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Article

Enhancing catalytic toluene oxidation over $\text{MnO}_2@\text{Co}_3\text{O}_4$ by constructing a coupled interface

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ABSTRACT

Herein, a bottom-down design is presented to successfully fabricate ZIF-derived Co_3O_4 , grown *in situ* on a one-dimensional (1D) $\alpha\text{-MnO}_2$ material, denoted as $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$. The synergistic effect derived from the coupled interface constructed between $\alpha\text{-MnO}_2$ and Co_3O_4 is responsible for the enhanced catalytic activity. The resultant $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ catalyst exhibits excellent catalytic activity at a $T_{90\%}$ (temperature required to achieve a toluene conversion of 90%) of approximately 229 °C, which is 47 and 28 °C lower than those of the pure $\alpha\text{-MnO}_2$ nanowire and Co_3O_4 -b obtained via pyrolysis of ZIF-67, respectively. This activity is attributed to the increase in the number of surface-adsorbed oxygen species, which accelerate the oxygen mobility and enhance the redox pairs of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$. Moreover, the result of *in situ* diffuse reflectance infrared Fourier transform spectroscopy suggests that the gaseous oxygen could be more easily activated to adsorbed oxygen species on the surface of $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ than on that of $\alpha\text{-MnO}_2$. The catalytic reaction route of toluene oxidation over the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ catalyst is as follows: toluene → benzoate species → alkanes containing oxygen functional group → CO_2 and H_2O . In addition, the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ catalyst shows excellent stability and good water resistance for toluene oxidation. Furthermore, the preparation method can be extended to other 1D MnO_2 materials. A new strategy for the development of high-performance catalysts of practical significance is provided.

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1. Introduction

Volatile organic compounds (VOCs) are considered as a series of gaseous contaminants, which are not only carcinogenic

to humans and animals, but also harmful to the environment [1–4]. Therefore, it is an urgent issue to minimize the emission of VOCs. Among the available technologies, the catalytic oxidation of VOCs is one of the most promising strategies owing to its

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lower operating temperature and less secondary pollution compared to those of direct thermal oxidation [5–7]. The catalysts, which play important roles in the catalytic oxidation, are classified into supported noble metal catalysts and transition metal oxide catalysts. Supported noble metal catalysts [8–10] exhibit high catalytic activity for VOC oxidation, while transition metal oxide catalysts, which are inexpensive and highly resistant to poisons, have attracted extensive attention. Among metal oxides, manganese oxides exhibit good catalytic activity in various catalytic oxidation reactions, such as HCHO oxidation [11], ethanol oxidation [12], and toluene oxidation [13], due to their naturally excellent physicochemical properties, including their controllable morphology [14], different crystal structures [15], and varied valences of Mn [16].

Nevertheless, the catalytic performance of individual metal oxides cannot satisfy the demands of practical applications; therefore, the formation of mixed metal oxides by introducing a hybrid metal is widely applied. Binary oxides, as the basic formation of mixed metal oxides, are common. Traditional methods, such as alkali-precipitation and impregnation, are applied to prepare the binary oxides [17,18]. For example, Deng *et al.* [17] investigated the MnO_2/NiO core-shell hybrid nanostructure, which was prepared by uniformly decorating NiO nanosheets on the MnO_2 nanowire, and reported that it displayed much better activity toward benzene oxidation than individual MnO_2 nanowires because MnO_2/NiO exhibits better low-temperature reducibility and has a high number of active surface oxygen species. Putla *et al.* [18] reported that $\text{MnO}_x/\text{CeO}_2$ composites, formed by the deposition of MnO_x on CeO_2 nanocubes by a wet impregnation method, exhibited outstanding catalytic activities toward both diesel soot oxidation and benzylamine oxidation compared to pure CeO_2 nanocubes. The synergistic effect between the CeO_2 and MnO_x components is responsible for the excellent catalytic activity of the $\text{MnO}_x/\text{CeO}_2$ composites.

Recently, metal-organic frameworks (MOFs), considered as effective sacrificial templates for the synthesis of catalysts for VOC catalytic oxidation, have been attracting extensive attention [6,19–21]. For instance, Jia *et al.* [19] revealed that a mesoporous CeO_2 -MOF/350 catalyst, synthesized through the pyrolysis of Ce-MOF, exhibited good catalytic performance for toluene combustion. Zhang *et al.* [20] reported that Mn-100-Ar-O derived from Mn-MIL-100 exhibited superior catalytic activity. Wang *et al.* [6] prepared Mn-Co oxides using MOF as the precursor, and they reported that MOF-Mn1Co1 displayed excellent catalytic activity for toluene combustion. Tang *et al.* [21] prepared CeCoO_x catalysts by the pyrolysis of a MOF, and they reported that the 3D mesoporous rosette CeCoO_x catalyst possessed superior catalytic activity for toluene total oxidation. Evidently, the preparation of individual metal oxides and binary oxide catalysts by the direct thermal decomposition of MOF is conventional. Moreover, it has been reported that binary oxides with a constructed coupled interface can be obtained by the pyrolysis of MOFs, to be applied in lithium-ion batteries [22] and NO reduction [23]. Zhong *et al.* [22] synthesized yolk-shell $\text{MnO}@/\text{ZnMn}_2\text{O}_4/\text{N-C}$ nanorods derived from $\alpha\text{-MnO}_2$ /zeolitic imidazolate frameworks-8 (ZIF-8),

which were applied as anode materials in lithium-ion batteries; they exhibited better electrochemical performances than pure MnO_x due to the synergistic effect between MnO and ZnMn_2O_4 in the unique yolk-shell nanorod structure. Wang *et al.* [23] revealed that the $\text{CeO}_2\text{-Co}_3\text{O}_4$ hybrid catalyst, obtained via the thermolysis of ZIF-67, exhibited better catalytic activity for NO reduction by CO than bare CeO_2 nanowires and Co_3O_4 catalysts, which was ascribed to the synergistic effect between the metal oxides. However, it is not common to synthesize binary oxides with a coupled interface constructed by the pyrolysis of a MOF, for application in catalytic toluene oxidation.

