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# Promoting effect of boron oxide on Cu/SiO<sub>2</sub> catalyst for glycerol hydrogenolysis to 1,2-propanediol

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## ABSTRACT

Cu/SiO<sub>2</sub> catalyst has been extensively applied in glycerol hydrogenolysis for its high selectivity to 1,2-propanediol, while suffering from severe deactivation easily. B<sub>2</sub>O<sub>3</sub> is frequently used as an additive for stabilizing active species. Thus, a series of Cu/SiO<sub>2</sub> catalysts with various B<sub>2</sub>O<sub>3</sub> loadings for glycerol hydrogenolysis were prepared via precipitation-gel method followed by impregnation with boric acid. These catalysts were fully characterized by ICP, BET, XRD (*in situ* XRD), N<sub>2</sub>O chemisorption, H<sub>2</sub>-TPR, NH<sub>3</sub>-TPD, IR, Raman, XPS, and TEM. Addition of B<sub>2</sub>O<sub>3</sub> to Cu/SiO<sub>2</sub> can greatly restrain the growth of copper particles and promote the dispersion of copper species upon calcination, reduction and reaction, which resulted in the enhanced catalytic activity and stability. The optimal 3CuB/SiO<sub>2</sub> reached complete conversion with 98.0% 1,2-propanediol selectivity. The strong correlation between 1,2-propanediol yield and Cu surface area gave direct evidence that the active Cu species were the primary active sites for glycerol hydrogenolysis.

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# 1. Introduction

Declining fossil fuel reserves and increasing environmental issues have stimulated intensive interest in developing renewable biomass and biofuels [1,2]. In this context, biodiesel emerges as a promising alternative to conventional fossil fuels for its non-toxic, carbon natural, and biodegradable properties. Biodiesel is currently produced by the transesterification of triglycerides with methanol or ethanol, which concurrently manufactures large amounts of byproduct glycerol equivalent to ca. 10 wt.% of the overall biodiesel production [3]. With the steady growth of biodiesel industry, huge surplus of glycerol has been currently produced, which makes the price of glycerol depreciate sharply. Moreover, the biomass-derivate glycerol is a nontoxic, edible, and sustainable compound containing highly multifunctional hydroxyl groups, making it as a versatile platform chemical for producing valuable derivatives [2,3]. Accordingly, significant work has been done to the transformation of glycerol by various catalytic processes, such as oxidation [4], hydrogenolysis [5–8], dehydration [9], reforming [10], acetalization [11], and esterification [12]. Among them, one of the most promising approaches is the catalytic hydrogenolysis of glycerol to

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1,2-propanediol (1,2-PDO) which is an important commodity chemical in the production of polyester resins, pharmaceuticals, tobacco humectants, paints, cosmetics, and antifreeze [13]. This process offers a sustainable and economically competitive route for the synthesis of 1,2-PDO from biomass-derived glycerol instead of petroleum-based propylene oxide.

Supported Pt, Ru, Ir, Rh, Pd, Ni, and Cu catalysts have been commonly employed for glycerol hydrogenolysis to 1,2-PDO [14-20]. Despite the high activity of noble metal and Ni-based catalysts, Cu-based catalysts generally afford excellent selectivity for producing 1,2-PDO due to their intrinsic ability to cleave the C–O bond in preference to the C-C bond in glycerol hydrogenolysis, which is regarded as crucial for 1,2-PDO formation. Various supports including SiO<sub>2</sub> [21], MgO [22], ZnO [23], Al<sub>2</sub>O<sub>3</sub> [24], Cr<sub>2</sub>O<sub>3</sub> [13] as well as zeolite [25] have been exhibited for Cu-based catalysts. Bienholz et al. [23] obtained a highly active Cu/ZnO catalyst prepared by oxalate gel method but with strong deactivation in water which was an unavoidable by-product of this reaction. Cu/Cr<sub>2</sub>O<sub>3</sub> [13] was identified as the most effective catalyst for relatively high performance and stability, while the toxic chromium limited its wide application for unresolved environmental issues. Among all the Cu-based catalysts investigated, Cu/SiO<sub>2</sub> [21,26-28] has been extensively studied and attracted considerable attention owing to its excellent selectivity, green benefit, and low cost in glycerol hydrogenolysis to 1.2-PDO. Several techniques [21,26-28] involving sol-gel, impregnation, ion exchange, co-precipitation, precipi-



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tation-deposition, and precipitation gel have been utilized to prepare Cu/SiO<sub>2</sub> catalysts. Nevertheless, there are still numerous technical problems to be addressed or disadvantages that need to be overcome. One of the most complicated issues is insufficient catalytic activity and stability for glycerol hydrogenolysis. Vasiliadou et al. [27] systematically investigated the deactivation behavior of Cu/SiO<sub>2</sub> catalyst in glycerol hydrogenolysis and suggested that the deactivation was mainly attributed to the agglomeration of active metallic phase.

To obtain highly dispersed and stable Cu nanoparticles has been supposed to be a dominant factor in achieving excellent catalytic performance for glycerol hydrogenolysis to 1,2-PDO. Modification of Cu-based catalyst by an effective promoter is needed to improve the catalytic activity and stability owing to the enhanced dispersion of Cu. specific surface area, and interaction between Cu and dopant. Zheng et al. [29] claimed that B<sub>2</sub>O<sub>3</sub>-modified Ni/SiO<sub>2</sub> catalyst possessed high metal dispersion together with suitable acidity and presented outstanding catalytic performance for hydrogenation of ethylbenzene because of the strong interaction between surface nickel and boron species. B<sub>2</sub>O<sub>3</sub> has emerged as a promising candidate for its sintering-resistant property and suitable acidity [29,30]. Appropriate acid components are essential for glycerol hydrogenolysis according to the dehydration-hydrogenation bifunctional mechanism, as elucidated by our previous reports [6,7]. Nevertheless, no literature has been published regarding structure-behavior correlation of B<sub>2</sub>O<sub>3</sub>-modified Cu/SiO<sub>2</sub> catalysts for glycerol hydrogenolysis. Thus, a series of B<sub>2</sub>O<sub>3</sub>-doped Cu/SiO<sub>2</sub> catalysts prepared by precipitation-gel procedure followed by impregnation with boric acid were first reported for selective hydrogenolysis of glycerol to 1,2-PDO. These catalysts were deeply characterized by various techniques including ICP, BET, XRD (in situ XRD), N<sub>2</sub>O chemisorption, H<sub>2</sub>-TPR, NH<sub>3</sub>-TPD, IR, Raman, XPS, and TEM. The structure-activity relationship of these B<sub>2</sub>O<sub>3</sub>-doped Cu/ SiO<sub>2</sub> catalysts in glycerol hydrogenolysis was also discussed in detail.

