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Pt/Co₃O₄/3DOM Al₂O₃: Highly effective catalysts for toluene combustion

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ABSTRACT

Three-dimensionally ordered macro-/mesoporous alumina (3DOM Al₂O₃)-supported cobalt oxide and platinum nanocatalysts (xPt/yCo₃O₄/3DOM Al₂O₃, Pt mass fraction (x%) = 0–1.4%, Co₃O₄ mass fraction (y%) = 0–9.2%) were prepared using poly(methyl methacrylate) templating, incipient wetness impregnation and polyvinyl alcohol-protected reduction. The resulting xPt/yCo₃O₄/3DOM Al₂O₃ samples displayed a high-quality 3DOM architecture with macropores (180–200 nm in diameter) and mesopores (4–6 nm in diameter) together with surface areas in the range of 94 to 102 m²/g. Using these techniques, Co₃O₄ nanoparticles (NPs, 18.3 nm) were loaded on the 3DOM Al₂O₃ surface, after which Pt NPs (2.3–2.5 nm) were uniformly dispersed on the yCo₃O₄/3DOM Al₂O₃. The 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ exhibited the best performance for toluene oxidation, with a T_{90%} value (the temperature required to achieve 90% toluene conversion) of 160 °C at a space velocity of 20000 mL g⁻¹ h⁻¹. It is concluded that the excellent catalytic performance of the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ is owing to well-dispersed Pt NPs, the high concentration of adsorbed oxygen species, good low-temperature reducibility, and strong interaction between the Pt and Co₃O₄ NPs, as well as the unique bimodal porous structure of the support.

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1. Introduction

Volatile organic compounds (VOCs), sulfur oxides, nitrogen oxides, carbon monoxide and particulate matter are all harmful to the environment and to human health. Many countries have issued increasingly strict regulations restricting the emissions of VOCs in the 21st century. Among the different strategies used to control VOC emissions, catalytic combustion has proven to be an effective technology. One key step in the further advancement of this technology is the development of highly

efficient catalysts.

In recent years, supported transition metal and noble metal catalysts have received much attention because these materials have several advantages, especially with regard to catalytic performance, compared with supported noble metal or transition metal catalysts. Among the supported noble metal catalysts, Pt, Pd or Rh on high surface area materials have been widely used due to the exceptional low-temperature activity and recyclability of such systems during the abatement of VOCs. However, these catalyst systems tend to exhibit low re-

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sistance to poisoning and are also costly compared with transition metal oxides [1,2]. Because catalytic activity varies depending on both the noble metal and the particular VOC, different activities are expected over different supported noble metal catalysts when applied to specific reactions [3]. For example, supported Rh catalysts are the most active for hexene oxidation but perform poorly during the oxidation of aromatics [3]. Supported Pd is more active in the oxidation of short-chain hydrocarbons, whereas supported Pt exhibits higher activity for the oxidation of long-chain hydrocarbons and aromatics [4,5]. Li et al. [6] prepared Pt/ γ -Al₂O₃ catalysts using a self-assembly method and observed that the temperatures required for the complete oxidation of toluene, isopropanol, acetone and ethyl acetate over 1.0% Pt/ γ -Al₂O₃ were 130, 135, 145 and 215 °C, respectively, at a space velocity (SV) of 18000 mL g⁻¹ h⁻¹. They proposed that the high catalytic activity of 1.0% Pt/ γ -Al₂O₃ is attributable to its enhanced surface area, and small size and good dispersion of Pt nanoparticles (NPs), reproducible low-temperature activity and greater concentration of hydroxyl species. Upon loading Pt NPs 1.3–2.3 nm in size on the surface of ZSM-5, Chen et al. [7] found that a Pt/ZSM-5 catalyst with a Pt particle size of 1.9 nm gave the best performance ($T_{98\%} = 150$ °C at SV = 30000 mL g⁻¹ h⁻¹) during the complete oxidation of toluene. This result was attributed to an optimum Pt dispersion and an ideal proportion of Pt⁰ species.

Supported transition metal catalysts not only show high oxidation reaction activities but are also less expensive and more resistant to poisoning compared with supported noble metal catalysts [8,9]. To date, numerous transition metal oxides, such as CuO, Co₃O₄, Cr₂O₃, NiO, Fe₂O₃ and MnO₂ [10], have been reported to be active for the catalytic combustion of typical VOCs. Among these, cobalt oxides exhibit excellent catalytic activity and selectivity [11]. It is also well known that the nature and extent of dispersion of the cobalt oxide species are the main factors determining the performance of these catalysts [12,13]. The preparation method [14,15], type of support [16–18] and transition metal loading [15,19] can all affect the state of the cobalt oxide species. Furthermore, the addition of a metal oxide can enhance the catalytic performance of supported platinum catalysts. Liu et al. [20] prepared Y- and Mn-doped Pt/Ce_{0.50}Zr_{0.50}O₂/ γ -Al₂O₃ catalysts and observed that 0.5% Pt/50% Ce_{0.40}Zr_{0.40}Y_{0.10}Mn_{0.10}O_x/ γ -Al₂O₃ exhibited the highest activity ($T_{10\%} = 170$ °C and $T_{90\%} = 216$ °C at SV = 12000 h⁻¹) during toluene combustion. Using a plasma- and ultrasound-assisted wet impregnation strategy, Haghighi and coworkers [21] found that an as-prepared 1% Pt/30 wt% CeO₂-Al₂O₃ catalyst showed good low-temperature activity ($T_{100\%} = 180$ °C at SV = 8400 mL g⁻¹ h⁻¹) and high stability during toluene oxidation. In these previous studies, porous alumina has been commonly used as the support material. To the best of our knowledge, however, there have been no reports concerning the preparation of three-dimensionally ordered macro-/mesoporous alumina (3DOM Al₂O₃)-supported Co₃O₄ and Pt NPs and their catalytic application to the combustion of toluene.

Recently, our group has prepared numerous 3DOM-sup-

ported transition metal oxide and/or noble metal catalysts, including MnO_x/3DOM LaMnO₃ [22], Co₃O₄/3DOM La_{0.6}Sr_{0.4}CoO₃ [23], Au/MnO_x/3DOM La_{0.6}Sr_{0.4}MnO₃ [24] and Au/MnO_x/3DOM SiO₂ [25]. It has been found that these porous materials perform well with regard to catalyzing the oxidation of CO and/or typical VOCs. We herein report the preparation, characterization and catalytic properties of xPt/yCo₃O₄/3DOM Al₂O₃ (Pt mass fraction $x\%$ = 0–1.4%; Co₃O₄ mass fraction $y\%$ = 0–9.2%) during the combustion of toluene.