Inspired by the above-mentioned works, we report a bottom-down approach for designing high-performance $\text{MnO}_2/\text{Co}_3\text{O}_4$ catalysts, which exhibit remarkable catalytic activities for toluene oxidation in comparison to pure MnO_2 and Co_3O_4 catalysts. The catalysts were synthesized via ZIF-67, grown *in situ* on MnO_2 with various crystal structures, followed by direct thermal decomposition. The structure-activity relationship is confirmed using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) studies, scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), hydrogen temperature-programmed reduction (H_2 -TPR), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption of oxygen (O_2 -TPD). *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed on pure $\alpha\text{-MnO}_2$ and $\alpha\text{-MnO}_2/\text{Co}_3\text{O}_4$ to further investigate the synergistic effect between $\alpha\text{-MnO}_2$ and Co_3O_4 on the catalytic toluene oxidation. The enhanced catalytic activity can be attributed largely to the synergistic effect between $\alpha\text{-MnO}_2$ and Co_3O_4 .

2. Experimental

2.1. Synthesis

Synthesis of $\alpha\text{-MnO}_2$: KMnO_4 (40 mmol) was dissolved in 150 mL of deionized water. After stirring for 30 min, the above solution was added to another homogeneous solution containing 50 mmol MnSO_4 in 50 mL of deionized water. After stirring for another 30 min, 5 mL of concentrated nitric acid (68 wt%) was introduced with vigorous stirring. Subsequently, the obtained dark brown slurry was refluxed at 100 °C for 24 h and then cooled to room temperature.

The sample was collected by rinsing, centrifugation, drying, and annealing at 350 °C for 3 h at a heating rate of 1 °C min⁻¹ in static air.

Synthesis of $\alpha\text{-MnO}_2/\text{ZIF-67}$: Seventy milligrams of the as-obtained $\alpha\text{-MnO}_2$ and 350 mg of polyvinyl pyrrolidone (PVP) were added to 25 mL of methanol. After the $\alpha\text{-MnO}_2$ sample was uniformly dispersed by ultrasonication for 30 min, the resultant solution was mixed with 291 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Thereafter, the slurry (A) was stirred for 30 min at room temperature. Subsequently, 493 mg of 2-methylimidazole was dissolved in 25 mL of methanol to form a solution (B), which was added to A under stirring for 30 min. The mixture was kept still for 12 h, after which the obtained precipitate was collected by

centrifugation, rinsed thoroughly with methanol several times to remove the residual ions, and finally dried at 80 °C for 12 h. The sample was denoted as $\alpha\text{-MnO}_2\text{@ZIF-67}$.

Synthesis of $\alpha\text{-MnO}_2\text{@Co}_3\text{O}_4$: The $\alpha\text{-MnO}_2\text{@ZIF-67}$ sample was annealing at 350 °C for 3 h at a heating rate of 1 °C min⁻¹ in static air.

Synthesis of $\beta\text{-MnO}_2$: 5 mmol MnSO_4 and an equal amount of $((\text{NH}_4)_2\text{S}_2\text{O}_8)$ were dissolved into 60 mL deionized water. After stirring for 30 min, the obtained homogeneous solution was transferred to a Teflon-lined autoclave with 100 mL capacity. Hydrothermal process was processed at 120 °C for 12 h, then the autoclave was cooled naturally to room temperature.

The sample was collected by rinsing, centrifuging, drying and annealing at 350 °C for 3 h with a heating rate of 1 °C min⁻¹ in static air.

Synthesis of $\beta\text{-MnO}_2\text{@ZIF-67}$: The synthesis of $\beta\text{-MnO}_2\text{@ZIF-67}$ was the same as $\alpha\text{-MnO}_2\text{@ZIF-67}$ except for the usage of $\beta\text{-MnO}_2$ instead of $\alpha\text{-MnO}_2$.

Synthesis of ZIF-67: The synthesis of ZIF-67 was the same as $\alpha\text{-MnO}_2\text{@ZIF-67}$ except for without $\alpha\text{-MnO}_2$.

The $\beta\text{-MnO}_2\text{@ZIF-67}$ and ZIF-67 samples annealed at 350 °C for 3 h with a heating rate of 1 °C min⁻¹ in static air were obtained $\beta\text{-MnO}_2\text{@Co}_3\text{O}_4$ and $\text{Co}_3\text{O}_4\text{-b}$, respectively.

2.2. Characterization

The surface morphologies and microstructure of samples were investigated by field-emission scanning electron microscopy (SEM, ZEISS) and transmission electron microscopy (TEM, JEOL JEM-2010F), respectively. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) element mapping were recorded on TEM instrument with a field emission gun operating at 200 kV. X-ray diffraction (XRD) were obtained on a Bruker D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 40 mA, scanning step = 0.02°) and further applied for determining the crystal structure of all samples. The chemical composition was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin-Elmer plasma 8000). The Brunauer-Emmett-Teller (BET) testing was measured with a Micromeritics ASAP 2020 instrument at -196 °C. Prior to the measurement, the sample was pretreated at 120 °C for 3 h under vacuum condition, and the Brunauer-Emmett-Teller (BET) model was used to calculate the specific surfaces area. The surface species was performed using XPS spectrum obtained by X-ray photoelectron spectroscopy (XPS) testing (Thermo ESCALAB 250Xi electron spectrometer), and every spectrum was referenced to the carbon 1s peak at 284.6 eV. Temperature-programmed reduction in H_2 ($\text{H}_2\text{-TPR}$) was conducted on a Micromeritics AutoChem II2920 instrument to get the reducibility information of the catalysts. Before each measurement, the catalyst (50 mg) in a U-shaped quartz reactor was heated 300 °C at a ramping rate of 10 °C min⁻¹ and maintained at the temperature for 1 h in high purity Ar (99.999%). After the pretreatment, reactor was cooled down to room temperature. 10% H_2/Ar flow (30 mL min⁻¹) was employed and the samples were heated up to 700 °C at a ramping

rate of 10 °C min⁻¹. For temperature-programmed desorption of O_2 ($\text{O}_2\text{-TPD}$), the catalyst (50 mg) in a U-shaped quartz reactor was heated 300 °C at a ramping rate of 10 °C min⁻¹ and maintained at the temperature for 1 h in high purity Ar (99.999%). After the pretreatment, reactor was cooled down to room temperature. 5 % O_2/He (30 mL min⁻¹) was switched into the reactor for 1 h, following by purging with high purity He (99.999%) at the same temperature for 30 min to remove the unadsorbed molecules of O_2 . The catalysts were heated from room temperature to 750 °C at a ramping rate of 10 °C min⁻¹ in high purity He (30 mL min⁻¹).