## 2. Experimental

#### 2.1. Catalyst preparation

The Cu/SiO<sub>2</sub> catalyst with 20 wt.% CuO loading was prepared by precipitation-gel method, according to previous reports [21,26]. A 28 wt.% ammonia (Sinopharm Chemical Reagent Co., Ltd., China (SCRC)) aqueous solution was dripped into  $Cu(NO_3)_2 \cdot 3H_2O$ (0.5 mol/L, SCRC) aqueous solution under vigorous stirring at 80 °C until the pH of mixed solution reached 6.5. Subsequently, a calculated amount of colloidal silica aqueous solution (SiO<sub>2</sub>, 30 wt.%, Qingdao Ocean Chemical CO., Ltd., China) was added into the remaining solution of the precipitate and then a gel was formed. After that, the gel was aged at 80 °C for 4 h, filtrated, washed with hot deionized water for 5 times, and dried overnight at 80 °C to form the powder of Cu/SiO<sub>2</sub> precursor. The B<sub>2</sub>O<sub>3</sub>-modified Cu/SiO<sub>2</sub> catalysts were prepared by incipient wetness impregnation of Cu/SiO<sub>2</sub> precursor with aqueous solutions containing the desired amount of H<sub>3</sub>BO<sub>3</sub> (SCRC). After impregnation, these samples were dried overnight at 80 °C and then calcined at 400 °C in static air for 4 h. The obtained catalysts are designated as xCuB/ SiO<sub>2</sub>, where the x represents the nominal mass loading of boron.

#### 2.2. Catalyst characterization

 $N_2$  adsorption-desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2420 instrument after degassing at 300 °C to remove physically adsorbed impurities for 8 h in vacuum. BET surface area and BJH pore size distribution were calculated according to the desorption branch of the isotherms.

ICP optical emission spectroscopy (Optima2100DV, PerkinElmer) was exhibited to check the chemical compositions of as-prepared samples.

Powder X-ray diffraction (XRD) patterns were recorded with a D2/max-RA X-ray diffractometer (Bruker, Germany) operating with Cu K $\alpha$  radiation at 30 kV and 10 mA with a scanning angle (2 $\theta$ ) ranging from 10° to 90° at the scanning rate of 5°/min. The mean crystallite size of Cu was calculated by Scherrer equation according to the full width at half maximum (FWHM) of Cu (111) diffraction at 2 $\theta$  of 43.2°. For *in situ* XRD measurement, the sample remained in pure H<sub>2</sub> at a flow rate of 30 cm<sup>3</sup> min<sup>-1</sup>. Temperature-ramping programs were exhibited from 25 °C to 150, 200, 250, 300, 350, and 400 °C at a heating rate of 5 °C min<sup>-1</sup>. The XRD patterns were obtained after the sample reached the preset temperature for 30 min.

H<sub>2</sub>-TPR measurements were conducted in Auto Chem. II 2920 equipment (Mircromeritics, USA) using 0.10 g sample for each run. Typically, the catalyst was pretreated in Ar at 150 °C for 30 min and then cooled to 30 °C. Subsequently, the Ar flow was switched to 10% H<sub>2</sub>-Ar mixed gas and a cold trap of 2-propanol-liquid nitrogen slurry was added to condense the water gas. The H<sub>2</sub>-TPR was started from 30 °C to 500 °C at a heating rate of 5 °C/min and simultaneously monitored by a thermal conductivity detector (TCD).

 $N_2O$  chemisorption was carried out in the same apparatus as above. The catalyst sample was placed into a U-shaped quartz tube and reduced according to the same  $H_2$ -TPR procedure described above. The specific surface area of Cu was performed by dissociative  $N_2O$  adsorption on the surface of copper with the pulse titration method based on the following equations: 2Cu  $(s) + N_2O \rightarrow N_2 + Cu_2O$  (s). Pure nitrogen was employed to detect the consumption of  $N_2O$ . The specific surface area of Cu was estimated from the total amount of  $N_2O$  consumption with  $1.46 \times 10^{19}$  copper atoms per square meter.

NH<sub>3</sub>-TPD was performed in the same apparatus as H<sub>2</sub>-TPR. Prior to the adsorption of NH<sub>3</sub>, the catalyst (0.30 g) was pretreated in He at 400 °C to clean the surface from moisture and other adsorbed gases for 1 h. After cooling to 100 °C, the catalyst was saturated with pure NH<sub>3</sub> for 30 min and then purged with He to remove the physisorbed NH<sub>3</sub> for 30 min. Subsequently, the sample was heated to 700 °C at a ramp rate of 5 °C/min and the NH<sub>3</sub> desorption was detected by a mass spectrometer (MS, Agilent).

The IR spectra were carried out on a Vertex 70 (Bruker) FT-IR spectrophotometer in the range of 400–4000 cm<sup>-1</sup>. The powder samples were mixed with KBr (2 wt.%) and pressed into translucent disks at room temperature.

Raman spectroscopy was performed on a Renishaw-UV-vis Raman System 1000 using a CCD detector at room temperature. The 532 nm of the air-cooled frequency-doubled Nd-Yag laser was employed as the exciting source with a power of 30 MW.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (XAES) were measured on a VG MiltiLab 2000 spectrometer with Mg K $\alpha$  radiation and a multichannel detector. Prior to each test, the calcined sample was reduced in H<sub>2</sub> at 250 °C for 2 h. The obtained binding energies were calibrated using the C1s peak at 284.6 eV as the reference. The experiment error was given within ±0.1 eV.

TEM measurement was performed with a JEM-1011 electron microscope operating at an 80 kV voltage. The samples were suspended in ethanol with an ultrasonic dispersion for 20 min and deposited on copper grids coated with amorphous carbon films.

#### 2.3. Catalytic test

Hydrogenolysis of glycerol was performed in a vertical fixedbed reactor (i.d. 12 mm, length 600 mm) made of a stainless steel tube. Typically, 4.0 g catalyst (20–40 mesh) was loaded into the constant temperature section of the reactor between two layers of quartz sand. Prior to each test, the catalyst was *in situ* reduced in flowing H<sub>2</sub> (100 cm<sup>3</sup> min<sup>-1</sup>) at 250 °C for 2 h at atmospheric pressure. After reduction, the system was cooled to 200 °C and pressured to 5.0 MPa. A 10 wt.% glycerol aqueous (or 2-propanol) solution was continuously pumped into the reactor with a high-pressure pump along with co-feeding H<sub>2</sub> of gas flowing at 150 cm<sup>3</sup> min<sup>-1</sup>. The liquid and gas products were condensed and collected in a gas-liquid separator immersed in an ice-water trap.

