Thermochimica Acta 600 (2015) 52–61

Contents lists available at ScienceDirect

Thermochimica Acta

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

TPD and DSC insights in the basicity of MCM-48-like silica and modified counterparts

Kamel Ghomari [a,c], Abdellah Benhamou [b], Rachida Hamacha [c], Abdelkader Bengueddach [c], Saadia Nousir [a], Tze Chieh Shiao [a], René Roy [a], Abdelkrim Azzouz [a,*]

[a] *Nanoqam, Department of Chemistry, University of Quebec at Montreal, H3C3P8, Canada*
[b] *Laboratory of Environmental Process Engineering, "M. Boudiaf" University of Sciences and Technology of Oran, Algeria*
[c] *Material Chemistry Laboratory, "Ahmed-Benbella"University of Oran, Algeria*

ARTICLE INFO

Article history:
Received 15 June 2014
Received in revised form 19 October 2014
Accepted 15 November 2014
Available online 25 November 2014

Keywords:
Mesoporous silica
MCM-48
Polyol loaded silica
Thermal programmed desorption
Differential scanning calorimetry
Basicity assessment

ABSTRACT

The basicity of MCM-48-like silica and modified counterparts was investigated by CO_2 thermal programmed desorption (TPD) and differential scanning calorimetry (DSC). Post-synthesis modifications were achieved through: (i) incorporation of dihexylamine (DHA); (ii) DHA removal by ethanol; (iii) calcination at 550 °C in air stream and (iv) incorporation of Boltorn H-20 dendrimer. After DHA incorporation, the specific surface area dropped from 953 down to 74 $m^2\,g^{-1}$, and the pore volume decreased from 0.41 to 0.13 $cm^3\,g^{-1}$. The surface basicity, expressed in terms of retained CO_2 amount decreased markedly after template removal, but was slightly revived after dendrimer loading. CO_2 was found to adsorb via physical or chemical interactions on two types of sites, according to the post-synthesis treatment. Correlating TPD and DSC measurements allows assessing the extent of the acidity attenuation and basicity adjustment for a wide variety of catalysts and adsorbents through suitable post-synthesis modifications.

1. Introduction

Carbon dioxide (CO_2) behaves as an acidic gas owing to its electron acceptor capacity, and is expected to readily react with water and bases. Given that the impact of the major CO_2 emission sources has become a major issue to be addressed, CO_2 retention by base-like compounds has focused fairly great interest in the published literature [1,3–32]. This involves strong chemical CO_2 interaction with the formation of carbamate groups. The latter can be reversed only upon heating or other energy-consuming chemical process.

Therefore, when assessed accurately, strong affinity towards CO_2 may be regarded as a precise indicator for estimating the base-like character of solid surfaces. Acidic surfaces such as mesoporous silicas, aluminosilicates, zeolites and clay minerals exhibit low affinity towards CO_2, but most of their synthetic counterparts obtained through hydrothermal procedures contain templating agents in their pores and cavities [11,33], and can interact with CO_2 via the formation of both carbamate and carbonate-like associations [28]. The special interest devoted to such materials is justified by their appreciable thermal and chemical stabilities, specific surface area, porosity and rigid frameworks that do not undergo compaction.

Supported amines or freshly prepared zeolite-like structures still containing amines [14,27,19,20,22,27], mesoporous silicas such as SBA-12 [34], SBA-15 [21,34], microspheres [2], MCM-41 and MCM-48 [23] showed appreciable affinity towards CO_2. In such structures, the number of adsorption sites accessible to CO_2 molecules is expected to depend on the pore size [16]. Among these materials, mesoporous silicas appear as interesting materials to investigate, due to their large pore aperture, which allows envisaging diverse modification procedures. For instance, pore-expanded MCM-41 displayed higher CO_2 uptakes than their conventional counterparts [12,32,33]. Reportedly, polyethylenimine-containing MCM-41-like silica showed a CO_2 retention capacity ca. 24 times higher than MCM-41 and twice higher than pure polyethylenimine [24]. However, the presence of amine within the pores and channels is supposed to generate major drawback by impeding the accessibility to the internal surface. Besides, when used in the reversible capture of gases, thermal

---

[*] Corresponding author. Tel.: +1 514 987 4119; fax: +1 514 987 4054.
E-mail address: azzouz.a@uqam.ca (A. Azzouz).

http://dx.doi.org/10.1016/j.tca.2014.11.014
0040-6031/© 2014 Elsevier B.V. All rights reserved.

regeneration is often required. This is expected to affect unavoidably the thermal stability by amine losses via evaporation and degradation.

Clay-supported polyalcohols and polyol dendrimers [4–9,26] were found to interact with CO_2 via much weaker interaction due to the slightly basic character of their hydroxyl groups. This finding stimulated research for obtaining mesoporous silica derivatives with various acid-base characters.

In the present study, a special interest was devoted to MCM-48-like silica, which possesses a tridimensional framework with high specific surface area and porosity [12,20]. Post-synthesis treatments of the freshly synthesized MCM-48 through the incorporation of dihexylamine (DHA), followed by DHA removal and calcination, along with incorporation of polyol dendrimer are expected to produce silica counterparts displaying interactions with CO_2 ranging from strong basicity of the organic moiety incorporated to weak acidity of the silica framework. Thermal programmed desorption of CO_2 (TPD) and differential scanning calorimetry (DSC) were used for this purpose. The CO_2 retention capacity (CRC) and the retention strength were correlated with the desorption heat and discussed in terms of both strength and extent of acid-base interaction.