In situ diffuse reflection infrared Fourier transform spectroscopy (in situ DRIFTS) was recorded on a Nicolet iS50R FTIR spectrometer equipped with a liquid nitrogen-cooled Mercury Cadmium Telluride (MCT) detector in the range of 700–3200 cm⁻¹ with 32 scans at a resolution of 4 cm⁻¹. A high temperature reaction chamber from Harrick Scientific Products Inc. was used as an environmental chamber, and a dome with two pieces of KBr windows (thickness = 2 mm, diameter = 15 mm) and one glass observation window were used in the chamber. The sample was placed into a sample cell in an atmospherically controllable chamber for in situ DRIFTS analysis. Meanwhile, looping water kept the outside of the chamber cool when operating at a high temperature. Prior to each experiment, the sample was pre-treated at 300 °C for 1 h in a gas flow of N_2 to remove any adsorbed impurities and then cooled to a desired temperature. The background spectrum were collected under N_2 and automatically subtracted from the sample spectra at the identical temperature. Afterward, 500 ppm of toluene balanced with N_2 was introduced to the cell at a flow rate of 30 mL min⁻¹, and then in situ DRIFTS were recorded. After adsorbed toluene for 250 min, the weakly adsorbed toluene was removed by purging with N_2 for 30 min, subsequently, 20% O_2/N_2 with the flow rate of 30 mL min⁻¹ was introduced into the cell to react with pre-adsorbed toluene. It is necessary to emphasis that the temperature is identical during the adsorption and oxidation of toluene to avoid two factors including both desorption of toluene from the surface of sample and the signal of in situ DRIFTS effected by the temperature variation.

2.3. Catalytic performance test

The catalytic activities of catalysts for toluene oxidation were carried out in a fixed-bed quartz tubular micro-reactor (i.d. = 6 mm, length = 500 mm) at atmospheric pressure under steady-state conditions. 100 mg of catalyst (40–60 mesh) mixed with 400 mg of quartz sands (40–60 mesh) minimizing the effect of hot spots was loaded in the quartz reactor with quartz wool packed at the both ends of the catalyst bed. A thermocouple was inserted inside the catalytic bed to measure the reaction temperature. A gas mixture composed of 1000 ppm of toluene, 20% O_2 , and balance N_2 was fed into the micro-reactor, and the total flow rate was held at 80 mL min⁻¹ via a mass flow controller, equivalent to a weight hourly space velocity (WHSV) of 48000 mL g⁻¹ h⁻¹. After the toluene oxidation reaction was stabilized for 15 min, the outlet products were continuously monitored using a gas chromatograph at a

Scheme 1. Illustration of the fabrication of α - MnO_2 @ Co_3O_4 samples.

given temperature for 8 times. Toluene conversions were monitored by a gas chromatograph (GC-2014C, Shimadzu) equipped with a flame ionization detector and the concentrations of CO_2 in the outlet gas was analyzed by other FID with a conversion furnace for converting CO_2 to CH_4 . In the case of water vapor addition, 2.0% of H_2O was introduced via a mass flow controller, which was achieved by a saturated H_2O vapor generator at 40 °C. The toluene conversion (η_{toluene}) was calculated as per the equations.

$$\eta_{\text{toluene}} = (C_{\text{toluene, in}} - C_{\text{toluene, out}}) / C_{\text{toluene, in}} \times 100$$

Herein, $C_{\text{toluene, in}}$ (ppm) and $C_{\text{toluene, out}}$ (ppm) are the concentrations of toluene in the inlet and outlet gas, respectively.

3. Results and discussion

A typical procedure based on a two-step strategy, as illustrated in Scheme 1, was applied to synthesize the α - MnO_2 @ Co_3O_4 hybrid materials. Firstly, α - MnO_2 was fabricated via a reflux method. Thereafter, the ZIF-67 rhombic dodecahedron was grown *in situ* on MnO_2 (denoted as α - MnO_2 @ZIF-67). The ZIF-derived Co_3O_4 , grown *in situ* on α - MnO_2 with a constructed coupled interface (denoted as α - MnO_2 @ Co_3O_4), was obtained after calcination at 350 °C for 3 h in static air.

3.1. Structure analysis

The XRD patterns of the as-obtained α - MnO_2 and α - MnO_2 @ Co_3O_4 samples are displayed in Fig. 1. The peaks displayed at 12.8°, 18.1°, 25.7°, 28.8°, 37.5°, 42.0°, and 49.9° are ascribed to the (110), (200), (220), (310), (211), (301), and (411) facets of the pure tetragonal α - MnO_2 catalyst (JCPDS card no. 44-0141), respectively [15]. After decorating Co_3O_4 on the α - MnO_2 , the original diffraction peaks of MnO_2 were adequately

Fig. 1. XRD patterns of the α - MnO_2 and α - MnO_2 @ Co_3O_4 samples.

maintained. In addition, several distinct peaks at 19.0°, 31.3°, 36.8°, 44.8°, 59.4°, and 65.2° are attributed to the (111), (220), (311), (400), (511), and (440) facets of the cubic spinel Co_3O_4 sample (JCPDS card no. 42-1467), respectively [3]. Moreover, the XRD patterns of the α - MnO_2 @ZIF-67, ZIF-67, and Co_3O_4 -b samples are displayed in Fig. S1. The Co/Mn molar ratio of the as-obtained α - MnO_2 @ Co_3O_4 is 0.44 (Table 1), as confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-OES), which is lower than the nominal Co/Mn molar ratio owing to the low yield of ZIF-67.

The N_2 adsorption-desorption isotherms and pore-size distribution curves of the α - MnO_2 , α - MnO_2 @ Co_3O_4 , and Co_3O_4 -b samples are shown in Fig. S2. The BET data are summarized in Table 1. The specific surface area of α - MnO_2 @ Co_3O_4 ($54.9 \text{ m}^2 \text{ g}^{-1}$) is slightly less than that of α - MnO_2 ($60.6 \text{ m}^2 \text{ g}^{-1}$). The BET result indicates that the specific surface area of the α - MnO_2 @ Co_3O_4 samples is determined by the physical structure of both α - MnO_2 and Co_3O_4 -b, considerably.

