Insight into the effect of manganese substitution on mesoporous hollow spinel cobalt oxides for catalytic oxidation of toluene

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HIGHLIGHTS

• The mesoporous hollow Mn-substituted Co 3O 4 are applied to toluene oxidation.
• The enhanced activity is related to small defective crystallite and high surface area.
• The chemical adsorbed oxygen is active species in toluene oxidation.
• DFT calculation and characterization elucidate the interaction between Co and Mn.

ABSTRACT

The cobalt oxides and manganese oxides have high-activity potential for catalytic oxidation of volatile organic compounds (VOCs), while the mesoporous hollow morphology is crucial to the mass transfer of reactant and product. Therefore, it is worth investigating the effect of manganese substitution in mesoporous hollow cobalt oxides on catalytic oxidation. Herein, a partially disordered spinel structure is formed by the Mn substitution in Co 3O 4 and the mesoporous hollow microsphere is improved in morphology homogeneity with the decrease of Co/Mn ratio in the range of 1.8–28.8. The 5Co1Mn (Mn-substituted Co 3O 4 with Co/Mn at 5.4) exhibits outstanding catalytic activity for toluene oxidation with 50% CO 2 generation at 237 °C, which is 21 °C lower than Co 3O 4. Moreover, the 5Co1Mn displays satisfactory stability in reusability, lifetime, and water resistance. The small defective crystallite, mesoporous hollow morphology, and high specific surface area endow Mn-substituted Co 3O 4 with more surface chemical adsorbed oxygen, enhancing the catalytic oxidation of toluene. Theoretical calculation on (311) plane of Co 3O 4 reveals that Mn 2+ or Mn 3+ substitution increases the formation energy of oxygen vacancy and makes it difficult to adsorb gaseous oxygen on the defective surface. The interaction between Co and Mn impedes the improvement of toluene oxidation because the mobility of lattice oxygen, the surface distribution of Co 3+, and the ratio of surface adsorbed oxygen to surface lattice oxygen are hindered by Mn substitution. The chemical adsorbed oxygen is more active than lattice oxygen in the oxidation of adsorbed intermediates (phenolate, benzoate species, etc.). The Langmuir–Hinshelwood mechanism dominates in the catalytic oxidation at 200–250 °C, while the catalytic oxidation follows both the
1. Introduction

Volatile organic compounds (VOCs) emitted from industrial, mobile, and domestic sources are major air pollutants that contribute greatly to the formation of ozone and photochemical smog [1,2]. Most VOCs are hazardous to human health because of their toxicity and carcinogenic effect. Due to the increasingly stringent environmental legislation, the control of VOCs emission has become an urgent task [3,4]. Currently, catalytic oxidation is regarded as the most effective and economical technique to transform VOCs into CO2, H2O, or other harmless compounds [5]. The key issue for catalytic oxidation is to develop a low-cost and high-efficiency catalyst with satisfactory stability. Noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability. Supported noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability. Supported noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability. Supported noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability. Supported noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability. Supported noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability. Supported noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability. Supported noble metals (Pd, Pt, Au, etc.) with superior catalytic activity are limited to high-efficiency catalyst with satisfactory stability.

Ordered mesoporous Co3O4 for dibromomethane oxidation has been synthesized by using mesoporous silica or silicon as a hard template, such as SBA-15 and KIT-6; however, the hard template must be etched by high-concentration strong base solution [12]. Suib et al. synthesize an efficient mesoporous Co3O4 for 2-propanol oxidation but the triblock copolymer (P123) as a soft template has to be washed off [13]. Owing to lightweight, tunable surface properties, and high storage capacity, attempts have been made to apply hollow Co-based catalysts into the oxidation of VOCs [14]. The hollow MCo3O4 (M = Co, Ni, Cu) are synthesized by a solvothermal alcoholysis method; however, the small specific surface area and limited mesopores of hollow MCo3O4 hinder further promotion in the oxidation of acetone [15]. The hollow Mn1−Co3−xO4 polyhedron for toluene oxidation can be obtained from the pyrolysis of metal-organic frameworks but the carcinogenic 2-methylimidazole is an indispensable chemical regent in preparation [16]. As such, one may expect to prepare mesoporous hollow Co3O4-based catalyst via an environment-friendly template-free method for VOCs oxidation.

Co3O4 displays spinel structure (AB2O4) with O2− arranged in a cubic close-packed lattice, in which the Co2+ occupies at the tetrahedral center (A site) and the Co3+ locates in the octahedral center (B site) [17]. With switchable oxidation states and similar ionic radius with Co, Mn is usually doped into spinel Co3O4 to enhance the catalytic oxidation of VOCs. Partial substitution of Co with Mn gives rise to more structural defects and faster oxygen mobility, and so it improves the catalytic performance of methane oxidation [18]. The synergistic effect between Co and Mn in redox capacity and oxygen mobility benefits the catalytic performance in 2-propanol oxidation [19]. Likewise, high specific surface area and abundant adsorbed oxygen species also contribute to the benzene and propane oxidation over spinel Co3O4 [20,21]. The effect of Mn substitution on the physiochemical properties and catalytic performance has been widely studied, whereas the underlying catalytic mechanism and interaction between Co and Mn still need to be further investigated.

The oxidation process on oxides is usually explained by Langmuir-Hinshelwood mechanism and Mars-van Krevelen mechanism above 250 °C. This work provides some enlightenment for exploring the role of surface oxygen species in VOCs oxidation and uncovering the interaction in binary spinel oxides.

