Effect of ZnO Facet on Ethanol Steam Reforming over Co/ZnO

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Abstract

The effects of ZnO facets on ethanol steam reforming (ESR) were investigated over Co/ZnO catalysts synthesized using ZnO with different fractions of (10-10) non-polar facet. Co supported on ZnO with a higher fraction of (10-10) non-polar facet shows higher C-C cleavage activity and higher selectivity to CO₂ (lower selectivity to CO) compared with Co supported on ZnO with less (10-10) non-polar facet exposed. The improved ethanol steam reforming performances are attributed to the high fraction of metallic Co stabilized by the ZnO (10-10) non-polar facet, which enhanced C-C cleavage and water-gas-shift (WGS) activities.

Key words: ethanol steam reforming; cobalt; ZnO; facet; water gas shift

1. Introduction

Over the last few decades, hydrogen production from ethanol steam reforming (ESR) has been widely studied due to its high hydrogen yield, increased availability and reduced cost of ethanol driven by the technical innovation of ethanol production from diversified biomass feedstock [1-4]. Typically, ESR involves steam reforming, water gas shift (WGS) and methanation reactions [4, 5]. WGS converts CO and water to CO₂ and H₂ which will reduce CO selectivity and increase H₂ yield in ESR which is highly desired.

Co based catalysts have been widely studied in ethanol steam reforming due to cobalt's high C-C cleavage activity and low methane selectivity [4, 6-9]. Numerous studies have revealed that both the nature of support material and the oxidation state of cobalt have significant effects on reaction pathway and catalyst deactivation [1, 2, 9-14]. It has been found that Co⁰ has a higher activity for C-C cleavage compared to Co²⁺ and has shown a higher selectivity to CO₂; in contrast, Co²⁺ has shown a higher activity for dehydrogenation of ethanol and a higher selectivity to CH₄ due to the methanation of CO and CO₂[15]. A high Co⁰/Co²⁺ ratio is crucial to maintain both C-C cleavage and WGS activity [15-18]. On the other hand, while support with high water dissociation and oxygen mobility could be highly efficient to remove CH_x*/C* species oxidation, it could also promote the oxidation of cobalt [9]. Therefore, it is desirable to control the surface chemistry of support for favorable water activation while minimizing the oxidation of metallic Co to achieve high activity and selectivity in ESR.

There have been numerous studies on ZnO polar and non-polar facets in ultra-high vacuum (UHV) system using model catalysts [19, 20]. For example, the growth and stability of cobalt on different ZnO facets, including ZnO (0001/000-1) polar facets and

ZnO (10-10) nonpolar facet, has been studied in UHV using ZnO single crystal [21-23]. It was found that lattice oxygen on polar ZnO (0001) and (000-1) facets became active at temperature above 700 K, leading to the oxidation of metallic cobalt to form CoO [23]. In contrast, metallic cobalt was found to be thermally stable up to 750 K on ZnO (10-10)[21], indicating different surface chemistry between ZnO polar and non-polar facet. Utilizing dominant facet ZnO powder, the effects of ZnO facet were studied in the Pd/ZnO system for methanol steam reforming under realistic reaction conditions [24]. Formation of stable β -PdZn was found more facile on polar ZnO (0001) facet than on nonpolar (10-10) facet, which led to lower CO selectivity in MSR. To our best knowledge, there are still no studies regarding ZnO facet effects on ESR over Co/ZnO catalyst. In this work we study and demonstrate the importance of ZnO facet on the ethanol steam reforming reaction over the Co/ZnO catalysts.

2. Experimental

2.1. Supports and catalysts preparation

The details for the synthesis of the supports and catalysts are shown supporting material. Briefly, two types of ZnO supports (ZnO-N and ZnO-S) with different fractions of (10-10) facet were prepared using the method reported by Wang et al. [25] with some modifications and 2 wt% Co/ZnO catalysts were prepared by incipient wetness impregnation. Cobalt acetate was used as cobalt precursor to avoid the potential damage of the facet on ZnO [26]. The catalysts were denoted as 2Co/ZnO-N and 2Co/ZnO-S, respectively.

