Catalysis Communications 28 (2012) 73–76

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

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

Short Communication

Base-free selective oxidation of glycerol with 3% H_2O_2 catalyzed by sulphonato-salen-chromium(III) intercalated LDH

Xiaoli Wang [a], Gongde Wu [a,*], Fang Wang [b], Keqiang Ding [a], Fang Zhang [a], Xianfeng Liu [a], Yunbo Xue [a]

[a] Department of Environment and Technology, Nanjing Institute of Technology, Nanjing, 211167, PR China
[b] College of Sciences, Nanjing University of Technology, Nanjing 210009, Jiangsu, PR China

ARTICLE INFO

Article history:
Received 12 July 2012
Received in revised form 13 August 2012
Accepted 13 August 2012
Available online 23 August 2012

Keywords:
Layered-double hydroxide
Schiff base
Selective oxidation
Glycerol
Dihydroxyacetone

ABSTRACT

A Mg – Al layered-double hydroxides (LDH) intercalated by sulphonato-salen-chromium(III) complex was used to the selective oxidation of glycerol (GLY) using 3% H_2O_2 as oxidant. The results revealed that the LDH hosted chromium complex was effective heterogeneous catalyst. And the main product was the C_3 oxygenated products of secondary alcohol-dihydroxyacetone (DHA). Under the optimal reaction conditions, the highest conversion of GLY reached 73.1% with 43.5% of the selectivity to DHA. Moreover, the catalytic performance remained after being recycled 6 times. In addition, the reaction probably involved an enzyme mimetic mechanism.

1. Introduction

GLY is a co-product of triglyceride transesterification in the production of fatty acid esters employed as biodiesel. For every 9 kg of biodiesel produced, about 1 kg of a crude GLY by-product is formed. With the increase of biodiesel production, the price of GLY will decrease sharply. GLY is expected to become a major platform chemical, and has been recently identified as an important building block for future biorefineries by the US Department of Energy (DOE) [1–3]. Therefore, GLY should find new outlets to optimize the economy of biodiesel production, and to synthesize the value-added chemicals. Various valuable conversion of GLY has been studied, including oxidation, reduction, halogenation and eterification. Among them, oxidation is one of the most intensively studied pathways. Because GLY is a highly functionalized molecule in comparison with hydrocarbons, the oxidation of GLY often shows a wild product distribution: DHA, glyceraldehyde (GLAD), glyceric acid (GLYAC), hydroxypyruvic acid (HYPAC), mesooxalic acid (MESAC), tartronic acid (TARAC), etc. These products are valuable chemical intermediates; particularly DHA was economically the most interesting one due to its applications in cosmetics. At present the commercially available DHA is generally produced in a fermentation process due to the quality requirements by good manufacturing practice regulation in cosmetics industry [4]. Therefore, in recent years, much effort has been paid to the selective catalytic oxidation of GLY to high-value DHA.

Most previous selective oxidation of GLY mainly used supported noble metals (Pd, Pt and Au) as catalysts [5–12]. However, noble metal catalysts were not only expensive, but also suffered catalytic deactivation with increasing reaction time. Therefore, in recent years the research had been focusing on the design of effective low-cost transition metal catalysts for selective oxidation of GLY. Unfortunately, up to now only a few of relevant reports were found. McMorn et al. reported that the transition metal-containing silicates and aluminophosphate catalysts could oxidize GLY in the presence of H_2O_2, but the main products were the low-value formic acid and a mono-formate ester of GLY [13]. Zhou et al. used Cu-containing layered double hydroxide (LDH) to the selective oxidation of GLY by O_2, and the main product was glyceric acid [3]. Shul'pin et al. reported the oxidation of GLY in the homogeneous manganese complex-H_2O_2-oxalic acid-acetonitrile system, whereas the yield of DHA did not surpass 15% [14]. Thus, there is still an urgent need to develop effective catalysts for selective oxidation of GLY to DHA.