The liquid products were determined by a gas chromatography (GC, Ruihong chromatogram analysis Co., Ltd., China) using a capillary column (DB-WAX, 30 m  $\times$  0.32 mm) and a flame ionization detector. The tail gas was off-line analyzed by a GC (Huaai chromatogram analysis Co., Ltd., China) using a capillary column (OV-101, 60 m  $\times$  0.25 mm) and a TCD. The obtained products were also identified by GC–MS (6890N, Agilent, USA). The conversion of glycerol and selectivity of products were calculated based on the following equations:

 $\begin{array}{l} \mbox{Conversion (\%)} = \frac{\mbox{moles of glycerol (in)} - \mbox{moles of glycerol (out)}}{\mbox{moles of glycerol (in)}} \\ \times \ 100 \end{array}$ 

Selectivity (%) = 
$$\frac{\text{moles of one product}}{\text{moles of all products}} \times 100$$

# 3. Results

#### 3.1. Characterization of the catalysts

#### 3.1.1. Physicochemical properties of the catalysts

The textural properties derived from N<sub>2</sub> adsorption-desorption isotherms of the Cu/SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>-doped catalysts are listed in Table 1. It can be observed that the BET surface area and average pore volume decreased obviously with increasing B<sub>2</sub>O<sub>3</sub> loading, while the average pore size enhanced. This may be attributed to pore blockage caused by B<sub>2</sub>O<sub>3</sub> molecules which are small enough to enter micropores of Cu/SiO<sub>2</sub>. As shown in Table 1, the bulk weight loadings of Cu and B elements determined by ICP test were close to the nominal values, despite small discrepancy owing to the loss in washing procedure. The dissociative N<sub>2</sub>O chemisorption (Table 1) on the reduced catalyst was to determine the Cu dispersion, specific surface area, and particle size. Doping B<sub>2</sub>O<sub>3</sub> to Cu/SiO<sub>2</sub> catalysts decreased Cu particle size significantly and simultaneously increased Cu dispersion and surface area remarkably. The role of B<sub>2</sub>O<sub>3</sub> in enhancing the dispersion was consistent well with the case of Ni-B/SiO<sub>2</sub> [29]. This tendency is explained by the fact that B<sub>2</sub>O<sub>3</sub> can be instrumental in preventing thermal transmigration and aggregation of Cu nanoparticles during the calcination and reduction, which may relate to the strong interaction between copper and boron species. Among them, 3CuB/SiO<sub>2</sub> afforded the highest Cu dispersion (23.9%) and lowest particle size (4.2 nm). However, further increase in  $B_2O_3$  loading (5CuB/SiO<sub>2</sub>) declined the Cu dispersion mildly, which was most probably ascribed to partial covering effect of surplus  $B_2O_3$  on the Cu surface (see below) [30].

#### 3.1.2. Structural properties of the catalysts

The XRD patterns of Cu/SiO<sub>2</sub> catalysts with different B<sub>2</sub>O<sub>3</sub> loadings after the calcination at 400 °C are displayed in Fig. 1A. The diffraction peaks at around 35.6° and 38.8° are assigned to CuO phase [31]. With the increasing  $B_2O_3$  loading, the intensity of diffraction peaks for CuO declined notably, and the peak width broadened gradually. These results meant that the crystallization degree of CuO and particle size calculated by Scherrer equation monotonically decreased with an increase in B<sub>2</sub>O<sub>3</sub> content. Moreover, the introduction of B<sub>2</sub>O<sub>3</sub> resulted in a slight shift of CuO diffraction peaks toward higher  $2\theta$  values. A detailed study of the predominant 32.0-42.0° reflections confirmed this effect, showing the continuous shift toward lower lattice parameters with an increase in boron content. This behavior was indicative of structure defects on the surface which might be originated from the incorporation of partial B<sup>3+</sup> into Cu<sup>2+</sup> cation [31]. Almost no peaks of B<sub>2</sub>O<sub>3</sub> were detected, most probably due to the homogeneous distribution of  $B_2O_3$  on the surface. Interestingly, only 5CuB/SiO<sub>2</sub> catalyst presented weak characteristic diffraction peak at 27.8° corresponding to B<sub>2</sub>O<sub>3</sub> [30], reflecting that surplus B<sub>2</sub>O<sub>3</sub> formed crystalline particle on the surface and covered partial cupreous species, as deduced by N<sub>2</sub>O chemisorption. In addition, a broad and diffuse diffraction peak centered at about 21.7° was observed for all the catalysts, which was assigned to amorphous SiO<sub>2</sub> [21].

The XRD patterns of Cu/SiO<sub>2</sub> with various B<sub>2</sub>O<sub>3</sub> contents after ex situ reduction at 250 °C were also checked. To prevent and diminish phase transformation that likely proceeded during exposure to air, the reduced samples were carefully collected and preserved in liquid paraffin at room temperature and sealed in glass bottles until XRD analysis. As compiled in Fig. 1B, for all the catalysts the broad and diffuse overlapping peak at around 19.3° was attributed to the collective contribution of amorphous silica and paraffin [21]. After reduction, the XRD diffraction peaks of CuO disappeared, while the peaks at around 43.2°, 50.4°, and 74.1° attributed to Cu emerged in these catalysts [32]. The Cu characteristic peaks enlarged and their intensities diminished apparently as a result of B<sub>2</sub>O<sub>3</sub> doping. The average Cu particle size calculated by Scherrer equation declined gradually from 17.6 nm for Cu/SiO<sub>2</sub> to 4.2 nm for 5CuB/SiO<sub>2</sub>. Due to the weak interaction between copper species and silica support, the copper particles tended to mobilize and aggregate to larger particles during the calcination and reduction processes. In contrast, the incorporation of B<sub>2</sub>O<sub>3</sub> was capable of controlling the growth of Cu particle size upon heat treatment, which led to the improved dispersion of Cu species. On the other hand, generally the average Cu particle size based on XRD was higher than that of N<sub>2</sub>O chemisorption. The nanoparticles below 4 nm cannot be detected by XRD, which can affect the accuracy

Table 1

The physicochemical properties and chemical compositions of B2O3-doped Cu/SiO2 catalysts.

Catalyst	$S_{BET} (m^2 g^{-1})$	D <sub>pore</sub> (nm)	$V_{\rm pore}~({\rm cm}^3{\rm g}^{-1})$	Cu content (wt.%) <sup>a</sup>	B content (wt.%) <sup>a</sup>	$d_{Cu} (nm)^{b}$	Cu dispersion (%) <sup>c</sup>	S <sub>Cu</sub> <sup>c</sup>	$d_{Cu} (nm)^{c}$
Cu/SiO <sub>2</sub>	146.6	8.8	0.392	14.65	0	17.6	7.7	7.6	13.0
0.5CuB/SiO <sub>2</sub>	117.4	9.2	0.380	14.31	0.50	14.2	13.7	12.9	7.3
1CuB/SiO <sub>2</sub>	104.7	9.3	0.348	13.88	1.06	12.3	15.8	15.7	6.3
3CuB/SiO <sub>2</sub>	98.8	10.9	0.337	13.95	2.73	6.8	23.9	23.6	4.2
5CuB/SiO <sub>2</sub>	92.5	11.1	0.294	13.52	4.59	4.2	22.1	20.2	4.5

<sup>a</sup> Determined by ICP.

