Ordered mesoporous spinel Co$_3$O$_4$ as a promising catalyst for the catalytic oxidation of dibromomethane

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ABSTRACT

The abatement of brominated volatile organic compounds (Br-VOCs) is an urgent task due to their serious harmfulness to human health and the environment. In this work, ordered mesoporous spinel Co$_3$O$_4$ was synthesized for the catalytic oxidation of dibromomethane (CH$_2$Br$_2$) as a model pollutant for Br-VOCs. The combined results of XRD, BET, and TEM suggested that ordered mesoporous spinel Co$_3$O$_4$ was successfully synthesized. Ordered mesoporous spinel Co$_3$O$_4$ showed a higher catalytic activity than bulk spinel Co$_3$O$_4$. Particularly, Co$_3$O$_4$-K showed the highest catalytic activity, and its T$_{90}$ value was only 271 °C. Meanwhile, Co$_3$O$_4$-K showed the highest selectivity to CO$_2$ at low temperature, and a good stability for at least 30 h. The superior catalytic activity was related to their ordered mesoporous channel structures with large specific surface area, high content of active Co$^{3+}$, and strong redox property. According to the results of product analysis and in situ DRIFT spectra, a reasonable mechanism for CH$_2$Br$_2$ oxidation over ordered mesoporous spinel Co$_3$O$_4$ was proposed.

1. Introduction

With the implementation of more stringent air pollutants emission standards, more and more people keep their eyes on the emission control of halogenated volatile organic compounds (HVOCs) due to their serious harmfulness to human health, and the environment [1,2]. Brominated volatile organic compounds (Br-VOCs) mainly come from the emission of pesticides, and petrochemicals. Meanwhile, Br-OVCs are also a typical pollutant from the generation of purified terephthalic acid (PTA), and their handling is extremely urgent, and full of challenges due to their difficulty in decomposition [3]. Catalytic oxidation is perceived as an economically viable, and environmentally friendly method to degrade Br-VOCs into CO$_2$, H$_2$O, and other harmless substances, making it a potential technology for abating Br-VOCs [4].

Our previous studies demonstrate that Co-based oxides (e.g., Ti-Co$_3$O$_4$, Co$_3$O$_4$/CeO$_2$) have a moderate activity for Br-VOCs oxidation due to their unique redox property, and high concentration of electrophilic oxide species [7]. However, the uses of their active cobalt species for Br-VOCs oxidation are still relatively small. It has been reported that controlling the morphology and structure of Co-based oxides can promote its catalytic activity due to more exposure of active sites [8,9]. Particularly, Co$_3$O$_4$ with ordered mesostructured significantly benefit its catalytic activity. Deng et al. compared conventional Co$_3$O$_4$ nanoparticles with order mesoporous Co$_3$O$_4$ for the degradation of chloramphenicol, and the results suggested that the catalytic performance decreased in the sequence of Co$_3$O$_4$-KIT6 > Co$_3$O$_4$-SBA15 > nano-Co$_3$O$_4$ [10]. Tüysüz et al. believed that order mesoporous Co$_3$O$_4$ with high porosity, and specific surface area exhibited better catalytic activity for water oxidation [11]. Song et al. found that mesoporous Co$_3$O$_4$ synthesized by an inverse surfactant micelle method, had high catalytic performance for CO oxidation at −60 °C [12]. However, research about ordered mesoporous spinel Co$_3$O$_4$ for Br-VOCs oxidation is rare.

In this work, ordered mesoporous spinel Co$_3$O$_4$ was synthesized by the nano-replication method using SBA-15, or KIT-6 selected as the template, and bulk spinel Co$_3$O$_4$ was synthesized using the co-precipitation method. The physicochemical properties of different Co$_3$O$_4$
were characterized by XRD, BET, TEM, XPS, and H2-TPR techniques. Dibromothane (CH2Br2) was explored as the model pollutant for Br-VOCs to evaluate the performance of different Co3O4. Product selectivity, and catalyst stability were also investigated. Finally, a reasonable mechanism for CH2Br2 oxidation over ordered mesoporous spinel Co3O4 was proposed.

