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Synthesis and characterization of porous magnesium aluminate spinel by hydrothermal process

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Abstract: Magnesium aluminate spinel has a great prospect in catalyst supports due to porous structure, good catalytic activity, high thermal stability and two active centers as acid and alkaline. The magnesium aluminate spinel powders synthesized by hydrothermal process were characterized by scanning electron microscope, transmission electron microscope, X-ray diffraction and N₂ adsorption-desorption isotherms. The particle surface is made up of laminated structure and it grows bigger with the increase of hydrothermal temperature and hydrothermal time. The spinel has wormlike porous structures and these structures grow smaller and better distributed at Hexadecyl trimethyl ammonium Bromide (CTAB) condition. The spinel phase emerges at 450 °C and the perfect crystalline structure emerges at 600 °C. The percent of MgAl₂O₄ spinel goes up with the increase of heat treatment temperature. The spinel has a large BET surface area and its special surface area diminishes continuously from 245.68 m²/g to 58.65 m²/g when the calcinating temperature increases from 500 °C to 1200 °C. Moreover, it reaches the maximum surface area of 195.1 m²/g with the addition of 1% CTAB according to BET analysis, yet excess of it has an adverse effect.

1 Introduction

In traditional ceramic industry, Magnesium aluminate spinel (MgAl₂O₄) has been used as refractory^[1-5]. Recently it exhibits high chemical inertness against both acidic and basic slag and average level of inertness to high-fluency neutron irradiation^[6]. MgAl₂O₄ spinel is widely used as catalysts or catalysis support in all types of catalytic reactions, such as hydrogenation^[7], desulfurization and sulfur-tolerant^[8-10], etc. With such feathers, MgAl₂O₄ plays a more and more significant role in catalyst or support in petrochemical industry, which renders the production of more homogeneous powders with higher specific surface areas powders highly important^[11]. In addition, the spinel has also been used as catalysts or supporters owing to its good catalytic activity, high thermal stability and two active centers as acid and alkaline^[12,13].

In recent years, various chemistry-based novel approaches have been applied to synthesize MgAl₂O₄ powders in order to improve its homogeneous, specific surface areas, pore volume and average pore diameter, such as co-precipitation of metal salts^[14], sol-gel^[15-17] and so on^[18]. Hydrothermal processing is one of the most important methods to fabricate porous spinel.



In this paper, powders have been synthesized by hydrolyzation of Magnesium-Aluminum alkoxide combined with hydrothermal method using Mg, Al and *n*-butanol as reactant. The powders are characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and N₂ adsorption-desorption isotherms.

2 Experiment

2.1 Preparation of MgAl₂O₄ powders

The stoichiometric magnesium (99.9%), aluminum (99.9%) and *n*-butanol were used as reactants ($n_{\text{Al}}:n_{\text{Mg}}=2:1$). The double alkoxides were prepared in a backflow using AlCl₃ as a catalyst. The synthesized alkoxides was hydrolyzed with deionized water under stirring until it turns into a homogeneous gel. The hydrolyzer was placed into high-pressure autoclave with magnetic stirrer for hydrothermal synthesis, and then dried at 100 °C for 24 h after natural cooling and calcination.

2.2 Characterization of MgAl₂O₄ powders

X-ray diffraction experiments were performed at room temperature in a Japan D/max-3B instrument. The crystallite size was determined from the XRD patterns using the Sherrer Eq. (1)

$$d = 0.89 \frac{\lambda}{\beta \cos \theta} \quad (1)$$

k is a constant, $k = 0.89$ where β is the half maximum (FWHM) of diffraction peak, θ is the angle of X-ray diffraction.

The cell parameter was calculated using the following Eq. (2)

$$a = d_{hkl} (h^2 + k^2 + l^2)^{1/2} \quad (2)$$

The morphology and microstructure of the powders were characterized by scanning electronic microscope in a Japan JSM-6360 LV instrument. The microstructure of the powders was observed by H800 JEOL-type transmission electron microscopy and the BET of MgAl₂O₄ supports were obtained by N₂ adsorption at −196 °C in the Quantachrome Corporation NOVA-1000 equipment.

3 Result and Discussion

3.1 Phase evolution of precursor and characterization

XRD patterns of heat-treated magnesium aluminate spinel are given in Fig.1. The spinel phase begins to emerge when the calcination starts at 450 °C. The perfect crystalline structure emerges obviously at 600 °C. The percent of MgAl₂O₄ spinel become more intense with the increase of heat treatment temperature, which is associated with an increase in the grain size. The dependence of the average grain size on calcination temperature and the average size of cell parameter are shown in Fig.2. The grain size of MgAl₂O₄ spinel increases with temperature yielding at 1200 °C, whose mean crystallize size is about 17.83 nm. However, the average size of cell parameter is quite similar to that of those from references, where $a = 0.80831$ nm for the well-crystallized spinel.

