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# Template-free Scalable Synthesis of Flower-like Co<sub>3-x</sub>Mn<sub>x</sub>O<sub>4</sub> Spinel Catalysts for Toluene Oxidation

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Abstract: The rational design of low-cost transition metal catalysts that exhibit high activity and selectivity may be the most significantly investigated in heterogeneous catalysis. In this study, Co3-xMnxO4 (x = 0.75, 1.0, and 1.5) mixed metal oxides were successfully synthesized by a controlled template-free autoclave strategy and studied for toluene oxidation. It is found that the Co-rich sample showed markedly enhanced activity and the 3D dandelion-like Co2.25Mn0.75O4 catalyst exhibited in the highest toluene oxidation rate (8.9 µmol/(g<sub>cat</sub>s)) and a 100 % toluene conversion at 239 °C. In situ DRIFTS study indicates that toluene was sequentially oxidized to benzyl radical, benzaldehyde, benzene, oxalic acid, and finally to CO<sub>2</sub> and H<sub>2</sub>O. The interaction between Co and Mn, in conjunction with the high concentration of surface oxygen species and rich surface oxygen vacancies, reasonably explains the elevated catalytic activity and thermal stability for toluene oxidation over 3D flower-like Co<sub>3-x</sub>Mn<sub>x</sub>O<sub>4</sub> spinel catalysts.

### Introduction

Volatile organic compounds (VOCs) emitted from certain solids or liquids in industrial processes and transport vehicles have short- and long-term health risks, and become a notable problem. In consideration of the environmental impact and energy-saving, low-temperature catalytic oxidation, one of frequently and widely distributed VOCs in the environment, is one promising strategy for the removal of toluene.

In the literature, precious metal catalysts (e.g., Pt, Pd, Ag, and Au) demonstrated higher activity as compared with transition

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Supporting information for this article is given via a link at the end of the document.

metal (e.g., Co and Mn) oxides for toluene oxidation. Normally, transition metal oxide catalysts show a complete conversion of trace toluene (> 99%) at temperatures above 250 °C,[1-2] whereas typical supported noble metal-based catalysts can achieve a complete conversion at temperatures below 200 °C. Even so, precious metal catalysts have some inevitable drawbacks, for instance, high cost, easy-poisoning tendency, and limited resources. It is hence desirable to make efforts on the development of efficient transition metal oxide catalysts with low cost and high thermal stability to substitute noble metal catalysts. Among the transition metal oxides, manganese and cobalt are recognized as the most promising ones because of their low price and adequate activities at relatively low temperatures. Kim and Shim [3] observed a catalytic activity order of  $Mn_3O_4 > \alpha - Mn_2O_3 > \beta - MnO_2$  for toluene and benzene oxidation. Mn with a high valence is more active in total oxidation. The further addition of alkali metal and alkaline earth metal improves the catalytic performance. Moreover, Co oxide is active due to the redox properties in toluene oxidation.

Apart from the catalyst composition, introducing porosity to a base metal oxide can increase surface area of the catalyst and improve its catalytic performance. This increase in surface area can decrease the initial reaction temperature of VOC oxidation and enhance the rate of the surface reaction. So it follows that the surface structure and properties of the catalyst are key to catalytic performance.[1-2, 4-8] To improve the catalytic activity of manganese and cobalt catalyst, many efforts have been made to adjust the synthetic methods to achieve appropriate crystal structures and morphologies. The impact of porosity in mesoporous/macroporous manganese and cobalt oxides on catalytic activity for toluene oxidation was investigated in our previous works. For example, we synthesized threedimensionally ordered macroporous (3DOM) Mn<sub>2</sub>O<sub>3</sub>-supported AuPd alloy catalyst with AuPd particle sizes of 2-4 nm by the PVA-protected reduction method.<sup>[9]</sup> Our recent research reported a robust process for the preparation of noble metal-free Ni/Co<sub>3</sub>O<sub>4</sub> catalyst with a hierarchically porous network that exhibited excellent catalytic activity for CO<sub>2</sub> methanation.<sup>[5]</sup>

