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Quantification of Brønsted Acid Sites of Grafted Amorphous Silica–Alumina Compounds and their Turnover Frequency in *m*-Xylene Isomerization

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The number and types of acid sites and the catalytic activity of amorphous silica–alumina, obtained by grafting silicon species to the surface of γ -alumina, varies with the synthesis conditions and the amount of grafted silicon. IR spectroscopy of the OH region proves that deposition occurs selectively, first on the (100) and then on the (110) facets. Grafting onto the (100) surface lowers the number of active sites in ethanol dehydration. Grafting onto the (110) surface yields Brønsted acid sites that are active in the dehydration of ethanol and that catalyze the isomerization of *m*-xylene. Strong Lewis acid sites, or

"defect sites", as detected by CO adsorption, also appear, although they are absent on the parent alumina. The stoichiometric dehydration of ethanol on Brønsted sites, monitored by using thermogravimetric analysis, enables the calculation of the turnover frequency of these sites in *m*-xylene isomerization $(1.4 \times 10^{-3} \text{ s}^{-1} \text{ site}^{-1} \text{ at } 350 \,^{\circ}\text{C}$, atmospheric pressure, 0.6 cm³ h⁻¹ of *m*-xylene, and 0.5 g of catalyst). This number is 22 times lower than on a USY zeolite without extraframework aluminum.

Introduction

Alumina and amorphous aluminosilicates (ASA) are often used as catalysts and catalyst supports for metals and alloys of Co, Ce, Au, Ni, Pt, and Pd, as well as for oxides and sulfides.^[1] They are active because of their acid/base properties. Brønsted acidity of ASAs hydroxyl groups results from the presence of both silicon and aluminum atoms in an oxide matrix. The characterization of the repartition and the detailed structure of the silicon and aluminum species in amorphous aluminosilicates is challenging, because these materials are usually obtained by different methods, leading to very dissimilar structures.^[2] These structures may have acid sites with a very different architecture. Nonetheless, the question as to the exact structure of the active site is of primary importance if we are to understand the relationship among surface chemistry, acidity, and catalytic activity.

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Because of their moderate acidity and mesoporosity, ASAs are tailored for the conversion of large hydrocarbon molecules to middle distillates during the oil-refining process. Moreover, numerous articles also report the use and characterization of alumina for catalytic reactions such as alcohol dehydration.^[3-5] Kwak et al. showed that the (100) surface of γ -alumina catalyzes the dehydration of ethanol to ethylene.^[4] Upon thermogravimetric analysis (TGA) after ethanol adsorption on the surface of alumina, they found that the active sites are either AI(VI)-OH groups (Brønsted acid sites, BAS) or coordinatively unsaturated AI(V) (Lewis acid sites, LAS) belonging to the (100) surface. The dehydration temperature depends on the type of site involved. Roy et al. applied the same technique to ethanol and other alcohols and compared the results to DFT calculations.^[5] They found no evidence that BAS are involved in alcohol dehydration, which they proposed to be exclusively catalyzed by LAS. The nature of the alcohol determines the temperature of dehydration. The BAS specific for zeolites also catalyze the dehydration of ethanol.^[6]

IR spectroscopy enables the differentiation of the different OH groups (stretching region, $\approx 3000 \text{ cm}^{-1}$ to 4000 cm^{-1}) that make up the surface of alumina, silica, and aluminosilicates.^[7-15] Based on DFT calculations, Digne et al. assigned the typical IR bands in the OH stretching region of γ -alumina.^[11] This model improves the previous assignment by Knözinger et al.^[16]

The adsorption of probe molecules, especially CO, monitored by using IR spectroscopy, reveals the nature and strength of the acidic sites (BAS, weak and strong LAS) of aluminas and ASAs^[12,17,18] based on the CO stretching frequency.

We developed a series of aluminosilicates by grafting.^[19] The materials, with a considerable variation in the Si/Al ratio and

surface structure, were synthesized by the deposition of Si(OEt)₄ (TEOS) on γ -alumina and Al(OiPr)₃ on silica. ²⁷Al and ²⁹Si NMR, time-of-flight secondary ion mass spectrometry (ToF–SIMS), and TEM results indicate that the type of deposit on the oxide support depends strongly on the temperature of grafting and the water content of the reaction mixture.

The present study determines the acidity of γ -alumina, silica, and Si/Al₂O₃ compounds. Assessment of their catalytic performance was achieved based on the isomerization of *m*-xylene to o- and p-xylene, catalyzed by acid solids such as ASAs and zeolites.^[20,21] BAS catalyze the isomerization from m- to o- and p-xylene through formation of a benzenium ion intermediate.^[20] IR spectroscopy measurements were performed before and after CO adsorption to monitor the development of BAS and LAS. Ethanol adsorption and TGA were employed to assess the nature and the number of sites that are active for dehydration. The comparison between the dehydration temperature and the IR spectra of the OH stretching region for Si/ Al₂O₃ samples, prepared under various conditions, reveals the selective grafting of silicon species onto surfaces (100) and (110) of alumina, and their relationship to the formation of LAS and BAS. BAS are active in both *m*-xylene isomerization and ethanol dehydration. As the amount of BAS is quantified, we were uniquely able to determine the turnover frequency (TOF) in *m*-xylene isomerization over BAS.

Results

The main characteristics of the materials used in this study and their synthesis conditions are given in Table 1. The temperature of grafting, the water content, and the amount of the alkoxide precursor were adapted to obtain materials displaying a wide range of compositions and surface structures, as described in Ref. [19]. In the following, deep blue labels correspond to alumina, silica, and materials prepared by chemical liquid deposition (CLD) in anhydrous conditions (entries 2–4), cyan labels correspond to materials prepared by CLD in aqueous conditions (entries 5 and 6), orange labels correspond to materials prepared by chemical sprepared by chemical sprepared by chemical sprepared by CVD at 250 °C, and red labels correspond to materials prepared by CVD at 400 °C.



Figure 1. Weight evolution during a TGA experiment (example: γ -alumina pretreated at 500 °C).

Preferential adsorption of ethanol on alumina surfaces

Ethanol adsorption on γ -alumina and silica

Figure 1 gives an example of the weight evolution of γ -alumina (entry 1 in Table 1) during a TGA experiment with pretreatment at 500 °C. Weight loss during pretreatment is ascribed to



Figure 2. Derivative of the TPD weight loss of ethanol on silica and alumina after pretreatment at 200 $^{\circ}$ C and 500 $^{\circ}$ C. Numbers in brackets correspond to entries in Table 1.

