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Article

Nanoplate-aggregate Co_3O_4 microspheres for toluene combustion

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ABSTRACT

Nanoplate-aggregate microspherical Co_3O_4 was prepared by an ethylenediamine-assisted hydrothermal route and characterized by means of numerous techniques. Their catalytic activities for toluene combustion were evaluated. The Co_3O_4 sample obtained using 1.0 ml of ethylenediamine and a hydrothermal treatment at 140 °C for 12 h had a nanoplate-aggregate microspherical morphology. This microspherical Co_3O_4 sample with a surface area of 66 $\text{m}^2 \text{g}^{-1}$ had a higher adsorbed oxygen concentration and better low-temperature reducibility than bulk Co_3O_4 . Over the Co_3O_4 microsphere sample, the temperatures required for 50% and 90% toluene conversions were 230 and 254 °C, respectively, at a space velocity of 20000 $\text{ml g}^{-1} \text{h}^{-1}$. The good catalytic performance of the Co_3O_4 microsphere sample was related to its large surface area, high oxygen adspecies concentration, and good low-temperature reducibility.

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1. Introduction

Most volatile organic compounds (VOCs) emitted from industrial and transportation activities are harmful to the environment and human health. Catalytic oxidation is one of the most effective ways to remove VOCs, and transition metal oxides are the most commonly used catalysts. Co_3O_4 is a versatile transition metal oxide and shows good catalytic performance for the oxidation of VOCs due to its excellent reducibility and plentiful oxygen vacancies [1–3]. The physicochemical properties of Co_3O_4 strongly depend on its morphology and exposed crystal faces [4–6]. In the past years, a large number of Co_3O_4 samples with different morphologies (nanowires [7,8], nanorods [4,9,10], nanocubes [5,11,12], and nanospheres [13,14]) have been fabricated, and some of them were applied for the

oxidation of VOCs. For instance, Co_3O_4 nanoparticles showed good activity in catalyzing VOC oxidation [15]. Xue et al. [16] observed a significant effect of Co_3O_4 morphology on catalytic activity of $\text{Au}/\text{Co}_3\text{O}_4$ for ethylene oxidation.

Previously, our group has used silica (SBA-16 or KIT-6)- and polymethyl methacrylate-templating, hydrothermal, and microemulsion methods to make ordered mesoporous Co_3O_4 [17,18], spherical Co_3O_4 [19], and porous Co_3O_4 nanowires and nanorods [2], and we found that they performed well in the combustion of VOCs. To the best of our knowledge, however, there have been no reports on catalytic oxidation of toluene over nanoplate-aggregate microspherical Co_3O_4 . In this work, we report the ethylenediamine-assisted hydrothermal preparation of Co_3O_4 microspheres and their catalytic performance for toluene combustion.

