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Carbon dioxide hydrogenation to light olefins over ZnO-Y₂O₃ and SAPO-34 bifunctional catalysts

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Abstract

Conversion of CO_2 using renewable hydrogen to produce valuable chemicals has recently become highly attractive. Light olefins are important basic monomers for the production of various commodities. This work developed a bifunctional catalyst composed of ZnO-Y₂O₃ oxide and SAPO-34 zeolite, which catalyzes the selective hydrogenation of CO₂ to light olefins with a selectivity in hydrocarbons reaching 83.9% at a conversion of 27.6% at 390 °C. The obtained results demonstrated that CO₂ conversion and product distribution are strongly dependent on the oxide composition and structure. This new bimetallic oxide catalyst appears promising for further development of practical CO₂ conversion to other valuable chemicals.

Keywords:

carbon dioxide, ZnO-Y2O3, bifunctional catalysts, light olefins.

1. Introduction

Alternative energy sources preferably renewable and environment protection are two major issues for a future sustainable society. Excessive carbon dioxide in the atmosphere is considered a major cause of ocean acidification and climate change [1].

It is widely agreed to control carbon dioxide emissions and more scientific discoveries have been inspired for effective valorization of CO_2 , which is an alternative way for its emissions reduction. In the meanwhile, utilization of CO_2 as a carbon source is also proposed, e.g., via electro-catalysis [2,3], photo-catalysis [4,5] and thermal catalysis [6,7]. Although there are still debates on the energy and carbon efficiency, as well as economic viability of heterogeneous catalytic hydrogenation of CO_2 , hydrogenation using renewable hydrogen might be a solution for the conversion of large-scale industrial CO_2 .

Light olefins, including ethylene, propylene and butylene, are important feedstocks for the production of a variety of chemicals, such as polymers and drugs. CO_2 can be hydrogenated to light olefins via a modified Fischer-Tropsch synthesis [8,9]. However, the distribution of hydrocarbon products over conventional Fischer-Tropsch synthesis catalysts is limited by the surface polymerization mechanism and it follows the Anderson-Schulz-Flory (ASF) distribution model. The selectivity of C_2 - C_4 hydrocarbons (including olefins and paraffins) is typically less than 58% [10-12]. For example, the sodium-containing Fe₃O₄ catalysts were used for carbon dioxide hydrogenation, which showed a selectivity of 46.6% for C_2 - C_4 light olefins among hydrocarbons at a CO_2 conversion of 40.5% [13].

We recently proposed a catalyst design concept of a bifunctional oxide-zeolite (OX-ZEO) system, which separates CO activation and C-C coupling onto two different types of active sites [12]. It was demonstrated to be an effective strategy to surpass the ASF distribution limit in CO hydrogenation to light olefins, which yields a selectivity of C_2 - C_4 hydrocarbons up to 94% [12]. By changing the zeolite to mordenite or HZSM, this OX-ZEO catalytic system allows syngas conversion to ethylene with a selectivity up to 73% and to aromatics 73.9%, respectively [14,15].

It was recently shown that this concept is also applicable for CO_2 hydrogenation. For example, by combining ZnO-ZrO₂ [16], ZnGa₂O₄ [17] and In₂O₃-ZrO₂ [18] with SAPO-34 zeolite as composite catalysts, CO₂ can be hydrogenated to light olefins with a selectivity in hydrocarbons reaching over 80%. Although the direct CO₂ conversion through bifunctional catalysts has gained wide attention, the catalytic

performance still needs to be improved and a better understanding of the reaction mechanism is also needed for further optimization of catalysts.

Herein, we report that $ZnO-Y_2O_3$ in combination with SAPO-34 as a composite catalyst gives a high selectivity towards light olefins (83.9%) in hydrocarbons with only 1.8% methane at a CO_2 conversion of 27.6%. The roles of ZnO and Y_2O_3 in the mixed oxide were studied, and results showed that this mixed oxide composition affects CO_2 conversion and product selectivity significantly.

2. Experimental

2.1. Catalyst preparation

The oxide catalysts were prepared by the co-precipitation method. A 6.7 wt% ZnO- Y_2O_3 catalyst was taken as an example to describe the synthesis procedures: 1.79 g Zn(NO₃)₂ · 6H₂O and 22.99 g Y(NO₃)₃ · 6H₂O were dissolved in 100 mL deionized water in a beaker A. 15.6 g aqueous ammonia (25 wt% solution) was added to a beaker B containing 100 mL water. The solution in beaker A and B were simultaneously added to a three-necked flask with 100 mL deionized water (at a flow rate of 5 mL min⁻¹) under vigorous stirring at 70 °C to form a precipitate. After aging for 2 h at 70 °C, the suspension was cooled to room temperature, filtered, and then washed five times with deionized water. The filter cake was dried at 110 °C for 12 h and then calcined at 500 °C in static air for 8 h. Other samples with different compositions x wt% ZnO- Y_2O_3 were synthesized by the same method, and x represents the ZnO content.

