Graphical Abstract

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 H₂O, and Fourier transform infrared spectroscopy analysis of adsorbed D₂O. 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.

Key words: Facet, Water dissociation, ZnO, ketonization, ethanol

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 photo-catalytic 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 CO₂ 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 ~72% (001)/(00-1) polar facets. The distinct surface chemistries of the two facets were further identified and unambiguously correlated to 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) were 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 hr.

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 $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ were sequentially added. The reaction mixture was then kept at 90 °C for 1 hr. 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 3hr.

2.2 Characterization

X-ray diffraction (XRD) spectra were recorded using a Philips X'pert MPD (Model PW3040/00) diffractometer with a copper anode ($K\alpha_1 = 0.15405 \text{ nm}$) and a scanning rate of 0.02-0.04° per second between $2\theta = 20^\circ$ -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 $K\alpha$ 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 hr. BET surface area was calculated using the Brunauer-Emmett-Teller (BET) model.

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

Fourier transform infrared spectrometry of D₂O (D₂O-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 hr under flowing He (50 SCCM). Before the D₂O adsorption, the sample was cooled down to 50 °C in He (50 SCCM) where the background was taken. D₂O adsorption was accomplished by flowing D₂O/helium gas through the catalyst samples at 50°C until the saturation of the catalyst surface was achieved, monitored by TCD. The D₂O/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 minutes 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 were packed by quartz wool in U-shaped tubes. Catalyst samples were pretreated under Helium at 400 °C for 1 hr, and then cooled down to 50 °C for the saturation of water vapor. After desorbing weakly 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 to 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

N₂ (50 ml/min) at 400 °C (ramping rate was 5 °C/min) for 1 hour. Then a mixture of H₂O/ethanol (or H₂O/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 1b show the TEM images of ZnO-N and ZnO-F. ZnO-N displays a needle-like morphology with 50-200 nanometers in length and 10-20 nanometers in width (Fig.S1a 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 characteristic of (100) and (101) on ZnO-N are significantly broadened (Fig. S2), suggesting the nano-scale 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-1d). Based on the dimensions from the TEM images of the two types of ZnO particles, the fraction of different facets were 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 (Fig. 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 3620 cm^{-1} is attributed to the OH on the polar O-ZnO (00-1) surface formed via dissociation of water on oxygen vacancy sites, while partially dissociated water on the mixed-terminated ZnO (100) surface yields both OH species with coadsorbed H_2O at 3672 cm^{-1} and the coexistent H_2O at ~ 3150 and 3687 cm^{-1} . The bands at 3639 and 3656 cm^{-1} represent isolated OH species formed on the mixed-terminated ZnO (100) surface, and interaction of water with oxygen defects forms $\text{O}-\text{H}\cdots\text{O}$ species at 3564 and 3448 cm^{-1} [28].

To investigate the effect of facet on the water activation and understand the nature of surface hydroxyl groups under realistic conditions, temperature programmed D_2O -FTIR was conducted on ZnO-N (Fig. 2A) and ZnO-F (Fig. 2B). The isotopic shift in D_2O -FTIR was used to unambiguously identify the hydroxyl groups on ZnO. Particularly, over the ZnO-F (Fig. 2B), a broad hump from 3750 to 3150 cm^{-1} (where OH groups were also identified) was observed. For comparison purposes, we also studied D_2O -FTIR on a commercial ZnO (ZnO-P) without any dominant facets (Fig. S6) and results are shown in Fig. 2C. Over ZnO-N pretreated under Helium at $400\text{ }^\circ\text{C}$, hydroxyl (OH) groups on both ZnO polar (3618 cm^{-1}) and non-polar facets (3677 cm^{-1}) were observed. Isolated OH groups on ZnO non-polar facets (3656 cm^{-1}) and $\text{O}-\text{H}\cdots\text{O}$ species (3565 and 3450 cm^{-1}) created via H_2O interaction with structural defects were also resolved. In addition, a weak narrow band at 3718 cm^{-1} is detected on ZnO-N only, which could be related to the non-H-bonded OH groups of a water molecule [28], adsorbed on the (100) nonpolar facet.

