Synthesis of hierarchical Mg-doped Fe₃O₄ micro/nano materials for the decomposition of hexachlorobenzene

Guijin Su *, Yexuan Liu, Linyan Huang, Huijie Lu, Sha Liu, Liewu Li, Minghui Zheng
State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

HIGHLIGHTS
- Mg-doped Fe₃O₄ micro/nano material for HCB decomposition was successfully prepared.
- As-prepared MgFe₂O₄–Fe₃O₄ exhibited superior reactivity compared to Fe₃O₄.
- Doping Fe₃O₄ matrices with Mg improved the dechlorination efficiency.

ARTICLE INFO
Article history:
Received 23 May 2013
Received in revised form 24 October 2013
Accepted 31 October 2013
Available online 28 November 2013
Keywords:
Micro/nano material
Mg-doped Fe₃O₄
Hexachlorobenzene decomposition
Dechlorination efficiency

ABSTRACT
An ethylene-glycol (EG) mediated self-assembly process was firstly developed to synthesize micrometer-sized nanostructured Mg-doped Fe₃O₄ composite oxides to decompose hexachlorobenzene (HCB) at 300 °C. The synthesized samples were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, energy dispersive X-ray spectroscopy and inductively coupled plasma optical emission spectrometer. The morphology and composition of the composite oxide precursor were regulated by the molar ratio of the magnesium acetate and ferric nitrate as the reactants. Calcination of the precursor particles, prepared with different molar ratio of the metal salts, under a reducing nitrogen atmosphere, generated three kinds of Mg doped Fe₃O₄ composite oxide micro/nano materials. Their reactivity toward HCB decomposition was likely influenced by the material morphology and content of Mg dopants. Ball-like MgFe₂O₄–Fe₃O₄ composite oxide micro/nano material showed superior HCB dechlorination efficiencies when compared with pure Fe₃O₄ micro/nano material, prepared under similar experimental conditions, thus highlighting the benefits of doping Mg into Fe₃O₄ matrices.

1. Introduction
Recently, the development of three-dimensional (3D) micro/nano structures for environmental remediation applications has received much attention because the sizes and morphology of such materials, which are generally believed to be key elements that determine their physical properties, can be tuned accordingly to fit the application of interest (Zhong et al., 2006; Zhong et al., 2007). Three-dimensional (3D) micro/nano materials consist of nano-sized hierarchical building blocks while the particle size is in the micrometer scale. Unlike common nanoparticles, 3D micro/nano particles allow for easy separation and recycling. Furthermore, aggregation can be effectively prevented, thus ensuring high mass transfer and high catalytic activity. Furthermore, its comparatively large total size can probably reduce the potential toxicity resulting from intrinsic nature (e.g. their size, shape or density) of traditional nanoparticles. Diverse and highly sophisticated 3D micro/nano architectures have been prepared by different techniques based on different mechanisms (Subramanian et al., 2005; Jiang et al., 2012; Hao et al., 2013). Recently, a simple and economical polyol-mediated process has been used to synthesize a series of 3D micro/nano metal oxides such as V₂O₅, CoO₃, Fe₂O₃, CuO, and CeO₂ (Cao et al., 2005, 2006; Zhong et al., 2006, 2007). However, these studies focus on the synthesis of single oxide materials only.

An important research direction in nanoparticles synthesis is the expansion from single component nanoparticles to doped multicomponent hybrid nanostructures featuring discrete domains of different materials arranged in a controlled fashion (Holesinger et al., 2008; Li et al., 2012). Doped multicomponent composite structures benefit from superior attributes such as multifunctionality that is otherwise limited in single component materials. To our knowledge, very few investigations on the preparation of 3D micro/nano multicomponent metal oxides by the polyol process have been carried out. More specifically, the development of 3D micro/nano multicomponent materials with
controllable morphology, orientation, and structure remains a challenge to this date.