SAPO-34 was synthesized hydrothermally using trithylamine (TEA) as the template. The molar composition was $1SiO_2 : 11Al_2O_3 : 18H_3PO_4 : 33TEA : 667H_2O$. The resulting gel mass was stirred for 2 h at room temperature, then transferred into 200 mL autoclave and heated for 24 h at 180 °C. The solid product was finally obtained through centrifugation, washed several times with deionized water till the pH of the supernate was 7.0-7.5, followed by drying overnight at 120 °C. Finally, the template was removed by calcination at 550 °C for 3 h.

2.2. Catalytic activity studies

The carbon dioxide hydrogenation reaction was performed in a tubular quartz fixed-bed reactor. Typically, 400 mg composite catalyst (20-40 mesh) with x wt% $ZnO-Y_2O_3/SAPO-34 = 1/1$ (mass ratio) was used, unless otherwise stated. The catalyst was treated at 400 °C with H₂ (900 mL h^{-1} g_{cat}⁻¹) for 2 h at 1 bar pressure prior to reaction, where the temperature was increased at a ramp of 1.5 °C min⁻¹. The temperature was then decreased to 390 °C and the feed gas flow was switched to a pre-mixed stream of CO₂, H₂ and Ar (19 vol% CO₂ + 76 vol% H₂ + 5 vol% Ar). Reaction was carried out using a H₂/CO₂ molar ratio of 4, P=4.0 MPa, T=390 °C and a GHSV of 1800 mL h^{-1} g_{cat}⁻¹. The composition of the effluent stream was analyzed by an online GC (Agilent 7890B), which was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Hayesep Q and 5A molecular sieves packed columns were connected to TCD, while HP-FFAP and HP-AL/S capillary columns were connected to FID. Oxygen-containing compounds and hydrocarbons up to C_{5+} were analyzed by the FID, while CO_2 , CO, CH_4 , C_2H_4 and C_2H_6 were analyzed by the TCD. CH_4 and C_2H_4 were taken as a reference bridge between FID and TCD. CO₂ conversion and product selectivities were calculated on a carbon atom basis according to the following Eqs. (1)-(3):

$$CO_2 Conversion = \frac{F(CO2 \text{ inlet}) - F(CO2 \text{ outlet})}{F(CO2 \text{ inlet})} \times 100\%,$$
(1)

where, $F(CO_{2 \text{ inlet}})$ and $F(CO_{2 \text{ outlet}})$ represent the molar flow rates of CO_{2} at the inlet and outlet, respectively. The CO selectivity was calculated according to:

$$CO Selectivity = \frac{F(CO \text{ outlet})}{F(CO2 \text{ inlet}) - F(CO2 \text{ outlet})} \times 100\%,$$
(2)

where $F(CO_{outlet})$ denotes the molar flow rate of CO at the outlet of reactor.

The selectivity of the individual hydrocarbon, C_nH_m among hydrocarbons was obtained according to:

$$C_{n}H_{m} \text{ Selectivity } = \frac{n F(CnHm \text{ outlet})}{F(CO2 \text{ inlet}) - F(CO2 \text{ outlet}) - F(CO \text{ outlet})}$$
(3)

The carbon balance fell in a range of 98%-102%.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) was carried out on an Empyrean-100 X-ray diffractometer with a Cu K α (λ = 1.541 Å), operated at 40 mA and 40 kV. XRD patterns were recorded in the range of 2θ = 5-80°.

Brunauer-Emmett-Teller (BET) surface area and the textural characteristics of x wt% ZnO- Y_2O_3 catalysts were characterized by nitrogen adsorption/desorption isotherms at 77 K using a Quantachrome autosorb iQ2 gas adsorption analyzer. The oxide samples were degassed at 300 °C for 2 h before measurements.

