ChemPubSoc Europe

DOI: 10.1002/cctc.201901728

CHEMCATCHEM Full Papers



NMR Spectroscopic Characterization of Flame-Made Amorphous Silica-Alumina for Cyclohexanol and Glyceraldehyde Conversion

Zichun Wang,[a, b] Yijiao Jiang,[a] Catherine Stampfl,[c] Alfons Baiker,[d] Michael Hunger,[e] and Jun Huang*[b]

This paper is dedicated to the memory of Prof. Dr. Jens Weitkamp in appreciation of his outstanding contribution to zeolites and catalysis.

Amorphous silica-aluminas (ASAs), possessing both Brønsted acid sites (BAS) and Lewis acid sites (LAS), are important bifunctional catalysts in various industrial applications. Solid-state NMR spectroscopy has been widely used for characterizing the local structure and the surface sites of ASAs with probe molecules. In this work, four-, five- and six-coordinated Al species have been observed on the flame-made ASAs by ^{27}Al MQ MAS NMR experiment. ^{1}H/^{27}Al TRAPDOR MAS NMR experiments confirmed that surface Al species contribute to the formation of BAS and protonate ammonia probe molecules. The adsorption of ammonia on Lewis acidic Al sites (δ_{1H} = 3.0 ppm) was evidenced by various ^{1}H MAS NMR experiments on samples dehydrated at different temperatures, allowing the distinction from ammonium ions (δ_{1H} = 6.7 ppm) formed at BAS. The signal of ammonia adsorbed on LAS increased with increasing Al content in the ASAs. These properties together with the absence of pore diffusional constraints render the flame-made ASAs excellent catalysts for cyclohexanol dehydration and the conversion of glyceraldehyde in ethanol to ethyl lactate, outperforming the performance of other ASAs or zeolites.

1. Introduction

Silica-aluminas, including crystalline zeolites and amorphous silica-aluminas (ASAs), are the most widely used solid catalysts in large-scale hydrocarbon conversions.[1–2] Their catalytic properties strongly depend on the active surface sites. Pure silica possesses no or only very weak acidity. Incorporation of Al atoms into the silica network/framework promotes the formation of Brønsted acid sites (BAS).[3–4] BAS can protonate hydrocarbons, forming carbocation intermediates, which promote important reactions, such as cracking, isomerization, alkylation, and aromatization.[5–7] Steam treatment or Al-exchange can introduce various Lewis acidic aluminum ions into zeolites, e.g. Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$,[8–9] while the defects in the alumina phase are related to the formation of Lewis acid sites (LAS) on the surface of ASAs due to the intrinsic inhomogeneity. LAS are able to abstract hydride or electron-rich groups (i.e. –OH) to form carbenium ions, and to drive the hydrocarbon reactions.[10–11] Therefore, characterizing the type and population density of surface acid sites, as well as their local structure is of great importance.

Solid-state NMR is widely used for investigating the acidic properties of silica-aluminas.[4,12] The density of BAS in zeolites can be determined by simulating the corresponding ^{1}H NMR spectra due to the low-field shift of the signals of bridging OH groups (BAS in zeolites), which can be clearly distinguished from the signals of weakly acidic SiOH groups.[7,9] Unlike, in zeolites the ^{1}H magic-angle-spinning (MAS) NMR signals of acidic OH groups in ASAs are often strongly overlapped by those of SiOH groups, which can be probed via adsorption of strongly basic probe molecules, such as ammonia. Adsorption of ammonia at BAS can generate ammonium ions with a well-distinguishable signal at low field (δ_{1H} = 6.5–7.0 ppm), which can be utilized to quantify the density of BAS on ASAs.[13–14]

However, the direct characterization of LAS of silica-aluminas is challenging. ^{13}C MAS NMR spectroscopy using 2-^{13}C-acetone as probe molecule is useful to identify the presence of BAS and LAS on silica-aluminas, providing chemical shifts of the carbonyl atoms at δ_{13C} = 213–225 ppm and 233–245 ppm,

[a] Dr. Z. Wang, Dr. Y. Jiang
Department of Engineering
Macquarie University
Sydney NSW-2109 (Australia)
[b] Dr. Z. Wang, Prof. J. Huang
Laboratory for Catalysis Engineering
School of Chemical and Biomolecular Engineering & Sydney Nano Institute
The University of Sydney
Sidney NSW-2006 (Australia)
E-mail: jun.huang@sydney.edu.au
[c] Prof. C. Stampfl
School of Physics
Sydney University
Sidney NSW-2006 (Australia)
[d] Prof. A. Baiker
Department of Chemistry and Applied Bioscience
ETH Zürich
Zürich CH-8093 (Switzerland)
[e] Prof. M. Hunger
Institute of Chemical Technology
University of Stuttgart
Stuttgart D-70550 (Germany)



This publication is part of a Special Collection on "Advanced Microscopy and Spectroscopy for Catalysis". Please check the ChemCatChem homepage for more articles in the collection.

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

respectively.[4] However, on strong LAS, acetone can be rapidly converted via aldol reactions, as reported for alumina and silica-zirconia.[15–16] ^{31}P NMR spectroscopy is another often applied technique in the study of surface acid sites, using trimethylphosphine (TMP) and trimethylphosphine oxide (TMPO) as probe molecules.[8,17] Since TMP is a toxic agent, the use of TMPO is more favorable. BAS with various strengths can be well determined via the ^{31}P MAS NMR shifts of adsorbed TMPO. However, the application of TMPO in the study of LAS is biased by the similar ^{31}P MAS NMR shifts with physisorbed TMPO on silica-alumina.[18–19]

Recently, ASAs before and after ammonia loading has been characterized by ^{27}Al-{^{1}H} dipolar-mediated heteronuclear multiple quantum correlation (D-HMQC) two-dimensional (2D) NMR experiments.[3] Upon loading with ammonia, the correlation between the occurrence of Al^{IV}/Al^{V} species and NH_4^+ ions revealed the formation of BAS based on the interaction of Al^{IV}/Al^{V} with neighboring SiOH groups, which has been evidenced by various DNP-enhanced homonuclear and heteronuclear correlation NMR experiments.[20] Moreover, correlations between the occurrence of Al^{IV}/Al^{V} species and ^{1}H MAS NMR signals at δ_{1H} = 2.2–2.6 ppm are also detected in ammonia-loaded ASAs. Ammonia is a Lewis base, which can be adsorbed at both BAS and LAS, and thus, the signals at δ_{1H} = 2.2–2.6 ppm are considered to be ammonia adsorbed at LAS. Since ammonia can be strongly adsorbed on LAS without further conversion, it is a potential candidate for the characterization of these sites.

