

Sustainable production of acetaldehyde from lactic acid over the carbon catalysts

Congming Tang^{*,†}, Jiansheng Peng^{*}, Xinli Li^{*}, Zhanjie Zhai^{*}, Hejun Gao^{*},
Wei Bai^{**}, Ning Jiang^{**}, and Yunwen Liao^{*}

^{*}Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, China West Normal University, Nanchong, Sichuan 637002, P. R. China

^{**}Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, P. R. China
(Received 26 November 2014 • accepted 7 May 2015)

Abstract—The synthesis of acetaldehyde from lactic acid over the carbon material catalysts was investigated. The carbon materials were characterized by scanning electron microscopy for morphologic features, by X-ray diffraction for crystal phases, by Fourier transform infrared spectroscopy for functional group structures, by N₂ sorption for specific surface area and by ammonia temperature-programmed desorption for acidity, respectively. Among the tested carbon catalysts, mesoporous carbon displayed the most excellent catalytic performance. By acidity analysis, the medium acidity is a crucial factor for catalytic performance: more medium acidity favored the formation of acetaldehyde from lactic acid. To verify, we compared the catalytic performance of fresh activated carbon with that of the activated carbon treated by nitric acid. Similarly, the modified activated carbon also displayed better activity due to a drastic increase of medium acidity amount. However, in contrast to fresh carbon nanotube, the treated sample displayed worse activity due to decrease of medium acidity amount. The effect of reaction temperature and time on stream on the catalytic performance was also investigated. Under the optimal reaction conditions, 100% lactic acid conversion and 91.6% acetaldehyde selectivity were achieved over the mesoporous carbon catalyst.

Keywords: Decarbonylation, Lactic Acid, Bulk Chemicals, Mesoporous Carbon, Biomass

INTRODUCTION

With the depletion of fossil resources and increasing demand for the acetaldehyde market, it is urgent to develop alternative routes to synthesize acetaldehyde from renewable resources [1-3]. A case in point is that acetaldehyde is produced through catalytic dehydrogenation of ethanol or partial oxidation of ethanol [4]. Acetaldehyde is also obtained from decarbonylation [5,6] of lactic acid (LA), which is mainly produced through fermentation or catalytic conversion using starch, cellulose, hemicellulose, sorbitol and sugar as raw materials [3,7,8]. Note that carbon monoxide always accompanies with the process of LA decarbonylation, resulting in decrease of atomic economic efficiency. However, carbon monoxide is often viewed as a valuable source for carbonylation or hydroformylation of alkenes, alkynes and alcohols to synthesize corresponding carbonyl compounds such as saturated organic acids and α,β -unsaturated acids [9-12]. Also, acetaldehyde is always reported as a by-product in the dehydration process of LA to acrylic acid in previous literatures [13-23]. Indeed, scarce research on decarbonylation or decarboxylation of LA to acetaldehyde has been reported. In recent years, silica supported heteropolyacids have been used to catalyze the decarbonylation of LA to acetaldehyde, achieving 91% conversion of LA as well as 81-83% yield of acetaldehyde [5]. More recently, our group has reported efficient catalysts of aluminum

sulfate and aluminum phosphate for decarbonylation of LA to acetaldehyde, achieving 100% LA conversion together with ~92.1% acetaldehyde selectivity [6,24].

Carbon materials with friendly environmental properties are widely used in catalysis, adsorption, and electrode material [25,26]. In catalysis, carbon materials are generally used for supports. For example, carbon-supported Pd-Ni₂P displays an efficient activity for oxidation of formic acid [27]. Besides, Pd/C without ligands or additives efficiently catalyzes the selective arylation of thiophenes under mild conditions [28]. Another case is that graphene supported ultrafine metal nanoparticles encapsulated with thin mesoporous SiO₂ layers display high catalytic activity and excellent high-temperature stability for oxidation and reduction reactions [29]. However, only carbon materials without active metals are rarely used as catalysts. Recently, activated carbon has been found to have a high activity for dehydration of oxylase into furfural [30]. So far, the research on activity comparison of different carbon materials as catalysts is rarely explored. To the best of our knowledge, direct conversion of LA to acetaldehyde with an excellent activity over the mesoporous carbon has never been reported. Carbon materials are known as water tolerant materials, which makes them an interesting catalyst alternative for synthesis of acetaldehyde from aqueous LA solution.

In this work, we present a simple and efficient way for synthesis of acetaldehyde from LA over the carbon catalysts. The catalysts are characterized by BET, NH₃-TPD, XRD, FT-IR and SEM to fully understand the catalysis for acetaldehyde synthesis from LA. Here we have focused on the effect of the acidity of carbon materials on catalytic performance for acetaldehyde synthesis from LA.

[†]To whom correspondence should be addressed.

E-mail: tcmtang2001@163.com

Copyright by The Korean Institute of Chemical Engineers.

EXPERIMENTAL

1. Materials

Lactic acid (analytic grade) was purchased from Chengdu Kelong Chemical Reagent Co. and was used for the synthesis of acetaldehyde. Triple-distilled water was prepared in the laboratory and used to dilute lactic acid for required concentration. Nitric acid, aluminum nitrate, phosphoric acid, citric acid (CA), acetaldehyde, acrylic acid, propionic acid, acetic acid, 2,3-pentanedione and n-butanol, together with hydroquinone were obtained from Sinopharm Chemical Reagent Co., Ltd. Activated carbon was purchased from Maoye Chemical Reagent Co. of Chongqing. Carbon nanotubes (CNTs) were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. Acrylic acid, propionic acid, acetic acid, 2,3-pentanedione and acetaldehyde were used for gas chromatograph reference materials, and n-butanol was used as internal standard material. Hydroquinone (0.3 wt%) was utilized as a polymerization inhibitor.