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2. Experimental

2.1. Catalyst preparation

The nanoplate-aggregate microspherical Co_3O_4 sample was prepared using the ethylenediamine-assisted hydrothermal method. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91 g) was dissolved in 30 ml deionized water, and 9 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous solution (28 wt% $\text{NH}_3 \cdot \text{H}_2\text{O} : \text{H}_2\text{O} = 1:3$, v/v) was then added dropwise to the $\text{Co}(\text{NO}_3)_2$ aqueous solution. After stirring for 0.5 h, 0.5, 1.0 or 2.0 ml ethylenediamine was added under stirring for 0.5 h. The mixed solution was transferred to a 50-ml Teflon-lined stainless steel autoclave, which was sealed and heated at 120, 140, 160, or 200 °C for 12 h. After the autoclave was cooled to room temperature (RT), the resulting precipitate was filtered out, washed with deionized water and absolute ethanol three times, dried in an oven at 60 °C for 24 h, and ground uniformly. Finally, the powder was calcined in air using a ramp of 1 °C min^{-1} from RT to 500 °C and maintained at this temperature for 4 h, thus generating the Co_3O_4 samples. The Co_3O_4 sample obtained with 1.0 ml ethylenediamine in the hydrothermal treatment at 140 °C for 12 h was denoted as Co_3O_4 microsphere. The Co_3O_4 samples obtained with 0, 0.5, and 2.0 ml ethylenediamine in the hydrothermal treatment at 140 °C for 12 h were denoted as Co_3O_4 -1, Co_3O_4 -2, and Co_3O_4 -3, respectively. The Co_3O_4 samples obtained with 1.0 ml ethylenediamine in the hydrothermal treatment at 120, 160, and 200 °C for 12 h were denoted as Co_3O_4 -4, Co_3O_4 -5, and Co_3O_4 -6, respectively. For comparison, a bulk Co_3O_4 (Co_3O_4 -bulk) sample was prepared by thermally decomposing $\text{Co}(\text{NO}_3)_2$ in air at 600 °C for 3 h. All of the chemicals (AR) were purchased from Beijing Chemical Reagent Company and used without further purification.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with $\text{Cu } K_\alpha$ radiation and nickel filter ($\lambda = 0.15406 \text{ nm}$). The scanning electron microscopic (SEM) images of the samples were recorded on a Gemini Zeiss Supra 55 apparatus (operating at 10 kV). BET (Brunauer-Emmett-Teller) surface areas of the samples were measured by N_2 adsorption at -196 °C on a Micromeritics ASAP 2020 analyzer. The samples were outgassed at 250 °C for 2.5 h under vacuum before measurement. X-ray photoelectron spectroscopy (XPS, VG CLAM 4 MCD analyzer) was used to determine the Co 2p, O 1s, and C 1s binding energies (BEs) of surface species using Mg K_α ($h\nu = 1253.6 \text{ eV}$) as the excitation source.

Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). The sample (40–60 mesh, 0.025 g) was loaded to a fixed-bed U-shaped quartz microreactor (i.d. = 4 mm) and pretreated in a O_2 flow (30 ml min^{-1}) at 500 °C for 1 h. After cooling in the same atmosphere to RT, a He flow (30 ml/min) was passed to purge the sample for 15 min. Finally, the pretreated sample was exposed to 5 vol% H_2/Ar mixture (50 ml min^{-1}) and heated at a ramp of 10 °C min^{-1} from RT to 550 °C. The H_2 concentration of the effluent

was monitored online by a chemical adsorption apparatus. The reduction peak was calibrated against that of the complete reduction of well-characterized CuO powders (Aldrich, 99.995%).

2.3. Catalytic evaluation

A continuous flow fixed-bed quartz microreactor (i.d. = 4 mm) was used to determine catalyst activity for the oxidation of toluene. To minimize the effect of hot spots, 0.6 g quartz sands (40–60 mesh) was used to dilute the sample (0.1 g). The total flow rate of the reactant mixture (0.1% toluene + O_2 + N_2 (balance)) was 33.3 ml min^{-1} , giving a toluene/ O_2 molar ratio of 1/400 and a space velocity (SV) of 20000 ml $\text{g}^{-1} \text{ h}^{-1}$. The toluene was obtained by passing a N_2 flow through a bottle containing pure toluene (AR) chilled in an ice-water isothermal bath. The SV was changed through the amount of sample. In the case of water vapor addition, 3.0 vol% H_2O was introduced by passing the feed stream through a water saturator at RT. Reactants and products were analyzed online by a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) using a stabilwax@-DA column (30 m in length) for VOC separation and a 1/8 in Carboxen 1000 column (3 m in length) for permanent gas separation. The carbon balance throughout the investigation was estimated to be 99.5%.

