Synthesis and adsorption properties of mesoporous MgAl2O4 spinel fibers by coaxial electospinning

Wen-Ling JI¹, Heng-Yong WEI¹,², Hui LI¹, Yi CUI¹, Shi-Lei HU¹, Pan LIU¹, Jing-Long BU¹, Jin-Meng YANG¹ and Ran WANG¹

¹College of Materials Science and Engineering, Hebei Provincial Key Laboratory of Inorganic Nonmetallic Materials, North China University of Science and Technology, Tangshan 063009, Hebei, China

Mesoporous magnesium aluminate (MgAl2O4) spinel fibers were prepared using a coaxial electospinning technique. The phase composition, porous structure and adsorption performance of the mesoporous MgAl2O4 spinel fibers were investigated. Differential thermal/thermo-gravimetric and X-ray-diffraction analysis revealed that gel fibers began to crystallize into the MgAl2O4 spinel phase at 700°C and became fully crystallized at 900°C. The morphology changes in the fibers were tracked by use of a scanning electron microscope and transmission electron microscope, which showed fibers with a mesoporous structure formed at 900°C. The Brunner-Emmet-Teller specific surface area of MgAl2O4 spinel fibers is 36.95 m²/g. In addition, the dye adsorption capacity of the fibers shows an adsorption percentage of over 80.0 % in 20 mg/l methylene blue after 2 min of adsorption. The kinetic study demonstrated that the adsorption data fit the pseudo-second-order kinetic model more naturally.

Key-words : MgAl2O4 fibers, Mesoporous, Electrospinning, Adsorption

1. Introduction

Due to their good chemical inertness and catalytic and adsorption properties, magnesium aluminate spinel (MgAl2O4) materials have been widely applied as adsorbents in waste-water treatment, especially for the removal of organic dyes.1) Compared with materials traditionally used for environmental remediation, MgAl2O4 spinel has a relatively complicated structure and positive potential in a wide range of pH, which can lead to longer life-times and better adsorption performance under acidic conditions.1)–3) MgAl2O4 spinel materials are thus in great demand as adsorbents. Apart from good chemical stability and excellent structural characteristics, a large specific surface area is a vital factor in improving the adsorption capacity of materials.3) Thus, mesoporous MgAl2O4 spinel materials with their large surface area, uniform pore size and large pore volume can be regarded as promising materials for environmental purification.

To date, the morphology of porous MgAl2O4 spinel materials used as adsorbents has mainly been powder.1)–4) Powder adsorbents are difficult to recover and recycle, however which adds unnecessary cost to their practical application. Compared with powder adsorbents, fibers are easy to recover after adsorption.5) Fibers materials have also attracted increased attention for adsorption applications due to their large length-to-diameter ratio and high surface-to-volume ratio, moreover, which could enhance their adsorption rate and capacity.6) 7) When it comes to practical environmental purification application, therefore, fiber materials are superior to the conventional powders, because fibers can be removed from liquid phases very easily and have large adsorption properties due to their one-dimensional structure.8),9) It is difficult to obtain porous MgAl2O4 fibers using conventional preparation methods, however, such as sol–gel pulling and extrusion processes.10),11)

Increasing attention has been paid to synthesizing porous ceramic fibers with coaxial electospinning techniques recently, because of their characteristics as simple processes with high efficiency and relatively.12) The advantages of coaxial electrospinning fibers lie in their large specific surface areas, ultrafine diameters, and abundant porosity, which can improve the application performance of the fibers as attractive candidates for absorption, filtration, thermal insulation and biomedical materials.13),14)

Mesoporous magnesium aluminate spinel fibers were therefore synthesized using the coaxial electrospinning method, and their adsorption performance with respect to methylene blue was investigated.

2. Experimental

2.1 Materials

The raw materials used in the experiment were anhy-
drous magnesium chloride (MgCl₂), anhydrous aluminum chloride (AlCl₃), methylene chloride (CH₂Cl₂), polyvinylpyrrolidone (PVP, Mn = 1300000), Triblock copolymer (P123, Mn = 5800), absolute ethyl alcohol (EtOH), liquid paraffin and N,N-dimethylformamide (DMF). All of the reagents were of analytically pure grade.