2. Preparation of Catalysts

According to the previous literature [31,32], the mesoporous carbon was prepared. Typically, H_3PO_4 (85 wt%) was dropped into a mixed aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and citric acid under vigorous stirring at ambient temperature, leading to a composition in molar ratio of 1.0 : 1.0 : 1.0 : 86 = $\text{Al}(\text{NO}_3)_3/\text{CA}/\text{H}_3\text{PO}_4/\text{H}_2\text{O}$. After that, an aqueous ammonia solution (10 wt%) was used to adjust the pH value of the solution to 5.0. The solid composite was formed after removing water and all other volatiles by heating the mixed solution at 363 K for 10 h. The porous carbon material was obtained via the following steps: the solid composite was first pretreated at 200 °C for a few minutes, and then carbonization of the composite was carried out at 800 °C for 6 h under an argon flow. The black carbonized composite was treated with 5 mol/L HNO_3 solution at 50 °C to remove AlPO_4 component, and was filtered and dried at 120 °C for 6 h to obtain the resulting mesoporous carbon material. Acid-modified activated carbon was also obtained with the following steps. Three g activated carbon was added to 20 mL HNO_3 aqueous solution (5 mol/L) and stirred for 8 h. Subsequently, it was filtered and dried 120 °C for 6 h to obtain the modified activated carbon with HNO_3 . Acid modified carbon nanotubes were also prepared using a similar method.

3. Catalyst Characterization

Powder X-ray diffraction measurement was conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-K α radiation. The FTIR spectra of the catalysts were recorded in

the range of 500–4,000 cm^{-1} on a Nicolet 6700 spectrometer. The morphologic features of the catalysts were observed using a scanning electron microscope (SEM, JSM-6510). The specific surface areas of catalysts were measured through nitrogen adsorption at 77 K using Autosorb IQ instrument (Autosorb-IQ-MP). Prior to adsorption, the samples were treated at 180 °C under vacuum for 18 h and the specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method. Pore size of catalysts was calculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model. Surface acidity of the catalyst was estimated by NH_3 -TPD using Quantachrome Instrument (Pulsa) and the desorbed species from catalyst surface was further confirmed by mass spectrometer (LC-D200).

4. Catalyst Evaluation

The synthesis of acetaldehyde from lactic acid over the catalysts was carried out in a fixed-bed quartz reactor with a 4 mm inner diameter operated at atmospheric pressure. The volume of loaded catalyst was fixed to 0.38 mL. The weight of loaded catalyst was changed with catalyst bulk density. The catalyst (0.08–0.42 g, 20–40 meshes) was placed in the middle of the reactor and quartz wool was placed in both ends. First, the catalyst was pretreated at the required reaction temperature (380 °C) for 1.0 h under N_2 with high purity (0.1 MPa, 1.0 mL/min). The feedstock (20 wt% solution of LA) was then pumped into the reactor (LA aqueous solution flow rate, 1.0 mL/h) and driven through the catalyst bed by carrier gas of nitrogen. The contact time of reactant over the catalyst is about 0.5 s, and the contact time is calculated by references [21,33]. The liquid products were condensed using ice-water bath and analyzed off-line using a SP-6890 gas chromatograph with a FFAP capillary column connected to a FID. Quantitative analysis of the products was by the internal standard method using *n*-butanol as the internal standard material. GC-MS analyses of the samples were performed with an Agilent 5973N mass selective detector attachment. The reaction tail gas was analyzed using GC with a packed col-

Table 1. BET data of catalysts

Catalyst	S_{BET} (m^2/g)	Vol (cm^3/g)	Pore size ^a (nm)
Mesoporous carbon	259.2	1.11	31.4
Activated carbon	86.3	0.10	3.7
Carbon nanotubes	111.2	1.62	63.3

^aCalculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model

Table 2. NH_3 -TPD results of catalysts

Catalyst	Acidity amount/mmol/g			Total acid amount/ mmol/g
	Weak (100–200 °C)	Medium (200–400 °C)	Strong (400–600 °C)	
Mesoporous carbon	0.243	1.125	0.766	2.134
Activated carbon	0.044	0.270	0.979	1.293
Activated carbon ^a	0.046	0.388	1.126	1.560
Carbon nanotubes	0.009	0.096	0.321	0.426
Carbon nanotubes ^a	0.003	0.041	0.296	0.340

^aImpregnated with 5 mol/L HNO_3 for 8 h

umn of TDX-01 connected to TCD detector. The conversion of LA and the selectivity toward acetaldehyde or other by-products were calculated as follows:

$$\text{Conversion}/\% = \frac{n_0 - n_1}{n_0} \times 100, \quad \text{Selectivity}/\% = \frac{n_p}{n_0 - n_1} \times 100$$

Where n_0 is the molar quantity of LA fed into reactor, n_1 is the molar quantity of LA in the effluent, and n_p is the molar quantity of lactic acid converted to acetaldehyde or other byproducts such as propionic acid, acrylic acid, acetic acid, 2,3-pentanedione.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

1-1. BET and NH_3 -TPD

The specific surface area of catalyst together with pore structure has an important influence in catalytic activity. Therefore, the specific surface area and pore structure of the catalysts were first evaluated (results given in Table 1). Clearly, the mesoporous carbon (PC) has the highest specific surface area ($259.2 \text{ m}^2/\text{g}$) and the medium mesopores (31.4 nm). And, activated carbon (AC) has the lowest specific surface area ($86.3 \text{ m}^2/\text{g}$) and the low mesopores (3.7

nm). As for LA and acetaldehyde molecules, their molecular dynamics diameters ($<1 \text{ nm}$) are far smaller than the pore sizes of the catalysts, indicating that diffusional limitation is very small [24,34,35]. According to the data of specific surface area of the catalysts, the increase order is: $\text{AC} < \text{CNTs} < \text{PC}$. Whereas, the increase order of catalytic activity characterized by LA conversion from Fig. 5 is: $\text{CNTs} < \text{AC} < \text{PC}$. Other factors except for specific surface area of the catalysts also have an important influence on catalytic activity.