Bifunctional BAS-LAS catalysts are widely used in the conversion of various platform chemicals to valuable products, for instance, biomass-derived dihydroxyacetone and glyceraldehyde can be readily converted into alkyl lactates.[21–23] The reaction mechanisms based on steam-treated zeolites suggested that these C_3 sugars are involved in a cascade reaction consisting of dehydration at BAS and an alcohol addition at LAS.[24] ASAs possess both BAS and LAS. Moreover, the improvement of the mass transfer by enhanced reactant/product diffusion provides ASAs excellent catalytic activity compared to zeolites, even at lower acidity.[25] Therefore, ASAs are potential high-performance catalysts for these bifunctional BAS-LAS reactions.

In this work, the interaction between ammonia and surface acid sites on ASAs has been studied by various solid-state NMR techniques. The interaction between ammonia and LAS on ASAs with various Si/Al ratios has been revealed by diverse ^{1}H MAS NMR experiments before and after ammonia loading and different desorption temperatures. The catalytic performance of ASAs was tested for the dehydration of a biomass-derived feedstock (cyclohexanol), where the ASA catalysts were shown to provide reaction rates 1–2 orders of magnitude higher than those prepared via conventional co-precipitation, atomic layer deposition (ALD) and chemical liquid deposition (CLD) techniques. Moreover, the concerted action of BAS and LAS provides ASAs with excellent catalytic performance in the conversion of glyceraldehyde, which is superior to that of dealuminated zeolites.

2. Results and Discussion

Solid-state NMR investigations. ^{27}Al solid-state NMR investigations of silica-aluminas are often performed using hydrated samples, which can reduce quadrupolar interactions of hydrated ^{27}Al atoms (spin I = 5/2) leading to a lower line broadening. In catalytic reactions, however, ASAs are often used in the dehydrated state, which results in a stronger coordination transfer as widely reported.[26–27] Therefore, the ^{27}Al MAS NMR spectra shown in Figure 1 were recorded with dehydrated ASAs. Only very broad and weak signals were detected for dehydrated SA/5x and SA/10x (SA/Xx stands for silica-alumina, X specifies atom% of Al and x indicates that xylene was used as a solvent in the flame-spray pyrolysis). The strong line broadening indicates that the Al species in SA/10x are involved in strong quadrupolar interactions. For ASAs with Al contents lower than 10%, a lack of correlation signals between Al species has been probed by ^{27}Al double-quantum single-quantum (DQ/SQ) NMR experiments (not shown). In terms of the homogeneous distribution of Al and Si at low Al contents,[26] it indicates that the Al species in these samples are well-distributed in the silica network. SiOH groups in the local structure of Al species inside the silica networks of ASAs can remarkably increase the local electric field gradient at the Al site, resulting in a strong quadrupole coupling constant C_{QCC}. Therefore, these Al species are assigned to Al species that are well-distributed throughout the silica network with neighboring SiOH groups. The signals of these ^{27}Al species are strongly enhanced with increasing Al content up to 70%. In order to safely identify the different ^{27}Al species in these ASA samples, ^{27}Al 3QMAS NMR experiments were carried out.[28] As shown in Figure 2, three signals at 56.7, 27.7, and 3.6 ppm could be identified, which were assigned to

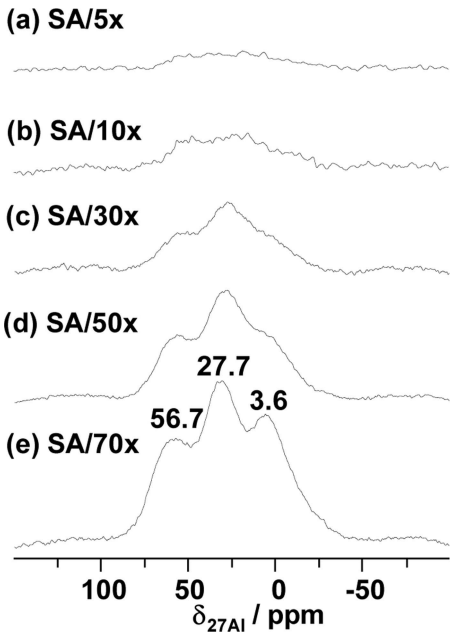


Figure 1. ^{27}Al MAS NMR spectra of ASAs: (a) SA/5x, (b) SA/10x, (c) SA/30x, (d) SA/50x, and (e) SA/70x. Recorded after SAx dehydrated at 723 K for 12 h at a pressure of less than 10^{-2} bar.

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

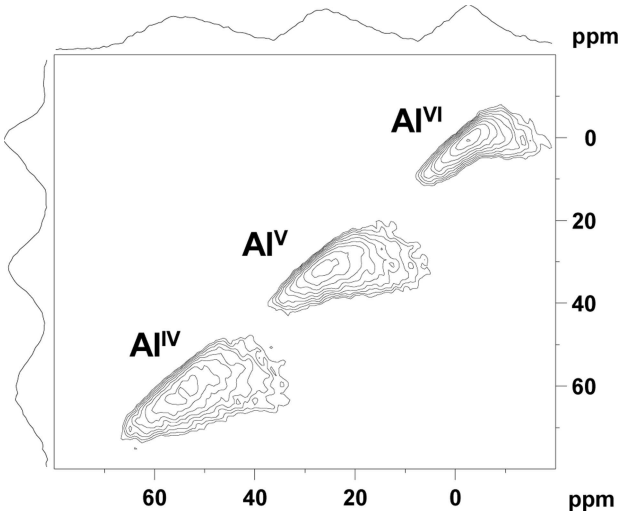


Figure 2. ^{27}Al MQMAS NMR spectrum of dehydrated SA/70x.