Table 1. Synthesis conditions and main characteristics of Si/Al ₂ O ₃ . ^[19]									
Entry	Sample	Sample ^[a]	SiO ₂	S _{BET}	Synthesis	Conditions (T [°C])			
	nature	name	[wt%]	[m²g ⁻ ']	technique	Pretreatment	Synthesis		
1	alumina	γ-alumina	0.0	235	_	_	-		
2	Si/Al ₂ O ₃	SA(7/anh)	7.3	200	CLD anhydrous	40, vacuum	110, toluene		
3		SA(12/anh)	12.2	180	CLD anhydrous (×2)	40, vacuum	110, toluene		
4		SA(17/anh)	17.1	160	CLD anhydrous (×3)	40, vacuum	110, toluene		
5		SA(17/4eqW)	16.5	175	CLD aqueous (4 equiv. H ₂ O)	40, vacuum	110, toluene		
6		SA(17/12eqW)	16.6	175	CLD aqueous (12 equiv. H ₂ O)	40, vacuum	110, toluene		
7		SA(17/CVD250)	17.2	165	CVD	250, air flow	250, air		
8		SA(19/CVD250)	19.4	165	CVD	250, air flow	250, air		
9		SA(17/CVD400)	16.5	170	CVD	250, N_2 flow	400, N ₂		
10		SA(28/CVD400)	28.0	125	CVD	250, N_2 flow	400, N ₂		
11	silica	silica	100.0	550	-	-	-		
[a] SA(X/Y) represents Si/Al ₂ O ₃ with X wt.% of SiO ₂ obtained by technique Y (CLD anhydrous: anh; CLD aqueous with 4 or 12 equiv. of water per precursor molecule: 4eqW and 12eqW, respectively; CVD at 250 °C or 400 °C: CVD250 and CVD400, respectively).									

both dehydration and dehydroxylation of the alumina surface. The uptake of ethanol is characterized by a steep increase in weight until saturation of the surface. The room-temperature purge results in weight loss because of desorption of the weakly bonded ethanol. The TPD is marked by a two-stage weight loss; at the end of the TPD, the weight of the sample is the same as that after pretreatment. Figure 2 gives the derivative of the weight loss of alumina and

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silica (entries 1 and 11 in Table 1, respectively) during TPD, after pretreatment at 200 °C and 500 °C. Both samples exhibit a first weight loss, between 30 °C and approximately 150 °C, at approximately 80 °C, which corresponds to desorption of medium strong bound ethanol.^[4] The second main desorption feature, only visible for alumina, relates to the formation and de-

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> Table 2. Surface density of adsorbed ethanol at different stages of TPD depending on the pretreatment conditions on pure alumina and silica.

Pretreatment temperature Total ^[a]		[a]	A On weak	mount of sites ^[b]	On dehydration sites ^[d]			
[°C]	Alumina	Silica	Alumina	Silica	Alumina	Silica	Alumina	Silica
200 500	3.5 3.8	3.2 3.0	1.2 1.0	1.3 1.7	1.8 2.0	1.9 1.3	0.5 0.8	0.0 0.0
[a] = [b] + [c] + [d]								

sorption of ethylene. The desorption temperature decreases when the pretreatment temperature increases, which is consistent with previous observations.^[4] Pretreatment at 500 °C leads to a larger amount of desorbed ethanol. Silica pretreated at 200 °C exhibits a larger amount of desorbed ethanol than at 500 °C pretreatment, in agreement with a high-temperature weight loss corresponding to dehydroxylation.

Table 2 gives the amounts of adsorbed and desorbed ethanol (per surface unit) at different stages of the TGA experiment on pure alumina and silica. According to the proposal of Golay et al.,^[22] the adsorption sites of ethanol fall into three categories:

- 1) Weak adsorption sites: ethanol desorbs at room temperature. Ethanol desorbs from these sites during purge;
- Medium strong adsorption sites: ethanol desorbs below 200°C;
- 3) Dehydration sites: ethanol remains adsorbed and is dehydrated to ethylene at a temperature above 200 °C. These sites are found on alumina, but not on silica.

The total amount of adsorbed ethanol on alumina is significantly higher than on silica. The high-temperature treatment on silica decreases the total amount of adsorbed ethanol and weakens its adsorption sites. Conversely, the high-temperature treatment on alumina increases the total amount of adsorbed ethanol and increases the amount of medium strong adsorption sites and dehydration sites.

Fraction of the alumina surface covered by silicon species on $\text{Si}/\text{Al}_2\text{O}_3$

Table 3 gives the amount of ethanol retained, that is, still adsorbed on the surface after the purge on various Si/Al_2O_3 after pretreatment at 500 °C. All the Si/Al_2O_3 samples retained a smaller amount of ethanol than pure alumina (entry 1). Values for SA(17/CVD250), SA(17/4eqW), and SA(17/CVD400) are close to that of SA(17/anh). Despite its high silica loading, the level of ethanol adsorption of SA(17/12eqW) is similar to that of SA(12/anh) with less silicon. The amount of ethanol left on SA(28/CVD400) is comparable to that on silica. Ethanol adsorption values in Table 3 confirm the results in Table 2, revealing the preferential adsorption of ethanol on alumina surfaces. Deposited silica lowers the number of ethanol adsorption sites.

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Table 3. Surface density of ethanol retained after purge following pretreatment at 500 $^\circ\text{C}.$

Entry	Sample	EtOH retained after purge [nm ⁻²]
1	γ-alumina	2.8
2	SA(7/anh)	2.4
3	SA(12/anh)	2.2
4	SA(17/anh)	1.7
5	SA(17/4eqW)	1.8
6	SA(17/12eqW)	2.2
7	SA(17/CVD250)	1.6
9	SA(17/CVD400)	1.8
10	SA(28/CVD400)	1.3
11	silica	1.3

From the values in Table 3, it is possible to estimate the ratio of exposed surface aluminum species by comparing the amount of ethanol retained after the purge of each sample to the minimum and maximum values obtained on pure silica (1.3 EtOH nm⁻²) and pure alumina (2.8 EtOH nm⁻²), respectively:

Experimental density of surface AI atoms [%] =

$$\frac{\text{amount of adsorbed ethanol } [nm^{-2}] - 1.3}{2.8 - 1.3} \times 100$$
(1)

The amount of deposited silicon atoms on Si/Al₂O₃ [Sinm⁻²] allows the calculation of the theoretical density of exposed surface aluminum atoms [Equation (2)]. On γ -alumina, this value is estimated to be between 9.3 Al nm⁻² and 14.5 Al nm⁻².^[16,23]

Theoretical density of surface AI atoms
$$[\%] = \frac{\text{density of AI atoms on alumina} - \text{density of grafted Si}}{\text{density of AI atoms on alumina}} \times 100$$
(2)

Equations (1) and (2) are valid, because the number of sites formed by Si deposition that are active for EtOH dehydration and *m*-xylene isomerization is at most 5% of the exposed Al atoms; for exposed Si atoms the value is only half of that.