2.2. Characterization

Nitrogen sorption measurements were conducted on a Micromeritics TriStar II 3020 physisorption analyzer at -196 °C using UHP N₂. The specific surface areas of the supports and catalysts were calculated based on the Brunauer-Emmett-Teller (BET) model. Catalysts were degassed at 300 °C for 1 h under vacuum before measurements.

Temperature-programmed reduction experiments by hydrogen (H₂-TPR) were performed on a Micromeritics AutoChem II 2920. Prior to the TPR experiment, samples were pretreated at 350 °C (5 °C/min) in helium flow (50 ml/min) for 1 h and then cooled down to 50 °C. During the H₂-TPR, sample is heated up to 600 °C (10 °C/min) in 10 % H₂/Ar flow (50 ml/min). The gas flow passed through a cold trap (-10 °C) was monitored with Thermal Conductivity Detector (TCD).

TEM images of the supports and catalysts were taken on a FEI Technai G2 20 Twin equipped with a LaB6 electron source. Samples were dispersed in ethanol via ultrasonic bath, and loaded onto the copper grid with ultrathin lacy carbon film. The diameter and length of ZnO supports were measured using ImageJ software[27].

XRD spectra were collected using Rigaku Miniflex II in the 2 θ angle between 20° and 80°, at a step of 0.02° and dwell time of 2.0 s. Refined XRD spectra were collected from 40° to 65° at a step size of 0.02° with a dwell time of 8.0 s. Before XRD measurements, catalysts were reduced in 50 ml/min H₂ flow at 400 °C for 2 hours and passivated in 50 ml/min 0.1% O₂/N₂ flow for 4 hours at room temperature. Cobalt particle size is calculated using Scherer equation.

Diffuse reflectance infrared fouries transform spectra (DRIFTS) were recorded on a Bruker Tenser 27 spectrometer equipped with DRIFT cell. Fine ZnO powder was filled into the sample holder which is covered by a dome with ZnSe coated window. ZnO

samples were first pretreated in flowing UHP helium (25 ml/min) up to 400 °C for 10 min and then in 10% O₂/He (25 ml/min) at 350 °C for 25 min to remove surface impurities and physisorbed water species on ZnO. After cooling to 50°C in helium, spectra were collected continuously with a spectral resolution of 4 cm⁻¹ and a time resolution of 60 s. KBr was used as the background.

2.3. Catalytic test

Ethanol steam reforming reactions were conducted under atmospheric pressure in a fixed bed quartz tubular reactor (I.D. 6.5 mm). 200 mg of 2 wt% Co/ZnO samples diluted with 9 times of inactive SiC (all 150-250 µm) were loaded and held between two quartz wool layers. A thermal couple was placed at the catalyst bed outside of the tube to monitor the reaction temperature. Before reaction, the catalyst was first reduced under 10 % H₂/Ar (50 ml/min) flow for 2 h at 400 °C. After reduction, N₂ flow (50 ml/min) was used to purge the reactor for 30 min. Ethanol (EtOH) solution (steam to carbon molar ratio of 5) was pumped into a vaporizer at 175 °C with a rate of 1 ml/h. The vaporized feed was carried into the reactor by N₂ flow (20 ml/min). The EtOH partial pressure (P_{EtOH}) was fixed at 4.2 kPa. Effluent gases passed through a cold trap and a Drierite column to remove condensable products and moisture. The dry gases were then sent to an Agilent CP490 microGC equipped with 4 parallel columns and TCDs for analysis. A 5 Å molecular sieve was used to separate and analyze H₂, N₂, CH₄ and CO. A PPQ column was used to separate and analyze CO₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈. An Al₂O₃ column was used to separate and analyze C₃H₆, C₃H₈ and C₄H₈, any additional hydrocarbons would appear on this column as well. Reaction was carried out at atmospheric pressure.

