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#### 1. Introduction

Volatile organic compounds (VOCs) generated from petrochemical-related production processes, product consumption behavior and motor vehicle exhaust are identified as dominant factors to air pollution and are harmful to human health.<sup>1-4</sup> Hence, it is urgent to eliminate the pollution of VOCs. In recent years, plenty of treatment ways such as physical, chemical and biological methods are used for the abatement of VOCs.<sup>5-7</sup> Among them, catalytic oxidation of VOCs is considered

# Enhanced catalytic benzene oxidation over a novel waste-derived Ag/eggshell catalyst<sup>†</sup>

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Catalytic oxidation plays a key role in transforming gaseous benzene into harmless matter, in which it is essential to look for a low-cost, environmentally friendly and efficient green catalyst/support. Herein, Ag nanoparticle (Ag NP) loaded-eggshell catalysts were successfully synthesized by a simple impregnation method, in which waste eggshells were used as an efficient template and catalyst support. SEM, XRD and ICP-OES results show that a different number of Ag NPs are uniformly distributed on the surface of eggshells, which are defined as Ag1/eggshell (10.8%), Ag2/eggshell (19.9%) and Ag3/eggshell (34.3%) catalysts according to the amounts of loaded Ag NPs. Then, the activity between the three catalysts and the pure Aq NPs was assessed based on the catalytic oxidation of benzene. Our results show that the Aq NP loaded-eggshell catalysts exhibit superior catalytic activity compared with the pure Ag NPs. Considering the balance between the cost and catalytic performance, the Ag<sub>2</sub>/eggshell catalyst was selected as the optimum research object in the subsequent work. The Aq<sub>2</sub>/eggshell catalyst calcined at 500 °C exhibited excellent catalytic activity, which is assigned to the unique channel structure of eqgshell, good low-temperature reducibility, and high dispersion of particles (sizes effects) on the surface of eggshell as well as the synergetic interaction between the Ag NPs and eggshell. Furthermore, the Ag<sub>2</sub>/eggshell catalyst exhibited predominant stability even after 200 h of on-stream reaction. The reaction mechanism is put forward based on the in situ FTIR experimental results, in which some carboxylate intermediate species are confirmed. Accordingly, the waste eggshell is considered as a promising supporting material for the large-scale synthesis of noble metal catalyst with high catalytic performance and stability for VOC oxidation.

> to be the most promising method and it can be performed at lower temperatures with low cost and high oxidation efficiency.<sup>6,8–10</sup> The key issue of catalytic oxidation is the preparation of inexpensive catalysts with high activity. Compared to transition-metal oxides, supported noble metals are widely used for the oxidation of VOCs because of their high catalytic performance and excellent stability. Generally, the activity of supported noble metals has a great relationship with the species of noble metals, the nature of support, *etc.*<sup>6,11</sup>

> In the past few decades, supported Ag catalysts have attracted much attention because of their low cost and relatively high catalytic performance.<sup>12,13</sup> Compared with other supported noble metal (Pd, Pt, Au, and Rh) catalysts,<sup>14–18</sup> the supported Ag catalyst shows a lot of merits. On one hand, Ag is one of the cheapest noble metals. On the other hand, Ag can also provide sufficient active sites for almost all kinds of catalytic oxidation reactions.<sup>2,19–21</sup> Therefore, the selectivity of Ag as the active site rather than other noble metals is essentially investigated. Recently, some literature studies reported the oxidation performance of VOCs on supported Ag catalysts, like Ag/  $Mn_2O_3$ ,<sup>2</sup> Ag/MnO<sub>2</sub>,<sup>22</sup> Ag/CeO<sub>2</sub>,<sup>11</sup> and Ag/Al<sub>2</sub>O<sub>3</sub>,<sup>23</sup> which demonstrate that Ag catalysts are promising for the reaction.



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However, most of the used catalyst supports are transition metal oxides, which have some obvious disadvantages with a high-cost, non-environmentally friendly and complex preparation process. Therefore, looking for an available supporting material with low-cost, green and simple preparation technology is urgently needed. Nature demonstrates a diverse species through evolution, affording us important inspiration for materials design and synthesis.12 Eggshell is a kind of natural biomaterial produced by poultry and composed of about 96% CaCO<sub>3</sub>, 1% MgCO<sub>3</sub>, 1% Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and organic materials (mainly proteins), as well as water.24,25 The eggshell support is composed of a foamy layer of cuticle, a calcite or calcium carbonate layer and two shell membranes, with 7000-17 000 funnel-shaped pore canals distributed unevenly on the shell surface.<sup>26</sup> Every day, a mass of eggshells is treated as waste in landfill, which becomes a source of environment pollution.27 In fact, eggshell has intrinsic pore and hierarchical structures and can be used as a calcium catalyst, additive and soil conditioner.24,28 Natural eggshell not only provides a cost-effective and environmentally sound feedstock to produce heterogeneous catalysts, but also acts as an excellent platform for the reduction, dispersion and stabilization of nanoparticles. More importantly, the hierarchical and porous structure is very much in favor of mass and energy transfer. To the best of our knowledge, few reports are available in the literature on the use of waste eggshell as a support to synthesize catalysts for VOC oxidation (most work focused on calcium sources for the synthesis of additives, biodiesel, tissue scaffolds and adsorbents).

Herein, we report a facile one-step route for preparing the Ag/eggshell catalysts, where the eggshell from kitchen waste is used as an efficient support and template. The Ag loaded-eggshell samples were utilized for the oxidation of benzene, and it is found that these catalysts show outstanding activity for the catalytic oxidation of benzene. It is believed that the facile synthesis, available large-scale production, environmental friendliness, low cost, non-toxic and excellent properties will make the eggshell support widely used in the practical application of VOC oxidation.

#### 2. Materials and methods

#### 2.1 Materials and agents

The waste eggshells were obtained from the canteen located in Quanzhou Normal University, China. The raw eggshells were carefully rinsed with deionized (DI) water several times and then dried overnight at room temperature. The dry eggshells were ground and sieved through a 100-mesh screen to obtain the eggshell powder. Silver nitrate (AgNO<sub>3</sub>) was purchased from Aladdin (Shanghai, China). Commercial CaCO<sub>3</sub> (com-CaCO<sub>3</sub>) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Guangzhou, China). All chemicals were of analytical grade and used as received. DI water was used throughout this work.

#### 2.2 Preparation of Ag catalysts

The typical impregnation method was used to prepare the Ag/eggshell catalysts. Firstly, an AgNO<sub>3</sub> solution with different

concentrations of 0.05, 0.1, and 0.2 mol L<sup>-1</sup> was added to a 100 mL conical flask, respectively. Afterwards, 2.0 g of eggshell powder was added to the above Ag precursor solution under magnetic stirring for 12 h. Then, the suspension was centrifuged and the solid in the retentate was dried at 60 °C in air for 6 h followed by calcination at 300, 400, 500 and 600 °C for 3 h with a ramp rate of 2 °C min<sup>-1</sup> in a muffle furnace, respectively. Finally, the different Ag loaded-eggshell catalysts were obtained (defined as Ag<sub>1</sub>/eggshell (10.8%), Ag<sub>2</sub>/eggshell (19.9%) and Ag<sub>3</sub>/ eggshell (34.3%)).

