ChemPhysChem

Review
doi.org/10.1002/cphc.202400513

Chemistry Europe
European Chemical Societies Publishing

www.chemphyschem.org

# Activation of $CH_4$, $NH_3$, and $N_2$ by Tantalum Ions, Clusters and Their Oxides: What Can Be Learnt from Studies of Ions in the Gas Phase

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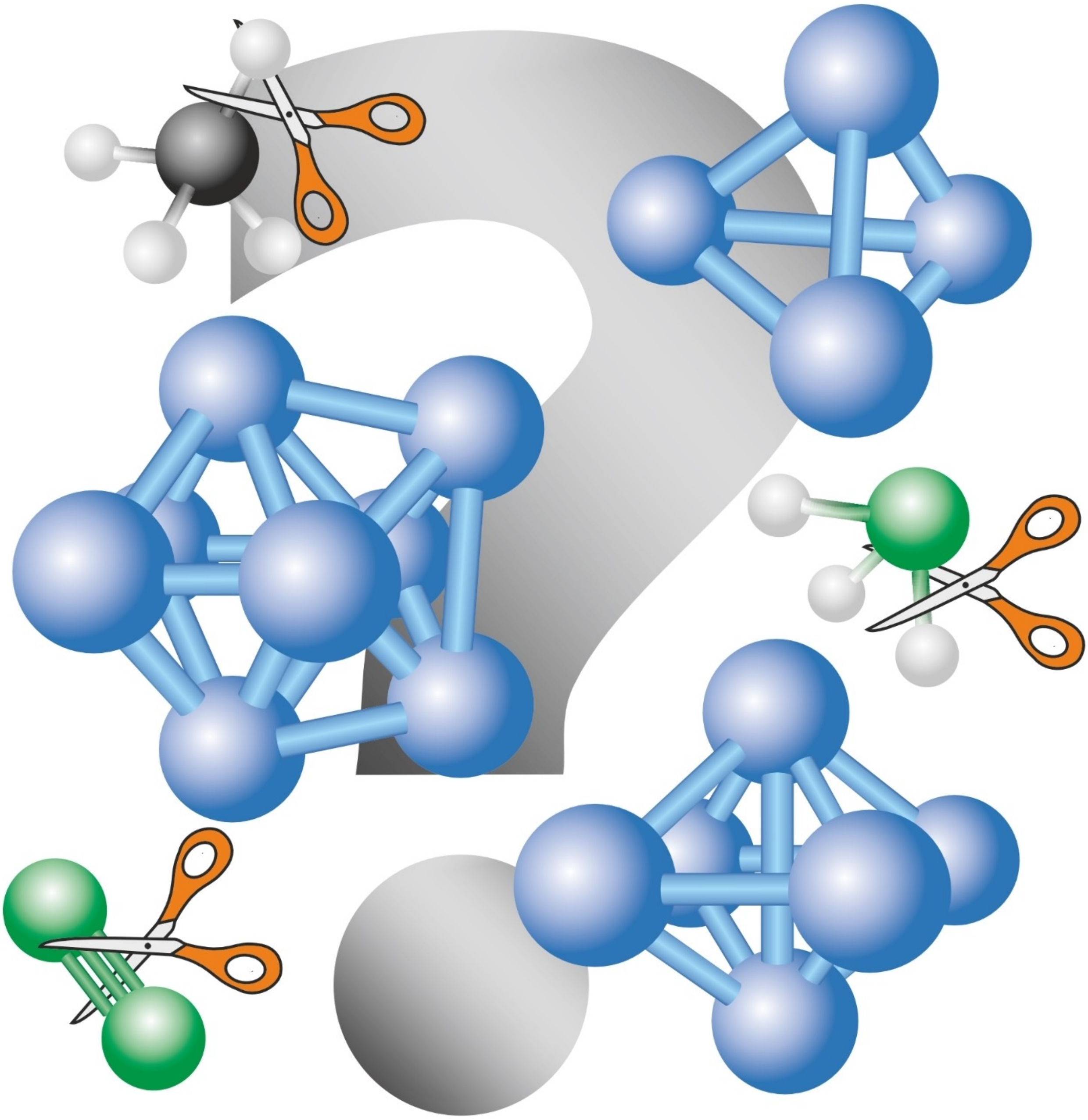

