



Article

Subscriber access provided by UNIVERSITY OF THE SUNSHINE COAST

Promotion Effect of Sn on Au/Sn-USY Catalysts for One-Pot Conversion of Glycerol to Methyl Lactate

Tianliang Lu, Xiaomin Fu, Lipeng Zhou, Yunlai Su, Xiaomei Yang, Li Han, Jianfeng Wang, and Chengying Song

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.7b02254 • Publication Date (Web): 12 Sep 2017 Downloaded from http://pubs.acs.org on September 12, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Promotion Effect of Sn on Au/Sn-USY Catalysts for One-Pot Conversion of Glycerol to Methyl Lactate

Tianliang Lu^{a,b}, Xiaomin Fu^b, Lipeng Zhou^b, Yunlai Su^b, Xiaomei Yang^{b,*}, Li Han^a, Jianfeng Wang^a, Chengying Song^a

^a Research Center of Heterogeneous Catalysis and Engineering Sciences, School of Chemical Engineering and Energy, Zhengzhou University, 100 Kexue Road, Zhengzhou 450001, China

^b College of Chemistry and Molecular Engineering, Zhengzhou University, 100 Kexue Road, Zhengzhou 450001, China

ABSTRACT: Herein, hierarchical bifunctional catalysts of Sn-USY supported Au nanoparticles were designed for the one-pot conversion of glycerol (GLY) to methyl lactate (MLA). Over Au/Sn-USY catalyst, 79% MLA yield can be given with a high selectivity (~90%). Promotion effect of Sn was investigated and the interaction between extra framework SnO_x and Au was confirmed by TEM, pyridine-FT-IR, CO-FT-IR and XPS. The interaction promotes the dispersion of Au particles (smaller and much more uniform). This is important for the oxidation of GLY to 1,3-dihydroxyacetone (DHA) and glyceraldehyde (GA) which are the intermediate species for the conversion of GLY to MLA. Meanwhile, introduction of Sn modified the acid property of the catalyst which is critical for the selective conversion of DHA and GA to MLA.

KEYWORDS: Au; Sn; Glycerol; Methyl lactate; Bifunctional catalysts; Zeolite

INTRODUCTION

Selective transformation of glycerol (GLY), which is the main byproduct of biodiesel industry, is an attractive prospect.^{1,2} Because of highly functionalized molecular structure of GLY, various high value-added chemicals can be obtained by kinds of processes including selective hydrogenolysis,³ dehydration,⁴ oxidation⁵ and esterification,⁶ Lactic acid and alkyl lactates are important chemicals widely used in food, pharmaceutical and chemical industries; and their derivative polylactic acid is a promising biodegradable polymer.^{7,8} Production of lactic acid and alkyl lactates from GLY attracts much attention of researchers nowadays.^{2,5,9-13} For both environmental and economical reasons, heterogenously catalytic conversion of GLY to lactic acid and alkyl lactates is desirable.¹⁴⁻²⁷ Recently, a variety of supported heterogenous catalysts including Au,¹⁴⁻¹⁷ Pt,¹⁸⁻²¹ Pd,²² and Cu^{23,24} metals were developed for the conversion of GLY to lactic acid in water. However, most of the above mentioned methods need high reaction temperature and/or addition of NaOH. Moreover, further esterification, distillation and hydrolysis are needed to produce lactic acid with high quality.²⁵ Methyl lactate (MLA) can be obtained directly with methanol as a solvent. This process does not need a separate esterification step compared to the aqueous medium. Furthermore, methanol is present in the crude GLY obtained from biodiesel. Taking methanol as a solvent eliminates the separation process for GLY/methanol. One-pot transfromation of GLY to MLA in methanol is attractive. Ye and coworkers applied CaO and CuO as catalysts to catalyze the conversion of glycerol to calcium lactate at 230 °C firstly; then methanol and CO₂ were charged to the reaction system, and calcium lactate was converted into MLA with 57% yield through ester transfer reaction at 200 °C.²⁶ Heeres and coworkers have reported the conversion of GLY to MLA over supported Au catalysts in base-free methanol.²⁷

Based on the previous reports,^{14-24,27} three continuous reactions are included in the conversion of GLY to MLA (Scheme 1): (1) oxidation of GLY to 1,3-dihydroxyacetone (DHA) and glyceraldehyde (GA), (2) dehydration of DHA and GA to pyruvaldehyde (PA), (3) alcohol addition of PA and isomerization to MLA. Thus, oxidation active sites (for reaction 1) and acid sites, particularly Lewis (L) acid sites (for reactions 2 and 3) should coexist in the designed catalysts for the conversion of GLY to MLA.



Scheme 1. Transformation of GLY to MLA in methanol.

As typical L acids, Sn-containing catalysts show excellent performance for selective production of MLA from DHA due to the unique activation ability of Sn for the carbonyl group.²⁸⁻³¹ Furthermore, the L acid property of Sn-containing catalysts, which is critical for obtaining high MLA yield, can be controled by adjustment of Sn content. We have reported that hierarchical Sn-USY is a highly active catalyst for the conversion of DHA to MLA. Even at ambient temperature (25-40 °C), DHA was completely converted to MLA with more than 95% yield.²⁸ So, we used hierarchical Sn-USY to provide the L acid sites. On the other hand, Au based catalysts were studied extensively for the conversion of GLY, and showed good activity and selectivity to produce DHA.³² Thus, in this work, the hierarchical bifunctional catalysts of Sn-USY supported Au nanoparticles were designed for the one-pot conversion of GLY to MLA in methanol. By a modified colloidal deposition method, hierarchical Au/Sn-USY were synthesized. The effects of Sn on Au particle size and its surface electronic property, which are

very important for the catalytic behavior, were studied in detail, and the influence of Au nanoparticles on the acid properties of Sn-USY was also investigated. By TEM, pyridine-FT-IR, CO-FT-IR and XPS, the interaction between Au and Sn, and the mechanism for preparation of Au/Sn-USY were established. Moreover, various preparation conditions were optimized to obtain Au/Sn-USY with excellent catalytic performance for one-pot conversion of GLY to MLA. Finally, the reaction conditions for selective conversion of GLY to MLA were optimized.

EXPERIMENTAL

Materials. Glycerol, methanol, HNO₃, H₂SO₄, NaBH₄, SnCl₄·5H₂O, HAuCl₄·4H₂O and naphthalene were obtained from commercial sources (AR grade). H-USY (Si/Al = 3.2) was purchased from Nankai University Catalyst Co., Ltd. (China). Polyvinyl alcohol (PVA; molecular weight = 9000 - 10000) was obtained from Sigma-Aldrich. Methyl lactate (>98%) was purchased from TCI Shanghai, China.

Preparation of Sn-DeAl-USY. Sn-USY zeolites were prepared using a method described in our previous report.²⁸ Typically, H-USY (8.0 g) was added to a nitric acid solution (200 mL, 8 M). After stirring at 85 °C for 8 h, the solid was separated from the suspension by centrifugation and washed to pH = 7 with deionized water. The obtained dealuminated solid was denoted as DeAl-USY. After drying at 100 °C for 12 h in air, the solid along with SnCl₄·5H₂O was ground thoroughly for 1 h in a mortar. Finally, the sample was calcined at 550 °C for 3 h after drying at 100 °C for 12 h. The obtained sample was denoted as *x*Sn-DeAl-USY where *x* represents the weight percent of Sn to Sn-DeAl-USY.

