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Article

Catalytic performance enhancement by alloying Pd with Pt on ordered mesoporous manganese oxide for methane combustion

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ABSTRACT

Ordered mesoporous Mn_2O_3 (meso- Mn_2O_3) and meso- Mn_2O_3 -supported Pd, Pt, and Pd-Pt alloy $x(\text{Pd,Pt})/\text{meso-Mn}_2\text{O}_3$; $x = (0.10\text{--}1.50)$ wt%; Pd/Pt molar ratio (y) = 4.9–5.1 nanocatalysts were prepared using KIT-6-templated and poly(vinyl alcohol)-protected reduction methods, respectively. The meso- Mn_2O_3 had a high surface area, i.e., $106 \text{ m}^2/\text{g}$, and a cubic crystal structure. Noble-metal nanoparticles (NPs) of size 2.1–2.8 nm were uniformly dispersed on the meso- Mn_2O_3 surfaces. Alloying Pd with Pt enhanced the catalytic activity in methane combustion; 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 gave the best performance; $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ (the temperatures required for achieving methane conversions of 10%, 50%, and 90%) were 265, 345, and 425 °C, respectively, at a space velocity of 20000 mL/(g·h). The effects of SO_2 , CO_2 , H_2O , and NO on methane combustion over 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 were also examined. We conclude that the good catalytic performance of 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 is associated with its high-quality porous structure, high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interactions between Pd-Pt alloy NPs and the meso- Mn_2O_3 support.

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1. Introduction

Methane is widely considered to be the cleanest available hydrocarbon energy source for transportation and industrial applications [1]. Methane itself, however, is a greenhouse gas, with a global warming effect 21–23 times greater than that of CO_2 [2], and more serious pollutants (e.g., CO, nitrogen oxides, and unburned hydrocarbons) are always detected in the outlets of methane flame combustion [3]. Catalytic combustion of methane has many advantages over conventional flame combus-

tion, e.g., suppression of NO_x and CO and emissions and more efficient energy use. Pd-based catalysts are commonly used for methane combustion because of their excellent low-temperature catalytic activities [4,5]. PdO is believed to be an important activity-controlling factor in catalyzing the oxidation of hydrocarbons, and the reduction of PdO to metallic Pd⁰ at high temperatures decreases the catalytic activity [6,7]; for example, Hellman et al. [8] found that the PdO (101) facet was more reactive than metallic Pd⁰ in methane combustion. Pd-based catalysts, however, have some major drawbacks: (1)

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they often have poor stability in steady-state methane combustion processes [9,10], and (2) their exposure to water or sulfur-containing compounds can significantly reduce the activity via formation of inactive $\text{Pd}(\text{OH})_2$ and stable palladium sulfate phases [5,11,12]. These problems can be overcome by adding a second metal to generate a bimetallic alloy catalyst. Pt-based catalysts are also good catalysts for the combustion of hydrocarbons. The addition of Pt can increase the low-temperature methane combustion activity or hinder the growth of Pd or PdO particles [13]. Doping of a supported Pd catalyst with a small amount of Pt improves the thermal stability [14,15] and enhances resistance to sulfur or water-vapor poisoning [12].

Transition-metal oxides (e.g., Mn [16,17], Co [18], Cu, Cr, and Ni [19]) have also been used as catalysts in methane combustion; they are cheaper, more stable at high temperatures [11], and more resistant to sulfur poisoning [19] than supported noble-metal catalysts. Among the transition-metal oxide catalysts developed so far, manganese oxides have been widely studied as possible alternative catalysts for methane combustion because of their varied and multiple oxidation states and oxygen-storage capacities [20]. Han's group [17] reported complete conversion of methane over $\alpha\text{-Mn}_2\text{O}_3$ at ca. 600 °C, and this catalyst has ultrahigh stability. Machocki and coworkers [21] found that Ag-loaded manganese-lanthanum oxides showed good catalytic activities in methane combustion, and the reaction rate was related to the surface $\text{Mn}^{4+}/\text{Mn}^{3+}$ molar ratio.

Recently, our group investigated a number of nanosized or porous catalysts (e.g., Au-Pd/meso- Co_3O_4 [22], Au-Pd/3DOM Co_3O_4 [23], Au-Pd/3DOM Mn_2O_3 [24], Au/3DOM Mn_2O_3 [25], Au/meso- Mn_2O_3 [26], Au-Pd/meso- Cr_2O_3 [27], and Ag/ Mn_2O_3 nanowires [28]), and found that most of them (especially the bimetallic catalysts) performed well in the oxidation of typical volatile organic compounds and/or CO. We introduced a small amount of Pt to generate Pd-Pt alloy nanoparticles (NPs) and loaded them via a poly(vinyl alcohol) (PVA)-protected reduction route on KIT-6-derived ordered mesoporous Mn_2O_3 (meso- Mn_2O_3) with specific redox properties to overcome the drawbacks of Pd-based catalysts. We investigated their physicochemical properties and evaluated their catalytic performances in methane combustion. Ordered meso- Mn_2O_3 has a good-quality porous structure and a high surface area, therefore its use as a support for metal alloy catalysts with a uniform particle distribution improves the catalytic activity and stability. To the best of our knowledge, there have been no reports of the preparation of three-dimensional ordered meso- Mn_2O_3 -supported metal alloy catalysts and their use as methane combustion catalysts.

2. Experimental

2.1. Catalyst preparation

Mesoporous silica (KIT-6) and ordered meso- Mn_2O_3 were synthesized using previously reported procedures [29,30]. In a typical synthesis, KIT-6 (1.0 g) was suspended in toluene (50 mL). The mixture was stirred at 65 °C for 0.5 h and $\text{Mn}(\text{NO}_3)_2$

aqueous solution (50 wt%, 20.00 mmol) was added under vigorous stirring. The mixture was stirred at 65 °C for 3 h. A powder was obtained by filtration and drying the residue at room temperature (rt). The precursor@silica composite was placed in a crucible and calcined in a muffle furnace from rt to 600 °C at a ramping rate of 1 °C/min; this temperature was maintained for 6 h. The silica template was removed by etching twice with hot NaOH aqueous solution (2.00 mol/L). Template-free meso- Mn_2O_3 was obtained by centrifugation, washing with deionized water and ethanol, and drying at 80 °C.

Ordered meso- Mn_2O_3 -supported Pd-Pt alloy catalysts were prepared via a PVA ($MW_{\text{aver.}} = 10000$ g/mol)-protected reduction route with NaBH_4 as a reducing agent [31]. The typical preparation procedure was as follows. A desired amount of PVA was added to an aqueous solution of PdCl_2 and H_2PtCl_4 (100 mg/L, Pd/Pt molar ratio = 5.0) in an ice bath; the mixture was stirred vigorously for 20 min. A certain amount of NaBH_4 aqueous solution (0.1 mol/L) was quickly added to the mixed solution, generating a dark-brown noble-metal sol. A desired amount of meso- Mn_2O_3 powder was added to the noble-metal sol (theoretical Pd-Pt loadings = (0.1, 1.0, and 1.5) wt%) and the mixture was stirred for 6 h. The mixture was filtered, washed with deionized water, and dried at 80 °C for 12 h. The dried powders were calcined in a muffle furnace from rt to 600 °C, at a ramping rate of 1 °C/min, and then this temperature was maintained for 6 h; $x(\text{Pd,Pt})/\text{meso-}\text{Mn}_2\text{O}_3$ samples were obtained. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the actual loadings (x) of the noble metals were (0.07, 0.72, and 1.41) wt%, respectively, and the corresponding y values were 4.9, 5.1, and 5.1.

