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Liquid phase microcalorimetry applied to evaluate surface polarity of MCM-41 type aluminosilicates

M.J. Meziani*, H. Benalla

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072, Université Montpellier II,
C.C. 015, Place E. Bataillon, 34095 Montpellier Cedex 5, France

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Abstract

Three calorimetric methods have been used to evaluate the surface polarity of three MCM-41 materials characterised by different Si:Al ratios (referred to as SiAl*x*C14, where *x* is the moles of Si:Al ratio, and 14 the chain length of the surfactant template). In the liquid phase, the heats of adsorption of 1-butanol from *n*-heptane and the heats of immersion in water, *n*-heptane and formamide were compared with the corresponding heat values obtained for two reference solids, viz. silica XOB015 and alumina. Surface (internal) energy of all MCM-41 samples appeared to be smaller than that of any reference solid, the differences being more marked in the case of alumina. In the gas phase, the combination of ammonia gas adsorption and mirocalorimetry measurements was used to evaluate the number and strength of acidic surface sites. With the exception of SiAl8C14, which contains 46% of strongly acidic sites, SiC14 and SiAl32C14 have low surface acidity. The broad distribution of adsorption energy values indicates the energetic heterogeneity of the acidic sites. Incorporating Al into the silicate matrix caused the surface polarity of the materials to increase. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Surface polarity; Microcalorimetry; MCM-41 materials

1. Introduction

The synthesis of inorganic materials using surfactants as structure directing agents has opened new perspectives in the field of adsorption and catalysis [1,2]. These well-defined structures can be regarded as model adsorbents to test the various methods of characterisation of porous solid substrates using gas and liquid adsorption [3–6]. They can be employed in various processes in which physical or chemical adsorption on solids with controllable pore shapes and sizes achieves desired results [7–9]. The determination of surface properties of such materials is crucial to their future applications.

In previous work [10,11], we have studied textural and surface characteristics of oxide-walled solids of ordered mesoporosity. The effect of incorporating aluminium into the silica matrix on the hydrophilic and acidic character of the surface of MCM-41 materials have been quantified using a variety of methods. In the present work, some surface properties of three materials prepared with different Si:Al ratio are compared to those of non-porous silica and alumina. The results of flow microcalorimetry measurements of 1-butanol adsorption from its solution in *n*-heptane are employed to describe the degree of surface polarity. The experimentally measured enthalpies of immersion in an apolar solvent (*n*-heptane) and two polar liquids

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* Corresponding author. Tel.: +33-467-14-33-34;
fax: +33-467-14-33-04.
E-mail address: jaouad@univ-montp2.fr (M.J. Meziani).

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(water and formamide) provide information about the surface enthalpy of the solids studied. The combination of ammonia gas adsorption and batch calorimetry measurements provides useful information about the number and strength distribution of surface acid sites. Surface polarity of all MCM-41 samples is compared to that of too reference solids, silica XOB015 and alumina.

2. Experimental

2.1. Materials

A purely siliceous sample, SiC14, and two aluminosilicate materials with framework Si:Al ratios of 32 and 8, SiAl32C14 and SiAl8C14, were prepared with the use of tetradecyltrimethylammonium bromide as structure directing agent and aluminium isopropoxide as a source of aluminium. The synthesis of these materials and their successive treatment were described in a previous article [10]. The following values of the BET specific surface area were obtained: 946 $m^2\,g^{-1}$, SiC14; 881 $m^2\,g^{-1}$, SiAl32C14; 900 $m^2\,g^{-1}$, SiAl8C14. The most probable value of the pore diameter, as determined from the BJH pore size distribution, was equal to 2.7 nm, irrespective of the sample. A macroporous Spherosil XOB015 (Rhône-Poulenc, France) and a non-porous alumina (carbon union) were used as powdered reference solids. The BET specific surface areas were equal to 29 $m^2\,g^{-1}$, XOB015 and 9.2 $m^2\,g^{-1}$, alumina.

The organic liquids used in calorimetric experiments, viz. 1-butanol, *n*-heptane and formamide, were Merck HPLC grade materials with purity exceeding 99%. Prior to measurement, they were additionally dried with zeolite molecular sieves. Water was deionised and purified with a Millipore Super Q System.

2.2. Methods

The integral heats of adsorption of *n*-butanol from its solution in *n*-heptane were measured using a microscale flow microcalorimeter [12]. The flow cell was filled with a known mass of powdered sample and evacuated to 0.01 Torr at 298 K. The adsorbent was then wetted with *n*-heptane. Once thermal equilibrium had been attained, the flow of solvent was exchanged for that of the 2 $g\,l^{-1}$ solution of 1-butanol in *n*-heptane. The related heat effect was recorded as a sharp thermal peak. Calibration of the area under this peak was carried out by dissipating a known amount of energy in the cell under the same flowing conditions (Joule heating using a calibration probe incorporated into the outlet tube). The ultimate heat effect was quantified as the integral heat of displacement per unit BET specific surface area, $\Delta_{dpl}H$.

