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Catalytic performance of cobalt oxide-supported gold-palladium nanocatalysts for the removal of toluene and *o*-xylene

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ABSTRACT

Using the molten salt and polyvinyl alcohol-protected reduction method, we fabricated Co₃O₄ octahedron-supported Au-Pd ($x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$; $x = (0.18, 0.47, \text{ and } 0.96) \text{ wt\%}$; $y (\text{Pd/Au molar ratio}) = 1.85\text{--}1.97$) nanocatalysts. The molten salt-derived Co₃O₄ sample possessed well-defined octahedral morphology, with an edge length of 300 nm. The Au-Pd nanoparticles, with sizes of 2.7–3.2 nm, were uniformly dispersed on the surface of Co₃O₄. The 0.96(AuPd_{1.92})/Co₃O₄ sample showed the highest catalytic activity for toluene and *o*-xylene oxidation, and the temperature required for achieving 90% conversion of toluene and *o*-xylene was 180 and 187 °C, respectively, at a space velocity of 40000 mL/(g·h). The high catalytic performance of Co₃O₄ octahedron-supported Au-Pd nanocatalysts was associated with the interaction between Au-Pd nanoparticles and Co₃O₄ and high concentration of adsorbed oxygen species.

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1. Introduction

It is well known that volatile organic compounds (VOCs, e.g., toluene and *o*-xylene) are not only detrimental to the environment but also harmful to human health [1–3]. Catalytic oxidation is considered to be one of the most effective methods for the removal of VOCs because of its high removal efficiency, absence of secondary pollution, and low fossil cost [4,5]. The key issue for this technology is the development of efficient catalysts.

Recently, supported noble metal (e.g., Au, Pd, Pt) nanocatalysts have gained much attention because of their high catalytic

performance for the removal of VOCs at low temperatures [6–14]. However, the presence of moisture can greatly inhibit the catalytic activity of supported single noble metal nanocatalysts [13,14]. In previous studies, researchers have reported that supported noble metal alloy nanocatalysts exhibit unique catalytic performance, compared with the corresponding supported single noble metal nanocatalysts [15–19]. For example, our group found that three-dimensionally ordered macroporous Mn₂O₃-supported Au-Pd nanocatalysts exhibited much better catalytic performance for toluene oxidation than supported Au or Pd nanocatalysts [16].

Among the transition metal (e.g., Mn, Fe, Zn, Ni and Co) ox-

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ides [20–24], cobalt oxides have been widely used as supports and catalysts for the removal of VOCs [15,25–28]. Recently, much attention has been paid to the support morphology because of its possible effects on the catalytic performance. Cobalt oxides with various morphologies (e.g., sphere, cube, belt, nanowire, and rod shapes) have been generated via the solution method [29–32]. Recently, our group found that the molten salt method is convenient for the preparation of transition oxides with defined morphologies (e.g., Mn_2O_3 nanowires) [33]. As an extension of this work, we fabricated Co_3O_4 octahedrons via the molten salt method and used them to support Au-Pd nanocatalysts fabricated via the polyvinyl alcohol (PVA)-protected reduction method; we then investigated their catalytic performance for the removal of toluene and *o*-xylene.

2. Experimental

2.1. Catalyst preparation

Co_3O_4 octahedrons were fabricated via the molten salt method. Typically, 29.4 g of NaNO_3 , 0.6 g of NaF, and 10 g of CoCl_2 were well ground and then calcined in a muffle furnace at 350 °C for 2 h. The as-obtained solid was dissolved in deionized water and washed several times to remove Na^+ , NO_3^- and F^- ions. The final Co_3O_4 octahedron sample was obtained after being dried in an oven at 80 °C.