Preparation of Au/Sn-DeAl-USY. Au was loaded on Sn-DeAl-USY via a modified colloidal deposition method as follows. First, desired amount of PVA was diluted with deionized water (25 mL). Then, desired volume HAuCl₄ (25 mmol L^{-1}) was added to the diluted PVA aqueous

solution. After stirring for 20 min, calculated volume NaBH₄ solution (0.1 mol L⁻¹, mole ratio of NaBH₄ to HAuCl₄ is 5) was added dropwise to the HAuCl₄ solution, and pH of the solution was adjusted to a certain value using H₂SO₄ (0.25 mol L⁻¹). Then, Sn-DeAl-USY was added to the solution. After stirring at room temperature for 6 h, the solid was obtained by rotary evaporation of the suspension at 40 °C. Finally, the solid was dried at 60 °C for 12 h, and calcined at 350 °C for 3 h. The obtained sample was denoted as *y*Au/*x*Sn-DeAl-USY where *y* represents the weight percent of Au to Au/Sn-DeAl-USY. For comparison, Au supported on H-USY (1Au/H-USY) and DeAl-USY (1Au/DeAl-USY) were also prepared by similar procedure.

Characterization. X-ray diffraction (XRD) was performed using a Panalytical X'pert PRO powder diffractometer with Cu-K α radiation ($\lambda = 0.15418$ nm) at 40 kV. N₂ adsorptiondesorption isotherms were measured with a Quantachrome Autosorb using N2 as adsorbate at -196 °C. Total surface area and pore size distributions (PSDs) were calculated according to Brunauer-Emmet-Taller (BET) method and Barrett-Joyner-Halenda (BJH) method (desorption branch of the isotherms), respectively. Transmission electron microscopy (TEM) images were obtained on a JEM2100 microscope operated at 200 kV. The FT-IR spectra of different catalysts with pyridine or deuterated acetonitrile (CD₃CN) adsorption were performed on a Bruker Tensor II spectrometer, and the resolution of the spectrometer is 4 cm⁻¹. The samples (9-12 mg) were evacuated in a pool under 350 °C for 3 h to remove water. After cooling down to room temperature, FT-IR spectra in the hydroxyl stretching vibration region of the sample were collected, and air was used as background reference. Then, another IR spectrum of the sample was collected and used as background reference for the following measurement. After that, pyridine or CD₃CN gas was introduced to the reactor pool at room temperature until adsorption saturation (15 min). Subsequently, a vacuum pump was used to desorb probe molecule under

different temperature for some time. Finally, the FT-IR spectrum of the catalyst with pyridine or CD₃CN adsorption was collected using the obtained IR spectrum mentioned above as background reference. FT-IR spectrum of CO adsorbed over 1Au/3Sn-DeAl-USY was collected on a Bruker Tensor 27 IR spectrometer. The sample was pressed into a self-supporting disk (13 mm diameter, 26.7 mg) and placed in a homemade IR cell attached to a closed glass-circulation system. Prior to CO adsorption, the sample disk was pretreated by heating at 250 °C for 1 h in vacuum (pressure $< 10^{-3}$ Pa) and then cooled to 20 °C, followed by the recording of a background at a resolution of 4 cm^{-1} , the sample disk was exposed to CO. IR spectrum of the chemisorbed CO was recorded after evacuation to eliminate physically adsorbed CO. X-ray photoelectron spectroscopy (XPS) was used to study the oxidation state of the elements on the catalyst surface. XPS experiments were carried out on a Kratos AXIS Supra photoelectron spectrometer with an Al K α radiation ($h\nu$ = 1486.6 eV). The instrument was run at 15.0 kV with a current of 10 mA. XPS data was analyzed on the software of XPSPEAK. The binding energy of C1s was taken as a reference at 284.6 eV. The Sn content in reaction solution after reaction was determined by induced coupled plasma-atomic emission spectroscopy (ICP-AES).

Catalytic Tests. The catalytic conversion of GLY to MLA was carried out in a stainless steel autoclave reactor with a magnetic stirrer and a temperature controller. Typically, GLY (1 mmol), Au/Sn-DeAl-USY (0.2 g) and methanol (5 mL) were added to the reactor. After the autoclave was sealed, the atmosphere over the solution was replaced four times with O_2 , and then the pressure of O_2 was charged to 0.5 MPa. Then, the reactor was heated to the reaction temperature under magnetic stirring. After reaction, the reactor was cooled down to ambient temperature and depressurized carefully.

ACS Catalysis

Product Analyses. Identification of the products in the reaction solution was based on Agilent 6890N GC/5973MS and compared with the authentic samples. Conversion of GLY was determined by external standard method on a Shimadzu LC-20AT HPLC with an Aminex HPX-87H column (300×7.8 mm, column temperature was 60 °C) and a RID-10A refractive index detector. Yield of MLA was analyzed on Agilent 7890A GC with HP-5 capillary column and flame ionization detector using naphthalene as the internal standard.

RESULTS AND DISCUSSION

Physicochemical Properties of Catalysts. XRD patterns of 3Sn-DeAl-USY and 1Au/3Sn-DeAl-USY shown in Figure S1 indicate that introduction of Sn and loading of Au did not destroy the crystalline structure of USY zeolite. Type IV isotherms of N₂ adsorption with H3 hysteresis loop (Figure S2) indicates that all the samples are micro-meso porous materials. Textural properties of the samples are summarized in Table 1. The external surface area and the mesopore volume of DeAl-USY increased dramatically compared to H-USY due to dealumination. However, the surface area and the pore volume of 3Sn-DeAl-USY decreased dramatically. This might be caused by the reconstitution during incorporation of Sn into the zeolite through grinding. Textural data of 1Au/H-USY, 1Au/3Sn-DeAl-USY and 1Au/DeAl-USY are similar to that of H-USY, 3Sn-DeAl-USY and DeAl-USY, respectively, indicating that the load of Au did not affect the textural properties of the samples dramatically.

