Uncovering selective and active Ga surface sites in gallia–alumina mixed-oxide propane dehydrogenation catalysts by dynamic nuclear polarization surface enhanced NMR spectroscopy†

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Gallia–alumina (Ga,Al)2O3 spinel-type solid solution nanoparticle catalysts for propane dehydrogenation (PDH) were prepared with four nominal Ga : Al atomic ratios (1 : 6, 1 : 3, 3 : 1, 1 : 0) using a colloidal synthesis approach. The structure, coordination environment and distribution of Ga and Al sites in these materials were investigated by X-ray diffraction, X-ray absorption spectroscopy (Ga K-edge) as well as 27Al and 71Ga solid state nuclear magnetic resonance. The surface acidity (Lewis or Brønsted) was probed using infrared spectroscopy with pyridine and 2,6-dimethylpyridine probe molecules, complemented by element-specific insights (Ga or Al) from dynamic nuclear polarization surface enhanced cross-polarization magic angle spinning15N{27Al} and 15N{71Ga} J coupling mediated heteronuclear multiple quantum correlation NMR experiments using 15N-labelled pyridine as a probe molecule. The latter approach provides unique insights into the nature and relative strength of the surface acid sites as it allows to distinguish contributions from Al and Ga sites to the overall surface acidity of mixed (Ga,Al)2O3 oxides. Notably, we demonstrate that (Ga,Al)2O3 catalysts with a high Al content show a greater relative abundance of four-coordinated Ga sites and a greater relative fraction of weak/medium Ga-based surface Lewis acid sites, which correlates with superior propene selectivity, Ga-based activity, and stability in PDH (due to lower coking). In contrast, (Ga,Al)2O3 catalysts with a lower Al content feature a higher fraction of six-coordinated Ga sites, as well as more abundant Ga-based strong surface Lewis acid sites, which deactivate through coking. Overall, the results show that the relative abundance and strength of Ga-based surface Lewis acid sites can be tuned by optimizing the bulk Ga : Al atomic ratio, thus providing an effective measure for a rational control of the catalyst performance.

Introduction

The growing demand for propene has motivated its on-purpose production through the propane dehydrogenation reaction (PDH, Scheme 1A). However, catalysts used at the industrial scale, i.e. CrOx/Al2O3 (Catofin process) or PtSn/Al2O3 (Oleflex process), still suffer from shortcomings, such as toxicity.

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Scheme 1 (A) Competing propane dehydrogenation (PDH) and propane cracking reactions. (B) A possible coordination geometry for a GaIV–O–GaIV surface linkage with the attribution of Lewis acidity strength according to the 15N chemical shift of bound pyridine probe molecule.12 SP stands for square pyramidal.

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concerns associated with the use of Cr⁶⁺ and the high cost of Pt.¹,² Catalysts based on gallium oxide (gallia) have been considered as possible alternatives to Cr₂O₃ and PtSn-based PDH catalysts.¹,² More recently, a PtGa/Al₂O₃ catalyst has been developed for the use in the FCDh (fluidized catalytic dehydrogenation) process, which allows energy usage (and therefore the carbon footprint) of PDH to be reduced.³ However, the role of platinum in PtGa catalysts is currently debated, ranging from a promoter of coordinately unsaturated Ga³⁺ active sites,⁴ to the active phase itself, such as site-isolated Pt atoms in metallic PtGa alloyed nanoparticles.⁵

In this context, the atomic-scale understanding of active sites in Ga₂O₃-based PDH catalysts is essential.⁶⁻⁸ It has been argued that the active sites in gallia catalysts are tetra coordinated (Ga₄⁷⁺) Lewis acidic Ga³⁺ surface sites,³⁻⁹ associated with weak Lewis acidity.¹⁰,¹¹ In β-Ga₂O₃, weak Lewis acid sites (LAS, assessed using pyridine as a probe molecule) active in PDH have been attributed to tricoordinated Ga sites (Ga₃m) with a neighboring oxygen vacancy (V₀, when x = 0 in Scheme 1B).¹² In contrast, stronger LAS have been associated with an accelerated catalyst deactivation through coking and linked to pentacoordinated gallia surfaces (Ga₅v, likely with square pyramidal (SP) geometry, formed when surface termination contains Ga in octahedral positions, Scheme 1B).¹³ In addition to coking, another undesired side reaction that competes with PDH is the cracking of propane, which forms methane and ethene (Scheme 1A). Cracking could be caused by either Lewis or Brønsted acidity.¹³ PDH and cracking reactions proceed on different sites in Ga₂O₃ catalysts since the rate of propene formation and propene selectivity decrease with time on stream (TOS) but the selectivity to cracking products and their rate of formation is stable with TOS.¹⁴

One strategy to control the distribution of bulk Ga₄v and Ga₅v sites, and thereby presumably also influence the coordination environment of surface Ga sites, is to exploit (Ga,Al)₂O₃ spinel-type solid solutions as alkane dehydrogenation catalysts.⁶,⁹,¹⁴ In these materials, the bulk Ga₄v : Ga₅v ratio can be varied since Al atoms preferentially occupy octahedral positions in the defect spinel-type structure of Ga₂O₃,¹⁵ increasing thereby the relative fraction of Ga₄v sites (i.e., the proposed active sites). For instance, gallia–alumina mixed oxides prepared by co precipitation demonstrated an improved activity and stability in PDH and lower coke-related deactivation relative to the γ-Ga₂O₃ benchmark.⁹ The reduced deactivation and increased activity might be related to the higher relative fraction of weak LAS in (Ga,Al)₂O₃ (as assessed by NH₃-TPD) and linked to a higher relative density of undercoordinated Ga sites, such as putative Ga₃m sites discussed above.⁹,¹² Note that the alkane dehydrogenation activity of various phases of Al₂O₃ (α-, δ-, γ-, θ-) is generally low and requires a pre-treatment with CO or H₂ at high temperature (600 °C) to become considerable.¹⁶⁻¹⁷ Due to their limited activity, Al₂O₃ catalysts are typically tested in PDH at substantially higher temperatures (600–630 °C) relative to Ga₂O₃ catalysts (550 °C).¹⁶,¹⁸

DFT studies proposed that doping (100) and (110) γ-Al₂O₃ surfaces with Ga could lead to Al-rich gallia–alumina solid solutions with an increased dehydrogenation activity.¹⁹,²⁰ The presence of Ga sites has been suggested to increase the activity of such surfaces by lowering the C–H activation barriers of the kinetically favored concerted alkane dehydrogenation pathway.¹⁹ In addition, the increase in PDH activity of the Ga-doped (110) γ-Al₂O₃ surface was attributed to vicinal Al₃m and Ga₃m sites.²⁰ However, an experimental determination of the coordination geometry, Lewis acidity and performance in PDH (i.e., activity, selectivity and stability) of Ga surface sites in the presence of Al surface sites on the surface of mixed (Ga,Al)₂O₃ catalysts is highly challenging.

Dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS) has emerged over the last decade as a unique approach to probe the surface structure of active sites in catalytic materials.²¹ For instance, it has been recently demonstrated that unique structural information could be obtained on the nature and relative strength of acid sites in alumina or silica-alumina materials from ¹⁵N DNP enhanced NMR spectroscopy using ¹⁵N-labelled pyridine as a probe molecule.²²⁻²⁴ In this work, we prepare nanocrystalline (Ga,Al)₂O₃ solid solution nanoparticles (NPs) via a colloidal route from Ga³⁺ and Al³⁺ acetylacetonate precursors and oleylamine. Al-rich (Ga,Al)₂O₃ (desired ratio of Al₂O₃: Ga₂O₃ 1:0.5) produces the least amount of coke (and deactivates least with TOS), while (Ga,Al)₂O₃ (desired ratio of Al₂O₃: Ga₂O₃ 1:3) is the most active catalyst (initial Ga-based activity). The variation of the PDH performance of (Ga,Al)₂O₃ NP catalysts is related to their surface acidity, assessed by Fourier transform infrared (FTIR) studies of adsorbed pyridine and 2,6-dimethylpyridine probe molecules, in addition to element-specific insights from a combination of DNP SENS experiments, namely cross-polarization magic angle spinning (CPMAS), ¹⁵N{²⁷Al} and ¹⁵N{⁷¹Ga} coupling mediated heteronuclear multiple quantum correlation (J-HMQC) experiments, using adsorbed ¹⁵N pyridine. These studies provide atomic level insights on the coordination geometry and Lewis acidity of surface sites, allowing one to categorize individual contributions of Al and Ga Lewis sites. In addition, we correlate element-specific Al and Ga Lewis acidity to the distribution of coordination environments of bulk Ga (Ga₄v and Ga₅v) and Al (Al₃m, Al₅v and Al₆i) sites obtained from fittings of ²⁷Al and ⁷¹Ga solid-state NMR spectra. The improved propene selectivity, stability and Ga-based activity of Al-rich catalysts is related to an increased relative abundance of surface Ga₄v–O–Al₃m linkages. These active sites feature a decreased Lewis acidity of Ga atoms relative to the Lewis acidity of Ga atoms in gallia-only or (Ga,Al)₂O₃ materials with low Al content, which is directly related to their high Ga-based catalytic activity, propene selectivity and stability in PDH.

Results
Synthesis and characterization
Colloidal solutions of gallia–alumina nanoparticles were prepared by heating Ga(acac)₃ and Al(acac)₃ precursors in oleylamine (200 °C, 7 h), using four nominal Ga : Al molar ratios, i.e. 1 : 6, 1 : 3, 3 : 1 and 1 : 0, the latter composition provided an Al-free γ-Ga₂O₃ NPs benchmark (Fig. 1).²⁵ The synthesis of colloidal Al₂O₃ NPs by the same method was
unsuccessful (i.e., no material could be isolated). The diameters of the as-synthesized NPs as determined by TEM were below 5 nm for all compositions (particle agglomeration prevents a more precise assessment of the particle size distribution, see Fig. 1 for a representative TEM image). After washing (see ESI† for details), the toluene colloidal solutions were dried and calcined (650 °C, 2 h) to give (Ga,Al)2O3 NPs, where x : y denotes the nominal molar Ga : Al ratio used.

The specific surface areas and pore diameters of the prepared materials were determined by applying the Brunauer–Emmett–Teller ( BET) method and Barrett–Joyner–Halenda ( BJH) model to the N2 physisorption data, respectively (Table S1†). The addition of Al(acac)3 in the synthesis of (Ga,Al)2O3 NPs leads to a notable increase of the BET surface area of the calcined materials, that is from 98 m2 g−1 for Ga2O3 NPs (x = y = 1 : 0) to ca. 245–286 m2 g−1 for Al-containing (Ga,Al)2O3 NPs; an increase of the BJH pore diameter accompanies the increase of the BET surface area (Table S1†).

Inductively coupled plasma – optical emission spectroscopy ( ICP-OES) measurements were performed to compare the experimental atomic Ga : Al ratios to the nominal compositions used (Table S1†). The ICP-OES determined Ga : Al ratio is closest to the nominal ratio in (Ga,Al)2O3(1 : 6) (1 : 5.6), and are ca. 2 : 1 and 1 : 2 for (Ga,Al)2O3(3 : 1) and (Ga,Al)2O3(1 : 3), respectively.

The X-ray powder diffractograms of the (Ga,Al)2O3 NPs materials display peaks of the γ-phase (cubic spinel-type structure, Fig. S1†). We have recently reported that calcination of γ-Ga2O3 NPs, prepared by a colloidal route from Ga(acac)3 and oleylamine, induces a phase transition of γ-Ga2O3 to the thermodynamically stable monoclinic β-Ga2O3 phase. This transition starts already at ca. 300 °C in the local environment of the Ga atoms, while the transformation of the periodic structure sets in at ca. 550 °C. Therefore, we assessed to which extent calcined (Ga,Al)2O3 NPs (650 °C, 2 h) have undergone this spinel-type-to-monoclinic phase transition. While the gallia-only material (Ga2O3) shows clearly peaks of the β-Ga2O3 phase (marked by red symbols in Fig. S1†), the X-ray diffraction ( XRD) patterns of Al-containing (Ga,Al)2O3 nanoparticles are consistent with a cubic spinel-type structure with no apparent transformation to the monoclinic phase (Fig. S1†), i.e. Al atoms stabilize notably the spinel structure.5,28–31 A linear increase of the lattice parameter (a) is observed with increasing Ga at% in (Ga,Al)2O3 NPs (Fig. S1†), explained by the lower atomic radius of Al compared to that of Ga (125 pm and 130 pm, respectively).22 Using the Scherrer equation,23 we estimated the average crystallite sizes in (Ga,Al)2O3 NPs and observed a decrease of the average crystallite size when Al is introduced into the structure of γ-Ga2O3, i.e. from ca. 5 nm in Ga-only (Ga2O3) to 2–3 nm in Al-containing materials (Table S1†). Overall, the XRD data is consistent with the formation of a solid solution with a spinel-type structure in all gallia-alumina materials.31