In addition, another type of Ag catalyst was also synthesized for comparison. The Ag<sub>2</sub>/com-CaCO<sub>3</sub> (19.9% and calcined at 500 °C for 3 h) catalyst was prepared by using the same method stated above except that com-CaCO<sub>3</sub> substituted for eggshell as a support. Ag NP solids were prepared according to the method developed by us with some slight modifications.<sup>29</sup> For a typical synthesis, 50 mg of ascorbic acid was added to the AgNO<sub>3</sub> solution (100 mL) with a concentration of 0.05 mol L<sup>-1</sup>; the mixture was stirred at room temperature for approximately 5 min followed by centrifuging and dried at 60 °C in air for 8 h. Finally, the Ag NPs were obtained.

#### 2.3 Catalyst characterization

The physicochemical properties of the eggshell support and Ag catalysts were characterized by using different techniques. Power X-ray diffraction (XRD) analysis was performed on an Xray diffractometer (Rigaku Ultima IV, Japan) with Cu Ka radiation at 40 kV and 30 mA to identify lattice parameters and to analyze the crystal phases. The surface morphology, pore structure, and composition of the samples as well as Ag NP size and dispersion on the supports were obtained by scanning electron microscopy (SEM) (ZEISS SIGMA, Germany) which was equipped with an EDS elemental composition analyzer. The Ag NP size of the supported Ag catalysts was estimated by using Sigma Scan Pro software (SPSS Inc., Version 4.01.003). Highangle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX) mapping were carried out by using using a Tecnai F30 microscope (TECNAI F30, USA) to identify the chemical compositions of the crystal phases. Textural properties were measured using a Micromeritics Tristar system (Tristar II3020, USA). Before the surface area measurement, all samples were degassed at 300 °C for 3 h. The actual loadings of Ag on the eggshell support were obtained by inductively coupled plasma optical emission spectrometry (ICP-OES) (5100 SVDV, USA). The surface elements and chemical states of Ag/eggshell were probed by X-ray photoelectron spectroscopy (XPS) using monochromated Al Ka (1486.7 eV) as an X-ray source in which the binding energies (BEs) were calibrated with C 1s 284.8 eV (Physical Electronics, USA). UV-vis diffuse reflectance spectrometry (UV-vis DRS) characterization was obtained in the wavelength range of 200-800 nm using a Cary 5000 spectrophotometer (Varian Cary 5000, USA) and dehydrated BaSO4 was used as the reference. Thermogravimetric (TG) characterization was performed from 30 to 800 °C in the temperature range at a heating rate of 10 °C min<sup>-1</sup> with an air flow of 50 mL min<sup>-1</sup>

over a thermobalance (SDT Q600, USA). FTIR spectra were performed on a Nicolet Avatar 660 (Nicolet 6700, USA), where the KBr powder was mixed with the samples and then pressed into an appropriate disk. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were performed on a chemical adsorption analyzer (MFTP-3060, China) by using a H<sub>2</sub>-Ar (5/95, v/v) mixture as a reducing gas. Prior to the H<sub>2</sub>-TPR operation, the samples were pretreated in an Ar flow of 30 mL min<sup>-1</sup> at 300 °C for 3 h, and the pretreated samples were heated from RT to 900 °C at a ramp rate of 5 °C min<sup>-1</sup> in the H<sub>2</sub>-Ar mixture of 50 mL min<sup>-1</sup>.

#### 2.4 Catalytic activity measurements

The catalytic activity of benzene was performed in a continuous flow fixed-bed quartz microreactor (inner diameter = 5 mm) using a catalyst amount of 50 mg. The reactant gas contains 1000 ppm benzene, where the benzene/ $O_2$  molar ratio was 1/400 and the remaining  $N_2$  was the balance gas, passing through the reactor bed with different flow rates, resulting in the different SV values of 20 000, 60 000, and 100 000 mL  $g^{-1}$   $h^{-1}$ , respectively. The temperatures of the column oven, gasification chamber and detector were 130, 240 and 250 °C, respectively for  $CO_2$  and benzene detection. To probe the effect of water vapor on the catalyst activity of benzene oxidation, 5.0 and 10.0 vol% water vapor were introduced into the reaction system by passing the reactant gas through a water saturator at 33 and 46 °C. In the case of analyzing the CO2 effect, 10.0 vol% CO2 was also introduced into the reaction system using a high-purity CO<sub>2</sub> cylinder. The gas concentrations from the microreactor were analyzed online by using a gas chromatograph (GC-9160, Ouhua China) equipped with double FID detectors. A TDX-01 packed column (1 m imes 2 mm) and a SE-54 capillary column (30 m imes 0.25 mm imes $0.5 \ \mu m$ ) were employed to analyze CO<sub>2</sub> and benzene concentrations with Ar and N2 as protective gases, respectively. In the catalytic activity experiments, the benzene conversion  $(X_{\text{benzene}})$ and  $CO_2$  selectivity  $(Y_{CO_2})$  were calculated according to the equations:

$$X_{\text{benzene}} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%$$
(1)

$$Y_{\rm CO_2} = \frac{C(\rm CO_2)_{out}}{C(\rm CO_2)_{complete}} \times 100\%$$
<sup>(2)</sup>

For the kinetic studies, the turnover frequencies  $(TOF_{Ag})$  were calculated according to the equation:

$$\text{TOF}_{Ag} = \frac{C_{\text{benzene}} X_{\text{benzene}} V_{\text{gas}}}{n_{Ag}} \quad (s^{-1}) \tag{3}$$

where  $C_{\rm in}$  and  $C_{\rm out}$  are the benzene concentration corresponding to the inlet and outlet, respectively,  $C(\rm CO_2)_{out}$  is the outlet  $\rm CO_2$  concentration and  $C(\rm CO_2)_{complete}$  is the  $\rm CO_2$  concentration of complete conversion of benzene to carbon dioxide, and  $V_{\rm gas}$  is the total molar flow rate,  $C_{\rm benzene}$  is the benzene concentration of the gas mixture, and  $n_{\rm Ag}$  is the molar amount of Ag in the catalyst.

#### 2.5 In situ FTIR

In situ Fourier transform infrared spectroscopy (abbreviated to in situ FTIR) was performed on a Nicolet Avatar 660 (Nicolet 6700, USA) at a resolution of 4  $cm^{-1}$  with 32 scans, which is equipped with an MCT detector (cooled with liquid nitrogen) and a stainless steel IR cell (CaF2 windows). Prior to each experiment, the IR cell was flushed with flowing N2 at a rate of 90 mL min<sup>-1</sup> for 2 h. At first, the catalyst (approximately 15 mg) was pressed into a supported disk. Then, the sample was under vacuum at 300 °C for 0.5 h and subsequently activated at 300 °C for 1 h in a 40%  $O_2/N_2$  (50 mL min<sup>-1</sup>) stream and then cooled to 260 °C. The background spectrum was collected under 40% O2/N2 and automatically subtracted from the next sample spectra. Afterward, 1000 ppm benzene/40% O2/N2 was introduced to the IR cell at a flow rate of 50 mL min<sup>-1</sup> at 260 °C, and subsequently the in situ FTIR spectra were measured at different times.

