available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article

Catalytic oxidation of glycerol to tartronic acid over Au/HY catalyst under mild conditions

Jiaying Cai^{a,b}, Hong Ma^a, Junjie Zhang^{a,b}, Zhongtian Du^a, Yizheng Huang^a, Jin Gao^a, Jie Xu^{a,*}^a Dalian National Laboratory for Clean Energy, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 30 March 2014

Accepted 28 April 2014

Published 20 October 2014

Keywords:

Catalytic oxidation

Glycerol

Gold

Tartronic acid

ABSTRACT

Gold nanoclusters or nanoparticles on various supports (CeO₂, activated carbon, HY, REY, and NaY) were investigated for glycerol oxidation in the aqueous phase under mild conditions. Compared with other catalysts, Au/HY showed remarkable catalytic performance in forming dicarboxylic acid (tartronic acid) over the monocarboxylic acid (glyceric acid) or the C–C cleavage product (oxalic acid). Au/HY achieved 98% conversion of glycerol and 80% yield of tartronic acid at 60 °C under 0.3 MPa O₂. Further characterization showed that the small size of Au clusters is the key factor for the high oxidation performance. In situ Fourier transform infrared spectroscopy revealed that glycerol was first transformed to glyceric acid, and then glyceric acid was directly oxidized to tartronic acid.

© 2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

As a major byproduct in biodiesel production, glycerol has received great attention with the rapid global development of biodiesel [1–5]. Glycerol has been recognized as an important biomass-based building block for valuable C3 molecules. The surplus of glycerol has inspired researchers to develop efficient methods to use glycerol [6–9]. Because glycerol is a highly functionalized molecule containing three hydroxyl groups, it is feasible to convert glycerol into valuable oxygenated derivatives via catalytic oxidation, such as tartronic acid (TARAC), glyceric acid (GLYA), and dihydroxyacetone (DIHA) [6,10,11]. Among these compounds, TARAC is a high value-added chemical that is widely used as a pharmaceutical and anti-corrosive protective agent, as well as for the monomer of biopolymers [12–15]. It is challenging and important to develop cost-efficient and environmentally friendly methods to oxidize

glycerol into TARAC using oxygen as oxidant and water as solvent under mild conditions. However, little research has been reported on this topic.

Currently, supported precious metal catalysts are used in glycerol oxidation. Au/C, Pd/C, and Pt/C are effective for producing GLYA but inefficient for producing TARAC [16–22]. Recently, Zope et al. [17] employed an Au/TiO₂ catalyst for the oxidation of glycerol and achieved 100% conversion with 20% selectivity of sodium tartronate. Kimura et al. [14] reported that glycerol oxidation over Pd/Pt-based catalyst yielded 58% disodium tartronate. These studies indicate that the unsatisfactory yield of TARAC results from the difficulty in further oxidation of GLYA and the occurrence of C–C cleavage or decarboxylation. To achieve a high yield of TARAC, it is imperative to develop new efficient heterogeneous catalysts avoiding C–C cleavage or decarboxylation. It is also important to investigate the reaction pathway of dicarboxylic acid formation.

* Corresponding author. Tel/Fax: +86-411-84379245; E-mail: xujie@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (20803074, 21233008) and the "Strategic Priority Research Program–Climate Change: Carbon Budget and Related Issues" of the Chinese Academy of Sciences (XDA050102).

DOI: 10.1016/S1872-2067(14)60132-7 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 10, October 2014

In our previous study, we found that gold-based catalysts are effective for alcohol oxidation [23]. Moreover, we have successfully encapsulated 1-nm Au nanoclusters in the supercage of HY zeolite. Au/HY showed high efficiency in 5-hydroxymethyl-2-furfural oxidation, achieving 99% yield of 2,5-furandicarboxylic acid [24]. In this study, inspired by its excellent performance in converting hydroxyl groups to carboxyl groups, we investigated supported Au catalysts for the oxidation of glycerol. We compared the catalytic performance of Au on different supports, investigated the oxidation pathway, and explored the conversion process of GLYA to TARAC.