3.2. Morphology and microstructure analyses

The SEM images reveal the morphologies of the α - MnO_2 samples (before and after calcination at 350 °C), α - MnO_2 @ZIF-67, and α - MnO_2 @ Co_3O_4 , as shown in Figs. 2(a),

Table 1

Physicochemical properties and conversion of toluene over the α - MnO_2 , α - MnO_2 @ Co_3O_4 , β - MnO_2 , β - MnO_2 @ Co_3O_4 , and Co_3O_4 -b samples.

Sample	A_{BET}^a ($\text{m}^2 \text{ g}^{-1}$)	Molar ratio of Co/Mn ^b	$\text{Mn}^{3+}/\text{Mn}^{4+}$	$\text{Co}^{3+}/\text{Co}^{2+}$	$\text{O}_{\text{ads}}/\text{O}_{\text{latt}}^c$	$T_{50\%}^d$ (°C)	$T_{90\%}^d$ (°C)
α - MnO_2	60.6	—	0.383	—	0.267	264	276
α - MnO_2 @ Co_3O_4	54.9	0.44	0.709	0.676	0.385	220	229
β - MnO_2	17.2	—	0.127	—	0.207	269	286
β - MnO_2 @ Co_3O_4	32.8	0.43	0.405	0.475	0.287	243	255
Co_3O_4 -b	34.1	—	—	0.420	0.279	245	257

^a Determined by BET.

^b Determined by ICP-OES.

^c Determined by XPS.

^d Reaction conditions: toluene concentration = 1000 ppm, WHSV = 48000 $\text{mL g}^{-1} \text{ h}^{-1}$, 20% O_2/N_2 , $m_{\text{cat}} = 0.1 \text{ g}$.

(b), 2(c), (d), and 2(e)–(f), respectively. It can be distinctly observed that the 1D α - MnO_2 nanowires have different lengths and diameters. As shown in Figs. 2(a), (b), the length of the α - MnO_2 nanowire is roughly 0.75 μm . The diameter of α - MnO_2 would be discussed in the section presenting the TEM results. After calcination, the morphology of the α - MnO_2 samples remained intact. Notably, the α - MnO_2 nanowire is embedded in the ZIF-67 rhombic dodecahedron, α - MnO_2 @ZIF-67 (highlighted by the faint yellow circles), as clearly shown in Fig. 2(c). Moreover, the schematic illustration of the α - MnO_2 @ZIF-67 samples is depicted in Fig. 2(d). After calcination at 350 $^{\circ}\text{C}$ in air, the morphology of the as-obtained α - MnO_2 @ Co_3O_4 is partly destroyed due to the high calcination temperature. Nevertheless, it is noteworthy that the as-obtained α - MnO_2 @ Co_3O_4 with a hierarchical nanostructure maintained a rhombic dodecahedron morphology to some extent, as can be distinctly observed from Fig. 2(e). Moreover, the schematic illustration of α - MnO_2 @ Co_3O_4 is displayed in Fig. 2(f).

The representative TEM images of α - MnO_2 and α - MnO_2 @ Co_3O_4 in Fig. 3 present more details about their microstructures. The diameter of the α - MnO_2 nanowires is roughly 25 nm, as shown in Figs. 3(a) and (b). The HRTEM images (Fig. 3(c)) display that the interplanar spacing of the fringe is 0.31 nm, which is consistent with the (310) plane of α - MnO_2 [24,25]. It can be observed that the α - MnO_2 nanomaterials are embedded in Co_3O_4 derived from ZIF-67, as illustrated in Figs. 3(d), (e). There are three typical lattice fringes of 0.48, 0.45, and 0.29 nm, corresponding well to the (200) plane of α - MnO_2 [25], and the (111) and (220) facets of Co_3O_4 , respectively, as illustrated in Fig. 3(f). Furthermore, the blue dotted line (Fig. 3(f)), at which point Co_3O_4 touches the surface of the α - MnO_2 nanowire, denotes the coupled interface. The effect of the coupled interface would be explained by further characterizations. The HAADF-STEM images of α - MnO_2 @ Co_3O_4 with a hierarchical nanostructure are exhibited in Fig. 3(g), which also confirm that the MnO_2 nanomaterials are embedded in Co_3O_4 derived

Fig. 3. Morphological and structural characterizations of α - MnO_2 and α - MnO_2 @ Co_3O_4 . TEM and HRTEM images of α - MnO_2 (a–c) and α - MnO_2 @ Co_3O_4 (d–f); HAADF-STEM, the corresponding elemental distribution maps, and line-scan images of α - MnO_2 @ Co_3O_4 (g–l).

from ZIF-67. Noticeably, as shown in the elemental distribution maps (Figs. 3(h)–(j)), Co is distributed on the surface of the 1D MnO_2 . The line-scan images (Fig. 3(k), (l)) further confirm the distribution of Co on the surface of the 1D MnO_2 nanowire. The HRTEM and HAADF-STEM images show that the ZIF 67-derived Co_3O_4 is successfully grown *in situ* on the α - MnO_2 nanomaterials with a constructed coupled interface.

3.3. Redox behavior and surface chemical states analyses

To investigate the reduction behavior over the α - MnO_2 @ Co_3O_4 catalyst, H_2 -TPR was employed using α - MnO_2 and Co_3O_4 -b as reference samples, as illustrated in Fig. 4. Generally, the reduction of MnO_2 proceeds via the sequence: $\text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$. For MnO_2 , the lower temperature reduction peak is ascribed to the reduction of MnO_2 to Mn_3O_4 , while the higher one is attributed to the reduction of Mn_3O_4 to MnO [11,25]. However, the reduction of MnO_2 may occur at a certain temperature range, which would combine the reduction peaks. For α - MnO_2 , the asymmetrical reduction peak manifests that the main reduction steps are processed together in the range of 200–370 $^{\circ}\text{C}$. In addition, the α - MnO_2 @ Co_3O_4 sample profile displays complex reduction peaks occurring at the range of 120–380 $^{\circ}\text{C}$, attributed to the reduction process of Co_3O_4 [26,27]. It can be clearly observed that the reduction peaks of α - MnO_2 @ Co_3O_4 shift toward lower temperatures in comparison to those of pure α - MnO_2 and Co_3O_4 -b (Fig. 4). According to the literatures [25,28,29], a catalyst shows a reduction peak at the lowest temperature, indicating that the highest amount of mobile oxygen species is present both at the surface and in the bulk. Therefore, α - MnO_2 @ Co_3O_4 shows higher oxygen mobility

Fig. 2. SEM images of the synthesized α - MnO_2 samples without calcination (a) and calcination at 350 $^{\circ}\text{C}$ (b) and α - MnO_2 @ZIF-67 (c); schematic of α - MnO_2 @ZIF-67 (d), α - MnO_2 @ Co_3O_4 (e), and α - MnO_2 @ Co_3O_4 (f).