#### 3. Results and discussion

# 3.1 Characterization of the pure eggshell and Ag/eggshell catalysts

3.1.1 XRD analysis. The crystalline structure of pure eggshell and the varying amounts of Ag NP loaded-eggshell catalysts was characterized by XRD. As shown in Fig. 1A, the main diffraction peaks of pure eggshell at  $2\theta = 23.2, 29.5, 31.6$ , 36.1, 39.5, 43.3, 47.7, 48.7, 57.6 and 60.8° were assigned to CaCO<sub>3</sub> (calcite, JCPDS PDF #29-0305). Compared with the pure eggshell, the additional peaks of varying amounts of Ag NP loaded-eggshell catalysts centered at 38.2, 44.4, 64.4, 77.4 and 81.5° were ascribed to metallic Ag (JCPDS PDF #04-0783).30 It can be seen that the peak intensities increased with the Ag loading amount, confirming the excellent incorporation of Ag NPs and the CaCO<sub>3</sub> support. In addition, it is worth noting that no extra diffraction peaks were observed from the XRD patterns, which indicated the pure phase of metallic Ag and CaCO<sub>3</sub>. Other components in the eggshell are too low in content to be observed from XRD patterns, which could also manifest the relatively pure Ag loaded-eggshell catalysts. Furthermore, the magnification patterns of Ag peaks are analyzed in Fig. 1B in detail. The diffraction peaks of Ag (111) and (200) become much stronger and sharper at increased Ag content, suggesting the formation of larger and more abundant concentration of Ag NPs. Comparably, almost no peak shifts were observed in the diffraction peaks of Ag (111) and (200), demonstrating that no related Ag compounds are formed, consistent with results in Fig. 1A.

**3.1.2 STEM observations and corresponding elemental mapping.** The morphologies of Ag NP loaded-eggshell catalysts can be observed from the STEM images. Fig. 2A–E show the HAADF-STEM and mapping images of the Ag<sub>2</sub>/eggshell catalyst. The EDX elemental mapping images were applied to elucidate the existence and the dispersion of Ag, Ca, C and O elements on the catalyst. The microstructure of Ag<sub>2</sub>/eggshell was also determined by HRTEM. As shown in Fig. 2F, the HRTEM image of the Ag<sub>2</sub>/eggshell catalyst demonstrates the lattice spacings of







Fig. 2 (A) HAADF-STEM image of Ag<sub>2</sub>/eggshell and the corresponding EDX elemental mapping images of (B) Ag, (C) Ca, (D) C and (E) O and (F) HRTEM image of Ag<sub>2</sub>/eggshell.

0.241 and 0.307 nm, which were ascribed to the (111) plane of Ag and (112) plane of  $CaCO_3$ , respectively according to the standard PDF cards of Ag (JCPDS PDF #04-0783) and  $CaCO_3$  (JCPDS PDF #29-0305). It can also be observed (from Fig. S1†) that a number of good-quality spherical Ag NPs were highly dispersed on the surface of the eggshell support. It is assured that plentiful Ag NPs were well generated on the surface of the eggshell. In addition, it can be seen from Fig. S2† that the pure Ag NPs are all spherical and have a uniform particle size, which is consistent with the Ag NPs dispersed on the eggshell support.

**3.1.3 BET analysis.** The textural properties of the eggshell support and Ag catalysts have an important effect on the catalytic performance. As shown in Fig. 3A and B, N<sub>2</sub> adsorption–desorption isotherm curves of eggshell and supported Ag catalysts show a characteristic isotherm pattern of non-porous materials (surface area 1–2 m<sup>2</sup> g<sup>-1</sup>). The existing porosity in the materials is due to interparticle meso/macroporosity (voids

created in between particles). Loading Ag onto the eggshell support did not obviously change the textural properties of the supported Ag catalyst, indicating that the majority of Ag NPs were highly dispersed on the eggshell (Table 1).

**3.1.4 XPS analysis.** XPS analysis was performed to characterize the electronic states of the Ag/eggshell catalysts with different Ag NP loadings. As shown in Fig. 4A, two binding energies with one doublet of Ag 3d are detected. The peaks at about 368.3 and 374.3 eV are assigned to the surface metallic  $Ag^0$  species. A shift to lower binding energy by 0.2 eV was observed for Ag of  $Ag_2$ /eggshell (368.2 eV), compared to  $Ag_1$ / eggshell and  $Ag_3$ /eggshell (368.4 eV). It has been reported that the Fermi energy levels would compromise to a new value in the case of a strong synergistic effect between Ag NPs and the support.<sup>19</sup> As a result, electron transfer from Ag NPs to the eggshell support occurred, decreasing the core-level binding energy of Ag. Hence, the lower shift for Ag of  $Ag_2$ /eggshell was

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Fig. 3 Nitrogen adsorption-desorption isotherm and the corresponding pore size distribution curves (inlet): (A) xAg/eggshell catalysts with different Ag loadings and (B) the optimum Ag<sub>2</sub>/eggshell calcined at different temperatures.

Table 1 Textural properties of various samples

Sample	BET surface area $(m^2 g^{-1})$	Pore volume <sup><i>a</i></sup> (cm <sup>3</sup> g <sup>-1</sup> )
Eggshell	<5	0.008
Ag <sub>1</sub> /eggshell	<5	0.005
Ag <sub>2</sub> /eggshell	<5	0.004
Ag <sub>3</sub> /eggshell	<5	0.003
Ag <sub>2</sub> /eggshell (300 °C)	<5	0.010
Ag <sub>2</sub> /eggshell (400 °C)	<5	0.007
Ag <sub>2</sub> /eggshell (600 °C)	<5	0.008
<i>a</i>	/	

<sup>*a*</sup> Calculated from the volume adsorbed at  $P/P_0 = 0.99$ .

a proof of the stronger synergistic effect between Ag nanoparticles and the eggshell support than that of  $Ag_1$ /eggshell and  $Ag_3$ /eggshell, resulting in improved catalytic properties.