NH_3 -TPD is an efficient measure for characterization of catalyst acidity, especially for the catalysts with dark color. The Hammett indicator method with *n*-butyl amine as an alkaline molecular probe is also an efficient measure to characterize the acidity of the catalysts [15,18]. But this method is only fit for those catalysts with light color. Therefore, we chose the NH_3 -TPD mean to estimate the acidity of carbon materials with dark color, and the results are given in Table 2 and Fig. 1. Although all catalysts belong to carbon materials, the acidity of the catalysts has a pronounced difference for each other. In terms of total acid amount and medium acid amount, the increase order is: $\text{CNTs} < \text{AC} < \text{PC}$. This order is consistent with those obtained from catalytic activity. Besides, it is expected that nitric acid is used to improve the acidity of catalyst surface. However, different results have been observed. As for AC catalyst, compared to the fresh AC, the surface acidity of the treated sample with nitric acid has been enhanced, whereas for CNTs, the surface acidity of the treated sample with nitric acid has reduced. For that reason, the catalytic performance displayed in AC and CNTs is evidently different between fresh sample and the treated sample.

1-2. FTIR and XRD

FTIR and XRD were used to investigate the functional groups and structures of catalysts to fully understand the catalysis in synthesis of acetaldehyde from LA, and the results are given in Fig. 2 and Fig. 3, respectively. The acidity of carbon materials originates from the carboxyl groups, hydroxyl groups, acid anhydride groups and other groups of the carbon surfaces. From Fig. 2(a), absorptions of $1,600 \text{ cm}^{-1}$ and $1,380 \text{ cm}^{-1}$ occur, indicating the existence of carboxylate anions, which are easily transformed into the carboxyl groups in the hydrothermal conditions [30,36]. Besides, the absorption band of $3,410 \text{ cm}^{-1}$ can be ascribed to hydroxyl groups. Thus, the acidity of mesoporous carbon formed and played a crucial role in catalytic synthesis of acetaldehyde from LA. From Fig. 2(b), the weak absorption bands of $1,860 \text{ cm}^{-1}$ and $1,800 \text{ cm}^{-1}$ can be ascribed to $\nu_{\text{C=O}}$ in acid anhydride. Together with the strong absorption band of $1,050 \text{ cm}^{-1}$ ($\nu_{\text{C-O-C}}$), we can deduce that an open chain anhydride group exists in activated carbon. Similarly, under the hydrothermal atmosphere an acid anhydride can be also transformed into a carboxyl group, resulting in the formation of activated carbon surface acidity. In addition, hydroxyl group ($3,420 \text{ cm}^{-1}$) also existed on the surface of activated carbon. Compared with patterns of Fig. 2(a) and 2(b), only the peak of hydroxyl group is very evident in Fig. 2(c), while other peaks representing acidic groups are very weak. Therefore, the acidity amount of CNTs is lower than that of mesoporous carbon and activated carbon.

We subsequently used XRD to investigate the structures of carbon catalysts. The XRD pattern of mesoporous carbon is given in Fig. 3(a). This sample exhibits two broad diffraction peaks centered at 26° and 44° , which can be generally indexed to (002), (101) dif-

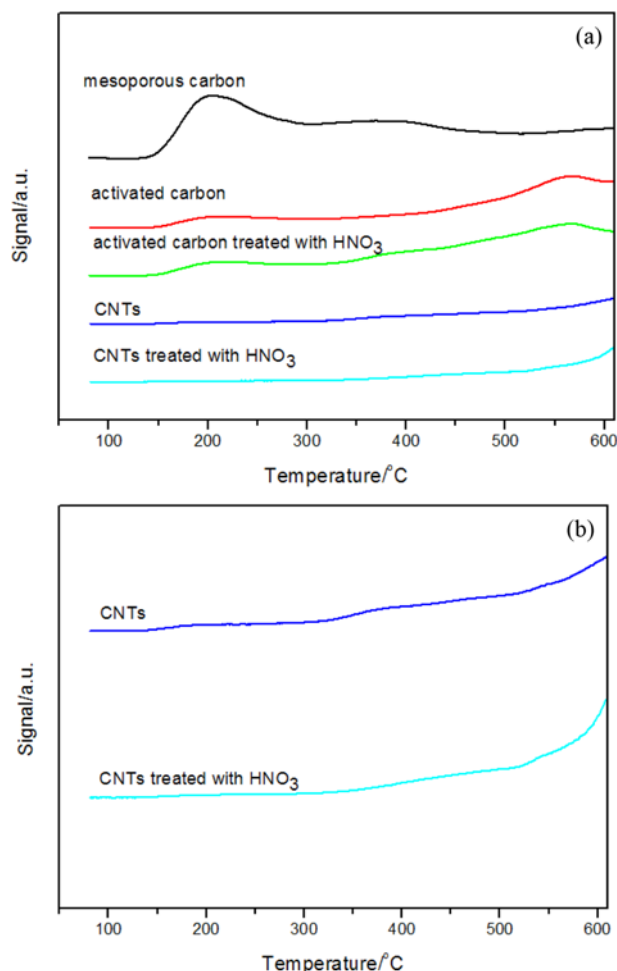


Fig. 1. NH_3 -TPD of catalysts (a) and (b) the amplified NH_3 -TPD for CNTs and CNTs treated with HNO_3 .

