

Sustainable production of 1,2-propanediol: Clean hydrogenolysis of glycerol over highly stable Cu-Ce/SiO₂ nanocatalyst

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ABSTRACT

The effects of preparation method and calcination temperature on the properties of CeO₂-incorporated Cu/SiO₂ catalysts for clean hydrogenolysis of glycerol to high value-added 1,2-propanediol were investigated. Experimental results showed that the incorporation of CeO₂ by all methods could improve the structure stability and thus the resistance to sintering of the Cu/SiO₂ catalysts. The resistance to sintering of the catalysts is highly dependent on the preparation method. Due to the covering of some part of active species, the doping of CeO₂ to some extent decreased the initial active of the Cu/SiO₂ catalyst. A synergistic effect was inferred to exist between copper and ceria, which was unobvious at low-temperature calcination but profoundly enhanced after high-temperature calcination. Due to the good promotion effect of cerium on the structure of Cu/SiO₂ catalyst, the long-term stability of the Ce incorporated catalyst in glycerol hydrogenolysis reaction largely increased.

Keywords: Cu/SiO₂ catalyst, cerium additive, glycerol, hydrogenolysis, 1,2-propanediol

1 INTRODUCTION

Large quantities of glycerol are available as a reaction coproduct owing to the rapid development of biodiesel production by transesterification of vegetable oils and animal fats. The hydrogenolysis of glycerol to propanediols is one process being evaluated to increase the profitability of biodiesel production. This process provides a clean and economically competitive route for the production of propanediols from renewable glycerol instead of from non-renewable petroleum [1]. Due to their low activity in the C-C bond cleavage and high activity in C-O hydrogenation, copper based catalysts exhibit high performance in the hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) [2-3].

Previously, we found that the Cu/SiO₂ catalyst with high dispersion prepared by precipitation-gel (PG) method exhibited high activity and selectivity in the hydrogenolysis of glycerol to 1,2-PDO [4]. We also found that the Cu/SiO₂ nanomaterials prepared by PG method showed high thermal stability in a wide CuO loadings [5]. Nonetheless, the long-term stability of this single-component Cu/SiO₂ catalyst during the time on-stream glycerol reaction is

unsatisfactory for industrial implication, as its activity deactivated fast after around 220 h reaction. In the searching of highly stable copper-based catalysts for glycerol hydrogenolysis, we found that Cerium (Ce) is a good promoter for the Cu/SiO₂ catalytic system [6]. In this work, we studied the effects of preparation method and calcination temperature on the structure and catalytic properties of Ce-incorporated Cu/SiO₂ catalysts for the clean hydrogenolysis of glycerol.

2 EXPERIMENTAL

Pure Cu/SiO₂ catalyst was prepared by a precipitation-gel (namely PG) method described in our previous report [4]. The Ce-doped Cu/SiO₂ catalysts were prepared by three different methods. The first method, namely PG-IM, was prepared by impregnating Ce onto the PG catalyst. The second method, namely CO-PG, was prepared by the coprecipitation of Ce(NO₃)₃ and Cu(NO₃)₂ with NaOH during the preparation of PG catalyst. The third method, namely PG-DP, was prepared by the deposition of Ce onto the slurry of PG catalyst with the additional adding of Ce(NO₃)₃ and NaOH. All the catalysts contain 30 wt % CuO and 6 wt % CeO₂ (except PG). The catalysts were calcined at two different temperatures, i.e. 450 and 750 °C, and accordingly the catalysts were referred as Method-T.

The X-ray powder diffraction (XRD) of the samples was carried out on a PANalytical X'pert Pro Diffractometer using nickel filtered Cu K α radiation with a scanning angle (2 θ) of 15–80°. The particle sizes of CuO and CeO₂ were calculated by using the Scherrer equation. X-ray photoelectron spectra (XPS) were obtained using a VG ESCALAB 210 spectrometer equipped with a Mg K α X-ray radiation source ($h\nu = 1253.6$ eV). All binding energies were calibrated using the Si2p peak at 103.4 eV as the reference. The BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. Temperature-programmed reduction (TPR) measurements were carried out in a quartz U-tube reactor with 20 mg of sample used for each measurement. Prior to the reduction, the sample was pretreated at 200 °C under He flow for 1 h. After cooling to room temperature, the sample was reduced with 5% H₂ in Ar at a flow rate of 50 mL/min and the temperature was increased to 500 °C at a ramping rate of 10 °C/min. H₂

consumption was continuously monitored by a thermal conductivity detector (TCD).

