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Graphical abstract
Urchin-Like Cobalt Incorporated Manganese Oxide OMS-2 Hollow Spheres:
Synthesis, Characterization and Catalytic Degradation of RhB Dye

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Abstract

Urchin-like \( \text{K}_x\text{Co}_y\text{Mn}_{8-y}\text{O}_{16} \) hollow spheres assembled from nanoplate building blocks were successfully fabricated via a one-pot hydrothermal route using cobalt acetate and potassium permanganate as raw material. The products were characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectrometer, field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) measurement. The thermal stability and surface areas of cobalt ion in the manganese sites of \( \text{KMn}_8\text{O}_{16} \) structures were clearly evidenced by TGA and \( \text{N}_2 \) adsorption-desorption isotherms curves. Based on time depended experiment results, a possible formation mechanism for this structures was proposed. The catalytic degradation of Rhodamine B (RhB) on \( \text{K}_x\text{Co}_y\text{Mn}_{8-y}\text{O}_{16} \) materials have, therefore been dependent for the molar precursor ratio and specific surface area of the as-fabricated products. UV-vis, LC-MS and barium hydroxide methods were utilized to monitor the temporal course of the catalytic reaction.

**Keyboard:** Cobalt-doped OMS-2, Hollow sphere, Surface area, Catalysis, Rhodamine B
1. Introduction

Over the past decades, the inorganic hollow structures have aroused considerable attention due to their unique chemical, physical properties and promising applications in nanoscale chemical reactors with enhanced selectivity, efficient catalysts drug-delivery carries, building blocks for photonic crystals, nanocapsules for hydrogen storage, and so forth [1-4]. Emulsion droplets, polymer or surfactant micelles, bubbles and sacrificial template were explored as technical strategies for growth and promotion of hollow structures materials [5-9]. Some of the other liquid phase chemical techniques using metal salts as a starting precursor, such as hydrothermal processes were intensively studied and applied to obtain manganese oxides nanomaterials, because it is low process temperature, simple operation, low cost, homogeneous reaction conditions resulting in narrow size distribution and shape controllability [10]. Recently, manganese oxides microspheres with and metals-doped manganese oxide urchin-like 3D nanostructure have, therefore been achieved by the redox reactions of MnO$_4^{-}$ and/or oxidizes of Mn$^{2+}$ [11-18].

Cryptomelane-type manganese oxide is one group of the OMS-2 family with the stoichiometry KMn$_8$O$_{16}$ and 1D-tunnel structure composed of 2x2 arrangement of edge-shared MnO$_6$ octahedral [19-22]. Due to porous structure and mixed valence of manganese species, OMS-2 were found to be an excellent heterogeneous catalyst for selective oxidation of volatile organic compounds [23,24], alcohols [25, 26], toluene [27], indene [28, 29], ethyl acetate [30], 2-thiophenemethanol [31], formaldehyde [32], 9H-fluorene [33], dehydrogenation of cyclohexane and decomposition of methylene blue [34]. In particular, the metal ion incorporated tunnel structured manganese oxides have also been exploited as-potential materials in the field of heterogeneous catalysis [35]. The nature and loading of the dopant elements have significantly been affected on both the conversion and selectivity in the oxidative dehydrogenation, olefin and acetaldehyde, removal of phenol and toxic metal ions from polluted aquatic systems [18, 36 and 37].
In this paper, we report single-step hydrothermal synthesis and characterization of urchin-like K\textsubscript{x}Co\textsubscript{y}Mn\textsubscript{8-y}O\textsubscript{16} hollow spheres assembled with 2D nanoplates. Furthermore, we are able to easily control the chemical composition, crystal structure, and morphology of the resultant nanostructures through the change of reaction time condition and precursor composition. Also, their catalytic activity for RhB degradation has been investigated. The possible reaction mechanism pathway of catalytic degradation was proposed by using UV-vis, LC-MS and barium hydroxide methods.