Fig. 4. H_2 -TPR profiles of the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$, $\alpha\text{-MnO}_2$, and $\text{Co}_3\text{O}_4\text{-b}$ samples.

than both pure $\alpha\text{-MnO}_2$ and $\text{Co}_3\text{O}_4\text{-b}$, which is attributed to the strong synergistic effect derived from the coupled interface constructed between $\alpha\text{-MnO}_2$ and Co_3O_4 and is beneficial for toluene oxidation [30].

The type of oxygen species was determined by O_2 -TPD, as depicted in Fig. 5. Generally, there are four types of oxygen species in a metal oxide [31,32]: the adsorbed oxygen molecule (ads-O_2), adsorbed oxygen molecule anion (ads-O_2^-), adsorbed oxygen anion (ads-O^-), and lattice oxygen (latt-O^{2-}). For the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ sample, the peak in the range of 60–200 °C is ascribed to the desorption of ads-O_2 and ads-O_2^- ; the peak between 300 and 650 °C is attributed to the ads-O^- and lattice oxygen species near the surface, while the peak above 650 °C belongs to the desorption of bulk-phase lattice oxygen species. At the range of 60–200 °C, the peak intensity of $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ is stronger than those of pure $\alpha\text{-MnO}_2$ and $\text{Co}_3\text{O}_4\text{-b}$, suggesting that a relatively high number of active oxygen species can be more easily released from the surface of the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ catalysts [3,32]. It is well known that the higher the number of surface oxygen vacancies, the easier the activation of the gaseous phase (O_2) to surface-active oxygen species (O_{ads}) [33]. In other words, the strong synergistic effect derived from the coupled interface constructed between $\alpha\text{-MnO}_2$ and Co_3O_4 is favorable to the formation of active oxygen species.

Subsequently, XPS is applied to determine the oxygen species and valence states of the elements in the surface atomic layers of the catalysts. It is well known that the surface oxygen species play an important role in the catalytic oxidation [34,35]. The XPS curves of O 1s for $\alpha\text{-MnO}_2$, $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$, and $\text{Co}_3\text{O}_4\text{-b}$ samples are fitted to distinguish the possible existence

Fig. 5. O_2 -TPD profiles of the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$, $\alpha\text{-MnO}_2$, and $\text{Co}_3\text{O}_4\text{-b}$ samples.

of different oxygen species, as illustrated in Fig. 6(c). The peak at about 529.7 eV is ascribed to the lattice oxygen (O_{latt}) species, and the shoulder peak at the higher binding energy of around 531.5 eV is assigned to the surface-adsorbed oxygen (O_{ads}) species, which are directly associated with the catalytic activity of toluene oxidation [36,37]. In comparison with the cases of pure $\alpha\text{-MnO}_2$ and $\text{Co}_3\text{O}_4\text{-b}$, the molar ratio of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ in $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ is notably increased by decorating Co_3O_4 on $\alpha\text{-MnO}_2$, which is favorable to the catalytic oxidation of toluene over the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ catalysts.

As shown in Fig. 6(a), the peaks of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ are centered at 642.2 and 653.9 eV, respectively [38]. The spin energy separation of 11.7 eV is in good agreement with the reported data of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ in MnO_2 [39]. The three components divided from the asymmetrical Mn $2p_{3/2}$ XPS profiles at 640.8, 642.2, and 643.7 eV are attributed to the surface Mn^{3+} , Mn^{4+} species, and the satellite, respectively [40,41]. Fig. 6(b) presents the Co 2p XPS profiles of the $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$ and $\text{Co}_3\text{O}_4\text{-b}$ samples. The asymmetrical Co $2p_{3/2}$ XPS profiles of all samples can be deconvoluted into two component peaks of Co^{3+} (779.5 eV) and Co^{2+} (780.8 eV). Generally, the cations of Mn^{3+} and Co^{2+} are considered to be involved in the formation of lattice oxygen, since the reversible valence transformation of cations ($\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+} + \text{e}$ and $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+} + \text{e}$) donates some electrons to activate oxygen during the catalytic reaction [42,43]. Based on the peak areas, the relative contents of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratios are summarized in Table 1. The $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratios are noticeably increased by the introduction of ZIF-67-derived Co_3O_4 on $\alpha\text{-MnO}_2$.

Fig. 6. Mn 2p (a), Co 2p (b), and O 1s (c) XPS profiles of the $\alpha\text{-MnO}_2$, $\alpha\text{-MnO}_2@\text{Co}_3\text{O}_4$, and $\text{Co}_3\text{O}_4\text{-b}$ samples.

Fig. 7. Toluene conversion curves over the α - MnO_2 , β - MnO_2 , α - MnO_2 @ Co_3O_4 , β - MnO_2 @ Co_3O_4 , and Co_3O_4 -b samples as a function of temperature. Reaction conditions: toluene concentration = 1000 ppm, 20% O_2/N_2 , WHSV = 48000 $\text{mL g}^{-1} \text{h}^{-1}$, $m_{\text{cat}} = 0.1 \text{ g}$.

From another perspective, the effect of valence change on the physicochemical properties is also explained. Chen *et al.* [43] recently reported that the interfacial effect existing in Ce-Mn composite oxides plays a key role in the modification of their physicochemical properties. The results of XPS indicated that the proportion of Ce^{3+} and Mn^{4+} cations is noticeably changed by the introduction of an appropriate amount of CeO_y . In other words, there is a strong synergistic interaction between Ce and Mn oxides. Moreover, the gaseous oxygen could be readily activated into active adsorbed oxygen species on the surface of α - MnO_2 @ Co_3O_4 by Co cations through the Zener exchange owing to the reversible electron transfer between Co^{3+} and Mn^{3+} , thereby leading to the formation of a significantly high amount of active oxygen species on the surface of α - MnO_2 @ Co_3O_4 [44], which is consistent with the result of O_2 -TPD.