2.2 Preparation of precursor sol solution
To prepare magnesium aluminate spinel precursor gel, 0.56 g of MgCl₂ powder with 1.6 g of AlCl₃ powder were entered into a beaker, after which 60 ml of CH₂Cl₂ and 2.0 ml of C₂H₅OH were slowly dropped into the beaker. The solution was stirred by magnetic stirrer until the powders were completely dissolved. The precursor sol solution was then taken placed in an oven, and heated from room temperature to 110°C for 5 h. After that, 4 g of PVP was added to 64 ml of anhydrous ethanol, to which 4 ml of DMF was then added to obtain the mixture solution. Finally, the precursor gel as-prepared was poured into the solution and the precursor sol solution was prepared by stirring for about 1 h at room temperature.

2.3 Fiber preparation
A coaxial electrospinning apparatus was set up horizontally. The precursor sol solution was entered into a glass syringe (30 ml) and liquid paraffin was dropped into another glass syringe. The two glass syringes were connected to the six coaxial nozzles of concentric rings using plastic piping. The liquid paraffin was injected into the exterior of the coaxial nozzles and the precursor sol solution was injected into the exterior of the coaxial nozzles by microsyringe pump (78-9100C Cole Parmer Instrument Company), respectively. The precursor sol solution flow rate was fixed at 3.0 ml/h and the paraffin wax flow rate was fixed at 0.2 ml/h. An aluminum collector and syringe needle were placed 15 cm apart under a constant voltage of 24.0 kV. The magnesium aluminate spinel precursor/PVP composite fibers were collected on the aluminum foil. The composite fibers were calcined between at 500 and 900°C for 1 h at the heating rate of 3 °C min⁻¹.

2.4 Adsorption studies
Adsorption experiments were performed with 0.175 g of mesoporous MgAl₂O₄ nanofibers added to 50 ml of the dye solution. The absorption spectra in concentrations of the methylene blue solution were determined through an ultraviolet–visible adsorption spectrophotometer at regular intervals. The calibration curves of the methylene blue were acquired by testing the absorbance values of its predetermined concentrations. The absorption spectrums of the filtrates were measured under the maximum absorption wavelength (628.5 nm) of methylene blue. All the tests were conducted at room temperature.

2.5 Characterization
The thermal performance of precursor/PVP composite fibers was measured with a differential thermal/thermo-gravimetric analyzer (DTA-TG, NETZSCH STA449C, Germany), with heating from room temperature to 1000°C at a rate of 10°C min⁻¹. The phase analysis of fibers was studied by X-ray-diffraction (XRD, D/MAX2500PC, Rigaku Corporation, Japan). Scans were conducted from 10 to 80° (2θ) at a speed of 10 °min⁻¹. Investigation of the fiber morphology was conducted with a scanning electron microscope (SEM, S-4800, Japan) and a transmission electron microscope (TEM, JEM-2010, Japan), respectively. Fourier transform infrared spectroscopy (FT-IR) studies were carried out on the facility (VERTEX70, Germany) using the KBr pellet method with a spectrophotometer ranging from 400 to 4000 cm⁻¹. The specific surface areas and pore sizes of the fibers obtained at 900°C were measured on an ASAP 2010 by the method of Brunner-Emmet-Teller (BET). Batch adsorption experiments were conducted and recorded by ultraviolet–visible spectra (SPECORD S600, Germany).

3. Results and discussion
Figure 1 shows an endothermic peak and two exothermic peaks on the DTA curve, which corresponding to the TG curve demonstrate that weight was lost in three main steps. As can be seen, the first step shows an endothermic peak at about 124°C accompanied by weight loss of about 30%, which is attributed to the decomposition of precursor gels. The second step appears a weak exothermic peak at about 463°C and corresponds to a fast rate of mass loss of about 48%. This is due to the removal of organic groups and paraffin in the precursor fibers. In addition, the formation of a periclase phase may occur at this stage. A wide endothermic peak between 600 and 800°C with no obvious weight loss in this step may be ascribed to a solid-state reaction between Al₂O₃ and MgO to form a MgAl₂O₄ phase. There is no significant change in the DTA curve at above 800°C.