Interestingly, the expected dominant OH hydroxyl groups detected on polar facets in UHV [28] was not observed in this study. Instead, only very weak hydroxyl bands at 3679, 3662, 3639, and 3614 cm^{-1} are resolved on ZnO-F with dominant (001)/(00-1) polar facets. Meanwhile, a broad hump between 3100 cm^{-1} and 3600 cm^{-1} is observed, which can be attributed to the H-bonded hydroxyl of molecularly adsorbed H_2O . Over ZnO-P, bands corresponding to both OH groups on both non-polar facet and polar facets are observed (Fig. 2C), similar to those on ZnO-N. However, non-H-bonded OH at 3718 cm^{-1} is not detected on ZnO-P, and the intensity of O-H $\cdots$ O species (3558 and 3446 cm^{-1}) is relatively lower than that of ZnO-N, likely due to the lower portion of (100) polar facet/oxygen defect on ZnO-P. More importantly, the H-bonded hydroxyl of molecular H_2O on polar facet is also observed as evidenced by the broad peak between 3100 cm^{-1} and 3350 cm^{-1} . The results reveal that, under realistic conditions, the ZnO hydroxyl groups observed in this study are generated from water dissociation on non-polar facets and possibly structural defects, while molecularly adsorbed H_2O might dominate on ZnO polar facets.

After saturating the samples with D_2O at 50 $^{\circ}\text{C}$, desorption spectra of D_2O at different temperatures are obtained. As can be seen in Fig. 2A (red curve), over the ZnO-N, bands associated with OH groups (3718, 3656, 3565, and 3450 cm^{-1}) decrease. Meanwhile a similar pattern of new bands associated with deuterioxyl groups (2740, 2711, 2698, 2667, 2632, and 2557 cm^{-1}) is detected at 50 $^{\circ}\text{C}$, evidenced by the isotopic ratios of $\nu(\text{OH}):\nu(\text{OD})$ of 1.35. The band at 2711 cm^{-1} corresponds to the OD group on ZnO (100) non-polar facets, and the one at 2667 cm^{-1} is related to the adsorption of OD on ZnO polar facets. The bands at 2740 cm^{-1} and 2698 cm^{-1} are attributed to isolated OD related to ZnO non-polar facets, and the broad bands at 2632 cm^{-1} and 2557 cm^{-1} correspond to O-D $\cdots$ O species. Upon increasing desorption temperature up to 400 $^{\circ}\text{C}$, the intensity of bands associated with both OH and OD barely changes. It is clear that the

water dissociation/H-D exchange reactions occur at 50 °C, suggesting the high activity of ZnO (100) non-polar facets. On the contrary, no band can be resolved in OD region on the ZnO-F regardless of desorption temperature, or even after a pretreatment in D₂O vapor at 450 °C (Fig. 2B, black curve). The broad peak between 3100 cm⁻¹ and 3600 cm⁻¹ also show negligible changes. It further confirms that the polar facet of ZnO-F shows low/no activity for water dissociation. It should be mentioned that ~28% of (100) non-polar facets present on ZnO-F (Table S1). The fact that no OD groups associated with non-polar facet are observed could be due to the low population of the OD groups registering below the detection limit of FTIR. It is still unclear why OH groups are present on the polar facet (3620 cm⁻¹), and there is H-D exchange (shown at 2667 cm⁻¹) on the ZnO-F (Figure 2A). We speculate that a substantial amount of defects might exist on the polar facet of ZnO-F, due to the small dimension of [100] (i.e., 17 nm). The presence of those defects could promote water dissociation, leading to the formation of OH groups.

Over the ZnO-P, bands associated with OH groups (3679, 3662, 3620, 3556, and 3448 cm⁻¹) decreases, and new bands associated with deuteroyl groups appear at 2706, 2669, 2628, and 2553 cm⁻¹. Different from ZnO-N, as desorption temperature increases, the intensity of the deuteroyls also increases (Fig. 2C), indicating its relatively lower activity for D₂O dissociation/H-D exchange. However, the broad hump between 3100 cm⁻¹ and 3350 cm⁻¹ still remains unchanged, further confirming the low/lack of activity of (001)/(00-1) polar facets on ZnO-P. To summarize, although the question regarding the interpretation of the band at ~3620 cm⁻¹ (OH on the polar facet) is still open to discussion, our FTIR results clearly indicate that dissociative adsorption of H₂O is favorable on ZnO (100) non-polar facets, while molecularly

adsorbed molecular water prevails on the ZnO (001)/(00-1) polar facets over the ZnO powder samples.

