

## Heterogeneous Catalysis

## Highly Dispersed SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> Catalysts Illuminate the Reactivity of Isolated Silanol Sites

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Abstract: The reaction of  $\gamma$ -alumina with tetraethylorthosilicate (TEOS) vapor at low temperatures selectively yields monomeric SiO<sub>x</sub> species on the alumina surface. These isolated (-AlO)<sub>3</sub>Si(OH) sites are characterized by PXRD, XPS, DRIFTS of adsorbed NH<sub>3</sub>, CO, and pyridine, and <sup>29</sup>Si and <sup>27</sup>Al DNP-enhanced solid-state NMR spectroscopy. The formation of isolated sites suggests that TEOS reacts preferentially at strong Lewis acid sites on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, functionalizing the surface with "mild" Brønsted acid sites. For liquid-phase catalytic cyclohexanol dehydration, these SiO<sub>x</sub> sites exhibit up to 3.5-fold higher specific activity than the parent alumina with identical selectivity.

 $\mathbf{S}$ ilica–aluminas are well-known solid acid catalysts and are employed in both laboratory organic synthesis and in largescale industrial processes.<sup>[1]</sup> These materials include amorphous silica-aluminas, typically prepared by coprecipitation or sol-gel methods,<sup>[2]</sup> and ion-exchanged, crystalline aluminosilicate zeolites such as H-ZSM-5 or H-Y.<sup>[3]</sup> Solid acids catalyze a variety of transformations, including dehydration, skeletal isomerization, and cracking,<sup>[4]</sup> and are used in processes such as fluid catalytic cracking (FCC) and methanol-to-gasoline (MTG) synthesis.<sup>[5]</sup> In crystalline zeolites, "strong" Brønsted-acidic sites arise from isomorphous Al<sup>3+</sup> substitution in the SiO<sub>2</sub> lattice, yielding "framework" protons as in Figure 1a.<sup>[6]</sup> Amorphous silica-aluminas also possess Brønsted acid sites (Figure 1b). Solid acids typically present a range of acid site strengths according to local coordination environments. Significant spectroscopic and physicochemical studies have been undertaken to characterize the strength and catalytic relevance of the different acid sites.<sup>[7]</sup>

In spite of advances in the synthesis and post-synthetic modification of solid acids, the non-uniformity of acid site strengths on solid acid catalysts remains a challenge. This nonuniformity can significantly compromise selectivity, leading to unwanted side products and ultimate deactivation by

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**Figure 1.** A) The pentasil unit of zeolite H-ZSM-5 with  $A^{3+}$  substitution (all lattice points, except Al, represent Si atoms, with Si–O bonds omitted for clarity). B) A proposed Brønsted-acidic site in amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

coking.<sup>[8]</sup> The attraction of tuning solid acid strength has been demonstrated in several organic transformations,<sup>[9]</sup> including recent work by Gazit and Katz<sup>[10]</sup> who reported the efficacy of mildly acidic silanol groups in  $\beta$ -glucan hydrolysis.<sup>[10]</sup> In recent work, van Bokhoven and co-workers demonstrated a controlled process for the synthesis of SiO<sub>2</sub>– Al<sub>2</sub>O<sub>3</sub> catalysts via chemical liquid deposition (CLD) grafting of Al and Si species on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supports.<sup>[7b,11]</sup> Here we report a new vapor phase approach to creating isolated, uniform, and weakly acidic SiO<sub>x</sub> sites on alumina, and explore their catalytic properties with respect to a transformation of biomass relevance. Cyclohexanol dehydration is diagnostic of solid acid catalytic activity<sup>[12]</sup> and permits assessment of selectivity with respect to unwanted side reactions and coking, a traditional challenge to solid acid catalysis.<sup>[13]</sup>

We employ a strategy here that combines the mild conditions of a low temperature vapor-phase deposition process and the specific surface reactivity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to realize a new class of SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts featuring well-defined, isolated Si active sites having the structure (-AlO)<sub>3</sub>Si-(OH) (Scheme 1). These species are characterized by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), <sup>29</sup>Si and <sup>27</sup>Al solid-state NMR enhanced by dynamic



**Scheme 1.** Vapor-phase synthesis of (-AlO)<sub>3</sub>Si(OH) sites on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Proposed active site in SiO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, **A**.

