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### 1. Introduction

Recently, the legislation has become more strict with regard to emission of industrial volatile organic compounds (VOCs), resulting in an increased attention to removal of VOCs.<sup>1</sup> Benzene, one of the widely utilized aromatic VOCs with high toxicity and significant carcinogenic effect, is harmful to the environment and human health.<sup>2,3</sup> Among the various methods employed for VOC elimination, catalytic combustion is one of the most effective and environmentally friendly pathways due to its advantages of good low-temperature removal efficiency and no secondary pollutant production.<sup>4–8</sup> Hence, it is needed to investigate highly active and stable catalysts for the removal of VOCs.

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# Pd/meso-CoO derived from *in situ* reduction of the one-step synthesized Pd/meso-Co<sub>3</sub>O<sub>4</sub>: highperformance catalysts for benzene combustion<sup>†</sup>

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The chemical state of Pd plays an important role in the catalytic combustion of volatile organic compounds (VOCs). In this work, we adopted a novel one-step modified KIT-6-templating strategy with nitrates of cobalt and palladium as the metal source to successfully synthesize the three-dimensionally ordered mesoporous  $Co_3O_4$ -supported Pd nanoparticles (0.85 wt% Pd/meso- $Co_3O_4$ , denoted as 0.85Pd/meso- $Co_3O_4$ ). The 0.93 wt% Pd/meso-CoO (denoted as 0.93Pd/meso-CoO) and 1.08 wt% Pd/meso- $Co_-CoO$  (denoted as 1.08Pd/meso-Co-CoO) samples were prepared *via in situ* reduction of 0.85Pd/meso- $Co_3O_4$  in a H<sub>2</sub> flow at 200 and 350 °C, respectively. Among these samples, 0.93Pd/meso-CoO exhibited the highest catalytic activity for benzene combustion ( $T_{50\%}$  = 167 °C and  $T_{90\%}$  = 189 °C at a space velocity of 40 000 mL (g h)<sup>-1</sup>). The chemical state of Pd on the 0.93Pd/meso-CoO surface was metallic Pd<sup>0</sup>, which favored oxygen activation to active adsorbed oxygen ( $O_{ads}$ ) species, hence rendering this sample to possess the largest desorption of  $O_{ads}$  species below 400 °C. The intermediates of formate, acetate, maleate, and phenolate were generated *via* the interaction of benzene and  $O_{ads}$  species. We conclude that the excellent catalytic performance of 0.93Pd/meso-CoO was related to the mainly formed Pd<sup>0</sup> species, good oxygen activation ability, and high surface area.

 $Co_3O_4$ , one of the most popular spinel-type metal oxides, is a catalytic material in a number of total oxidation of pollutants (e.g., CO and  $CH_4$  as well as benzene, toluene, and xylene (BTX)) because of its good redox property and low cost.<sup>9-11</sup> It has been proven that Co<sup>2+</sup> species contribute to generation of active O<sub>2</sub><sup>-</sup> and  $O_2^{2-}$  species, which favor the enhancement in catalytic performance.<sup>12</sup> Since a catalytic reaction occurs on the catalyst surface, a rise in surface area could improve catalytic activity. Recently, three-dimensionally (3D) ordered mesoporous Co<sub>3</sub>O<sub>4</sub> has attracted much attention.<sup>12-14</sup> Such material can be synthesized using a facile nanocasting method. The highly ordered mesoporous structure favors dispersion of the noble metals as well as adsorption and diffusion of the reactant molecules. Up to now, many studies have been focused on supported noble metal catalysts, in which Pd-based materials exhibited excellent catalytic activities for organics combustion.<sup>15–19</sup> The loading of Pd on the surface of Co<sub>3</sub>O<sub>4</sub> could generate the noble metal-metal oxide interfaces that were beneficial for improving oxygen activation ability and hence the catalytic activity.<sup>20-23</sup> It has been reported that the PdO-doped mesoporous  $Co_3O_4$  catalyst derived from an *in situ* nanocasting route showed better activity for o-xylene oxidation than the PdO-loaded mesoporous Co<sub>3</sub>O<sub>4</sub> catalyst obtained by the post-impregnation method, which was possibly due to the presence of a large amount of the well-dispersed PdO species in the former sample.<sup>21</sup>



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Pretreatment of a Pd-based catalyst in a reducing  $(H_2)$  or oxidative  $(O_2 \text{ or air})$  atmosphere can induce a change in the chemical state of the Pd species. It has been demonstrated that the reduction pretreatment led to a positive effect on the activity of the Pd-based catalysts for acetylene hydrogenation and VOC oxidation.<sup>16,24</sup> For example, Wang et al.<sup>25</sup> attributed the superior activity of the Al<sub>2</sub>O<sub>3</sub>-, TiO<sub>2</sub>-, SiO<sub>2</sub>-, CeO<sub>2</sub>-, MnO<sub>2</sub>- or Co<sub>3</sub>O<sub>4</sub>-supported catalyst for *o*-xylene combustion to formation of the metallic Pd<sup>0</sup> species. For VOC combustion, the supported Pd catalysts with metallic Pd<sup>0</sup> species were more active than the ones with PdO species.<sup>20</sup> Metallic Pd<sup>0</sup> with a strong ability to adsorb o-xylene was the main phase on mesoporous CoO (meso-CoO), resulting in a high catalytic activity (o-xylene conversion = 90% at 173 °C).<sup>20</sup> However, there is a controversial viewpoint on the effect of the Pd chemical state on VOC combustion. Some authors recognized that the catalysts with a mixture of PdO and Pd<sup>0</sup> performed better than the ones with only Pd<sup>0</sup>.<sup>21,26</sup> Our previous work also found that catalytic activity was associated with the increased amount of Pd<sup>2+</sup> species.<sup>27</sup> Therefore, it is important to investigate active sites of the Pd catalysts supported on meso-Co<sub>3</sub>O<sub>4</sub>.

In one of our previous works,<sup>20</sup> we investigated the role of the interface between Pd and meso-CoO, and found that the highly active Pd-CoO interface was responsible for the excellent catalytic performance of the Pd/meso-CoO sample for o-xylene oxidation. In the present work, however, we focus our attention to the in situ reduction in H<sub>2</sub> at different temperatures of the one-step prepared Pd/meso-Co<sub>3</sub>O<sub>4</sub> (nominal Pd loading was 1 wt%) to Pd/meso-CoO and catalytic benzene combustion mechanisms by the in situ diffuse reflection infrared Fourier transform spectroscopic (DRIFTS) technique, and the reaction mechanisms are discussed and correlated with the chemical state of Pd. It should be pointed out that compared with the Pd/meso-Co<sub>3</sub>O<sub>4</sub> and Pd/meso-CoO samples derived from the traditional impregnation method, those prepared by the one-step approach possessed better Pd dispersion that would enhance the catalytic activity of the as-obtained samples. Furthermore, the one-step approach simplified the preparation procedure, as compared with the traditional two-step fabrication method.