2. Experimental

2.1. Catalyst preparation and characterization

The catalysts were prepared based on the methods in our previous work [24]. A certain amount of support was added to HAuCl₄ aqueous solution (50 mL, 0.1 mol/L). After stirring at 60 °C for 2 h, sodium citrate solution was added. The obtained mixture was stirred for another 2 h. After centrifugation and washing with distilled water, the sample was treated at 100 °C in H₂ atmosphere (0.1 MPa) for 6 h. The Au loading for these catalysts was 1.5 wt%.

Transmission electron microscopy (TEM) studies were performed in a FEI Tecnai G2 F30 S-Twin electron microscope. The real-time in situ Fourier transform infrared spectroscopy (FT-IR) measurements were carried out with a Mettler Toledo ReactIR 45m spectrometer. An Infrared Associates liquid nitrogen-cooled AgX fiber conduit diamond-attenuated total reflection probe was used.

2.2. Glycerol oxidation and product analysis

A typical reaction procedure was as follows. Glycerol (2.5 mmol), H₂O (4.6 g), NaOH (0.4 g), and catalyst (0.3 g, 0.023 mmol) were added into the autoclave. The autoclave was charged with dioxygen (0.3 MPa), maintained at 60 °C for 9 h, and then cooled. The reaction mixture was acidified and analyzed by high-performance liquid chromatography (HPLC) on a Waters 2695 system.

3. Results and discussion

3.1. Catalytic performance

Initially, we employed Au catalysts with different supports (CeO₂, activated carbon (AC), HY, REY, and NaY) on glycerol oxidation reaction at 60 °C under 0.3 MPa O₂ in water. As the reactions were conducted in alkaline solution, the final products were in the form of glycerate, tartronate, and oxalate. Thus, acidification to the carboxylic acid form was required for analysis. The catalysts had remarkably different performance for glycerol oxidation (Table 1). When gold was supported on CeO₂, it gave 98% conversion. However, the main product was oxalic acid (OXALA, 55% yield), and the yield of TARAC was only 24%, suggesting that the oxidation process was accompa-

Table 1

Catalytic oxidation of glycerol over Au catalysts with different supports.

Catalyst	<i>D</i> _{Au} (nm)	Conversion (%)	Product yield (%)			
			GLYA	TARAC	OXALA	Others
Au/AC	15	90	80	6	2	2
Au/CeO ₂	10	98	2	24	55	17
Au/NaY	6	98	26	43	4	25
Au/REY	2	99	5	69	6	19
Au/HY	1	98	3	80	12	3
HY	—	4	4	0	0	0

Reaction conditions: 0.23 g glycerol in 4.6 g H₂O, 0.4 g NaOH, 0.3 g catalyst (1.5 wt% Au), 60 °C, *p*(O₂) = 0.3 MPa, 9 h, the Au/glycerol molar ratio 1/150.

GLYA: Glyceric acid; TARAC: Tartronic acid; OXALA: Oxalic acid.

nied by C–C cleavage with formic acid and OXALA as the degradation products. In the case of Au/AC, glycerol was efficiently oxidized to GLYA with 80% yield, but the yield of TARAC was low (6%), which is consistent with previous studies that GLYA was the main product over Au/AC [16]. For the Au/HY, Au/REY, and Au/NaY catalysts, there was a higher yield of TARAC than for the Au/AC and Au/CeO₂ catalysts. Gold nanoclusters on HY zeolite had extremely high activity, achieving 98% conversion with 80% yield of TARAC. However, the HY support alone only had very low activity. Over the Au/REY catalyst, 90% conversion with 69% yield of TARAC was achieved, and Au/NaY only gave 43% yield of TARAC.