Furthermore, the signals of the metallic Ag become stronger and stronger  $(Ag_3/eggshell > Ag_2/eggshell > Ag_1/eggshell)$  with the increased Ag loadings. Besides, no other peaks were observed, which elucidated the complete conversion of oxidation valence state  $Ag^+$  to metallic Ag during the preparation process. It was also in accordance with the results of XRD (Fig. 1). Fig. 4B shows the Ca 2p spectra of the three catalysts, and one can see that a set of peaks occurred corresponding to the Ca  $2p_{3/2}$  and  $2p_{1/2}$  electronic states. The peaks at 347.2 eV reflect the Ca  $2p_{3/2}$  features while the peaks with a binding energy of about 350.6 eV belong to Ca  $2p_{1/2}$ . As a result, the peak position spacing between Ca  $2p_{3/2}$  and Ca  $2p_{1/2}$  from all the catalysts was around 3.5 eV. Then, the C 1s peaks (Fig. 4C) of the silver supported catalysts have two binding energies with one double, which is located at around 284.7 and 289.7 eV. The peak corresponding to C-C/C-H bonds was observed in all the samples at approximately 284.7 eV assigned to the carbon from inadequate combustion of organics, and this peak was always elucidated as a reference calibration.<sup>31,32</sup> Besides, the peak obtained at 289.7 eV demonstrated the presence of the carbonate group in the Ag/eggshell catalysts.33 Furthermore, it can be seen from Fig. 4D that there are two binding energy peaks at around

531.2 eV and 532.9 eV, which can be derived from the asymmetrical element O 1s of the catalysts. The binding energy peak at 531.2 eV pertains to the  $O_{latt}$  (lattice oxygen) in CaCO<sub>3</sub>,<sup>34</sup> and the other at 532.9 eV can be ascribed to the adsorbed oxygen species  $O_{ads}$  (adsorbed oxygen, *e.g.*,  $O_2^-$ ,  $O^-$  or  $O_2^{2-}$ ).<sup>35,36</sup>

3.1.5 TG and FTIR analysis. TG characterization was carried out to investigate the decomposition of the pure eggshell and xAg/eggshell catalysts. The TG curves of all the samples are shown in Fig. 5A. The TG curve of the pure eggshell support demonstrated a slight decline at 217-373 °C and a sharp decrease at 560-769 °C, which is attributed to the decomposition of the eggshell membrane and CaCO<sub>3</sub>, respectively. And the weight loss of the eggshell membrane was accounted for 2.1 wt%. Compared with the pure eggshell, all the xAg/eggshell catalysts showed an extra decrease in the range of 130 to 250 °C, which is attributed to the decomposition of AgNO<sub>3</sub>. Furthermore, the weight loss of the different Ag/ eggshell catalysts between 130-250 °C is obviously different (ranked as  $Ag_3/eggshell > Ag_2/eggshell > Ag_1/eggshell$ ), which is consistent with the data obtained by ICP-OES. In addition, the FTIR spectra of the eggshell and xAg/eggshell catalysts were obtained to validate the existence of different functional groups. As shown in Fig. 5B, nine characteristic absorption bands were observed in every spectrum. This indicates that they have similar FTIR absorption. Moreover, the positions and intensities of the absorption bands were not affected by the loading of Ag NPs on the eggshell. The characteristic absorption band centering at 3434 cm<sup>-1</sup> was assigned to -OH stretching vibration from adsorbed water.<sup>37</sup> The weak band centering at 2976, 2875 and 1800  $\text{cm}^{-1}$  can be ascribed to C=O bands derived from carbonate. The moderate absorption peak at 2517  $\rm cm^{-1}$ was the characteristic peak of CaCO<sub>3</sub>. Another two well-defined characteristic absorption peaks at 1422 and 878 cm<sup>-1</sup> correspond to the C-O stretching and bending modes of CaCO<sub>3</sub>, respectively.<sup>38</sup> The peak at 1639 cm<sup>-1</sup> can be attributed to N–H bending mode. The absorption band at 709  $cm^{-1}$  can be assigned to Ca-O bonds.<sup>39</sup> In summary, these peaks are characteristic functional groups of eggshell.

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Fig. 4 XPS spectra of (A) Ag 3d, (B) Ca 2p, (C) C 1s and (D) O 1s for the xAg/eggshell catalysts.

**3.1.6** H<sub>2</sub>-**TPR** analysis. H<sub>2</sub>-**TPR** experiments were performed to demonstrate the reducibility of the samples. According to the H<sub>2</sub>-**TPR** profiles in Fig. 6, there is only one reduction peak in all the samples. The profile of pure eggshell (Fig. 6A) showed a single peak at 759 °C, which is ascribed to  $CO_2$  generation from the decomposition of eggshell. No peaks assigned to the reduction of AgO to Ag were observed, which indicated that all the Ag precursors were completely converted into Ag<sup>0</sup> in this preparation method. It can be seen from Fig. 6A

that when Ag NPs were loaded onto the eggshell support, the reduction peak of all the catalysts shifted to a lower temperature than the one of pure eggshell which indicated that Ag NP loading could obviously enhance the reducibility of the eggshell. As the Ag loading increases, the reduction peak gradually shifted to a lower temperature. Based on the Marsvan Krevelen (redox) mechanism,<sup>6,40</sup> such shifts demonstrate a strong interaction between Ag NPs and the eggshell support, which could benefit the low-temperature reducibility of the



Fig. 5 (A) Simultaneous TG profiles and (B) FTIR spectra of pure eggshell and xAg/eggshell materials.



Fig. 6  $H_2$ -TPR profiles of (A) xAg/eggshell catalysts with different Ag loadings and (B) the optimum Ag<sub>2</sub>/eggshell calcined at different temperatures.

supported Ag catalysts and enhance the catalytic performance. As shown in Fig. 6B, despite all the catalysts containing the same Ag contents, the reduction peaks shifted to higher temperature with respect to the increased calcination temperature of the Ag<sub>2</sub>/eggshell, affirming that higher calcination conditions could decrease the reducibility of the catalysts. In conclusion, when Ag NPs were loaded on the eggshell, the reducibility of the eggshell was enhanced, demonstrating a synergistic effect between the Ag and eggshell in Ag<sub>2</sub>/eggshell.

**3.1.7 UV-vis DRS analysis.** UV-vis DRS was further applied to identify the Ag oxidation state of the *x*Ag/eggshell catalysts. It can be seen from Fig. 7A that no peaks were observed above 300 nm on pure eggshell. In contrast, when Ag NPs were loaded onto the eggshell support, the absorption bands of *x*Ag/eggshell at about 314 and 348 nm were ascribed to the oxidized silver clusters (Ag<sub>n</sub><sup> $\delta$ +</sup>), which were formed by the interaction between the eggshell and metallic silver.<sup>41</sup> And the peak intensities at 314 nm became stronger as the Ag NP loading increased, which was helpful for the catalytic oxidation of benzene. As is well known, Ag<sup>0</sup> and oxidized silver clusters (Ag<sub>n</sub><sup> $\delta$ +</sup>) are active species with respect to ethylene epoxidation, as opposed to Ag<sup>+</sup>.<sup>41,42</sup> The absorption bands of *x*Ag/eggshell (Fig. 7A) at 389 and 405 nm

were assigned to  $Ag^0$  species.<sup>43</sup> And no absorption bands at about 200 nm associated with  $Ag^+$  were observed in the three samples, which demonstrated that all the Ag precursors were reduced completely. As for Fig. 7B, all the  $Ag_2$ /eggshell catalysts calcined at different temperatures have similar peak positions and intensities, which indicated that they have the same Ag species and content.

#### 3.2 Catalytic performance in benzene oxidation

The pure eggshell did not have any catalytic activity for the oxidation of benzene until the reaction temperature reached 380 °C (Fig. S3†). The effect of Ag loading on the catalytic performance of benzene was further investigated. As can be seen in Fig. 8A, the catalytic performance of Ag/eggshell catalysts (all calcined at 500 °C) was significantly improved by immobilizing the Ag NPs onto the eggshell, compared with the pure eggshell. What is more, the higher Ag loading resulted in higher benzene conversion at a certain temperature. However, the benzene conversion increase became not obvious when the Ag NP loading exceeded 19.9%. Hence, Ag<sub>2</sub>/eggshell was determined to be an optimal Ag loading, in which the  $T_{90\%}$  (the temperature for achieving 90% benzene conversion) was 225 °C,



Fig. 7 UV-vis DRS profiles of (A) xAg/eggshell catalysts with different Ag loadings and (B) the optimum Ag<sub>2</sub>/eggshell calcined at different temperatures.



