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Fabrication of nano-sized $Ca(OH)_2$ with excellent adsorption ability for N_2O_4

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ABSTRACT

Uniform nano-sized calcium hydroxide ($Ca(OH)_2$) monocrystal powder was synthesized from calcium oxide in a surfactant solution via a digestion method by decreasing the surface tension of the reaction system to control the growth of crystalline $Ca(OH)_2$. The $Ca(OH)_2$ monocrystal powder samples were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and Fourier transform-infrared spectroscopy (FT-IR). The NO_x adsorption ability of the samples was evaluated, and the influence of various types and concentrations of surfactants on powder agglomeration and then the specific surface area in the precipitation process were studied. The specific surface area of the samples was found as high as 58 m^2/g and 92 m^2/g and the particle size, 300–400 nm and 200–300 nm in the presence of 10 wt% PEG600 and 0.086 mL/L SDS at a reaction time of 5 h, respectively. The product has an exceptionally strong adsorption ability for NO_x, which makes it a highly promising adsorbent for emission control and air purification.

1. Introduction

N_2O_4, often used as a liquid rocket propellant in space launch, can quickly generate high concentration of NO_2 at ambient temperature and pressure, to cause pulmonary edema, chemical pneumonia, and even death from suffocation. NO_2 also forms photochemical smog and acid rain in air, resulting in serious environmental pollution (Pandey, Khan, Joseph, & Kumar, 2002). How to prevent propellant N_2O_4 leakage effectively is an important problem. Alkaline and alkaline-earth metal oxides and hydroxides have been widely used to adsorb acidic gas due to their strong neutralizing effect (Beruto, Botter, & Searcy, 1984; Koper, Lagadic, Volodin, & Klabunde, 1997; Philipp & Fujimoto, 1992; Philipp, Omata, Aoki, & Fujimoto, 1992; Renedo, González, Pesquera, & Ferández, 2006; Withum & Yoon, 1989). Up to now, $Ca(OH)_2$ powder has been focused upon by many researchers and applied industrially to prevent N_2O_4 leakage due to its low cost, non-toxicity, simple preparation and good neutralizing effect on strong acidic gases.

The ability of $Ca(OH)_2$ powder to adsorb N_2O_4 depends on its specific surface area, which can be improved by increasing powder fineness and porosity. Nano-sized CaO has been much reported (Bellobono, Selli, Righetto, & Muffato, 1988; Bellobono, Castellano, & Tozzi, 1991; Koper et al., 1997; Tang, Claveau, Corcuff, Belkacemi, & Arul, 2008), though not much for nano-sized $Ca(OH)_2$. Sotirchos and Smith (2004) synthesized porous CaO powders with specific surface area of 24 m^2/g from calcium grease by a corrosion decomposition method, while Wu, Uddin, and Sasaoka (2005) synthesized porous CaO powder with a specific surface area of 15 m^2/g by a water–acetic acid swelling method. In their study on CaO with high surface area as the final product and $Ca(OH)_2$ as the intermediate product, Liu et al. (2007) synthesized porous CaO with a specific surface area of 139 m^2/g from activated carbon as hard template and calcium nitrate as the calcium source, by means of a nanocasting fabrication method. Liu, Zhang, et al. (2008) produced 3D porous CaO with a specific surface area between 181 and 257 m^2/g from a 24 to 72 h reaction of CaO by hydrothermal synthesis in the presence of surfactants (P123, CTAB, PEG) at 160–240 °C. During his study on $Ca(OH)_2$ as the final product, Zhao (2006) synthesized $Ca(OH)_2$ nanotubes with outer diameters of 120–200 nm and wall thickness of 40–80 nm in an aqueous solution of $CaCl_2$ and NaOH in the presence of Triton X-100 as a surfactant under 15 d (days) agitation at ambient temperature, but the specific surface area was not characterized. Chain-shaped $Ca(OH)_2$ powder with diameters of 500–1000 nm and the specific surface area of 30 m^2/g was produced by Xu, Qian, Xiao, Liu, and Chen (2008) by a coprecipitation method in the presence of polyethylene glycol as the template

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agent. Jiang, Chen, Xu, Liu, and Xiao (2006) synthesized $Ca(OH)_2$ powder with a diameter of 1 μm and the specific surface area of 35 m^2/g from polyacrylamide by an in situ synthesis process. None of the above methods is, however, suitable for industrial production. At present, industrial $Ca(OH)_2$ powders are produced from lime by the digestion process and used as chemical, medicinal and building materials. Industrial $Ca(OH)_2$ powders generally have specific surface areas of 20–25 m^2/g and particle diameters of 5–20 μm (Deng & He, 2007; Iwashita et al., 1998; Salvadori & Dei, 2001).

To produce nanosized $Ca(OH)_2$ crystal powders with large specific surface area and excellent adsorption ability, suitable for industrial production, uniform and porous $Ca(OH)_2$ monocrystals with specific surface area as high as 96 m^2/g were produced from CaO by a digestion method in sodium dodecyl sulfate (SDS) or polyethylene glycol (PEG) aqueous solution by decreasing the surface tension of the reaction system and utilizing the structure-directing effect of the micelle to control the crystal $Ca(OH)_2$ powder growth. This process is low-cost and adaptable for industrial production. The nano-sized $Ca(OH)_2$ produced using this method has been applied to the space industry in China with very promising results.