2. Experimental

2.1 Catalysts preparation

All the chemical reagents were purchased from Shanghai Chemical Reagent Co. China. For a typical synthesis of K\textsubscript{x}Co\textsubscript{y}Mn\textsubscript{8-y}O\textsubscript{16} microspheres, KMnO\textsubscript{4} and Co(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{2}•4H\textsubscript{2}O were completely dissolved in 35 mL distilled water. The ratio of Co/Mn was varied from 1/1 to 1/6. The obtained solutions were transferred into a 40 mL Teflon-lined stainless steel autoclave, which was subsequently sealed and maintained at 140 °C for 14h. The precipitates were filtered and washed with distilled water and absolute ethanol by using centrifugation at 8000 rpm for 10 min for several times, and then dried in a vacuum at 50 °C for 12 h.

2.2. Catalysts characterization

X-ray data of the crystal structure were obtained on an X-ray diffractometer (Panalytical χ' Pert Pro; Netherlands) using a Cu K\textsubscript{α} target (λ =1.5418 Å) at an angular 20 speed of 2 degrees per minute. A Fourier-transform infrared (FT-IR) spectrum was measured on an Equinox 55 Burker FT spectrometer employing a KBr beam splitter. EDAX Eagle III energy-dispersive micro-XRF (μXRF) spectrometer was used to identify of elements presents. The field emission scanning electron microscope (FE-SEM) observations were performed with a FEI Sirion 200, Netherlands. The transmission electron microscopy (TEM) images were examined by using a Tecnai G\textsuperscript{2}20, Netherlands. A high-resolution transmission electron microscopy (HR-TEM) image was carried out on a JEM-2010 FEF TEM at an acceleration voltage of 200 kV. Thermogravimetric analysis (TGA) was estimated on a Perkin Elmer Pyris at rate of
10° C min⁻¹ under argon condition. The temperature range was scanned at 40 -800°C. The BET surface areas were measured by a Micromeritics ASAP 2010 system.

2.3. Degradation experiments

The catalytic degradation of RhB process was carryout in a three-neck glass under a reflux condenser, magnetic stirring and oxygen air bubbling. 1.0 mmol catalyst powders were suspended in an aqueous solution containing 0.15 g/L of RhB. Samples was taken from the three-neck glass reactor at regular intervals during the experiment that lasted 32 min. At the end of each experiment, the catalytic powder was removed by filtration and centrifuging. The decolorization of dye was analyzed by using a UV-vis spectrophotometer (Shimadzu, Model No. 2450). The degradation rate of RhB was calculated based on the following equation [D% = (1−A_t/A_o)/100].

2.4. LC-MS analysis

After reaction, the catalytic powder was removed through filter paper and centrifuge to analysis by LC-MS spectrum with an Agilent 1100 series LC system (Agilent Technologies, Palo Alto, CA), performed with a binary pump, 1100 UV-vis diode array detector, an autosample and column thermostat. The LC-MS system was equipped with a Zorbax C18 column (150 mm x 4.6 mm i.d., 5µm). The mass spectrometer was conducted with an ESI source and operated in positive polarity. Solvent methanol: water 80:20 % v:v was used as a mobile phase with a flow rate of 0.8 mL min⁻¹. The LC-MS experiment was performed in the mass range from 50 to 600 m/z.

3. Results and discussion

3.1. Morphology and structure

The phase structures of the as-prepared samples with different molar ratio of Co/Mn were investigated by XRD. Fig 1 (a) shows the almost intensity of the diffraction peaks of XRD patterns can be index to tetragonal phase of KMn₈O₁₆ with lattice parameters of a=9.84Å and c=2.87Å corresponded to JCPDS card no. 12-706. Peak at 20.20° indicates the cobalt derivative is presented. FT-IR spectrum of the as-synthesized products shown in Fig. 1(b) revealing the absorption peaks at 474 and
531 cm\(^{-1}\) are assigned to the Mn-O vibrations of MnO\(_6\) octahedra [30, 38]. The transmision bands at 3432.68 and 1639.31 cm\(^{-1}\) correspond to the O-H vibrating mode of traces of absorbed water. However, the peak appears at 722 cm\(^{-1}\) has, maybe, been attributed to cobalt substituted in KMn\(_8\)O\(_{16}\) structures.