As shown in Fig. 1, the Au particle size varies immensely on different supports. For AC and CeO₂ supports, Au particles had average sizes of 15 and 10 nm, respectively. Their different catalytic performance may be attributed to the differences in C–C cleavage active sites on the supports and the metal support interaction. For Au/HY, the Au nanoclusters had a size around 1 nm, which has been demonstrated by detailed characterizations in our previous study [24]. It seems that the yield of TARAC increased from 43% to 80% when the Au nanoparticle size decreased from 6 to 1 nm. These results suggest that the formation of TARAC can be significantly increased by decreasing the Au particle size. Therefore, the small size of the Au nanoclusters is the main reason for the formation of TARAC when choosing Y type zeolite as support.

3.2. Reaction course and proposed catalytic route

In the reaction, TARAC may be produced either by the consecutive reaction in which glycerol is first converted to GLYA and then to TARAC, or by parallel reactions where two hydroxyl groups are simultaneously oxidized and glycerol is directly transformed to TARAC in one step. For the Au/AC catalyst, glycerol was efficiently oxidized to GLYA with production of a small amount of TARAC (Table 1). Moreover, glycerol oxidation over Au/HY showed 10% yield of GLYA. It is proposed that GLYA may be the intermediate substance. To study the process, the influence of reaction time on the catalytic performance of Au/HY was investigated. As shown in Fig. 2(a), the conversion of glycerol increased with time and reached 98% after 3 h. The yield of GLYA increased in the initial 2 h and reached a maximum value of 38%. Then the amount of GLYA gradually de-

Fig. 1. Representative TEM images and size distributions of (a) Au/AC, (b) Au/CeO₂, (c) Au/REY, and (d) Au/NaY.

creased, and the yield was low (2%) after 9 h. The trend of GLYA concentration went through a volcano curve, which is consistent with the character of consecutive reaction, suggesting that glycerol may first convert to GLYA and then GLYA is oxidized to TARAC [22].

Real-time in situ FT-IR spectroscopy further confirms the conversion of the monocarboxylic acid to the dicarboxylic acid during the glycerol oxidation process over Au/HY (Fig. 2). Be-

fore the reaction, the IR spectra of glycerol, TARAC, GLYA, and the Au/HY catalyst were recorded under reaction conditions (Fig. 2(b)) [25]. In the beginning, only the characteristic peaks of glycerol and the catalyst are observed at 1045 and 1640 cm⁻¹, respectively. After 1 h reaction time, IR bands at 1340 and 1600 cm⁻¹ appeared (Fig. 2(b) and (c)), indicating the production of TARAC. In addition, the intensity of the glycerol peak at 1045 cm⁻¹ decreased with time (Fig. 2(d)). It should be noted

Fig. 2. Reaction course (a) and a segment of the in situ FT-IR spectra (b-d) for glycerol oxidation on the Au/HY catalyst.

that although the peak of GLYA at 1420 cm^{-1} maintained a low intensity, it initially increased and then decreased during the reaction.

Through calculation, the glycerol oxidation rate was calculated to be $44\text{ mol}_{\text{glycerol}}/(\text{mol}_{\text{Au}}\cdot\text{h})$ for the initial 2 h. The generation rates of TARAC and GLYA were 20 and $19\text{ mol}_{\text{product}}/(\text{mol}_{\text{Au}}\cdot\text{h})$, respectively. The similar rate values for TARAC and GLYA can be explained by the fact that they were obtained via resemble oxidation processes and the reaction was composed of consecutive processes [26]. Each step of the consecutive process involves the oxidation of one hydroxyl group.

