Catalysis Communications 11 (2010) 493-497

Contents lists available at ScienceDirect

Catalysis Communications

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



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ARTICLE INFO

Article history: Received 16 September 2009 Received in revised form 5 November 2009 Accepted 4 December 2009 Available online 11 December 2009

Keywords: Carbothermal reduction Glycerol hydrogenolysis Potassium borohydride Propylene glycol

1. Introduction

Catalytic conversion of renewable biomass resources into valuable chemicals is a challenging and promising process. Glycerol, which is the by-product of biodiesel manufactures [1] and also derived from sugars or sugar alcohols [2], is an important biomassderived compound. The low price and rich availability make it a potential feedstock for the manufacture of high value-added chemicals, especially 1,2-propylene glycol (1,2-PG). 1,2-PG is of great demand for producing polymers and resins, as well as pharmaceuticals, foods, cosmetics or functional fluids. The current industrial production of 1,2-PG is from petroleum derivatives by chemical catalytic routes via hydration of propylene oxide [3]. Comparably, as an alternative route, the catalytic converting of glycerol to 1,2-PG seems to be more advantageous. A number of reports were published for the catalytic hydrogenolysis of glycerol. Noble metal catalysts of Ru, Rh, Pd and Pt [4-9] were explored in this reaction; however, the majority of noble metal catalysts were not so efficient. Over Ru/C plus Amberlyst, the conversion is only 12.9% [4,5]; Rh/SiO₂ only gave 19.6% conversion with 34.6% selectivity of 1,2-PG [6]. In recent years, non-noble metals had attracted increasing attention and Raney Ni, Cu-Cr, Cu-ZnO, and Cu/SiO₂ [10-14] were reported for glycerol hydrogenolysis. The research of supported non-noble Ni catalyst was slightly reported in this kind of reaction.

ABSTRACT

It reported a novel procedure for preparing Ni/AC catalyst for the glycerol hydrogenolysis, which involved carbothermal reduction of supported nickel nitrate and further treatment with KBH₄. The activity of the as-prepared catalyst was remarkably enhanced compared with KBH₄, H₂ or carbothermal reduced Ni/AC catalyst. The Ni particles and the variation of oxygen-containing surface groups (OSGs) were studied by XRD, TEM, FT–IR, He-TPD and NH₃–TPD techniques. The high dispersed Ni and the acidity generated by the OSGs have the synergy effect on the activity of glycerol hydrogenolysis.

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Carbon supported nickel catalyst was an excellent non-noble hydrogenation catalyst used in various hydrogenation reactions [15–17]. The rich oxygen-containing surface groups (OSGs) in the carbon supports, i.e. carboxylic, phenolic, quinone, lactonic and etheric groups, strongly influenced the hydrogenation performance [18-21]. It demonstrated that the OSGs have positive effect including: (1) enhancing the metal dispersion due to the metal particles anchored by selective groups [18,20]; (2) change the surface polarity to facilitate the adsorption of organic reactant [19]; (3) adjusting the surface acidity or basicity to promote the hydrogenation activity [21]. The composition and amount of OSGs played important roles on hydrogenation reaction. In this work, it reported a novel procedure for preparing Ni/AC (activated carbon) catalyst by the treatment of KBH₄ on carbothermal reduced catalyst, and investigated the effect of OSGs on catalytic activity in glycerol hydrogenolysis.

2. Experimental

 $Ni(NO_3)_2/AC$ was prepared by incipient wetness impregnation method as follows: AC (coconut shell, 80–100 mesh, 1318 m²/g BET surface area) was immersed in desired amount of 1.2 M $Ni(NO_3)_2$ aqueous solution for 24 h at room temperature and then dried overnight at 393 K. The loading amount of nickel in the catalyst was all 10 wt.%. The carbothermal reduction and H₂ reduction of $Ni(NO_3)_2/AC$ were carried out in tubular furnace with 90 min ramp and a 180 min hold at 723 K under flow N₂ and H₂ (99.999% purity). The samples were denoted as Ni/AC-C and





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Fig. 1. XRD patterns of (a) Ni/AC-C, (b) Ni/AC-CB, (c) Ni/AC-H, (d) Ni/AC-HB and (e) NiB/AC.