2	
3	
4	
5	
6	
7	
2 2	
0	
9	
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	
20	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	
30	
31	
32	
33	
24	
34	
35	
36	
37	
38	
39	
40	
41	
42	
43	
44	
45	
46	
<u>⊿</u> 7	
-+1 10	
40	
49	
50	
51	
52	
53	
54	
55	
56	
57	
58	
~~~	

1

Table 1. Textural Parameters of the	e Samples
-------------------------------------	-----------

Sample	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$	Total pore volume (mL g ⁻¹ )	$S_{\text{External}}^{a}$ (m ² g ⁻¹ )	Mesopore volume ^{$a$} (mL g ⁻¹ )
H-USY	427	0.31	77	0.12
DeAl-USY	505	0.40	121	0.20
3Sn-DeAl-USY	421	0.34	82	0.17
1Au/H-USY	418	0.30	62	0.12
1Au/DeAl-USY	486	0.39	115	0.20
1Au/3Sn-DeAl-USY	422	0.33	96	0.16

^{*a*}  $S_{\text{External}} = S_{\text{BET}} - S_{\text{Micropore}}$ ; mesopore volume = total pore volume – micropore volume, where the micropore surface area and volume were determined by the *t*-plot method at a relative pressure of 0.05-0.70.

**Morphology of Catalysts.** Particle size is very important for the catalytic performance of gold. In general, Au nano-particles (Au NPs) smaller than 10 nm are proper for many catalytic reaction. To obtain small (< 10 nm) and uniform Au NPs, preparation conditions and parameters including solution pH, Au/PVA weight ratio and Sn content were studied firstly.



**Figure 1**. TEM images of 1Au/3Sn-DeAl-USY catalysts prepared with different solution pH value (Au/PVA weight ratio = 4).

The solution acidity has a marked effect on the size of the prepared Au NPs.^{33,34} To illustrate the acidity effects, 1Au/3Sn-DeAl-USY samples were synthesized at different pH value (pH = 1 to 7) with a fixed Au/PVA weight ratio. TEM images in Figure 1 show that the size of the Au NPs decreased in the beginning as the pH increased, and followed by an increase of the Au NPs size. When the pH values were 3 and 5, size of most of Au NPs was smaller than 10 nm. Lower (pH = 1) or higher (pH = 7) pH value caused the formation of lager Au NPs (> 10 nm). In acidic solution (pH < 7), hydroxyl groups on PVA chains were protonated. Thus, the polymer chains are extended in acidic solution due to the electrostatic repulsions between the positive charges of protonated PVA chains. This prevents Au particles from aggregating.³³ However, much lower

pH value (pH = 1) might lead to partial decomposition of PVA and destruction of NaBH₄, which caused the growth of Au particles.



**Figure 2**. TEM images of 1Au/3Sn-DeAl-USY prepared with different Au/PVA weight ratio (solution pH value = 3).

TEM images and particle distributions of 1Au/3Sn-DeAl-USY catalysts prepared with Au/PVA weight ratio of 4, 1 and 0.25 are presented in Figure 2. When the Au/PVA weight ratio was adjusted to 4, average gold particle diameter of 7.8 nm was observed along with a broad particle size distribution of 5-30 nm. At the same Au concentration, decreasing the Au/PVA weight ratio from 4 to 1 produced smaller Au NPs. Average particle diameter of 6.2 nm and a narrower particle size distribution (4-10 nm) were obtained. However, further decreasing the Au/PVA weight ratio from 1 to 0.25 resulted in the formation of large Au NPs, and average particle diameter of Au NPs increased from 6.2 nm to 8.5 nm with a broader particle size distribution (4-22 nm). Thus, there is an optimum Au/PVA weight ratio of 1 for the formation of small and uniform Au NPs in this work. When PVA is insufficient, Au NPs would be unstable and growth of some particles might occur, which lead to the formation of a few large particles and the broader Au NPs would exist due to more difficult immobilization of the Au NPs onto the support. Similar results were reported in literature.^{35,36}



**Figure 3**. TEM images of 1Au/*x*Sn-DeAl-USY catalysts prepared with Au/PVA weight ratio of 1 and solution pH of 3.

Sn dopped hierarchical USY was applied as the support in this study. Figure 3 shows the morphology of 1Au/xSn-DeAl-USY catalysts. Surprisingly, the average Au NPs diameter and the particle size distribution were affected significantly by the Sn content in USY. When Sn was absent, large Au NPs with average particle size of 18.7 nm was observed associated with a broad particle size distribution in the range of 8 nm to 32 nm. Increasing the Sn content to 1 wt%, a dramatic decrease of average Au NPs diameter from 18.7 nm to 9.4 nm was observed along with a narrower particle size distribution from 4 nm to 16 nm. Further increase of the Sn content from 1 wt% to 2 wt%, 3 wt% and 4 wt% resulted in a decrease of average Au NPs size from 9.4 nm to 6.8 nm, 6.2 nm and 5.5 nm, respectively. These results demonstrate that the presence of Sn promoted the formation of small and uniform Au NPs. Growth or aggregation of Au particles

mainly exist in the reduction process of Au(III) to Au(0) in the gel and immobilization of the Au NPs onto the support (including the calcination process). Size of most Au NPs in the gel synthesized at the fixed conditions (solution pH = 3, Au/PVA weight ratio = 1 and Sn content = 3 wt%) is in the range of 2 nm to 5 nm (Figure 4a). Taking the unsupported Au NPs sample (Figure 4a) to calcine directly, huge lump of Au formed (Figure S3). Thus, immobilization of Au NPs onto Sn-DeAl-USY depressed the growth or aggregation of Au caused by the calcination, although size of Au NPs on Au/Sn-DeAl-USY was larger than that of unsupported Au NPs. However, different Sn content in Sn-DeAl-USY brought on different degree of depression effect as described above.

Introduction of Sn into DeAI-USY was realized by the post-synthesis method via dealumination of H-USY zeolite with nitric acid and solid-state ion-exchange with SnCl₄. Plenty of mesopores formed in Sn-DeAI-USY due to the dealumination as described in our previous work,²⁸ diameter of mesopores in Sn-DeAI-USY is mainly in the range of 5 nm to 30 nm which was further confirmed by the TEM images of Sn-DeAI-USY in Figure 4b. By this method, there would be some Sn sites at the surrounding of the mesopores. By analyzing the sites of Au on 1Au/xSn-DeAI-USY (for example, partial enlarged view of 1Au/4Sn-DeAI-USY in Figure 3), it was found that Au NPs located at the surrounding of the mesopores. Thus, it is reasonable that the interaction between Au and Sn made Au NPs tend to locate at the Sn sites around the mesopores, and this prevented Au NPs from aggregation. Zhang and coworkers prepared Au-Sn/C catalyst, and illustrated that strong interaction between Au and Sn made the Au species disperse well.³⁷ In this work, the interaction between Au and Sn was further confirmed by CO-FT-IR, pyridine-FT-IR and XPS in the following sections.