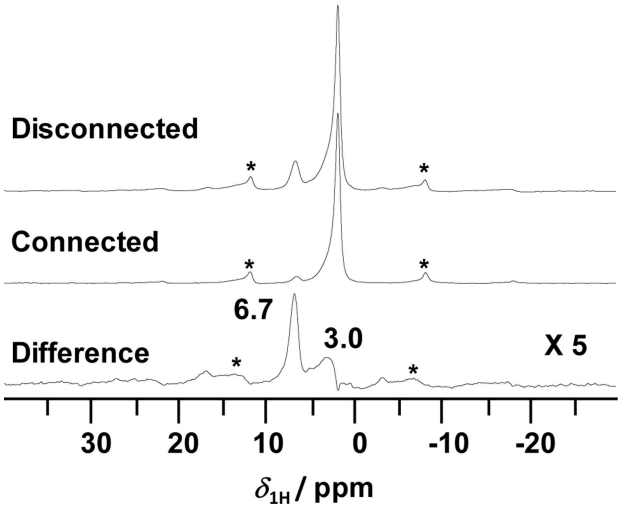


Figure 3. ^{1}H/^{27}Al TRAPDOR MAS NMR spectra of dehydrated and ammonia-loaded SA/70x recorded without (top) and with (middle) ^{27}Al irradiation.

Al^{IV}, Al^{V}, and Al^{VI} species, respectively. It has been widely accepted that BAS are formed by SiOH groups having Al^{IV}/Al^{V} species in the vicinity.[3] The presence of Al^{V} and Al^{VI} species is often related to the formation of Al domains in the ASAs, which may lead to the formation of surface LAS.[29–30]

A high distribution of Al atoms in the silica network of ASAs can enhance the acid strength of neighboring SiOH groups, acting as BAS. The incorporation of Al atoms has been demonstrated by a simultaneous low chemical shift of silica signals in the Si MAS NMR spectra.[31] The spatial proximities of Al atoms and neighboring SiOH groups could be directly probed by ^{1}H/^{27}Al TRAPDOR MAS NMR experiments. As recently reported,[28] mainly a ^{1}H MAS NMR signal at $\delta_{1H}=1.8$ ppm was observed in the difference spectra obtained without and with Al irradiation for dehydrated SA/70x without ammonia loading. This finding demonstrates that some of the SiOH groups ($\delta_{1H}=$ 1.8 ppm) are in proximity to Al atoms, while no strong signals of AlOH groups could be observed.[4] The incorporation of Al atoms in the local structure of SiOH groups withdraws electron density from neighboring oxygen atoms, thereby enhancing the acid strength of the SiOH groups acting as BAS. These BAS can protonate adsorbed NH_3 into ammonium ions ($\delta_{1H}=$ 6.7 ppm). As shown in Figure 3, the difference spectrum recorded in the ^{1}H/^{27}Al TRAPDOR MAS NMR experiment of ammonia-loaded SA/70x sample demonstrates that ammonium ions ($\delta_{1H}=6.7$ ppm) are formed in proximity to surface Al species that are involved in BAS. Interestingly, a signal at $\delta_{1H}=$ 3.0 ppm was also detected in the difference spectrum, which was not observed in the previous spectrum without ammonia loading. This signal is accompanied by strong and broad spinning sidebands, which was not observed with SiOH groups or BAS. The strong and broad sidebands indicate that ammonia molecules are strongly adsorbed on these surface sites, i.e. on surface LAS via electron pairs.[32]

The signal at $\delta_{1H}=3.0$ ppm was further investigated using ASAs with different Al content. As shown in Figure 4, the signal

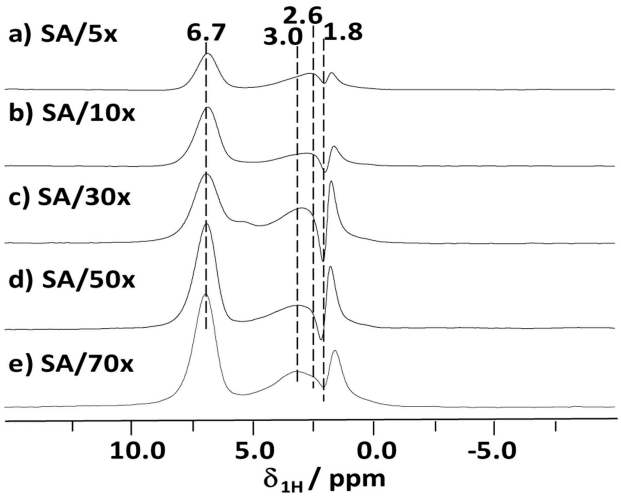


Figure 4. ^{1}H MAS NMR difference spectra recorded before and after ammonia loading on dehydrated ASAs with different Al content.

of ammonium ions at $\delta_{1H}=6.7$ ppm became more prominent with increasing Al content up to 70%. Moreover, a decrease of the signal at $\delta_{1H}=1.8$ ppm confirmed that BAS are generated from acidic SiOH groups in ASAs. The signal at $\delta_{1H}=2.6$ ppm was observed with ASAs having Al contents of $\leq$10%. This signal gradually shifted to $\delta_{1H}=3.0$ ppm with increasing Al content up to 70%. The signal at $\delta_{1H}=2.6$ ppm is caused by the formation of hydrogen-bonded SiOH groups, which decreases sharply with increasing Al content.[33] With increasing Al content, Al domains are formed in the ASA particles, as indicated by the occurrence of Al^{VI} species. Defect sites in Al domains are related to the formation of LAS. The low-field shift of the ammonia signal from 2.6 to 3.0 ppm indicates the formation of surface LAS with increasing strength. These observations are in line with those of ^{13}C MAS NMR investigations using 2-^{13}C-acetone as probe molecules.[31] In the

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

above-mentioned work, virtually no LAS could be detected on SA/10x, while significant amounts of LAS were generated on SA/70x.