The Co_3O_4 octahedron-supported gold-palladium ($x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$) samples were prepared using the PVA-protected reduction method. The typical preparation procedures were as follows. A 0.6, 1.5, or 3 mL of PVA aqueous solution (2.0 g/L) was added to a PdCl_2 (1.5 mmol/L) and HAuCl_4 (1.5 mmol/L) mixed aqueous solution in an ice bath under vigorous stirring for 30 min. Then, 0.7, 1.7, or 3.4 mL of NaBH_4 aqueous solution (2.0 g/L) was quickly injected into the mixed noble metal aqueous solution, generating a dark-brown sol. Subsequently, 0.5 g of the Co_3O_4 support was added to the dark-brown sol and vigorously stirred for 8 h. The mixture solution was filtered and washed with deionized water, until no Cl^- ions in the supernatant were detected using AgNO_3 (0.1 mol/L) aqueous solution. The obtained wet solid was dried at 80 °C for 10 h and calcined in a muffle furnace at a ramp rate of 1 °C/min from room temperature (RT) to 300 °C and maintained at this temperature for 4 h, thus obtaining the $x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$ samples. The results of inductively coupled plasma atomic emission spectroscopic (ICP-AES) investigations reveal that the real loadings of noble metals were (0.18, 0.47, and 0.96) wt% in $x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$, respectively, and the corresponding real Pd/Au molar ratios were 1.85, 1.93, and 1.92.

For comparison, the $x(\text{AuPd}_y)/\text{bulk Co}_3\text{O}_4$ samples were also prepared using thermal decomposition of cobalt nitrate at 600 °C for 4 h and the PVA-protected reduction method. The results of the ICP-AES studies reveal that the real Au-Pd loading (x) was 0.95 wt% in the $x(\text{AuPd}_y)/\text{bulk Co}_3\text{O}_4$ sample, with the real Pd/Au molar ratio being 1.97.

All chemicals (A.R. in purity) were purchased from Beijing Chemical Reagent Company and used without further purification.

2.2. Catalyst characterization

Elemental analysis of the noble metal loadings was performed using the ICP-AES technique on a Thermo Electron IRIS Intrepid ER/S spectrometer. X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with $\text{Cu } K_\alpha$ radiation and a nickel filter ($\lambda = 0.15406$ nm). Scanning electron microscopy (SEM) images of the samples were recorded on a Gemini Zeiss Supra 55 apparatus (operating at 10 kV). Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns of the samples were obtained using a JEOL-2010 (operating at 200 kV). High-angle annular dark field (HAADF) images and element mapping were acquired on an FEI G2 80–200/Chemi-STEM Cs-corrected transmission electron microscope with a probe corrector. BET (Brunauer-Emmett-Teller) surface areas of the samples were measured via N_2 adsorption at –196 °C on a Micromeritics ASAP 2020 analyzer with the samples being degassed at 250 °C for 2.5 h under vacuum before measurement. X-ray photoelectron spectroscopy (XPS, VG CLAM 4 MCD analyzer) was used to determine the Co 2p, O 1s, Au 4f, Pd 3d, and C 1s binding energies (BEs) of surface species using Mg K_α ($h\nu = 1253.6$ eV) as the excitation source. To remove the adsorbed water and carbonate species on the surface, the samples were pre-treated in O_2 (flow rate = 20 mL/min) at 300 °C for 1 h and then cooled to RT, followed by transferring the pre-treated samples into the spectrometer in a transparent Glove Bag (Instruments for Research and Industry, USA) filled with helium. The pre-treated samples were outgassed in the preparation chamber (10^{-5} Torr) for 0.5 h and then introduced into the analysis chamber (3×10^{-9} Torr) for XPS spectrum recording. The C 1s signal at 284.6 eV was taken as a reference for BE calibration.

Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before TPR measurement, ca. 50 mg of the sample (40–60 mesh) was loaded to a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and pre-treated in an O_2 flow of 30 mL/min at 250 °C for 1 h. After being cooled under the same atmosphere to 30 °C, the sample was purged with a helium flow of 30 mL/min for 15 min. Finally, the pretreated sample was exposed to a flow (30 mL/min) of 5% H_2 -95% Ar (v/v) mixture and heated at a ramp rate of 10 °C/min from 30 °C to 900 °C. The alteration in H_2 concentration of the effluent was monitored online by the chemical adsorption analyzer. The reduction peak was calibrated against that of the complete reduction of a known standard powdered CuO (Aldrich, 99.995%).

Oxygen temperature-programmed desorption (O_2 -TPD) was carried out on the same apparatus used in the H_2 -TPR experiments. Prior to O_2 -TPD experiment, 30 mg of the sample was preheated in an O_2 flow of 30 mL/min at 300 °C for 1 h. After cooling to RT, the sample was kept in the same flow for another 1 h. Before the sample was heated from RT to 750 °C at a ramp of 10 °C/min, a helium flow of 40 mL/min was employed to remove the O_2 for 1 h. The oxygen concentration in the effluent was continuously monitored by a thermal conductivity detec-

tor. The oxygen desorption peak was calibrated according to the results of the oxygen pulse experiment.