Figure 2 exhibits the XRD spectra of the precursor fibers heat-treated at different calcination temperatures for 1 h. The XRD peaks of the precursor fibers heat-treated at 500°C indicate the mainly formed periclase phase. In addition, the XRD pattern shows a gradual crystallization of the MgAl₂O₄ spinel phase. When the calcination temperature was increased to 700°C, the MgAl₂O₄ spinel appeared, which was consistent with the DTA result. The
MgAl$_2$O$_4$ spinel phase formed at relatively low temperatures may be attributed to reaction of Mg$^{2+}$ and Al$^{3+}$ ions through coordination polymerization to achieve uniform distribution in the precursor gels.\(^{18,19}\) Well-defined diffraction peaks of MgAl$_2$O$_4$ were detected, moreover, which gradually became stronger with increases in the temperature to 900°C. This suggests that increasing the calcination temperature can improve the crystallinity of the MgAl$_2$O$_4$ phase.

Figure 3 displays FT-IR spectra of MgAl$_2$O$_4$ precursor fibers and MgAl$_2$O$_4$ spinel fibers obtained at different temperatures: 500, 700 and 900°C. MgAl$_2$O$_4$ spinel phase formed at relatively low temperatures may be attributed to reaction of Mg$^{2+}$ and Al$^{3+}$ ions through coordination polymerization to achieve uniform distribution in the precursor gels.\(^{18,19}\) Well-defined diffraction peaks of MgAl$_2$O$_4$ were detected, moreover, which gradually became stronger with increases in the temperature to 900°C. This suggests that increasing the calcination temperature can improve the crystallinity of the MgAl$_2$O$_4$ phase.

Figure 3 displays FT-IR spectra of the fibers prepared at various temperatures. The analysis of samples contains a broad band at about 3400 cm$^{-1}$ and a band about at 1650 cm$^{-1}$, which correspond to the O–H stretching vibrations and H$_2$O deformation vibrations, respectively.\(^{15}\) This may be due to exposure of the samples to ambient humidity during operational testing.\(^{20-22}\) In the precursor fibers, bands appearing within the range of 1500–1200 cm$^{-1}$ were caused by vibration of the organic group, including the CH$_2$ and CH$_3$ stretching modes of PVP.\(^{23}\) The intensities of these organic vibration peaks decreased with increased in the calcination temperature, clearly indicating that organic matter was gradually removed from the samples, which is well consistent with the DTA-TG curve. For the sample calcined at 700°C, all organic bands disappeared and two new high-frequency absorption peaks appeared at about 518 and 692 cm$^{-1}$, which are related to the AlO$_6$ octahedra\(^{24}\) and Mg–O stretching.\(^{25,26}\) This demonstrated that the crystalline phase of MgAl$_2$O$_4$ spinel could be formed at this temperature. In addition, the bands related to Mg–O–Al became stronger at higher calcination temperatures.\(^{27}\)

The SEM micrographs shown in Fig. 4 reveal the microstructure of the prepared fibers, which changed significantly with increasing calcination temperatures. The surfaces of the precursor fibers are very smooth and the diameters of this fibers were concentrated mainly at about 500 nm. After calcination at 500°C, the fibers became thinner with uniform diameters of about 280 nm. This phenomenon is due to the decomposition and evaporation of paraffin, PVP and inorganic salts. The diameters of the fibers became slightly coarse with increasing in the calcination temperatures up to 700°C, which was probably caused by a slight volume expansion in the processing of periclase into spinel. When the calcining temperature was increased further to 900°C, a porous structure appeared to some degree on the fiber surface.