Figure 4. TEM images of the unsupported Au NPs in the gel (a) and 3Sn-DeAl-USY (b).

Acid Property of Catalysts. Figure 5 shows the FT-IR spectra in the hydroxyl stretching vibration region. Several characteristic bands at 3740 cm⁻¹, 3470 cm⁻¹, 3630 cm⁻¹ and 3561 cm⁻¹ were observed for these samples. Bands at 3740 cm⁻¹ and 3470 cm⁻¹ can be ascribed to the external Si-OH groups and the internal Si-OH groups in the framework formed in the process of dealumination, respectively.³⁸⁻⁴⁰ Bands at 3630 cm⁻¹ and 3561 cm⁻¹ belonged to bridging hydroxyls Si-OH-Al in zeolite cages.^{38,39} Spectrum of 1Au/H-USY (Figure 5b) is similar to that of H-USY (Figure 5a) indicating the introduction of Au has little impact on the hydroxyl of H-USY without dealumination. For DeAl-USY (Figure 5c), intensity of bands at 3740 cm⁻¹ and 3470 cm⁻¹ increased dramatically compared to the parent H-USY zeolite (Figure 5a) implying the formation of a large amount of Si-OH groups. After introduction of Sn, both the intensity of band at 3470 cm⁻¹ and band at 3740 cm⁻¹ decreased (3Sn-DeAl-USY, Figure 5d). This phenomenon indicates that the internal Si-OH groups react with SnCl₄ to form framework Sn, and the external Si-OH groups can also react with SnCl₄ to form extra framework Sn. Interestingly, after introduction of Au into DeAl-USY (1Au/DeAl-USY Figure 5e), band at 3470 cm⁻¹ also decreased indicating that Au species can react with the Si-OH groups too. FT-IR spectrum in the hydroxyl stretching vibration region of 1Au/3Sn-DeAl-USY (Figure 5f) was

similar to that of 3Sn-DeAl-USY (Figure 5d). Thus, for 1Au/3Sn-DeAl-USY, Si-OH groups in DeAl-USY mainly react with Sn species.



**Figure 5.** FT-IR spectra in the hydroxyl stretching vibration region for samples of (a) H-USY, (b) 1Au/H-USY, (c) DeAl-USY, (d) 3Sn-DeAl-USY, (e) 1Au/DeAl-USY and (f) 1Au/3Sn-DeAl-USY.

Figure S4 and Figure S5 show the pyridine-FT-IR spectra of 1Au/3Sn-DeAl-USY prepared with different solution pH and different Au/PVA weight ratio, respectively. Three obvious IR bands at 1453 cm⁻¹, 1543 cm⁻¹ and 1490 cm⁻¹ observed in all the 1Au/3Sn-DeAl-USY samples were ascribed to pyridine adsorption on the Lewis (L) acid sites, Brönsted (B) acid sites and L/B acid sites, respectively.^{28,38,41} According to the area of the corresponding peak, the amount of L and B acid sites was calculated and listed in Table S1. In general, with a fixed Au/PVA weight ratio of 4, high pH value (5 and 7) leads to more L acid sites, which are important for this reaction, and fewer B acid sites compared to low pH value (1 and 3). Meanwhile, Au/PVA weight ratio did not affect the amount of L acid sites of the catalysts significantly. Figure 6

Page 15 of 34

# **ACS Catalysis**

shows the effect of Sn content on the acid property of 1Au/xSn-DeAl-USY. The amount of acidic sites is listed in Table 2. There are few L and B acid sites in DeAl-USY sample due to dealumination. Additional IR bands at 1460 cm⁻¹ was observed obviously for 1Au/DeAl-USY and 1Au/1Sn-DeAl-USY. So, IR bands at 1460 cm⁻¹ can be ascribed to pyridine adsorption on the L acid sites created by the introduction of Au. Introduction of Au into DeAl-USY leads to the increase in the amount of both L and B acid sites by 29.5 and 8.9 µmol g⁻¹, respectively. When the Sn content increased from 0 wt% to 2 wt%, the intensity of band at 1453 cm⁻¹ became stronger, indicating the increase of L acid sites created by the formation of framework Sn. Meanwhile, the intensity of the band at 1460 cm⁻¹ became lower, implying that L acid sites created by the introduction of Au decreased. This might be caused by the competition of Sn. Total amount of L acid sites (according to the total area of bands at 1453 and 1460  $\text{cm}^{-1}$ ) increased dramatically from 43.2 to 83.5  $\mu$ mol g⁻¹ when the Sn content increased from 0 wt% to 2 wt%. Further increasing the Sn content to 4 wt%, the amount of L acid sites increased slightly to 97.5 umol g⁻¹. The introduced Sn can react with the internal Si-OH and the external Si-OH. When the Sn loading is low (< 2 wt%), introduced Sn mainly react with the internal Si-OH. With the increase of the Sn loading ( $\geq 2 \text{ wt\%}$ ), more and more introduced Sn would react with the external Si-OH around the mesopores, and these extra framework Sn species  $(SnO_r)$  are favorable for the dispersion of Au NPs.



**Figure 6.** FT-IR spectra of (a) DeAl-USY, (b) 1Au/DeAl-USY, (c) 1Au/1Sn-DeAl-USY, (d) 1Au/2Sn-DeAl-USY, (e) 1Au/3Sn-DeAl-USY and (f) 1Au/4Sn-DeAl-USY after pyridine adsorption and evacuation at 150 °C for 30 min.

Sample	Lewis acid sites (µmol g ⁻¹ )	Brönsted acid sites (µmol g ⁻¹ )	L/B ratio	
DeAl-USY	13.7	4.4	3.1	
1Au/DeAl-USY	43.2	13.3	3.3	
1Au/1Sn-DeAl-USY	53.3	9.2	5.8	
1Au/2Sn-DeAl-USY	83.5	24.9	3.4	
1Au/3Sn-DeAl-USY	85.2	24.8	3.4	
1Au/4Sn-DeAl-USY	97.5	27.0	3.6	

Table 2. Amount of Lewis and Brönsted Acid Sites of Au/Sn-USY with Different Sn Content.^a

^{*a*} Calculating by the equation given in literature.⁴² The integrated molar extinction coefficient of pyridine adsorbed to Lewis acid sites is  $1.42 \text{ cm} \mu \text{mol}^{-1}$ .