Here we reported the efficient selective oxidation of GLY to DHA with 3% H_2O_2 catalyzed by sulphonato-salen-chromium(III) complex intercalated LDH. The catalytic performance of LDH hosting complex was compared with that of LDH, homogeneous complex and the immobilized complex on mesoporous MCM-41, and an in-depth study on the differences in their catalytic performance was carried out. Moreover, the roles of reaction conditions in the catalytic

* Corresponding author. Tel. /fax: +86 25 86118960.
E-mail address: wugongde@njit.edu.cn (G. Wu).

1566-7367/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2012.08.014

performance of catalyst, the stability of catalyst as well as the reaction mechanism were also discussed in detail.

2. Experimental

2.1. Catalyst preparation and characterization

The homogeneous sulphonato-salen-chromium complex was prepared, and then was intercalated into LDH, The so-obtained homogeneous complex and intercalated complex were denoted as Cr(SO_3-salen) and LDH-[Cr(SO_3-salen)], respectively. The synthetic and characterization procedures had been described in our previous report [15].

For comparison, Cr(SO_3-salen) was also immobilized on mesoporous MCM-41 by a similar procedure [16], except Cr(SO_3-salen) was used in place of Cr(salen). The so-obtained immobilized complex [abbreviated as Cr(SO_3-salen)-MCM-41] was characterized by various physicochemical measurements such as FT-IR, UV–vis, XRD, N_2 sorption and elemental analysis (see supplementary information).

2.2. Catalytic test

The catalytic glycerol oxidation experiments were carried out under atmospheric pressure in a three neck flask (100 mL) equipped with a heat-gathering style magnetism mixer (DF-II). For each reactor, 0.2 g of catalyst was suspended in 50 mL aqueous solution of glycerol (0.2 mol L^{-1}). Once the required temperature reached, 3% H_2O_2 was introduced into the reactor. After reaction, catalyst was filtered off, and the aqueous solution was analyzed using an Agilent 1200 series high-performance liquid chromatography (HPLC) equipped with refractive index detector and UV–vis detectors. Product separation in the HPLC was carried out using an Aminex HPX-87 H column (Bio-Rad) operating at 333 K with 0.01 mol/L H_2SO_4 as eluent flowing at 0.5 mL/min. An injection volume of 10 μL and a measure time of 30 min were adjusted. The retention times and calibration curves were found using known concentrations of products. During the oxidation reaction, gas in the effluent was collected and analyzed by a BALZERS OMNISTAR QMS200 mass spectrometer. H_2O_2 consumption was determined after the reactions by iodometric titration.

3. Results and discussion

3.1. Catalytic performance

Without any organic solvent, phase transfer catalyst or additive, the so-obtained catalysts were used to the selective oxidation of GLY. In order to ensure the identical concentration of active chromium complex present in the catalytic system, the amounts of different catalysts was determined according to their elemental composition. Under the conditions used herein, only five products DHA, GLYAC, TARAC, formic acid and oxalic acid were detected. Other products, if any, present as minor constituents could not be detected.

When O_2 was used as oxidant, it was noted that the oxidation reaction did not take place under the present non-alkaline conditions (see Table 1). This indicated that when 3% H_2O_2 was used as oxidant, the disproportionation decomposition of H_2O_2 to O_2 was unproductive for GLY oxidation. Obviously, if a catalyst was inactive to disproportionately decompose H_2O_2, namely showed high H_2O_2 efficiency, it would exhibit high catalytic activity. This could explain the almost identical profiles of H_2O_2 efficiency and GLY conversion over different catalysts in Table 1.

