A Molecular Analogue of the C–H Activation Intermediate of the Silica-Supported Ga(III) Single-Site Propane Dehydrogenation Catalyst: Structure and XANES Signature

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Dedicated to P. Kündig on the occasion of his 75th birthday

Propane dehydrogenation is an important field of research due to an increasing world-wide demand of propene while classical production routes through naphtha cracking are in decline. In that context, silica-supported Ga(III) sites, synthesized from surface organometallic chemistry principles, show high selectivity and stability in the propane dehydrogenation reaction. This performance is in significant contrast to the reported fast deactivation and lower selectivity of most Ga₂O₃ and CrO₃ based materials. The Ga-catalyzed propane dehydrogenation reaction is proposed to proceed through the formation of Ga alkyl intermediates for which it would be desirable to have detailed structural and spectroscopic information. Here, we prepare a consistent series of Ga(III) molecular complexes with varying numbers of alkyl and siloxide ligands; they are characterized by single crystal X-Ray diffraction and X-Ray Absorption Near Edge Structure analysis, which is known to be highly sensitive to the Ga coordination environment. We report in particular the structure and the spectroscopic signatures of [Ga(iPr)(OSi(OTBu)₃)(HOSi(OTBu)₃)]₂, a molecular mimic of the key proposed reaction intermediates in the Ga-catalyzed PDH reaction.

Keywords: C–H activation, dehydrogenation, gallium, molecular gallium complexes, propane dehydrogenation, X-ray absorption spectroscopy, X-ray structure.

Introduction

The production of light olefins, such as ethene and propene, are important industrial processes as these molecules are key intermediates for the production of a large number of bulk and fine chemicals as well as polymers.1,2 While these olefins were mostly produced from cracking of naphtha, the increasing availability of shale gas led to changes in cracking technology, resulting in decreased propene production. Thus, the direct dehydrogenation of the corresponding alkane has become the dominating alternative approach for the (on-purpose) production route of olefins in recent years. The highly endothermic nature of the reaction (Δ_H°₂₉₈ = 137 kJ mol⁻¹, 124.3 kJ mol⁻¹ and 117.6 kJ mol⁻¹ for ethane, propane and isobutane, resp.) necessitates high reaction temperatures (>500 °C) to achieve economical levels of conversion. Such harsh reaction conditions promote deactivation through both sintering and coke formation for the main industrially employed catalysts CrO₃/Al₂O₃ and Pt–M/Al₂O₃ (M = Sn or Ga) (Catofin®, UOP Oleflex™ and DOW FCDh).3,4 Frequent regeneration cycles are required for these systems, decreasing the efficiency and catalyst lifetime. The search for alternative PDH catalysts, tackling these stability and...
selectivity issues has thus been an important field of research.\textsuperscript{[1,5]}

Ga\textsubscript{2}O\textsubscript{3} is one metal oxide that has received significant interest due to its promising initial activity and selectivity in alkane dehydrogenation. However, this system undergoes rapid deactivation likely due to the reduction of Ga\textsubscript{2}O\textsubscript{3}\textsuperscript{[6–12]} While Ga\textsubscript{2}O\textsubscript{3}-based materials readily deactivate and cannot be used on industrial scales for PDH, the corresponding Ga-zeotype catalysts are used to convert propane into aromatics in the commercial Cyclar\textsuperscript{©} process; this process is proposed to also involve propane dehydrogenation as a key step on isolated Ga sites before the further conversion of propene to aromatics on acid sites.\textsuperscript{[13–16]} These unique catalytic properties have led to the synthesis of isolated Ga sites at the surface of non-reducible bulk materials such as silica to generate stable propane dehydrogenation catalysts.\textsuperscript{[17–19]}

One methodology to achieve such isolation is a two-step approach combining surface organometallic chemistry (SOMC) and the thermolytic molecular precursor approach (TMP).\textsuperscript{[20,21]} Using this approach isolated Ga(III) sites, but also Cr(III) and Co(II), have shown activity in the dehydrogenation of alkanes and the corresponding hydrogenation reactions.\textsuperscript{[17,22,23]} For isolated Ga(III) sites, the preparation involves grafting of the molecular precursor [Ga(OSi(O^tBu)_3)_3(THF)] (1) onto partially dehydroxylated SiO\textsubscript{2} followed by a thermal treatment (Scheme 1,a). The resulting Ga/SiO\textsubscript{2} catalyst showed high activity and stability in propane dehydrogenation among other Ga-based catalysts, a performance attributed to the stabilization of active four-coordinate Ga(III) ions on a redox-inactive support that suppresses facile reduction processes associated with some bulk materials like Ga\textsubscript{2}O\textsubscript{3}.

Similar to its Cr-analogues, the proposed mechanism involves three steps, namely the heterolytic C–H bond cleavage of the alkane to form a M–C and an O–H bond, a subsequent β-H elimination step to form the alkene, and the regeneration of the catalyst by H\textsubscript{2} formation (Scheme 1,b).\textsuperscript{[22,24,25]} One of the key reaction intermediates in this proposed mechanism is a Ga(III) alkyl species. In fact, alternative synthetic approaches have used molecular Ga alkyl compounds as precursor to generate PDH catalysts.\textsuperscript{[18]}

In trying to understand the evolution of Ga sites during PDH (formation and evolution of reaction intermediates), Ga K-edge X-Ray Absorption Near Edge Structure Spectroscopy (XANES) has been used because it is highly sensitive to the Ga coordination environment and structure.\textsuperscript{[26]} However, interpretation of Ga XANES can be complicated because the XANES spectra signatures of Ga(III) alkyl can overlap with reduced Ga sites, making interpretation ambiguous.\textsuperscript{[26]}

In addition, one of the main issues when interpreting X-Ray Absorption Spectroscopy (XAS) spectra is the use of bulk reference compounds while surface species have intrinsically very different coordination environments.\textsuperscript{[27]}

Since molecular metal siloxide complexes have been shown to be a successful approach to model surface species in particular for silica-supported heterogeneous catalysts,\textsuperscript{[28–30]} we therefore present the synthesis of a series of tailored molecular Ga(III) complexes, containing a varying number of siloxide and alkyl ligands to mimic possible reaction intermediates, and structural characterization through single crystal X-Ray Diffraction (XRD) as well as XAS. We report in particular the isolation of a molecular analogue of the proposed mono-propyl Ga(III) intermediate (Scheme 1,b) and provide its XANES signature.

\textbf{Scheme 1.} a) Preparation of Ga/SiO\textsubscript{2} from partially dehydroxylated SiO\textsubscript{2} and [Ga(OSi(O^tBu)_3)_3(THF)] (1). b) Proposed reaction mechanism of the Ga/SiO\textsubscript{2} catalyzed PDH reaction showing the two possible Ga(III) alkyl reaction intermediates.
Results and Discussion

Based on the molecular complex [Ga(OSi(ΟBu))3(THF)] (1) developed in an earlier study, we were first interested in developing a consistent set of Ga complexes with an increasing amount of Ga–C and decreasing amount of Ga–OSi bonds as a benchmark for a detailed Ga K-edge XAS analysis in view of the high sensitivity of the edge energy to the ligand σ/π-donation. For this purpose we decided to use -OSi(ΟBu) and neopentyl as the ligands of choice. The reaction of [Ga(CH₂Bu)] with one equivalent of HOSi(ΟBu) at 55°C yielded the dimeric complex [Ga₂(OSi(ΟBu))(CH₂Bu)2] (2) after 12 h in 88% yield (Scheme 2,a) as subsequently evidenced by X-Ray crystallography (vide infra).

This complex does not further react with HOSi(ΟBu) at 55°C, most likely due to its intrinsic stability. To trigger full ligand exchange, three equivalents of HOSi(ΟBu) were stirred with [Ga(CH₂Bu)] at 70°C for 12 h, to yield the monomeric monoalkyl complex [Ga(CH₂Bu)(OSi(ΟBu))(HOSi(ΟBu))] (3) in 87% yield. Interestingly, a silanol adduct was formed instead of protonating the last neopentyl ligand which again must be due to a high kinetic barrier of further exchange. These results caught our interest as the structure of complex 3 closely resembles one of the proposed structures of the first reaction intermediate in the Ga-catalyzed PDH reaction, that is associated with the heterolytic bond cleavage of the C–H bond on a Ga(III)–O site.

These results prompted us to synthesize the monomeric propyl and isopropyl Ga complexes. In a first attempt, we tried to synthesize propyl analogues of the neopentyl containing complexes. An analogues dimeric complex could be obtained by stirring three equivalents of HOSi(ΟBu) with [Ga(Pr)] at room temperature overnight resulting in [Ga₂(OSi(ΟBu))(Pr)] (4; Scheme 2,b) in 30% yield. Unfortunately, further transformation of this dimeric complex has remained so far unsuccessful. Reaction at 70°C – in analogy to the synthesis of 3 – resulted in no reaction while subsequent increase of the reaction temperature ultimately resulted in decomposition and no monomeric product could be isolated. Next, we targeted the synthesis of the isopropyl analogue through a direct route, which could be obtained by stirring of [Ga(Pr)] with three equivalents of HOSi(ΟBu) in C₄H₆ for 12 hours at 50°C resulting in complex [Ga(Pr)(OSi(ΟBu))(HOSi(ΟBu))] (5). Steric differences are the most likely reason why [Ga(Pr)] underwent more facile ligand exchange compared to [Ga(Pr)] or [Ga(CH₂Bu)].

All complexes were obtained in high purity and single crystals could be obtained amenable for XRD studies (see Figure 1). Crystals for the neopentyl containing complexes 2 and 3 were obtained from concentrated (Me₃Si)₂O and pentane solutions, respectively. The XRD data could confirm the identity proposed by EA as well as the dimeric and monomeric nature of the complexes. In 2, the two Ga atoms are crystallographically independent but both bridged by a siloxide ligand with narrow O–Ga–O angles of 80.8°. The C–Ga–C angles of 135.7° (Ga1) and 134.7° (Ga2) are much wider resulting in a strongly distorted tetrahedral environment for both Ga1 (τ₄ = 0.75) and Ga2 (τ₄ = 0.77). In 3, the Ga–siloxide distances (Ga1–O1, 1.816(2); Ga1–O9, 1.811(2) Å), are noticeably shorter than the Ga–OHsilanol distance (Ga1–O5, 2.050(2) Å). The coordination geometry around Ga is best described as pseudo-tetrahedral (τ₄ = 0.82).

Interestingly in the propyl containing dimeric structure 4, the two Ga atoms are crystallographically equivalent. While the O–Ga–O angle is the same as the one in 2 (80.8°), the C–Ga–C angle is more acute with only 127.8° – attributed to steric reasons – resulting in a pseudo-tetrahedral environment for both Ga atoms (τ₄ = 0.85). For complex 5, a similar trend can be observed compared to 3 with Ga–Osiloxide distances.
(Ga2–O10, 1.806(2) Å; Ga2–O13, 1.828(2) Å) being similarly shorter than the Ga–OHsilanol distance (Ga2–O1, 2.042(2) Å) and a very similar pseudo-tetrahedral coordination environment ($\tau_4 = 0.83$). The significant lengthening of one of the Ga–O bonds in both complexes can be used for the assignment of the coordinated silanol ligand in the solid-state structure. The absence of occupational disorder also allows for the conclusion that the hydrogen atom is stabilized on one of the oxygen atoms in the solid-state structure.

To further investigate the stabilization of the silanol hydrogen in 3 and 5 we performed an energy optimization of the –OH hydrogen atom in both complexes using Gaussian 09 (See Supporting Information for computational details). The obtained structures reveal a strong hydrogen bonding interaction of the –OH hydrogen with a neighboring O-atom that is not directly coordinated to the Ga center (Figure 2), making a six-membered cyclic structural motif with wide O–H–O angles of 164.1° (3) and 162.1° (5) and very short O–H contacts of only around 1.7 Å for both complexes. This supports a strong hydrogen bonding interaction, consistent with the X-Ray data and most likely responsible for the kinetic stability of such complexes, preventing the simple protonation of the alkyl moieties. In fact, this –OH can easily be observed by solution $^1$H-NMR (Figures S3 and S7) at 5.62 and 5.77 ppm for compounds 3 and 5, respectively. This deshielded chemical shift compared to free HOSi(OtBu)$_3$ (2.30 ppm) and the narrow line width are both consistent with the conservation of this H-bonding interaction in solution.

We then recorded XAS data at the Ga K-edge to obtain insight into the effect of alkyl and siloxide ligands on the edge structure and energy. First, we analyzed the series of complexes (Np$_0$–Np$_3$ corresponding to 1, 3, 2 and [Ga(CH$_2$tBu)$_3$], respectively) with consecutively increasing amounts of neopentyl ligands (Figure 3,a). The data clearly shows a correlation between decreasing edge energy and increasing number of alkyl ligands with the Ga K-edge energy spanning 10366.3 – 10371.4 eV. While the complexes are all formally Ga(III), the shifts in energy can be explained by the varying ligand environment and complex structure, in accordance with previously published work on carbosilyl ligand containing Ga(III) complexes.[26] The trigonal planar [Ga(CH$_2$Bu)$_3$] has a distinct feature at lower energy which can be attributed to a transition from the Ga 1s into the non-bonding Ga 4pz orbital.[26] The three distorted tetrahedral structures (Np$_0$–Np$_2$) show more similar edge structures with several convoluted features – a result of energetically similar Ga 1s to 4p transitions – that cannot easily be assigned. Figure 3,b shows the Ga K-edge energy dependency of all investigated complexes on the number of alkyl ligands coordinated to the Ga center. Despite the electronic and structural differences of the complexes, an almost linear trend can be observed among the neopentyl series. The other complexes...
investigated – namely the propyl and isopropyl complexes – fit very well in the trend with only small differences compared to the neopentyl containing complexes.

Overall, the presented data show that there is a significantly decreasing edge energy with increasing numbers of alkyl ligands following a linear correlation. The Ga K-edge XANES signature can thus be used for the facile establishment of the coordination environment and the number of siloxide and alkyl ligands in Ga(III) complexes. In fact, this Ga K-edge corresponds to what is observed for the silica-supported Ga(III) sites during PDH (see Figures S18–S21 and Table S5), suggesting the formation of similar coordination motifs whose structure(s) would need to be ascertained by complementary techniques.

Conclusions

A set of easily accessible Ga complexes with systematically changing numbers of oxygen (OSi(O\textsuperscript{t}Bu)\textsubscript{3}) and alkyl (CH\textsubscript{2}tBu, iPr and Pr) ligands was synthesized. The complexes were analyzed by XRD revealing the identity and coordination environment around the Ga centers which can be described as pseudo-tetrahedral in all cases. While di-alkyl species are dimeric, both mono alkyl species are monomeric due to the coordination of an additional silanol ligand to the Ga center. In particular, we isolated a molecular analogue of a proposed key reaction intermediate in the Ga/SiO\textsubscript{2}-catalysed PDH reaction, a Ga(III) alkyl interacting with an adjacent silanol that corresponds to the proposed C–H activation product of propane on silica-supported Ga(III) isolated sites. Furthermore, a spectroscopic investigation by means of XAS shows that the Ga K-edge XANES signature depends on the number of alkyl ligands as previously discussed; a decrease in Ga K-edge energy follows an almost linear correlation with a decrease in number of alkyl ligands which can be mostly attributed to energy differences in the Ga 4p orbitals due to differences in the \(\sigma/\pi\) donation ability of oxygen-based compared to carbon-based ligands. It is noteworthy that the XANES signature of the spent Ga/SiO\textsubscript{2} catalyst closely resembles features of the mono-alkyl species. Hence, we are intrigued to carry out a more detailed \textit{operando} investigation of Ga single-site based PDH catalysts, to track the active sites and reaction intermediates. Such work will be reported in due course.

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Author Contribution Statement

#L. R. and K. S. contributed equally. Both authors contributed to the design, the execution and the development of the project in the current form. D. N. contributed to single crystal XRD measurements. S. R. D. contributed to obtaining crystals for single crystal
XRD measurements and to XAS measurements. D. G. contributed to the computational optimization of molecular structures. C. C. designed and led the project. All authors contributed to writing the manuscript.

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