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Efficient conversion of glycerol to 1, 2-propenadiol over ZnPd/ZnO-3Al catalyst: The significant influences of calcination temperature

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ABSTRACT

ZnPd bimetallic nanoparticles supported on the Al-doped ZnO support showed efficient catalytic performance for glycerol hydrogenolysis to 1,2-propanediol (1,2-PDO). The Al species in the ZnPd/ZnO-3Al catalyst were highly related to the reaction activity of the catalysts. It was confirmed that the $Al_A^{(IV)}$ species in the ZnPd/ZnO-3Al catalyst determined the reduction of ZnO, the size of ZnPd, oxygen vacancy density, and the reaction activity. Calcination temperature had significant influences on the distribution and migration of $Al^{(IV)}$ in ZnO lattice, and hence affected the reaction activity.

1. Introduction

Doping a small fraction of guest cations into host oxide supports (into lattice or surface layers) is an effective strategy for improving the catalytic performance of heterogeneous catalysts. Although the doping level is low (commonly less than 5%), both structural and electronic properties of the host can be greatly modified upon the doping [1–3]. The dispersion of metal nanoparticles (NPs) [4,5], reducibility of support [6], surface charge distribution [7,8], metal-support interaction [9], acidic and basic characters [10], and oxygen vacancy density [7,11] in the catalysts could be altered. They consequently cause an essential improvement in the catalytic performance. For instance, the oxygen vacancy density was improved by doping lanthanide ions to CeO_2, hence its activity for the CO oxidation was increased [12]. The addition of Mg^{2+} to ZnO led to a stronger metal-support interaction (SMSI), and resulted in an enhancement of the stability of Pd/ZnO catalyst [13]. Al_2O_3-ZnO mixed oxide is one of the most efficient supports, for example, Cu/ZnO/Al_2O_3 catalyst has been extensively studied for stream reforming of methanol, Water-Gas shifts, hydrogenation, and so on. The mixed oxide of Al_2O_3-ZnO is intrigue owing to that very low concentration of Al doped into ZnO lattice could lead to a defect-enriched support [9,14–16]. However, the influences of doped Al on metal dispersion, surface defect, and catalyst activity are not very clear yet. Besides, how does the synthetic procedure (such as calcination temperature) affect the distribution and migration of Al species is highly desired.

Increasing demand for biodiesels results in a large surplus of glycerol, a main by-product of biodiesels production. Consequently, the utilization of glycerol is of essence for reducing the cost of biodiesels production [17,18]. Glycerol hydrogenolysis to 1,2-PDO is considered one of the most promising routes for glycerol utilization because the current manufacture pathways (chlorohydrin process and hydroperoxide process) to 1,2-PDO are not environmental benign enough [19–21]. ZnPd alloy has very similar valence electron density as Cu, and it shows advanced catalytic performance in some catalysis reactions where Cu-based catalysts are required, such as the methanol steam reforming [22–24]. Besides, ZnPd alloy catalysts are expected to have better stability than Cu, especially in the aqueous solution under harsh conditions [25–27]. In our previous study, the excellent catalytic performances of ZnPd/ZnO-3Al catalysts have been reported for hydrogenolysis of glycerol to 1,2–PDO (~ 92% selectivity), and the relationship between the activity and oxygen vacancy density was revealed [28]. As the supplement and continuation of our previous study, we further investigate the influences of calcination temperature on Al distributions and migrations, as well as clarify the roles of different kinds of Al species. A relative lower calcination temperature favoured the retaining of $Al_A^{(IV)}$ in ZnO support, which facilitated the dispersion of ZnPd, reduction of ZnO, as well as the formation of oxygen vacancies. We believe this study should provide helpful knowledge for the design of catalysts with ZnO-Al_2O_3 supports.

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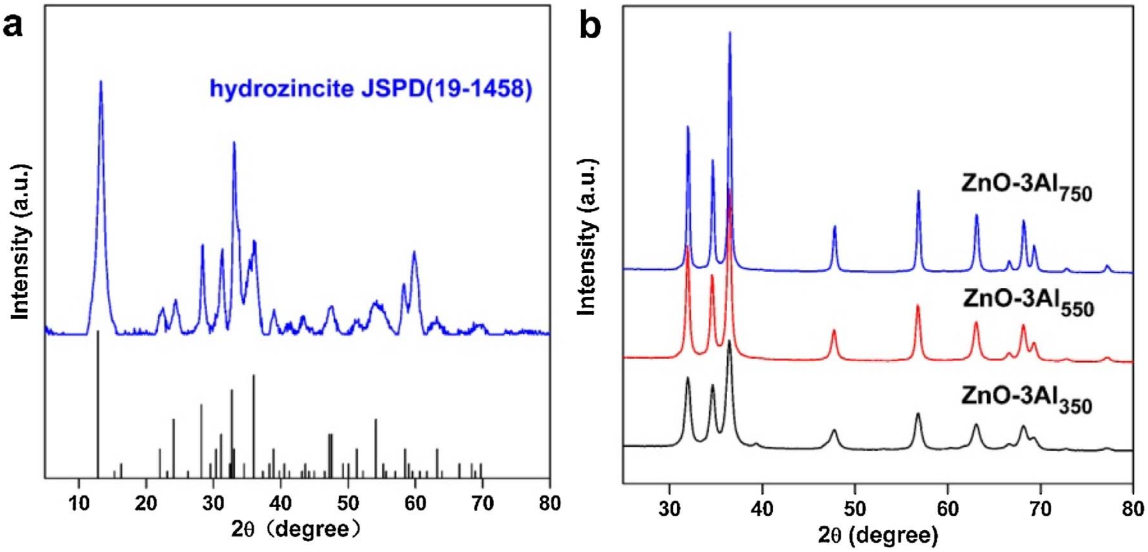

Fig. 1. XRD patterns of the precipitates (a); and the ZnO-3Al supports calcinated at 350 °C, 550 °C, and 750 °C (b).