### 2. Experimental

#### 2.1. Catalyst preparation

3D ordered mesoporous silica (KIT-6) was synthesized using the method reported in the literature.<sup>28</sup> The 1 wt% Pd/3D ordered mesoporous  $Co_3O_4$  (1.0Pd/meso- $Co_3O_4$ ) sample was prepared using a modified KIT-6-templating strategy, by which formation of meso- $Co_3O_4$  and loading of Pt nanoparticles (NPs) were achieved concurrently. 1.0 g of KIT-6 was outgassed in a vacuum oven for 3 h and then dispersed in 50 mL of toluene. After the above solution was ultrasonically treated at room temperature for 0.5 h and stirred at 65 °C for 0.5 h, a well ground mixture of 2.0 g of  $Co(NO_3)_2 \cdot 6H_2O$  and 14 mg of Pd( $NO_3)_2 \cdot 2H_2O$  was added to the above solution at 65 °C, and the mixture was stirred for 3 h. After filtering and drying at

120 °C for 12 h, a brown powder was obtained which was thermally treated in a muffle furnace at a heating rate of 1 °C min<sup>-1</sup> from room temperature to 450 °C and kept at 450 °C for 4 h. The silica template was removed using a hot (80 °C) sodium hydroxide aqueous solution (2.0 mol  $L^{-1}$ ). After filtering, washing with deionized water and ethanol three times, and drying at 70 °C for 12 h, the Pt/meso-Co<sub>3</sub>O<sub>4</sub> sample was obtained. The Pt/meso-Co<sub>3</sub>O<sub>4</sub> sample was pretreated in a 3.5 vol% H<sub>2</sub>/96.5 vol% Ar flow of 30 mL min<sup>-1</sup> at 200 or 350 °C for 1 h. The X-ray diffraction (XRD) patterns demonstrate that the cobalt oxide support was reduced at 200 and 350 °C to CoO and Co-CoO, respectively. We used the inductively coupled plasma-atomic emission spectroscopic (ICP-AES) technique to measure the actual Pd contents in the samples, and the results showed that the actual Pd loadings in the three samples were 0.85, 0.93, and 1.08 wt%, respectively, and they were denoted as 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, 0.93Pd/meso-CoO, and 1.08Pd/meso-Co-CoO, respectively.

#### 2.2. Catalyst characterization

Physicochemical properties of the samples were characterized using the ICP–AES, XRD, TEM, HAADF-STEM, EDX, BET, XPS, Raman, H<sub>2</sub>-TPR, O<sub>2</sub>-TPD, and *in situ* DRIFTS techniques. The detailed characterization procedures can be found in the ESI.†

#### 2.3. Catalytic activity evaluation

We evaluated the catalytic activities of the samples in a continuousflow fixed-bed quartz tubular microreactor (i.d. = 6.0 mm). A gas mixture containing 1000 ppm benzene + 20 vol%  $O_2$  +  $N_2$  (balance) at a total flow of 33.3 mL min<sup>-1</sup> was fed into the microreactor, in which 0.5 g of the catalyst (40–60 mesh) was diluted with 1.5 g of quartz sand (40–60 mesh), giving rise to a space velocity (SV) of *ca.* 40 000 mL (g h)<sup>-1</sup>. The 1000 ppm benzene gas was generated using a  $N_2$  flow that was bubbled in a saturator filled with liquid benzene at 6 °C. The reactants and products were online analyzed on a Shimadzu GC-14C apparatus. The detailed procedures are described in the ESI.†

### Results and discussion

#### 3.1. Catalytic performance

The catalytic activities of the samples for benzene combustion are shown in Fig. 1. We used the temperatures  $T_{10\%}$ ,  $T_{50\%}$ , and  $T_{90\%}$  (which corresponded to benzene conversions of 10, 50, and 90%) to evaluate the activities of the samples. As revealed by the data in Fig. 1 and Table 1, catalytic activity dropped in the order of 0.93Pd/meso-CoO > 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> > 1.08Pd/meso-Co–CoO. The 0.93Pd/meso-CoO sample showed the highest activity ( $T_{10\%}$  = 142 °C,  $T_{50\%}$  = 167 °C, and  $T_{90\%}$  = 189 °C), while the 1.08Pd/meso-Co–CoO sample exhibited the lowest activity ( $T_{10\%}$  = 187 °C,  $T_{50\%}$  = 246 °C, and  $T_{90\%}$  = 275 °C) at SV = 40 000 mL (g h)<sup>-1</sup>. The above results demonstrate that the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample obtained after reduction at 200 °C was much more active than the unreduced sample or the sample obtained after reduction at 350 °C. We detected the products of benzene combustion, and the CO<sub>2</sub> yields were



**Fig. 1** (A) Benzene conversion as a function of temperature, (B)  $T_{10\%}$ ,  $T_{50\%}$ , and  $T_{90\%}$ , (C) CO<sub>2</sub> yield over 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, 0.93Pd/meso-CoO, and 1.08Pd/meso-Co–CoO for benzene oxidation, and (D) benzene conversion as a function of on-stream reaction time over 0.93Pd/meso-CoO for benzene oxidation at 170 °C and SV = 40 000 mL (g h)<sup>-1</sup>.

Table 1	Catalytic	activities	over	the	samples	at	SV =	40,000	ml	$(a h)^{-}$
Tuble 1	Cututytic	activities	Over	uic.	Jumpics	u	5	10 000		(g ii)

	Benze tempe	ne oxida rature	ition	CO <sub>2</sub> yield temperature			
Sample	<i>T</i> <sup>10%</sup> (°C)	<i>T</i> <sub>50%</sub> (°C)	<i>T</i> 90% (°C)	<i>T</i> <sup>10%</sup> (°C)	<i>T</i> <sub>50%</sub> (°C)	<i>T</i> 90% (°C)	
0.85Pd/meso-Co <sub>3</sub> O <sub>4</sub> 0.93Pd/meso-CoO 1.08Pd/meso-Co-CoO	160 142 187	197 167 246	214 189 275	162 147 200	200 168 250	220 192 280	

calculated, as shown in Fig. S1 and Fig. 1C (ESI<sup>†</sup>).  $CO_2$  yield rose with increasing temperature, which was similar to the tendency in benzene conversion. As shown in Table 1, lower temperature was required for benzene conversion than for  $CO_2$ yield, which was consistent with the results reported in the literature.<sup>29,30</sup> Liu *et al.*<sup>29</sup> analyzed the compositions of the effluent gases on a GC–MS apparatus when benzene conversion was less than 20%, and found that 5-hexen-1-ol, phenol, and malic acid were the main byproducts of the partial oxidation of benzene; in the meanwhile some unidentified organics with high molecular weights were also detected. These unidentified organics tended to form carbon deposit, leading to higher temperatures required for deep oxidation of benzene. In addition, no significant loss in activity was detected over 0.93Pd/meso-CoO after 10 h of on-stream benzene oxidation (Fig. 1D), indicating that this sample was catalytically stable. A piece of evidence for such a deduction was from one of our previously reported works, in which the *in situ* XRD results demonstrated that CoO was not oxidized to Co<sub>3</sub>O<sub>4</sub> after CoO was pretreated in air at 270 °C for 1 h.<sup>12</sup> That is to say, the phase of CoO in 0.93Pd/meso-CoO was stable in an oxidative atmosphere below 270 °C.

