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

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## **I.1. 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<sub>2</sub>O and D<sub>2</sub>O adsorbed on Lewis sites before and after addition of CO.

## **I.2. Highlights**

Unwanted H<sub>2</sub>O adsorption modifies acidity distribution in standard conditions

A procedure is proposed to suppress water readsorption during acidity measurement

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First time report of the position of the bands of D<sub>2</sub>O adsorbed on undercoordinated Al  
Water adsorption on Lewis sites leads to Brønsted sites stronger than the native ones

### **Keywords**

Brønsted acidity, Lewis acidity, amorphous silica-alumina, ASA, CO adsorption, BAS,  
LAS

### **I.3. 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.  $\{\equiv\text{Si-OH}; \square\text{Al}\equiv\}$  pair [2]) and/or pseudo-bridging silanols (i.e. an  $\{\equiv\text{Si-OH}; \square\text{Al}\equiv\}$  pair that becomes Si-O<sup>-</sup>-Al, BH<sup>+</sup> in presence of a basic molecule B [3, 4, 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,  $\text{NH}_3$ ..., 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  $2139\text{ cm}^{-1}$ ) the stronger the acid site. Moreover, the adsorption of CO on a Brønsted acid site leads to a shift of the  $\nu(\text{OH})$  (low frequency shift) band of several tens/hundreds of  $\text{cm}^{-1}$  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 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  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  adsorbed on Lewis sites before and after addition of CO.

#### **I.4. Experimental**

The ASA sample used for this study was graciously provide by Grace Davison and has the following characteristics: it contains 13 wt %  $\text{Al}_2\text{O}_3$ , has a BET surface area of  $575\text{ m}^2\cdot\text{g}^{-1}$  and the total number of Brønsted and Lewis sites, measured by  $\text{NH}_3$ -TPD, is ca.  $400\text{ }\mu\text{mol}\cdot\text{g}^{-1}$ .

The transmission FTIR spectra of adsorbed CO were collected on a Bruker Vertex 70 spectrometer using a MCT detector (resolution  $2\text{ cm}^{-1}$ , 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<sub>2</sub> container that surrounds the cell. The self-supported wafer of about 15 mg.cm<sup>-2</sup> was first calcined *in situ* under O<sub>2</sub> (30 mL.min<sup>-1</sup>) at 723 or 973 K and then evacuated under secondary vacuum (5.10<sup>-6</sup> Torr) at this temperature for 1h. Three procedures have been followed after this pretreatment 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 1h hour, after what the wafer is lowered to the lower part of the cell which has been cooled down to ca. 100K 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 100K): FC-723 and FC-973. **Procedure with Water exposure:** the sample is either exposed to pulses of H<sub>2</sub>O or D<sub>2</sub>O (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 323K 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. 100K (spectra W-723, W-973 and D-973, where W stand for H<sub>2</sub>O and D for D<sub>2</sub>O). 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≈10<sup>-5</sup> 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.

## I.5. Results

The figure 1 shows the OH range of the spectra after pretreatment at 723K 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  $\text{cm}^{-1}$  together with a broad shoulder at ca. 3625  $\text{cm}^{-1}$  associated with hydrogen bounded silanols, whereas the sample obtained after water exposure present three extra bands at 3687, 3609 and 1606  $\text{cm}^{-1}$ . These positions are shifted but consistent with antisymmetric and symmetric stretching and with bending mode of water in the gas phase ( $\nu_{\text{as}}(\text{OH}_2)=3756 \text{ cm}^{-1}$ ,  $\nu_{\text{as}}(\text{OH}_2)=3656 \text{ cm}^{-1}$ ,  $\delta(\text{OH}_2)=1595 \text{ cm}^{-1}$ ). IR bands have been previously observed at similar position (3697, 3611, 1605  $\text{cm}^{-1}$ ) by Garrone et al. on the difference spectra after CO adsorption of Al-MCM-41 materials and assigned respectively to  $\nu_{\text{as}}(\text{OH}_2)$ ,  $\nu_{\text{s}}(\text{OH}_2)$  and  $\delta(\text{OH}_2)$  of water adsorbed on the Lewis sites (undercoordinated  $\text{Al}^{3+}$ ) of silica-aluminas [8]. These values are also close to values reported for similar systems (3686 and 3616  $\text{cm}^{-1}$  for  $\nu_{\text{as}}(\text{OH}_2)$ ,  $\nu_{\text{s}}(\text{OH}_2)$  of  $\text{H}_2\text{O}$  in  $\text{Ni}^+(\text{H}_2\text{O})$ , [16]). This is nevertheless the first observation of these bands at RT on the spectrum before CO adsorption. The spectrum after the Standard cooling procedure (S-723) shows no visible difference with the one measured after the Fast Cooling procedure (FC-723).

The difference spectra of FC-723, W-723 and S-723 after addition of 1, 2 and 11 doses of CO (0.45, 0.9, 5  $\mu\text{mol}$  of CO) are shown on figure 2. The last amount was chosen as it corresponds to a saturation of the strong and mild Lewis and Brønsted sites for all samples.

The three wavenumber ranges of interest ( $3800-3200\text{ cm}^{-1}$  for  $\nu(\text{OH})$  and  $\nu(\text{CO}\dots\text{OH})$ ,  $2300-2100\text{ cm}^{-1}$  for  $\nu(\text{CO})$  and  $\nu(\text{CO}\dots\text{OH})$  and  $1700-1500\text{ cm}^{-1}$  for  $\delta(\text{H}_2\text{O})$ ) have been displayed with the same Y scale but various X scales in order to facilitate the observation of the IR bands.

The spectra of the sample after Fast Cooling procedure (figure 2 (a) FC-723, dotted line) shows the bands characteristic of a silica-alumina sample: in the  $\nu(\text{CO})$  range the two bands at  $2231$  and  $2190\text{ cm}^{-1}$  are characteristic of CO adsorbed respectively on strong and mild Lewis sites whereas the third band at  $2172\text{ cm}^{-1}$  could be associated with CO in interaction with either a Lewis or a Brønsted sites. However, the adsorption of CO on Brønsted sites being ascertained by the modifications in the  $\nu(\text{OH})$  range, it must necessarily be due to Brønsted sites. Its position is characteristic of relatively mild average Brønsted acidity. In the  $\nu(\text{OH})$  range, two bands are observed at  $3718$  (negative band) and  $3550\text{ cm}^{-1}$ . As they grow simultaneously with CO loading, they can be assigned to the  $\nu(\text{OH})$  and  $\nu(\text{CO}\dots\text{OH})$  of the same Brønsted sites. Their position and the shift of the  $\nu(\text{OH})$  ( $\Delta\nu(\text{OH})=-168\text{ cm}^{-1}$ ) with CO are characteristic of mild Brønsted sites and, according to the correlation established by Crepeau et al, should correspond to a  $\nu(\text{CO}\dots\text{OH})$  band at ca.  $2164\text{ cm}^{-1}$  [2]. These sites are often associated with silanols in close vicinity with an Al Lewis site [2]. A shoulder on the right side of the band at  $3550\text{ cm}^{-1}$ , whose position is difficult to determine precisely (ca.  $3480-3450\text{ cm}^{-1}$ ), indicates the presence of Brønsted sites of stronger acidity. Increasing the CO loading to  $0.9\text{ }\mu\text{mol}$ , leads, in the CO range, to an increase in the intensities of the  $\nu(\text{CO})$  bands associated with CO on mild and strong Lewis sites ( $2231$  and  $2190\text{ cm}^{-1}$ ) and of the  $\nu(\text{CO}\dots\text{OH})$  band associated with Brønsted sites. A shoulder becomes visible on the right side of this band that can be assigned to CO interacting with Brønsted sites of very weak acidity. The corresponding bands in the  $\nu(\text{OH})$  range are located at  $3745\text{ cm}^{-1}$  (negative band)

