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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.¹ Benzene, one of the widely utilized aromatic VOCs with high toxicity and significant carcinogenic effect, is harmful to the environment and human health.^{2,3} 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.^{4–8} Hence, it is needed to investigate highly active and stable catalysts for the removal of VOCs.

^b Petrochina Petrochemical Research Institute, Beijing 102206, China

^c CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Center for Nanoscience and Technology, Beijing 100190, China

Pd/meso-CoO derived from *in situ* reduction of the one-step synthesized Pd/meso-Co₃O₄: highperformance catalysts for benzene combustion[†]

Xingtian Zhao,^a Ran Zhang,^b Yuxi Liu,^a Jiguang Deng,^b Peng Xu,^{ac} Sijie Lv,^a Shuang Li,^a Wenbo Pei,^a Kunfeng Zhang^a and Hongxing Dai^b*^a

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 H₂ 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)⁻¹). The chemical state of Pd on the 0.93Pd/meso-CoO surface was metallic Pd⁰, 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 Pd⁰ 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.⁹⁻¹¹ It has been proven that Co²⁺ species contribute to generation of active O₂⁻ and O_2^{2-} species, which favor the enhancement in catalytic performance.¹² Since a catalytic reaction occurs on the catalyst surface, a rise in surface area could improve catalytic activity. Recently, three-dimensionally (3D) ordered mesoporous Co₃O₄ has attracted much attention.¹²⁻¹⁴ 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.^{15–19} The loading of Pd on the surface of Co₃O₄ could generate the noble metal-metal oxide interfaces that were beneficial for improving oxygen activation ability and hence the catalytic activity.²⁰⁻²³ 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 Co₃O₄ 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.²¹



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^a Beijing Key Laboratory for Green Catalysis and Separation, Key Laboratory of Beijing on Regional Air Pollution Control, Key Laboratory of Advanced Functional Materials, Education Ministry of China, Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China. E-mail: hxdai@bjut.edu.cn

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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.^{16,24} For example, Wang et al.²⁵ attributed the superior activity of the Al₂O₃-, TiO₂-, SiO₂-, CeO₂-, MnO₂- or Co₃O₄-supported catalyst for *o*-xylene combustion to formation of the metallic Pd⁰ species. For VOC combustion, the supported Pd catalysts with metallic Pd⁰ species were more active than the ones with PdO species.²⁰ Metallic Pd⁰ 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).²⁰ 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 Pd⁰ performed better than the ones with only Pd⁰.^{21,26} Our previous work also found that catalytic activity was associated with the increased amount of Pd²⁺ species.²⁷ Therefore, it is important to investigate active sites of the Pd catalysts supported on meso-Co₃O₄.

In one of our previous works,²⁰ 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 H₂ at different temperatures of the one-step prepared Pd/meso-Co₃O₄ (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-Co₃O₄ 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.²⁸ 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⁻¹ 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-Co₃O₄ sample was obtained. The Pt/meso-Co₃O₄ sample was pretreated in a 3.5 vol% H₂/96.5 vol% Ar flow of 30 mL min⁻¹ 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-Co₃O₄, 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, H₂-TPR, O₂-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⁻¹ 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)⁻¹. 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-Co₃O₄ > 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)⁻¹. The above results demonstrate that the 0.85Pd/meso-Co₃O₄ 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 CO₂ yields were



Fig. 1 (A) Benzene conversion as a function of temperature, (B) $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$, (C) CO₂ yield over 0.85Pd/meso-Co₃O₄, 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)⁻¹.

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 ₂ yield temperature			
Sample	<i>T</i> ^{10%} (°C)	<i>T</i> _{50%} (°C)	<i>T</i> 90% (°C)	<i>T</i> ^{10%} (°C)	<i>T</i> _{50%} (°C)	<i>T</i> 90% (°C)	
0.85Pd/meso-Co ₃ O ₄ 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[†]). 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.^{29,30} Liu *et al.*²⁹ 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 Co₃O₄ after CoO was pretreated in air at 270 °C for 1 h.¹² That is to say, the phase of CoO in 0.93Pd/meso-CoO was stable in an oxidative atmosphere below 270 °C.