For comparison, $x\text{Pd}/\text{meso-}\text{Mn}_2\text{O}_3$, $x\text{Pt}/\text{meso-}\text{Mn}_2\text{O}_3$, and $x(\text{Pd,Pt})/\text{bulk-}\text{Mn}_2\text{O}_3$ samples were also prepared using the same method. ICP-AES showed that the actual Pd, Pt, and Pd-Pt loadings (x) were (1.40, 1.42, and 0.70) wt% in $x\text{Pd}/\text{meso-}\text{Mn}_2\text{O}_3$, $x\text{Pt}/\text{meso-}\text{Mn}_2\text{O}_3$, and $x(\text{Pd,Pt})/\text{bulk-}\text{Mn}_2\text{O}_3$, respectively; the actual Pd/Pt molar ratio (y) in $x(\text{Pd,Pt})/\text{bulk-}\text{Mn}_2\text{O}_3$ was 4.9.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and a Ni filter ($\lambda = 0.15406$ nm). Elemental analyses of the noble-metal loadings were performed using ICP-AES (Thermo Electron IRIS Intrepid ER/S spectrometer). Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were performed using a JEOL-2010 instrument operated at 200 kV. High-angle annular dark-field and scanning transmission electron microscopy (HAADF-STEM) were used to acquire HAADF and element mapping images (FEI G2 80-200/Chemi-STEM Cs-corrected transmission electron microscope with probe corrector). The Brunauer-Emmett-Teller (BET) surface areas of the samples were determined based on N_2 adsorption at -196 °C (Micromeritics ASAP 2020 analyzer); the samples were outgassed at 250 °C for 2.5 h under vacuum before the measurements. Their pore-size distributions were calculated based on the desorption branches

of the isotherms. X-ray photoelectron spectroscopy (XPS; VG CLAM 4 MCD analyzer) was used to determine the Mn 2p, O 1s, Pd 3d, Pt 4f, and C 1s binding energies (BEs) of surface species, using Mg $K\alpha$ ($h\nu = 1253.6$ eV) as the excitation source.

Temperature-programmed H_2 reduction (H_2 -TPR) experiments were performed using a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before the TPR measurements, the catalyst (40–60 mesh, ca. 0.050 g) was loaded into a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and pretreated in O_2 flow (20 mL/min) at 250 °C for 1 h. After cooling to rt in the same atmosphere, the system was purged with He flow (30 mL/min) for 15 min. The pretreated sample was exposed to a flow (50 mL/min) of 5% H_2 -95% Ar and heated from rt to 900 °C at a ramping rate of 10 °C/min. Changes in the H_2 concentration in the effluent were monitored online using the chemical adsorption analyzer. The reduction peak was calibrated against that for complete reduction of a known standard, i.e., powdered CuO (Aldrich, 99.995%).

The Fourier-transform infrared (FT-IR) spectrum of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ (1 wt% sample + 99 wt% KBr) was recorded in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1} (Bruker Vertex 70 spectrometer). Before the spectrum was recorded, the sample was activated in O_2 and methane, with the introduction of 100 ppm SO_2 , 5.0 vol% CO_2 , 3.0 vol% H_2O , and 1.0 vol% NO.

2.3. Catalytic evaluation

The catalytic activities of the samples were evaluated using a continuous-flow fixed-bed quartz tubular microreactor (i.d. = 6.0 mm). The sample (40–60 mesh, 50 mg) was diluted with quartz sand (40–60 mesh, 0.25 g) to minimize the effects of hot spots. Before the test, each sample was treated in O_2 flow (20 mL/min) at 250 °C for 1 h. The reactant mixture consisted of 2.5 vol% CH_4 + 20 vol% O_2 + 77.5 vol% N_2 (balance), and the total flow was 16.6 mL/min, giving a CH_4/O_2 molar ratio of 1/8 and a space velocity (SV) of ca. 20000 mL/(g·h). A mass flow

controller was used to introduce 100 ppm SO_2 , 5.0 vol% CO_2 , and 1.0 vol% NO from the corresponding SO_2 , CO_2 , and NO cylinders (balanced with N_2) into the reaction system. Water vapor (3.0 vol% H_2O) was introduced by passing the feed stream through a water saturator at a certain temperature. The reactants and products were analyzed online using a gas chromatograph (GC-14C, Shimadzu) equipped with a flame ionization detector and a thermal conductivity detector; a Stabilwax column (length 30 m) was used for methane separation and a Carboxen 1000 column (length 3 m) was used for permanent gas detection. The balance of carbon throughout the catalytic system was estimated to be 99.5%. The catalytic activities of the samples were evaluated based on the temperatures ($T_{10\%}$, $T_{50\%}$, and $T_{90\%}$) required for achieving methane conversions of 10%, 50%, and 90%. The methane conversion was defined as $(C_{inlet} - C_{outlet})/C_{inlet} \times 100\%$, where C_{inlet} and C_{outlet} are the methane concentrations in the inlet and outlet feed streams, respectively.

3. Results and discussion

3.1. Crystal phase composition, morphology, surface area, and particle size distribution

Fig. 1 shows the XRD patterns of the prepared samples. A comparison with the XRD pattern of a standard Mn_2O_3 sample (JCPDS PDF# 41-1442) shows that all the Bragg diffraction peaks (Fig. 1(a)) of the meso- Mn_2O_3 and $x(Pd,Pt)/meso-Mn_2O_3$ samples can be indexed to a cubic crystal structure.

The sizes of the Mn_2O_3 (Table 1) crystallites in meso- Mn_2O_3 and the supported noble-metal samples, calculated using the Scherrer equation, were in the range 19.1–20.3 nm, whereas that of Mn_2O_3 in 0.07(Pd_{4.9}Pt)/bulk- Mn_2O_3 was 70.7 nm. No diffraction signals from noble-metal phases were detected because of the low loadings of noble metals and their good dispersion. The diffraction peak at $2\theta = ca. 1^\circ$ in the small-angle XRD pattern (Fig. 1(b)) of meso- Mn_2O_3 and the supported no-

Fig. 1. (a) Wide-angle and (b) small-angle XRD patterns of (1) meso- Mn_2O_3 , (2) 0.07(Pd_{4.9}Pt)/meso- Mn_2O_3 , (3) 0.72(Pd_{5.1}Pt)/meso- Mn_2O_3 , (4) 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 , (5) 1.40Pd/meso- Mn_2O_3 , (6) 1.42Pt/meso- Mn_2O_3 , and (7) 0.07(Pd_{4.9}Pt)/bulk- Mn_2O_3 .

Table 1

BET surface areas, pore volumes, average pore sizes, Mn_2O_3 crystallite sizes ($D_{\text{Mn}_2\text{O}_3}$), noble-metal particle sizes, real Pd or Pt contents, and real Pd/Pt molar ratios of samples.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	$D_{\text{Mn}_2\text{O}_3}$ ^a (nm)	Nobel metal particle size ^b	Real Pd/Pt content ^c (wt%)	Real Pd/Pt molar ratio ^c
meso- Mn_2O_3	105.6	0.37	11.2	19.5	—	—/—	—
0.07(Pd _{4.9} Pt)/meso- Mn_2O_3	95.3	0.40	12.6	19.6	—	0.051/0.019	4.9
0.72(Pd _{5.1} Pt)/meso- Mn_2O_3	76.5	0.38	9.6	19.1	2.4	0.53/0.19	5.1
1.41(Pd _{5.1} Pt)/meso- Mn_2O_3	85.1	0.36	9.6	19.4	2.2	1.04/0.37	5.1
1.40Pd/meso- Mn_2O_3	89.9	0.35	9.3	20.2	2.8	1.40/—	—
1.42Pt/meso- Mn_2O_3	83.5	0.35	9.9	20.3	2.5	—/1.42	—
0.07(Pd _{4.9} Pt)/bulk- Mn_2O_3	4.5	0.03	—	70.7	2.1	0.051/0.019	4.9

^a Data were calculated according to the Scherrer equation using the FWHM of the (222) line of Mn_2O_3 ;

^b Data were estimated according to the TEM images;

^c Data were determined by the ICP-AES technique.

ble-metal samples indicates formation of an ordered mesoporous structure, but no small-angle XRD peaks were detected in 0.07(Pd_{4.9}Pt)/bulk- Mn_2O_3 .