2. Experimental

2.1. Catalyst preparation

A well-packed, monodisperse colloidal crystal template composed of poly(methyl methacrylate) (PMMA) microspheres with an average diameter of approximately 300 nm was synthesized using a previously described approach [26]. The 3DOM Al₂O₃ with three-dimensionally ordered mesoporous walls was fabricated by employing the triblock copolymer Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) as a soft template and the PMMA microspheres as a hard template. It has been determined that the use of aluminum isopropoxide as the Al source tends to produce higher quality 3DOM Al₂O₃ [26], and so this reagent was applied during the preparation of the 3DOM Al₂O₃ in the present work. A typical preparation procedure began with the dissolution of 4.0 g F127 in 20.0 g of a 95% ethanol solution, and stirring until a homogeneous mixture was obtained (termed Solution A). Simultaneously, 4.8 mL of concentrated nitric acid 65%–68% was added to 24.0 mL of absolute ethanol and the mixture was stirred for 15 min. Next, 8.16 g of aluminum isopropoxide was gradually added to the above inorganic acid-ethanol solution until the Al precursor was completely dissolved, giving Solution B. Solution B was gradually poured into Solution A with continuous stirring and, after stirring for an additional 15 min, Solution C was obtained. Finally, 4.0 g of the colloidal crystalline PMMA microspheres was added to Solution C. After the PMMA microspheres were thoroughly wetted, the excess solution was removed using a Buchner filter funnel connected to a vacuum. After drying under ambient conditions for 48 h, the obtained solid was calcined in an oven, applying a ramp of 1 °C/min from room temperature (RT) to 300 °C and then holding the sample at this temperature for 3 h. Subsequently, the same ramp was applied to raise the temperature from 300 to 600 °C, and the sample was held at 600 °C for 5 h, generating the 3DOM Al₂O₃ support.

The yCo₃O₄/3DOM Al₂O₃ sample with a theoretical value of $y = 10$ was prepared via incipient wetness impregnation. It should be noted that the 3DOM architecture would have been degraded when using water as the solvent to prepare the yCo₃O₄/3DOM Al₂O₃ during the subsequent thermal treatment process. To avoid this, we instead used isopropyl alcohol as the solvent during the fabrication of the yCo₃O₄/3DOM Al₂O₃. In a typical preparation procedure, the required amount of a 10% aqueous Co(NO₃)₂ solution was diluted with a specific volume of isopropyl alcohol, and the diluted solution was added dropwise to 0.2 g of the 3DOM Al₂O₃ support until the support was

completely wetted. Following this, the wetted sample was held at RT for 0.5 h and then dried in an oven overnight at 80 °C. In the final step, the resulting solid was calcined in air, applying a ramp of 1 °C/min from RT to 500 °C, and it was maintained at this temperature for 4 h, thus generating the $\gamma\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$.

The $x\text{Pt}/\gamma\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ specimens (with theoretical values of $x = 0.5, 1.0$ and 2.0) were prepared using a polyvinyl alcohol (PVA)-protected reduction method [27]. In a typical preparation procedure, the required amount of PVA ($M_r = 10000$) was added to a 0.01 mol/L aqueous H_2PtCl_6 solution (Pt/PVA mass ratio = 1.0:1.5) in an ice-water bath under vigorous stirring over the span of 10 min. After rapidly injecting aqueous NaBH_4 solution (0.1 mol/L, Pt/ NaBH_4 molar ratio = 1.0:5.0) and continuously stirring for 20 min, a sol was obtained. The necessary amount of the $\gamma\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ support was subsequently added to a specific quantity of this sol, and the resulting suspension was sonicated at 60 kHz for 30 s. Nitrogen bubble-assisted stirring was then applied to agitate the suspension system for 10 h until complete adsorption of the colloidal noble metals. The solid product was then filtered, washed with 2.0 L of deionized water, dried at 80 °C for 12 h, and finally calcined at a ramp of 1 °C/min from RT to 450 °C and maintained at this temperature for 4 h to produce the $x\text{Pt}/\gamma\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Electron IRIS Intrepid ER/S) analysis demonstrated that the actual Pt loading ($x\%$) in the $x\text{Pt}/\gamma\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ ranged from 0.3% to 1.4%, while the actual Co_3O_4 loading levels ($y\%$) were 9.2% in the $\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ and 8.9% in the $x\text{Pt}/\gamma\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$.

To better compare the catalytic activities of the different materials, we also prepared a commercial Al_2O_3 -supported Co_3O_4 and Pt sample. The commercial alumina (hydrophilic fumed alumina, Degussa AEROIDE Alu C, denoted as com- Al_2O_3) had a surface area of 110 m^2/g . In addition, a 1.2Pt/8.8 Co_3O_4 /com- Al_2O_3 sample was prepared via the above incipient wetness impregnation and PVA-protected reduction routes. All the chemicals employed in this work were of A.R. grade purity and were purchased from the Beijing Sinopharm Chemical Reagents Company (Beijing, China) and used without further purification.

2.2. Catalyst characterization

The actual Co_3O_4 and Pt concentrations in the samples were determined using ICP-AES. For these analyses, the samples were dissolved in a mixture of concentrated HCl and HNO_3 (3:1 (V:V)). X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu K_α radiation and a nickel filter ($\lambda = 0.15406$ nm). Scanning electron microscopy (SEM) images of the samples were obtained with a Gemini Zeiss Supra 55 apparatus operating at 10 kV. Transmission electron microscopy (TEM) images and selected-area electron diffraction patterns of the samples were acquired using a JEOL-2010 instrument operating at 200 kV. The Brunauer-Emmett-Teller (BET) surface areas of samples were determined via N_2 adsorption at -196 °C, employing a Micromeritics

Tristar 3000 analyzer, with degassing of specimens at 250 °C for 3 h under vacuum prior to measurements. X-ray photoelectron spectroscopy (XPS, VG CLAM 4 MCD analyzer) was used to determine the Co 2p, O 1s, Pt 4d, and C 1s binding energy (BE) of surface species, applying a Mg K_α ($h\nu = 1253.6$ eV) excitation source. Surface adsorbed water and carbonate species were removed by pretreating samples in O_2 (flow rate = 20 mL/min) at 450 °C for 1 h followed by cooling to RT and transferring the pretreated samples into the spectrometer, all within a transparent glove bag (Instruments for Research and Industry, USA) filled with helium. The pretreated samples were outgassed in the preparation chamber of the instrument (at 1.33 mPa) for 0.5 h and then introduced into the analysis chamber (at 0.4 μPa) to acquire XPS spectra. The C 1s signal at 284.6 eV was used as a reference for BE calibration. Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were carried out with a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Prior to TPR measurements, approximately 0.02 g of the catalyst (40–60 mesh) was loaded into a fixed-bed, U-shaped quartz microreactor (i.d. = 4 mm) and pretreated in an O_2 flow of 30 mL/min at 300 °C for 1 h. After cooling to RT under the same atmosphere, the pretreated sample was exposed to a 50 mL/min flow of a 5% H_2 –95% Ar mixture and then heated from RT to 800 °C at a ramp of 10 °C/min. Variations in the H_2 concentration of the effluent were monitored via an on-line chemical adsorption analyzer. The reduction peak was calibrated by comparison with the peak obtained from the complete reduction of standard powdered CuO (99.995%, Aldrich).