2. Experimental

2.1. Synthesis procedure and post-synthesis treatments

MCM-48-like silica was synthesized via hydrothermal procedure, using cetyl-trimethyl-ammonium bromide (CTMABr) as the templating agent and tetraethyl ortho-silicate (TEOS) as the silica source according to previous methods [13,30]. Thus, NaOH and CTMABr were dissolved in deionized water, and then TEOS was added under vigorous stirring for 2 h. The initial gel with a molar chemical composition of 1.0 SiO_2, 0.48 CTMAB, 0.48 NaOH, 55 H_2O was initially heated at 100 °C for 3 days in a sealed Teflon-lined autoclave. The final product was recovered as a white powder after vacuum filtration. The latter was repeatedly washed with deionized water and dried overnight at room temperature.

For post-synthesis treatment, the as-synthesized MCM-48-0 (5 g) was added to an emulsion of dihexylamine (DHA) (7 g) in distilled water (78 g) under continuous stirring for 30 min, and the resulting mixture was heated at 120 °C in the same autoclave for 72 h. After vacuum filtration, the product, designated as MCM-48-1, was repeatedly washed with deionized water and then dried. In a second step [30,31]. MCM-48-1 was washed twice with ethanol (9.7 mL per g of adsorbent) at room temperature (MCM-48-2). The resulting material was further calcined in air stream at 550 °C for 6 h [30], giving rise to a purely inorganic material (MCM-48-3).

In order to provide clear evidence of the role of the OH groups, polyol-MCM-48 materials (denoted by MCM-48-OH) were prepared using aqueous solutions of 0.5, 1.0 and 3.0 wt% in Boltorn dendrimer H20 (supplied by Perstorpt Polyol, Inc., Toledo, Ohio). The idealized structure (Scheme S1) consists of an hyperbranched polyester with molecular weight of 1749.8 g/mol. Intercalation was achieved by mere electrostatic self-assembly in aqueous media between a MCM-48 suspension and the organic polyol species. For this purpose, attempts were performed by impregnating samples of these materials in powder form (500 mg) with a diluted aqueous solution containing the dendritic polyalcohol. The resulting mixture was then stirred overnight at room temperature. The organo-mesoporous samples (denoted by MCM-48-OH_1, MCM-48-OH_2 and MCM-48-OH_3) were dried overnight at room temperature and then at 80 °C for 6 h until total evaporation before being smoothly crushed.

2.2. Samples characterization

The morphology and particle size of MCM-48 samples were analyzed through scanning electronic microscopy (SEM) using a Hitachi S-4300SE/N-VP-SEM instrument. Deeper insights in the structure and pore shape uniformity were achieved by means of a Jeol JEM-2100F Transmission Electron Microscope (TEM), coupled to a field effect cannon that operates at a 200 KV acceleration voltage and an X-ray Energy Dispersion Spectrometer (EDS). The structure and crystallinity were investigated by X-ray diffraction (XRD with Co-K_{alpha} radiation at 1.7890 Å) by means of a Siemens D5000 instrument.

Nitrogen adsorption–desorption equilibria on samples previously outgassed at 100 °C for 6 h were achieved at 77 K, using a Micromeritics ASAP 2000 equipment. The specific surface area (SSA) values were calculated from the BET isotherm plots. The pore distribution was obtained using the BJH method. FT-IR spectroscopy (Bruker Vector 22 FTIR spectrometer) was performed to identify the chemical functional groups present in the MCM-48 samples. For this purpose, finely crushed MCM-48 powders were dispersed in a proportion of up to 10 wt% in anhydrous KBr pills. Thermal gravimetry (TG) and differential thermal gravimetry (DTG) analyses were performed in the temperature 20–900 °C using a TG/TDA6200 Seiko thermal analyzer under a 100 ml min^{-1} air or N_2 stream, at a 5 °C min^{-1} heating rate.

2.3. CO_2 thermal desorption measurements

The hydrophilic character and base-like behavior of the different MCM-48 samples with defined particle size (0.05–0.1 mm) were evaluated via thermal programmed desorption of carbon dioxide (CO_2-TPD) and water (H_2O-TPD) between 20 and 90 °C, as fully described elsewhere [10,26]. The amounts of desorbed CO_2 and water were measured by means of a Li-840A CO_2/H_2O gas analyzer. Here, CO_2-TPD measurements are intended to provide three kinds of data, i.e., (1) the CO_2 retention capacity (CRC), which corresponds to the number of adsorption sites; (2) the peak area ratios, which account for the distribution of the basicity strength; (3) the temperature of the desorption peak, which provides information on the basicity strength. The latter will be correlated with the desorption heat as determined through DSC measurements

Qualitative plotting of the TPD pattern and quick estimation of the maximum desorption temperature were achieved after a dynamic saturation of the sample with 0.0615 mmol of pure dry CO_2 within the TPD reactor under 15 mL min^{-1} dry nitrogen stream. Accurate assessment of the CRC was made after a static saturation mode without nitrogen stream and total evacuation of the non-adsorbed CO_2 excess by 15 mL min^{-1} of nitrogen stream. In both modes, TPD measurements were performed between 20 °C and 90 °C at a heating rate of 5 °C min^{-1} and nitrogen flow rate of 15 mL min^{-1} (dynamic mode) or 1 mL min^{-1} (static mode of saturation). The CRC was expressed in terms of μmol CO_2 desorbed per gram of dry sample between 20 °C and 90 °C, and corresponds to the area described by the TPD pattern within this temperature range. Because of possible fluctuations of the amounts of adsorbed CO_2 and water during adsorption, accurate CRC assessment required TPD measurements through repetitive adsorption-desorption cycles between 20 °C and 90 °C. This upper temperature limit was determined by TG-DTG measurements, which revealed higher thermal stability for MCM-48-OH samples (up to 160–180 °C) as compared to their other counterparts (110–120 °C).