The TOF<sub>Pd</sub> (TOF<sub>Pd</sub> =  $xC_0/n_{Pd}$ , where x,  $C_0$  (mol s<sup>-1</sup>), and  $n_{Pd}$  (mol) are the benzene conversion at 160 °C, initial benzene

concentration per second, and Pd molar amount, respectively) and specific reaction rates were calculated according to the activity data and Pd molar amounts, as summarized in Table S1 (ESI<sup>†</sup>). Obviously, 0.93Pd/meso-CoO showed a catalytic activity (TOF\_{Pd} = 1.46  $\times$   $10^{-3}~s^{-1}$  and specific reaction rate = 13.74  $\mu$ mol (g<sub>Pd</sub> s)<sup>-1</sup>) much higher than that over 0.85Pd/ meso-Co\_3O\_4 (TOF\_{Pd} = 0.62  $\times$   $10^{-3}~s^{-1}$  and specific reaction rate = 5.85  $\mu$ mol (g<sub>Pd</sub> s)<sup>-1</sup>) and 1.08Pd/meso-Co–CoO (TOF<sub>Pd</sub> =  $0.07 \times 10^{-3} \text{ s}^{-1}$  and specific reaction rate = 0.62 µmol (g<sub>Pd</sub> s)<sup>-1</sup>), respectively. Summarized in Table S1 (ESI<sup>+</sup>) are the activities of the supported noble metal catalysts reported in the literature. It can be observed that the TOF<sub>Pd</sub> (1.46  $\times$  10<sup>-3</sup> s<sup>-1</sup>) and specific reaction rate (13.74  $\mu mol~(g_{Pd}~s)^{-1})$  at 160  $\,^\circ C$  over 0.93Pd/meso-CoO were significantly higher than those over 6.5Au/meso-Co<sub>3</sub>O<sub>4</sub> (0.33  $\times$  10<sup>-3</sup> s<sup>-1</sup> and 1.68  $\mu$ mol (g<sub>Pd</sub> s)<sup>-1</sup>),<sup>31</sup>  $0.53 Pd/Co_{3}O_{4}~(0.30~\times~10^{-3}~s^{-1}$  and 2.82  $\mu mol~(g_{Pd}~s)^{-1}),^{32}$  and K/Ag-OMS-40 (1.28  $\times$  10<sup>-3</sup> s<sup>-1</sup> and 11.90  $\mu$ mol (g<sub>Pd</sub> s)<sup>-1</sup>),<sup>5</sup> but lower than those over 1.0Pd/Al<sub>2</sub>O<sub>3</sub> ( $2.72 \times 10^{-3}$  s<sup>-1</sup> and 24.37  $\mu$ mol (g<sub>Pd</sub> s)<sup>-1</sup>).<sup>5</sup>

In practical applications, the effects of  $H_2O$  and  $CO_2$  on the activity of a catalyst should be taken into account. Benzene combustion over 0.93Pd/meso-CoO was carried out when 3.0 or 5.0 vol%  $H_2O$  was introduced into the reaction system. It is seen from Fig. 2 that addition of 3.0 or 5.0 vol%  $H_2O$  to the feedstock at 185 °C led to a decrease of 5–8% in benzene conversion. Nevertheless, benzene conversion was recovered to its original levels after water vapor was cut off. It has been reported that there was a reversible inhibition on VOC oxidation by water, and the significant drop in activity was induced by competitive adsorption of  $H_2O$  and VOC molecules.<sup>4,33,34</sup> After 5.0 vol% CO<sub>2</sub> was introduced into the reaction system, a slow decrease in benzene conversion from 86 to 75% was observed. Even if CO<sub>2</sub> was removed from the feed stream, benzene conversion was maintained at 77%. Wang *et al.*<sup>35</sup> pointed out that the



Fig. 2 Effects of (a) 3.0 or 5.0 vol% H<sub>2</sub>O, (b) 5.0 vol% CO<sub>2</sub>, and (c) 3.0 vol% H<sub>2</sub>O + 5.0 vol% CO<sub>2</sub> on benzene conversion over the 0.93Pd/meso-CoO sample at 185 °C and SV = 40 000 mL (g h)<sup>-1</sup>.

carbonate species formed on the surface of the catalyst resulted in a loss in activity, and such a deactivation induced by  $CO_2$  was reversible. In the case of simultaneous addition of 3.0 vol% H<sub>2</sub>O and 5.0 vol% CO<sub>2</sub>, the changing trend in activity was rather similar to that in the presence of 5.0 vol% CO<sub>2</sub>. Therefore, the above results reveal that addition of H<sub>2</sub>O and/or CO<sub>2</sub> to the feedstock induced a negative impact on benzene combustion.