2. Experimental section

2.1. Preparation

SBA-15, and KIT-6 were prepared by the hydrothermal method. Tetraethoxysilane (TEOS) was used as the silica source, and P123 (EO20PO70EO20) was used as the structure-directing agent. Ordered mesoporous spinel Co3O4 was synthesized by the nano-replication method using SBA-15 or KIT-6 as the template. First, 1.0 g of SBA-15 or KIT-6 was added into a Co(NO3)2·6H2O ethanol solution (30 mL, 1.0 mol/L). After stirred for 1 h, the ethanol was evaporated at 80 °C, and obtained particles were calcined at 200 °C for 6 h in air. The particles were re-impregnated, and calcined at 500 °C for 3 h in air. SBA-15, and KIT-6 were removed using a NaOH solution (2 mol/L) in 80 °C water bath under magnetic stirring for 16 h. The particles were separated by suction filtration, and then washed with ultrapure water three times. Lastly, the particles were dried at 100 °C for 10 h. The obtained particles were labeled as Co3O4-S, and Co3O4-K, respectively. Bulk spinel Co3O4 (Co3O4-B) was synthesized by the co-precipitation method.

2.2. Characterization

The wide-angle X-ray diffraction pattern (XRD), low-angle XRD pattern, Brunauer-Emmett-Teller (BET) surface area, morphology and microstructure, X-ray photoelectron spectroscopy (XPS), H2-temperature programmed reduction (H2-TPR), and in situ DRIFT spectra were monitored on an X-ray diffractometer (Shimadzu, XRD-6100), a SAXS, a N2 adsorption apparatus (Quantachrome, 2200e), a transmission electron microscopy (TEM, JEOL-2100F), a X-ray photoelectron spectroscopy (Shimadzu-Kratos, AXIS UltraDLD), a chemical adsorption apparatus (AutoChem II, 2920), and a Fourier transform infrared spectrometer (FTIR, Nicolet 6700), respectively.

2.3. Activity test

CH2Br2 oxidation was conducted in a quartz tube microreactor and the reaction temperature ranged from 150 to 300 °C. The mass of catalyst with 40–60 mesh was generally 80 mg and the total gas flow was 150 mL min⁻¹, resulting in a (GHSV of 112,500 cm³ g⁻¹ h⁻¹. The simulated smelting flue gas contained approximately 500 ppm of CH2Br2, 10% of O2, 500 ppm of p-xylene (PX) (when used), 2% of H2O (when used), and the rest being N2. The concentration of gaseous CH2Br2 was monitored using a gas chromatographer (GC-2010 Plus) equipped with an electron capture detector (ECD). CH2Br2 conversion represented the catalytic activity, and it was described as follows:

\[ X_{\text{CH2Br2}} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \]  

Where \( C_{\text{in}} \) and \( C_{\text{out}} \) are the CH2Br2 concentrations in the inlet and outlet, respectively.

The products of CH2Br2 oxidation were monitored using a GCMS-QP2010. The HBr and Br2 concentrations were determined using the titration method. First, the gas flow consisting of HBr and Br2 was entirely absorbed in a KI solution. Then, the Br2 concentration was determined using the titration method. The bromide ion concentration was determined using an ion chromatography. The CO and CO2 concentrations were determined using a gas chromatographer (GC-14B).

The selectivity to CO, CO2, Br2, and HBr can be described as follows,

\[ S_{\text{CO}} = \frac{C_{\text{CO}}}{C_{\text{in}} - C_{\text{out}}} \times 100\% \]  
\[ S_{\text{CO2}} = \frac{C_{\text{CO2}}}{C_{\text{in}} - C_{\text{out}}} \times 100\% \]  
\[ S_{\text{Br2}} = \frac{C_{\text{Br2}}}{C_{\text{in}} - C_{\text{out}}} \times 100\% \]  
\[ S_{\text{HBr}} = \frac{C_{\text{HBr}}}{2(C_{\text{in}} - C_{\text{out}})} \times 100\% \]

Where \( C_{\text{CO}} \) and \( C_{\text{CO2}} \) were the CO and CO2 concentrations, \( C_{\text{Br2}} \) and \( C_{\text{HBr}} \) were the Br2 and HBr concentrations, respectively.

3. Results and discussion

3.1. Characterization

The ordered mesoporous structure of different Co3O4 is determined by the low-angle XRD patterns, and the results are shown in Fig. 1(a). It is significant to see that the low-angle XRD patterns of both Co3O4-S, and Co2O3-K displayed a new reflection at 0.5–1.0°, corresponding to the lower symmetry compared with its parent silica. It suggested that
ordered mesoporous structure of Co3O4 was formed.

