earth elements (La, Ce, Nd and Pr) on the performance of Cu/Zn/Zr catalyst for CH₃OH synthesis from CO₂

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Abstract

A series of Cu/Zn/Zr (CZZ) catalysts with different rare earth elements (La, Ce, Nd and Pr) were prepared by co-precipitation method and tested for CO₂ hydrogenation to methanol. The influence of modifier (La, Ce, Nd and Pr) on the physicochemical properties of CZZ catalysts was studied. The results of catalytic test reveal that CO₂ conversion was correlated to the introduction of different promoters. The introduction of La and Ce favor the production of methanol, Nd and Pr modified CZZ catalysts show relative low activity compared with the reference CZZ catalyst.

Keywords: Rare-earth elements, CO₂ hydrogenation, Cu/Zn/Zr catalyst

1. Introduction

In recent years, chemical fixation of carbon dioxide has attracted additional attention as a possible way to manufacture useful chemicals, which is becoming one of the most promising ways to mitigate global warming problems caused by greenhouse gas. Methanol is an important chemical feedstock for several valuable chemicals and may be used as a fuel additive or clean fuel [1-3]. It can also be converted to high-octane gasoline by MTG, olefin by MTO, hydrocarbons by MTH [4]. Based on the great significance of methanol synthesis from CO_2 hydrogenation, Olah et al proposed a new concept of "methanol economy" [1].

Cu/Zn/Al catalysts have been widely used for methanol synthesis from CO₂ containing syngas; however, they exhibited a relative poor catalytic reaction performance for CO₂ hydrogenation to methanol [5]. The reason can be ascribed to the poisoning effect of water on the rate of methanol formation and the strong hydrophilic characteristic of alumina [6]. Promoters such as Ga [7], La [8], Pd [9] on the Cu/ZnO based methanol synthesis catalyst have been investigated. Among the various metal oxides, ZrO₂ is of special interest because of its mechanical and thermal stability, its high specific surface and its semiconducting properties [10]. Zirconia-supported copper catalyst has been reported to have better performance than conventional Cu/ZnO/Al₂O₃ catalyst [6, 11]. The interaction of ZrO₂ and metal Cu particles could lead to the stability of

 $Cu^{\delta+}$ sites and a "mix" of Cu^{0} , $Cu^{\delta+}$ and oxide basic sites concurring to the adsorption of H₂, CO and CO₂ [12]. Thus, zirconia-supported copper catalysts have gained an increasing interest for its high activity in recent years [6, 13-17]. And it was well established in literatures that the addition of promoters, such as La₂O₃, Mn, Cr, B₂O₃ and Ga₂O₃, could also enhance the catalytic performance of methanol synthesis [8, 18, 19]. Słoczyński et al. [20] reported that the addition of Mn and Mg promoters could improve copper dispersion and the adsorptive properties of the $Cu/ZnO/ZrO_2$ catalysts for the synthesis of methanol from CO_2 hydrogenation. They also reported the effect of B, Ga, In and Gd oxides modified CZZ catalyst on the catalytic activity, and found the Ga_2O_3 additive was especially useful [21]. Moreover, some rare-earth elements such as La, Ce and Y can also increase the Cu surface area, as well as effectively increase the strength of the interaction and facilitated spillover of H₂ between Cu and ZrO₂ and therefore stabilized the active center of the catalyst. It could also improve the resistance to thermal sintering and prevent the quick deactivation of Cu species in the presence of water and CO₂ [22-25].

It has been shown in the earlier studies that the catalytic performance was influenced by the different promoter. Especially the incorporation of rare earth element (La_2O_3) could enhance the interaction of reactant and catalyst [8]. It was not reported in detail the effect of different rare earth

elements on the properties of catalyst and reaction performance. The objective was to study the different interaction between components and to investigate the effect of rare earth element on Cu species, which were responsible for the catalytic performance.

In the present study, the CZZX (X =La, Ce, Nd and Pr) catalysts were prepared and characterized by XRD, BET, XPS and TPR techniques. The aim of this work has been a systematic study of the influence of the rare-earth elements on the structure and activity of CZZ catalyst in the synthesis of methanol from CO₂ hydrogenation.