#### 3.2. Crystal structure and textural property

The XRD, Raman, N<sub>2</sub> adsorption-desorption, HRTEM, and HAADF-STEM techniques were used to characterize the crystal phase compositions, morphologies, and textural properties of the samples. The small-angle XRD pattern (Fig. S2 (ESI<sup>+</sup>)) of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> showed significant diffraction peaks in the region of  $2\theta = 0.8-2.8^{\circ}$  assignable to the (211) and (332) crystal planes, indicative of formation of a good-quality ordered mesoporous structure. There were well-resolved reflections in the wide-angle XRD pattern (Fig. 3) of the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample, which were assignable to the cubic Co<sub>3</sub>O<sub>4</sub> phase (JCPDS 74-1657). After 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> was pretreated in H<sub>2</sub> at 200 °C, the obtained 0.93Pd/meso-CoO sample displayed a decreased ordering of the mesoporous structure due to the disappearance of the (322) crystal phase in the low-angle XRD pattern. Meanwhile, the wide-angle pattern of 0.93Pd/meso-CoO showed two weak diffraction peaks at  $2\theta = 36.6^{\circ}$  and  $42.5^{\circ}$ . indicating the formation of the cubic CoO or  $CoO_x$  phase (JCPDS 48-1719).<sup>12</sup> For the 1.08Pd/meso-Co-CoO sample, new peaks at  $2\theta = 44.2^{\circ}$  and 75.8° appeared, which were assignable to the metallic Co<sup>0</sup> phase (JCPDS 15-0806), although the CoO or  $CoO_x$  phase was still detected. No significant signals were recorded in the low-angle XRD pattern of 1.08Pd/meso-Co-CoO, suggesting that most of the ordered mesoporous structure was damaged after treatment in H<sub>2</sub> at 350 °C. We detected five characteristic bands at 193, 477, 516, 617, and 687  $\text{cm}^{-1}$  in the Raman spectrum (Fig. S3 (ESI<sup>†</sup>)) of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, which were attributable to the  $F_{2g}(1)$ ,  $E_g$ ,  $F_{2g}(2)$ ,  $F_{2g}(3)$ , and  $A_{1g}$ symmetries of Co<sub>3</sub>O<sub>4</sub>,<sup>11</sup> respectively. Obviously, the reduction treatment exerted a significant impact on the Raman spectrum



Fig. 3 Wide-angle XRD patterns of the samples.

of the sample. After reduction of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, the Raman signals were weakened. There was a significant red shift (*ca.* 12 cm<sup>-1</sup>) in the A<sub>1g</sub> symmetry of the 0.93Pd/meso-CoO sample (at 675 cm<sup>-1</sup>), which was much lower than that of the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample. The results demonstrate that lattice distortion and residual stress of the spinel crystal were generated during the reduction process.<sup>11,36</sup> Theoretically, a more amount of oxygen vacancies can be formed due to more lattice defects, which would favor activation of O<sub>2</sub> to the active oxygen adspecies and hence greatly enhance the activity of a catalyst.

The 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> and 0.93Pd/meso-CoO samples displayed an IV-type N<sub>2</sub> adsorption–desorption isotherm and a H1-type hysteresis loop (Fig. 4), suggesting formation of an ordered mesoporous structure. The hysteresis loop of the 0.93Pd/meso-CoO sample was slightly shifted to the higher relative pressure, a result possibly due to partial sintering of the mesoporous structure.<sup>12</sup> The average pore diameter of the 0.93Pd/meso-CoO sample was 5.0 nm, which was similar to that (4.8 nm) of the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample. Summarized in Table 2 are textural parameters of the samples. BET surface areas of the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, 0.93Pd/meso-CoO, and 1.08Pd/meso-Co–CoO samples were 91.2, 88.5, and 52.6 m<sup>2</sup> g<sup>-1</sup>, respectively. The results indicate that the reduction treatment induced an obvious change in the mesoporous structure.

TEM images (Fig. S4 (ESI<sup>†</sup>)) of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, 0.93Pd/meso-CoO, and 1.08Pd/meso-Co–CoO show highly ordered mesopore arrays. A rise in reduction temperature to 350 °C resulted in significant agglomeration of Pd nanoparticles (NPs) and enlargement in mesopore diameter. It should be noted that no distinct Pd NPs could be seen in the TEM image of the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> or 0.93Pd/meso-CoO sample. Fig. 5 shows HAADF-STEM images and element mappings of the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> and 0.93Pd/meso-CoO samples. Apparently, Pd

NPs were well distributed on the surface of each sample and no significant Pd NP agglomeration was observed.

#### 3.3. Surface property

Illustrated in Fig. 6 are the Co 2p<sub>3/2</sub>, Pd 3d, and O 1s XPS spectra of the samples, and their surface parameters are listed in Table 2. The asymmetrical Co 2p<sub>3/2</sub> XPS spectrum (Fig. 6A) of each sample contained three components at BE = 779.8 eV (assignable to the surface  $Co^{3+}$  species), 781.8 eV (attributable to the surface  $Co^{2+}$  species), and 786.2 eV (the shake-up satellite of Co<sup>2+</sup>).<sup>27</sup> After reduction of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> at 200 or 350 °C, the surface  $Co^{2+}/Co^{3+}$  molar ratio rose from 0.58 to 0.86, *i.e.*, the surface  $Co^{2+}$  concentration increased. That is to say, compared with the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample, the reduced samples showed a more amount of oxygen vacancies on the surface. The asymmetrical Pd 3d XPS spectrum of the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample (Fig. 6B) was decomposed into four components at BE = 335.3 and 340.5 eV (attributed to the surface Pd<sup>0</sup> species) and 336.9 and 342.2 eV (assigned to the surface Pd<sup>2+</sup> species).<sup>16,19,27</sup> Only Pd<sup>0</sup> species, however, were detected on the surface of 0.93Pd/meso-CoO and 1.08Pd/meso-Co-CoO. The above results confirm that the H<sub>2</sub> pretreatment exerted a significant influence on the oxidation state of the surface metals. The asymmetrical O 1s XPS spectrum of each sample (Fig. 6C) was deconvoluted into three components at BE = 529.0, 530.9, and 532.7 eV, which could be assignable to the surface lattice oxygen (O<sub>latt</sub>), adsorbed oxygen (O<sub>ads</sub>, e.g., O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup> or O<sup>-</sup>), and hydroxyl and/or carbonate species,<sup>27</sup> respectively. The Oads/Olatt molar ratio increased in the sequence of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> (0.85) < 0.93Pd/meso-CoO (1.52) < 1.08Pd/meso-Co-CoO (2.68) (Table 2). It was reported that the more the surface oxygen vacancy amount, the easier the activation of O<sub>2</sub>, leading to better performance for VOC combustion.<sup>19,20</sup> The higher O<sub>ads</sub> concentration is an indication



Fig. 4 (A) Nitrogen adsorption-desorption isotherms and (B) pore-size distributions of (a) 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, (b) 0.93Pd/meso-CoO, and (c) 1.08Pd/meso-Co-CoO.