Figure 3 gives the plot of the relative amount of adsorbed ethanol [%] after purge at room temperature in [Eq. (1)], reflecting the experimental surface density of aluminum atoms (Y-axis) versus the theoretical density [Eq. (2)] (X-axis). When the theoretical density of surface aluminum atoms equals the experimental density (dashed line), each deposited silicon



Figure 3. Fraction of the alumina surface accessible to ethanol adsorption and retained after purging: theoretical *X* values (based on the composition data) versus experimental *Y* values (based on ethanol adsorption). Numbers in brackets correspond to entries in Table 1.

atom covers one aluminum atom of alumina. Si/Al₂O₃ samples prepared under anhydrous conditions (Table 3, entries 2–4) show this behavior. The results for SA(17/4eqW) (entry 5) are similar to those of SA(17/anh) (entry 4). The deposition of silicon species by chemical vapor deposition (SA(17/CVD400), entry 9 and SA(17/CVD250), entry 7) is less regular but remains close to the ideal line. Owing to the large excess of water during deposition, the silicon species form aggregates on SA(17/12eqW) (entry 6), maintaining a large fraction of accessible alumina. The surface of SA(28/CVD400) (entry 10) has the same number of available adsorption sites as silica (entry 11). This corresponds to a complete coverage of the alumina surface by silicon species.

Dehydration of ethanol

Figure 4a gives the derivative of the weight loss during TPD on alumina and on Si/Al₂O₃ prepared under anhydrous conditions. All the samples have similar ethanol desorption features at approximately 80 °C and dissimilar ethanol dehydration peaks between 200 °C and 280 °C. At silica loadings below 12% (SA(7/anh) and SA(12/anh), Table 1, entries 2 and 3), the intensity of the ethanol dehydration peak is lower and is shifted towards a higher temperature compared to that of pure alumina (entry 1). At higher loadings (17% SiO₂: SA(17/anh), entry 4) the intensity of the dehydration peak intensity is lower and has shifted back towards a lower temperature.

Figure 4 b gives the results for samples prepared by CVD and by CLD in the presence of water. SA(17/4eqW) (Table 1, entry 5) and SA(17/CVD250) (entry 7) exhibit similar ethanol dehydration peaks (both the intensity and temperature) as that of SA(17/anh). Conversely, SA(17/12eqW) (entry 6) and SA(17/CVD400) (entry 9) exhibit higher intensities than SA(17/ anh) but still significantly lower ones than for alumina. The position of the ethanol dehydration peak of SA(17/CVD400) is very similar to that of pure alumina (≈ 250 °C) whereas that of SA(17/12eqW) has shifted (Table 4).

Table 4 gives the amount of dehydrated ethanol. For the Si/Al₂O₃ samples prepared in anhydrous conditions, in the presence of four water equivalents per TEOS molecule and by CVD at 250°C (entries 1-7), a decrease in the amount of ethanol that undergoes dehydration is observed when the free alumina surface decreases. SA(17/CVD400) is an exception: although its alumina surface is mainly covered by silicon species, it dehydrates a large amount of ethanol per surface unit. 15% of the ethanol remaining after the purge undergoes dehydration, which, though 50% less than on pure alumina, is a significantly more than that on the other Si/Al₂O₃ compounds. Entries 1-7 first show a decrease (entries 1-3 and 6) and then an increase (entries 4, 5, and 7) in the amount of dehydrated ethanol per exposed aluminum atom when the free alumina surface decreases. SA(17/CVD400) clearly follows a different trend than the other Si/Al₂O₃.

m-Xylene isomerization

Table 5 gives the rates of *m*-xylene isomerization per gram of catalyst and per surface area of alumina, silica, and Si/Al_2O_3 ,



Figure 4. Derivative of TPD weight loss of ethanol on Si/Al₂O₃ grafted samples after pretreatment at 500 °C: a) prepared by anhydrous CLD; b) prepared by various methods (\approx 17% SiO₂). The intensities are normalized by the surface area of each sample. Numbers in brackets correspond to entries in Table 1.

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Table 4. Ethanol dehydration over Si/Al_2O_3 grafted samples as function of the percentage of free aluminum species.

Entry	Sample	Free alumina surface [%] ^[a]	EtOH unde Isosurface [nm ⁻²] ^[b]	rgoing dehydration Per exposed Al atom [×10 ⁻²] ^[c]	Fraction of EtOH dehydrated [%] ^[d]	Position of EtOH dehyd. peak [°C]
1	γ-alumina	100	0.83	7	30	252
2	SA(7/anh)	70	0.27	3	11	262
3	SA(12/anh)	57	0.23	3	11	270
4	SA(17/anh)	29	0.17	5	10	249
5	SA(17/4eqW)	34	0.20	5	11	246
6	SA(17/12eqW)	61	0.22	3	10	256
7	SA(17/CVD250)	17	0.16	7	10	250
9	SA(17/CVD400)	35	0.27	6	15	250
11	silica	0	0.00	-	0	-

[a] Calculated by using [Eq. (2)]. [b] Based on the total surface area. [c] Based on the fraction of alumina not covered by silicon species. [d] Relative to total EtOH desorbed during TPD.

Table 5. Conversion of *m*-xylene over Si/Al₂O₃ grafted samples and wavenumber in the CO region corresponding to the first CO adsorption on OH groups.

Entry	Sample	Rate o Isoweight ^[a]	f <i>m</i> -xylene co lsosurface ^[b]	nverted at 10 min Per exposed Al atom ^[c]	First-pulse wavenumber of CO band $[cm^{-1}]^{[d]}$
1	γ-alumina	3	7.9	0.6	2162
2	SA(7/anh)	7	21.8	2.5	2170
3	SA(12/anh)	16	54.0	7.6	2172
4	SA(17/anh)	25	94.1	26.5	2173
5	SA(17/4eqW)	29	98.3	22.9	2175
6	SA(17/12eqW)	16	55.4	7.3	2173
7	SA(17/CVD250)	22	78.1	36.4	2175
8	SA(19/CVD250)	17	64.2	23.2	2171
9	SA(17/CVD400)	7	24.9	5.6	2166
11	silica	3	2.9	-	2156
[a] ln	$[\times 10^{-2} mmol h^{-1}]$	g _{cat} ⁻¹]. [b] ln	[×10 ⁻² mole	cule h ⁻¹ nm ⁻²], based o	on the total surface area. [c] In [×

 10^{-2} molecule h⁻¹], based on the fraction of alumina not covered by silicon species. [d] Upon CO adsorption on OH groups.

and per exposed aluminum atom. All the catalysts deactivate over time; hence, the conversion data in Table 5 were obtained after only 10 min in *m*-xylene stream. Entries 1–7 first show an increase and then a decrease in the rate of *m*-xylene conversion when the fraction of free alumina surface decreases. The highest rates are reached when approximately 30% of the alumina surface is still uncovered. Once again, SA(17/CVD400) (entry 9) does not follow the same trend and exhibits a rate of conversion four times lower than expected for such coverage of the alumina surface. Data normalized by the density of the exposed aluminum atoms follow the same trend as the isoweight and isosurface data.