The crystal texture of different Co3O4 is monitored through the wide-angle XRD patterns, and the results are shown in Fig. 1(b). All the samples showed eight diffraction peaks, which were related to the face-centered cubic spinel Co3O4 [14]. However, the intensity of diffraction peaks for Co3O4-S and Co3O4-K was weaker than that of Co3O4-B, suggesting that ordered mesoporous spinel Co3O4 had lower crystallinity and smaller crystallite size. By calculating the Scherrer equation applied for (311) plane, the crystalline sizes of Co3O4-B, Co3O4-S, and Co3O4-K were 28.4, 15.5, and 12.8 nm, respectively.

The microscopic morphology and structure information of different Co3O4 are shown in Fig. 2. The N2 adsorption-desorption isotherms, which were related to the face-centered cubic spinel Co3O4 [14]. However, the intensity of diffraction peaks for Co3O4-S and Co3O4-K was weaker than that of Co3O4-B, suggesting that ordered mesoporous spinel Co3O4 had lower crystallinity and smaller crystallite size. By calculating the Scherrer equation applied for (311) plane, the crystalline sizes of Co3O4-B, Co3O4-S, and Co3O4-K were 28.4, 15.5, and 12.8 nm, respectively.

The N2 adsorption-desorption isotherms and pore size distributions of different Co3O4 are shown in Fig. 2. The N2 adsorption-desorption isotherms of Co3O4-S and Co3O4-K were attributed to type IV with a type H1 hysteresis loop, and their capillary condensation ranges were broad starting at approximately P/P0 = 0.45 and extending almost to P/P0 = 0.95 (Fig. 2(a)), suggesting typically mesoporous structure features. Meanwhile, the hysteresis loop of Co3O4-K was larger than that of Co3O4-S, suggesting that they had different porous channel structure. The BJH pore size distributions, calculated through the desorption isotherms, showed that Co3O4-S and Co3O4-K had a unimodal pore-size distribution centered at 3.9, and 3.6 nm, respectively, which further demonstrates that Co3O4-S, and Co3O4-K perfectly remained the replica structures of their templates. Textural parameters of different Co3O4 estimated by N2 physisorption are summarized in Table 1. The BET specific surface areas of Co3O4-S, and Co3O4-K were 86.2, and 94.0 m2 g⁻¹, respectively, which were larger than that of Co3O4-B (0.2 m² g⁻¹). Similarly, the average pore volumes of Co3O4-S, and Co3O4-K were also larger than that of Co3O4-B. The results suggested that constructing ordered mesoporous structure could significantly improve the BET specific surface area, and average pore volume.

To ascertain the oxidation states of Co, and O on the surface, XPS was performed, and the related spectra are shown in Fig. 4. All the samples had two main peaks, appeared at 779.0–779.5 eV, and 794.8–795.3 eV (Fig. 4(a)), which was ascribed to Co 2p3/2, and Co 2p1/2, respectively. The Co 2p3/2 XPS spectra could be decomposed into two components, and their binding energy approximately appeared at 778.7–779.4, and 797.8–780.5 eV, which was belong to Co3+ and Co2+, respectively [17]. The Co3+/Co2+ ratio was 0.30, 0.37, and 0.39 for Co3O4-B, Co3O4-S, and Co3O4-K, respectively (Table 2). The results suggested that ordered mesoporous spinel Co3O4 had more Co3+ species, which favored bringing more surface oxygen and promoting gas molecule adsorption (Table 3).

The O 1s spectra of different Co3O4 were resolved into two peaks (Fig. 4(b)). The binding energy appeared at 529.0–529.7 eV were ascribed to the lattice oxygen (Olat), and the binding energy appeared at 530.4–531.2 eV was assigned to surface adsorbed oxygen (Oads) [18]. Co3O4-B had the largest Oads/Olat ratio, followed by Co3O4-S, and Co3O4-B was the least Oads/Olat ratio (Table 2). The results suggested that ordered mesoporous spinel Co3O4, especially Co3O4-K, had abundant surface active oxygen.