Ga K-edge X-ray absorption near edge structure ( XANES) spectra of (Ga,Al)2O3 NPs provide information about the relative abundances of GaIV and GaIII sites in the prepared materials. The features at ca. 10.375 eV and 10.380 eV are related to GaIV and GaIII sites, respectively.24 Consistent with previous studies,31 increasing the content of Al atoms in (Ga,Al)2O3 NPs materials leads to a higher relative fraction of GaIV sites, as seen from the increased intensity of the white line feature of the GaIV sites (and the correspondingly decreased intensities of GaIII features), in particular for (Ga,Al)2O3(1 : 6) and (Ga,Al)2O3(1 : 3) (Fig. 2A). The local environment around Ga, was investigated by the extended X-ray absorption fine structure ( EXAFS), exhibiting two distinguishable peaks due to Ga–O and Ga–Ga/Al coordination shells (Fig. 2B). The corresponding fittings provided average coordination numbers ( CN) and average interatomic distances. We modeled the EXAFS data using one average Ga–O shell and two Ga–Ga/Al subshells. In general, shorter average Ga–O distances and lower average Ga–O coordination numbers can be related to a higher fraction of GaIV sites. The fitting results presented in Table S2 and Fig. S2† show a decrease in the average Ga–O distances and coordination numbers with increasing Al loadings in the (Ga,Al)2O3 NPs materials, consistent with the corresponding XANES data. In particular, the average Ga–O distance decreases from 1.91(1) to 1.89(1), 1.86(1) and 1.84(1) Å for (Ga,Al)2O3(1 : 3) NPs with increasing nominal Al content from 1 : 0 to 3 : 1, 1 : 3 and 1 : 6 (Table S2†).

The relative distributions of Ga and Al sites between tetrahedral and octahedral geometries were then assessed quantitatively using 27Al and 71Ga magic-angle spinning nuclear magnetic resonance spectroscopy ( MAS NMR).27 Al MAS NMR spectra feature asymmetric peaks due to distorted AlIV and AlIII sites centered at ca. 70 and 15 ppm, respectively, although an additional minor peak at ca. 35 ppm, attributed to AlV sites, appears in Al-rich (Ga,Al)2O3(1 : 3) (Fig. 2C).35 71Ga MAS NMR spectra show two peaks located at ca. 150 and 30 ppm, associated with distorted GaIV and GaIII sites, respectively (Fig. 2D).31 Quantification of the relative ratios, average isotropic chemical shift (δiso), distribution of isotropic chemical shift (Δδiso) and average quadrupolar coupling constant (CQ) of the Ga and Al sites in the materials was performed using the Gaussian isotropic model ( GIM) or Czjzek model implemented in the DMFit software (Fig. S3, Tables S3 and S4†).36–38 In the case of 71Ga, the quadrupolar interaction is significantly larger than the spinning speed, and the computation takes into account the latter to reproduce the many spinning sidebands observed for this nuclei. The relative abundance of GaIV sites in the prepared materials increases with Al content, i.e. from 57% in (Ga2O3)–O3(1 : 1) to 72% in (Ga,Al)2O3(1 : 3) and 86% in (Ga,Al)2O3(1 : 6)
tetrahedral and octahedral positions, as in the case of (Ga,Al)\(_2\)O\(_3\)(1 : 3). (I) Shows an ADF-STEM model for the spinel structure along the \([100]\)-zone axis, where the arrows indicate preferential occupation of tetrahedral sites by Ga. The spinel model in (H) shows Ga occupying both tetrahedral and octahedral positions, as in the case of (Ga,Al)\(_2\)O\(_3\)(1 : 3). (I) Shows an ADF–STEM model for the spinel structure along the \([100]\)-zone axis, where Ga and Al occupy tetrahedral and octahedral positions, respectively.

The highest amount of Al\(_{IV}\) sites (92%) is found in (Ga,Al)\(_2\)O\(_3\)(1 : 3), and this amount decreases to 88% and 66% for (Ga,Al)\(_2\)O\(_3\)(1 : 3) and (Ga,Al)\(_2\)O\(_3\)(1 : 6), i.e. with increasing Al content. In Al-rich (Ga,Al)\(_2\)O\(_3\)(1 : 6), the fitted fraction of Al\(_{IV}\) sites is 22%, and decreases to 12% and 8% in (Ga,Al)\(_2\)O\(_3\)(1 : 3) and (Ga,Al)\(_2\)O\(_3\)(1 : 1), respectively (Fig. S3, Table S4†). The fitted fraction of Al\(_{VI}\) sites in (Ga,Al)\(_2\)O\(_3\)(1 : 6) is 12%. This value appears to be slightly higher than the Al\(_{VI}\) values reported for \(\gamma\)-Al\(_2\)O\(_3\) (5–10%). Residual amounts of Al\(_{IV}\) sites (<10%) could be possibly present in (Ga,Al)\(_2\)O\(_3\)(1 : 3), but their low intensity and high intrinsic error in the fit (due to strongly overlapping contributions) does not allow to accurately quantify them. Besides a slight decrease in the chemical shifts with increasing Al content, no notable changes could be observed neither in the average chemical shifts nor in the average quadrupolar couplings between the different (Ga,Al)\(_2\)O\(_3\) materials (Fig. S3, Table S4†). The spectra of (Ga,Al)\(_2\)O\(_3\)(1 : 6) are complicated by the coexistence of \(\gamma\) and \(\beta\) polymorphs, and no robust simulations could be performed in this case. The \(\beta\) polymorph is nevertheless known to show both Ga\(_{IV}\) and Ga\(_{IV}\) environments with \(\delta_{iso} = 40\) and 200 ppm and \(C_Q = 13.4\) and 17.5 MHz, respectively.