#### **ACS Catalysis**

FT-IR spectra of adsorbed CD₃CN over DeAl-USY, 3Sn-DeAl-USY, 1Au/DeAl-USY and 1Au/3Sn-DeAl-USY were also collected (Figure S6). According to the previous report, bands at 2310 cm⁻¹ and 2274 cm⁻¹ could be assigned to the interaction of the CN group with isolated framework Sn sites and silanols in Sn-substituted zeolites.^{28,42} As shown in Figure S6, no obvious band can be observed at 2310 cm⁻¹ in DeAl-USY (Figure S6a) and 1Au/DeAl-USY (Figure S6c) implying there is no framework Sn sites in these samples. L acid sites detected in DeAl-USY (13.7 µmol g⁻¹) and 1Au/DeAl-USY (43.2 µmol g⁻¹) by pyridine-FT-IR were caused by the residue Al species and the introduction of Au. For 3Sn-DeAl-USY and 1Au/3Sn-DeAl-USY, a band at 2310 cm⁻¹ was observed indicating the formation of framework Sn sites. We calculated the amount of framework Sn sites according to the FT-IR spectra of CD₃CN adsorption shown in Figure S6 by a reported method.⁴² The results are shown in Table S2. Introduction of Au reduces the framework Sn sites in 3Sn-DeAl-USY. This might be due to that Au NPs located at the surrounding of the mesopores hinder the interaction of the CN group with some framework Sn sites nearby. Meanwhile, some introduced Au might interact with the framework Sn leading to the shift of peak at 2310 cm⁻¹ to lower wave number region as shown in Figure S6d.

**Chemical States.** XPS was conducted to examine the chemical state of Au and Sn (Figure 7 and Figure S7). Figure 7 shows the Sn3d in 3Sn-DeAl-USY and 1Au/3Sn-DeAl-USY. In the Sn3d region, signals positioned at 487.2, 487.8, 495.6 and 496.2 eV can be observed for both 3Sn-DeAl-USY and 1Au/3Sn-DeAl-USY samples. Binding energy values of 487.8 and 496.2 eV were ascribed to  $3d_{5/2}$  and  $3d_{3/2}$  photoelectrons of tetrahedrally coordinated framework Sn species, 487.2 and 495.6 eV should be ascribed to  $3d_{5/2}$  and  $3d_{3/2}$  photoelectrons of extra framework Sn species which probably come mainly from the Sn sites at the surrounding of the

mesopores of USY mentioned above.^{43,44} Compared to 3Sn-DeAl-USY, two additional signals at lower binding energy (486.6 and 495.0 eV) were observed for 1Au/3Sn-DeAl-USY indicating the interaction of Au and Sn. When Au was introduced to 1Au/3Sn-DeAl-USY, Au NPs preferentially located at the extra framework Sn sites around the mesopores of USY and transferred some electrons into the extra framework SnO_x. Similar results have been reported in many previous literature.^{37,45} Au 4f in 1Au/DeAl-USY and 1Au/3Sn-DeAl-USY are shown in Figure S7. Because Au species are nanoparticles which including hundreds or thousands of Au atoms, electron transfer between Au NPs and extra framework SnO_x does not affect the electron structure of Au NPs significantly. Thus, similar peak profile of Au4f (87.3/83.6 eV) were obtained for 1Au/DeAl-USY and 1Au/3Sn-DeAl-USY.

To confirm the existence of positively charged Au further, FT-IR spectrum of 1Au/3Sn-DeAl-USY with CO adsorption was collected (Figure S8). According to the previous literature,⁴⁶⁻⁴⁸ the band at 2131 cm⁻¹ can be assigned to adsorption of CO on positively charged Au. This result proves the existence of positively charged Au in 1Au/3Sn-DeAl-USY.



Figure 7. XPS spectra of Sn3d in 3Sn-DeAl-USY and 1Au/3Sn-DeAl-USY.

#### **ACS Catalysis**

**Interaction between Au and Sn.** Based on the results of TEM, FT-IR and XPS discussed above, the interaction between Au and Sn in the sample can be confirmed. After dealumination, few L acid site can be observed in DeAI-USY sample. The formation of L acidic Sn sites in Sn-DeAI-USY is due to the tetrahedrally coordinated framework  $Sn^{4+}$  centers. When the Sn content (for example 3 wt% or 4 wt%) is high, many Sn species can react with the Si-OH around the mesopores to form extra framwork Sn sites (SnO_x). The electron on Au surface is transferable. In the loading process, Au NPs preferentially located at the extra framework SnO_x around the mesopores of USY and transferred some electrons into the SnO_x. This intereaction depressed the further growth and agregation of Au NPs in the loading process. Based on the results mentioned above, we proposed a scheme for the preparation of 1Au/3Sn-DeAI-USY catalyst (Scheme 2).



Scheme 2. Formation of 1Au/3Sn-DeAl-USY catalyst

**Catalytic Results.** Effects of the synthesis conditions of the catalysts, including pH of the Au gel, weight ratio of Au/PVA, Sn content and Au loadings, on the conversion of GLY to MLA

were investigated (Table 3). The pH value of Au gel affects the catalytic performance of the catalysts significantly (Table 3, entries 1 to 5). When the pH value of Au gel was 3, the prepared catalyst showed the best catalytic performance; 72% GLY conversion and 60% yield of MLA were obtained. Both lower and higher pH value led to the decrease of GLY conversion and MLA yield. For example, when the pH = 1, 66% GLY conversion and 49% MLA yield were obtained. GLY conversion and MLA yield were 51% and 34% at the pH of 7. As mentioned above (Figure 1), when the pH = 1 or 7, average particles size of Au became much larger than that at pH = 3, and this caused the lower catalytic activity of Au NPs. Conversion of GLY to MLA includes oxidation of GLY to 1,3-dihydroxyacetone (DHA) and/or glyceraldehyde (GA), and conversion of DHA and/or GA to MLA. Acid properties especially the L acid sites are important for the selective conversion of DHA and/or GA to MLA. The pH value also affects the mole ratio of L acid sites to B acid sites (L/B ratio) of the prepared catalyst (Table S1). L/B ratio might influence the selectivity of MLA. When pH = 1, L/B ratio of the sample (1.8) is much lower than that (4.6) synthesized at pH = 3. Although these two samples have comparable amount of L acid sites (71.4) and 67.1  $\mu$ mol g⁻¹), MLA selectivity for pH =1 (74%) is lower than that for pH = 3 (83%). The effect of Au/PVA weight ratio was also studied (Table 3, entries 6 to 10). In a broad range of 2 to 0.5, high GLY conversion (~80%) and high MLA yield (~70%) can be obtained. Much more PVA used in the catalyst synthesis would be unfavorable for the catalytic performance. GLY conversion and MLA yield were only 50% and 41% respectively when the Au/PVA weight ratio was 0.25. This is consistent with the TEM results (Figure 2) that size of Au NPs was larger when the Au/PVA weight ratio was 0.25. Furthermore, as shown in Table S1, all the L/B ratios of the samples with different Au/PVA weight ratio (4, 1 and 0.25) are larger than 3. The MLA selectivity for these samples is higher than 80%. It is known that Sn content affects the acid