The TOF_{Pd} (TOF_{Pd} = xC_0/n_{Pd} , where x, C_0 (mol s⁻¹), 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[†]). Obviously, 0.93Pd/meso-CoO showed a catalytic activity (TOF_{Pd} = 1.46 \times $10^{-3}~s^{-1}$ and specific reaction rate = 13.74 μ mol (g_{Pd} s)⁻¹) 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 μ mol (g_{Pd} s)⁻¹) and 1.08Pd/meso-Co–CoO (TOF_{Pd} = $0.07 \times 10^{-3} \text{ s}^{-1}$ and specific reaction rate = 0.62 µmol (g_{Pd} s)⁻¹), respectively. Summarized in Table S1 (ESI⁺) are the activities of the supported noble metal catalysts reported in the literature. It can be observed that the TOF_{Pd} (1.46 \times 10⁻³ s⁻¹) 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-Co₃O₄ (0.33 \times 10⁻³ s⁻¹ and 1.68 μ mol (g_{Pd} s)⁻¹),³¹ $0.53 Pd/Co_{3}O_{4}~(0.30~\times~10^{-3}~s^{-1}$ and 2.82 $\mu mol~(g_{Pd}~s)^{-1}),^{32}$ and K/Ag-OMS-40 (1.28 \times 10⁻³ s⁻¹ and 11.90 μ mol (g_{Pd} s)⁻¹),⁵ but lower than those over 1.0Pd/Al₂O₃ (2.72×10^{-3} s⁻¹ and 24.37 μ mol (g_{Pd} s)⁻¹).⁵

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.^{4,33,34} After 5.0 vol% CO₂ was introduced into the reaction system, a slow decrease in benzene conversion from 86 to 75% was observed. Even if CO₂ was removed from the feed stream, benzene conversion was maintained at 77%. Wang *et al.*³⁵ pointed out that the



Fig. 2 Effects of (a) 3.0 or 5.0 vol% H₂O, (b) 5.0 vol% CO₂, and (c) 3.0 vol% H₂O + 5.0 vol% CO₂ on benzene conversion over the 0.93Pd/meso-CoO sample at 185 °C and SV = 40 000 mL (g h)⁻¹.

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% H₂O and 5.0 vol% CO₂, the changing trend in activity was rather similar to that in the presence of 5.0 vol% CO₂. Therefore, the above results reveal that addition of H₂O and/or CO₂ to the feedstock induced a negative impact on benzene combustion.

3.2. Crystal structure and textural property

The XRD, Raman, N₂ 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⁺)) of 0.85Pd/meso-Co₃O₄ 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-Co₃O₄ sample, which were assignable to the cubic Co₃O₄ phase (JCPDS 74-1657). After 0.85Pd/meso-Co₃O₄ was pretreated in H₂ 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° . indicating the formation of the cubic CoO or CoO_x phase (JCPDS 48-1719).¹² 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 Co⁰ 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 H₂ at 350 °C. We detected five characteristic bands at 193, 477, 516, 617, and 687 cm^{-1} in the Raman spectrum (Fig. S3 (ESI[†])) of 0.85Pd/meso-Co₃O₄, which were attributable to the $F_{2g}(1)$, E_g , $F_{2g}(2)$, $F_{2g}(3)$, and A_{1g} symmetries of Co₃O₄,¹¹ 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-Co₃O₄, the Raman signals were weakened. There was a significant red shift (*ca.* 12 cm⁻¹) in the A_{1g} symmetry of the 0.93Pd/meso-CoO sample (at 675 cm⁻¹), which was much lower than that of the 0.85Pd/meso-Co₃O₄ sample. The results demonstrate that lattice distortion and residual stress of the spinel crystal were generated during the reduction process.^{11,36} Theoretically, a more amount of oxygen vacancies can be formed due to more lattice defects, which would favor activation of O₂ to the active oxygen adspecies and hence greatly enhance the activity of a catalyst.