Annuar dark-field scanning transmission electron microscopy imaging (ADF-STEM) was carried out to obtain insight into the distribution of Ga and Al sites (distinguished by a brighter contrast for Ga atoms relative to Al atoms) on the surface of (Ga,Al)\(_2\)O\(_3\)(1 : 3) and (Ga,Al)\(_2\)O\(_3\)(1 : 6) nanoparticles. While the particles are often found to be poorly crystalline (Fig. S4†), we observe that the terminating surfaces have an enhanced contrast over the bulk (marked by arrows in Fig. 2E, corresponding to (Ga,Al)\(_2\)O\(_3\)(1 : 3)). For \(\gamma\)-Al\(_2\)O\(_3\), it has been suggested that this enhanced contrast is due to aluminum-terminated (111) and (100) planes. This literature result is similar to what we have reported for \(\gamma\)-Ga\(_2\)O\(_3\) nanoparticles, which feature Ga-terminated (111) facets in solely octahedral positions. In a mixed (Ga,Al)\(_2\)O\(_3\) oxide, the enhanced contrast at the particle edge could be due to a mixture of Ga and Al cations. However, given that Al atoms feature lower line profile intensities relative to Ga atoms, the intensity line profile suggests that the particle edge contains mainly aluminum cations (Fig. S5†).

Based on ADF-STEM images of (Ga,Al)\(_2\)O\(_3\)(1 : 3) particles (boxed region in Fig. 2F) and (Ga,Al)\(_2\)O\(_3\)(1 : 6) (Fig. 2G), we can observe an atomic arrangement that is characteristic for a spinel-type structure (Fig. 2H) oriented along the [100]-zone axis (FFT pattern in the top right inset in Fig. 2F). The spinel tetrahedral and octahedral positions are distinguishable along this zone axis. The non-spinel positions are not shown due to their low occupancies and, therefore, low contribution to the contrast of the ADF-STEM image. The analysis of the ADF-STEM image shows that Ga atoms (bright dots) can be found in both tetrahedral and octahedral positions (Fig. 2F). In
(Ga,Al)2O₃(1 : 6), Ga atoms are found to occupy mainly tetrahedral positions (marked by arrows in Fig. 2G), which is consistent with the NMR and X-ray absorption spectroscopy (XAS) results discussed above. Fig. 2I shows an ADF-STEM model for the spinel structure oriented along the [100] zone axis, built on the assumption that Ga occupies solely tetrahedral sites, while Al occupies octahedral sites. A clear resemblance is observed between the model in Fig. 2I and the experimental ADF image shown in Fig. 2G, confirming the preferential Ga occupancies of tetrahedral sites in (Ga,Al)2O₃(1 : 6). An additional discussion of the results of the electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) is provided in the ESI (Fig. S13 and S14, respectively).

Catalytic tests and coke deposition

Catalytic tests were performed at 550 °C and at a weight hourly space velocity (WHSV) = 7.2 h⁻¹ using 10% propane in N₂. The changes of the Ga weight-normalized (ICP based) rates of formation of propene and cracking products (methane and ethene) as well as the selectivity to propene with time on stream are plotted in Fig. 3. The activity of the tested catalysts is normalized by the Ga content determined by ICP-OES measurements (mol C₃H₆ mol Ga⁻¹ h⁻¹) because, as we have discussed above, the activity of unsupported Al-based catalysts in PDH becomes significant only at higher temperatures (600–630 °C) and requires a CO pre-treatment.⁶³⁻⁶⁷ Both of those requirements are not available in our experiments. Therefore, we consider Al sites inactive when tested in the present conditions. Table S5† summarizes the propane conversions and propene selectivities after 4 and 144 min TOS. The amount of coke deposited by the catalysts (determined in a separate thermogravimetric analysis (TGA) experiment) is presented as weight gain (%) normalized by either BET surface area or Ga wt% (Table S5†). Surface area-normalized activities (based on the surface area of the calcined NPs and expressed in μmol C₃H₆ m⁻² h⁻¹) are also presented in Fig. S6† and summarized in Table S6†.

The initial Ga-normalized activity after 4 min TOS decreases as following: [Ga,Al]₂O₃(3 : 1) > [Ga,Al]₂O₃(1 : 6) > [Ga,Al]₂O₃(3 : 1) > (Ga,Al)₂O₃(1 : 0) (4.48, 3.41, 2.24 and 1.21 mol C₃H₆ mol Ga⁻¹ h⁻¹, respectively, Fig. 3A). While all catalysts deactivate, the activity of [Ga,Al]₂O₃(1 : 6) increases first to 4.51 mol C₃H₆ mol Ga⁻¹ h⁻¹ within 24 min TOS, before deactivation also sets in for this catalyst. After 144 min of TOS, the catalysts have deactivated to varying extents, i.e. the decrease of activity is less pronounced for the Ga-poor materials (Ga,Al)₂O₃(1 : 6) and (Ga,Al)₂O₃(3 : 1) (decrease to 3.32 and 2.67 mol C₃H₆ mol Ga⁻¹ h⁻¹, respectively) and more noticeable for the Ga-rich materials (Ga,Al)₂O₃(1 : 0) and especially (Ga,Al)₂O₃(3 : 1) (decrease to 0.6 and 0.2 mol C₃H₆ mol Ga⁻¹ h⁻¹, respectively). When comparing the productivity, (Ga,Al)₂O₃(3 : 1) also outperforms the other three catalysts, showing productivities of 0.80 and 0.47 g C₃H₆ gcat h⁻¹ after 4 and 144 min TOS, respectively (Fig. S7, Table S6†).