Chlorinated aromatic compounds are ubiquitous pollutants found in sediments, soil, and water (Javedankherad et al., 2013; Ozurek et al., 2013; Villanenau et al., 2013). Many of these compounds are highly toxic, difficult to degrade and easily enriched in the food chain. Because of the hazard they present to both the environment and humans, the control of chlorinated aromatic pollution is a matter of public concern. Among various chlorinated aromatic compounds, hexachlorobenzene (HCB) has been identified as a notorious organic pollutant, as listed under the “Stockholm Convention” in priority. HCB is widely used as a seed dressing to prevent fungal growth on crops, and it is also used in the production of rubber and pyrotechnics (Barber et al., 2005). Upon release into the environment, HCB can be converted to poly-chlorinated dibenzo-p-dioxins and dibenzofurans that are highly carcinogenic and mutagenic. Because of its structure and environmental hazard, HCB has often been used as a model pollutant to assess the efficiency of treatment technologies for chlorinated aromatic compounds.

Of the numerous metal oxides that have been widely examined for the catalytic degradation of chlorinated organic compounds, iron oxide is a promising material because of its non-toxicity and low-cost (Hooker and Klabunde, 1994; Morlando et al., 1997). More specifically, the magnetic properties of Fe3O4 afford easy separation from the solution medium, following treatment, via the application of an external magnetic field. In our former studies (Jia et al., 2011), we investigated 3D hierarchical flower-like iron oxide micro/nano materials that were synthesized using an ethylene-glycol (EG)-mediated self-assembly process, for the decomposition of HCB at 300 °C. It was found that as-prepared Fe3O4 micro/nano materials exhibited much higher reactivity toward the degradation of HCB than as-prepared α-Fe2O3 micro/nano material. However, the considerable amounts of lower chlorinated benzene degradation products were observed on the Fe3O4 catalyst surface. The key step for the detoxification of chlorinated organics is to destruct their chemical structure, and to reduce and remove the existence of the chlorine elements attached on the carbon backbone. Thus, there is a need to improve the dechlorination reactivity of as-prepared Fe3O4 micro/nano material toward HCB while keeping its higher degradation reactivity. Many studies have demonstrated that the reactivity of iron oxides towards chlorinated organic compounds can be increased by the addition of alkaline earth metal elements such as Mg (Jiang et al., 1998; Decker et al., 2002; Ma et al., 2005).

In this study, we investigated the use of EG-mediated self-assembly process to fabricate 3D micro/nano Mg-doped Fe3O4 composite oxides for the degradation of HCB. The morphology and composition of the hybrid oxide precursors were controlled by varying the relative concentrations of the metal salts (Mg(CH3COO)2·4H2O and Fe(NO3)3·9H2O) as the reactants during synthesis. The formation mechanism of the resulting architectures was evaluated. The synthesized Mg doped Fe3O4 composite oxides were assessed for the catalytic degradation of HCB and the performance of ball-like MgFe2O4–α-Fe2O3 were compared with those of pure Fe3O4 materials prepared using the same method.

2. Experimental

2.1. Chemicals

Hexachlorobenzene (HCB, purity 99.9%), analytic grade Fe(NO3)3·9H2O, Mg(CH3COO)2·4H2O, urea, polyethylene glycol 10000 (PEG), EG, and ethanol were purchased from Beijing Chemical Plant of China and used without further purification. Pesticide grade hexane was purchased from Fisher Scientific Inc.

2.2. Preparation and characterization of materials

Mg-Fe composite oxides were synthesized using an EG-mediated self-assembly method. A total of 0.9 g urea, 1.5 g PEG, and known amounts of Mg(CH3COO)2·4H2O and Fe(NO3)3·9H2O were added to 60 mL EG in a 250 mL round-bottom flask at room temperature. The concentration of the metal salts was fixed at 25 mM while the molar ratios of Mg(CH3COO)2·4H2O to Fe(NO3)3·9H2O were varied at 2:1, 1:1, and 1:2. The resulting mixture was stirred and heated under reflux at 230 °C, in an oil-bath, for 60 min, then cooled to room temperature. The precipitate, named as the precursor, was collected by centrifugation and washed with ethanol four times, then dried in an oven at 80 °C for 6 h. The resulting precipitate was calcined in a tube furnace at 350 °C for 3 h in 60 mL min−1 air or highly pure nitrogen.