The 0.85Pd/meso-Co₃O₄ and 0.93Pd/meso-CoO samples displayed an IV-type N₂ 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.¹² 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-Co₃O₄ sample. Summarized in Table 2 are textural parameters of the samples. BET surface areas of the 0.85Pd/meso-Co₃O₄, 0.93Pd/meso-CoO, and 1.08Pd/meso-Co–CoO samples were 91.2, 88.5, and 52.6 m² g⁻¹, respectively. The results indicate that the reduction treatment induced an obvious change in the mesoporous structure.

TEM images (Fig. S4 (ESI[†])) of 0.85Pd/meso-Co₃O₄, 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-Co₃O₄ or 0.93Pd/meso-CoO sample. Fig. 5 shows HAADF-STEM images and element mappings of the 0.85Pd/meso-Co₃O₄ 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_{3/2}, Pd 3d, and O 1s XPS spectra of the samples, and their surface parameters are listed in Table 2. The asymmetrical Co 2p_{3/2} 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 Co²⁺).²⁷ After reduction of 0.85Pd/meso-Co₃O₄ 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-Co₃O₄ 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-Co₃O₄ sample (Fig. 6B) was decomposed into four components at BE = 335.3 and 340.5 eV (attributed to the surface Pd⁰ species) and 336.9 and 342.2 eV (assigned to the surface Pd²⁺ species).^{16,19,27} Only Pd⁰ species, however, were detected on the surface of 0.93Pd/meso-CoO and 1.08Pd/meso-Co-CoO. The above results confirm that the H₂ 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_{latt}), adsorbed oxygen (O_{ads}, e.g., O₂⁻, O₂²⁻ or O⁻), and hydroxyl and/or carbonate species,²⁷ respectively. The Oads/Olatt molar ratio increased in the sequence of 0.85Pd/meso-Co₃O₄ (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 O₂, leading to better performance for VOC combustion.^{19,20} The higher O_{ads} concentration is an indication



Fig. 4 (A) Nitrogen adsorption-desorption isotherms and (B) pore-size distributions of (a) 0.85Pd/meso-Co₃O₄, (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, H₂ consumption, and oxygen desorption of the samples

	Textural parameter				Surface elem	ient	H_2 consumption (mmol g ⁻¹)	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 ²⁺ /Co ³⁺ molar ratio	O _{ads} /O _{latt} molar ratio	Above 200 $^{\circ}\mathrm{C}$	Below 400 °C	Above 400 $^{\circ}C$
0.85Pd/meso-Co ₃ O ₄	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-Co₃O₄ 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-Co₃O₄ 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 H₂-TPR profiles of the as-prepared samples. The 0.85Pd/meso-Co₃O₄ 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 Pd⁰, Co³⁺ to Co²⁺, and Co²⁺ to Co⁰, respectively. The H₂ 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 Pd⁰. Secondly, the lower temperatures were

required for reduction from Co^{3+} to Co^{2+} or from Co^{2+} to Co^{0} in 0.93Pd/meso-CoO and 1.08Pd/meso-Co-CoO. Dacquin et al.37 reported the reduction of Co³⁺ to Co²⁺ at *ca.* 200 °C due to the H₂ spillover effect. In the present work, the H₂ 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 H₂-TPR profiles can obtain H₂ consumption of the samples (Table 2). Theoretically speaking, the H₂ 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 Co²⁺ and only Co³⁺ and are reduced to Co^0 , respectively. Apparently, the H₂ 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.³⁸ More importantly, H₂ consumption (16.12 mmol g^{-1}) of 0.85Pd/meso-Co₃O₄ 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⁻¹) of the 1.08Pd/meso-Co-CoO sample, however, decreased dramatically, indicating that part of Co³⁺ and/or Co²⁺ were reduced to Co⁰. On the basis of the H2-TPR results, we can realize that PdO could be reduced to metallic Pd⁰ in 3.5 vol% H₂/96.5 vol% Ar below 200 °C, but most

Fig. 6 (A) Co 2p_{3/2}, (B) Pd 3d, and (C) O 1s XPS spectra of (a) 0.85Pd/meso-Co₃O₄, (b) 0.93Pd/meso-CoO, and (c) 1.08Pd/meso-Co-CoO.