The initial surface area-normalized activity shows a different activity trend, i.e. (Ga,Al)₂O₃(3 : 1) > (Ga,Al)₂O₃(1 : 6) > (Ga,Al)₂O₃(1 : 3) > (Ga,Al)₂O₃(1 : 0) (125, 77, 66 and 39 μmol C₃H₆ m⁻² h⁻¹, respectively, Fig. S6, Table S6†), which is explained by decreasing the surface density of active sites (Ga atoms) with increasing Al content. Therefore, comparing the catalysts’ activity after normalization by their Ga content (as presented in Fig. 3) may reflect the intrinsic activities of the active sites more precisely, at least for (Ga,Al)₂O₃(3 : 1), (Ga,Al)₂O₃(1 : 6) and (Ga,Al)₂O₃(3 : 1) catalysts that feature similar specific surface areas (Table S1†). Noteworthy, the surface area-normalized PDH activity and propene selectivity of the bulk γ-Al₂O₃ reference catalyst is poor, i.e. ca. 8 μmol C₃H₆ m⁻² h⁻¹, ca. 15 times lower than the initial areal activity of (Ga,Al)₂O₃(1 : 0), and 42%, respectively (Fig. S8†).

Interestingly, while the selectivity to propene declines with TOS from 87% to 62% for (Ga,Al)₂O₃(1 : 0) and from 76% to 68% for Ga-rich (Ga,Al)₂O₃(3 : 1) (after a ca. 20 min initial increase of propene selectivity for this catalyst), the propene selectivity is high and stable at ca. 86–90% for the Al-rich (Ga,Al)₂O₃(3 : 1) and (Ga,Al)₂O₃(1 : 6) materials (Fig. 3B, Table S5†). (Ga,Al)₂O₃(1 : 0), and the Al-rich catalysts (Ga,Al)₂O₃(3 : 1) and (Ga,Al)₂O₃(1 : 6), crack propane to methane and ethene with similar stable activities of ca. 0.1 mol (C₁ + C₂⁻) mol Ga⁻¹ h⁻¹. (Ga,Al)₂O₃(3 : 1) shows an initial cracking activity of ca. 0.4 mol (C₁ + C₂⁻) mol Ga⁻¹ h⁻¹ that decreases within the first ca. 24 min TOS and then stabilizes at ca. 0.16 mol (C₁ + C₂⁻) mol Ga⁻¹ h⁻¹ (Fig. 3C).

In situ TGA measurements under reaction conditions show that (Ga,Al)₂O₃(1 : 0) deposits higher amounts of coke per surface area relative to the other catalysts studied and that the amount of deposited coke decreases with the increasing Al content (Table S5†). In contrast, the reference γ-Al₂O₃ material shows no detectable coke deposition. If the amount of coke is normalized per Ga content, (Ga,Al)₂O₃(1 : 3) deposits the highest amounts of carbon while Al-rich (Ga,Al)₂O₃(3 : 1) deposits the lowest amounts of carbon.

Acidity of surface sites by Py-FTIR

To probe the nature of the surface acid sites (i.e., Brønsted vs. Lewis), their strengths and distributions, a Fourier-transform infrared spectroscopy study was performed using pyridine as a probe molecule (Py-FTIR). Pyridine was adsorbed at room temperature on self-supporting pellets of the catalysts that had been previously outgassed at 500 °C under ca. 10⁻³ mbar for 2 h, followed by pyridine desorption at room temperature, 100, 200 and 300 °C.⁴⁴⁻⁴⁷ The spectra and description of results obtained are presented in the ESI (Fig. S9–S11. Table S7†). In brief, we observe that bands assigned to Py on weak LAS are more abundant in Al-rich (Ga,Al)₂O₃(3 : 1) and (Ga,Al)₂O₃(1 : 3) NPs. Strong LAS are present in all four (Ga,Al)₂O₃ catalysts, but their relative fraction is lowest in Al-rich (Ga,Al)₂O₃(1 : 6). Experiments were also performed using 2,6-dimethylpyridine as the probe molecule, but these experiments did not yield additional insights relative to the Py-FTIR results (Fig. S12†).

Acidity of surface sites by DNP SENS of adsorbed ¹⁵N pyridine

In order to obtain further insight into the strength, the distribution and the nature of LAS and BAS on the surface of...
(Ga,Al)2O3 NPs, dynamic nuclear polarization surface enhanced NMR spectroscopy\(^\text{46}\) of adsorbed \(^{15}\text{N}\)-labelled pyridine was applied. This surface selective spectroscopy has been recently shown to be a powerful approach to characterize acid surface sites because the \(^{15}\text{N}\) chemical shifts are sensitive to the nature and strength of pyridine adsorption onto Lewis or Bronsted surface sites.\(^\text{12,22,23,49}\)

DNP enhanced \(^{15}\text{N}[^1\text{H}]\) CPMAS spectra were acquired for (Ga,Al)\(_2\)O\(_3(1:6)\), (Ga,Al)\(_2\)O\(_3(1:3)\), (Ga,Al)\(_2\)O\(_3(3:1)\) and (Ga,Al)\(_2\)O\(_3(1:0)\) (Fig. 4A). Three major peaks resonating at ca. 240, 265 and 281 ppm are identified from the CPMAS spectrum of (Ga,Al)\(_2\)O\(_3(1:0)\), which are assigned to strong, medium and weak gallium LAS, respectively (Fig. 4A).\(^\text{12}\) A minor peak is also observed at ca. 305 ppm corresponding to pyridine adsorbed on weak BAS. It should be noted that the peak at 281 ppm has been commonly linked to the presence of weak or mild BAS, in particular in silica- and silica-alumina supported materials with abundant surface silanols; however, we have recently shown, based on DFT modeling and chemical shift calculations on gallia materials, that a peak at this chemical shift is related to weak LAS rather than to weak or mild BAS (i.e., GaOH sites).\(^\text{12}\) In the CPMAS spectrum of (Ga,Al)\(_2\)O\(_3(3:1)\) the three mentioned LAS peaks are observed as well, while the minor peak at ca. 305 ppm disappears, suggesting that the amount of weak BAS associated with Ga is reduced when Al is introduced. Deconvolution of the CPMAS spectra of (Ga,Al)\(_2\)O\(_3(1:3)\) and (Ga,Al)\(_2\)O\(_3(1:6)\) clearly demonstrates that increasing further the content of Al results in weak LAS rather than to weak or mild BAS (i.e., GaOH sites).\(^\text{12}\) We observe that the intensity of weak LAS peak at ca. 281 ppm decreases with the incorporation of Al (from 14% to 11–9%, see Table S8\(^\dagger\)). Varying further the ratio between Ga and Al in a large range (i.e., from 3 : 1 to 1 : 6 nominal ratio) does not significantly change the relative amount of weak LAS (ca. 10%). In parallel, we observe clearly that the intensity of the strong LAS peak at around 241 ppm decreases with increasing Al content.