Pure Fe3O4 and α-Fe2O3 were prepared by an EG-mediated self-assembly method, as previously reported (Zhang et al., 2006; Jia et al., 2011). Briefly, Fe(NO3)3·9H2O (25 mM), 0.9 g urea, and 1.5 g PEG were added to 60 mL EG in a 250 mL round-bottom flask at room temperature. The precipitate was collected and then calcined at 350 °C for 3 h in a tube furnace in highly pure nitrogen and air, which were identified to be Fe3O4 and α-Fe2O3. BET surface area of Fe3O4 and α-Fe2O3 are 59 m2·g−1 and 25 m2·g−1, respectively.

Characterization of the prepared samples were conducted on scanning electron microscope (SEM, Hitachi S-3000N), energy-disperse X-ray analyzer analyzer (EDX) (IXRF system, Model 550i) coupled with SEM (Hitachi, SU8020), high-resolution SEM (Zeiss Supra 55), transmission electron microscope (TEM, Hitachi-7500), high-resolution TEM (JEOL JEM-2100), X-ray powder diffractometer (XRD, X’pert Pro MPD, Cu Kα radiation), and a surface area analyzer (Micromeritics ASAP 2020). Quantification analysis of the elements in the Mg-Fe composite precursors was performed using an Optima 2000 DV model (Perkin–Elmer, USA) inductively coupled plasma optical emission spectrometer (ICP–OES). Sample solutions were prepared by dissolving the precursors in 1 M HNO3 aqueous solution.

2.3. Degradation of HCB

The degradation experiments were carried out in sealed glass ampoules with a volume of ~1.0 mL under air. 0.5 mg HCB (1754 nmol) was mixed with 50 mg of as-prepared materials and heated at 300 °C for 10 min. A blank test was also carried out without the catalysts at 300 °C for 10 min. All experiments were performed in triplicate to ensure repeatability of the results.

After the reaction, the ampoules were crushed and the reaction mixture was extracted with hexane. The extracts were analyzed on an Agilent 6890 gas chromatograph (GC) equipped with a DB-5 MS capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) and a detector (Agilent 5973 N MSD). Quantitative analyses were performed on a selected ion monitoring mode using the two most abundant ions of the molecular ion clusters.

The degradation efficiency (DgE) and dechlorination efficiency (DcE) were calculated using Eqs. (1) and (2), respectively. The result of the blank test was included into Table 1. The DgE and DcE of HCB, in the absence of catalyst, were 7% with 93% recovery. This suggested that HCB can barely be degraded in the absence of catalysts.

\[
D_{gE} = \left(1 - \frac{R_{HCB}}{I_{HCB}}\right) \times 100\% 
\]

\[
D_{cE} = \left(1 - \frac{\sum_{x=1}^{6} X \cdot R_{HCB}}{6 \cdot I_{HCB}}\right) \times 100\%
\]

where \(I_{HCB}\) (nmol) is the initial amount of HCB, \(R_{HCB}\) (nmol) is the amount of residual HCB, and \(R_{HCB}\) (nmol) is the amount of chlorinated benzenes produced after the reaction was complete.
 Decomposition of hexachlorobenzene (1754 nM) and associated degradation products over different dosage of MgFe$_2$O$_4$–Fe$_3$O$_4$ and Fe$_3$O$_4$, and in the absence of catalyst (amount of products: nM; n = 3; RSD < 10%).

