Intrinsic affinity of acid-activated bentonite towards hydrogen and carbon dioxide

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ABSTRACT

The effect of acid activation on bentonite affinity toward carbon dioxide (CO_2) and hydrogen (H_2) was investigated at ambient conditions. Characterization through X-ray diffraction and fluorescence, thermal gravimetric analysis, nitrogen adsorption-desorption isotherms, Fourier Transform Infrared spectroscopy and differential scanning calorimetry allowed correlating newly induced textural and structural features with adsorptive properties. Optimum acid treatment improved the specific surface area and porosity. The resulting decrease in dehydration temperature indicates decay in hydrophilic character. The affinity improvement towards hydrogen was due to Brønsted acidity suppression and surface basicity attenuation, which are essential requirements for adsorption on aluminosilicates (AS) via weak Lewis Acid-Base interactions, but excessive acid attack was detrimental. Low Si/Al surfaces should be suitable for CO_2 capture, while moderately acid-treated clays should be interesting candidates as hydrogen adsorbents. This allows envisaging promising prospects for low-cost AS-based materials intended for selective CO_2-free capture and storage of hydrogen without energy and safety constraints.

Introduction

Power fluctuations imposes energy storage, and this concept is of great importance, more particularly for renewable energy sources [1]. One of these sources is hydrogen, which appears as probably the most promising fuel for a future hydrogen-based economy. However, hydrogen storage without severe safety and economic constraints still remains a major challenge to be addressed. The current research trend in this regard focuses on hydrogen adsorption on solid matrices [2—6]. Among the wide variety of more or less porous adsorbents tested so far [2,3,7—18]. Si-containing matrices exhibit intrinsic affinity towards hydrogen through their silicon atoms.

As a general tendency, the chemical approaches appear to prevail at the expense of physical hydrogen storage, relegating to the background the very concept of truly reversible capture of hydrogen under ambient conditions. This concept should be regarded as an essential requirement for a sustainable hydrogen-based economy, and, paradoxically, does not necessarily need the synthesis of highly porous materials. Indeed, low surface organoclays were found to display appreciable surface affinity towards hydrogen under ambient conditions [19—22]. A part of this affinity was attributed to the inorganic support, i.e. to the presence of silicon atoms.

In this regard, a special interest is devoted to clay materials such as bentonite, which are natural, low cost, widely

available and probably the most promising materials because of their high content of lamellar aluminosilicate (montmorillonite). The latter displays interesting surface properties that can be judiciously tailored for various applications through specific modification procedures [23–32]. Among these, acid activation using various acids *such as HCl, H$_2$SO$_4$, or HNO$_3$* has widely been studied to tailor the Si/Al ratio [30–33]. The subsequent Al, Fe, and Mg atoms dissolution induces changes in crystallinity and/or rearrangement of the structural ions [30]. This results in a decay of the cation exchange capacity (CEC) [34] and the genesis of additional silanol groups [35]. An optimum acid activation should generate higher number of silanol groups without causing structure collapse that affects the porosity and specific surface area. This requires a rigorous control of the acid concentration, temperature and contact time along with an appropriate acid/clay ratio [23,35–38].

The increase of Si content is expected to improve the intrinsic affinity towards hydrogen of the aluminosilicate surface [7]. This is the main argument that justifies the present investigations. Since changes in Si content should induce changes in the acid-base properties, thermal programmed desorption of CO$_2$ will be used to correlate the surface basicity to surface affinity for hydrogen. Correlating the retention capacities of CO$_2$ and H$_2$ is expected to provide valuable information on the role of the chemical composition of bentonite and acid-base properties on the ability of bentonite to reversibly capture hydrogen. To the best of our knowledge such an approach has barely been tackled so far.

Experimental

Acid activation of bentonite

Samples of a commercial bentonite supplied by Aldrich (200 g) were treated with 1000 mL of aqueous 5 M sulphuric acid solution at 80 °C for various contact times under mild stirring, according to a conventional procedure [35,37]. The powder was filtered and repeatedly washed with distilled water until neutral pH, and then dried at 100 °C for 12 h. The different samples were denoted as Bent, AAB1, AAB4, AAB8, AAB15 and AAB24 after acid treatment during 0, 1, 4, 8, 15 and 24 h, respectively. Each sample was then washed with water, centrifuged, and repeatedly dialyzed overnight with distilled water in cellulose bags to remove the residual excess of unreacted salts. The as-activated bentonite was softly ground and sieved into a 75 μm particle size (200 mesh ASTM) using a porcelain mill.

