Selective Hydrogenation



# Nitrogen-Doped Carbon Nanotube Confined Co–N<sub>x</sub> Sites for Selective Hydrogenation of Biomass-Derived Compounds

Wanbing Gong, Yue Lin, Chun Chen, Mohammad Al-Mamun, Hai-Sheng Lu, Guozhong Wang, Haimin Zhang,\* and Huijun Zhao\*

Biomass is the most abundant renewable resource on earth and developing high-performance nonprecious selective hydrogenation (SH) catalysts will enable the use of biomass to replace rapidly diminishing fossil resources. This work utilizes ZIF-67-derived nitrogen-doped carbon nanotubes to confine Co nanoparticles (NPs) with Co– $N_x$  active sites as a high-performance SH catalyst. The confined Co NPs with Co– $N_x$  exhibit excellent catalytic activity, selectivity, and stability toward a wide range of biomass-derived compounds. Such active sites can selectively hydrogenate aldehyde, ketone, carboxyl, and nitro groups of biomass-derived compounds into value-added fine chemicals with 100% selectivity. The reported approach could be adopted to create other forms of catalytically active sites from other nonprecious metals.

Biomass represents the most abundant renewable resource on earth. With suitable catalysts, biomass can be used to replace the rapidly diminishing fossil resource for production of fuels and chemicals.<sup>[1]</sup> The heterogeneous catalytic selective hydrogenation (SH) has been one of the most widely used approaches in fine chemical production. It is especially important for conversion of biomass-derived organic molecules into value-added chemicals due to their rich oxygen contents.<sup>[1c]</sup> Till now, the industrial hydrogenation catalysts are almost exclusively made of precious metals such as Pt, Au, Pd,

University of Science and Technology of China Hefei 230026, P. R. China

Dr. M. Al-Mamun, Prof. H. Zhao Centre for Clean Environment and Energy Griffith University

Gold Coast Campus, Southport, Queensland 4222, Australia

D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201808341.

#### DOI: 10.1002/adma.201808341

Ru, etc.<sup>[2]</sup> The development of cheap and earth-abundant material-based catalysts is therefore urgently needed to sustain the future demands. This is, however, a challenging task as nonprecious materials normally possess inferior catalytic activity, selectivity, and stability.<sup>[1a,3]</sup> Recently reported evidences indicate that introducing new types of catalytic active sites can empower nonprecious materials with superior catalytic activity for SH of biomass-derived compounds.<sup>[4]</sup> Among them, Wu's group reported the use of synergistic interactions between Cu and Ni in alloy catalysts to achieve SH of furfural (FAL).<sup>[4b]</sup> Moon et al. showed that creating novel threefold hollow Ni and neighboring

P sites can empower  $\rm Ni_2P/SiO_2$  with high catalytic activity toward guaiacol hydrodeoxygenation.  $^{[4c]}$  In addition, the MoS\_2 monolayer sheets decorated with isolated Co atoms that covalently bond to sulfur vacancies exhibit high activity, selectivity, and stability for SH of 4-methylphenol.  $^{[4d]}$ 

The metal–organic frameworks (MOFs) have been used as sacrificial templates to fabricate nonprecious catalysts with highly dispersed active sites. Li's group reviewed various MOF-derived carbon-based nanostructured catalysts for different reactions.<sup>[5]</sup> Recently, the thermally reduced MOFs' node ions were used as growth catalyst to convert MOFs into N-doped carbon nanotubes (N-CNTs).<sup>[6]</sup> Mai's<sup>[6a]</sup> and Wang's groups<sup>[6b]</sup> have, respectively, reported the use of MOF-derived N-CNTs as high-performance electrocatalysts for oxygen reduction and evolution reactions. They attributed the excellent electrocatalytic properties to the synergistic effects of chemical compositions (appropriate N doping) and multilevel hollow structures.<sup>[6a,b]</sup> However, the catalytic potentials of N-CNT confined metal nanoparticles (NPs) have not been explored.