<table>
<thead>
<tr>
<th>Chlorobenzenes</th>
<th>MgFe$_2$O$_4$/Fe$_3$O$_4$ (BET surface area 59.6 m$^2$ g$^{-1}$)</th>
<th>Fe$_3$O$_4$ (BET surface area 59 m$^2$ g$^{-1}$)</th>
<th>HCB blank reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1,3-DCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1,4-DCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1,2-DCB</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1,3,5-TrCB</td>
<td>ND</td>
<td>2.7</td>
<td>ND</td>
</tr>
<tr>
<td>1,2,4-TrCB</td>
<td>ND</td>
<td>10.7</td>
<td>ND</td>
</tr>
<tr>
<td>1,2,3-TrCB</td>
<td>ND</td>
<td>2.5</td>
<td>ND</td>
</tr>
<tr>
<td>1,2,4,5/-1,2,3,5-TrCB</td>
<td>ND</td>
<td>4.2</td>
<td>ND</td>
</tr>
<tr>
<td>1,2,3,4-TecB</td>
<td>ND</td>
<td>3.4</td>
<td>ND</td>
</tr>
<tr>
<td>FeCB</td>
<td>ND</td>
<td>3.3</td>
<td>22.1</td>
</tr>
<tr>
<td>HCB</td>
<td>203.7</td>
<td>0.3</td>
<td>1131.9</td>
</tr>
<tr>
<td>D$_g$(%)</td>
<td>88.4</td>
<td>~100</td>
<td>35.5</td>
</tr>
<tr>
<td>D$_e$(%)</td>
<td>88.4</td>
<td>99.1</td>
<td>34.4</td>
</tr>
<tr>
<td>ND</td>
<td>Not detected.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Diversification of precursor morphologies and compositions

The EG solution containing Mg(Ch$_2$COO)$_2$-4H$_2$O, Fe(NO$_3$)$_2$-9H$_2$O, and urea and PEG was heated at refluxing temperature 230°C for 60 min, which led to the precipitation of Mg–Fe composite oxide precursor. A series of experiments were conducted with the vailed molar ratios of two metal salts, while keeping other process parameters constant as described in the Experimental Section. It aims at revealing the effect of the initial molar ratios on the compositions and morphologies of the synthesized Mg–Fe composite oxide precursors. The obtained results are presented in Fig. 1. A mixture of cube-like and non-defined structures, as seen in Fig. 1a, were obtained when the molar ratio of Mg(Ch$_2$COO)$_2$-4H$_2$O to Fe(NO$_3$)$_2$-9H$_2$O was set at 2:1. The precursor was essentially composed of carbon, iron, magnesium, and oxygen as seen in the EDX spectra in Fig. 1b. This confirms the coexistence of Mg and Fe in the precursor. ICP–OES, which is ideal for quantification of elements based on a macroscopic analysis, was used to determine the Mg/Fe ratios in the precursors. The analysis results showed that Mg/Fe atomic ratio in this precursor is around 1:1.5 (Table S1). The observed atomic ratio values were lower than that at 2:1 in the two metal salts. When the molar ratio of Mg(Ch$_2$COO)$_2$-4H$_2$O to Fe(NO$_3$)$_2$-9H$_2$O was adjusted to 1:1, the precursor adopted the uniform ball-like configuration in shape with the minimal surface energy, as observed in Fig. 1c. The particles displayed a high degree of monodispersity because of the spherical configuration, resulting in very small contact areas between the particles (Bain et al., 2008). EDX spectroscopy in Fig. 1d shows that the precursor still consists of carbon, iron, magnesium, and oxygen, which indicates both Mg and Fe still coexist in the precursor. This set of particles displayed a similar EDX pattern (Fig. 1d) to the one described above. The Mg/Fe atomic ratio determined by ICP–OES was about 1:12, which is less than that at 1:1 in the two metal salts as well. A change in morphology, to a flower-like configuration, resulting in very small contact areas. The number of experiments confirmed that the precursors synthesized by EG-mediated method are made of the metal alkoide, which is the results of the coordination and subsequent oligomerization of EG with the metal ions. The representative XRD pattern of the Mg–Fe composite oxide precursor in Fig. 2e showed two peaks in the low-angle region at ca. 10° and 17°. These two peaks are often found in organometallic precursors synthesized by a similar polyol-mediated process (Fuls et al., 1970; Larcher et al., 1998, 2003; Wang et al., 2003; Jiang et al., 2004; Chakroune et al., 2005), which is indicative of the formation of a metal alkoide. In particular, the strong peak located at ca. 10° is a characteristic feature of the occurrence of coordination and oligomerization processes in EG (Wang et al., 2003; Jiang et al., 2004). This type of organic precursors is generally characterized by stacked metal–oxygen sheets separated by bonded alcoholate anions. The XRD pattern suggests the presence of interlayer spacings in lamellar structures. According to the reported results regarding metal alkoxides (Fuls et al., 1970; Larcher et al., 1998, 2003; Wang et al., 2003; Chakroune et al., 2005), the characteristic strong peak at 10° can be indexed as (001). The interlayer distance was evaluated to be 8.17 Å, which is comparable to those of iron alkoxides (8.11 Å) (Fuls et al., 1970), cobalt alkoxide with 8.31 Å (Chakroune et al., 2005), and manganese alkoxide with 8.32 Å (Larcher et al., 1998).