IR spectroscopy

IR spectra of the OH stretching region

Figure 5 gives the OH stretching vibrations between 3200 cm⁻¹ and 4000 cm⁻¹ of alumina and Si/Al₂O₃ prepared under anhydrous conditions. Entry 1 (γ -alumina, Table 1) has five main contributions. The assignment of the peaks to local Al–OH

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structures is based on the computational study by Digne et al., as shown in the figure.[11] The 3590 cm^{-1} and the 3770 cm^{-1} bands correspond to the Al-OH groups on the (100) surface of alumina. The 3671 cm⁻¹ and the 3730 cm⁻¹ peaks as well as the 3793 cm⁻¹ shoulder are Al–OH groups on the (110) surface. The deposition of the first silicon atoms on SA(7/anh) causes the 3770 cm⁻¹ band to disappear and the attenuation of the $3590-3600 \text{ cm}^{-1}$, the 3670- 3680 cm^{-1} , and the 3790-3793 cm⁻¹ bands. The 3730 cm⁻¹ band remains, and a new band at 3740 cm⁻¹, corresponding to isolated silanol, appears.^[9] The only remaining feature of alumina on SA(12/anh) is the attenuated 3730 cm⁻¹ shoulder. A broad absorption band becomes at visible approximately 3600 cm⁻¹. This band is often visible on silicated aluminas and other ASAs and sometimes ascribed to Al-OH groups, rendered inaccessible to probe molecules owing to the deposition of silicon species, and to Si-OH and Al-OH groups interacting with each other and with water.^[8, 10, 12, 13] A computational study by Leydier et al.[15] indi-

cates the presence of pseudo-bridging silanols (PBS, that is, silanol groups bridging aluminum atoms under certain conditions) and other H-bonded groups between 3600 cm^{-1} and 3700 cm^{-1} . Zaki et al. also locate the origin of the acidity of ASAs in the broad band at approximately 3600 cm^{-1} .⁽⁷⁾ On SA(17/anh) there are no longer any visible OH groups of alumina; apart from the isolated silanols, the main feature is the broad band at 3600 cm^{-1} .

Figure 6 gives the IR spectra of Si/Al₂O₃ (\approx 17% SiO₂) prepared under various conditions. The spectrum of SA(17/4eqW) (Table 1, entry 5) is similar to that of SA(17/anh) (entry 4) and only shows the peak corresponding to isolated silanols (3745 cm⁻¹) and a broad band at approximately 3600 cm⁻¹; there is no visible characteristic signal of the pure alumina surfaces. The spectrum of SA(17/12eqW) (entry 6) is dominated by the peak of the silanol groups. The peaks at 3681 cm⁻¹, 3730 cm⁻¹, and 3795 cm⁻¹ are still visible and are the last remaining features of the (110) surface of alumina. The spectrum of SA(17/CVD250) (entry 7) is close to that of SA(17/anh) and SA(17/4eqW) except for the lower intensity of the broad band at 3600 cm⁻¹. Among the Si/Al₂O₃, SA(17/CVD400) is the only



Figure 5. IR spectra (OH region) of Si/Al₂O₃ prepared by anhydrous CLD: a) γ -alumina; b) SA(7/anh); c) SA(12/anh); d) SA(17/anh). Top: ascriptions of the vibrational stretching frequencies of Al–OH and Si–OH groups.^[9,11] Numbers in brackets correspond to entries in Table 1; (100) or (110): surfaces of γ -alumina. For each spectrum the intensity is adapted so all spectra can be compared.

material with a remaining peak at 3771 cm^{-1} , characteristic of the (100) surface of alumina. Peaks at 3672 cm^{-1} and 3795 cm^{-1} are also visible; the 3730 cm^{-1} band has disappeared and the silanol peak is visible. It is not clear whether the broad signal at approximately 3600 cm^{-1} is a remaining band of the alumina support or the OH signal similar to those for materials in entries 3–5 and 7.

IR spectra of the CO stretching region upon CO adsorption

Figure 7 gives the characteristic CO stretching region after stepwise dosing of CO and saturation on alumina and Si/Al₂O₃. On pure alumina (Table 1, entry 1), two peaks are visible. One, located between 2175 cm⁻¹ and 2215 cm⁻¹, is redshifted with increasing CO dosing; it corresponds to CO adsorption on medium-strength LAS.^[12,24] Digne et al.^[11] and Zecchina et al.^[24] agree on the tetrahedral coordination of the aluminum atoms of these sites. The progressive shift of the peak (2209 cm⁻¹ \rightarrow





Figure 6. IR spectra (OH region) of Si/Al₂O₃ prepared by various grafting techniques: a) γ -alumina; b) SA(17/anh); c) SA(17/4eqW); d) SA(17/12eqW); e) SA(17/CVD250); f) SA(17/CVD400). Top: ascriptions of vibrational stretching frequencies of Al–OH and Si–OH groups.^[9,11] Numbers in brackets correspond to entries in Table 1; (100) or (110): surfaces of γ -alumina. For each spectrum the intensity is adapted so all spectra can be compared.

2182 cm⁻¹) is associated with the adsorption on sites of lower strength.^[24] The other peak, at approximately 2160 cm⁻¹, ranks second in the order of CO adsorption and is ascribed to weaker LAS formed by octahedrally^[24] or pentacoordinated^[11] aluminum atoms, to low-acidic OH groups,^[12,25] or to hydrogen bonding to Al–OH groups.^[7] Adsorption of CO on pure silica



Figure 7. IR spectra (CO region) at increasing doses of CO adsorbed on Si/ Al₂O₃ prepared by anhydrous CLD: a) γ -alumina; b) SA(7/anh); c) SA(12/anh); d) SA(17/anh). LAS: Lewis acid sites. Numbers in brackets correspond to entries in Table 1. Full spectra are shown in Figure S1 and S2.