**Element-specific (Ga or Al) acidity of surface peaks**

In the materials containing both Ga and Al, the surface acidity can be associated with either Ga or Al atoms. To further characterize the nature of the LAS observed in the \(^{15}\text{N}[^1\text{H}]\) CPMAS spectra, 1D \(^{15}\text{N}[^{27}\text{Al}]\) J-HMQC spectra were acquired for (Ga,Al)\(_2\)O\(_3(1:6)\), (Ga,Al)\(_2\)O\(_3(1:3)\) and (Ga,Al)\(_2\)O\(_3(3:1)\) (Fig. 4B). This experiment relies on the existence of a sizeable \(J\) coupling between \(^{15}\text{N}\) and \(^{27}\text{Al}\) spin pair and therefore can be used to probe Al-based LAS; the one-bond \(J[^{15}\text{N}–^{27}\text{Al}]\) coupling value increasing with Lewis acidity. We first note that the signal-to-noise ratio of the \(^{15}\text{N}[^{27}\text{Al}]\) J-HMQC spectrum of (Ga,Al)\(_2\)O\(_3(3:1)\) is relatively low due to the low Al content. Nevertheless, the spectrum clearly shows that the aluminum Lewis acid sites contribute to the resonances observed in the 260–280 ppm chemical shift range. Strong aluminum LAS peaks are also identified at 234 ppm in the spectra of (Ga,Al)\(_2\)O\(_3(1:6)\) and (Ga,Al)\(_2\)O\(_3(1:3)\), with relative intensities around 19 and 20%, respectively (Fig. 4B; Table S9\(^\dagger\)).

These results agree well with what we observe in the corresponding CPMAS spectra (Fig. 4A), i.e. confirming that the resonance at around 234 ppm relates exclusively to strong Al-based LAS. The deconvolution also shows the presence of a weak resonance at ca. 242 ppm in these two spectra. The intensity of this peak increases with the content of Al, which is contrary to its behavior in the CPMAS spectra of Fig. 4A. In addition, there is a difference between the full widths at half maximum (FWHM, in ppm) of this resonance...
in (Ga,Al)$_2$O$_3$ (1 : 6) and (Ga,Al)$_2$O$_3$ (1 : 3), decreasing from ca. 15 and 15.6, respectively, in the CPMAS spectra to around 9.3 ppm in $^{15}$N($^{27}$Al) $^J$-HMQC spectra (see Tables S8 and S9†). This implies that the resonance at around 242 ppm has contributions both from Ga and Al Lewis acid sites and that the relative amount of Ga-based strong LAS decreases when the content of Al is increased. The Al-based medium LAS peak that resonates at ca. 263–264 ppm is slightly shifted upfield (by 1 to 3 ppm) with respect to the chemical shift extracted from the CPMAS spectra, and its linewidth increases with Al content, viz. from a FWHM of 16 ppm in (Ga,Al)$_2$O$_3$ (3 : 1) to 20 and 23 ppm. This is in contrast to what is observed for the medium LAS peak in the CPMAS spectra, where the linewidth remains within 26.4 and 23.3 ppm in all materials (Table S8†). These two observations indicate that both Ga- and Al-based medium LAS contribute to the shifts in the 260–265 ppm range. Finally, the peak resonating at ca. 275–277 ppm can be assigned to Al-based weak LAS. The relative intensity of this peak decreases when the Al content increases, i.e. from 28% in (Ga,Al)$_2$O$_3$ (3 : 1) to 16% in (Ga,Al)$_2$O$_3$ (1 : 3) and 6% in (Ga,Al)$_2$O$_3$ (1 : 6). In the corresponding CPMAS spectra, the weak LAS peak appears at 282 ppm and its intensity remains between 9–11% in the Ga–Al materials. This indicates that weak LAS also have contributions from both Ga and Al. A 1D $^{15}$N($^{71}$Ga) $^J$-HMQC spectrum of (Ga,Al)$_2$O$_3$ (3 : 1) (natural abundance of $^{71}$Ga is 30.8%) has also been recorded and is presented in Fig. 4C. While the signal-to-noise ratio does not allow for the unambiguous observation of the strong gallium Lewis acid sites at around 240 ppm in (Ga,Al)$_2$O$_3$ (3 : 1), we observe clearly a broad resonance in the 260–280 ppm range, with a maximum at ca. 276 ppm, which confirms the presence of Ga-based weak LAS at this chemical shift (and rules out the assignment of this peak to Py on weak/mild BAS).

**Discussion**

Our study shows that an increasing Al content leads to higher amounts of GaIV sites in (Ga,Al)$_2$O$_3$ nanoparticle catalysts, influencing thereby the distribution and properties of the surface sites and in turn the catalytic performance of the materials. In particular, an increased selectivity and stability was reported for (Ga,Al)$_2$O$_3$ catalysts with high Al contents, i.e. with a high fraction of GaIV sites. Results of the present study further advance our understanding of (Ga,Al)$_2$O$_3$ catalysts by disentangling element-specific contributions of Ga or Al sites to the overall Lewis acidity and by correlating these new insights to catalytic properties and the relative populations of bulk GaIV.