Fig. 2 shows the TEM images and SAED patterns of the samples. The meso- Mn_2O_3 and supported noble-metal samples had high-quality ordered mesoporous structures with a pore size of

Fig. 2. TEM images and SAED patterns (insets) of (a, b) meso- Mn_2O_3 , (c, d) 0.07(Pd_{4.9}Pt)/meso- Mn_2O_3 , (e, f) 0.72(Pd_{5.1}Pt)/meso- Mn_2O_3 , (g, h) 1.41(Pd_{5.1}Pt)/meso- Mn_2O_3 , (i, j) 1.40Pd/meso- Mn_2O_3 , (k, l) 1.42Pt/meso- Mn_2O_3 , and (m, n) 0.07(Pd_{4.9}Pt)/bulk- Mn_2O_3 .

ca. 14 nm (Fig. 2(b) and (d)). Noble-metal NPs were highly dispersed on the Mn_2O_3 surfaces. The particle sizes of more than 70 noble-metal NPs in the supported samples were measured; the results are shown in Table 1 and Fig. 3. The average sizes of the noble-metal NPs in the supported samples were in the range 2.2–2.8 nm. The multiple bright electron diffraction rings in the SAED patterns (Fig. 2(a), (c), (e), (g), (i), (k), and (m)) of the samples indicate that these materials were polycrystalline.

Fig. 4 shows the HAADF-STEM and element mapping images of $1.41(\text{Pd}_{5.1}\text{Pt})/\text{meso-Mn}_2\text{O}_3$. The figure clearly shows that a Pd-Pt alloy was formed using the PVA-protected reduction strategy with NaBH_4 as the reducing agent.

Fig. 5 shows the N_2 adsorption-desorption isotherms and

pore-size distributions of the samples. The meso- Mn_2O_3 and supported noble-metal samples had type IV isotherms with a hysteresis loop in the relative pressure range 0.5–1.0 (Fig. 5(a)), indicating generation of a mesoporous structure in these samples. The pore-size distribution curves (Fig. 5(b)) had two peaks, in the ranges 2–6 and 10–16 nm, respectively.

The BET surface areas and pore volumes of meso- Mn_2O_3 and the supported noble-metal samples were in the ranges 76.5–105.6 m^2/g and 0.35–0.40 cm^3/g , respectively, much higher than those (4.52 m^2/g and 0.03 cm^3/g) of 0.70($\text{Pd}_{4.9}\text{Pt}$)/bulk- Mn_2O_3 (Table 1). The meso- Mn_2O_3 -supported noble-metal catalysts were prepared using the incipient wetness impregnation method, followed by

Fig. 3. Noble-metal particle size distributions of (a) 0.72($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 , (b) 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 , (c) 1.40Pd/meso- Mn_2O_3 , (d) 1.42Pt/meso- Mn_2O_3 , and (e) 0.07($\text{Pd}_{4.9}\text{Pt}$)/bulk- Mn_2O_3 .

Fig. 4. (a–d) HAADF-STEM images and (e–h) element mapping images of 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 .

Fig. 5. (a) N₂ adsorption-desorption isotherms and (b) pore-size distributions of (1) meso-Mn₂O₃, (2) 0.07(Pd_{4.9}Pt)/meso-Mn₂O₃, (3) 0.72(Pd_{5.1}Pt)/meso-Mn₂O₃, (4) 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃, (5) 1.40Pd/meso-Mn₂O₃, and (6) 1.42Pt/meso-Mn₂O₃.

calcination at 600 °C for 6 h. During impregnation and calcination, changes in the porous structure occurred and the quality

of the mesoporous structure decreased, leading to changes in the surface areas of the samples.

Fig. 6. (a) Mn 2p_{3/2}, (b) O 1s, (c) Pd 3d, and (d) Pt 4f XPS of (1) meso-Mn₂O₃, (2) 0.07(Pd_{4.9}Pt)/meso-Mn₂O₃, (3) 0.72(Pd_{5.1}Pt)/meso-Mn₂O₃, (4) 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃, (5) 1.40Pd/meso-Mn₂O₃, (6) 1.42Pt/meso-Mn₂O₃, and (7) 0.07(Pd_{4.9}Pt)/bulk-Mn₂O₃.

3.2. Surface composition, metal oxidation state, and oxygen species

XPS is an effective technique for investigating the surface element contents, metal oxidation states, and adsorbed oxygen species of an oxide catalyst. Fig. 6 shows the Mn 2p_{3/2}, O 1s, Pd 3d, and Pt 4f XPS of the samples. Each sample gave an asymmetric Mn 2p_{3/2} XPS signal (Fig. 6(a)), which was decomposed to three components with BE = 640.0, 641.3, and 642.8 eV together with a weak shake-up satellite at BE = 644.7 eV, assignable to surface Mn²⁺, Mn³⁺, and Mn⁴⁺ species [32,33], respectively. Fig. 6(b) shows that each sample gave a broad, asymmetric O 1s XPS peak, which was decomposed into two components, at BE = 529.6 and 531.2 eV, ascribable to surface lattice oxygen (O_{latt}) and adsorbed oxygen (O_{ads}, e.g., O₂⁻, O₂²⁻, or O⁻) species [21,34], respectively. Curve fitting enabled deconvolution of the asymmetric Pd 3d and Pt 4f XPS signals of 0.72(Pd_{5.1}Pt)/meso-Mn₂O₃, 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃, 1.40Pd/meso-Mn₂O₃, and 1.42Pt/meso-Mn₂O₃ into four components, at BE = 335.4, 337.3, 340.8, and 342.6 eV and at BE = 71.7, 72.6, 74.6, and 75.7 eV (Fig. 6(c) and (d)), respectively. The signals at BE = 335.5 and 340.8 eV are assigned to surface metallic Pd⁰ species and those at BE = 337.8 and 342.9 eV are attributed to surface Pd²⁺ species [35]. Similarly, the components at BE = 71.7 eV and 74.6 eV are ascribed to surface metallic Pt⁰ species, and those at BE = 72.6 eV and 75.7 eV are ascribed to surface oxidized Pt (Pt²⁺) [36,37]. The Pd 3d and Pt 4f XPS of the other samples are not shown because their weak signals could not be decomposed accurately.

XPS was used for quantitative analysis of the samples to determine the surface element contents; the results are summarized in Table 2. The O_{ads}/O_{latt} molar ratios decreased in the order 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ (0.77) > 1.40Pd/meso-Mn₂O₃ (0.69) > 0.72(Pd_{5.1}Pt)/meso-Mn₂O₃ (0.65) > 1.42Pt/meso-Mn₂O₃ (0.63) > 0.07(Pd_{4.9}Pt)/meso-Mn₂O₃ (0.53) > 0.07(Pd_{4.9}Pt)/bulk-Mn₂O₃ (0.52) > meso-Mn₂O₃ (0.45); this sequence corresponds to the order of the catalytic performances (discussed below).

A catalyst with a higher adsorbed oxygen species concentration promotes redox-based reactions [38–40]. Generally, O₂ molecules can be adsorbed at the oxygen vacancies of a metal oxide [41]. Pd, Pt, or Pd-Pt loading enhanced the adsorbed oxygen species concentrations of the samples; 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ had the highest adsorbed oxygen species concentration, and therefore gave the best catalytic

Fig. 7. H₂-TPR profiles of (1) meso-Mn₂O₃, (2) 0.07(Pd_{4.9}Pt)/meso-Mn₂O₃, (3) 0.72(Pd_{5.1}Pt)/meso-Mn₂O₃, (4) 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃, (5) 1.40Pd/meso-Mn₂O₃, (6) 1.42Pt/meso-Mn₂O₃, and (7) 0.07(Pd_{4.9}Pt)/bulk-Mn₂O₃.

performance. Strong interactions can occur between the noble-metal or alloy NPs and the Mn₂O₃ support (possibly via the reaction Pd (Pt or Pd-Pt) + 2Mn⁴⁺ → Pd²⁺ (Pt²⁺ or Pd²⁺-Pt²⁺) + 2Mn³⁺), therefore the surface Mn⁴⁺/Mn³⁺ molar ratios were similar (0.60–0.67) at similar loadings ((1.40–1.42) wt%) of Pd, Pt, or Pd-Pt NPs.