To further confirm the formation of K\(_x\)Co\(_y\)Mn\(_{8-y}\)O\(_{16}\) samples with different molar ratios of Co/Mn in range between 1:1 to 1:6 EDS spectrum analysis were measured. Fig. 2(a) clearly shows the peaks of K, Co and Mn elements in the spectrum of as-prepared products, while the peak of oxygen is not observed owing to X-ray instrumen. The Co/Mn percentages increased with increase of cobalt concentration, meanwhile, the K/Mn ratio become decreases (Table1). The TGA curve of the samples shown Fig. 7(b) depicting the average weight losses of 13.359-15.188% at the temperature range from 100 to 250°C are generally corresponding to the water content of 0.602-0.70 per unit formula, respectively.

Fig. 3(a) shows the typical FE-SEM micrograph of K\(_x\)Co\(_y\)Mn\(_{8-y}\)O\(_{16}\) hollow spheres prepared via a hydrothermal treatment of same molar ratio of reactors is shown Fig. 3(b), depicts that the architecture microspheres consisted of plate-like nanostructure with an average size diameter of 1.2±0.2 µm, shell thickness of 150±20 nm and the diameter of the hollow cavity of 350±50 nm. The edge length and thickness of the nanoplate are about 80±20 nm and 20±10 nm, respectively. As for Fig. 3(c), the morphology of microspheres was also investigated by TEM images, which is in agreement with the FE-SEM observation. The selected area electron diffraction (SA-ED) pattern inserted in Fig. 3(c), shows the product can be indexed as a polycrystalline K\(_x\)Co\(_y\)Mn\(_{8-y}\)O\(_{16}\) microsphere. Fig. 3(d) shows a typical high-resolution transmission electron microscopy (HR-TEM) image of the product. The image clearly reveals that the fringes of \{110\} lattice planes with a lattice spacing of approximately 0.686 nm can be observed. We probed the effect of chemical reaction on the crystallite morphology of the pristine material using FE-SEM. As shown in panel (a)-(c) of Fig. 4, the samples were prepared with mole ratio \(\leq 1/2\) at 140 °C for 14 h. The precursor the K\(_x\)Co\(_y\)Mn\(_{8-y}\)O\(_{16}\) consists of micropherical particles without visible cavities even with the lower Co/Mn ratios. The microspheres with edge size diameters in range from one to two micrometer.
The formation process of the hierarchical hollow spheres utilized, whereas both Co and Mn were consumed in same concentration exposure in time-dependent experiments. Fig. 5(a) shows the particles with randomly a few plate-like structures are formed when the reaction sealed at 140 °C for 4h. At the same temperature, but the time required to 8 h, the particles are aggregated together through self-assembling to form hierarchical leaf-like nanosheets (Fig. 5(b)). When the reaction-time is prolonged to 12h, the nanosheets are bonded together to form the urchin-like microspheres structures (Fig. 5(c)). Whereas the explosion of hierarchically structures from microspheres occurred by sealing hydrothermal reaction for 14h (Fig. 5(d)). The possible growth mechanism of $K_xCo_yMn_{8-x}O_{16}$ hollow sphere maybe is proposed by Ostwald ripening (OR) process, which is similar to those reported in literatures [10, 39, 40]. Due to the energy difference, Ostwald ripening includes the formation of aggregates with primary crystallites, followed by the gradual migration of crystallites through a re-crystallization process. Three-step growth model are proposed, display the formation of such a hollow nanostructure. First step, the particles appeared in the solution, and they might act as the primary particles for the formation of nanoplate structure. In the second step, the plates-like structure are aggregate together to composed 2D sheet-like structure. Then sheet crystallites of the aggregate went to the solid spheres as in the third step. Due to a dissolution-recrystallization process, the hole of microspheres may be occurred.

Nitrogen adsorption isotherms for the samples are indicated in Fig. 6. All of the isotherms exhibit stepwise adsorption and desorption (type IV isotherms), indicating a typical mesoporous structure. As listed in Table 1, the present materials are expanded surface area of 292.03 m²/g for the hierarchical $K_xCo_yMn_{8-x}O_{16}$ hollow sphere with Co/Mn ratio of 1/1 and 130-86 m²/g for other nanostructured microspheres with Co/Mn ratio <1/1, respectively. The enhancement of surface area underscores the overall formation of microstructured materials. The surface area increased dramatically with the concentration of cobalt-substituted in $KMn_8O_{16}$ and hollow sphere assembly of nanoplates structures when compared to the microspheres is attributable to their nonaggregated morphology and less cobaltation of the as-prepared product.