2. Experimental

2.1. Catalyst preparation

The investigated catalysts with weight ratio of CuO:ZnO:ZrO₂=5:3:2 and CuO:ZnO:ZrO₂:X=5:3:1.5:0.5 (X represents La, Ce, Nd and Pr oxide) were prepared by a conventional co-precipitation method as described in detail by our previous work [11, 26]. Typically, two aqueous solutions, a metal salts solution of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, ZrO(NO₃)₂·2H₂O, and in necessary, La(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, Nd(NO₃)₃·6H₂O or Pr(NO₃)₃·6H₂O (all Wako, total cation concentration 1 *M*) and a mixed solution of Na₂CO₃ precipitant, were added dropwise at 65°Cto final pH of 7. The precipitate was then filtered, dried, and then calcined in air at 400°C for 5 h. Finally, the resultant powder was shaped into granules and to 20-40 meshes for the reaction.

2.2. Catalyst characterization

XRD patterns of catalyst samples were measured under ambient atmosphere with a RIGAKU X-ray diffract meter equipped with a Cu-K α radiation. The composition of every sample was determined by X-ray fluorescence on HITACH ZSX101-e instrument. The specific surface area of the catalysts was determined by BET method using a Micromeritics ASAP 2010. X-ray photoelectron spectra (XPS) of the calcined catalysts were recorded on an ESCALAB 250 spectrometer using Al K α radiation (1486.6 eV). The binding energies were calculated with respect to C1s

peak at 284.6 eV.

TPR carried out with a BELCAT-B instrument. The sample (50mg) was previously treated in He flow up to 350°C and kept for 2 h followed by cooling to 50°C. The 10% H₂/He mixture was passed over samples at a flow rate of 30 ml/min with a heating rate of 10°C/min up to 400°C. The effluent gas was passed over a molecular sieve trap to remove the generated water and then analyzed by GC equipped with TCD.

2.3. Procedures for catalytic reaction and product analysis

A pressurized flow type reaction apparatus with a fixed-bed reactor was used for this study. The apparatus was equipped with an electronic temperature controller for a furnace, a tubular reactor with an inner diameter of 8 mm, thermal mass flow controllers for gas flows and a back-pressure regulator. A thermocouple was set at the axial center of the tubular reactor. One gram of catalyst was placed in the reactor with inert quartz sands above and under the catalyst. All catalysts were reduced in the flow of 5% H₂ in nitrogen at 250°C for 4 h before reaction. All the products from the reactor were analyzed by on line gas chromatograph (GC). The effluent gas component including CO, CO₂ and CH₄ were analyzed by a GC equipped with the thermal conductivity detector (TCD) and a column of activated charcoal, and methanol and other by-products were analyzed by another GC equipped with the flame ionization detector (FID) and a capillary column of Porapak-Q.

3. Results

3.1. Characterizaiton

The data on BET surface area, pore volume and average diameter of the calcined catalysts are shown in Table 1. It is found that the BET specific surface area for the CZZX (X=La, Ce, Nd and Pr) samples are lower than that for CZZ and increase in series: CZZCe < CZZNd < CZZLa < CZZPr< CZZ. The chemical composition of catalysts after calcination was determined by XRF as summarized in Table 1, which generally agrees to the weight ratio of the starting precursor salts added.

Fig.1 shows the XRD patters of the samples after calcination. Some broad peaks due to a poorly crystallized CuO phase $(2\theta=35.4^{\circ}, 38.7^{\circ}, 66.0^{\circ}, 74.5^{\circ})$ are detectable for the all the samples. It is also observed that some diffraction peaks appear at 20 of $31.3^{\circ}, 47.5^{\circ}, 56.4^{\circ}, 62.0^{\circ}, 67.9^{\circ}$, which was overlapping, indicating the present of crystalline ZnO [27]. But crystallization of ZrO₂ is not obviously observed. For CZZCe and CZZLa samples, the new phases of CeO₂ and La₂O₃ (this part is enlarged in the same figure) with weak intensity are segregated. No crystalline Pr or Nd oxide phase is detected when Pr or Nd is added. This may be attributed to the fact that these elements may be exist in the amorphous state as low calcination temperature (400°C) does not favor the formation of metal oxide crystalline.

