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Creation of Brønsted Acidity by Grafting Aluminum Isopropoxide on Silica under Controlled Conditions: Determination of the Number of Brønsted Sites and their Turnover Frequency for *m*-Xylene Isomerization

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There is not a unique Brønsted acid site for aluminosilicates (ASAs). IR spectroscopy following CO adsorption proves the creation of Brønsted acid sites on Al/SiO_2 ASAs, which are synthesized by the deposition of aluminum species on hydroxylated silica. These sites are active for ethanol dehydration and *m*-xylene isomerization. Controlled deposition under anhydrous conditions optimizes the number of sites, whereas the

Introduction

Owing to the increasing need for middle distillates, the development and optimization of catalysts to convert the heavy fraction of crude oil are of fundamental importance. Thanks to their Brønsted acidity, amorphous aluminosilicates (ASAs) are materials of interest. However, their diversity in the distribution of silicon and aluminum species throughout the material and their amorphous character render a straightforward correlation between surface structure and acidity difficult. Therefore, the nature and number of Brønsted sites on ASAs are regular topics of discussion.^[1-4]

We have described the synthesis of ASAs by grafting.^[5] Al/ SiO₂ was obtained by depositing $Al(OiPr)_3$ on an amorphous silica gel under controlled conditions. Such Al/SiO_2 materials display Brønsted acidic character, which is not the case of the parent support.^[6-12] For example, Al/SiO_2 materials catalyze the cracking of cumene.^[9,10,13] The deposition of Pd leads to bifunctional catalysts, which are active in hydrogenation/dehydro-

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presence of water leads to alumina agglomerates with no Brønsted acidity. The turnover frequency for *m*-xylene isomerization $(4.3 \times 10^{-4} \text{ s}^{-1} \text{ site}^{-1} \text{ at } 350 \,^{\circ}\text{C}$, atmospheric pressure, and 0.6 cm³ h⁻¹ of *m*-xylene) is approximately 3 times lower than that of the Brønsted acid sites of Si/Al₂O₃ and 75 times lower than that of an ultrastable Y-type zeolite without extra-framework aluminum.

genation.^[11,12,14] Hensen et al. found that the Brønsted acidity of Al/SiO₂, prepared by homogeneous deposition–precipitation of aluminum nitrate on silica, results from the diffusion of a limited amount of tetrahedral aluminum atoms through the silica lattice, which leads to negative charge compensation by labile acidic protons, hence Brønsted acidity, similar to what occurs in zeolites.^[14] The choice of the preparation technique for obtaining ASAs—co-gelation, grafting, and so on—strongly influences the spread of silicon and aluminum atoms through the particles and can lead to dissimilar structures.^[15]

The nature of the OH groups upon the grafting of aluminum can be monitored by observing the OH stretching region (\approx 3000 to 4000 cm⁻¹) by IR spectroscopy. The adsorption of CO leads to changes in the 2100 to 2250 cm⁻¹ range (CO stretching); each band thus obtained is ascribable to a specific type of acidic site.

We already demonstrated the relevance of ethanol adsorption followed by thermogravimetry to evaluate the development of Brønsted acid sites (BAS) on Si/Al₂O₃ ASAs.^[16] The dehydration of ethanol to ethylene is catalyzed by the Lewis acid sites (LAS) of γ -alumina and the Brønsted acid sites (BAS) of zeolites and ASAs.^[17-22] Knowing the number of BAS enables the calculation of the turnover frequency (TOF) in Brønsted acid demanding reactions, such as *m*-xylene isomerization. On Si/Al₂O₃, the TOF is $1.4 \times 10^{-3} \text{ s}^{-1} \text{ site}^{-1}$, and on an ultrastable Y-type (USY) zeolite without extra-framework aluminum the TOF is $3.1 \times 10^{-2} \text{ s}^{-1} \text{ site}^{-1}$.^[16]

The aim of this study was to determine the acidity of Al/SiO_2 by grafting aluminum isopropoxide on silica. The catalytic activity to *m*-xylene isomerization was measured and indicated the emergence of Brønsted acidity upon grafting of silica with aluminum species. This was confirmed by recording the IR

spectra of the CO stretching region after CO adsorption. We performed the adsorption of ethanol followed by thermogravimetry. This enabled the determination of the surface coverage of aluminum species, similar to Si/Al_2O_3 .^[16] The TOF of Al/SiO₂ for *m*-xylene isomerization was calculated.

Results

Adsorption of ethanol followed by thermogravimetry

Surface coverage of aluminum species on Al/SiO₂

The main characteristics of Al/SiO_2 and its composition were tuned by adapting the amount of precursor in the reaction mixture (Table 1). Anhydrous conditions led to a uniform deposition of aluminum species (entries 2–7), whereas the presence of water favored a heterogeneous deposit (entries 8 and 9).^[5] In the rest of the document, blue labels correspond to alumina, silica, and materials prepared under anhydrous conditions (entries 1 to 7 and 10) and purple/pink labels correspond to materials prepared under aqueous conditions (entries 8 and 9).