3.3. Low-temperature reducibility

According to the literature [32,42], the reduction of manganese oxides can be divided into consecutive steps: Mn₂O₃ → Mn₃O₄ → MnO. However, the reduction peaks in the H₂-TPR profile may also arise from reduction of species in different local environments [42]. Fig. 7 shows the H₂-TPR profiles of the samples, and their H₂ consumptions are summarized in Table 2.

There were two main reduction peaks, centered at 397 and 558 °C, for meso-Mn₂O₃, attributable to the reduction of Mn₂O₃ to Mn₃O₄ and of Mn₃O₄ to MnO [32,42,43], respectively. After noble-metal loading, the reduction peaks of the samples shifted to lower temperatures, particularly in the case of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃. This indicates improved

Table 2

Surface element contents of samples and H₂-TPR results.

Sample	Surface element composition (molar ratio)				H ₂ consumption (mmol/g)		
	Mn ⁴⁺ /Mn ³⁺	O _{ads} /O _{latt}	Pd ²⁺ /Pd ⁰	Pt ²⁺ /Pt ⁰	Below 120 °C	Above 120 °C	Total
meso-Mn ₂ O ₃	0.65	0.45	—	—	—	14.85	14.85
0.07(Pd _{4.9} Pt)/meso-Mn ₂ O ₃	0.48	0.53	—	—	0.68	12.21	12.89
0.72(Pd _{5.1} Pt)/meso-Mn ₂ O ₃	0.57	0.65	5.40	0.96	1.19	12.00	13.19
1.41(Pd _{5.1} Pt)/meso-Mn ₂ O ₃	0.67	0.77	4.50	1.18	2.34	11.81	14.15
1.40Pd/meso-Mn ₂ O ₃	0.61	0.69	11.48	—	2.19	11.52	13.71
1.42Pt/meso-Mn ₂ O ₃	0.60	0.63	—	0.92	0.82	11.42	12.24
0.07(Pd _{4.9} Pt)/bulk-Mn ₂ O ₃	0.49	0.52	—	—	—	14.10	14.10

low-temperature reducibility. The reduction shoulders below 120 °C can be ascribed to the reduction of oxidized noble metals, and those above 120 °C can be assigned to the reduction of Mn_2O_3 to Mn_3O_4 or further to MnO . The total H_2 consumptions (14.10–14.85 mmol/g) of the meso- Mn_2O_3 and 0.07($\text{Pd}_{4.9}\text{Pt}$)/bulk- Mn_2O_3 samples were close to or slightly higher than those (12.24–14.15 mmol/g) of the meso- Mn_2O_3 -supported noble-metal samples; the latter gave a low-temperature (below 120 °C) H_2 consumption of 0.68–2.34 mmol/g, showing that the low-temperature reducibilities of the porous Mn_2O_3 -supported samples were better than those of the bulk- Mn_2O_3 -supported and noble-metal-free samples. The 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 sample showed the best low-temperature reducibility.

3.4. Catalytic performance

In a blank experiment (only quartz sand was loaded in the microreactor), no methane conversion was detected under the conditions 2.5 vol% CH_4 , CH_4/O_2 molar ratio = 1/8, $\text{SV} = 20000$ mL/(g·h), less than 600 °C, i.e., no homogeneous reactions occurred in the catalytic system under the conditions used. Fig. 8(a) and (b) show the catalytic activities of the obtained samples and the effect of the SV on the catalytic activity of 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 in methane combustion, respectively.

Fig. 8(a) shows that the catalytic activity increased monotonously with increasing temperature, and loading of noble-metal NPs improved the catalytic activity. At similar noble-metal NP loadings, the catalytic activity of the sample loaded with Pd-Pt alloy NPs was better than those of the samples loaded with Pd only (1.40Pd/meso- Mn_2O_3) or Pt only (1.42Pt/meso- Mn_2O_3). The 0.70($\text{Pd}_{4.9}\text{Pt}$)/meso- Mn_2O_3 sample outperformed the 0.70($\text{Pd}_{4.9}\text{Pt}$)/bulk- Mn_2O_3 sample. The 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 sample gave the best performance. These results show that the presence of a porous structure and the alloying of noble metals improved the catalytic activity. It is

more convenient to compare the catalytic activities of the samples using $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$; these data are summarized in Table 3.

The 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 sample performed best, giving $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ values of 265, 345, and 425 °C, respectively, at $\text{SV} = 20000$ mL/(g·h). The $T_{90\%}$ values were 495 °C over 1.42Pt/meso- Mn_2O_3 , 485 °C over 0.72($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 , and 460 °C over 1.40Pd/meso- Mn_2O_3 . The methane conversion over 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 decreased with increasing SV (Fig. 8(b)), as a result of shortening of the contact time.

Generally, it is more accurate to use the turnover frequencies (TOFs) and specific reaction rates to evaluate the inherent catalytic activities. For the Mn_2O_3 -supported noble-metal catalysts, noble metals and Mn_2O_3 are the active sites, and it is difficult to calculate the TOFs of such samples accurately. The TOF_M values [$= zC_0/n_M$, where z is the conversion at a certain temperature, C_0 (mol/s) is the initial methane concentration, and n_M (mol) is the molar amount of metal or oxide ($M = \text{Pd}, \text{Pt}, \text{Pd-Pt}$ or Mn_2O_3)] and the specific reaction rates at a typical temperature (400 °C) were calculated based on the activity data and amounts of Pd and/or Pt and Mn_2O_3 in the samples; the results are summarized in Table 3. Fig. 9 shows the specific reaction rates normalized per gram of catalyst, noble metal, or Mn_2O_3 . Fig. 9 and the data in Table 3 shows that 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 had the highest TOF (1.02 ms^{-1}) for noble metal and the highest specific reaction rates ($6.39 \mu\text{mol}/(\text{g}\cdot\text{s})$ for catalyst and $6.48 \text{ mmol}/(\text{g}\cdot\text{s})$ for Mn_2O_3) at 400 °C; however, the highest TOF (0.50 ms^{-1}) for Mn_2O_3 and specific reaction rate normalized per gram of noble metal ($4.11 \text{ mmol}/(\text{g}\cdot\text{s})$) at 400 °C were achieved over 0.07($\text{Pd}_{4.9}\text{Pt}$)/meso- Mn_2O_3 . The specific reaction rates normalized per gram of catalyst or Mn_2O_3 (Fig. 9(a) and (b)) changed in a similar manner to the catalytic activities of the samples. The only difference was in the case of the specific reaction rates normalized per gram of noble metal, in which the 0.07($\text{Pd}_{4.9}\text{Pt}$)/meso- Mn_2O_3 and 0.07($\text{Pd}_{4.9}\text{Pt}$)/bulk- Mn_2O_3 sam-

Fig. 8. (a) Methane conversion as function of reaction temperature for (1) meso- Mn_2O_3 , (2) 0.07($\text{Pd}_{4.9}\text{Pt}$)/meso- Mn_2O_3 , (3) 0.72($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 , (4) 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 , (5) 0.07($\text{Pd}_{4.9}\text{Pt}$)/bulk- Mn_2O_3 , (6) 1.40Pd/meso- Mn_2O_3 , and (7) 1.42Pt/meso- Mn_2O_3 at $\text{SV} = 20000$ mL/(g·h); and (b) effect of SV on methane oxidation over 1.41($\text{Pd}_{5.1}\text{Pt}$)/meso- Mn_2O_3 .

