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Research Note

Distinct water activation on polar/non-polar facets of ZnO nanoparticles

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ABSTRACT

ZnO nanoparticles with differing dominant facets were prepared and characterized by a complimentary of techniques such as X-ray diffraction, electron microscopy, temperature programmed desorption of H_2O, and Fourier transform infrared spectroscopy analysis of adsorbed D_2O. For the first time, water interaction/activation is compared on ZnO polar and non-polar facets. We report that non-polar facets exhibit high activity in water activation, which favors reactions such as ketonization and steam reforming in which dissociated water is involved. The distinct water dissociation on ZnO non-polar facets could be related to its facile formation of oxygen vacancies under realistic reaction conditions.

1. Introduction

A fundamental understanding of the structure–function relationship is essential in the rational design of catalysts. In addition to particle size or quantum confinement [1], morphology of catalyst particles may also influence the catalytic performances [2]. Previous studies on the facet effect of metal/metal oxide catalysts were exclusively conducted on single-crystal model surfaces with limited surface area in an ultra-high vacuum (UHV) system [3–7]. Studies on high surface area materials are limited to only a few metal oxides with controlled morphologies including Co_3O_4 [2,8], and CeO_2 [9–12]. High surface area materials with well-defined morphologies are still highly desired which allow for meaningful kinetic measurement under realistic conditions without the concerns of material and pressure gaps.

Commercial fermentation of biomass produces bio-ethanol (~20 wt% ethanol in water). With the increasing availability of bio-ethanol, its further conversion to value-added chemicals/fuels without unnecessary water separation is highly desired [13–15], which requires the fundamental understanding of interactions between water and the catalyst surface. ZnO has been widely used as a support and a promoter in alcohol conversion [14]. The effect of ZnO on the water activation has been studied recently in methanol steam reforming (MSR) [16–19], ethanol steam reforming (ESR) [20–22], and bio-ethanol to isobutene conversion [11,13], etc. Although numerous studies have been reported on the unique catalytic properties of polar and non-polar facets on ZnO [5–7,23], those were mainly focused on the studies in UHV using model catalysts. For example, studies on ethanol reaction over model ZnO (001)/(00−1) polar facets and ZnO (100) non-polar facets revealed that both acetaldehyde and ethylene form over ZnO polar facets between 410–490 K, while ethylene is mainly produced on ZnO nanowires with dominant (100) non-polar facets at 517 K [5,7]. It was also found that oxygen vacancies on both polar and non-polar facets play a key role in ethanol reaction [5,7]. In photocatalysis, hexagonal plate-like ZnO was found to exhibit more than 5 times higher activity than rod-shaped particles in the photocatalytic decomposition of methylene blue [24]. Recently, we synthesized stable ZnO nanoflakes with dominant polar facets, and investigated the influence of ZnO facet on MSR [16,25]. It was found that ZnO with dominant polar (001) and (00−1) facets exhibited higher activity but lower CO_2 selectivity, compared with commercial ZnO without any dominant facets in MSR [16]. In addition, even with loaded Pd, the facet exhibited significant effect on the formation of PdZn alloys and thus catalytic performances of the Pd/ZnO catalyst in MSR [25]. Apparently, polar and non-polar facets exhibit different surface chemistries; however, the inherent mechanism is still yet to be uncovered. Herein, we prepared two ZnO samples: one is needle-like ZnO (ZnO-N) with ~96% (100) non-polar facets and the other is flake-like ZnO (ZnO-F) with

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~72% (001)/(00−1) polar facets. The distinct surface chemistries of the two facets were further identified and unambiguously correlated with the water activation.

2. Materials and methods

2.1. Materials preparation

ZnO needles were synthesized by a surfactant assisted alcohol thermal procedure according to our previous reported method [26]. In a typical synthesis, 3.0 g of polyvinylpyrrolidone (PVP) (Sigma–Aldrich; $M = 40{,}000$) was dissolved in 180 ml of ethanol and then 0.75 g of zinc acetate dihydrate was slowly added into the solution. The resulting reaction mixture was stirred for several minutes, followed by the addition of 4.5 g of NaOH. A turbid solution was stirred and loaded into autoclave. It was then sealed and maintained at 80 °C for 24 h. The obtained material was washed with ethanol and distilled water for several times, respectively. The ZnO needle was obtained followed by calcinations at 350 °C for 3 h.

ZnO flakes were synthesized by surfactant directed crystallization according to the reported method [27] with some modifications. 2.0 g of Polyvinylpyrrolidone (PVP) (Sigma–Aldrich; $M = 40{,}000$) was dissolved in 200 ml of pentanol, and then 8 ml of a 0.15 M aqueous NaOH solution and 6 ml of a 0.1 M ethanol solution of $Zn(NO_3)_2 \cdot 6\ H_2O$ were sequentially added. The reaction mixture was then kept at 90 °C for 1 h. The obtained material was washed with ethanol and distilled water for several times, respectively. The ZnO flake was obtained followed by calcinations at 350 °C for 3 h.

