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Selective hydrogenolysis of glycerol to propylene glycol on Cu–ZnO catalysts

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Hydrogenolysis of biomass-derived glycerol is an alternative route to sustainable production of propylene glycol. Cu–ZnO catalysts were prepared by coprecipitation with a range of Cu/Zn atomic ratio (0.6–2.0) and examined in glycerol hydrogenolysis to propylene glycol at 453–513 K and 4.2 MPa H_2. These catalysts possess acid and hydrogenation sites required for bifunctional glycerol reaction pathways, most likely involving glycerol dehydration to acetol and glycidol intermediates on acidic ZnO surfaces, and their subsequent hydrogenation on Cu surfaces. Glycerol hydrogenolysis conversions and selectivities depend on Cu and ZnO particle sizes. Smaller ZnO and Cu domains led to higher conversions and propylene glycol selectivities, respectively. A high propylene glycol selectivity (83.6%), with a 94.3% combined selectivity to propylene glycol and ethylene glycol (also a valuable product) was achieved at 22.5% glycerol conversion at 473 K on Cu–ZnO (Cu/Zn = 1.0) with relatively small Cu particles. Reaction temperature effects showed that optimal temperatures (e.g. 493 K) are required for high propylene glycol selectivities, probably as a result of optimized adsorption and transformation of the reaction intermediates on the catalyst surfaces. These preliminary results provide guidance for the synthesis of more efficient Cu–ZnO catalysts and for the optimization of reaction parameters for selective glycerol hydrogenolysis to produce propylene glycol.

KEY WORDS: selective hydrogenolysis; glycerol; propylene glycol; Cu–Zn catalysts.

1. Introduction

Propylene glycol, i.e. 1,2-propanediol, is an important commodity chemical. It is used as biodegradable functional fluids such as de-icing reagents, antifreezes and coolants, and as precursors in the syntheses of unsaturated polyester resins and pharmaceuticals, etc. [1–3]. Propylene glycol is currently produced from petroleum-derived propylene via the process involving propylene selective oxidation to propylene oxide and its subsequent hydrolysis [1,2]. But this process is restricted by the supply of propylene due to the dwindling petroleum resource, which stimulates the efforts for searching for renewable substitutes for propylene. In this respect, bio-renewable glycerol has emerged as a promising candidate. It is readily available as a by-product of manufacturing biodiesel via transesterification of vegetable oils or animal fats, stemming from the incentives to the development of biodiesel worldwide [2–5]. It can be hydrogenolyzed to propylene glycol [2–9], providing an alternative route to sustainable production of propylene glycol.

Selective hydrogenolysis of glycerol to propylene glycol requires cleavage of C–O bonds by H_2 without attacking C–C bonds in the glycerol molecule. For this purpose, a number of solid catalysts have been explored, among which Cu-containing catalysts exhibit superior performances [2–6, 9]. For example, Chaminand et al. [2] found that on a Cu–Zn-based catalyst, glycerol hydrogenolysis is 100% selective to propylene glycol at ~20% conversion at 453 K, but it is not reactive and thus the reaction takes 90 h in a high H_2 pressure (8 MPa). Dasari et al. [3] reported that Cu–Cr (copper–chromite) catalysts catalyze glycerol hydrogenolysis to propylene glycol with a high selectivity of 85.0% at ~55% conversion (after 24 h) at 473 K and ~1.4 MPa H_2, much milder conditions than in previous studies. However, the increasing concerns over green chemistry make these Cu–Cr catalysts undesirable because of their toxicity associated with chromium.

These considerations led us to focus on Cu–Zn-based catalysts, albeit with the reported low reactivity. We here examine catalytic hydrogenolysis of glycerol to propylene glycol on the Cu–Zn-based catalysts, with the aim of getting insights into the connections between the structure of the catalysts and their catalytic properties and the effects of reaction parameters on the production of propylene glycol.