The discontinuous glycerol reaction was carried out in a 100 mL stainless steel autoclave. The catalysts were prereduced by H₂ stream at 280 °C for 3 h. The reaction was carried out under the following conditions: 180 °C, 9.0 MPa of H₂ pressure, 20 g of 80 wt % glycerol aqueous solution, 1 g of reduced catalyst, 10 h. The liquid-phase products were analyzed by using a gas chromatograph with a SE-54 capillary column (50 m × 0.32 mm) and a flame ionization detector. The gas products were analyzed by using a gas chromatograph (Porapak Q column (4 m × 3 mm)) equipped with a thermal conductivity detector. Conversions and selectivities were calculated on a carbon basis. The continuous glycerol reaction was performed in a fixed-bed reactor at 6.0 MPa total pressure. Before the reaction, the catalysts were reduced with a hydrogen flow at 280 °C for 3 h. The reaction media contained 40 wt % of glycerol, 10 wt % of water and 50 wt % of methanol. Standard reaction conditions were: WHSV of 0.25 h⁻¹, glycerol to hydrogen mol ratio 1 : 23, 180 °C. The reaction products were analyzed as indicated above.

3. RESULTS AND DISCUSSION

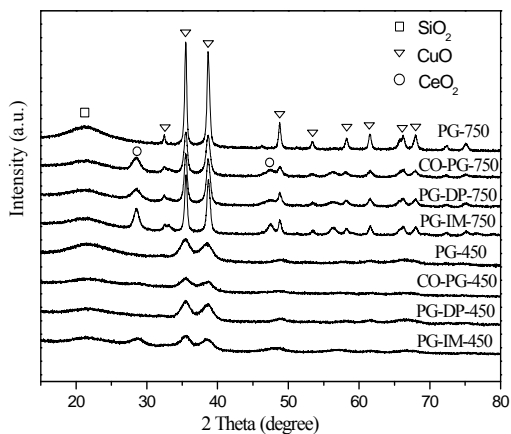


Fig.1 X-ray diffraction patterns of catalysts prepared by different methods calcined at 450 and 750 °C.

XRD characterization of the catalysts without and with the incorporation of Ce calcined at 450 °C showed that an additional broad diffraction associating with CeO₂ appeared in PG-IM-450 and CO-PG-450 catalysts after the incorporation of Ce, with its diffraction more intense in the former catalyst (Fig. 1). In contrast, it is hard to observe the diffraction peak of CeO₂ in PG-DP-450 catalyst, showing the higher dispersion of Ce in this catalyst. Crystalline size analysis showed that there is no big difference between the catalysts without and with the incorporation of Ce calcined at 450 °C, whereas preparation method strongly influenced the BET surface areas of the Ce-doped catalysts (Table 1). After the incorporation of Ce, the surface area of the catalyst prepared by CO-PG slightly increased, whereas a

slight and a large decrease of surface areas were observed over PG-IM-450 and PG-DP-450 catalysts, respectively. The decrease of surface areas for PG-IM-450 and PG-DP-450 catalysts could be explained by the blockage of some pores due to the doping of CeO₂ nanoparticles, whereas the increase of surface area for CO-PG-450 might be resulted by the increase of the dispersion of catalyst after the incorporation of Ce, as can be seen from its rather broader and lower XRD diffraction peaks of CuO.

Table 1 Crystalline sizes and BET surface areas of the catalysts prepared by different methods calcined at 450 and 750 °C.