Fig. 4 Deconvoluted CPMAS (A) and $^{15}$N($^{27}$Al) $^J$-HMQC (B) spectra of (Ga,Al)$_2$O$_3$ materials. The peak intensities are normalized with respect to the most intense peak in each spectrum. Peak maxima and fitting results are summarized in Tables S8 and S9†. $^{15}$N-Py was desorbed at 100 °C. (C) Comparison of $^{15}$N($^{71}$Ga) $^J$-HMQC spectrum with CPMAS and $^{15}$N($^{27}$Al) $^J$-HMQC spectra of (Ga,Al)$_2$O$_3$. The red box marks the feature at ca. 276 ppm attributed to Py on weak Ga LAS. Panel (D) shows a sketch explaining the observed variation of Lewis acidity of Ga–O–Ga and Ga–O–Al linkages with increasing substitution of Ga atoms in octahedral positions by Al atoms.
and Ga\textsubscript{VI} sites as well as Al\textsubscript{IV}, Al\textsubscript{V}, and Al\textsubscript{VI} sites. Our experimental results are graphically summarized in Fig. 5 and discussed in detail below.

We observe that in contrast to the Ga-only benchmark (Ga,Al\textsubscript{2})O\textsubscript{3}(1 : 0), which transforms after calcination at 650 °C partially into the monoclinic β-phase, Al-containing (Ga,Al\textsubscript{2})O\textsubscript{3} materials retain their cubic spinel-type structure (γ-phase) characteristic of the as-prepared (Ga,Al\textsubscript{2})O\textsubscript{3} NPs. The addition of Al decreases the average crystallite size of (Ga,Al\textsubscript{2})O\textsubscript{3} NPs (from ca. 5 nm in (Ga,Al\textsubscript{2})O\textsubscript{3}(1 : 0) to ca. 2–3 nm in (Ga,Al\textsubscript{2})O\textsubscript{3}(1 : 1), (Ga,Al\textsubscript{2})O\textsubscript{3}(1 : 3) and (Ga,Al\textsubscript{2})O\textsubscript{3}(1 : 6) and increases the specific surface area of the Al-containing materials, by ca. 2.5–2.9 times (note that the molecular weight of Al is ca. 2.6 times lower than that of Ga). Ga K-edge XAS, 27\textsuperscript{Al} and 71\textsuperscript{Ga} MAS NMR data confirm that increasing the fraction of Al in the materials leads to a higher fraction of Ga\textsubscript{IV} sites, with Al cations found hexa-
notable, the presence of strong Al-based LAS in (Ga,Al)2O3(1 : 6) (as well as the presence of mostly weak/mild Ga-based LAS in this material) does not lead to coking, which is in contrast to other (Ga,Al)2O3 catalysts studied here that contain strong Ga-based LAS and produce coke. This result suggests that strong Al-based LAS are not involved in coking.

While the relative fraction of Py on Al-based medium LAS associated with the peak at 263–264 ppm changes in the 15N-(57)Al J-HMQC spectra from 65% in (Ga,Al)2O3(3 : 1) to 60% and 71% in (Ga,Al)2O3(1 : 3) and (Ga,Al)2O3(1 : 6), respectively, the relative fraction of Py on weak Al-based LAS (peak at 275–277 ppm) decreases constantly, i.e. from 28% in (Ga,Al)2O3(3 : 1) to 16% in (Ga,Al)2O3(1 : 3) and to 6% in (Ga,Al)2O3(1 : 6). That being said, the fittings of the CPMAS spectra, which capture contributions from Al-based and Ga-based LAS, reveal that the fraction of weak LAS (centered at 281–282 ppm) remains stable at around 10% in Al-containing (Ga,Al)2O3 catalysts, and is higher at 14% only in (Ga,Al)2O3(1 : 6). These results suggest that in Al-containing catalysts, the relative fraction of Ga-based weak LAS increases with the increasing Al content. Importantly, the presence of the weak LAS peak resonating at 276 ppm in the 15N-(57)Ga J-HMQC spectrum of (Ga,Al)2O3(3 : 1) demonstrates unequivocally the attribution of this peak to weak Ga-based LAS sites rather than to weak/medium BAS sites. We have reported previously that the higher catalytic activity of β-Ga2O3 is linked to a notably higher relative fraction of weak LAS in this material relative to the γ-Ga2O3 polymorph, identified by the 15N peak at 281 ppm. Therefore, we explain the higher relative fraction of weak LAS in (Ga,Al)2O3(1 : 6) as compared to the Al-containing (Ga,Al)2O3 catalysts by the presence of the β-Ga2O3 phase in (Ga,Al)2O3(1 : 0), which follows from the XRD results in Fig. S1.† Indeed, the presence of Al stabilizes notably the γ-spinel-type structure of the (Ga,Al)2O3 catalysts against the transformation to the β-polymorph, and the β-Ga2O3 phase is not observed in Al-containing (Ga,Al)2O3 catalysts.

CPMAS and 15N-(57)Al J-HMQC experiments reveal a fundamental divergence of the Lewis acidity strength related to the respective Al4+/Ga4+ (and Al3+/Ga3+) sites (Fig. 4A and B). We discussed above that Al atoms preferentially occupy octahedral sites in the (Ga,Al)2O3 materials, but with increasing Al content, also tetrahedral sites become occupied and comprise 8, 12 and 22% in (Ga,Al)2O3(3 : 1), (Ga,Al)2O3(1 : 3) and (Ga,Al)2O3(1 : 6), respectively, according to the quantitative fittings of the 27Al NMR spectra. Although these values reflect the quantity of bulk Al4+ sites, a qualitative correlation is found with the relative amount of strong Al-based LAS, fitted to 7% of the total area in (Ga,Al)2O3(3 : 1) but increasing to ca. 20–25% in (Ga,Al)2O3(1 : 3) and (Ga,Al)2O3(1 : 6) (Table S9†). In line with these results, the Al-poor (Ga,Al)2O3(1 : 3) catalyst contains 92% of bulk Al4+ sites and features a fitted area of weak/medium LAS peaks totaling to 93%. This data allows us to associate strong Al-based Lewis acidity in (Ga,Al)2O3 catalysts with Al4+ sites and weak/medium Lewis acidity with Al surface sites in SP geometry (Scheme 1B), consistent with the previous data on γ-Al2O3. Analysis of CPMAS results discussed above displays the opposite correlation (relative to Al sites) between the coordination geometry and Lewis acidity of Ga LAS in γ-(Ga,Al)2O3 spinels. Specifically, an increasing amount of bulk Ga4+ sites (57, 72 and 86% in (Ga,Al)2O3(3 : 1)), (Ga,Al)2O3(1 : 3) and (Ga,Al)2O3(1 : 6), respectively) correlates with the increasing fraction of weak/medium LAS. In turn, the respective decreasing amount of bulk Ga4+ sites correlates with a decreasing fraction of strong Ga LAS. Therefore, strong Ga-based Lewis acidity is associated with Ga LAS in Ga2O3 surface termination positions, which likely yields Ga surface sites in square pyramidal geometry, and weak/medium Lewis acidity with Ga4+ positions, providing Ga4+ and Ga3+ (next to a Va site) surface sites. The underlying physical reason why SP surface Ga sites are strong LAS in Ga2O3 and γ-(Ga,Al)2O3 materials is currently unclear, but is consistent with reported DFT calculations.12