The properties of BAS and LAS of the ASAs were further studied after desorption of ammonia at different evacuation temperatures. As shown in Figure 5, the ammonium ions at former BAS were decomposed resulting in a rapid release of ammonia with increasing evacuation temperature from 383 K to 523 K, while the signal at 3.0 ppm was only slightly affected. This behavior suggests strong adsorption of ammonia at surface LAS, which are more stable adsorbate complexes than ammonium ions formed at BAS. After evacuation at 623 K, both the ammonia adsorbed at BAS and LAS are desorbed.

For adsorption of ammonia at LAS of dealuminated H-ZSM-5, Yin *et al.* reported a ^{1}H MAS NMR signal at $\delta_{1H}=2.6$ ppm corresponding to an IR band at 1625 cm^{-1}.[34] For ammonia adsorption at LAS on MCM-22, such as Lewis acidic Al^{3+} ions, a ^{1}H MAS NMR signal at ca. $\delta_{1H}=4.6$ ppm was observed, which was confirmed by ^{31}P MAS NMR studies.[30] The difference in the chemical shifts of the above-mentioned ^{1}H MAS NMR signals can be explained by the presence of Al ions with various Lewis acid strength. More recently, Lang *et al.* performed a systematic study of alumina and metal-exchanged zeolites using various probe molecules, such as 2-^{13}C-acetone, TMPO, and ammonia.[32] By comparison with the results of other probe molecules, these authors suggested that adsorption of ammonia on LAS causes ^{1}H MAS NMR signals in the chemical shift range of $\delta_{1H}=-0.5$ to 3.0 ppm, which agrees well with the current observation of ammonia adsorbed on LAS in ASAs.

In summary, the signal at ca. $\delta_{1H}=3.0$ ppm was identified as LAS on flame-made SAx with an Al content above 30%, while the signal at ca. $\delta_{1H}=2.2$–2.6 ppm was assigned to hydrogen-bonded SiOH groups at an Al content less than 10%. Therefore, the signal intensities at ca. $\delta_{1H}=3.0$ ppm in the corresponding ^{1}H MAS NMR spectra were utilized to quantified the density of LAS on flame-made SAx, as shown in Figure 6 and summarized in Table 1. In line with the spectra shown in Figure 4, the density of LAS strongly increased with increasing Al content in SAx, as expected.

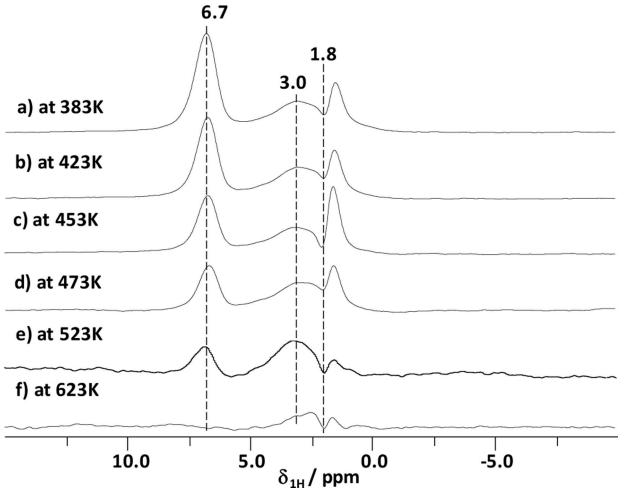


Figure 5. ^{1}H MAS NMR difference spectra of dehydrated and ammonia-loaded SA/70x, recorded after evacuated at a temperature of (a) 383 K, (b) 423 K, (c) 453 K, (d) 473 K, (e) 523 K, and (f) 623 K.

Cyclohexanol dehydration. The catalytic activity of ASA materials was examined using the cyclohexanol dehydration, a frequently applied test reaction for silica-alumina catalysts.[35,37] The results of these studies are summarized in Table 1. Al_2O_3 was used as a reference catalyst because of the presence of large amounts of alumina in some of the ASA materials under study. In agreement with a previous report,[35] Al_2O_3 proved to be virtually inactive under the conditions used, i.e. offering much lower cyclohexanol conversion (1.5%) than those obtained with ASA catalysts (6–30%). As shown in Table 1, SA/10x exhibits a cyclohexanol conversion of 18.9%, which is over 2 times higher than that achieved with an ALD-prepared ASA or ASAs made by conventional co-precipitation method. The cyclohexanol conversion increased with increasing Al content of the flame-made ASAs, which may be attributed to an enhanced BAS strength, as observed earlier.[31] The lower conversion obtained with SA/70x is likely due to the formation of some alumina phase domains at the surface (*vide supra*), which may affect the surface diffusion of reactant molecules.

Table 1. Catalytic reaction results of cyclohexanol (CH) dehydration over ASA catalysts prepared by different methods. TOF: CH molecules converted per BAS and per second. R: rate of CH conversion per unit surface area of ASA and per second.[a]

	Surface area [m^2 g^{-1}]	BAS[c] [mol g^{-1}]	LAS[d] [mol g^{-1}]	Conversion [%]	Selectivity [%]	TOF [BAS s^{-1}]	*R* [mol m^{-2} s^{-1}]	Ref.
Al_2O_3			–	1.5		–	1.6×10^{-8}	This work
SA/30[b,c]	286	5.2×10^{-2}	–	7.2	94.8	0.006	1.0×10^{-6}	This work
SA/10[c]	344	8.4×10^{-2}	–	5.9	98.2	0.003	7.2×10^{-7}	This work
SA/70x	241	19.8×10^{-2}	26.3×10^{-2}	25.4	38.1	0.011	8.8×10^{-6}	This work
SA/50x	267	15.8×10^{-2}	15.0×10^{-2}	29.1	47.5	0.015	9.1×10^{-6}	This work
SA/30x	289	14.8×10^{-2}	12.5×10^{-2}	23.6	84.1	0.013	6.8×10^{-6}	This work
SA/10x	369	7.4×10^{-2}	–	18.9	95.3	0.021	4.3×10^{-6}	This work
ALD ASA			–	9.1			6.6×10^{-8}	Ref.[35]
CLD ASA			–			–	4.7×10^{-8}	Ref.[35]