The temperature-programmed desorption of CO₂ and CO (CO₂-TPD and CO-TPD) of x% ZnO-Y₂O₃ catalysts were conducted on an AutoChem 2910 adsorption/desorption system. In a typical CO₂-TPD run, a 100-mg sample was treated *in situ* in a H₂ gas stream (30 mL min⁻¹) at 400 °C for 2 h, flushed with He gas (30 mL min⁻¹) at 400 °C for 30 min, and then cooled to 50 °C. The inlet gas flow was then switched to CO₂ to allow adsorption for 60 min. Afterwards, the sample was flushed with He until a stable baseline was obtained. Then the sample was heated from 50 to 600 °C at the heating ramp of 10 °C min⁻¹, while the composition of effluent was monitored by a TCD and an OmniStar 300 mass spectrometer. The adsorption amounts of CO₂ and CO were estimated based on the peak area of CO₂ and CO calibration pulses.

Hydrogen temperature-programmed reduction (H₂-TPR) was carried out in a tubular quartz reactor. A 100- mg of each sample was placed in the reactor and treated with pure He at 120 °C for 1 h, then cooled to 50 °C in He flow. The sample was then heated in 1 vol% H₂/Ar at the ramp of 10 °C min⁻¹ from 50 to 800 °C, while the composition of effluent was monitored by the *on-line* mass spectrometer.

High-resolution transmission electron microscopy studies (HRTEM) were conducted on a JEM 2100 microscope. Scanning electron microscopy studies (SEM) were conducted on a ZEISS Orion nanoFab.

3. Results and discussion

Table 1 lists the catalytic performance of various ZnO-Y₂O₃ combined with SAPO-34 zeolite bifunctional catalysts towards CO₂ hydrogenation, where the mass ratio of ZnO/(ZnO+Y₂O₃) was varied. Y₂O₃+SAPO-34 catalyst gives a CO₂ conversion of 6.6%, producing only CO and no light olefins. By the addition of ZnO, light olefins $C_2^{=}$ -C₄⁼ products start to appear. In the meanwhile, the catalytic activity is gradually improved with the increasing amount of ZnO, and CO₂ conversion reaches a maximum value (ca. 27.6%) when the oxide contains 6.7 wt% ZnO. However, by further increasing the ZnO content results in a declining CO₂ conversion. Since the same SAPO-34 zeolite has been used, the different performance between these bifunctional catalysts should be attributed to the ZnO-Y₂O₃ mixed oxides phase. In order to understand the role of these oxides in the catalytic system, a series of characterizations were applied.

X-ray diffraction (XRD) patterns (Fig. 1) show crystal phases of the ZnO-Y₂O₃ oxides. As shown in Fig. 1, diffraction peaks at $2\theta = 31.7$, 34.4 and 36.3° are assigned to the (100), (002) and (101) plane facets of the hexagonal ZnO crystal (JCPDS 36-1451), respectively. In the single component Y₂O₃ sample, the diffraction peaks at $2\theta = 20.5$ and 29.2° are assigned to the (211) and (222) plane facets of Y₂O₃ crystal (JCPDS 41-1105), respectively. Only pure ZnO and Y₂O₃ diffraction peaks are detected for the single components of ZnO and Y₂O₃ samples. For the bi-component ZnO-Y₂O₃ samples, there is no new crystal phase observed. However, the relative peak intensity for each oxide varies with their contents as expected. In addition, the ZnO crystal phase is not detected when ZnO content is less than 6.7 wt%, indicating that ZnO is dispersed well (< 4.0 nm primary crystal particles). However, the crystal plane (101) of hexagonal ZnO crystal is still discernible in the transmission electron microscopy (TEM) images recorded for the 6.7 wt% ZnO-Y₂O₃, as shown in Fig. S1 (see ESI). This also indicates that ZnO still retains the hexagonal crystal phase in this mixed oxide system.

Scanning electronic microscopy (SEM) images of ZnO-Y₂O₃ oxides shown in Fig. S2 (see ESI) exhibit different morphologies. The morphology of bi-component oxides appears fluffy and more finely dispersed. BET measurement indicates that

these samples exhibit higher specific surface areas (SSA) than either of the parent single metal oxide (see Table S1, ESI). It indicates that the addition of ZnO increases the pore volume and surface area, which then it is reasonably expected to offer a larger number of surface catalytic sites, thus enhancing catalytic activity.

H₂-TPR was used to elucidate the reducibility of the solid samples. As displayed in Fig. 2, there is a weak and broad reduction peak for ZnO centered at ~ 405 °C. In comparison, Y_2O_3 is much more difficult to reduce than ZnO, as its reduction starts only above 400 °C showing a peak maximum at 497 °C. Therefore, it appears that under reaction conditions, Y_2O_3 is not expected to be found in a partially reduced form. With the addition of ZnO into Y_2O_3 , the reduction gradually becomes more facile.