2.3. Catalytic performance evaluation

Catalytic activities of the samples were evaluated in a continuous flow fixed-bed quartz tubular microreactor (i.d. = 6.0 mm). 50 mg of the sample (40–60 mesh) was diluted with 0.25 g of quartz sand (40–60 mesh). Prior to the measurement, the sample was pretreated in an O₂ flow of 20 mL/min at 250 °C for 1 h. After being cooled to a given temperature, the reactant gas containing toluene or *o*-xylene was passed through the catalyst bed. The reactant mixture gas was 0.1% toluene or *o*-xylene + O₂ + N₂ (balance), and the total flow was 33.6 mL/min, giving a toluene or *o*-xylene/O₂ molar ratio of 1/400 and a space velocity (SV) of ca. 40000 mL/(g·h). The 0.1% toluene or *o*-xylene was generated by passing a N₂ flow through a bottle containing pure toluene or *o*-xylene in a low-temperature thermostatic bath. In the case of water vapor introduction, 3.0 vol% H₂O was introduced by passing the feed stream through a water saturator at 24 °C. Reactants and products were analyzed online by gas chromatography (GC-14C, Shimadzu) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), using a stabilwax column (30 m in length) for toluene or *o*-xylene separation and a Carboxen 1000 column (3 m in length) for permanent gas detection. Conversion was defined as $(c_{\text{inlet}} - c_{\text{outlet}})/c_{\text{inlet}} \times 100\%$, where c_{inlet} and c_{outlet} are the inlet and outlet toluene or *o*-xylene concentrations in the feed stream, respectively. We used a mass spectrometer (Hiden HPR20) to detect the products and found that CO₂ and H₂O were the only products in the combustion of toluene and *o*-xylene. The balance of carbon throughout the investigation was estimated to be $(99.5 \pm 1.5)\%$.

3. Results and discussion

Fig. 1. XRD patterns of (1) Co₃O₄, (2) 0.18(AuPd_{1.85})/Co₃O₄, (3) 0.47(AuPd_{1.93})/Co₃O₄, (4) 0.96(AuPd_{1.92})/Co₃O₄, and (5) 0.95(AuPd_{1.97})/bulk Co₃O₄.

3.1. Characterization results

Fig. 1 shows the XRD patterns of the as-prepared samples. Compared with the XRD pattern of the standard Co₃O₄ sample (JCPDS PDF #42-1467), it is clear that cobalt oxide in 0.95(AuPd_{1.97})/bulk Co₃O₄ and $x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$ was cubic in crystal structure, and all of the diffraction peaks could be well indexed (Fig. 1(5)). The loading of Au-Pd nanoparticles did not cause any changes in the crystal structure of Co₃O₄. In addition, diffraction peaks ascribed to the Au, Pd, or Au-Pd phases were not detected, indicating that the noble metal nanoparticles might be well dispersed on the surface of Co₃O₄.

As can be seen from Fig. 2, the Co₃O₄ support derived via the molten salt method possessed octahedral morphology, with an edge length of 300 nm, while the Co₃O₄ support derived via the thermal decomposition of nitrates had an irregular morphology.

Fig. 2. SEM images of (a,b) Co₃O₄ and TEM images and SAED patterns (insets) of (c,d) 0.18(AuPd_{1.85})/Co₃O₄, (e,f) 0.47(AuPd_{1.93})/Co₃O₄, (g,h) 0.96(AuPd_{1.92})/Co₃O₄, and (i,j) 0.95(AuPd_{1.97})/bulk Co₃O₄.

Fig. 3. Au-Pd particle size distributions of (a) 0.18(AuPd_{1.85})/Co₃O₄, (b) 0.47(AuPd_{1.93})/Co₃O₄, (c) 0.96(AuPd_{1.92})/Co₃O₄, and (d) 0.95(AuPd_{1.97})/bulk Co₃O₄.

gy. There were uniformly dispersed Au-Pd nanoparticles on the surface of octahedral Co₃O₄. The average sizes of Au-Pd nanoparticles were in the range of 2.7–3.2 nm (Fig. 3 and Table 1). The lattice spacings (d value) of Co₃O₄ in the x (AuPd _{y})/Co₃O₄ and 0.95(AuPd_{1.97})/bulk Co₃O₄ samples was estimated to be ca. 0.461 nm (Fig. 2(f, h, j)), rather close to that of the (111) plane of standard Co₃O₄ (JCPDS PDF #42-1467). The linearly aligned bright electron diffraction spots in the SAED patterns (insets of Fig. 2(d, f, h, and j)) suggest that the Co₃O₄ supports were single crystalline.