(entry 11, Figure S2) also leads to a peak from 2150 cm⁻¹ to 2160 cm⁻¹. Thus, it is attributed to CO adsorption on weak OH groups rather than on LAS.^[18,26]

SA(7/anh) (Table 1, entry 2) shows a 2200 cm⁻¹ peak of low intensity and a shoulder at approximately 2135–2140 cm⁻¹, corresponding to physisorption on silanols.^[11,12,18,24-26] This is consistent with the consumption of the alumina surface and the grafting of silicon species. The OH peak is redshifted ($\approx 6 \text{ cm}^{-1}$), indicative of a stronger H-bond donor or, generally, of a stronger acidity.^[7,11,12,24,25,27]

SA(12/anh) (Table 1, entry 3) is also characterized by a less intense 2200 cm⁻¹ peak and a more intense peak at 2135 cm⁻¹. However, the first CO molecules adsorbed cause the appearance of a low-intensity peak at approximately 2230 cm⁻¹, which is usually not related to the presence of silicon species but to the existence of strong LAS on the γ -alumina surface,^[12,18] viewed as surface defects.^[24] Based on thermodynamic calculations, these sites can probably be formed only upon high-temperature dehydroxylation of alumina and correspond to tri-coordinated aluminum species.^[11] Wischert et al. showed, however, that the optimal temperature for obtaining such tricoordinated species was approximately 700 °C.^[28] Herein, strong LAS are not observed on pure γ -alumina, but only after the grafting of a certain number of silicon species.

SA(17/anh) (Table 1, entry 4) exhibits more intense peaks at 2230 cm⁻¹ and 2135 cm⁻¹ and a less intense peak at 2200 cm⁻¹. This is in line with the tendency observed on SA(12/anh). The position of the peaks of the OH groups is approximately the same as for SA(7/anh) and SA(12/anh).

Figure 8 gives the effect of the synthesis conditions of Si/ Al_2O_3 on the adsorption of CO. The CO stretching region of



Figure 8. IR spectra (CO region) of increasing doses of CO adsorbed on Si/ Al₂O₃ prepared by anhydrous CLD: a) γ -alumina; b) SA(7/anh); c) SA(12/anh); d) SA(17/anh). LAS: Lewis acid sites. Numbers in brackets correspond to entries in Table 1. Full spectra are shown in Figure S1 and S2.

SA(17/4eqW) (Table 1, entry 5) is similar to that of SA(17/anh) (entry 4). With a larger fraction of the alumina surface uncovered, SA(17/12eqW) (entry 6) exhibits a higher amount of weak and medium LAS and a less intense silanol shoulder. SA(17/ CVD250) (entry 7) is characterized by a large amount of strong LAS; the silanol shoulder is comparable to those of the shoulders of SA(17/anh) and SA(17/4eqW). Even though SA(17/ CVD400) (entry 9) also has a silanol shoulder similar to those of entries 4, 5, and 7, the amount of weak and medium LAS is significantly higher, and it exhibits fewer strong LAS.

The peaks for CO adsorbed on OH groups of the silica, alumina, and Si/Al₂O₃ samples (\approx 2150–2160 cm⁻¹) do not exhibit the same evolution with increasing amounts of adsorbed CO. Some of the redshift is caused by the interaction of neighboring CO molecules,^[18] and some also depends on the wavenumber for the first CO doses on the OH groups (Table 5). The higher the wavenumber, the stronger the acidic character. The highest wavenumbers for the first CO doses on the OH groups are obtained for SA(17/4eqW) and SA(17/CVD250), the lowest for pure silica and alumina. The values increase from SA(7/anh) to SA(17/anh). Although higher than for pure alumina, the wavenumber for SA(17/CVD400) is markedly lower than for the other Si/Al₂O₃. The higher the wavenumber of CO on OH groups, the higher the rate of conversion of *m*-xylene (Table 5). High conversion rates are thus associated with OH groups with the strongest acidity.

The integration of the 2230 cm⁻¹ and 2200 cm⁻¹ peaks yields an estimate of the amounts of weak, medium, and strong LAS. Normalization of the data by the weight of the sample wafer and the surface area enables a comparison of the surface density of LAS of the different samples. The absorption coefficients for each type of LAS are similar;^[29] thus, the fraction of strong LAS among the total amount of LAS can be estimated as follows:

Fraction of strong LAS in total LAS =
$$\frac{A_{\text{peak strong LAS}}}{\overline{A_{\text{peak strong LAS}} + A_{\text{weak & medium LAS}}}}$$
(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, or weak and medium LAS: peak at 2200 cm⁻¹).

The plot of the fraction of strong LAS among the total LAS versus the free alumina surface is given in Figure 9. There is no strong LAS on γ -alumina and SA(7/anh) (Table 1, entry 2). Strong LAS appear at higher silica loadings (entries 3–7), and



Figure 9. Evolution of the percentage of strong Lewis acid sites (LAS) as a function of the available alumina surface. Numbers in brackets correspond to entries in Table 1.

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their percentage correlates with the area of uncovered alumina. Again, SA(17/CVD400) (entry 9) deviates and shows a much lower percentage of strong LAS than SA(17/4eqW) (entry 5).

Discussion

Surface occupancy and distribution of silicon species on $\gamma\text{-alumina}$

The amount of ethanol adsorbed and retained at room temperature enables the calculation of the fraction of the alumina support occupied by silicon species (Figure 3). Data show a regular deposition of silicon species for samples prepared under anhydrous conditions (Table 1, entries 2-4), with four equivalents of water per precursor molecule (entry 5), and for those prepared by CVD at 250 °C (entry 7). In these cases, the coverage of the alumina surface is proportional to the amount of deposited silicon. High heterogeneity is observed on SA(17/ 12eqW) (entry 6) prepared in excess water, in agreement with our previous data.^[19] This confirms the relevance and accuracy of ethanol adsorption as a probe for determining the fraction of occupied and unoccupied alumina surface. In particular, the data reveal the similarity between the surface states of SA(12/ anh) and SA(17/12eqW), despite the different silica loading, as also detected by ²⁹Si NMR.^[19]

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

Stepwise grafting of silicon atoms on the facets of γ -alumina by CLD and CVD-250 °C

IR spectroscopy (Figure 5 and 6) demonstrates the uneven decrease in the alumina OH stretching absorption bands when silicon is grafted to its surface. The first silicon atoms are grafted on the (100) facet, as indicated by the disappearance of the band at 3770 cm⁻¹ (Al^{VI}–OH). Kwak et al. showed the preferential grafting of BaO on the (100) facet of γ -alumina.^[4,30] On SA(12/anh), Al^{IV}–OH and (Al^{VI})₂–OH are no longer visible, and the intensity of the Al^V–OH band is notably reduced. This means that silicon is also grafted on the (110) facet. A further increase in silica loading results in the complete covering of the alumina surface. Thus, the IR data reveal that the grafting is selective with regard to the facets, the (100) one grafted first, the (110) afterwards, whereas the adsorption of ethanol suggests the progressive and regular coverage of the alumina surface by silicon species.