[a] Reaction conditions: catalyst (0.04 g) was added into 2 mL of cyclohexane solution containing 0.1 mmol cyclohexanol, the reaction was carried out at 448 K for 10 min. The reaction rate was determined using the conversion at this time, [b] ASAs were prepared by a conventional co-condensation method,[36] [c] The number of BAS of ASA samples was determined by quantitative ^{1}H MAS NMR measurement. Before measurement, the samples were dehydrated at 723 K, followed by ammonia loading and evacuated at 393 K for 1 h. BAS of flame-made SAs were determined in the same way and obtained from ref [31], [d] LAS were determined by quantitative ^{1}H MAS NMR measurement with the signal intensity at ca. $\delta_{1H}=3.0$ ppm shown in Figure 6.

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

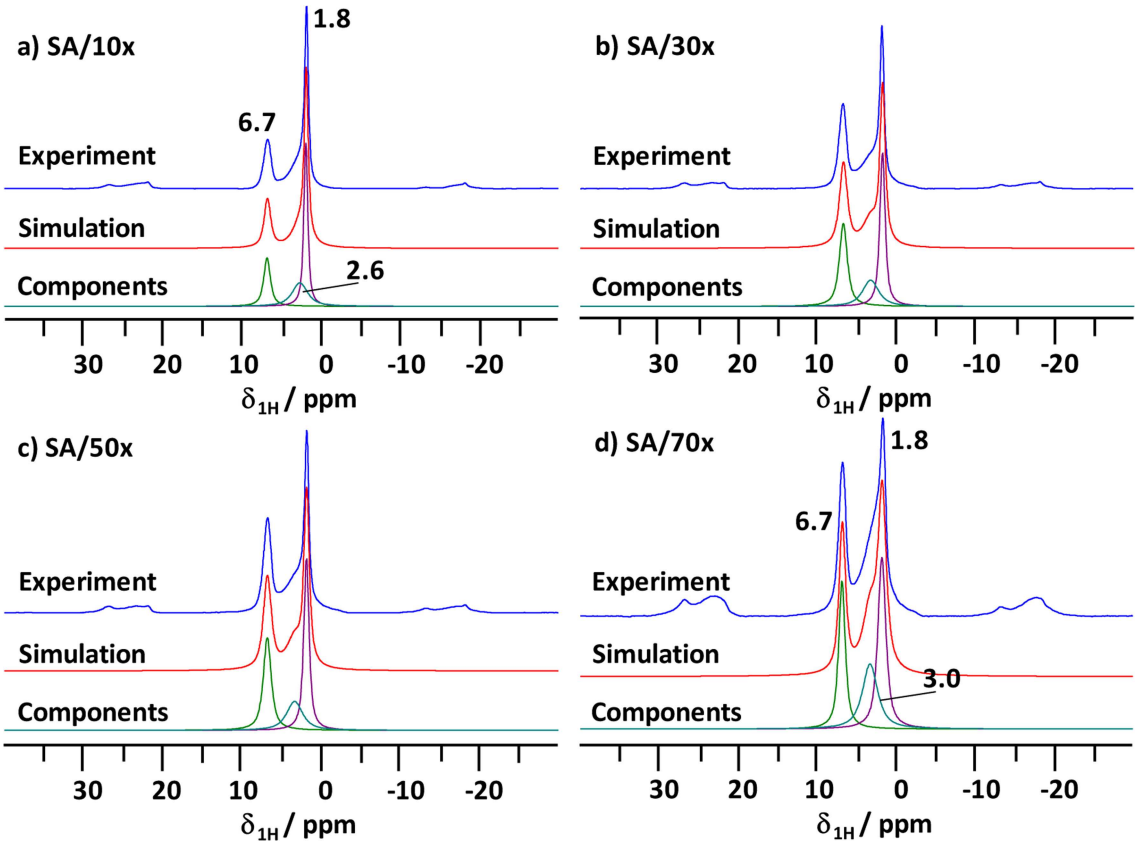


Figure 6. ^{1}H MAS NMR spectra of dehydrated and ammonia-loaded ASAs (a) SA/10x, (b) SA/30x, (c) SA/50x and (d) SA/70x, recorded after evacuated at 383 K.

The catalytic performance of ASAs was also evaluated by comparing the rates of cyclohexanol dehydration. SA/10x and SA/30x provided 7 times higher reaction rates than their co-condensed counterparts. With SAx materials, further improvement of the catalytic performance could be achieved by increasing the Al content up to 50%. A similar reaction rate was obtained with SA/70x, in spite of its higher BAS surface density compared to SA/50x. Again, this can be attributed to the presence of larger alumina phase domains in SA/70x, which can adsorb cyclohexanol and slow down its surface diffusion. The SAx catalysts yielded reaction rates that were two orders of magnitude higher than those of ASA catalysts prepared by surface modification methods, such as ALD and CLD.[35] We attribute this difference to the smaller particle size and higher surface area of ASAs prepared by flame spray pyrolysis (241–369 m^2/g, 7–20 nm) compared to those synthesized via commercial γ-alumina (60 m^2/g, <3 μm),[35] and to the larger number of BAS due to the homogeneous distribution of Al sites. In addition, the cyclohexanol dehydration reaction requires only moderate Brønsted acidity while strong Brønsted acidity can result in side reactions.[37] In flame-made SAx catalysts, the BAS strength is strongly enhanced with increasing Al content,[31] leading to a decrease of the cyclohexene selectivity as shown in Table 1. The high selectivity achieved with SA/10 and conventional ASAs is attributed to their moderate Brønsted acidity. Since cyclohexanol conversion is mainly catalyzed by BAS, we have also examined the bifunctional properties of the flame-made SAx catalysts, using the conversion of glyceraldehyde in alcohols as an example.