<sup>b</sup> Average Cu particle size calculated by XRD.

 $^{\rm c}\,$  Determined by  $N_2O$  chemisorption.



Fig. 1. XRD patterns of B<sub>2</sub>O<sub>3</sub>-doped Cu/SiO<sub>2</sub> catalysts upon (A) calcination; (B) reduction.

[33]. This may explain the discrepancy between XRD and  $N_2O$  chemisorption results.

To further explore the phase evolution of representative Cu/SiO<sub>2</sub> and 3CuB/SiO<sub>2</sub>, the in situ XRD technique was exhibited in flowing H<sub>2</sub> under different reduction temperatures. As illustrated in Fig. S1 (in the Supplementary material), the Cu/SiO<sub>2</sub> sample displayed two obvious peaks at ca. 35.6° and 38.8° characteristic of CuO at 25 °C. These two peaks became remarkably weak while new peaks at ca. 43.2°, 50.4°, and 74.1° characteristic of Cu appeared with the increasing temperature to 150 °C. With continuous increasing reduction temperature, these metallic Cu characteristic peaks sharpened gradually, due to the inevitable sintering and aggregation of copper particles upon heat treatment. Based on Scherrer equation, the mean copper particle size significantly increased from 15.7 to 25.5 nm, when the reduction temperature enhanced from 200 to 400 °C. Similar trend of phase evolution has been observed in the case of 3CuB/SiO<sub>2</sub> (Fig. S2). Nevertheless, the mean copper particle size grew moderately from 4.2 to 7.8 nm with the increasing temperature from 200 to 400 °C, indicating that the  $B_2O_3$  played a role in immobilizing copper species and suppressing sintering of Cu nanoparticles upon heat treatment.

Interestingly, it has been observed that the calcined  $Cu/SiO_2$  sample presented mainly dark color while the color of  $B_2O_3$ -doped samples gradually became blue with the increasing  $B_2O_3$  content (Fig. S3), indicating the appearance of at least two copper species

due to B<sub>2</sub>O<sub>3</sub> doping. To gain further insight into the structure information, the FTIR spectra of these calcined samples were conducted. As shown in Fig. 2, the Cu/SiO<sub>2</sub> sample displayed three characteristic bands which centered at 1110, 800, and 470 cm<sup>-1</sup> corresponding to the various vibration modes of Si-O bonds in the amorphous SiO<sub>2</sub> [21]. Compared to bulk SiO<sub>2</sub>, these bands still preserved and actually unchanged even addition of B<sub>2</sub>O<sub>3</sub> to Cu/SiO<sub>2</sub>, revealing the weak interaction between CuO and SiO<sub>2</sub>, consistent well with the Raman results (see below). A weak band centered at 670 cm<sup>-1</sup> was ascribed to cupric phyllosilicate over Cu/SiO<sub>2</sub> sample [34]. The intensity ratio for IR bands at 670 and 800 cm<sup>-1</sup> enhanced continuously with the increasing B<sub>2</sub>O<sub>3</sub> loading, suggesting that the relative content of cupric phyllosilicate to amorphous silica improved gradually. The cupric phyllosilicate which is a kind of copper silicate with lamellar structure may originate from the unique precipitation-gel method. The structure is formed through the reaction of Cu<sup>2+</sup> complex with the silanol groups of silica surface via hydrolytic adsorption to produce = SiOCu<sup>II</sup> monomer and consecutive polymerization [34]. Addition of B<sub>2</sub>O<sub>3</sub> into Cu/SiO<sub>2</sub> may facilitate to stabilize this complex on the surface that would decompose to form cupric phyllosilicate upon calcination at 400 °C. Therefore, it can be inferred that the black color was attributed to the CuO species while the blue color was due to the formation of partial cupric phyllosilicate on the surface. Meanwhile, the band at approximately 1420 cm<sup>-1</sup> appeared and the intensity in-

400 600 800 1000 1200 1400 1600 1800 2000 Wavenumber (cm<sup>-1</sup>)

1100

1420

f

e

d c

Fig. 2. FTIR spectra of calcined (a) SiO<sub>2</sub>, (b) Cu/SiO<sub>2</sub>, (c) 0.5CuB/SiO<sub>2</sub>, (d) 1CuB/SiO<sub>2</sub>, (e) 3CuB/SiO<sub>2</sub>, and (f) 5CuB/SiO<sub>2</sub>.

creased with the increasing boron content, which was assigned to the vibration of  $B_2O_3$  [35].

The Raman spectra of  $Cu/SiO_2$  catalysts with and without  $B_2O_3$ dopants are illustrated in Fig. 3. For comparison, the Raman spectra of bulk CuO were also examined, which presented three characteristic bands at 293, 340 and 627 cm<sup>-1</sup>, respectively [36]. For  $B_2O_3$ free Cu/SiO<sub>2</sub> catalyst, these characteristic bands remained and practically unchanged, suggesting that CuO and SiO<sub>2</sub> did not interact substantially. However, these bands underwent obvious shift toward lower wavenumbers and widened gradually with the increasing boron content. Specifically, the vibration band in  $A_g$ mode of CuO [36] ranged from 293 cm<sup>-1</sup> for Cu/SiO<sub>2</sub> to 282 cm<sup>-1</sup> for 5CuB/SiO<sub>2</sub>. These features could be related to the structure defects generated by incorporation of heterovalent atoms [36]. The incorporation of smaller ions (B3+) into CuO structure and consequent lattice contraction of CuO as well as Cu-O vibration frequency may induce shift in the CuO characteristic band position, as evidenced by XRD measurements. The generation of surface defects in the CuO structure due to the incorporation of B<sup>3+</sup> was indicative of the existence of close contact between copper and boron



Fig. 3. Raman spectra of bulk CuO and calcined B<sub>2</sub>O<sub>3</sub>-doped Cu/SiO<sub>2</sub> catalysts.



Fig. 4. H<sub>2</sub>-TPR profiles of B<sub>2</sub>O<sub>3</sub>-doped Cu/SiO<sub>2</sub> catalysts.

species on the support surface, reflecting the strong CuO and  $B_2O_3$  interaction. Moreover, it can be observed that only the 5CuB/SiO<sub>2</sub> emerged two bands at 143 and 247 cm<sup>-1</sup> corresponding to  $B_2O_3$  [35], suggesting that the  $B_2O_3$  species were highly dispersed on the surface in the other modified catalysts, in agreement with the XRD results.