and at  $3650\text{ cm}^{-1}$ . These bands are generally associated with silanols on the surface of silica-like domains [2]. After addition of  $5\text{ }\mu\text{mol}$  of CO (saturation of the strong and mild Brønsted and Lewis sites), the intensities of all the  $\nu(\text{CO})$  bands increase further and the position of the  $\nu(\text{CO}\dots\text{OH})$  is shifted to  $2169\text{ cm}^{-1}$ . This shift could indicate that the proportion of mild Brønsted sites has increased or that CO is adsorbed on milder Brønsted sites. The bands associated with weak Brønsted ( $\nu(\text{OH})=3745\text{ cm}^{-1}$ ,  $\nu(\text{CO}\dots\text{OH})=3650\text{ cm}^{-1}$ ) and  $\nu(\text{CO})=2157\text{ cm}^{-1}$ ) become the main bands and physisorbed CO is detected (band at  $2140\text{ cm}^{-1}$ ). One can also note, whatever the CO loading, the absence of any band in the  $\delta(\text{OH}_2)$  range for this procedure.

Whatever the CO loading the spectra after the water exposure procedure ((b), W-723, dashed line) are radically different from those of FC-723. In the  $\nu(\text{CO})$  range, the  $\nu(\text{CO})$  bands at  $2226$  and  $2190\text{ cm}^{-1}$  are notably weaker and only detected at high loading. This indicates that the amounts of Lewis sites (strong and mild) are significantly lowered by water adsorption. Simultaneously, the intensity of the  $\nu(\text{CO}\dots\text{OH})$  band is considerably increased whatever the loading and its position is shifted to higher wavenumber ( $2176\text{ cm}^{-1}$  for low and intermediate CO loading and  $2170\text{ cm}^{-1}$  with a right shoulder at ca.  $2174\text{ cm}^{-1}$  at high loading). This position is indicative of strong Brønsted sites (with strength similar, for example, to that of Brønsted sites in HY zeolites [2, 17]). This conclusion is confirmed by the analysis of the  $\nu(\text{OH})$  range where three bands are detected at low CO loading: two negative  $\nu(\text{OH})$  bands at  $3688$  and  $3609\text{ cm}^{-1}$  and a broad band centred at ca  $3440\text{ cm}^{-1}$  which appears to be the juxtaposition of two bands at ca.  $3455$  and  $3410\text{ cm}^{-1}$ . Increasing the CO loading leads to an increase of these four bands and to the observation of two more bands: a negative shoulder at  $3715\text{ cm}^{-1}$  and a positive shoulder at ca.  $3530\text{ cm}^{-1}$ . These last two bands have already been observed with the previous pretreatment procedure and can therefore be assigned to native mild Brønsted sites. The position of the negative bands at  $3688$  and  $3609\text{ cm}^{-1}$  and the



simultaneous growth, in the  $\delta(\text{H}_2\text{O})$  range, of a negative band at  $1604\text{ cm}^{-1}$  are consistent with CO adsorption on the sites responsible for the bands observed before CO adsorption at  $3687$ ,  $3609$  and  $1606\text{ cm}^{-1}$  (Figure 1) and assigned to water molecule interacting with Al Lewis sites. It is interesting to note the absence of any clearly visible positive band in the  $\delta(\text{H}_2\text{O})$  range that could be associated with the bending mode of  $\text{OC}\dots\text{H-O-H}\dots\text{CO}$ . This question has already been addressed by Garrone et al. [8] who suggested, based on ab initio calculation, that this band was expected to appear at  $1628\text{ cm}^{-1}$  but could hardly be detected because its extinction coefficient was significantly lower than the one of the band associated with the bending mode of H-O-H. We will come back to this point later. This is a confirmation of the Brønsted acid character of these sites as already observed by Garrone et al.. If one takes into account the fact that these negative bands grow simultaneously with the positive bands at  $3455$  and  $3410\text{ cm}^{-1}$ , these two last bands are likely  $\nu_{\text{as}}(\text{CO}\dots\text{OH})$  and  $\nu_{\text{s}}(\text{CO}\dots\text{OH})$  due to the adsorption of two molecules of CO per chemisorbed water molecule (formation of  $\text{OC}\dots\text{H-O-H}\dots\text{CO}$ ). These values are close to those predicted by Garrone et al using theoretical calculations ( $3385$  and  $3440\text{ cm}^{-1}$ ) [8]. The shift of the  $\nu(\text{OH})$  upon adsorption of CO for these bands (which should be calculated as  $1/2(\nu_{\text{as}}(\text{CO}\dots\text{OH}) + \nu_{\text{s}}(\text{CO}\dots\text{OH})) - (\nu_{\text{as}}(\text{OH}) + \nu_{\text{s}}(\text{OH}))$ ) is ca.  $-215\text{ cm}^{-1}$ , which is significantly larger than the value calculated for the native mild Brønsted sites of the sample ( $-168\text{ cm}^{-1}$ ). Another interesting result of these experiments is that both mild and strong Lewis sites chemisorb  $\text{H}_2\text{O}$  (the intensities of the bands of CO adsorbed on these two sites undergo a similar decrease in presence of water), but that only one type of chemisorbed water is observed (only one set of  $\nu_{\text{as}}(\text{OH})$  and  $\nu_{\text{s}}(\text{OH})$ ). One can propose two interpretations for this observation: either  $\text{H}_2\text{O}$  is chemisorbed dissociatively on one of the type of Lewis sites (but it is unlikely as no new Al-OH band is detected) or, more likely, the two types of Lewis sites become identical after  $\text{H}_2\text{O}$  adsorption.