Following pretreatment at 500 °C, ethanol was adsorbed at room temperature, and weakly bonded molecules were desorbed by purging. With increasing alumina content (Table 2, entries 1–7), a higher amount of ethanol was retained after the purge. Similar to our previous observations,^[16] this indicated a greater number of strong ethanol adsorption sites on the alumina surfaces. Despite a similar aluminum loading, entries 8 and 9, synthesized in the presence of water, showed a smaller amount of retained ethanol than entry 5, which was prepared under anhydrous conditions.

As for the Si/Al₂O₃ materials,^[16] the surface coverage by aluminum species on the Al/SiO₂ materials was calculated by comparing the amount of ethanol retained after the purge to the minimum and maximum amounts on pure silica (1.3 EtOH nm⁻²) and pure alumina (2.8 EtOH nm⁻²), respectively [Eq. (1)]:

Experimental density of surface Al atoms [%] $_$ amount of adsorbed ethanol [nm⁻²]-1.3 > 100

Table 2. Surface density of ethanol retained after purge following pretreatment at 500 $^\circ\text{C}.$					
Entry	Sample	Ethanol retained after purge [nm ⁻²]			
1	silica	1.3			
2	AS(3/anh)	1.3			
3	AS(6/anh)	1.5			
4	AS(10/anh)	1.6			
5	AS(15/anh)	2.0			
6	AS(25/anh)	2.2			
7	AS(35/anh)	2.6			
8	AS(16/1eqW)	1.6			
9	AS(17/3eqW)	1.4			
10	γ-alumina	2.8			

The theoretical coverage of Al/SiO_2 by aluminum species was estimated as follows [Eq. (2)]:⁽¹⁶⁾

$$\begin{array}{l} \mbox{Theoretical density of surface Al atoms [\%]} \\ = & \frac{\mbox{density of grafted Al}}{\mbox{density of Al atoms on alumina}} \times 100 \end{tabular} \end{tabular}$$

In the plot of the experimental density of aluminum atoms (*y* axis) versus the theoretical plot (*x* axis, Figure 1), the dashed line corresponds to the experimental density, which is the same as the theoretical density, as found upon depositing the aluminum atoms uniformly on the surface. Thus, samples that were prepared under anhydrous conditions (entries 3–7) display a homogeneous deposition of species. The higher the surface density of aluminum atoms, the higher the amount of strong adsorption sites for ethanol. Conversely, entries 8 and 9 show inhomogeneous deposition, which confirms previous observations.^[5] The higher the water content during synthesis, the lower the density of the aluminum atoms accessible to ethanol, which is indicative of the presence of clusters of alumina species.

The difference in ethanol retained after purge between silica and AS(3/anh) is not accurate enough to calculate the surface ratio of surface aluminum; thus, it is not reported in Figure 1, and the surface ratio of aluminum species of AS(3/anh) used further in the document corresponds to the theoretical one.

Table 1. Synthesis conditions and main characteristics of Al/SiO2.							
Entry	Sample nature	Sample name ^[a]	Al ₂ O ₃ [wt%]	S _{BET} [m ² g ⁻¹]	Synthesis technique	^ح [° Pretreatment	C], Synthesis
1 2 3 4 5 6 7 8 9 10	silica Al/SiO ₂ Al/SiO ₂ Al/SiO ₂ Al/SiO ₂ Al/SiO ₂ Al/SiO ₂ Al/SiO ₂ alumina	silica AS(3/anh) AS(6/anh) AS(10/anh) AS(15/anh) AS(25/anh) AS(16/1eqW) AS(17/3eqW) γ-alumina	0.0 2.8 5.7 10.3 15.0 24.8 34.9 16.1 16.7 100.0	550 505 460 430 400 330 185 420 420 235	 CLD anhydrous CLD anhydrous CLD anhydrous CLD anhydrous CLD anhydrous (× 2) CLD anhydrous (× 3) CLD anhydrous (1 equiv. H₂O) CLD anhydrous (3 equiv. H₂O) 	- 30, vacuum 30, vacuum 30, vacuum 30, vacuum 30, vacuum 30, vacuum 30, vacuum	- 110, toluene 110, toluene 110, toluene 110, toluene 110, toluene 110, toluene 110, toluene 110, toluene
[a] AS(x/y): Al/SiO ₂ with x wt% of Al ₂ O ₃ and obtained by technique y (CLD anhydrous: anh; CLD aqueous with 1 or 3 equiv. water per precursor molecule: 1eqW and 3eqW).							