Herein, we report, for the first time, the use of N-CNT confined Co NPs (Co@N-CNTs) with Co– $N_x$  active sites derived from ZIF-67 as highly active and stable catalyst for SH of various biomass-derived organic compounds. Such type of active sites can selectively hydrogenate aldehyde, ketone, carboxyl, and nitro groups of biomass-derived compounds into value-added fine chemicals at room temperature. The Co@N-CNTs were synthesized via a facile two-step thermal treatment of ZIF-67 (Figure S1, Supporting Information). The synthesized ZIF-67 exhibits uniform dodecahedral morphology, high crystallinity, and specific surface area with microporous structures

Dr. W. Gong, Dr. C. Chen, Dr. H.-S. Lu, Prof. G. Wang, Prof. H. Zhang, Prof. H. Zhao Key Laboratory of Materials Physics Centre for Environmental and Energy Nanomaterials Anhui Key Laboratory of Nanomaterials and Nanotechnology CAS Center for Excellence in Nanoscience Institute of Solid State Physics Chinese Academy of Sciences Hefei 230031, P. R. China E-mail: zhanghm@issp.ac.cn; h.zhao@griffith.edu.au Dr. Y. Lin Hefei National Laboratory for Physical Sciences at the Microscale



ADVANCED MATERIALS

(Figure S2 and Table S1, Supporting Information).<sup>[6b]</sup> The first step involving low-temperature pyrolysis (440 °C) leads to the formation of Co@N-CNTs (denoted as Co-440) with an average Co particle size of 6.8 nm, while the dodecahedral structure of ZIF-67 is well preserved (Figure S3, Supporting Information). The obtained Co-440 is then subjected to the second step involving high-temperature treatment at 900 °C. In this work, the yield of Co-900 is ≈55%. The optimization experimental results indicate that a 10 vol% H<sub>2</sub>/Ar atmosphere can provide a balanced rate of reduction for Co ion and 2-methylimidazole ligand to achieve complete conversion of ZIF-67 to N-CNTs. The typical field emission scanning electron microscopy (FESEM) images of the resultant product (denoted as Co-900) reveal that ZIF-67 has been fully transformed into N-CNTs with wellretained size and shape of ZIF-67 (Figure 1a). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images confirm uniformly distributed Co NPs throughout the entire assembled structure (Figure 1b). The high-resolution transmission electron microscopy (HRTEM) image indicates that all Co NPs are confined on the tips of N-CNTs with an average size of 10.4 nm (Figure 1c). Figure 1d shows that N-CNTs possess a lattice fringe of ≈0.36 nm, assignable to the plane of C (002). It also shows that the confined Co NPs have a lattice distance of 0.204 nm, corresponding to the (111) planes of metallic Co. These results are consistent with the X-ray diffraction (XRD) and Raman spectra data (Figures S4 and S5, Supporting Information). The X-ray photoelectron spectroscopy (XPS) spectra of Co-440 show the signature characteristics of cobalt oxide species ( $CoO_x$ , 780.3 eV), while for Co-900, the high-resolution Co  $2p_{3/2}$  peaks appearing at the binding energies of 778.7 and 780.7 eV can be, respectively, attributed to Co<sup>0</sup> and N-coordinated Co (Co-N<sub>x</sub>) (Figure 1e).<sup>[6d]</sup> XPS N 1S spectra infer that the conversion of pyridinic-N (398.5 eV) and pyrrolic-N (400.1 eV) to graphitic-N (401.1 eV) has occurred during the second step involving high-temperature treatment (Figure 1f; Table S1, Supporting Information), which could be an indication that the graphitic-N is favorable for the formation of  $Co-N_x$ .<sup>[7]</sup> To further confirm the active site structure, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed. The obtained Co K-edge absorption edge of Co-900 is almost identical to that of Co<sup>0</sup> (Figure 1g). Importantly, the EXAFS spectra (Figure 1h) confirm the existence of Co-N (1.60 Å) in Co-900, corresponding to the tetrahedrally coordinated Co in a sodalite crystal form.<sup>[8]</sup> Besides, the Brunauer-Emmett–Teller surface areas are 267 and 157  $m^2 g^{-1}$  for Co-440 and Co-900, respectively (Figure S6 and Table S1, Supporting Information). Also, similar Co contents in Co-440 (45.1 wt%) and Co-900 (42.5 wt%) are confirmed by the inductively coupled plasma (ICP) analysis, suggesting that nearly 100% Co node ions in ZIF-67 have been converted to Co NPs (Table S1, Supporting Information).