3.2. Catalytic activities
The contamination of water supplies by organic molecules is an increasing problem mainly because many of these molecules are not readily degraded by conventional methods for the treatment of effluents. This problem has increased with the development of the textile industry because many of the pollutants are dyes used by them [41, 42]. Among dyes, Rhodamine B is an important factor in environmental pollution from the textile industry and study of degradation mechanism to be quite well [43,44]. In this area, the degradation of RhB with oxygen air babbles catalyzed by $K_xCo_yMn_{8-y}O_{16}$ microspheres was occurred without adjust of pH and under atmospheric pressure at room temperature. Fig. 7(a) depicts the UV-visible spectrum of RhB has consists of two main characteristic absorption bands. One is (554 nm) and another in UV region (332 and 222 nm). The absorption in the visible region can be attributed to chromophore containing azine linkage, whereas the bands obtained in UV region can be assigned to aromatic rings. When RhB solution was treated by $K_xCo_yMn_{8-y}O_{16}$ microspheres, the absorption intensity of both peaks is decreased with times, suggesting RhB is gradually degraded, including degradation of the aromatic structure.

On the basis of the surface characterization results described above, it is now instructive to compare the catalytic activities of the as-prepared $K_xCo_yMn_{8-y}O_{16}$ samples with different mole ratio of reactants. Curve I in Fig. 7(b) reveals the RhB could hardly be decomposed in the presence of air babble and absences of catalyst powder. As shown in curve II of Fig. 7(b), the degradation percentage of RhB over $K_xCo_yMn_{8-y}O_{16}$ hollow spheres in absence air babbles is about 23%. This analysis displayed that the higher surface area of catalyst, meanwhile, the presence of $O_2$ is necessary but the oxygen flow rate has no significant effect on the degradation process. Furthermore, the degradation percentages of RhB is occurred of 98% by $K_xCo_yMn_{8-y}O_{16}$ hollow sphere with higher molar of Co/Mn ratio (curve VI), has better catalytic activity than the other samples with the lower Co/Mn ratio~78-65% (curves III, IV and V). This result underscored that the positive impact of cobalt substitution and it also confirm the comparison between the microstructured samples with nearly the same Co content but with different structure kinds.
The mechanism of this reaction can be considered a pseudo first order due to the oxygen excess. With the same assumption, the plots of \( \log(A_o/A_t) \) versus times, as represented in Fig. 7 (c). The slope gives a good linear correlation \( (R^2 = 0.99904) \) also suggesting the reaction follows a pseudo-first order. According to the rate constant formula \( [k = (2.303/t) \log(A_o/A_t)] \). The rate constant of the catalytic degradation of RhB by \( K_xCo_yMn_{8-y}O_{16} \) hollow sphere prepared with same mole of reactors of about 0.095 min\(^{-1}\) (VI), is faster than other samples ~ 0.064- 0.032 min\(^{-1}\) (III, IV and V curves).

Fig. 7(d) shows the LC-MS analysis degradation RhB catalyzed by \( K_xCo_yMn_{8-y}O_{16} \) microsphere after reaction follows for 0, 30 min and 60 min, respectively. The RhB and N-de-ethylation of RhB have chromatographed peaks at 9.66, 8.8 and 1.9 min with mass spectra of 443, 415 and 359 m/z, reveals that the degradation pathways of dye (Scheme 1). The decomposition of RhB pollutants solution is also qualified by a saturated solution of barium hydroxide. The pale white precipitate of barium carbonate indicates the carbon dioxide is formed by an oxo-metal complex of the dye molecule on the catalyst surface [34].

4. Conclusions

In conclusion, urchin-like \( K_xCo_yMn_{8-y}O_{16} \) hollow spheres were synthesized via a one-pot hydrothermal method without the use of a solid-state precursor prepared at elevated temperature. Through altering synthesis parameters, it was found that the hydrothermal reaction time played an important role in the formation of \( K_xCo_yMn_{8-y}O_{16} \) hierarchical hollow structures. The catalytic degradation efficiency of RhB by as-prepared products was compared with different partial Co substitution for the micro-structured manganese oxides. The decomposition reaction of RhB follows first order kinetics. LC-MS spectrum and barium hydroxide test were employed to analysis the catalytic degraded products and a possible reaction mechanism pathway was suggested. All results postulate that \( K_xCo_yMn_{8-y}O_{16} \) promising applications in the oxidative degradation of dye, like RhB.