#### 3.1.3. Reducibility and surface acidic properties

In order to explore the reduction behavior of these catalysts, the H<sub>2</sub>-TPR technique was measured. As displayed in Fig. 4, the Cu/SiO<sub>2</sub> sample presented an asymmetric reduction peak, implying at least two different Cu species, which can be deconvoluted into two peaks centered at about 165 and 236 °C, respectively. All the TPR patterns of these samples can be roughly divided in two reductive peaks which were designated as low-temperature peak  $\alpha$  and high-temperature peak  $\beta$ , respectively. Irrespective of peak  $\alpha$  or β, these peaks shifted toward higher temperature with the increasing B<sub>2</sub>O<sub>3</sub> content, most presumably owing to the strong interaction between CuO and B<sub>2</sub>O<sub>3</sub>. According to previous reports [26,31,36], the low temperature peak can be assigned to the reduction of highly dispersed CuO with small nanoparticles while the high-temperature peak can be related to the reduction of bulk CuO with large size. Thus, the copper species in Cu/SiO<sub>2</sub> sample was mainly present in the form of bulk CuO, indicating the weak meal-support interaction, which was probably stemmed from the poor interaction between the precipitated species copper hydroxide and the surface of silica support [21]. With the promotion of  $B_2O_3$ , the peak area of low-temperature peak  $\alpha$  was elevated considerately, reflecting that addition of B<sub>2</sub>O<sub>3</sub> was beneficial for the formation of large amounts of highly dispersed CuO nanoparticles. This may be associated with the close contact between CuO and  $B_2O_3$  on the SiO<sub>2</sub> surface, which facilitates to inhibit the aggregation of copper species and form small nanoparticles upon heat treatment. The nanoparticles possessing a lower average CuO size presented kinetically faster reduction than that of bulk CuO. Indeed, the H<sub>2</sub>-TPR results demonstrate that there is strong interaction between copper and boron species, consistent with the Raman spectra results.

It is well established that the acidity plays an important role in determining the catalytic performance of glycerol hydrogenolysis on the basis of bi-functional reaction mechanism [6,14,37]. Thus, the accessible surface acidic sites of these catalysts were probed by NH<sub>3</sub>-TPD. As shown in Fig. 5, the NH<sub>3</sub>-TPD profile of Cu/SiO<sub>2</sub> catalyst presented a broad peak centered at 375 °C, indicating that

470

Absorbance

670 800



Fig. 5. NH<sub>3</sub>-TPD profiles of B<sub>2</sub>O<sub>3</sub>-doped Cu/SiO<sub>2</sub> catalysts.

medium acid sites existed on the catalyst surface [30]. The NH<sub>3</sub> desorption peak area improved gradually with the enhancement of boron content, maximized on 3CuB/SiO<sub>2</sub>, and then decreased slightly. Meanwhile, the NH<sub>3</sub> desorption temperature shifted toward higher temperature with an increase in boron loading. Thus, it can be inferred that addition of boron species increased acidic amount and also enhanced acidic strength, in well agreement with the previous reports [29,38].

#### 3.1.4. Surface chemical states

XPS analysis was used to identify surface chemical states after reduction and the compositions of these catalysts; the results are summarized in Table 2. According to previous reports [32,39], the Cu<sup>+</sup> was almost not detected for all the catalysts, as indicated by XAES spectra. Therefore, the two peaks (Fig. 6A) centered at ca. 932.5 and 952.5 eV were mainly ascribed to Cu 2p<sub>3/2</sub> and Cu  $2p_{1/2}$  peaks of Cu<sup>0</sup>, respectively [30,39]. Meanwhile, at all cases the absence of satellite peaks at 944–945 eV related to Cu<sup>2+</sup> were observed [39], suggesting that the Cu<sup>2+</sup> species (from copper oxide and cupric phyllosilicate) were reduced completely, consistent with the XRD results. As shown in Fig. 6B, the B 1s peak at about 193.5 eV was indicative of B<sup>3+</sup>. The lack of a peak at 188.7 eV revealed that no B<sup>0</sup> was present, which was different from the report by Zhao et al. [32]. The disparity may stem from the different reduction procedure as Zhao et al. used 350 °C as reduction temperature at which partial  $B^{3+}$  can be reduced to  $B^{0}$ .

As listed in Table 2, there was almost no variation in the binding energy of Si 2p. The Cu  $2p_{3/2}$  peak shifted to higher binding energy when adding  $B_2O_3$  to Cu/SiO<sub>2</sub>, while the B 1s moved to lower binding energy. The diminishing electron density in the Cu<sup>0</sup> nucleus arose from the electron scavenging property of  $B_2O_3$  [30]. Thus, an electron donor–acceptor interaction between Cu and  $B_2O_3$  may occur on the silica surface. These results demonstrated the existence of strong interaction between copper and boron species wherein the electron likely transferred from Cu<sup>0</sup> to B<sup>3+</sup>. Additionally, despite

#### Table 2

XPS results for  $B_2O_3$ -doped Cu/SiO<sub>2</sub> catalysts.



Fig. 6. Cu 2p (A) and B 1s (B) XPS photoemission peaks of reduced  $B_2O_3\text{-doped}$  Cu/  $SiO_2$  catalysts.

almost the same bulk Cu loading, the surface concentration of Cu over Cu/SiO<sub>2</sub> increased greatly due to  $B_2O_3$  doping, indicating that the incorporation of  $B_2O_3$  apparently enhanced Cu dispersion and thus generated more active sites, in well line with N<sub>2</sub>O chemisorption results. The Cu/B atomic molar ratio estimated from XPS analysis was much lower than the values determined by ICP test. The low detection of Cu on the surface was possibly ascribed to the fact that partial Cu species were covered by  $B_2O_3$  as a consequence of the unique preparation method, which was also in accordance with the results deduced by N<sub>2</sub>O chemisorption.

### 3.2. Catalytic performance of the catalysts

The catalytic performance of  $B_2O_3$ -doped Cu/SiO<sub>2</sub> catalysts was tested in a continuous fixed-bed reactor at 200 °C and 5.0 MPa

Catalyst	Binding energy (eV)			Surface element	Cu/B molar ratio	
	Cu 2p <sub>3/2</sub>	B 1s	Si 2p	Cu	В	
Cu/SiO <sub>2</sub>	932.5	-	103.4	2.9	-	_
0.5CuB/SiO <sub>2</sub>	932.7	193.5	103.4	3.5	3.0	1.2 (4.9) <sup>a</sup>
1CuB/SiO <sub>2</sub>	932.8	193.4	103.4	4.4	4.2	1.0 (2.2)
3CuB/SiO <sub>2</sub>	932.9	193.2	103.4	5.1	6.4	0.80 (0.87)
5CuB/SiO <sub>2</sub>	933.0	193.1	103.4	4.5	11.0	0.41 (0.50)

<sup>a</sup> Values in parenthesis are determined by ICP test.