2. Experimental

Cu–Zn oxide (denoted as Cu–ZnO) catalysts were prepared by coprecipitation of aqueous solutions of

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$Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with urea (All from Beijing Chemicals, AR grade) [10,11]. The concentrations of Cu^{2+} and Zn^{2+} in the solutions were varied to change the Cu/Zn atomic ratio by keeping a constant cation (Cu^{2+} + Zn^{2+}) concentration of 0.05 M. The concentrations of urea were kept at 0.5 M in the solutions. The solutions were heated to 363 K and maintained at 363 K for 2 h to form precipitates. The precipitates were aged at 333 K for 2 h, followed by filtration and thoroughly washing with deionized water until the filtrates were neutral. These precipitates were treated in ambient air at 383 K overnight, and then at 573 K for 3 h. ICP (Vario EL) analysis results show that the Cu/Zn atomic ratios for the resulting three catalysts were 0.6, 1.0, and 2.0. For comparison, bulk ZnO and CuO were also prepared in the same way by coprecipitation of an aqueous solution of only $Zn(NO_3)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ with urea.

BET surface areas were measured by N_2 physisorption at its normal boiling point using an ASAP 2010 analyzer (Micromeritics) after samples were evacuated (< 2.66 Pa) at 393 K for 4 h. X-ray diffraction (XRD) patterns were obtained in the 2θ range 10–80 ° on a Rigaku D/MAX-2400 diffractometer using Cu Kα1 radiation ($\lambda = 1.5406$ Å) operated at 30 eV and 15 mA. The average crystallite sizes (D) of ZnO, CuO and Cu in the samples were estimated by Scherrer equation, [12] $D = 0.90\lambda/\beta \cos\theta$, where θ is the diffraction angle and β is the full width at half-maximum (FWHM).

Glycerol hydrogenolysis reactions were carried our in a Teflon-lined stainless steel autoclave (150 mL) at a stirring speed of 500 rpm. 15 g glycerol diluted in 65 mL deioninized water (20 wt% glycerol in the aqueous solutions) and catalysts were introduced to the autoclave. Unless specifically stated, Cu–ZnO samples without pre-reduction by H_2 stream were used as the catalysts in this work. The autoclave after it was flushed with H_2 was pressurized with H_2 ($> 99.99\%$, Beijing Huayuan) to 4.2 MPa, and then heated to reaction temperatures. Reactants and products were analyzed by gas chromatography (Shimadzu 2010 GC) using two capillary columns (PEG-20M: 3 m × 4 mm × 0.5 μm; OV-101: 30 m × 0.25 mm × 0.33μm) connected to flame ionization detector (FID) and thermal conductivity detectors (TCD), respectively. *t*-Butanol was used as external standard for analysis. Detected liquid products mainly include propylene glycol, ethylene glycol, and trace amounts of 1,3-propanediol, 1-propanol, 2-propanol, methanol and ethanol, and gas products mainly methane, dimethylether, diethylether, and methyl-ethylether. Selectivities are reported on a carbon basis. Only selectivities to propylene glycol and ethylene glycol were discussed in this study by considering both the amounts detected and commercial importance.

3. Results and discussion

Table 1 shows glycerol hydrogenolysis conversions and selectivities to propylene glycol and ethylene glycol (also a valuable product) at 473 K on Cu–ZnO catalysts with different Cu/Zn atomic ratios at a constant Cu content (7.5 mmol), and for comparison on bulk CuO and ZnO. Bulk CuO catalyzed glycerol conversion to propylene glycol with a high selectivity of 76.8% at a low conversion of 4.0%. ZnO showed an activity solely for glycerol dehydration without forming any hydrogenolysis products, indicating that ZnO surfaces possess acid sites only for dehydration, and hydrogenation occurs on Cu surfaces. Higher glycerol conversions were obtained on the Cu–ZnO catalysts containing combined acid and hydrogenation functions (Table 1). As the Cu/Zn ratio increased from 0.6 to 2.0, glycerol conversions decreased from 22.5% to 7.8% and propylene glycol selectivities concurrently increased from 20.4% to 51.3%; ethylene glycol selectivities increased from 1.3% to 6.4% (Table 1).

Fresh Cu–ZnO catalysts, as shown by XRD results (Figure 1), contained merely ZnO and CuO crystallites, and no any mixed Cu–Zn oxide phases were detected [11]. After glycerol hydrogenolysis reaction, CuO was reduced to Cu, as evidenced by the concurrent appearance of Cu crystallite diffraction peaks at 43.3 °, 50.6 ° and 74.2 ° and disappearance of CuO diffraction peaks (at 35.1 °, 38.7 ° and 48.8 °, etc) [11] in figure 1. Relative to the fresh samples, the crystallite sizes increased after the reaction, but they fell in the similar ranges of 27.6–32.2 nm for ZnO and 37.0–38.7 nm for Cu (Table 2), irrespective of the Cu/Zn atomic ratio, indicating that these crystallites agglomerate in aqueous solutions under the reaction conditions. Surface areas of these samples were also similar after the hydrogenolysis reaction, being around 15 m^2/g.