Acknowledgments
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References


Tables

Table 1 The ratios of Co/Mn, k/Mn, water content and surface area of $K_{x}Co_{y}Mn_{8-y}O_{16}$ materials

Figures Caption

Fig. 1(a) XRD pattern and (b) FT-IR spectrum of the materials prepared at 140 °C for 14 h with different molar ratios Co/Mn of 1/1, 1/2, 1/4, 1/6 and *Co substitution.

Fig. 2(a) EDAX spectra and (b) TGA curves of the materials synthesized with the various molar ratios of Co/Mn at 140 °C for 14 h.

Fig. 3 (a) low-, (b) high-magnification SEM images, (c) TEM images (insert, a SA-ED) and (d) HR-TEM images of the $K_{x}Co_{y}Mn_{8-y}O_{16}$ microsphere prepared by hydrothermal method with the molar ratio Co/Mn of 1:1 at 140 °C for 14 h.

Fig. 4 FE-SEM image of the $K_xCo_yMn_{8-y}O_{16}$ samples synthesized by hydrothermal method with the different Co/Mn molar ratios varied from 1/2 to 1/6 at 140 °C for 14 h.

Fig. 5 FE-SEM images of the samples synthesized with the molar ratio Co/Mn of 1:1 at 140 °C for ambient times (a) 4 h, (b) 8 h, (c) 12h and (d) 14h.

Fig. 6 (a) N$_2$ adsorption-desorption isotherms of $K_xCo_yMn_{8-y}O_{16}$ microspheres obtained with the different molar ratios at 140 °C for 14 h.

Fig. 7 (a) UV-visible absorption of degradation RhB by $K_xCo_yMn_{8-y}O_{16}$ hollow spheres with times; (b) D% of RhB under different conditions: (I) in the absence of catalysts; (II) in presences of $K_xCo_yMn_{8-y}O_{16}$ without $O_2$; with the Co/Mn ratios in the precursor of (III)1/6, (IV)1/4,(V)1/2 and (VI)1/1; (c) the degradation rate constant of RhB and MR catalyzed by $K_xCo_yMn_{8-y}O_{16}$ with different Co/Mn molar ratios of (III) 1/6, (IV)1/4,(V)1/2 and (VI)1/1; (d) HPLC chromatogram of degraded samples for 0 min, 30min and 60 min.

Scheme 1 the probable mechanisms diagram for the catalytic degradation of RhB dye by $K_xCo_yMn_{8-y}O_{16}$ hollow spheres.
Table 1

<table>
<thead>
<tr>
<th>Sample [Co$^{2+}$/Mn$^{7+}$]</th>
<th>Co/Mn</th>
<th>K/Mn</th>
<th>H$_2$O content</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.89</td>
<td>0.14</td>
<td>0.65</td>
<td>292.03</td>
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<tr>
<td>1:2</td>
<td>0.47</td>
<td>0.23</td>
<td>0.63</td>
<td>129.1</td>
</tr>
<tr>
<td>1:4</td>
<td>0.38</td>
<td>0.28</td>
<td>0.67</td>
<td>107.4</td>
</tr>
<tr>
<td>1:6</td>
<td>0.20</td>
<td>0.29</td>
<td>0.70</td>
<td>85.7</td>
</tr>
</tbody>
</table>
Figure 1

(a) X-ray diffraction patterns of Co/Mn films with different Co/Mn ratios.

(b) FTIR spectra of Co/Mn films with different Co/Mn ratios.
Figure 2

(c) K\textsubscript{CoMn} and K\textsubscript{Cnt}

(b) Weight loss (%) vs Temperature (°C)
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7

(a) Abs (a.u.) vs mn

(b) Degradation% vs Time (min)

(c) log(Ao/At) vs Time (min)

(d) Intensity (a.u.) vs Time (min)
Scheme 1

Oxidative degradation

\[ \text{CO}_2 + \text{H}_2\text{O} \]