3.2. Ball-like precursor

Based on the findings discussed above, further analysis was carried out on the ball-like structured precursor since such a structure has the uniform morphology and markable coexistence of Mg and Fe entities. As seen in Fig. 2a, the high-resolution SEM image in the large scale showed that the diameter of the ball-like precursor varied in the range of 0.4–1.0 μm (Fig. 2a). High-resolution SEM image magnified from the individual ball-like architecture in Fig. 2b clearly reveals that its surface is covered by the accumulation of cladate structure with the length less than 100 nm. The surface of the cladate structure is relatively smooth, which is believed to occur through Ostwald ripening (Cheng et al., 2005). TEM image in Fig. 2c shows the very dense structure of the ball-like precursor particles. High-resolution TEM image, which was conducted on the edge of the ball-like precursor particles, as shown in Fig. 2d, revealed that the particles were mostly amorphous with weak lattice fringes occasionally observed in localized areas. The number of experiments confirmed that the precursors synthesized by EG-mediated method are made of the metal alkoide, which is the results of the coordination and subsequent oligomerization of EG with the metal ions. The representative XRD pattern of the Mg–Fe composite oxide precursor in Fig. 2e showed two peaks in the low-angle region at ca. 10° and 17°. These two peaks are often found in organometallic precursors synthesized by a similar polyol-mediated process (Fuls et al., 1970; Larcher et al., 1998, 2003; Wang et al., 2003; Jiang et al., 2004; Chakroune et al., 2005), which is indicative of the formation of a metal alkoide. In particular, the strong peak located at ca. 10° is a characteristic feature of the occurrence of coordination and oligomerization processes in EG (Wang et al., 2003; Jiang et al., 2004). This type of organic precursors is generally characterized by stacked metal–oxygen sheets separated by bonded alcoholate anions. The XRD pattern suggests the presence of interlayer spacings in lamellar structures. According to the reported results regarding metal alkoxides (Fuls et al., 1970; Larcher et al., 1998, 2003; Wang et al., 2003; Chakroune et al., 2005), the characteristic strong peak at 10° can be indexed as (001). The interlayer distance was evaluated to be 8.17 Å, which is comparable to those of iron alkoxides (8.11 Å) (Fuls et al., 1970), cobalt alkoxide with 8.31 Å (Chakroune et al., 2005), and manganese alkoxide with 8.32 Å (Larcher et al., 1998).

3.3. Proposed mechanism for the precursor formation

The growth mechanism of the nanomaterial precursor remained an open question despite the great achievements in the
preparations and applications of the nanomaterials. Based on the comprehensive findings from SEM, EDX, XRD and ICP–OES, a probable mechanism for the formation of Mg-doped Fe composite oxide precursor is proposed. The illustration of the formation mechanism for ball-like Mg–Fe composite oxide precursor, as an example, is illustrated in Scheme 1 (Wang et al., 2003; Jiang et al., 2004). The slightly lower Mg/Fe atomic ratio value observed for the precursor particles relative to that in the initially added metal salts might be due to the competitive coordination reactions of EG with Mg$^{2+}$ and Fe$^{3+}$. Typically the chemistry of the coordination complexes is dominated by interactions between a central atom or ion and the ligands via coordinate covalent bond. In such coordination complexes, the central atom or ion acts as an electron-pair acceptor (Lewis acid) and the ligand acts as an electron-pair donor (Lewis base). Fe$^{3+}$ is known to be a very strong Lewis acid. As a result, Fe$^{3+}$ coordinates more easily with EG than Mg$^{2+}$ does. The formed complexes eventually form longer chains via an oligomerization process, and further self-assemble into the morphological structures through van der Waals interactions (Wang et al., 2003).