Glyceraldehyde conversion in ethanol. The catalytic results of the glyceraldehyde conversion in ethanol are summarized in Table 2. Dealuminated HY zeolite (De–Al-HY) and parent HY zeolites were used as references. De–Al-HY exhibits much higher activity than the parent HY zeolite, which is attributed to the presence of extra-framework Al species in the De–Al-HY zeolite.[38]

Table 2. Catalytic reaction results of glyceraldehyde conversion in ethanol over ASA catalysts.[a]

	Conversion	Yield	Selectivity	TOF[b]
SA/10x	43	41	90	36.9
SA/30x	49	47	96	21.2
SA/50x	66	65	99	27.4
SA/70x	65	63	97	21.2
HY	8	6	4	–
De–Al–HY	51	46	89	3.9

[a] Conditions: 1.25 mL aqueous ethanol (water/ethanol = 1:1 in volume ratio) solution containing 0.25 M glyceraldehyde, 0.05 g catalyst, at 363 K for 6 h with stirring. [b] Dealuminated zeolite De–Al–HY (Si/Al = 5.4) was obtained by steaming zeolite H–Y (Si/Al = 2.7) at 748 K for 2.5 h, having BAS density of 0.865 mmol/g,[40] [b] Average TOFs were calculated on the basis of Brønsted density and the conversion after 6 h of reaction.

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Over ASA catalysts, the enhanced acidity at higher Al contents can strongly promote the conversion of glyceraldehyde. It is well-known that BAS promote the glyceraldehyde dehydration, which is in line with the increasing conversion. The similar conversion obtained with both SA/50x and SA/70x could be attributed to the presence of stronger LAS, which affects the surface diffusion of glyceraldehyde. Glyceraldehyde dehydration results in pyruvic aldehyde, which undergoes redox disproportionative conversion with ethanol to form ethyl lactate at LAS. As shown in ^{1}H MAS NMR studies, SAx exhibits an enhanced Lewis acidity with increasing Al content. Therefore, the yield of ethyl lactate is expected to be enhanced at higher Al contents, which is well in line with the catalytic results. As shown in Table 2, all SAx catalysts provide high ethyl lactate selectivity over 90%. The yield of ethyl lactate increased from 41% to 65%, with increasing Al content. For comparison, SA/50x, with much lower Brønsted and Lewis acidity, afforded 15% higher conversion and 19% higher yield after 6 h of reaction than the De–Al-HY zeolite. The SAx catalysts exhibited a slightly lower yield but higher selectivity to ethyl lactate than those reported in the literature using dealuminated zeolites (yield of 76% and selectivity of 83%).[38] The lower performance of SAx catalysts could be attributed to the weak acidity and lower reaction temperature applied in this work.

A comparison of the average turnover frequencies (TOFs) confirms the high activity of SAx in glyceraldehyde conversion (Table 2). The average TOFs obtained with SAx were in the range of 21.2 ~ 36.9 h^{-1}, which is up to ~10 times higher than that achieved with De–Al-HY (3.9 h^{-1}). Since SAx possess both lower acidity and surface areas compared to the De–Al-HY zeolite, the excellent activity of the non-porous SAx catalysts is attributed to the high external diffusion rates of reactant and product compared to the constrained internal diffusion occurring in the cages and narrow channels of zeolites. The absence of pore diffusion limitations in the SAx catalysts facilitates high TOFs similar to those reported earlier.[25,39]

3. Conclusions

The acidic properties of flame-made ASAs have been examined using solid-state NMR methods in combination with ammonia as probe molecules. We show that BAS can be identified and quantified via the ^{1}H MAS NMR signals of ammonium ions formed at these sites, and that ammonia adsorbed at LAS on ASAs result in signals with a chemical shift of $\delta_{1H} = 2.6–3.0$ ppm, providing an alternative method for characterizing LAS on ASAs.

The flame-made ASAs under study exhibit excellent catalytic performance in the dehydration of cyclohexane and the conversion of glyceraldehyde to ethyl lactate. The enhanced Brønsted acidity promotes the cyclohexane dehydration providing TOFs up to 7 times higher than those obtained with their co-condensed counterparts and 20 times higher reaction rates based on unit surface area (mol m^{-2} s^{-1}) than those prepared by ALD and CLD. In the conversion of glyceraldehyde to ethyl lactate, the flame-made ASAs, which contain both BAS and LAS, afford a yield up to 65% at 66% glyceraldehyde conversion, a performance higher than that achieved with dealuminated zeolite HY with stronger Brønsted and Lewis acidity.

Experimental Section

Preparation of ASAs. Aluminum acetylacetonate ($Al(acac)_3$, purity ≥99.9%), tetraethyl orthosilicate (TEOS) (purity ≥99.9%), and xylene (purity ≥98.5%) were all purchased from Sigma-Aldrich and used for producing the amorphous silica-alumina catalysts. The precursor solutions used for the preparation of ASAs by flame-spray pyrolysis (FSP) technique were obtained by dissolving appropriate amounts of the precursor materials in xylene (0.5 M concentration by metal), followed by filtration using a glass filter. Then, the FSP precursor solutions were applied in the FSP process as described previously.[33] In brief, the precursor solutions were pumped through a capillary at a rate of 5 mL/min, and nebulized in 5 L/min O_2. The resulting spray was ignited by an annular supporting methane/oxygen flame (1.5/0.9 L/min). Particles were collected on a cooled Whatman GF6 filter (257 mm diameter). A Busch SV 1040C vacuum pump aided in particle recovery. The synthesized silica-alumina powders are designated as SA/Xx, where X is 5, 10, 30 and 70, representing the atom% of Al in the precursor and x indicates the use of xylene as solvent to distinguish from the methanol/acetic acid (denoted as SA/X) used in the earlier work.[33]