Ni/AC-*H*, respectively. Then, the reduced samples of Ni/AC-*C* and Ni/AC-*H* were treated by 2.0 M KBH₄ containing 0.2 M NaOH with continuous stirring. The catalysts were named as Ni/AC-*CB* and Ni/AC-*HB*, respectively. The NiB/AC amorphous alloy catalyst was prepared by the reduction of the dried Ni $(NO_3)_2$ /AC with the 2.0 M KBH₄ solution containing 0.2 M NaOH.

The identification of crystal phases was performed by X-ray powder diffraction (XRD) using Rigaku D/Max 3400 powder diffraction system with Cu K α radiation (λ = 0.1542 nm) at 40 kV and 200 mA with a scanning rate of 5°/min. The microstructures

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The characteristics of the as-prepared Ni/AC catalysts.

Catalysts	S_{BET}	V _{total}	d _{XRD} ^a	d _{TEM}	CO ^b
	(m ² /g)	(cm ³ /g)	(nm)	(nm)	(µmol/g)
Ni/AC-C	1095	0.44	16.5	20.8	368.2
Ni/AC-CB	1056	0.43	16.9	23.3	385.8
Ni/AC-H	1295	0.58	20.4	26.4	160.5
Ni/AC-HB	1317	0.53	28.9	29.6	257.7
NiB/AC	1135	0.46	-	24.7	299.2

^a Average crystallite size calculated by Scherrer equation according to the Ni (111).

^b Amount of CO evolved in He-TPD test.

of the catalysts were examined by transmission electron microscopy (TEM) on a JEOL JEM-2000EX electron microscope. The surface area of catalysts was measured with the BET method by using N₂ adsorption–desorption measurements at 77 K in a Quantachrome Autosorb-1. Fourier transform infrared spectra (FT–IR) were collected on a Bruker Tensor 27 FT–IR spectrometer. He-temperature-programmed desorption (He-TPD) and NH₃-temperature-programmed desorption (NH₃-TPD) were used to study the surface groups and catalyst acidity on a Micromeritics Auto-Chem II 2920 instrument.

Hydrogenolysis of glycerol was carried out in a 600 mL batch autoclave reactor (Parr Instrument Co.). The reactor was initially loaded with glycerol aqueous solution (25 wt.%) and the catalyst. After air had been flushed out, the reactor was heated to 473 K and pressurized with 5 MPa of H₂, and then the reaction was started. The pressure was kept constant by supplying H₂ during the reaction. The products were identified by Agilent 6890N GC/



Fig. 2. TEM micrographs of Ni based catalysts (a) Ni/AC-C, (b) Ni/AC-CB, (c) NiB/AC, (d) Ni/AC-H, (e) Ni/AC-HB and (f) their particle size distribution.

5973 MS detector and quantified by Agilent 4890D GC equipped with FID detector and a HP-5 ($30 \text{ m} \times 0.53 \text{ mm} \times 0.6 \mu \text{m}$) capillary column with the internal standard method. Conversion is defined as the molar ratio of the consumed glycerol in the reaction to the initial added glycerol. Selectivity is defined as the molar ratio of the product to the consumed glycerol in the reaction [11].

3. Results and discussion

Fig. 1 showed the XRD patterns of these catalysts. The Ni/AC-C displayed three typical peaks of metallic Ni around 44° , 52° , and 76° of 2θ [22]. For Ni/AC-*CB*, the typical peaks of metallic Ni still existed and the Ni crystallite size slightly changed from 16.5 to 16.9 nm according to Scherrer calculation. It was indicated that KBH₄ treatment did not change the metallic Ni. The XRD curve of Ni/AC-*H* (-*HB*) still showed the peak of metallic Ni, however, the Ni crystallite size of Ni/AC-*HB* was much larger (Table 1). Differently, NiB/AC had the typical amorphous alloy characteristics [23] with a weak and broad peak at 44° of 2θ .