The STEM and HAADF element mapping images of the 0.96(AuPd_{1.92})/Co₃O₄ sample (Fig. 4) confirmed that Au and Pd species were uniformly dispersed on the surface of octahedral Co₃O₄. In other words, an Au-Pd alloy may have been formed.

Shown in Fig. 5 are the Co 2p_{3/2}, O 1s, Au 4f, and Pd 3d XPS spectra of the samples. The asymmetrical Co 2p_{3/2} XPS spectrum (Fig. 5(a)) of each sample could be decomposed into two components at BE = 780.1 and 781.7 eV, attributed to the surface Co³⁺ and Co²⁺ species [14,34], respectively. The weak satellite signal at BE = 785.7 eV also confirmed the presence of surface Co²⁺ in the samples [35]. Because of the interaction between noble metal NPs and Co₃O₄ (Au⁰ + Co³⁺ → Au^{δ+} + Co²⁺ or Pd⁰ + Co³⁺ → Pd²⁺ + Co²⁺), the surface Co³⁺/Co²⁺ molar ratios of the samples decreased from 1.41 to 0.90 with an increase in the loading of Au-Pd nanoparticles from (0 to 0.96) wt% (Table 2). The asymmetrical O 1s XPS spectrum (Fig. 5(b)) of each sample could be decomposed to three components at BE = 529.9,

531.5, and 533.3 eV, assignable to the surface lattice oxygen (O_{latt}), adsorbed oxygen (O_{ads}, e.g., O₂⁻, O₂²⁻, or O⁻), and carbonate or adsorbed water species [36,37], respectively. It is well known that the surface adsorbed oxygen species play an important role in deep oxidation of organics [38]. An increase in the surface O_{ads} species could enhance the catalytic activity of a catalyst. As shown in Table 2, the surface O_{ads}/O_{latt} molar ratio increased from 0.49 to 2.36 with an increase in the loading of Au-Pd nanoparticles from (0 to 0.96) wt%. The Au 4f XPS spectrum of each sample could be decomposed into four components at BE = 83.5, 84.5, 87.2, and 88.3 eV (Fig. 5(c)). The ones at BE = 83.5 and 87.2 eV were attributed to the surface metallic gold (Au⁰) species, whereas the ones at BE = 84.5 and 88.3 eV were attributed to the surface oxidized gold (Au^{δ+}) species [39,40]. As shown in Fig. 5(d), the Pd 3d spectrum of each sample could be deconvoluted into four components at BE = 335.5, 337.9, 340.9, and 343.2 eV. The components at BE = 335.5 and 340.9 eV were due to the surface metallic palladium (Pd⁰) species, while the ones at BE = 337.9 and 343.2 eV were due to the surface oxidized palladium (Pd²⁺) species [41–43]. Apparently, the surface Au^{δ+}/Au⁰ or Pd²⁺/Pd⁰ molar ratio also increased with a rise in the loading of Au-Pd nanoparticles because of the interaction between Au-Pd nanoparticles and Co₃O₄ [39,44].

The H₂-TPR profiles of the present catalysts are shown in Fig. 6. For the Co₃O₄ octahedron sample, there were two asymmetrical reduction peaks, at 386 and 497 °C, because of

Table 1

BET surface areas, average Au-Pd particle sizes, real Au and Pd contents, and real Pd/Au molar ratios of the as-prepared samples.

Sample	Surface area (m ² /g)	Average Au-Pd particle size ^a (nm)	Real content ^b (wt%)		Real Pd/Au molar ratio ^b
			Au	Pd	
Co ₃ O ₄	1.2	—	—	—	—
0.18(AuPd _{1.85})/Co ₃ O ₄	1.2	2.8	0.09	0.09	1.85
0.47(AuPd _{1.93})/Co ₃ O ₄	1.3	2.9	0.23	0.24	1.93
0.96(AuPd _{1.92})/Co ₃ O ₄	1.3	2.7	0.47	0.49	1.92
0.95(AuPd _{1.97})/bulk Co ₃ O ₄	8.6	3.2	0.46	0.49	1.97

^a Estimated according to the estimation of noble metal particles in the TEM images of the samples.

^b Determined by the ICP-AES technique.

Fig. 4. HAADF-STEM and elemental scanning images of 0.96(AuPd_{1.92})/Co₃O₄.

Fig. 5. (a) Co $2p_{3/2}$, (b) O $1s$, (c) Au $4f$, and (d) Pd $3d$ XPS spectra of (1) Co_3O_4 , (2) $0.18(\text{AuPd}_{1.85})/\text{Co}_3\text{O}_4$, (3) $0.47(\text{AuPd}_{1.93})/\text{Co}_3\text{O}_4$, (4) $0.96(\text{AuPd}_{1.92})/\text{Co}_3\text{O}_4$, and (5) $0.95(\text{AuPd}_{1.97})/\text{bulk Co}_3\text{O}_4$.

the reduction of Co_3O_4 to CoO and CoO to metallic cobalt [45,46], respectively. When the Au-Pd nanoparticles were loaded on the surface of octahedral or bulk Co_3O_4 , the two reduction peaks were shifted to lower temperatures because of the interaction between Au-Pd nanoparticles and the support. This interaction enhanced the low reducibility of the supported catalysts, which could greatly improve the catalytic activity of these samples. The H_2 consumption of the present catalysts was in the range of 13.03–14.27 mmol/g.

Shown in Fig. 7 are the O_2 -TPD profiles of the as-prepared samples. The weak signal at low temperature ($< 600^\circ\text{C}$) is due to the desorption of surface chemisorbed oxygen (O_2^- , O_2^{2-} or O^-) species [26,47]. The peaks above 600°C are attributable to the desorption of lattice oxygen (O^{2-}) species. To some extent, the loading of AuPd nanoparticles enhanced the adsorbed oxygen species amount of the sample (Table 2), indicating that the loading of AuPd nanoparticles improved the oxygen activation ability of $x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$ [48,49].

Table 2

Surface element compositions, O_2 desorption, and H_2 consumption of the samples.

Sample	$\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio	$\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio	$\text{Au}^{\delta+}/\text{Au}^0$ molar ratio	$\text{Pd}^{2+}/\text{Pd}^0$ molar ratio	H_2 consumption ^a (mmol/g)					O_2 desorption ^b (mmol/g)	
					I	II	III	IV	Total	200–600 $^\circ\text{C}$	
Co_3O_4	1.41	0.49	—	—	—	—	2.70	10.59	13.29	0.089	
$0.18(\text{AuPd}_{1.85})/\text{Co}_3\text{O}_4$	1.28	1.20	0.28	0.36	1.90	2.87	5.40	2.86	13.03	0.072	
$0.47(\text{AuPd}_{1.93})/\text{Co}_3\text{O}_4$	1.07	1.38	0.44	0.53	3.38	3.78	3.47	2.65	13.28	0.095	
$0.96(\text{AuPd}_{1.92})/\text{Co}_3\text{O}_4$	0.90	2.36	0.49	0.56	3.78	3.91	3.74	1.61	13.04	0.120	
$0.95(\text{AuPd}_{1.97})/\text{Bulk Co}_3\text{O}_4$	1.09	0.62	0.32	0.39	1.64	2.83	6.09	3.71	14.27	0.046	

^a Estimated by quantitatively analyzing the reduction peaks in the H_2 -TPR profiles.

^b Estimated by quantitatively analyzing the desorption peaks in the O_2 -TPD profiles.

Fig. 6. H₂-TPR profiles of (1) Co₃O₄, (2) 0.18(AuPd_{1.85})/Co₃O₄, (3) 0.47(AuPd_{1.93})/Co₃O₄, (4) 0.96(AuPd_{1.92})/Co₃O₄, and (5) 0.95(AuPd_{1.97})/bulk Co₃O₄.