Solid-state NMR investigations. Before the ^{1}H and ^{27}Al MAS NMR experiments, the samples filled into glass tubes were dehydrated at 723 K for 12 h at a pressure of less than 10^{-2} bar. These dehydrated samples were sealed in glass tubes or directly loaded with ammonia on a vacuum line. Subsequently, the loaded samples were evacuated at 383 K for 1 h to remove weakly physisorbed molecules. Then, the samples were transferred into the MAS NMR rotors under dry nitrogen gas inside a glove box. ^{1}H and ^{27}Al MAS NMR investigations were performed on a Bruker Avance III 400 WB spectrometer with a 9.4 Tesla superconducting magnet operating at resonance frequencies of 400.1 and 104.3 MHz, respectively, with a sample-spinning rate of 8 kHz using 4 mm MAS rotors. ^{1}H MAS NMR spectra were recorded after single-pulse $\pi/2$ excitation with a repetition time of 20 s. ^{27}Al MAS NMR spectra were recorded after single-pulse $\pi/6$ excitation with a repetition time of 0.5 s.

^{27}Al MQMAS NMR spectra were recorded on a Bruker Avance III 700 spectrometer with a 16.4 Tesla superconducting magnet operating at a resonance frequency of 182.5 MHz and 700 MHz for ^{27}Al and ^{1}H nuclei, respectively. The samples were packed into 4 mm zirconia MAS rotors inside a glove box to prevent any exposure to ambient air and moisture. The MAS rotors were spun with 14 kHz in a 4 mm H–X double resonance probe. The MQMAS spectra were acquired using a three-pulse z-filter sequence.[28] The 2D spectra were sheared with xfshear program. Excitation and reconversion pulses lasted $\tau_p = 4.2$ and 1.4 μs, respectively, with $\nu_{rf} = 100$ kHz, the central-transition (CT) selective $\pi/2$ last pulse was 20 μs with $\nu_{rf} =$ 4.17 kHz, and a repetition time of 0.3 s was used.

Cyclohexanol dehydration. Dehydrated (activated) ASA catalysts (0.04 g) were added to a 2 mL cyclohexane (CH) solution containing 0.1 mmol of cyclohexanol in a glass pressure reactor. 10 mg of adamantane was used as an internal standard. The reaction was carried out in an oil bath at 448 K under stirring for ca. 10 min. The reaction mixture was then cooled down to room temperature for sample collection. Reaction products were analyzed using a Shimadzu GCMS QP2010 Ultra (Rtx-5MS column 30 m × 0.25 mm × 0.25 μm) and a Shimadzu GC2010 (25QC3/BP1 column 25 m × 0.32 mm × 5 μm).

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Glyceraldehyde conversion in ethanol. Before reaction, the catalysts (0.05 g) were activated at 723 K under N_2 flow of 150 mL/min for 3 h. In a typical run, the activated catalyst (0.05 g) was transferred into a pressure vessel, together with an ethanol solution (5 mL) containing glyceraldehyde (0.4 M). The reaction was carried out in a tightly closed pressure vessel, under controlled temperature for 6 h under stirring. The reaction products were collected at regular time intervals and prepared in ethanol for GC analysis. A Shimadzu GCMS-QP2010 Ultra furnished with a RTX-5MS capillary column (30 m $\times$0.25 mm$\times$0.25 μm) and a Shimadzu GC-FID equipped with a RTX-5 capillary column (25 m $\times$0.32 mm$\times$5 μm) were employed for the product determination and quantification, respectively. The selectivity *Si* to specific product *i* was calculated as S_i (%) = 100$\times$(*i*)/[(glyceraldehyde)$_0$-(glyceraldehyde)], where (*i*) is the molar concentration of the product and (glyceraldehyde)$_0$ and (glyceraldehyde) correspond to the molar concentration of glyceraldehyde before and after the reaction, respectively.

Acknowledgments

This work was supported by the Australian Research Council Discovery Projects (DP150103842) and Discovery Earlier Career Research Project (DE190101618), and SOAR fellowship from the University of Sydney.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: silica-alumina · acidity · solid-state NMR · cyclohexane dehydration · glyceraldehyde conversion