Fig. 2 exhibited the morphology of the fresh prepared catalysts. It could be observed that the particles in Ni/AC-*C* and Ni/AC-*CB* were highly and evenly dispersed on AC support. The size distribution of particles was much narrower, and the average size of the metal particles was appropriately close. However, for Ni/AC-H (-*HB*) and NiB/AC, the dispersion of particles was unsatisfactory and the size turned bigger.

The specific surface areas of the catalysts were shown in Table 1. For Ni/AC-*C* (-*CB*) and NiB/AC, the BET surface area was decreased obviously in comparison with AC, suggesting surface was probably changed or partial pores were blocked. However, the catalysts still maintain a rather high surface area. The surface area of Ni/AC-*H* (-*HB*) slightly changed compared to AC, which indicated that this treatment had no effect on the catalysts.

Fig. 3 showed the He-TPD spectra results of all the samples treated by different methods. The amount of CO₂ releasing in all the catalyst was much less than the CO releasing. Compared with AC. the OSGs of Ni/AC-C catalyst was increased evidently. There were two obviously CO peaks in the 920 K and 1080 K, which could be attributed to the phenolic and carbonyl group, respectively [24]. It was probably because the released HNO₃ and NO_x from nickel nitrate decomposition [25] would oxygenate partial surface of AC. For the Ni/AC-CB, the CO peak in the 1070 K was weakened and the peak of 920 K was strengthened, which indicated that the carbonyl group was reduced to phenolic group during the KBH₄ treating. The total amount of evolved CO was almost approaching (Seen in Table 1). For Ni/AC-H and Ni/AC-HB, same phenomenon could be seen; however, the amount of OSGs was low. For NiB/AC, the He-TPD was similar to that of Ni/AC-CB, and the releasing amount of CO was between that of Ni/AC-CB and Ni/AC-HB. The results indicated that KBH₄ could reduce the carbonyl group to phenolic group which leaded to the redistribution of OSGs.

FTIR spectra were another proof for the OSGs change (seen in Fig. 4). The peak in 1560 cm⁻¹ was attributed to quinone structure [26]. It was strengthened for Ni/AC-*C* in comparison with AC and then weakened for Ni/AC-*CB*. The phenomenon was in accordance with the results of He-TPD analysis.

Catalysts were in further tested by NH₃-TPD analysis to estimate the acidity, and the results were shown in Fig. 5. For Ni/AC-*CB*, the strength and the amount of acidity were enhanced remarkably and it owned the highest acidity in all the catalysts. The obvious increasing of acidity probably resulted from KBH₄ reducing the carbonyl structure to phenolic hydroxyls, which was considered as one kind of the acid groups in AC [27].

Catalytic performances were tested in the hydrogenolysis of glycerol (Table 2). Ni/AC-*H* and Ni/AC-*C* only gave 7.4% and 6.3%



Fig. 3. He-TPD profiles for (a) Ni/AC-*C* and Ni/AC-*CB*, (b) Ni/AC-*H* and Ni/AC-*HB* and (c) NiB/AC.

of glycerol conversion, respectively. The further KBH₄ treating resulted in their activity obviously increased. The glycerol conversion



Fig. 4. FT-IR spectra of the catalysts of (a) AC, (b) Ni/AC-C and (c) Ni/AC-CB.



Fig. 5. NH₃-TPD curves of (a) AC, (b) NiB/AC, (c) Ni/AC-*H*, (d) Ni/AC-*HB*, (e) Ni/AC-*C* and (f) Ni/AC-*CB*.

increased to 10.8% over Ni/AC-*HB* and 43.3% over Ni/AC-*CB* catalyst. NiB/AC amorphous alloy was in further investigated and the glycerol conversion was 16.6%, which was between the Ni/AC-*CB* and Ni/AC-*HB*. The activity of Ni/AC-*CB* was the highest among these catalysts. The conversion was increased by about 6 times in comparison with Ni/AC-*C*, and the selectivity of 1,2-PG was obviously improved to 76.1%. The result was better than that of some already reported catalysts in similar condition [4–6]. When extending the reaction time to 24 h, the conversion reached 63.2% with 77.4% selectivity of 1,2-PG. The activity sequence was that Ni/AC-*CB* > NiB/AC > Ni/AC-*HB* > Ni/AC-*C* \approx Ni/AC-*H*.