Table 2 BET surface area, pore size, pore volume, Pd content, surface element composition, H<sub>2</sub> consumption, and oxygen desorption of the samples

	Textural parameter				Surface elem	ient	$H_2$ consumption (mmol g <sup>-1</sup> )	Oxygen desorption $(\mu mol g^{-1})$	
Sample	Surface area $(m^2 g^{-1})$	Pore size (nm)	Pore volume $(cm^3 g^{-1})$	Pd content (wt%)	Co <sup>2+</sup> /Co <sup>3+</sup> molar ratio	O <sub>ads</sub> /O <sub>latt</sub> molar ratio	Above 200 $^{\circ}\mathrm{C}$	Below 400 °C	Above 400 $^{\circ}C$
0.85Pd/meso-Co <sub>3</sub> O <sub>4</sub>	91.2	4.8	0.17	0.85	0.58	0.85	16.12	7.0	33.8
0.93Pd/meso-CoO	88.5	5.0	0.15	0.93	0.70	1.51	15.19	37.1	10.6
1.08Pd/meso-Co-CoO	52.6	10.0	0.13	1.08	0.86	2.68	8.49	17.4	7.4



Fig. 5 HAADF-STEM images and elemental mappings of (a-d) 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> and (e-h) 0.93Pd/meso-CoO.

that the reduction favored formation of the active oxygen species, hence enhancing the catalytic activity of the sample. As demonstrated above, the 1.08Pd/meso-Co–CoO sample exhibited the highest molar ratios of surface  $\text{Co}^{2+}/\text{Co}^{3+}$  (0.86) and  $O_{ads}/O_{latt}$  (2.68). However, the 0.93Pd/meso-CoO sample performed the best for benzene combustion. This fact clearly suggests that other factors might govern the activity of the sample except for oxygen activation ability and  $O_{ads}$  species concentration. In our present work, the 350 °C-reduction pretreatment of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> resulted in the 1.08Pd/meso-Co–CoO sample with the lowest surface area, which was possibly associated with its worst activity for benzene combustion.

#### 3.4. Redox property

Illustrated in Fig. 7A are the H<sub>2</sub>-TPR profiles of the as-prepared samples. The 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample showed three peaks at 130 °C (peak I), 300 °C (peak II), and 375 °C (peak III), which were the reduction of PdO to Pd<sup>0</sup>, Co<sup>3+</sup> to Co<sup>2+</sup>, and Co<sup>2+</sup> to Co<sup>0</sup>, respectively. The H<sub>2</sub> reduction treatment brought about a significant change in reduction behavior. Firstly, the peak at 130 °C owing to PdO reduction in 0.93Pd/meso-CoO and 1.08Pd/meso-Co-CoO disappeared, indicating that Pd was present in metallic Pd<sup>0</sup>. Secondly, the lower temperatures were

required for reduction from  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  or from  $\text{Co}^{2+}$  to  $\text{Co}^{0}$  in 0.93Pd/meso-CoO and 1.08Pd/meso-Co-CoO. Dacquin et al.37 reported the reduction of Co<sup>3+</sup> to Co<sup>2+</sup> at *ca.* 200 °C due to the H<sub>2</sub> spillover effect. In the present work, the H<sub>2</sub> spillover effect could also exist in the reduction of  $Co^{3+}$  to  $Co^{2+}$  or  $Co^{2+}$  to  $Co^{0-}$ . Quantitative analysis of the reduction peaks above 200 °C in the H<sub>2</sub>-TPR profiles can obtain H<sub>2</sub> consumption of the samples (Table 2). Theoretically speaking, the H<sub>2</sub> consumption is 13.33 and 18.07 mmol  $g^{-1}$  supposing that the Co ions in cobalt oxide are present in the form of only Co<sup>2+</sup> and only Co<sup>3+</sup> and are reduced to  $Co^0$ , respectively. Apparently, the H<sub>2</sub> consumption corresponding to the reduction peaks above 200 °C was 13.33–18.07 mmol  $g^{-1}$  (Table 2). This result suggests that cobalt ions in these samples were present in mixed oxidation states (*i.e.*,  $Co^{3+}$  and  $Co^{2+}$ ), which was in good consistency with the reported results.<sup>38</sup> More importantly, H<sub>2</sub> consumption (16.12 mmol  $g^{-1}$ ) of 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> was higher than that (15.19 mmol  $g^{-1}$ ) of 0.93Pd/meso-CoO, revealing that there was a less amount of  $Co^{3+}$  in the latter than in the former.  $H_2$ consumption (8.49 mmol g<sup>-1</sup>) of the 1.08Pd/meso-Co-CoO sample, however, decreased dramatically, indicating that part of Co<sup>3+</sup> and/or Co<sup>2+</sup> were reduced to Co<sup>0</sup>. On the basis of the H2-TPR results, we can realize that PdO could be reduced to metallic Pd<sup>0</sup> in 3.5 vol% H<sub>2</sub>/96.5 vol% Ar below 200 °C, but most



Fig. 6 (A) Co 2p<sub>3/2</sub>, (B) Pd 3d, and (C) O 1s XPS spectra of (a) 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, (b) 0.93Pd/meso-CoO, and (c) 1.08Pd/meso-Co-CoO.



Fig. 7 (A) H<sub>2</sub>-TPR and (B) O<sub>2</sub>-TPD profiles of (a) 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, (b) 0.93Pd/meso-CoO, and (c) 1.08Pd/meso-Co-CoO.

of the  $\text{Co}^{3^+}$  and  $\text{Co}^{2^+}$  species were retained in the 0.93Pd/meso-CoO sample. Some authors proposed that the samples with high amounts of the  $\text{Co}^{2^+}$  species and high  $O_{ads}$  species concentrations possessed more amounts of oxygen vacancies, which were beneficial for the activation of gas-phase oxygen to active  $O_{ads}$  species. It is known that oxygen is involved in adsorption, activation, consumption, and replenishment in VOC combustion over a catalyst. The active oxygen species were vital in the oxidation of intermediates on the catalyst surface.<sup>13,27,39</sup> Hence, the more the  $\text{Co}^{2+}$  and  $O_{\text{ads}}$  species in/on the sample, the better the catalytic activity for the redox-involving reactions (*e.g.*, benzene combustion). The 1.08Pd/meso-Co–CoO sample

contained a large amount of inactive Co<sup>0</sup> species that resulted in a decrease of catalytic activity. Moreover, the poor mesoporous structure and low surface area were also accountable for the drop in the catalytic activity of 1.08Pd/meso-Co–CoO.