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nuclear polarization (DNP), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed NH<sub>3</sub>, CO, and pyridine, followed by catalytic studies. A linear relationship is demonstrated between the Si site density and surface Brønsted acidity. We also show that these SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts are competent for the catalytic dehydration of cyclohexanol to cyclohexene, exhibiting up to 3.5-fold higher specific activity than the parent  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with no loss in selectivity and with negligible coking.

Silica–alumina catalysts with multiple SiO<sub>2</sub> surface layers were previously prepared by chemical vapour deposition (CVD).<sup>[14]</sup> Atomic layer deposition (ALD) growth of SiO<sub>2</sub> on Si(100) wafers was achieved by George<sup>[15]</sup> using SiCl<sub>4</sub> + H<sub>2</sub>O, while Ferguson obtained similar results using Si(OEt)<sub>4</sub> (TEOS) + H<sub>2</sub>O.<sup>[16]</sup> Due to the low reactivity of SiO<sub>2</sub>, an NH<sub>3</sub> co-feed was required in both cases to achieve efficient growth. However, Ma<sup>[17]</sup> reported that more nucleophilic Au/TiO<sub>2</sub> substrates nucleate SiO<sub>2</sub> growth using Si(OMe)<sub>4</sub> (TMOS) + H<sub>2</sub>O without NH<sub>3</sub>.

In the present strategy,  $SiO_x/Al_2O_3$ catalysts are prepared at 50 °C by TEOS ALD on phase-pure  $\gamma$ -alumina (Alfa-Aesar, 60 m<sup>2</sup>g<sup>-1</sup>) in the viscous flow reactor described previously.<sup>[18]</sup> The ALD A-B type growth sequence (Figure S9; Supporting Information) is:

1) gaseous TEOS flow over the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for 120 s; 2) chamber purge for 240 s; 3) water vapor flow over the alumina for 300 s from a 25°C reservoir; 4) chamber purge for 300 s (see Supporting Information for more details). After the ALD growth, the catalysts are calcined for 18 h at 550 °C in flowing O<sub>2</sub>. Before deposition, no surface species other than C, Al, and O are detected on the alumina by XPS. The coverages of the deposited Si on the alumina (1.5–3.2 Si/nm<sup>2</sup>) were assayed by inductively coupled plasma (ICP) analysis (Figure 2A) with confirmation by XPS. Note here that the Si deposition saturates, independent of TEOS exposure time. Despite the A-B-type reaction sequence, substrate rehydroxylation does not result in further silica growth. Thus, the highest loading obtained is 3.2 Si/nm<sup>2</sup>. Due to the low loading of Si, little change in Al surface character is observed spectroscopically (see below), as only a small fraction of surface sites are occupied by Si atoms. Brunauer-Emmett-Teller (BET) surface area analysis indicates constant surface area after ALD across all SiO<sub>x</sub> loadings (Figure S9, representative isotherms in Figure S10), and scanning electron microscopy (SEM) evidences no obvious morphological changes, with the particle size remaining  $<3 \,\mu m$  by SEM (Figures S9 and S11). X-ray powder diffraction patterns of the catalysts remain unchanged after Si saturation, confirming the assign-



**Figure 2.** A) Si surface coverage in Si/nm<sup>2</sup> as determined by ICP. B) Si (2p) XPS spectrum of SiO<sub>x</sub> catalysts. C) DNP-enhanced <sup>29</sup>Si CPMAS NMR spectra before and after calcining. Spectra were obtained at 100 K using MAS rate  $\nu_R = 10$  kHz, recycle delay  $\tau_{RD} = 1.5$  s, contact time  $\tau_{CP} = 3$  ms, number of scans NS = 2048, acquisition time AT = 50 min. The surface structures Si(3Al,OH), Si(Al,Si,2OH), Si(2Al,2OH), Si(2Al,Si,OH), and Si(3Al,Si) are depicted on the right. Note that Si(3Al,OH) is the principle species in the calcined sample.

ment of  $SiO_x$  as a surface species, neither intercalating into the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure nor altering the catalyst crystallite size (Figure S12).