Dry gas conversion was calculated with equation 1. "n" is the number of carbon atoms in gas products C_n .

$$\text{Dry gas conversion (\%)} = \frac{\sum n \cdot \text{molar flow rate of } C_n \text{ products}}{2 \cdot \text{molar feed rate of EtOH}} \times 100 \quad (1)$$

Equation 2 was used to calculate selectivity to C_1 products.

$$C_1 \text{ selectivity (\%)} = \frac{\text{molar flow rate of } C_1 \text{ product}}{\sum \text{molar flow rate of } C_1 \text{ products}} \times 100 \quad (2)$$

Equation 3 was used to calculate C-C cleavage of ethanol.

$$C - C \text{ cleavage (\%)} = \frac{\sum \text{molar flow rate of } C_1 \text{ products}}{2 \cdot \text{molar feed rate of EtOH}} \times 100 \quad (3)$$

3. Results and Discussion

3.1 Characterization of support and catalysts

The textural properties of ZnO supports and Co/ZnO catalysts are shown in Table 1. ZnO-N has a surface area of 37 m²/g, and the surface area of ZnO-S is 7 m²/g. The decreased surface area suggests that the high calcinations temperature (i.e., 550 °C) changed the morphology of ZnO-N, which can be further confirmed by the TEM observation discussed below. After adding Co to ZnO-N support, the surface area of 2Co/ZnO-N decreased slightly from 37 to 34m²/g. The decreased surface area is likely due to the minor change of the morphology of the ZnO-N support which will be further discussed in the following part. The surface area of 2Co/ZnO-S, in contrast, increased from 7 to 12 m²/g.

TEM images of ZnO-N, ZnO-S, 2Co/ZnO-N and 2Co/ZnO-S are shown in Fig. 1.

Images of samples were used to estimate the fraction of ZnO (10-10) facet. TEM of ZnO-N shows a long needle-shape morphology with a diameter around 10~20 nm (Fig. 1a). The estimated (10-10) fraction is ~93% (Table 1). Consistent with the decreased

surface area, TEM (Fig. S2) and SEM (Fig. S3) of ZnO-S reveal that its morphology changed significantly from long needle to irregular shaped particles with diameter of 50~100 nm , which makes the determination of the fraction of the (10-10) facet difficult. It was found that surface hydroxyl groups on the ZnO (10-10) and ZnO (000-1) facet showed different band frequencies [28]. Here, DRIFTS was further conducted to differentiate the different facet on the ZnO-N and ZnO-S supports, as shown in Fig. 2. While the bands at 3680, 3659 (3639) cm^{-1} are related to the hydroxyl group on ZnO (10-10) facet, the one at 3618 cm^{-1} is attributed to the hydroxyl groups on ZnO (000-1) facet [28]. The peaks at 3558 and 3446 cm^{-1} are related to the interaction of water with oxygen defects forms $\text{O}-\text{H}\cdots\text{O}$ species. It is clear that the intensity of bands at 3680 and 3659 cm^{-1} are much stronger on ZnO-N than on ZnO-S. It suggests a higher fraction of (10-10) facet on ZnO-N than on ZnO-S, consistent with the TEM observations. It is interesting to note that the band at 3558 cm^{-1} on ZnO-N is also much stronger than that on ZnO-S, indicating that $\text{O}-\text{H}\cdots\text{O}$ species might also be related to the (10-10) facet. Upon addition of cobalt, it was found that the length of the needle-like ZnO (ZnO-N) became shorter and the diameter also increases slightly (Fig. 1c). However, the needle-like shape is still conserved with ~89% (10-10). On the other hand, the morphology of ZnO-S showed little change (Fig. 1d). From TEM, the average cobalt particle sizes of 2Co/ZnO-N and 2Co/ZnO-S catalysts were very close which were 6.7 nm and 7.6 nm, respectively.

Fig. 3 shows the XRD patterns of Co/ZnO catalysts. A broad and weak diffraction peak at 2θ of 44° , characteristic of metallic Co peaks, were identified. The average cobalt particle sizes were calculated using Scherrer equation (Table 1). Both 2Co/ZnO-N and

2Co/ZnO-S catalyst have a similar average cobalt particle size of 4.4 nm and 5.5 nm, which are smaller compared with TEM observation due to possible peak broadening caused by multiple factors such as instrumental effects, and micro-stresses[29].

However, both techniques suggest the particle size on the two supports was similar.