The CO₂-TPD profiles shown in Fig. 3a exhibit three CO₂ desorption peaks for Y_2O_3 , 0.18 wt% ZnO- Y_2O_3 and 6.7 wt %ZnO- Y_2O_3 solids. However, there is almost no CO₂ adsorption over ZnO. The total amount of CO₂ adsorption estimated on ZnO is two orders of magnitude lower than that estimated over the other three oxides (see Table S2, ESI). Surprisingly, the total amount of CO₂ adsorption gradually increases with increasing ZnO content, implying that ZnO can promote the adsorption of CO₂ over Y_2O_3 . Therefore, CO₂ likely adsorbs on Y_2O_3 , and the presence of ZnO likely promotes its adsorption on Y_2O_3 . The three CO₂-TPD peaks observed over Y_2O_3 , 0.18 wt% ZnO- Y_2O_3 and 6.7 wt% ZnO- Y_2O_3 fall in a similar temperature range. The peak at ~ 94 °C is assigned to weakly adsorbed CO₂, while the other two peaks at ~ 203 °C and 390 °C belong to strongly adsorbed CO₂.

Although single component Y_2O_3 metal oxide exhibits the highest capacity of CO_2 adsorption, its CO_2 hydrogenation activity appears to be the lowest (CO_2 conversion only 6.6%) among these mixed-metal oxides when combined with SAPO-34 (see Table 1). Furthermore, CO is the only product over Y_2O_3 combined with SAPO-34. In contrast, even though ZnO exhibits a very poor CO_2 adsorption capacity it gives a 16% CO_2 conversion when combined with SAPO-34. This might be related with the H₂ activation ability of the metal oxide phase, as this is considered as a critical step for hydrogenation.

In fact, ZnO is known to be active towards activation of molecular H₂ [19]. Liu and co-workers [20] observed the formation of hydroxyl (OH) species on the ZnO ($10\overline{1}0$) surface at room temperature when the solid was exposed to 0.3 mbar H₂. This result indicated the dissociative adsorption of H₂. Griffin and co-workers [21] reported the dissociation of H₂ on commercial ZnO, as evidenced by the bond-stretching frequencies recorded at 1710 and 3490 cm⁻¹ in their IR studies. It was shown that H₂ adsorbed rapidly and reversibly to form active hydrogen species at room temperature [22, 23], which could be reactive for the hydrogenation of H₂ for Y₂O₃ to the best of our knowledge.

The above results and discussion show that Y_2O_3 is active for CO_2 adsorption, while H₂ adsorption and activation are likely taking place at the ZnO surface. This may explain the activity behaviour of ZnO-Y₂O₃ mixed oxides for the CO₂ hydrogenation. However, there is no linear relationship between CO₂ conversion and the content (wt%) of ZnO. Furthermore, the co-precipitated ZnO-Y₂O₃ solid exhibits a much higher activity and light olefin selectivity than its physical mixture counterpart (ZnO+Y₂O₃) (see Table 2). For example, the co-precipitated 6.7 wt% ZnO-Y₂O₃ catalyst gives a 27.6% CO₂ conversion, while the physical mixture counterpart gives only a 17.4% CO₂ conversion. The co-precipitated oxide is also more active than the impregnated (6.7 wt% ZnO/Y₂O₃) one with same chemical composition. It is suggested that this activity behaviour is likely attributed to the interface developed between ZnO and Y₂O₃ during the co-precipitation process of synthesis followed by the calcination step, which seems to play an important role for the simultaneous CO₂ and H₂ activation, hence the hydrogenation reaction. As a result, the 6.7 wt% ZnO-Y₂O₃+SAPO-34 catalyst exhibits the best CO₂ hydrogenation activity.

CO-TPD studies were also conducted in order to gain some good understanding about the high selectivity of CO in the present CO_2 hydrogenation reaction. It can be seen from Fig. 3b that ZnO gives almost no CO desorption up to 500 °C. This is surprising because it has been demonstrated in our previous study that ZnO is active in CO hydrogenation for light olefin synthesis when combined with SAPO-34 [25].