At low CO loading the spectra obtained after the Standard cooling procedure ((c) S-723, solid line) have characteristics of both FC-723 and W-723 spectra. Indeed, in the  $\nu(\text{CO})$  range, the bands characteristic of CO adsorbed on mild and strong Lewis sites are, as for FC-723, detected at 2230 and 2193  $\text{cm}^{-1}$  but their intensities are lower than on the spectrum of FC-723. On the other side, the intensity of the  $\nu(\text{CO}\dots\text{OH})$  is stronger than for FC-723 and its position (2175  $\text{cm}^{-1}$ ) is closer to the one observed for W-723 (2176  $\text{cm}^{-1}$ ) than for FC-723 (2172  $\text{cm}^{-1}$ ). In the  $\nu(\text{OH})$  range the bands assigned to water adsorbed on Lewis sites are detected at 3690, 3608  $\text{cm}^{-1}$  (negative bands) and 3440  $\text{cm}^{-1}$  (together with the band assigned to the milder sites at 3550  $\text{cm}^{-1}$ ) and in the  $\delta(\text{H}_2\text{O})$  range the characteristic band at 1605  $\text{cm}^{-1}$  is also observed. However, upon increasing the CO loading the intensities of the bands corresponding to adsorbed water increase barely (this is particularly clear for the  $\delta(\text{H}_2\text{O})$  and, after saturation of the Brønsted and Lewis sites, the band assigned to the mild (native) Brønsted sites at 3550  $\text{cm}^{-1}$  is clearly the main band (this is confirmed by the position of the  $\nu(\text{CO}\dots\text{OH})$  band at saturation: 2169  $\text{cm}^{-1}$  i.e. the same position as for FC-723). Nevertheless the presence of a much larger fraction of strong Brønsted sites following the Standard procedure than the Fast Cooling procedure is still evident when one compare, in the  $\nu(\text{OH})$  range, the spectra after addition of 11 CO pulses.

These three series of experiments clearly show the impact of water traces on the nature and strength of the acid sites detected by CO adsorption. They also show that the appropriate procedure to ensure the absence of  $\text{H}_2\text{O}$  adsorption on the Lewis sites is a fast cooling of the sample from its pretreatment temperature (which is too high for water adsorption) to the measurement temperature (ca. 100 K) without any intermediate cooling step to RT.

In order confirm the assignment proposed for the  $\nu(\text{OH}_2)$ ,  $\nu(\text{OC}\dots\text{H-O-H}\dots\text{CO})$  and  $\delta(\text{OH}_2)$  bands during this first series of experiments, we have performed a second set of experiments for which the wafer has been pretreated at a higher temperature (973 instead of

723 K) in order to decrease the amount of native (strong and mild) Brønsted sites and increase the amount of Lewis sites by dehydroxylation (or by homolytic decomposition as suggested recently by Nash et al. [18]). The wafer was afterwards either rapidly cooled to 100K (FC-973) or exposed to water (W-973) or D<sub>2</sub>O (D-973) and subsequently treated under vacuum to remove physisorbed water.

The spectra prior to addition of CO are shown on figure 3 in the  $\nu(\text{OH})$ ,  $\nu(\text{OD})$  and  $\delta(\text{H}_2\text{O})$  ranges. As already reported for pretreatment at 723 K, the spectra in absence of water ((a), FC-973, dotted line) present only one peak at  $3752\text{ cm}^{-1}$ , that can be assigned to isolated silanols (the shift to higher position of this peak after pretreatment at high temperature is consistent with previous reports [19]). The bump on the right side of this peak that was clearly visible after pre-treatment at 723 K (figure 1) and had been assigned to H-bonded silanols is not detected anymore which is consistent with a higher degree of dehydroxylation for the sample after high temperature pretreatment. As for W-723 (figure 1), the spectra after addition of H<sub>2</sub>O ((c), W-973, solid line) presents the three bands characteristic of water adsorption on the Lewis sites ( $3693$ ,  $3613$  and  $1604\text{ cm}^{-1}$  for respectively  $\nu_{\text{as}}(\text{OH}_2)$ ,  $\nu_{\text{s}}(\text{OH}_2)$  and  $\delta(\text{H}_2\text{O})$ ). Their intensities are higher than on W-723, which is consistent with a higher amount of Lewis sites after high temperature pretreatment. Interestingly, the spectra after addition of D<sub>2</sub>O ((b), D-973, dashed line) also shows, in the  $\nu(\text{OH})$  and  $\delta(\text{H}_2\text{O})$  ranges, the bands characteristic of H<sub>2</sub>O adsorption on the Lewis sites. As the D<sub>2</sub>O sample we used did not contain a significant amount of H<sub>2</sub>O, this confirms that H<sub>2</sub>O traces present in the setup compete with D<sub>2</sub>O intentionally introduced for adsorption on the Lewis sites. Moreover, a third band is observed in the  $\nu(\text{OH})$  range at  $3655\text{ cm}^{-1}$ . The position of this last band which is almost at the exact average position of  $\nu_{\text{as}}(\text{OH}_2)$  and  $\nu_{\text{s}}(\text{OH}_2)$   $(3693+3612)/2=3653\text{ cm}^{-1}$  allows us to assign it to  $\nu(\text{D-OH})$  (for water in the gas phase the half sum of  $\nu_{\text{as}}(\text{OH}_2)$  and  $\nu_{\text{s}}(\text{OH}_2)$  is  $3706.5\text{ cm}^{-1}$  compared to  $\nu(\text{D-OH})=3707.5\text{ cm}^{-1}$  [20]). This HOD could, for example, be formed by

reaction of D<sub>2</sub>O with H<sub>2</sub>O adsorbed on the Lewis sites. The presence of adsorbed HOD is confirmed by the band at 1418 cm<sup>-1</sup> in the bending mode range whose position is consistent with  $\delta(\text{HOD})$  ( $\delta(\text{HOD})=1403.5 \text{ cm}^{-1}$  in the gas phase [20]). This result is also a confirmation of the attribution proposed by Garrone et al. of the bands at ca. 3690 and 3610 cm<sup>-1</sup> to  $\nu_{\text{as}}(\text{OH}_2)$  and  $\nu_{\text{s}}(\text{OH}_2)$  of H<sub>2</sub>O shifted by adsorption on Lewis sites [8]. The spectra of D-973 shows some similarities in the  $\nu(\text{OD})$  compared to the  $\nu(\text{OH})$ . In this range four bands are detected at 2764, 2749, 2689 and 2637 cm<sup>-1</sup>. The first band can be assigned to Si-OD of silica like domains (reported at 2761 cm<sup>-1</sup>, [21]). For the other three, the half sum of the positions of the first and third bands  $(2746+2637)=2693 \text{ cm}^{-1}$  compares rather well with the position of the second band (2689 cm<sup>-1</sup>). These three bands can therefore be assigned to  $\nu_{\text{as}}(\text{OD}_2)$ ,  $\nu(\underline{\text{DO}}\text{-H})$  and  $\nu_{\text{s}}(\text{OD}_2)$  (in the gas phase the positions of  $\nu_{\text{as}}(\text{OD}_2)$  and  $\nu_{\text{s}}(\text{OD}_2)$  are 2787.7 and 2671.7 cm<sup>-1</sup>, half sum 2729.7 cm<sup>-1</sup> compared to 2723.7 for  $\nu(\underline{\text{DO}}\text{-H})$  [22]).