3. Results and discussion

3.1. Crystal phase composition, morphology, and surface area

Figure 1 shows the XRD patterns of the Co_3O_4 samples. The two samples possessed a cubic Co_3O_4 crystal structure with well-indexed planes (JCPDS PDF #74-1657). The difference in diffraction intensity reflected the discrepancy in crystallinity. As can be seen from Fig. 2, the particles of the Co_3O_4 bulk sample were irregular polyhedra. The Co_3O_4 sample derived from the ethylenediamine-assisted hydrothermal route was composed of microspherical entities as several layers of a number of nanoplates (Fig. 2(b)–(d)). With a change in the preparation

Fig. 1. XRD patterns of Co_3O_4 bulk (1) and Co_3O_4 microspheres (2).

Fig. 2. SEM images of Co_3O_4 bulk (a) and Co_3O_4 microspheres (b–d).

Fig. 3. SEM images of Co_3O_4 -1 (a), Co_3O_4 -2 (b), Co_3O_4 -3 (c), Co_3O_4 -4 (d), Co_3O_4 -5 (e), and Co_3O_4 -6 (f).

conditions (added amount of ethylenediamine or hydrothermal temperature), the morphology of the Co_3O_4 samples obtained was irregular (Fig. 3). Therefore, we investigated in detail only the Co_3O_4 bulk and Co_3O_4 microsphere samples. The surface areas of the Co_3O_4 bulk and Co_3O_4 microsphere samples were 9.8 and 66.2 $\text{m}^2 \text{g}^{-1}$, respectively, whereas the Co_3O_4 - i ($i = 1$ –6) samples showed a surface area of 33.2, 43.5, 50.1, 39.3, 54.2, and 26.9 $\text{m}^2 \text{g}^{-1}$, respectively.

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

Figure 4(a) illustrates the Co $2p_{3/2}$ XPS spectra of the samples. The Co $2p_{3/2}$ signal at 780.0 eV showed the presence of surface Co^{3+} species, while the Co $2p_{3/2}$ signal at 781.9 eV together with the shake-up satellite at 785.5 eV confirms the presence of surface Co^{2+} species [20]. It can be observed from Table 1 that the surface $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio (1.44) of the

Fig. 4. Co $2p_{3/2}$ (a) and O $1s$ (b) XPS spectra of Co_3O_4 bulk (1) and Co_3O_4 microspheres (2).

Table 1Surface element compositions, H₂ consumption, and catalytic activities of the Co₃O₄ bulk and Co₃O₄ microsphere samples.

Sample	Surface element composition		H ₂ consumption (mmol g ⁻¹)		Catalytic activity		
	Co ³⁺ /Co ²⁺ molar ratio	O _{ads} /O _{latt} molar ratio	≤ 250 °C	> 250 °C	T _{10%} (°C)	T _{50%} (°C)	T _{90%} (°C)
Co ₃ O ₄ bulk	1.65	0.38	3.22	12.86	230	273	304
Co ₃ O ₄ microsphere	1.44	1.03	3.10	12.38	190	230	254

Reaction conditions: toluene concentration = 0.1%, toluene/O₂ molar ratio = 1/400, SV = 20000 ml g⁻¹ h⁻¹.

Co₃O₄ microsphere was lower than that (1.65) of Co₃O₄ bulk, indicating a higher surface Co²⁺ concentration in the former. That is, the Co₃O₄ microsphere sample possessed more oxygen vacancies than the bulk counterpart. It is well known that the adsorbed oxygen species concentration is associated with the oxygen vacancy density. For an oxygen-deficient material, more oxygen vacancies give a higher oxygen adspecies concentration. This was substantiated by the O 1s XPS result. As shown in Fig. 4(b), an asymmetrical O 1s XPS signal was recorded for each sample, which was deconvoluted into the peaks of several kinds of surface oxygen species. The oxygen adspecies at 529.3, 530.3, 531.8, and 533.4 eV were assignable to the surface lattice oxygen (O_{latt}), adsorbed oxygen (O_{ads}, e.g., O₂⁻, O₂²⁻, or O⁻), hydroxyl and/or carbonate species, and adsorbed molecular water [21,22], respectively. Compared to the Co₃O₄ bulk sample, the O_{ads}/O_{latt} molar ratio of the microspherical Co₃O₄ sample was much higher, indicating a higher O_{ads} concentration.

