Applied Clay Science 46 (2009) 109–113

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Selective adsorption of carbon dioxide over nitrogen on calcined synthetic hectorites with tailor-made porosity

Radheshyam R. Pawar, Hasmukh A. Patel, Govind Sethia, Hari C. Bajaj *

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar-364 002, Gujarat, India

ARTICLE INFO

Article history:
Received 18 March 2009
Received in revised form 7 July 2009
Accepted 13 July 2009
Available online 18 July 2009

Keywords:
Synthetic hectorites
Adsorption
Carbon dioxide
Nitrogen
Selectivity

ABSTRACT

Hectorites were synthesized using 1-butyl-3-methylimidazolium bromide, 1,3-didecyl-2-methylimidazolium chloride and 1-decyl-3-methylimidazolium chloride as synthesis directing agents at condensation temperature for 48 h. Calcinations of synthetic hectorites resulted mesoporous materials with pore diameters ranging from 3.4 to 5.5 nm. The pore diameters depended on the directing agent. Synthetic and calcined hectorites were characterized by powder X-ray diffraction. Adsorption properties of CO_2 and N_2 on calcined hectorites were investigated by volumetric measurements. The adsorption capacity for CO_2 and N_2 decreased with increasing pore diameter. The calcined hectorites showed very good selectivity for CO_2 over N_2 at lower as well as higher partial pressure at 303 K.

1. Introduction

The issue of global warming resulting from increased atmospheric concentrations of CO_2 is arguably the most important environmental challenge facing the world today. Therefore, the capture and sequestration of CO_2 generated by large point sources, such as fossil fuel fired power gasification plants, is very important (Yue et al., 2006). Current technologies being considered for CO_2 sequestration comprise disposal of CO_2 in deep oceans; depleted oil and gas fields; deep saline formations (aquifers); recovery of enhanced oil, gas and coal-bed methane; and CO_2 separation and capture from flue gas or other gas by liquid amine based scrubbing systems (Gray et al., 2004; Filburn et al., 2005). However, the current cost and complicated operations for the utilization of these types of technologies have been proven to be too expensive. Consequently, reducing the cost for the capture of CO_2 will be a critical step in the overall carbon management program.

Though the research efforts focusing on solid adsorbents such as zeolite, pillared clays and hydrotalcite were developed, loading amines on silica gel, carbon and polymeric materials were also found to be promising way for achieving effective adsorption of CO_2 (Katoh et al., 2000; Xu et al., 2003; Jaramillo and Chandross, 2004; Shen et al., 2004). Yue et al. (2006) reported SBA-15 modified by tetraethylenepentamine showed adsorption capacity of 148 mg g^{-1}, while SBA-15 modified by propylamine showed an adsorption capacity of 9–18 mg g^{-1}. Xu et al. (2003) reported that MCM-41 modified by polyethylenimine had an adsorption capacity of 133 mg g^{-1} at 75 °C adsorption temperature.

Synthetic smectites are attractive class of materials for extending the industrial applications of natural smectites. Among the synthetic smectites, hectorite is popular due to its formation under relatively mild conditions (Barrer and Dicks, 1967; Kloprogge et al., 1999; Carrado, 2000; Patel et al., 2006; Bergaya et al., 2006). Carrado (1992) reported the hydrothermal crystallization of organo-hectorite from gels containing organic or organometallic compounds, which were subsequently intercalated. Numerous organic compounds have been used as synthesis directing agent for crystallization of hectorites. The synthesis directing agent should be soluble in water, thermally stable and cationic or non-ionic for synthesis of hectorite. Cationic organic compounds (poly(dimethydiallylammonium), tetramethylammonium, tetraethylammonium, ruthenium and cobalt complexes etc.) and non-ionic species (poly(vinylpyrrolidone), poly(vinylalcohol), poly(acrylonitrile), hydroxyethyl cellulose etc.) have been extensively used synthesis directing agent (Carrado, 1992; Carrado et al., 1997a,b,c).