3.2. Catalyst activity

The complete oxidation of toluene and *o*-xylene was used to evaluate the catalytic activities of the as-prepared samples. In the blank experiments (only quartz sand was loaded in the micro-reactor) under the conditions of toluene or *o*-xylene concentration = 0.1%, toluene or *o*-xylene/O₂ molar ratio = 1/400, and SV = 40000 mL/(g·h), no significant toluene and *o*-xylene conversions were observed at 400 °C for toluene or *o*-xylene combustion. These results indicate that no significant homogeneous reactions took place under the adopted reaction conditions. The catalytic activities of the present catalysts are shown in Fig. 8. Apparently, the conversions of toluene and *o*-xylene increased with a rise in the reaction temperature. The loading of Au-Pd nanoparticles on the surface of octahedral Co₃O₄ benefited the catalytic combustion of toluene and

Fig. 7. O₂-TPD profiles of (1) Co₃O₄, (2) 0.18(AuPd_{1.85})/Co₃O₄, (3) 0.47(AuPd_{1.93})/Co₃O₄, (4) 0.96(AuPd_{1.92})/Co₃O₄, and (5) 0.95(AuPd_{1.97})/bulk Co₃O₄.

o-xylene. Furthermore, with an increase in the loading of Au-Pd nanoparticles, the present $x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$ catalyst exhibited higher catalytic activity, and the 0.96(AuPd_{1.92})/Co₃O₄ sample performed best. Under the mentioned reaction conditions, the temperatures required for 10%, 50%, and 90% conversion of toluene or *o*-xylene (denoted $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$) over the present catalysts are summarized in Table 3. With an increase in the loading of Au-Pd nanoparticles from 0 to 0.96 wt%, $T_{50\%}$ and $T_{90\%}$ over the $x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$ nanocatalysts decreased from 262 to 171 °C and from 268 to 180 °C, respectively, for toluene oxidation; and from 285 to 181 °C and from 293 to 187 °C, respectively, for *o*-xylene oxidation. The 0.96(AuPd_{1.92})/Co₃O₄ sample exhibited higher catalytic activity than the 0.95(AuPd_{1.97})/bulk Co₃O₄ sample. $T_{50\%}$ and $T_{90\%}$ over the molten salt-derived Co₃O₄ supported Au-Pd nanocatalysts decreased by 20–30 °C.

For the transition metal oxide-supported noble metal cata-

Fig. 8. (a) Toluene conversion and (b) *o*-xylene conversion as a function of reaction temperature over (1) Co₃O₄, (2) 0.18(AuPd_{1.85})/Co₃O₄, (3) 0.47(AuPd_{1.93})/Co₃O₄, (4) 0.96(AuPd_{1.92})/Co₃O₄, and (5) 0.95(AuPd_{1.97})/bulk Co₃O₄ under the conditions of toluene or *o*-xylene concentration = 0.1%, toluene or *o*-xylene/O₂ molar ratio = 1/400, and SV = 40000 mL/(g·h).

Table 3

Catalytic activities of the catalysts at SV = 40000 mL/(g·h).

Sample	Toluene oxidation (°C)			<i>o</i> -Xylene oxidation (°C)		
	<i>T</i> _{10%}	<i>T</i> _{50%}	<i>T</i> _{90%}	<i>T</i> _{10%}	<i>T</i> _{50%}	<i>T</i> _{90%}
Co ₃ O ₄	238	262	268	276	285	293
0.18(AuPd _{1.85})/Co ₃ O ₄	175	200	206	190	210	223
0.47(AuPd _{1.93})/Co ₃ O ₄	165	183	192	173	193	203
0.96(AuPd _{1.92})/Co ₃ O ₄	153	171	180	165	181	187
0.95(AuPd _{1.97})/bulk Co ₃ O ₄	170	195	200	190	200	215

lysts, it is difficult to define the active sites and to calculate the number of active sites. In the present study, all of the species, such as Au, Pd, and AuPd nanoparticles, and the interface between AuPd nanoparticles and Co₃O₄, could act as active sites for VOC oxidation. That is to say, the accurate calculation of TOFs might be impossible. However, the redox ability and oxygen vacancy concentration of the catalyst certainly played an important role in the oxidation removal of VOCs. As can be seen from the results of H₂-TPR, O₂-TPD, and XPS characterizations, the loading of AuPd nanoparticles on the surface of Co₃O₄ enhanced the low-temperature reducibility and surface oxygen species. Therefore, it is understandable that 0.96(AuPd_{1.92})/Co₃O₄ performed better than Co₃O₄, 0.18(AuPd_{1.85})/Co₃O₄, and 0.47(AuPd_{1.93})/Co₃O₄. Because of the high price of Au and Pd, we did not investigate the catalytic activities of supported catalysts with larger loadings (> 1 wt%) of AuPd nanoparticles.