3.3. Reducibility

Figure 5(a) illustrates the H₂-TPR profiles of the Co₃O₄ samples. The reduction of Co₃O₄ proceeds *via* the sequence of Co₃O₄ → CoO → Co⁰ [9]. The first peak at 227–230 °C was due to the reduction of Co³⁺ to Co²⁺ and the removal of oxygen adspecies. The reduction peaks at 279–292 and 316–341 °C corresponded to the reduction of Co²⁺ to Co⁰ [23]. If the cobalt ions in Co₃O₄ were only Co³⁺ and only Co²⁺ and reduced to Co⁰, the H₂ consumption would be 18.07 and 13.33 mmol g⁻¹, respectively. Actually, the H₂ consumptions of the Co₃O₄ bulk and Co₃O₄ microsphere samples were 16.08 and 15.48 mmol g⁻¹, respec-

tively. Furthermore, the low-temperature H₂ consumption (3.22 mmol g⁻¹) of the Co₃O₄ bulk sample was higher than that (3.10 mmol g⁻¹) of the Co₃O₄ microsphere sample, indicating that there was more Co³⁺ in Co₃O₄ bulk (i.e., the Co₃O₄ microsphere sample possessed a higher oxygen vacancy concentration and hence a higher oxygen adspecies concentration). Therefore, the cobalt species in the Co₃O₄ samples were present in a mixed valence (Co³⁺ and Co²⁺), which was in good agreement with the XPS results.

It is better to evaluate the low-temperature reducibility of a sample using the initial (where less than 25% oxygen in the sample was removed for the first reduction peak) H₂ consumption rate [24]. Figure 5(b) shows the initial H₂ consumption rate as a function of inverse temperature of the Co₃O₄ samples. Obviously, the initial H₂ consumption rate of the nanoplate-aggregate Co₃O₄ microsphere sample was higher than that of the Co₃O₄ bulk sample. This difference in low-temperature reducibility was in consistent with the difference in their O_{ads} concentrations and catalytic performance.

3.4. Catalytic performance

In the quartz sand blank experiment, no conversion of toluene was observed below 400 °C, indicating that under the adopted conditions there was no occurrence of homogeneous reactions. Figure 6(a) shows catalytic activity of the samples for toluene combustion. It can be clearly seen that the microspherical Co₃O₄ sample outperformed the bulk counterpart, with the T_{10%}, T_{50%}, and T_{90%} (temperatures required for toluene conversion of 10%, 50%, and 90%, respectively) of 190, 230, and 254 °C at SV = 20000 ml g⁻¹ h⁻¹ (Table 1), respectively. Toluene was completely

Fig. 5. H₂-TPR profiles (a) and initial H₂ consumption rate as a function of inverse temperature (b) of Co₃O₄ bulk (1) and Co₃O₄ microspheres (2).

Fig. 6. Toluene conversion (a), specific reaction rate normalized by catalyst amount (b), and specific reaction rate normalized by the surface area of the catalyst (c) as a function of temperature over Co_3O_4 bulk (1) and Co_3O_4 microspheres (2). Reaction conditions: 0.1% toluene, toluene/ O_2 molar ratio = 1/400, $\text{SV} = 20000 \text{ ml g}^{-1} \text{h}^{-1}$.

oxidized to CO_2 and H_2O over the Co_3O_4 samples, and there were no incomplete oxidation products, as substantiated by the carbon balance (99.5%) in each run. To better evaluate the catalytic activity of the samples, we use the specific reaction rates (normalized by weight amount and surface area of the sample) *versus* reaction temperature, as shown in Fig. 6(b) and (c), respectively. It is observed that the changing trend in specific reaction rate normalized by weight amount of the sample *versus* temperature was rather similar to that for toluene conversion *versus* temperature, but different from the specific reaction rate normalized by surface area of the sample *versus* temperature. This result indicated that the surface area had an important influence on the catalytic activity of the sample.