The emission control of harmful compounds and greenhouse gases and the development of alternative, sustainable fuel sources is a major focus in current research. A solution for this problem lies in the development of efficient catalytic materials. Here, gas phase model systems represent prominent examples for obtaining fundamental insights on reaction properties of prospective catalytic systems. In this work, we review results from studies of tantalum clusters and their oxides in the gas phase and discuss insights with a potential relevance for applied systems. We focus on reactions that are essential for sustainable chemistry in the future. In detail, we address the activation of methane, which may enable the transformation of a greenhouse gas to a chemical feedstock, and we discuss the activation of $NH_3$, which may function as an alternative energy carrier whose unwanted emission needs to be curbed in future applications. Finally, we consider the activation of $N_2$ as a third reaction, since reducing the high energy demand of ammonia synthesis still bears significant challenges. While tantalum may be an interesting catalytic material, the discussed studies may also serve as benchmark for investigations of other materials.

## 1. Introduction

Transition metals are a prominent choice when looking for efficient catalytic materials. Due to their partially filled d-orbitals, they can either donate or accept electrons easily from reactants, which often explains their catalytic activity. Moreover, they can exist in a large number of oxidation states, which change over the course of the reaction and can form complexes. Transition metals are thus often found as an essential component in catalytically active materials.[1] A less prominent member of the group of catalytically active d-block metals is tantalum. It is one of the rarest elements in the solar system,[2] but its relative abundance on earth is comparably high and exceeds that of other catalytically active materials, e.g., platinum, by several orders of magnitude.[3] While it indeed shows significant catalytic activity in some important reactions, e.g., in the non-oxidative coupling of methane (NOCM),[4] the origin of this activity and the associated pathways are often not understood. Therefore, research on the identification of these catalytic properties is essential to understand the underlying mechanisms. Here, reactions of isolated ions in the gas phase can serve as model systems to obtain insights on a molecular level for different reactions. Fostered by the idea of gas phase clusters mimicking catalytically active centers,[5,6] such studies are usually pursued in order to develop “concepts rather than recipes”.[7] While the absence of a support material comes with the expense of direct comparability with realistic catalyst materials (and the development of “recipes”), the study of gas phase clusters features different advantages over deposited systems. On the one hand, these studies enable the detection of reaction intermediates bound to the clusters with high sensitivity, which are in conventional studies often only accessible with highly demanding operando techniques with potential unwanted side effects (e.g., beam damages). On the other hand, the composition of the clusters is well defined in gas phase studies and can be tuned precisely, for example by using different charge states or altering the stoichiometry of the clusters (e.g., by their (partial) oxidation state). Furthermore, spectroscopic techniques in the gas phase, such as infrared multiple photon dissociation (IRMPD) spectroscopy,[8] can be exploited to obtain precise structural information on the metal particles, the reaction products, and intermediates. Hence, such studies yield detailed insights into possible reaction pathways, mechanistic concepts, and relevant properties (structural and electronic ones) of potential catalytic materials.

In this work, we review the insights from studies of tantalum ions, clusters, and their oxides in the gas phase for three different important reactions: methane conversion, ammonia oxidation, and nitrogen activation. While methane is a potent greenhouse gas, it is also the smallest hydrocarbon and a source of molecular hydrogen.[9] Its selective and mild conversion to value-added chemicals is therefore not only of interest when considering the global methane budget,[10] but may also be economically attractive. $NH_3$ is another source of molecular hydrogen. Due to its beneficial shipping properties in comparison to methane and hydrogen, it may be an attractive alternative for the replacement of conventional fossil liquid fuels.[11] However, it is also a caustic and hazardous gas and, when being burnt, a potential source of harmful nitrogen oxides.[12] Emissions of $NH_3$ from technical applications, the so-called ammonia slip, should thus be avoided, fostering the research on efficient ammonia slip catalysts. As a last reaction, this article addresses the activation of nitrogen. An efficient production of ammonia is still important, but currently also challenging,[13] in particular when it comes to a production in small, decentralized facilities.[14] With an efficient activation of $N_2$, a crucial step toward improved $NH_3$ conversions will be made.