Page 21 of 34

#### **ACS Catalysis**

property of the catalysts. The L/B ratios of the samples with 1 wt%, 2 wt%, 3 wt% and 4 wt% Sn content are all higher than 3. When these samples were applied as catalysts, 85% to 90% MLA selectivity was obtained except for 1Au/1Sn-DeAl-USY. For 1Au/1Sn-DeAl-USY, the MLA selectivity is 73%. The L/B ratio of 1Au/1Sn-DeAl-USY is 5.8, but the total amount of L acid sites is 53.3 µmol g⁻¹. Considering other L acid sites generated by the residue Al, the introduction of Au and the extra framework Sn, the amount of L acidic Sn sites might be not enough. The importance of L acidic Sn sites can also be proved by the catalytic result (19% MLA selectivity) of 1Au/DeAl-USY (L/B ratio = 3.3). Thus, both adequate amount of L acidic Sn sites and high L/B ratio are necessary to obtain a high MLA selectivity. Considering the effect of Sn on the oxidation performance of Au which determined the conversion of GLY, 3 wt% Sn content was proper for this study. Au is the active component for the oxidation of GLY to DHA and/or GA, so we also studied the effect of Au amount on GLY conversion. In the absence of Au, no MLA was detected (Table 3, entry 15). It means that no oxidation of GLY to DHA and/or GA occurred, although 10% GLY conversion was observed. For 0.5Au/3Sn-DeAl-USY, 1Au/3Sn-DeAl-USY and 2Au/3Sn-DeAl-USY, GLY conversions are 25%, 81% and 84%, and MLA yields are 22%, 69% and 68%. It can be seen that when the amount of Au increased from 0.5 wt% to 1 wt%, GLY conversion and MLA yield increased dramatically. However, further increasing the amount of Au to 2 wt%, similar GLY conversion and MLA yield were observed as that for 1Au/3Sn-DeAl-USY. So, the proper Au content is 1 wt% in this work. Thus, the optimized synthesis conditions of the catalysts including pH of the Au gel (pH = 3), weight ratio of Au/PVA (1), Sn content (3 wt%) and Au loadings (1 wt%) were obtained.

**Table 3**. Modification of the Synthesis Conditions of the Catalysts.^a

Entry	pН	Au/PVA weight	Sn content	Au loading	Conversion of	Yield of MLA
-	-	ratio	(wt%)	(wt%)	GLY (%)	(%)

-	1	1	4	3	1	66	49
	2	2	4	3	1	62	48
	3	3	4	3	1	72	60
	4	5	4	3	1	61	52
	5	7	4	3	1	51	34
	6	3	8	3	1	76	58
	7	3	2	3	1	81	68
	8	3	1	3	1	81	69
	9	3	0.5	3	1	81	67
	10	3	0.25	3	1	50	41
	11	3	1	0	1	48	9
	12	3	1	1	1	62	45
	13	3	1	2	1	54	46
	14	3	1	4	1	63	57
	15	-	-	3	0	10	0
	16	3	1	3	0.5	25	22
	17	3	1	3	2	84	68

 a  Reaction conditions: 0.2 g of catalyst, 1 mmol of GLY, 5 mL of methanol, 0.5 MPa O₂, 140 °C, 10 h.



**Figure 8.** Conversion of GLY to MLA catalyzed by various catalysts. Reaction conditions: 1 mmol of GLY, 5 mL of methanol, 0.2 g of catalyst, 0.5 MPa O₂, 140 °C, 10 h. ^{*a*} Physical mixture of 1Au/DeAl-USY (0.2 g) and 3Sn-DeAl-USY (0.2 g).

To get more information about the effect of Sn on the performance of 1Au/3Sn-DeAl-USY catalyst, reactions over various catalysts including H-USY, 3Sn-DeAl-USY, 1Au/H-USY, 1Au/DeAl-USY, 1Au/3Sn-DeAl-USY and physical mixture of 1Au/DeAl-USY and 3Sn-DeAl-USY were carried out (Figure 8). As anticipated, only 1% GLY was converted and no MLA was observed without catalyst. No MLA formed with H-USY or 3Sn-DeAl-USY as catalyst, although 15% or 10% conversion of GLY was obtained, respectively. In our previous report we proved that Sn-DeAl-USY is an excellent catalyst for the conversion of DHA to MLA.²⁸ Thus, it is confirmed that Au plays a crucial role for the oxidation of GLY to DHA and/or GA. When 1Au/H-USY and 1Au/DeAl-USY were used as catalysts, 45% and 48% GLY conversion were obtained. However, MLA yields were only 14% and 9% respectively. In contrast, 1Au/3Sn-DeAl-USY exhibited remarkable activity and selectivity for the conversion of GLY to MLA, and

81% GLY conversion with 69% MLA yield was obtained under the same reaction conditions as that for 1Au/H-USY and 1Au/DeAl-USY. Physical mixture of 1Au/DeAl-USY and 3Sn-DeAl-USY was also applied as catalyst for this reaction, 38% GLY conversion and 13% MLA yield were obtained. Thus, introduction of Sn promotes both the conversion of GLY and the selectivity of MLA. First, GLY conversion is determined by the catalytic activity of Au. The presence of Sn promoted the formation of small and uniform Au particles due to the interaction between Au and extra framework Sn. It is known that Au particle size is important for its catalytic activity. Secondly, introduction of Sn increased the L acid sites dramatically which are very beneficial for the conversion of DHA to MLA. So, introduction of Sn is critical for the high GLY conversion and MLA yield.



**Figure 9.** Catalytic performance of 1Au/3Sn-DeAl-USY at different reaction temperature. Reaction conditions: 1 mmol of GLY, 5 mL of methanol, 0.2 g of catalyst, 0.5 MPa O₂, 10 h.

Effects of the reaction conditions including reaction temperature, reaction time, substrate concentration, catalyst amount and initial O₂ pressure were also investigated. Figure 9 shows the catalytic performance of 1Au/3Sn-DeAl-USY at different reaction temperature. With the

 elevation of the reaction temperature from 100 to 140 °C, GLY conversion increased sharply from 12% to 81% and MLA yield increased from 12% to 69%. Further elevated the temperature to 180 °C, both GLY conversion and MLA yield increased gradually. When the reaction temperature was 160 °C or 180 °C, the same MLA yield was obtained (79%). However, the MLA selectivity obtained at 180 °C was lower than that at 160 °C. High reaction temperature would lead to the formation of over-oxidation products, such as methyl glycerate (MGA). This would be further discussed in the following section.



**Figure 10.** Time course of the reaction over 1Au/3Sn-DeAl-USY. Reaction conditions: 1 mmol of GLY, 5 mL of methanol, 0.2 g of catalyst, 0.5 MPa O₂, 160 °C.

To understand the reaction mechanism over Au/Sn-USY catalyst, time courses of the reactants and products in the presence of 1Au/3Sn-DeAl-USY are provided in Figure 10. 1Au/3Sn-DeAl-USY shows high activity, 80% GLY conversion can be obtained in 1 h. Further increasing the reaction time to 10 h, GLY conversion increased to 88%. Meanwhile, with the increase of time, MLA yield also increased sharply in first 1.5 h, and then increased slowly in the following reaction time. As a by-product, MGA was formed due to over-oxidation. 4% MGA yield was

