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Maxime Caillot, Alexandra Chaumonnot, Mathieu Digne, Jeroen A. van Bokhoven. The variety of Brønsted acid sites in amorphous aluminosilicates and zeolites.. *Journal of Catalysis*, 2014, 316 (July), pp.47-56. 10.1016/j.jcat.2014.05.002 . hal-01070397

**HAL Id: hal-01070397**

**<https://ifp.hal.science/hal-01070397>**

Submitted on 1 Oct 2014

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1 **The variety of Brønsted acid sites in amorphous aluminosilicates and zeolites**

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## 1 ABSTRACT

2 Brønsted acid sites of similar strength to those in zeolites are found in ASAs prepared  
3 by cogelation, as shown by thermogravimetric study of the dehydration of ethanol to  
4 ethylene. ASAs prepared by grafting and a commercial ASA (Siralox 30) show  
5 Brønsted acid sites that differ from those of zeolites. CO respectively ethanol adsorption  
6 followed by infrared spectroscopy identified the OH stretching frequency of the  
7 Brønsted acid sites specific to Si/Al<sub>2</sub>O<sub>3</sub> and Al/SiO<sub>2</sub> materials obtained by grafting to be  
8 ca. 3600 cm<sup>-1</sup> and 3640 cm<sup>-1</sup>, respectively, although the intensity of the corresponding  
9 band is weak. These sites, contrary to those of a H-USY zeolite with very few extra-  
10 framework aluminium, are highly sensitive to the surface hydration state: Their number  
11 decreases with increasing temperature. The surface structure of Siralox 30 resembles  
12 that of Si/Al<sub>2</sub>O<sub>3</sub> prepared in anhydrous conditions, showing similar isosurface acidic  
13 properties and distribution of silicon species.

## 14 Keywords

15 ASA; zeolite; Brønsted acidity; Siralox; TGA.

16

## 17 **1. Introduction**

18 Aluminosilicates are widely used in the field of catalysis due to their Brønsted acidic  
19 properties that enable the conversion of hydrocarbons. However, the reasons why  
20 crystalline zeolites are much more active than amorphous aluminosilicates (ASAs)  
21 remain unclear. It has been proposed that the lower catalytic activity of ASAs is due to a  
22 smaller number of Brønsted acid sites (BAS) whose structure, i.e. a tetrahedral

1 aluminium substituting a silicon atom in a silica lattice, is the same in both ASAs and  
2 zeolites [1-4]. Alternatively, specific structures of the site in ASAs are proposed: The  
3 acidity of the proton of a silanol is enhanced due to the vicinity of a coordinatively  
4 unsaturated aluminium atom, but not bridging the aluminium atom like in zeolites [5].  
5 CO and pyridine adsorption followed by infrared (IR) spectroscopy and their theoretical  
6 evaluation based on DFT, also suggested a non-permanently bridging nature of the  
7 Brønsted acid sites of ASAs [6]. A recent study made a distinction between strong  
8 Brønsted acid sites of zeolitic sites of ASAs and weaker Brønsted acid sites, which  
9 density is higher and which might be formed by silanol groups interacting with strong  
10 Lewis acid sites [4]. The diversity of ASAs surfaces may originate from the numerous  
11 techniques for synthesis [7]. We chose to rationalize this by directly comparing ASAs  
12 synthesized by grafting and cogelation. Molecular precursors of silicon and aluminium  
13 were deposited on alumina and silica to obtain, respectively, Si/Al<sub>2</sub>O<sub>3</sub> and Al/SiO<sub>2</sub> [8].  
14 By tuning the synthesis conditions (activation temperature and water content during  
15 synthesis) we obtained materials showing a diversity of surfaces. Thanks to  
16 thermogravimetric measurements and catalytic characterization; we found that the  
17 grafting of silicon and aluminium species creates Brønsted acid sites, and that the  
18 intrinsic activity of these is lower than that of a H-USY zeolite.

19 IR spectroscopy enables the characterization of the surface hydroxyl groups of ASAs  
20 and zeolites. The IR spectroscopy of adsorbed CO yields the nature and relative amount  
21 of Brønsted acid sites and strong and weak/medium Lewis acid sites [9-12]. Sites of  
22 similar strength were found in ASAs and steamed zeolites [9], acknowledging the  
23 complexity of the Brønsted acidity in ASAs and zeolites [12]. By evaluating ASAs  
24 (Siral from Sasol, ex Condea) from 0 to 100% wt.% SiO<sub>2</sub>, a mixed silica-alumina phase

1 was found for compositions below 30 wt.% SiO<sub>2</sub>, possessing bridged zeolitic Brønsted  
2 acid sites, as well as the encapsulation of the alumina surface by silicon species above  
3 30 wt.% SiO<sub>2</sub> with decreasing acidity.

4 Thermogravimetric analysis after ethanol adsorption is a relevant tool for  
5 investigating the surface percentage of silicon and aluminium species [13-18]. It enables  
6 the quantification of the number of Brønsted acid sites, which enables to calculate the  
7 turnover frequency of Brønsted-acid catalyzed reactions, such as the isomerization of *m*-  
8 xylene. This gives the intrinsic acidity of the Brønsted acid sites. On grafted Si/Al<sub>2</sub>O<sub>3</sub>  
9 the turnover frequency is  $1.4 \times 10^{-3} \text{ s}^{-1} \text{ site}^{-1}$ , on grafted Al/SiO<sub>2</sub>  $4.3 \times 10^{-4} \text{ s}^{-1} \text{ site}^{-1}$  and on  
10 a H-USY zeolite with very few extra-framework aluminium  $3.1 \times 10^{-2} \text{ s}^{-1} \text{ site}^{-1}$ . The IR  
11 study of adsorbed ethanol is useful for evaluating the intermediate that leads to ethylene  
12 upon dehydration [19].

13 In the present study, we demonstrate the variety of Brønsted acidities in zeolites and  
14 ASAs. The model Si/Al<sub>2</sub>O<sub>3</sub> and Al/SiO<sub>2</sub> ASAs that were previously prepared by  
15 grafting and characterized are compared to ASAs prepared by cogelation. A cogel ASA,  
16 prepared by mixing molecular precursors of silicon and aluminium species, and whose  
17 structure is expected to differ from that of the grafted samples, shows a heterogeneous  
18 structure and the presence of zeolitic sites that are not found in the ASAs made by  
19 grafting. A Siralox reference from Sasol (Siralox 30, 30 wt.% SiO<sub>2</sub>) is compared to  
20 Si/Al<sub>2</sub>O<sub>3</sub> samples that we made by grafting. We uniquely give evidence of the presence  
21 of specific structures for the BAS of ASAs made by grafting thanks to CO and ethanol  
22 adsorption followed by IR.