3.4. Catalytic activity and stability

The catalytic activities of toluene oxidation over the α - MnO_2 , α - MnO_2 @ Co_3O_4 , and Co_3O_4 -b catalysts are evaluated under the conditions of toluene concentration = 1000 ppm, WHSV = 48 000 $\text{mL g}^{-1} \text{h}^{-1}$, and 20% O_2/N_2 as balance gas, as illustrated in

Fig. 7. For pure α - MnO_2 , the reaction temperatures for toluene conversions of 50% ($T_{50\%}$) and 90% ($T_{90\%}$) are 264 and 276 °C, respectively, as listed in Table 1. Over pure Co_3O_4 -b, the reaction temperatures for $T_{50\%}$ and $T_{90\%}$ are 245 and 257 °C, respectively. Interestingly, α - MnO_2 @ Co_3O_4 is more active than pure α - MnO_2 and Co_3O_4 -b. The $T_{50\%}$ and $T_{90\%}$ values of α - MnO_2 @ Co_3O_4 are 220 and 229 °C, respectively, which are 44 and 47 °C lower than those of pure α - MnO_2 , and 25 and 28 °C lower than those of Co_3O_4 -b, respectively. The results suggest that the synergistic effect derived from the coupled interface constructed between the α - MnO_2 and Co_3O_4 catalysts significantly promotes the toluene oxidation catalytic activity. In addition, the catalytic activities of typical samples for toluene oxidation are summarized in Table 2. Evidently, the catalytic activity over the α - MnO_2 @ Co_3O_4 hybrid catalyst is considerably better than those previously reported for other catalysts, such as $\text{Mn}_{10}\text{Cu}_1\text{-S}$ ($T_{90\%} = 258 \text{ °C}$) [45], Mn-Co (1:1) ($T_{90\%} = 249 \text{ °C}$) [46], $7.4\text{Au}/\text{Co}_3\text{O}_4$ ($T_{90\%} = 250 \text{ °C}$) [47], $1\% \text{Pt}/\text{Al}_2\text{O}_3$ ($T_{90\%} = 258 \text{ °C}$) [48], $0.12\text{Ag}/\text{Mn}_2\text{O}_3\text{-redn}$ ($T_{90\%} = 250 \text{ °C}$) [49], and $\text{Pd}/\text{Co}_3\text{AlO}$ ($T_{90\%} = 230 \text{ °C}$) [31].

Moreover, to investigate the effect of water vapor on the catalytic performance, we carried out a toluene oxidation experiment in the presence of 2% water vapor over the α - MnO_2 @ Co_3O_4 catalyst at 240 °C, as shown in Fig. S8(a). It is distinctly observed that the incorporation of 2% water vapor at 240 °C led to a decrease in the toluene conversion by ca. 15%, which is ascribed to the competitive adsorption of H_2O and reactant molecules (oxygen molecules and toluene molecules) over the α - MnO_2 @ Co_3O_4 catalyst [50,51]. When the water vapor is cut off, the toluene conversion is almost restored to the initial value, which indicates that α - MnO_2 @ Co_3O_4 possesses good water-resistant ability in toluene oxidation.

We subsequently extended the fabrication method to other 1D MnO_2 nanomaterials. β - MnO_2 , β - MnO_2 @ZIF-67, and β - MnO_2 @ Co_3O_4 were synthesized. The metal Co/Mn molar ratios of these β - MnO_2 @ Co_3O_4 materials were determined by ICP-OES. The characterizations by XRD, BET, SEM, TEM, HRTEM, EDS elemental analysis, H_2 -TPR, O_2 -TPD (Figs. S1–S6), and XPS (Fig. S7) generated a similar structural picture to that

Table 2

Main data from research papers on VOC over Mn (Co)-based oxide catalysts.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	VOC type	VOC conc. (ppm)	GHSV ($\text{mL g}^{-1} \text{h}^{-1}$)	Catalytic activity (°C)		Ref.
					$T_{50\%}$	$T_{90\%}$	
γ - MnO_2	83.7	Toluene	1000	60000	219	251	[52]
Co_3O_4 microspheres	17.4	Toluene	1000	20000	266	285	[47]
$7.4\text{Au}/\text{Co}_3\text{O}_4$	22.4	Toluene	1000	20000	242	250	[47]
MnCo-1	32.2	Toluene	1000	40000	240	—	[53]
$\text{Mn}_{10}\text{Cu}_1\text{-S}$	21.3	Toluene	1000	30000	238	258	[45]
LCO-0	3.8	Toluene	1000	60000	239	263	[54]
$\text{Mn}_{0.3}\text{Zr}_{0.7}\text{O}_2$	178.7	Toluene	1000	60000	231	235	[55]
$25\text{Mn}/\text{Cr}_2\text{O}_3\text{-M}$	51.8	Toluene	1000	20000	264	269	[56]
Ga-Co spinel	84.5	Toluene	1000	60000	275	288	[57]
$1\% \text{Pt}/\text{Al}_2\text{O}_3$	—	Toluene	1200	60000	234	258	[48]
$0.12 \text{Ag}/\text{Mn}_2\text{O}_3\text{-redn}$	75–80	Toluene	1000	40000	225	250	[49]
Mn-Co (1:1)	27.9	Toluene	1000	30000	236	249	[46]
$\text{Pd}/\text{Co}_3\text{AlO}$	93	Toluene	800	30000	220	230	[31]
C3M1-C	48	Toluene	500	67500	217	237	[58]
$\text{Cu}_2\text{Mn}_1\text{O}$	44.9	Toluene	1000	60000	229	234	[59]
α - MnO_2 @ Co_3O_4	54.9	Toluene	1000	48000	220	229	present work

of the $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ analog: 1D MnO_2 embedded in the Co_3O_4 rhombic dodecahedron (Figs. S4(d), (e)). The key properties of materials are summarized in Table 1. We tested the catalytic activity of $\beta\text{-MnO}_2@ \text{Co}_3\text{O}_4$ toward toluene oxidation under the conditions of toluene concentration = 1000 ppm, WHSV = 48 000 $\text{mL g}^{-1} \text{h}^{-1}$, and 20% O_2/N_2 as balance gas, as illustrated in Fig. 7. The activities of the pure $\beta\text{-MnO}_2$ and $\text{Co}_3\text{O}_4\text{-b}$ catalysts were measured for comparison. The results of the catalytic activity tests of the catalysts are summarized in Table 1. In addition, $\beta\text{-MnO}_2@ \text{Co}_3\text{O}_4$ displayed a good water-resistant ability in toluene oxidation, as illustrated in Fig. S8(b). The foremost conclusion from these results is that the structure of 1D $\text{MnO}_2@ \text{Co}_3\text{O}_4$ dictates its catalytic ability, which underscores the utility of our synthetic methodology. The performance of the $\beta\text{-MnO}_2@ \text{Co}_3\text{O}_4$ catalyst is comparable to that of the $\text{Co}_3\text{O}_4\text{-b}$ catalyst because the Co content of $\beta\text{-MnO}_2@ \text{Co}_3\text{O}_4$ is low (Table 1).