2. Experimental section

2.1. Catalyst preparation

All chemicals were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. They are in analytical grade and used without further purification. In the synthesis of Co3O4, 4 mmol Co(NO3)2⋅6H2O were dissolved into a mixed solvent of 50 mL isopropanol and 14 mL glycerol to form a pink transparent solution. Subsequently, the solution was transferred into 100 mL Teflon-lined stainless steel autoclave and stayed at 170 °C for 6 h. After cooling to room temperature naturally, the pink precipitates in Fig. S1a were washed by ethanol and then were dispersed in 64 mL distilled water. Afterward, the suspension was transferred into an autoclave and kept at 150 °C for 3 h. The collected green solid in Fig. S1b after hydrothermal treatment was washed by distilled water and dried in a vacuum oven at 80 °C overnight. Finally, the ground precursor was calcined in air at 350 °C for 2 h at a rate of 2 °C min−1. Similarly, the Mn-substituted Co3O4 and MnO2 were obtained by tuning the molar ratio of Co/Mn, in which the 50 wt% Mn(NO3)2 solution was used as the Mn source. The resulting Mn-substituted Co3O4 were labeled as 29Co1Mn, 14Co1Mn, 5Co1Mn, and 2Co1Mn, respectively, where the molar ratio of Co/Mn was obtained by tuning the molar ratio of Co/Mn, in which the 50 wt% Mn(NO3)2 solution was used as the Mn source. The resulting Mn-substituted Co3O4 were labeled as 29Co1Mn, 14Co1Mn, 5Co1Mn, and 2Co1Mn, respectively, where the molar ratio of Co/Mn was obtained by tuning the molar ratio of Co/Mn, in which the 50 wt% Mn(NO3)2 solution was used as the Mn source.
diffraction (XRD), Raman spectroscopy, Electron spin resonance (ESR), and high-resolution transmission electron microscopy (HR-TEM) for microstructure; hydrogen temperature-programmed reduction (H₂-TPR) for reducibility; oxygen temperature-programmed desorption (O₂-TPD) for oxygen mobility; X-ray photoelectron spectroscopy (XPS) for surface oxidation state; temperature-programmed surface reaction (TPSR) for the reactivity of oxygen species; in situ diffuse reflectance infrared Fourier Transform spectroscopy (in situ DRIFTS) for adsorbed intermediates in toluene oxidation; density functional theory (DFT) calculation for the formation energy (E_{vo}) of oxygen vacancy and the adsorption energy (E_{ads}). The characterization details were provided in Text S1.

2.3. Catalytic evaluations

The periodic steady-state activity for toluene oxidation was tested in a fixed-bed reactor under atmospheric pressure. The feeding gas contains 1000 ppm toluene and synthetic air (21% O₂ balanced by N₂), corresponding to a weight hourly space velocity (WHSV) of 60 000 mL g⁻¹ C₀⁻¹ h⁻¹. Each catalyst was evaluated three times and the standard deviation was set to the error bar. The kinetic test was carried out less than 20% CO₂ generation to obtain the apparent activation energy. The specific CO₂ generation rate was normalized by BET specific surface area to evaluate the intrinsic activity. The catalytic stability was evaluated by cyclic test for three times, lifetime test at 240 °C for 24 h, and water-resistance test under 5% H₂O. The analysis details were provided in Text S2.

3. Results and discussion

3.1. Microstructure and morphology properties

For Co₃O₄ and Mn-substituted Co₃O₄, diffraction patterns in Fig. 1a at 19, 31, 39, 56, 59, 65, 74, 78, and 79° corresponds to the (111), (220), (311), (222), (400), (422), (511), (440), (620), (533), and (622) planes of cubic spinel Co₃O₄ phase, respectively [26]. The main diffraction patterns of MnO₂ belong to the spinel Mn₃O₄ ( hausmannite); however, weak patterns of tetragonal MnO₂ (pyrolusite) emerge at 37.3 and 43.0°, assigned to (011) and (1 1 1) planes, respectively [27]. With the increase of Mn substitution, diffraction patterns gradually become broad and the average crystallite size decreases from 19.3 to 8.4 nm. The decreasing trend of crystallite size is inversely correlated with the variation of specific surface area (Table 1). The pattern of (3 1 1) plane shifts towards the low 2θ angle as the Mn substitution increases (Fig. 1b), indicating an enlargement of d spacing. The substitution of Co²⁺ (0.58 Å) in tetrahedral sites by Mn²⁺ (0.66 Å) and the Co³⁺ (0.61 Å) in octahedral sites by Mn³⁺ (0.65 Å) will result in lattice expansion [28], so that the a₀ increases from 8.077 to 8.138 Å. Nevertheless, the XRD analysis cannot confirm all Mn cations are doped in the spinel structure because mixed oxides with amorphous structure may exist at a high Mn concentration[29].

The Raman spectrum of Co₃O₄ in Fig. 2a show five active modes at 192 cm⁻¹ (F₂g^3), 467 cm⁻¹ (Eg), 512 cm⁻¹ (F₂g^2), 604 cm⁻¹ (F₁g^1), and 672 cm⁻¹ (A₁g) [30]. The spectra of 2₉Co₁Mn, 1₄Co₁Mn, and 5Co₁Mn are similar to that of Co₃O₄, implying the successful Mn substitution in the spinel structure. Particularly, it is difficult for Raman scattering of 2Co₁Mn to be detected during tests. The Raman spectrum of MnO₂ is also characterized by the A₁g mode of hausmannite at 654 cm⁻¹ [31]. There are two remarkable changes in Raman spectra with the incorporation of Mn in Co₃O₄: the broadening of bands and the red shift of bands. The phonons can be confined in space by crystal boundaries or defects so that the shifting and broadening of Raman bands increase as the crystallite size decreases and lattice distortion intensifies [5,32].