The biomass-derived aldehydes can be converted into valueadded alcohols as important intermediates in chemical, pharmaceutical, and agrochemical industries.<sup>[1a,b]</sup> In this work, SH of FAL to furfuryl alcohol (FOL) in liquid phase was chosen as a model reaction to evaluate the catalytic performance of Co-900 for aldehyde compounds. As can be seen from **Figure 2**, 100% FOL selectivity can be achieved from all reaction conditions

employed in this work and no by-products such as tetrahydrofurfural, tetrahydrofurfuryl alcohol, furan, or tetrahydrofuran are detectable. FAL conversion efficiency is dependent on H<sub>2</sub> pressure (Figure 2a). An increase in H<sub>2</sub> pressure leads to an increased FAL conversion and 100% conversion can be achieved under 2 MPa H<sub>2</sub> pressure. The strong H<sub>2</sub> pressure influence observed at lower pressure range (e.g., <1 MPa) indicates that Co-900 has high capacity to dissolve hydrogen at lower temperatures. When other reaction conditions are fixed, an increase in the reaction time leads to an increased FAL conversion (Figure 2b) and 100% conversion can be achieved after 5 h. The effect of solvent was investigated (Figure 2c). FAL conversion efficiencies of 89.8%, 74.2%, 65.3%, and 100% can be, respectively, achieved from methanol, ethanol, 2-propanol, and water solvents. Different 2-propanol-water mixture solvents were also evaluated. An increased water portion in the solvent mixture results in an increase in FAL conversion. Obviously, water is the best-performing solvent among others. Such increased trends in FAL conversion efficiencies indicate that SH of FAL favors solvent with high polarity. The reusability was examined (Figure 2d). Well-retained catalytic activity of Co-900 is confirmed by the catalytic performance obtained from five consecutive runs, indicating a superior stability of Co-900. The Co concentration in the reaction solution was determined using ICP spectroscopy to confirm whether any Co leaching occurred. No detectable Co in the reaction solution can be found, suggesting that the leached Co in the reaction solution is below the ICP detection limit. TEM images (Figure S7a,b, Supporting Information), XRD patterns (Figure S8, Supporting Information), and XPS spectra (Figure S9, Supporting Information) of Co-900 before and after five consecutive runs reveal no noticeable change in morphology, crystal structure, Co NP size (Figure S7c, Supporting Information), and, more importantly, Co-N bonding state, further confirming the superior stability of Co-900. To the best of our knowledge, the demonstrated FAL conversion performance by Co-900 under mild reaction conditions surpasses many reported precious metal-based catalysts.<sup>[9]</sup>

The SH catalytic performances of Co-900 under room temperature (25 °C) to convert FAL and other biomass-derived aldehydes, including benzaldehyde, hydroxymethylfurfural, vanillin, and cinnamaldehyde, into alcohols were also investigated (entries 1–5, **Table 1**). Co-900 exhibits high catalytic activity with 100% conversion efficiency toward all aldehydes investigated. An essentially 100% selectivity can be achieved for FAL, benzaldehyde, and cinnamaldehyde, while 86.1% and 92.1% are achieved for hydroxymethylfurfural and vanillin, respectively.

The room-temperature SH performances of Co-900 for biomass-derived ketone-, carboxyl-, and nitro-containing compounds were systematically investigated (**Figure 3** and Table 1, entries 6–14). Table 1 (entries 6–8) shows the SH conversion of biomass-derived ketone compounds into alcohols, a class of important intermediates for chemical and pharmaceutical synthesis.<sup>[1a]</sup> It was found that 100% selectivity can be achieved for all ketones investigated. For cyclohexanone, the conversion efficiency linearly increased to 95.7% within 11 h of reaction and further increased to 96.3% when the reaction proceeded to 12 h (Figure 3a). Interestingly, the selectivity of other