obtained in first 1 h. Prolonged the reaction time to 10 h, 7% MGA yield achieved. When the reaction time is 10 h, 88% GLY conversion, 79% MLA yield and 7% MGA yield were obtained, and only 2% other unknown by-product formed. However, shorter reaction time caused lower MLA selectivity, and MGA yield was minor. This is a consecutive reaction including oxidation of GLY to intermediate species (DHA and/or GA) and further conversion to MLA. Because of the high reaction temperature, no DHA and/or GA was detected in the products even in the first 0.5 h. Thus, some other unknown intermediate species formed from DHA and/or GA in this process. Furthermore, the unknown intermediate species can also be converted to DHA and/or GA reversibly when prolonged the reaction time. To confirm this assumption, DHA was applied as reactant at 160 °C under 0.5 MPa O₂ without catalyst. After 0.5 h, 92% DHA conversion and 9% MGA yield were obtained. No other product was detected. This result implied that, under 160 °C, DHA was converted to the unknown intermediate species mentioned above which might be the condensation or polymerization products. This would be investigated in detail in the future work.

Effect of reactant concentration was studied (Figure S9). As anticipated, with the increase of GLY concentration, both the GLY conversion and the MLA yield decreased. Effect of catalyst amount was also investigated (Figure S10). Compared to 0.2 g of 1Au/3Sn-DeAl-USY, slight decrease of GLY conversion and MLA yield was observed when 0.1 g of catalyst was applied. Further decreasing the catalyst amount to 0.05 g, GLY conversion and MLA yield decreased significantly. Initial O₂ pressure has little impact on the catalytic performance of the catalyst (Figure S11).

The yield and the selectivity of MLA are higher than those described in previous report.²⁷ To the best of our knowledge, this is the first example of such a high MLA selectivity ( $\sim$ 90%) with a

high MLA yield (> 75%) for the conversion of GLY to MLA directly. TOF value of 1Au/3Sn-DeAl-USY was tested (Table 4). To avoid the mass transfer limitations, the test was carried out with a small amount of catalyst (0.05 g) and high stirring speed. After 0.5 h reaction time, the MLA yield was 12% which corresponds to a TOF of 94.6 mol_{MLA} mol_{Au}⁻¹ h⁻¹. For comparison, TOFs of 1Au/H-USY and 1Au/DeAl-USY were also tested. However, no MLA was detected at the same reaction conditions.

Entry	Sample	GLY conversion (%)	MLA yield (%)	TOF (mol _{MLA} mol _{Au} ⁻¹ h ⁻¹ )
1	1Au/H-USY	7.5	0	0
2	1Au/DeAl-USY	4.6	0	0
3	1Au/3Sn-DeAl-USY	14.4	12	94.6

Table 4. Catalytic Activity of 1Au/H-USY, 1Au/DeAl-USY and 1Au/3Sn-DeAl-USY^a

 a  Reaction conditions: 1 mmol of GLY, 5 mL of methanol, 0.05 g of catalyst, 0.5 MPa O₂, 160  o C, 0.5 h.

**Catalyst Stability.** Stability of the prepared catalyst was investigated. Figure 11 shows the XRD patterns of 1Au/3Sn-DeAl-USY before and after reaction. Crystalline structure of the zeolite did not alter significantly. So, the crystalline structure of the catalysts is stable. Furthermore, GLY conversion was 26% after 1 h under 160 °C when the 1Au/3Sn-DeAl-USY was used as catalyst. Then, the catalyst was removed from the reaction by hot-filtration. After reaction for another 1 h, the conversion of glycerol did not increase dramatically (27%). Thus, this reaction is heterogeneous and there is no leaching of Au NPs in the reaction.



Figure 11. XRD patterns of 1Au/3Sn-DeAl-USY (a) before and (b) after the reaction.

We further examined the recyclability of 1Au/3Sn-DeAl-USY (Figure 12). 77% MLA yield with 88% GLY conversion was obtained in the second run, which is comparable to the first run (79% MLA yield and 88% GLY conversion). However, for the third run, 66% MLA yield and 81% GLY conversion were given. Figure 13 shows TEM images of 1Au/3Sn-DeAl-USY before and after reaction. It can be seen that the average size of Au NPs increased slightly after reaction. So, the decrease of GLY conversion might be caused by the aggregation of Au NPs and/or the exfoliation of smaller Au NPs from the support. To explain the decrease of the MLA selectivity, the Sn content in the reaction solution after reaction was tested by ICP, only 0.0037 wt% Sn leaching was observed. Furthermore, the acid properties of the used catalyst after 2 runs were measured (Figures S12 and S13 and Table S3). After reaction, the amount of L acid sites decreased, especially the framework Sn sites. This might be caused by the strong chemisorption of chemicals on the framework Sn sites, the active sites for the conversion of DHA to MLA. So, the recyclability of the catalyst would be further improved in the future study.



**Figure 12.** Reuse test of 1Au/3Sn-DeAl-USY in the conversion of GLY to MLA. Reaction conditions: 1 mmol of GLY, 5 mL of methanol, 0.2 g of catalyst, 0.5 MPa O₂, 160 °C, 10 h.



Figure 13. TEM images of 1Au/3Sn-DeAl-USY (a) before and (b) after the reaction.

# CONCLUSIONS

In summary, we developed hierarchical bifunctional catalysts of Sn-USY supported Au nanoparticles for one-pot conversion of glycerol to methyl lactate. High methyl lactate yield can be obtained with a high selectivity (~90%). Interaction between Au and extra framework  $SnO_x$  around the mesopores of DeAl-USY promotes the dispersion of Au particles (smaller and much more uniform), which is important for the oxidation of glycerol to 1,3-dihydroxyacetone and

glyceraldehydes. On the other hand, the introduction of Sn modified the acid property of the catalyst, which is critical for the selective conversion of 1,3-dihydroxyacetone and glyceraldehydes to methyl lactate.

# ASSOCIATED CONTENT

Supporting Information. Additional XRD patterns, nitrogen sorption isotherms, TEM image, pyridine-FT-IR, CD₃CN-FT-IR, CO-FT-IR, XPS and related activity tests results.