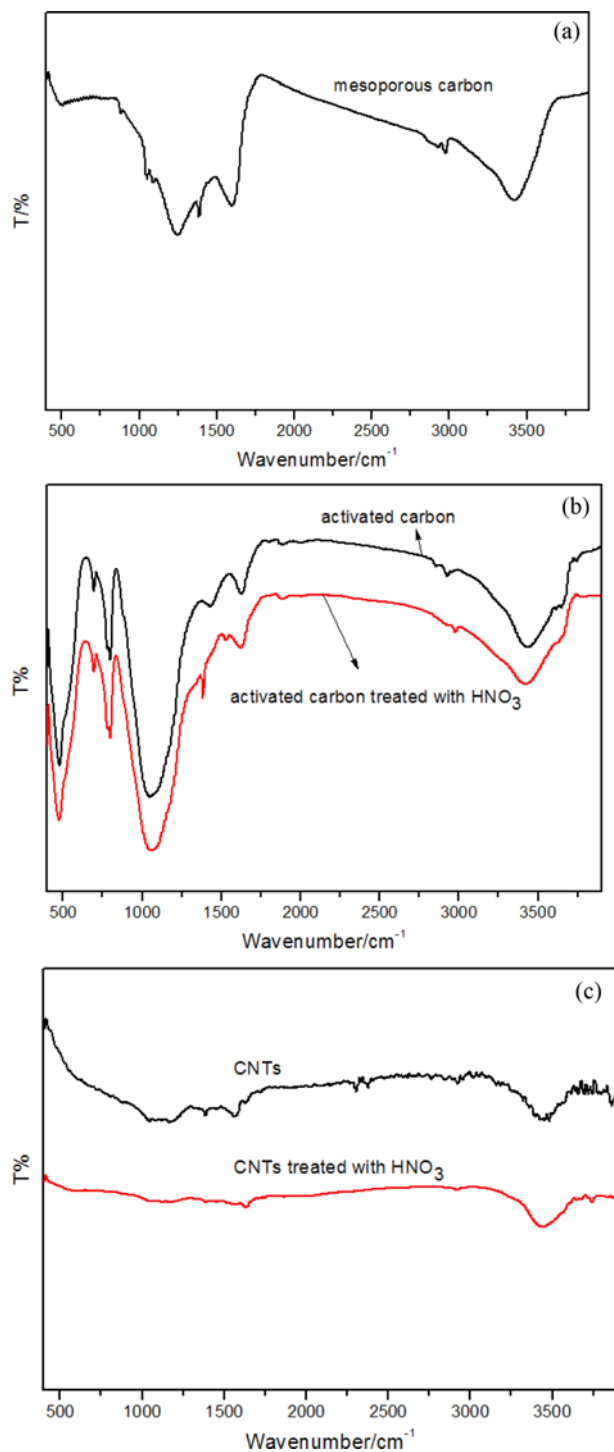


Fig. 2. FT-IR of catalysts. (a) Mesoporous carbon; (b) activated carbon and activated carbon treated with HNO_3 ; (c) CNTs and CNTs treated with HNO_3 .

fraction for glass carbons bearing graphitic characteristic. This result is in accord with that reported in previous work [31]. From the XRD patterns given in Fig. 3(b) and 3(c), fresh activated carbon and fresh CNTs can be well identical to corresponding samples treated with nitric acid, demonstrating that carbon materials are very stable in acidic aqueous solutions.

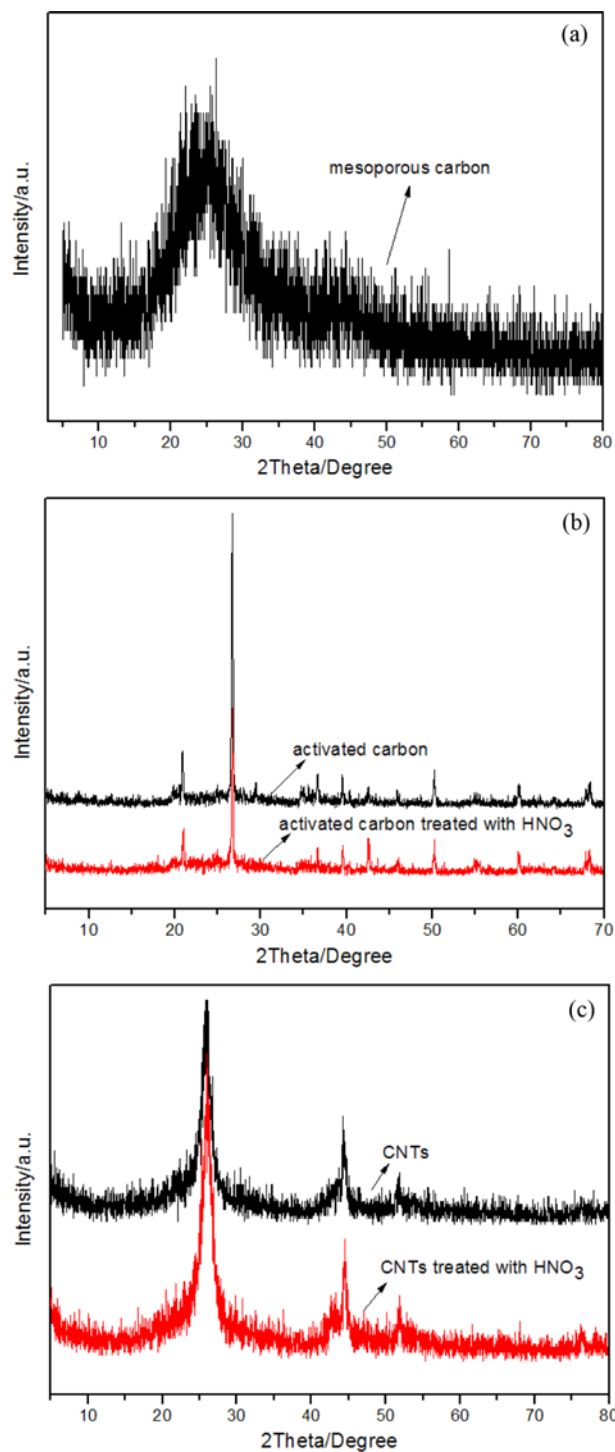


Fig. 3. XRD of catalysts. (a) Mesoporous carbon; (b) activated carbon and activated carbon treated with HNO_3 ; (c) CNTs and CNTs treated with HNO_3 .