Fig. 8 Benzene conversion as a function of reaction temperature over (A) pure Ag NPs and. xAg/eggshell catalysts with different Ag loadings and (B) effect of calcination temperature of Ag<sub>2</sub>/eggshell at SV = 20 000 mL  $g^{-1} h^{-1}$ .

which is lower than that of reported other kinds of catalysts (Table S2<sup>†</sup>). Besides, the catalytic oxidation ability of pure Ag NPs was also tested and the conversion was lower than that of Ag<sub>2</sub>/eggshell and Ag<sub>3</sub>/eggshell catalysts at a certain temperature. The TOF<sub>Ag</sub> values were calculated at low conversions at 190  $^\circ C$ under a kinetically controlled regime for the oxidation of benzene. It is demonstrated that the  $\text{TOF}_{Ag}(10^{-4} \text{ s}^{-1})$  values of the samples decreased in the sequence of  $Ag_2/eggshell (0.153) >$  $Ag_3/eggshell (0.129) > Ag_1/eggshell (0.073) > pure Ag NPs (0.005),$ with the lowest  $\mathrm{TOF}_{\mathrm{Ag}}$  value being observed over pure Ag NPs and highest TOFAg value of Ag2/eggshell. This calculation result explains why Ag<sub>2</sub>/eggshell was chosen as the catalyst support. Considering the characterization analysis of Fig. 6A and 7A, the observed enhanced catalytic activity for benzene oxidation results from a synergistic interaction between the eggshell and Ag NPs.

Besides, SEM images and size histograms of Ag NPs with different Ag contents are shown in Fig. S4.† It is obvious that the spherical Ag NPs were uniformly distributed on the eggshell supports. The mean diameter of Ag NPs increased from 237.5 to 308.8 nm, with the increase of Ag content from 10.8 to 34.3%, which is consistent with the phenomenon observed in Fig. 1. The superior performance observed for the highest Ag loading might be ascribed to the larger Ag content and presence of active Ag sites which results in a higher catalytic activity for benzene oxidation.

Calcination is necessary to decompose the AgNO<sub>3</sub> for the formation of Ag loaded-eggshell catalysts. Therefore, different calcination temperatures might influence the size, morphology and polymorphism of the resulting products, and finally, the catalytic activity.<sup>44</sup> Considering the Ag<sub>2</sub>/eggshell catalyst as the optimum option in the system, we tested its catalytic activity calcined at 300, 400, 500 and 600 °C. As shown in Fig. 8B, the benzene conversion increased as the temperature increased from 300 to 500 °C, but declined significantly as the temperature reached 600 °C. Hence, 500 °C was regarded as the optimal calcination temperature. The TOF<sub>Ag</sub> values were calculated at 190 °C corresponding to the low conversions. It is conducted that the TOF<sub>Ag</sub> (10<sup>-4</sup> s<sup>-1</sup>) values of the samples decreased in the

sequence of Ag<sub>2</sub>/eggshell-500 °C (0.153) > Ag<sub>2</sub>/eggshell-400 °C (0.112) > Ag<sub>2</sub>/eggshell-300 °C (0.080) > Ag<sub>2</sub>/eggshell-600 °C (0.026), which is consistent with the catalytic curves observed in Fig. 8B. Furthermore, it can be seen from the XRD patterns (Fig. S5†) that with the increase of calcination temperature, the peaks belonging Ag NPs tended to become narrow, which demonstrated that the sizes of the generated Ag NPs were increasing. This observation was further confirmed by the SEM images, as shown below.

SEM images and size distributions (insets) of the  $Ag_2/$ eggshell calcined at different temperatures are described in Fig. S6.<sup>†</sup> It can be seen that the spherical Ag NPs were highly distributed on the surfaces of the eggshell supports. The average particle size increased slowly as the calcination temperature increased from 300 to 500 °C, which corresponded to 197.7, 246.5, and 276.3 nm, respectively. Nevertheless, the average particle size of Ag NPs dramatically increased to 402.0 nm when the calcination temperature was 600 °C, which suggested the obvious agglomeration of the Ag NPs at this temperature. In general, the smaller the noble nanoparticles of supported noble metal catalysts, the greater the number of active sites and interfaces, and it will be beneficial to the catalytic activity enhancement. However, according to the H2-TPR analysis in Fig. 6B, as the calcined temperature of the Ag<sub>2</sub>/ eggshell increased, the reduction peaks shifted to higher temperature, which leads to the decrease of catalytic activity. Therefore, the catalytic performance of Ag NP loaded-eggshell catalysts is a comprehensive effect of Ag NP dispersion/size and synergistic effect. Therefore, choosing an available calcination temperature for preparing the catalyst is extremely important to the catalytic activity of the reaction system. As mentioned, the optimal catalytic activity of Ag<sub>2</sub>/eggshell was obtained at 500 °C.

#### 3.3 Stability of the Ag<sub>2</sub>/eggshell catalyst

It is obvious that both the catalytic performance and stability are equally important parameters in various industrial applications. Thus, the durability of the as-prepared Ag<sub>2</sub>/eggshell

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catalyst was determined. As shown in Fig. 9, the benzene conversion remains constant ( $\sim$ 95%) within 200 h of testing, which demonstrated the excellent durability of the catalyst. In order to explore what happened to the catalyst before and after reaction, a series of experiments including SEM, TG/DTG, XRD, XPS and UV-vis DRS are carried out. As indicated in Fig. S7,† all these characterization results of the catalyst after 200 h at 230 °C reaction are much the same as the unreacted one. No obvious changes in terms of textural/surface properties were observed for Ag catalysts after 200 h reaction. Compared to the catalyst before reaction, slight binding energy shifts of Ag 3d and O 1s after reaction were found. The peaks slightly shifted to lower binding energy, assigned to the differential charging effect by the interaction between Ag and the support, as discussed above.19 These results also indicated an optimum stability of the catalyst under long-term reaction conditions.

#### 3.4 Effects of space velocity, water vapor and CO<sub>2</sub>

To meet the requirements of industrial applications, the treatment of VOCs is usually carried out at a high space velocity. Furthermore, the high SV will have an essential influence on the catalytic performances of the Ag/eggshell catalysts. Therefore, the influence of various SV values ranging from 20 000 to 100 000 mL g<sup>-1</sup> h<sup>-1</sup> on the catalytic activity of the Ag<sub>2</sub>/eggshell catalyst was investigated. As shown in Fig. S8,† it is a general fact that benzene conversion and CO<sub>2</sub> yield decreased with the increase of SV at the same reaction temperature. In the case of the biggest SV (100 000 mL  $(g^{-1} h^{-1})$ ), the complete conversion of benzene and total CO<sub>2</sub> yield of Ag<sub>2</sub>/eggshell were obtained at a temperature of about 280 °C, which is lower than that of reported other kinds of catalysts,45,46 revealing the good performances of the Ag/eggshell based catalyst. Moreover, one can see that the benzene conversion is equated with the CO<sub>2</sub> yield on the whole, indicating that benzene is completely oxidized into CO2 over the Ag2/eggshell catalyst, and no byproducts are produced through the catalytic reaction.