(1)

Dehydration of ethanol

The derivative of the weight loss of silica, γ -alumina, and various Al/SiO₂ (prepared under anhydrous conditions) during the thermoprogrammed desorption (TPD) of adsorbed ethanol from room temperature to 400 °C shows a desorption feature at approximately 80 °C, associated with ethanol desorption from medium/strong sites, visible for all materials (Figure 2 a). Above 200 °C, ethylene desorbs from the dehydration sites.^[17,23] Dehy-

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Figure 1. Fraction of available alumina surface: theoretical *x* values (based on the composition data) versus experimental *y* values (based on of ethanol adsorption). Numbers in parentheses correspond to entries in Table 1. CLD = chemical liquid deposition.

dration occurs only on materials possessing surface aluminum species, and the amount increases with the aluminum content. The dehydration peak of Al/SiO₂ is constantly located at approximately 270 °C, except for AS(3/anh) (entry 2), the dehydration temperature of which is slightly higher (275 °C). The dehydration temperature is notably higher than that of γ -alumina (entry 10), which is indicative of a different surface.

For Al/SiO₂ prepared in the presence of water (Figure 2 b), the higher the water content during synthesis, the higher the dehydration temperature [280 °C for AS(16/3eqW), entry 9] and the lower the intensity. Compared to that of AS(16/anh) (entry 5), the dehydration peak of AS(16/3eqW) is particularly asymmetric.

For samples prepared under anhydrous conditions, high aluminum loading is associated to a higher amount of dehydrated ethanol (Table 3, column 4). Samples in entries 8 and 9, prepared by aqueous grafting, have fewer dehydration sites than the sample in entry 5. At low aluminum loading [AS(3/anh), entry 2], one fifth of the exposed atoms form a dehydration

Entry	Sample	Surface coverage of aluminum species [Eq. (1)] [%]	EtOH underg Isosurface [nm ⁻²] ^[a]	oing dehydration Per Al atom ^[b]	Fraction of EtOH dehy- drated [%] ^[c]	
1	silica	0	0.00	-	0	
2	AS(3/anh)	$\approx 5^{[d]}$	0.12	\approx 0.2	10	
3	AS(6/anh)	11	0.20	0.15	13	
4	AS(10/anh)	15	0.26	0.14	20	
5	AS(15/anh)	46	0.45	0.08	22	
6	AS(25/anh)	56	0.61	0.09	28	
7	AS(35/anh)	83	0.65	0.05	20	
8	AS(16/1eqW)	21	0.38	0.14	23	
9	AS(17/3eqW)	7	0.27	0.33	19	
10	γ-alumina	100	0.83	0.07	30	
[a] Based on the total surface area. [b] Based on the surface coverage of aluminum species. [c] Relative to total EtOH desorbed during TPD. [d] Based on the theoretical density of grafted atoms, by considering a uniform deposition.						



Figure 2. Derivative of the TPD weight loss of ethanol on Al/SiO₂-grafted samples after pretreatment at 500 °C: a) prepared by anhydrous CLD; b) prepared by various methods with similar loading (\approx 15–17% Al₂O₃). The intensities are normalized by the surface area of each sample. Numbers in parentheses correspond to entries in Table 1.

site (Table 3, column 5). At a higher aluminum loading (entries 3–7), the number of dehydration sites per exposed aluminum atoms decreases. Consistent with their small amount of exposed aluminum, AS(16/1eqW) and AS(17/3eqW) show a large number of dehydration sites per exposed atom, especially AS(17/3eqW), for which one third of the exposed aluminum atoms are associated to a dehydration site. For entries 2–6, 8 and 9, the more aluminum atoms present on the surface, the greater the percentage of adsorbed ethanol molecules that undergo dehydration (Table 3, column 6). For AS(35/

> anh) (entry 7), only 20% of the ethanol is dehydrated; thus, the number of aluminum atoms that form medium/strong adsorption sites (at which ethanol adsorbs but does not react) increases more than the number of aluminum atoms that form dehydration sites.

CO adsorption followed by IR spectroscopy

IR spectra of the OH stretching region

In Figure 3, pure silica (entry 1) shows a main band at 3745 cm⁻¹ corresponding to isolated silanols.^[24] The low-wavenumber tail between 3400 and 3700 cm⁻¹ corresponds to weakly interacting silanol groups,^[24] which is consistent with the high density of surface OH groups (3.3 OH nm⁻²). The first deposited aluminum atoms (entry 2) do not change the global shape of the spectra, except for a small bump at approxi-

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Figure 3. IR spectra of Al/SiO₂ prepared by anhydrous CLD: a) silica, b) AS(3/ anh), c) AS(6/anh), d) AS(10/anh), e) AS(15/anh), f) AS(25/anh), and g) AS(35/ anh). Numbers in parentheses correspond to entries in Table 1. For each spectrum the intensity is adapted so that all spectra can be compared.

mately 3600 cm⁻¹, which is also detected at higher loading (entry 5). A broad band of low intensity at approximately 3850 cm⁻¹, also visible for entry 4, corresponds to a torsional mode resonance of silanols.^[24] Increasing the aluminum loading (entries 3–7) causes a decrease in the tail from 3400 to 3700 cm⁻¹ and, hence, less bonding between silanol groups. At the same time, a broad band centered at approximately 3650 cm⁻¹ increases. This was observed for our Si/Al₂O₃ materials^[16] and corresponds to interacting Al–OH and Si–OH groups. The acidic hydroxy groups of ASAs could be located in this area.^[25,26] Even at high loadings, the band corresponding to isolated silanols is still visible.