The difference spectra after CO addition on FC-973 ((a),dotted black line), W-973 ((b), solid black line) ( $\nu(\text{OH})$  and  $\nu(\text{CO})$  ranges) and D-973 ((c), solid gray line) ( $\nu(\text{OD})$  range) after saturation of the strong and mild Lewis and Brønsted sites (addition of 11 pulses of CO, ca. 5  $\mu\text{mol}$  of CO) are shown on figure 4. For comparison, the spectrum of FC-723 is also shown on this figure ((d), dashed black line). The comparison of FC-723 and FC-973, shows an increase in the amount of mild and strong Lewis sites ( $\nu(\text{CO})$  at 2232 and 2188 cm<sup>-1</sup>) and a decrease in the amount of Brønsted sites ( $\nu(\underline{\text{CO}}\dots\text{OH})=2169 \text{ cm}^{-1}$ ) which are consistent with the transformation, at least partial, of Brønsted sites in Lewis sites by high temperature dehydroxylation. The loss of most of the Brønsted sites in FC-973 sites is confirmed by the analysis of the  $\nu(\text{OH})$  range for this spectrum, where only mild Brønsted site are detected ( $\nu(\text{CO}\dots\underline{\text{OH}})=3580 \text{ cm}^{-1}$ ) and in smaller quantity compared to FC-723. Addition of H<sub>2</sub>O, leads, as observed after pretreatment at 723 K, to a decrease in the amount of mild and strong Lewis

sites. This not only confirms the adsorption of H<sub>2</sub>O on these sites, but also allows to clearly identify the bands associated with H<sub>2</sub>O adsorbed on the Lewis sites:  $\nu_{as}(\text{OH}_2)=3698\text{ cm}^{-1}$   $\nu_s(\text{OH}_2)=3612\text{ cm}^{-1}$  and  $\delta(\text{H}_2\text{O})=1604\text{ cm}^{-1}$  (not shown). This experiment also confirms the presence of two bands of OH in interaction with CO for these sites:  $\nu(\text{CO}\dots\text{OH})=3452\text{ cm}^{-1}$  and  $3421\text{ cm}^{-1}$  that most probably correspond to asymmetric and symmetric stretching of  $\text{OC}\dots\text{H-O-H}\dots\text{CO}$ , and the very strong acidity of these sites as testified by the position of the  $\nu(\text{CO})$  at  $2177\text{ cm}^{-1}$  i.e. at the same position as, for example a HY zeolite (Si/Al=5.4) [2]. Moreover the position of the corresponding bands in presence of D<sub>2</sub>O can be identified at  $2737$  and  $2638\text{ cm}^{-1}$  (antisymmetric and symmetric stretching of D<sub>2</sub>O) and the remaining negative bands can be assigned to  $\nu(\text{DO-H})$  ( $2688\text{ cm}^{-1}$ ) and  $\nu(\text{Si-OD})$  of Si-OD from silica like domains ( $2764\text{ cm}^{-1}$ ). A band corresponding to OD in interaction with CO is located at  $2536\text{ cm}^{-1}$ . Considering the higher intensity of  $\nu(\text{DO-H})$  compared to  $\nu_{as}(\text{D-O-D})$  and  $\nu_a(\text{D-O-D})$ , the position of this band is likely related to  $\nu(\text{CO}\dots\text{DO-H})$  and the weak shoulders on both side could be due to  $\nu_{as}(\text{OC}\dots\text{D-O-D}\dots\text{CO})$  and  $\nu_s(\text{OC}\dots\text{D-O-D}\dots\text{CO})$ , but the exact positions of these bands cannot be determined.

According to the theoretical calculation reported by Garrone et al. [8], the first and the second molecules of CO adsorb on the water molecule with very similar heat of adsorption ( $-15\text{ kJ}\cdot\text{mol}^{-1}$  for the first CO molecule and  $-14\text{ kJ}\cdot\text{mol}^{-1}$  for the second) but the adsorption of the first CO molecule reflects slightly stronger sites ( $\Delta\nu(\text{OH})=298\text{ cm}^{-1}$  for a single CO molecule per H<sub>2</sub>O vs.  $239\text{ cm}^{-1}$  for two molecules of CO). We checked whether we could detect this band for W-973 and D-973 by performing an experiment at low CO coverage (addition of  $0.1\text{ }\mu\text{mol}$  of CO) and also by measuring a spectrum after saturation followed by desorption at  $10^{-5}$  Torr. The spectra in the  $\nu(\text{OH})$  and  $\nu(\text{CO})$  ranges (W-973) and in the  $\nu(\text{OD})$  range (D-973) are shown on figure 5. To facilitate the comparison the intensities of the

spectra at low CO coverage (dotted lines) have been multiplied by a factor of ca. 10. In the  $\nu(\text{OH})$  and  $\nu(\text{OD})$  ranges the negative bands characteristics of adsorbed  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$  &  $\text{HOD}$ ) are clearly visible on all spectra and at the same positions as those reported after saturation of the Brønsted and Lewis sites, but the  $\nu(\text{CO}\dots\text{OH})$  and  $\nu(\text{CO}\dots\text{OD})$  bands of strong Brønsted sites are shifted to lower wavenumbers with regards to the spectra recorded at saturation as they are observed respectively at 3395 and 2508  $\text{cm}^{-1}$  (compared to  $(3452+3421)/2=3436$  and 2536  $\text{cm}^{-1}$ ). Moreover, the position of the  $\nu(\text{CO}\dots\text{OH})$  band is shifted to 2180  $\text{cm}^{-1}$  (compared to 2177  $\text{cm}^{-1}$  at saturation). This indicates a very strong acidity for the water molecules adsorbed on the Lewis sites at low CO coverage and is consistent with the adsorption of a single CO molecule per water molecule at low coverage. Moreover the similarity between the spectra at low coverage and after saturation followed by desorption at  $10^{-5}$  Torr indicates that it is possible to selectively remove one of the CO molecule under vacuum. When a single molecule of CO is adsorbed per water molecule, a band corresponding to the free OH ( $\text{H-O-H}\dots\text{CO}$ ) is expected to appear. Although the position is similar to the one of  $\nu(\text{CO}\dots\text{OH})$  of silanols, we can propose that this OH is responsible for the narrow band at 3676  $\text{cm}^{-1}$ , as no band characteristic of CO adsorbed on silanol is detected in the  $\nu(\text{CO})$  range on these spectra and this position would be consistent with the position predicted for this band by Garrone et al (3674  $\text{cm}^{-1}$ ) [8].

As mentioned above, the adsorption of CO on  $\text{Al}\square\text{OH}_2$  should lead, in the  $\delta(\text{H}_2\text{O})$  range, not only to the negative band at 1604  $\text{cm}^{-1}$  but also to a positive band (corresponding to the bending mode of  $\text{H-O-H}\dots\text{CO}$  or  $\text{CO}\dots\text{H-O-H}\dots\text{CO}$ ). The difficulty to observe these positive bands has been already discussed by Garrone et al. [8] and assigned, based on ab initio calculation, to their weak extinction coefficients and close proximity to the  $\delta(\text{Al}\square\text{OH}_2)$  (predicted values: 44  $\text{cm}\cdot\mu\text{mol}^{-1}/1628 \text{ cm}^{-1}$  for  $\text{Al}\square\text{OH}_2(\text{CO})_2$ , 78  $\text{cm}\cdot\mu\text{mol}^{-1}/1619 \text{ cm}^{-1}$  for  $\text{Al}\square\text{OH}_2\text{C}$ , and 131  $\text{cm}\cdot\mu\text{mol}^{-1}/1605 \text{ cm}^{-1}$  for  $\text{Al}\square\text{OH}_2$ ). Nevertheless the absence of these

bands could also be regarded as indicative of a dissociation of adsorbed water molecules upon CO adsorption.  $(=(\text{OH}_2)\text{Al-O-Si}\equiv \rightarrow =(\text{OH})\text{Al-OH-Si}\equiv)$ . In order to discriminate between these two possibilities, we have examined the 1800-1400 range of the W-973 difference spectra (figure 6) after saturation of all the acid sites ((a), dotted line) and after evacuation at  $10^{-5}$  torr ((b), solid line). A weak positive band is observed on the two spectra -located at  $1623 \text{ cm}^{-1}$  after evacuation (i.e. at low CO loading) it is positioned at  $1654 \text{ cm}^{-1}$  and broader at high CO loading, which supports the assignment previously proposed by Garrone et al.