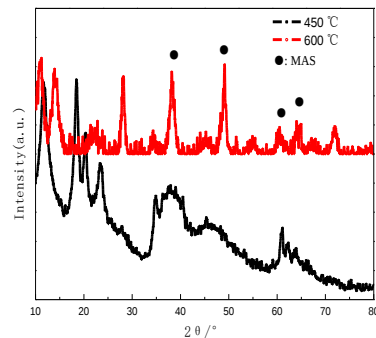


Fig. 1 XRD patterns of heat-treated magnesium aluminate spinel

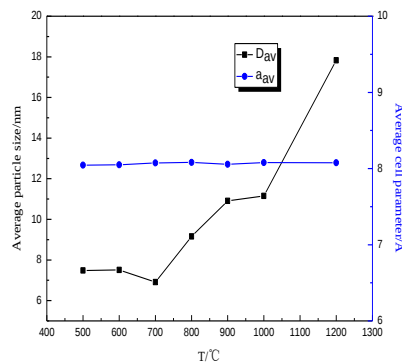


Fig. 2 Dependence of grain size and average size of cell parameter on calcination temperature

3.2 Hydrothermal temperatures

SEM images of samples prepared by hydrothermal process at 80, 120, 160, 250 °C for 6 h and calcined at 700 °C are shown in Fig.3. The surface of the sample consists of large grains during the hydrothermal process at 80 °C. While the sample surface is made of small and regularly-arranged laminated structure at 120 °C, the laminated structures grow bigger and bigger with the increase of hydrothermal temperatures. In addition, the samples have irregular growth of laminated structures at high hydrothermal temperatures. The results indicated that there is not enough energy to drive the particle to grow into sheet structures at low temperatures. Yet it provides enough energy to grow into the laminated structures when hydrothermal temperature reaches 120 °C.

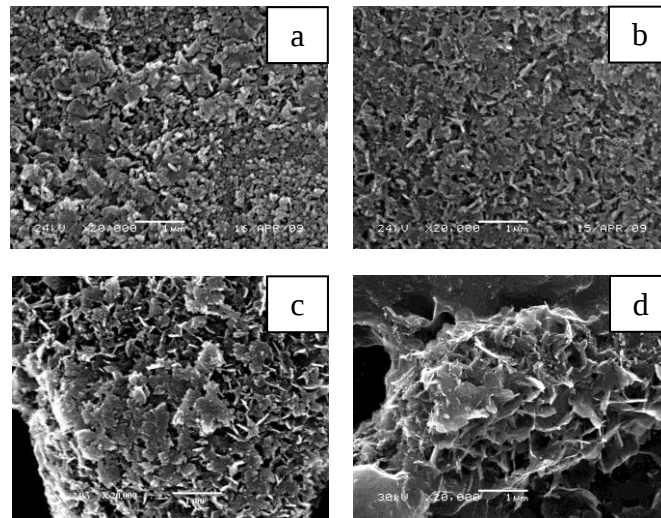


Fig. 3 SEM images of samples at different hydrothermal temperatures (a) 80 °C (b) 120 °C (c) 160 °C (d) 250 °C

3.3 Hydrothermal time

Fig.4 shows SEM images of samples that are prepared at 160 °C for different time by hydrothermal process, then calcined at 700 °C. It can be seen that the laminated structures of sample particles by hydrothermal process for 6 h grow regularly and are uniform in size. With the increase of hydrothermal time, the laminated structures of sample gradually grow bigger. The result indicates that the formation rate of crystal nucleus is fixed when hydrothermal temperatures are the same. The system provides enough energy to promote grain to aggregate and grow bigger as the hydrothermal process lasts longer. Accordingly, the same effects apply to make laminated structures large by increasing hydrothermal temperature and hydrothermal time.