1-3. SEM

Fig. 4 shows the SEM image of fresh mesoporous carbon catalyst. One can clearly observe the porous structure of the carbon catalyst, which offers the catalyst with a high specific surface area ($259.2 \text{ m}^2/\text{g}$) for catalytic reaction of acetaldehyde synthesis from LA.

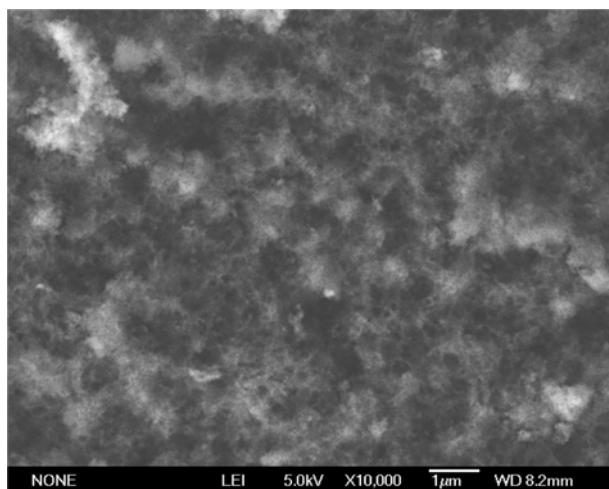


Fig. 4. SEM of mesoporous carbon.

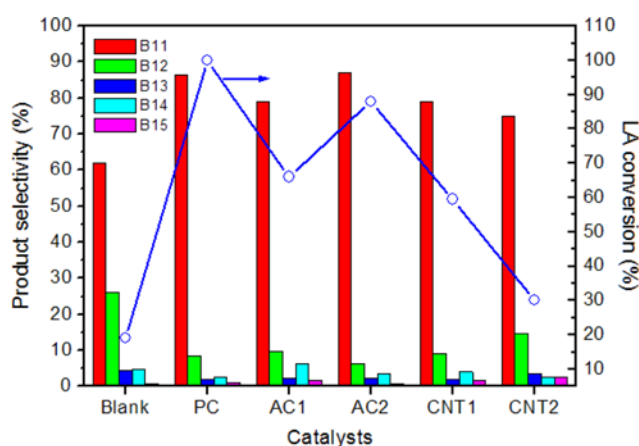


Fig. 5. Comparison of different catalysts at 380 °C. a Conditions: catalyst: PC (mesoporous carbon), 0.08 g, AC1 (fresh activated carbon), 0.42 g, AC2 (treated activated carbon with HNO_3), 0.42 g, CNT1 (fresh carbon nanotubes), 0.12 g, CNT2 (treated carbon nanotubes with HNO_3), 0.11 g. Particle size: 20–40 meshes, carrier gas N_2 : 1 mL/min, feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water. b Product selectivity: B11, acetaldehyde, B12, propionic acid, B13, acetic acid, B14, acrylic acid, B15, 2,3-pentanedione. c: impregnated with 5 mol/L HNO_3 for 8 h (AC2, CNT2), d: Blank represented reaction without catalyst.

2. Activity

2-1. Screening of Carbon Catalysts

First, we compared catalytic activity of three kinds of carbon materials with different acidity for decarboxylation of LA to acetaldehyde (Fig. 5). Decarboxylation of LA clearly occurs without catalyst at 380 °C, achieving 25% conversion of LA as well as 62.0% selectivity toward acetaldehyde. However, when the carbon catalysts were used, the reaction performance was greatly enhanced at the identical reaction conditions, indicating that the carbon materials indeed displayed catalysis. In terms of LA conversion, different carbon materials have a drastic difference. For example, over the modified CNTs with HNO_3 , LA conversion is the lowest, only