Next, an alternative growth mode in which all TEOS pulses were performed in sequence, followed by  $H_2O$  pulses, was investigated to determine if Si saturation occurs without A-B-cycling. While Si growth is again observed in this procedure, coverages reach only ca. 60% of those observed for comparable numbers of A-B growth cycles. We speculate that deposition is sterically hindered by the presence of surface EtOH groups, consistent with previous observations in ALD processes.<sup>[19]</sup>

The SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> sites were next characterized by XPS. The adventitious C(1s) carbon peak is referenced here to a binding energy (BE) of 285.0 eV. A higher energy feature assignable to C–O species<sup>[20]</sup> is not detected, even in uncalcined catalysts. The absence of residual surface –OEt moieties is further corroborated by solid-state NMR spectroscopy (see below). The Al(2p) BE occurs at 74.4 ± 0.2 eV for all catalysts after calcination, while the Al(2p) BE of reference  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is found at 74.4 eV. Representative Al XPS spectra are shown in the Supporting Information (Figures S15–S17). The Si(2p) BE of the calcined SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> sites is found at 102.4 ± 0.2 eV for all Si loadings (Figure 2B) and differs from that of bulk SiO<sub>2</sub>,

found here at 104.1 eV, in agreement with the literature.<sup>[21]</sup> Lower Si BEs relative to bulk silica are observed in other aluminosilicates, and have been assigned to Si-O-M structures<sup>[22]</sup> where  $M \neq Si$ . Increased acidity in the silanol proton is attributable to this electronic effect.

The surface geometry of the ALD-derived SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> sites was next probed by DNP-enhanced <sup>29</sup>Si{<sup>1</sup>H} crosspolarization magic angle spinning (CPMAS) NMR spectroscopy (Figure 2C, i-ii).<sup>[23]</sup> The DNP technique boosts the sensitivity of conventional CPMAS by ca. 2 orders of magnitude through excitation of the exogenously administered biradicals at their ESR resonance frequency and concomitant transfer of magnetization to the nuclear spins (due to the low Si loadings of these catalysts, conventional <sup>29</sup>Si CPMAS NMR gave no detectable signals even after 40000 scans). In the uncalcined materials, the spectrum is assignable to sites Si(2Al,Si,OH), Si(Al,Si,2OH) and Si(3Al,Si) species which are all expected at  $\delta = -85$  to -90 ppm.<sup>[24]</sup> Contributions from other sites, such as Si(2Al,2OH) and Si(3Al,OH), cannot be excluded a priori.<sup>[25]</sup> Furthermore, surface ethoxy groups cannot be detected by DNP-enhanced  ${}^{13}C{}^{1}H$ CPMAS NMR (Figure S13), arguing that hydrolysis is essentially complete under the growth conditions.

The NMR results indicate that calcination enhances the Si site homogeneity and increases the density of Si-O-Al linkages, evidenced by narrowing and downfield displacement of the <sup>29</sup>Si signal. Moreover the  $\delta = -81$  ppm position suggests that the major Si surface species after calcination has an Si(3Al,OH) geometry (Figure 2C, ii).<sup>[25b]</sup> Minor responses from the other species noted above are in principle possible; however, the spectroscopic and catalytic data (see below) argue that their contributions are minimal. Signals characteristic of Si(4Si) (ca.  $\delta = -110 \text{ ppm}$ ) and Si(3Si,OH) (ca.  $\delta = -100 \text{ ppm}$ ) sites<sup>[24]</sup> are also negligible, demonstrating, in agreement with the XPS data, that the Si deposition is limited by surface reactivity. Note that the present <sup>29</sup>Si NMR findings are consistent with other studies arguing that the final stable geometry of surface silica is a tridentate Si(3Al,OH) structure.<sup>[26]</sup> We speculate that here the geometry after calcination is a result of Si atom spatial isolation. Although the deposition process appears to yield some Si-O-Si linkages, polymeric SiO<sub>2</sub> does not form, so that during the 550 °C calcination, the Si surface atoms reconstruct in a final geometry dictated solely by the underlying  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> struture.