Catalyst	Crystalline size (nm)		BET surface area (m ² /g)
	CuO	CeO ₂	
PG-450	5.6	—	180
CO-PG-450	5.5	—	195
PG-DP-450	5.7	—	129
PG-IM-450	6.0	5.3	162
PG-750	24.9	—	27
CO-PG-750	15.6	7.7	52
PG-DP-750	16.9	6.3	34
PG-IM-750	20.7	10.5	38

After calcination at a much high temperature of 750 °C, the diffractions of CuO in all catalysts intensified with the non-Ce incorporated PG catalyst much more intense and stronger; and big difference in crystalline sizes of CuO was observed (Table 1). The crystalline size of CuO in all the Ce-doped catalysts were smaller than that of the non-Ce incorporated PG catalyst with the crystalline sizes of CO-PG-750 and PG-DP-750 much smaller. On the contrary, the BET surface areas of all the Ce-doped catalysts were larger than that of the non-Ce incorporated PG catalyst with the surface area of CO-PG-750 much larger, which is almost two times that of PG-750 catalyst. The above results suggest that the incorporation of Ce to PG catalyst could inhibit the sintering of the catalyst and thus maintain high thermal stability of the Ce-incorporated catalysts. Taking the preparation method into consideration, the Cu-Ce/SiO₂ catalysts prepared by CO-PG and PG-DP showed a higher dispersion of CeO₂ in the catalysts than that of the catalyst prepared by PG-IM (Fig. 1). It appears that the higher the dispersion of Ce in the Cu-Ce/SiO₂ catalysts, the higher the thermal stability of the catalysts.

The TPR profiles of the catalysts without and with the incorporation of Ce were shown in Fig. 2. As can be seen, after the incorporation of Ce, the onset reduction temperatures and the main peak temperatures of all the Ce-incorporated catalysts shifted to lower temperatures with that of the CO-PG-450 and PG-DP-450 catalysts around 14 °C lower than that of the none-Ce promoted PG-450 catalyst. It is reported that CeO₂ is not substantially reduced at temperature below 360 °C [7]. Thus the above findings suggest that the incorporation of Ce could facilitate the reduction of copper species in the catalyst, which generally

follow the trend that the higher the dispersion of Ce species in the catalyst, the larger the decrease of the peak reduction temperature. Shiao et al [8] also found that the doping of Ce in Cu/ γ -Al₂O₃ catalyst could decrease the reduction temperature of CuO in the catalyst.

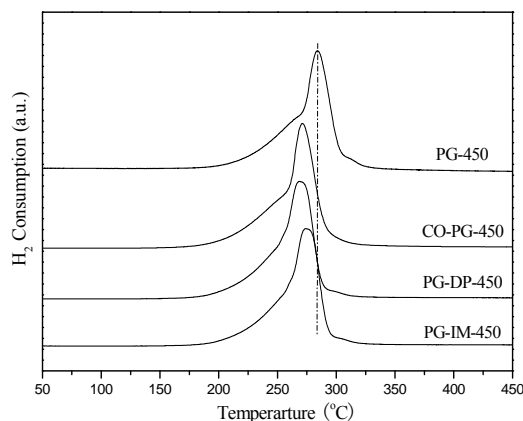


Fig.2 H₂-TPR profiles of the catalysts prepared by different methods calcined at 450 °C.

The XP spectra of pure Cu/SiO₂ catalyst prepared by PG method and the Ce-incorporated Cu-Ce/SiO₂ catalyst prepared by PG-IM method calcined at different temperatures are reported in Fig. 3. The intense and broad photoelectron peak at somewhat above 933.8 eV (Cu2p_{3/2}) along with the presence of the characteristic shakeup satellite peaks suggests that the copper oxidation state is +2 in all calcined samples [9]. The binding energy (BE) of pure CuO prepared by precipitation was determined at around 934.0 eV; thus the large positive BE shift of the Cu2p core level for the PG-450 and PG-IM-450 samples is indicative of a charge transfer from the metal ions toward the support matrix, that is, a strong interaction between the metal ions and the matrix [10]. According to our previous report [5], the high BE of the both samples would be resulted by the formation of copper phyllosilicate. After calcination at 750 °C, the BE of both catalysts decreased to around 933.9 eV, suggesting that the copper phyllosilicate species in both samples were decomposed to CuO and SiO₂. It appears that the BEs of Ce3d_{5/2} for both PG-IM-450 and PG-IM-750 catalysts were not affected much by calcination temperature, as which maintained around 883.1–883.2 eV. A slight electron transfer between Ce and Cu is inferred to exist in the Ce-incorporated PG-IM-450 catalyst, as the BE of Cu2p_{3/2} at each calcination temperature is slightly lower than its corresponding pure Cu/SiO₂ catalyst (Table 2).

