Synthesis of High Surface Area Calcium Aluminate ($Ca_{12}Al_{14}O_{33}$) with Carbon Template by Solid State Calcination Method

[1]Ruiyuan Tang, [2]Junhui Hao, [1]Kai Liu, [2]Yingyun Qiao, [1]Juntao Zhang and [2]Yuanyu Tian*
[1]Research Center of Petroleum Processing & Petrochemicals, Xi'an Shiyou University, Xi'an 710065, Shaanxi, China.
[2]State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao Shandong 266580, China.
tianyy1008@126.com*

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Summary: High surface area calcium aluminate is synthetized within a short time by using a carbon template solid state calcination method which involved addition of carbon black into the $CaCO_3$ and Al_2O_3 powders, calcination, and carbon removal by steam. Vary carbon black dosage changed the textural properties of the calcium aluminate, such as the surface area. By varying carbon black dosage from 0 to 10.0 wt%, the calcium aluminate with a surface area ranging from 21.5 to 41.2 $m^2 \cdot g^{-1}$ are successfully synthesized within 14.0 h. Furthermore, the nanometer sized $CaCO_3$ and Al_2O_3 powders comprising carbon black could markedly reduce the calcination temperature without reducing the surface area. This research might lead to the cost-effective synthesis of calcium aluminate ($Ca_{12}Al_{14}O_{33}$) in a short synthesis period.

Key words: Solid-state; $Ca_{12}Al_{14}O_{33}$; High surface area; Carbon template; Short synthesis period.

Introduction

Calcium aluminate ($Ca_{12}Al_{14}O_{33}$) could find wide applications in catalysis, adsorption, conductor and advanced ceramics as optical ceramics [1–5], because of its high anticarbon and antisulfur characteristics [6, 7], reactivity, conductivity and stability. Conventionally, the calcium aluminate is synthesized by solid state reactions between calcium carbonate ($CaCO_3$), or lime (CaO) and alumina (Al_2O_3) [7–10] at temperature around 1400 °C. Powders prepared by this method typically display very low surface areas (<2.0 $m^2 \cdot g^{-1}$) [11]. To enhance surface area of the calcium aluminate, some other prepare methods are developed such as sol gel [4], hydrothermal and coprecipitation [12, 13]. Nevertheless, these methods suffer from discharge of operability and consumption of longer synthesis periods (19.5 to 85 h) [4, 12, 13].

In this research, we reported a simple, time saving and facile method to synthesis high surface area calcium aluminate by simple addition carbon black in the course of the solid state synthesizing. By using this method, calcium aluminate with the surface area up to 41.2 $m^2 \cdot g^{-1}$ was synthesized within 14 h. Also, nanometer sized $CaCO_3$ and Al_2O_3 powders in presence of carbon black could markedly reduce the calcination temperature without reducing surface area. The study is potentially attractive for preparing high surface area calcium aluminate convert into the useful material applicability in the fields of fine chemical industry and adsorption.

Experiment

Materials

Micrometer sized $CaCO_3$ and Al_2O_3 (about 20 μm) are bought from the Tianjin Kemiou Chemical Reagent Co., Ltd, China. Nanometer sized $CaCO_3$ (about 30 nm) and Al_2O_3 (about 15 nm) are bought from NanoMaterials Technology Co., Ltd, China. Nanometer sized carbon black is purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Catalysts preparation

Micrometer sized $CaCO_3$ and Al_2O_3 powders (or the nanometer sized $CaCO_3$ and Al_2O_3 powders) mixed with a molar ratio of 12:7 (namely, $n(CaCO_3):n(Al_2O_3)=12:7$) was dissolved in 100 mL ethyl alcohol at 70 °C for 1.5 h, followed with addition of 0-10 wt% carbon black. And then was stirred for 1 h to obtain solid mixtures. After calcined in Ar at 1100 or 900 °C for 5 h with a heating rate of 8 $°C \cdot min^{-1}$. When cooled to 800 °C, the samples were exposed to steam for 1 h to remove the remaining carbon.

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[*]To whom all correspondence should be addressed.

Afterwards, the steam treated samples were cooled to room temperature under Ar flow. The samples were recorded as the CaAl-x-y, where x and y meant the calcination temperature and carbon black dosage, respectively. For instance, the CaAl-1100-5.0% catalyst represented the obtained sample prepared by addition of 5.0 wt% carbon black and calcination at 1100 °C.

