On the influence of water traces on the acidity measurement of amorphous aluminosilicates

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ABSTRACT

For the measurement of their acidity, amorphous aluminosilicates are beforehand treated at temperature of 450 °C or higher in order to remove water adsorbed on their surface. We will show in this study that, during the standard course of an acidity measurement by low temperature CO adsorption, traces of water present in the setup may perturb the acidity measurement by desorbing from the setup and adsorbing on the sample. We will also demonstrate that the interaction of water occurs on mild and strong Lewis sites and leads to the detection of stronger Brønsted sites than those natively present in the amorphous aluminosilicate. We will finally propose an experimental procedure that allows avoiding the adsorption on water on the sample and will clearly identify the position of the band associated with H_2O and D_2O adsorbed on Lewis sites before and after addition of CO.

1. Introduction

Many chemical processes in oil refining, petrochemistry and fine chemicals production rely on heterogeneous acid catalysts. Silica-alumina materials, which combine high surface areas and Lewis and Brønsted acidic properties, are widely used in these applications. These materials can be divided into two families: 1) zeolites which are crystalline and microporous and 2) amorphous silica-aluminas (ASA) which are mesoporous. Zeolites contain mainly Brønsted sites arising from the presence of Si—OH—Al bridges. In ASA, the exact nature of the Brønsted acid sites is more obscure: a small fraction of Si—OH—Al bridges (as in zeolites [1]) and/or silanol of enhanced acidity by a neighbouring Lewis aluminium (i.e. {≡Si—OH;—Al≡} pair [2]) and/or pseudo-bridging silanols (i.e. an {≡Si—OH;—Al≡} pair that becomes Si—O⁻—Al, BH⁺ in presence of a basic molecule B [3–5]. ASA contain also Lewis acid sites, associated with the presence of undercoordinated aluminium. The transformation of Lewis acid sites to Brønsted acid sites in presence of water has been reported almost fifty years ago [6] and used for example to determine the absorption coefficient of pyridine chemisorbed

on Brønsted and Lewis sites [7]. However, the nature and strength of the resulting Brønsted sites has only very recently been investigated by computational and/or spectroscopic tools [8–10] and still needs clarification.

Many efforts have recently been devoted to the study of the nature and strength of the acid sites of ASA by spectroscopic characterization of adsorbed basic probe molecules [2,11–13], with the general purpose to understand the origin of the lower acidity of ASA compared to zeolite. Among the molecules used as acidity probes (either strong bases such as pyridine, lutidine, $NH_3 \cdots$, or weak bases such as n-hexane or benzene···), carbon monoxide (CO) has received a great deal of attention due to its suitability for both qualitative and semiquantitative analysis. Its small size, softness (in terms of basicity), non-reactivity (at low temperature) and sensitivity make it ideal for the investigation of samples with both Brønsted and Lewis acid sites. CO adsorption on acid sites leads to a high frequency shift of the C—O stretching mode. The larger the CO shift (compared to free CO located at 2139 cm^{-1}) the stronger the acid site. Moreover, the adsorption of CO on a Brønsted acid site leads to a shift of the ν(OH) (low frequency shift) band of several tens/hundreds of cm^{-1} and the importance of this shift is also related to the strength of the acid site.

We will present results that will demonstrate that, in standard measurements conditions, traces of water present in the setup may adsorb on the Lewis sites and form stronger Brønsted sites than

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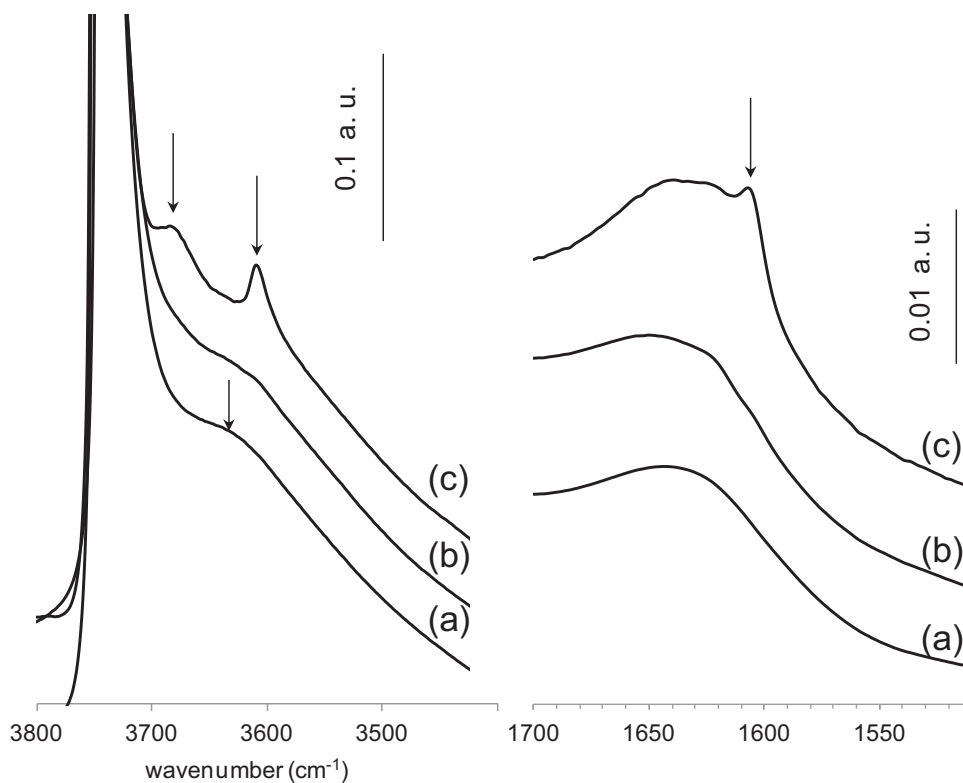   E-mail address: juliette.blanchard@upmc.fr (J. Blanchard).