The XPS intensity ratio of Cu2p/Si2p values for both samples are also included in Table 2, which reflects the copper dispersion on silica support. A remarkable decrease of Cu/Si ratio (30.8%) was seen as the calcination temperature of pure Cu/SiO₂ catalyst was raised up to 750 °C. After the incorporation of Ce, the decrease of Cu/Si ratio for PG-IM catalyst declined to 17.5% during the same procedure. These findings suggest that the incorporation of

Ce could inhibit the sintering of copper species, which is in line with the results of XRD and BET analysis.

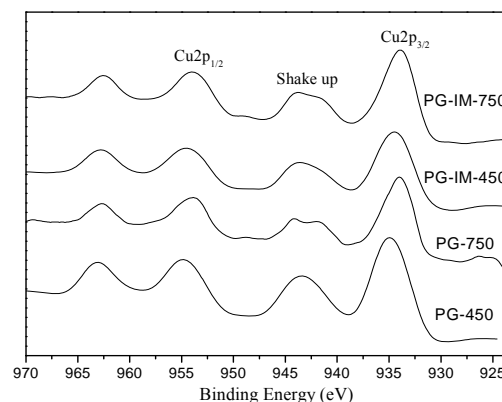


Fig. 3 XPS spectra of catalysts prepared by PG and PG-IM methods calcined at different temperatures.

Table 2 XPS analysis of catalysts prepared by PG and PG-IM methods calcined at different temperatures.

Catalyst	BE of Cu2p _{3/2} (eV)	BE of Ce3d _{5/2} (eV)	Atomic ratio	
			Cu/Si	Ce/Si
PG-450	934.9	—	0.39	—
PG-750	933.9	—	0.27	—
PG-IM-450	934.7	883.2	0.40	0.011
PG-IM-750	933.8	883.1	0.33	0.0094

Catalytic activity test in the hydrogenolysis of glycerol in non-continuous autoclave showed that the incorporation of Ce to some extent decreased the activity of the Cu/SiO₂ catalyst (Table 3). The activities of the catalysts without and with the incorporation of Ce were in an order of PG-450 > PG-IM-450 > PG-DP-450 > CO-PG-450. It is widely accepted that Cu⁰ is the active site for glycerol hydrogenolysis reaction [4, 11-12]. The decrease of activity for the Ce incorporated catalysts may be resulted by the covering some of the active sites of the Cu/SiO₂ catalyst. Nonetheless, after calcination at 750 °C, the activity of the none Ce-promoted PG750 catalyst sharply decreased to almost one third that of PG450, whereas only slight decrease of activity was observed over PG-IM-750 and PG-DP-750 catalysts, suggesting the doping of Ce could maintain the reactive stability of the Cu/SiO₂ catalyst. Differently, a large increase of activity was seen over CO-PG-750 catalyst as comparison to CO-PG-450, although obvious but slightest sintering was seen over this catalyst after calcination at 750 °C. Considering that pure CeO₂/SiO₂ was almost inactive in glycerol hydrogenolysis reaction (Table 3), it seems that there exists a synergistic effect between copper and cerium, which is enhanced after high temperature calcination and promotes the catalytic activity of the CO-PG-750 catalyst. This synergistic effect may also exist in the Cu-Ce/SiO₂ catalysts prepared by PG-

IM and PG-DP methods, however, due to a more serious sintering of these catalysts (Table 1), a slight decrease of the activities was seen after calcined at 750 °C, as compared with their corresponding samples calcined at 450 °C.

Table 3 Catalytic activity of glycerol hydrogenolysis over catalyst with different Ce addition methods calcined at 450 and 750 °C^a

Catalyst	Conversion (%)	Selectivity (%)
CeO ₂ /SiO ₂	—	—
PG-450	73.3	92.2
CO-PG-450	44.5	94.0
PG-DP-450	56.9	91.7
PG-IM-450	62.7	93.4
PG-750	24.7	94.5
CO-PG-750	60.0	93.5
PG-DP-750	51.8	91.8
PG-IM-750	50.6	93.5

^a Reaction condition: 1.0 g catalyst (reduced), 200 °C, 8 MPa H₂, 10 h, 20 g 80 wt % glycerol aqueous solution.