2.3. Catalyst evaluation

The catalytic activities of the samples were evaluated in a continuous flow, fixed-bed quartz microreactor (i.d. = 4 mm). To minimize the effects of hot spots, each sample (50 mg, 40–60 mesh) was diluted with 0.25 g of quartz sand (40–60 mesh). Prior to each test, the sample was treated in O_2 (20 mL/min) at 250 °C for 1 h. After cooling to the desired temperature, the reactant gas (1000 ppm toluene + O_2 + N_2 (balance)) was passed through the catalyst bed at a total flow rate of 16.7 mL/min, equivalent to a toluene/ O_2 molar ratio of 1/400, and an SV of approximately 20000 $\text{mL g}^{-1} \text{h}^{-1}$. The 1000 ppm toluene concentration in the gas mixture was generated by passing the N_2 flow through a bottle containing pure toluene and chilled in an ice water bath. The toluene concentration in the gas stream was varied from 2000 to 3000 ppm by changing the N_2 flow rate through the bottle. Water vapor was introduced into the stream at a level of 5.0% by passing the reactant mixture flow through a water saturator device held at 33 °C. Both reactants and products exiting the reactor were analyzed online by a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector and a thermal conductivity detector in conjunction with a Stabilwax@-DA column (30 m in length) for VOCs separation and a Carboxen 1000 column (3.175 mm in diameter and 3 m in length) for permanent gas separation. Products were also analyzed by mass spectrometry (Hiden HPR20), and it was determined that CO_2 and H_2O were the only

products generated during the combustion of toluene. The carbon balance throughout the investigation was estimated to be $(99.5 \pm 1.5)\%$.

3. Results and discussion

3.1. Crystal phase composition

Fig. 1 shows the XRD patterns of the as-prepared samples. By comparing these to the XRD pattern of the standard Al_2O_3 sample, it is evident that the three broad diffraction peaks at $2\theta = 26.0^\circ$, 42.0° and 66.0° can be assigned to the amorphous Al_2O_3 phase in $1.4\text{Pt}/3\text{DOM Al}_2\text{O}_3$. In addition, the peaks at $2\theta = 32.8^\circ$, 34.5° , 39.5° , 45.6° and 67.0° are ascribable to the $\delta\text{-Al}_2\text{O}_3$ phase (JCPDS PDF #16-0394) in $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$. Those at $2\theta = 19.0^\circ$, 31.2° , 36.8° , 49.9° , 55.7° , 59.4° , 65.1° and 77.2° result from the cubic Co_3O_4 phases (JCPDS PDF #42-1467) in $9.2\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, $0.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, $0.6\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ and $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$. Following loading of the Pt NPs, no peaks due to the Pt phase are seen in the $x\text{Pt}/y\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ and $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$ patterns, indicating that the Pt NPs were highly dispersed on the Al_2O_3 support surfaces.

3.2. Morphology, pore structure, and surface area

Fig. 2 presents SEM and TEM images of the $3\text{DOM Al}_2\text{O}_3$ and $9.2\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ samples. It can be clearly seen that the $3\text{DOM Al}_2\text{O}_3$ displays a high-quality 3DOM architecture with a macropore diameter of 180–200 nm (Fig. 2(a) and (b)). Furthermore, the formation of ordered mesopores on the walls of the macropores is evident in Fig. 2(b). Additionally, the loading of Co_3O_4 NPs did not degrade the porous structure of the $3\text{DOM Al}_2\text{O}_3$, and the Co_3O_4 NPs were uniformly dispersed (Fig. 2(c) and (d)). As shown in Fig. 3(a), (c), (e), (g) and (i), the high quality 3DOM structure contained interconnected macropores. It is worth pointing out that ordered mesopores with 4–6-nm

Fig. 1. XRD patterns of (1) $9.2\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, (2) $0.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, (3) $0.6\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, (4) $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, (5) $1.4\text{Pt}/3\text{DOM Al}_2\text{O}_3$, and (6) $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$.

Fig. 2. (a, c, d) SEM and (b) TEM images of (a, b) $3\text{DOM Al}_2\text{O}_3$ and (c, d) $9.2\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$.

diameters were generated within the macroporous skeleton. Therefore, the $x\text{Pt}/y\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ samples possessed a hierarchically ordered macro-/mesoporous morphology. The $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$ sample, however, exhibits a worm-hole-like mesoporous structure (Fig. 3(k) and (l)), and a number of Co_3O_4 and/or Pt NPs are uniformly dispersed on the Al_2O_3 surfaces. The lattice spacings (d values) of the Co_3O_4 NPs in the $9.2\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, $x\text{Pt}/y\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ and $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$ samples were approximately all 0.46 nm (Fig. 3(b), (d), (f), (h) and (l)), a value that is in good agreement with the (111) plane spacing in a standard Co_3O_4 (JCPDS PDF #42-1467) sample. The d values of the Pt NPs in the $x\text{Pt}/y\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ and $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$ were estimated to be approximately 0.23 nm (Fig. 3(d), (f), (h), (j) and (l)), which is close to that of the (111) plane of a standard Pt (JCPDS PDF #87-0644) sample. The Co_3O_4 NPs in the $9.2\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ and $x\text{Pt}/y\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ were 18.3 nm in size, whereas the average size of the Co_3O_4 NPs in the $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$ was 15.8 nm (Table 1 and Fig. 4). The average Pt particle sizes in the $0.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, $0.6\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$, $1.4\text{Pt}/3\text{DOM Al}_2\text{O}_3$ and $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$ were 2.3, 2.4, 2.6, 2.5 and 3.2 nm (Table 1 and Fig. 4), respectively. It is known that the crystalline phase of alumina can influence the thermal stability of its supported catalyst. We found that the amorphous Al_2O_3 used in this work could be converted to crystalline $\gamma\text{-Al}_2\text{O}_3$ after calcination at 800°C for 5 h (Fig. 5), but the ordered mesopores within the skeletons were totally destroyed. It is also well known that the surface area, porous structure extent of noble metal NP dispersion are all important factors governing the performance of a catalyst. Therefore, we fabricated meso-/macroporous Al_2O_3 with an amorphous phase as the support material.