Fig. 7 (A) H₂-TPR and (B) O₂-TPD profiles of (a) 0.85Pd/meso-Co₃O₄, (b) 0.93Pd/meso-CoO, and (c) 1.08Pd/meso-Co-CoO.

of the Co^{3^+} and Co^{2^+} species were retained in the 0.93Pd/meso-CoO sample. Some authors proposed that the samples with high amounts of the 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.^{13,27,39} Hence, the more the Co^{2+} and O_{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 Co⁰ 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 O₂-TPD profiles of the samples (Fig. 7B). According to the literature,^{9,11,39} the peaks below 400 °C were due to desorption of the O_{ads} species, the ones in the range of 400-500 °C were ascribed to desorption of the coordinately unsaturated surface O_{latt} species, and the ones above 700 °C were assigned to desorption of the coordinately saturated O_{latt} species. For the 0.85Pd/meso-Co₃O₄ sample, the peaks at 165 and 280 °C were assignable to desorption of the O_{ads} species, whereas the one at 810 °C was attributable to desorption of the O_{latt} species in Co₃O₄. Differently from the 0.85Pd/meso-Co₃O₄ 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 Co₃O₄ 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_{ads} species below 400 °C significantly increased after the H₂ reduction pretreatment, and the changing trend decreased in the sequence of 0.93Pd/meso-CoO (37.1 μ mol g⁻¹) > 1.08Pd/ meso-Co-CoO (17.4 μ mol g⁻¹) > 0.85Pd/meso-Co₃O₄ (7.0 μ mol g⁻¹). The desorbed oxygen species could be ascribed to the Oads species bound to the Co³⁺ sites since the Co²⁺ species were first easily oxidized into the Co³⁺ species by gas-phase O₂ and then the surface oxygen species were bound to the Co³⁺ 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⁺)) 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⁻¹ 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⁺)), we can tentatively assign all of the absorption bands of the samples. The bands at 3657-3705, 1700-2000, and 600-1100 cm^{-1} were due to the adsorbed gaseous benzene (not shown),¹³ the one at 1596 cm^{-1} was attributed to the anti-symmetric vibration of C-O in the formate species,40 the ones at 1555-1565 cm⁻¹ were ascribed to the

anti-symmetric vibration of C-O in the acetate species,12,41,42 the ones at 1532 and 1307 cm⁻¹ were due to the maleate species,^{42–44} the one at 1400 cm⁻¹ (which was slightly shifted to 1422 cm⁻¹) was attributed to the symmetric vibration of C–O in the acetate species,^{12,42} the ones at 1481–1493 and 1443 cm⁻¹ were ascribable to the skeletal C-C vibration,^{40,44,45} and the one at 1469 cm⁻¹ were attributable to the C–H deformation vibration of the aromatic ring, 40,44,45 and the one at 1242 cm⁻¹ 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.^{39,42,46-48} 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.^{39,48} As discussed in the XPS characterization results, H₂ reduction pretreatment increased the amount of O_{ads} 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-Co₃O₄ 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.⁴⁵ 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-Co₃O₄ in a 20 vol% O₂ (N₂ 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⁻¹ 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.¹² 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-Co₃O₄ samples after benzene pre-adsorption at 150 °C were carried out by elevating the temperature in a N₂ 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_{ads} species at 250 $^{\circ}$ C to generate CO₂ and H₂O.

Furthermore, the integral DRIFTS area of the representative acetate species centered at 1422-1400 cm⁻¹ 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-Co₃O₄, implying that the metallic Pd⁰ 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 O₂ 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⁻¹ disappeared over 0.93Pd/ meso-CoO at 200 °C and over 0.85Pd/meso-Co₃O₄ 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-Co₃O₄ in a N₂ 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⁻¹) 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⁻¹) on (A) 0.93Pd/meso-CoO and (B) 0.85Pd/meso-Co₃O₄ 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 CO₂ and H₂O.

4. Conclusions

The 0.85Pd/meso-Co₃O₄ 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-Co₃O₄ sample in H₂ at 200 and 350 °C, respectively. The H₂ reduction treatment led to partial mesostructure destroying in meso-Co₃O₄, 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 Pd⁰ 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)⁻¹). A higher temperature was required for CO₂ 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 Pd⁰ species, good oxygen activation ability, and high surface area.

Conflicts of interest

There are no conflicts of interest to declare.

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