Herein, we demonstrate the rational design of low-cost transition metal-based catalysts (flower-like spinel Co-Mn solid solutions) derived from a template-free route for toluene oxidation, in which the porous architecture of flower-like structure provided easy access to the active sites, and allowed for the accessible deposition of the active phases. Details on sample preparation (Fig. S1) were described in the Supporting Information. Toluene oxidation activity evaluation over the as-obtained samples was performed according to the procedures depicted in the Supporting Information. All of the catalysts were characterized by the techniques, such as  $N_2$  adsorption-desorption (Brunauer-Emmett-Teller, BET), inductively coupled plasma atomic

emission spectroscopy (ICP–AES), field emission scanning electron microscopy (FESEM), field-emission high resolution transmission electron microscopic (FE–HRTEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR), temperature-programmed desorption of oxygen (O<sub>2</sub>-TPD), *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (*in-situ* DRIFTS). The detailed characterization procedures and catalytic activity evaluation were described in the Supporting Information.

### **Results and Discussion**

The  $Co_{3-x}Mn_xO_4$  (x = 0.75, 1.0, and 1.5) samples, which were denoted as MnCo-3, MnCo-2, and MnCo-1, respectively, were successfully fabricated by a controlled template-free autoclave strategy. The results of ICP-AES investigations reveal that the Co/Mn molar ratio was 1.09, 2.35, and 4.38, respectively, which were close to the theoretical molar ratios of 1, 2, and 4 in the samples, respectively (Table 1). The small discrepancy in theoretical and measured Co/Mn molar ratios was due to the instrumental errors during ICP-AES measurement processes. The 3D flower-like Co-Mn oxide was generated through primary configuration of nano-cores and successively anisotropic growth through the direction followed by Ostwald ripening, as shown in Fig. S2. The illustration of the step-wise process for the formation of flower-like MnCo-3 was presented in Scheme 1. As shown in reactions (Eqs. 1-4), the thermal decomposition of urea occurred rapidly after being heated to 100 °C, followed by the release of NH<sub>3</sub> and CO<sub>2</sub>. Metal cations (Mn and Co) slowly reacted with NH<sub>3</sub>/OH<sup>-</sup> in an aqueous solution. The thermodynamically controlled protocol and reasonably slow nucleation rate gave pointed, radial nuclei leading to the observed anisotropic growth. Finally, with the growth of nuclei and the extension in the Ostwald-ripening process, Mn and Co nanoparticles would self-assemble into a porous structure, which was composed of 3D flake-like (MnCo-1) or 3D flower-like subunits (MnCo-2 and MnCo-3). The relevant chemical reactions involved could be described by the following equations:[10]

$CO(NH_2)_2 \rightarrow C_3H_6N_6 + 6NH_3 + 3CO_2$	Eq. 1
$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$	Eq. 2
$Mn + Co + 6OH^{-} \rightarrow MnCo_2(OH)_6$	Eq. 3
$2MnCo_2(OH)_6 + O_2 \rightarrow 2MnCo_2O_4 + 6H_2O$	Ea. 4

The morphologies and structures of the synthesized 3D Co<sub>3-</sub>  $_xMn_xO_4$  samples were characterized by the FESEM and FE-HRTEM techniques. It is noticed that the as-obtained Co<sub>3-</sub>  $_xMn_xO_4$  samples with different Co/Mn molar ratios (Fig. 1) followed by different growth mechanisms. SEM images in Fig. 1a further reveal that the MnCo-1 particles (lower Co/Mn molar ratio) had a flake-like framework (5-6 µm in diameter). The 3D flake-like structures were composed of numerous twodimensional nanoplates (Fig. 1b). The high magnification FESEM image of MnCo-1 shows the interconnected nanopetals with an average thickness of 20 nm (Fig. S3). The multilayer structure of flake-like MnCo-1 increased the surface area (32.2 m<sup>2</sup>/g) of the composite, which was beneficial for toluene oxidation. The morphology of MnCo-2 (higher Co/Mn molar ratio) as shown in Fig. 1c and d was considerably different from that of MnCo-1. The size of the 3D structure decreased gradually and the morphology became a flower-like structure formed by the network of nanoneedles.