H₂-TPR was further studied to compare the reducibility properties of 2Co/ZnO-N and 2Co/ZnO-S as shown in Fig.4. For 2Co/ZnO-S catalyst (Fig. 4 a), two major hydrogen consumption peaks were detected at 240 °C and 410 °C, which can be ascribed to cobalt reduction from Co³⁺ to Co²⁺ and Co²⁺ to metallic Co, respectively [7]. Moreover, separate H₂ TPR experiments over both ZnO (Fig.S4) and 5 wt% Co/ZnO (Fig. S5) were also conducted to confirm the peak assignment. Over 2Co/ZnO-N, a similar reduction peak for Co³⁺ to Co²⁺ was also observed at 240 °C. Unlike 2Co/ZnO-S, 2Co/ZnO-N showed two reduction peaks at higher temperature, 370 °C and 440 °C, both of which are attributed to the reduction of Co²⁺ to metallic Co. The peak at 370 °C could be related to the reduction of Co²⁺ species that have less interaction with ZnO (10-10) surface. The peak at 440 °C was attributed to the reduction of cobalt that strongly interacted with ZnO polar surface as suggested by the work of Hyman et al. [23] Assuming the high-temperature reduction peak is due to the reduction of Co²⁺, a further quantification of hydrogen consumption reveals that the reduction extent of Co²⁺ on 2Co/ZnO-N and 2Co/ZnO-S are 64% and 62%, respectively. It indicates that there are still irreducible Co²⁺ species on ZnO, likely due to the strong metal-support interaction. In addition, the formation of two types of Co²⁺ species with different reducibility indicates a unique surface chemistry of the (10-10) non-polar facet, which will be further addressed in the following ESR reactions.

3.2 Ethanol steam reforming

Under the conditions studied for ethanol steam reforming deactivation of catalysts was observed. To best investigate the effects of ZnO (10-10) facet on ethanol steam reforming over Co/ZnO catalysts the initial catalyst activity was primarily investigated; experimental data collected and averaged within 30 minutes of time-on-stream was used to compare the activity and selectivity with the minimal influence of catalyst deactivation. Reactions were performed at 400 °C where it is found that ZnO-N support exhibited a relatively high stability [24].

Prior to the catalyst test on Co/ZnO, the performance of ZnO-N and ZnO-S supports were tested in ethanol steam reforming reaction as ZnO was also found active for ethanol steam reforming [30]. Under the current reaction conditions, however, both ZnO-N and ZnO-S supports showed no detectable C1 products suggesting negligible steam reforming activity. This could be due to the different reaction conditions employed in the two cases (i.e., lower S/C ratio and much higher ethanol partial pressure and space velocity than that reported [30]). Over Co/ZnO, selectivity and yield to CO₂ were compared and shown in Fig. 5. Under the identical reaction conditions, C1 products including CO₂, CO and CH₄ were the most significant products and less than 1% selectivity to C2 and C3 products were observed. 2Co/ZnO-N catalyst showed a much higher activity than 2Co/ZnO-S in terms of C-C bond cleavage (49.7% vs. 33.5%) with similar cobalt particle sizes. In addition, selectivity to CO₂ on 2Co/ZnO-N catalyst was also higher than over 2Co/ZnO-S catalyst (68.0% vs. 49.7%). CO selectivity on 2Co/ZnO-N catalyst was significantly lower than that of 2Co/ZnO-S catalyst (22.5% vs. 40.6%). However, methane selectivity between the two catalysts did not show much

difference. The large difference in CO selectivity and small difference in CH₄ selectivity suggested that the higher selectivity to CO₂ is due to an enhanced WGS activity on 2Co/ZnO-N catalysts, converting CO into CO₂.