Oxidation of GLYA accompanying with real-time in situ FT-IR experiments was performed to determine whether it could be further oxidized to TARAC (Fig. 3). During the first 6 h, GLYA was gradually oxidized to TARAC. The reaction achieved 95% conversion with 75% yield of TARAC (Fig. 3(a)) after 9 h, which is consistent with the peak at 1115 cm^{-1} (GLYA) decreasing and peak at 1340 cm^{-1} (TARAC) increasing in the real-time in situ FT-IR spectrum (Fig. 3(b)) within 5 h oxidation reaction time. This experiment suggests that GLYA is the intermediate in glycerol oxidation. In addition, there is no detection of aldehyde production such as glyceraldehyde. The proposed reaction pathway for glycerol oxidation is shown in Scheme 1. Glycerol was first directly oxidized to GLYA, and then GLYA was further oxidized to TARAC.

Fig. 3. Reaction course (a) and a segment of the in situ FT-IR spectra (b) for GLYA oxidation over the Au/HY catalyst.

Scheme 1. Proposed reaction pathway for the formation of TARAC over Au/HY catalyst.

3.3. Effects of pressure and temperature on glycerol oxidation

The effect of oxygen pressure on glycerol oxidation was investigated, and the results are shown in Fig. 4. The conversion of glycerol gradually increased with increasing pressure from 0.1 to 0.5 MPa. In addition, the yield of TARAC increased from 30% to 80% when the O_2 pressure was increased from 0.1 to 0.3 MPa. However, further increasing the pressure to 0.5 MPa did not further increase the yield of TARAC. In fact, the yield of TARAC decreased to 58% at 0.5 MPa, which may be caused by over-oxidation. Hence, the optimum O_2 pressure was 0.3 MPa.

Figure 5 shows the effect of reaction temperature on glycerol oxidation over Au/HY. At 20 and 40°C , the yield of TARAC was less than 60%. Increasing the temperature tended to increase the yield of TARAC. However, at 80°C the yield of

Fig. 4. Effect of pressure on glycerol conversion and TARAC production

Fig. 5. Effect of reaction temperature on glycerol conversion and TARAC production.

TARAC decreased to 60%. Thus, the optimal oxidation temperature was 60 °C.

4. Conclusions

We have successfully fabricated an Au/HY catalyst for the oxidation of glycerol to tartronic acid (TARAC) with 98% conversion and 80% yield of TARAC under mild conditions. The high efficiency of Au/HY in the production of TARAC was attributed to the small size of the Au nanoclusters on the HY support. Real-time in situ FT-IR experiments combining with reaction course revealed that glycerol was initially oxidized to glyceric acid and then further oxidized to TARAC. These results have important implications for the oxidation of biomass-derived hydroxyl compounds. Further application of the Au/HY

catalyst to the oxidation of other biomass-derived hydroxyl compounds is in progress.