The results in Table 1 also showed no significant amount of GLY was oxidized without catalyst or with MCM-41 as catalyst. In contrast, the GLY conversion was 6.4% over parent LDH, but the overoxidation product of formic acid was found to be the main dominant product (Sel. 92.6%). In the presence of homogeneous Cr(SO_3-salen), the GLY conversion reached 36.1%. Simultaneously, a small amount C_3 oxygenated products of DHA and GLAD was detected (Sel. 9.5 and 13.7%, respectively); though formic acid was still the main product (Sel. 75.8%). This indicated that Cr(SO_3-salen) Schiff base complex contributed to the oxidation of secondary alcohol in GLY. When Cr(SO_3-salen)-MCM-41 was used as catalyst, compared to the catalytic performance of homogeneous complex, only the GLY conversion was slightly increased to 45.9%, no significantly enhanced selectivity to DHA was found. Interestingly, when the reaction was performed over LDH-[Cr(SO_3-salen)], the GLY conversion was remarkably increased to 71.3%, while the main product was DHA (Sel. 43.5%) instead of GLAD (Sel. 20.9%) and formic acid (Sel. 35.2%). Considering the similar content of active Cr(SO_3-salen) complex in LDH-[Cr(SO_3-salen)] and Cr(SO_3-salen)-MCM-41, the differences in their catalytic performance could be related to their different supports. It was known that the weak base LDH host (OH^-) benefited the cleavage of peroxide bond in H_2O_2 due to the formation of H-bonding between the OH^- and the hydrogen atom of H_2O_2, which could significantly improve the oxidation capacity of H_2O_2 [15]. On the other hand, the weak base environment could also enhance the catalytic performance by facilitating the formation of intermediate product alkoxide [5]. Therefore, the synergistic effect of chromium Schiff base complex and the weak base LDH host made LDH-[Cr(SO_3-salen)] an effective catalyst for the selective oxidation of GLY to DHA with 3% H_2O_2.

It is known that, when O_2 was used as oxidant, basic environment can significantly enhance both the catalytic activity and the selectivity to C_3 oxidation products of primary alcohol — GLYAC [1,5,11], while

Table 1
Catalytic performance of samples in GLY oxidation.[a]

Catalysts	Cr wt.%	Amounts of catalysts (g)	GLY Con. (mol %)	Sel. (mol %)					H_2O_2 Efficiency (mol %)
				DHA	GLAD	TARAC	Formic acid	Oxalic acid	
Blank	……	……	0	0	0	0	0	0	0
MCM-41	……	0.58	0	0	0	0	0	0	0
LDH	……	0.20	6.4	0	1.6	0.2	92.6	5.6	9.7
Cr(SO_3-salen)	11.50	0.11	36.1	9.5	13.7	0.8	75.8	0.2	40.2
Cr(SO_3-salen)-MCM-41	2.20	0.58	45.9	9.7	13.5	0	76.7	0.1	52.0
LDH-[Cr(SO_3-salen)]	6.36	0.20	71.3	43.5	20.9	0	35.2	0.4	77.5
LDH-[Cr(SO_3-salen)][b]	6.36	0.20	71.2	43.0	21.5	0	33.0	2.5	77.0
LDH-[Cr(SO_3-salen)][c]	6.36	0.20	72.0	42.7	21.2	0.2	34.1	1.6	78.5
LDH-[Cr(SO_3-salen)][d]	6.36	0.20	70.5	43.5	19.8	0	35.4	1.3	76.2
LDH-[Cr(SO_3-salen)][e]	6.36	0.20	0	0	0	0	0	0	0

[a] Reaction conditions: GLY (10 mmol), 3% H_2O_2 (25 mL), 60 °C, 4 h.
[b] Adding pyrocatechol (20 mmol).
[c] Adding resorcinol (20 mmol).
[d] Adding hydroquinone (20 mmol).
[e] Reaction conditions: GLY (10 mmol), O_2 60 mL min^{-1}, 60 °C, 4 h.

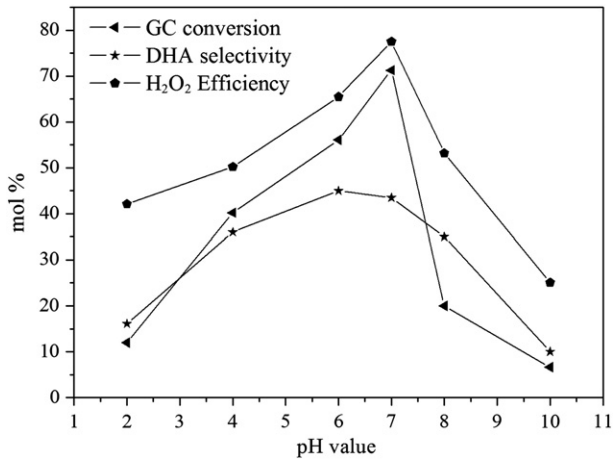

Fig. 1. Effect of pH value on the catalytic performance of LDH-[Cr(SO_3-salen)].