It has been generally accepted that water vapor introduced into the feed steam has an important effect on the catalytic



Fig. 9 Benzene conversion as a function of on-stream reaction time over Ag<sub>2</sub>/eggshell. Reaction conditions:  $SV = 20\ 000\ mL\ g^{-1}\ h^{-1}$  and reaction temperature = 230 °C.

activity of the catalysts.35,47 In order to examine the influence of water vapor on the catalytic performance of the Ag<sub>2</sub>/eggshell catalyst, the on-stream benzene oxidation experiments in the presence of 5.0 and 10.0 vol% water vapor were carried out. As shown in Fig. 10A, when the 5.0 vol% water vapor was introduced into the feed steam, the benzene conversion and  $CO_2$ yield were reduced from 98.6 and 98.9% to 83.2 and 77.4%, respectively. When the content of water vapor was further increased to 10.0 vol%, the benzene conversion and CO2 yield decreased to 80.3 and 73.4%, respectively. Thus, with the increase of water vapor content, the conversion is increasingly reduced. However, after water vapor is cut off, the benzene conversion would be restored to the original values again. These results show that the structural integrity of the Ag/eggshell catalyst is kept even for long term water vapor running tests. Obviously, water vapor plays a negative role in catalyzing benzene oxidation, which is attributed to the competitive adsorption between water vapor and benzene.14,35

As another product of benzene oxidation-CO<sub>2</sub>, its effect on benzene conversion was also examined. As can be seen in Fig. 10B, the introduction of 10.0 vol% CO<sub>2</sub> in the feed steam caused a decrease (by ca. 14.4% for 280 °C and ca. 6.5% for 300 °C, respectively) in the catalytic performance of the Ag<sub>2</sub>/ eggshell catalyst. However, the benzene conversion will be almost restored to the original values when the CO2 was cut off. The negative effect might be due to the surface active site deactivation of the Ag<sub>2</sub>/eggshell, which was caused by the formed carbonate species coating. It is noticeable that the benzene conversion decreased about 14.4% for a reaction temperature of 280 °C, compared to 6.5% for 300 °C. The reason is that higher temperature would promote the decomposition rate of carbonate species. The resulting benzene conversion of the CO<sub>2</sub> introduction is a balance of carbonate species accumulation and degradation. These carbonate species would be almost decomposed after CO<sub>2</sub> was cut off, which led to the recovery of the surface active sites of the catalyst. The conversion after the cut off of CO<sub>2</sub> is about 1.9% lower than the original values, suggesting that fewer carbonate species are still on the active sites of the Ag<sub>2</sub>/eggshell catalyst.

# 3.5 Comparison between Ag<sub>2</sub>/eggshell and Ag<sub>2</sub>/com-CaCO<sub>3</sub> catalysts

As shown in Fig. 11, the benzene oxidation conversion was done using  $Ag_2/eggshell$  and  $Ag_2/com-CaCO_3$  catalysts. It is worth noting that both catalysts had the same preparation method and corresponded with the same Ag loading amount (19.9%). From it, one can see that the activity of the Ag\_2/eggshell catalyst significantly outperformed that of the Ag\_2/com-CaCO\_3 catalyst. To find out the possible reason, SEM observation and BET analysis were also performed for the Ag\_2/com-CaCO\_3 catalyst.

As shown in Fig. S9,† the Ag NPs were distributed inhomogeneously on the surface of com-CaCO<sub>3</sub>, and their sizes are either too large or too small. By calculation, the average Ag NP size of the Ag<sub>2</sub>/com-CaCO<sub>3</sub> (627.1  $\pm$  284.3 nm) was much larger than that of the Ag<sub>2</sub>/eggshell (276.3  $\pm$  90.7 nm shown in Fig. S6c†). Therefore, it is concluded that the Ag NPs in the



Fig. 10 Benzene conversion over Ag<sub>2</sub>/eggshell (A) in the presence or absence of water vapor at 280 °C and (B) effects of 10.0 vol% CO<sub>2</sub> at 280 and 300 °C at SV = 100 000 mL g<sup>-1</sup> h<sup>-1</sup>.

Ag/com-CaCO<sub>3</sub> catalyst tended to agglomerate to form oversized particles during the preparation process. The reason for this agglomeration may be due to the difference in the supports. As mentioned above, eggshell is a kind of natural biomaterial containing CaCO<sub>3</sub> and a layer of membrane (proteins and polysaccharides). Thus, the eggshell membrane plays a crucial role in regulating the size and distribution of Ag NPs during the preparation process because of the strong metal-protein bonding interactions.<sup>24,48</sup> In addition, it can be seen from Fig. S10<sup>†</sup> that the eggshell is composed of porous structure characters, which increased the contact area and was beneficial for the reaction gas and energy transmission. In order to explore the textural properties in detail, BET analysis of com-CaCO3 and Ag<sub>2</sub>/com-CaCO<sub>3</sub> was also carried out in comparison. As shown in Fig. S11 and Table S1,<sup>†</sup> the BET surface areas of eggshell and Ag<sub>2</sub>/eggshell are very similar as compared to com-CaCO<sub>3</sub> and  $Ag_2$ /com-CaCO<sub>3</sub>. The difference in the morphology and chemical composition may be the reason for different catalytic activity. On one hand, the oversized Ag NPs will reduce the surface area of the active sites. On the other hand, the interaction between the oversized-Ag NPs and the CaCO<sub>3</sub> support will be significantly weakened, thereby decreasing the catalytic performance.

#### 3.6 In situ FTIR studies

In situ FTIR characterization was performed to explore the intermediate species along with the oxidation of benzene, and the result of the Ag<sub>2</sub>/eggshell catalyst is shown in Fig. 12. It can be observed that the Ag<sub>2</sub>/eggshell catalyst demonstrated similar spectra at different reaction time intervals. The band at 3055 cm<sup>-1</sup> can be assigned to the phenylic C–H vibration of the aromatic ring.49 The band located at 2938 cm<sup>-1</sup> is associated with the C-H stretching vibrations.<sup>50</sup> The band at 1619 cm<sup>-1</sup> can be ascribed to the vibration of the aromatic ring which was adsorbed parallel to the catalyst surface.<sup>51</sup> It is commonly accepted that the band at  $1570 \text{ cm}^{-1}$  should be attributed to the phenolate species.<sup>52</sup> In addition, the band at 1710 cm<sup>-1</sup> can be specially assigned to the C=O from quinone species.53 Besides, the bands at 1306, 1438, and 1519–1542  $cm^{-1}$  are characteristic of maleate species.53 The bands at 1349-1355 cm<sup>-1</sup> (CH<sub>3</sub> stretching vibration) should be assigned to the acetate species.54 Besides, the band at 1400 cm<sup>-1</sup> was attributed to *o*-benzoquinone.<sup>55</sup> Furthermore, the band at 1595 cm<sup>−1</sup> can be assigned to carboxylate species (ring vibrations), derived from the oxidation of the breaking ring.50 These results above are in accordance with previous research on the oxidation of benzene.