Since the single positively charged oxygen vacancy (Vₒ⁺) is occupied by one electron and consequently paramagnetic, the ESR can provide the information of oxygen vacancy [33]. The ESR signal of the Vₒ center with g = 2.000 measured at room temperature shows an asymmetrical line shape (Fig. 2b), and its peak-to-peak line width is 0.04 mT. Neither a line splitting nor a line broadening is detectable with the increase of Mn substitution, but the signal of the Vₒ center gradually increases. The result suggests the Mn substitution can increase the amount of oxygen vacancy in
Co$_3$O$_4$, and this may be related to the lattice distortion caused by Mn substitution. Fig. 3 and Fig. S3 exhibit the morphological evolution with the increase of Mn substitution. The Co$_3$O$_4$ presents many 1–2 lm broken hollow mesoporous microspheres and fragments of shells that are interwoven together (Fig. 3a and d). Upon the introduction of Mn into Co$_3$O$_4$, more flower-like hollow microspheres with plenty of intraparticle voids appear in 29Co1Mn than in Co$_3$O$_4$ (Fig. 3b and e). The microspheres in 14Co1Mn are more uniform in shape than in 29Co1Mn (Fig. 3c), though the hollow sphere with a loophole still can be found in some regions (Fig. 3f). The 5Co1Mn presents a core-shell structure, in which the shell still preserves abundant flower-like sheets. The further increase of Mn/Co ratio leads to the generation of hierarchical particle-stacked microspheres with clear boundaries in 2Co1Mn. The MnO$_x$ turns into irregular bulk agglomerates with the flocculent surfaces in the absence of Co. In comparison, the homogeneity of microspheres is improved with the increase of Mn. The diameter of microspheres, which is the independence of the Co/Mn ratio, is in the range of 1–2 lm.

TEM image of Co$_3$O$_4$ in Fig. 4a1 presents a broken hollow microsphere with 1.4 lm in diameter, which is composed of particles at ca. 20 nm in size. One particle in Co$_3$O$_4$ displays highly-ordered and well-defined lattice fringes of (022) and (311) plane of Co$_3$O$_4$ with the angle of 64.8°, indicating a relatively high crystallinity (Fig. 4a3–a4). It can be observed perfect hollow core-shell structured microspheres with mesoporous shells in 14Co1Mn, 5Co1Mn, and 2Co1Mn. Compared with Co$_3$O$_4$ and 29Co1Mn, 5Co1Mn and 2Co1Mn exhibit smaller particles and dense mesopores (Fig. 4a2, b2, d2, and e2). Inconsistency with the XRD result, the crystallite size of Mn-substituted Co$_3$O$_4$ gradually decreases with the increase of Mn substitution, which is evidenced by more blurry and anisotropic lattice fringes. The edge dislocation is found in one crystallite of 14Co1Mn (Fig. 4c3), where the (222) plane gradually transfers into (111) plane. Likewise, the crystal-plane slip can be found in 5Co1Mn and 2Co1Mn, where the lattice fringes of (400) and (311) in one crystallite are not in a line. Since the shape of crystallites is rough and ruleless, the surface of crystallite contains many imperfections (kinks, steps, edges, or terraces), where cations are in low coordination (Fig. S4). Therefore, the introduction of Mn into Co$_3$O$_4$ inhibits the growth of crystallites and brings about surface imperfections.

The N$_2$ adsorption-desorption isotherms in Fig. S5a show mixed characteristics of type II and IV according to the IUPAC definitions [34]. Little uptake of N$_2$ at low P/P$_0$ indicates that the micropores are rare and the H3-type hysteresis loops suggest the predominance of mesopores. All isotherms exhibit a sharp uptake at P/P$_0$ 0.8–1.0, implying the presence of macropores. The macropores mainly originate from the network of microspheres and the cavity between core and shell. The distribution of mesopores in Co$_3$O$_4$ is broad but the mesopore volume gradually narrows towards 15 nm with the increase of Mn substitution (Fig. S3b). The mesopore volume initially increases from 0.12 to 0.35 cm$^3$ g$^{-1}$ but then decreases to 0.27 cm$^3$ g$^{-1}$ over 2Co1Mn (Table 1). The decreasing pore volume for 2Co1Mn might be associated with the morphologic change from the flower-like microsphere to the particle-stacked microsphere. Besides, the specific surface area increases from 40

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET SSA/m² g⁻¹</th>
<th>Mesopore volume/cm³ g⁻¹</th>
<th>Crystallite size/nm</th>
<th>Lattice constant a/Å</th>
<th>Bulk ratio of Co/Mn</th>
<th>Surface ratio of Co/Mn</th>
</tr>
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<tbody>
<tr>
<td>Co$_3$O$_4$</td>
<td>40</td>
<td>0.12</td>
<td>19.3</td>
<td>8.077</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>29Co1Mn</td>
<td>59</td>
<td>0.24</td>
<td>16.2</td>
<td>8.085</td>
<td>28.8</td>
<td>17.0</td>
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<tr>
<td>14Co1Mn</td>
<td>81</td>
<td>0.31</td>
<td>13.2</td>
<td>8.089</td>
<td>14.4</td>
<td>8.8</td>
</tr>
<tr>
<td>5Co1Mn</td>
<td>114</td>
<td>0.33</td>
<td>9.1</td>
<td>8.111</td>
<td>5.4</td>
<td>3.8</td>
</tr>
<tr>
<td>2Co1Mn</td>
<td>131</td>
<td>0.27</td>
<td>8.4</td>
<td>8.138</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>MnO$_x$</td>
<td>63</td>
<td>0.19</td>
<td>14.7</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

a Specific surface area obtained by BET method at P/P$_0$ 0.05–0.25.
b Cumulative mesopore volume estimated from the BJH adsorption branch.
c Average crystallite size calculated from the patterns of (111), (220), (311), (400), (511), and (440) planes by the Scherrer equation.
d Lattice constant refined by the Rietveld method.
e Bulk ratio of Co/Mn determined by ICP-OES.
f Surface ratio of Co/Mn obtained by XPS.
to 131 m² g⁻¹. Thus, the Mn/Co ratio of Mn-substituted Co₃O₄ not only regulates the nanostructure but also changes the pore structure and specific surface area.