References

- [1] Ragauskas A J, Williams C K, Davison B H, Britovsek G, Cairney J, Eckert C A, Frederick W J Jr, Hallett J P, Leak D J, Liotta C L, Mielenz J R, Murphy R, Templer R, Tschaplinski T. *Science*, 2006, 311: 484
- [2] Bozell J J. *Clean Soil Air Water*, 2008, 36: 633
- [3] Bozell J J, Petersen G R. *Green Chem*, 2010, 12: 539
- [4] Kohse-Höinghaus K, Osswald P, Cool T A, Kasper T, Hansen N, Qi F, Westbrook C K, Westmoreland P R. *Angew Chem Int Ed*, 2010, 49: 3572
- [5] Huber G W, Iborra S, Corma A. *Chem Rev*, 2006, 106: 4044
- [6] Clark I T. *Ind Eng Chem*, 1958, 50: 1125
- [7] Rennard D C, Kruger J S, Michael B C, Schmidt L D. *Ind Eng Chem Res*, 2010, 49: 8424
- [8] Zhang M Y, Liang D, Nie R F, Lü X Y, Chen P, Hou Z Y. *Chin J Catal* (张梦媛, 梁丹, 聂仁峰, 吕秀阳, 陈平, 侯昭胤. 催化学报), 2012, 33: 1340
- [9] Zhao J, Yu W Q, Li D C, Ma H, Gao J, Xu J. *Chin J Catal* (赵静, 于维强, 李德财, 马红, 高进, 徐杰. 催化学报), 2010, 31: 200
- [10] Berchmans H J, Hirata S. *Bioresour Technol*, 2008, 99: 1716
- [11] Liang D, Cui S Y, Gao J, Wang J H, Chen P, Hou Z Y. *Chin J Catal* (梁丹, 崔世玉, 高静, 王军华, 陈平, 侯昭胤. 催化学报), 2011, 32, 1831
- [12] Pagliaro M, Rossi M. *The Future of Glycerol*. Cambridge: Royal Society of Chemistry, 2008
- [13] Biesiada A, Nawirska A, Kucharska A, Sokol-Letowska A. *Ecol Chem Eng A*, 2011, 18: 9
- [14] Kimura H, Imanaka T, Yokota Y. JP Patent 06279352A. 1994
- [15] Caselli G, Monatovanini M, Gandolfi C A, Allegretti M, Fiorentino S, Pellegrini L, Melillo G, Bertini R, Sabbatini W, Anacardio R, Calvanna G, Sciortino G, Teti A. *J Bone Miner Res*, 1997, 12: 972
- [16] Villa A, Chan-Thaw C E, Prati L. *Appl Catal B*, 2010, 96: 541
- [17] Zope B N, Davis S E, Davis R J. *Top Catal*, 2012, 55: 24
- [18] Yakusheva T S. *Bull Exp Biol Med*, 1958, 45: 52
- [19] Gandolfi C A, Cotini L, Mantovanini M, Caselli G, Clavenna G, Omini C. WO Patent 9 410 127. 1994
- [20] Dimitratos N, Lopez-Sanchez J A, Lennon D, Porta F, Prati L, Villa A. *Catal Lett*, 2006, 108: 147
- [21] Dimitratos N, Messi C, Porta F, Prati L, Villa A. *J Mol Catal A*, 2006, 256: 21
- [22] Dimitratos N, Porta F, Prati L. *Appl Catal A*, 2005, 291: 210

Graphical Abstract

Chin. J. Catal., 2014, 35: 1653–1660 doi: 10.1016/S1872-2067(14)60132-7

Catalytic oxidation of glycerol to tartronic acid over Au/HY catalyst under mild conditions

Jiaying Cai, Hong Ma, Junjie Zhang, Zhongtian Du, Yizheng Huang, Jin Gao, Jie Xu*
Dalian Institute of Chemical Physics, Chinese Academy of Sciences;
University of Chinese Academy of Sciences

Tartronic acid has been produced as the dominant product in glycerol oxidation over Au/HY catalyst. Real-time in situ FT-IR showed that glycerol was first oxidized to glyceric acid and then to tartronic acid.

- [23] Ma H, Nie X, Cai J Y, Chen C, Gao J, Miao H, Xu J. *Sci China Chem*, 2010, 53: 1497
[24] Cai J Y, Ma H, Zhang J J, Song Q, Du Z T, Huang Y Z, Xu J. *Chem Eur J*,

- 2013, 19: 14215
[25] Simões M, Baranton S, Coutanceau C. *Appl Catal B*, 2010, 93: 354
[26] Kimura H, Yokota Y, Sawamoto Y. *Catal Lett*, 2005, 99: 133

温和条件下Au/HY催化剂催化氧化丙三醇制丙醇二酸

蔡嘉莹^{a,b}, 马红^a, 张俊杰^{a,b}, 杜中田^a, 黄义争^a, 高进^a, 徐杰^{a,*}

^a中国科学院大连化学物理研究所, 催化基础国家重点实验室, 洁净能源国家实验室(筹), 辽宁大连116023

^b中国科学院大学, 北京100049

摘要: 研究了不同载体负载的Au催化剂催化丙三醇水相选择性氧化制丙醇二酸. 与Au/CeO₂, Au/AC, Au/REY和Au/NaY催化剂相比, Au/HY上获得了高收率的丙醇二酸. 在60 °C和0.3 MPa氧气压力下, 丙三醇转化率达98%, 丙醇二酸收率为80%. 表征结果表明, 小尺寸的Au纳米颗粒对生成丙醇二酸有明显促进作用; 反应过程中丙三醇先被催化氧化生成甘油酸, 再被进一步氧化生成丙醇二酸.