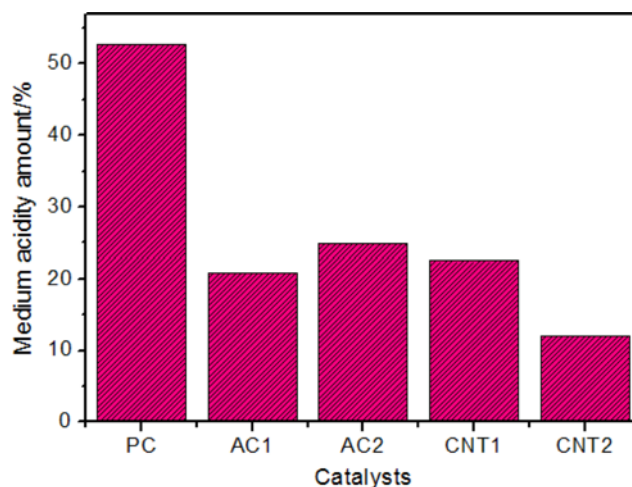
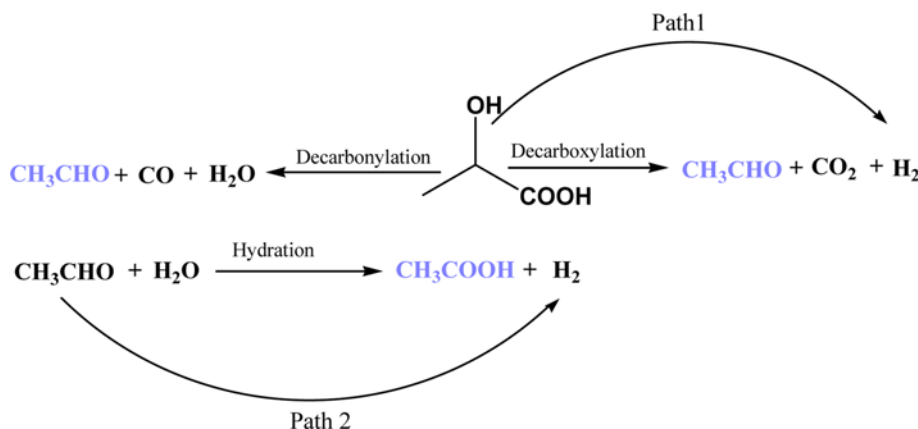
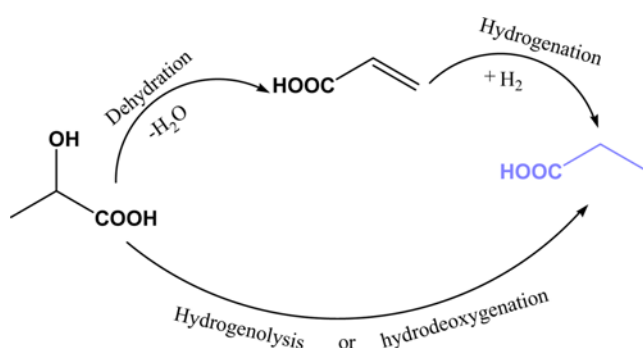


Fig. 6. Medium acidic site percentage in carbon catalysts.

30%, and as for PC, LA conversion is the highest, up to 100%. Nitric acid is usually utilized to modify carbon materials to enhance the acidity; however, we observed inconsistent results between activated carbon and CNTs. As for activated carbon, the acidity increased as it was modified with nitric acid, while for the CNTs the acidity decreased (seen in Table 2). Combined with the data of the total acid amount in carbon catalysts, the activity of catalysts increases with an increase of catalyst total acid amount. Product selectivity is also influenced by catalyst acidity. Similar to that of LA conversion influenced by catalyst acidity, selectivity toward acetaldehyde increased with an increase of the catalyst total acid amount. Also, the formation of acetaldehyde is related to medium acidic active sites. That is, medium acidic active sites favored to the formation of acetaldehyde. This result accords with that in our previous report [6]. Medium acidity amount percentage in total acid amount was calculated according to the data of Table 2 (the results are given in Fig. 6). In addition, from the data shown in Table 2, indeed, weak acid sites in mesoporous carbon are far more than others. But, the highest selectivity of acetaldehyde was achieved in mesoporous carbon catalyst. Based on these results, we can determine that weak acidity also slightly favors catalytic decarboxylation of lactic acid into acetaldehyde, or has not destroyed at least. Propionic acid as a major by-product is also related to catalyst acidity. A trend is clearly observed that the weaker the acidity is, the higher the propionic acid is. A case is that propionic acid selectivity attains to 14.6% for CNTs modified with nitric acid, while for PC and AC2, the propionic acid selectivities are 8.5% and 6.2%, respectively. Besides, an interesting phenomenon is also observed that higher propionic acid selectivity usually accompanies with higher acetic acid selectivity, while the acetaldehyde selectivity is lower. Based on the results obtained from Fig. 5, we can deduce that hydrogenolysis/hydrodeoxygenation of LA or hydrogenation of acrylic acid to form propionic acid occurs, while oxygenation of acetaldehyde with water to form acetic acid occurs, resulting in decrease of acetaldehyde and formation of hydrogen. To verify whether acetaldehyde was oxygenated with water, the experiment on acetaldehyde used as feedstock in water solution was at similar reaction conditions. Indeed, we found that a small quantity of acetic acid as well as hydrogen



Scheme 1. Synthesis of acetaldehyde and acetic acid accompanying with formation of hydrogen.



Scheme 2. Formation of propionic acid via hydrogenolysis/hydrodeoxygenation of LA or hydrogenation of the intermediate acrylic acid.

formed from acetaldehyde. The other hydrogen source can be obtained from the decarboxylation of LA. This view can be further confirmed by analysis of tail gas. In the process of catalytic reac-

tion, we detected hydrogen, CO_2 and CO in tail gas. The reaction paths are given in Schemes 1 and 2, respectively. To achieve the highly selective conversion of LA to acetaldehyde, PC is an evident substitute as an efficient catalyst for synthesis of acetaldehyde from lactic acid.

2-2. Effect of Reaction Temperature

The effect of reaction temperature on the reaction performance was investigated as for PC catalyst at the fixed other reaction conditions (Fig. 7). Reaction temperature clearly has an important influence on the reaction performance. LA conversion drastically increases with an increase of reaction temperature. For example, LA conversion is 84% at 300°C , while it increases to 100% at 350°C . For PC at 300°C the catalytic performance bears comparison with that of the CARiACT Q-15 supported silicotungstic acid catalyzed the decarbonylation of LA at 275°C (In terms of acetaldehyde yield, the former is 79.8% while the latter is about 81%) [5]. As for acetaldehyde selectivity, it decreases with an increase of reaction temperature. For example, the selectivity toward acetaldehyde is 94.9% at 300°C , while the selectivity to acetaldehyde decreases to 86.3% at 380°C . For propionic acid as a major by-product, the selectivity greatly increases with an increase of reaction tempera-