To further investigate the nature and amounts of different oxygen species, we recorded the O<sub>2</sub>-TPD profiles of the samples (Fig. 7B). According to the literature,<sup>9,11,39</sup> the peaks below 400 °C were due to desorption of the O<sub>ads</sub> species, the ones in the range of 400-500 °C were ascribed to desorption of the coordinately unsaturated surface O<sub>latt</sub> species, and the ones above 700 °C were assigned to desorption of the coordinately saturated O<sub>latt</sub> species. For the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample, the peaks at 165 and 280 °C were assignable to desorption of the O<sub>ads</sub> species, whereas the one at 810 °C was attributable to desorption of the O<sub>latt</sub> species in Co<sub>3</sub>O<sub>4</sub>. Differently from the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample, 0.93Pd/meso-CoO showed three strong oxygen desorption signals at 160, 305, and 348 °C, assignable to desorption of the Oads species in the different coordination environments. In addition, a desorption peak appeared at 439 °C, which was assignable to desorption of lattice oxygen in CoO. We observed similar oxygen desorption profiles in the 1.08Pd/meso-Co-CoO sample. It should be pointed out that no apparent signals attributable to desorption of lattice oxygen at 810 °C were recorded in the 0.93Pd/meso-CoO and 1.08Pd/meso-Co-CoO samples, indicating that the Co<sub>3</sub>O<sub>4</sub> phase was converted to the CoO and/or Co phase. We quantitatively analyzed the oxygen desorption of the samples in a certain temperature range (Table 2). Desorption of the O<sub>ads</sub> species below 400 °C significantly increased after the H<sub>2</sub> reduction pretreatment, and the changing trend decreased in the sequence of 0.93Pd/meso-CoO (37.1  $\mu$ mol g<sup>-1</sup>) > 1.08Pd/ meso-Co-CoO (17.4  $\mu$ mol g<sup>-1</sup>) > 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> (7.0  $\mu$ mol g<sup>-1</sup>). The desorbed oxygen species could be ascribed to the Oads species bound to the Co<sup>3+</sup> sites since the Co<sup>2+</sup> species were first easily oxidized into the Co<sup>3+</sup> species by gas-phase O<sub>2</sub> and then the surface oxygen species were bound to the Co<sup>3+</sup> sites.

# 3.5. Possible intermediates formed during the benzene oxidation process

The in situ DRIFTS characterization was performed to determine the intermediate species generated on the surface of the samples, so that benzene combustion mechanisms could be investigated. In situ DRIFTS spectra (Fig. S5 and S6 (ESI<sup>+</sup>)) of the samples were collected as a function of time after 1000 ppm benzene + N2 (balance) was introduced into the reaction cell at 150 °C. With the introduction of benzene, numerous absorption bands were recorded. The absorption bands cannot be distinguished precisely in the region of 1800–1100 cm<sup>-1</sup> since a large number of different species have overlapping absorption bands in this region. On the basis of the assignments reported in the literature (Table S2 (ESI<sup>+</sup>)), we can tentatively assign all of the absorption bands of the samples. The bands at 3657-3705, 1700-2000, and 600-1100  $\text{cm}^{-1}$  were due to the adsorbed gaseous benzene (not shown),<sup>13</sup> the one at 1596  $\text{cm}^{-1}$  was attributed to the anti-symmetric vibration of C-O in the formate species,40 the ones at 1555-1565 cm<sup>-1</sup> were ascribed to the

anti-symmetric vibration of C-O in the acetate species,12,41,42 the ones at 1532 and 1307 cm<sup>-1</sup> were due to the maleate species,<sup>42–44</sup> the one at 1400 cm<sup>-1</sup> (which was slightly shifted to 1422 cm<sup>-1</sup>) was attributed to the symmetric vibration of C–O in the acetate species,<sup>12,42</sup> the ones at 1481–1493 and 1443 cm<sup>-1</sup> were ascribable to the skeletal C-C vibration,<sup>40,44,45</sup> and the one at 1469 cm<sup>-1</sup> were attributable to the C–H deformation vibration of the aromatic ring,  $^{40,44,45}$  and the one at 1242 cm<sup>-1</sup> was assignable to the surface phenolate species.42 It is clearly seen that the intensity of these absorption bands of the 0.93Pd/meso-CoO sample increased monotonically with the exposure time, indicating that the organic byproducts were accumulated on the sample surface. Partially oxidized products (e.g., acetate, maleate, formate, and phenolate species) were formed during the adsorption treatment process in the absence of O2, suggesting involvement of the Oads species in the benzene combustion process. Up to now, there have been a number of research works on the role of surface oxygen species in the catalytic oxidation of organic compounds in the literature.<sup>39,42,46-48</sup> Some authors attributed the cleavage of the benzene ring to the amount of the electrophilic  $O_{ads}$  ( $O_2^-$ ,  $O_2^{2-}$  or  $O^-$ ) species, and thought that oxidation of small carboxylate molecules was associated with the oxidation ability of the nucleophilic Olatt species.<sup>39,48</sup> As discussed in the XPS characterization results, H<sub>2</sub> reduction pretreatment increased the amount of O<sub>ads</sub> species in the 0.93Pd/meso-CoO sample, and the enhanced Oads species could efficiently attack the adsorbed benzene molecules to form the products in the absence of gas-phase oxygen. It should be pointed out that the surface Olatt species with highly negative charge and nucleophilic property could favor the oxidation of carboxylates.

When the atmosphere was switched from benzene to  $N_2$  and after  $N_2$  purging for 1 h, the absorption bands attributable to the gaseous benzene molecules and aromatic ring disappeared. Acetate, maleate, and phenolate species were retained in the flow of  $N_2$  (Fig. S7 (ESI†)). The same process of benzene adsorption on the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample was carried out and the *in situ* DRIFTS spectra were recorded. It is seen that there were absorption bands attributable to the acetate, maleate and phenolate species after  $N_2$  purging, similar to the *in situ* DRIFTS spectra of the 0.93Pd/meso-CoO sample. Hence, it can be concluded that benzene underwent the same activation pathway on the surface of the two samples.

The benzene-adsorbed 0.93Pd/meso-CoO sample was then consecutively exposed to a flow of  $O_2$  to testify the reactivity of the formed intermediates at different temperatures. As shown in Fig. 8A, there were slight decreases in the intensity of the *in situ* DRIFTS signals (especially in the intensity of the signal due to the acetate species). This observation suggests that the  $O_{ads}$  species generated from  $O_2$  activation reacted with the intermediates, and the reactivity of the acetate species was higher than that of the other intermediates.<sup>45</sup> Moreover, no new absorption bands were recorded, indicating that the intermediates had already been generated *via* the interaction of benzene and  $O_{ads}$  species. When the temperature was increased to 180 or 200 °C, these intermediate bands became weak in intensity or



Fig. 8 In situ temperature-dependent DRIFTS spectra of (A) 0.93Pd/meso-CoO and (B) 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> in a 20 vol% O<sub>2</sub> (N<sub>2</sub> as balance) flow after benzene pre-adsorption at 150  $^{\circ}$ C.

even disappeared. The decreasing trend in the intensity of the species in the 1800–1100 cm<sup>-1</sup> region suggests that these species were the main intermediates in the catalytic combustion of benzene, and that they were further catalytically oxidized into  $CO_2$  and  $H_2O$ . This finding coincided with that reported by other researchers.<sup>12</sup> Comparatively, the intermediates formed on the 0.85Pd/meso- $CO_3O_4$  sample disappeared at a higher temperature (Fig. 8B). This result well explained the changing trend in the catalytic activity of the samples. Therefore, we conclude that the 0.93Pd/meso-CoO sample favored the dissociative adsorption of  $O_2$  at a lower temperature, as demonstrated by the  $O_2$ -TPD and XPS results.