The redox property of the catalyst has a significant impact on catalytic reaction, it can be determined using H2-TPR experiment, and the results are shown in Fig. 5. Co3O4-B had two reduction peaks appeared at 337, and 387 °C, which corresponded to the reduction of Co3+ to Co2+, and Co2+ to Co0, respectively [19]. The area of low temperature reduction peak was lower than that of high temperature reduction peak, suggesting that the amount of Co3+ was higher than that of Co2+, which was consistent with the XPS results. Co3O4-S had three reduction peaks appeared at 305, 366, and 458 °C. The first reduction peak was related to the reduction of Co3+ to Co2+, while the latter two reduction

### Table 1: Textural parameters of different Co3O4.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>Average pore diameter (nm)</th>
<th>Average pore volume (cm³ g⁻¹)</th>
<th>D_{Co3O4} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co3O4-B</td>
<td>0.2</td>
<td>23.0</td>
<td>0.02</td>
<td>28.4</td>
</tr>
<tr>
<td>Co3O4-S</td>
<td>86.2</td>
<td>3.9</td>
<td>0.15</td>
<td>15.5</td>
</tr>
<tr>
<td>Co3O4-K</td>
<td>94.0</td>
<td>3.6</td>
<td>0.12</td>
<td>12.8</td>
</tr>
</tbody>
</table>

D_{Co3O4}, Co3O4 crystallite size calculated by Scherrer equation from XRD.
peaks corresponded to the reduction of $\text{Co}^{2+}$ to $\text{Co}^0$. The similar result was also observed for Co$_3$O$_4$-K, except the reduction peaks shifted to lower temperature. However, the first reduction peak area for Co$_3$O$_4$-K was larger than that for Co$_3$O$_4$-S, suggesting that Co$_3$O$_4$-K had more $\text{Co}^{3+}$. As well known, the more $\text{Co}^{3+}$ ions generated the more anionic defects, which was in favor of bringing surface oxygen and promoting the adsorption of reactant molecule. Moreover, Co$_3$O$_4$-K had the strongest redox ability owing to the lowest reduction temperature, which was conducive to the catalytic reaction.

3.2. Activity

CH$_2$Br$_2$ conversion curves as function of temperature over different Co$_3$O$_4$ are shown in Fig. 6. Co$_3$O$_4$-B presented the worst oxidation activity, and its $T_{90}$ (the temperature required for 90% conversion) value was approximately 287 °C. Co$_3$O$_4$-S had better activity, and its $T_{90}$ value was approximately 274 °C. Co$_3$O$_4$-K displayed the highest catalytic activity with a $T_{90}$ value of approximately 271 °C, by reason of the three dimensional porous channels and the large specific surface area of Co$_3$O$_4$-K made it easily adsorb CH$_2$Br$_2$ molecules. The results suggested that ordered mesoporous spinel Co$_3$O$_4$ were in favor of CH$_2$Br$_2$ oxidation owing to their unique porous structures.

3.3. Product analysis

It is common knowledge that the ideal products of Br-VOCs oxidation are CO$_2$, and HBr, or Br$_2$, however, the current catalysts hardly achieve fully mineralization. Hence, it is essential to analyze the product composition, and product selectivity to the ideal products when developing a novel catalyst. The products over Co$_3$O$_4$-B, Co$_3$O$_4$-S, and Co$_3$O$_4$-K at different temperature were detected by GCMS, and the results are shown in Table S1, S2, and S3. The products were CO, CO$_2$, HBr, and H$_2$O at low temperature, and no other Br-containing by-products were monitored. Fig. 7 presents the selectivity to CO, CO$_2$, HBr, and Br$_2$ at different temperatures over Co$_3$O$_4$-B, Co$_3$O$_4$-S, and Co$_3$O$_4$-K. For Co$_3$O$_4$-B, the selectivity to CO$_2$ and Br$_2$ gradually increased with the increase of temperature, while that to CO, and HBr gradually decreased (Fig. 7(a)). Similar phenomena were also observed for Co$_3$O$_4$-S, and Co$_3$O$_4$-K. The selectivity to CO$_2$ was approximately 23%, 47%, 61%, and 91% at 150, 175, 200, and 225 °C, respectively, and was 100% above 250 °C. The increase in selectivity to CO$_2$ was attributed to the deep oxidation of CO at higher temperatures. Additionally, Br$_2$ was
formed when the temperature was exceed 175 °C, which was due to the occurrence of Deacon reaction (4HBr + O2 → 2Br2 + H2O) [20], and the selectivity to Br2 was 61% at 300 °C. For Co3O4-S and Co3O4-K, the selectivity to CO2 and Br2 were higher than that to Co3O4-B. The results suggested that ordered mesoporous spinel Co3O4 was beneficial to the deep oxidation of CO to CO2 and promoted the formation of Br2.