Table 3

Catalytic activities, TOF values, and specific reaction rates of samples at SV = 20000 mL/(g·h).

Sample	Methane combustion activity			Methane combustion at 400 °C				
	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	TOF _{Noble metal} (ms ⁻¹)	TOF _{Mn2O3} (ms ⁻¹)	Specific reaction rate for catalyst (μmol/(g·s))	Specific reaction rate for Mn ₂ O ₃ (μmol/(g·s))	Specific reaction rate for noble metal (mmol/(g·s))
meso-Mn ₂ O ₃	370	455	—	0.23	—	1.44	1.44	—
0.07Pd _{4.9} Pt/meso-Mn ₂ O ₃	320	425	—	0.45	0.50	2.88	2.88	4.11
0.72Pd _{5.1} Pt/meso-Mn ₂ O ₃	285	382	485	0.75	0.08	4.70	4.74	0.65
1.41Pd _{5.1} Pt/meso-Mn ₂ O ₃	265	345	425	1.02	0.05	6.39	6.48	0.45
1.40Pd/meso-Mn ₂ O ₃	280	380	460	0.80	0.04	4.97	5.04	0.35
1.42Pt/meso-Mn ₂ O ₃	305	400	495	0.62	0.05	3.85	3.90	0.27
0.07Pd _{4.9} Pt/bulk-Mn ₂ O ₃	320	455	—	0.40	0.04	2.54	2.54	3.63

Fig. 9. Specific reaction rates normalized per gram of (a) catalyst, (b) Mn₂O₃, and (c) noble metal as a function of temperature for (◆) meso-Mn₂O₃, (■) 0.07(Pd_{4.9}Pt)/meso-Mn₂O₃, (●) 0.72(Pd_{5.1}Pt)/meso-Mn₂O₃, (▲) 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃, (Δ) 1.40Pd/meso-Mn₂O₃, (◇) 1.42Pt/meso-Mn₂O₃, and (□) 0.07Pd_{4.9}Pt/bulk-Mn₂O₃.

ples showed higher specific reaction rates normalized per gram of noble metal above 300 °C (Fig. 9(c)), possibly because of the low loadings of noble-metal NPs. These results also suggest that other factors (e.g., adsorbed oxygen species concentration, low-temperature reducibility, and noble metal-support interactions) affected the catalytic performances of the supported samples.

Fig. 10 shows the methane consumption rates and TOF_{Mn2O3} values of the samples at 300 and 400 °C as a function of the $O_{\text{ads}}/O_{\text{latt}}$ molar ratio. Either the methane consumption rate or the TOF_{Mn2O3} increased with increasing O_{ads} concentration, showing that a higher O_{ads} concentration enhanced the catalytic performance [44].

Hutchings and coworkers [45] pointed out that the Au in supported Au-Pd alloy catalysts can act as an electronic promoter for Pd. It has also been reported that the performances of bimetallic Au-Pd/CeO₂ catalysts in toluene oxidation are better than those of single-metal Au/CeO₂ or Pd/CeO₂ catalysts because of a mutual promotional effect [46]. In the present work, 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ performed better than 1.40Pd/meso-Mn₂O₃ or 1.42Pt/meso-Mn₂O₃, possibly because of Pd-Pt interactions. PdO is usually considered to be an activity-controlling factor in catalyzing hydrocarbon oxidation. According to the literature [47,48], however, a small amount of metallic Pd on the PdO particles in pure Pd catalysts enhances

the activity compared with that of fully oxidized PdO particles. A good contact surface between Pd and PdO particles is therefore important. In the case of supported bimetallic Pd-Pt catalysts, the metallic phase is retained, even in an oxidizing atmosphere, because of Pd-Pt alloy formation. The catalytic activity of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ might therefore be better than that of a monometallic Pd catalyst, despite the slightly lower surface PdO content. Another possible reason for the higher activity of the supported Pd-Pt alloy catalyst is easier oxygen adsorption and activation than on the PdO phase.

In recent years, a number of studies of methane combustion over Mn-based and supported noble-metal catalysts have been reported in the literature; the results are shown in Table 4.

Clearly, the $T_{50\%}$ and $T_{90\%}$ values over 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ were much lower than those over La_{0.7}Ag_{0.3}MnO₃ [49], La_{0.7}Sr_{0.3}MnO₃ [49], La_{0.7}Ce_{0.3}MnO₃ [49], 1.0 wt% Pd/Al₂O₃ [50], 1.0 wt% Pd/ZrO₂ [50], 1 mol% Pd in LaMnPd [51], 2 mol% Rh in LaMnRh [51], and 1.1 wt% Pt/3DOM Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ [52]. The specific activity over 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ was much higher than those over La_{0.7}Ag_{0.3}MnO₃ [49], La_{0.7}Sr_{0.3}MnO₃ [49], La_{0.7}Ce_{0.3}MnO₃ [49], 1 mol% Pd in LaMnPd [51], and 2 mol% Rh in LaMnRh [51], and close to those over 1.1 wt% Pt/3DOM Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ [52], but lower than those over 1.0 wt% Pd/Al₂O₃ [50] and 1.0 wt% Pd/ZrO₂ [50].

Fig. 10. (a) Methane consumption rates and (b) $\text{TOF}_{\text{Mn}_2\text{O}_3}$ values at various temperatures as function of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratios of samples.

Table 4

Comparison of methane oxidation activities of samples with those reported in the literature.

Catalyst	Reaction condition	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	Specific activity at $T_{50\%}$ (mol/(g·min))	Specific activity at $T_{90\%}$ (mol/(g·min))	Ref.
1.41Pd _{5.1} Pt/meso-Mn ₂ O ₃	2.5% CH ₄ , SV = 20000 mL/(g·h)	345	425	2.28×10^{-4}	4.10×10^{-4}	This work
La _{0.7} Ag _{0.3} MnO ₃	1% CH ₄ , SV = 10000 mL/(g·h)	690	750	1.81×10^{-5}	2.66×10^{-5}	[49]
La _{0.7} Sr _{0.3} MnO ₃	1% CH ₄ , SV = 10000 mL/(g·h)	720	780	1.69×10^{-5}	2.57×10^{-5}	[49]
La _{0.7} Ce _{0.3} MnO ₃	1% CH ₄ , SV = 10000 mL/(g·h)	740	810	1.68×10^{-5}	2.52×10^{-5}	[49]
1.0 wt% Pd/Al ₂ O ₃	5% CH ₄ , SV = 30000 mL/(g·h)	640	710	3.57×10^{-4}	4.72×10^{-4}	[50]
1.0 wt% Pd/ZrO ₂	5% CH ₄ , SV = 30000 mL/(g·h)	600	650	3.88×10^{-4}	5.15×10^{-4}	[50]
1 mol% Pd, LaMnPd	1% CH ₄ , SV = 5000 mL/(g·h)	425	475	1.21×10^{-5}	1.85×10^{-5}	[51]
2 mol% Rh, LaMnRh	1% CH ₄ , SV = 5000 mL/(g·h)	445	515	1.17×10^{-5}	1.79×10^{-5}	[51]
1.1 wt% Pt/3DOM Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	2% CH ₄ , SV = 30000 mL/(g·h)	479	598	2.41×10^{-4}	4.33×10^{-4}	[52]

Methane oxidation over the Pd-based catalysts can proceed via the Mars-van Krevelen mechanism, in which the reaction takes place via a redox cycle of the catalyst [19,53,54]. At low temperatures, methane can react with chemisorbed oxygen to yield CO₂ and H₂O; however, at higher temperatures, the lattice oxygens in oxidized noble metals are involved in methane oxidation, resulting in catalyst reduction. The gas-phase O₂ molecules can be activated at the oxygen vacancies of Mn₂O₃ or near the interface between oxidized Pd and/or Pt and Mn₂O₃ to give active oxygen species, replenishing the lattice oxygens of oxidized Pd and/or Pt consumed in methane oxidation and re-oxidizing the reduced catalyst. In the case of the Mn₂O₃-supported Pd-Pt alloy catalysts, the metallic phase is maintained, even in an oxidizing atmosphere, because of formation of a Pd-Pt alloy, resulting in better activity compared with those of the Mn₂O₃-supported Pd or Pt catalyst. Alloying of Pd with Pt significantly promotes the adsorption and activation of oxygen, possibly enhancing the migration of activated oxygen to the noble-metal alloy-Mn₂O₃ interface. The excellent catalytic activity of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ could result from its enhanced oxygen activation ability and better low-temperature reducibility.