3.2. Surface oxidation state, reducibility, and oxygen mobility

The H₂-TPR curve of Co₃O₄ displays two obvious reduction peaks (Fig. 5a), which are assigned to the reduction of Co³⁺ to Co²⁺ and Co²⁺ to Co⁰, respectively [35]. The area ratio of Co³⁺ to Co²⁺ over Co₃O₄ is 35.1%, which is close to the theoretical ratio (33.3%) (Eqs. (1) and (2)). In the H₂-TPR curve of Mn-substituted Co₃O₄, the first peak is the reduction of Co³⁺ to Co²⁺ and the second peak is the overlapping reduction of Co²⁺ to Co⁰ and Mn³⁺ to Mn²⁺ [36]. The reduction peak of Mn³⁺ to Mn²⁺ is unclear in the broad peak of Co²⁺ to Co⁰. Since the H₂ consumption for Mn³⁺ to Mn²⁺ is half of that for Co²⁺ to Co⁰, the high-temperature reduction peak decreases from 12.5 to 8.8 mmol g⁻¹ with the increase of Mn substitution (Table 2). From the XRD analysis, the MnOₓ is composed of Mn₃O₄ and a small quantity of MnO₂. Due to the strong Jahn-Teller effect of octahedral Mn³⁺, there are two main kinds of Mn³⁺–O²⁻ bonds in spinel Mn₃O₄, i.e. octahedral long Mn³⁺–O²⁻ and octahedral short Mn³⁺–O²⁻ [37]. Thus, the curve of MnOₓ consists of three reduction peaks centered at 204, 268, and 392 °C, which are assigned to Mn⁴⁺ → Mn³⁺ of MnO₂ and Mn³⁺ → Mn²⁺ at different coordination environments in Mn₃O₄, respectively. In addition, the 2Co1Mn exhibits a minor reduction peak centered at 220 °C, which is related to the reduction of Mn⁴⁺ → Mn³⁺. This observation confirms the existence of amorphous MnO₂ in 2Co1Mn.

From the view of crystal field theory, Mn³⁺ with octahedral site preference energy (OSPE) at 95.4 kJ mol⁻¹ prefers to coordinate octahedrally than Co³⁺ with OSPE at 79.5 kJ mol⁻¹, while Co²⁺ with tetrahedral crystal-field stabilization energy (CFSE) at 62.0 kJ mol⁻¹ is prior to Mn²⁺ with tetrahedral CFSE at 0 kJ mol⁻¹ in competition for the tetrahedral site [38,39]. Considering the redox couples of Mn³⁺/Mn²⁺ (E° = 1.54 V) and Co³⁺/Co²⁺ (E° = 1.92 V), the Mn³⁺ tends to be oxidized by Co³⁺ [40]. Therefore, the balance between these cations is determined by their structural and redox properties. In this case, the H₂ consumption of Co²⁺ → Co³⁺ for Co₃O₄ and
Mn-substituted Co$_3$O$_4$ is in the narrow range of 4.2–4.4 mmol g$^{-1}$ regardless of Co/Mn ratio, suggesting that Mn substitution leads to the partially disordered spinel structure [41]. There is no obvious deviation of reduction temperature in the reduction of Co$^{3+}$ → Co$^{2+}$ after Mn substitution, but the reduction of Co$^{2+}$ → Co$^{0}$ and Mn$^{3+}$ → Mn$^{2+}$ shifts to the high temperature as divided by the red dotted line. The result indicates that the reducibility is hindered by Mn substitution. Moreover, there is a minor reduction peak at 50–180 °C in Fig. 5b, which is assigned to the reduction of chemical adsorbed oxygen (O$_2$) or O$_2^-$ (or O$^-$) [8,42].

In Fig. 5c, the O$_2$-TPD curves of Co$_3$O$_4$, 29Co1Mn, 14Co1Mn, and 5Co1Mn can be divided into two regions: the O$_2$ located at low temperatures (<210 °C) is assigned to the desorption of physically adsorbed oxygen (Eq. 39) and chemical adsorbed oxygen (Eq. S10) [43], and the O$_2$ at medium temperatures (210–450 °C) is contributed by the evolution of surface lattice oxygen (Eq. S11). In addition, the desorption of O$_2$ at high temperatures (>450 °C) corresponds to bulk lattice oxygen through oxygen vacancies after the desorption of surface lattice oxygen (Fig. S6, Eq. S12) [19,24].

Owing to increasing specific surface area and decreasing crystallite size, the desorption of O$_2$ and O$_3$ gradually increases from Co$_3$O$_4$ to 5Co1Mn. However, the desorption temperature of O$_2$ gradually shifts from 317 °C (Co$_3$O$_4$) to 341 °C (5Co1Mn), implying that the release of surface lattice oxygen is more difficult. Since the desorption temperature of O$_2$ for MnO$_2$ ranges from 400 to 800 °C in Fig. S6 [44], two strong desorption peaks of MnO$_2$ centered at 465 and 534 °C are attributed to the release of bulk lattice oxygen of MnO$_2$. Similarly, the oxygen desorption peak centered at 484 °C for 2Co1Mn is associated with the release of bulk lattice oxygen from amorphous MnO$_2$. Consequently, the desorption temperatures of O$_2$ and O$_3$ over 2Co1Mn are inconsistent with the desorption temperatures of Co$_3$O$_4$, 29Co1Mn, 14Co1Mn, and 5Co1Mn.

