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# Studies on continuous selective hydrogenolysis of glycerol over supported Cu-Co bimetallic catalysts

Narsinga. Raju, Voggu. Rekha, Burri. Abhishek, Peddagolla. Mahesh Kumar, Chenna. Sumana and Nakka. Lingaiah\*

Copper-cobalt supported on alumina catalysts were made and screened for continuous hydrogenolysis of glycerol to 1,2propanediol at atmospheric pressure. BET surface area, temperature-programmed reduction, X-ray diffraction, pulse N<sub>2</sub>O chemisorption, transmission electron microscopy and X-ray photoelectron spectroscopy techniques were used to derive catalysts characteristics. The presence of Co in Cu/alumina significantly increased the reducibility of CuO species and also metallic Cu surface area. The catalyst with 10%Cu-7%Co on Al<sub>2</sub>O<sub>3</sub> afforded complete glycerol conversion with 77% selectivity to 1,2-propanediol. The catalysts activity was mainly owing to the existence of Cu in highly dispersed state with high metal surface area and synergistic interaction between Cu-Co moieties. The reaction parameters influence was screened and best possible parameters were provided. The most active catalyst showed high stability during time on stream analysis.

### Introduction

Biodiesel, a potential environmentally friendly diesel fuel to substitute petro-diesel can be obtained from transesterification of animal fats or vegetable oils. The global biodiesel production expected to grow rapidly to 36.9 MMT by 2020 [1-2]. Glycerol, smallest polyol, available as a main side product in biodiesel synthesis, which is approximately 10% of total biodiesel production. Technical challenges and economic factors limited the consumption of glycerol [3-4]. Glycerol is a well functionalized chemical and can be renewed into high value products by diverse catalytic process such as steam reforming, hydrogenolysis, dehydration, oxidation, carbonvlation. esterification, acetalization and chlorination, etc [5-7]. Among these catalytic interventions, selective glycerol hydrogenolysis (GH) to 1,2-propanediol (1,2-PD) represents as a green and lowcost approach for its utilization. In general, 1, 2-PD is manufactured mainly by propylene oxide hydration derived from petroleum. It is a foremost commodity chemical extensively utilized in antifreeze functional fluids. pharmaceuticals, paints, food products, polyester resins, etc. GH is carried over supported metals, namely Pt, Ru, Pd, Cu, Ag, Ir, Ni and Co are used as effective catalysts for 1,2-PD preparation [8-10].

The popular reaction in glycerol to 1,2-PD conversion is the C-O hydrogenolysis where glycerol dehydration followed by hydrogenation takes place [11]. This reaction needs multifunctional catalytic system especially acid sites for dehydration to intermediate hydroxyacetone and its hydrogenation over transition metals. Further, Lewis and Brønsted acid catalysed hydrogenolysis proceed via different intermediate formation yielding the same 1,2-PD [12]. The existing literature suggested that catalysts with noble metals are by and large efficient than other transition metal catalysts for this reaction. Most of these catalysts are studied at high pressure in batch mode. The disadvantages of liquid phase glycerol to 1,2-PD is that the adsorption of intermediates and by-products on the surface of the catalyst resulting low catalytic activity and selectivity [13].

Continuous glycerol hydrogenolysis is the best alternative to overcome the disadvantages but it is less investigated at atmospheric pressure. The continuous hydrogenolysis was reported by few researchers. Zheng et al. reported MOF based Cu/ZnO catalyst system for continuous glycerol hydrogenolysis at 20 bar pressure [14]. The Ce promoting effect on Cu-Co-Al catalyst was reported for continuous hydrogenolysis with 1,2-PD yield up to 95% at 35 bar pressure [15]. Amadeo group studied vapor phase GH to 1,2-PD at ambient pressure over Cu deposited on mesoporous alumina [16]. In these studies, no indication about the catalyst stability. We also studied continuous glycerol hydrogenolysis over Ni-Ag/y-Al<sub>2</sub>O<sub>3</sub> catalysts. However, the stability of the catalyst was limited [17]. The main drawback in continuous hydrogenolysis at atmospheric pressure is catalysts deactivation. The bimetallic catalysts demonstrated better stability compared to monometallic catalysts for glycerol hydrogenolysis. The supported Cu based bi-metallics, such as Cu-Zn, Cu-Ni, Cu-Ag and Cu-Pd were explored for GH in batch mode at high pressure [18-22]. These catalysts showed varied activities at different reaction conditions. Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst showed high conversion under pressure conditions with low stability. Ag-Cu/