The grafting of silicon species in aqueous CLD follows the same rules (Figure 6). If a small amount of water is added to the reaction mixture (SA(17/4eqW), Table 1, entry 5), no difference is found compared to the equivalent prepared under anhydrous conditions (SA(17/anh), entry 4): IR analysis shows high coverage of the alumina surface. If a larger amount of water is added (SA(17/12eqW), entry 6), some of the TEOS polymerizes, and a smaller fraction of the alumina surface is covered (39%). As a consequence, the distribution of the alumina OH groups on the surface, visible in IR spectroscopy, is

close to that of SA(7/anh) (70% alumina uncovered) and SA(12/anh) (57% alumina uncovered), respectively (Table 1, entries 2 and 3; Figure 5): The (100) surface is grafted and the (110) surface is partially grafted.

The IR spectrum of SA(17/CVD250) (Table 1, entry 7; Figure 6) shows a general pattern that is similar to that for SA(17/anh) and SA(17/4eqW) but with a more intense silanol peak, which is associated to a higher degree of coverage and more regular deposition of silicon species on the surface, thus maximizing the density of surface SiOH. On SA(17/CVD400) (entry 9; Figure 6), all of the OH groups of the alumina support are equally affected, which is evidence of the nonselective grafting of the silicon species under such conditions, irrespective of the alumina facets.

Thus, for samples prepared by CLD or by CVD at 250 °C (Table 1, entries 2–7), silicon species are first grafted on the (100) surface and only at higher coverage on the (110) surface. It is noteworthy that strong LAS only appear in the presence of a minimum amount of grafted silicon (Figure 9), and they are located on the (110) surface, as confirmed by a computational study of the γ -alumina surface, which shows that the "defect sites" or strong LAS are located on the (110) surface.^[11,28] Here, they are not visible on γ -alumina and result from the change in the nature of the (110) surface after the grafting of the silicon species.

Nature of the active sites for ethanol dehydration and m-xylene isomerization

Figure 10a gives the amount of dehydrated ethanol (per surface unit) as a function of uncovered alumina surface and the nature of the grafted facet ((100) or (110)) for CLD and CVD-250 °C-prepared Si/Al₂O₃ (Table 1, entries 1–7). The grafting of silicon on the (100) facet is accompanied by a strong decrease in the amount of dehydrated ethanol. In agreement with the conclusions of Kwak et al., this confirms that the sites of alumina that are active for ethanol dehydration are on the (100) facet.^[4] According to IR spectra of the OH stretching region, these active sites are, thus, the hydroxylated or dehydroxylated form of Al^{VI} –OH or $(Al^{VI})_3$ –OH, visible at 3770 cm⁻¹ and 3600 cm⁻¹, respectively.

Figure 10b gives the evolution of the number of weak/ medium and strong LAS as a function of the alumina coverage and the nature of the grafted facet. As the (100) surface is covered by silicon species, the number of weak and medium LAS decreases, whereas strong LAS and BAS do not form. Weak and medium LAS on the (100) surface thus are, depending on the activation temperature, the sites of γ -alumina that are active for ethanol dehydration.

Covering the (110) surface with silicon species hardly leads to a change in ethanol dehydration (Figure 10a). However, there are still dehydration sites on the surface, despite the full coverage of the (100) surface; thus, these sites form by deposition of silicon on the (110) surface. If this occurs, the ethanol dehydration peak shifts back towards lower temperatures (Table 1, entries 4, 5, and 7; Figure 4). The coverage of the (110) surface is associated with a loss of the weak and



Figure 10. Impact of the grafting mode of silicon on a) the catalytic performance and b) the amount (per surface unit) of weak/medium and strong LAS of Si/Al₂O₃ prepared by CLD or CVD-250 °C (Table 1, entries 1–7). (100) and (110): surfaces of alumina. Numbers in brackets correspond to entries in Table 1.

medium LAS, especially between SA(7/anh) (entry 2) and SA(12/anh) (entry 3; Figure 10 b). Strong LAS form as a result of the deposition of silicon on the (110) surface. SA(17/CVD250) reveals the largest amount of strong LAS but the smallest number of dehydration sites, indicating that strong LAS on the (110) surface are not the active sites.

Figure 10a also shows the development of the rate of *m*-xylene conversion (per surface unit) for CLD and CVD-250 °Cprepared Si/Al₂O₃ (Table 1, entries 1–7). The rate per surface unit remains low when the (100) surface undergoes grafting. Thus, (nearly) no active sites for *m*-xylene conversion are formed. The rate increases strongly as soon as silicon is deposited on the (110) surface, which indicates that active sites for *m*-xylene isomerization are on the (110) surface and that they require the presence of silicon. The isomerization of *m*-xylene requires Brønsted acidity, and it takes place over zeolites such as HZSM-5, zeolite beta, and mordenite.^[20,31] The correlation

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between the wavenumber at the lowest CO coverage on the OH groups (Table 5) and *m*-xylene isomerization reactivity (Table 5) suggests that these OH sites catalyze the reaction.

Similarly, and in accord with the IR data, we associate the remaining sites for ethanol dehydration with the same BAS on the (110) surface of γ -alumina, formed following deposition of the silicon species. The formation of BAS is accompanied by the formation of strong Lewis acidity on the same surface (Figure 10b). However, as mentioned above, the strong LAS are not responsible for EtOH or *m*xylene conversion.

When the surface is almost fully covered by silicon species

(Table 1, entries 4, 5, and 7), the rate of conversion of *m*-xylene passes the maximum (Figure 10a). At the same time, there is a slight decrease in the amount of dehydrated ethanol. We ascribe these evolutions to the grafting of precursor molecules to the BAS, thus removing the active site. Once the TEOS molecules are grafted to the (100) and (110) surfaces of γ -alumina, anchorage sites for new precursor molecules become fewer and it is likely that TEOS is grafted to the most reactive of the available OH groups, hence decreasing the number of BAS. Conversely, the deposition of the same amount of silicon in one step and in the presence of water (SA(17/4eqW), entry 5) leaves more of the BAS ungrafted because of the uncontrolled deposition. The grafting to BAS explains the decrease in the rate of *m*-xylene conversion between SA(17/CVD250) and SA(19/CVD250) (Table 5). Thus, there is an optimum γ -alumina coverage, between 70% and 80%, above which deposition of silicon species no longer takes place exclusively on alumina, but leads to the consumption of BAS in anhydrous CLD or CVD-250 °C. As BAS are grafted, the number of strong LAS increases further (Figure 10b).

by silicon species.