The formation and thermal stability of hydroxyl groups on ZnO has been widely studied to differentiate the surface structure and chemistry of (00-1) polar and (100) non-polar facet in UHV. No OH bands were observed on (100) non-polar and (001)/(00-1) polar facets of ZnO single crystal, but oxygen vacancies were noted. Upon exposure to water, water dissociation took place on the oxygen vacancies, leading to the observation of surface hydroxyl groups. Thermal stability of hydroxyl groups evidenced by temperature programmed desorption (TPD) reveal that recombinative desorption of hydroxyl groups on (100) surface occurs at temperatures as low as 300 °C, while those on O-terminated (00-1) surface are stable up to more than 500 °C [28, 29]. Consistent with this observation, our H₂O-TPD experiments (Fig. 3) reveal that the H₂O desorption peak temperature of ZnO-F is much higher than that of ZnO-N (~520 °C versus ~420 °C). Different from the observations in UHV [28], FTIR characterizations only show a broad hump with poor resolved hydroxyl peaks on ZnO-F with dominant (001)/(00-1) polar facet (Fig. 2B). Further D₂O-FTIR experiments at an increased temperature (i.e, 400 °C) also revealed no water dissociation/H-D exchange reactions (Fig. 2B). The question of the H₂O desorption observed at high-temperature (>500 °C) by H₂O-TPD (Fig. 3) is thus open to the further discussion. While it is unclear why water dissociation was not observed on ZnO-F contradictory to what was observed in UHV, the surface reconstruction and formation of oxygen vacancy must be vital to the water dissociation on the powder ZnO. We propose that the ability to form oxygen vacancy on the ZnO polar facet is much harder than that on ZnO non-polar facet under realistic conditions. Indeed, our H₂O-FTIR reveals that oxygen vacancy on ZnO-N is much more pronounced than that on ZnO-F, evidenced by the bands at 3558 and 3446 cm⁻¹ shown in Figure

2A & 2B.. However, a high temperature (i.e., 400 °C) pretreatment in flowing hydrogen for 12 h is required to create the oxygen vacancy on ZnO-F with dominant polar facets [16]. The current results suggest that while activation using H₂ is required to generate the oxygen vacancy over ZnO polar facets, ZnO with dominant non-polar facet could favor the formation of oxygen vacancy and thus reactions involving water activation under realistic conditions.

Water has been found to play essential roles in the bio-ethanol-to-acetone conversion[11, 13, 15], and the water activation on the base or balanced acid-base pairs is believed to be essential to enhance the oxidation of acetaldehyde to form acetone via a possible ketonization pathway [15]. To further verify the distinct activity of water activation observed on the ZnO polar and non-polar facets, bio-ethanol conversion was performed on the ZnO-N and ZnO-F catalysts. Fig. 4 shows the evolution of products with bio-ethanol conversion. Dehydration reaction takes place on both catalysts. However, it plays a minor role in the overall reaction as evidenced by the low ethylene selectivity (< 8%), consistent with our previous observation [13]. On the contrary, dehydrogenation was found to be the dominant reaction pathway, evidenced by the primary formation of acetaldehyde at low conversion. Kinetic analysis reveals that the ethanol conversion rate on the ZnO-F is almost two times higher than that on the ZnO-N (Table 1). This observation indicates that the dehydrogenation of ethanol to acetaldehyde could occur on both ZnO (001)/(00-1) polar facets and ZnO (100) non-polar facets, however ZnO (001)/(00-1) polar facet is more active than ZnO (100) non-polar facet, which is consistent with our previous report [16]. As ethanol conversion increases, acetone selectivity increases at the expense of acetaldehyde, suggesting that acetone is a secondary product formed from acetaldehyde. Moreover, the bio-ethanol to acetone reaction is limited by acetaldehyde conversion. Crotonaldehyde was also observed. However, different from those studies using high purity ethanol as a feed [15],

crotonaldehyde selectivity is less than 1% for both catalysts in the current bio-ethanol (20 wt% ethanol in H₂O) reaction. Apparently, the acetaldehyde to acetone conversion is favored in the presence of water [15] due to the acetaldehyde oxidation by dissociated water.