关键词: 催化氧化; 丙三醇; 金; 丙醇二酸

收稿日期: 2014-03-30. 接受日期: 2014-04-28. 出版日期: 2014-10-20.

*通讯联系人. 电话/传真: (0411)84379245; 电子信箱: xujie@dicp.ac.cn

基金来源: 国家自然科学基金(20803074, 21233008); 中国科学院战略性先导科技专项—应对气候变化的碳收支认证及相关问题(XDA050102).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

1. 前言

随着生物柴油工业的发展, 丙三醇作为生物柴油副产物受到了普遍关注^[1–5]. 丙三醇是一种重要的生物质基平台化合物, 可以转化制备多种具有较高附加值的C3化合物. 近年来丙三醇产量过剩, 推动和刺激着科研人员开发高效转化和利用丙三醇的新方法^[6–9]. 丙三醇催化氧化转化制备高价值的C3含氧化合物是一类原子经济性较高的反应, 譬如选择氧化制丙醇二酸(TARAC)、甘油酸(GLYA)和二羟基丙酮(DIHA)等^[6,10,11]. 在诸多氧化产物中, 丙醇二酸是一类高附加值化学品, 在医药、抗腐蚀及生物质基高分子等领域有重要的潜在应用^[12–15]. 目前丙醇二酸制备成本较高, 需要开发一条成本较低且环境友好的高效制备路线. 从丙三醇出发在温和条件下以分子氧为氧源选择性氧化制丙醇二酸具有重要意义, 但目前这方面的研究报道较少.

目前, 关于负载型贵金属催化剂在丙三醇氧化中的催化性能已有较多报道. Au/C, Pd/C和Pt/C对丙三醇氧化制甘油酸表现出催化活性, 但对制备丙醇二酸则活性欠佳^[16–22]. 近来, Zope等^[17]采用Au/TiO₂催化丙三醇氧化, 转化率为100%, 丙醇二酸钠选择性为20%. Kimura等^[14]报道了Pd/Pt基催化剂上丙三醇氧化结果, 丙醇二酸钠选择性为58%. 丙三醇氧化为甘油酸后, 进一步氧化困难, 易发生C–C键氧化断裂, 导致丙醇二酸收率较低, 使得丙三醇氧化制丙醇二酸具有挑战性. 因此, 需进一

步发展新的高效催化体系, 实现高选择性氧化羟基, 并同时避免C–C键裂解和脱羧反应发生. 羟基氧化为羧酸的反应机理也需进一步研究和认识, 为进一步的催化剂设计和制备提供基础.

在我们前期工作中, 已将Au催化剂用于醇的催化氧化, 并且进一步制备了新型Au/HY催化剂, 即在HY分子筛超笼内成功封装了1 nm的Au簇, 该催化剂在5-羟甲基糠醛氧化制2,5-呋喃二甲酸的反应中表现出很高活性, 达到99%转化率和99%的2,5-呋喃二甲酸选择性^[23,24]. 该研究表明此催化剂对氧化羟基制羧酸的反应有效. 受该研究启发, 本文将Au/HY催化剂应用于丙三醇的氧化, 结果显示在60 °C和0.3 MPa氧气压力下丙三醇水相氧化达到98%的转化率和80%的丙醇二酸收率. 同时本文对不同的载体进行了研究, 并探索了Au高活性的原因. 采用实时原位红外跟踪监测的方法研究了丙三醇氧化过程.