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#### Page 2 of 8

#### ARTICLE

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59 60  $Al_2O_3$  has been reported to work under ambient pressure with a gradient reaction temperature with complete glycerol conversion and high selectivity more than 98% with stability up to 1-5 h. The main drawback in continuous hydrogenolysis at atmospheric pressure is catalysts deactivation. The catalysts activity depends on how efficiently the dehydration flowed by hydrogenation reaction takes place during hydrogenolysis of glycerol. The metal surface area, acidity are the important characteristics of the catalysts for this reaction [23]. It is thought bimetallic catalysts based on Cu may be stable and active for glycerol hydrogenolysis if the catalyst contains high metal surface area and acidity.

In this work, Cu-Co bimetallic supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were systematically evaluated for continuous GH at atmospheric pressure to 1,2-PD. The catalysts were characterized to assess metal surface area, dispersion and other structural characteristics. The hydrogenolysis activity majorly discussed up on the catalysts physico-chemical characteristics derived from various characterization techniques.

#### **Results and discussion**

#### **Catalysts Physico-chemical properties**

Table 1 presents the physical characteristics of the catalysts. In comparison to mono  $Cu/Al_2O_3$ , bimetallic  $Cu-Co/Al_2O_3$  catalysts exhibited high surface area. The Co addition to Cu led to enhancement in surface area. This is distinct when Co content increased from 3 to 7 wt. %. Further, raise in Co content to 13 wt. %, a trivial drop was detected in surface area. This could be owed to the formation of bulk cobalt oxide species and these large particles could block the micro pores of  $Al_2O_3$ . A similar trend was also noticed in Ce-Cu/MgO and Ni-Cu/Al<sub>2</sub>O<sub>3</sub> bimetallic catalysts [26, 27].

Table 1: Physico-chemical properties of Cu-Co/Al<sub>2</sub>O<sub>3</sub> catalysts.

S. No	Catalyst	BET S. A. (m²/g)	Avg. Pore Dia. (nm)	Disp. (%)	Cu S. A. (m²/g)	H₂ Uptake (μmol)
1	$AI_2O_3$	167	8.2	-	-	
2	10Cu/ Al <sub>2</sub> O <sub>3</sub>	115	8.0	34.5	233.7	286
3	10Cu-3Co/	125	7.6	27.7	175.9	512
4	Al <sub>2</sub> O <sub>3</sub> 10Cu-5Co/ Al <sub>2</sub> O <sub>3</sub>	132	6.5	25.9	187.7	1079
5	10Cu-7Co/	142	5.1	49.9	337.9	1434
	Al <sub>2</sub> O <sub>3</sub>					
6	10Cu-10Co/	130	4.7	37.1	251.5	1065
7	AI <sub>2</sub> O <sub>3</sub> 10Cu-13Co/ Al <sub>2</sub> O <sub>3</sub>	123	4.0	21.1	143.1	1032

The dispersion of Cu metal and metal surface area measured from  $N_2O$  dissociative approach improved with increase in Co loading up to 7 wt. % in the catalyst. A small decrease in Cu dispersion and metal surface area was noticed with raise in Co

content beyond 7 wt. %. The lowering of Cu dispersion at high Co contents linked to the growth of surface bulk cobait oxides species. The 10Cu-7Co/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited more Cu dispersion and metal surface area. This may be owed to the close interactions among Cu and Co species which aid to reduce the thermal transmigration and sintering of Cu particles [28].

XRD patterns of calcined catalysts are displayed in Fig.1. The patterns showed mainly the characteristic peaks of CuO,  $Co_3O_4$ , and CuCo<sub>2</sub>O<sub>4</sub> phases. Additionally, reflections corresponding to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were observed at 20 of 45.9° and 67.0° [29]. The intense peaks corresponding to CuO were observed at 32.5°, 35.5° and 38.8° [30]. The diffraction peaks at 31.2°, 36.8°, 44.8°, 59.2° and 64.9° indicates the presence of Co<sub>3</sub>O<sub>4</sub> or CuCo<sub>2</sub>O<sub>4</sub> spices in the catalyst [31]. It is difficult to distinguish the phases between Co<sub>3</sub>O<sub>4</sub> and CuCo<sub>2</sub>O<sub>4</sub> because of similar cubic framework and identical unit cell parameters [32]. The intensities of the peaks related to CuCo<sub>2</sub>O<sub>4</sub> or Co<sub>3</sub>O<sub>4</sub> were increased with an increase in Co loading beyond 7 wt. %.