Table 1

Glycerol hydrogenolysis conversions and selectivities at 473 K on Cu–ZnO catalysts with Cu/Zn atomic ratios of 0.6, 1.0, and 2.0 and on bulk CuO and ZnO[a]

Catalyst	Conversion (%)	Selectivity (%)	
		Propylene glycol	Ethylene glycol
Cu–ZnO (0.6)[b]	22.5	20.4	1.3
Cu–ZnO (1.0)[b]	17.2	29.4	2.6
Cu–ZnO (2.0)[b]	7.8	51.3	6.4
CuO	4.0	76.8	–
ZnO[c]	3.6	–	–

[a] 20 wt% glycerol (15 g glycerol in 65 mL H_2O), 4.2 MPa H_2, 12 h, 7.5 mmol Cu.

[b] Number in the parenthesis represents Cu/Zn atomic ratio measured by ICP.

[c] ZnO content used for bulk ZnO is equivalent to that for Cu–ZnO (1/1).

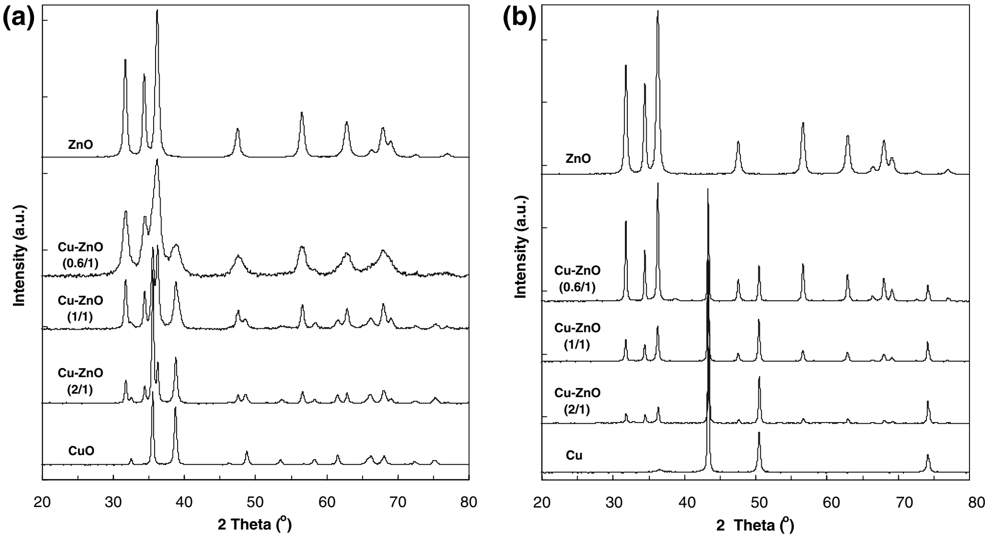


Figure 1. X-ray diffraction patterns for Cu–ZnO catalysts with different Cu/Zn atomic ratios (0.6, 1.0 and 2.0) and for bulk CuO and ZnO before (a) and after (b) glycerol hydrogenolysis for 12 h at 273 K and 4.2 MPa H_2.

Table 2

Crystallite sizes for Cu–ZnO and bulk CuO before and after glycerol hydrogenolysis at 473 K[a]