Considering the different surface areas and the dependence of the acetone selectivity on ethanol conversion, product selectivity (i.e., acetaldehyde and acetone) is compared at same ethanol conversion by adjusting the space velocity (Fig. 4). Interestingly, acetone selectivity on ZnO-N with dominant (100) non-polar facets is always higher than that on ZnO-F with dominant (001)/(00-1) polar ones. This result agrees well with the favorite water dissociation on (100) facets evidenced by D₂O-FTIR, as well as a much higher surface area of (100) non-polar facets on ZnO-N compared to on ZnO-F (~35 m²/g vs 1.4 m²/g, Table S1). Further kinetic analysis shows that the acetone formation rate on ZnO-N normalized by total surface area is more than three times higher than that of ZnO-F (Table 1). However, the acetone formation rate normalized by the surface area of (100) non-polar facets are comparable on both ZnO-N and ZnO-F catalysts (7.31 vs 8.31, $\times 10^{-5}$ mol acetone.s⁻¹. m₍₁₀₀₎⁻², Table 1 and S1). Moreover, the apparent activation energy for acetaldehyde to acetone conversion on the two catalysts is similar (145 vs 152 kJ/mol). These results further suggest that acetaldehyde to acetone conversion is limited by water activation on ZnO (100) non-polar facets, and that ZnO (001)/(00-1) polar facets do not seem to be involved in the water dissociation.

4. Conclusions

In summary, we found that the water activation/dissociation occurs mainly on oxygen vacancy of the ZnO powder samples. Under realistic conditions, the formation of oxygen vacancies on (100) non-polar facets is much more facile than on the ZnO (001)/(00-1) polar facets. Both FTIR and H₂O-TPD suggest that H₂O might be strongly adsorbed on ZnO (001)/(00-1) polar facets,

which inhibits the formation of the oxygen vacancy and thus adsorption/dissociation of H₂O on the ZnO-F. In the bio-ethanol reactions, both the ZnO (100) non-polar facet and the ZnO (001)/(00-1) polar facets are active for ethanol dehydrogenation to form acetaldehyde. However, the subsequent acetaldehyde reaction to form acetone via the ketonization pathway mainly occurs on the ZnO (100) non-polar facet on which water dissociation is highly favored. The current work provides a fundamental understanding of H₂O dissociation as affected by the facet of the metal oxide catalyst, and consequently its relations with the water consuming reactions, such as ketonization and steam reforming.

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Supplementary material

Supplementary data associated with this article can be found in the online version.

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Fig. 1. TEM/SEM images of ZnO catalysts: a) ZnO needle; b-d) ZnO flake.

Fig. 2. D₂O-FTIR on ZnO-N (A), ZnO-F (B) and ZnO-P (C).

Fig. 3. H₂O-TPD (m/z=17) over ZnO flake (ZnO-F) and needle (ZnO-N).

Fig. 4. Product selectivity as a function of ethanol conversion over ZnO flake (ZnO-F) and needle (ZnO-N) catalysts.

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Fig. 4. Product selectivity as a function of ethanol conversion over ZnO flake (ZnO-F) and needle (ZnO-N) catalysts.

Table 1. Activity comparison of ZnO needle and flake for catalytic bio-ethanol conversion

Catalysts	Surface area (m ² /g)	Ethanol Con.(%)	Acetaldehyde Sel. (%)	Acetone Sel. (%)	Ethanol rate ^a (mol.s ⁻¹ .m ⁻²)	Acetone rate ^a (mol.s ⁻¹ .m ⁻²)	Acetone rate ^b (mol.s ⁻¹ .m ₍₁₀₀₎ ⁻²)
ZnO-N	36	19.3	74.8	11.7	9.00e-4	7.01e-5	7.31e-5
ZnO-F	5	21.8	84.3	1.9	1.83e-3	2.32e-5	8.28e-5

10:1 molar H₂O/ethanol, 4.24% ethanol, T= 400 °C. a, rate normalized by total surface area; b, rate normalized by surface area of non-polar facet