Fig. 1. X-ray diffraction patterns of calcined catalysts (a)  $10Cu/Al_2O_{3,}$ (b)  $10Cu-3Co/Al_2O_{3,}$ (c)  $10Cu-5Co/Al_2O_{3,}$ (d)  $10Cu-7Co/Al_2O_{3}$ , (e) $10Cu-10Co/Al_2O_{3,}$ (f)  $10Cu-13Co/Al_2O_{3,}$ (g)  $10Co/Al_2O_{3,}$ 

The reduced catalysts diffraction patterns are shown in Fig. 2. The main diffraction peaks of  $Al_2O_3$  remain unaltered. All the peaks correspond to CuO have been compromised after reduction. The intense peaks were noticed at 43.9°, 50.66° and 74.1° and these were evidently related to metallic copper moieties [33]. The reduced XRD patterns of bimetallic catalysts majorly exhibited metallic copper species and no diffraction peaks observed for metallic cobalt species. As it is observed in Fig. 1 are not dominantly scene. This suggests that the  $Co_3O_4$  is partly reduced or the surface is mostly covered with CuO species. Interestingly, a new peak evolved right next to the main Cu (43.9°) peak, which can be related to reduced cobalt oxide.

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#### ARTICLE

The catalysts reduction tendency was studied by temperature-programmed reduction and the profiles are made known in the insert of Fig. 3. The TPR results of mono metallic Cu, Co along with bimetallic 10Cu-7Co on  $Al_2O_3$  are shown in the figure 3 for sake of clarity.



 $\label{eq:Fig.2.X-ray diffraction patterns of reduced catalysts (a) 10Cu/Al_2O_3, (b) 10Cu-3Co/Al_2O_3, (c) 10Cu-5Co/Al_2O_3, (d) 10Cu-7Co/Al_2O_3, (e) 10Cu-10Co/Al_2O_3, (f) 10Cu-13Co/Al_2O_3.$ 

The monometallic CuO/Al<sub>2</sub>O<sub>3</sub> showed a two-stage reduction in between 210 to 230 °C. The peak at low temperature was linked to the reduction of Cu<sup>+2</sup> to Cu<sup>+1</sup> and further reduction of Cu<sup>+1</sup> to Cu<sup>0</sup> is noticed at high temperature. The monometallic Co catalyst showed a reduction peak at 355 °C which is the easy reduction step of  $Co^{+3}$  to  $Co^{+2}$  and a broad peak ranging from 480 to 650 °C due to the reduction of Co<sup>+2</sup> to Co<sup>0</sup>. The catalyst with 10%Cu-3%Co showed distinct reduction peaks where, it showed a reduction pattern at low temperature, related to the reduction of CuO to Cu<sup>0</sup> and the high temperature peak related to the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO as this peak intensity is higher than the monometallic CuO/Al<sub>2</sub>O<sub>3</sub> catalyst. The catalysts with high Co content showed indistinguishable two low temperatures reduction peaks at < 350 °C. These reduction peaks might be associated with the reduction of Cu-Co oxides. The existence of Cu effectively decreases cobalt oxide reduction temperature. This might be related to the hydrogen activation on Cu metal sites which helps in easy reduction of Cu-Co mixed oxides. Similar observations were reported by Wang et.al [34]. They discussed about addition of small amount of Cu to Co/Al<sub>2</sub>O<sub>3</sub>, the reduction peak temperature lowered dramatically. As it is observed, in case of the Cu-Co catalysts with 5Co and 7Co content showed two peak maxima which can be attributed to the reduction of both CuO and  $Co_3O_4$ . In case of 7Co catalyst the peak is broader compared to 5Co catalyst indicating the presence of more reducible oxides on the surface. The peak at lower temperature considered due to reduction of Cu<sup>2+</sup> to Cu<sup>+1</sup> reduction peak is not observed, which may be due to the formation of more CuCo<sub>2</sub>O<sub>4</sub> species and less availability of CuO. The peak is mostly related to reduction of Co<sub>3</sub>O<sub>4</sub> species. The catalysts with 10Co and 13Co showed different

pattern with three reduction peak maxima, attributed to the reduction of Cu and Co species. When Compared TRA TRATE monometallic 10Co, no broad reduction peak at high temperature was noticed in case of 10Cu-10Co catalyst, which may be because of the Co-Cu interactions as observed from XRD results.