2. 实验部分

2.1. 催化剂的制备和表征

催化剂制备基于我们之前的报道^[24]. 将一定量载体加入到HAuCl₄溶液中(50 mL, 0.1 mol/L), 在60 °C下搅拌2 h, 加入柠檬酸钠溶液, 得到的混合溶液继续搅拌2 h. 将得到的反应液离心, 并用去离子水洗涤数次至中性. 得到的样品在100 °C氢气气氛下处理6 h. 催化剂中金的负载量为1.5 wt%.

电镜观察在FEI Tecnai G2 F30 S-Twin上进行. 实时原位红外光谱在Mettler toledo ReactIR™ 45 m上进行, 采用特制的原位反应器, 同时配有液氮冷却的AgX纤维导管和金刚石ATR探头.

2.2. 丙三醇氧化及产物分析

将丙三醇(2.5 mmol), H₂O (4.6 g), NaOH (0.4 g)和催化剂(0.3 g, 0.023 mmol)加入反应釜中, 充入0.3 MPa的氧气后密封, 升温至60 °C进行反应. 反应结束后用冷却水降温. 取出反应液, 离心酸化后采用Waters 2695高效液相色谱仪分析.

3. 结果与讨论

3.1. 丙三醇催化氧化

将不同载体(包括CeO₂、活性炭、HY、REY和NaY等)负载的Au催化剂用于丙三醇氧化反应, 丙三醇氧化产物主要以钠盐形式存在, 反应结果如表1所示. 可以看出, 不同催化剂的反应性能差别较大. 当Au负载在CeO₂上, 丙三醇氧化转化率为98%, 其中55%的产物为草酸钠, 而丙醇二酸收率仅为24%. 这表明Au/CeO₂催化剂具备一定的催化C–C键断裂能力, 甲酸和草酸是C–C键裂解产物. Au/C催化剂则可较好地氧化丙三醇制甘油酸, 达到80%的收率, 但只产生了6%的丙醇二酸, 表明Au/C催化剂对生成甘油酸有利, 有报道也观察到了类似的现象^[16]. Au/HY, Au/REY和Au/NaY催化剂则表现出不同的丙醇二酸生成活性. 在这三者之中, Au纳米簇包覆于HY超笼的催化剂表现出很高的活性, 达到98%的丙三醇转化率和80%的丙醇二酸收率. 而单独的HY分子筛则在反应过程中几乎没有活性, 转化率仅为4%. Au/REY上丙三醇转化率为90%, 丙醇二酸收率为69%, 而Au/NaY则只给出了43%的丙醇二酸.

如图1所示, Au粒子的尺寸在不同载体上的变化较大. 对于活性炭和CeO₂载体, Au的平均尺寸分别约为15和10 nm. 不同催化剂具有不同的催化活性, 这与催化剂对C–C键裂解以及金属-载体之间的强相互作用有关. 我们曾对Au/HY催化剂进行过详细表征^[24], 其中的Au纳米簇约为1 nm. 另外, 当Au的尺寸从6 nm减小到1 nm时, 丙醇二酸收率从43%增加到80%, 说明Au粒子尺寸对丙醇二酸的生成有较大影响, 小尺寸的Au粒子有利于生成丙醇二酸.

3.2. 反应进程及可能机理

丙三醇氧化过程中丙醇二酸可通过连续反应产生, 即丙三醇氧化生成甘油酸, 之后进一步氧化为丙醇二酸;

也可通过丙三醇中两个伯羟基同时氧化生成丙醇二酸. 丙三醇在Au/C催化剂上产生甘油酸的同时生成少量丙醇二酸(表1); 而在Au/HY上氧化则产生10%的甘油酸, 提示甘油酸可能是丙三醇氧化反应的中间产物. 为了进一步揭示氧化过程, 对Au/HY催化剂上丙三醇及其产物随时间进程的变化进行了研究. 如图2(a)所示, 丙三醇转化率随着时间延长逐渐增加, 在3 h达到98%. 甘油酸收率在初始的2 h内达到最大值38%, 在随后的7 h中逐渐下降, 在9 h得到了2%的收率. 甘油酸在反应过程中的变化趋势符合火山型曲线, 具有连续反应的特征, 表明丙三醇氧化可能首先转化为甘油酸, 之后再进一步氧化为丙醇二酸^[22].