The catalytic stability was examined by performing on-stream methane combustion over 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ at 425 °C and SV = 20000 mL/(g·h) for 25 h; the results are shown in Fig. 11. No significant loss in catalytic activity was observed within 25 h of on-stream reaction. The 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ sample was therefore cat-

alytically stable under the reaction conditions used.

3.5. Effects of SO₂, CO₂, H₂O, and NO addition on catalytic activity

The effects of SO₂, CO₂, water vapor, and NO on the catalytic activity were investigated by performing methane combustion over 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ in the presence of 100 ppm SO₂, 5.0 vol% CO₂, 3.0 vol% H₂O, or 1.0 vol% NO; the results are shown in Fig. 12(a).

It is clear that the catalytic activities of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ in the presence and absence of 100 ppm SO₂ or 5.0 vol% CO₂ were similar, i.e., this catalyst was

Fig. 11. Methane conversion versus on-stream methane oxidation time over 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ at SV = 20000 mL/(g·h) and at 425 °C.

Fig. 12. (a) Effects of 100 ppm SO₂, 5.0 vol% CO₂, 3.0 vol% H₂O, and 1.0 vol% NO on methane conversion at SV = 20000 mL/(g·h); and (b) FT-IR spectra of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ (1) after activation in O₂ flow (16.6 mL/min) at 250 °C for 1 h and after methane combustion in presence of (2) 100 ppm SO₂, (3) 5.0 vol% CO₂, (4) 3.0 vol% H₂O, or (5) 1.0 vol% NO.

strongly resistant to SO₂ or CO₂ poisoning. This is possibly because the introduction of a small amount of Pt prevents blocking of the active sites by adsorption of sulfur or carbon oxides. Corro et al. [55] reported that the presence of Pt⁰ might be necessary to prevent interactions between SO₂ and Pd surface species. In the case of 3.0 vol% water vapor addition, methane conversion over 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ decreased by ca. 10%, as a result of formation of hydroxyl groups on the support surface, which hindered oxygen exchange between the support and active sites [56]. It has been reported that $T_{50\%}$ increased by ca. 100 °C over Pd/Al₂O₃ in the presence of 10.0 vol% water vapor [12], by ca. 35 °C over PdO/Al₂O₃ in the presence of 3.0 vol% water vapor [57], and by ca. 120 °C over Pd/ZrO₂, Pd/Zr-CeO₂, and Pd/La-CeO₂ in the presence of 18.0 vol% water vapor [58]. The introduction of Pt therefore increased the resistance of the Pd-based catalysts to water vapor poisoning. An activity drop (ca. 30%) was observed over 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ in the presence of 1.0 vol% NO. The introduction of NO into the reaction system could interfere with methane combustion because of selective catalytic reduction of NO with methane, which could occur simultaneously with methane combustion [59]:

We used FT-IR spectroscopy to elucidate the surface species in 1.41Pd_{5.1}Pt/meso-Mn₂O₃ after activation in an O₂ flow (16.6 mL/min) at 250 °C for 1 h and after methane combustion in the presence of 100 ppm SO₂, 5.0 vol% CO₂, 3.0 vol% H₂O, and 1.0 vol% NO; the spectra are shown in Fig. 12(b). According to the literature [18,60,61], the absorption bands at 3400, 2360 and 2340, 1625, 1410, and 930 cm⁻¹ can be ascribed to the stretching vibrations of OH⁻, atmospheric CO₂, bending vibrations of adsorbed water molecules, stretching vibrations of C–H bonds,

and stretching and bending vibrations of Mn–O bonds, respectively. The absorption bands at 1125 and 1146 cm⁻¹ [Fig. 12(b)(1)] can be assigned to oxygen species (e.g., O₂⁻ and O₂²⁻) [18,62]. The absorption band at 1042 cm⁻¹ indicates formation of SO₃²⁻ or SO₄²⁻ species [19]. No corresponding carbonate or OH⁻ groups were detected (Fig. 12(b)(2) and (3)), possibly because of decomposition of carbonate or OH⁻ species at high temperatures. The strong absorption band at 1140 cm⁻¹ for the sample after methane combustion in the presence of 1.0 vol% NO can be assigned to NO adsorption on the support or noble-metal NPs [63]; this decreased the catalytic activity of the sample [59].

Fig. 13 shows TEM images of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ after activation in O₂ at 250 °C for 1 h, after methane combustion in the presence of 100 ppm SO₂, 5.0 vol% CO₂, 3.0 vol% CO₂, or 1.0 vol% NO, and after 25 h of on-stream reaction. The images clearly show that all the samples maintained their high-quality mesoporous structure and the Pd–Pt alloy NPs were well distributed on the surface of the meso-Mn₂O₃ support (similar to the images in Fig. 2(g) and (h)).

4. Conclusions

We prepared meso-Mn₂O₃ and x(Pd_yPt)/meso-Mn₂O₃ nanocatalysts using KIT-6-templating and PVA-protected reduction methods, respectively. The porous samples had surface areas of 77–106 m²/g and noble-metal NPs of size 2–3 nm, and were highly dispersed on the surfaces of the cubic crystalline meso-Mn₂O₃ support. Alloying Pd with Pt enhanced the catalytic performance in methane combustion; 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ showed the highest activity ($T_{10\%}$ = 265 °C, $T_{50\%}$ = 345 °C, and $T_{90\%}$ = 425 °C at SV = 20000 mL/(g·h)). Introduction of a small amount of Pt increased re-

Fig. 13. TEM images of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃ (a, b) after activation in O₂ flow (16.6 mL/min) at 250 °C for 1 h; after methane combustion in the presence of (c, d) 100 ppm SO₂, (e, f) 5.0 vol% CO₂, (g, h) 3.0 vol% H₂O, or (i, j) 1.0 vol% NO; and (k, l) after 25 h of on-stream reaction at 425 °C and SV = 20000 mL/(g·h).

sistance to SO₂, CO₂, and water vapor poisoning. However, NO addition negatively affected methane combustion because of selective catalytic reduction of NO with methane. It is concluded that a large surface area, high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interactions between the Pd-Pt alloy NPs and meso-Mn₂O₃ were responsible for the excellent catalytic performance of 1.41(Pd_{5.1}Pt)/meso-Mn₂O₃.