Table 2: Catalytic activity of glycerol hydrogenolysis over Cu-Co/Al $_2O_3$  catalysts.

	Chaoral	Selectivity %				
Catalysts	Conv. (%)	1,2-	EG	Acetol	Other	
		PDO			S	
$10Cu/Al_2O_3$	92.4	52.4	1.8	41.5	4.3	
$10Cu-3Co/Al_2O_3$	86.7	53.5	1.9	41.1	3.5	
$10Cu-5Co/Al_2O_3$	88.3	62.5	2.1	33.2	2.2	
$10Cu-7Co/Al_2O_3$	98.5	77.2	3.2	18.1	1.5	
$10Cu-10Co/Al_2O_3$	95.4	68.4	3.6	23.9	4.1	
$10Cu-13Co/Al_2O_3$	86.4	58.3	6.7	28.2	6.8	
10Co/Al <sub>2</sub> O <sub>3</sub>	84.2	30.8	26.2	20.7	22.3	

Reaction Conditions: Glycerol conc: 20 wt.%, Reaction Temp.: 200 °C, Cat. Wt: 1g, LHSV: 2.5  $h^{\rm -1}$ 

An interesting observation has been made from the TPR profiles that the H<sub>2</sub> consumption is increasing with the addition of Co to Cu up to a Co content of 7% as shown in Table 1. The  $H_2$  consumption for the 10Cu-7Co catalyst is 1434 µmol. Pure Cu/Al<sub>2</sub>O<sub>3</sub> catalyst showed the lowest amount of H<sub>2</sub> consumption which indicates the presence of low amount of reducible CuO particles on the surface of the catalyst. The Co/Al<sub>2</sub>O<sub>3</sub> catalyst also showed high  $H_2$  consumption of 1260 µmol. The variation in Co amount there is change in the Cu surface area and CuO reducibility. The main factors responsible for H<sub>2</sub> consumption are the availability and reducibility of CuO. As it is seen in all the catalysts the amount of CuO is the same with varying Co amount. The variation in TPR profiles can be attributed to the influence of Cu on cobalt oxide. The catalyst with optimal amount of Co (10Cu-7Co) showed the highest amount of H<sub>2</sub> consumption along with high Cu surface area that attributed to the synergetic effect between Co and Cu.

The surface chemical states of Cu-Co bimetallic samples were systematically probed by XPS technique. The binding energy (B.E) values of calcined, reduced and spent 10%Cu-7%Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples are displayed in Fig. 4. The calcined Cu-Co catalysts B.E values of Cu2p<sub>3/2</sub> and Cu2p<sub>1/2</sub> were noticed at 933.8 and 953.8eV, respectively. The B.E of Cu2p<sub>1/2</sub> was noticeably high (more than 20eV) as a result of a spin-orbit coupling. Indeed, there were no satellite peaks at 934 and 954 eV in calcined Cu-Co bimetallic catalysts [35, 36]. This suggests

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#### **Journal Name**

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that Cu is in the form of CuO. B.E values of  $Co2p_{3/2}$  and  $Co2p_{1/2}$ were observed at 781.8 and 797 eV respectively. The BE separation for the catalyst between the spin-orbit doublets of Co2p levels was consistent at 15eV, that distinguish the presence of Co<sub>3</sub>O<sub>4</sub> spinal. The reduced Cu-Co samples exhibited B.E values at 932.5 and 952.5 eV respectively for Cu2p<sub>3/2</sub> and  $Cu2p_{1/2}$ . These values are ascribed to the presence of  $Cu^0$ metallic species. It was obvious that facile reduction of surface CuO particles into Cu<sup>0</sup> particles takes place during reduction. In case of Co species, no change in the binding energy values was observed. This indicates that  $Co_3O_4$  is not reduced during reduction step. The presence of cobalt oxide moieties in reduced Cu-Co catalyst, clearly indicates that cobalt oxide particles may possibly had efficient interaction with tetrahedral voids of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, thus obviously retard the easy reduction of cobalt oxide.