The heats of immersion in water, *n*-heptane and formamide were measured with a Calvet differential calorimeter at 301 K [13]. The solid sample, outgassed at 433 K for 12 h, was placed in a glass bulb under vacuum. The bulb was closed by a brittle tail and introduced into the calorimetric cell, which had been previously filled with about 15 ml of immersional liquid. After attaining thermal equilibrium, the glass tail was broken and the immersional liquid penetrated into the bulb. The total heat effect was corrected for thermal effects coming from breaking the tail and those related to changes in the dead volume of the calorimetric cell and the bulb upon experiment. The resulting heat of immersion, $\Delta_{imm}H$, was expressed per unit BET surface area.

The differential enthalpies of NH_3 gas adsorption were determined using heat flow microcalorimeter of the Tian-Calvet type (C80 from Setaram), with an on-line injection system permitting the introduction of successive small pulses of the reactive gas. After every adsorption step, the equilibrium pressure was measured by means of a datametrics differential pressure gauge. Successive gas doses were sent onto the sample until a final equilibrium pressure of 0.6 Torr was attained. Prior to adsorption measurements, the samples were degassed overnight at 433 K. In order to reduce physisorption of ammonia on the solid surface, the adsorption temperature was maintained at 353 K. At the end of the first adsorption cycle, the sample was pumped at 353 K and the secondary adsorption cycle was then performed at the same temperature.

3. Results and discussion

The 1-butanol molecules are capable of interacting with both polar and non-polar sites exposed on the solid surface. At the solid–liquid interface, the adsorption of 1-butanol from its solution in *n*-heptane has a competitive character. When the solid sample is initially immersed in the inert solvent and then brought into contact with the solution, the alcohol molecules can displace *n*-heptane only from polar surface sites. The concentration of 1-butanol in the solution used in calorimetric measurements is low enough for each polar site to be occupied by only one alcohol molecule. For MCM-41 materials, the diameter of cylindrical pores is much greater than the molecular length of butanol (<0.5 nm) and, probably, all surface sites are occupied. Therefore, the heat of displacement per unit surface area may be considered as the measure of the surface polarity for a given solid substrate. Notice that the value of $\Delta_{\mathrm{dpl}}H$ includes both the number of polar sites and their relative strength averaged over all accessible surface domains.

The experimental heats of displacement for two reference solids are as follows: 79.3 mJ m^{-2}, silica XOB015; 150.4 mJ m^{-2}. Therefore, alumina has higher surface polarity than silica. The results of calorimetric measurements for the three MCM-41 materials are presented in Fig. 1, in which the ratio of the heat of displacement for a given sample to the heat of displacement for a reference sample is plotted as a function of the reciprocal of Si:Al ratio.

As can be seen, the generalised surface polarity of mesoporous samples is smaller than those of reference solids. With silica XOB015 taken as reference, the values of $\Delta_{\mathrm{dpl}}H/\Delta_{\mathrm{dpl}}H_{\mathrm{ref}}$ are doubled but they are still smaller than 100%. The incorporation of aluminium into the silica matrix causes the surface polarity to increase, though the difference between SiAl32C14 and SiAl8C14 is not very pronounced.

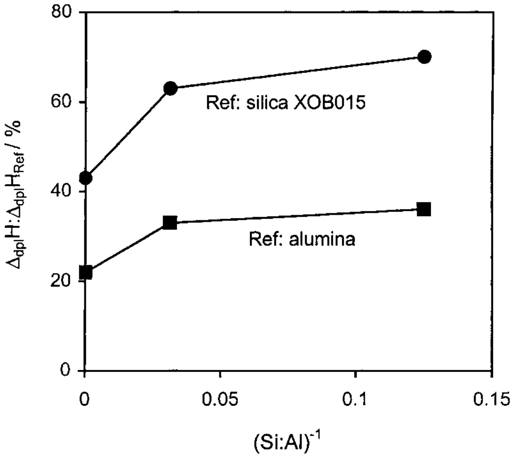

Fig. 1. The ratio of the heat of displacement of *n*-heptane by 1-butanol from a 2 g l^{-1} butanol solution on a MCM-41 material to the corresponding heat of displacement on a non-porous reference solid plotted as a function of the reciprocal of the molar Si:Al ratio.

The more precise image of surface polarity can be obtained using the experimental heats of immersion in polar liquids, viz. water and formamide. Thermal effects of immersion in *n*-heptane provide information about the non-polar character of the solid surface.

The following heats of immersion have been obtained for XOB015 silica: 78 mJ m^{-2}, *n*-heptane; 365 mJ m^{-2}, water; 305 mJ m^{-2}. For alumina, the corresponding values are as follows: 162 mJ m^{-2}, *n*-heptane; 704 mJ m^{-2}, water; 585 mJ m^{-2}. Fig. 2 shows the various heats of immersion in these three liquids for MCM-41 materials expressed as

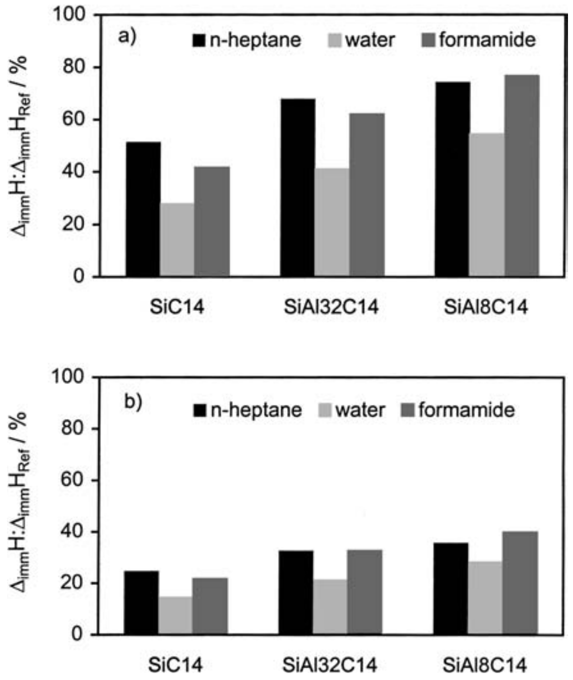

Fig. 2. Schematic representation of the results of immersional calorimetry measurements performed on three MCM-41 samples in *n*-heptane, water, formamide; the ratio of the heat of immersion for a given sample to the corresponding heat of immersion for a reference solid: (a) silica XOB015 as a reference; (b) alumina as a reference.

percentages of the appropriate heats of immersion for the two reference solids.

The heats of immersion values obtained for SiC14, SiAl32C14 and SiAl8C14 in *n*-heptane, water and formamide are again smaller than those of the reference samples. This points to the small total surface (internal) energy of the MCM-41 samples. The heat effects on immersion in polar liquids is very sensitive to the aluminium content in the silicate framework and this tendency is similar to that deduced from the results of the adsorption of 1-butanol in *n*-heptane. The values of $\Delta_{\mathrm{imm}}H$ in formamide are greater than those in water, indicating a predominant acidic character of the oxide-walled materials studied. The increase in heat of immersion in apolar *n*-heptane is less considerable, but shows that the presence of aluminium also modifies to some extent the dispersive forces operating at the MCM-41 surface.

In the gas phase, the determination by flow microcalorimetric, of the pseudo-differential enthalpy $\Delta_{\mathrm{ads}}H$ of ammonia chemisorption at 80°C remains a more precise method to evaluate quantitatively the strength distribution of surface acid sites. The strength distributions of acid sites in the three samples are shown in Fig. 3. On the purely siliceous SiC14, a single strength value of about -40 kJ mol^{-1} has been observed. It corresponds mainly to ammonia adsorption on terminal silanol groups and Si–O–Si bridging oxygen atoms in the pore walls. These adsorption sites are very homogeneous. In the case of SiAl32C14, the changes in the strength distribution of acid sites, ranging between -45 and -70 kJ mol^{-1} are very small and do not go beyond the critical value of -80 kJ mol^{-1}, characteristic of ammonia chemisorption on strongly acidic sites. This would mean the presence of surface sites with lower acid strength which are distributed unequally on the surface (e.g. regrouped on some surface patches). This nature of distribution could be ascribed to NH_3 adsorption on the pore walls, Si–O–Si and Si–O–Al bridging oxygen atoms and the terminal surface silanol groups. Concerning the case of SiAl8C14, the maximum amount of strong sites showing NH_3 chemisorption enthalpy greater than -80 kJ mol^{-1} is about 46% of the total amount of acid sites. This means that the distribution of adsorption energy values is quite broad and the sample surface is heterogeneous. The energetic heterogeneity of acid sites may be ascribed to important flexibility of the amorphous framework and to various contributions from sites containing Al atoms, as evidenced clearly by the results of NMR study [11]. Moreover, additionally to the Lewis sites, the existence of two types of Brönsted sites, i.e. Si(OH)Al and Si–Al(OH)–Si, cannot be excluded. It is clear that the incorporation of Al into the MCM-41 network leads to the creation of strong Brönsted acid sites and Lewis acid sites.

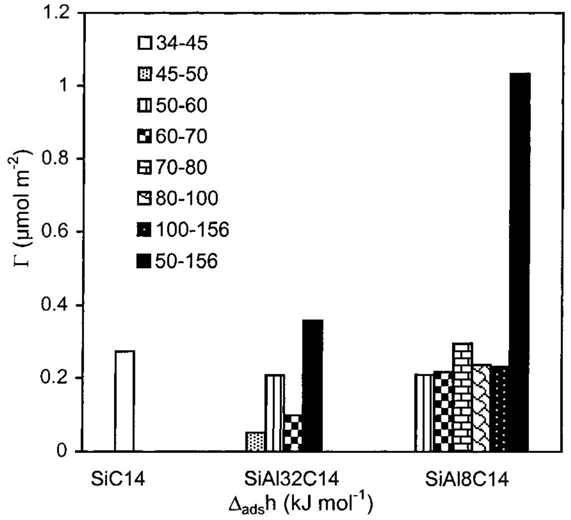

Fig. 3. Schematic representation of the strength distribution of acid sites on the three MCM-41 samples.

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