References

- [1] M. N. Debbagh, C. S. M. de Lecea, J. Pérez-Ramírez, *Appl. Catal. B*, **2007**, 70, 335–341.
- [2] Z. Q. Yang, J. R. Grace, C. J. Lim, L. Zhang, *Energy Fuels*, **2011**, 25, 975–980.
- [3] L. A. Graham, G. Rideout, D. Rosenblatt, J. Hendren, *Atmos. Environ.*, **2008**, 42, 4665–4681.
- [4] P. Gélin, M. Primet, *Appl. Catal. B*, **2002**, 39, 1–37.
- [5] D. Ciuparu, M. R. Lyubovsky, E. Altman, L. D. Pfefferle, A. Datye, *Catal. Rev. Sci. Eng.*, **2002**, 44, 593–649.
- [6] J. Xu, L. K. Ouyang, W. Mao, X. J. Yang, X. C. Xu, J. J. Su, T. Z. Zhuang, H. Li, Y. F. Han, *ACS Catal.*, **2012**, 2, 261–269.
- [7] J. D. Grunwaldt, N. van Vegten, A. Baiker, *Chem. Commun.*, **2007**, 44, 4635–4637.
- [8] A. Hellman, A. Resta, N. M. Martin, J. Gustafson, A. Trinchero, P. A. Carlsson, O. Balmes, R. R. Felici, R. van Rijn, J. W. M. Frenken, J. N. Andersen, E. Lundgren, H. Grönbeck, *J. Phys. Chem. Lett.*, **2012**, 3, 678–682.
- [9] A. Ersson, H. Kusar, R. Carroni, T. Griffin, S. Järås, *Catal. Today*, **2003**, 83, 265–277.
- [10] K. Persson, A. Ersson, K. Jansson, N. Iverlund, S. Järås, *J. Catal.*, **2005**, 231, 139–150.
- [11] T. V. Choudhary, S. Banerjee, V. R. Choudhary, *Appl. Catal. A*, **2002**, 234, 1–23.
- [12] P. Gélin, L. Urfels, M. Primet, E. Tena, *Catal. Today*, **2003**, 83, 45–57.
- [13] N. M. Kinnunen, J. T. Hirvi, M. Suvanto, T. A. Pakkanen, *J. Mol. Catal. A*, **2012**, 356, 20–28.
- [14] H. Yoshida, T. Nakajima, Y. Yazawa, T. Hattori, *Appl. Catal. B*, **2007**, 71, 70–79.
- [15] A. Barrera, S. Fuentes, G. Diaz, A. Gomez-Cortes, F. Tzompantzi, J. C. Molina, *Fuel*, **2012**, 93, 136–141.
- [16] K. Ramesh, E. Widjaja, S. Chilukoti, I. K. Surjani, J. S. Chen, *J. Catal.*, **2008**, 253, 261–268.
- [17] K. Ramesh, L. W. Chen, F. X. Chen, Z. Y. Zhong, J. H. Chin, H. W. Mook, Y. F. Han, *Catal. Commun.*, **2007**, 8, 1421–1426.
- [18] J. H. Li, X. Liang, S. C. Xu, J. M. Hao, *Appl. Catal. B*, **2009**, 90, 307–312.
- [19] S. Ordóñez, J. R. Paredes, F. V. Díez, *Appl. Catal. A*, **2008**, 341, 174–180.
- [20] M. R. Morales, B. P. Barbero, L. E. Cadús, *Appl. Catal. B*, **2006**, 67,

- 229–236.
- [21] A. Machocki, T. Ioannides, B. Stasinska, W. Gac, G. Avgouropoulos, D. Delimaris, W. Grzegorzczak, S. Pasieczna, *J. Catal.*, **2004**, 227, 282–296.
- [22] Z. X. Wu, J. G. Deng, Y. X. Liu, S. H. Xie, Y. Jiang, X. T. Zhao, J. Yang, H. Arandian, G. S. Guo, H. X. Dai, *J. Catal.*, **2015**, 332, 13–24.
- [23] S. H. Xie, J. G. Deng, S. M. Zang, H. G. Yang, G. S. Guo, H. Arandian, H. X. Dai, *J. Catal.*, **2015**, 322, 38–48.
- [24] S. H. Xie, J. G. Deng, Y. X. Liu, Z. H. Zhang, H. G. Yang, Y. Jiang, H. Arandian, H. X. Dai, C. T. Au, *Appl. Catal. A*, **2015**, 507, 82–90.
- [25] S. H. Xie, H. X. Dai, J. G. Deng, H. G. Yang, W. Han, H. Arandian, G. S. Guo, *J. Hazard. Mater.*, **2014**, 279, 392–401.
- [26] Y. X. Liu, H. X. Dai, J. G. Deng, S. H. Xie, H. G. Yang, W. Tan, W. Han, Y. Jiang, G. S. Guo, *J. Catal.*, **2014**, 309, 408–418.
- [27] Z. X. Wu, J. G. Deng, S. H. Xie, H. G. Yang, X. T. Zhao, K. F. Zhang, H. X. Lin, H. X. Dai, G. S. Guo, *Microporous Mesoporous Mater.*, **2016**, 224, 311–322.
- [28] J. G. Deng, S. N. He, S. H. Xie, H. G. Yang, Y. X. Liu, G. S. Guo, H. X. Dai, *Environ. Sci. Technol.*, **2015**, 49, 11089–11095.
- [29] F. Kleitz, S. H. Choi, R. Ryoo, *Chem. Commun.*, **2003**, 2136–2137.
- [30] X. H. Sun, Y. F. Shi, P. Zhang, C. M. Zheng, X. Y. Zheng, F. Zhang, Y. C. Zhang, N. J. Guan, D. Y. Zhao, G. D. Stucky, *J. Am. Chem. Soc.*, **2011**, 133, 14542–14545.
- [31] S. H. Xie, J. G. Deng, S. M. Zang, H. G. Yang, G. S. Guo, H. Arandian, H. X. Dai, *J. Catal.*, **2015**, 322, 38–48.
- [32] V. P. Santos, M. F. R. Pereira, J. J. M. Órfão, J. L. Figueiredo, *Appl. Catal. B*, **2010**, 99, 353–363.
- [33] Y. J. Wei, L. Y. Yan, C. Z. Wang, X. G. Xu, F. Wu, G. Chen, *J. Phys. Chem. B*, **2004**, 108, 18547–18551.
- [34] K. Jiratova, J. Mikulova, J. Klempa, T. Grygar, Z. Bastl, F. Kovanda, *Appl. Catal. A*, **2009**, 361, 106–116.
- [35] H. Q. Dong, Y. Y. Chen, M. Han, S. L. Li, J. Zhang, J. S. Li, Y. Q. Lan, Z. H. Dai, J. C. Bao, *J. Mater. Chem. A*, **2014**, 2, 1272–1276.
- [36] Y. B. He, G. R. Li, Z. L. Wang, Y. N. Ou, Y. X. Tong, *J. Phys. Chem. C*, **2010**, 114, 19175–19181.
- [37] J. Prabhuram, T. S. Zhao, C. W. Wong, J. W. Guo, *J. Power Sources*, **2004**, 134, 1–6.
- [38] B. Solsona, T. García, S. H. Taylor, G. J. Hutchings, M. Makkee, *Appl. Catal. A*, **2009**, 365, 222–230.
- [39] H. J. Wu, L. D. Wang, J. Q. Zhang, Z. Y. Shen, J. H. Zhao, *Catal. Commun.*, **2011**, 12, 859–865.
- [40] D. S. Zhang, L. Zhang, C. Fang, R. H. Gao, Y. L. Qian, L. Y. Shi, J. P. Zhang, *RSC Adv.*, **2013**, 3, 8811–8819.
- [41] Y. X. Liu, H. X. Dai, Y. C. Du, J. G. Deng, L. Zhang, Z. X. Zhao, C. T. Au, *J. Catal.*, **2012**, 287, 149–160.
- [42] W. Gac, *Appl. Catal. B*, **2007**, 75, 107–117.
- [43] R. Xu, X. Wang, D. S. Wang, K. B. Zhou, Y. D. Li, *J. Catal.*, **2006**, 237, 426–430.
- [44] S. Rousseau, S. Loridant, P. Delichere, A. Boreave, J. P. Deloume, P. Vernoux, *Appl. Catal. B*, **2009**, 88, 438–447.
- [45] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science*, **2006**, 311, 362–365.
- [46] D. S. Lee, Y. W. Chen, *J. Taiwan Inst. Chem. Eng.*, **2013**, 44, 40–44.
- [47] J. N. Carstens, S. C. Su, A. T. Bell, *J. Catal.*, **1998**, 176, 136–142.
- [48] K. Persson, A. Ersson, K. Jansson, J. L. G. Fierro, S. G. Järås, *J. Catal.*, **2006**, 243, 14–24.
- [49] F. Teng, W. Qu, G. D. Wen, Z. M. Wang, Z. J. Tian, X. M. Yang, P. Xu, Y. F. Zhu, G. X. Xiong, *Microporous Mesoporous Mater.*, **2008**, 111, 620–626.
- [50] W. R. Schwartz, D. Ciuparu, L. D. Pfefferle, *J. Phys. Chem. C*, **2012**, 116, 8587–8593.
- [51] P. Hurtado, S. Ordóñez, H. Sastre, F. V. Díez, *Appl. Catal. B*, **2004**, 51, 229–238.
- [52] S. Ordóñez, L. Bello, H. Sastre, R. Rosal, F. V. Díez, *Appl. Catal. B*, **2002**, 38, 139–149.
- [53] L. Ren, P. P. Wang, Y. S. Han, C. W. Hu, B. Q. Wei, *Chem. Phys. Lett.*, **2009**, 476, 78–83.
- [54] K. Sasaki, O. Tanaike, H. Konno, *Can. Mineral.*, **1998**, 36, 1225–1235.
- [55] G. Corro, C. Cano, J. L. G. Fierro, *J. Mol. Catal. A*, **2010**, 315, 35–42.
- [56] A. T. Gremminger, H. W. P. de Carvalho, R. Popescu, J. D. Grunwaldt, O. Deutschmann, *Catal. Today*, **2015**, 258, 470–480.
- [57] D. Ciuparu, E. Perkins, L. Pfefferle, *Appl. Catal. A*, **2004**, 263, 145–153.
- [58] S. Eriksson, M. Boutonnet, S. Järås, *Appl. Catal. A*, **2006**, 312, 95–101.
- [59] Y. H. Chin, D. E. Resasco, *Catalysis*, **1999**, 14, 1–39.
- [60] S. M. Li, Y. L. Wang, M. G. Ma, J. F. Zhu, R. C. Sun, F. Xu, *Crop. Prod.*, **2013**, 43, 751–756.
- [61] X. Y. Wang, L. Liu, X. Y. Wang, L. H. Yi, C. Y. Hu, X. Y. Zhang, *Mater. Sci. Eng. B*, **2011**, 176, 1232–1238.
- [62] Z. H. Li, G. H. Xu, G. B. Hoflund, *Fuel Process. Technol.*, **2003**, 84, 1–11.
- [63] A. Martinez-Arias, J. Soria, J. C. Conesda, X. L. Seoane, A. Arcoya, R. Cataluna, *J. Chem. Soc. Faraday Trans.*, **1995**, 91, 1679–1687.