We can now relate results of DNP SENS experiments to the catalytic performance of the studied materials. The high and stable selectivity to propane displayed by (Ga,Al)2O3(3 : 1) and (Ga,Al)2O3(1 : 6) catalysts, at ca. 90 and 85%, respectively) and the high activity (Ga-content normalized) of these catalysts is associated with the low relative amounts of strong Ga-based LAS and high relative amounts of weak and medium Ga-based LAS assigned to tetra- or tricoordinated Ga surface sites. When the relative amount of weak/mild Ga LAS decreases and the relative amount of strong Ga LAS increases, as in (Ga,Al)2O3(3 : 1), the activity and propane selectivity decline. Interestingly, while Ga sites in octahedral positions at surface termination (GaA surface sites with SP geometry, Scheme 1B) can be linked to deactivation by coking,12 the current results show that surface Al sites in these positions do not coke significantly; yet, strong Al-based LAS (Al4+) do not coke either. However, in addition to deactivation by coking, we cannot exclude that strongly bound surface hydrides contribute to the observed deactivation.

We also note that another parameter changing alongside the Al loading in (Ga,Al)2O3 catalysts is the oxygen basicity, which is linked with the electron density on the oxygen atom.29 For instance, oxygen basicity has been shown to increase with the increasing content of the framework Al sites in zeolites.30 Therefore, it is likely that the basicity of surface oxygen atoms is higher in Al-rich (Ga,Al)2O3 catalysts, which is beneficial for the proton transfer step during the C–H activation of propane;22 a higher electron density on the oxygen atoms can also decrease Lewis acidity of Ga in Ga–O–Al surface linkages. The progress in understanding the relation between oxygen acidity and Lewis acidity in Ga-based PDH catalysts will be reported in due course.

A control experiment with γ-Al2O3 (S BET = 100 m2 g−1) showed a surface area-normalized activity that is ca. 15 times lower than the initial activity of (Ga,Al)2O3(3 : 1), and it showed a poor propane selectivity of 42%, consistent with previous reports.36,53 No coke deposition could be detected in this material by TGA. While a higher activity of alumina for PDH was reported to require a high temperature CO pre-treatment,13,14,54,55 such pre-treatment was not performed in the present work. Crystalline alumina-based catalysts also require higher reaction temperatures (600–630 °C), as was already mentioned above. Thus, the activity trends of (Ga,Al)2O3 catalysts in this work are related to Ga sites, that are influenced by the coordination geometry of both Ga and Al atoms, and the
replacement on the surface of Ga-O-Ga linkages in Ga-rich materials by Ga-O-Al linkages in Al-rich materials (Fig. 4D). High resolution TEM imaging of (GaAl)3O4(1:3) nanoparticles showed that the atomic termination rows contain AlO4 cations.

Overall, the experimental results suggest that the high catalytic activity, stability and selectivity in PDH is related to the weak/mild Lewis acidity of Ga-based active sites, presumably residing in GaO–O–AlVI surface linkages, that is when Ga and Al are in tetrahedral and octahedral positions in atomic termination rows, respectively (Fig. 4D). The replacement of Ga by Al in (GaAl)3O4 spinel-type solid solutions attenuates the relative fraction of strong Lewis acidity of Ga-based sites and increases the relative fraction of weak and mild Ga-based sites. Thus, weak and mild Lewis acidity is associated with Ga atoms that produce little coke and yield high propene selectivity, and that are in tetrahedral atomic termination rows with tetra- or tricoordinated (if in the vicinity of a Vp site) geometry of Ga sites. Since the presence of strong Al-based LAS in Al-rich (GaAl)2O3 catalysts does not induce coking, it is the strongly Lewis acidic Ga sites found in GaO–O–AlO4 atomic termination rows that are most likely responsible for deactivation by coke deposition.

Conclusions

We have described how control over the Ga : Al atomic ratio in (GaAl)3O4 spinel-type solid solutions allows one to improve the catalytic performance (activity, selectivity, stability) of these materials in the dehydrogenation of propane. The presence of Al atoms in (GaAl)2O3 nanoparticles stabilizes the spinel-type structure, leads to a higher relative fraction of bulk and surface GaIV sites and, for Al-rich compositions, provides a relatively high fraction of weak/mild Ga-based surface Lewis acid sites. These weak/mild Ga LAS that suffer less from catalyst deactivation (owing to decreased coke deposition during PDH) while retaining a high activity and selectivity are ascribed to GaIV–O–AlO4 surface linkages. (GaAl)2O3 catalysts that are rich in Ga display a higher presence of bulk GaVI sites, a higher relative fraction of stronger Ga-based surface LAS and this correlates with a faster deactivation by coke deposition.

Data availability

Data are available within the article or in the ESI file.

Author contributions

P. C.-F. and A. F. conceived the research project and planned the experimental work. P. C.-F. prepared materials, characterized and tested the catalysts, and analyzed the data. M. K. and Z. W. planned and performed DNP SENS solid-state NMR experiments, supervised by A. L., analysed and described results. D. M. performed 27Al and 71Ga solid-state NMR experiments. E. K. performed part of Py-FTIR experiments. E. W. performed ADF-STEM imaging and EELS characterization. P. M. A. supervised XAS experiments and data analysis. The data were discussed among all co-authors. P. C.-F. and A. F. wrote the first draft that was edited by all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