Fig. 6 presents the N_2 adsorption-desorption isotherms and pore size distributions of the samples. Each of the $3\text{DOM Al}_2\text{O}_3$ -supported samples displayed a type II isotherm with an H3 hysteresis loop in the relative pressure (p/p_0) range of

Fig. 3. TEM images of (a, b) 9.2Co₃O₄/3DOM Al₂O₃, (c, d) 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (e, f) 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃, (g, h) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (i, j) 1.4Pt/3DOM Al₂O₃, and (k, l) 1.2Pt/8.8Co₃O₄/com-Al₂O₃.

0.8–1.0, indicating the presence of macropores (Fig. 6(a)–(1–5)) [28]. In addition, mesopores were formed, as confirmed by the pore size distributions (Fig. 6(b)–(1–5)). These data indicated that the 3DOM Al₂O₃-supported samples possessed bimodal (macro-/mesoporous) structures. The N₂ adsorption-desorption isotherm of the 1.2Pt/8.8Co₃O₄/com-Al₂O₃ sample exhibited a type IV isotherm with an H1 hysteresis loop, characteristic of cylindrical mesopores (Fig. 6(a)–(6)). The broad pore size distribution indicates that the 1.2Pt/8.8Co₃O₄/com-Al₂O₃ did not contain uniform mesopores (Fig. 6(b)–(6)). Table 1 summarizes the textural parameters of the as-prepared samples. The BET surface areas (94–100 m²/g) of the 3DOM

Al₂O₃-supported samples were slightly lower than that (110.2 m²/g) of the 1.2Pt/8.8Co₃O₄/com-Al₂O₃ sample.

3.3. Surface composition, metal oxidation state and adsorbed oxygen species

The XPS technique was used to investigate the surface element compositions, metal oxidation states and adsorbed oxygen species of the as-prepared samples, and Fig. 7 shows the Co 2p_{3/2}, O 1s and Pt 4d XPS spectra of the samples. The asymmetrical Co 2p_{3/2} signal of each sample (Fig. 7(a)) could be deconvoluted to three components at BE values of 780.2, 781.9 and

Table 1

BET surface areas, pore volumes, average pore sizes, average Pt and Co₃O₄ particle sizes and actual Pt and Co₃O₄ concentrations of catalyst samples.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	Particle size ^a (nm)	
				Pt	Co ₃ O ₄
9.2Co ₃ O ₄ /3DOM Al ₂ O ₃	97.8	0.52	20.5	—	18.3
0.3Pt/8.9Co ₃ O ₄ /3DOM Al ₂ O ₃	93.5	0.47	19.6	2.3	18.3
0.6Pt/8.9Co ₃ O ₄ /3DOM Al ₂ O ₃	100.4	0.57	18.3	2.4	18.3
1.3Pt/8.9Co ₃ O ₄ /3DOM Al ₂ O ₃	102.2	0.56	17.9	2.6	18.3
1.4Pt/3DOM Al ₂ O ₃	100.3	0.48	21.7	2.5	—
1.2Pt/8.8Co ₃ O ₄ /com-Al ₂ O ₃	110.2	0.31	11.3	3.2	15.8

^a Estimated based on TEM images.

Fig. 4. Co_3O_4 and Pt particle size distributions of (a) 9.2 Co_3O_4 /3DOM Al_2O_3 , (b) 0.3Pt/8.9 Co_3O_4 /3DOM Al_2O_3 , (c) 0.6Pt/8.9 Co_3O_4 /3DOM Al_2O_3 , (d) 1.3Pt/8.9 Co_3O_4 /3DOM Al_2O_3 , (e) 1.4Pt/3DOM Al_2O_3 , and (f) 1.2Pt/8.8 Co_3O_4 /com- Al_2O_3 .

786.5 eV, which were assignable to the surface Co^{3+} and Co^{2+} species [29] and the satellite of the surface Co^{2+} species [30], respectively. Table 2 summarizes the surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratios of the samples, from which it is evident that the surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio decreased (that is, the surface Co^{2+} concentration increased) after loading the Pt NPs on the 9.2 Co_3O_4 /3DOM Al_2O_3 surface. The surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio (1.95) of the 9.2 Co_3O_4 /3DOM Al_2O_3 was much higher than those (0.89–1.15) of the $x\text{Pt}/y\text{Co}_3\text{O}_4$ /3DOM Al_2O_3 and 1.2Pt/8.8 Co_3O_4 /com- Al_2O_3 . The 1.3Pt/8.9 Co_3O_4 /3DOM Al_2O_3 sample exhibited the lowest surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio

(0.89), and the surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio (0.95) of the 1.2Pt/8.8 Co_3O_4 /com- Al_2O_3 was lower than that (1.15) of the 0.3Pt/8.9 Co_3O_4 /3DOM Al_2O_3 and that (1.01) of the 0.6Pt/8.9 Co_3O_4 /3DOM Al_2O_3 . These results demonstrate that there were more surface oxygen vacancies on the Pt and Co_3O_4 -loaded samples than on the 9.2 Co_3O_4 /3DOM Al_2O_3 [31]. Such structural defects can facilitate the adsorption and activation of gas phase oxygen molecules, thereby enhancing the catalytic performance of the materials for toluene oxidation [32].

As shown in Fig. 7(b), the asymmetrical O 1s spectrum of each sample could be deconvoluted to two components, one with BE = 530.5 eV, ascribable to surface lattice oxygen (O_{latt}) species, and the other at BE = 531.6 eV, attributable to surface adsorbed oxygen (O_{ads} , such as O_2^- , O_2^{2-} and O^-) species [33]. Following the loading of Pt on the 9.2 Co_3O_4 /3DOM Al_2O_3 surface, the surface $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio increased markedly (Table 2), with the highest $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio (2.45) being achieved on the 1.3Pt/8.9 Co_3O_4 /3DOM Al_2O_3 sample. The changes in the $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratios of the samples display a trend similar to that of the surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratios.

Fig. 7(c) presents the Pt 4d XPS spectra of the $x\text{Pt}/y\text{Co}_3\text{O}_4$ /3DOM Al_2O_3 , 1.4Pt/3DOM Al_2O_3 and 1.2Pt/8.8 Co_3O_4 /com- Al_2O_3 . Since the Al 2p and Pt 4f lines overlap, the Pt 4d line was used in the present study. The Pt 4d spectrum of each sample could be deconvoluted into three components. The component at BE = 313.2 eV was assigned to surface metallic Pt (Pt^0) species [34], while that at BE = 315.6 eV was attributed to typical surface PtO species [35], and the component at BE = 318.6 eV

Fig. 5. XRD patterns of the 3DOM Al_2O_3 samples obtained after calcination at (1) 600 °C, (2) 700 °C, and (3) 800 °C.