In order to distinguish the impacts of  $O_{ads}$  and gas-phase  $O_2$ , in situ DRIFTS experiments on the 0.93Pd/meso-CoO and 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> samples after benzene pre-adsorption at 150 °C were carried out by elevating the temperature in a N<sub>2</sub> atmosphere (Fig. 9). It is noteworthy that the two samples displayed similar DRIFTS spectra with only slightly decreased intensity at 180 and 200 °C, as compared with that at 150 °C. At 250 °C, however, all of the absorption bands disappeared. The results demonstrate that the intermediate species were stable below 200  $^{\circ}$ C, and could react with the O<sub>ads</sub> species at 250  $^{\circ}$ C to generate CO<sub>2</sub> and H<sub>2</sub>O.

Furthermore, the integral DRIFTS area of the representative acetate species centered at 1422-1400 cm<sup>-1</sup> was plotted as a function of time, as shown in Fig. 10 and 11. After making a quantitative analysis (Fig. 10A), one can know that the acetate formation rate was higher over 0.93Pd/meso-CoO than that over 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub>, implying that the metallic Pd<sup>0</sup> species possessed a stronger benzene activation ability than the oxidized Pd species. It is reasonably inferred from Fig. 10B and 11 that the atmosphere exerted a little effect on the formation of the acetate species at 150  $^{\circ}$ C, but further introducing O<sub>2</sub> resulted in a decrease in the intensity of the acetate species due to their reaction. The integral DRIFTS area of each sample also declined with the elevated temperature (Fig. 11A and B). Finally, the band at 1422-1400 cm<sup>-1</sup> disappeared over 0.93Pd/ meso-CoO at 200 °C and over 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> at 250 °C, indicating that the acetate species were completely eliminated.



Fig. 9 In situ temperature-dependent DRIFTS spectra of (A) 0.93Pd/meso-CoO and (B) 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> in a N<sub>2</sub> flow after benzene pre-adsorption at 150 °C.



**Fig. 10** Time-dependent trends of integral DRIFTS areas corresponding to the acetate species (at 1400–1422 cm<sup>-1</sup>) on the samples in a flow of (A) 1000 ppm benzene +  $N_2$  (in the range of 1–60 min) and (B)  $N_2$  (in the range of 61–120 min).



Fig. 11 Time-dependent trends of integral DRIFTS areas corresponding to the acetate species (at 1400–1422 cm<sup>-1</sup>) on (A) 0.93Pd/meso-CoO and (B) 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> in a flow of 20 vol%  $O_2 + N_2$  at different temperatures.

By combining the above *in situ* DRIFTS results as well as those reported in the literature, we propose the five-step catalytic benzene oxidation mechanism over the cobalt oxidesupported Pd samples: (i) benzene adsorption, (ii) formation of phenolate, (iii) breaking of the benzene ring due to the attack of the active surface species, (iv) generation of the oxygenate species (carbonate bidentate, formate, acetate, and maleate), and (v) further reaction of the intermediate species with the  $O_{ads}$  species to produce CO<sub>2</sub> and H<sub>2</sub>O.

### 4. Conclusions

The 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample was synthesized *via* a one-step KIT-templating nanocasting route, and the 0.93Pd/meso-CoO and 1.08Pd/meso-CoO samples were prepared by reducing

the 0.85Pd/meso-Co<sub>3</sub>O<sub>4</sub> sample in H<sub>2</sub> at 200 and 350 °C, respectively. The H<sub>2</sub> reduction treatment led to partial mesostructure destroying in meso-Co<sub>3</sub>O<sub>4</sub>, decrease in surface area, increase in pore size, and big Pd NPs in 1.08Pd/meso-Co-CoO. The 0.93Pd/meso-CoO sample with the surface Pd<sup>0</sup> being the dominant species exhibited the highest benzene oxidation activity ( $T_{10\%}$  = 142 °C,  $T_{50\%}$  = 167 °C, and  $T_{90\%}$  = 189 °C at a SV of 40 000 mL (g h)<sup>-1</sup>). A higher temperature was required for CO<sub>2</sub> yield than for benzene conversion. Carbonate bidentate, formate, acetate, maleate, and phenolate were the main intermediate species during the benzene combustion process, and the 0.93Pd/meso-CoO sample exhibited the strongest oxygen activation ability among all of the samples. It is concluded that the outstanding catalytic performance of 0.93Pd/meso-CoO was related to the mainly formed Pd<sup>0</sup> species, good oxygen activation ability, and high surface area.

# Conflicts of interest

There are no conflicts of interest to declare.