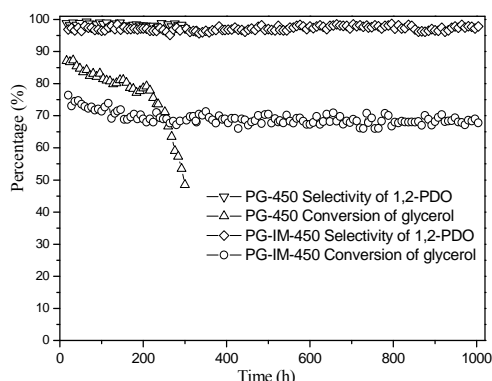


Fig. 4 Time on-stream behavior of PG-450 and PG-IM-450 catalysts. Reaction conditions: WHSV of 0.25 h⁻¹, glycerol to hydrogen mole ratio 1:23, pressure 6.0 MPa, 180 °C.

To study whether the incorporation of cerium could improve the long-time stability of the Cu/SiO₂ catalyst or not, the reaction was carried out by using a fixed-bed flow reactor over PG-450 and PG-IM-450 catalysts. As shown in Fig. 4, a slight decrease of initial activity but a remarkable increase of stability was seen over PG-IM-450 catalyst as compared to PG-450 catalyst. The decrease of initial activity over PG-IM-450 catalyst in continuous fixed-bed flow reactor is in agreement with the results obtained in non-continuous autoclave reaction that the incorporation of cerium could inhibit the initial activity of pure Cu/SiO₂ catalyst. The remarkable increase of long-time stability of

the PG-IM-450 could be ascribed to the promotion effect of Ce on the structural stability of the Cu/SiO₂ catalyst.

4 CONCLUSION

The effects of the addition method of the rare earth additive of Ce on the structure stability and catalytic performance in glycerol hydrogenolysis of Cu/SiO₂ catalysts were studied. Both the resistance to sintering and the catalytic activity of the catalysts are highly dependent on the preparation method. The incorporation of Ce by all methods could inhibit the sintering and thus improve the thermal stability and reactive stability of the Cu/SiO₂ catalyst. Nonetheless, due to the covering of some active sites, the initial activities of the Cu-Ce/SiO₂ catalysts were to some extent lost after the incorporation of Ce. There may exist a synergistic effect between copper and cerium, which was further enhanced after high-temperature calcination and promoted the catalytic activity. The Ce incorporated Cu-Ce/SiO₂ catalyst exhibited high activity, selectivity and long-term stability in the clean hydrogenolysis of glycerol to 1,2-PDO, showing high potential in the industrial utilization of this catalyst.

5 ACKNOWLEDGEMENT

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6 REFERENCES

- [1] Y. Zheng, X. Chen, Y. Shen, Chem. Rev., 10, 5253-5277, 2008.
- [2] M.A. Dasari, P.-P. Kiatsimkul, W.R. Sutterlin, G.J. Suppes, Appl. Catal. A., 281, 225-231, 2005.
- [3] S. Wang, H. Liu, Catal. Lett., 117, 62-67, 2007.
- [4] Z. Huang, F. Cui, H. Kang, J. Chen, X. Zhang, C. Xia, Chem. Mater., 20, 5090-5099, 2008.
- [5] Z. Huang, F. Cui, J. Xue, J. Zuo, J. Chen, C. Xia, J. Phys. Chem. C., 114, 16104-16113, 2010.
- [6] F. Cui, J. Chen, C. Xia, H. Kang, X. Zhang, J. Tong, X. Li, US 7586016-B2, 2009.
- [7] G. Águila, F. Gracia, P. Araya, Appl. Catal. A., 343, 16-24, 2008.
- [8] C.-Y. Shiau, M.W. Ma, C.S. Chuang, Appl. Catal. A., 301, 89-95, 2006.
- [9] K.V.R. Chary, K.K. Seela, G.V. Sagar, B. Sreedhar, J. Phys. Chem. B., 108, 658-663, 2004.
- [10] A. Auroux, A. Gervasini, C. Guimon, J. Phys. Chem. B., 103, 7195-7205, 1999.
- [11] R. Mane, A. Hengne, A. Ghalwadkar, S. Vijayanand, P. Mohite, H. Potdar, C. Rode, Catal. Lett., 135, 141-147, 2010.
- [12] A. Bienholz, F. Schwab, P. Claus, Green Chem., 12, 290-295, 2010.