3.4. Preparation and characterization of Mg-doped Fe composite oxides

Subjecting metal alkoxides to a thermal treatment is a simple route to synthesize metal oxides (Larcher et al., 2003). However, the calcination conditions, such as atmosphere, can highly influence the phase composition of the products. The effect of the calcination atmosphere (nitrogen or air) on the formation of Mg-doped Fe composite oxides using the ball-like precursor was examined. Fig. 3a shows the wide-angle XRD pattern of the resulting Mg-doped Fe composite oxides calcined in air. However, the resulting Mg-doped Fe composite oxides featured $\alpha$-Fe$_2$O$_3$ (JCPDS 80-2377) and MgFe$_2$O$_4$ (JCPDS 88-1936) crystalline phases. If the atmosphere was switched to nitrogen, the diffraction peaks of the calcined product in Fig. 3b matched those for the mixture of MgFe$_2$O$_4$ with Fe$_3$O$_4$ instead of $\alpha$-Fe$_2$O$_3$. The formation of MgFe$_2$O$_4$ was reported to be attributed to the reductive ability of the organic species (glycolates) in the precursor under nitrogen protection (Zhong et al., 2006). The relatively
Fig. 2. (a) SEM, (b) high-resolution SEM, (c) TEM and (d) high-resolution TEM images of the Mg–Fe composite oxide precursor, prepared with a 1:1 molar ratio of Mg(CH₃COO)₂·4H₂O to Fe(NO₃)₃·9H₂O and (e) the associated XRD pattern.

Scheme 1. Schematic illustration of the formation mechanism for ball-like Mg–Fe composite oxide precursor.
broad diffraction peaks indicate that the MgFe₂O₄–Fe₃O₄ structured materials are composed of very small crystallites. The diffraction peaks of Fe₃O₄ coincide with those of MgFe₂O₄, which might be due to the same cubic spinel configurations in both oxides. The specific surface areas of MgFe₂O₄–Fe₃O₄ was measured at 59.6 m²/g, which is higher than that of MgFe₂O₄–α-Fe₂O₃ at 31 m²/g. Fig. 4 reveals the morphological feature of MgFe₂O₄–Fe₃O₄ after the calcination 3 h in nitrogen, the subsequent calcination had no noticeable effect on the total superficial morphology of the material. The initial ball-like morphology of precursor was well-preserved and the particles also featured clavate-like structures on the surface (Fig. 4a), as discussed earlier. The preservation of superficial morphology after the calcination has been reported during the preparation of single oxides such as Co₃O₄, CuO, and CeO₂ using EG-mediated approaches (Cao et al., 2006, 2007; Zhong et al., 2007). However, TEM imaging revealed the development of a highly porous structure, following calcination, consisting of interconnected nanoparticles with diameters of less than 50 nm, as observed in Fig. 4b. This is likely due to the pyrolysis of organic species during the calcination treatment (Zhong et al., 2006).

High-resolution TEM imaging also revealed the presence of two distinct sets of lattice fringes with spacings of 0.25 nm and 0.29 nm that correspond to the (3 1 1) and (2 2 0) planes of the cubic spinel structure, respectively (Fig. 4c and d). Hence, 3D hierarchical ball-like Mg-doped Fe₃O₄ micro/nano materials were successfully prepared under a reducing nitrogen atmosphere.

Based on the result obtained above, the majorly cube-like and flower-like precursors prepared by using Mg(CH₃COO)₂·4H₂O:Fe(NO₃)₃·9H₂O molar ratios of 2:1 and 1:2, were calcined selectively in highly pure nitrogen to obtain Mg-doped Fe₃O₄ composite oxides with different morphology.