Characterization

The specific surface area (SSA), porosity and pore size distribution of samples previously dried and outgassed at 100–150 °C for 4 h under a 10 Torr vacuum were assessed by nitrogen adsorption-desorption isotherms at −195.7 °C, using a Quantachrome device with an Autosorb automated gas system control. Thermal gravimetric Analysis (TG and DTG) was performed by means of a TG/TDA-6200 thermal analyzer (Seiko instrument Inc.), under a 100 mL min^{-1} nitrogen stream and 5 °C.min^{-1} heating rate. The synthesized materials were

also characterized through X-ray diffraction (XRD) using a Siemens D5000 equipment (Co-Kα at 1.7890Å), Fourier transform Infrared spectroscopy by means of a Model Nicolet 6700 FTIR instrument, operating in attenuated total reflectance (ATR) mode (Diamond ATR crystal) between 600 and 4000 cm^{-1}, and differential scanning calorimetry (DSC) on a Mettler Toledo TGA-SDTA 851e, under dry nitrogen stream of 20 mL.min^{-1} and heating rate of 5 °C.min^{-1}.

Adsorption-desorption tests

The surface basicity and hydrophilic character were assessed by CO$_2$-thermal programmed desorption (CO$_2$-TPD) measurements of the CO$_2$ and water retention capacity (CRC and WRC, respectively) between 20 and 200 °C, according to a procedure fully described elsewhere [39]. Prior to TPD, dynamic impregnation of the adsorbent was carried out with 200 mL of CO$_2$ at 20 °C under a 15 mL.min^{-1} dry nitrogen stream, followed by a purge under similar conditions for evacuating the non-adsorbed CO$_2$ excess. TPD measurements were achieved under a 1 mL min^{-1} of dry nitrogen stream within a tubular oven coupled to a CO$_2$-detector (Li-840A CO$_2$/H$_2$O Gas Analyzer) [40,41]. Each sample (40 mg, particle size of 0.05–0.1 mm) was dried at 80–160 °C for 1 h, then cooled down to 20 °C and saturated at this temperature with dry CO$_2$ in static mode without nitrogen stream for accurate assessment of the CRC and WRC values. The CO$_2$ excess was further evacuated by 5 mL.min^{-1} nitrogen stream until no CO$_2$ was detected. The values of CRC and WRC were expressed in μmol of desorbed gas per gram of adsorbent under 5 mL.min^{-1} nitrogen stream and 5 °C.min^{-1} heating rate between 20 and 80 or 100 °C depending on the limit of stability of each sample as given by thermal gravimetric results.

Ammonia TPD measurements were achieved to assess the surface acidity for only some samples using 200 mg clay sample having a 0.1–0.2 mm particle size, introduced as a 2–3 cm height fixed clay-bed in the cylindrical glass microreactor (2 mm internal diameter) of the TPD device. TPD tests were run under 80 mL.min^{-1} dry N60 nitrogen stream at normal pressure. Such operations conditions are essential requirements for achieving adsorption–desorption equilibrium and to prevent from diffusion hindrance. Ammonia was injected through the clay fixed bed till saturation, and the excess of the probe gas was purged. Saturation was attained when the amount of probe gas injected in the TPD microreactor is equal to that of the probe gas evacuated into the titration solution. Further, NH$_3$-TPD was performed with a constant heating rate of ca. 75 °C.h^{-1} between 80 and 500 °C. The desorbed ammonia was evacuated by the carrier gas, then bubbled during 15–18 min in 2 mL samples of a 0.02 N sulfuric acid solution or NaOH through a 2 mm × 20 mm cylindrical porous glass bubbler and assessed by back titration using a 0.01 N NaOH or H$_2$SO$_4$ solution using Tashiro's indicator or by potentiometry.

Hydrogen retention capacity (HRC) was measured on samples previously saturated at room temperature with dry hydrogen in a similar procedure as previously, at room temperature and ambient air pressure. The amount of desorbed hydrogen was measured through both DSC and TGA measurements in dry helium, between 20 and 80 or 100 °C