3.5. In situ DRIFTS analysis

In situ DRIFTS experiments were performed to track the intermediates and investigate the reaction mechanisms of toluene oxidation over pure $\alpha\text{-MnO}_2$ and $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$; the results are illustrated in Fig. 8. The samples were firstly pre-treated under N_2 atmosphere at 300 °C for 1 h, after which they were cooled to 180 °C under N_2 . Subsequently, the samples were exposed under a flow of 500 ppm toluene/ N_2 at 180 °C, as shown in Figs. 8(a) and 8(c). For pure $\alpha\text{-MnO}_2$ (Fig. 8(a)), it was evident that the intensities of the aromatic ring vibration

peaks at about 1558 and 1595 cm^{-1} [6,60,61] and the peak at 1450 cm^{-1} associated with the asymmetric methyl bending vibrations of toluene [62] were increased with time, which indicated the accumulation of adsorbed toluene on the surface of $\alpha\text{-MnO}_2$. Notably, the peak at approximately 1545 cm^{-1} is assigned to the carboxylate group ($-\text{COOH}$); simultaneously, the peaks at 1414 and 1521 cm^{-1} are ascribed to the symmetric C–O stretching vibration and antisymmetric C–O stretching vibration of benzoate species, respectively [61]. Further, the intensity of the bands (benzoate species) gradually ascends with time in the presence of 500 ppm toluene/ N_2 , indicating that the benzoate species are the key intermediates in the toluene oxidation over $\alpha\text{-MnO}_2$. In addition, it is necessary to mention that the desorption temperatures of ads-O_2 and ads-O_2^- are in the range of 60–200 °C, according to the result of O_2 -TPD. Therefore, it is reasonable to speculate that the adsorbed oxygen species (ads-O_2 and ads-O_2^-) may be involved in the transformation of adsorbed toluene into benzoate species without the gas-phase oxygen at 180 °C. Moreover, the peaks at 2339 and 2362 cm^{-1} are attributed to CO_2 [53]. It can be distinctly observed that the toluene molecules are partially oxidized to intermediates (benzoate species), even to CO_2 , further suggesting that the adsorbed oxygen species (ads-O_2 and ads-O_2^-) on the surface of the catalyst may participate in the deep oxidation of toluene. For $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ (Fig. 8(c)), a distinct increasing trend can be observed for toluene (1601 and 1445 cm^{-1}) [6,62], the benzoate species (1545 and 1402 cm^{-1}) [61], and CO_2 (2339 and 2362 cm^{-1}) [53] with time.

After the adsorption of toluene over the catalysts for 250

Fig. 8. *In situ* DRIFTS of toluene adsorption for different periods over $\alpha\text{-MnO}_2$ (a) and $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ (c) at 180 °C; after inputting 20% O_2/N_2 over $\alpha\text{-MnO}_2$ (b) and $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ (d) at 180 °C.

min, the weakly adsorbed toluene molecules were removed by purging with N₂ for 30 min; subsequently, 20% O₂/N₂ was flowed into the reaction chamber at 180 °C. For pure α -MnO₂ (Fig. 8(b)), it was observed that the peak intensities did not decrease significantly even at 250 min, indicating that the adsorbed toluene (1450, 1558, and 1595 cm⁻¹) [6,62] and the benzoate species (1414, 1521 and 1545 cm⁻¹) [61] were barely further oxidized at 180 °C in 20% O₂/N₂. Contrarily, for α -MnO₂@Co₃O₄ (Fig. 8(d)), the peak intensities of toluene (1445, 1560, and 1601 cm⁻¹) and the benzoate species (1402 and 1545 cm⁻¹) distinctly decreased at 50 min and even completely disappeared at 250 min. The reason is that the gaseous oxygen (O₂) could be more easily activated into active adsorbed oxygen species (O_{ads}) on the surface of α -MnO₂@Co₃O₄ according to the XPS and O₂-TPD results, which gives rise to the oxidation of toluene into key intermediate benzoate species and, finally, into CO₂ over the α -MnO₂@Co₃O₄ catalyst.

Based on the *in situ* DRIFTS characterization, we can speculate the possible reaction path over α -MnO₂@Co₃O₄, as follows [63,64]: adsorbed toluene → benzoate species → alkanes containing oxygen functional group (such as maleic anhydride) → CO₂ and H₂O. Moreover, it was observed that toluene can be more easily completely oxidized over α -MnO₂@Co₃O₄ than over the pure α -MnO₂ catalyst at the same temperature, which is consistent with the results of the catalytic activity tests for toluene oxidation. The results further indicated that the synergistic effect between α -MnO₂ and Co₃O₄ in the α -MnO₂@Co₃O₄ catalyst is beneficial to the toluene oxidation.

Since the synergistic effect derived from the coupled interface constructed between MnO₂ and Co₃O₄ has a significant influence on the catalytic performance, the inner relationship is investigated by the combination of physico-chemical properties. It is recognized that a large specific surface area is beneficial for enhancing the adsorption and retention time of gaseous toluene. However, although α -MnO₂ possesses the highest specific surface area, it does not exhibit the best catalytic activity for toluene oxidation; this indicates that the specific surface area is not the primary factor in the enhancement of the catalytic activity. The chemical properties of the catalysts play important roles in enhancing the catalytic activity. The H₂-TPR result suggests that the oxygen mobility of α -MnO₂@Co₃O₄ is notably enhanced by the synergistic effect derived from the constructed coupled interface, which can accelerate the oxidation process. Combining the XPS and O₂-TPD results, it is established that synergistic effect owing to the constructed coupled interface distinctly facilitates the augmentation of adsorbed oxygen species on α -MnO₂@Co₃O₄. Generally, a high number of adsorbed oxygen species is beneficial for the oxidation of toluene, and adsorbed oxygen species play key roles in the catalytic oxidation process [30,64,65]. In addition, the reversible valence transformation of cations ($\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+} + \text{e}$ and $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+} + \text{e}$) donates some electrons to activate oxygen during the catalytic reaction [42,43]. Furthermore, the results of *in situ* DRIFTS demonstrated that the gaseous oxygen could be more easily activated into active adsorbed oxygen species on the surface of α -MnO₂@Co₃O₄ than on that of α -MnO₂. Therefore, the α -MnO₂@Co₃O₄ catalyst with the constructed coupled interface

exhibits better catalytic activity for toluene oxidation than α -MnO₂.