The broad and asymmetrical O 1s spectrum gradually shifts from 529.6 to 530.2 eV with the increase of Mn (Fig. 6a), and this is caused by the change of surface oxygen coordination environment [28]. The O 1s spectra can be fitted with two components, i.e. lattice oxygen (O$_{\text{latt}}$) and adsorbed oxygen (O$_{\text{ads}}$) species. The ratio of O$_{\text{ads}}$/O$_{\text{latt}}$ for Co$_3$O$_4$ (0.56) is slightly higher than that of Mn-substituted Co$_3$O$_4$ (0.41–0.48) (Fig. S8a). In Fig. 6b, Mn 2p$_{3/2}$ spectra show a peak centered at 641.6 eV, demonstrating that the Mn is in a similar oxidation state regardless of Co/Mn ratio. The splitting of Mn 3s peak (ΔE) for MnO$_2$, Mn$_2$O$_3$, and MnO are 4.7, 5.5, and 6.0 eV, respectively, indicating that the ΔE is the diagnostic of oxidation state [5]. In Fig. S8b, the Mn 3s spectra exhibit ΔE of 5.3 eV, indicating that Mn is mainly in a trivalent state on average.
Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_2$-TPR $P_1$/mmol g$^{-1}$</th>
<th>$P_2$/mmol g$^{-1}$</th>
<th>XPS</th>
<th>$Co^{3+}$/Co</th>
<th>$O_{ads}$/O$_{lat}$</th>
<th>Co$^{3+}$/Co + Mn</th>
</tr>
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<tr>
<td>Co$_3$O$_4$</td>
<td>4.4</td>
<td>12.5</td>
<td>3.0</td>
<td>0.56</td>
<td>0.75</td>
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<tr>
<td>29Co1Mn</td>
<td>4.2</td>
<td>11.7</td>
<td>1.1</td>
<td>0.46</td>
<td>0.50</td>
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<tr>
<td>14Co1Mn</td>
<td>4.2</td>
<td>11.5</td>
<td>0.8</td>
<td>0.46</td>
<td>0.41</td>
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</tr>
<tr>
<td>5Co1Mn</td>
<td>4.3</td>
<td>10.8</td>
<td>0.5</td>
<td>0.48</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>2Co1Mn</td>
<td>4.3</td>
<td>8.8</td>
<td>0.3</td>
<td>0.41</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The $H_2$ consumption amount of Co$^{3+}$ → Co$^{2+}$ in $H_2$-TPR.

$^b$ The total $H_2$ consumption amount of Co$^{3+}$ → Co$^{2+}$ and Mn$^{3+}$ → Mn$^{2+}$.
The Co 2p 3/2 spectra can be fitted with three components: octahedral Co 3+ centered at 779.6 ± 0.2 eV, tetrahedral Co 2+ centered at 781.2 ± 0.3 eV, and satellite with instrument background at 785.8 ± 1.1 eV [28]. The binding energy of Co 2p 3/2 spectra shifts from 779.1 to 779.9 eV, suggesting a remarkable change of oxidation state (Fig. 6c). In Table 2, the order of surface Co 3+/Co 2+ ratio is Co 3O 4 (3.0) > 29Co1Mn (1.1) > 14Co1Mn (0.8) > 5Co1Mn (0.5) > 2Co1Mn (0.3), indicating that the introduction of Mn leads to the following surface redox reaction: Mn 2+ + Co 3+ → Mn 3+ + Co 2+. Consequently, the average oxidation state of Mn on the surface is mainly in +3 and the ratio of Co 3+/Co 2+ decreases. Compared with the bulk ratio of Co/Mn determined by ICP-OES, the surface ratio of Co/Mn obtained by XPS is much lower, indicating that the Mn enriches on the surface (Table 1).

3.3. Catalytic performance for toluene oxidation

The catalytic oxidation of toluene was used as a probe reaction to evaluate catalytic efficiency of VOCs (Fig. 7). The toluene conversion at 225 °C is in the range of 20–29%, but the CO 2 generation is less than 12%. Due to the negligible CO in the outlet gas, the carbon imbalance suggests that the toluene and intermediates are adsorbed on the surface, and this is also verified in the following in situ DRIFT and TPSR experiments. When the temperature increases to 275 °C, the CO 2 generation rate is close to the toluene conversion rate, indicating that the CO 2 selectivity is approaching 100%. In Table 3, the temperature of 50% CO 2 generation (T 50) gradually decreases from 258 °C (Co 3O 4) to 237 °C (5Co1Mn), and then stays at 238 °C (2Co1Mn). This trend is also evidenced by the activity order of T 50 on toluene conversion. Table S1 summarizes cobalt-based catalyst in toluene oxidation from previous studies, suggesting that 5Co1Mn presents a satisfactory catalytic activity.

Owing to the best activity among the prepared catalysts, the 5Co1Mn is chosen as the model catalyst to evaluate catalytic stability. In Fig. S9a, no obvious decrease in CO 2 generation is found after three cyclic experiments. The toluene conversion and CO 2 generation at 240 °C vary in the narrow range of 31–38% and 28–33% for 24 h, respectively (Fig. S9b). After twenty-four-hour lifetime tests, the collected 5Co1Mn is evaluated for toluene oxidation again and it still shows an almost identical light-off curve to fresh 5Co1Mn. The effect of 5% H 2O on catalytic oxidation is investigated at 240 and 275 °C. The CO 2 generation drops less than 8% when 5% H 2O is introduced into feed gas for 60 min, and it gradually recovers when the introduction of H 2O stops (Fig. S9c).

Besides, the specific CO 2 generation rates normalized by BET surface area (r *CO2) for Co 3O 4 and Mn-substituted Co 3O 4 are close at 210, 220, and 230 °C (Fig. S10a). For example, the r *CO2 at 210, 220, and 230 °C for Co 3O 4 is 2.2 × 10 10, 3.4 × 10 10, and 6.4 × 10 10 mol m 2 s 1, while they are 2.2 × 10 10, 3.3 × 10 10, and 6.9 × 10 10 mol m 2 s 1 for 5Co1Mn. Fig. S10b displays the Arrhenius plots of the catalysts, and the apparent activation energies are summarized in Table 3. The results display that the Ea value of Co 3O 4 (111 kJ mol 1) is in the range of that of Mn-substituted Co 3O 4 (105–112 kJ mol 1) and the fluctuation of Ea may be in the error range.