## 2. Structure of Tantalum Clusters and Oxides

The precise knowledge of structures in the gas phase is essential for the elucidation of structure-reactivity relationships and the identification of structural and associated electronic motifs governing the reaction properties. The reactivity of small clusters can drastically change by the addition of a single

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atom.[15] On the one hand, this is attributed to electronic charge effects within the cluster (e.g., the difference between open-shell vs. noble gas configurations), which are usually most pronounced when the clusters only comprise a few atoms.[16] On the other hand, the structure of small clusters often varies strongly, even if their stoichiometry differs only by one atom.[17] Therefore, the structural determination with atomic precision is required until structural motifs develop, which stay dominant over a large size range (e.g., in the case of Pd anions[18]).

The structures of anionic tantalum clusters were determined by trapped ion electron diffraction (TIED) studies,[19] while cationic clusters were studied with IRMPD spectroscopy.[20] Due to the challenges associated with the experimental structure determination of neutral clusters, their geometries were only investigated by theoretical density functional theory (DFT) approaches.[21,22] Interestingly, the charge state of the clusters does not influence their structure strongly. Tantalum clusters ($Ta_n$) with $n > 3$ of different charges exhibit compact structures (see Figure 1) with the atoms forming a framework with high coordination numbers.[19–21] For $Ta_3$, only theoretical structures are reported for the cationic and neutral clusters. Again, similar results are found for both charge states with all calculations suggesting a triangular structure.[21–25] $Ta_4$ clusters already exhibit a three-dimensional, tetrahedral structure and $Ta_5$, $Ta_6$, and $Ta_7$ form trigonal, tetragonal and pentagonal bipyramides. The structures of $Ta_8$ to $Ta_{13}$ represent an icosahedral growth sequence, as determined in IRMPD[20] and TIED[19] experiments. Depending on the cluster size and the electronic state, distortion of the ideal symmetries are possible.[19]

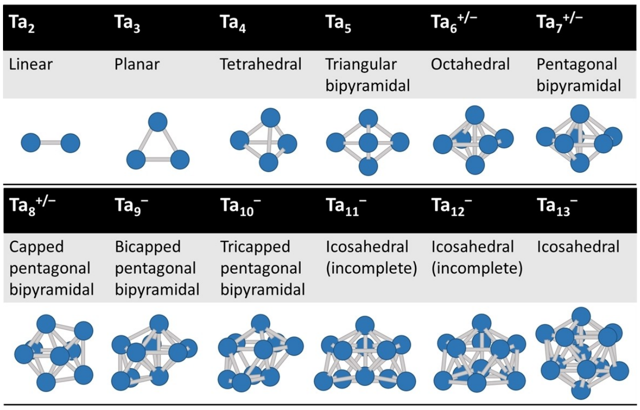

**Figure 1.** Structure of $Ta_2$ - $Ta_{13}$ for different charge states, which are all of similar geometry for clusters of the same size. A given charge state in the cluster's name indicates that the structure is supported by experimental data, either from IR-measurements or electron diffraction.[19,20] Tantalum atoms are shown in blue.

Fielicke et al. also investigated the structures of oxidized cationic tantalum clusters with low oxygen stoichiometry by IRMPD spectroscopy.[20] The results suggest that the geometry of the bare metal cluster is largely preserved (see Figure 2). The oxygen atoms are added in bridging positions for all investigated clusters. The oxidation can lead to slight distortions in the clusters and therefore a deviation from the symmetry of the bare tantalum species. The position of the first oxygen atom depends on the Ta–Ta bond lengths in the bare metal cluster and determines the edge where the bridging occurs. The second oxygen atom is usually bound in a position adjacent to the first Ta-O–Ta bridge. DFT calculations for the oxides of $Ta_3^+$ and $Ta_4^+$ further reveal that these motifs can continue for higher oxidation states until Ta–Ta bonds are cleaved by

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Martin Tschurl studied chemistry at the TU Graz (Austria), finishing with his Diploma Thesis on ESR spectroscopy with Günther Grampp. Later, he joined the TU Munich (Germany) for his PhD on the laser mass-spectrometry of anions with Ulli Boesl. After a post-doc stay at UC Berkeley (U.S.A.) with Richard Saykally, working on fs-CARS spectroscopy, he re-joined the TU Munich for his Habilitation with Ueli Heiz on model systems in catalysis. His research interests focus on the identification of reaction properties and mechanisms in different environments and applications.