The attributions of the FTIR bands discussed in this work have been summed up in Table 1.

## I.6. Conclusion

The CO adsorption experiments reported in this paper clearly show the impact of water on the nature and strength of the acid sites detected by CO adsorption. They confirm the adsorption of CO on Lewis sites and indicate that both strong and mild Lewis sites are concerned and that they are likely both transformed in identical strong acid sites upon adsorption of water. These experiments also show that water traces present in the set-up can modify significantly the distribution of Lewis and Brønsted sites and increase substantially the amount of strong Brønsted acid sites detected by CO adsorption. Indeed, although strong Brønsted sites are probably natively present in ASA, the present work demonstrates that care must be taken during the evaluation of the amount of these strong Brønsted sites, because the strong acid sites formed by adsorption of water may contribute significantly to the total amount of strong Brønsted sites. Adsorption of water, unbeknownst to the experimenter, can therefore give a false impression of the strength of the acid sites of ASA and complicate the determination of their true nature. It is therefore important to have a clear signature for unwanted water readsorption: although the presence of water on the Lewis sites is associated with several bands ( $3693$ ,  $3613$  and  $1604 \text{ cm}^{-1}$  for respectively  $\nu_{\text{as}}(\text{OH}_2)$ ,  $\nu_{\text{s}}(\text{OH}_2)$  and  $\delta(\text{H}_2\text{O})$ )

some of these bands may be difficult to detect because their position is too close to other FTIR band occurring during a CO adsorption experiment. This is in particular the case for the band at  $3696\text{ cm}^{-1}$  that can be easily masked by the positive (and very strong) band of  $\nu(\text{CO}\dots\text{OH})$  of the silanols of the silica-like domains. However (at least for CO adsorption) the  $\delta(\text{H}_2\text{O})$  band should constitute a clear indication of the presence of adsorbed water as it occurs in a spectral range where no other band is expected in the difference spectra. This band should therefore be used as fingerprint of the presence of adsorbed water.

As the elimination of every water traces in the set-up is probably impossible, we have proposed an alternative procedure that ensure the absence of CO adsorption (as evidenced by the absence of the  $\delta(\text{H}_2\text{O})$  band): fast cooling of the sample from its pretreatment temperature (which is too high for water adsorption) to the measurement temperature (ca. 100 K) prevents the desorption of water from the set up in the vicinity of the wafer, whereas an intermediate cooling step from pretreatment temperature to RT is favourable to water adsorption.

In order to determine precisely the positions of the bands assigned to  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  adsorbed on Lewis sites, a second series of experiment has been performed on a highly dehydroxylated ASA (to decrease the amount of native Brønsted sites and increase the amount of Lewis sites, the sites responsible for water adsorption). The positions of the  $\nu(\text{CO})$ ,  $\nu(\text{OH})$ ,  $\nu(\text{OD})$  bands for water/ $\text{D}_2\text{O}$  adsorbed on Lewis sites are summed up in Table 1 and could be used for a new evaluation of previously published results taking into account the possibility of water adsorption. Moreover, this experiment has shown that severe dehydroxylation followed by rehydration transforms the weak native Brønsted sites ( $\nu(\text{CO}\dots\text{OH})=2172\text{ cm}^{-1}$ ), in much stronger sites ( $\nu(\text{CO}\dots\text{OH})=2180\text{-}2178\text{ cm}^{-1}$  with an acidity strength similar to that of zeolites.



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## I.9. Figure captions

Figure 1: IR spectra of FC-723 (a), S-723 (b) and W-723 (c) in the  $\nu(\text{OH})$  (3800-3200  $\text{cm}^{-1}$ ) and  $\delta(\text{H}_2\text{O})$  (1700-1500  $\text{cm}^{-1}$ ) ranges.

Figure 2: IR difference spectra after CO adsorption on FC-723 ((a), dotted line), S-723 ((b), solid black line) and W-723 ((c), dashed line) in the  $\nu(\text{OH})$  ( $3800\text{-}3200\text{ cm}^{-1}$ ),  $\nu(\text{CO})$  ( $1700\text{-}1500\text{ cm}^{-1}$ ) and  $\delta(\text{H}_2\text{O})$  ( $1700\text{-}1500\text{ cm}^{-1}$ ) ranges: (I) after adsorption of  $0.45\text{ }\mu\text{mol}$  of CO; (II) after adsorption of  $0.9\text{ }\mu\text{mol}$ ; (III) after adsorption of  $5\text{ }\mu\text{mol}$  of CO (saturation of all, mild and strong, Lewis and Brønsted, sites).

Figure 3: IR spectra of FC-973 ((a), dotted line), D-973 ((b), dashed line) and W-973 ((c), solid line) in the  $\nu(\text{OH})$  ( $3800\text{-}3200\text{ cm}^{-1}$ ),  $\nu(\text{OD})$  range ( $2800\text{-}2500\text{ cm}^{-1}$ ) and  $\delta(\text{H}_2\text{O})$  ( $1700\text{-}1500\text{ cm}^{-1}$ ) ranges.

Figure 4: IR difference spectra after adsorption of  $5\text{ }\mu\text{mol}$  of CO (saturation of all, mild and strong, Lewis and Brønsted, sites) on: FC-973 ((a) dotted black line), W-973 ((b) solid black line), FC-723 ((d) dashed black line) in the  $\nu(\text{OH})$  ( $3800\text{-}3200\text{ cm}^{-1}$ ) and  $\nu(\text{CO})$  ( $1700\text{-}1500\text{ cm}^{-1}$ ) ranges and of D-973 ((c) solid gray line) in the  $\nu(\text{OD})$  range ( $2800\text{-}2500\text{ cm}^{-1}$ ).