The DNP-enhanced <sup>27</sup>Al{<sup>1</sup>H} CPMAS NMR measurements were carried out to selectively detect Al sites on the surface while excluding signals from underlying bulk Al<sub>2</sub>O<sub>3</sub>. The spectra of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3.2 Si/nm<sup>2</sup> SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> before and after calcination (Figure S14) show two Al peaks assignable to octahedral sites (Al<sup>VI</sup>,  $\delta$  = 5 ppm) and tetrahedral sites (Al<sup>IV</sup>,  $\delta$  = 65 ppm).<sup>[24]</sup> Deposition of Si converts a fraction of Al<sup>VI</sup> sites to Al<sup>IV</sup> sites, with no peak shift or new signal apparent. The spectral intensities do not undergo any further change upon calcination, suggesting that the surface reconstruction by calcination involves primarily the Si species, a result corroborated by infrared spectroscopy (see below). Note that a small upfield shift (ca. 5 ppm) in the Al<sup>IV</sup> peak is expected upon conversion of Al-OH to Al-O-Si bonds; however, due to the low Si loading only a small fraction of  $Al^{IV}$  sites have Al-O-Si bonds, precluding further interpretation of peak shape.

Ambient DRIFTS spectra of the catalysts were recorded at 100°C after drying samples at 500°C for 1 hour, using a KBr background (Figure S18). The spectral features are consistent with those previously noted in the literature.<sup>[27]</sup> Importantly, there is no shift in the position of the hydroxy signatures, hence no attenuation of the O-H bond strength, although there is lessened intensity of the bands at 3790 cm<sup>-1</sup> and 3730 cm<sup>-1</sup> similar to that previously reported for Si deposition on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>[27b]</sup> This contrasts with the analogous but liquid-phase CLD process, which reveals attenuation under comparable conditions.<sup>[11a]</sup> Notable is the appearance of a sharp feature at  $3723 \text{ cm}^{-1}$  in the present  $\text{SiO}_x/\text{Al}_2\text{O}_3$ catalyst, assignable to surface Si-OH species. Previously this peak was assigned at 3725-3745 cm<sup>-1</sup>,<sup>[27b,28]</sup> with the lower frequency mode associated with greater O-H bond ionicity, signifying enhanced Brønsted acidity. The 3723 cm<sup>-1</sup> position is thus consistent with the present assignment of the Si-O-H sites as Brønsted acid sites.

NH<sub>3</sub> DRIFTS experiments were next conducted to probe surface acid sites, with catalyst surfaces exposed to NH<sub>3</sub> at 100 °C, then purged with Ar. The resulting spectra (Figure 3 A,B) show that NH<sub>3</sub> interaction with the neat  $\gamma$ -alumina hydroxy groups gives rise to Al<sub>n</sub>-OH…NH<sub>3</sub> features at 3769, 3727, and 3671 cm<sup>-1</sup> (Figure 3 A, i, ii) in agreement with the literature.<sup>[29]</sup> On ALD-derived SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, an additional band at 3741 cm<sup>-1</sup> (Figure 3 A, iii, iv) is assigned to Si-OH…NH<sub>3</sub> species by analogy to similar modes in amorphous silica–aluminas.<sup>[8a,30]</sup> The acid-site DRIFTS spectral region



**Figure 3.** A) DRIFTS spectra of NH<sub>3</sub> treated SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> for: i) uncalcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ii) calcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, iii) uncalcined SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> with 3.2 Si/nm<sup>2</sup>, and iv) calcined SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> with 3.2 Si/nm<sup>2</sup>. B) DRIFTS acid region spectra of NH<sub>3</sub>-treated SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. C) Ratio of Brønsted-to-Lewis acid DRIFTS peak areas for NH<sub>3</sub> treated SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> samples.

(Figure 3B, i–iv) shows three NH<sub>3</sub> bands on neat  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 1620, 1471, and 1268 cm<sup>-1</sup>. Those at 1620 and 1268 cm<sup>-1</sup> are assignable to NH3 bound to weak and strong Al Lewis acid sites, respectively, while the feature at 1471 cm<sup>-1</sup> is assigned to a Brønsted acid site-derived NH<sub>4</sub><sup>+</sup> mode.<sup>[31]</sup> In contrast, the DRIFTS spectrum of NH<sub>3</sub> on uncalcined SiO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> exhibits only an Si–OH mode at 3741 cm<sup>-1</sup> (Figure 3 A, iii), indicating that the majority of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> hydroxy groups are consumed in the ALD process. While the band at  $3769 \text{ cm}^{-1}$  is usually associated with the most reactive Al-OH groups,<sup>[27a]</sup> here we find that all the alumina hydroxy groups react with gaseous TEOS. The SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> DRIFTS acid region spectrum also indicates selective consumption of the strong Lewis acid sites related to the band at 1268 cm<sup>-1</sup> (Figure 3 B, iii), leaving the other acid sites unperturbed. It thus appears that the present ALD process involves coordination to, and presumably TEOS cleavage at, strong Lewis acid sites. When these sites are consumed, film growth ceases since the Si-OH units are insufficiently reactive to protonolyze the TEOS Si-OR linkage.