利用实时原位FT-IR光谱进一步研究了丙三醇的氧化过程(图2(b), (c)和(d)). 在反应前, 首先对丙醇二酸、甘油酸和Au/HY催化剂进行红外表征并进行了相应的归属(图2(b))^[26]. 在反应初始, 只观察到丙三醇和催化剂的特征峰, 分别在1045和1640 cm⁻¹. 反应1 h后, 1340和1600 cm⁻¹处出现了吸收峰(图2(b)和(c)), 表明丙醇二酸开始生成. 同时, 1045 cm⁻¹处丙三醇的吸收峰随着时间增加而逐渐降低. 另外, 甘油酸在1420 cm⁻¹处吸收峰在整个反应过程中维持了较低的强度, 并经历了先增加后降低的过程.

通过计算每摩尔Au上丙三醇消耗速率和产物生成速率可以比较反应速率. 在反应开始的2 h内每摩尔Au丙三醇氧化的速率为44 mol_{glycerol}/(mol_{Au}·h). 丙醇二酸和甘油酸分别为20和19 mol_{product}/(mol_{Au}·h). 丙醇二酸和甘油酸相似的反应速率暗示着丙三醇氧化为丙醇二酸是经连续反应过程进行的^[25]. 丙三醇氧化一个羟基得到甘油酸, 甘油酸氧化羟基得到丙醇二酸. 在这两步中都分别氧化了一个羟基, 具有相似的反应速率. 这与观察的实验结果一致.

为了验证甘油酸能否氧化为丙醇二酸, 进行了甘油酸的氧化实验. 氧化过程由实时原位FT-IR进行监测. 从图3可知, 在反应过程中甘油酸的典型吸收峰(1115 cm⁻¹)降低, 而丙醇二酸的吸收峰相应增强(1340 cm⁻¹), 表明在反应过程中甘油酸氧化为丙醇二酸. 另外, 实时原位红外没有检测到醛类产物生成. 结合上述实验, 丙三醇氧化的过程可能如图式1所示, 即丙三醇经历了首先被氧化为甘油酸之后再进一步被氧化为丙醇二酸的过程.

3.3. 反应温度和压力的影响

进一步研究了氧气压力对丙三醇氧化反应的影响,

反应分别在0.1, 0.3和0.5 MPa氧气压力下进行. 随着氧气压力的增加, 丙三醇达到相同转化率的反应时间缩短, 当压力从0.1 MPa增加到0.3 MPa时, 丙醇二酸收率从30%增加到80%; 但进一步提高反应压力到0.5 MPa时, 丙醇二酸的收率降低到58%, 这可归因于丙三醇及其产物的过度氧化. 因此, 生成丙醇二酸的优化反应压力为0.3 MPa.

温度对Au催化剂上丙三醇反应的影响如图5所示. 在20和40 °C下, 丙醇二酸收率低于60%. 升高温度时丙醇二酸收率也进一步增加; 但当温度达到80 °C时, 丙醇二酸收率降低到60%. 因此生成丙醇二酸的优化反应温

度为60 °C.

4. 结论

本文在Au/HY催化剂上实现了温和条件下丙三醇氧化制丙醇二酸, 转化率为98%, 收率为80%. Au/HY催化剂中小尺寸的Au纳米簇是高效氧化丙三醇生成丙醇二酸的重要原因. 结合反应时间进程的原位实时红外光谱研究表明, 丙三醇首先被氧化为甘油酸, 之后进一步氧化为丙醇二酸. 本研究为选择氧化生物质基多羟基化合物提供了参考. Au/HY催化剂在其他生物质基化合物氧化中的催化性能研究正在开展.