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### References

- 1 M. S. Kamal, S. A. Razzk and M. M. Hossain, *Atmos. Environ.*, 2016, **140**, 117–134.
- 2 M. Hakim, Y. Y. Broza, O. Barash, N. Peled, M. Phillips,
  A. Amann and H. Haick, *Chem. Rev.*, 2012, **112**, 5949–5966.
- 3 A. L. Bolden, C. F. Kwiatkowski and T. Colborn, *Environ. Sci. Technol.*, 2015, **49**, 5261–5276.
- 4 L. F. Liotta, Appl. Catal., B, 2010, 100, 403-412.
- 5 H. Deng, S. Y. Kang, J. Z. Ma, C. B. Zhang and H. He, *Appl. Catal.*, *B*, 2018, **239**, 214–222.
- 6 Z. Y. Chen, J. X. Mao and R. X. Zhou, *Appl. Surf. Sci.*, 2019, 465, 15–22.
- 7 H. X. Dai, Sci. Bull., 2015, 60, 1708–1710.
- 8 H. B. Huang, Y. Xu, Q. Y. Feng and D. Y. C. Leung, *Catal. Sci. Technol.*, 2015, **5**, 2649–2669.
- 9 Z. Wang, W. Z. Wang, L. Zhang and D. Jiang, *Catal. Sci. Technol.*, 2016, **6**, 3845–3853.
- 10 F. G. Wang, L. J. Zhang, L. L. Xu, Z. Y. Deng and W. D. Shi, *Fuel*, 2017, 203, 419–429.
- 11 W. X. Tang, W. Xiao, S. B. Wang, Z. Ren, J. Ding and P. X. Gao, *Appl. Catal.*, *B*, 2018, **226**, 585–595.
- 12 S. H. Xie, Y. X. Liu, J. G. Deng, J. Yang, X. T. Zhao, Z. Han, K. F. Zhang and H. X. Dai, *J. Catal.*, 2017, 352, 282–292.
- 13 X. Y. Wang, Y. Liu, T. H. Zhang, Y. J. Luo, Z. X. Lan, K. Zhang, J. C. Zuo, L. L. Jiang and R. H. Wang, ACS Catal., 2017, 7, 1626–1636.
- J. González-Prior, R. López-Fonseca, J. I. Gutiérrez-Ortiz and B. D. Rivas, *Appl. Catal.*, B, 2018, 222, 9–17.
- 15 S. Zhao, K. Z. Li, S. Jiang and J. H. Li, *Appl. Catal.*, B, 2016, 181, 236–248.
- 16 Y. B. Li, C. B. Zhang, J. Z. Ma, M. Chen, H. Deng and H. He, *Appl. Catal.*, B, 2017, 217, 560–569.
- 17 C. B. Zhang, Y. B. Li, Y. F. Wang and H. He, *Environ. Sci. Technol.*, 2014, 48, 5816–5822.
- 18 C. H. Liu, C. Y. Lin, J. L. Chen, K. T. Lu, J. F. Lee and J. M. Chen, J. Catal., 2017, 350, 21–29.
- 19 S. Zhao, F. Y. Hu and J. H. Li, ACS Catal., 2016, 6, 3433-3441.
- 20 S. H. Xie, Y. X. Liu, J. G. Deng, J. Yang, X. T. Zhao, Z. Han, K. F. Zhang, Y. Wang, H. Arandiyan and H. X. Dai, *Catal. Sci. Technol.*, 2018, 8, 806–816.
- 21 Y. F. Wang, C. B. Zhang, F. D. Liu and H. He, *Appl. Catal.*, *B*, 2013, **142–143**, 72–79.
- 22 G. Ercolino, P. Stelmachowski, G. Grzybek, A. Kotarba and S. Specchia, *Appl. Catal., B*, 2017, **206**, 712–725.

- 23 T. J. Hua, Y. Wang, L. N. Zhang, T. Tang, H. Xiao, W. W. Chen, M. Zhao, J. F. Jia and H. Y. Zhu, *Appl. Catal.*, *B*, 2019, 243, 175–182.
- 24 S. C. Kim and W. G. Shim, Appl. Catal., B, 2009, 92, 429-436.
- 25 Y. F. Wang, C. B. Zhang and H. He, *ChemCatChem*, 2018, **10**, 998–1004.
- 26 H. Tan, J. Wang, S. Yu and K. Zhou, *Environ. Sci. Technol.*, 2015, 49, 8675–8682.
- 27 S. H. Xie, J. G. Deng, S. M. Zang, H. G. Yang, G. S. Guo, H. Arandiyan and H. X. Dai, *J. Catal.*, 2015, **322**, 38–48.
- 28 F. Kleitz, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136–2137.
- 29 L. Z. Liu, J. X. Li, H. B. Zhang, L. Li, P. Zhou, X. L. Meng, M. M. Guo, J. P. Jia and T. H. Sun, *J. Hazard. Mater.*, 2019, 362, 178–186.
- 30 J. Chen, X. Chen, W. J. Xu, Z. Xu, H. P. Jia and J. Chen, *Appl. Catal.*, B, 2018, 224, 825–835.
- 31 Y. X. Liu, H. X. Dai, J. G. Deng, S. H. Xie, H. G. Yang, W. Tan, W. Han, Y. Jiang and G. S. Guo, *J. Catal.*, 2014, 309, 408–418.
- 32 J. Q. Li, W. H. Li, G. Liu, Y. Z. Deng, J. Yang and Y. F. Chen, *Catal. Lett.*, 2016, **146**, 1300–1308.
- 33 Y. J. Luo, K. C. Wang, J. C. Zuo, Q. R. Qian, Y. X. Xu, X. P. Liu, H. Xue and Q. H. Chen, *Mol. Catal.*, 2017, 436, 259–266.
- 34 R. Gholami, M. Alyani and K. J. Smith, *Catalysts*, 2015, 5, 561–594.
- 35 H. Wang, W. Yang, P. H. Tian, J. Zhou, R. Tang and S. J. Wu, *Appl. Catal.*, *A*, 2017, **529**, 60–67.
- 36 Q. Liu, L. C. Wang, M. Chen, Y. Cao, H. Y. He and K. N. Fan, J. Catal., 2009, 263, 104–113.
- 37 J. P. Dacquin, C. Dujardin and P. Granger, J. Catal., 2008, 253, 37–49.
- 38 Z. X. Wu, J. G. Deng, Y. X. Liu, S. H. Xie, Y. Jiang, X. T. Zhao, J. Yang, H. Arandiyan, G. S. Guo and H. X. Dai, *J. Catal.*, 2015, **332**, 13–24.
- 39 W. Jiang, Y. J. Pang, L. L. Gu, Y. Yao, Q. Su, W. J. Ji and C. T. Au, *J. Catal.*, 2017, 349, 183–196.
- 40 C. P. O'Brien and I. C. Lee, J. Catal., 2017, 347, 1-8.
- 41 X. Y. Wang, W. T. Zhao, X. W. Wu, T. H. Zhang, Y. Liu, K. Zhang, Y. H. Xiao and L. L. Jiang, *Appl. Surf. Sci.*, 2017, 426, 1198–1205.
- 42 W. Deng, Q. G. Dai, Y. J. Lao, B. B. Shi and X. Y. Wang, *Appl. Catal.*, *B*, 2016, **181**, 848–861.
- 43 X. L. Liu, J. L. Zeng, W. B. Shi, J. Wang, T. Y. Zhu and Y. F. Chen, *Catal. Sci. Technol.*, 2017, 7, 213–221.
- 44 K. Yang, Y. X. Liu, J. G. Deng, X. T. Zhao, J. Yang, Z. Han,
  Z. Q. Hou and H. X. Dai, *Appl. Catal.*, *B*, 2019, 244, 650–659.
- 45 X. C. Sun, J. Lin, H. L. Guan, L. Li, L. Sun, Y. H. Wang, S. Miao, Y. Su and X. D. Wang, *Appl. Catal.*, B, 2018, 226, 575–584.
- 46 Y. B. Li, X. Y. Chen, C. Y. Wang, C. B. Zhang and H. He, ACS Catal., 2018, 8, 11377–11385.
- 47 Y. S. Wu, S. S. Yuan, R. Feng, Z. C. Ma, Y. Z. Gao and S. T. Xing, *Mol. Catal.*, 2017, 442, 164–172.
- 48 V. P. Santos, M. F. R. Pereira, J. J. M. Órfão and J. L. Figueiredo, *Appl. Catal.*, *B*, 2010, **99**, 353–363.