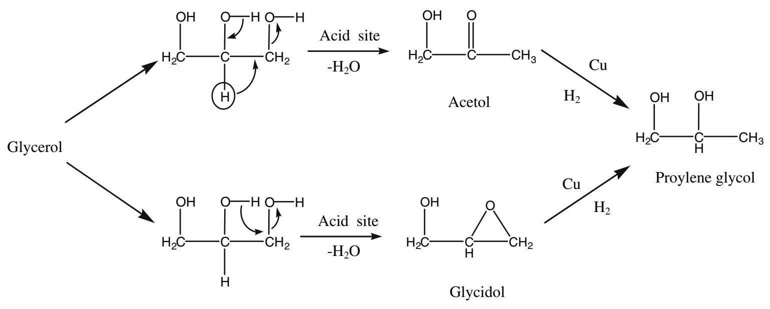
Catalyst	Before reaction (nm)		After reaction (nm)	
	ZnO	CuO	ZnO	Cu
Cu–ZnO (0.6)[b]	7.5	4.6	2.2	33.7
Cu–ZnO (1.0)[b]	19.1	10.1	27.6	32.9
Cu–ZnO (2.0)[b]	25.0	17.7	31.8	32.3
CuO	–	20.7	–	23.9

[a] 20 wt% glycerol (15 g glycerol in 65 mL H_2O), 4.2 MPa H_2, 12 h, 7.5 mmol Cu.

[b] Number in the parenthesis represents Cu/Zn atomic ratio measured by ICP.

Taken together, these results indicate that the observed changes in the conversions and selectivities with changing the Cu/Zn ratio (at the fixed Cu content) may not be related to the difference in structure of these catalysts but to the effects of their relative ZnO and Cu contents on the glycerol reaction pathways. The pathways may involve glycerol dehydration to dehydrated intermediates on acid sites of ZnO surfaces, followed by hydrogenation of the intermediates on Cu surfaces, as shown in Scheme 1, where the two proposed dehydrated intermediates, acetol (1-hydroxyacetone) and glycidol (3-hydroxy-1,2-epoxypropane), were indeed detected by GC-MS. Dasari et al. [3] validated acetol as the intermediate for propylene glycol synthesis from glycerol on Cu–Cr catalysts. Quantum mechanical calculations proposed that glycidol is an energetically favorable dehydrated product in the presence of acid [13].

It appears to be clear that the observed decrease in glycerol conversions at the constant Cu contents with increasing the Cu/Zn ratio is due to the decrease in the ZnO contents required for catalyzing glycerol dehydration, and thus that such dehydration step may determine the glycerol conversions. Acetol and glycidol intermediates are unstable and susceptible to decomposition to form formaldehyde and acetaldehyde, etc [13], which are most likely the precursors of the observed byproducts such as methane, methanol, ethanol and their ethers in this study. Thus, efficient hydrogention of these intermediates, once they are formed, to propylene glycol on Cu surfaces is required for minimizing their decomposition to achieve high propylene glycol selectivities. Such requirements may account for the observed difference in



Scheme 1. Proposed bifunctional glycerol hydrogenolysis reaction pathways.

Table 3

Effects of initial pH value on glycerol hydrogenolysis conversions and selectivities at 473 K on Cu–ZnO (Cu/Zn atomic ratio = 1.0) as well as on its crystallite sizes measured after glycerol hydrogenolysis[a]

Initial pH	Conversion (%)	Selectivity (%)		Crystallite size (nm)	
		Propylene glycol	Ethylene glycol	ZnO	Cu
2	10.4	27.9	1.4	41.1	33.5
7	21.1	29.4	2.6	27.6	32.9
12	33.9	77.5	4.9	13.3	26.3

[a] 20 wt% glycerol (15 g glycerol in 65 mL H_2O), 4.2 MPa H_2, 12 h, 7.5 mmol Cu.

the propylene glycol selectivities at different Cu/Zn ratio (Table 1).

Table 3 shows the effects of initial pH value (adjusted by H_2SO_4 or NaOH) of the reaction solutions on glycerol hydrogenolysis on Cu–ZnO (Cu/Zr = 1.0) at 473 K. Increasing the pH value from 2 to 7 led to an increase in glycerol conversions from 10.4% to 21.1%, which further increased to 33.9% at pH of 12. Propylene glycol selectivities slightly changed (27.9%–29.4%) in the pH range 2–7, while they reached as high as 77.5% at pH of 12. Ethylene glycol selectivities increased monotonically from 1.4% to 4.9% in the pH range 2–12. The pH values of the reaction solutions were essentially constant, i.e. ~6.5, after the glycerol reactions, irrespective of their initial pH. Further measurements found that these constant pH values were indeed reached rapidly under the reaction conditions. This reflects the amphoteric nature of ZnO supports, which can react with both H^+ and OH^- ions in acid and basic solutions. So the constant pH values measured indicate that the observed effects of the initial pH value on the conversions and selectivities may not be due to their effects on the bifunctional glycerol reaction pathways, but to the effects on the catalyst structure as discussed below.