Scheme 1 illustrates the evolution, on the (110) surface, of the sites that are grafted and of the active sites, depending on the coverage of alumina by silicon species. On γ -alumina, Al^{VI}– OH sites on the (100) surface are the first to dehydroxylate with increasing temperature;^[11] they can readily dehydroxylate to form LAS that are active in ethanol dehydration. Conversely, Al^{IV}–OH sites on the (110) surface are not dehydroxylated (top panel). When silicon is deposited on the (110) surface (Scheme 1, middle panel), Al^V–OH sites (peak at 3730 cm⁻¹ in the IR spectrum) disappear as a result of the grafting. Strong LAS, which were not present on γ -alumina, form; they are probably three-coordinated.^[11] Interaction of these strong LAS with silanol, provided that the coordination of the aluminum is flexible, form BAS, according to the hypothesis of Trombetta et al.^[32] In contrast to zeolites, the silanol does not permanently bridge the aluminum atom, but rather pseudo-bridging occurs, according to the definition of Chizallet et al.^[33] Depending on the SiOH–Al distance, angle, and activation temperature, either BAS or strong LAS are detected. As all these parameters probably have a large spread, it is impossible to detect a clear stretching frequency of OH in the IR. Above 70% coverage of alumina by silicon species, new species are grafted to the BAS (low panel). The number of strong LAS, which are no longer in interaction with silanols, increases.

Turnover frequency in m-xylene isomerization

Based on the stoichiometric adsorption and desorption of ethanol, it is possible to calculate the total density of ethanol dehydration sites (Table 6). Once the whole (100) surface is grafted (entries 4, 5, and 7), both the dehydration of ethanol and *m*-xylene isomerization take place exclusively on the BAS. The number of BAS equals the amount of ethanol dehydration sites, which is known. As the isosurface rate of *m*-xylene conversion is also known, the TOF of BAS, expressed in s⁻¹ site⁻¹, can be calculated as follows:

$$\mathsf{TOF}\ [\mathsf{s}^{-1}\ \mathsf{site}^{-1}] = \frac{\mathsf{rate}\ \mathsf{of}\ m\mathsf{-xylene}\ \mathsf{converted}\ \mathsf{at}\ 10\ \mathsf{min}}{\mathsf{EtOH}\ \mathsf{dehydration}\ \mathsf{sites}} \times \frac{1}{3600} \tag{4}$$

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

Table 6 gives the TOFs for entries 4, 5, and 7. The entries yield similar results, approximately 1.4×10^{-3} s⁻¹ per BAS, which indicates that they have similar BAS. This value is approximately 22 times lower than that $(3.1 \times 10^{-2} \text{ s}^{-1} \text{ per BAS})$ obtained over a USY zeolite, that has no or few extraframework aluminum (CBV720 from Zeolyst).^[34] The number of BAS of this zeolite was determined by ethanol dehydration (yield 0.18 BAS nm⁻²), which is virtually identical to the value obtained by TPD of pyridine. Assuming that all the Si/Al₂O₃ sam-



Table 6. Comparison of the density of *m*-xylene conversion sites and ethanol conversion sites over Si/Al₂O₃-grafted samples and the degree of coverage of the (100) surface of alumina by silicon species.

Entry	Sample	EtOH dehyd. sites [nm ⁻²]	TOF $[\times 10^{-3} \text{ s}^{-1} \text{ site}^{-1}]$	lsosurface [nm ⁻²] ^[a]	BAS Per exposed AI atom $[\times 10^{-2}]^{[b]}$	Per exposed Si atom $[\times 10^{-2}]^{[b]}$	Fraction of BAS in EtOH dehyd. sites [%] ^[c]	Fraction of free alumina surface [%]	Fraction of free (100) surface [%] ^[d]
1	γ-alumina	0.83	-	0.02	0.1	-	2	100	98
2	SA(7/anh)	0.27	-	0.04	0.5	1.2	16	70	27
3	SA(12/anh)	0.23	-	0.11	1.5	2.0	47	57	14
4	SA(17/anh)	0.17	1.5	0.19	5.2	2.1	\approx 100	28	0
5	SA(17/4eqW)	0.20	1.3	0.20	4.5	2.4	\approx 100	34	1
6	SA(17/12eqW)	0.22	-	0.11	1.4	2.2	50	61	13
7	SA(17/CVD250)	0.16	1.3	0.16	7.2	1.5	pprox 100	17	2
9	SA(17/CVD400)	0.27	-	0.05	1.1	0.6	18	35	26

[a] Calculated on the basis of an average TOF value of 1.4×10^{-3} s⁻¹ site⁻¹ calculated for SA(17/anh), SA(17/4eqW), and SA(17/CVD250) for *m*-xylene conversion. Values are obtained by assuming that all the EtOH dehydration sites of the materials are BAS [Eq. (5)]. [b] Calculated on the basis of the fraction of alumina surface covered/not covered by silicon species. [c] Calculated by dividing the number of BAS by the total number of dehydration sites [Eq. (7)]. [d] (100) surface of γ -alumina, calculated by dividing the difference between the number of EtOH dehydration sites and the number of *m*-xylene conversion sites by the number of EtOH dehydration sites on γ -alumina, where they are exclusively located on the (100) surface [Eq. (6)].

ples have the same TOF, the number of BAS (per surface unit) of the other Si/Al_2O_3 can be estimated based on the average TOF for entries 4, 5, and 7 (Table 6):

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$$BAS [nm^{-2}] = \frac{\text{rate of } m\text{-xylene conversion at 10 min}}{\text{TOF}} \times \frac{1}{3600}$$
(5)

in which the rate is in $[h^{-1}\,nm^{-2}]$ and the TOF is $1.4\times10^{-3}\,s^{-1}\,site^{-1}.$

The number of BAS for entries 4, 5, and 7 in Table 6 is equal to the number of ethanol dehydration sites. Other samples reveal a smaller number of BAS than of dehydration sites, which means that some of the dehydration sites are still on the (100) surface, in general agreement with the characterization of the sample.^[19]

The density of the BAS is low with respect to the exposed aluminum and silicon (Table 6). In Figure 11, the density of BAS per exposed silicon (a) and aluminum (b) is shown as a function of the fraction of accessible alumina. The density per atom of the (110) surface is calculated by estimating that the (100) and (110) surfaces represent 20% and 75%, respectively, of the total γ -alumina surface^[11] and by determining the coverage of the (100) surface (see below). Figure 11a reveals that among the silicon atoms grafted on the whole alumina surface, the percentage of silicon atoms that form the BAS reaches a maximum (2%) when the (110) surface is grafted. This value is even lower at the initial grafting of silicon on the (100) surface. Approximately 4% of the silicon atoms that are grafted on the (110) surface give rise to BAS. Thus, most of the grafted silicon atoms do not form BAS. When grafting to the BAS occurs, at high coverage of the alumina surface, the density of the BAS per silicon atom decreases. Figure 11b reveals that, at most, 7% of the total exposed aluminum atoms, and 8% of the aluminum atoms of the (110) surface, relate to a BAS (on SA(17/CVD250)). The deposition of silicon species by CVD-400 °C is much less efficient when it comes to the formation of BAS than when it occurs by CLD and CVD-250 °C.