The present study was undertaken to develop synthetic hectorites with tuned porosity for selective adsorption of CO_2 over N_2. They were prepared using short/long alkyl imidazolium cations as synthesis directing agents. The effect of alkyl chain length on the specific surface area, pore size and pore volume is described. Isothermal adsorptions of CO_2 and N_2 on the calcined hectorites were carried out to study the adsorption capacity and selectivity of CO_2 over N_2.

---

* Corresponding author. Tel.: +91 278 2471793; fax: +91 278 2567562.
E-mail address: hcbajaj@csmcri.org (H.C. Bajaj).

0169-1317/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2009.07.009

2. Experimental

2.1. Materials

1-butyl-3-methylimidazolium bromide (BMI), 1,3-didecyl-2-methylimidazolium chloride (DDMI) and 1-decyl-3-methylimidazolium chloride (DMI) were purchased from IoLiTec Ionic Liquids Technologies GmbH & Co. KG, Germany. Ludox HS-40, a Na^+-stabilized 40% silica sol (DuPont) was purchased from Sigma-Aldrich, USA. Magnesium chloride hexahydrate and sodium hydroxide were purchased from S. D. Fine Chemicals, India. Ultra high-purity (>99.99%) CO_2 and N_2 (Inox Air Products Ltd, Maharashtra India) were used in all equilibrium adsorption measurements. All chemicals and gases were used as received.

2.2. Synthesis of organo-hectorites and hectorite

The detailed procedure for the hydrothermal crystallization of hectorites was reported earlier (Carrado et al., 1997c). In typical synthesis, reactants in the molar ratios of $LiF:MgO:SiO_2 = 0.266:1.00:1.52$ were refluxed for 48 h as 2 mass% aqueous dispersion. This corresponded to the ideal hectorite composition: $M_{.66}[Li_{0.66}Mg_{5.34}Si_8O_{20}(OH)_4]$, where M^+ = exchangeable cations. In synthetic hectorite without organic modifier, Li^+ is the exchangeable cation. For quaternary imidazolium cations, 0.066 mol were used and only 0.2 mol of LiF were needed. The source of MgO was a freshly synthesized $Mg(OH)_2$ slurry.

0.72 g BMI, 1.32 g DDMI, and 0.85 g DMI (3.3 mmol) of imidazolium salts were individually dissolved in 200 ml deionized water in a three round-bottom flask, 0.26 g of LiF was added with vigorous stirring. Separately, 10.16 g of $MgCl_2{\cdot}6H_2O$ were dissolved in 400 ml of deionized water and reacted with 77 ml of 1 N NaOH. The $Mg(OH)_2$ precipitate was allowed to settle, then decanted and washed with deionized water until removal of chloride ions. The fresh $Mg(OH)_2$ slurries, concentrated down to 150 ml, were added to the imidazolium salts-LiF solutions and stirred for 20 min. In each round-bottom flask, 11.42 g of Ludox HS-40 was added and the total volume were brought up to 400 ml to achieve ca. 2% gel concentration. The dispersions were refluxed at 383 K with stirring for 48 h, then filtered, washed and dried at 383 K for 10–12 h. The synthesized hectorites were denoted as STH1 (imidazolium salt: BMI), STH2 (imidazolium salt: DDMI) and STH3 (imidazolium salt: DMI). For hectorite without organic modifier, 0.35 g of LiF was used and was processed as reported above and was denoted as STH. All hectorites were calcined at 723 K for 12 h and denoted as STHC, STH1C, STH2C and STH3C.

2.3. Characterization

Powder X-ray diffraction (PXRD) analysis was carried out with the Philips X'Pert MPD system using PW3123/00 Ni-filtered Cu-Kα radiation with slow scanning of 0.3°/s. Fourier transform infrared spectra (FTIR) were measured with the Perkin-Elmer, GX-FTIR instrument using KBr pellets. The specific surface area was determined from N_2 adsorption data at 77.35 K (ASAP 2020, Micromeritics Inc., USA) after activating the sample at 423 K under high vacuum. The micropore surface area was determined by the *t* method (Panfitt and Sing, 1976). The slope of the *t*-plot is directly proportional to the surface area of the sample. Any upward deviation from linearity is due to the capillary condensation inside the pores and the initial slope is proportional to the micropore surface area. CO_2 and N_2 adsorption was measured at 288, 303 and 318 K using a static volumetric system (ASAP 2020, Micromeritics Inc., USA). The temperature during adsorption and desorption was kept constant using Julabo F 25 water circulator. Prior to adsorption measurements, the samples were dried at 353 K for 24 h. The samples were further activated in situ by increasing the temperature at a heating rate of 1 K min^{-1} up to 423 K under vacuum (5×10^{-3} mmHg) and the temperature and vacuum was maintained for 8 h before the sorption measurements.