Fig. 6. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distributions of (1) 9.2Co₃O₄/3DOM Al₂O₃, (2) 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (3) 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃, (4) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (5) 1.4Pt/3DOM Al₂O₃, and (6) 1.2Pt/8.8Co₃O₄/com-Al₂O₃.

Fig. 7. (a) Co 2p_{3/2}, (b) O 1s, and (c) Pt 4d XPS spectra of (1) 9.2Co₃O₄/3DOM Al₂O₃, (2) 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (3) 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃, (4) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (5) 1.4Pt/3DOM Al₂O₃, and (6) 1.2Pt/8.8Co₃O₄/com-Al₂O₃.

Table 2

Surface element compositions and H₂ consumption values of catalyst samples.

Sample	Co ³⁺ /Co ²⁺ molar ratio	O _{ads} /O _{latt} molar ratio	Pt ^{δ+} /Pt ⁰ molar ratio	H ₂ consumption ^a (mmol/g)			
				< 300 °C	300–400 °C	> 400 °C	Total
9.2Co ₃ O ₄ /3DOM Al ₂ O ₃	1.95	0.81	—	—	—	1.16	1.16
0.3Pt/8.9Co ₃ O ₄ /3DOM Al ₂ O ₃	1.15	1.02	1.04	—	0.23	1.14	1.37
0.6Pt/8.9Co ₃ O ₄ /3DOM Al ₂ O ₃	1.01	1.19	1.22	0.27	—	1.98	2.25
1.3Pt/8.9Co ₃ O ₄ /3DOM Al ₂ O ₃	0.89	2.45	2.82	0.30	0.95	2.23	3.48
1.4Pt/3DOM Al ₂ O ₃	—	1.44	1.62	0.23	1.16	—	1.39
1.2Pt/8.8Co ₃ O ₄ /com-Al ₂ O ₃	0.95	1.68	2.07	0.41	—	1.61	2.02

^a Estimated by quantitatively analyzing the H₂-TPR profiles.

was higher than expected for pure PtO₂ [36]. The detection of surface Pt^{δ+} species indicates a strong interaction between Pt and the Co₃O₄ NPs via the reaction Pt⁰ + Co³⁺ → Pt^{δ+} + Co²⁺. The surface Pt^{δ+}/Pt⁰ molar ratio (2.82) of the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ was much higher than those (1.04–2.07) of the other supported Pt samples (Table 2). Therefore, the 1.3Pt/8.9Co₃O₄/

3DOM Al₂O₃ possessed the highest O_{ads}/O_{latt} and Pt^{δ+}/Pt⁰ molar ratios as well as the lowest Co³⁺/Co²⁺ molar ratio. The increased O_{ads} concentration resulting from a greater number of oxygen vacancies would be beneficial in terms of enhancing the catalytic performance of the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ sample for toluene oxidation.

Fig. 8. (a) H₂-TPR profiles and (b) initial H₂ consumption rates as functions of inverse temperature for (1) 9.2Co₃O₄/3DOM Al₂O₃, (2) 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (3) 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃, (4) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (5) 1.4Pt/3DOM Al₂O₃, and (6) 1.2Pt/8.8Co₃O₄/com-Al₂O₃.

3.4. Reducibility

Given that the reducibility of a catalyst can play an important role in redox-based reactions, we carried out TPR experiments to investigate the reducibility of the as-prepared samples, and the resulting profiles are shown in Fig. 8(a). There were two reduction peaks for the 9.2Co₃O₄/3DOM Al₂O₃ (Fig. 8(a)-(1)). The peak centered at 495 °C was due to the reduction of Co₃O₄ to CoO, whereas the peak at 606 °C was attributed to the reduction of CoO to Co⁰ [37]. In the case of the 1.4Pt/3DOM Al₂O₃ (Fig. 8(a)-(5)), two weaker reduction peaks appeared at 273 and 394 °C, ascribed to the reduction of chemically adsorbed oxygen species on the highly dispersed Pt NPs (that is, from Pt-O_x to Pt⁰) [38–40]. After loading of the Pt NPs, the xPt/8.9Co₃O₄/3DOM Al₂O₃ and 1.2Pt/8.8Co₃O₄/com-Al₂O₃ reduction peaks (Fig. 8(a)-(2, 3, 4, 6)) were shifted to lower temperatures, especially in the case of the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ sample (Fig. 8(a)-(4)). This result implies a strong interaction between the Pt and the Co₃O₄ NPs, resulting in improved low-temperature reducibility. By quantifying the reduction peaks, one can obtain the total H₂ consumption of the samples, as summarized in Table 2. It can be seen that the total H₂ consumption values of the 9.2Co₃O₄/3DOM Al₂O₃, xPt/8.9Co₃O₄/3DOM Al₂O₃, 1.4Pt/3DOM Al₂O₃ and 1.2Pt/8.8Co₃O₄/com-Al₂O₃ were 1.16, 1.37–3.48, 1.39 and 2.02 mmol/g, respectively. In addition to the highest total H₂ consumption (3.48 mmol/g), the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ also possessed the highest low-temperature H₂ consumption (0.41 mmol/g), demonstrating that this sample exhibited the best low-temperature reducibility.

To better evaluate the low-temperature reducibility of the samples, we calculated the initial H₂ consumption rates (the rates up to the point at which less than 25% of the oxygen was removed for the first reduction peak) [41], as shown in Fig. 8(b). The initial H₂ consumption rate (equivalent to the low-temperature reducibility) increased in the order of 9.2Co₃O₄/3DOM Al₂O₃ < 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃ < 0.6Pt/

8.9Co₃O₄/3DOM Al₂O₃ < 1.4Pt/3DOM Al₂O₃ < 1.2Pt/8.8Co₃O₄/com-Al₂O₃ < 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃. This trend in the low-temperature reducibility was in good agreement with the observed O_{ads} concentration and catalytic performance data, as presented below.

3.5. Catalytic performance

A blank trial in which only quartz sand was loaded in the microreactor and the temperature was maintained below 400 °C was carried out using a toluene concentration of 1000 ppm, a toluene/O₂ molar ratio of 1/400 and an SV of 20000 mL g⁻¹ h⁻¹. No significant conversion of toluene was detected under these conditions, demonstrating that there were no obvious homogeneous reactions under the adopted reaction conditions. Fig. 9 summarizes the catalytic activities of the as-prepared samples during the oxidation of toluene. The toluene conver-

Fig. 9. Toluene conversion as a function of reaction temperature over the as-prepared catalysts at an SV of 20000 mL g⁻¹ h⁻¹. (1) 9.2Co₃O₄/3DOM Al₂O₃; (2) 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃; (3) 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃; (4) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃; (5) 1.4Pt/3DOM Al₂O₃; (6) 1.2Pt/8.8Co₃O₄/com-Al₂O₃.