Figure 11. Evolution of the number of BAS a) per exposed silicon atom and b) per exposed aluminum atom of the whole surface and of the (110) surface. Filled symbols: CLD or CVD-250 °C materials (Table 1, entries 2–7); empty symbols: CVD-400 °C (entry 9).

Especially for samples with only partial coverage of alumina surfaces, the difference between the number of ethanol dehydration sites and the number of BAS enables the calculation of the percentage of free (100) surface (Table 6): Part of (100) uncovered [%] =

in which the EtOH dehydration sites of pure alumina are fixed at 0.83 nm^{-2} and the fraction of BAS of the total number of ethanol dehydration sites (Table 6):

Fraction of BAS in EtOH dehydration sites
$$[\%] =$$

These data prove the preferential deposition of the first silicon species, at an early stage of the grafting, under relatively mild synthesis conditions, on the (100) surface of γ -alumina (Table 6, entries 1–7): the degree of coverage of the (100) surface is always higher than that of the whole alumina surface. There are virtually no BAS on pure alumina. On SA(7/anh), most of the dehydration sites are still on the (100) surface. SA(12/anh) and SA(17/12eqW) reveal that some of the dehydration sites on the (100) surface are still present while some BAS appear. On SA(17/anh), SA(17/4eqW), and SA(17/CVD250), the (100) surface is completely covered.

Nonselective grafting of silicon atoms on the facets of γ -alumina by CVD-400 °C

The process of grafting differs in the case of CVD-400°C. Despite the similar coverage of the alumina surface to that of SA(17/anh), SA(17/4eqW), or SA(17/CVD250), shown by the amount of ethanol bound to the surface (Figure 3), and consistent with our previous data,^[19] SA(17/CVD400) (Table 6, entry 9) has a smaller number of BAS and strong LAS. The IR spectrum shows a nonpreferential decrease in the alumina OH bands (Figure 6); the position of the ethanol dehydration peak is similar (although less intense) to that of γ -alumina. This indicates that, at high grafting temperature, the facets of γ -alumina are nonselectively grafted by the silicon species. By calculating the percentage of the free (100) surface (Table 6), we confirm that the value (26%) is close to the overall percentage of the free alumina surface (35%). The remaining sites on the (100) surface allow the dehydration of ethanol in a similar way to that on γ-alumina.

Conclusions

Silicon grafting on γ -alumina takes place preferentially on the (100) surface if grafting occurs under mild conditions. When this whole surface is covered, the (110) surface is grafted. At almost complete coverage of the (110) surface, silicon is grafted on the previously deposited silicon species. Lewis acid sites (LAS) on the uncovered γ -alumina (100) surface are the active sites for ethanol dehydration; these sites are hydroxylated or dehydroxylated forms of Al^{VI}–OH or (Al^{VI})₃–OH. Brønsted acid sites (BAS) and strong LAS are created by silicon grafting on the (110) surface. These BAS are responsible for *m*-xylene isomerization and are also active in the dehydration of ethanol.

As the Brønsted active sites are the same for ethanol dehydration and *m*-xylene isomerization, we were able to determine the TOF in *m*-xylene isomerization: $1.4 \times 10^{-3} \text{ s}^{-1} \text{ site}^{-1}$. This value is 22 times lower than obtained over the BAS of a USY zeolite without extraframework aluminum.

Experimental Section

TGA experiments were performed with a Mettler Toledo apparatus (TGA/SDTA851e) according to the procedure of Kwak et al.^[4] Before the measurements, the samples were pretreated in a flow of helium (60 mL min $^{-1})$ at 200 and 500 $^{\circ}\text{C},$ respectively, 10 $^{\circ}\text{C}\,\text{min}^{-1},$ for 2 h to eliminate physisorbed water from the surface and/or to activate sites. Samples were cooled to RT. Helium was passed through a saturator containing ethanol at RT for approximately 30 min, and the increase in the weight of the sample was determined. Weakly bonded ethanol molecules were evacuated by means of a helium purge at RT for 1 h. TPD of ethanol was performed at a rate of 10°C min⁻¹ until 400°C. The intensity of the desorption features was measured by calculation of the first derivative of weight loss during TPD with respect to temperature, and normalized by the surface area of the sample. The release of ethanol and ethylene was confirmed by mass spectrometry. The amount of dehydrated ethanol determined from the TGA results was calculated as follows:

ethanol retained after purge
$$\times \frac{A_{\text{peak ethylene}}}{A_{\text{ethylene}} + A_{\text{peak ethanol}}}$$
 (8)

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

The *m*-xylene isomerization test consisted of reacting a catalyst bed of 0.5 g with gaseous *m*-xylene (0.6 cm³ h⁻¹). Catalysts were first preheated in an air flow at 350 °C, followed by xylene conversion at 350 °C in a flow of nitrogen. Analysis of the products was performed by on-line gas chromatography by means of a Hewlett Packard 6850 apparatus, equipped with a flame ionization detector (FID) and an FFAP column. *m*-Xylene was isomerized to *p*- and *o*xylene or disproportionated to toluene and isomers of trimethylbenzene. In the latter case, the reaction of trimethylbenzene with toluene or xylene may also lead to the formation of isomers of xylene by a bimolecular mechanism (Supporting Information, Figure S3). The rate of *m*-xylene conversion measured after the first 10 min of reaction is given in Equation (9):

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

$$[\sum_{i}^{\text{species}} \frac{A_{i}}{N_{\text{C atoms }i}} / (\sum_{i}^{\text{species}} \frac{A_{i}}{N_{\text{C atoms }i}} + \frac{A_{m\text{-xylene}}}{8})] \qquad (9)$$
$$\times \frac{\text{flow rate} \times \text{density}_{m\text{-xylene}}}{M_{m\text{-xylene}} \times m_{\text{catalyst}}} \times \frac{N_{\text{A}}}{S_{\text{BET}}}$$

in which A_i is the area of the GC peak of species i (i=toluene, *p*-xylene, *o*-xylene, trimethylbenzenes) (6.02×10²³ mol⁻¹), flow rate is in [cm³ h⁻¹], N_A is the Avogadro number, and S_{BET} in [nm²g⁻¹] the surface area of the catalyst.

IR spectra were recorded by a Nexus Fourier transform instrument. Samples (self-supported pellets of compressed powder) were pretreated in situ under vacuum ($\approx 10^{-5}\,mbar$) for 10 h at 450 °C

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(heating rate of $5 \,^{\circ}$ Cmin⁻¹) including a plateau at $150 \,^{\circ}$ C for 1 h. CO adsorption was achieved by adding increasing amounts of CO to the sample at liquid nitrogen temperature.

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