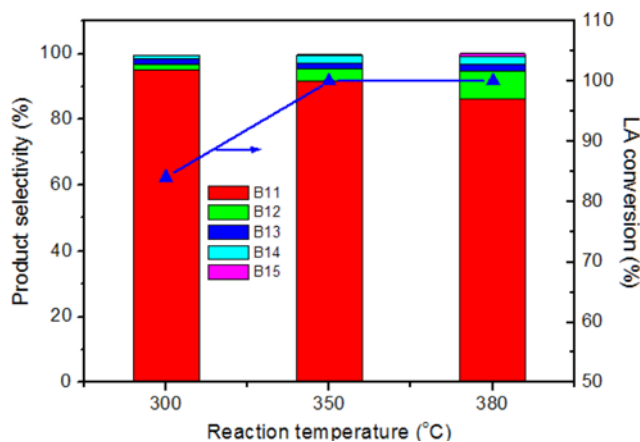


Fig. 7. Effect of reaction temperature a Conditions: PC (mesoporous carbon) catalyst, 0.08 g, particle size: 20-40 meshes, carrier gas N_2 : 1 mL/min, feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water. b Product selectivity: B11, acetaldehyde, B12, propionic acid, B13, acetic acid, B14, acrylic acid, B15, 2,3-pentanedione.

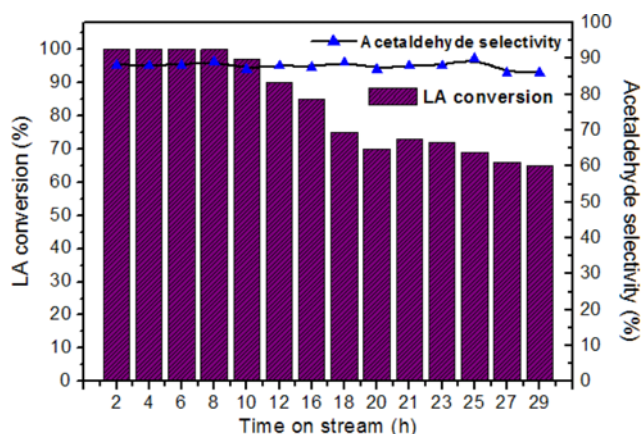


Fig. 8. Catalytic stability of mesoporous carbon. a Conditions: reaction temperature 380°C , catalyst: Mesoporous carbon, 0.08 g, particle size: 20-40 meshes, carrier gas N_2 : 1 mL/min, feed flow rate: 1 mL/h, LA feedstock: 20 wt% in water.

ture, indicating that the elevated temperature favors formation of propionic acid via hydrogenolysis of LA with an in-situ formed hydrogen from decarboxylation of LA.

2-3. Catalytic Stability

Long-term stability is a very important characteristic for a heterogeneous catalyst [1,2,37-39]. The catalytic stability of mesoporous carbon was investigated at 380 °C (see Fig. 8). LA can be almost completely converted to other high value chemicals such as acetaldehyde, propionic acid, acetic acid and acrylic acid within an initial 10 h on stream. However, the conversion of LA markedly decreased with an increase of time on stream. For example, LA conversion decreased from 97% at 10 h time on stream to 70% at 20 h time on stream. Subsequently, LA conversion slightly fluctuated from 65% to 73% with a further increase of time on stream. Although LA conversion was drastically influenced with time on stream in terms of the whole reaction process, acetaldehyde selectivity remained a slight fluctuation.

CONCLUSIONS

This work presents a simple and efficient way to synthesize acetaldehyde from lactic acid. Among the tested carbon materials, mesoporous carbon displayed the best catalytic performance due to a high amount of medium acidity. The other factor is that mesoporous carbon has a high specific surface area (259.2 m²/g) and appropriate mesoporous structure (31.4 nm), respectively. The selectivity of acetaldehyde increases with a decrease of reaction temperature. However, LA conversion decreases with a decrease of reaction temperature. To achieve a high yield of acetaldehyde, appropriate reaction temperatures (350-380 °C) should be chosen. We believe that mesoporous carbon catalyst has a potential application in synthesis of bulk chemicals such as acetaldehyde from lactic acid.

ACKNOWLEDGEMENTS

This work was supported by Scientific Research Fund of Sichuan Provincial Educational Department with project number of 14ZA0128, Scientific Research Fund of Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province with project number of CSPC-2014-3-1, and Scientific Research Fund of China West Normal University with project number of 12B019.