Previous studies have shown that Co particle size plays an important role in water dissociation and thus CO oxidation to CO₂ [31]. However, both TEM and XRD suggest that 2Co/ZnO-N and 2Co/ZnO-S catalysts have similar cobalt particle size. The complication introduced by Co particle size can be thus excluded. Karim et al. investigated effects of Co⁰/Co²⁺ on ethanol steam reforming over Co/MgO catalysts finding that Co⁰ was much more active than Co²⁺ for ethanol conversion, C-C cleavage, and WGS reaction, while Co²⁺ promoted methanation of CO and CO₂ to CH₄ [15]. More importantly, recent UHV study of cobalt deposited on ZnO single crystal suggest that metallic cobalt nanoparticles are more resistant to oxidation on ZnO (10-10) nonpolar facet due to the less reducible nature of the facet [21]. It is thus hypothesized that the high C-C bond cleavage on 2Co/ZnO-N catalyst and high yield to CO₂ could be due to a higher fraction of metallic Co maintained on the ZnO nonpolar facet during ESR.

4. Conclusions

The effects of ZnO facet on ethanol steam reforming were investigated over Co/ZnO catalysts. Cobalt nanoparticles of similar particle size were prepared on ZnO-N and ZnO-S supports with different percentages of ZnO (10-10) facet exposed. Under similar reaction conditions, Co/ZnO-N catalyst with a higher fraction of ZnO (10-10) facet exhibited a higher C-C cleavage activity compared to the Co/ZnO-S catalyst. Moreover, higher CO₂ selectivity and lower CO selectivity were also observed on Co/ZnO-N. This phenomenon can be related to the high fraction of metallic Co maintained on the ZnO

(10-10) facet in ESR over the 2Co/ZnO-N catalyst. For the first time, the present study demonstrated that ZnO (10-10) can prevent metallic cobalt from oxidation in realistic Co/ZnO catalyst, evidenced by the favorable C-C cleavage and WGS reactions in ethanol steam reforming. The finding of the unique property of ZnO (10-10) could direct rational design of catalysts for ethanol steam reforming reactions.

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Table 1. Textural properties of ZnO supports and Co/ZnO catalysts.

Fig.1. TEM images of (a) ZnO-N, (b) ZnO-S, (c) 2Co/ZnO-N and (d) 2Co/ZnO-S reduced and passivated.

Fig. 2. DRIFT spectra of ZnO-N (a) and ZnO-S (b).

Fig. 3. XRD patterns of different Co/ZnO catalysts: 2Co/ZnO-N (a); 2Co/ZnO-S (b).

Fig. 4 H₂-TPR profile of 2Co/ZnO-S catalyst (a) and 2Co/ZnO-N catalyst (b).

Fig. 5. Comparison of CO₂ selectivity and yield between 2Co/ZnO-N and 2Co/ZnO-S.

200mg catalysts diluted with 9 times of SiC, S/C=5:1, W/F=0.32 g s ml⁻¹, P_{EtOH}= 4.2 kPa, 400 °C.

Table 1. Textural properties of ZnO supports and Co/ZnO catalysts.

Sample name	BET surface area(m ² /g)	Fraction of ZnO (10-10) facet (%) ^c	Co particle size (nm) ^a	Co particle size (nm) ^b
ZnO-N	37	93±5	-	-
ZnO-S	7	-	-	-
2Co/ZnO-N	34	89±5	6.7	4.4
2Co/ZnO-S	12	-	7.6	5.5

^a Cobalt particle size based on TEM images; ^b Cobalt particle size from XRD; ^c the fraction of facet was estimated by assuming a hexagonal prism morphology of the ZnO-N support albeit their different dimensions.

Fig.1. TEM images of (a), ZnO-N; (b), ZnO-S; (c), 2Co/ZnO-N; (d), 2Co/ZnO-S reduced and passivated.

Fig. 2. DRIFT spectra of ZnO-N (a) and ZnO-S (b).

Fig. 3. XRD patterns of (a), 2Co/ZnO-N; (b), 2Co/ZnO-S.

Fig. 4. H₂-TPR profile of 2Co/ZnO-S (a) catalyst and 2Co/ZnO-N (b) catalyst.

Fig. 5. Comparison of CO₂ selectivity and yield over 2Co/ZnO-N and 2Co/ZnO-S.

200mg catalysts diluted with 9 times of SiC, S/C=5:1, W/F=0.32 g s ml⁻¹, P_{EtOH}= 4.2 kPa, 400 °C.