TPR measurements were carried out to highlight the reduction patter of

CZZ and CZZX (X=La, Ce, Nd and Pr) catalysts. The reduction profiles of the studied catalysts are shown in Fig. 2. All of the systems display reduction profiles characterized by a main peak between 150 and 190°C. The reduction curve is not uniform and shows a shoulder at 164°C for CZZ. It was reported that the two reduction steps are due to the consecutive reduction of Cu^{2+} first to Cu^+ and then to Cu [28]. Whereas the peak is much more symmetrical for CZZX, and the peak of CZZLa and CZZCe is sharper than the reference catalyst CZZ, suggesting relative strong interaction between La, Ce with CuO than other investigated rare-earth elements.

Changes to surface bonding with rare-earth elements were monitored by measuring the binding energies (BE) of Cu2p3 core electron, as seen in Fig. 3. The BE of Cu2p_{3/2} gave value of 933.6eV, corresponding to CuO. The presence of Cu²⁺ species can be readily identified by a strong satellite peak at ~940 eV [29]. This satellite peak implies copper species on the catalyst exist in the Cu²⁺ oxidation state. The lack of a peak at 932eV indicates negligible Cu⁰ or Cu⁺ is present on the catalyst surface [30]. The shift in BEs when comparing the different rare-earth element provides evidence of an interaction between the copper and rare-earth element. Inclusion of rare-earth elements into the system shifted the Cu2p_{3/2} peak from 933.6 eV to 933.3 eV for La, 933.6 eV to 933.7 eV for Pr, no obvious shift for Ce and Nd, respectively, demonstrating an interaction

between CuO and rare-earth element oxide.

3.2. Catalytic performance

3.2.1. General features of CO₂ hydrogenation over Cu/ZnO-based catalysts

When a mixture of CO_2/H_2 was contacted with these catalysts at the operating conditions (3MPa; 230°C; $H_2/CO_2=3/1$), the main products of the reaction were methanol, CO and water. Methane was not detected as the significant byproduct.

3.2.2. Reaction performance of CZZ and CZZX (X = La, Ce, Nd and Pr oxide) catalysts

The catalytic performance of a CZZ and CZZX (X = La, Ce, Nd and Pr) catalysts are listed in Table 2. Compared with the CZZ, the conversion of CO₂ increased by 4.6% for CZZLa and by 16.3% for CZZCe, and the CH₃OH selectivity was enhanced significantly with introduction of La and Ce, achieving 49.8% for CZZLa and 53.0% for CZZCe, which are 12.2% and 19.4% higher than that on the CZZ. CZZNd and CZZPr catalysts exhibit relative lower activity in comparison with that obtained over CZZ. The CH₃OH yield is also accordance with the order of CO₂ conversion. A maximum CH₃OH yield of 3.2 mol· h^{-1,} kg⁻¹ with the CO₂ conversion of 22.8% is obtained over the CZZCe at 230°C.

The reaction performance with regard to the conversion of CO₂ and

selectivity of methanol is obvious, indicating the influence of addition of different rare earth element. Recently, Arena et al [17] investigated the reaction of CO₂ hydrogenation on CZZ and proposed the reaction mechanism, the adsorption and dissociation of hydrogen occur over the Cu site, while the adsorption of CO₂ takes place on the ZrO₂ site. Then, the atomic hydrogen transports from the surface of Cu onto the surface of ZrO_2 via spillover and hydrogenates the adsorbed carbon containing species to methanol. On this account, it is reasonable to draw a conclusion that appropriate adsorption amount and adsorption strength of CO_2 are favorable for the hydrogenation of CO_2 . CeO_2 was reported to have an excellent oxygen storage capacity, which leads to a marked increase in oxygen vacancies of CZZ, resulting in high activity [31-33] among all investigated dopants. The XPS results also support this point, that is, the addition of CeO_2 changed the electron environment of Cu, promoting the synergistic effect between CuO and the surface oxygen vacancies of ceria, which was related to the activity and methanol selectivity [34].

Similar to CZZCe, CZZLa also shows relative high activity compared with CZZ, which could be related to its high ability of hydrogen adsorption. The relatively low catalytic activity of CZZPr and CZZNd was possibly attributed to the relative low ability of hydrogen adsorption.