Table 3
Catalytic activity from light-off curves and CO 2 generation from TPSR curves.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Toluene conversion temperature/°C</th>
<th>CO 2 generation temperature/°C</th>
<th>CO 2 generation amount/mmol</th>
<th>Apparent Ea/kJ mol 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T 50</td>
<td>T 90</td>
<td>T 50</td>
<td>T 90</td>
</tr>
<tr>
<td>Co 3O 4</td>
<td>255</td>
<td>271</td>
<td>258</td>
<td>271</td>
</tr>
<tr>
<td>29Co1Mn</td>
<td>248</td>
<td>269</td>
<td>253</td>
<td>270</td>
</tr>
<tr>
<td>14Co1Mn</td>
<td>239</td>
<td>267</td>
<td>241</td>
<td>266</td>
</tr>
<tr>
<td>5Co1Mn</td>
<td>232</td>
<td>247</td>
<td>237</td>
<td>248</td>
</tr>
<tr>
<td>2Co1Mn</td>
<td>233</td>
<td>248</td>
<td>238</td>
<td>249</td>
</tr>
<tr>
<td>MnO x</td>
<td>238</td>
<td>264</td>
<td>240</td>
<td>264</td>
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<td>2.3</td>
<td>2.3</td>
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<td>2.2</td>
</tr>
</tbody>
</table>

*T 50 and *T 90 are the temperatures of 50% and 90% toluene conversion, respectively.

*T 50 and *T 90 are the temperatures of 50% and 90% CO 2 generation, respectively.

r *CO2 in O 2-TPSR and r *CO2 in N 2-TPSR are the molar amount of CO 2 generation in O 2-TPSR and N 2-TPSR, respectively.
3.4. Structure-activity relationship and reaction mechanism

The O$_2$-TPSR shows a broad CO$_2$ generation peak centered at 280–290 °C (Fig. 8a), while the N$_2$-TPSR curves present two broad peaks centered at 317–326 °C and 410–428 °C, respectively (Fig. 8b). The temperature gap between O$_2$-TPSR and T50 from light-off curves is caused by two different temperature programming, i.e. dynamic heating and steady state. The CO$_2$ generation in N$_2$-TPSR indicates that bulk lattice oxygen participates in the oxidation of adsorbed toluene and intermediates. The second CO$_2$ generation peak at 410–428 °C becomes stronger with the increase of Mn substitution. As the Co$^{3+}$–O$_2$ starts to be reduced before Co$^{3+}$–O$^{2-}$ and Mn$^{3+}$–O$^{2-}$ do in H$_2$-TPR, the first CO$_2$ generation peak is associated with the reaction between Co$^{3+}$–O$^{2-}$ and adsorbed intermediates, while the second peak is related to the oxidation of adsorbed intermediates by Co$^{3+}$–O$^{2-}$ and Mn$^{3+}$–O$^{2-}$. The temperature of CO$_2$ peak in O$_2$-TPSR is lower than that in N$_2$-TPSR, implying that the chemical adsorbed oxygen on the surface is more active than lattice oxygen in the oxidation of adsorbed intermediates. The CO$_2$ generation in O$_2$-TPSR and N$_2$-TPSR increases with the increment of Mn substitution (Table 3). This suggests that the high specific surface area and abundant mesopores provides more surface sites for adsorption, so the Mn-substituted Co$_3$O$_4$ supplies more chemical adsorbed oxygen and lattice oxygen for toluene oxidation. On one hand, as evidenced by H$_2$-TPR and O$_2$-TPD, the reducibility and oxygen mobility are hindered by Mn introduction. On the other hand, the distribution of Co$^{3+}$ on the surface declines after Mn substitution. As a result, the CO$_2$–generation temperature in TPSR gradually shifts to a high temperature as the Mn substitution increases.

Previous studies have shown that lattice oxygen and adsorbed oxygen species play a vital role in the catalytic oxidation reaction [44,45]. The CO or hydrocarbon molecules react with lattice oxygen and then the gaseous O$_2$ replenish the oxygen vacancies when the catalytic oxidation follows the MVK mechanism. The L-H mechanism indicates that the adsorbed oxygen species on oxygen vacancies are reactive species to participate in the oxidation of CO or hydrocarbon molecules. Thus, the formation energy of oxygen vacancy and the adsorption energy of O$_2$ are significant. The (311) plane of Co$_3$O$_4$, which is commonly found in HR-TEM images (Fig. 4), is chosen to obtain E$_{vo}$ and E$_{ads}$ by DFT + U method (Fig. 9). The Co$_3$O$_4$ has the lowest E$_{vo}$ (1.76 eV), which is smaller than the Mn$^{3+}$-substituted Co$_3$O$_4$ (2.18 eV) and Mn$^{2+}$-substituted Co$_3$O$_4$ (2.81 eV). The theoretical calculation supports that Mn substitution suppresses the reducibility and oxygen mobility [46]. The O$_2$ molecule is parallelly adsorbed on the defective (311) plane of Co$_3$O$_4$ (Fig. 9d), on which one oxygen atom is bonded on Co$^{3+}$ and the other interacts with Co$^{2+}$. The bond length between adsorbed O$_2$ and surface Co (1.847–1.853 Å) is shorter than the bond length of Co$^{3+}$–O$^{2-}$ (1.939 Å) and Co$^{2+}$–O$^{2-}$ (1.934 Å), while the bond length of adsorbed O$_2$ (1.354 Å) is longer than that of isolated O$_2$ (1.209 Å). Besides, the absolute E$_{ads}$ (2.14 eV) is higher than the E$_{vo}$ (1.76 eV). The above finding indicates that the O$_2$ molecule is chemically adsorbed on the defective (311) plane. The O$_2$ molecule is perpendicularly adsorbed on the Mn$^{3+}$-substituted Co$_3$O$_4$, resulting in the slip of adjacent Co$^{3+}$ in the supercell (Fig. 9e). On the (311) plane of Mn$^{3+}$-substituted Co$_3$O$_4$, the stable adsorption configuration is the O$_2$ perpendicularly bonded with the Co$^{3+}$ where a Co$^{3+}$ is between oxygen vacancy and the Co$^{3+}$–O$_2$ (Fig. 9f). Although the stable adsorption configurations are different, the binding strength of O$_2$ on defective Co$_3$O$_4$ (–2.14 eV) is slightly stronger than that on defective Mn$^{3+}$-substituted Co$_3$O$_4$ (–1.92 eV) and defective Mn$^{2+}$-substituted Co$_3$O$_4$ (–1.22 eV). This can explain the ratio of O$_{ads}$/O$_{latt}$ for Co$_3$O$_4$ is 0.56 but the ratios of O$_{ads}$/O$_{latt}$ for Mn-substituted Co$_3$O$_4$ are in the range of 0.41–0.48.