Figure 4 gives the spectra for AS(16/1eqW) and AS(17/ 3eqW), which were prepared in the presence of water. The spectrum of AS(16/1eqW) (entry 8) is similar to that of entry 4 (with 10% Al₂O₃) in Figure 3, which has a similar coverage of aluminum species (Figure 1). Similarly, the spectrum of AS(17/





Figure 4. IR spectra of Al/SiO₂ prepared by various grafting techniques: a) AS(16/1eqW) and b) AS(17/3eqW). Numbers in parentheses correspond to entries in Table 1. For each spectrum the intensity is adapted so that all spectra can be compared.

3eqW) (entry 9) is close to that of entry 2 (with $3 \% \text{ Al}_2\text{O}_3$). Both samples show a small bump at approximately 3600 cm⁻¹.

IR spectra of the CO stretching region upon CO adsorption

Upon progressive dosing of CO until saturation on pure silica, the CO stretching region displays two main bands (Figure 5a). In the CO stretching region, the higher the CO stretching frequency of the OH groups, which are characterized by bands in the 2140 to 2180 cm⁻¹ region, the higher the acidity.^[27] CO adsorption first causes an increase in the band at approximately 2155 cm⁻¹. This corresponds to adsorption on weak OH groups.^[3] Further, CO adsorption yields a shoulder at approximately 2140 cm⁻¹, which corresponds to physisorption on silanols.^[3, 28-30] CO adsorption on the sample with the lowest number of grafted aluminum [AS(3/anh), entry 2] causes the appearance of a band at 2179 cm^{-1} , which corresponds to CO adsorption on strong BAS.^[3] Such high wavenumbers are usually obtained for the strong BAS of zeolites.^[31] Thus, for this sample, the BAS are the only sites that differ from the sites of pure silica. A higher aluminum loading (entries 3-7) induces the appearance of strong (2230 cm⁻¹) then weak/medium (\approx 2200 cm⁻¹) LAS.^[3,28] Their number increases with the aluminum content. At the same time, CO adsorption on the BAS increases, and CO physisorption on silanols decreases.

AS(16/1eqW) and AS(17/3eqW), prepared in the presence of water, are characterized by the presence of strong and weak/ medium LAS and BAS, even at the first doses of CO (Figure 6). The number of strong LAS on AS(16/1eqW) is particularly high. The peak corresponding to the BAS is similar in both samples. The peak corresponding to CO physisorption on silanols is better defined on AS(17/3eqW) than on AS(16/1eqW).

The integration of the peaks for CO adsorption on the strong LAS (2230 cm⁻¹) and the weak/medium LAS (2200 cm⁻¹), normalized by the weight of the pellet and the surface area of the sample, yields a comparative estimate of

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Figure 5. IR spectra of CO adsorbed on Al/SiO_2 prepared by anhydrous CLD: a) silica, b) AS(3/anh), c) AS(6/anh), d) AS(10/anh), e) AS(15/anh), f) AS(25/ anh), and g) AS(35/anh). Numbers in parentheses correspond to entries in Table 1. Full spectra are shown in Figure S1.

the number of sites. The fraction of strong LAS of the total LAS is estimated as follows [Eq. (3)]:^{16]}

Fraction of strong LAS in total LAS = $\frac{A_{\text{band stro}}}{A_{\text{band stro}}}$

$$= \frac{A_{\text{band strong LAS}}}{A_{\text{band strong LAS}} + A_{\text{weak/medium LAS}}}$$
(3)

in which A_i is the area of the CO peak of species *i*, normalized by the weight of the wafer and the surface area of the material (*i*=strong LAS: peak at 2230 cm⁻¹; weak/medium LAS: peak at 2200 cm⁻¹).



Figure 6. IR spectra of CO adsorbed on Al/SiO_2 prepared in the presence of water: a) AS(16/1eqW) and b) AS(17/3eqW). Numbers in parentheses correspond to entries in Table 1. Full spectra are shown in Figure S1.



Figure 7. Evolution of the fraction of strong Lewis acid sites (LAS) of the total number of LAS. Numbers in parentheses correspond to entries in Table 1.