To explore the pore size distribution of the MgAl$_2$O$_4$ spinel fibers calcined at different temperatures, BET tests were conducted to study the specific surface areas and porosity of the fibers. As can be seen from Fig. 5(a), the hysteresis loops were all composed of an adsorption isotherm with a steady rise and a desorption isotherm with a steep drop, which revealed the existence of remarkable mesoporous structures in the fibers.\(^{29}\) In addition, N$_2$
adsorption isotherms of the fibers obtained at 500, 700 and 900°C were identified as type IV isotherms with a rapid increase of the adsorption capacity at $P/P_0 = 0.3, 0.4, 0.6$, respectively, demonstrating once again the existence of well-developed mesopores in the MgAl$_2$O$_4$ spinel fibers. The specific surface areas of the fibers calcined at 500, 700 and 900°C were 93.30, 59.14 and 36.95 m$^2$/g, respectively, according to the BET analysis shown in Table 1. A large specific surface area appeared in the fibers calcined at 500°C because of the removal of PVP and phase-separation solvent (liquid paraffin). A decline in the specific surface areas of the fibers at from 500 to 900°C may be ascribed, however, to grain growth and cross-linking of pores at high temperatures. The grain growth could cause some small pores to become cross-linked with each other and incorporated to form large pores, which is conductive to dye diffusion.

Based on the above results, the MgAl$_2$O$_4$ spinel fibers were found to have a mainly mesoporous structure. The schematic process of coaxial electrospinning is demonstrated in Fig. 6. Liquid paraffin was injected into the interior of the coaxial nozzles and precursor solution was injected into the exterior of the coaxial nozzles simultaneously by microsyringe pump. The two kinds of immiscible fluid formed cylinder-shaped compound fluid jets according to the structure of the original nozzles. Under sufficiently high electric field conditions, the precursor and paraffin immiscible compound droplets can be ejected in a trickle by overcoming the surface tension, and the droplet jet can then be stretched and a large quantity of solvent rapidly vaporized. Meanwhile, as there are difficulties in miscibility between the precursor and paraffin, liquid paraffin may be randomly distributed in precursor droplets during the stretching process, and a specific structure thus formed via phase separation. When a charged droplet jet was ejected on the collecting plate, paraffin core/precursor shell structure composite fibers were formed. Mg$_2$Al$_2$O$_4$ spinel fibers with a porous structure can thus be obtained by high-temperature calcination to remove the organic and liquid paraffin.

What is more, the fibers calcined at 900°C are purer than the fibers prepared at 700°C, although the surface area of the latter is slightly higher. The following analysis of TEM and the adsorption experiments were therefore implemented for a typical sample (MgAl$_2$O$_4$ spinel fibers calcined at 900°C).

The TEM micrographs and selected area electron diffraction pattern (SAED) of a typical sample are shown in Fig. 7. It can be seen that these fibers were composed of nanoparticles, the average size of which was 20 nm. These small nanoparticles connected mutually to form mesoporous fibers. The TEM images show abundant pore structures accumulated by nanoparticles in the fibers, with
most of the pore diameters measuring about 10 nm. The SAED pattern shows clear diffraction rings, which confirm that the MgAl$_2$O$_4$ spinel fibers have a crystalline structure.

The as-prepared MgAl$_2$O$_4$ spinel porous fibers have potential applications in the adsorption field because of their special mesoporous structure. Here, the fibers obtained at 900°C are tested for their adsorption performance with respect to methylene blue. Figure 8(a) depicts the methylene blue adsorption process employing MgAl$_2$O$_4$ spinel porous fibers. The percentage of methylene blue removal from its solution was tested by ultraviolet visible adsorption spectroscopy at specified time intervals. The obvious absorbance decrease indicated that MgAl$_2$O$_4$ spinel fibers have excellent dye adsorption performance. This might result from the large pore size of the mesoporous fibers as well as from their small diameters, which enable the methylene blue molecules to enter rapidly. In addition, the fibrous configuration can also enhance the capture probability, which may benefit from the interconnected voids formed by entanglement of the fibers. The absorbance of methylene blue at around 628.5 nm was used to account quantitatively for the adsorption characteristics. In addition, the removal rate ($\mu$) was calculated by the following equation:

$$\mu = \frac{C_0 - C_t}{C_0} \times 100\%$$

where $C_0$ and $C_t$ represent the concentrations of methylene blue before and after time $t$, respectively. The original concentration of methylene blue $C_0$ was 20 mg/l. The relationship between the removal rate of methylene blue and the adsorption time is shown in Figure 8(b). As can be seen, the whole adsorption process can be divided into two steps for description. The first step shows that the adsorption rate was very high and that methylene blue was adsorbed almost immediately, with about 80.0% adsorbed within 2 min. In the second step, the adsorption percentage increased very slowly over between 2 and 40 min. When the adsorption time reached 40 min, about 89.6% of the methylene blue had been removed from the solution. This result shows that the first stage is rapid adsorption and the second is gradual adsorption.

The relative adsorption capacity is evaluated below:

$$q_{ads} = \frac{(C_0 - C_t) \cdot V}{m}$$

where the adsorption quantity, $q_{ads}$ (mg/g) was calculated by the original concentration $C_o$ (mg/l), concentration after anytime $t$, $C_t$ (mg/l), solution volume, $V$ (l) and the fiber quality, $m$ (g).

This calculation revealed that the adsorption capacity increased sharply until it almost became a constant and that the maximum adsorption was 5.121 mg/g at 40 min. Possibly as a result of the pore sizes and the total volume of the fibers’ pores, relatively large, straight tunnels can make the methylene blue enter the porous fibers rapidly. In addition, the concentration gradient between the solution and solvent makes methylene blue pass through the mesoporous channels so quickly in the beginning.

To compare the adsorption properties of MgAl$_2$O$_4$ spinel fibers with those of powders, mesoporous MgAl$_2$O$_4$ spinel powders were prepared by the method reported in our previous work. During this process, 1.5 g of P123 was added as a template to a solution of C$_2$H$_5$OH and CH$_2$Cl$_2$. The morphologies of the MgAl$_2$O$_4$ spinel powders obtained at 900°C are shown in Figure 9. It was found that the MgAl$_2$O$_4$ spinel powders were approximately spherical and that the average particle size was about 20 nm. Some mesoporous structures also appeared in spherical particle agglomeration. Figure 10 displays the N$_2$ ad/desorption and pore size distribution of the as-prepared MgAl$_2$O$_4$ nanowires. The isotherm was classified as type IV and the hysteresis loop as type H3, both typical of mesoporous structures. The pore sizes of the powders were mostly concentrated at 12 nm, which was similar to
the size of the mesoporous MgAl\textsubscript{2}O\textsubscript{4} spinel fibers. Thus, the adsorption performance of the MgAl\textsubscript{2}O\textsubscript{4} spinel powders was measured by the same absorption experiment as shown in Fig. 11. It showed that about 69.6\% of the methylene blue was absorbed quickly in two minutes and that the maximum removal rate was 74.2\% at equilibrium. These suggested that the adsorption ability of as-prepared MgAl\textsubscript{2}O\textsubscript{4} powders was lower than that of the fibers. These results indicated that the interconnected voids formed from entanglement of the fibers might improve the adsorption probability.\textsuperscript{30}

The adsorption data for the MgAl\textsubscript{2}O\textsubscript{4} spinel fibers synthesized at 900°C were obtained by fitting to various isotherm models and through comparison of $R^2$ values. The experimental data clearly conform to the Freundlich model. The equation for the Freundlich isotherm is given below:\textsuperscript{1),34}

\[
\ln q_{\text{ads}} = \ln K_F + \frac{\ln C_{\text{eq}}}{n}
\]

where $C_{\text{eq}}$ (mg/l) represents the concentration at equilibrium. From Fig. 12, $lnq_{\text{ads}}$ (mg/g) shows an approximately linear relationship with $lnC_{\text{eq}}$ (mg/l), which agrees with the equation. $K_F$ is a constant used to represent the degree of adsorption. In addition, $n$ may be considered to be a heterogeneous factor associated with the fitting value of 2.67. The value of $n$ describes the adsorption characteristics and $n > 1$ expresses its support for interaction adsorption.\textsuperscript{1)}

Research on the kinetics of the data obtained was conducted by studying the adsorption mechanism and the reaction pathways. Kinetics equations of the pseudo-first-order and pseudo-second-order can be applied to study the kinetics of methylene blue adsorption on the MgAl\textsubscript{2}O\textsubscript{4} spinel fiber surfaces, respectively:\textsuperscript{1)}

\[
\ln\left(\frac{q_t}{q_e} - \frac{q_t}{q_e} - K_{P-1} \cdot t\right) = \ln q_e - K_{P-1} \cdot t
\]

\[
\frac{t}{q_t} = \frac{1}{K_{P-2} \cdot q_e^2} + \frac{t}{q_e}
\]

where $q_e$ (mg/g) and $q_t$ (mg/g) represent the adsorption quantity at the moment of equilibrium and time $t$ (min) of methylene blue, respectively. The rate constants of pseudo-first-order kinetics and pseudo-second-order kinetics were $K_{P-1}$ (min$^{-1}$) and $K_{P-2}$ (g/mg·min), respectively.

According to the calculation, the coefficient of associations of the pseudo-first-order kinetics was relatively lower. Large amounts of the data, however, fit the pseudo-first-order kinetics model more naturally and the correlation coefficient is greater than 0.99 as shown in Fig. 13. In addition, the intercept of the plot expresses the rate
constant of pseudo-second-order. The original absorption rate and half adsorption time \((t_{1/2})\) can be calculated by the equations given in Table 2. This model indicated that the adsorption rate of methylene blue was dependent on the “surface reaction” or “chemisorption mechanism”, \(^{1,3}\)

### 4. Conclusion

In summary, mesoporous \(\text{MgAl}_2\text{O}_4\) spinel fibers can be obtained successfully by the coaxial electrospinning route. It was found that the removal of polymers and liquid paraffin is an important factor for forming a porous structure. The typical sample prepared at 900°C has a high-purity \(\text{MgAl}_2\text{O}_4\) spinel phase and high specific surface area, which leads to an excellent removal ratio (89.6%) with respect to methylene blue. In general, prepared mesoporous \(\text{MgAl}_2\text{O}_4\) spinel nanofibers offer great potential as dye absorption materials in environmental purification.

**Acknowledgments**

The research was supported by the National Nature Science Foundation of China (51302064 and 51472072).

**References**

1. B. Ismail, S. T. Hussain and S. Akram, *Chem. Eng. J.*, 219, 395–402 (2013).
2. H. Wang, C. Jia, J. Yang, X. Zhao, Y. L. Li, H. G. Sun and W. L. Fan, *RSC Adv.*, 5, 77973–77985 (2015).
3. J. Y. Tian, P. Tian, G. L. Ning, H. C. Pang, Q. Song, H. Cheng and H. X. Fang, *RSC Adv.*, 5, 5123–5130 (2015).
4. E. L. Foleto, S. L. Jahn and R. F. P. M. Moreira, *Separ. Sci. Technol.*, 44, 2132–2145 (2009).
5. J. Y. Shen, Z. H. Li, Y. N. Wu, B. Zhang and F. T. Li, *Chem. Eng. J.*, 264, 48–55 (2015).
6. D. Vu, Z. Y. Li, H. N. Zhang, W. Wang, Z. J. Wang, X. R. Xu, B. Dong and C. Wang, *J. Colloid Interf. Sci.*, 387, 429–435 (2012).
7. K. Choi, W. Lee, S. Lee and C. Lim, *Mater. Lett.*, 158, 36–39 (2015).
8. C. Pen, J. L. Zhang, Z. G. Xiong, B. H. Zhao and P. C. Liu, *Micropor. Mesop. Mat.*, 215, 133–142 (2015).
9. Y. Wang, W. Li, X. L. Jiao and D. R. Chen, *J. Mater. Chem. A.*, 1, 10720–10726 (2013).
10. J. M. Boulton, K. Jones and H. G. Emblem, *J. Mater. Sci. Lett.*, 9, 914–915 (1990).
11. Y. Liu and R. M. Laine, *J. Eur. Ceram. Soc.*, 19, 1949–1999 (1999).
12. D. Li, J. T. McCann, Y. Xia and M. Marquez, *J. Am. Chem. Soc.*, 89, 1861–1869 (2006).
13. H. Y. Chen, J. C. Di, N. Wang, H. Dong, J. Wu, Y. Zhao, J. H. Yu and L. Jiang, *Small*, 7, 1779–1783 (2011).
14. Z. Li and C. Wang, *Springer* (2013).
15. B. Alinejad, H. Sarpoonlakay, A. Beitollahi, A. Beitollahi, A. Saberi and S. Afshar, *Mater. Res. Bull.*, 43, 1188–1194 (2008).
16. A. Vioux, *Chem. Mater.*, 9, 2292–2299 (1997).
17. G. J. Li, Z. R. Sun, C. H. Chen, X. J. Cui and R. M. Ren, *Mater. Lett.*, 61, 3585–3588 (2007).
18. A. K. Adka, S. K. Saha and P. Pramanik, *J. Mater. Sci. Lett.*, 16, 234–235 (1997).
19. L. Z. Pei, W. Y. Yin, J. F. Wang, J. Chen, C. G. Fan and Q. F. Zhang, *Mater. Res.*, 13, 339–343 (2010).
20. A. Aboulaich, O. Lorret, B. Boury and P. H. Mutin, *Chem. Mater.*, 21, 2577–2579 (2009).
21. A. Aboulaich, B. Boury and P. H. Mutin, *Chem. Mater.*, 22, 4519–4521 (2010).
22. A. Aboulaich, B. Boury and P. H. Mutin, *Eur. J. Inorg. Chem.*, 2011, 3644–3649 (2011).
23. B. H. Sturt, *Exp. Therm.*, 4, 325–385 (2004).
24. X. L. Du, Y. Q. Liu, L. Q. Li, W. C. Chen and Y. T. Cui, *J. Mater. Res.*, 29, 2921–2926 (2014).
25. E. N. Alvar, M. Rezaeei and H. N. Alvar, *Powder Technol.*, 198, 275–278 (2008).
26. A. Saberi, F. Golestani-Fard, H. Sarpoonlakay, M. Willert-Porada, T. Gerdes and R. Simon, *J. Alloy. Compd.*, 462, 142–146 (2008).
27. N. Thanabodeekij, M. Sathupuya, A. M. Tamieson and S. Wongkasemjit, *Mater. Charact.*, 55 (2015).
28. M. K. And and M. Jaroniec, *Chem. Mater.*, 13, 3169–3183 (2001).
29. M. Thommes, B. Smarsly, M. Groenewolt, P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 22, 756–764 (2006).
30. J. Z. Ma, H. J. Ji, Y. Teng, G. P. Dong, J. J. Zhou, D. Z. Tan and J. R. Qiu, *J. Colloid Interf. Sci.*, 358, 547–533 (2012).
31. K. Y. Foo and B. H. Hameed, *Chem. Eng. J.*, 156, 2–10 (2010).
32. H. Li, H. Y. Wei, Y. Cui, R. L. Sang, J. L. Bu, Y. N. Wei, J. Lin and J. H. Zhao, *J. Ceram. Soc. Jpn.*, 125, 100–104 (2017).
33. S. Sanjabi and A. Obeydavi, *J. Alloy. Compd.*, 645, 535–540 (2015).
34. J. H. Park, I. Jang, B. Kwon, S. C. Jang and S. G. Oh, *Mater. Res. Bull.*, 48, 469–475 (2013).