To examine the effect of water vapor on the catalytic performance, we conducted toluene oxidation in the presence of 3.0 vol% water vapor over the microspherical Co_3O_4 sample. As shown in Fig. 7, the addition of water vapor at 260 °C did not lead to a significant decrease in toluene conversion, but introduction of water vapor at 220 °C induced a drop in toluene conversion by 4%. This result was possibly due to the competitive adsorption of water, toluene, and oxygen. When the water vapor was cut off, toluene conversion at 220 °C was restored to almost the initial value in the absence of water vapor. There-

fore, the deactivation due to water vapor introduction was reversible.

Figure 8 shows the effect of SV on the catalytic activity of the Co_3O_4 microsphere sample. As expected, the toluene conversion increased with the drop in SV. In order to examine the catalytic stability, we carried out the 100 h on-stream reaction experiment over the Co_3O_4 microsphere sample at 250 °C and $20000 \text{ ml g}^{-1} \text{h}^{-1}$. As shown in Fig. 9, no significant loss in activity was ob-

Fig. 8. Toluene conversion as a function of reaction temperature at different SV values over the nanoplate-aggregate microspherical Co_3O_4 catalyst. Reaction conditions: 0.1% toluene, toluene/ O_2 molar ratio = 1/400.

Fig. 7. The effect of 3.0 vol% water vapor on the catalytic activity at 220 °C (1) and 260 °C (2) over Co_3O_4 microspheres. Reaction conditions: 0.1% toluene, toluene/ O_2 molar ratio = 1/400, $\text{SV} = 20000 \text{ ml g}^{-1} \text{h}^{-1}$.

Fig. 9. Toluene conversion as a function of on-stream reaction time over the nanoplate-aggregate microspherical Co_3O_4 sample. Reaction conditions: 0.1% toluene, toluene/ O_2 molar ratio = 1/400, $\text{SV} = 20000 \text{ ml g}^{-1} \text{h}^{-1}$, 250 °C.

Table 2

Comparison on the activity of various catalysts for toluene combustion.

Catalyst	Reaction condition		Specific reaction rate (mmol g ⁻¹ h ⁻¹)		Ref.
	Toluene concentration (%)	SV (ml g ⁻¹ h ⁻¹)	At 150 °C	At 250 °C	
Co ₃ O ₄ microspheres	0.1	20000	0.0376	0.711	This work
Co ₃ O ₄ -HT-CTAB	0.1	20000	0.164	0.818	[2]
Bulk Co ₃ O ₄	0.1	20000	0.0164	0.246	[17]
Mesoporous Co ₃ O ₄	0.1	20000	0.246	0.818	[17]
Mesoporous Co ₃ O ₄	0.1	20000	0.778	0.818	[18]
Mn ₃ O ₄	0.1	15000	0	0.522	[25]
α -Mn ₂ O ₃	0.1	15000	0	0.00614	[25]
β -MnO ₂	0.1	15000	0	0	[25]
LaMnO ₃	0.19	178 h ⁻¹	0.000277	0.00554	[26]
5 wt% Au/CeO ₂	0.7	186	0	0.00533	[27]
0.5 wt% Pd/LaMnO ₃	0.1328	18000 h ⁻¹	0.293	0.880	[28]

served. This result demonstrated that the microspherical Co₃O₄ sample was stable under the adopted conditions.

In the past years, many materials have been used as the catalyst for toluene combustion. The activities of these catalysts are summarized in Table 2. Usually, the specific reaction rate normalized by the sample amount is used to compare the catalytic activity of different samples. At a given reaction temperature (150 or 250 °C), the specific reaction rate (0.0376 mmol g⁻¹ h⁻¹ at 150 °C or 0.711 mmol g⁻¹ h⁻¹ at 250 °C) over the Co₃O₄ microspheres was much higher than those over Mn₃O₄ [25], α -Mn₂O₃ [25], β -MnO₂ [25], bulk Co₃O₄ [17], LaMnO₃ [26], and 5 wt% Au/CeO₂ [27], but lower than those over Co₃O₄-HT-CTAB [2], mesoporous Co₃O₄ [17,18], and 0.5 wt% Pd/LaMnO₃ [28].