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Catalytic performance of the as-prepared Ni/AC catalysts.

Catalysts	Conversion (%)	Selectivity (%)	Selectivity (%) ^a	
		1,2-PG	EG	
Ni/AC-C Ni/AC-CB Ni/AC-CB ^c Ni/AC-H Ni/AC-HB	7.4 43.3 63.2 6.3 10.8	18.3 76.1 77.4 38.2 63.5	n.d. ^b 8.0 7.9 29.1 n.d.	
N1B/AC	16.6	38.3	n.d.	

Reaction conditions: 150 g 25 wt.% glycerol aqueous solution, 0.695 g Ni in the catalyst, 5 MPa $\rm H_2,\,473$ K, 6 h.

^a Other byproducts mainly including methanol, ethanol and propane.

^b Not detected.

^c 24 h of reaction time.

The high activity of the as-prepared Ni/AC-CB could attribute to synergy effect of hydrogenation center and acidity generated from the variation of OSGs. The carbothermal reduction process formed the metallic Ni as the hydrogenation center, and simultaneously generated large amount of OSGs, which could anchor the new formed metallic Ni [20] and lead to high dispersion. However, the activity of such catalyst (Ni/AC-C) was unsatisfactory. It indicated only metallic Ni was not efficient for glycerol hydrogenolysis. When it was further treated with KBH₄ to reduce the carbonyl group, the glycerol conversion was enhanced immediately. NH₃-TPD verified that the acidity was greatly increased by the transformation of OSGs. The high acidity combined with the metallic Ni corporately enhanced the activity. The mechanism of glycerol hydrogenolysis was consistent with the recent reports [3,9,14]. Over Ni/AC-CB, glycerol was first dehydrated to the intermediate of acetol over the acid sites generated by the variation of OSGs, and this process was a rate-determining step. After the step was finished, the hydrogenation of acetol was quickly realized on the high dispersed Ni metal formed by carbothermal reduction. However, for Ni/AC-C, Ni/AC-H, Ni/AC-HB and NiB/AC, they had low amount of acid, which make the rate-determining step could not effectively progress and absolutely resulted in the lower activity.

4. Conclusions

The efficient catalyst was successfully prepared by KBH₄ treating the carbothermal reduced Ni/AC. The XRD, TEM, FT–IR, He-TPD and NH₃-TPD characterization indicated that carbothermal reduction provided the Ni active sites and simultaneously generated large amount of OSGs in AC support, and further KBH₄ treating reduced the carbonyl group to phenolic group which greatly increased the catalyst acidity. The as-prepared catalyt gave 43.3% conversion of glycerol and 76.1% selectivity for 1,2-PG over Ni/ AC-CB catalyst at 200 °C under 5 MPa H₂ after 6 h, and 63.2% conversion with 77.4% selectivity for 1,2-PG after 24 h. The result was much better than that of catalysts prepared by KBH₄ reduction, carbothermal reduction, and H₂ reduction. It suggested that the highly dispersed Ni and the acidity generated from OSGs have the synergy effect on the activity of glycerol hydrogenolysis.