Table 3
Catalytic performance of glycerol hydrogenolysis over different catalysts. <sup>a</sup>

Catalyst	TOF <sup>b</sup> (h <sup>-1</sup> )	Conversion (%)	Selectivity (%)			
			1,2- PDO	Acetol	EG	Others <sup>c</sup>
Cu/SiO <sub>2</sub> 0.5CuB/ SiO <sub>2</sub>	0.88 1.24	62.1 83.3	89.5 92.1	6.0 3.6	2.6 1.2	1.9 3.1
1CuB/SiO <sub>2</sub> 3CuB/SiO <sub>2</sub> 5CuB/SiO <sub>2</sub>	1.38 1.53 1.47	91.3 100 98.5	94.7 98.0 96.7	2.1 0.5 1.3	1.0 0.3 0.6	2.2 1.2 1.4

 $^a$  Reaction conditions: 200 °C, 5.0 MPa, 10 wt.% glycerol aqueous solution,  $H_2/$  glycerol = 123:1 (molar ratio), WHSV = 0.075  $h^{-1}.$ 

<sup>b</sup> TOF is moles of glycerol converted per mole of surface Cu sites and per hour. Reaction conditions: 200 °C, 5.0 MPa, 10 wt.% glycerol aqueous solution,  $H_2/glyc$ -erol = 123:1 (molar ratio), WHSV = 0.3  $h^{-1}$ .

<sup>c</sup> Others include ethanol, methanol, propane, etc.

using water as solvent; the results are summarized in Table 3. For B<sub>2</sub>O<sub>3</sub>-free Cu/SiO<sub>2</sub> catalyst, the conversion of glycerol and selectivity to 1,2-PDO were 62.1% and 89.5%, respectively. As B<sub>2</sub>O<sub>3</sub> was introduced into Cu/SiO<sub>2</sub> catalysts, the catalytic activity and 1,2-PDO selectivity were improved significantly. Among the catalysts employed, the 3CuB/SiO<sub>2</sub> catalyst achieved the superior performance, up to complete glycerol conversion with 98.0% 1,2-PDO selectivity, which is among the best reported results for the previous Cu-based catalysts [21-25,28]. However, further increase in B<sub>2</sub>O<sub>3</sub> amount resulted in minor decline of conversion and 1,2-PDO selectivity. Turnover frequency (TOF) is calculated to reflect the intrinsic activity; the results are also listed in Table 3. Compared to Cu/SiO<sub>2</sub>, the addition of B<sub>2</sub>O<sub>3</sub> increased TOF dramatically. The  $3CuB/SiO_2$  catalyst achieved the highest TOF, up to  $1.53 h^{-1}$ , which was superior or at least compared to the previous Cu/SiO<sub>2</sub> catalysts [21,28]. The combined results clearly confirmed the high efficiency of B<sub>2</sub>O<sub>3</sub>-modified Cu/SiO<sub>2</sub> catalyst. Concurrently, the selectivity to acetol diminished with the increasing B<sub>2</sub>O<sub>3</sub> loading. minimized on 3CuB/SiO<sub>2</sub>, and then increased slightly. The introduction of B<sub>2</sub>O<sub>3</sub> into Cu/SiO<sub>2</sub> impaired the selectivity of ethylene glycol (EG), indicating that the C-C cleavage reaction was suppressed to some extent, which was related to the increased acidity [40].

As stability was critical for the practical application for glycerol hydrogenolysis, the long-term performance of representative Cu/ $SiO_2$  and  $3CuB/SiO_2$  catalysts was conducted. As shown in Fig. 7, the Cu/ $SiO_2$  catalyst presented serious deactivation after only



**Fig. 7.** The long-term performance of Cu/SiO<sub>2</sub> and 3CuB/SiO<sub>2</sub> catalysts. Reaction conditions: 200 °C, 5.0 MPa, 10 wt.% glycerol aqueous solution (or 2-propanol), H<sub>2</sub>/ glycerol = 123:1 (molar ratio), WHSV = 0.075 h<sup>-1</sup>.



Fig. 8. XRD patterns of spent Cu/SiO<sub>2</sub> and 3CuB/SiO<sub>2</sub> catalysts.

24 h, when using water as solvent. Contrarily, the 3CuB/SiO<sub>2</sub> catalyst can stabilize to 56 h under the identical reaction conditions. However, further prolonging reaction time led to distinct decrease in glycerol conversion. Bienholz et al. [23] asserted that water can cause serious aggregation of Cu nanoparticles and result in a tremendous loss of copper surface area. Similar results have been obtained in our B<sub>2</sub>O<sub>3</sub>-modified Cu/SiO<sub>2</sub> catalysts, as evidenced by XRD and TEM techniques. As illustrated in Fig. 8, the Cu particle size of spent Cu/SiO<sub>2</sub> after 33 h in water increased remarkably from 17.6 to 34.2 nm owing to the significant agglomeration of copper species. In contrast, the Cu particle size of spent 3CuB/SiO<sub>2</sub> catalyst grew moderately from 6.8 to 12.1 nm despite with longer reaction time (72 h). The TEM results of spent catalysts are displayed in Fig. 9, which can give direct information on the distribution of Cu particles and morphology. Big copper particles with an average diameter up to 30 nm were present over spent Cu/SiO<sub>2</sub>, consistent well with the XRD results. Furthermore, the majority of them underwent extremely serious aggregation and formed irregularly shaped large clusters. Compared with spent Cu/SiO<sub>2</sub>, the large amounts of copper nanoparticles were homogenously distributed on 3CuB/SiO<sub>2</sub>, while some of them moderately aggregated. The above results indicated that B<sub>2</sub>O<sub>3</sub> can be instrumental in controlling the Cu particle size and suppressing the aggregation of copper species during the reaction.

To address this issue, the glycerol hydrogenolysis was performed over 3CuB/SiO<sub>2</sub> using 2-propanol as solvent. As shown in Fig. 7, no obvious decline in the activity was observed even after 150 h time-on-stream over 3CuB/SiO<sub>2</sub> catalyst. Concurrently, the product distribution did not show any appreciable fluctuation during the complete test. These results demonstrated that the 3CuB/ SiO<sub>2</sub> catalyst was rather robust under 2-propanol solvent for glycerol hydrogenolysis. As shown in Fig. 8, the mean Cu particle size of spent 3CuB/SiO<sub>2</sub> in 2-propanol solvent only grew mildly up to 9.6 nm. In addition, the Cu nanoparticles in TEM image (Fig. 9C) were spherical and distributed uniformly on the surface without obvious aggregation. It can be concluded that the solvent had important impact on the stability of Cu-based catalysts, in well line with the report by Bienholz et al. [23].