**Scheme 1.** Schematic illustration of the preparation process of the 3D flowerlike spinel catalysts.

When the molar ratio of Co and Mn increased to two (MnCo-3), the morphology of the MnCo-3 sample remained similar to that of MnCo-2, but the diameter of the particles increased to ca. 7  $\mu$ m (Fig. 1e and f). The flower-like morphology gradually became more clearly defined. As shown in Fig. 1f, the MnCo-3 particles had a 3D dandelion-like structure. Numerous nanoneedles radiated from the center of the spherical particles (Fig. S4).

(a)	MnCo-1	(b)	MnCo-1
<u>10 µm</u>		<u>3 μm</u> Fla	ake-like framework
(C)	MnCo-2	(d)	MnCo-2
A 2 2			
<u>10 μm</u>		<u>3 μm</u>	wer-like structure
(e)	MnCo-3	(f)	MnCo-3
10 µm		3 µm	lelion-like structure

Fig. 1 SEM and FESEM images of (a, b) MnCo-1, (c, d) MnCo-2, and (e, f) MnCo-3.

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Fig. 2 (a, b) TEM and (c) FE-HRTEM images of the MnCo-3 sample, inset EDS intensity line profiles extracted from the spectrum image along the line drawn on image (d), and (d-h) EDS elemental maps for the MnCo-3 sample.

To further demonstrate the composition of the as-obtained MnCo-3 sample, the auxiliary-mapped via EDS was utilized to detect the integrated intensity of Mn, Co, and O signals as a function of the beam position when the FE-HRSEM/EDS was operated in scanning mode (Fig. S5). To better characterize the size and morphology of the 3D dandelion-like structure, TEM and FE-HRTEM images of the MnCo-3 sample were obtained (Fig. 2). The MnCo-3 structure consisted of nanoneedles growing radially in the length of 500–800 nm with a hollow core (2-3  $\mu$ m in diameter). The EDS element maps and line profile analysis of the MnCo-3 sample show that the three elements of Mn, Co, and O were homogeneously distributed in the entire particle (Fig. 2d-h).

Further evidence of the porous architecture can be seen from the N<sub>2</sub> adsorption-desorption isotherms (Fig. 3a), in which all of the catalysts exhibited a similar type II isotherm, suggesting the presence of macropores and mesopores in the samples. Hysteresis loops of types H3 in the relative pressure  $(p/p_0)$  range of 0.8-1.0 was observed in the MnCo-3 sample, while the H2type hysteresis loops were seen in the  $p/p_0$  range of 0.4–0.8 for the MnCo-1 and MnCo-2 samples. The result shown in MnCo-3 was related to the capillary condensation taking place in the dandelion-like structure, affirming the formation of mesoporous structure within the hollow core. An inset of Fig. 3a illustrates the Barrett-Joyner-Halenda (BJH) pore-size distributions of the samples. The results include one peak in the range of 3-5 nm, indicating the existence of textural mesopores within the structures, which was also confirmed by the FESEM and FE-HRTEM results (Figs. 1 and 2). The BET surface areas, pore volumes, and pore sizes of samples are summarized in Table 1. The pore volumes of the as-obtained samples were in the range of 0.06-0.016 cm<sup>3</sup>/g. The MnCo-3 sample, with a Co loading of x = 2.25 was found to have the a relatively large surface area of 41.3 m<sup>2</sup>/g. The MnCo-1 at x = 1.5 Co gave a surface area of 32.2 m<sup>2</sup>/g and MnCo-2 (x = 1) gave the lowest surface area of 22.9 m<sup>2</sup>/g. Hence the surface area decreases with increasing Co loading. This might be caused by formation of the thinner dandelion-like structure which contributed to the extra surface area of the MnCo-3 sample.