Figure 5: IR difference spectra after adsorption of  $0.1\text{ }\mu\text{mol}$  of CO ((a), (b), dotted lines) and after saturation of the Lewis and Brønsted sites followed by desorption under vacuum at  $10^{-5}$  Torr ((c), (d) solid lines) in the  $\nu(\text{OH})$  ( $3800\text{-}3200\text{ cm}^{-1}$ ) and  $\nu(\text{CO})$  ( $1700\text{-}1500\text{ cm}^{-1}$ ) ranges (W-973) and in the  $\nu(\text{OD})$  range ( $2800\text{-}2500\text{ cm}^{-1}$ ) (D-973). The spectra after addition of  $0.1\text{ }\mu\text{mol}$  of CO have been multiplied by 10 to facilitate the comparison (the absorbance scales refer to the spectra (b) & (d) ie. after saturation)

Figure 6: IR difference spectra of W-973 in the  $1800\text{-}1400$  range after saturation of the acid sites ((a), dotted line) followed by desorption under vacuum at  $10^{-5}$  torr ((b), solid line)

• **Table 1: Assignment of the FTIR bands associated with Brønsted sites**

| $\nu(\text{OX})^{(a)}$<br>( $\text{cm}^{-1}$ )            | $\nu(\text{CO}\dots\text{OX})^{(a)}$<br>( $\text{cm}^{-1}$ ) | $\Delta\nu(\text{OX})^{(a)}$<br>( $\text{cm}^{-1}$ ) | $\nu(\text{CO}\dots\text{OX})^{(a)}$<br>( $\text{cm}^{-1}$ ) | assignment   |
|---|--|--|--|--|
| 3745  | 3650   | 95   | 2156   | Si-OH, weak Brønsted sites   |
| 2764  | Not observed<br>(expected at 2698)                           |  | 2156   | Si-OD, weak Brønsted sites   |
| 3718  | 3550   | 160  | 2169   | Mild (native) Brønsted sites (possibly silanols in close proximity with Lewis Al)  |
| ?   | 3450   |  | ?  | Moderate/Strong (native) Brønsted sites  |
| 3690 ( $\nu_{\text{as}}$ )<br>3610 ( $\nu_{\text{s}}$ )   | 3450 ( $\nu_{\text{as}}$ ) & 3420 ( $\nu_{\text{s}}$ )       | 215  | 2177   | Strong Brønsted sites formed by adsorption of H <sub>2</sub> O on Lewis sites at high coverage (two CO per water molecule) |
| 2740 ( $\nu_{\text{as}}$ )<br>& 2637 ( $\nu_{\text{s}}$ ) | Accurate position undetermined                               |  | 2177   | Strong Brønsted sites formed by adsorption of D <sub>2</sub> O on Lewis sites at high coverage (two CO per water molecule) |
| 2689  | 2536   | 153  | 2177   | Strong Brønsted sites formed by adsorption of  |

|                                       |                               |     |      |  |
|---------------------------------------|-------------------------------|-----|------|--|
|                                       |                               |     |      | HOD on Lewis sites at high coverage (two CO per water molecule)  |
| 3690 ( $v_{as}$ )<br>& 3610 ( $v_s$ ) | 3396 + (3676 for the free OH) | 254 | 2180 | Strong Brønsted sites formed by adsorption of H <sub>2</sub> O on Lewis sites at high coverage (one CO per water molecule) |
| 2689                                  | 2508                          | 181 | 2180 | Strong Brønsted sites formed by adsorption of HOD on Lewis sites at high coverage (one CO per water molecule)              |

<sup>(a)</sup> where X stands for H or D

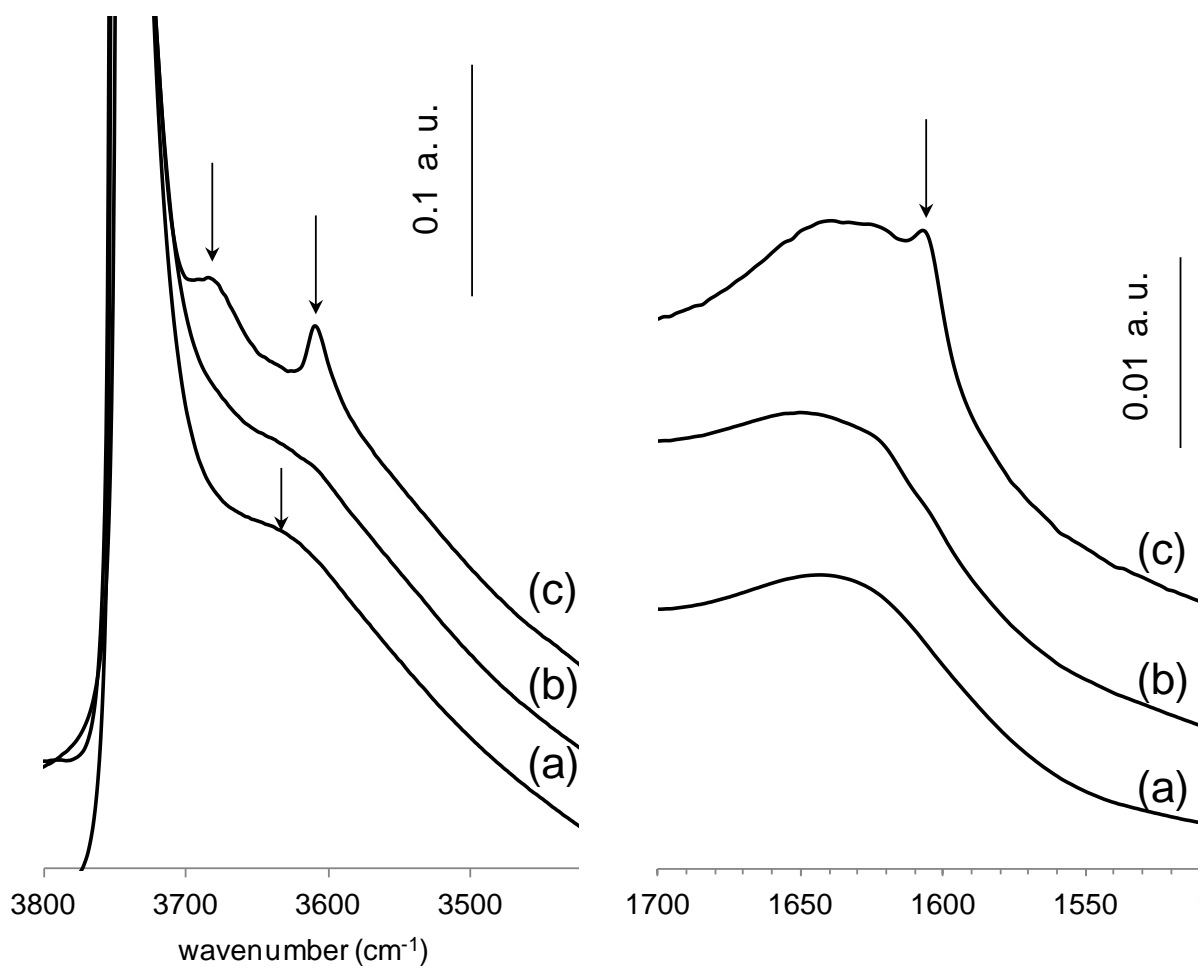


Figure 1

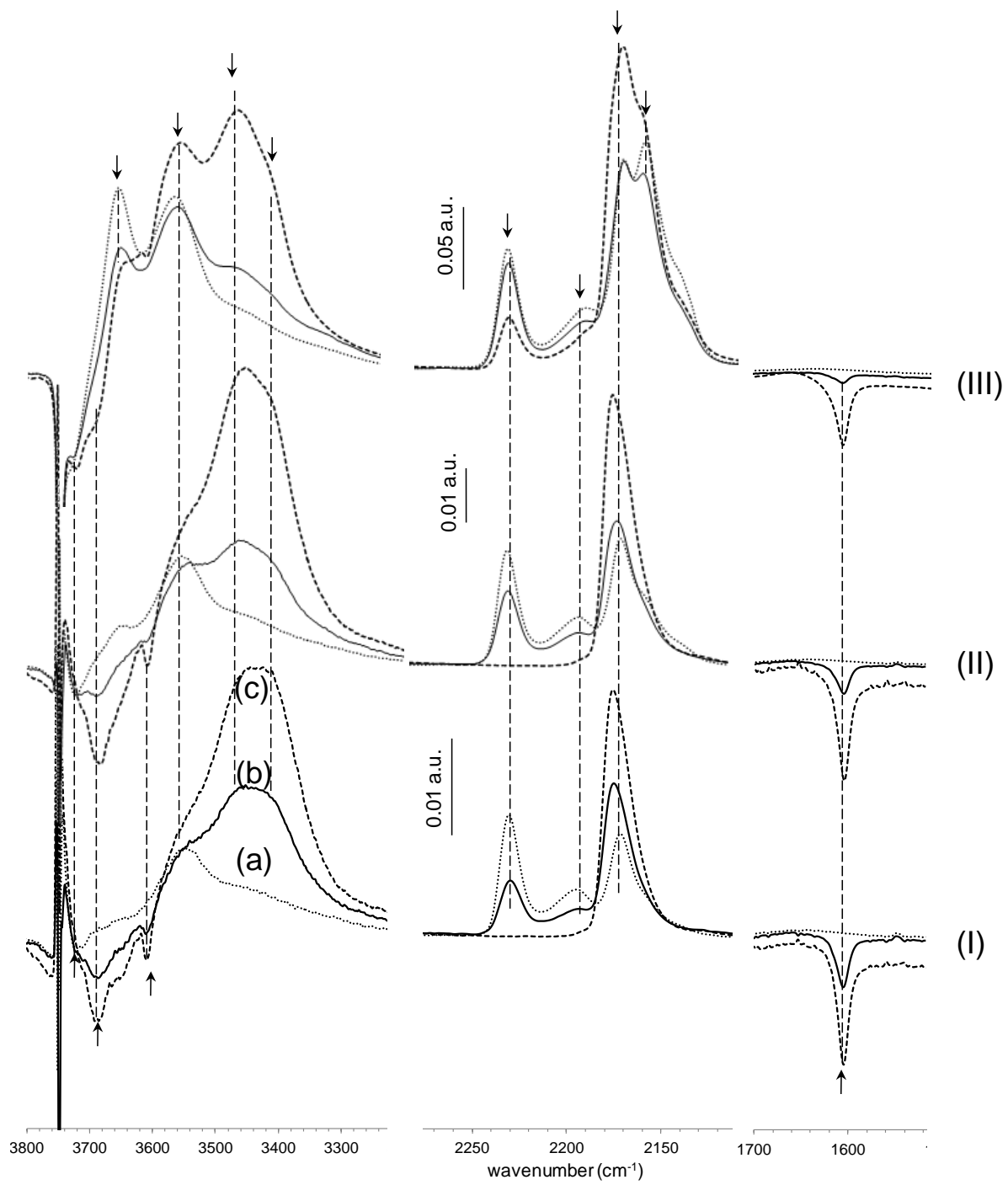


Figure 2

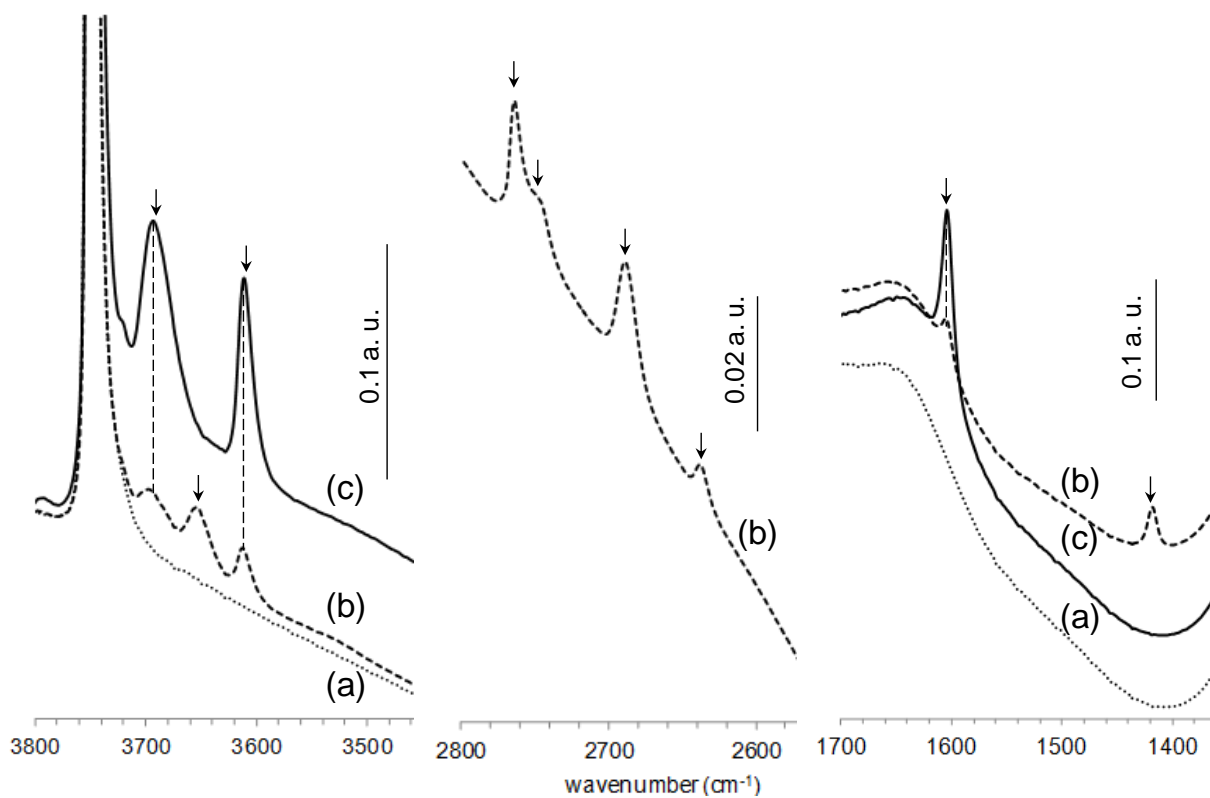


Figure 3

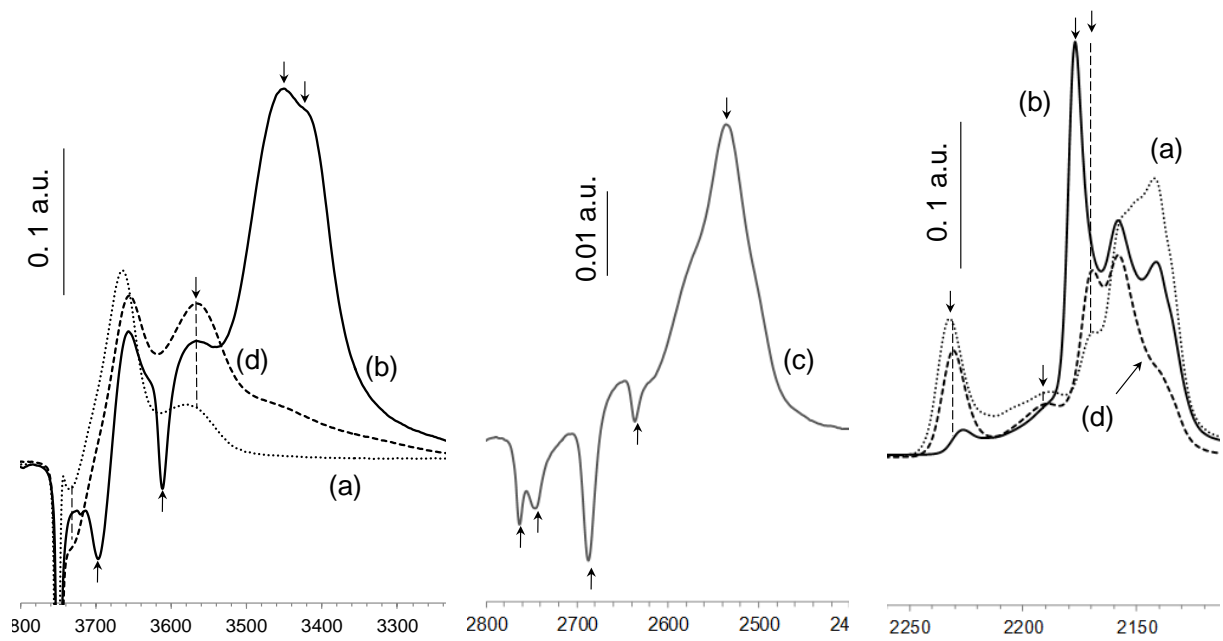


Figure 4



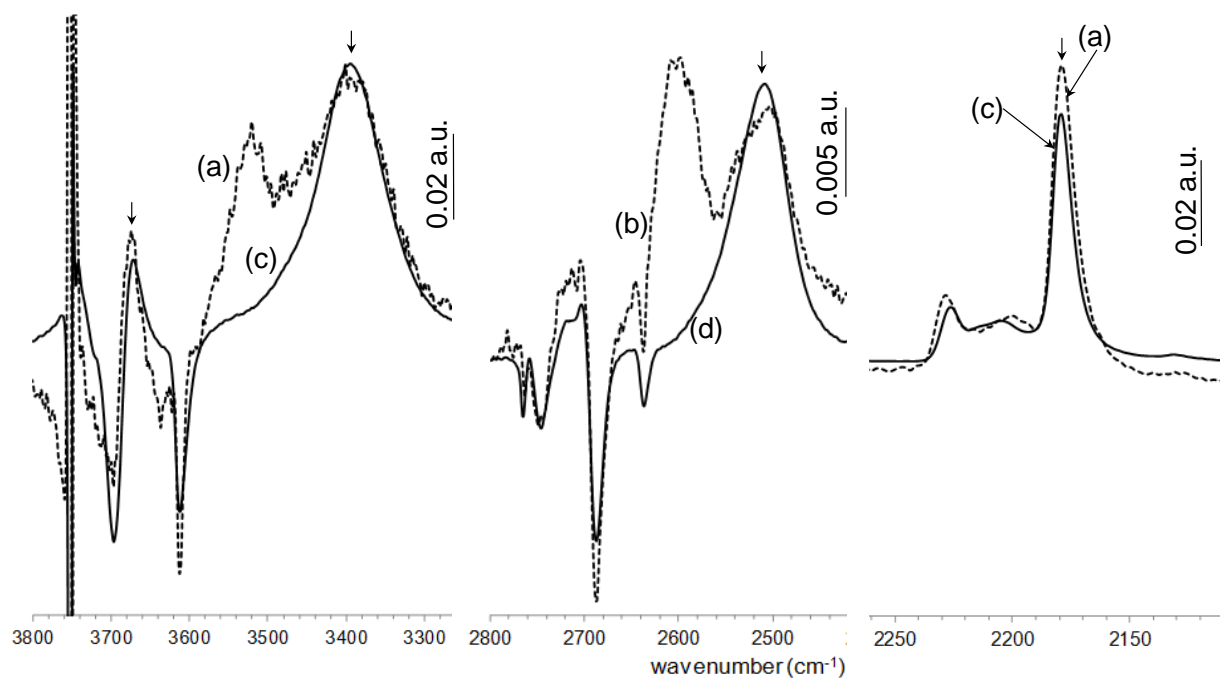


Figure 5

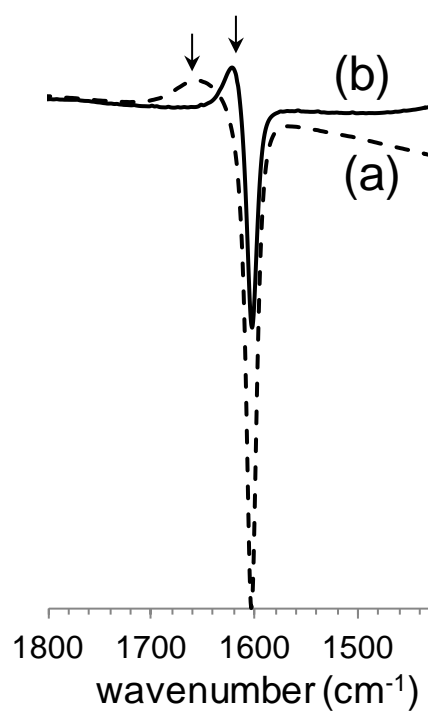
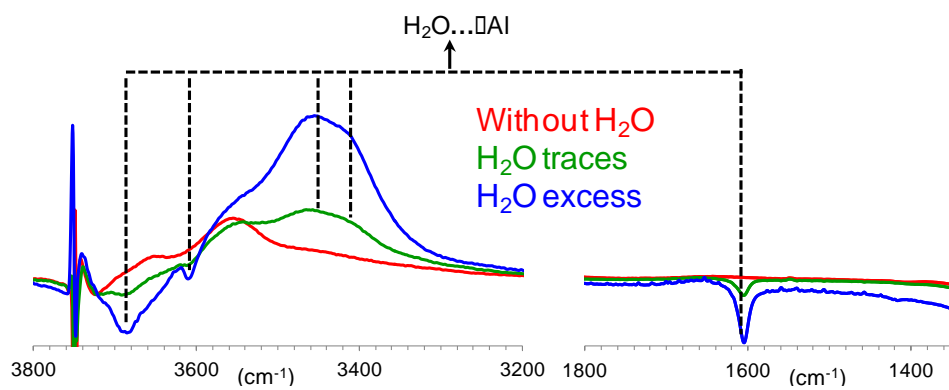


Figure 6



Graphical abstract