2. Experimental

2.1. Synthesis

Nanosized $Ca(OH)_2$ powder was synthesized from calcium oxide by a digestion process induced by the surfactants SDS or PEG, analytically pure and from Sinopharm Chemical Reagent Co. Ltd. Each 20 g of CaO powder is added into a 100 mL Erlenmeyer flask before 10 wt%, 5 wt% and 2 wt% PEG600 solutions and 0.0172 mol/L, 0.0430 mol/L and 0.0860 mol/L SDS solutions were prepared, respectively. The above aqueous solution concentrations were selected to obtain the micelle in various experiments. Then 25.7 g of each surfactant solution is added into the Erlenmeyer flask with CaO powder for hydrolysis reaction under strong agitation for 20–30 min and slow agitation for 1–5 h at room temperature. After complete reaction, the product was filtered, washed with distilled water three times, washed with ethanol for the 4th time, and dried at 60 °C for 24 h under vacuum. The product samples were denoted as P-*a*-*b*, S-*a*-*b*, and B-*a*-*b*, where P stands for PEG600, S for SDS, B for no surfactant, *a* for concentration, and *b* for reaction time.

2.2. Characterization

The phase compositions of the obtained samples were characterized by X-ray diffraction (XRD) on a Rigaku D/MAX-II X-ray diffractometer operating at 35 kV, 35 mA with a scan rate of 4°/min and a step of 0.02° using Cu Kα radiation and a Ni filter. Morphology was observed on a JEOL 6500 F field-emission scanning electron microscope (SEM) working at 30 kV. High-resolution transmission electron microscopic (HRTEM) images and selected area electron diffraction (SAED) patterns of the catalysts were obtained using a JEOL JEM-2010 instrument. The specific surface area and pore size distributions of powders were calculated according to Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods respectively, by employing a Micromeritics ASAP2020 automatic surface area and porosity analyzer. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Vertex 70 spectrometer under a detecting range of 600–4000 cm^{-1} with a resolution of 0.4 cm^{-1} of the 1 wt% sample and 99 wt% KBr samples.

NO_2 gas can quickly be generated after N_2O_4 leakage, so the N_2O_4 adsorption ability of the samples was evaluated with the NO_x (N_2O_4, NO_2) as the test objectives by the catalyst activity testing apparatus WPF-101 with a Shimadzu single loop controller SR52 of high quality and a chemiluminescence detection system ML-9841AS NO_x from Monitor Labs.

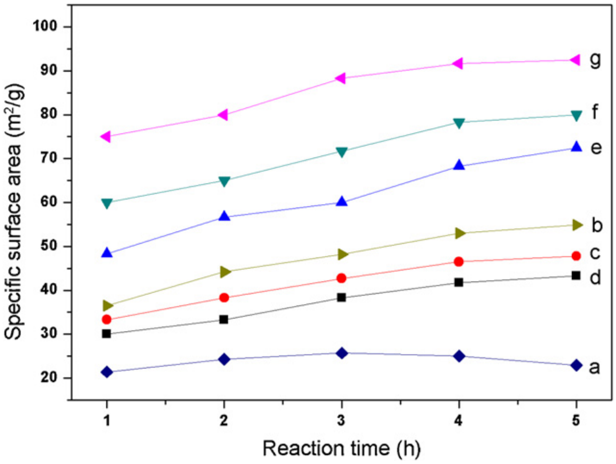

Fig. 1. Specific surface area as a function of reaction time for 5 samples: (a) B-0-3, (b) P-10-5, (c) P-5-5, (d) P-2-5, (e) S-0.017-5, (f) S-0.043-5 and (g) S-0.086-5.

3. Result and discussion

3.1. Effect of surfactants on surface area and XRD

Fig. 1 shows the effects of PEG and SDS concentration and reaction time on specific surface area of $Ca(OH)_2$. Curve (a) shows the specific surface area vs. reaction time in the blank test without surfactant. Curves (b)–(d) show specific surface area vs. reaction time using 10 wt%, 5 wt% and 2 wt% PEG600 respectively. Curves (e)–(g) show specific surface area vs. reaction time using 0.0172, 0.0430 and 0.0860 mol/L SDS respectively.

It can be seen from Curve (a) in Fig. 1 that the specific surface area is almost independent of reaction time while without any surfactant. Moreover, the surface area reaches a maximum value of 28 m^2/g at the reaction time of 3 h and decreases thereafter. The particle size is about 3–8 μm, as illustrated in its SEM image shown in Fig. 3(c). The CaO hydration is so rapid and exothermic that the produced ionic crystal of $Ca(OH)_2$ can have strong polarity and grow easily. Thus it is difficult to prepare $Ca(OH)_2$ crystal in such a reaction system.

Curves (b)–(d) of Fig. 1 show that the specific area increases with increasing PEG concentration and reaction time. Take the Sample P-10-5, Curve (b), for example, the specific surface area reaches 58 m^2/g and the particle size is between 500 and 800 nm at the reaction time of 5 h using 10% PEG, because, as shown in Fig. 3(a), PEG, which is soluble in water, can spontaneously form spherical or rod macromolecular aggregates (Pan & Wang, 2006; Shen & Wang, 1991) in aqueous solution and such aggregates will guide the growing morphology of the $Ca(OH)_2$ crystal and prevent the development of big particles.

SDS can enhance the specific surface area more significantly than PEG, and both SDS concentration and reaction time help increase the specific surface area as shown in Curves (e)–(g) of Fig. 1. Sample S-0.086-5 has a specific surface area as high as 92 m^2/g at the reaction time and SDS concentration of 5 h and 0.086 mol/L (10 times CMC, 0.0086 mol/L) respectively. Such significantly increased specific surface area can be attributed to the lower surface free energy and the micelles formed from SDS which can control the growth process and particle size of the $Ca(OH)_2$ crystals.