2.2. Characterization

X-ray diffraction (XRD) spectra were recorded using a Philips X'pert MPD (Model PW3040/00) diffractometer with a copper anode ($K\alpha_1 = 0.15405$ nm) and a scanning rate of 0.02–0.04° per second between $2\theta = 20$–$70°$. The diffraction patterns were analyzed using Jade 5 (Materials Data Inc., Livermore, CA) and the Powder Diffraction File database (International Center for Diffraction Data, Newtown Square, PA). The particle size of the ZnO crystals was estimated from the XRD patterns using the Scherrer equation ($d = 0.89\lambda/B\cos\theta$, where λ is the wavelength of Cu Kα radiation, B is the calibrated full width at half-maximum (FWHM) of the peak in radians, and θ is the diffraction angle of the crystal plane).

Nitrogen sorption experiments were recorded on a Micromeritics TriStar II 3020 automatic physisorption analyzer. Before adsorption analysis, samples were degassed under vacuum at 300 °C for 1 h. BET surface area was calculated using the Bru nauer–Emmett–Teller (BET) model.

Transmission electron microscopy (TEM) was conducted using a JEOL 2010 high-resolution analytical electron microscope operating at 200 kV with a LaB_6 filament. Scanning electron microscopy (SEM) was done on FEI SEM Quanta 200 F microscope.

Fourier transform infrared spectrometry of D_2O (D_2O-FTIR), using a Bruker Tensor 27 Fourier Transform Infrared Spectrometer (FTIR) operated in the mode of *in situ* Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS), was used to understand how water interacts with ZnO surfaces. Sample was loaded in the DRIFTS cell and pretreated at 400 (or 500) °C for 1 h under flowing He (50 SCCM). Before the D_2O adsorption, the sample was cooled down to 50 °C in He (50 SCCM) where the background was taken. D_2O adsorption was accomplished by flowing D_2O/helium gas through the catalyst samples at 50 °C until the saturation of the catalyst surface was achieved, monitored by TCD. The D_2O/helium was generated by flowing He (20 SCCM) through a bubble generator. The absorbance spectra were recorded at 50 °C after heating sample at different temperatures (50 °C, 150 °C, 250 °C, 350 °C, 400 °C) for 30 min under helium (50 SCCM).

Temperature programmed desorption (TPD) of water was recorded in an AutoChem II 2920 chemisorption analyzer with a vapor generator. Typically, 50–100 mg catalyst was packed by quartz wool in U-shaped tubes. Catalyst samples were pretreated under Helium at 400 °C for 1 h, and then cooled down to 50 °C for the saturation of water vapor. After desorbing weekly adsorbed water with Helium at 50 °C, the temperature was ramped to 600 °C with a rate of 10 °C/min under Helium. MS signals ($m/z = 16$, 17 and 18) were recorded by ThermoStars 200 AMU mass spectrometer.

2.3. Catalytic reaction

Bio-ethanol conversion reactions were conducted in a fixed-bed stainless steel reactor (i.d. 5 mm), which has been described elsewhere [13]. Typically, 50–100 mg of catalyst was packed and sandwiched by quartz wool beds. The thermocouple was placed in the middle of the catalyst bed to monitor the reaction temperature. Before the reaction, catalysts were firstly pre-treated in N_2 (50 ml/min) at 400 °C (ramping rate was 5 °C/min) for 1 h. Then a mixture of H_2O/ethanol (or H_2O/acetaldehyde) (a 10:1 molar ratio) was introduced into the evaporator (180 °C) by a syringe pump and carried into the reactor by flowing nitrogen gas (4.24% ethanol). The product line was heated to 150 °C before a cold trap to avoid the condensation of liquid products.

3. Results and discussion

Fig. 1a and b shows the TEM images of ZnO-N and ZnO-F. ZnO-N displays a needle-like morphology with 50–200 nm in length and 10–20 nm in width (Figs. 1a and S1). On the other hand, ZnO-F displays a flake-like morphology, 200–400 nm in width and tens of nanometers in thickness (Fig. 1c). XRD patterns for both ZnO-N and ZnO-F samples display Wurtzite structure (Fig. S2). It is noteworthy that the peaks, characteristics of (100) and (101) on ZnO-N, are significantly broadened (Fig. S2), suggesting the nanoscale dimensions along [100] and [101] and the dominant non-polar facets (Fig. S3). According to the Scherer equation, the calculated dimensions for ZnO-N are 17 nm, 48 nm, and 16 nm, corresponding to the crystal diameter normal to (100), (002) and (101). It suggests that the particles are elongated along [001] such that the polar ZnO surfaces are located at the tips of the ZnO needles (Fig. S3), consistent with our previous results [25]. In contrast, ZnO-F shows the average dimensions of 79 nm, 59 nm, and 69 nm perpendicular to (100), (002) and (101) planes of ZnO, indicating that (001)/(00−1) polar planes are dominant on ZnO-F, which can be further evidenced by TEM observation (Fig. 1b–d). Based on the dimensions from the TEM images of the two types of ZnO particles, the fraction of different facets was calculated and the results are summarized in Table S1. XRD results and TEM images of two spent samples suggest that dominant planes are still maintained even after bio-ethanol reactions at 400 °C although the overall dimensions increased (Figs. S2, S4 and S5). It should be noted that dominant facets of ZnO are maintained under the conditions studied, suggesting that the ZnO-N and ZnO-F materials are hydrothermally/thermally stable under these conditions, which is pivotal to study the effects of ZnO facet on bio-ethanol conversion.

The water interaction and identification of OH bands on different facets of ZnO has been previously studied in UHV using both ZnO single crystal and ZnO nanoparticles [28]. The band at