Table 3Catalytic activities, apparent activation energies (E_a), and toluene oxidation rates of the catalysts at 160 °C.

Sample	$T_{10\%}/^{\circ}\text{C}$	$T_{50\%}/^{\circ}\text{C}$	$T_{90\%}/^{\circ}\text{C}$	$E_a/(\text{kJ/mol})$	Toluene oxidation rate at 160 °C		
					For catalyst ($\mu\text{mol g}^{-1} \text{s}^{-1}$)	For Co_3O_4 ($\text{mmol mol}^{-1} \text{s}^{-1}$)	For Pt ($\text{mmol mol}^{-1} \text{s}^{-1}$)
$9.2\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$	240	290	326	85.2	0.002	0.007	—
$0.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$	184	210	220	78.3	0.007	0.032	0.762
$0.6\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$	160	189	200	73.6	0.026	0.118	1.419
$1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$	106	140	160	42.6	0.222	1.003	5.557
$1.4\text{Pt}/3\text{DOM Al}_2\text{O}_3$	155	180	197	67.2	0.029	—	0.667
$1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$	140	164	180	55.8	0.086	0.528	2.333

sion is seen to have increased monotonically with increasing temperature. It is preferable to use the reaction temperatures $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ (corresponding to toluene conversions of 10%, 50% and 90%) to evaluate the catalytic performance of the samples, as summarized in Table 3. The $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ sample exhibited the best performance, with $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ values of 106, 140 and 160 °C at $\text{SV} = 20000 \text{ mL g}^{-1} \text{ h}^{-1}$. In addition, the Pt- and/or Co_3O_4 -loaded samples outperformed the sample loaded with only Co_3O_4 . The activity over the $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ was much higher than that ($T_{10\%} = 140$ °C, $T_{50\%} = 164$ °C and $T_{90\%} = 180$ °C) over the $1.2\text{Pt}/8.8\text{Co}_3\text{O}_4/\text{com-Al}_2\text{O}_3$.

Table 4 summarizes the activities for toluene oxidation over various catalysts that have been reported in the references. By comparing the activities of these samples with that of the best-performing $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ from the present study, it is evident that the catalytic activity ($T_{90\%} = 160$ °C at $20000 \text{ mL g}^{-1} \text{ h}^{-1}$) over the $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ was superior to that ($T_{90\%} = 215$ °C at $18000 \text{ mL g}^{-1} \text{ h}^{-1}$) obtained from 1.0% Pt/ $\gamma\text{-Al}_2\text{O}_3$, as well as that ($T_{90\%} = 215$ °C at $8400 \text{ mL g}^{-1} \text{ h}^{-1}$) over 1% Pt/ Al_2O_3 –30 wt% CeO_2 and ($T_{90\%} = 226$ °C at $20000 \text{ mL g}^{-1} \text{ h}^{-1}$) over 4.6% Au/macroporous LaMnO_3 . The value from this work was also similar to the value ($T_{90\%} = 170$ °C at $20000 \text{ mL g}^{-1} \text{ h}^{-1}$) over 6.4% Au/ $3\text{DOM La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, but inferior to that ($T_{90\%} = 138$ °C at $20000 \text{ mL g}^{-1} \text{ h}^{-1}$) over 6.5% Au/meso- Co_3O_4 and ($T_{90\%} = 149$ °C at $30000 \text{ mL g}^{-1} \text{ h}^{-1}$) over 1.0% Pt/ZSM-5. Compared with Au, Pt is more expensive, and a loading of 1.3% is relatively high. Thus, with regard to practical applications, it is necessary to reduce the loading of Pt in these catalysts. Doping with a base transition metal such as Co might be an effective means of reducing the noble metal loading without a significant loss in catalytic activity. In fact, we

have recently found that supported Pt-Co nanocatalysts exhibit excellent performance for the catalytic oxidation of typical VOCs, which will be reported in the future.

To examine the catalytic stability of these materials, a 48-h on-stream toluene oxidation experiment was conducted using the best-performing $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ sample at 160 °C and $\text{SV} = 20000 \text{ mL g}^{-1} \text{ h}^{-1}$, with the results shown in Fig. 10(a). In addition, Fig. 10(b) shows the catalytic activities over fresh and used $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ after toluene oxidation at $\text{SV} = 20000 \text{ mL g}^{-1} \text{ h}^{-1}$ in the presence of 1000, 2000 or 3000 ppm toluene for 30, 9 and 9 h, respectively. It is apparent that no significant loss in catalytic activity occurred. Furthermore, the change in toluene concentration had no obvious impact on the catalytic activity of the $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$. Therefore, the $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ was catalytically durable under the adopted conditions.

Fig. 11 shows the effect of moisture on the catalytic activity during toluene oxidation over the $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$. A 5.0% water vapor concentration was introduced to the reaction system gas mixture feed after the catalytic activity at 160 °C and $\text{SV} = 20000 \text{ mL g}^{-1} \text{ h}^{-1}$ became stable. It can be seen from these data that the water vapor decreased the activity by approximately 5%. After the water vapor feed was cut off, the activity was restored to that of the fresh sample, indicating that deactivation of the $1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$ induced by water vapor addition was reversible. The negative effect of moisture on toluene oxidation is attributed to the competitive adsorption of water in place of toluene or oxygen molecules. It is worth noting that the doping of Al_2O_3 with CeO_2 can improve the moisture tolerance of the catalyst. Recently, we determined that the introduction of water vapor to the reaction system when using the $x\text{Pt}/3\text{DOM CeO}_2\text{-Al}_2\text{O}_3$ catalyst has a positive

Table 4

Catalytic activities of various catalysts for the oxidation of toluene as reported in the references.