Acknowledgements

This work was financially supported by the Key Program of CAS Action Plan of Science and Technology for Revitalization of Northeast China and Forefront Program of Knowledge Innovation Project of CAS (K2006D1). W. Yu et al./Catalysis Communications 11 (2010) 493-497

References

- [1] C. Chiu, Ind. Eng. Chem. Res. 45 (2006) 791-795.
- [2] T.A. Werpy, J.G. Frye Jr., A.H. Zacher, D.J. Miller, US Pat. 6,677,385 (2004).
- [3] A. Alhanash, E.F. Kozhevnikova, I.V. Kozhevnikov, Catal. Lett. 120 (2008) 307-311.
- [4] T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, J. Catal. 240 (2006) 213– 221.
- [5] T. Miyazawa, S. Koso, K. Kunimori, K. Tomishige, Appl. Catal. A 318 (2007) 244– 251.
- [6] I. Furikado, T. Miyazawa, S. Koso, A. Shimao, K. Kunimori, K. Tomishige, Green Chem. 9 (2007) 582–588.
- [7] E.P. Maris, W.C. Ketchie, M. Murayama, R.J. Davis, J. Catal. 251 (2007) 281-294.
- [8] E.P. Maris, R.J. Davis, J. Catal. 249 (2007) 328-337.
 [9] M. Balaraju, V. Rekha, P.S. Sai Prasad, B.L.A. Prabhavathi Devi, R.B.N. Prasad, N.
- [9] M. Balaraju, V. Rekna, P.S. Sal Prasad, B.L.A. Prabnavatni Devi, R.B.N. Prasad, N. Lingaiah, Appl. Catal. A 354 (2009) 82–87.
- [10] A. Perosa, P. Tundo, Ind. Eng. Chem. Res. 44 (2005) 8535-8537.
- [11] M.A. Dasari, P.-P. Kiatsimkul, W.R. Sutterlin, G.J. Suppes, Appl. Catal. A 281 (2005) 225–231.
- [12] J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel, C. Rosier, Green Chem. 6 (2004) 359–361.
- [13] S. Wang, H.C. Liu, Catal. Lett. 117 (2007) 62-67.
- [14] Z.W. Huang, F. Cui, H.X. Kang, J. Chen, X.Z. Zhang, C. Xia, Chem. Mater. 20 (2008) 5090-5099.

- [15] W.H. Wu, J. Xu, R. Ohnishi, Appl. Catal. B 60 (2005) 129-137.
- [16] Y.G. He, M.H. Qiao, H.R. Hu, J.F. Deng, K.N. Fan, Appl. Catal. A 228 (2002) 29–37.
 [17] A. Nieto-Márquez, S. Gil, A. Romero, J.L. Valverde, S. Gómez-Quero, M.A. Keane,
- Appl. Catal. A 363 (2009) 188–198. [18] A. Sepúlveda-Escribano, F. Coloma, F. Rodríguez-Reinoso, Appl. Catal. A 173
- (1998) 247–257. [19] M.L. Toebes, Y.H. Zhang, J. Hájek, T.A. Nijhuis, J.H. Bitter, A.J. van Dillen, D.Yu.
- Murzin, D.C. Koningsberger, K.P. de Jong, J. Catal. 226 (2004) 215–225.
- [20] A.E. Aksoylu, M.M.A. Freitas, J.L. Figueiredo, Appl. Catal. A 192 (2000) 29–42.
 [21] V.Z. Radkevich, T.L. Senko, K. Wilson, L.M. Grishenko, A.N. Zaderko, V.Y. Diyuk,
- Appl. Catal. A 335 (2008) 241–251. [22] Y. Li, B.C. Zhang, X.W. Xie, J.L. Liu, Y.Y. Xu, W.J. Shen, J. Catal. 238 (2006) 412–
- 424. [23] B. Mile, D. Stirling, M.A. Zammitt, A. Lovell, M. Webbs, J. Catal. 114 (1988) 217– 229.
- [24] J.L. Figueiredo, M.F. Pereira, M.M. Freitas, J.J.M. Órfão, Carbon 37 (1999) 1379– 1389.
- [25] L.M.S. Silva, J.J.M. Órfão, J.L. Figueiredo, Appl. Catal. A 209 (2001) 145-154.
- [26] V. Gomez-Serrano, J. Pastor-Villegas, A. Perez-Florindo, C. Duran-Valle, C. Valenzuela-Calahorro, J. Anal. Appl. Pyrol. 36 (1996) 71–80.
- [27] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Carbon 37 (1999) 1379-1389.