The XRD, Raman, and HR-TEM results reveal that most Mn cations are successfully doped into the spinel structure, resulting in small crystallites with defective structures. From the ESR results, more oxygen vacancies are generated in Co$_3$O$_4$ with the increase of Mn. The hollow mesoporous structure is confirmed by the observation of SEM and TEM. The specific surface area gradually increases with the decrease of crystallite size. The hard/soft templates are commonly used to prepare mesoporous Co$_3$O$_4$ but they must be etched off or washed off in preparation [13,47]. This brings about the waste of alkaline solution or organic solvent. The hollow Mn$_n$-Co$_{3-x}$O$_{4-y}$ is obtained by the pyrolysis of metal-organic frameworks but the carcinogenic ligands are necessary chemicals [16]. Herein, the precursor of mesoporous hollow Mn-substituted Co$_3$O$_4$ is prepared by using safe and cheap organic chemicals, i.e. isopropanol and glycerol. Compared with the previous solvothermal alcoholysis method [15], our method increases the production of precursor and modifies the mesoporous hollow structure of Mn-substituted Co$_3$O$_4$.

The mesoporous shells are beneficial for the toluene molecule to penetrate into the cavity and to be oxidized on the surface of the core. The small crystallites expose considerable surface imperfections which facilitate the adsorption and transformation of O$_2$. Both surface adsorbed oxygen and surface lattice oxygen on

Fig. 8. The CO$_2$ generation in the temperature-programmed surface reaction (TPSR) under synthetic air (a) and N$_2$ (b). Reaction condition: catalyst mass = 10 mg and flow rate = 100 ml min$^{-1}$. 721
Mn-substituted Co₃O₄ increase in the total amount due to the large surface area. The surface octahedral Co³⁺–O₂⁻/Co is generally considered as the active center in CO oxidation as well as VOCs oxidation [48, 49], while the reducibility and oxygen mobility are two key factors for the catalytic activity. The correlation between T50 of CO₂ generation and characterization parameters is built to confirm the structure-activity relationship. In Fig. S11, the linear fitting result reveals that the BET specific surface area, intensity of ESR signals, and the amount of CO₂ generation in O₂-TPSR are negatively correlated with the T50, while the H₂ consumption amount in H₂-TPR, the desorption temperature of surface lattice oxygen in O₂-TPD, and the surface ratio of Co³⁺/(Co + Mn) are positively correlated with the T50. The Mn substitution not only contribute to a mesoporous hollow spherical Co₃O₄ with small defective crystallites and high surface area but also presents a negative side—the decrease of reducibility, the weakening of oxygen mobility, and the shrinkage in the distribution of surface Co³⁺ and adsorbed oxygen. Even so, the T50 gradually decreases from 258 to 237°C, whereas the specific reaction rates and apparent activation energies show the independence of the Co/Mn ratio. Accordingly, the enhanced physical properties are of importance in the catalytic oxidation of toluene.

To monitor the intermediates in toluene oxidation, the in situ DRIFTS was conducted under toluene/synthetic air in the temperature range of 100–250 °C. The 5Co₁Mn exhibits similar DRIFTS with Co₃O₄ but shows remarkably different spectra from MnOₓ (Fig. 10 and Fig. S12). The bands at 2950 and 2871 cm⁻¹ are assigned to skeletal vibration of the aromatic ring [50]. The bands at 2950 and 2871 cm⁻¹ are the asymmetric stretching vibration of the methyl group (CH₃), suggesting the presence of adsorbed toluene. The band at 1347 and 1289 cm⁻¹ are assigned to in-plane bending and rocking vibration from the methylene group, indicating that the methyl group of toluene has been cleaved into the methylene group to form benzyl (Ph–CH₂–) [51]. The band at 3361 cm⁻¹ is assigned to the O–H stretching vibration and the bands at 1179 and 1112 cm⁻¹ are recognized as the C–O stretching vibration of benzyl alcohol (Ph–CH₂–OH) [50]. The weak bands at 1213 and 1141 cm⁻¹ are assigned to C–O stretching vibration of benzoate (C₆H₅–COO⁻) and the strong bands at 1528 and 1408 cm⁻¹ are asymmetric and symmetric stretching vibrations of COO⁻, respectively [30]. The band at 1240 cm⁻¹ is characteristic of the C–O stretching vibration of phenolate [52]. Additionally, the characteristic carbonyl C=O stretching vibration of benzoic acid is absent in the range of 1600–1800 cm⁻¹.