Catalyst	Toluene concentration (ppm)	Toluene/oxygen molar ratio	Space velocity ($\text{mL g}^{-1} \text{ h}^{-1}$)	$T_{90\%}/^{\circ}\text{C}$	Ref.
$1.3\text{Pt}/8.9\text{Co}_3\text{O}_4/3\text{DOM Al}_2\text{O}_3$	1000	1/400	20000	160	This work
1.0% Pt/ $\gamma\text{-Al}_2\text{O}_3$	1000	1/200	18000	215	[6]
1% Pt/ Al_2O_3 –30% CeO_2	1000	1/200	8400	215	[5]
4.6% Au/macroporous LaMnO_3	1000	1/400	20000	226	[42]
6.4% Au/ $3\text{DOM La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	1000	1/400	20000	170	[43]
6.5% Au/meso- Co_3O_4	1000	1/400	20000	138	[44]
1.0% Pt/ZSM-5	1000	1/200	30000	149	[7]

Fig. 10. (a) Toluene conversion as a function of on-stream reaction time over 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ at 160 °C and an SV of 20000 mL g⁻¹ h⁻¹; (b) Catalytic activity over fresh (1) and used (2) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ samples after 30, 9 and 9 h of toluene oxidation at an SV of 20000 mL g⁻¹ h⁻¹ in the presence of 1000, 2000 or 3000 ppm toluene, respectively.

effect on the catalytic activity during the oxidation of toluene.

Toluene consumption rates versus reaction temperature over the as-prepared samples are shown in Fig. 12. Toluene consumption rates were found to increase in a linear fashion with rising temperature. It is known that there are several different types of active sites (such as noble metals, transition-metal oxides and interfaces between noble metals and transition-metal oxides) in reducible metal oxide-supported noble metal catalysts, making it difficult to identify a single type of active site. Therefore, the accurate calculation of the turnover frequency can be challenging. For comparison purposes, however, we calculated the toluene oxidation rate (r) as xV_0/m_{cat} (or n_M), where x is the conversion at a given temperature, V_0 is the initial toluene concentration per second, m_{cat} is the mass of catalyst, and n_M ($M = \text{Pt}$ or Co_3O_4) is the molar amount of M . Table 3 summarizes the toluene oxidation rates at 160 °C over the samples. It can be seen that the r value increased in the order of 9.2Co₃O₄/3DOM Al₂O₃ < 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃ < 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃ < 1.4Pt/3DOM Al₂O₃ < 1.2Pt/8.8Co₃O₄/com-Al₂O₃ < 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ when normalized by grams of catalyst, and in the order of 9.2Co₃O₄/3DOM Al₂O₃ < 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃ < 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃ < 1.2Pt/8.8Co₃O₄/com-Al₂O₃ < 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ when normalized by moles of Co₃O₄. However, the r value of the 1.4Pt/3DOM Al₂O₃ was 0.667

Fig. 11. Effect of H₂O on toluene conversion at 160 °C over the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃.

mmol mol⁻¹ s⁻¹) for Pt. This value was lower than those (0.762 to 5.557 mmol mol⁻¹ s⁻¹) obtained from the xPt/8.9Co₃O₄/3DOM Al₂O₃ and 1.2Pt/8.8Co₃O₄/com-Al₂O₃, possibly owing to the much higher Pt loading in the former sample. Therefore, the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ showed the highest toluene oxidation rate. In addition to the Co₃O₄ and Pt NP active sites, the interaction between the Pt and the Co₃O₄ NPs might also play an important role in enhancing the oxidation of toluene over 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃. The presence of a hierarchically ordered macro-/mesoporous structure would be expected to facilitate the dispersion of the Pt and the Co₃O₄ NPs on the pore surfaces [45] and render these active sites more accessible to the reactant molecules, thereby improving the catalytic activity.

Fig. 13 shows the toluene consumption rate for catalysts at 160 °C as a function of the $O_{\text{ads}}/O_{\text{latt}}$ molar ratio in each sample. It is evident that a higher O_{ads} concentration enhances the catalytic activity of the sample, and that the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ exhibited the highest toluene oxidation rate and $O_{\text{ads}}/O_{\text{latt}}$ molar ratio. The toluene consumption rate (0.222 μmol g⁻¹ s⁻¹)

Fig. 12. Toluene consumption rate as a function of reaction temperature over the catalysts at SV = 20000 mL g⁻¹ h⁻¹. (1) 9.2Co₃O₄/3DOM Al₂O₃; (2) 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃; (3) 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃; (4) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃; (5) 1.4Pt/3DOM Al₂O₃; (6) 1.2Pt/8.8Co₃O₄/com-Al₂O₃.

Fig. 13. Toluene consumption rates for catalysts at 160 °C and SV = 20000 mL g⁻¹ h⁻¹ as a function of the O_{ads}/O_{latt} molar ratios of the samples.

over the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ was 111, 7.6 and 2.6 times the values obtained over the 9.2Co₃O₄/3DOM Al₂O₃, 1.4Pt/3DOM Al₂O₃ and 1.2Pt/8.8Co₃O₄/com-Al₂O₃ (0.002, 0.029 and 0.086 μmol g⁻¹ s⁻¹), respectively. This variation in activity was due to the interactions between the Pt and the Co₃O₄ NPs and the ordered macro-/mesoporous structures. Similar interactions between precious metals (such as Pt, Pd, Rh, Ru and Ag) and a CeO₂ support were also observed by Acerbi et al. [46]. The interaction between the Pt and the Co₃O₄ NPs could possibly facilitate the activation of O₂ molecules to generate active O_{ads} species and thus enhance the catalytic activity of the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃. It is well known that the reducibility of metal oxides is associated with the formation of oxygen vacancies. Kleitz et al. [47] found that a metal oxide could induce surface defects more readily if it was more reducible, and thus could produce a higher O_{ads} concentration. Based on the characterization and activity evaluations, we conclude that the excellent catalytic performance of the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ results from highly dispersed Pt NPs, an elevated O_{ads} concentration, good low-temperature reducibility, strong interactions between the Pt and the Co₃O₄ NPs, and a hierarchically ordered macro-/mesoporous structure.

3.6. Apparent activation energy

It has been generally believed that the oxidation of VOCs over transition metal oxides obeys first-order reaction kinetics with regard to VOC concentration and zero-order kinetics with regard to oxygen concentration [48]. Therefore, it is reasonable to assume that toluene oxidation in the presence of excess oxygen (toluene/O₂ molar ratio = 1/400) should follow a first-order reaction mechanism with respect to the VOC concentration (*c*), such that $r = -k c = (-A \exp(-E_a/RT))c$, where *r*, *k*, *A* and *E_a* are the reaction rate (mol/s), rate constant (s⁻¹), pre-exponential factor and apparent activation energy (kJ/mol), respectively. Fig. 14 presents the Arrhenius plots for toluene oxidation over the as-prepared samples, and the calcu-

Fig. 14. Arrhenius plots for toluene oxidation at SV = 20000 mL g⁻¹ h⁻¹ over (1) 9.2Co₃O₄/3DOM Al₂O₃, (2) 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (3) 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃, (4) 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃, (5) 1.4Pt/3DOM Al₂O₃, and (6) 1.2Pt/8.8Co₃O₄/com-Al₂O₃.

lated *E_a* values are summarized in Table 3. It can be seen that the *E_a* decreased in the order of 9.2Co₃O₄/3DOM Al₂O₃ > 0.3Pt/8.9Co₃O₄/3DOM Al₂O₃ > 0.6Pt/8.9Co₃O₄/3DOM Al₂O₃ > 1.4Pt/3DOM Al₂O₃ > 1.2Pt/8.8Co₃O₄/com-Al₂O₃ > 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃. The *E_a* (42.6 kJ/mol) over the best-performing 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ catalyst was much lower than the values (120–144 kJ/mol) obtained from CuO/Al₂O₃ and MnO_x/Al₂O₃ [49] as well as those (54–76 kJ/mol) over Au/3DOM Mn₂O₃ [50], but close to the values (45–55 kJ/mol) reported for Au/meso-Co₃O₄ [44]. These results indicate that toluene oxidation proceeds more readily over the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ sample.