Characterization

Textural properties of the tested samples were characterized by N_2 adsorption/desorption measurements at –196 °C with a Tristar II 3020 apparatus (Micromeritics Corp., USA). The isotherms are applied to obtain surface area (S_{BET}), mesopore pore volume (V_{meso}), total pore volume (V_t), the mesopore fraction ($V_{\mathrm{meso}}/V_{\mathrm{t}}$) is obtained by dividing mesopore volume (V_{meso}) with total volume (V_{t}). Fourier transformed infrared spectroscopy (FT-IR) spectra is recorded by using a Tensor 27 FT-IR spectrometer range in the 4000–500 cm^{-1}. The X-ray diffraction patterns are recorded by X-ray diffractometer X'Pert PRO MPD (PANalytical Netherlands) by using an acceleration voltage of 40 kV and 40 mA from 5° to 75° with the step of $8^{\circ}\cdot min^{-1}$. Microscopic feature of the catalysts are observed by a cold field scanning electron microscopy (SEM) (S–4800, Hitachi, Japan). Before the test, the catalysts samples are coated with gold to increase the electroconductivity.

Results and Discussion

Table-1 shows the textural properties of calcium aluminate. The highest surface area of calcium aluminate ($Ca_{12}Al_{14}O_{33}$) reached to 41.2 $m^2\cdot g^{-1}$ (average of three replicates), which is fairly comparable to the reported surface area (0.9–68.9 $m^2\cdot g^{-1}$) of calcium aluminate [5, 7–10, 12]. It should be mentioned that the total synthesis period in this research is shorter than 13 h, while the reported synthesis periods are all longer than 20 h. Therefore, the main reason for reducing the synthesis periods is understandable. In literature, the preparation of high surface area calcium aluminate sample usually requires time consuming hydrolysis condensation and coprecipitation method to form the precursors [5, 12 –14], whereas the method proposed in this study does not need the time consuming steps, and thus rendering the synthesis process time saving and facile.

Table-1: Textural properties of calcium aluminate.

Samples	$S_{BET}/m^2\cdot g^{-1}$	$V_t/cm^3\cdot g^{-1}$	$V_{meso}/cm^3\cdot g^{-1}$	V_{meso}/V_t(%)	D/nm
CaAl-1100-0%	**21.5**	**0.15**	**0.14**	**93.3**	**10.0**
CaAl-1100-5.0%	**23.7**	**0.21**	**0.20**	**95.2**	**11.2**
CaAl-1100-10.0%	**27.8**	**0.18**	**0.17**	**94.4**	**13.1**
CaAl-900-10.0%	**41.2**	**0.16**	**0.15**	**93.8**	**13.7**

Table-1 shows that the V_{meso}/V_t ratio of the calcium aluminate is all above 93.3% and the mesopore volume changed slightly (ranged from 0.14 to 0.20 $cm^3\cdot g^{-1}$). These observations suggest that (1) the samples are abundant in mesopores and lacking in micropores and (2) the addition of carbon black has little effects on pore structure of calcium aluminate. Table-1 also shows that increasing the dosage of carbon black and used the nanometer sized powders are conducive to the surface area. Of which the nanometer sized $CaCO_3$ and Al_2O_3 powders with carbon black assisted can evidently improve the surface area (reached to 41.2 $m^2\cdot g^{-1}$). Also, to test whether the addition of carbon black affects structure of calcium aluminate, we conducted FT-IR and XRD analysis, with the results discussed below.

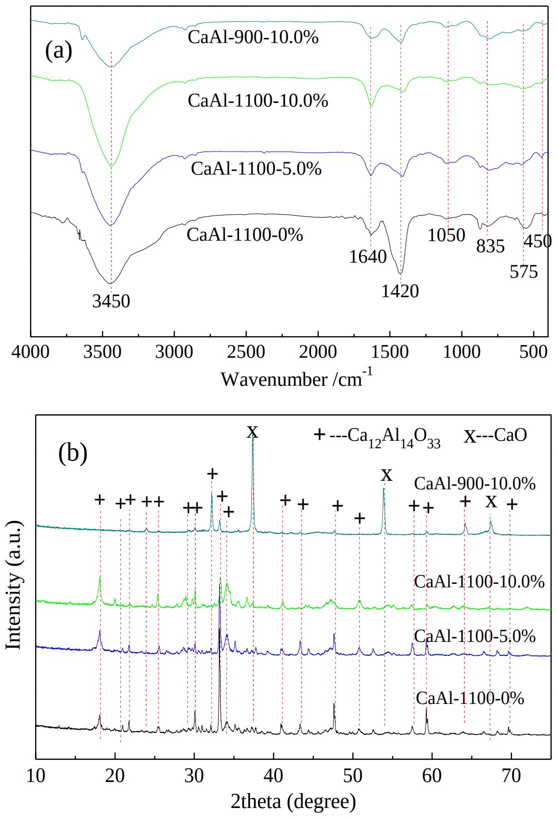

Fig. 1: FT-IR spectra (a) and XRD curves (b) of the obtained calcium aluminate.