**Figure 1.** a–d) Typical SEM images (inset: high-magnification image), HAADF-STEM images (inset: high-magnification image), and HRTEM images (inset: Co NP size distribution) of Co-900. e, f) Co 2p and N 1s spectra of Co-440 and Co-900. g) Co K-edge XANES spectra of Co foil, Co-440, and Co-900. h) Comparative k3-weighted x(k)-function of EXAFS spectra of Co-440 and Co-900.

ketone compounds (e.g., cyclopentanone and acetophenone) exhibits similar reaction time independency characteristics. Cyclopentanone and acetophenone can achieved 87.9% and

100% conversion efficiencies within 16 and 12 h, respectively (entries 7 and 8, Table 1). Reusability values of Co-900 for SH of cyclohexanone are given in Figure 3b. No performance decay







**Figure 2.** a) Effect of  $H_2$  pressure (solvent: water; reaction time: 6 h), b) reaction time (solvent: water;  $H_2$  pressure: 2 MPa), and c) solvent (reaction time: 6 h;  $H_2$  pressure: 2 MPa; 1: methanol; 2: ethanol; 3: 2-propanol; 4: water; 5: 2-propanol/water = 7/3; 6: 2-propanol/water = 5/5; 7: 2-propanol/water = 3/7) on conversion efficiency and selectivity. d) Reusability of Co-900 (solvent: water;  $H_2$  pressure: 2 MPa; reaction time: 0.5 h). All reactions were carried out using 20 mg Co-900 + 1.0 mmol FAL in 10 mL solvent at 60 °C.

was observed after five consecutive runs, indicating the superior stability of Co-900 toward SH of ketone compounds.

Levulinic acid (LA) is a typical biomass-derived carboxylic acid and its hydrogenated product,  $\gamma$ -valerolactone, has been widely used as biofuel and food additive.<sup>[1]</sup> The catalytic performance of Co-900 for SH of LA to produce  $\gamma$ -valerolactone is summarized in Table 1 (entry 9). As shown in Figure 3c, the conversion of LA rapidly increased with reaction time up to 20 h and can achieve 82.8% conversion efficiency at 24 h. Meanwhile, the selectivity toward  $\gamma$ -valerolactone is almost independent of reaction time, changing slightly from 92.2% at 1 h to 96.1% at 24 h. No noticeable performance decay was observed after five consecutive runs, indicating the superior stability of Co-900 (Figure 3d) toward SH of LA.

The SH conversion of nitroarenes to aromatic amines is another class of important hydrogenation reactions to produce fine and bulk chemicals for a wide range of industrial and pharmaceutical applications.<sup>[2b,c]</sup> The SH performances of Co-900 to convert nitroarenes to corresponding aromatic amines are summarized in Table 1 (entries 10–14). For nitrobenzene, an increase in reaction time up to 4 h leads to a rapidly increased conversion efficiency to 96.1% and 100% conversion can be achieved at 6 h (Figure 3e). In contrast, a 100% selectivity can be retained throughout the entire reaction period. Other nitroarenes exhibit similar behaviors and can readily achieve 100% selectivity under the reaction conditions employed (entries 11–14, Table 1). For nitroarenes containing -OHand  $-CH_3$ , such as *p*-nitrophenol and *p*-nitrotoluene, 100% conversion can be obtained within 6 h (entries 11 and 12, Table 1). Impressively, halogen-substituted nitroarenes such as *p*-nitrochlorobenzene and *p*-nitrobromobenzene can be 100% converted to corresponding haloaromatic amines within 12 h and without any dehalogenation-type by-products (entries 13 and 14, Table 1). Again, superior stability of Co-900 is confirmed by the results obtained from seven consecutive reuse cycles (Figure 3f).

The catalytic performances described above, especially the room-temperature performances, demonstrate the superiority of Co-900 as an SH catalyst. The achieved SH performance by Co-900 surpasses many state-of-the-art precious and nonprecious metal-based heterogeneous catalysts (Tables S2 and S3, Supporting Information). Remarkably, Co-900 possesses superior SH catalytic activities toward a wide spectrum of biomass-derived aldehyde, ketone, carboxyl, and nitro compounds.