The XRD patterns of the as-obtained samples are illustrated in Fig. 3b. The Co-rich ( $MnCo_2O_4$ ) sample tended to form a tetragonal spinel structure (JCPDS PDF# 00-077-0471), while

the Mn-rich (CoMn<sub>2</sub>O<sub>4</sub>) sample was likely to form a cubic spinel structure (JCPDS PDF# 00-001-1130), as shown in Figs. 3b and S6. The  $Co_3O_4$  sample showed a cubic  $Co_3O_4$  spinel and the diffraction peaks corresponded to the standard sample (JCPDS PDF# 00-074-2120). After the incorporation of Mn into the host spinel matrix, the diffraction peaks of the MnCo samples were broadened and the peak position was shifted to a lower degree as compared with the pure Co<sub>3</sub>O<sub>4</sub> (Fig. S7), which might be caused by the changes of the lattice parameters and stress from lattice mismatching between Co and Mn. The crystallite size of the MnCo sample reduced after Mn doping and such a behavior was due to the restriction in the grain boundary movement in the alien element-doped system with different ionic radii. The MnCo-1 (Mn/Co molar ratio = 1) exhibited a homogeneous mixed phase of tetragonal MnCo<sub>2</sub>O<sub>4</sub> spinel and cubic CoMn<sub>2</sub>O<sub>4</sub> at  $2\theta$  = 18.2°, 32.9°, and 60.7°. Homogeneity of the sample could improve the distribution of the Co-Mn mixed oxide, which was in agreement with the EDS elemental mapping analysis (Fig. S5). The reducibility and surface re-oxidizability of the as-obtained

Co-Mn oxide samples were studied using the H<sub>2</sub>-TPR and O<sub>2</sub>-TPD techniques, and the results are illustrated in Fig. 3c and d, respectively. There were two peaks in the H2-TPR profile of each sample. The first reduction peak was in the range of 294-310 °C, which was correlated with the stepwise reduction of  $Co_3O_4 \rightarrow$ CoO and  $MnO_2 \rightarrow Mn_3O_4$ .<sup>[11]</sup> The second reduction peak in the range of 366-460 °C was broad, which was associated with the subsequent reduction of CoO  $\rightarrow$  Co<sup>0</sup> and Mn<sub>3</sub>O<sub>4</sub>  $\rightarrow$  MnO.<sup>[12]</sup> It is noticed that the small peak at 197-224 °C was caused by the reduction of surface oxygen species formed at the oxygen vacancies in the Co-Mn oxides. The result was in good agreement with the results of the O2-TPD as described below. The similar results were also reported by Shi et al. who studied the Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> oxides for formaldehyde oxidation <sup>[12]</sup> and Jha et al. who used the MnCo-MO catalyst for aerobic oxidation of vanillyl alcohol.[11]

As revealed in Fig. 3d of the O<sub>2</sub>-TPD profiles, three oxygen desorption peaks were observed: the one below 200 °C, the one below 400 °C, and the one above 650 °C, corresponding the release of surface active oxygen (O<sub>ads</sub>, e.g., O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup> or O<sup>-</sup>), surface lattice oxygen, and the thermal decomposition of the bulk metal oxides (CoO<sub>x</sub>, MnO<sub>x</sub> and CoMnO<sub>x</sub>) (O<sub>latt</sub>). As shown in Fig. 3d, the  $O_{latt}$  decomposition of the MnCo-3 sample was much larger and broader (in the range of 650-800 °C) than that of the other samples. Since the transfer of the bulk oxygen to the surface sites happens first during the decomposition of lattice oxygen in bulk oxides, the presence of surface oxygen vacancies plays a critical role in bulk oxide decomposition.<sup>[13]</sup> A shift to a lower temperature (298 °C) was observed in the O<sub>ads</sub> peak for the MnCo-3 sample, demonstrating the richness of O<sub>ads</sub> species on the surface of MnCo-3 and improved Olatt mobility with of the rise in Co content. This strongly indicates that Olatt mobility is significantly improved with the addition of cobalt to manganese oxide. This would increase the O-vacancies, which in turn increases the low-temperature adsorption. Overall decreasing the activation of O2 molecules on the surface of the MnCo-3 sample. It is quite consistent with the results of the H2-TPR investigations. Hence, lower onset temperatures of oxygen ChemCatChem



desorption ( $O_{ads}$ ) and higher intensity of desorption peaks ( $O_{iatt}$ ) of the MnCo-3 sample resulted in better catalytic performance.