4. Conclusions

In this work, *x*Pt/*y*Co₃O₄/3DOM Al₂O₃ samples were prepared via PMMA-templating, incipient wetness impregnation and PVA-protected reduction. The *x*Pt/*y*Co₃O₄/3DOM Al₂O₃ samples displayed a hierarchical 3DOM architecture (with macropore diameters from 180 to 200 nm and mesopore diameters from 4 to 6 nm) and surface areas in the range of 94 to 102 m²/g. Co₃O₄ NPs that were 18.3 nm in size and Pt NPs with sizes from 2.3 to 2.5 nm were uniformly dispersed on the surfaces of the 3DOM Al₂O₃. Among the *x*Pt/*y*Co₃O₄/3DOM Al₂O₃ catalysts, the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ had the highest O_{ads} concentration and the best low-temperature reducibility, and thus exhibited the highest catalytic activity (*T*_{90%} = 160 °C at SV = 20000 mL g⁻¹ h⁻¹) for toluene oxidation. Based on the activity data and characterization results, we conclude that the superior performance of this material can be attributed to well dispersed Pt NPs, an elevated O_{ads} concentration, superior reducibility at low temperatures and significant Pt to Co₃O₄ NP interactions. The hierarchically ordered macro-/mesoporous structure of this material is also believed to have been partly responsible for the excellent catalytic abilities of the 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃.

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Graphical Abstract

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Pt/Co₃O₄/3DOM Al₂O₃: Highly effective catalysts for toluene combustion

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The xPt/yCo₃O₄/3DOM Al₂O₃ nanocatalysts perform well in toluene combustion. The well-dispersed Pt nanoparticles, high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interaction between Pt and Co₃O₄ account for the excellent activity of 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃.

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Pt/Co₃O₄/3DOM Al₂O₃: 甲苯燃烧的高效催化剂

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摘要: 与硫氧化物、氮氧化物、一氧化碳以及悬浮颗粒一样, 大部分挥发性有机物 (VOCs) 污染大气环境. 控制 VOCs 排放有多种方法, 其中催化氧化法是一种有效技术, 关键在于获得高效催化剂.

近年来, 负载过渡金属和贵金属催化剂因具有比单纯负载贵金属和单纯负载过渡金属氧化物更好的催化性能而备受关注. 在负载贵金属催化剂中, 高比表面积载体负载 Pt, Pd 或 Rh 催化剂得到广泛而深入的研究, 尽管这些催化剂成本较高, 但是其对 VOCs 氧化反应显示了很高的低温催化活性. 众所周知, 催化活性取决于贵金属和 VOCs 的种类, 不同负载贵金属催化剂对特定反应会表现出不同的催化活性. 负载 Pt 催化剂对长链碳氢化合物和芳香族化合物氧化反应表现出更高的活性. 相对于负载贵金属催化剂, 负载过渡金属氧化物催化剂不仅具有良好的氧化活性, 而且价格低廉. 迄今已发现许多过渡金属氧化物 (如 Co₃O₄, Cr₂O₃ 和 MnO₂ 等) 对典型 VOCs 氧化反应具有催化活性, 其中 Co₃O₄ 的催化活性尤为突出. 研究表明, Co₃O₄ 的性质和分散度是决定其性能的关键因素, 制备方法、载体性质和过渡金属氧化物负载量对 Co₃O₄ 的物化性质具有重要影响, 而且在负载 Pt 催化剂中添加金属氧化物能改善其催化性能. 尽管多孔氧化铝是一种常用的载体材料, 但目前尚无文献报道三维有序大孔-介孔氧化铝负载 Co₃O₄ 和 Pt 纳米粒子催化剂的制备及其对甲苯氧化反应的催化性能.

本文采用聚甲基丙烯酸甲酯微球胶晶模板法、等体积浸渍法和聚乙烯醇保护的硼氢化钠还原法制备了三维有序大孔-介孔 (3DOM Al₂O₃) 负载 Co₃O₄ 和 Pt (xPt/yCo₃O₄/3DOM Al₂O₃, Pt 的质量分数 (x%) 为 0–1.4%, Co₃O₄ 的质量分数 (y%) 为 0–9.2%) 纳米催化剂. 通过电感耦合等离子体原子发射光谱、X 射线衍射、氮气吸附-脱附、扫描电子显微镜、透射电子显微镜、选区电子衍射、X 射线光电子能谱及氢气程序升温还原等技术表征了催化剂的物化性质, 利用固定床微型石英反应器评价了催化剂对甲苯氧化反应的催化活性. 结果表明, xPt/yCo₃O₄/3DOM Al₂O₃ 催化剂具有多级孔结构 (大孔孔径为 180–200 nm, 介孔孔径为 4–6 nm), 比表面积为 94–102 m²/g. 粒径为 18.3 nm 的 Co₃O₄ 纳米粒子和粒径为 2.3–2.5 nm 的 Pt 纳米粒子均匀分散在 3DOM Al₂O₃ 表面. 在 xPt/yCo₃O₄/3DOM Al₂O₃ 催化剂中, 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ 拥有最高的 O_{ads} 浓度、最好的低温还原性和最高的甲苯氧化反应催化活性 (当空速为 20000 mL g⁻¹ h⁻¹ 时, 甲苯转化率达 90% 的反应温度为 160 °C). 基于催化剂的活性数据和结构表征, 我们认为, 1.3Pt/8.9Co₃O₄/3DOM Al₂O₃ 优异的催化性能与其高分散的 Pt 纳米粒子、高的 O_{ads} 浓度、好的低温还原性、Pt 和 Co₃O₄ 纳米粒子间的强相互作用以及多级孔结构相关.

关键词: 三维有序大孔; 氧化铝负载氧化钴催化剂; 负载铂催化剂; 甲苯燃烧

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