## 23 **2. Experimental**

1 The characteristics and synthesis conditions of the materials evaluated in this study  
2 are given in Table 1. Grafted samples, which synthesis is described in [8], were  
3 prepared by contacting, in controlled conditions, a silicon precursor (tetraethyl  
4 orthosilicate, TEOS) to alumina, leading to Si/Al<sub>2</sub>O<sub>3</sub> materials (entries 3-7), and an  
5 aluminium precursor (aluminium isopropoxide) to silica, leading to Al/SiO<sub>2</sub> materials  
6 (entry 8). Both Si/Al<sub>2</sub>O<sub>3</sub> and Al/SiO<sub>2</sub> materials underwent final calcination at 550°C.  
7 The commercial ASA reference was a Siralox 30 from Sasol (ASA(comm.), entry 10)  
8 obtained by impregnation of alumina with a silica gel. The cogel sample (entry 9) was  
9 prepared by mixing molecular precursors of both aluminium (aluminium sulfate) and  
10 silicon (sodium metasilicate), followed by washing, drying and calcination at 550°C.  
11 The zeolite reference (entry 11) was a ultra-stabilized Y zeolite, H form, from Zeolyst.

12 CO-infrared studies were performed on a Nexus Fourier transform apparatus  
13 (resolution 4 cm<sup>-1</sup>). The samples, pressed into pellets, were pretreated *in situ* under  
14 vacuum ( $\approx 10^{-5}$  mbar) for 10 h at 450°C (heating rate of 5°C/min) including a plateau at  
15 150°C for 1 h. In order to evaluate the influence of the activation temperature prior to  
16 CO adsorption, two of the grafted ASAs were activated at 250°C instead of 450°C.  
17 Spectra were taken before and after adsorption of increasing doses of CO, at liquid  
18 nitrogen temperature, up to a total amount of 600 μmol. Ethanol-infrared studies were  
19 performed on a Bio-RAD Fourier transform spectrometer (resolution 4 cm<sup>-1</sup>). The  
20 samples were pressed into pellets and pretreated *in situ* under high vacuum ( $\approx 10^{-8}$   
21 mbar) for 10 min at 200°C or 400°C (heating rate of 2°C/min). Spectra were taken after  
22 adsorbing increasing doses of ethanol at room temperature into the chamber where the  
23 sample was hold. Ethanol was then desorbed by gradually heating the sample up to  
24 400°C.

1 The thermogravimetric study of ethanol adsorption and desorption followed the  
 2 protocol given by Kwak et al. [20] that we previously used for Si/Al<sub>2</sub>O<sub>3</sub> [17] and  
 3 Al/SiO<sub>2</sub> [18] materials. The samples (≈ 20-30 mg) were put in crucibles and inserted  
 4 into a Mettler Toledo apparatus (TGA/SDTA851e) and activated in a flow of helium  
 5 (60 mL.min<sup>-1</sup>) at 500°C (heating rate 10 °C.min<sup>-1</sup>) for two hours, to eliminate  
 6 physisorbed water. After cooling to room temperature, ethanol was adsorbed by passing  
 7 helium through a saturator of ethanol until saturation of the weight gain (approx. 30  
 8 min). The weakly adsorbed ethanol molecules were desorbed by purging for 1 h at room  
 9 temperature, and the strongly adsorbed molecules were desorbed during the thermo-  
 10 programmed desorption step (TPD) by heating the sample from room temperature to  
 11 400°C. This resulted, when calculating the first derivative of the weight loss during  
 12 TPD with respect to temperature, in two main desorption features corresponding to  
 13 ethanol and ethylene release. The amount of dehydrated ethanol was calculated as  
 14 follows:

$$16 \text{ Ethanol dehydrated (nm}^{-2}\text{)} = \text{Ethanol retained after purge (nm}^{-2}\text{)} \times \frac{A_{\text{peak ethylene}}}{A_{\text{peak ethylene}} + A_{\text{peak ethanol}}} \quad (1)$$

18  
 19 where  $A_{\text{peak } i}$  is the area of the peak corresponding to the desorption of species  $i$  when  
 20 calculating the derivative of the weight loss of ethanol during TPD.

21 For the *m*-xylene isomerization test, the samples were first activated in a flow of air at  
 22 350°C, and gaseous *m*-xylene (0.6 cm<sup>3</sup>h<sup>-1</sup>) was reacted with the bed of catalyst at 350°C  
 23 in a flow of nitrogen. The products were analyzed by on-line chromatography by means  
 24 of a Hewlett Packard 6850 apparatus equipped with a flame ionization detector (FID)

1 and an FFAP column. Because the catalysts deactivated fast when submitting to *m*-  
 2 xylene flow, the rate of conversion of *m*-xylene to its products was calculated after 10  
 3 min on stream [4]. The value was given by:

4

5 Rate (molecule h<sup>-1</sup> nm<sup>-2</sup>) =

$$6 \frac{\sum_i^{\text{species}} \frac{A_i}{\text{number of carbons}_i}}{\sum_i^{\text{species}} \frac{A_i}{\text{number of carbons}_i} + \frac{A_{m\text{-xylene}}}{8}} \times \frac{\text{flow rate (cm}^3\text{h}^{-1}) \times \text{density}_{m\text{-xylene}} (\text{g cm}^{-3})}{M_{m\text{-xylene}} (\text{g mol}^{-1}) \times m_{\text{catalyst}} (\text{g})} \times \quad (2)$$

7  $\frac{N_A}{S_{\text{BET}} (\text{nm}^2\text{g}^{-1})}$

8

9 where  $A_i$  is the area of the GC peak of species  $i$  ( $i$  = toluene, *p*-xylene, *o*-xylene,  
 10 trimethylbenzenes),  $N_A$  the Avogadro number ( $6.02 \times 10^{23}$  mol<sup>-1</sup>), and  $S_{\text{BET}}$  the surface  
 11 area of the catalyst.