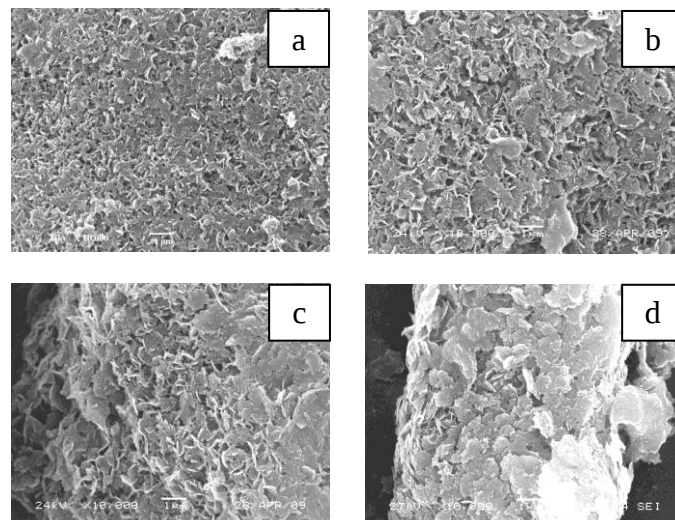


Fig. 4 SEM images of samples with hydrothermal process for different times (a) 6 h (b) 24 h (c) 48 h (d) 96 h

3.4 Effects of Hexadecyl trimethyl ammonium Bromide (CTAB)

The microstructure and morphology of samples prepared by hydrothermal process at 160 °C for 6 h are shown in TEM images in Fig.5. It can be seen that the particles of samples consist of lots of worm-like pore structure with irregular arrangement and nonuniform form by comparing precursor in Fig.5(a) with calcined sample in Fig.5(b). It is a relic of the morphology even after calcination and regarded as topological transformation. The TEM images of samples by adding CTAB, are shown in Fig.5(c) which is precursor and Fig.5(d) which is calcined at 700 °C. The wormlike pore structures of particles grow smaller and better distributed on account of faintish coordination interaction force between precursor and CATB, which can induce the accumulation of colloidal particle effectively. The result indicates that the composites have no obvious long-distance ordered porous structure, but the order of porous structure increases distinctly. The TEM image in Fig.5(b) indicates that the products of MgAl_2O_4 spinel and polycrystalline powder, namely MgAl_2O_4 spinel catalyst supports, have grain structure.

3.5 Effects of CTAB contents and Calcination Temperatures

The specific surface area of samples with different calcinations temperatures and different CTAB contents are shown in table 1. The specific surface area decreases from 245 m^2/g at 500 °C to 58.65 m^2/g as the temperature hits 1200 °C which still presents high heat stability of spinel catalyst support. The CTAB has an important influence on the specific surface area. It can be seen that the specific surface

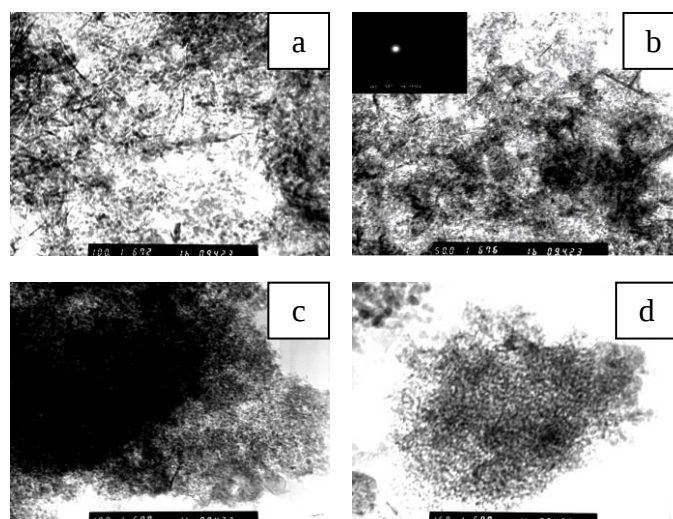


Fig. 5 TEM images of samples of precursor and spinel
(a) images of precursors and (b) images of samples calcined at 700 °C without CTAB
(c) images of precursors and (d) images of samples calcined at 700 °C with CTAB

area is 179.01 m^2/g when 0.2% CTAB is added. It reaches maximum BET surface area, about 195.11 m^2/g with the addition of 1% CATB. Afterward the surface area diminishes gradually with the increase of CTAB to 76.92 m^2/g with 5% CTAB, which is attributed to over roasting because the excessive surfactants precipitate out from solutions and they are inclined to be absorbed on the surface of precursor.

Table 1. The specific surface areas of samples with different CTAB contents

Calcination temperature/ °C	BET/ (m ² /g)	CTAB content/ wt%	BET/ (m ² /g)
R. T.	142.07	0.2	179.01
400	233.32	0.5	177.41
500	245.68	1	195.11
700	162.06	2	140.24
800	156.92	3	115.01
1000	82.78	4	100.74
1200	58.65	5	76.92

4 Conclusion

The spinel powders particle surface is made up of laminated structure prepared by hydrothermal process combined with alkoxide hydrolysis. It reveals wormlike porous structures and a large special surface area in such structure. The laminated structure of MgAl₂O₄ powders particle surface grow larger with the increase of hydrothermal temperature and hydrothermal duration. The spinel phase comes into being at 450 °C and the perfect crystalline structure emerges at 600 °C. The spinel phase increases gradually, the crystalline grain grows bigger and its specific surface area diminishes continuously from 245.68 m²/g to 58.65 m²/g when the roasting temperatures increase from 500 °C to 1200 °C. Additionally, the laminated structures of particle surface grow regularly by adding the amount of surfactant CTAB below 1%, while the excessive of surfactant CTAB has an adverse effect.

References

- [1] Li X N, Chen H Y (2008). Preparation and properties of Al₂O₃–MgAl₂O₄ composites for aluminum refining furnace. *Journal of the Chinese Ceramic Society*, 36(1): 49-53.
- [2] Zhang W J, Shao G Q (2009). Synthesis of yttria stabilized Zirconia/MgAl₂O₄ composite powders and their sintering activation energy. *Journal of the Chinese Ceramic Society*, 37(11):1813-1817.
- [3] Gao Z X, He Z Y (2011). Structure of β-Al₂O₃ in Synthetic Magnesium Aluminate Spinel. *Journal of the Chinese Ceramic Society*, 39(11): 1747-1751.
- [4] Xu X H, Ma X H (2012). In-Situ Preparation and Thermal Shock Behavior of Corundum–Mullite–Magnesium Aluminate Spinel Composite Ceramic. *Journal of the Chinese Ceramic Society*, 2012, 40(10):1187-1193.
- [5] Yin G X, Li Y (2014). Effect of heat treatment temperature on mechanical properties of MgO–MgAl₂O₄–ZrO₂ eutectic materials. *Journal of the Chinese Ceramic Society*, 42(3):367-371.
- [6] Carmen B, Rafael M (1995). High-temperature mechanical behavior of stoichiometric magnesium spinel. *Jam Ceram Soc*, 78(7):1857-1862.
- [7] Sonia A, Alberto A (2007). Characterization and catalytic behavior in the n-butanedehydrogenation of trimetallic InPtSn/MgAl₂O₄ catalysts. *Applied Catalysis A: General*, 333(1): 49-56.
- [8] Tan Y F, Li X (1997). Performance and industrial application of QCS-01 sulfur-tolerant shift catalyst (in Chinese) *J. Gongye Cuihua (Industrial Catalysis)*, 4: 41-46.
- [9] Qian M S, Awad A N (1997). Studies on DE-SO_x additives by acidic method (in Chinese). *Journal-East China University of Science and Technology*, 23(2): 182-186.
- [10] Guo J J, Luo H (2004). Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels. *Applied Catalysis A: General*, 273: 75-82
- [11] C. PACURARIU, I. LAZAU (2007). Synthesis methods of MgAl₂O₄ spinel, *Journal of the European Ceramic Society*, 27: 707-710.
- [12] Guo J J, Luo H (2004). Novel synthesis of high surface area MgAl₂O₄ spinel as catalyst support. *Mater Lett*, 58: 1920-1923.

- [13] Guo J J, Luo H (2007). The deposition of coke from methane on a Ni/MgAl₂O₄ catalyst. *J. Carbon*, 45:1314-1321.
- [14] STEVEN C, JORIS N (2008). Influence of composition of MgAl₂O₄ supported NiCeO₂ZrO₂ catalyst on coke formation and catalyst stability for dry reforming of methane. *Catalysis Today*, 138(1-2):28-32.
- [15] OWEN R. EVANS, ALEXIS T. BELL (2004). Oxidative dehydrogenation of propane over vanadia-based catalysts supported on high-surface-area mesoporous MgAl₂O₄. *Journal of Catalysis*, 226(2): 292-300.
- [16] EDWIN H. WALKER JR (2002). The novel low temperature synthesis of nanocrystalline MgAl₂O₄ spinel using “gel” precursors. *Materials Research Bulletin*, 37:1041-1050.
- [17] Zhao Y Q, Zhao H L (2008). Preparation and gelatination mechanism of CuO(CoO, MnO)/SiO₂ nanocomposite aerogel as catalyst carrier by the SOL-GEL process (in Chinese). *Journal of the Chinese Ceramic Society*, 36(5):658-662.
- [18] Ibram G, Bakki S (2004). Microwave assisted solid state reaction synthesis of MgAl₂O₄ spinel powders. *Journal of the European Ceramic Society*, 24: 201-207.