Materials stemming from anhydrous synthesis show a decrease in the fraction of strong LAS as the coverage by aluminum species increases (Figure 7). Under such preparation conditions, the first LAS are strong (entries 2 and 3). At a high aluminum loading, the percentage of strong LAS remains constant and low. The percentage of strong LAS of AS(16/1eqW) is consistent with its coverage of aluminum species. Given its even lower coverage, the structure of the alumina deposit of AS(17/3eqW) differs, with a low percentage of strong LAS. Pure γ -Al₂O₃ (entry 10) shows no strong LAS.

m-Xylene isomerization

The grafting of aluminum species under anhydrous conditions first led to an increase (entries 2–6) and then to a decrease (entry 7) in the isosurface rate of *m*-xylene conversion (Table 4, column 3). AS(16/1eqW) and AS(17/3eqW) showed values consistent with their surface ratio of exposed aluminum. The rates per exposed aluminum atom (Table 4, column 4) decreased

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Table 4. Conversion of <i>m</i> -xylene over Al/SiO ₂ -grafted samples.						
Entry	Sample	Rate of <i>m</i> -xylene converted at 10 minIsosurfacePer Al atom $[\times 10^{-2} \text{ molecule h}^{-1} \text{ nm}^{-2}]^{[a]}$ $[\times 10^{-2} \text{ molecule h}^{-1}]^{[b]}$				
1	silica	2.9	-			
2	AS(3/anh)	20.7	34.5			
3	AS(6/anh)	31.2	23.6			
4	AS(10/anh)	47.1	25.0			
5	AS(15/anh)	59.1	10.3			
6	AS(25/anh)	78.9	11.2			
7	AS(35/anh)	42.2	4.1			
8	AS(16/1eqW)	43.7	16.3			
9	AS(17/3eqW)	30.8	37.4			
10	γ-alumina	7.9	0.6			
[a] Based on the total surface area. [b] Based on the surface coverage of aluminum species						

continuously with increasing surface coverage of aluminum species. The highest rate was obtained on AS(17/3eqW). During this reaction, *m*-xylene was either isomerized (I) or disproportionated to toluene and trimethylbenzenes (D). The latter can further form isomers of xylene. The ratio isomerization/disproportionation increased with the isosurface catalytic activity; AS(3/anh) displayed the lowest value (I/D = 0.49) and AS(15/anh) displayed the highest value (I/D = 0.85).

Discussion

Surface occupancy and distribution of aluminum species on silica

Anhydrous conditions during synthesis yield regular and uniform deposition of aluminum species on silica: the coverage is proportional to the surface density of the grafted species. The IR spectra of the CO stretching region also show the disappearance of silanols physisorbing CO, which is directly related to the coverage of aluminum species. Water during synthesis, even at low concentration (1 equiv. per precursor molecule), favors the polymerization of the precursor to aggregates, which causes a lower coverage of the silica surface: the higher the water concentration, the higher the degree of aggregation. These findings agree with our previous findings based on time-of-flight secondary ion mass spectrometry, NMR spectroscopy, and TEM data.^[5]

The IR spectra of the OH stretching region (Figure 3) show that grafting of the silica surface caused a disruption of H-bonding among the silanol groups. Considering a "chain" model of silanols that interact with each other,^[3] the grafting of aluminum species not only consumes silanols by condensation with the OH groups, but it also disturbs the long-distance interaction of these groups. When this occurs, the remaining silanols are, for the most part, isolated; they remain visible even at high aluminum loading, and this confirms that the coverage onto silica is not complete. New OH groups, typically found on ASAs, become visible in the OH region upon grafting of enough aluminum. Interestingly, three of the samples (entries 2, 8, and 9), which have low alumina coverage, show

bumps at approximately 3600 to 3650 $\rm cm^{-1}$ that emerge from a broader band of OH groups. These may result from the interaction of deposited aluminum with the silanols of the silica support. $^{[3,32]}$

Brønsted acid sites as active sites for ethanol dehydration and *m*-xylene isomerization

Active sites for ethanol dehydration and *m*-xylene isomerization

As probed by CO, grafting of the first aluminum species (entry 2) causes a steep increase in the number of BAS (Figure 8a). With increasing aluminum loading, the number of BAS increased more slowly.



Figure 8. Evolution of the number of a) Brønsted acid sites (BAS) and b) strong Lewis acid sites (LAS) (——) and weak or medium LAS (-----) of Al/ SiO₂, probed by CO adsorption followed by IR spectroscopy. Numbers in parentheses correspond to entries in Table 1.

For samples prepared under anhydrous conditions, the number of strong LAS first increased [particularly pronounced between entry 2 (3% Al_2O_3) and entry 3 (6% Al_2O_3)] and then decreased above 10% Al_2O_3 (Figure 8b). Up to 10% Al_2O_3 , no weak/medium LAS were visible. Although the number of strong LAS decreased, weak and medium LAS appeared and their number increased. Thus, increasing the aluminum loading caused a weakening of the LAS. Contrary to the BAS, the evolution of the number of LAS was strongly related to the structure of the deposit. Samples prepared in the presence of water

to entries in Table 1.



(-----), and the number of Brønsted acid sites (BAS), as probed by CO (+----). Numbers in parentheses correspond

on sites other than weak LAS. The evolution of the number of strong LAS, which was highest at approximately 10% Al₂O₃, did not parallel the amount of dehydrated ethanol, which was highest at approximately 25% Al₂O₃. Thus, strong LAS cannot be the exclusive sites for ethanol dehydration.