ZnO and Cu particle sizes after the glycerol reactions were estimated by XRD, which decreased with increasing the initial pH value, as shown in Table 3. ZnO sizes decreased sharply from 41.1 nm to 13.3 nm in the pH range 2–12, while Cu particle sizes slightly varied (33.5 nm vs. 32.9 nm) at pHs 2 and 7, and then decreased to 26.3 nm at pH 12, likely as a result of the higher surface potentials of ZnO and Cu crystallites at higher pH values, preventing their aggregation according to the DLVO theory [14,15]. These changes in the ZnO and Cu domain sizes, as shown in figure 2, inversely parallel the observed changes in the conversions and selectivities, showing that smaller ZnO and Cu sizes lead to higher glycerol conversions and propylene glycol selectivities, respectively. These results further confirm that glycerol conversions are determined by the ZnO-catalyzed glycerol dehydration step, while Cu hydrogenation performances correlate with the propylene glycol selectivities, as seen more clearly in Table 4 shown below.

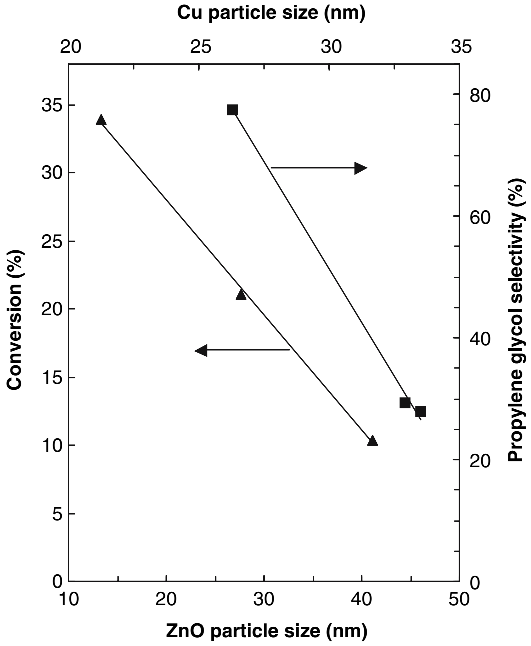


Figure 2. Glycerol hydrogenolysis conversions and propylene glycol selectivities at 473 K on Cu–ZnO (Cu/Zn atomic ratio = 1.0), respectively, as a function of ZnO and Cu crystallite size measured after glycerol hydrogenolysis (20 wt% glycerol, 4.2 MPa H_2, 12 h, 7.5 mmol Cu).

Table 4

Glycerol hydrogenolysis conversions and selectivities at 473 K on Cu–ZnO (Cu/Zn atomic ratio = 1.0) with and without pre-reduction by H_2 stream (at 623 K), and the corresponding crystallite sizes measured after glycerol hydrogenolysis[a]

	Conversion (%)	Selectivity (%)		Crystallite size (nm)	
		Propylene glycol	Ethylene glycol	ZnO	Cu
Non pre-reduction	21.1	29.4	2.6	27.6	32.9
Pre-reduction	22.5	83.6	10.7	25.7	22.8

[a] 20 wt% glycerol (15 g glycerol in 65 mL H_2O), 4.2 MPa H_2, 12 h, 7.5 mmol Cu.

Table 4 shows the glycerol conversions and selectivities at 473 K on Cu–ZnO (Cu/Zn = 1.0) with and without pre-reduction by H_2 stream before it was loaded to the reactor. Pre-reduction of Cu–ZnO (Cu/Zn = 1.0) led to smaller Cu sizes of 22.8 nm compared to 32.9 nm after the glycerol reactions, while ZnO sizes (27.6 nm vs. 25.7 nm) were essentially unaffected. Consequently, this reduction in the Cu size led to a propylene glycol selectivity of as high as 83.6% on the pre-reduced catalyst at 22.5% glycerol conversion, a comparable conversion to that on the non-prereduced catalyst but with a much lower selectivity (29.4%). Noticeably, small