Fig. 11 Benzene oxidation catalyzed by the Ag catalysts with different supports as a function of temperature at SV = 100 000 mL g<sup>-1</sup> h<sup>-1</sup>, (A) benzene conversion and (B) CO<sub>2</sub> yield.



Fig. 12 In situ FTIR spectra in a 1000 ppm benzene/40% O<sub>2</sub>/N<sub>2</sub> stream at 260 °C over Ag<sub>2</sub>/eggshell at different times.

In order to determine the source of oxygen required for the initiation step of catalytic benzene oxidation, the in situ FTIR experiments of 1000 ppm benzene/N2 adsorption over the Ag2/ eggshell catalyst at 260 °C were also performed. It can be seen from Fig. S12<sup>†</sup> that four broad bands centered at 3058, 1700, 1495 and 1388 cm<sup>-1</sup> can be observed, respectively. It demonstrated similar band regions, compared to Fig. 12. It is calculated that the band intensities were weaker than the spectra characterized by the 1000 ppm benzene/O2/N2, and the reason may be that the oxygen supply is insufficient in the oxygen-consuming process. Comparing Fig. 12 with Fig. S12,† it is generally accepted that benzene first reacted with the active oxygen species of the catalyst, other than the oxygen gas. When the active oxygen was consumed, the oxygen gas was transformed into active oxygen on the catalysts, thereby achieving the oxygen circulation process of the catalytic performance on the catalyst.

#### 3.7 Reaction mechanism

Combining the characterization discussed above, the reaction mechanisms can be demonstrated in Fig. 13. As is well known,



**Fig. 13** Proposed mechanism for the catalytic benzene oxidation over the Aq<sub>2</sub>/eqgshell catalyst.

Oads species play essential roles during the VOC catalytic oxidation. On the basis of the O 1s spectra and in situ FTIR results (Fig. 12 and S12<sup>†</sup>), it was demonstrated that benzene reacted with the active oxygen species. The surface active oxygen species could be supplemented by gas phase oxygen along with the catalytic benzene oxidation process. Benzene first reacted with the active oxygen species at the Ag-eggshell interface and produced phenolate species (A); the phenolate species possess an oxygen-containing functional group which is reserved as an ortho-para position director and an electron provider.53 Therefore, benzoquinones are further generated through the transformation of the phenolate species (B); as the reaction proceeds, the active oxygen species would give rise to the cleavage of benzene rings resulting in the formation of carboxylate species (C), which are the main intermediate species during the catalytic process; finally, the carboxylate species can further react with active oxygen species into the final products (*i.e.*,  $CO_2$  and  $H_2O)$  (D).

#### 4. Conclusions

Waste eggshells were firstly used as a template and support to prepare Ag/eggshell catalysts, and their application to VOC catalytic oxidation is investigated. The strategy is facile, environmentally friendly and economical. Due to the involvement of biomolecules, the limited-sized Ag NPs were well dispersed on the surface of the eggshell. Compared with the Ag/com-CaCO<sub>3</sub> catalyst, the Ag/eggshell showed an outstanding catalytic oxidation performance towards benzene, which is attributed to the even particle size distribution and channel structures. The optimal parameter of  $T_{90\%}$  with the Ag<sub>2</sub>/eggshell is 257 °C at SV = 100 000 mL g<sup>-1</sup> h<sup>-1</sup>. In addition, it keeps excellent stability even after 200 h of on-stream reaction. The introduction of water vapor into the feed steam induced a decrease in the catalytic activity, and the introduction of CO<sub>2</sub> also led to a decrease in the catalytic activity. However, they did not affect the structure of the catalysts. In situ FTIR results show that carboxylate species are the main intermediate species in the catalytic benzene oxidation, which would be finally oxidized to

the products– $CO_2$  and  $H_2O$ . Based on these results, the reaction mechanism for the catalytic oxidation of benzene over the Ag/ eggshell catalyst was proposed. The present work clearly showed the potential use of waste eggshell-derived Ag catalysts for VOC oxidation and gave us a valuable insight into designing eggshell-based catalysts/supports for industrial applications.

## Conflicts of interest

There are no conflicts to declare.

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### References

- 1 L. Xu, D. Chen, J. Qu, L. Wang, J. Tang, H. Liu and J. Yang, *J. Mater. Chem. A*, 2018, **6**, 17032–17039.
- 2 J. Deng, S. He, S. Xie, H. Yang, Y. Liu, G. Guo and H. Dai, *Environ. Sci. Technol.*, 2015, **49**, 11089–11095.
- 3 W. Zhang, X. Pan, P. Long, X. Liu, X. Long, Y. Yu and Z. Yi, *J. Mater. Chem. A*, 2017, **5**, 18998–19006.
- 4 S. Mo, S. Li, W. Li, J. Li, J. Chen and Y. Chen, *J. Mater. Chem. A*, 2016, 4, 8113–8122.
- 5 Q. Ren, S. Mo, R. Peng, Z. Feng, M. Zhang, L. Chen, M. Fu, J. Wu and D. Ye, *J. Mater. Chem. A*, 2018, **6**, 498–509.
- 6 H. Huang, Y. Xu, Q. Feng and D. Y. C. Leung, *Catal. Sci. Technol.*, 2015, 5, 2649–2669.
- 7 H. Zhao, J. Song, X. Song, Z. Yan and H. Zeng, *J. Mater. Chem. A*, 2015, **3**, 6679–6684.
- 8 Z. Zhang, Z. Jiang and W. Shangguan, *Catal. Today*, 2016, **264**, 270–278.
- 9 H. Yang, C. Ma, Y. Li, J. Wang, X. Zhang, G. Wang, N. Qiao, Y. Sun, J. Cheng and Z. Hao, *Chem. Eng. J.*, 2018, 347, 808– 818.
- 10 C. Chen, Q. Wu, F. Chen, L. Zhang, S. Pan, C. Bian, X. Zheng, X. Meng and F.-S. Xiao, *J. Mater. Chem. A*, 2015, 3, 5556–5562.
- 11 Y. Wang, H. Arandiyan, J. Scott, A. Bagheri, H. Dai and R. Amal, *J. Mater. Chem. A*, 2017, **5**, 8825–8846.
- 12 J. Huang, L. Lin, D. Sun, H. Chen, D. Yang and Q. Li, *Chem. Soc. Rev.*, 2015, **44**, 6330–6374.
- 13 H. Yang, C. Ma, X. Zhang, Y. Li, J. Cheng and Z. Hao, ACS Catal., 2018, 8, 1248–1258.
- 14 Y. Liu, H. Dai, J. Deng, S. Xie, H. Yang, W. Tan, W. Han, Y. Jiang and G. Guo, *J. Catal.*, 2014, **309**, 408–418.
- 15 S. Xie, Y. Liu, J. Deng, X. Zhao, J. Yang, K. Zhang, Z. Han and H. Dai, *J. Catal.*, 2016, **342**, 17–26.