NH<sub>3</sub> adsorption on either uncalcined or calcined y-Al<sub>2</sub>O<sub>3</sub> reveals no obvous DRIFTS spectral differences (Figure 3 A,B, i, ii). For NH<sub>3</sub> adsorportion on calcined Si-saturated SiO<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub>, similar Al–OH features at 3769, 3727, and 3671 cm<sup>-1</sup> are visible (Figure 3 A, , iv), however the Si–OH group signature at 3741 cm<sup>-1</sup> remains strong, arguing that the Si species are not incorporated into the bulk  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. A strong Lewis acid peak at 1268 cm<sup>-1</sup> is also evident (Figure 3 B, iv) and resembles that of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The Brønsted acidity of the SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> series was next assayed from the DRIFTS peak area ratio of Brønsted NH<sub>4</sub><sup>+</sup> to Lewis site ... NH<sub>3</sub> species (Figure 3C). The linear correlation of this ratio with the Si surface density argues for enhanced Brønsted acidity of the new active sites. Additionally, the DRIFTS of adsorbed pyridine (Figure S20) confirms that there is no perturbation of the catalyst Lewis acid sites after Si deposition and calcination. DRIFTS of NH<sub>3</sub> spectra for individual catalyst loadings are shown in Figure S21.

CO DRIFTS was used to further probe surface hydroxy groups, since the O–H stretchinig frequency observed upon CO adsorption is sensitive to the Brønsted acidity, due to Al-OH…CO hydrogen-bonding.<sup>[32]</sup> At 100 °C, the DRIFTS spectrum of CO on pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Figure S19) reveals bands at 3794 and 3774 cm<sup>-1</sup>, assignable to terminal tetrahedral and octahedral Al–OH groups, in excellent agreement with the literature.<sup>[33]</sup> ALD deposition of Si on the catalyst surface does not affect these peak positions, although a reduction in the 3794 cm<sup>-1</sup> band intensity is noticable. A new OH band appears at 3726 cm<sup>-1</sup> in the 3.2 Si/nm<sup>2</sup> catalyst spectrum, which is assigned here to isolated Si-OH groups on the basis of previous reports.<sup>[3b]</sup> Thus, the CO DRIFTS confirms the presence of isolated Si–OH sites, with no discernable attenuation of existing Al–OH groups.

The catalytic properties of the calcined  $SiO_x/Al_2O_3$ materials were next evaluated for cyclohexanol dehydration in a batch reactor (see Figures S6 and S7 for details); catalytic data are compiled in Table S22, and summarized in Figure 4. It is seen that the present  $SiO_x/Al_2O_3$  catalysts possess sufficiently strong Brønsted acid sites to catalyze this trans-



**Figure 4.** Cyclohexanol dehydration kinetics over  $SiO_x/Al_2O_3$ . A) Turnover frequencies for 0.0–3.2 Si/nm<sup>2</sup> SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. Units: mol substrate/(m<sup>2</sup> cat s). B) Rate difference per mol Si on  $SiO_x/Al_2O_3$  catalysts. The rate of pure alumina is subtracted from the rate of each catalyst to approximate the specific activity of the Si sites, expressed as the slope *m* of the linear regression. Units: mol substrate/(mol Si s).

formation but without formation of carbonaceous deposits typical of strong solid acids.<sup>[34]</sup> For ALD-derived SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, no products except cyclohexene are observed by GC-MS, and the carbon balance determined by an independent calibration of both cyclohexanol and cyclohexene is invariably 95–102%. Since the cyclohexanol dehydration rate over SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> exhibits a first-order dependence on [cyclohexanol], the rate constant *k* is determined from the slope of the cyclohexanol conversion versus time plot under differential conditions, i.e., when [cyclohexanol] is not significantly altered (Figure S22).