## 12 3. Results

### 13 3.1. Ethanol adsorption and dehydration followed by thermogravimetric 14 analysis

15 Fig. 1 gives the derivative of the weight loss during TPD on various ASAs and H-  
 16 USY. The first peak at around 80°C corresponds to the desorption of ethanol; its  
 17 position is the same for all samples. The second peak above 150°C corresponds to the  
 18 release of ethylene from dehydration of ethanol. No release of diethylether was  
 19 detected. On Si/Al<sub>2</sub>O<sub>3</sub> materials prepared under anhydrous conditions (Fig. 1a), the  
 20 ethanol dehydration peak first shifts to higher temperatures, then to lower temperatures,  
 21 which is indicative of the consumption of LAS and to the formation of BAS,  
 22 respectively [17]. In terms of intensity and position of the peaks, ASA(comm.) (entry



1 10) shows ethanol and ethylene desorption features very similar to those of SA(12/anh)  
2 (entry 4). Fig. 1b gives the results for ASAs and H-USY. The increasing ethanol  
3 dehydration temperature from H-USY to SA(17/anh) and AS(25/anh), for which ethanol  
4 dehydration takes place exclusively on BAS, relate to a decreasing strength of the BAS  
5 [18]. ASA(cogel) shows a low amount of ethanol desorbing, and its ethanol dehydration  
6 peak has the same position as that of H-USY. The weight loss above 250°C is ascribed  
7 to dehydroxylation.

8 Table 2 gives the amount of ethanol retained after purge, and the amount of ethanol  
9 undergoing dehydration. ASA(cogel) and  $\gamma$ -alumina show, respectively, the minimum  
10 and maximum values of ethanol retained after purge (col. 3). The calculation of the  
11 percentage of free alumina surface, in column 4, is based on the preferential adsorption  
12 of ethanol on alumina surfaces compared to the silica surface [17,18]. Given its specific  
13 crystalline structure, this calculation has no meaning for H-USY. The low amount of  
14 ethanol retained on ASA(cogel) is evidence of a highly dehydroxylated surface, without  
15 sites typical of alumina, such as LAS. Except for silica, all samples possess ethanol  
16 dehydration sites (col.5). We demonstrated that these sites are LAS on alumina, BAS on  
17 AS(25/anh), SA(17/anh) and H-USY, and a sum of LAS and BAS on SA(7/anh) and  
18 SA(12/anh) [17,18].

## 19 **3.2. Infrared spectroscopy**

### 20 **3.2.1. Infrared spectra of the OH stretching region upon ethanol adsorption**

21 Fig. 2 gives the difference spectra of the IR stretching region, recorded after  
22 adsorption of ethanol on alumina and Si/Al<sub>2</sub>O<sub>3</sub> samples, following a pretreatment at  
23 200°C. Infrared spectra of the OH stretching region of the materials are shown in a

1 previous paper [17]. Ethanol adsorption on the OH groups of the support causes a  
2 decrease of intensity in the OH stretching region ( $3600\text{ cm}^{-1}$  to  $3800\text{ cm}^{-1}$ ), and the  
3 appearance of peaks in the  $\text{CH}_2\text{-CH}_3$  stretching region ( $2800\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$ ) [13]. H-  
4 bonding between ethanol molecules and hydroxyl groups of the support is characterized  
5 by a broad positive band in the  $3000\text{ cm}^{-1}$  to  $3600\text{ cm}^{-1}$  [21]. On alumina, ethanol  
6 molecules are mainly adsorbed on Al(VI)-OH groups of the (100) surface, as indicated  
7 by the negative peak at  $3770\text{ cm}^{-1}$ . Upon heating and dehydration of ethanol, these OH  
8 groups are restored (not shown here). These observations confirm the role of the (100)  
9 surface of  $\gamma$ -alumina in the dehydration of ethanol [17,20]. To a lesser extent, Al-OH  
10 groups of the (110) surface (at  $3790\text{ cm}^{-1}$  and  $3730\text{ cm}^{-1}$ ) also contribute to the  
11 adsorption of ethanol. On SA(7/anh), ethanol adsorption takes place on silanol groups  
12 ( $3745\text{ cm}^{-1}$ ) and OH groups of the (110) surface of alumina ( $3730\text{ cm}^{-1}$ ). The OH groups  
13 of the (100) surface are grafted with silicon species and can no longer adsorb ethanol  
14 [17], hence the absence of a negative peak at  $3770\text{ cm}^{-1}$ . On SA(12/anh), due to grafting  
15 of the (110) surface with silicon species [17], the intensity of the negative bands  
16 corresponding to the OH groups of the (110) surface ( $3790\text{ cm}^{-1}$  and  $3730\text{ cm}^{-1}$ )  
17 decreases. The ethanol dehydration sites of SA(17/CVD250) are exclusively BAS [17].  
18 On SA(17/CVD250), silanols are the main adsorption sites, but the negative band  
19 extends until  $3650\text{ cm}^{-1}$ .

20 On alumina, the  $\text{CH}_2\text{-CH}_3$  stretching region is characterized by four main peaks. The  
21 peaks at  $2967\text{ cm}^{-1}$  and  $2926\text{ cm}^{-1}$  are ascribed to the asymmetric stretching vibration of  
22  $\text{CH}_3$  ( $\nu_a(\text{CH}_3)$ ) and  $\text{CH}_2$  ( $\nu_a(\text{CH}_2)$ ), respectively; the peaks at  $2895\text{ cm}^{-1}$  and  $2868\text{ cm}^{-1}$   
23 are ascribed to the symmetric stretching vibration of  $\text{CH}_2$  ( $\nu_s(\text{CH}_2)$ ) and  $\text{CH}_3$  ( $\nu_s(\text{CH}_3)$ ),  
24 respectively [13]; H-bonding confirms the adsorption of ethanol on OH groups. From

1 alumina to SA(7/anh), the four peaks are blue-shifted, and the intensity of  $\nu_s(\text{CH}_3)$   
2 decreases. When the silica loading increases,  $\nu_a(\text{CH}_3)$  is red-shifted, the intensity of  
3  $\nu_s(\text{CH}_3)$  decreases, and H-bonding is more pronounced.