Fig. 4. XPS patterns of 10Cu-7Co/Al<sub>2</sub>O<sub>3</sub> catalysts.

The binding energies of CoO species slightly moved to higher values for  $Co2p_{3/2}$  at 782.5 eV and  $Co2p_{1/2}$  at 798.4 eV with absence of satellite peaks at 786 and 803 eV. This considerably shows that the  $Co^{3+}$  species were reduced partially to  $Co^{2+}$  in Cu-Co bimetallic catalysts [37, 38]. Even after, the prolonged time-on-stream activity the spent Cu-Co catalysts displays a similar peak as that of virgin catalyst. The results suggest that more number of Cu species are available over the surface of the catalyst rather than Co particles. XPS result also confirms that addition of Co to Cu appreciably enhanced the dispersion of

metallic copper particles, which was in fulfilment with the

results of dissociative  $N_2O$  adsorption results  $^{10.1039/C9NJ04945B}$ 

7Co/Al<sub>2</sub>O<sub>3</sub> catalysts are shown in Fig.5. The particles of Cu-Co

catalysts were distributed uniformly with different phases on

the support Al<sub>2</sub>O<sub>3</sub>. A few overlapped springs specie showed in

circles were observed in the catalyst. The d spacing of 0.47 nm

illustrated the formation of  $CuCo_2O_4$ , and  $Co_3O_4$  phase in the

calcined sample. Besides, d (111) spacing 0.23 nm and 0.28 nm

mostly ascribed to higher number of finely dispersed CuO

species, which is in better correlation with reported ones [34].

Transmission electron microscopy (TEM) images of 10Cu-

Fig. 5. TEM image of 10Cu-7Co/Al<sub>2</sub>O<sub>3</sub> catalysts

#### **Glycerol hydrogenolysis activity**

The hydrogenolysis of glycerol activity of  $Cu/Al_2O_3$  and  $Cu-Co/Al_2O_3$  catalysts are shown in Table 2. Based on initial screening of the catalysts 10% Cu on  $Al_2O_3$  was selected as optimal Cu content for glycerol hydrogenolysis. This catalyst showed about 99% glycerol conversion with 56% selectivity towards 1,2-PD at steady sate condition (after 3h of reaction time).



Fig. 6. Influence of reaction temperature on glycerol hydrogenolysis.

Cu-Co bimetallic supported on Al<sub>2</sub>O<sub>3</sub> catalysts exhibited better catalytic activity in terms of high glycerol conversion and selectivity to 1,2-PD compared to Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. In case of the monometallic catalysts both Cu and Co both showed different selectivities. Cu/Al<sub>2</sub>O<sub>3</sub> catalyst is more selective

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#### Journal Name

towards acetol and 1,2-PD whereas Co/Al<sub>2</sub>O<sub>3</sub> showed high selectivity to EG and other by-products. The 10Cu-3Co/Al<sub>2</sub>O<sub>3</sub> catalyst displayed about 86% glycerol conversion with limited selectivity to 1,2-PD. Further increase in Co, the 10Cu-5Co/Al<sub>2</sub>O<sub>3</sub> catalyst achieved higher catalytic activity with about 62% selectivity towards 1,2-PD. The catalyst with 10Cu-7Co on Al<sub>2</sub>O<sub>3</sub> showed exceptional glycerol hydrogenolysis activity among all the Cu-Co catalysts. This catalyst showed about 100% conversion of glycerol with 77% of 1,2-PD selectivity. Further increase in Co content in the catalysts, there was no improvement in activity and a decrease in selectivity towards 1,2-PD was observed. The activity results of these catalysts can be justified based on their characteristics. The high activity of 10Cu-7Co/ Al<sub>2</sub>O<sub>3</sub> is mainly related to the presence of high Cu metal surface area and its dispersion. The existence of Cu is its metallic form and having strong interaction with Co species as evidence from TPR analysis might led to exceptional hydrogenolysis activity for this catalyst. The presence of Co in its lower oxidation state (CoO) rather than Co<sub>3</sub>O<sub>4</sub> in the catalysts also favours the hydrogenolysis as Co is well known for its hydrogenation activity. The main text of the article should appear here with headings as appropriate.

#### Effect of reaction temperature

Glycerol hydrogenolysis was carried out at different temperature ranging from 180 to 240 °C over most preferable  $10Cu-7Co/Al_2O_3$  catalyst and the results are presented in Fig. 6. Glycerol conversion was about 90% at 180 °C with 48% 1,2-PD selectivity. At a moderate reaction temperature of 180 °C, probably dehydration of glycerol to acetol takes place and its further hydrogenation is limited. These results are in well agreement with reported ones [39]. With rise in reaction temperature to 200 °C, a complete glycerol conversion was observed with 77% selectivity. Further rise in reaction temperature beyond 200 °C, 1,2-PD selectivity was drastically declined. In general, at high reaction temperature over hydrogenated products (methanol, 1-propanol, 2-propanol, and ethanol) formation was favorable and accordingly desired product selectivity is decreased. The preferred reaction temperature is 200 °C for selective formation of 1,2-PD in hydrogenolysis of glycerol over the present catalytic system.



Fig. 7. The role of glycerol concentration on hydrogenolysis activity.

#### Effect of glycerol concentration

Glycerol hydrogenolysis was evaluated in the concentration range of 10 to 40wt% and the outcomes are displayed in Fig.7. The conversion of glycerol increased with enhancement in glycerol concentration up to 20wt% and then a gradual fall in conversion was noticed. About 20wt% glycerol concentration could afford full conversion with 77% 1,2-PD selectivity. Further increase in the glycerol concentration more than 20%, the conversion of glycerol and selectivity of 1,2-PD was considerably decreased. At high glycerol concentration decrease in conversion of glycerol was because of unavailability of more number of active sites of catalyst for the largely present glycerol as the amount of catalyst is constant. Based on different reactant concentrations, 20% glycerol was the optimum concentration to get highest activity.



Fig.8. The effect of LHSV on hydrogenolysis of glycerol.

#### Role of liquid hourly space velocity (LHSV) on catalytic activity

The significant influence of LHSV on catalytic activity during continuous hydrogenolysis of glycerol is shown in Fig. 8. These results intimate that the conversion of was constant up to LHSV

ARTICLE

#### ARTICLE

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Page 6 of 8

Journal Name

of 2.5 h<sup>-1</sup> and then decreased with further increase in LHSV value to 3.3 h<sup>-1</sup>. This was expected as the numbers of active sites available were constant and at higher LHSV the selectivity towards 1,2-PD decreased and the selectivity towards acetol is increased. This indicates that the acidic sites of the catalyst were sufficient for dehydration of glycerol and the active Cu metal sites are not sufficient to hydrogenate acetol to 1,2-PD. The elevated activity of the catalyst relatively at higher LHSV values reiterates the efficiency of the Cu-Co/Al<sub>2</sub>O<sub>3</sub> catalysts towards glycerol hydrogenolysis.

#### Time on stream analysis

The main disadvantage in case of vapor phase hydrogenolysis is the longevity of the catalyst. The Cu based catalysts prone to deactivation during glycerol hydrogenolysis because of the significant growth in Cu particle size and sintering under reaction conditions [41]. Therefore, stability of the catalyst is the main concern for continuous hydrogenolysis of glycerol. In order to check the stability, the reaction was carried for 24 h over 10Cu-7Co/Al<sub>2</sub>O<sub>3</sub> catalyst at 200 °C and results are shown in Fig.9. The monometallic Cu/Al<sub>2</sub>O<sub>3</sub> catalyst also studied for time on stream analysis to know its stability and the results are shown in the same figure. The conversion and selectivity were decreased continuously with time for monometallic Cu catalyst. The decrease in activity of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst might be due to sintering and agglomeration of Cu species [42]. The Cu-Co/Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst exhibited stable activity for the entire period of 24 h with constant glycerol conversion and selectivity to 1,2-PD. This result suggested that the Cu-Co bimetallic catalyst is stable with consistent activity even at atmospheric pressure. It is a potential catalyst for practical application for hydrogenolysis of glycerol.



Fig. 9. Time on stream analysis during glycerol hydrogenolysis over Cu and Cu-Co/ $\gamma$ -Al $_2O_3$  catalysts.

