



Short communication

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.

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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 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) non-polar 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 Co⁰ [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

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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 $-196\text{ }^{\circ}\text{C}$ using UHP N_2 . The specific surface areas of the supports and catalysts were calculated based on the Brunauer–Emmett–Teller (BET) model. Catalysts were degassed at $300\text{ }^{\circ}\text{C}$ for 1 h under vacuum before measurements.

Temperature-programmed reduction experiments by hydrogen (H_2 -TPR) were performed on a Micromeritics AutoChem II 2920. Prior to the TPR experiment, samples were pretreated at $350\text{ }^{\circ}\text{C}$ ($5\text{ }^{\circ}\text{C}/\text{min}$) in helium flow ($50\text{ ml}/\text{min}$) for 1 h and then cooled down to $50\text{ }^{\circ}\text{C}$. During the H_2 -TPR, sample is heated up to $600\text{ }^{\circ}\text{C}$ ($10\text{ }^{\circ}\text{C}/\text{min}$) in $10\%\text{ H}_2/\text{Ar}$ flow ($50\text{ ml}/\text{min}$). The gas flow passed through a cold trap ($-10\text{ }^{\circ}\text{C}$) 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 2θ 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 $50\text{ ml}/\text{min}$ H_2 flow at $400\text{ }^{\circ}\text{C}$ for 2 h and passivated in $50\text{ ml}/\text{min}$ $0.1\%\text{ O}_2/\text{N}_2$ flow for 4 h at room temperature. Cobalt particle size is calculated using Scherer equation.

Diffuse reflectance infrared fourier transform spectra (DRIFTS) were recorded on a Bruker Tensor 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 ($25\text{ ml}/\text{min}$) up to $400\text{ }^{\circ}\text{C}$ for 10 min and then in $10\%\text{ O}_2/\text{He}$ ($25\text{ ml}/\text{min}$) at $350\text{ }^{\circ}\text{C}$ for 25 min to remove surface impurities and physisorbed water species on ZnO. After cooling to $50\text{ }^{\circ}\text{C}$ 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 $150\text{--}250\text{ }\mu\text{m}$) 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 $10\%\text{ H}_2/\text{Ar}$ ($50\text{ ml}/\text{min}$) flow for 2 h at $400\text{ }^{\circ}\text{C}$. After reduction, N_2 flow ($50\text{ ml}/\text{min}$) 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 $175\text{ }^{\circ}\text{C}$ with a rate of 1 ml/h. The vaporized feed was carried into the reactor by N_2 flow ($20\text{ ml}/\text{min}$). 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 $5\text{ }\text{\AA}$ molecular sieve was used to separate and analyze H_2 , N_2 , CH_4 and CO. A PPQ column was used to separate and analyze CO_2 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 . An Al_2O_3 column was used to separate and analyze C_3H_6 , C_3H_8 and C_4H_8 , any additional hydrocarbons would appear on this column as well. Reaction was carried out at atmospheric pressure.

Dry gas conversion was calculated with Eq. (1). “ n ” is the number of carbon atoms in gas products C_n .

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

Eq. (2) was used to calculate selectivity to C_1 products.

$$\text{C}_1 \text{ selectivity}(\%) = \frac{\text{molar flow rate of } \text{C}_1 \text{ product}}{\sum \text{molar flow rate of } \text{C}_1 \text{ products}} \times 100 \quad (2)$$

Eq. (3) was used to calculate C–C cleavage of ethanol.

$$\text{C–C cleavage}(\%) = \frac{\sum \text{molar flow rate of } \text{C}_1 \text{ products}}{2 \cdot \text{molar feed rate of EtOH}} \times 100 \quad (3)$$

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 $37\text{ m}^2/\text{g}$, and the surface area of ZnO–S is $7\text{ m}^2/\text{g}$. The decreased surface area suggests that the high calcinations temperature (i.e., $550\text{ }^{\circ}\text{C}$) 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 $34\text{ m}^2/\text{g}$. 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 $12\text{ m}^2/\text{g}$.

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 $10\text{--}20\text{ nm}$ (Fig. 1a). The estimated (10–10) fraction is $\sim 93\%$ (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 a diameter of $50\text{--}100\text{ nm}$, 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 $\text{O–H}\cdots\text{O}$ 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

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.

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