[1] G. Busca, *Chem. Rev.* **2007**, *107*, 5366–5410.
[2] Y. Li, L. Li, J. H. Yu, *Chem* **2017**, *3*, 928–949.
[3] Z. C. Wang, Y. J. Jiang, O. Lafon, J. Trebosc, K. D. Kim, C. Stampfl, A. Baiker, J. P. Amoureux, J. Huang, *Nat. Commun.* **2016**, *7*, 13820.
[4] Y. Jiang, J. Huang, W. Dai, M. Hunger, *Solid State Nucl. Magn. Reson.* **2011**, *39*, 116–141.
[5] G. A. Olah, *Angew. Chem. Int. Ed.* **1973**, *12*, 173–212.
[6] Z. Wang, H. Ling, J. Shi, C. Stampfl, A. Yu, M. Hunger, J. Huang, *J. Catal.* **2018**, *358*, 71–79.
[7] Z. C. Wang, L. Wang, Z. Zhou, Y. Y. Zhang, H. T. Li, C. Stampfl, C. H. Liang, J. Huang, *J. Phys. Chem. C* **2017**, *121*, 15248–15255.
[8] X. Yi, K. Liu, W. Chen, J. Li, S. Xu, C. Li, Y. Xiao, H. Liu, X. Guo, S. B. Liu, A. Zheng, *J. Am. Chem. Soc.* **2018**, *140*, 10764–10774.
[9] Z. Wang, L. Wang, Y. Jiang, M. Hunger, J. Huang, *ACS Catal.* **2014**, *4*, 1144–1147.
[10] J. Huang, Y. Jiang, V. R. R. Marthala, M. Hunger, *J. Am. Chem. Soc.* **2008**, *130*, 12642–12644.
[11] K. Larmier, C. Chizallet, S. Maury, N. Cadran, J. Abboud, A. F. Lamic-Humblot, E. Marceau, H. Lauron-Pernot, *Angew. Chem. Int. Ed.* **2017**, *56*, 230–234; *Angew. Chem.* **2017**, *129*, 236–240.
[12] A. M. Zheng, S. H. Li, S. B. Liu, F. Deng, *Acc. Chem. Res.* **2016**, *49*, 655–663.
[13] Z. Wang, S. Pokhrel, M. Chen, M. Hunger, L. Mädler, J. Huang, *J. Catal.* **2013**, *302*, 10–19.
[14] K. D. Kim, S. Pokhrel, Z. C. Wang, H. J. Ling, C. F. Zhou, Z. W. Liu, M. Hunger, L. Madler, J. Huang, *ACS Catal.* **2016**, *6*, 2372–2381.
[15] Z. Wang, Y. Jiang, M. Hunger, A. Baiker, J. Huang, *ChemCatChem* **2014**, *6*, 2970–2975.
[16] A. I. Biaglow, R. J. Gorte, D. White, *J. Catal.* **1994**, *150*, 221–224.
[17] A. Zheng, S. B. Liu, F. Deng, *Chem. Rev.* **2017**, *117*, 12475–12531.
[18] S. Hayashi, K. Jimura, N. Kojima, *Microporous Mesoporous Mater.* **2014**, *186*, 101–105.
[19] E. F. Rakiewicz, A. W. Peters, F. Wormsbecher, K. J. Sutovich, K. T. Mueller, *J. Phys. Chem. B* **1998**, *102*, 2890–2896.
[20] F. A. Perras, Z. Wang, T. Kobayashi, A. Baiker, J. Huang, M. Pruski, *Phys. Chem. Chem. Phys.* **2019**, *21*,19529–19537.
[21] F. de Clippel, M. Dusselier, R. Van Rompaey, P. Vanelderen, J. Dijkmans, E. Makshina, L. Giebeler, S. Oswald, G. V. Baron, J. F. M. Denayer, P. P. Pescarmona, P. A. Jacobs, B. F. Sels, *J. Am. Chem. Soc.* **2012**, *134*, 10089–10101.
[22] Z. Wang, J. Huang, *Production of Biofuels and Chemicals with Bifunctional Catalysts* (Ed.: Z. Fang, R. L. Smith Jr., Springer Nature, Singapore, **2017**, pp. 99–136.
[23] K. D. Kim, Z. Wang, Y. Jiang, M. Hunger, J. Huang, *Green Chem.* **2019**, *21*, 3383–3393.
[24] R. M. West, M. S. Holm, S. Saravanamurugan, J. Xiong, Z. Beversdorf, E. Taarning, C. H. Christensen, *J. Catal.* **2010**, *269*, 122–130.
[25] Z. Wang, Y. Jiang, A. Baiker, J. Huang, *ACS Catal.* **2013**, *3*, 1573–1577.
[26] Z. Wang, Y. Jiang, X. Yi, C. Zhou, A. Rawal, J. Hook, Z. Liu, F. Deng, A. Zheng, M. Hunger, A. Baiker, J. Huang, *Sci. Bull.* **2019**, *64*, 516–523.
[27] A. Omegna, J. A. van Bokhoven, R. Prins, *J. Phys. Chem. B* **2003**, *107*, 8854–8860.
[28] J. P. Amoureux, C. Fernandez, S. Steuernagel, *J. Magn. Reson. Ser. A* **1996**, *123*, 116–118.
[29] D. Coster, A. L. Blumenfeld, J. J. Fripiat, *J. Phys. Chem.* **1994**, *98*, 6201–6211.
[30] D. Ma, X. W. Han, S. J. Xie, X. H. Bao, H. B. Hu, S. C. F. Au-Yeung, *Chem. Eur. J.* **2002**, *8*, 162–170.
[31] Z. Wang, Y. Jiang, F. Jin, C. Stampfl, M. Hunger, A. Baiker, J. Huang, *J. Catal.* **2019**, *372*, 1–7.
[32] S. Lang, M. Benz, U. Obenaus, R. Himmelmann, M. Hunger, *ChemCatChem* **2016**, *8*, 2031–2036.
[33] J. Huang, N. van Vegten, Y. Jiang, M. Hunger, A. Baiker, *Angew. Chem. Int. Ed.* **2010**, *49*, 7776–7781; *Angew. Chem.* **2010**, *122*, 7942–7947.
[34] F. Yin, A. L. Blumenfeld, V. Gruver, J. J. Fripiat, *J. Phys. Chem. B* **1997**, *101*, 1824–1830.
[35] D. Ma, X. W. Han, S. J. Xie, X. H. Bao, H. B. Hu, S. C. F. Au-Yeung, *Chem. A Euro. J.* **2002**, *8*, 162–170.
[36] A. R. Mouat, C. George, T. Kobayashi, M. Pruski, R. P. van Duyne, T. J. Marks, P. C. Stair, *Angew. Chem. Int. Ed.* **2015**, *54*, 13346–13351; *Angew. Chem.* **2015**, *127*, 13544–13549.
[37] J. Datka, B. Gil, O. Vogt, J. Rakoczy, *Stud. Surf.Sci. Catal., Vol. 125* (Eds.: I. Kiricsi, G. PalBorbely, J. B. Nagy, H. G. Karge), Elsevier, Amsterdam **1999**, pp. 409–415.
[38] P. P. Pescarmona, K. P. F. Janssen, C. Delaet, C. Stroobants, K. Houthoofd, A. Philippaerts, C. De Jonghe, J. S. Paul, P. A. Jacobs, B. F. Sels, *Green Chem.* **2010**, *12*, 1083–1089.
[39] Z. Wang, Y. Jiang, R. Rachwalik, Z. Liu, J. Shi, M. Hunger, J. Huang, *ChemCatChem* **2013**, *5*, 3889–3896.
[40] J. Huang, Y. J. Jiang, V. R. R. Marthala, Y. S. Ooi, M. Hunger, *ChemPhysChem* **2008**, *9*, 1107–1109.

Manuscript received: September 13, 2019
Revised manuscript received: October 11, 2019
Accepted manuscript online: October 16, 2019
Version of record online: December 3, 2019

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim