Catalysis Today 164 (2011) 447–450

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Role of promoters in copper chromite catalysts for hydrogenolysis of glycerol

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ARTICLE INFO

Article history:
Received 1 July 2010
Received in revised form
28 September 2010
Accepted 2 October 2010
Available online 3 December 2010

Keywords:
Glycerol hydrogenolysis
1,2-Propylene glycol
Acetol
Ammonia TPD
Surface acidity

ABSTRACT

Various copper chromite catalysts with and without promoters were prepared by simultaneous co-precipitation and digestion technique and the role of promoters (Al, Ba and Zn) was investigated for hydrogenolysis of glycerol to 1,2-propylene glycol (1,2-PG) in both batch and continuous operations. Among various promoters studied, copper chromite catalyst with Ba as a promoter showed the highest activity and selectivity of 85% to 1,2-PG. This catalyst was found to be active for more than 800 h in a continuous operation also. Ammonia TPD results showed that barium promoted copper chromite catalyst had the highest acidity which facilitates the dehydration of glycerol to acetol which is the first step in hydrogenolysis of glycerol to 1,2-PG. The effect of barium content and variation in the promoters combination was also studied.

1. Introduction

Large amount of glycerol is formed as a byproduct due to the rapid development of biodiesel industries. Being a highly functionalized molecule glycerol can be converted into value added chemicals by various transformations such as hydrogenolysis to propanediol, oxidation to glyceric acid, dehydration to hydroxyacetone or acrolein and reforming to syngas [1,2]. Among these processes, selective catalytic hydrogenolysis of glycerol represents a low cost and green route for 1,2-propylene glycol which is a major commodity chemical used in the production of antifreeze functional fluids, paints, humectants, and polyester resins [2,3]. The commercial route for propylene glycol involves the hydration of propylene oxide derived from petroleum based propylene by chlorohydrin process or the hydroperoxide process [4,5]. Hence, catalytic hydrogenolysis of glycerol to 1,2-PG is a sustainable process based on renewable bio-feedstock.

Several studies are reported for hydrogenolysis of glycerol using noble metal catalysts [6–9] as well as other transition metals mainly copper and zinc on active carbon, SiO_2, Al_2O_3 [10–12]. Mono- as well as bimetallic combination of noble metals such as Ru, Rh, and Pt are well known for hydrogenolysis of glycerol [13,14]. Tomishige et al. have studied in detail the combination of Ru/C and amberlyst resin for glycerol hydrogenolysis achieving glycerol conversion of 79.3% with the highest selectivity of 82% to 1,2-PG at 393 K and 80 bar initial H_2 pressure for 10 h [15–17]. Unfortunately, Ru based catalysts often promote excessive C–C cleavage, resulting in the formation of degradation products such as ethylene glycol and methane. Since, 1,2-PG formation via glycerol hydrogenolysis involves selective cleavage of C–O bond without breaking C–C bond, copper based catalysts were found to show superior performance in the hydrogenolysis reaction due to their high efficiency for C–O bond hydrogenolysis and poor activity for C–C bond cleavage [18]. Chaminand et al. reported Cu–Zn based catalysts for glycerol hydrogenolysis with 100% selectivity to 1,2-PG at ~20% conversion at 453 K, however the reaction time reported was incredibly high (90 h) under 8 MPa H_2 pressure conditions [19]. Wang and Liu proposed bifunctional Cu–ZnO catalysts and obtained 84% selectivity to 1,2-PG with 23% glycerol conversion in 12 h [20]. Another composition of Cu–ZnO catalyst has been reported to give highest selectivity of 93% to 1,2-PG with 34% glycerol conversion in 16 h reaction time [21]. Cu:Al nano structured catalyst system has been recently reported by Mane et al. for the hydrogenolysis of glycerol under relatively milder conditions giving >47% glycerol conversion in 5 h [22]. Using Cu–Cr based catalysts, Dasari et al. efficiently converted glycerol to 1,2-PG with high selectivity of 85% at ~55% conversion (after 24 h) at 473 K [18]. It is well known that one or more metals from groups II and III are usually incorporated as promoters in copper chromite catalyst systems. These promoters play a vital role in enhancing the catalyst activity as well as the product selectivity particularly in case of glycerol hydrogenolysis, in which the first step involves the acid catalyzed dehydration to acetol [18] and also for controlling the formation of degradation products such as ethylene glycol, methanol, and 1-propanol. Recently, Rode et al. reported continuous hydrogenolysis of glycerol for >800 h over Cu–Cr catalyst [23]. In continuation of this work,

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doi:10.1016/j.cattod.2010.10.032

a systematic study on the role of promoters in Cu–Cr catalysts is reported here.

Therefore, the main objective of the present work was to study systematically the additive effect of each promoter such as Al, Ba and Zn separately and with their combination, on the activity and selectivity of copper chromite catalysts for hydrogenolysis of glycerol. For this purpose, copper chromite catalysts with different combinations of aluminum, barium and zinc were prepared by co-precipitation method and screened for glycerol hydrogenolysis reaction. Among various promoters studied, Ba showed the highest activity with 34% conversion of glycerol and 85% selectivity to 1,2-PG whereas Cu–Cr without any promoter showed the least catalyst activity with 16% conversion of glycerol. Catalyst characterization results revealed that the higher acidity and the stabilization of Cu^0 state due to the presence of Ba were mainly responsible for its higher activity and selectivity in hydrogenolysis of glycerol.

2. Experimental

2.1. Materials

Glycerol (99.9%), ethylene glycol were purchased from Merck Specialties, Mumbai, India and acetol, 1,2-propylene glycol, and 2-propanol were procured from Sigma–Aldrich, Bangalore, India. 30% aqueous ammonia, copper nitrate, ammonium dichromate, zinc nitrate, aluminium nitrate, barium nitrate were purchased from Loba Chemie, Mumbai, India. Hydrogen and nitrogen of high purity were obtained from Inox, India.

2.2. Catalyst preparation

Copper chromite catalysts with and without promoters with different compositions of Cu (30–66%) (designated as NMT006, NMT002, T1, T2, T3, T4, NMT005 and NMT008) along with promoters such as Al, Zn and Ba were prepared by the co-precipitation method by adding respective amounts of ammonium chromate solution to the nitrate solutions of metal precursors under stirring in a thin stream. After complete addition, reddish brown precipitate was obtained which was then filtered, dried at 373 K, calcined (673 K) and activated under H_2 flow.

Activity measurement for glycerol hydrogenolysis was carried out in both batch reactor of 300 mL capacity autoclave (Parr Instruments Co., USA) and high pressure continuous fixed bed SS single tube reactor of 25 g catalyst holding capacity under standard conditions: 20 wt% glycerol solution, temperature 493 K. Liquid samples were analyzed using Varian 3600 GC with FID detector and FFAP capillary column with a temperature programming of 353–463 K.

2.3. Physico-chemical characterization

X-ray powder diffraction patterns were recorded on a Rigaku, D-Max III VC model, using nickel filtered CuKα radiation. The samples were scanned in the 2θ range of 10–80 °C. For acidity measurements, ammonia TPD measurements were carried out on a Quantachrome CHEMBET 3000 instrument by (1) pre-treating the samples from room temperature to 473 K under nitrogen flow rate of 65 mL/min, (2) adsorption of ammonia at room temperature and (3) desorption of adsorbed ammonia with a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ starting from the adsorption temperature to 973 K.

2.4. Catalytic activity test

Glycerol hydrogenolysis reactions were carried out in a Parr autoclave of 300 mL capacity. Typical hydrogenolysis conditions were: temperature, 493 K; glycerol concentration, 20 wt%; catalyst loading, 1 g; and hydrogen pressure, 5 MPa. The prepared catalysts were pre-reduced under H_2 at 473 K for 12 h.

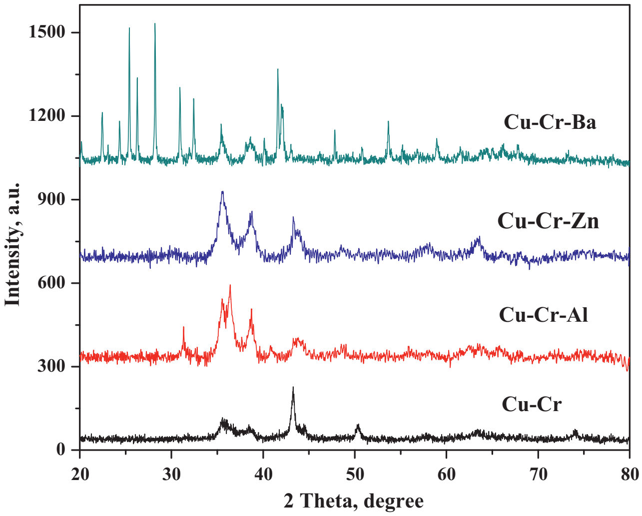

Fig. 1. XRD patterns of Cu–Cr catalyst with and without promoters.

The progress of reaction was observed by decrease in hydrogen pressure as a function of time, during the reaction. The reactant and obtained products withdrawn from the reactor from time to time were also analyzed by GC system (Varian 3600) equipped with FID detector and capillary HP-FFAP (Free Fatty Acid Phase) (30 m length × 0.53 mm i.d. × 1 μm film thickness) column. The products detected during glycerol hydrogenolysis mainly included 1,2-PG, acetol and ethylene glycol. Glycerol conversion and product selectivity were calculated using following equations:

$$\text{Conversion}\,(\%) = \frac{\text{initial moles of glycerol} - \text{final moles of glycerol}}{\text{initial moles of glycerol}} \times 100 \qquad (1)$$

$$\text{Selectivity}\,(\%) = \frac{\text{moles of a product formed}}{\sum \text{moles of all the products}} \times 100 \qquad (2)$$

3. Results and discussion

Fig. 1 shows XRD patterns of the various activated Cu–Cr catalyst samples without and with Al, Ba and Zn promoters. In all these samples content of Cu as well as that of different promoters were kept constant at 52% and 30% respectively. Copper chromite without any promoter showed predominant peaks at 2θ values of 43.2° and 50.1° [24] which could be attributed to Cu^0 while two small peaks at 35.4° and 38.4° showed the presence of Cu^{2+} [20]. While the XRD spectrum of the Ba promoted copper chromite catalyst showed peaks at 2θ values of 22.4°, 25.4°, 28.2°, 41.6°, 41.9°, 43° and 30.9° which correspond to $BaCrO_4$ phase [25]. A peak at 2θ value of 43.2° was due to Cu^0 while no peak corresponding to Cu^{2+} or Cu^{1+} was observed. Al promoted Cu–Cr showed a major peak at 2θ of 36.4° which was due to Cu^{1+} state and two minor broad peaks at 2θ of 35.4° and 38.4° for Cu^{2+}. Cu–Cr catalyst with Zn also showed the presence of Cu^{2+} with only small amount of metallic copper. This clearly showed that the presence of Ba was responsible for stabilizing Cu^0 state in copper chromite catalysts which is mainly responsible for hydrogenolysis of glycerol as indicated by the activity results shown in Fig. 2. It is also interesting to note that crystallite sizes obtained from diffraction peaks for Cu^0 (2θ 43.2°) state in Cu–Cr catalysts without and with promoters varied as follows: 156 nm (Cu–Cr) > 149 nm (Cu–Cr–Zn) > 95 nm (Cu–Cr–Al) > 69 nm (Cu–Cr–Ba). Thus Ba was found to be responsible for inhibiting the

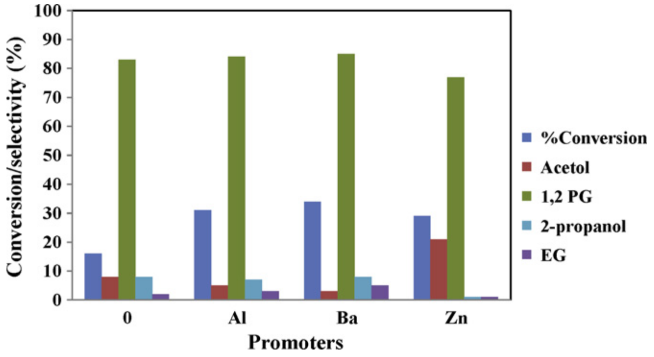

Fig. 2. Effect of promoters on glycerol hydrogenolysis. Reaction conditions: temperature, 493 K; 20 wt% glycerol; pH_2, 52 bar; solvent, 2-propanol; catalyst, 0.01 g/ml; reaction time, 5 h.

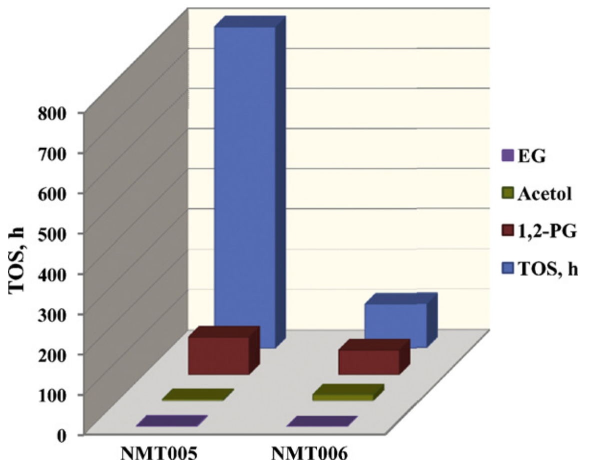

Fig. 3. Time on stream activity of Cu–Cr–Ba (NMT005) and Cu–Cr (NMT006) catalysts. Reaction conditions: catalyst wt., 23 g; solvent, 2-propanol; 20 wt% glycerol; feed flow rate, 30 ml/h; H_2 flow rate, 10 NL/h; pressure, 40 bar; temperature, 493 K.

agglomeration which also has been reported earlier [26]. The inhibition of agglomeration by Ba leading to a longer catalyst activity was also evidenced by time on stream activity of >7 fold than of only Cu–Cr catalyst for continuous hydrogenolysis of glycerol, as shown in Fig. 3.

The first step of glycerol hydrogenolysis involves its dehydration to acetol which is said to be catalyzed by acid sites of the catalyst/support. Hence, the strength and nature of acid sites of our catalysts were also determined by NH_3-TPD and the results are presented in Table 1. Cu–Cr catalyst showed the least acidity (0.3414 mmol NH_3/g) while Cu–Cr–Ba (NMT005) sample showed the highest acidity (1.2444 mmol NH_3/g). Although, both Al and Ba promoters showed similar acidity in lower temperature region (region I), acidity for Ba promoted sample increased substantially in region II (temperature range of 473–673 K) which corresponds to the reaction temperature used in this work. Hence the activity of Ba promoted catalyst was also found to be higher than that for Al promoted catalyst.

Table 1
Ammonia TPD results of Cu–Cr catalysts with different promoters.

Sr. no.	Catalyst	Promoter	NH_3 desorbed region wise			Total NH_3 desorbed (mmol/g)
			Region I	Region II	Region III	
1	NMT006	Nil	0.0208	0.2299	0.0907	0.3414
2	NMT001	Al	0.1255	0.3743	0.3562	0.856
3	NMT005	Ba	0.1255	0.8684	0.2505	1.2444
4	NMT011	Zn	0.0910	0.3452	0.3494	0.7856

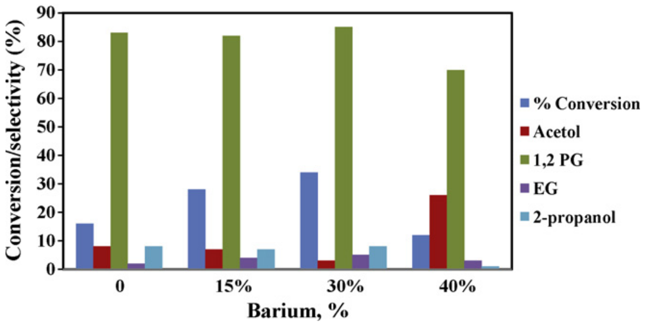

Fig. 4. Effect of Ba content on glycerol hydrogenolysis. Reaction conditions: temperature, 493 K; 20 wt% glycerol; pH_2, 52 bar; solvent, 2-propanol; catalyst, 0.01 g/ml; reaction time, 5 h.

It was observed that Cu–Cr without any promoter showed the least activity (16% conversion) towards glycerol hydrogenolysis (Fig. 2). While Cu–Cr catalyst with barium showed highest glycerol conversion of 34% in comparison with the other promoters as aluminium and zinc which gave about 29 and 24% glycerol conversion respectively. From the activity results and characterization of catalysts described above, the highest activity of barium promoted Cu–Cr catalyst was mainly due to the following reasons. (i) Higher acidity responsible for catalyzing the first step of dehydration of glycerol to acetol, more efficiently. (ii) Formation of $BaCrO_4$ phase that inhibits the growth of crystallites contributing to prolonged catalyst activity under high temperature reaction conditions [26].

Since, Ba was found to be the best promoter, effect of barium content was also studied in the range of 15–40% and the results are shown in Fig. 4. It was observed that the activity increased with the increase in barium content up to 30%, after which it decreased substantially (from 34 to <20% conversion) for higher barium content of 40%. XRD pattern of the catalysts with different Ba contents showed the decrease in diffraction peak intensity for Cu^0 state with increase in Ba content up to 30% whereas at higher 40% Ba content diffraction peak for Cu^0 state diminished (Fig. 5). This could be due to fact that the critical concentration of Ba exists beyond which the $BaCrO_4$ inhibits the migration of Cu from the bulk to the surface hence decreasing the hydrogenation activity. Ba content beyond

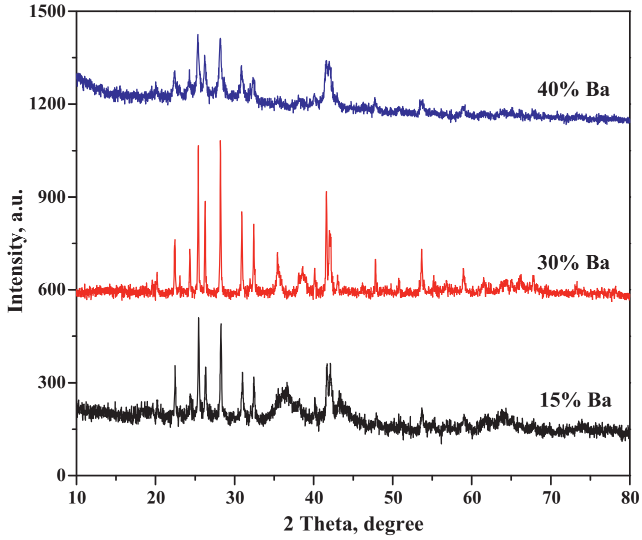

Fig. 5. XRD patterns of Cu–Cr catalyst with different barium contents.

Table 2
Ammonia TPD results of Cu–Cr catalysts with different Ba contents.

Sr. no.	Catalyst	Ba	NH_3 desorbed region wise			Total NH_3 desorbed (mmol/g)
			Region I	Region II	Region III	
1	NMT006	0	0.0208	0.2299	0.0907	0.3414
2	T3	15	0.1255	0.8684	0.2505	0.482
3	NMT005	30	0.0241	0.1713	0.2866	1.2444
4	T4	40	0.0610	0.6675	0.5843	1.3128

Table 3
Activity of Cu–Cr catalysts with promoter combinations.

Catalyst	Promoters (%)			% conversion	% selectivity			
	Al	Ba	Zn		Acetol	1,2-PG	EG	2-Propanol
NMT006	–	–	–	16	8	83	2	8
T2	39	–	11	34	4	90	1	5
T1	11	–	39	17	6	85	5	4
NMT008	19	10		26	16	71	10	3

40% also affected the selectivity pattern. With increase in Ba content from 30 to 40%, acetol selectivity increased substantially from <5% to 25% and at the same time 1,2-PG selectivity decreased from 84% to 70% (Table 2). As the Ba content increased, the enhanced acidity was responsible for the dehydration of glycerol to acetol while the second step of acetol hydrogenation was retarded due to less number of Cu atoms on the catalyst surface.

As can be seen from Fig. 3 and also discussed above, time on stream activity of Ba containing Cu–Cr catalyst (NMT005) showed much higher activity and stability than Cu–Cr catalyst without a promoter (NMT006) confirms that the choice of an appropriate promoter is necessary for a stable activity under reaction conditions.

Since, the activity achieved was almost double for Cu–Cr catalyst containing both Al and Ba as promoters (Fig. 2), effect of combination of both these promoters together (NMT008) on the activity was also evaluated and the results are shown in Table 3. Surprisingly, 1,2-PDO selectivity obtained for NMT008 catalyst was much lower (71%) than the catalysts containing a single promoter. Lowering in 1,2-PG selectivity for a catalyst containing both Al and Ba promoters was mainly due to the formation of cracked product like ethylene glycol (10%) from glycerol and also due to accumulation of an intermediate acetol (selectivity 16%) indicating slower kinetics of acetol hydrogenation. Further work on detail catalyst characterizations as well as kinetics of the various steps involved in glycerol hydrogenolysis is in progress.

4. Conclusions

The role of promoters in copper chromite catalysts was found to be very important in determining the activity as well as the selectivity in hydrogenolysis of glycerol. Effect of three promoters viz. Al, Zn and Ba was studied individually as well as in combination with each other for the hydrogenolysis of glycerol. Cu–Cr catalyst with Ba as a promoter showed the highest conversion of 34% with highest selectivity of 85% to 1,2-PG in a batch operation while in a continuous operation it gave still higher conversion of 65% with a higher (>7 fold) catalyst stability as compared to Cu–Cr catalyst without any promoter. Highest activity and selectivity with Ba was mainly due to enhanced acidity catalyzing the first step of dehydration of glycerol to acetol and due to $BaCrO_4$ phase stabilizing the crystallite size of Cu^0 at a lower value (69 nm) than that compared to ∼150 nm incase of bare Cu–Cr catalyst.

Acknowledgement

We gratefully acknowledge Council of Scientific and Industrial Research, New Delhi for its financial support to this work under NMITLI program (TLP 002326).

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