the acidic environment assisted the formation of the C_3 oxidation product of secondary alcohol – DHA [1,6]. Here, we also investigated the role of pH value in the catalytic performance of LDH-[Cr(SO_3-salen)] in the selective oxidation of GLY with 3% H_2O_2. Basic and acidic environment was provided by adding NaOH and $NaHSO_3$ at the beginning of the reaction, respectively. The results in Fig. 1 revealed that both acidic and basic environments were not conducive to the oxidation reaction. It had been prevailing accepted that Schiff base complex was susceptible to be inactive due to oxidative degradation under acidic environment. In contrast, basic environment promoted the invalid decomposition of H_2O_2 to O_2 though the catalyst was stable. Therefore, in the present catalytic oxidation system, neutral environment favored the selective oxidation of GLY.

In order to obtain the best catalytic results, the effect of condition parameters on the catalytic performance of LDH-[Cr(SO_3-salen)] was investigated. It was found that the amount of oxidant and catalyst, the reaction time and temperature all significantly influenced the catalytic performance of this intercalated complex (see Fig. 2). When the reaction run for 4 h at 60 °C over 0.2 g catalyst with 25 mL 3% H_2O_2, the best GLY conversion of 71.3% with 43.5% of the selectivity to DHA were achieved.

The mechanistic probe for the selective oxidation of alcohols with H_2O_2 by oxometal complexes was attracting continuous interests, and the prevailing accepted ones were the enzyme mimetic mechanism (the heterolytic bond cleavage of peroxide) and the free-radical mechanism (the homolytic bond cleavage of peroxide) [17,18]. To check the presence of radicals, the inhibition experiments were designed by the use of three radical scavengers (pyrocatechol, resorcinol and hydroquinone). No significant lowering of the conversion of GLY was observed (see Table 1), suggesting the involvement of enzyme mimetic mechanism.

In addition, a further study on the stability of LDH-[Cr(SO_3-salen)] was also carried out. After the first catalytic run, the catalyst was separated from the reaction solution, washed several times with water to remove any physisorbed molecules, dried and then reused in another five catalytic runs. The results in Fig. 3 revealed that the catalyst was still active until being reused for six times. Chemical analysis revealed that the recovered catalyst after six times held almost the same chromium content (Cr wt%: 6.35) as the fresh catalyst, indicating that the chromium leaching was negligible. The nature of the above recovered catalyst had also been followed by FTIR spectrum (see Fig. 4), and no significant change was observed. This further indicated that the obtained LDH hosted chromium complex was stable in the present reaction conditions. Therefore, the significantly decreasing catalytic performance over the recovered catalyst after the sixth runs might