#### Experimental

#### **Catalysts preparation**

Alumina supported copper-cobalt bimetallic catalysts were synthesized by impregnation method. Calculated amount of Cu

 $(NO_3)_2.3H_2O$  and Co  $(NO_3)_2.6H_2O$  were mixed in whether indicated water and added to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. With continuous stimms the excess water was evaporated slowly on hot plate. After removal of water the semi-dried catalyst samples were further dried at 120 °C for overnight and calcined at 400 °C for 3 h to obtain finished catalyst. The Cu content was fixed at 10 wt. % and the Co weight ratio was varied from 3 wt. % to 13wt. %. The catalysts are named as  $10Cu3Co/Al_2O_3$  where the indicate the catalyst contains 10 wt. % Cu and 3wt % Co.

#### **Catalysts characterizations**

Powder X-ray diffraction (XRD) patterns of the samples were recorded on Rigaku X-ray diffract meter using Ni-filtered CuK $\alpha$  radiation ( $\lambda$  = 1.5406 Å) under continuous scan with a speed of 2°min<sup>-1</sup> at 30 kV and 15mA.

BET surface areas were measured by  $N_2$  adsorption isotherm at -196 °C using BELSORP II (BEL Japan. Inc.) adsorption unit. Approximately 0.2 g of catalyst is used for measurement. The catalysts were pre-treated by degassing at 300 °C for 3 h to remove adsorbed gases and moisture.

Temperature-programmed reduction (TPR) was carried using BELCAT II (BEL Japan, Inc.) equipment. Before the TPR run, samples were pre-treated with Ar (60 ml/min) gas for 2 h at 300 °C. After pretreatment, Ar gas was replaced by 5% H<sub>2</sub>/Ar mixed gas and the sample was subjected to temperature programmed heating with ramping of 10°C min<sup>-1</sup> up to 800 °C. Thermal conductivity detector (TCD) was used to monitor H<sub>2</sub> consumption.

The morphological features of the catalysts were captured by transmission electron microscopy (TEM). The TEM images were captured using a Philips Tecnai FEI F20, operating at 120 kV. The sample was prepared by dispersing the catalyst in ethanol by ultrasonic dispersion for 30 min. The suspension drops of were layered on a copper grid prior to the measurements.

XPS analysis was carried out using a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using the Mg K<sub> $\alpha$ </sub> anode. The XPS experimental details are reported elsewhere [17].

The dissociative  $N_2O$  adsorption method was carried out on same BELCAT II instrument used for TPR analysis. The details of the experimental procedure to determine copper metal surface area, dispersion and particle size are reported in our earlier publication [24].

#### Evaluation of glycerol hydrogenolysis reaction

In a typical reaction, about 1g of catalyst is loaded which is sandwiched in a quartz reactor of 10 mm ID between two quartz wool plugs. This reactor was placed in a tubular furnace equipped with programmable temperature controller and monitored by thermocouple placed middle of the catalyst bed. The reactions are done by changing temperature in the range of 180-240 °C at ambient pressure. The catalyst was reduced prior to the reaction at 400 °C with hydrogen flow of 70 ml/min for 2 h. Then the catalyst bed cooled to the required temperature and the feed were introduced at a flow rate LHSV of 2.5 h<sup>-1</sup> into the preheater before passing into the reactor by a microprocessor-based feed pump (Braun Corp. Germany). The outlet of the reactor is connected to the condenser to collect

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the products. The products are analyzed using gas chromatography fitted with flame ionization detector by separating the products using an Inno-wax capillary column. The products and the details of the calculations are reported elsewhere [25].

#### Conclusions

Co-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared with high Cu dispersion and metal surface area. These are highly active for hydrogenolysis of glycerol at ambient pressure to produce 1,2-PD selectively. The presence of Cu significantly improved the reduction of cobalt oxide species. The facile reducibility and high dispersion of Cu particles are accountable for high activity of the catalyst. The catalyst with 10%Cu and 7%Co on Al<sub>2</sub>O<sub>3</sub> exhibited complete glycerol conversion with 77% yield towards 1,2-PD. Different reaction parameters like reaction temperature, influence of reactant flow rates, and glycerol concentration were optimized. The catalyst is highly stable with constant activity for long period of operation.

### **Conflicts of interest**

"There are no conflicts to declare".

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## Studies on continuous selective hydrogenolysis of glycerol over supported Cu-Co bimetallic catalysts

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