Because the adopted reaction conditions have a great influence on the catalytic performance, comparison is difficult among various catalysts in terms of activity, selectivity, and stability. Table 4 summarizes the catalytic activities of 0.96(AuPd_{1.92})/Co₃O₄ and catalysts reported in the literature for toluene or *o*-xylene oxidation under similar reaction conditions. We can see that 0.96(AuPd_{1.92})/Co₃O₄ performed better than 0.90(Au₁Pd₂)/Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ (*T*_{90%} = 218 °C at SV = 20000 mL/(g·h)) [17], 1.5Pd-Au/Ti-Zr (*T*_{90%} = 230 °C at SV = 200 h⁻¹) [50], 1.5Pd-Au/TiO₂ (*T*_{90%} = 220 °C at SV = 200 h⁻¹) [51], 1.0Pd/*meso*-Co₃O₄ (*T*_{90%} = 230 °C at SV = 200 h⁻¹) [52], 1.0Pd/*meso*-Co₃O₄ (*T*_{90%} = 249 °C at SV = 200 h⁻¹) [48], and 7.4Au/Co₃O₄ (*T*_{90%} = 218 °C at SV = 20000 mL/(g·h)) [29], and exhibited similar or inferior catalytic activity to 1.0Au-Pd/3DOM Co₃O₄ (*T*_{90%} = 179 °C at SV = 20000 mL/(g·h)) [15], 0.97(Au₁Pd₂)/*meso*-Cr₂O₃ (*T*_{90%} = 176 °C at SV = 20000

Fig. 9. Toluene conversion as a function of on-stream reaction time over the 0.96(AuPd_{1.92})/Co₃O₄ sample at 180 °C and SV = 40000 mL/(g·h).

mL/(g·h)) [53] and 6.5Au/*meso*-Co₃O₄ (*T*_{90%} = 138 °C at SV = 20000 mL/(g·h)) [12].

To probe the catalytic stability of 0.96(AuPd_{1.92})/Co₃O₄, we conducted a 30-h on-stream reaction experiment at 180 °C, and the result is shown in Fig. 9. Apparently, there were no significant losses in catalytic activity within 30 h of on-stream reaction time, indicating that the 0.96(AuPd_{1.92})/Co₃O₄ sample was catalytically stable. As expected, toluene or *o*-xylene conversion increased with a decrease in SV (Fig. 10(a) and (b)) from 60000 to 20000 mL/(g·h), indicating that the extension in contact time was favorable for the conversion of toluene or *o*-xylene.

To examine the effect of moisture on the catalytic activity of 0.96(AuPd_{1.92})/Co₃O₄, we introduced 3 vol% water vapor, and the result is shown in Fig. 11. It can be seen that because of the competitive adsorption between water vapor and toluene molecules on the surface of the catalyst, toluene conversion decreased from 80% to 74% with the addition of 3 vol% water vapor. However, when the water vapor was cut off, toluene conversion returned to its original values. That is to say, the deactivation was reversible.

4. Conclusions

Octahedral Co₃O₄ and its supported Au-Pd nanocatalysts were fabricated via the molten salt and PVA-protected reduction methods, respectively. The molten salt-derived Co₃O₄ octahedron was cubic, with a single crystalline structure. The

Table 4

Comparison of catalytic activities over various catalysts for the oxidation of VOCs as reported in the references.

Catalyst	Reactant	VOCs concentration (ppm)	Space velocity (mL/(g·h))	<i>T</i> _{90%} (°C)	Ref.
0.96(AuPd _{1.92})/Co ₃ O ₄	Toluene	1000	40000	180	This work
1.5Pd-Au/Ti-Zr	Toluene	1000	200 h ⁻¹	230	[50]
1.0Au-Pd/3DOM Co ₃ O ₄	Toluene	1000	40000	179	[15]
0.90(Au ₁ Pd ₂)/Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	Toluene	1000	20000	218	[17]
1.5Pd-Au/TiO ₂	Toluene	1000	200 h ⁻¹	220	[51]
1.0Pd/ <i>mes</i> -Co ₃ O ₄	<i>o</i> -xylene	150	200 h ⁻¹	204	[52]
0.97(Au ₁ Pd ₂)/ <i>mes</i> -Cr ₂ O ₃	Toluene	1000	20000	176	[53]
1.0Pd/ <i>mes</i> -Co ₃ O ₄	<i>o</i> -xylene	150	60000	249	[48]
7.4Au/Co ₃ O ₄	Toluene	1000	20000	285	[35]
6.5Au/ <i>mes</i> -Co ₃ O ₄	Toluene	1000	20000	138	[12]

Fig. 10. Effect of space velocity on (a) toluene and (b) *o*-xylene oxidation over the 0.96(AuPd_{1.92})/Co₃O₄ sample. (1) 20000 mL/(g·h); (2) 40000 mL/(g·h); (3) 60000 mL/(g·h).