Fig. 3 (a)  $N_2$  adsorption-desorption isotherms (inset figure of BJH pore-size distributions), (b) XRD patterns, (c) H<sub>2</sub>-TPR profiles, and (d) O<sub>2</sub>-TPD profiles of the MnCo-1, MnCo-2, and MnCo-3 samples.

XPS is an effective surface analysis technique to study the metal oxidation states and adsorbed species of a solid solution sample. Fig 4a illustrates the asymmetrical Co  $2p_{3/2}$  XPS spectra of each sample which could be decomposed into two components. The component at binding energy (BE) of 780.4 eV was due to the surface Co<sup>3+</sup> species, whereas the one at BE = 782.8 eV demonstrated the presence of the surface Co<sup>2+</sup> species.<sup>[14]</sup> The Co<sup>3+</sup>/Co<sup>2+</sup> molar ratio increased in the sequence of MnCo-1 < MnCo-2 < MnCo-3. It appears that the higher the amount of exposed Co<sup>3+</sup> sites in the Co sample make oxidation more favourable.<sup>[15-16]</sup> Hence, the MnCo-3 sample could show the maximal oxidation activity.

The complete oxidation of toluene over the Co-Mn oxide samples was carried out in a fixed-bed microreactor in the range of 150-300 °C. Under the conditions of toluene (concentration 1000 ppm) +  $O_2$  +  $N_2$  (balance) and the total flow rate of 33.4 mL/min, toluene conversion increased with the rise in temperature. Evaluation of the catalytic performance of the samples was conducted according to the procedure described in Fig. S9. Toluene was fully oxidized to H<sub>2</sub>O and CO<sub>2</sub> over the Co-Mn oxide catalysts, and there were no products of incomplete oxidation, as confirmed by the carbon balance (ca. 99.5%). In order to compare catalytic activities of the samples, we used the temperatures  $T_{10\%}$ ,  $T_{50\%}$ , and  $T_{90\%}$  (corresponding to toluene conversion =10, 50, and 90%). It can be observed that with a rise in Co/Mn molar ratio from 1.0 (MnCo-1) to 4.0 (MnCo-3), the T<sub>90%</sub> decreased from 240 to 214 °C (Fig. S10). Toluene oxidation rates at 230 °C normalized per gram of catalyst of the samples are illustrated in Fig. 4b. Clearly, the catalytic performance was improved with the rise in Co content. Toluene oxidation rate at 230 °C (3.55 µmol/(g<sub>cat</sub> s)) over MnCo-2 was much higher than that at 230 °C (0.72 µmol/(g<sub>cat</sub>s)) over MnCo-1. This result suggests that Co was the active sites for the oxidation of toluene. Among all of the samples, the MnCo-3 sample showed the highest toluene oxidation rate (8.9 µmol/(g<sub>cat</sub>s)), which was much higher than that (3.3 µmol/(g<sub>cat</sub>s)) over 3.4Au/3DOM La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>,<sup>[17]</sup> that (1.14 µmol/(g<sub>cat</sub>s)) over 1.0Pt/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>,<sup>[18]</sup> that (4.54 µmol/(g<sub>cat</sub>s)) over 0.3Pd/Al<sub>2</sub>O<sub>3</sub>,<sup>[19]</sup> that (5.51 µmol/(g<sub>cat</sub>s)) over 1.99AuPd/3DOM Co<sub>3</sub>O<sub>4</sub>,<sup>[20]</sup> and that (5.70 µmol/(g<sub>cat</sub>s)) over 1.99AuPd/3DOM Co<sub>3</sub>O<sub>4</sub>,<sup>[21]</sup> Table S1 lists the catalytic activities of various catalysts reported in the literature for toluene oxidation. To probe the catalytic stability, an onstream reaction experiment was conducted over the CoMn-3 sample. The result showed that no obvious loss in catalytic activity was detected within 70 h of reaction (Fig. S10).



Fig. 4 (a) Co  $2p_{3/2}$  XPS spectra, and (b) toluene reaction rate versus temperature over the MnCo-1, MnCo-2, and MnCo-3 samples.

In this study, we used the in situ DRIFTS that is an efficient technology to monitor the transient species and states adsorbed on the catalyst surface. The MnCo-3 sample with the highest activity towards toluene oxidation was taken as an example to study the reaction mechanism over the manganese-cobalt catalyst. IR spectra of the MnCo-3 sample are shown in Fig. 5a. The absorption band at 3800-3600 cm<sup>-1</sup> was ascribed to the u(M-OH) vibration and water molecules coordinated to the surface metal cations M=Co and Mn, and the broad band centered at ca.3400 cm<sup>-1</sup> was assigned to the vibration band of the H-bonding.<sup>[22]</sup> The bands in the two regions of 3200-2800 and 1600-1250 cm<sup>-1</sup> were attributed to the features of toluene. Four bands at 3068, 3028, 2925, and 2872 cm<sup>-1</sup> in the 3200-2800 cm<sup>-1</sup> region were assigned to the  $u_{C-H}$  stretching.<sup>[23]</sup> The bands at 3068 and 3028 cm<sup>-1</sup> were attributed to the C-H stretching of the aromatic ring, and the bands at 2925 and 2872 cm<sup>-1</sup> were assigned to the symmetric C-H stretching vibration of methyl. In the low wavenumber range (Fig. 5b), the bands at 1596, 1538, and 1494 cm<sup>-1</sup> were ascribed to the skeleton stretching vibrations of the aromatic ring.[24] With the rise in temperature, the intensity of toluene bands decreased gradually, and at the same time, some new IR bands appeared. The bands at 1450 and 1415 cm<sup>-1</sup> were caused by the asymmetric methyl bending vibrations, and the ones at 1354 and 1304 cm<sup>-1</sup> were caused by the bending vibrations of a methylene group (u(CH<sub>2</sub>)).<sup>[25-26]</sup> The bands at 1754, 1724, and 1672 cm<sup>-1</sup> were assigned to the u(C=O) of an aldehyde group, together with the evidence of u(C=C) (at 1649 and 1564 cm<sup>-1</sup>) in the skeleton vibrations of the aromatic ring, which demonstrated the gneration of benzaldehyde.[24]

 Table 1. Weight percentages and Co/Mn molar ratio, BET surface areas, pore volumes, and pore sizes of MnCo-1, MnCo-2, and MnCo-3 samples.

Catalyst	Formula	Weight percentage <sup>a</sup>		Weight percentage <sup>a</sup> Co/Mn molar ratio		olar ratio	BET	Pore volume	Pore size
		Co (wt%)	Mn (wt%)	Theoretical	Measured	surface area m²/g	cm³/g	nm	
MnCo-1	Co <sub>1.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>	39.7	33.9	1	1.09	32.2	0.11	6.24	
MnCo-2	Co <sub>2</sub> Mn <sub>1</sub> O <sub>4</sub>	52.3	20.7	2	2.35	22.9	0.06	6.15	
MnCo-3	Co <sub>2.25</sub> Mn <sub>0.75</sub> O <sub>4</sub>	60.0	12.8	4	4.38	41.3	0.16	6.75	

<sup>a</sup> The data were obtained by the ICP-AES technique.



Fig. 5 (a-c) *In-situ* DRIFT spectra of toluene oxidation over the MnCo-3-sample.