Note that the present SiO<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts provide higher initial turnover frequencies (normalized to catalyst surface area, Figure 4A) versus the parent  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> TOF reaches a maximum of  $6.6 \times 10^{-8}$  mol substrate/(m<sup>2</sup> cats) at the highest Si loading, a 3.5-fold increase over that of  $\gamma$ - $Al_2O_3$ ,  $1.9 \times 10^{-8}$  mol substrate/(m<sup>2</sup> cat s). SiO<sub>2</sub> was found to be catalytically inert under the same conditions, differentiating the Brønsted acidity of the isolated SiO<sub>x</sub> site from polymeric SiO<sub>2</sub>. A commercially available 6.5 wt % SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was screened for comparison. While the TOF of the commercial catalyst  $(1.4 \times 10^{-7} \text{ mol substrate}/(\text{m}^2 \text{ cat s}))$  was found to be 2 times that of our highest TOF ( $6.6 \times 10^{-8}$  mol substrate/  $(m^2 \text{ cat s}))$ , the carbon balance of the reaction was only 68%, indicating significant carbon loss consistent with heavy product formation (Figure S22). We hypothesize that this difference in carbon balance is a result of the milder acidity of the SiO<sub>x</sub> species relative to strong Brønsted sites in conventional SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and demonstrates the value of tuning the strength and homogeneity of solid acid catalysts.



Since the DNP-enhanced CPMAS NMR and infrared spectroscopies indicate (see above) that the  $SiO_x/Al_2O_3$  alumina character is largely unchanged after calcination, it is reasonable to assume the parent alumina catalytic activity remains approximately constant at all Si loadings. This allows for subtraction of the alumina rate contribution from the apparent  $SiO_x/Al_2O_3$  rates (Figure 4B). The resulting linear increase in rate per mol Si strongly argues that all surface Si sites are uniformly active in the cyclohexanol dehydration, and the slope of the linear regression yields a turnover frequency per Si site of  $1.5 \times 10^{-2}$  mol substrate/(mol Sis).

As a further comparison, a surface-acid SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared according to the wet chemical CLD technique of van Bokhoven.[11b] This catalyst was selected because it represents an umambiguous, direct comparison to our own, being prepared from the same precursors, TEOS and y-Al<sub>2</sub>O<sub>3</sub>, but under different synthetic conditions. In addition, the physical and acidic properties of such catalysts have been extensively characterized.<sup>[7b,11]</sup> The catalyst was prepared with a single Si deposition reaction using an y-Al<sub>2</sub>O<sub>3</sub> identical to that in the ALD syntheses (further description in Figure S9). The liquid-phase technique yields a catalyst of substantially similar surface area (56  $m^2g^{-1}$ ), particle size  $(<3 \,\mu\text{m})$ , and Si content (2.8 Si/nm<sup>2</sup>). However, the catalytic results (Figures S22 and S23) deviate from those observed with the ALD-derived catalysts. Analysis of catalytic activity and selectivity is hampered by apparent leaching of Si from the catalyst under reaction conditions, as Si-containing species are observed by GC-MS and <sup>29</sup>Si NMR (principally cyclohexyl ethers of Si). Selectivity to cyclohexene is low (<20%), and other products, including dicyclohexyl ether and cyclohexylcyclohexane, are observed. Despite the leaching, catalytic activity comparable to SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts on a surface area basis  $(4.7 \times 10^{-8} \text{ mol substrate}/(\text{m}^2 \text{cats}))$  was observed, but based on the catalyst Si content, the Si sites do not show the same activity as those in  $SiO_x/Al_2O_3$  (<1.5×  $10^2$  mol substrate/(mol Sis)). The origin of this difference is at present unclear and promises a rich question for future study. In addition some structural differences in previously prepared CLD catalysts are noted, as characterized by FTIR<sup>[11a]</sup> and DNP-enhanced CPMAS SSNMR.<sup>[11c]</sup>

In summary, we report the synthesis of a novel class of highly dispersed SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts by the vapor-phase reaction of TEOS with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Significant surface Brønsted acidity is observed that tracks the Si coverage in a linear fashion, implying along with XPS, NMR, and DRIFTS spectroscopic data, an (-AlO)<sub>3</sub>Si(OH) active site assignment. The silanol proton is catalytically competent, and the SiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> sites exhibit higher catalytic activity than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sites in cyclohexanol dehydration. In contrast to stronger Brønsted acid sites in a conventional silica–alumina catalyst, no carbon loss is detected, demonstrating the attraction of more uniform/less acidic SiO<sub>x</sub> sites.

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