Since polycrystalline particles exhibit crystalline anisotropy and contain sites associated with terraces, edges, kinks, and vacancies, the Co₃O₄ and Mn-substituted Co₃O₄ exhibit complex catalytic sites with different activities. Consequently, the intermediates with different oxidation degrees are adsorbed on the surface of the catalyst together. The intermediates gradually accumulate with time-on-stream as the oxidation reaction proceeds (Fig. S13). In our previous results of proton transfer reaction mass spectrometer (PTR-TOF-MS), ring-opened by-products, such as maleic acid, acetic acid, ketone, etc. are found in the outlet gas [30]; however, it is difficult to observe and identify the bands of above intermediates in DRIFTS, and this might suggest that the breakage of an aromatic ring is the rate-determining step in toluene oxidation.
oxidation. A possible reaction pathway for toluene oxidation is proposed: gaseous toluene → adsorbed toluene → benzyl → benzyl alcohol → benzoate → phenolate → CO₂ and H₂O. As the temperature increases from 100 to 200 °C, major bands are still strong in intensity, indicating that the deep oxidation of intermediates is limited. This explains why CO₂ generation in light-off curves is below 200 °C. The accumulation of intermediates is rare on Co₃O₄ at 225 °C but the bands of benzoate species still can be found on 5Co₁Mn. The result is in agreement with the finding of TPSR that the decomposition temperature of adsorbed toluene and intermediates over 5Co₁Mn is higher than over Co₃O₄.

To identify the role of chemical adsorbed oxygen and surface lattice oxygen in toluene oxidation, the on-stream reaction at 240 °C was performed under O₂-containing or O₂-free atmosphere alternatively (Fig. 11a). When the 1000 ppm toluene/synthetic air is switched by 1000 ppm toluene/N₂, the CO₂ generation immediately decreases from 30% to 6%, and then gradually decreases to 2%. As the toluene/synthetic air is introduced into feed gas again, the CO₂ generation recovers to 25–30%. The CO₂ generation of 5Co₁Mn still keeps at 24% after three cycles. The above findings indicate that the chemical adsorbed oxygen is more active than lattice oxygen over 5Co₁Mn in toluene oxidation.

The isolated DRIFTS is also recorded under 500 ppm toluene/synthetic air or 500 ppm toluene/N₂ to determine the intermediates at 240 °C during the cyclic reaction (Fig. 11b). The band intensity of benzoate is negligible under toluene/synthetic air but the characteristic bands of benzoate appear at 1406 and 1534 cm⁻¹ under toluene/N₂. This means that the 5Co₁Mn cannot provide enough active lattice oxygen to participate in the complete oxidation of toluene, so the toluene molecules are adsorbed or incompletely oxidized on the surface under toluene/N₂. When the gaseous O₂ is introduced, the newly-formed chemical adsorbed
oxygen acts as the main oxygen source in oxidation products, i.e. CO₂ and H₂O, and so the coverage of intermediates on 5Co1Mn is rare.

Fig. S14 shows in situ DRIFTS of toluene/intermediates desorption under air or N₂ over 5Co1Mn at different temperatures. Since the 5Co1Mn is pretreated with a flow of N₂ at 300 °C for 60 min, the chemical adsorbed oxygen on the surface is removed. The bands at 1402, 1240, and 1179 cm⁻¹ appear in the spectrum when the toluene/N₂ is introduced into the chamber at 150 °C, indicating the adsorbed toluene is partially oxidized into benzoate, phenolate, and benzyl alcohol by the surface lattice oxygen. Prior to the introduction of air, the pure N₂ flows in the chamber to remove the residual toluene. The characteristic bands of benzoate and phenolate increase in area at 150 °C under air and this is related to the oxidation of adsorbed toluene. As the temperature increases to 225 °C, the band area of benzoate and phenolate sharply drops (Fig. S15). However, the spectrum of toluene desorption under N₂ at 225 °C still shows strong bands of benzoate and phenolate, which sharply decreases until the temperature increases to 275 °C. Although the lattice oxygen can participate in the incomplete oxidation of toluene as electron donor and oxygen source at 150 °C, the surface/bulk Co–O and Mn³⁺–O₂⁻ is not active enough to oxidize the toluene completely below 250 °C. In contrast, the O₂ can be activated into electrophilic oxygen species (O₂, O²⁻ and O⁻) on surface defects, especially on oxygen vacancies. Then these chemical adsorbed oxygen species are prone to attack the toluene in the region of high electron density, leading to complete oxidation of toluene or intermediates above 200 °C. The chemical adsorbed oxygen is the active species according to L-H mechanism, whereas the surface lattice oxygen is the active site on the basis of MVK mechanism. Therefore, the toluene oxidation over 5Co1Mn is dominated by L-H mechanism at 200–250 °C, while toluene oxidation following MVK mechanism starts proceeding above 250 °C (Fig. 12).

4. Conclusion

In this work, we present mesoporous hollow Mn-substituted spinel Co₃O₄ with safe and cheap organic chemicals, i.e. isopropanol and glycerol. The synthesized Mn-substituted Co₃O₄ exhibits promising activity and stability in the catalytic oxidation of toluene. The Mn substitution reduces the crystallite size, increases the surface area, and improves the homogeneity of mesoporous core-shell microspheres. It is found that the improved activity by Mn substitution is attributed to the above enhanced physical properties. Namely, the small defective crystallites of Mn-substituted Co₃O₄ expose more active sites (defects and lattice oxygen) on the surface and accelerate the adsorption and transformation of reactants. In contrast, the interaction between Co and Mn results in negative effects, such as the decrease of reducibility, the weakening of lattice-oxygen mobility, and the shrinkage in the distribution of surface Co³⁺ and adsorbed oxygen. The chemical adsorbed oxygen on Mn-substituted spinel Co₃O₄ is more active than lattice oxygen in toluene oxidation. Moreover, the toluene oxidation is dominated by Langmuir–Hinshelwood mechanism at 200–250 °C, while toluene oxidation following Mars-van Krevelen mechanism also proceeds above 250 °C. This work demonstrates a potential mesoporous hollow cobalt-based catalyst in the elimination of volatile organic compounds, reveals the role of surface oxygen species in catalytic oxidation, and clarifies the interaction between Co and Mn in the spinel structure.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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