It can thus be postulated that the ethanol dehydration sites are a combination of BAS and LAS. Figure 9 gives a good correlation between the number of BAS and the amount of ethanol dehydration sites for entries 1–6, 8, and 9.

showed a high number of LAS, which were strong LAS, even at low coverage. γ -Al₂O₃ (entry 10) showed neither BAS nor strong LAS but a large number of weak LAS.

The isomerization of *m*-xylene requires BAS.^[33-37] This was confirmed by the good correlation for entries 1–6, 8, and 9 between the rate of *m*-xylene conversion and the number of BAS as a function of the coverage of aluminum species (Figure 9): the BAS of Al/SiO₂ are responsible for *m*-xylene isomerization. γ -Al₂O₃, which has no BAS, did not catalyze *m*-xylene isomerization. At high aluminum loading, AS(35/anh) (entry 7) showed discrepant results: Whereas the number of BAS probed by CO still increased, the rate of conversion of *m*-xylene decreased. The reason for this is not immediately clear.

The dehydration of ethanol can take place on both Lewis acid sites of alumina and Brønsted acid sites of Si/Al_2O_3 .^[16] AS(3/anh) (entry 2) was active in both ethanol dehydration and *m*-xylene isomerization (Figure 9), despite the absence of weak LAS and a low number of strong LAS (Figure 8 b). Conversely, the number of BAS in this sample is high, despite its low aluminum loading (Figure 8a). Although entries 2 and 3 do not have weak LAS, these materials still dehydrated ethanol (Figure 9). This showed that ethanol dehydration can be done

In another study, we showed that on Si/Al₂O₃ the temperature of the ethanol dehydration peak is associated with the nature of the active site.^[16] In the present study, all the samples prepared under anhydrous conditions showed similar ethanol dehydration temperatures (≈ 270 °C). Thus, the ethanol dehydration sites of entry 2, with BAS but almost no LAS, are the same as those of entries 3 to 6. Furthermore, the dehydration temperature was higher than that of γ -Al₂O₃ (252 °C), for which ethanol dehydration occurs on LAS.^[16] Therefore, we assume that the BAS of Al/SiO₂, detected by CO adsorption and probed by ethanol dehydration, are the active sites for *m*-xylene isomerization and that for samples 2–6 their number is probed by the amount of dehydrated ethanol.

Turnover frequency for *m*-xylene isomerization

We already showed that the BAS of ASAs dehydrate ethanol, which enabled us to estimate their number and to calculate their TOF for *m*-xylene isomerization.^[16] On the basis of the number of ethanol dehydration sites (Table 5, column 3) and by assuming that they are exclusively BAS, the TOF of BAS in s^{-1} site⁻¹ was calculated as follows [Eq. (4)]:

Table 5	Table 5. Density of m-xylene conversion sites and ethanol conversion sites over Al/SiO2-grafted samples.							
Entry	Sample	EtOH dehyd. sites	TOF BAS			Fraction of BAS	Surface coverage	
		[nm ⁻²]	[×10 ⁻⁴ s ⁻¹ site ⁻¹]	[nm ⁻²] ^[a]	atom $[\times 10^{-2}]^{[b]}$	atom $[\times 10^{-2}]^{[b]}$	sites [%] ^[c]	[%]
2	AS(3/anh)	0.12	4.7	0.14	22.5	1.1	≈100	≈5
3	AS(6/anh)	0.20	4.4	0.20	15.4	1.8	\approx 100	11
4	AS(10/anh)	0.26	5.0	0.31	16.3	2.9	\approx 100	15
5	AS(15/anh)	0.45	3.6	0.39	6.7	5.7	\approx 100	46
6	AS(25/anh)	0.61	3.7	0.52	7.3	9.4	\approx 100	56
7	AS(35/anh)	0.50	-	0.28	2.7	12.8	55 ^[d]	83
8	AS(16/1eqW)	0.38	-	0.29	10.7	2.9	76 ^[e]	21
9	AS(17/3eqW)	0.27	-	0.20	24.5	1.7	73 ^[e]	7

[a] Calculated on the basis of an average TOF value of $4.25 \times 10^{-4} \text{ s}^{-1} \text{ site}^{-1}$ obtained on samples 2–6 for *m*-xylene conversion. Values were obtained by assuming that all the EtOH dehydration sites of these materials are BAS [Eq. (4)]. [b] Calculated on the basis of the surface coverage of aluminum species. [c] Calculated by dividing the number of BAS by the total number of dehydration sites. [d] < 100 as a result of accessibility: a higher number of sites is accessible to EtOH than to *m*-xylene. [e] < 100 as a result of the composite nature of the EtOH dehydration sites.

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 $TOF \ \left[s^{-1} \ site^{-1}\right]$

$$= \frac{\text{rate of } m\text{-xylene converted at 10 min}}{\text{EtOH dehydration sites}} \times \frac{1}{3600}$$
(4)

in which the rate is in $[molecule h^{-1} nm^{-2}]$.