Fig. 1. IR spectra of FC-723 (a), S-723 (b) and W-723 (c) in the $\nu(OH)$ (3800–3200 cm^{-1}) and $\delta(H_2O)$ (1700–1500 cm^{-1}) ranges.

those initially present in the amorphous aluminosilicate. We will also propose an experimental procedure that allows avoiding the adsorption on water on the sample, and clearly identify the position of the band associated with H_2O and D_2O adsorbed on Lewis sites before and after addition of CO.

2. Experimental

The ASA sample used for this study was graciously provide by Grace Davison and has the following characteristics: it contains 13 wt% Al_2O_3, has a BET surface area of 575 m^2 g^{-1} and the total number of Brønsted and Lewis sites, measured by NH_3-TPD, is ca. 400 µmol g^{-1}.

The transmission FTIR spectra of adsorbed CO were collected on a Bruker Vertex 70 spectrometer using a MCT detector (resolution 2 cm^{-1}, 64 scans per spectrum). The in situ set-up used for this study has been described in details in [14]. The upper part is used for the pretreatment of the sample and the sample is move from the upper part to the lower part (for FTIR measurements) with a magnet attached to the sample holder. The lower part can be cooled down to about 100 K thanks to a liquid N_2 container that surrounds the cell. The self-supported wafer of about 15 mg cm^{-2} was first calcined in situ under O_2 (30 mL min^{-1}) at 723 or 973 K and then evacuated under secondary vacuum (5×10^{-6} Torr) at this temperature for 1 h. Three procedures have been followed after this pretreament step and prior to the CO adsorption measurement itself. Standard procedure: the sample wafer is left to cool down to RT under secondary vacuum during 1 h, after what the wafer is lowered to the lower part of the cell which has been cooled down to ca. 100 K beforehand (S-723). Fast Cooling procedure: the wafer is directly moved from the upper part (heated either at 723 or at 973 K) to the lower part (cooled to 100 K): FC-723 and FC-973. Procedure with Water exposure: the sample is either exposed to pulses of H_2O or D_2O (ca.

1.5 µmol) or left under static vacuum in the cell overnight. It is then evacuated under secondary vacuum, the temperature is increased to 323 K and the sample is left 30 min at this temperature. After that the wafer is quickly lowered to the measurement cell cooled down at ca. 100 K (spectra W-723, W-973 and D-973, where W stand for H_2O and D for D_2O). For the three procedures, prior to the addition of CO, a He pulse (10 Torr, about 0.7 µmol He) is added in order to speed up thermal equilibration [14,15]. The purpose of this step is to allow the wafer to reach its equilibrium temperature. Indeed, under vacuum, thermal equilibrium is very slow and very difficult to obtain before the addition of the first CO pulse. The progressive increase in pressure in the cell upon CO addition will results in a progressive decrease of the temperature of the wafer and therefore a shift of all the infrared peaks. As explained by Trukhan et al. [15], this usually leads, in difference spectra, in distorted peaks and possibly to the appearance of artefact ones. Addition of a small amount of He increases the pressure in the cell sufficiently to reach thermal equilibrium in a few minutes. Spectra were recorded after addition of each successive CO pulse (6 Torr, 0.45 µmol CO) and also during the desorption step at $P \approx 10^{-5}$ mbar. The difference spectra reported in this study were obtained by subtracting the spectra of the sample before addition of any CO pulse from those recorded after adsorption of successive doses of CO.

3. Results

The Fig. 1 shows the OH range of the spectra after pretreatment at 723 K followed by different cooling procedures (Standard S-723, Fast Cooling FC-723, and Water exposure W-723). The differences between FC-723 and W-723 are clearly visible: the spectrum obtained after Fast Cooling only shows the narrow peak associated with free silanols at 3750 cm^{-1} together with a broad shoulder at ca. 3625 cm^{-1} associated with hydrogen bounded silanols, whereas