3.5. Activity measurement

The degradation of HCB over the ball-like, majorly cube-like and flower-like Mg-doped Fe₃O₄ composite oxides, which were obtained by calcinating in nitrogen the precursors prepared by varying Mg(CH₃COO)₂·4H₂O:Fe(NO₃)₃·9H₂O at 1:1, 2:1 and 1:2, were carried out at 300 °C for 10 min. The degradation products were identified by GC–MS. Various chlorinated benzenes, including pentachlorobenzene (PeCB), three tetrachlorobenzenes (1, 2, 4, 5-TeCB, 1, 2, 3-TeCB, 1,2,3,4-TeCB), and three trichlorobenzenes (1,3,5-TrCB, 1,2,4-TrCB, 1,2,3-TrCB), were detected as the degradation products.
products. The detection of varying types of chlorinated benzenes indicates that HCB undergoes a stepwise hydrodechlorination process during decomposition. From Table S2, one can observe that the ball-like Mg-doped Fe3O4 prepared at a 1:1 molar ratio of Mg(CH2COO)2·4H2O:Fe(NO3)3·9H2O, exhibited slightly lower but noticeably higher DGE and DCE than majorly cube-like and flower-like Mg-Fe composite oxides prepared with 2:1 and 1:2 molar ratio of the metal salts, respectively. The reactivity of three types of materials which were prepared by varying the Mg(CH2COO)2·4H2O:Fe(NO3)3·9H2O at 2:1, 1:1 and 2:1, was likely affected by their different morphologies and content of Mg dopants. The morphological effect on the reactivity has been reported by Lin et al. (2011) that cabbage-like Co3O4 exhibited the higher reactivity than one with both the cabbage-like and plate-like morphologies toward the degradation of 1,2,4-trichlorobenzene. However, the ball-like Mg-doped Fe3O4 with relatively higher reactivity was proposed for the treatment of chlorinated aromatics, due to the architecture stability with easy preparation.

The activity of 3D hierarchical ball-like MgFe2O4–Fe3O4 toward HCB degradation at 300 °C for 10 min, was further compared with that of pure Fe3O4, as shown in Table 1, and with those of ball-like MgFe2O4–α-Fe2O3 and pure α-Fe2O3, as shown in Table S3. With the dosage of the materials at 50 mg, the MgFe2O4–Fe3O4 composite oxides achieved DGE of ~100%, which was slightly higher than that of Fe3O4 (93.7%)(Table 1). However, the MgFe2O4–Fe3O4 composite oxides achieved a superior DCE of 99.1%, in comparison with the single oxide Fe3O4 (62.2%), thereby highlighting the benefits of Mg doping in the Fe3O4 matrices. (Fig. 5 compared the typical GC–MS chromatograms, following the degradation reaction of HCB by 50 mg MgFe2O4–Fe3O4 and 50 mg Fe3O4). Mg dopants improved the reactivity toward the degradation of HCB. Mg dopants not only improved the dechlorination efficiency, but also maintained high HCB degradation efficiencies. This phenomena is even more evident if the dosage of MgFe2O4–Fe3O4 and Fe3O4 reduced from 50 mg to 5 mg for the degradation of HCB with the amount fixed at 1754 nM. Both DGE and DCE of HCB over 5 mg Mg-doped Fe3O4 reached 88.4%, which are significantly higher than those over 5 mg Fe3O4 with 35.5% and 34.4%. On the other hand, the benefits of Mg dopant can be also reflected by the higher DGE and DCE of HCB over MgFe2O4–α-Fe2O3 than those over pure α-Fe2O3 (Table S3). However, both DGE and DCE of HCB over MgFe2O4–α-Fe2O3 are much lower than those over MgFe2O4–Fe3O4. Therefore, as expected, the ball-like Mg-doped Fe3O4 herein developed are advantageous for the degradation of HCB.