4 The temperature of activation of alumina impacts the type of adsorption of ethanol  
5 (Fig. 3). Upon ethanol adsorption after a pretreatment at 400°C, no-H-bonding is  
6 visible. The negative signal in the OH region only appears for high ethanol coverage,  
7 and it is not centered at 3770  $\text{cm}^{-1}$ , which indicates that most of the ethanol molecules  
8 are not adsorbed on OH groups. The absence of disturbances, in the OH stretching  
9 region, between 3750  $\text{cm}^{-1}$  and 3800  $\text{cm}^{-1}$ , confirms that the (100) surface has no  
10 hydroxyl group. In fact, upon dehydroxylation of the (100) surface by pretreatment at  
11 high temperature, LAS form and become the adsorption sites of ethanol instead of OH  
12 groups. However, whatever the activation temperature, the four peaks in the  $\text{CH}_2\text{-CH}_3$   
13 stretching region have the same ratios of intensity and the same positions. This means  
14 that the shape of the  $\text{CH}_2\text{-CH}_3$  stretching region is not sensitive to the nature of the  
15 adsorption site (BAS or LAS), but rather to the local environment of the site (aluminium  
16 or silicon atoms).

17 Fig. 4 compares the results of ethanol adsorption on ASAs (SA(17/CVD250) and  
18 AS(25/anh)) to that on a zeolite (H-USY), following a pretreatment at 200°C. On  
19 AS(25/anh), the OH and  $\text{CH}_2\text{-CH}_3$  stretching regions are very similar to that of  
20 SA(17/CVD250), and silanols are the main adsorption sites of ethanol. On H-USY,  
21 ethanol first adsorbs on OH groups of the supercages (SiOHAl HF, 3630  $\text{cm}^{-1}$ ) and  
22 sodalite cages (SiOHAl LF, 3564  $\text{cm}^{-1}$ ) [22], then finally on silanols, which confirms  
23 that ethanol is a good probe of the BAS. As for ASAs, H-bonding of ethanol is visible  
24 and the  $\text{CH}_2\text{-CH}_3$  stretching region is dominated by the peak of  $\nu_a(\text{CH}_3)$ . Thus, this

1 stretching region has a characteristic shape when ethanol is adsorbed on BAS of ASAs  
2 and zeolites. However, contrary to H-USY, there is no wavenumber specific to the OH  
3 stretching of BAS of ASAs. These might be hidden because of the appearance of the  
4 broad H-bonding band.

### 5 **3.2.2. Infrared spectra of the OH stretching region and CO stretching region** 6 **upon CO adsorption**

7 Fig. 5 gives the evolution of the OH and CO stretching regions of H-USY upon CO  
8 adsorption following a pretreatment at 450°C. Due to the formation of the OH-CO  
9 bond, the stretching wavenumber of the adsorbing OH groups is shifted towards lower  
10 values. On a difference spectrum, the wavenumber shift due to adsorption on OH  
11 groups results in a negative peak indicating the original wavenumber of the OH group,  
12 and a positive band at lower wavenumber relating to the new OH-CO complex [12].  
13 The intensity of the shift ( $\Delta\nu$ ) is proportional to the acidic strength of the OH group [9].  
14 CO first adsorbs on strong Lewis acid sites ( $2230\text{ cm}^{-1}$ , ①) (Fig. 5a). This causes a shift  
15 of the OH stretching peak of isolated silanols ( $3745\text{ cm}^{-1}$ ) and SiOHAl HF ( $3632\text{ cm}^{-1}$ )  
16 towards higher wavenumbers. This phenomenon was observed by Crépeau et al. and it  
17 was ascribed to thermal effects caused by the temperature gap between CO and the  
18 temperature of the cell [11]. One can also postulate that silanol groups are disturbed due  
19 to the introduction of the first CO molecules. Further adsorption of CO molecules is  
20 characterized by a peak at  $2180\text{ cm}^{-1}$  (CO-OH(a)) in the CO region (②). The  
21 simultaneous appearance of a negative band at  $3632\text{ cm}^{-1}$  in the OH stretching region  
22 confirms the adsorption on strong BAS (SiOHAl HF, **OH(a)**). Upon CO adsorption, this  
23 OH band is shifted to  $3280\text{ cm}^{-1}$  (CO-**OH(a)**). The CO adsorption on silanols (③)

1 causes the appearance of several peaks in the CO stretching region (**CO-OH(b)** and (c)).  
2 The silanol peak (**OH(b-c)**) is shifted to  $3660\text{ cm}^{-1}$  (**CO-OH(b-c)**) upon CO adsorption.

3 Fig. 6 gives the parallel evolution of the OH and CO stretching region of AS(25/anh)  
4 upon the adsorption of CO following a pretreatment at  $450^\circ\text{C}$ . The first CO molecules  
5 are adsorbed on strong ( $2230\text{ cm}^{-1}$ , ①) then weak/medium LAS ( $2200\text{ cm}^{-1}$ , ②) (Fig.  
6 6a) [9-11,23]. Further CO adsorption causes the appearance of a peak at  $2177\text{ cm}^{-1}$ ,  
7 which is associated to adsorption on BAS (③) [11]. As for zeolites (Fig. 5), negative  
8 and positive bands are visible in the OH stretching region. Studies about ASAs have  
9 shown the presence of positive bands corresponding to perturbed OH bands, but they  
10 have failed to locate the original wavenumber of BAS, which has lead to various  
11 hypotheses aiming at explaining its absence: structure of BAS differing from that of  
12 zeolites [5,11] or low number of bridged sites [10], for example. Here, we observe both  
13 the shifted wavenumber of the CO-OH complex starting at around  $3400\text{ cm}^{-1}$  (**CO-**  
14 **OH(A)**), the original wavenumber of the BAS at  $3640\text{ cm}^{-1}$ , (**OH(A)**) and the stretching  
15 frequency of CO on BAS at  $2177\text{ cm}^{-1}$  (**CO-OH(A)**). In agreement with the  
16 observations of Cairon et al. and Crépeau et al. [9,11], CO is then chemisorbed on  
17 weaker OH groups (④), hence higher wavenumber for **CO-OH(B)** ( $3550\text{ cm}^{-1}$ ) and  
18 lower wavenumber for **CO-OH(B)** ( $2157\text{ cm}^{-1}$ ). The right part of the silanol peak ( $3745$   
19  $\text{cm}^{-1}$ ) becomes negative, which suggests that weak-acidic silanols in interaction with  
20 each other are the adsorbing sites (**OH(B)**). Physisorption of CO causes the appearance  
21 of a third component in the OH stretching region (**CO-OH(C)**,  $3660\text{ cm}^{-1}$ ) and in the  
22 CO stretching region (**CO-OH(C)**,  $2135\text{ cm}^{-1}$ ). The global silanol peak becomes  
23 negative, which shows that both isolated and interacting silanols undergo the  
24 physisorption of CO.

1 The OH and CO stretching regions of SA(17/anh), SA(17/4eqW) and  
2 SA(17/CVD250) (entries 5, 6, and 7, respectively) upon CO adsorption after  
3 pretreatment at 450°C are similar to the OH and CO stretching region of AS(25/anh).  
4 However, no negative band for BAS in the OH region nor specific peak for BAS in the  
5 CO region is detected.

6 The relative number of LAS and BAS of each sample are compared by integrating the  
7 corresponding band, in the CO stretching region, at saturation of its intensity. The  
8 values, reported in Table 3, are normalized by the weight of the wafer and the surface  
9 area. Entries 4 to 6 and 10 show no peak that can be exclusively ascribed to BAS, hence  
10 no values are reported. ASA(comm.) has the same number of strong LAS as SA(12/anh)  
11 and the same amount of weak/medium LAS as SA(17/anh). Consistent with its low  
12 amount of extra-framework aluminium species, H-USY shows almost no LAS.

13 On ASAs, there is an impact of the activation temperature of the sample on the  
14 amount of CO adsorbed on BAS and LAS. Fig. 7 gives the results for AS(25/anh) and  
15 SA(17/4eqW), which possess the highest surface density of BAS of Si/Al<sub>2</sub>O<sub>3</sub> and  
16 Al/SiO<sub>2</sub>, respectively [17,18], on the OH and CO stretching regions. At high activation  
17 temperature, the number of LAS (2180 cm<sup>-1</sup> to 2240 cm<sup>-1</sup>) and BAS (**OH(A)**) of  
18 AS(25/anh) (Fig. 7a) is lower; physisorption (**OH(C)**) is constant. Integration of the  
19 peaks (Table 3) confirms a lower number of strong LAS (-69%), weak/medium LAS (-  
20 31%), and BAS (-30%) at 450°C versus 250°C. Although their quantification is more  
21 difficult in the absence of a proper peak to integrate in the CO region, the number of  
22 silanol groups of SA(17/4eqW) (Fig. 7b), measured during physisorption of CO, is  
23 constant whatever the activation temperature. On SA(17/4eqW), the number of strong  
24 and weak/medium LAS increases (+115% and +32%, respectively) when the activation

1 temperature increases; the number of silanol groups of SA(17/4eqW) also increases ( $\approx$   
2 +30%). The negative peak at around  $3600\text{ cm}^{-1}$  in the OH stretching region indicates the  
3 presence of BAS at a lower wavenumber than for AS(25/anh) ( $3640\text{ cm}^{-1}$ ), and which  
4 are hardly visible at high activation temperature. The CO dose which is adsorbed on the  
5 BAS of SA(17/4eqW) leads to a more intense **CO-OH(A/B)** band in the CO region, at a  
6 higher wavenumber than for the following CO doses ( $2173\text{ cm}^{-1}$  vs.  $2156\text{ cm}^{-1}$ ), as  
7 previously observed[12].

### 8 **3.3. Isomerization of *m*-xylene**

9 Table 4 gives the rates of conversion of *m*-xylene. These and the turnover frequency  
10 (TOF) of the BAS of Si/Al<sub>2</sub>O<sub>3</sub> (entries 3, 4, and 5), Al/SiO<sub>2</sub> (entry 8), and H-USY  
11 (entry 11) were determined based on the amount of ethanol dehydration exclusively  
12 occurring on BAS, as previously calculated [17,18]. The density of BAS is assumed to  
13 correspond to the density of adsorbed ethanol that is converted to ethylene upon  
14 temperature-programmed desorption. ASA(cogel) shows the highest isoweight and  
15 isosurface rates of conversion, and the highest TOF of the ASAs. However, compared  
16 to SA(17/anh) and AS(25/anh), showing the best catalytic performance of their  
17 respective category, the number of BAS per surface unit is low. Furthermore, the level  
18 of conversion and the TOF are much lower than for H-USY. The isosurface conversion  
19 rate of ASA(comm.) is intermediary between that of SA(12/anh) and that of  
20 SA(17/anh); but due to a higher surface area, its isoweight conversion rate is much  
21 higher. Considering that the surface structure of ASA(comm.) can be rationalized as that  
22 of a Si/Al<sub>2</sub>O<sub>3</sub> material (vide infra), hence by using the same TOF, the number of BAS  
23 per surface unit can be estimated. The value is, again, between those of SA(12/anh) and  
24 SA(17/anh).

## 1 4. Discussion

### 2 4.1. Zeolitic Brønsted acid sites in ASAs

3 Table 5 summarizes the main conclusions about Brønsted acidity of ASAs and  
4 zeolite. The ethanol dehydration temperature of ASA(cogel) is lower than that of other  
5 ASAs and equal to that of H-USY. It means that, contrary to the other ASAs,  
6 ASA(cogel) has BAS of zeolitic strength. The presence of such strong BAS was already  
7 demonstrated in ASAs prepared by cogelation and homogeneous deposition of  
8 aluminium on silica using selective poisoning of these site by lutidine during *m*-xylene  
9 isomerization [4]. However, the TOF for *m*-xylene isomerisation of ASA(cogel) is five  
10 times lower than that of H-USY. ASA(cogel) and H-USY have the same intrinsic  
11 activation energy for catalytic reactions but different rates because of different surface  
12 structures affecting the adsorption and the number of active sites [3]. The higher pore  
13 diameter of ASA(cogel) (ca. 20 nm) compared to the micropores of the zeolite and  
14 amorphous structure, resulting in a lower confinement and fitting of the reactant  
15 molecule to the pore and the active site, lowers the heat of adsorption. The low amount  
16 of ethanol retained on the surface of ASA(cogel) after purge (Table 2) and the large  
17 amount of water lost during pretreatment (20% of the total sample weight) indicate that  
18 the surface of the sample is sensitive to heating and highly dehydroxylated upon  
19 activation at 500°C. The study of the OH stretching region in IR spectroscopy confirms  
20 the low number of silanol groups (not shown here). Moreover, the surface contains  
21 almost no aluminium species that form LAS, which would retain ethanol even after  
22 dehydroxylation. Thus, the cogelation synthesis does not lead to a homogeneous  
23 polymerization of species, and most of the minor component (silicon species) ends up  
24 on the outermost surface of the material. The core contains the major component



1 (aluminium species), which explains the high pore diameter and low surface area. The  
2 few aluminium species on the surface might be incorporated in the silica matrix, and  
3 would lead to zeolitic BAS (Table 5), by bridging silanols. In contrast, the surface of H-  
4 USY is more stable against thermal deactivation (10% weight loss during activation)  
5 and shows a higher amount of ethanol retained after purge (Table 2); thus, its surface  
6 silanols condensate to a lesser extent than those of ASA(cogel) upon heating. The  
7 stretching frequency of the BAS of ASA(cogel) could not be determined upon CO  
8 adsorption followed by IR spectroscopy; this can be the consequence of the low surface  
9 area and number of BAS, and the high amount of water despite pretreatment.

#### 10 **4.2. Diversity of Brønsted acid sites in zeolites and ASAs**

11 In all ASAs other than ASA(cogel), the ethanol dehydration temperature is higher  
12 than that of H-USY, which indicates higher activation energy and lower strength of the  
13 site. Hence, they are of a different nature (Table 5). Such ASAs may, however, catalyze  
14 the isomerization of *m*-xylene to its products. This proves that sites other than zeolitic  
15 BAS and weaker than zeolitic BAS may catalyze the isomerization of *m*-xylene, which  
16 contradicts former results [4].

17 Based on computational data, sites that are specific to ASAs have been proposed [6].  
18 The temperature range in which these pseudo-bridging silanols (PBS) can be obtained is  
19 narrow, as a certain hydration state of the surface is required. In the present study, CO  
20 adsorption on Si/Al<sub>2</sub>O<sub>3</sub> after activation at 250°C or 450°C shows that the number of  
21 both strong LAS and silanols increases and BAS are less visible when the activation  
22 temperature increases (Fig. 7b). Basing on our model of BAS for Si/Al<sub>2</sub>O<sub>3</sub> [17], it  
23 means that the interaction between the aluminium species and the silicon species, which  
24 can be assimilated to a PBS structure, is weaker at high temperatures, leaving the two

1 species isolated and causing the increase of the strong Lewis acidity and the decrease of  
2 the Brønsted acidity. On Al/SiO<sub>2</sub>, the number of both LAS and BAS decreases when  
3 increasing the activation temperature, while the number of silanols remains constant  
4 (Fig. 7a). There is no clear explanation for this observation, but it confirms the role of  
5 the hydration state of the surface in the number of BAS. NMR on AS(25/anh) showed  
6 no change in the distribution of coordination of the aluminium atoms upon adsorption of  
7 ethanol, as it is expected for PBS.

8 In the OH stretching region of the infrared spectra of AS(25/anh) upon CO  
9 adsorption, a Brønsted acid site with a stretching frequency of 3640 cm<sup>-1</sup> can be  
10 identified in Al/SiO<sub>2</sub> (Fig. 6). Because of the lower surface area of AS(25/anh), the  
11 negative peak observed during CO adsorption is less intense than those of H-USY. As a  
12 consequence, this peak is hidden by the H-bonding following the adsorption of ethanol  
13 (Fig. 4). The broadness of the band at 3640 cm<sup>-1</sup> in IR-CO indicates a certain variety of  
14 sites, which correlates to a broad ethanol dehydration peak (Fig. 1b), contrary to H-  
15 USY. The lower wavenumber of the BAS of Si/Al<sub>2</sub>O<sub>3</sub> (3600 cm<sup>-1</sup>) and the lower ethanol  
16 dehydration temperature (Fig. 1b) confirm a different nature and environment of the  
17 sites between the two types of ASAs.

18 On H-USY, we show that both the dehydration of ethanol and the adsorption of CO  
19 followed by IR probe the BAS of the supercages. These sites show constant ethanol  
20 dehydration temperature and amount of ethanol dehydrated whatever the pretreatment  
21 temperature. The number of BAS probed by CO adsorption is similar after activation at  
22 250°C and 450°C (not shown here), which confirms the high stability to temperature of  
23 the bridged BAS of H-USY. The shift of the OH band ( $\Delta\nu$ ) upon CO adsorption is  
24 higher for the BAS of H-USY ( $\Delta\nu = 352 \text{ cm}^{-1}$ ) than for the BAS of AS(25/anh) ( $\Delta\nu =$

1 240  $\text{cm}^{-1}$ ) and for the silanol groups ( $\Delta\nu = 85 \text{ cm}^{-1}$  for both H-USY and AS(25/anh)),  
2 which is consistent with a higher acidity of the BAS of the zeolite [9]. A similar  
3 conclusion had been obtained by calculating the turnover frequencies (TOF) of the BAS  
4 of these materials for *m*-xylene isomerisation [18].

5 We found no impact of the type of zeolite (H-USY with and with very few EFAL, H-  
6 ZSM-5) nor of the activation conditions (200°C or 500°C) on the dehydration  
7 temperature of ethanol (ca. 210°C, see Supporting Information). However, the nature of  
8 the intermediate leading to ethylene, either a carbenium ion [24] or an alkoxy [15,20], is  
9 debated. On alumina, the reactivity of ethanol depends on the activation temperature of  
10 the catalyst. After a pretreatment at 500°C, ethanol is adsorbed at room temperature on  
11 the LAS of the (100) surface, and is further dehydrated upon heating at ca. 250°C  
12 according to a mechanism of the E<sub>2</sub>-type, i.e. concerted [25]. Our results show that after  
13 a pretreatment at 200°C, ethanol is adsorbed on the Al(VI)-OH groups of the (100)  
14 surface. Contrary to the OH groups of silica [17], these sites are strong enough not to  
15 desorb ethanol upon heating at 200°C. Above 200°C LAS are formed, which enables  
16 the formation of ethoxy species. These species are further transformed into ethylene  
17 upon heating at ca. 270°C. In a recent study, Phung et al. claim that the formation of  
18 ethoxy species on alumina occurs whatever the hydroxylation state of the surface.[19]  
19 However, the more silicon atoms are grafted on the surface of alumina, the smaller the  
20 effect of the pretreatment temperature on the ethanol dehydration temperature. This  
21 confirms that the active Lewis acid sites of the bare alumina surface are responsible for  
22 the lower ethanol dehydration temperature after pretreatment at 500°C. On Al/SiO<sub>2</sub>  
23 materials, this effect of the pretreatment temperature is limited (between 1°C and 7°C).

#### 24 **4.3. Grafted ASAs as a model for the variety of commercial ASAs**

1 Our ASA(comm.) is prepared by impregnation of alumina, obtained by hydrolysis of  
2 an aluminium alkoxide, with orthosilicic acid [26]. The results obtained for this sample  
3 (percentage of free alumina surface, position of the ethanol dehydration peak, number of  
4 strong and weak/medium LAS, and isosurface rate of conversion of *m*-xylene) are  
5 systematically close to those of SA(12/anh), despite dissimilar synthesis techniques.  
6 Thus, the deposition of silicon species must proceed in a similar way, that leads to the  
7 stepwise grafting of the  $\gamma$ -alumina facets [17]. Assuming that ASA(comm.) has the  
8 same BAS as Si/Al<sub>2</sub>O<sub>3</sub> materials (Table 5), hence the same turnover frequency for *m*-  
9 xylene isomerization (TOF), the distribution of species on the surfaces can be calculated  
10 [17] (Table 6). The results confirm the partial coverage of the facets of ASA(comm.) in  
11 a similar way as SA(12/anh). This conclusion confirms and provides further  
12 clarification on the deposition process of silicon species in Siral materials as described  
13 by Daniell et al. [10]. These materials do not possess bridged zeolitic BAS.

## 14 **5. Conclusion**

15 Zeolitic-like Brønsted acid sites are found on an ASA prepared by cogelation (20%  
16 SiO<sub>2</sub>), despite a heterogeneous core-shell structure exhibiting essentially silicon surface  
17 species. Grafted ASAs possess specific Brønsted acid sites that differ from those of  
18 zeolites, with high sensitivity to temperature. The grafting approach of Si/Al<sub>2</sub>O<sub>3</sub>  
19 materials that we previously described, including stepwise grafting of silicon species on  
20 the facets of  $\gamma$ -alumina, is convincingly extended to a commercial ASA reference  
21 (Siralox). We confirm the relevance of ethanol as a probe of the Brønsted acid sites of  
22 ASAs and zeolites and OH and Lewis acid sites of  $\gamma$ -alumina.

## 23 **Appendix A. Ethanol adsorption and dehydration followed by thermogravimetry**

1 Fig. S1 gives the derivative of the weight loss during TPD on various zeolites. The  
2 values of the derivatives are normalized by the surface area of each sample. The first  
3 peak at around 80°C corresponds to the desorption of ethanol. The second peak at  
4 around 210°C corresponds to ethylene stemming from the dehydration of ethanol. The  
5 nature of the zeolite (H-ZSM-5 or USY) and the aluminium content impact the amount  
6 of ethanol dehydrated, but the dehydration temperature is the same for all samples and  
7 activation temperatures. Table S1 gives the number of Brønsted acid sites (BAS),  
8 quantified by the amount of ethanol dehydrated. One every two aluminium atoms of H-  
9 ZSM-5 forms a BAS and one every four or five aluminium atoms of USY forms a BAS.  
10 CBV 712, which possesses extra framework aluminium species (EFAL), shows the  
11 lower ratio of BAS per aluminium atom.

## 12 **Acknowledgments**

13 The authors thank Anne-Agathe Quoineaud, Emmanuel Soyer, and Laurent Lemaître  
14 from IFP Energies nouvelles for IR–CO measurements. Amaia Beloqui Redondo,  
15 Matthew A. Brown, and Daniel Fodor were very helpful in setting the equipment for IR  
16 observations of adsorbed ethanol. We acknowledge financial support from IFP Energies  
17 nouvelles.

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- 34

1 **Tables**

2 **Table 1**

3 **Synthesis conditions and main characteristics of the materials [7].**

Entry	Sample nature	Sample name	wt.% SiO <sub>2</sub>	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Synthesis technique	Pretreatment conditions (temperature, mode)	Synthesis conditions (temperature, media)
(1)	Alumina	γ-alumina	0.0	235	-	-	-
(2)	Silica	Silica	100.0	550	-	-	-
(3)	ASA (Si/Al <sub>2</sub> O <sub>3</sub> )	SA(7/anh)	7.3	200	CLD anhydrous	40°C, vacuum	110°C, toluene
(4)		SA(12/anh)	12.2	180	CLD anhydrous (x2)	40°C, vacuum	110°C, toluene
(5)		SA(17/anh)	17.1	160	CLD anhydrous (x3)	40°C, vacuum	110°C, toluene
(6)		SA(17/4eqW)	16.5	175	CLD aqueous (4 eq. water)	40°C, vacuum	110°C, toluene
(7)		SA(17/CVD250)	17.2	165	CVD	250°C, air flow	250°C, air
(8)	ASA (Al/SiO <sub>2</sub> )	AS(25/anh)	24.8	330	CLD anhydrous (x2)	30°C, vacuum	110°C, toluene
(9)	ASA (cogel)	ASA(cogel)	20.0	160	cogelation	-	-
(10)	ASA (comm. reference)	ASA(comm.)	30.0	315	impregnation of alumina with silica gel	-	-
(11)	Zeolite	H-USY	94.6	780	-	-	-

4

5 **Table 2**

6 **Surface density of ethanol retained after purge and undergoing dehydration (nm<sup>-2</sup>)**

7 **following a pretreatment at 500°C.**

Entry	Sample	Ethanol retained after purge (nm <sup>-2</sup> ) (col. 3)	Percentage of free alumina surface (%) (col. 4)	Ethanol undergoing dehydration (nm <sup>-2</sup> ) <sup>a</sup> (col. 5)
(1)	γ-alumina	2.8	100	0.83
(2)	silica	1.3	0	0.00
(3)	SA(7/anh)	2.4	70	0.27
(4)	SA(12/anh)	2.2	57	0.23
(5)	SA(17/anh)	1.7	29	0.17
(8)	AS(25/anh)	2.2	56	0.61
(9)	ASA(cogel)	1.1	0	0.12
(10)	ASA(comm.)	2.1	55	0.27
(11)	H-USY	1.4	-	0.18

8 <sup>a</sup> Based on the total surface area.

9

10 **Table 3**

1 Number of sites probed by CO (a.u. isosurface data: intensity of the band in the CO  
 2 region after integrating and dividing by the weight of the wafer and the surface area of  
 3 the sample).

Entry	Sample	Activation temperature (°C)	Strong LAS	Weak/medium LAS	BAS <sup>a</sup>	Silanols
(4)	SA(12/anh)	450	39	374	-	
(5)	SA(17/anh)	450	76	272	-	
(6)	SA(17/4eqW)	250	34	333	-	605
(6)	SA(17/4eqW)	450	73	441	-	802
(8)	AS(25/anh)	250	88	219	781	468
(8)	AS(25/anh)	450	27	152	547	456
(10)	ASA(comm.)	450	38	278	-	
(11)	H-USY	450	8	14	1250	

4 <sup>a</sup> Entries 4-6 and 10: no peak specific to BAS. Entry 11: integration of all the bands  
 5 corresponding to CO adsorption on OH groups.

6

7 Table 4

8 *m*-xylene conversion over ASAs and zeolites.

Entry	Sample	Rate of <i>m</i> -xylene converted @ 10 min		TOF ( $\times 10^{-3} \text{ s}^{-1} \text{ site}^{-1}$ )	BAS (nm <sup>-2</sup> ) <sup>b</sup>
		Isoweight (mmol h <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> )	Isosurface (molecule h <sup>-1</sup> nm <sup>-2</sup> )		
(3)	SA(7/anh)	7	21.8	1.4	0.04
(4)	SA(12/anh)	16	54.0	1.4	0.11
(5)	SA(17/anh)	25	94.1	1.4	0.19
(8)	AS(25/anh)	43	78.9	0.4	0.52
(9)	ASA(cogel)	69	259.6	6.0	0.12
(10)	ASA(comm.)	42	80.0	1.4 <sup>a</sup>	0.16
(11)	H-USY	2640	2034.8	31.4	0.18

9 <sup>a</sup> Based on the hypothesis that ASA(comm.) is similar to Si/Al<sub>2</sub>O<sub>3</sub> material, for which  
 10 the TOF is 0.14 s<sup>-1</sup> site<sup>-1</sup>.

11 <sup>b</sup> Based on the TOF.

12

13 Table 5

14 Main conclusions on the BAS of grafted and commercial ASAs and zeolites.



Entry	Sample name	Type of Brønsted acid site (BAS)	Evolution of the number of BAS with increasing temperature	Characteristic wavenumber in IR (cm <sup>-1</sup> )
(5)	SA(17/anh)	ASA (Si/Al <sub>2</sub> O <sub>3</sub> )	decreases (upon heating, formation of a strong Lewis acid site and a silanol)	3600 <sup>a</sup>
(6)	SA(17/4eqW)			
(7)	SA(17/CVD250)			
(10)	ASA(comm.)			
(8)	AS(25/anh)	ASA (Al/SiO <sub>2</sub> )	decreases	3640
(11)	H-USY	zeolitic	stable	3630 <sup>b</sup>
(9)	ASA(cogel)			

1 <sup>a</sup> As found in SA(17/4eqW), which contains the highest number of active sites,  
2 following a pretreatment at 250°C before CO adsorption.

3 <sup>b</sup> The stretching frequency of Brønsted acid sites of ASA(cogel) is supposed to be the  
4 same as that of H-USY, but no evidence was found in IR-CO.

5

6 Table 6

7 Percentage of free (100) and (110) surfaces on Si/Al<sub>2</sub>O<sub>3</sub> and ASA(comm.).

Entry	Sample	Part of free (100) surface (%)	Part of free (110) surface (%)
(3)	SA(7/anh)	27	81
(4)	SA(12/anh)	14	68
(5)	SA(17/anh)	0	36
(10)	ASA(comm.)	14	65

8

9 Table S1

10 Number of Brønsted acid sites (BAS).

Zeolite	BAS	
	Isosurface (nm <sup>-2</sup> )	Per Al atom (Al atom <sup>-1</sup> )
H-ZSM-5	0.75	0.51
H-USY CBV 760	0.11	0.24
H-USY CBV 720	0.18	0.21
NH <sub>4</sub> -USY CBV 712	0.45	0.20

1 **Figure captions**

2

3 Fig. 1. Derivative of TPD weight loss of ethanol on ASAs and H-USY after  
4 pretreatment at 500°C: (a) Si/Al<sub>2</sub>O<sub>3</sub> prepared by anhydrous CLD [16] (entries 3 to 5)  
5 and commercial reference (entry 10); (b) Si/Al<sub>2</sub>O<sub>3</sub> (entry 5), Al/SiO<sub>2</sub> (entry 8), and  
6 cogel (entry 9) ASAs and H-USY (entry 11). Numbers in brackets correspond to entries  
7 in Table 1.

8

9 Fig. 2. Infrared spectra (OH and CH<sub>2</sub>-CH<sub>3</sub> stretching region) of Si/Al<sub>2</sub>O<sub>3</sub> after  
10 adsorption of ethanol, following pretreatment at 200°C. (x): entries in Table 1; (100) or  
11 (110): surfaces of  $\gamma$ -alumina.

12

13 Fig. 3. Infrared spectra (OH and CH<sub>2</sub>-CH<sub>3</sub> stretching region) of  $\gamma$ -alumina after  
14 adsorption of ethanol, following pretreatment at 200°C and 400°C.

15

16 Fig. 4. Infrared spectra (OH and CH<sub>2</sub>-CH<sub>3</sub> stretching region) of Si/Al<sub>2</sub>O<sub>3</sub>, Al/SiO<sub>2</sub>, and  
17 H-USY after adsorption of ethanol, following pretreatment at 200°C. Numbers in  
18 brackets correspond to entries in Table 1.

19

20 Fig. 5. Progressive adsorption of CO on H-USY (entry 10) followed by infrared  
21 spectroscopy after pretreatment at 450°C.

1

2 Fig. 6. Progressive adsorption of CO on Al/SiO<sub>2</sub> (AS/25anh, entry 8) followed by  
3 infrared spectroscopy after pretreatment at 450°C.

4

5 Fig. 7. Impact of the activation temperature on CO adsorption: (a) AS(25/anh); (b)  
6 SA(17/4eqW). Dotted lines correspond to CO adsorption on BAS.

7

8 Fig. S1. Derivative of TPD weight loss of various zeolites after pretreatment at 200°C  
9 and 500°C: (a) Si/Al<sub>2</sub>O<sub>3</sub> prepared by anhydrous CLD; (b) various ASAs and H-USY.  
10 EFAL: extra-framework aluminium species.