Fig. 11. Effect of water vapor on toluene conversion over the 0.96(AuPd_{1.92})/Co₃O₄ sample at 176 °C and SV = 40000 mL/(g·h).

Au-Pd nanoparticles were uniformly dispersed on the surface of the Co₃O₄ octahedron. Among the present $x(\text{AuPd}_y)/\text{Co}_3\text{O}_4$ ($x = (0.18, 0.47, \text{ and } 0.96) \text{ wt\%}; y = 1.85\text{--}1.97$) catalysts, the 0.96(AuPd_{1.92})/Co₃O₄ sample exhibited the best catalytic performance. Under the reaction conditions of space velocity = 40000 mL/(g·h), the temperature required for achieving 90% conversion of toluene and *o*-xylene was 180 and 187 °C, respectively. The deactivation caused by water vapor addition was reversible. We deduced that the high catalytic performance of 0.96(AuPd_{1.92})/Co₃O₄ was associated with the proper interaction between Au-Pd nanoparticles and Co₃O₄ and high concentration of surface adsorbed oxygen species.

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Graphical Abstract

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Catalytic performance of cobalt oxide-supported gold-palladium nanocatalysts for the removal of toluene and *o*-xylene

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Co₃O₄ octahedron-supported Au-Pd nanocatalyst exhibited high catalytic activity for toluene and *o*-xylene elimination because of the interaction between Au-Pd nanoparticles and Co₃O₄ and high concentration of adsorbed oxygen species.

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四氧化三钴负载金钯纳米催化剂催化消除甲苯和邻二甲苯

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摘要: 挥发性有机物(VOCs, 例如甲苯和二甲苯)不仅危害人身健康, 而且对大气环境造成严重污染. 由于去除效率高、无二次污染以及耗能低等优点, 催化氧化法被认为是消除VOCs的有效方法之一. 该方法的关键是高效催化剂的研发. 由于具有良好的低温催化氧化性能, 过渡金属氧化物负载的贵金属催化剂备受关注. 相比于单组分贵金属负载型催化剂, 双组分贵金属负载型催化剂的催化活性、水热稳定性和抗硫中毒性能均有显著提高.

本文采用熔融盐法和聚乙烯醇保护的硼氢化钠还原法制备了八面体状Co₃O₄负载的AuPd ($x(\text{AuPd})/\text{Co}_3\text{O}_4$; AuPd负载量 $x = (0.18, 0.47, 0.97) \text{ wt}\%$; Pd/Au摩尔比 $y = 1.85, 1.93, 1.92$)合金纳米催化剂. 采用X射线衍射、扫描电子显微镜、透射电子显微镜、选区电子衍射、氢气程序升温还原、氧气程序升温脱附和X射线光电子衍射等技术对催化剂物化性质进行了表征. 利用固定床微型反应器评价了催化剂对甲苯和邻二甲苯完全氧化反应的催化性能. 研究表明, 采用熔融盐法制得

的 Co_3O_4 具有规整八面体形貌, 棱长约为300 nm. AuPd合金纳米粒子均匀分布在 Co_3O_4 表面, 粒径为2.7–3.2 nm. 在所得催化剂中, $0.96(\text{AuPd}_{1.92})/\text{Co}_3\text{O}_4$ 催化剂对甲苯和邻二甲苯完全氧化反应表现出较高的催化活性. 在空速为40000 mL/(g·h)时, 甲苯和邻二甲苯转化率达到90%所需的温度分别为180和187 °C. 我们认为 $0.96(\text{AuPd}_{1.92})/\text{Co}_3\text{O}_4$ 催化剂较为优异的催化性能与AuPd纳米粒子和 Co_3O_4 之间的强相互作用和较高的吸附氧浓度有关.

关键词: 熔融盐; 四氧化三钴; AuPd纳米粒子; 挥发性有机物; 催化氧化

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