It is well established that the oxidation of organics over a transition metal oxide involves a Mars–van Krevelen mechanism, where organic molecules are oxidized by the lattice oxygen of the metal oxide, and the partially reduced metal oxide is then re-oxidized by the gas phase oxygen [29–31]. Wang et al. [31] attributed the higher reactivity of manganese oxide to the improvement in oxygen activation ability, which enhanced the combustion of ethanol and acetaldehyde. In the case of Co₃O₄, lattice oxygen could be consumed by reaction with toluene and then replenished by gas phase oxygen [32,33]. Thus, the lattice oxygen of cobalt oxide is of great importance in toluene oxidation. The low-temperature reducibility reflects the reactivity of the lattice oxygen in Co₃O₄. As shown in Fig. 5, the lattice oxygen reactivity (i.e., low-temperature reducibility) of the Co₃O₄ microspheres was higher than that of Co₃O₄ bulk. Surface oxygen vacancies also have an important role to play [34,35]. The presence of oxygen vacancies favors the activation of oxygen molecules to active oxygen adspecies. The microspherical Co₃O₄ sample possessed a higher oxygen adspecies concentration (which is related to the surface oxygen vacancy density) than the Co₃O₄ bulk sample, in good agreement with their catalytic activity sequence. In addition, the surface area (66 m² g⁻¹) of nanoplate-aggregate Co₃O₄ microspheres was much higher than that (10 m² g⁻¹) of Co₃O₄ bulk. Therefore, we conclude that the large surface area, high oxygen adspecies concentration, and good low-temperature reducibility accounted for the good catalytic performance of the nanoplate-aggregate Co₃O₄ microspheres for toluene combustion.

4. Conclusions

The nanoplate-aggregate microspherical Co₃O₄ catalyst was prepared using an ethylenediamine-assisted hydrothermal strategy. This catalyst had a cubic crystal structure and was comprised of nanoplate-aggregate microspheres. The microspherical Co₃O₄ sample outperformed the bulk counterpart, giving the $T_{50\%}$ and $T_{90\%}$ of 230 and 254 °C at SV = 20000 ml g⁻¹ h⁻¹, respectively. The large surface area, high surface oxygen adspecies concentration, and good low-temperature reducibility of the Co₃O₄ microspheres were responsible for its high catalytic performance.

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Graphical Abstract

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Nanoplate-aggregate microspherical Co_3O_4 prepared by the ethylenediamine-assisted hydrothermal route exhibits good catalytic performance for toluene oxidation because of its high surface area and concentration of adsorbed oxygen and good low-temperature reducibility.

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纳米片聚结 Co_3O_4 微球催化甲苯燃烧

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摘要: 采用乙二胺辅助的水热法制备了纳米片聚结的 Co_3O_4 微球. 利用多种分析技术表征了其物化性质, 并评价了其对于甲苯燃烧的催化活性. 结果表明, 由添加1.0 ml乙二胺经140 °C水热处理12 h后制得的 Co_3O_4 样品呈纳米片聚结的微球状表面形貌. Co_3O_4 微球样品的比表面积约为66 m² g⁻¹. 与体相 Co_3O_4 样品相比, Co_3O_4 微球样品具有较高的氧吸附物种浓度和较好的低温还原性. 当空速为20000 ml g⁻¹ h⁻¹时, 在 Co_3O_4 微球样品上甲苯转化率达到50%和90%时的反应温度分别为230和254 °C. 这与该样品具有较大的比表面积、较高的氧吸附物种浓度和较好的低温还原性相关.

关键词: 氧化钴微球; 纳米片形貌; 表面活性剂辅助水热合成; 甲苯燃烧

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