The amount of CO desorption increases stepwise with reducing content (wt%) of ZnO. The Y₂O₃, 0.18 wt% ZnO-Y₂O₃ and 6.7 wt% ZnO-Y₂O₃ metal oxides all exhibit two CO desorption peaks. The first one appears at ~ 85 °C is attributed to some weakly chemisorbed adsorbed CO, and the second one in the 260-290 °C range corresponds to a more strongly chemisorbed CO. Note that the total amount of CO₂ desorbed is dozens of times higher than that of CO over the mixed oxides containing Y₂O₃ (see Table S2, ESI), and that the CO desorption temperature overlaps with that of CO₂ desorption. Therefore, there is likely competitive adsorption between CO₂ and CO over these metal oxides, thus further adsorption and conversion of CO might be suppressed. This might be one reason for a high selectivity of CO in the CO₂ hydrogenation reaction in this work.

4. Conclusions

In summary, we reported that a bifunctional ZnO- Y_2O_3 +SAPO-34 catalyst largely promotes the CO₂ hydrogenation into C₂-C₄ olefins with an outstanding selectivity. The activity and selectivity varied with composition and structure of the metal oxides, which is likely attributed to their different functions, i.e. CO₂ adsorption and activation over Y_2O_3 and H_2 over ZnO. Hence, the co-precipitated composite 6.7 wt% ZnO- Y_2O_3 catalyst gave the highest CO₂ conversion and light olefin selectivity when combined with SAPO-34, ca. selectivity to light olefins in hydrocarbons 83.6% at a single pass CO₂ conversion of 27.6%.

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Oxide sample	CO ₂ Conv.	Hydrocarbon distribution [%]				
		CU	0=0=		C	- CO
	[%]	CH_4	C_2 - C_4	C_2 - C_4	C_{5+}	Sel. [%]
Y_2O_3	6.6	0	0	0	0	100
0.18 wt% ZnO- Y_2O_3	17.7	5.1	81.4	8.6	4.9	97.4
6.7 wt% ZnO-Y ₂ O ₃	27.6	1.8	83.9	12.9	1.4	85.0
19.4 wt% ZnO-Y ₂ O ₃	17.4	1.4	82.8	13.5	2.3	89.3
ZnO	16.0	1.4	88.6	8.4	1.6	75.8

Table 1. Hydrocarbons distribution and CO_2 conversion over different ZnO-Y₂O₃ samples in combination with SAPO-34 as bifunctional catalysts for the hydrogenation of CO_2^{a} .

^a Reaction conditions: $CO_2/H_2 = 1/4$, 390 °C, 4.0 MPa, GHSV = 1800 mL g⁻¹ h⁻¹.

1. ./4, 390 °C

		Hydrocarbons distribution [%]				-
Oxide sample	CO ₂ -	CH ₄	$C_2^{=}-C_4^{=}$	$C_2^{-}-C_4^{-}$	C ₅₊	CO Sel. [%]
6.7 wt% ZnO- Y_2O_3 -CP ^b	27.6	1.8	83.9	12.9	1.4	85.0
$6.7 \text{ wt\% } \text{ZnO/Y}_2\text{O}_3\text{-I}^c$	19.3	2.9	78.1	16.9	2.1	84.3
6.7 wt% ZnO+93.3 wt% Y_2O_3 -M ^d	17.4	4.9	64.6	26.7	3.8	91.4

Table. 2. Hydrocarbons distribution and CO_2 conversion over different preparation methods of ZnO-Y₂O₃ oxides combined with SAPO-34 as bifunctional catalysts of CO₂ hydrogenation^a.

^a Reaction conditions: $CO_2/H_2 = 1/4$, 390 °C, 4.0 MPa, GHSV = 1800 mL g⁻¹ h⁻¹.

 b 6.7 wt% ZnO-Y₂O₃-CP was prepared by co-precipitation.

 $^{\circ}$ 6.7 wt% ZnO/Y2O3-I was prepared by impregnation of ZnO to Y2O3.

 d 6.7 wt% ZnO+93.3% wt% $Y_2O_3\text{-}M$ was prepared by grinding the ZnO and Y_2O_3 mixture with a mass ratio of 6.7/93.3.

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Figure captions

- Fig. 1. XRD patterns of ZnO-Y₂O₃ oxides.
- Fig. 2. H₂-TPR profiles of ZnO-Y₂O₃ oxides.
- Fig. 3. TPD profiles of ZnO-Y₂O₃ oxides (a) CO₂-TPD; (b) CO-TPD.

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Graphical abstract:

Highlights

- CO₂ hydrogenation to light olefins over bifunctional catalyst (ZnO-Y₂O₃ + SAPO-34).
- A high CO₂ conversion (27.6%) was achieved through interaction between ZnO and Y_2O_3 .
- A selectivity for $C_2^{=}-C_4^{=}$ was up to 83.9% in hydrocarbons with 1.8% CH₄.

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