Adsorption data obtained were fitted by the virial equation (Eq. (1)) and values for Henry's constant, *K*, were determined from the first virial coefficient using Eq. (2) (Sebastian et al., 2005; Sebastian and Jasra, 2005; Peter et al., 2005). Virial equation;

$$\ln {}^{P}\!\Big/_{q} = A + Bq + Cq^2 + \ldots\ldots \tag{1}$$

Henry's Constant;

$$K = \exp(-A) \tag{2}$$

where *q* is the amount of gas adsorbed per unit mass of the adsorbent, *P* is the equilibrium pressure, *A*, *B* and *C* are the first, second and third virial coefficients respectively.

Adsorption capacity, selectivity and isosteric heat of adsorption were determined from the adsorption isotherms measured at 288, 303 and 318 K. The component selectivity of gases A and B was calculated by using the equation (Sebastian et al., 2005; Sebastian and Jasra, 2005; Peter et al., 2005).

$$\alpha_{A/B} = \left[{}^{V_A}\Big/_{V_B}\right]_{P,T} \tag{3}$$

where, V_A and V_B are the volumes of gas A and B respectively adsorbed at any given pressure *P* and temperature *T*.

Isosteric heats of adsorption were calculated from the adsorption data collected at 288, 303 and 318 K using the Clausius–Clapeyron equation (Sebastian et al., 2005; Sebastian and Jasra, 2005; Peter et al., 2005).

$$\Delta_{ad}H^o = R\left[{}^{\partial \ln P}\Big/_{\partial(1/T)}\right]_\theta \tag{4}$$

where, *R* is the universal gas constant, *θ* is the fraction of the adsorbed sites at a pressure *P* and temperature *T*. The errors in the Henry constant, adsorption selectivity and heat of adsorption estimated from propagation of error method were 0.5%, 0.4%, and 0.4% respectively.

3. Results and discussion

3.1. PXRD and FTIR study

The degree of hectorite crystallization and intercalation of imidazolium cation was studied by PXRD (Fig. 1). STH, with Li^+ as exchangeable cations displayed a basal spacing of 1.12 nm. Peaks at 4.6 Å (about 19.4° 2*θ*), 2.6 Å (35.8° 2*θ*), 1.7 Å (52.9° 2*θ*), and 1.5 Å (60.6° 2*θ*) represented the (110, 020), (130, 200), (150, 240, 310), and (060, 330) reflections of hectorite, respectively. Brucite $Mg(OH)_2$ was only crystalline product in the starting materials and there was no sign of any unreacted $Mg(OH)_2$ which would display reflections at 4.77 Å (18.6° 2*θ*) and 2.37 Å (38.0° 2*θ*) for (001) and (101) reflections. The basal spacing for STH1, STH2 and STH3 was 1.32, 1.42 and 1.66 nm, respectively. The imidazolium cations with variable alkyl chain length formed monolayer to bilayer arrangements within the interlayer space (Vaia et al., 1994; Patel et al., 2008). The (060) values of STH, STH1, STH2 and STH3 were determined to be nearly 1.52 Å, indicating the trioctahedral nature of synthesized samples. All reflections at about $2\theta = 7°, 19°, 28°, 36°, 53°$ and $61°$ suggest synthesize samples to have a structure similar to hectorite. In the case of calcined samples, the (001) reflection disappeared; however, the layered structure remained stable as indicated by other reflections.

All peaks observed in FTIR spectra (Fig. 2) were due to either hectorite structure or imidazolium moieties. The higher frequency band at 3678 cm^{-1} was recognized to the Mg–OH stretching vibration. Other