3.4. The influence of H2O or PX

Water vapor generally exists in the Br-VOCs-containing industrial exhaust gas, herein, the influence of water vapor on the catalytic activity for CH2Br2 oxidation was investigated, and Fig. 8 shows CH2Br2 conversion over Co3O4-K as a function of temperature in the presence of 2% H2O. To our surprise, CH2Br2 conversion was slightly increased at low temperature in comparison with the result without H2O, and the T10 (the temperature required for 10% conversion) value decreased by approximately 9 °C. However, with the increase of temperature, CH2Br2 conversion was obviously decreased, and T90 value shifted to higher temperature, which was related to the competitive adsorption of H2O with CH2Br2 molecules at the active sites.

Generally, various organic compounds exist in the Br-VOCs-
containing industrial exhaust gas, but it is unrealistic to simultaneously inspect the influence of various organic compounds on CH₂Br₂ oxidation. Hence, we mainly studied the reaction behaviors touching upon a binary mixture of organic compounds, and CH₂Br₂ conversion over Co₃O₄-K as a function of temperature in the presence of PX as a model PTA-exhaust-gas organic compound is also shown in Fig. 8. When the presence of PX, CH₂Br₂ conversion was remarkably decreased, and T₉₀ increased to 294 °C. The depressing influence might be related to the reduction of active sites because of PX oxidation.

3.5. Catalyst stability

For an industrial application, it is essential to investigate the catalyst stability. The stability test was carried out by feeding an air flow comprising 500 ppm of CH₂Br₂, 10% of O₂, and the rest being N₂ at 250 °C with GHSV of 112,500 cm³ g⁻¹ h⁻¹, and the results for Co₃O₄-B, Co₃O₄-S, and Co₃O₄-K catalysts are shown in Fig. 9. All the samples displayed highly stable activity for 30 h with CH₂Br₂ conversion of approximately 49, 61, and 66%, respectively. Meanwhile, the positions and intensities of the characteristic peaks corresponding to spinel Co₃O₄ had almost no change after reaction for 30 h, which implied that the structure and composition of the active sites were stable. The deposition of bromine species on the catalyst is often perceived as the primary reason for decrease in activity. XPS analysis shows that the bromine contents de of Co₃O₄-B, Co₃O₄-S, and Co₃O₄-K were 1.07, 1.04, and 1.02%, respectively. The results suggested that ordered mesoporous spinel Co₃O₄ can promote the removal of bromine species from the catalyst surface and enhanced catalyst stability. Stability of Co₃O₄-K for CH₂Br₂ oxidation in the presence of 2% of H₂O or 500 ppm of PX at 250 °C was also investigated (Figure. S2), and the results suggested that Co₃O₄-K could exhibit superior stability for long-term CH₂Br₂ oxidation in the presence of H₂O, and PX, making it potential for industrial application.
Combined with the results of product analysis, and in situ DRIFT study, a reasonable mechanism for CH$_2$Br$_2$ oxidation over ordered mesoporous spinel Co$_3$O$_4$ was proposed, and the results are shown in Fig. 11: (1) adsorption of CH$_2$Br$_2$ molecules on Co active sites through Br atoms; (2) dissociation of adsorbed CH$_2$Br$_2$ through the breakage of C-Br bonds into formate species; (3) adsorption of gas-phase oxygen on the surface to supply the consumed oxygen; (4) formation of CO and CO$_2$ through the formate species oxidized by active oxygen species; and (5) the removal of adsorbed Br species from the catalyst surface in the form of Br$_2$ and HBr.

4. Conclusion

In this work, ordered mesoporous spinel Co$_3$O$_4$ were synthesized for the catalytic oxidation of CH$_2$Br$_2$ as the model pollutant for Br-VOCs. It is found that ordered mesoporous spinel Co$_3$O$_4$ exhibited superior catalytic activity than bulk spinel Co$_3$O$_4$. Particularly, Co$_3$O$_4$-K showed the highest catalytic activity, and its $T_{90}$ value was only 271°C. Meanwhile, Co$_3$O$_4$-S showed the highest selectivity to CO$_2$ at low temperature and a good stability for at least 30 h. The superior catalytic activity of ordered mesoporous spinel Co$_3$O$_4$ was related to their high specific surface areas, high content of Co$^{3+}$, and strong redox property. In situ DRIFT study showed that formate species were the main intermediate products generated on the surface of ordered mesoporous spinel Co$_3$O$_4$, and a reasonable mechanism for CH$_2$Br$_2$ oxidation over ordered mesoporous spinel Co$_3$O$_4$ was proposed. Consequently, ordered mesoporous spinel Co$_3$O$_4$ can be a promising catalyst for industrial application.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2018.10.001.

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