Moreover, similar bands (at 1760, 1725, 1690, 1660, 1645, 1558, 1547 and 1512 cm<sup>-1</sup>) have been reported for benzaldehyde adsorption on TiO2 and Degussa P25.[25-26] The results revealed that weakly adsorbed benzaldehyde was formed during the reaction.<sup>[26]</sup> Benzaldehyde molecules resulting from the partial oxidation of toluene weakly interacted with the catalyst surface and subsequently reacted with the hydroxyl groups on the surface generated from the adsorbed water molecules. The bands at 1709, 1691, and 1420 cm<sup>-1</sup> were attributed to the C=O, C-O, and C-C vibration of oxalic acid, which implies the occurrence of the attack by the activated oxygen species or hydroxyl radicals upon the carbon structures, confirming the opening of the aromatic ring.<sup>[24, 27]</sup> From the whole range of 1200-4000 cm<sup>-1</sup> spectra in Fig. 5c, the responses corresponding to CO<sub>2</sub> (at 2360 and 2341 cm<sup>-1</sup>) were negative, which was due to the deduction of background during the DRIFTS analysis. A similar result was reported in ref.<sup>[24]</sup> The formation of CO<sub>2</sub> along with the increase of temperature was proven by the decrease of the negative peaks. Fig. S12(A and B) show the desorption of toluene before reaction (Fig. S12(A)) and the intermediates and products after reaction (Fig. S12(B)). It is observed that, with increasing the desorption time, the adsorption peaks referred to the toluene features decreased in intensity. After 60 min of

reaction, however, there were some obvious toluene peaks remained, suggesting the strong adsorption of toluene on the surface of the Mn-Co catalyst. The signal intensity of each peak except CO<sub>2</sub> (at 2360 and 2341 cm<sup>-1</sup>) in Fig. S12(B) did not decrease obviously, indicating that the intermediate species had a strong interaction with the catalyst surface. Combining the results of DRIFTS characterization and previous works,<sup>[24, 26, 28-29]</sup> the oxidation of toluene could follow the pathways: benzyl radical  $\rightarrow$  benzaldehyde  $\rightarrow$  benzene  $\rightarrow$  oxalic acid, and finally to CO<sub>2</sub> and H<sub>2</sub>O. Between the benzaldehyde and oxalic acid, there were possible intermediate products, such as benzoic acids.

#### Conclusions

In summary, the low-cost transition metal-based Mn-Co catalysts with a flower-like morphology were synthesized using a simple template-free autoclave strategy. The  $Co_{2.25}Mn_{0.75}O_4$  spinel sample with rich Co composition and well defined 3D flower-like structure exhibited the best catalytic activity (100 % toluene conversion at 239 °C) and stability (no obvious activity drop after 70 h of on-stream reaction). The *in situ* DRIFTS results have revealed the possible reaction pathway on the synthetic Mn-Co catalyst, following the dissociation steps as toluene to benzyl radical, benzaldehyde, benzene, oxalic acid, and finally to CO<sub>2</sub> and H<sub>2</sub>O. The good activity and stability of toluene oxidation on the resulted Mn-Co complex is raised from the integrated effects by the large surface area, porous morphology, rich surface oxygen vacancies and Mn-Co interaction.

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**Keywords:** 3D flower-like catalyst;  $Co_{3-x}Mn_xO_4$  spinel; oxidation of toluene; scalable synthesis; template-free strategy.

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Flower-like spinel Co-Mn solid solution are self-assembled using the template-free strategy. The low-cost transition metal-based catalysts are active for toluene oxidation. High adsorbed oxygen species enhance catalytic performance. Yuan Wang<sup>[a]</sup>, Hamidreza Arandiyan<sup>[a],[b],\*</sup>, Yuxi Liu<sup>[c]</sup>, Yijing Liang<sup>[c]</sup>, Yue Peng<sup>[d]</sup>, Stuart Bartlett<sup>[b]</sup>, Hongxing Dai<sup>[c]</sup>, Sadegh Rostamnia<sup>[e]</sup> and Junhua Li<sup>[d]</sup>

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Template-free Scalable Synthesis of Flower-like Co<sub>3-x</sub>Mn<sub>x</sub>O<sub>4</sub> Spinel Catalysts for Toluene Oxidation



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