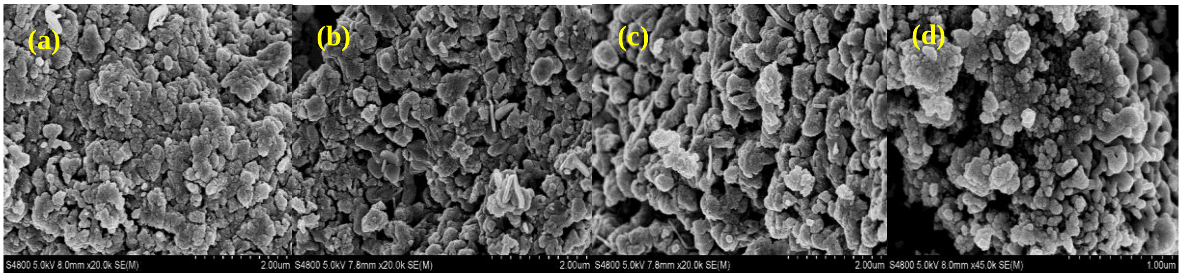

Fig. 2: SEM images of (a) CaAl-1100-0% sample of 2 μm, (b) CaAl-1100-5.0% sample of 2 μm, (c) CaAl-1100-10.0% sample of 2 μm and (d) CaAl-900-0% sample of 1.0 μm.

Fig.1 (a) shows FT-IR spectra of the calcium aluminate samples. For all samples, a broad O-H stretching vibration peak at 3450 cm^{-1} is observed, which corresponded to O-H bonds of free water and hydrogen bonds of structural hydroxyl [15]. A weak O-H bending vibration peak at 1640 and 1420 cm^{-1} is attributed to the H_2O absorbed from air in the samples or KBr [16]. Two absorption peaks at 575 and 1050 cm^{-1} are observed, which are owing to the Al-O vibration [17]. A weak absorption peak at 450 cm^{-1} was assigned to the absorption peak of the Ca-O stretching vibration [18]. An absorption peak at 835 cm^{-1} is ascribable to the stretching vibration peak of the Al-O bond in the tetrahedron (AlO_4) [19], this indicates that the calcium aluminate ($Ca_{12}Al_{14}O_{33}$) was successfully synthesized by the proposed with carbon template by the solid state calcination method.

The XRD patterns in Fig.1 (b) shows that all the calcium aluminate samples represented high crystallinity degree, and only the diffraction peak intensity of CaAl-900-10.0% sample is slightly weakened. For all samples, the crystal diffraction peaks corresponding to $Ca_{12}Al_{14}O_{33}$ phase, while the CaAl-900-10.0% sample remained with the presence of few diffraction peaks owing to the CaO crystal phase [14], suggesting that the extra unreacted Ca species could be transferred to form calcium oxide after the calcination process [20]. Hence, it was concluded that the addition of carbon black has not influenced calcium aluminate crystal structure.

All prepared samples could be describable by SEM characterization as shown in Fig.2. It appears that addition of carbon black in the synthesis process could improve the quantity of interparticle voids caused by the aggregation of uniform size lamellar or rod like morphology. The particles size of calcium aluminate samples (a-c) in ranged of 1-10 μm, while aggregates with similar particle morphologies are observed in the CaAl-900-10.0% sample (d). And the smaller aggregates are contributed to the rise in its surface area.

Conclusions

Calcium aluminate ($Ca_{12}Al_{14}O_{33}$) with the surface area of 41.2 m^2·g^{-1} was successfully synthesized within a short period (<14.0 h) by solid state calcination of micrometer sized (or nanometer sized) powders comprising carbon black. Also, the nanometer sized $CaCO_3$ and Al_2O_3 powders in presence of carbon black can markedly reduce the calcination temperature (about 900 °C) without reducing surface area.

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