# **AUTHOR INFORMATION**

* Corresponding Author Tel.: +86 371 67781780; E-mail addresses: <u>vangxiaomei@zzu.edu.cn</u>

#### ACKNOWLEDGEMENTS

We are grateful to the NSFC-Henan Joint Foundation (U1304209), the Key Scientific Research Projects for University in Henan Province (16A530009) and the Outstanding Young Talent Research Fund of Zhengzhou University (1521316006) for the financial supports.

# REFERENCES

- (1) Zheng, Y.; Chen, X.; Shen, Y. Chem. Rev. 2008, 108, 5253-5277.
- (2) Sharninghausen, L. S.; Campos, J.; Manas, M. G.; Crabtree, R. H. Nat. Commun. 2014, 5, 5084
- (3) Wołosiak-Hnat, A.; Milchert, E.; Lewandowski, G. Org. Process Res. Dev. 2013, 17, 701– 713.
- (4) Katryniok, B.; Paul, S.; Dumeignil, S. ACS Catal. 2013, 3, 1819–1834.
- (5) Morales, M.; Dapsens, P. Y.; Giovinazzo, I.; Witte, J.; Mondelli, C.; Papadokonstantakis, S.;

Hungerbühler, K.; Pérez-Ramírez, J. Energy Environ. Sci. 2015, 8, 558–567.

1
2
3
4
т 5
5
6
7
8
9
10
11
12
12
13
14
15
16
17
18
10
20
20
21
22
23
24
25
26
20
21
28
29
30
31
32
33
24
34
35
36
37
38
39
40
<u></u>
41
42
43
44
45
46
47
18
40
49
50
51
52
53
54
55
22
56
57
58
59
~~

(6) Rastegari, H.; Ghaziaskar, H. S.; Yalpani, M. Ind. Eng. Chem. Res. 2015, 54, 3279-3284.

- (7) Mäki-Arvela, P.; Simakova, I. L.; Salmi, T.; Murzin, D. Yu. Chem. Rev. 2014, 114, 1909– 1971.
- (8) Huang, T.; Miura, M.; Nobukawa, S.; Yamaguchi, M. *Biomacromolecules* **2015**, *16*, 1660–1666.
- (9) Dusselier, M.; Wouwe, P. V.; Dewaele, A.; Makshina, E.; Sels, B. F. *Energy Environ. Sci.* **2013**, *6*, 1415–1442.
- (10) Yin, H.; Zhang, C.; Yin, H.; Gao, D.; Shen, L.; Wang, A. Chem. Eng. J. 2016, 288, 332–343.
- (11) Li, Y.; Nielsen, M.; Li, B.; Dixneuf, P. H.; Junge, H.; Beller, M. Green Chem. 2015, 17, 193–198.
- (12) Sharninghausen, L. S.; Mercado, B. Q.; Crabtree, R. H.; Hazari, N. *Chem. Commun.* 2015, *51*, 16201–16204.
- (13) Lu, Z.; Demianets, I.; Hamze, R.; Terrile, N. J.; Williams, T. J. ACS Catal. 2016, 6, 2014–2017.
- (14) Shen, Y.; Zhang, S.; Li, H.; Ren, Y.; Liu, H. Chem. Eur. J. 2010, 16, 7368-7371.
- (15) Xu, J.; Zhang, H.; Zhao, Y.; Yu, B.; Chen, S.; Li, Y.; Hao, L.; Liu, Z. Green Chem. 2013, 15, 1520–1525.
- (16) Lakshmanan, P.; Upare, P. P.; Le, N.-T.; Hwang, Y. K.; Hwang, D. W.; Lee, U-H.; Kim, H.
  R.; Chang, J.-S. *Appl. Catal.*, A 2013, 468, 260–268.
- (17) Purushothaman, R. K. P.; van Haveren, J.; van Es, D. S.; Meeldijk, J. D.; Heeres, H. J. *Appl. Catal., B* **2014**, *147*, 92–100.
- (18) Cho, H. J.; Chang, C.-C.; Fan, W. Green Chem. 2014, 16, 3428-3433.

- (19) Ftouni, J.; Villandier, N.; Auneau, F.; Besson, M.; Djakovitch, L.; Pinel, C. *Catal. Today* **2015**, *257*, 267–273.
- (20) Oberhauser, W.; Evangelisti, C.; Tiozzo, C.; Vizza, F.; Psaro, R. ACS Catal. 2016, 6, 1671– 1674.
- (21) Komanoya, T.; Suzuki, A.; Nakajima, K.; Kitano, M.; Kamata, K.; Hara, M. *ChemCatChem***2016**, *8*, 1094–1099.
- (22) Marques, F. L.; Oliveira, A. C.; Filho, J. M.; Rodríguez-Castellón, E.; Cavalcante Jr., C. L.;Vieira, R. S. *Fuel Process. Technol.* 2015, *138*, 228–235.
- (23) Roy, D.; Subramaniam, B.; Chaudhari, R. V. ACS Catal. 2011, 1, 548–551.
- (24) Yang, G.-Y.; Ke, Y.-H.; Ren, H.-F.; Liu, C.-L.; Yang, R.-Z.; Dong, W.-S. *Chem. Eng. J.* **2016**, *283*, 759–767.
- (25) Su, C.-Y.; Yu, C.-C.; Chien, I-L.; Ward, J. D. Ind. Eng. Chem. Res. 2015, 54, 6932-6940.

(26) Ren, S.; Ye, X. P.; Ayers, P. D. RSC Adv. 2015, 5, 53230–53239.

- (27) Purushothaman, R. K. P.; van Haveren, J.; Melián- Cabrera, I.; van Eck, E. R. H.; Heeres, H. J. *ChemSusChem* 2014, *7*, 1140–1147.
- (28) Yang, X.; Wu, L.; Wang, Z.; Bian, J.; Lu, T.; Zhou, L.; Chen, C.; Xu, J. *Catal. Sci. Technol.* **2016**, *6*, 1757–1763.
- (29) Román-Leshkov, Y.; Davis, M. E. ACS Catal. 2011, 1, 1566–1580.
- (30) Tolborg, S.; Meier, S.; Sádaba, I.; Elliot, S. G.; Kristensen, S. K.; Saravanamurugan, S.; Riisager, A.; Fristrup, P.; Skrydstrup, T.; Taarning, E. *Green Chem.* **2016**, *18*, 3360–3369.
- (31) Yang, X.; Bian, J.; Huang, J.; Xin, W.; Lu, T.; Chen, C.; Su, Y.; Zhou, L.; Wang, F.; Xu, J. *Green Chem.* **2017**, *19*, 692–701.
- (32) Liu, S.-S.; Sun, K.-Q.; Xu, B.-Q. ACS Catal. 2014, 4, 2226–2230.

#### **ACS Catalysis**

- (33) Zhai, C.; Liu, X.; Chen, X.; Li, L.; Sun, F.; Ma, H. J. Inorg. Organomet. Polym. 2015, 25, 687–693.
- (34) Briñas, R. P.; Hu, M.; Qian, L.; Lymar, E. S.; Hainfeld, J. F. J. Am. Chem. Soc. 2008, 130, 975–982.
- (35) Shimmin, R. G.; Schoch, A. B.; Braun, P. V. Langmuir 2004, 20, 5613–5620.
- (36) Dimitratos, N.; Villa, A.; Prati, L.; Hammond, C.; Chan-Thaw, C. E.; Cookson, J.; Bishop,
  P. T. *Appl. Catal.*, A 2016, *514*, 267–275.
- (37) Dong, Y.; Zhang, H.; Li, W.; Sun, M.; Guo, C.; Zhang, J. J. Ind. Eng. Chem. 2016, 35, 177– 184.
- (38) Zhu, Z.; Xu, H.; Jiang, J.; Liu, X.; Ding, J.; Wu, P. Appl. Catal., A 2016, 519, 155-164.
- (39) Li, Y.; Armor, J. N. Appl. Catal., A 1999, 183, 107–120.
- (40) Verboekend, D.; Keller, T. C.; Mitchell, S.; Perez-Ramirez, J. Adv. Funct. Mater. 2013, 23, 1923–1934.
- (41) Daniell, W.; Topsøe, N.-Y.; Knözinger, H. Langmuir 2001, 17, 6233-6239.
- (42) Harris, J. W.; Cordon, M. J.; Di Iorio, J. R.; Vega-Vila, J. C.; Ribeiro, F. H.; Gounder, R. J. *Catal.* **2016**, *335*, 141–154.
- (43) Tang, B.; Dai, W.; Wu, G.; Guan, N.; Li, L.; Hunger, M. ACS Catal. 2014, 4, 2801–2810.
- (44) Mäki-Arvela, P.; Kumar, N.; Diáz, S. F.; Aho, A.; Tenho, M.; Salonen, J.; Leino, A.-R.;

Kordás, K.; Laukkanen, P.; Dahl, J.; Sinev, I.; Salmi, T.; Murzin, D. Y. J. Mol. Catal. A: Chem. **2013**, *366*, 228–237.

(45) Ishimoto, T.; Hamatake, Y.; Kazuno, H.; Kishida, T.; Koyama, M. Appl. Surf. Sci. 2015, 324, 76–81.

(46) Abad, A.; Concepción, P.; Corma, A.; García, H. Angew. Chem., Int. Ed. 2005, 44, 4066–4069.

- (47) Guzman, J.; Carrettin, S.; Corma, A. J. Am. Chem. Soc. 2005, 127, 3286-3287.
- (48) Carrasquillo-Flores, R.; Ro, I.; Kumbhalkar, M. D.; Burt, S.; Carrero, C. A.; Alba-Rubio, A.
- C.; Miller, J. T.; Hermans, I.; Huber, G. W.; Dumesic, J. A. J. Am. Chem. Soc. 2015, 137, 10317–10325.

# TOC