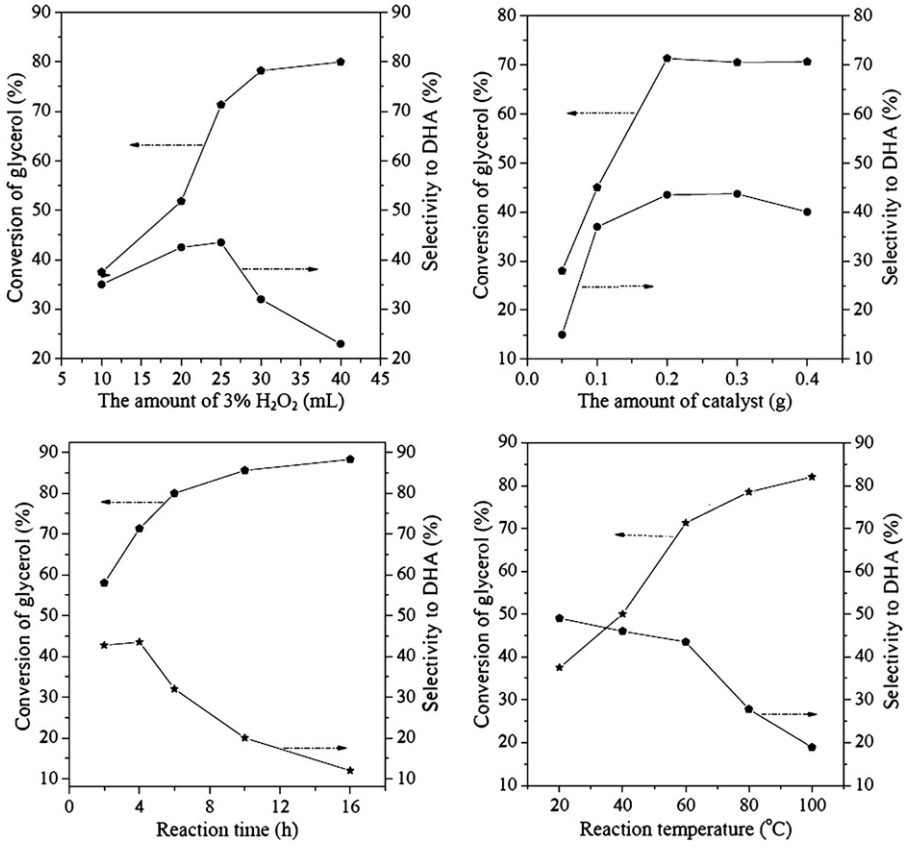

Fig. 2. Effect of condition parameters on the catalytic performance of LDH-[Cr(SO_3-salen)].

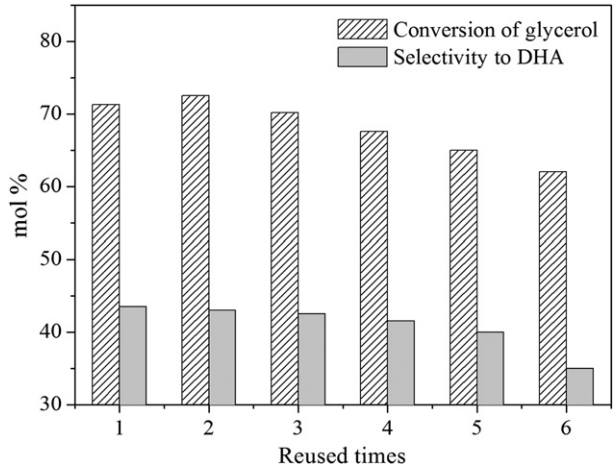

Fig. 3. Reusability of LDH-[Cr(SO_3-salen)]. Reaction conditions: GLY (10 mmol), 3% H_2O_2 (25 mL), catalyst (0.2 g), 60 °C, 4 h.

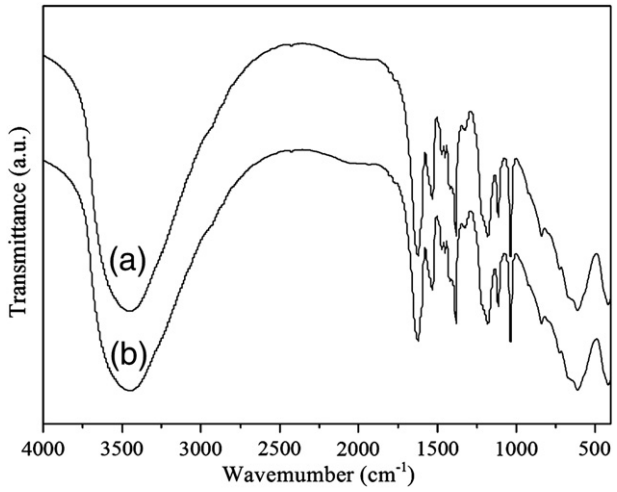

Fig. 4. FTIR spectra of LDH-[Cr(SO3-salen)]: (a) as prepared, (b)used six times.

be related to the increasing residual adsorbed molecules which prevented the reactants from accessing the active sites.