Graphical Abstract

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Catalytic performance enhancement by alloying Pd with Pt on ordered mesoporous manganese oxide for methane combustion

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Alloying Pd with Pt enhanced the catalytic performance in methane combustion. 1.41(Pd₅1Pt)/meso-Mn₂O₃ showed the highest activity because of its large surface area, high O_{ads} concentration, good low-temperature reducibility, and strong Pd-Pt alloy and Mn₂O₃ interactions.

有序介孔三氧化二锰负载PdPt合金：一种高效的甲烷催化燃烧催化剂

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摘要: 甲烷作为一种清洁廉价的碳氢能源, 广泛应用于运输业和其它工业领域. 但是其本身是一种比二氧化碳导致全球变暖效应更强的温室气体, 而且甲烷直接燃烧会产生其它污染物, 比如一氧化碳、氮氧化物、未充分燃烧的碳氢化合物等. 因此有必要开展有关甲烷催化燃烧的研究工作, 以大幅度降低起燃温度, 提高燃烧效率, 有效地减少污染副产物的产生. 由于具有较好的低温催化活性, Pd基催化剂常用于甲烷的催化燃烧. 但是Pd基催化剂也存在一些亟需解决的问题, 比如在催化燃烧过程中活性相结构不稳定. PdO通常被认为是碳氢化合物催化氧化中的活性相, 但是在高温下PdO分解为Pd, 导致催化活性下降. PdO遇到含水或硫的化合物时会生成惰性的Pd(OH)₂或稳定的硫化物, 造成活性物种的流失, 从而降低催化剂的性能. 如果在材料中添加另一种贵金属Pt, 使之与Pd一起形成贵金属合金, 则可提高其低温催化燃烧的活性, 增加Pd基催化剂的热稳定性以及抗水和抗硫能力. 另一方面, 过渡金属氧化物价格便宜, 热稳定性以及抗硫性较好, 也常作为甲烷燃烧的催化剂. 其中三氧化二锰由于具有可变的氧化态以及较好的储氧能力受到了广泛关注. 本课题组采用KIT-6作为硬模板, 先合成具有有序介孔结构的Mn₂O₃(meso-Mn₂O₃)纳米催化剂, 然后通过聚乙烯醇(PVA)保护的液相共还原法分别制备meso-Mn₂O₃负载Pd, Pt及PdPt合金的纳米催化剂(x(Pd₅Pt)/meso-Mn₂O₃; x = (0.10–1.50) wt%; Pd/Pt摩尔比(y) = 4.9–5.1).

XRD结果表明, 合成的meso-Mn₂O₃具有立方相晶体结构. 其BET比表面积为106 m²/g. 由TEM照片可观察到粒径范围为2.1–2.8 nm的贵金属纳米颗粒均匀分散在meso-Mn₂O₃表面. 通过XPS分析可知, 结合能在529.6和531.2 eV的峰可分别归属于晶格氧(O_{latt})和表面吸附氧(O_{ads}). Pd⁰和Pd²⁺以及Pt⁰和Pt²⁺也均可通过曲线拟合后进行分峰确定. XPS定量分析结果表明, 样品的 O_{ads}/O_{latt} 摩尔比有如下顺序: 1.41(Pd₅Pt)/meso-Mn₂O₃ (0.77) > 1.40Pd/meso-Mn₂O₃ (0.69) > 0.72(Pd₅Pt)/meso-Mn₂O₃ (0.65) > 1.42Pt/meso-Mn₂O₃ (0.63) > 0.07(Pd₄Pt)/meso-Mn₂O₃ (0.53) > 0.07(Pd₄Pt)/bulk-Mn₂O₃ (0.52) > meso-Mn₂O₃ (0.45), 这与其催化活性的顺序相一致. 该结果表明, 高的吸附氧物种浓度有利于甲烷催化燃烧. 负载Pd, Pt或PdPt以后的样品的表面吸附氧物种浓度显著提高, 催化活性最好的1.41(Pd₅Pt)/meso-Mn₂O₃样品具有最高的吸附氧物种浓度.

负载PdPt合金可有效提高催化剂对甲烷燃烧的催化活性. 1.41(Pd₅Pt)/meso-Mn₂O₃催化剂的活性最好: 在空速为20000 mL/(g·h)的条件下, 甲烷燃烧的T_{10%}, T_{50%}和T_{90%}分别为265, 345和425 °C. 此外, 还考察了引入一定量的SO₂, CO₂, H₂O和NO对甲烷在1.41(Pd₅Pt)/meso-Mn₂O₃催化剂上氧化反应的影响, 发现引入少量的Pt可提高催化剂抗SO₂, CO₂和H₂O的能力, 但是NO对甲烷燃烧的还原效应也不可忽视. 基于催化剂物化性质的表征结果和活性数据, 我们认为1.41(Pd₅Pt)/meso-Mn₂O₃优异的催化性能与其拥有高质量的三维有序多孔结构、高的吸附氧物种浓度、优良的低温还原性以及Pd-Pt合金与meso-Mn₂O₃载体之间的强相互作用有关.

关键词: 有序介孔三氧化二锰; PdPt合金纳米颗粒; 负载贵金属催化剂; 金属-载体强相互作用; 甲烷燃烧

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