#### 4. Discussion

# 4.1. The effect of $B_2O_3$ doping on the structural and surface features of $Cu/SiO_2$ catalysts

It is generally accepted that B<sub>2</sub>O<sub>3</sub> is considered as an additive of thermal stability and applied widely for various catalysts



Fig. 9. TEM images of spent (A) Cu/SiO<sub>2</sub> using water as solvent, (B) 3CuB/SiO<sub>2</sub> using water as solvent, and (C) 3CuB/SiO<sub>2</sub> using 2-propanol as solvent.

[29,41,42]. The quantum mechanics calculations reveal that boron atoms are thermodynamically stable at step and subsurface sites over CoB/Al<sub>2</sub>O<sub>3</sub> catalyst under Fischer-Tropsch synthesis conditions which are even harsher than ours [41]. However, the underlying mechanism by which the stabilizing effect occurs is still subject to some debate. In the presence of Ni-B/SiO<sub>2</sub> catalyst prepared by sol-gel approach. Zheng et al. [29] ascribed the enhancement in the dispersion of active species to the strong interaction between surface Ni and B<sub>2</sub>O<sub>3</sub>. On the other hand, Tupabut et al. [42] claimed that the strong interaction between Co<sub>3</sub>O<sub>4</sub> and support MCM-41 induced by B<sub>2</sub>O<sub>3</sub> doping can suppress sintering of Co<sub>3</sub>O<sub>4</sub> particles and improve the dispersion of active species. In a series of research on CuB/HMS catalysts by Yin et al. [38], boron loading, boron source, and the preparation method were found to affect Cu particle size and catalytic performance of dimethyl oxalate hydrogenation. They argued that B<sub>2</sub>O<sub>3</sub> can make Cu-based catalysts expose more active sites or a synergetic effect may lie in between the copper and boron species. It seems that all of them provide plausible explanations which are highly dependent on the catalytic systems and preparation methods.

In our case, the stabilizing effect of  $B_2O_3$  on copper species can be explained as follows. Firstly, the strong interaction between copper and boron species is capable of retarding the aggregation of copper species as well as the growth of crystalline particles during the processes of calcination, reduction and reaction, which results in remaining high dispersion of copper species. Based on FTIR, Raman and TPR results, the interaction between CuO and support SiO<sub>2</sub> is rather weak, which readily leads to the transmigration of copper species and further coagulation during thermal treatment. Contrarily, as revealed by Raman, XPS and TPR results, the strong interaction between copper and boron species can effectively confine the lateral growth of Cu nanoparticles and improve thermal stability, even in hydrothermal reaction. He et al. [30] have proposed that the acidity and electron affinity of  $B_2O_3$  are higher than that of SiO<sub>2</sub>, which is favorable to the formation of strong interaction between copper and boron species. Secondly, addition of B<sub>2</sub>O<sub>3</sub> to Cu/SiO<sub>2</sub> catalysts facilitates to induce the generation of cupric phyllosilicate which can provide more stable copper species during the course of reduction [32,34]. Note that all the spent catalysts presented red and the blue color disappeared, confirming that the blue cupric phyllosilicate can be reduced to red copper. This was also verified by undetectable Cu<sup>2+</sup> from XPS. The cupric phyllosilicate species cannot only enhance the dispersion of copper species, but also stabilize the active species during heat treatment. Finally, the doping of B<sub>2</sub>O<sub>3</sub> positively generates new surface defects which are typically more reactive than fully coordinated species, consistent well with the report by Zhao et al. [32]. The XRD and Raman characterization results implied that partial Cu<sup>2+</sup> was likely substituted by B<sup>3+</sup>, which can affect planes, corner, and edge atoms, correspondingly change both surface structure and electronic property and eventually form new surface defects. Natesakhawat et al. [39] suggested that surface defects contained coordinately unsaturated sites and were more reactive in CO<sub>2</sub> hydrogenation to methanol. Guo et al. [31] indicated that the new formation of surface defects can hinder the crystallization of catalyst components and growth of crystal grain over La-doped Cu/ZrO<sub>2</sub> catalyst.

On the other hand, the partial surface Cu might be occupied by boron species on the surface, as evidenced by XPS results. Additionally,  $B_2O_3$  can also be utilized to adjust acidity. Likewise, the improvement of boron oxide in acidic property has been demonstrated by others [29,38]. Moreover, the introduction of  $B_2O_3$  also affected BET surface area and pore size distribution to some extent, although the nature of mesoporous material was not changed.

# 4.2. The effect of $B_2O_3$ doping on the catalytic behavior of Cu/SiO<sub>2</sub> catalysts

Bienholz et al. [28] proposed that there was a linear relationship between the copper specific surface area and catalytic performance of glycerol hydrogenolysis, irrespective of the preparation proce-



**Fig. 10.** 1,2-PDO yield and copper dispersion as a function of copper surface area for the  $B_2O_3$ -doped Cu/SiO<sub>2</sub> catalysts. Reaction conditions: 200 °C, 5.0 MPa, 10 wt.% glycerol aqueous solution,  $H_2$ /glycerol = 123:1 (molar ratio), WHSV = 0.075 h<sup>-1</sup>.

dure, additive, and support. For Cu-based catalysts, the similar linear correlation between activity and copper surface area has also been widely reported, including dimethyl oxalate hydrogenation [43], 5-methylfurfuryl alcohol hydrogenolysis [44], and carbon dioxide hydrogenation to methanol [39]. Thereby, the metallic copper surface area was supposed to be the predominant factor in the structure–activity relationship for Cu-based catalysts during glycerol hydrogenolysis. Accordingly, the best catalytic performance of optimal  $3CuB/SiO_2$  (Table 3) was tentatively ascribed to the most Cu surface area and highest Cu dispersion which could be originated from the formation of abundant highly dispersed Cu nanoparticles due to  $B_2O_3$  modification.

To gain further insight into the nature of active species in glycerol hydrogenolysis over  $B_2O_3$ -doped Cu/SiO<sub>2</sub> catalysts, we attempted to correlate 1,2-PDO yield at 200 °C with the Cu surface area determined by N<sub>2</sub>O chemisorption. As compiled in Fig. 10, a closely linear relationship between 1,2-PDO yield and Cu surface area was obtained, giving clear evidence that metallic Cu involved as the active site in glycerol hydrogenolysis. The surface metallic Cu site density was mainly responsible for the catalytic activity, which can offer a rational explanation for the boron content effect on the catalytic performance. Moreover, it is expected that the Cu dispersion and specific surface area are strongly correlated because the dispersion is inversely proportional to the radius of spherical particle [39], as confirmed by TEM.