A series of purposely designed experiments were performed to identify possible catalytic active sites responsible for high SH performance. FAL, cyclohexanone, LA, and nitrobenzene were selected to represent aldehyde, ketone, carboxyl, and nitro compounds. Experimental results are summarized in Table S4 in the Supporting Information. It can be seen that ZIF-67 is catalytically inactive for all listed compounds in the table. Both Co-440 and Co-900 exhibit hydrogenation catalytic activities for all listed compounds. However, Co-900 displays much higher catalytic activities than that of Co-440 for all cases investigated. In addition, the turnover frequency (TOF) and activation energy of both catalysts for SH of FAL were determined (Table S5 and Figure S10, Supporting Information). The Co-900 possesses higher TOF (30.7  $h^{-1}$  at

# ADVANCED SCIENCE NEWS

www.ad	vanced	sciencer	iews.com	

Table 1. Room-temperature	SH of various	substrates b	y Co-900. <sup>a)</sup>
---------------------------	---------------	--------------	-------------------------



www.advmat.de

Entry	Group	Substrate	Product	Time [h]	Conversion [%] <sup>b)</sup>	Selectivity [%] <sup>b)</sup>
1	R-CHO	0	О	12	100	100
2		0	ОН	6	100	100
3		ОСОСОН	но он	14	100	86.1
4		он он	CH <sub>2</sub> OH	12	100	92.1
5			ОН	14	100	100
6	R1-(C=O)-R2		ОН	12	96.3	100
7			ОН	16	87.9	100
8			ОН	12	100	100
9	R–COOH	ОН		24	82.8	96.1
10	R-NO <sub>2</sub>	NO <sub>2</sub>	NH <sub>2</sub>	6	100	100
11		OH NO2	OH NH2	6	100	100
12		CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> NH <sub>2</sub>	6	100	100
13			CI NH2	12	100	100
14		Br NO <sub>2</sub>	Br NH <sub>2</sub>	12	100	100

a) Reaction conditions: 20 mg Co-900 + 1 mmol substrate in 10 mL water under 2 MPa H2 at room temperature (25 °C); b) Determined by GC-MS.

333 K) and lower activation energy (68.2 kJ mol<sup>-1</sup>) than those of Co-440 (2.58 h<sup>-1</sup> at 333 K, 81.8 kJ mol<sup>-1</sup>). As confirmed by the obtained results (Figure 1; Figures S3–S6 and Table S1, Supporting Information), both catalysts possess almost identical structural, morphological, and compositional characteristics. They contain essentially same percentage of Co contents that exist in the same nanoparticle form and confined in the same way on the tips of N-CNTs (Figure 1; Figure S3, Supporting Information). The only noticeable difference between the two catalysts is that Co-900 contains Co–N<sub>xy</sub> while Co-440 does not (Figure 1e–h). Two  $Co-N_x$ -free Co NP catalysts were synthesized to further confirm that  $Co-N_x$  is responsible for the enhanced SH performance. One contains Co NPs confined by CNTs derived from Co-BTC, a nitrogen-free MOF (Co-900-B; Figure S11, Supporting Information), and another directly embedded Co NPs in active carbon (AC) supporting substrate (Co/AC; Figure S12, Supporting Information). As shown in Table S4 in the Supporting Information, when compared to Co-900, both Co-900-B and Co/AC display inferior SH catalytic activity toward all functional







Figure 3. a,c,e) Influence of reaction time over the Co-900 catalyst. Reaction conditions: 20 mg Co-900 + 1 mmol substrate in 10 mL water under 2 MPa  $H_2$  at room temperature. b,d,f) Reusability of Co-900 catalyst. Reaction conditions: reaction time = 3, 8, and 1 h, respectively.

groups investigated. These results confirm again that the  $Co-N_x$  plays a significant role for the enhanced SH performance by Co-900. The improved activity of  $Co-N_x$  in other catalytic reactions has recently been confirmed by a number of eminent research groups.<sup>[10]</sup> It is therefore reasonable to claim that the superior SH catalytic activity of Co-900 results from  $Co-N_x$ .

In summary, we have successfully utilized the ZIF-67-derived N-doped carbon nanotubes to confine Co NPs with Co–N<sub>x</sub> active sites. We have also demonstrated that the resultant catalyst possesses excellent catalytic activity, selectivity, and stability toward SH of aldehyde, ketone, carboxyl, and nitro functional groups of biomass-derived compounds. Such a wide spectrum SH catalytic activity could be further extended to transform other biomass-derived compound into value-added chemicals. The reported synthetic approach could be applicable to create other forms of catalytic active structures from other nonprecious metals.

#### **Experimental Section**

Chemicals: 2-Methylimidazole, 1,3,5-benzenetricarboxylic acid, and activated carbon were purchased from Aladdin Reagent Company. Methanol, ethanol, 2-propanol, cobalt nitrate hexahydrate ( $Co(NO_3)_2$ · $6H_2O$ ), and cobalt acetate tetrahydrate ( $C_4H_6CoO_4$ · $4H_2O$ ) were purchased from Sinopharm Chemical Reagent Co. Ltd. Unless otherwise stated, all other solvents and chemicals were of commercially available analytical grade and used without any further treatment.

Synthesis of ZIF-67 Precursors: ZIF-67 precursors were synthesized according to several previous reports with some modification.<sup>[6a,b]</sup> In a typical synthesis, 2-methylimidazole (1.97 g) was dissolved in a mixed solution of 20 mL methanol and 20 mL ethanol.  $Co(NO_3)_2$ ·6H<sub>2</sub>O (1.746 g) was dissolved in another mixed solution of 20 mL methanol and 20 mL ethanol. The above two solutions were then mixed under continuous stirring for 10 s, and the final solution was kept for 20 h at room temperature. The purple precipitate was collected by centrifugation, washed in ethanol several times, and dried at 70 °C in air for 12 h.

Synthesis of ZIF-Derived Cobalt Catalysts: The ZIF-derived cobalt catalysts were synthesized according to the literature with some

www.advancedsciencenews.com



modification.<sup>[6a,b]</sup> First, the 1.0 g ZIF-67 particles were mounted in a ceramic boat and heated to 440 °C with the heating ramp of 2 °C min<sup>-1</sup> and held for 8 h under continuous flow of 10 vol%  $H_2/Ar$ . The obtained sample was denoted as Co-440. Afterward, the temperature in the furnace was further raised to 900 °C at a heating rate of 2 °C min<sup>-1</sup> and maintained for 2 h in a tube furnace. After the system cooled down naturally, a 0.55 g of product (55% yield) was obtained (denoted as Co-900).

*Synthesis of BTC-Derived Cobalt Catalyst*: The Co-BTC was synthesized according to the reported method described in the reported literature.<sup>[11]</sup> The obtained Co-BTC was used as the precursor and subjected to the same thermal treatment procedure used for Co-900. The obtained product was denoted as Co-900-B.

Synthesis of Co/AC Catalyst: The commercial activated carbon was first washed by deionized water and ethanol, followed by drying at 80 °C in air overnight. Then, 0.5 g of pretreated AC was dispersed into 0.5 mL of 3.0 M Co(NO<sub>3</sub>)<sub>2</sub> solution, and then dried at 80 °C in air for 12 h. The obtained AC sample with adsorbed Co was thermally treated at 500 °C with a ramp rate of 5 °C min<sup>-1</sup> for 2 h in N<sub>2</sub> atmosphere. The obtained sample was denoted as Co/AC.