Entries 2 to 6, that is, materials showing consistent results between the number of BAS probed by CO, the amount of dehydrated ethanol, and the rate of conversion of *m*-xylene (Figure 9), and having similar ethanol dehydration temperatures (Figure 2a), yielded comparable TOFs (Table 5, column 4), the average of which $(4.3 \times 10^{-4} \text{ s}^{-1} \text{ per BAS})$ is approximately 75 times lower than that obtained for a USY zeolite without extra-framework aluminum (CBV720 from Zeolyst): 3.1× 10^{-2} s^{-1} per BAS.^[16] Assuming that all the Al/SiO₂ materials have the same TOF, this average value enabled the calculation of the number of BAS (Table 5, column 5). The number of BAS in entries 2 to 6 is the same as the number of ethanol dehydration sites. For entries 7 to 9, the number of dehydration sites is higher than the number of BAS. A non-negligible percentage (24 to 45%; Table 5, column 8) of the ethanol dehydration sites of these materials is not active in *m*-xylene isomerization (see below).

On AS(35/anh) (entry 7), this difference might be due to the accessibility of the reactant molecules to the active sites: Figure 9 shows that although CO probes a higher number of BAS if the alumina loading was increased from 25 (entry 6) to 35% Al₂O₃ (entry 7), ethanol dehydration and *m*-xylene isomerization indicate an opposite trend. The adsorption of 2,6-lutidine, with a similar size to that of *m*-xylene, followed by IR spectroscopy, also showed a decrease in the number of BAS if the alumina loading was increased from entry 6 to entry 7 (Supporting Information, Figures S2 and S3).

AS(16/1eqW) (entry 8) and AS(17/3eqW) (entry 9) both showed a higher ethanol dehydration temperature than the materials prepared under anhydrous conditions as well as asymmetric ethanol dehydration peaks. This indicates that the active sites for ethanol dehydration are different to those of entries 2 to 7. We assume that these samples have additional sites, other than BAS, that dehydrate ethanol and contribute to a composite ethanol peak resulting from their combined effects. These sites might be LAS, which are more numerous on water-prepared samples than on the other samples (Figure 8b). Nonetheless, BAS are major active sites and represent between 73 and 76% of the dehydrated ethanol.

Table 5, columns 6 and 7 give the density of BAS per surface aluminum and silicon atoms. If the surface density of aluminum species increases, the density of silicon atoms decreases; thus, the number of BAS per surface silicon increases. Given that the number of surface aluminum species increases faster than the number of BAS, the number of BAS per surface aluminum decreases. At low aluminum loading [AS(3/anh)], one out of five aluminum atoms is related to a BAS.

There is a strong correlation, even for samples with dissimilar surface structures (entries 1–6, 8, and 9), between the number of BAS, probed by different means, and the coverage by aluminum species (Figure 9 and Table 5). Conversely, despite a similar coverage, the number of LAS is higher on materials with alumina clusters (entries 8 and 9) than on materials with well-dispersed aluminum species (entries 3 and 4) (Figure 8b). Thus, BAS are associated with well-dispersed aluminum species, whereas clusters favor the presence of LAS.

Comparison with Si/Al₂O₃ grafting and zeolite

Table 6 gives a comparison between the main features of Al/ SiO_2 and Si/Al_2O_3 from our previous study and those of a H-USY zeolite that is free of extra-framework aluminum (EFAL) species. $^{\rm [16]}$ In both Si/Al_2O_3 and Al/SiO_2, the number of BAS decreases at high loading of grafted species, but for different reasons: On Si/Al₂O₃, new species are grafted on top of the BAS at the highest loadings, whereas on Al/SiO₂, the accessibility of large molecules, such as *m*-xylene, to the BAS might be difficult if the alumina deposit is too thick. The number of BAS per nm² is generally higher on Al/SiO₂ than on Si/Al₂O₃, but these sites are less active: the TOF for *m*-xylene isomerization is 3.3 times lower than that on Si/Al_2O_3 and 75 times lower than that on a USY zeolite without EFAL. This is also reflected by the average ethanol dehydration temperature (269 °C), which is higher than that of the BAS of Si/Al₂O₃ (248°C) and much higher than that of the zeolite (211 °C). The dehydration peak is also broader on Al/SiO₂, which suggests a larger spread in local structure. On γ -alumina, the LAS on the (100) surface are responsible for the large number of ethanol dehydration sites. Calculation of the rates of *m*-xylene conversion per unit of surface stresses the impact of the high surface area of zeolites:

Table 6. Main catalytic properties of Al/SiO ₂ and Si/Al ₂ O ₃ materials prepared under anhydrous conditions and H-USY without (w/o) extra-framework aluminum (EFAL).							
	Al/SiO ₂	$Si/Al_2O_3^{[16]}$	H-USY w/o EFAL (CBV720) ^[16]				
Evolution of the number of BAS upon grafting guest species under mild conditions	increases	goes through a max.	_				
Max. number of BAS [nm ⁻²]	0.52	0.18	0.18				
Sample name	AS(25/anh)	SA(17/4eqW)					
Max. number of EtOH dehyd. sites [nm ⁻²]	0.61	0.83	0.18				
Sample name	AS(25/anh)	pure γ-alumina					
TOF for <i>m</i> -xylene isomerization [s ⁻¹ active site ⁻¹]	4.3×10^{-4}	1.4×10 ⁻³	3.1×10 ⁻²				
Max. rate of <i>m</i> -xylene converted at 10 min [mmol $h^{-1}g_{cat}^{-1}$]	43	29	2640				
Sample name	AS(25/anh)	SA(17/4eqW)					
Average EtOH dehyd. temperature (if exclusively catalyzed by BAS) [°C]	269	248	211				

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The isoweight rate of the USY zeolite is 61 and 91 times higher than that on AI/SiO_2 and Si/AI_2O_3 , respectively.

Conclusions

Controlled deposition of aluminum species on silica occurred under anhydrous conditions and created Brønsted acid sites, the number of which increased with the aluminum loading. Ethanol dehydration followed by thermogravimetry, combined with IR spectroscopy after CO adsorption, yielded the number of Brønsted acid sites and the TOF of these sites for *m*-xylene isomerization: $4.3 \times 10^{-4} \text{ s}^{-1}$ site⁻¹. This value is 3.3 times lower than that of Si/Al₂O₃ and 75 times lower than that of a USY zeolite without extra-framework aluminum. This confirms that the nature of the Brønsted acid sites strongly depends on the method of ASA synthesis. Strong Lewis acid sites also appeared during grafting; they became weaker as the concentration of the guest species was increased. Under aqueous conditions, grafting was less controlled and alumina agglomerates possessing weak and medium Lewis acid sites but no Brønsted acidity were formed.

Experimental Section

For IR spectroscopy studies, samples were pressed into pellets and pretreated in situ under vacuum (10^{-5} mbar) for 10 h at 450 °C (heating rate of 5 °C min⁻¹) including a plateau at 150 °C for 1 h. Samples were then cooled down at liquid-nitrogen temperature and increasing amounts of CO, up to a total amount of 600 µmol, were admitted into the chamber. Spectra were recorded after each dose of CO, by a Nexus Fourier transform apparatus (resolution 4 cm⁻¹).

Adsorption and desorption of ethanol, followed by thermogravimetry, were performed in a similar manner as the method described by Kwak et al.^[17] and previously used for our Si/Al₂O₃ materials.^[16] Samples were first activated under a flow of helium at 500 °C for 2 h. After cooling to room temperature, helium was passed through a saturator of ethanol for approximately 30 min. Ethanol molecules on weak adsorption sites were then evacuated by purging with helium at room temperature for 1 h. Strongly adsorbed molecules were desorbed during the thermoprogrammed desorption of ethanol (TPD), from room temperature to 400 °C, at a heating rate of 10 °C min⁻¹. The intensity of the two main desorption features (ethanol and ethylene) was measured by calculating the first derivative of the weight loss during TPD with respect to temperature. The amount of dehydrated ethanol was calculated as follows [Eq. (5)]:

= ethanol retained after purge
$$\times \frac{A_{\text{peakethylene}}}{A_{\text{peakethylene}} + A_{\text{peakethanol}}}$$
 (5)

in which $A_{\text{peak }i}$ is the area of the peak corresponding to the desorption of species i upon calculating the derivative of the weight loss of ethanol during TPD.

The *m*-xylene isomerization test was performed by passing gaseous *m*-xylene (0.6 cm³ h⁻¹) through a bed of catalyst (0.5 g) at 350 °C. The catalyst had been preheated in an air flow at 350 °C. Analysis of the products was performed by online gas chromatography by means of a Hewlett Packard 6850 apparatus, equipped

with a flame ionization detector (FID) and an FFAP column. The calculation of the rate of conversion was based on the conversion of *m*-xylene into its products (*o*- and *p*-xylene, toluene, and trimethylbenzenes) after 10 min on-stream [Eq. (6)]:

Rate [molecule
$$h^{-1} nm^{-2}$$
]

$$= \left[\sum_{i}^{\text{species}} \frac{A_{i}}{N_{\text{C_atoms_i}}} / \left(\sum_{i}^{\text{species}} \frac{A_{i}}{N_{\text{C_atoms_i}}} + \frac{A_{m-xylene}}{8}\right)\right] \quad (6)$$
$$\times \frac{\text{flowrate} \times \text{density}_{m-xylene}}{M_{m-xylene} \times m_{\text{catalyst}}} \times \frac{N_{\text{A}}}{S_{\text{BET}}}$$

in which A_i is the area of the GC peak of species *i* (*i*=toluene, *p*-xylene, *o*-xylene, trimethylbenzenes), flow rate is in [cm³ h⁻¹], N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$), and S_{BET} [nm⁻² g⁻¹] is the surface area of the catalyst.

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Keywords: acidity · coverage degree · ethanol · silicates · thermogravimetry

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