2. Experiment

2.1. Synthesis of ZnO and ZnO-3Al support

The ZnO and Al-doped ZnO supports were prepared by a co-precipitation method as reported elsewhere [28]. In a typical process, 11.16 g $Zn(NO_3)_2{\cdot}6H_2O$ and 0.42 g $Al(NO_3)_3{\cdot}9H_2O$ (mole percentage of Al was 3%) were dissolved in deionized water, and the total metal ion concentration in the solution was 1.5 mol/L. Then, the metal ions were precipitated by dropping of Na_2CO_3 solution (4 g Na_2CO_3 in 20 mL deionized water). After aging at 65 °C for 2 h, the precipitate was collected, washed, and dried at 80 °C overnight, and finally calcined in air for 5 h. The carrier was denoted as ZnO and ZnO-3Alx for ZnO with and without Al, in which the “x” refers to the calcination temperature.

2.2. Synthesis of catalysts

Catalysts with a Pd-loading of 5 wt.% were prepared by the incipient wetness impregnation method. Acetone solution of $Pd(C_2H_3O_2)_2$ was added drop-wisely to form a support slurry, and then the slurry was dried overnight, and followed by calcination in air at 300 °C for 2 h. Prior to usage, the catalysts were pre-reduced with H_2 at 400 °C for 2 h with a heating rate of 2.5 °C/min. For the preparation of ZnPd/ZnO-3Al (R) catalyst, the ZnO-3Al support was firstly reduced under H_2 at 400 °C for 2 h, and then Pd was loaded by incipient wetness impregnation method as described above.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) measurement was carried on a Bruker D8 ADVANCE diffractmeter, using Cu-Kα radiation ($\lambda = 0.154$ nm). The ^{27}Al nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP magic angle spinning (MAS) probehead whose X channel was tuned to 104.27 MHz for ^{27}Al, using a magnetic field of 9.39T at 297 K. The dried and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap which were spun at 5 kHz rate, with a $\pi/12$ pulse. A total of 256 scans were recorded with 2 s recycle delay for each sample. All ^{27}Al MAS chemical shifts are referenced to the resonances of $Al(H_2O)_6^{3+}$ standard. Temperature-programmed reduction (TPR) was carried out on Micromeritics Autochem II 2920 chemisorption instrument using 10% H_2 diluted Ar (50 ml/min). The amount of catalyst was 0.05 g, and temperature was increased from 50 °C to 600 °C at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) measurements were carried on the VG Microtech 3000 Multilab. The electronic properties of O 1s, Pd 3d and Zn 2p were determined. All XPS spectra were corrected to the C 1 s peak at 284.6 eV. Transmission electron microscopy (TEM) images were performed on a JEOL JEM-2010 instrument operating at an accelerating voltage of 200 kV. N_2 adsorption-desorption experiments were performed with a Micromeritics ASAP 2020 surface area and porosity analyzer.

2.4. Catalytic testing

The hydrogenolysis of glycerol was performed in a 50-mL stainless steel reactor with an inner Teflon coating. The autoclave was charged with desired amount of catalysts and glycerol aqueous solution, then flushed with H_2 for more than three times and pressurized to 3.0 MPa. Then the reactor was placed in the preheated oil bath at 230 °C. When the temperature of reactor was up to 230 °C(about 15 min), the reaction started at the beginning of the stirring with a speed of 1300 rpm. After reaction, the vessel was cooled to room temperature, and the liquid phase was analysed with a gas chromatograph (Shimadzu, 14C) equipped with a capillary column (Restek Stabilwax 30 m × 0.53 mm × 1 μm,) and a flame ionization detector (FID) and n-butanol as internal standard.

3. Results and discussion

3.1. Structural characterization

The ZnO and ZnO-3Al ([Al]/[Zn] + [Al] = 3%) supports were prepared by the co-precipitation of Zn^{2+} and Al^{3+} ions and followed by the calcination. The X-ray diffraction patterns of the precipitates and the ZnO-3Al calcined at different temperatures are presented in Fig. 1. The low doping concentration (3%) of Al and the co-precipitate process ensured the uniform distribution of Al in the ZnO [29–31]. The diffraction peaks of the precursor matched well with the hydrozincite $Zn_5(CO_3)_2(OH)_6$ (JSPDF 19–1458), except for a slight right shift of 2θ values, which was resulted from the doping of Al. Al doping caused the lattice contraction of ZnO, hence diffraction peak shifted rightwards [1,32]. The diffraction peaks of the calcined samples can be easily indexed to hexagonal wurtzite ZnO (JSPDF 65–3411). The doping of Al caused lattice contraction and local disorder of atom arrangements of Zn, and led to the obviously broadening of diffraction peaks. In view of