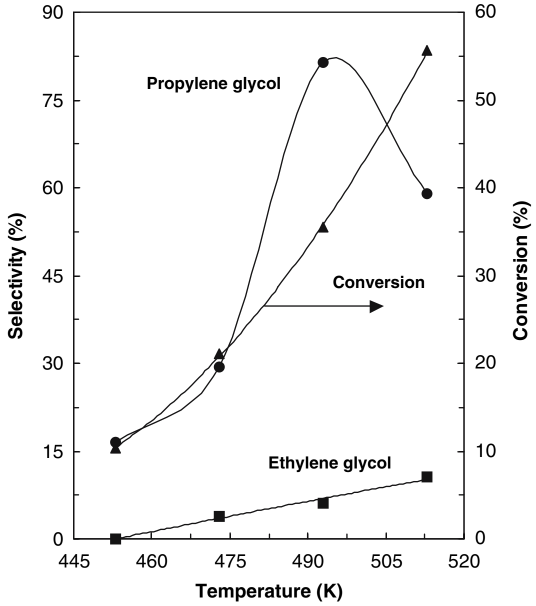


Figure 3. Effects of reaction temperature on glycerol hydrogenolysis conversions and selectivities to propylene glycol and ethylene glycol at 473 K on Cu–ZnO (Cu/Zn atomic ratio = 1.0, 20 wt% glycerol, 4.2 MPa H_2, 12 h, 7.5 mmol Cu).

Cu particles obtained upon such pre-reduction led to a combined selectivity to propylene glycol and ethylene glycol of 94.3%, which is much higher than that (32.0%) without the pre-reduction (Table 4). Reuse of this pre-reduced catalyst did not show any significant declines in both glycerol conversions and selectivities to propylene glycol and ethylene glycol.

We have also explored the effects of reaction temperature on glycerol conversions and selectivities on Cu–ZnO (Cu/Zn = 1.0). As shown in figure 3, glycerol conversions increased from 10.3% to 55.7% with increasing the temperature in the range 453–513 K. Propylene glycol selectivities increased sharply from 16.5% to 81.4% as the temperature increased from 453 K to 493 K, then declined to 59.0% at 513 K. Ethylene selectivities increased monotonically from 0 to 7.1% in this whole temperature range. The catalysts possessed similar Cu particle sizes (31.9–32.9 nm) after the glycerol reactions at different temperatures, while ZnO particle sizes did not change (~27.6 nm) until the reaction temperature reached 513 K, increasing to 33.6 nm. This indicates that the temperature effects on the propylene glycerol selectivities are not due to the effects of Cu structure discussed above. They may be due to the effects on rates of intrinsic adsorption/desorption and transformations of the dehydrated glycerol intermediates on ZnO and Cu surfaces. Lower temperatures favor strong adsorption of the intermediates leading to high probability of their decomposition, while higher temperatures favor their desorption and also breaking of their C–C and C–O bonds leading to over-hydrogenolyzed products, as reflected by the higher ethylene glycol selectivities at higher temperatures (figure 3). Thus, high propylene glycol selectivities require optimal temperatures facilitating the selective conversions of the dehydrated intermediate, as was found at 493 K in figure 3.

4. Conclusions

Co-precipitated Cu–ZnO catalysts catalyze glycerol hydrogenolysis to propylene glycol at 453–513 K, most likely via bifuncational reaction pathways including glycerol dehydration to acetol and glycidol intermediates on acidic ZnO surfaces, followed by their hydrogention on Cu surfaces. Glycerol hydrogenolysis conversions and selectivities are dependent on Cu and ZnO particle sizes; smaller ZnO and Cu particles lead to higher conversions and propylene glycol selectivities, respectively. The smaller particles are found to be formed in basic reaction solutions, likely as a result of the higher surface potentials of ZnO and CuO particles at higher pH values (e.g. at pH = 12), discouraging their aggregation, and via pre-reduction of fresh Cu–ZnO catalysts by H_2 stream as a result of avoiding the water effects on the aggregation of Cu particles in situ formed (i.e. the general procedure employed in this work) in the reaction solutions. Reaction temperature effects show that optimal reaction temperatures are required for optimizing the adsorption and transformation of the reaction intermediates required for high propylene glycol selectivity. These preliminary results about the size and temperature effects provide basis for synthesis of novel Cu–ZnO catalysts and for optimization of reaction parameters for achieving high propylene glycol productivities.

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