- 16 C. Chen, F. Chen, L. Zhang, S. Pan, C. Bian, X. Zheng, X. Meng and F. S. Xiao, *Chem. Commun.*, 2015, **51**, 5936– 5938.
- 17 Z. Wu, J. Deng, Y. Liu, S. Xie, Y. Jiang, X. Zhao, J. Yang,
   H. Arandiyan, G. Guo and H. Dai, *J. Catal.*, 2015, 332, 13–24.
- 18 M. Manzoli, F. Vindigni, T. Tabakova, C. Lamberti, D. Dimitrov, K. Ivanov and G. Agostini, *J. Mater. Chem. A*, 2017, 5, 2083–2094.
- 19 F. Yang, J. Huang, T. Odoom-Wubah, Y. Hong, M. Du,
   D. Sun, L. Jia and Q. Li, *Chem. Eng. J.*, 2015, 269, 105–112.
- 20 F. Yang, X. Jing, J. Huang, D. Sun and Q. Li, *Ind. Eng. Chem. Res.*, 2015, **54**, 5373–5380.
- 21 X. Jing, J. Huang, H. Wang, M. Du, D. Sun and Q. Li, *Chem. Eng. J.*, 2016, **284**, 149–157.
- 22 B. Bai, Q. Qiao, H. Arandiyan, J. Li and J. Hao, *Environ. Sci. Technol.*, 2016, **50**, 2635–2640.
- 23 H. Einaga and A. Ogata, Environ. Sci. Technol., 2010, 44, 2612.
- 24 M. Nasrollahzadeh, S. M. Sajadi and A. Hatamifard, *Appl. Catal.*, *B*, 2016, **191**, 209–227.
- 25 G. Chen, R. Shan, J. Shi and B. Yan, *Bioresour. Technol.*, 2014, 171, 428–432.
- 26 A. Laca, A. Laca and M. Diaz, *J. Environ. Manage.*, 2017, **197**, 351–359.
- 27 S. J. Abbas, P. V. R. K. Ramacharyulu, H. H. Lo, S. I. Ali and S. C. Ke, *Appl. Catal.*, B, 2017, 210, 276–289.
- 28 R. Mallampati and S. Valiyaveettil, ACS Sustainable Chem. Eng., 2014, 2, 855–859.
- 29 D. P. Yang, S. Chen, P. Huang, X. Wang, W. Jiang, O. Pandoli and D. Cui, *Green Chem.*, 2010, **12**, 2038–2042.
- 30 C. Lee, J.-I. Park, Y.-G. Shul, H. Einaga and Y. Teraoka, *Appl. Catal.*, B, 2015, 174–175, 185–192.
- 31 Y. Huang, W. Fan, B. Long, H. Li, W. Qiu, F. Zhao, Y. Tong and H. Ji, *J. Mater. Chem. A*, 2016, 4, 3648–3654.
- 32 B. Chen, A. S. Susha, C. J. Reckmeier, S. V. Kershaw, Y. Wang,
  B. Zou, H. Zhong and A. L. Rogach, *Adv. Mater.*, 2017, 29, 1604284.
- 33 J. Wang, C. Luo, T. Gao, A. Langrock, A. C. Mignerey and C. Wang, *Small*, 2015, **11**, 473–481.
- 34 X. Ma, M. Zhao, Q. Pang, M. Zheng, H. Sun, J. Crittenden,
   Y. Zhu and Y. Chen, *Appl. Catal.*, A, 2016, 522, 70–79.
- 35 S. Xie, J. Deng, S. Zang, H. Yang, G. Guo, H. Arandiyan and H. Dai, *J. Catal.*, 2015, **322**, 38–48.
- 36 S. Xie, J. Deng, Y. Liu, Z. Zhang, H. Yang, Y. Jiang, H. Arandiyan,
   H. Dai and C. T. Au, *Appl. Catal.*, A, 2015, 507, 82–90.
- 37 Y. Xu, Y. Chen and W. F. Fu, Appl. Catal., B, 2018, 236, 176– 183.
- 38 J. S. Markovski, D. D. Marković, V. R. Đokić, M. Mitrić, M. Đ. Ristić, A. E. Onjia and A. D. Marinković, *Chem. Eng. J.*, 2014, 237, 430–442.
- 39 W. You, Y. Weng, W. Xiu, Z. Zhuang and Y. Yan, ACS Appl. Mater. Interfaces, 2016, 8, 33656–33665.
- 40 Y. Liu, H. Dai, J. Deng, S. Xie, H. Yang, T. Wei, W. Han, J. Yang and G. Guo, *J. Catal.*, 2014, **309**, 408–418.
- 41 X. Jing, H. Wang, H. Chen, J. Huang, Q. Li and D. Sun, *RSC Adv.*, 2014, **4**, 27597–27603.
- 42 D. Sun, H. Wang, G. Zhang, J. Huang and Q. Li, *RSC Adv.*, 2013, **3**, 20732.

- 43 X. She and M. Flytzanistephanopoulos, *J. Catal.*, 2006, 237, 79–93.
- 44 W. Tang, X. Wu, D. Li, Z. Wang, G. Liu, H. Liu and Y. Chen, *J. Mater. Chem. A*, 2014, 2, 2544–2554.
- 45 C. Lee, Y. G. Shul and H. Einaga, *Catal. Today*, 2017, **281**, 460–466.
- 46 W. Tang, Y. Deng and Y. Chen, *Catal. Commun.*, 2017, **89**, 86–90.
- 47 S. Xie, H. Dai, J. Deng, Y. Liu, H. Yang, Y. Jiang, W. Tan, A. Ao and G. Guo, *Nanoscale*, 2013, 5, 11207–11219.
- 48 Y. Gao and C. Xu, Catal. Today, 2012, 190, 107-111.
- 49 S. Zhao, K. Li, S. Jiang and J. Li, *Appl. Catal.*, *B*, 2016, **181**, 236–248.

- 50 X. Wang, Y. Liu, T. Zhang, Y. Luo, Z. Lan, K. Zhang, J. Zuo, L. Jiang and R. Wang, ACS Catal., 2017, 7, 1626–1636.
- 51 S. Pan, H. Lin, J. Deng, P. Chen, X. Chen, Z. Yang and H. Peng, *Adv. Energy Mater.*, 2015, 5, 1401438.
- 52 L. Mino, A. Zecchina, G. Martra, A. M. Rossi and G. Spoto, *Appl. Catal.*, *B*, 2016, **196**, 135–141.
- 53 X. Liu, J. Zeng, W. Shi, J. Wang, T. Zhu and Y. Chen, *Catal. Sci. Technol.*, 2017, 7, 213–221.
- 54 V. V. Kaichev, Y. A. Chesalov, A. A. Saraev, A. Y. Klyushin,
  A. Knop-Gericke, T. V. Andrushkevich and
  V. I. Bukhtiyarov, *J. Catal.*, 2016, 338, 82–93.
- 55 J. Zeng, X. Liu, J. Wang, H. Lv and T. Zhu, *J. Mol. Catal. A: Chem.*, 2015, **408**, 221–227.