Characterization: FESEM images of the samples were taken on a FESEM (SU8020) operated at an accelerating voltage of 10.0 kV. TEM (JEOL-2010) images were obtained with the instrument operated at an acceleration voltage of 200 kV. STEM images of the samples were recorded by a high-resolution TEM (Philips TecnaiG2 F20) operated at an acceleration voltage of 200 kV. Powder XRD patterns were analyzed on a Philips X-Pert Pro X-ray diffractometer using the Ni-filtered monochromatic Cu K $\alpha$  radiation ( $\lambda_{K\alpha 1} = 1.5418$  Å) at 40 keV and 40 mA. The surface area and porosity of samples were measured at 77 K using a surface area and porosity analyzer (Autosorb iQ Station 2). XPS analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA) equipped with Al  $K\alpha_{1,2}$  monochromatized radiation at 1486.6 eV X-ray source. Raman spectra of the samples were recorded on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) using an Ar ion laser operating at 632 nm. The metal content in the composite structure was determined by the inductively coupled plasma spectroscopy after microwave digestion of the samples (ICP 6300, Thermo Fisher Scientific). The X-ray absorption fine structure spectra data (Co K-edge) were collected at 1W1B station in Beijing Synchrotron Radiation Facility (operated at 2.5 GeV with a maximum current of 250 mA). The data were collected in fluorescence excitation mode using a Lytle detector. All samples were pelletized as disks of 13 mm diameter with 1 mm thickness using graphite powder as a binder.

Evaluation of the Catalytic Performance for Hydrogenation Reactions: The catalytic hydrogenation reactions were carried out in a 25 mL stainless steel autoclave equipped with a mechanical stirrer, a pressure gauge, and automatic temperature control apparatus. In a typical experiment, the reaction solutions of reactant (1 mmol), catalyst (20 mg), and H<sub>2</sub>O (10 mL) were loaded into the reactor. The reactor was sealed, purged three times with N<sub>2</sub> at 1 MPa, and then pressurized with H<sub>2</sub> to a setting point. The reactor was then heated to the desired temperature with continuous stirring at 700 rpm, which eliminates the diffusion effects. After reaction, the autoclave was cooled down quickly. The autoclave contents were transferred to a centrifuge tube, and the catalyst was separated by centrifugation. The products were extracted by ethyl acetate from the liquid and analyzed.

The liquid product was identified by gas chromatography–mass spectrometry (GC–MS, Thermo Fisher Scientific-TXQ Quantum XLS, column-TG-WAXMS, 30 m  $\times$  0.25 mm  $\times$  0.25 µm), and was quantitatively analyzed by GC (Shimadzu, GC-2010 Plus), equipped with flame ionization detector and a 30 m  $\times$  0.25 mm  $\times$  0.25 µm KB-WAX capillary column (Kromat Corporation, USA). The mass balance (based on carbon) was checked in every experimental run and detected to be higher than 96%.

During the catalyst stability test, the catalyst was reused without any further treatment. More specifically, following the first hydrogenation reaction, the reaction mixture was centrifuged or filtered to recover the catalyst, which was washed first with water and then with ethanol followed by drying under vacuum oven at 60  $^{\circ}$ C and employed for the next test.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

# Acknowledgements

W.G. and Y.L. contributed equally to this work. This work was supported by the Natural Science Foundation of China (Grant Nos. 51432009 and 51872292) and the CAS Pioneer Hundred Talents Program. The authors thank the 1W1B station for XAFS measurement in Beijing Synchrotron Radiation Facility.

## **Conflict of Interest**

The authors declare no conflict of interest.

### **Keywords**

biomass-derived molecules, cobalt nanoparticles, Co– $N_x$ , metal–organic frameworks, selective hydrogenation

Received: December 27, 2018 Revised: January 7, 2019 Published online:

- a) M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* 2014, 114, 1827;
   b) D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Chem. Soc. Rev.* 2012, 41, 8075;
   c) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem., Int. Ed.* 2007, 46, 7164.
- [2] a) M. Zhao, K. Yuan, Y. Wang, G. Li, J. Guo, L. Gu, W. Hu, H. Zhao, Z. Tang, *Nature* 2016, *539*, 76; b) A. Corma, P. Serna, *Science* 2006, *313*, 332; c) Y. Tan, X. Y. Liu, L. Zhang, A. Wang, L. Li, X. Pan, S. Miao, M. Haruta, H. Wei, H. Wang, F. Wang, X. Wang, T. Zhang, *Angew. Chem., Int. Ed.* 2017, *129*, 2753; d) P. Liu, Y. Zhao, R. Qin, S. Mo, G. Chen, L. Gu, D. M. Chevrier, P. Zhang, Q. Guo, D. Zang, B. Wu, G. Fu, N. Zheng, *Science* 2016, *352*, 797; e) T. L. Cui, W. Y. Ke, W. B. Zhang, H. H. Wang, X. H. Li, J. S. Chen, *Angew. Chem., Int. Ed.* 2016, *55*, 9178; f) J. Tan, J. Cui, X. Cui, T. Deng, X. Li, Y. Zhu, Y. Li, *ACS Catal.* 2015, *5*, 7379.
- [3] M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B. C. Gates, M. R. Rahimpour, *Energy Environ. Sci.* 2014, 7, 103.
- [4] a) L. He, F. Weniger, H. Neumann, M. Beller, Angew. Chem., Int. Ed. 2016, 55, 12582; b) J. Wu, G. Gao, J. Li, P. Sun, X. Long, F. Li, Appl. Catal. B 2017, 203, 227; c) J.-S. Moon, E.-G. Kim, Y.-K. Lee, J. Catal. 2014, 311, 144; d) G. Liu, A. W. Robertson, M. M.-J. Li, W. C. H. Kuo, M. T. Darby, M. H. Muhieddine, Y.-C. Lin, K. Suenaga, M. Stamatakis, J. H. Warner, S. C. E. Tsang, Nat. Chem. 2017, 9, 810.
- [5] K. Shen, X. Chen, J. Chen, Y. Li, ACS Catal. 2016, 6, 5887.
- [6] a) J. Meng, C. Niu, L. Xu, J. Li, X. Liu, X. Wang, Y. Wu, X. Xu, W. Chen, Q. Li, Z. Zhu, D. Zhao, L. Mai, J. Am. Chem. Soc. 2017, 139, 8212; b) B. Y. Xia, Y. Yan, N. Li, H. B. Wu, X. W. Lou, X. Wang, Nat. Energy 2016, 1, 15006; c) P. Xiong, X. Zhao, Y. Xu, ChemSusChem 2017, 11, 202; d) S. Liu, Z. Wang, S. Zhou, F. Yu, M. Yu, C. Y. Chiang, W. Zhou, J. Zhao, J. Qiu, Adv. Mater. 2017, 29, 1700874; e) Z. Chen, R. Wu, Y. Liu, Y. Ha, Y. Guo, D. Sun, M. Liu, F. Fang, Adv. Mater. 2018, 30, 1802011.
- [7] Y. He, S. Hwang, D. A. Cullen, M. A. Uddin, L. Langhorst, B. Li, S. Karakalos, A. J. Kropf, E. C. Wegener, J. Sokolowski, M. Chen,

# **ADVANCED** SCIENCE NEWS

www.advancedsciencenews.com



D. J. Myers, D. Su, K. L. More, G. Wang, S. Litster, G. Wu, *Energy Environ. Sci.* 2019, 12, 250.

- [8] a) P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei, Y. Li, *Angew. Chem., Int. Ed.* **2016**, *55*, 10800; b) Y. Chen, S. Ji, Y. Wang, J. Dong, W. Chen, Z. Li, R. Shen, L. Zheng, Z. Zhuang, D. Wang, Y. Li, *Angew. Chem., Int. Ed.* **2017**, *56*, 6937; c) X. Sun, A. I. Olivos-Suarez, D. Osadchii, M. J. V. Romero, F. Kapteijn, J. Gascon, J. Catal. **2018**, *357*, 20.
- [9] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sadaba, M. L. Granados, Energy Environ. Sci. 2016, 9, 1144.
- [10] a) R. V. Jagadeesh, K. Murugesan, A. S. Alshammari, H. Neumann, M.-M. Pohl, J. Radnik, M. Beller, *Science* 2017, *358*, 326; b) C. Tang, A.-E. Surkus, F. Chen, M.-M. Pohl, G. Agostini, M. Schneider, H. Junge, M. Beller, *Angew. Chem., Int. Ed.* 2017, *56*, 16616.
- [11] a) O. M. Yaghi, H. Li, T. L. Groy, J. Am. Chem. Soc. 1996, 118, 9096;
  b) H. Liu, G. Xia, R. Zhang, P. Jiang, J. Chen, Q. Chen, RSC Adv. 2017, 7, 3686.