Based on the above discussion, it is reasonably to infer that the TOF value may have obvious correlation with Cu particle size. As illustrated in Fig. 11, the TOF value linearly declined with the increasing Cu particle size over these catalysts, providing direct evidence that glycerol hydrogenolysis was a structure-sensitive reaction [27]. However, these results cannot rule out the role of other factors, such as the textural properties, chemical environmental of copper species and surface acid sites, which may also affect the catalytic behavior of glycerol hydrogenolysis.

It is well-known that glycerol hydrogenolysis to 1,2-PDO proceeds dehydration of glycerol primary hydroxyl group to acetol and subsequent hydrogenation [6]. Our previous report [45] revealed that an approximately stoichiometric relationship was existed between acetol and 1,2-PDO. Similar tendency was also obtained over  $B_2O_3$ -modified Cu/SiO<sub>2</sub> catalysts. As shown in Table 3, addition of  $B_2O_3$  to Cu/SiO<sub>2</sub> catalyst improved 1,2-PDO selectivity moderately at the expense of acetol, implying that the surplus acetol over Cu/SiO<sub>2</sub> can be converted into 1,2-PDO. This can be explained by the enhanced surface Cu species due to  $B_2O_3$  doping. Thereby, it can be inferred that the  $B_2O_3$ -free Cu/SiO<sub>2</sub> catalyst in the cu/SiO<sub>2</sub> catalyst in the surplus acetol by the enhanced surface Cu species due to  $B_2O_3$  doping. Thereby, it can be inferred that the  $B_2O_3$ -free Cu/SiO<sub>2</sub> catalyst in the cu/SiO<sub>2</sub> catalyst in the cu/SiO<sub>2</sub> catalyst is curved to the cu/SiO<sub>2</sub> catalyst in the surplus acetol by the enhanced surface Cu species due to  $B_2O_3$  doping. Thereby, it can be inferred that the curve cu/SiO<sub>2</sub> catalyst in the curve curv



**Fig. 11.** TOF value as a function of copper particle size for the  $B_2O_3$ -doped Cu/SiO<sub>2</sub> catalysts. Reaction conditions: 200 °C, 5.0 MPa, 10 wt.% glycerol aqueous solution,  $H_2$ /glycerol = 123:1 (molar ratio), WHSV = 0.3 h<sup>-1</sup>.

alyst could provide enough acidic sites to proceed dehydration of glycerol, while lacking adequately available surface copper sites to undergo hydrogenation, which led to the formation of much acetol. Furthermore, the linear correlation between 1,2-PDO yield with Cu surface area also indicates that acetol hydrogenation over active copper sites may be the rate-determining step [46]. However, the surface acidic sites play indispensable role in glycerol hydrogenolysis as they can protonate the hydroxyl group of glycerol and promote glycerol dehydration. To sum up, the optimal catalytic activity of 3CuB/SiO<sub>2</sub> is supposed to be the combined contribution of the most surface Cu sites and acidic sites.

# 4.3. The effect of $B_2O_3$ doping on the stability of Cu/SiO<sub>2</sub> catalysts

It is well established that Cu-based catalysts are susceptible to agglomeration of active metallic phase during glycerol hydrogenolysis in aqueous solution, which is the primary factor for strong deactivation [23,27,47,48]. Accordingly, a number of additives including ZnO [47], Ru [27], Ga<sub>2</sub>O<sub>3</sub> [48], and Cr<sub>2</sub>O<sub>3</sub> [13] have been employed to immobilize copper particle size. The stability of copper catalysts can be distinctly improved by  $B_2O_3$  doping, such as in the hydrogenation of dimethyl oxalate [30]. As mentioned above, the strong interaction between copper and boron species was supposed to stabilize active copper species and suppress surface transmigration of small nanoparticles during glycerol hydrogenolysis, resulting in good catalytic stability (Fig. 7). Moreover, the formation of cupric phyllosilicate also favored to provide stable copper nanoparticles upon reduction, which may play a role in improving the stability.

However, the frequent transition of copper species induced by water presumably impaired the strong interaction between copper and boron species and led to the accelerated sintering of copper nanoparticles [30], which finally caused the deactivation of 3CuB/SiO<sub>2</sub>. Contrarily, the 3CuB/SiO<sub>2</sub> catalyst presented extremely excellent stability in 2-propanol solvent. The combined results indicated that the reaction solvent played a key role in preventing the aggregation of copper species. Recently, Zhou et al. [49] concluded that sintering due to the combined contribution of water, hydrogen, glycerol, temperature, and duration was responsible for the deactivation of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst in glycerol hydrogenolysis. Based on our results, it can be speculated that the deactivation was mainly attributed to water and reaction duration for Cu-based catalysts.

# 5. Conclusions

It has been demonstrated that the  $B_2O_3$  dopant can substantially interact with copper species, induce the formation of cupric phyllosilicate, and generate surface defects, which can be instrumental in preventing the aggregation of Cu nanoparticles and promoting the dispersion of copper species upon heat treatment and reaction.

Addition of suitable  $B_2O_3$  to Cu/SiO<sub>2</sub> catalyst pronouncedly enhanced the activity, 1,2-PDO selectivity, and stability for glycerol hydrogenolysis. Among the catalysts tested, 3CuB/SiO<sub>2</sub> afforded the best catalytic performance, up to complete conversion with 98.0% 1,2-PDO selectivity. The close linear relationship between 1,2-PDO yield and copper surface area revealed that the active Cu surface area was predominantly responsible for the catalytic behavior of glycerol hydrogenolysis. Moreover, glycerol hydrogenolysis was structure-sensitive, as corroborated by the strong correlation between TOF value with Cu particle size.

Compared to Cu/SiO<sub>2</sub>, the 3CuB/SiO<sub>2</sub> catalyst exhibited superior long-term performance when using water as solvent, which was mainly related to the stabilizing effect of B<sub>2</sub>O<sub>3</sub> on Cu nanoparticles and strong interaction between copper and boron species. Nevertheless, the 3CuB/SiO<sub>2</sub> catalyst still suffered from deactivation after 56 h time-on-stream, presumably due to the sintering and aggregation of active metallic species. The lifespan of 3CuB/SiO<sub>2</sub> can be greatly extended to 150 h, when 2-propanol was employed as the reaction solvent, instead of water. The important role of solvent on the stability for Cu-based catalysts will be further investigated in our future work.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.03.018.

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