4. Conclusions

In summary, we have designed a bottom-down approach to successfully synthesize ZIF-derived Co₃O₄ grown *in situ* on a 1D α -MnO₂ material, denoted as α -MnO₂@Co₃O₄. The enhanced catalytic activity over α -MnO₂@Co₃O₄ is attributed to the synergistic effect owing to the coupled interface constructed between α -MnO₂ and Co₃O₄. Compared to the pure α -MnO₂ nanowire and Co₃O₄-b obtained via thermolysis of ZIF-67, the resultant α -MnO₂@Co₃O₄ catalyst exhibits better catalytic activity for toluene oxidation, which is ascribed to the increased number of surface-adsorbed oxygen species, which accelerate the oxygen mobility and enhance the redox pairs of Mn⁴⁺/Mn³⁺ and Co²⁺/Co³⁺. In addition, the *in situ* DRIFTS result indicates that α -MnO₂@Co₃O₄ possessed a stronger ability to activate gaseous oxygen into adsorbed oxygen species than α -MnO₂. The reaction route over α -MnO₂@Co₃O₄ is as follows: toluene → benzoate species → alkanes containing oxygen functional group → CO₂ and H₂O. Furthermore, the benzoate species are key intermediates in toluene oxidation. Moreover, the α -MnO₂@Co₃O₄ catalyst shows outstanding stability and good water resistance in toluene oxidation. Furthermore, the fabrication method can be extended to other 1D MnO₂ materials. Our work provides a new avenue for the development of high-performance catalysts of practical significance.

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Graphical Abstract

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Enhancing catalytic toluene oxidation over $\text{MnO}_2@ \text{Co}_3\text{O}_4$ by constructing a coupled interface

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The resultant $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ catalyst with a coupled interface shows better catalytic activity than the pure $\alpha\text{-MnO}_2$, which is ascribed to the increased number of surface-adsorbed oxygen species, which accelerate the oxygen mobility and enhance the redox pairs of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$.

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构筑耦合界面提高 $\text{MnO}_2@ \text{Co}_3\text{O}_4$ 催化氧化甲苯性能

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摘要: 挥发性有机化合物(VOCs)是大气主要污染物之一, 它不仅危害人类健康, 而且也危害环境。催化氧化是消除VOCs最有前景的方法之一。过渡金属氧化物由于其低成本、环境友好、高催化活性等优点, 而越来越受到VOCs氧化领域的重视。一般认为, 具有耦合界面的多组分金属氧化物比单组分金属氧化物表现出更好的催化性能。因此, 本文在一维(1D) $\alpha\text{-MnO}_2$ 纳米线上原位生长ZIF衍生的 Co_3O_4 ($\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$)。由于 $\alpha\text{-MnO}_2$ 和 Co_3O_4 之间耦合界面的协同效应, 使得 $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 表现出优异的催化活性, 甲苯转化率达到90%的反应温度($T_{90\%}$)约为229 °C, 分别低于 $\alpha\text{-MnO}_2$ 纳米线的(47 °C)和热解ZIF-67产生的 Co_3O_4 -b的(28 °C)。本文采用氢气程序升温还原(H_2 -TPR), 氧气程序升温脱附(O_2 -TPD), X射线光电子能谱(XPS), 原位漫反射红外光谱(in situ DRIFTS)等手段研究了具有 $\alpha\text{-MnO}_2$ 和 Co_3O_4 耦合界面的 $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 催化剂表现更优异甲苯氧化性能的原因。

H_2 -TPR结果表明, 相比于 $\alpha\text{-MnO}_2$ 纳米线和热解ZIF-67产生的 Co_3O_4 -b, $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 催化剂因具有耦合界面而表现出更好的氧流动性。 O_2 -TPD结果表明, 具有耦合界面的 $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 催化剂表面有更多的表面氧空位, 从而使气相氧更容易活化为表面活性氧物种。XPS结果表明, 具有耦合界面的 $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 催化剂表面有更多的活性氧物种, 并且增强了 $\text{Mn}^{4+}/\text{Mn}^{3+}$ 和 $\text{Co}^{2+}/\text{Co}^{3+}$ 氧化还原对。原位漫反射红外结果表明, 催化剂在180 °C下吸附甲苯/ N_2 250 min后, 通入 N_2 吹扫30 min, 然后将气氛切换为20% O_2/N_2 , 温度保持在180 °C, 反应进行250 min时, $\alpha\text{-MnO}_2$ 表面吸附甲苯和苯甲醛的特征峰强度没有明显降低的趋势。相反, 在反应进行50 min时, $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 表面吸附甲苯和苯甲醛的特征峰强度明显减弱, 至250 min时, 这些特征峰几乎完全消失。这进一步表明, 在 $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 表面, 气相氧可能更容易活化为吸附氧物种, 且甲苯在 $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 催化剂的可能催化反应路径如下: 甲苯 → 苯甲酸 → 含氧官能团的烷烃 → CO_2 和 H_2O , 而更多的吸附氧物种有利于甲苯的催化氧化, 且它们在催化氧化过程中起着重要的作用。另一方面, 在催化反应中, 阳离子的可逆价态转变($\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+} + \text{e}$ 和 $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+} + \text{e}$)为活化氧分子提供了电子。因此, 具有耦合界面的 $\alpha\text{-MnO}_2@ \text{Co}_3\text{O}_4$ 催化剂表现出更好的甲苯催化性能。此外, 该制备方法可推广到其它一维 MnO_2 材料, 为开发具有实际意义的高性能催化剂提供了一种新的策略。

关键词: $\text{MnO}_2@ \text{Co}_3\text{O}_4$; 甲苯氧化; 协同作用; 耦合界面; 原位漫反射红外光谱

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