REFERENCES

1. J. M. Sun, K. K. Zhu, F. Gao, C. M. Wang, J. Liu, C. H. F. Peden and Y. Wang, *J. Am. Chem. Soc.*, **133**, 11096 (2011).
2. M. S. Holm, S. Saravanamurugan and E. Taarning, *Science*, **328**, 602 (2010).
3. Y. L. Wang, W. P. Deng, B. J. Wang, Q. H. Zhang, X. Y. Wan, Z. C. Tang, Y. Wang, C. Zhu, Z. X. Cao, G. C. Wang and H. L. Wan, *Nat. Commun.*, **4**, 2141 (2013).
4. I. Abdullahi, T. J. Davis, D. M. Yun and J. E. Herrera, *Appl. Catal. A-Gen.*, **469**, 8 (2014).
5. B. Katryniok, S. Paul and F. Dumeignil, *Green Chem.*, **12**, 1910 (2010).
6. Z. J. Zhai, X. L. Li, C. M. Tang, J. S. Peng, N. Jiang, W. Bai, H. J. Gao and Y. W. Liao, *Ind. Eng. Chem. Res.*, **53**, 10318 (2014).
7. D. Esposito and M. Antonietti, *ChemSuschem*, **6**, 989 (2013).
8. C. A. Ramirez-Lopez, J. R. Ochoa-Gomez, S. Gil-Rio, O. Gomez-Jimenez-Aberasturi and J. Torrecilla-Soria, *J. Chem. Technol. Biot.*, **86**, 867 (2011).
9. C. M. Tang, Y. Zeng, X. G. Yang, Y. C. Lei and G. Y. Wang, *J. Mol. Catal. A-Chem.*, **314**, 15 (2009).
10. C. M. Tang, Y. Zeng, P. Cao, X. G. Yang and G. Y. Wang, *Catal. Lett.*, **129**, 189 (2009).
11. A. Brennfuhrer, H. Neumann and M. Beller, *Chemcatchem*, **1**, 28 (2009).
12. C. M. Tang, X. L. Li and G. Y. Wang, *Korean J. Chem. Eng.*, **29**, 1700 (2012).
13. J. F. Zhang, Y. L. Zhao, X. Z. Feng, M. Pan, J. Zhao, W. J. Ji and C.-T. Au, *Catal. Sci. Technol.*, **4**, 1376 (2014).
14. C. M. Tang, J. S. Peng, G. C. Fan, X. L. Li, X. L. Pu and W. Bai, *Catal. Commun.*, **43**, 231 (2014).
15. J. S. Peng, X. L. Li, C. M. Tang and W. Bai, *Green Chem.*, **16**, 108 (2014).
16. J. H. Hong, J.-M. Lee, H. Kim, Y. K. Hwang, J.-S. Chang, S. B. Halligudi and Y.-H. Han, *Appl. Catal. A-Gen.*, **396**, 194 (2011).
17. J. M. Lee, D. W. Hwang, Y. K. Hwang, S. B. Halligudi, J. S. Chang and Y. H. Han, *Catal. Commun.*, **11**, 1176 (2010).
18. C. M. Tang, J. S. Peng, X. L. Li, Z. J. Zhai, N. Jiang, W. Bai, H. J. Gao and Y. W. Liao, *RSC Adv.*, **4**, 28875 (2014).
19. P. Sun, D. H. Yu, K. M. Fu, M. Y. Gu, Y. Wang, H. Huang and H. H. Ying, *Catal. Commun.*, **10**, 1345 (2009).
20. T. M. Aida, A. Ikarashi, Y. Saito, M. Watanabe, R. L. Smith and K. Arai, *J. Supercrit. Fluid.*, **50**, 257 (2009).
21. J. F. Zhang, J. P. Lin and P. L. Cen, *Can. J. Chem. Eng.*, **86**, 1047 (2008).
22. H. J. Wang, D. H. Yu, P. Sun, J. Yan, Y. Wang and H. Huang, *Catal. Commun.*, **9**, 1799 (2008).
23. V. C. Ghantani, S. T. Lomate, M. K. Dongare and S. B. Umbarkar, *Green Chem.*, **15**, 1211 (2013).
24. C. M. Tang, J. S. Peng, X. L. Li, Z. J. Zhai, W. Bai, N. Jiang, H. J. Gao and Y. W. Liao, *Green Chem.*, **17**, 1159 (2015).
25. N. Li, J. X. Xu, H. Chen and X. Y. Wang, *J. Nanosci. Nanotechnol.*, **14**, 5157 (2014).
26. M. Ruthiraan, N. M. Mubarak, R. K. Thines, E. C. Abdullah, J. N. Sahu, N. S. Jayakumar and P. Ganesan, *Korean J. Chem. Eng.*, **32**, 446 (2015).
27. J. F. Chang, L. G. Feng, C. P. Liu, W. Xing and X. L. Hu, *Angew. Chem. Int. Edit.*, **53**, 122 (2014).
28. D. T. D. Tang, K. D. Collins, J. B. Ernst and F. Glorius, *Angew. Chem. Int. Edit.*, **53**, 1809 (2014).
29. L. Shang, T. Bian, B. H. Zhang, D. H. Zhang, L. Z. Wu, C. H. Tung, Y. D. Yin and T. R. Zhang, *Angew. Chem. Int. Edit.*, **53**, 250 (2014).
30. E. Sairanen, K. Vilonen, R. Karinen and J. Lehtonen, *Top. Catal.*, **56**, 512 (2013).
31. G. Liu, Y. Liu, Z. L. Wang, X. Z. Liao, S. J. Wu, W. X. Zhang and M. J. Jia, *Micropor. Mesopor. Mater.*, **116**, 439 (2008).
32. L. Borchardt, M. Oschatz, S. Graetz, M. R. Lohe, M. H. Rummell and S. Kaskel, *Micropor. Mesopor. Mater.*, **186**, 163 (2014).
33. J. F. Zhang, Y. L. Zhao, M. Pan, X. Z. Feng, W. J. Ji and C. T. Au, *ACS Catal.*, **1**, 32 (2011).

34. G. Sastre, A. Chica and A. Corma, *J. Catal.*, **195**, 227 (2000).
35. F. Jimenez-Cruz and G. C. Laredo, *Fuel*, **83**, 2183 (2004).
36. J. Dong, F. R. van de Voort, A. A. Ismail, E. Akochi-Koble and D. Pinchuk, *Lubric. Eng.*, **56**, 12 (2000).
37. M. Behrens, F. Studt, I. Kasatkin, S. Kuhl, M. Havecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. L. Kniep, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlögl, *Science*, **336**, 893 (2012).
38. L. Deiana, Y. Jiang, C. Palo-Nieto, S. Afewerki, C. A. Incerti-Pradillos, O. Verho, C. W. Tai, E. V. Johnston and A. Cordova, *Angew. Chem. Int. Edit.*, **53**, 3447 (2014).
39. X. J. Jin, K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Edit.*, **53**, 455 (2014).