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

2

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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/Al₂O₃ and Al/SiO₂ materials obtained by grafting to be
8 ca. 3600 cm⁻¹ and 3640 cm⁻¹, 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/Al₂O₃ 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/Al₂O₃ and Al/SiO₂ [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.% SiO₂, a mixed silica-alumina phase

1 was found for compositions below 30 wt.% SiO₂, possessing bridged zeolitic Brønsted
2 acid sites, as well as the encapsulation of the alumina surface by silicon species above
3 30 wt.% SiO₂ 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/Al₂O₃
9 the turnover frequency is $1.4 \times 10^{-3} \text{ s}^{-1} \text{ site}^{-1}$, on grafted Al/SiO₂ $4.3 \times 10^{-4} \text{ s}^{-1} \text{ site}^{-1}$ 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/Al₂O₃ and Al/SiO₂ 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.% SiO₂) is compared to
20 Si/Al₂O₃ 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/Al₂O₃ materials (entries 3-7), and an
5 aluminium precursor (aluminium isopropoxide) to silica, leading to Al/SiO₂ materials
6 (entry 8). Both Si/Al₂O₃ and Al/SiO₂ 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⁻¹). 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 μ mol. Ethanol-infrared studies were
19 performed on a Bio-RAD Fourier transform spectrometer (resolution 4 cm⁻¹). 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/Al₂O₃ [17] and
 3 Al/SiO₂ [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⁻¹) at 500°C (heating rate 10 °C.min⁻¹) 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 cm³h⁻¹) 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⁻¹ nm⁻²) =

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

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 (6.02×10^{23} mol⁻¹), and S_{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/Al₂O₃ 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 γ -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/Al₂O₃ 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 cm^{-1} to 3800 cm^{-1}), and the
3 appearance of peaks in the $\text{CH}_2\text{-CH}_3$ stretching region (2800 cm^{-1} to 3000 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 cm^{-1} to 3600 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 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 γ -alumina in the dehydration of ethanol [17,20]. To a lesser extent, Al-OH
10 groups of the (110) surface (at 3790 cm^{-1} and 3730 cm^{-1}) also contribute to the
11 adsorption of ethanol. On SA(7/anh), ethanol adsorption takes place on silanol groups
12 (3745 cm^{-1}) and OH groups of the (110) surface of alumina (3730 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 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 cm^{-1} and 3730 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 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 cm^{-1} and 2926 cm^{-1} are ascribed to the asymmetric stretching vibration of
22 CH_3 ($\nu_a(\text{CH}_3)$) and CH_2 ($\nu_a(\text{CH}_2)$), respectively; the peaks at 2895 cm^{-1} and 2868 cm^{-1}
23 are ascribed to the symmetric stretching vibration of CH_2 ($\nu_s(\text{CH}_2)$) and 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 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 cm^{-1} and 3800 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 cm^{-1}) and
22 sodalite cages (SiOHAl LF, 3564 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 cm^{-1} , ①) (Fig. 5a). This causes a shift
15 of the OH stretching peak of isolated silanols (3745 cm^{-1}) and SiOHAl HF (3632 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 cm^{-1} (CO-OH(a)) in the CO region (②). The
21 simultaneous appearance of a negative band at 3632 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 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 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°C . The first CO molecules
5 are adsorbed on strong (2230 cm^{-1} , ①) then weak/medium LAS (2200 cm^{-1} , ②) (Fig.
6 6a) [9-11,23]. Further CO adsorption causes the appearance of a peak at 2177 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 cm^{-1} (**CO-**
14 **OH(A)**), the original wavenumber of the BAS at 3640 cm^{-1} , (**OH(A)**) and the stretching
15 frequency of CO on BAS at 2177 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 cm^{-1}) and
18 lower wavenumber for **CO-OH(B)** (2157 cm^{-1}). The right part of the silanol peak (3745
19 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 cm^{-1}) and in the
22 CO stretching region (**CO-OH(C)**, 2135 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/Al₂O₃ and
16 Al/SiO₂, respectively [17,18], on the OH and CO stretching regions. At high activation
17 temperature, the number of LAS (2180 cm⁻¹ to 2240 cm⁻¹) 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 cm^{-1} in the OH stretching region indicates the
3 presence of BAS at a lower wavenumber than for AS(25/anh) (3640 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 cm^{-1} vs. 2156 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/Al₂O₃ (entries 3, 4, and 5), Al/SiO₂ (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/Al₂O₃ 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/Al₂O₃ 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/Al₂O₃ [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/SiO₂, 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⁻¹ can be
10 identified in Al/SiO₂ (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⁻¹ 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/Al₂O₃ (3600 cm⁻¹) 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 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 E₂-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/SiO₂
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 γ -alumina facets [17]. Assuming that ASA(comm.) has the
8 same BAS as Si/Al₂O₃ 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 SiO₂), 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/Al₂O₃
19 materials that we previously described, including stepwise grafting of silicon species on
20 the facets of γ -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 γ -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.

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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 ₂	S _{BET} (m ² g ⁻¹)	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 ₂ O ₃)	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 ₂)	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⁻²)**

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

Entry	Sample	Ethanol retained after purge (nm ⁻²) (col. 3)	Percentage of free alumina surface (%) (col. 4)	Ethanol undergoing dehydration (nm ⁻²) ^a (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 ^a 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 ^a	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 ^a 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 ⁻²) ^b
		Isoweight (mmol h ⁻¹ g _{cat} ⁻¹)	Isosurface (molecule h ⁻¹ nm ⁻²)		
(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 ^a	0.16
(11)	H-USY	2640	2034.8	31.4	0.18

9 ^a Based on the hypothesis that ASA(comm.) is similar to Si/Al₂O₃ material, for which
 10 the TOF is 0.14 s⁻¹ site⁻¹.

11 ^b 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 ⁻¹)
(5)	SA(17/anh)	ASA (Si/Al ₂ O ₃)	decreases (upon heating, formation of a strong Lewis acid site and a silanol)	3600 ^a
(6)	SA(17/4eqW)			
(7)	SA(17/CVD250)			
(10)	ASA(comm.)			
(8)	AS(25/anh)	ASA (Al/SiO ₂)	decreases	3640
(11)	H-USY	zeolitic	stable	3630 ^b
(9)	ASA(cogel)			

1 ^a 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 ^b 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/Al₂O₃ 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 ⁻²)	Per Al atom (Al atom ⁻¹)
H-ZSM-5	0.75	0.51
H-USY CBV 760	0.11	0.24
H-USY CBV 720	0.18	0.21
NH ₄ -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/Al₂O₃ prepared by anhydrous CLD [16] (entries 3 to 5)
5 and commercial reference (entry 10); (b) Si/Al₂O₃ (entry 5), Al/SiO₂ (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 CH₂-CH₃ stretching region) of Si/Al₂O₃ after
10 adsorption of ethanol, following pretreatment at 200°C. (x): entries in Table 1; (100) or
11 (110): surfaces of γ -alumina.

12

13 Fig. 3. Infrared spectra (OH and CH₂-CH₃ stretching region) of γ -alumina after
14 adsorption of ethanol, following pretreatment at 200°C and 400°C.

15

16 Fig. 4. Infrared spectra (OH and CH₂-CH₃ stretching region) of Si/Al₂O₃, Al/SiO₂, 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/SiO₂ (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/Al₂O₃ prepared by anhydrous CLD; (b) various ASAs and H-USY.
10 EFAL: extra-framework aluminium species.