4. Conclusions

LDH hosted sulphonato-salen-chromium(III) complex was a promising catalyst for the selective oxidation of GLY to DHA with 3% H_2O_2. This could be attributed to the synergistic effect between chromium Schiff base complex and the weak base LDH host. The chromium Schiff base complex contributed to the oxidation of secondary alcohol in GLY, while the weak base LDH host could improve H_2O_2 efficiency, and could also facilitate the formation of intermediate product alkoxide. The highest GLY conversion reached 73.1%, with 43.5% of the selectivity to DHA, when the reaction ran at 60 °C for 4 h over 0.2 g catalyst with 25 mL 3% H_2O_2. Moreover, the catalytic performance remained after being recycled 6 times. We believe that the more efficient intercalated catalysts for the selective oxidation of GLY can be prepared by modifying the structure and composition of Schiff base complex and LDH host, which will exhibit more wildly application prospect. This work will be of significance for high effective heterogeneous catalyst design.

Acknowledgements

The authors acknowledge the financial supports from the National Natural Science Foundation of China (21003073, 21203093), the Program to Cultivate Outstanding Young Key Teachers of Colleges and Universities of Jiangsu Province and the Innovation Technology Funding Project of Nanjing Institute of Technology (CKJ2010012).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.08.014.

References

[1] Ch.H. Zhou, J.N. Beltramini, Y.X. Fan, G.Q. Lu, Chemical Society Reviews 37 (2008) 527–549.
[2] L. Prati, P. Spontoni, A. Gaiassi, Topics in Catalysis 52 (2009) 288–296.
[3] Ch.H. Zhou, J.N. Beltramini, Ch.X. Lin, Zh.P. Xu, G.Q. Lu, A. Tanksale, Catalysis Reviews: Science and Technology 1 (2011) 111–122.
[4] B. Katryniok, J. Kimura, E. Skrzyńska, J.-S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul, F. Dumeignil, Green Chemistry 13 (2011) 1960–1979.
[5] L. Prati, A. Villa, C.E. Chan-Thaw, R. Arrigo, D. Wang, D.S. Su, Faraday Discussions 152 (2011) 253–365.
[6] H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi, Y. Inaya, Applied Catalysis A: General 96 (1993) 217–228.
[7] A. Tsuji, K.T.V. Rao, Sh. Nishimura, A. Takagaki, K. Ebitani, ChemSusChem 4 (2011) 542–548.
[8] A. Villa, G.M. Veith, L. Prati, Angewandte Chemie 122 (2010) 4601–4604.
[9] A. Villa, G.M. Veith, L. Prati, Angewandte Chemie International Edition 49 (2010) 4499–4502.
[10] G.L. Brett, Q. He, C. Hammond, P.J. Miedziak, N. Dimitratos, M. Sankar, A.A. Herzing, M. Conte, J.A. Lopez-Sanchez, Ch.J. Kiely, D.W. Knight, S.H. Taylor, G.J. Hutchings, Angewandte Chemie International Edition 50 (2011) 1–4.
[11] B.N. Zope, D.D. Hibbitts, M. Neurock, R.J. Davis, Science 330 (2010) 74–77.
[12] M. Sankar, N. Dimitratos, D.W. Knight, A.F. Carley, R. Tiruvalam, Ch.J. Kiely, D. Thomas, G.J. Hutchings, ChemSusChem 2 (2009) 1145–1151.
[13] P. McMorn, G. Roberts, G.J. Hutchings, Catalysis Letters 63 (1999) 193–197.
[14] G.B. Shul'pin, Y.N. Kozlow, L.S. Shul'pina, T.V. Strelkova, D. Mandelli, Catalysis Letters 138 (2010) 193–204.
[15] G. Wu, X.L. Wang, J.P. Li, N. Zhao, W. Wei, Y.H. Sun, Catalysis Today 131 (2008) 402–407.
[16] X.L. Wang, G.D. Wu, W. Wei, Y.H. Sun, Transition Metal Chemistry 35 (2010) 213–220.
[17] L. Roecker, T.J. Meyer, Journal of the American Chemical Society 109 (1987) 746–754.
[18] B.-H. Éva, S. Gábor, Journal of Molecular Catalysis A: Chemical 230 (2005) 79–83.