3.2.3. The effect of reaction temperature

Methanol synthesis over the CZZ and CZZX (X = La, Ce, Nd and Pr) catalysts was studied in the temperature range from 210 to 250°C, and the results are shown in Fig.4. The conversion of CO₂ increases with the increasing temperature and reach the maximum value when the temperature arrives 230°C. However, the methanol selectivity decreased with increasing temperature. Therefore, it can be deduced that the control factor for methanol synthesis shifts from kinetics to thermodynamics. From the results, it can be seen that the maximum conversion is obtained at 230°C under tested conditions.

3.2.4. The effect of space velocity

In order to clarify whether methanol is produced indirectly via the intermediate formation of carbon monoxide and then hydrogenation or directly by the carbon dioxide hydrogenation, the influence of the space velocity on the methanol selectivity was investigated (as shown in Fig. 5). It is well known that the reverse water gas shift reaction (RWGS) and methanol synthesis reactions coexist in carbon dioxide hydrogenation presented as

$$CO_2(g) + 3H_2 \leftrightarrow CH_3OH(g) + H_2O(g)$$
 (1)

 $CO(g) + 2H_2 \leftrightarrow CH_3OH(g)$ (2)

 $CO_2(g) + H_2 \leftrightarrow CO(g) + H_2O(g)$ (3)

It is clearly note that carbon monoxide was the main product at short contact time for CZZX (X = La, Ce, Nd and Pr) catalysts and then the

yield to methanol increases quickly and to carbon monoxide decrease slowly with the increase of space velocity. At the same time, it is also interesting to note that slight amount of methanol can be formed even at short contact time. The results indicate the activation of carbon dioxide to methanol by CZZA could pass through two parallel routes: one is the direct process from CO_2 and another is the one which pass through CO.

4. Conclusions

It is concluded that, the doped Ce in CZZ catalyst was the most active giving CO₂ conversion at 22.8% and methanol selectivity at 53.0%. The methanol formation from CO₂ over CZZr and CZZX (X = La, Ce, Nd and Pr) were assumed to pass through two parallel routes: one is the direct process from CO₂ and another is the one which pass through CO. Compared with CZZ, the presence of La and Ce was favorable for improving the overall activity, the doping of Nd and Pr appeared to decrease the activity.

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Table 1

Physicochemical properties of the studied catalysts.

Sample	BET	Pore Volume	Pore size	Chemical composition			
	(m^2/g)	(cm^3/g)	(nm)	CuO	ZnO	ZrO_2	Х
CZZ	83.3	0.46	16.4	56.2	26.7	17.1	
CZZLa	72.5	0.47	20.0	55.5	26.5	13.0	5.0
CZZCe	61.2	0.50	20.1	54.7	25.7	14.0	5.6
CZZNd	67.4	0.54	21.6	54.8	26.0	14.2	5.0
CZZ Pr	74.1	0.50	20.2	55.0	26.1	13.6	5.3

Table 2

Reaction performance of the catalysts.							
Cat	CO_2	Methanol Productivity	Methanol Selectivity (%)				
	Conv.(%)	$(\text{mol } \text{h}^{-1} \text{kg}^{-1})$					
CZZ	19.6	2.3	44.4				
CZZLa	20.5	2.7	49.8				
CZZCe	22.8	3.2	53.0				
CZZNd	19.0	2.0	40.5				
CZZPr	19.3	2.2	42.0				

K

Reaction conditions: 3 MPa; 230 °C; H₂/CO₂=3/1, W/F=10 g·cat·h/mol.

K K K



Fig. 1. XRD patters of CZZ and CZZX (X = La, Ce, Nd and Pr)



Fig. 2. TPR profiles of CZZ and CZZX (X = La, Ce, Nd and Pr) catalysts.

K K K



Fig. 3. XPS spectra of CZZ and CZZX (X = La, Ce, Nd and Pr) catalysts.



Fig.4. Effect of reaction temperature.

Test conditions: 3.0 MPa, 230 $^{\rm o}C$, H_2/CO2=3.





Test conditions: 3.0 MPa, 230 $^{\circ}$ C, H₂/CO₂=5.



Highlights

- CZZCe was proved to be effective catalyst for CO₂ hydrogenation.
- La and Ce was favorable for improving the overall activity.
- Methanol formation over CZZ and CZZX were assumed to pass through parallel route.

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