The results obtained above suggested that, the surface properties of the Mg doped Fe3O4 may be different from that of Fe3O4 before doping. A similar case has been reported by Liu et al. that the impurities of silicon and phosphorous within titanium dioxide nanoparticles change the surface charge and electrostatic interaction of nanoparticles (Liu et al., 2011). Lin et al. also found that the cerium in the cobalt oxide nanomaterial could improve the mobility of the oxygen on the surface (Lin et al., 2012). The higher reactivity of alkaline earth metal-iron composite oxides relative to iron oxide towards chlorinated organic compounds has been reported to be attributed to the Cl−/O2− exchange (Jiang et al., 1998; Decker et al., 2002; Ma et al., 2005). Mg dopants are thought to improve a chlorine ion sink during the dechlorination process of HCB over Mg-doped Fe composite oxide (Ma et al., 2005). Coordination theory shows that metallic ions (Lewis acid) on the surfaces of metal oxides are unsaturated and are prone to bond with ligands (Lewis base). It was tentatively hypothesized that HCB molecules adsorbed on the surface of MgFe2O4–Fe3O4 via the coordination interaction between the iron ions (strong Lewis acid) and Cl (Lewis base). This step was followed by the breakage of C–Cl bond and the simultaneous production of chlorine ions on iron ion sites during the heating process. The newly formed chloride ion may migrate over the Mg-doped composite oxide surface. This behavior has been confirmed during the destructive adsorption of CCl4, CHCl3 and C2H4Cl2 over the core–shell nanoparticles of Fe3O4/MgO, Fe2O3CoO, and V2O5/MgO (Jiang et al., 1998; Decker et al., 2002). The chloride ions may travel along the surfaces of the Cl⋅−/O2− exchange jump, i.e. anion replacement readily occurred, probably as a consequence of surface migration (Jenny and Overstreet, 1939). Ion exchange occurs whenever an ion enters the oscillation volume of another ion, provided conditions for ion exchange are satisfied. The mobile chloride ion may then be deposited onto Mg2+ sites. The occurrence of such process may be due to the lower ΔHf of MgCl2 (~642 kJ/mol) relative to that of FeCl3 (~405 kJ/mol) (Koper et al., 1993), which results in a higher thermodynamic stability of the former than the latter. The removal of chlorine from the carbon backbone is repeated. Hence, the dechlorination process has been accelerated. The direct reaction of Mg dopants with HCB resulting in its dechlorination may coexist as well. The reactivity of Mg doped Fe3O4 could be also affected by the morphology and content of Mg dopants. However, further work is required to fully understand the increased dechlorination activity as displayed by the Mg-doped Fe3O4 materials.

4. Conclusion

Mg-doped Fe3O4 composite oxides, with a 3D hierarchical micro/nano structure, were synthesized via a simple EG-mediated self-assembly route, and assessed for the decomposition of HCB at 300 °C. By varying the molar ratios of Mg(CH2COO)2·4H2O to Fe(NO3)3·9H2O as the reactants, both the morphology and composition of the composite oxide precursor were readily tuned. The Mg/Fe atomic ratio in the precursors is rather lower than their initial molar ratios in two metal salts. The relative decrease of the molar ratio was attributed to the likelihood of weaker coordination reactions of EG with Mg2+ than with Fe3+. Mg-doped Fe3O4 composite oxides micro/nano materials were obtained by calcination of the precursor particles under a reducing nitrogen atmosphere. Their reactivity toward HCB decomposition was likely influenced by the morphology and content of Mg dopants. HCB decomposition by 3D hierarchical ball-like MgFe2O4–Fe3O4 and pure Fe3O4 was compared. Relative to 3D hierarchical MgFe2O4–Fe3O4, MgFe2O4–Fe3O4 showed superior dechlorination performances towards the degradation of HCB, demonstrating the importance of doping Fe3O4 matrices with Mg on facilitating the dechlorination processes.

Fig. 5. GC–MS chromatogram showing the degradation products following decomposition of HCB with nanomaterials at 300 °C for 10 min by (a) MgFe2O4/Fe3O4 and (b) Fe3O4.
Acknowledgements

This study was supported by the Chinese Academy of Sciences (Grant No. KZCX2-YW-QN407), the National 863 Program (2012AA062803), the National Natural Science Foundation of China (2087049, 51078346, 21177141), the Project sponsored by SRF for ROCS, SEM, and Youth Innovation Promotion Association, CAS.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.10.090.

References


G. Su et al. / Chemosphere 99 (2014) 216–223