Dr. Detlef Schooss received his PhD from the University of Karlsruhe in 1999. After a postdoctoral stay at Harvard University, he joined the Institute of Nanotechnology at the Karlsruhe Institute of Technology in 2001. His research interests focus on structural and optical properties of molecules and clusters in the gas phase.

Ueli Heiz explores properties of cluster-assembled materials in the non-scalable size regime for different applications. After studying chemistry in Bern, he received his PhD with E. Schumacher. He conducted research at ExxonMobil Research & Engineering Company and at the University of Pittsburgh with J.T. Yates, Jr with two scholarships (Andrew W. Mellon Foundation / Swiss National Science Foundation). He habilitated in Physics at the University of Lausanne with W.-D. Schneider. After stays in Japan and Berlin (Alexander von Humboldt Fellow), he was appointed to the University of Ulm. He became Chair of Physical Chemistry at TU Munich in 2004.

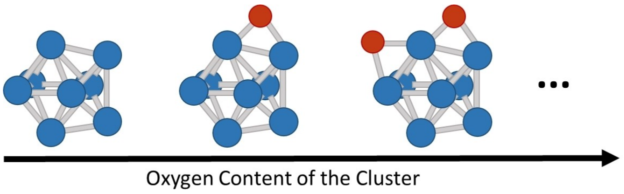

**Figure 2.** Structures of clusters with low degrees of oxidation shown on the example of $Ta_8^+$. Within the oxidation process of the cluster, the bicapped octahedron structure of the pure metal cluster remains largely preserved. Oxygen atoms are drawn in red, tantalum atoms in blue.

oxygen atoms, which then act as a bridge between two tantalum atoms.[26]

## 3. Methane Activation in the Gas Phase

Methane can be converted in different catalytic processes.[27–29] The two most common ones are the full oxidation of the molecule (i.e., its full combustion) and the steam reforming of methane (SRM). While the first one is applied to remove undesired methane emissions (e.g., by "flaring"),[30] the latter one represents an important method for $H_2$ generation and was the dominant process in 2019, as pointed out in a recent review article.[31] In both cases, large amounts of $CO_2$ are created. While this molecule is intrinsically produced in the full oxidation reaction, there are significant efforts undertaken to reduce $CO_2$ emissions in SRM and make the current processes more efficient.[9,31,32] The avoidance of $CO_2$ emissions is also a reason for other conversion pathways to enter the spotlight in research, which focus on the carbonaceous by-products of the reaction. Possible reactions are the partial oxidation of methane, which includes SRM, but also the conversion with $O_2$, methane dry reforming with $CO_2$, the catalytic decomposition of methane (CDM) and coupling reactions with methane, which can be either oxidative (OCM) or non-oxidative (NOCM). All these reactions are associated with different advantages and shortcomings.[27,33] For both reactions, the first activation steps are crucial for the overall reactions and an understanding of the reaction pathways is desired to interpret and improve the conversion efficiency and the reaction's selectivity. These aspects foster reaction studies of isolated ions with $CH_4$.[7]

When a methane molecule approaches a catalyst, it may be activated by different pathways (see Figure 3). i) If the catalyst interacts primarily with one of the hydrogen atoms, one of the C–H bonds will be weakened, which may ultimately cause a hydrogen-atom transfer (HAT) to the catalyst. This may be accompanied by the release of $CH_3$ radicals into the gas phase, as described by Wang and Lundsford on Li-doped MgO.[28] This mode of activation is also found on the oxide $[V_4O_{10}]^+$ and may be governed by the spin density on oxygen atoms.[34] ii) One atom of the catalyst may insert into the C–H bond of the approaching methane molecules. The driving force of this process could be the energy gain in the resulting bond formation between one of the atoms in the catalyst and the carbon atom of methane. Ultimately, this effect may lead to the cleavage of the C–H bond and even to consecutive C–H bond cleavages, followed by the desorption of $H_2$. iii) $CH_4$ may also react with the catalyst by a proton-coupled electron transfer (PCET) reaction. This process requires the existence of a Lewis acid-base pair on the catalyst.[35] Therefore, at least two different atoms of the catalyst are involved in this reaction, while only one atom would, in principle, suffice for the activation of $CH_4$ in the former activation schemes. The activation of methane via a PCET may also occur on metal oxides, similarly to the HAT. Both processes have been found to compete with each other if oxygen atoms with notable spin densities and centers with

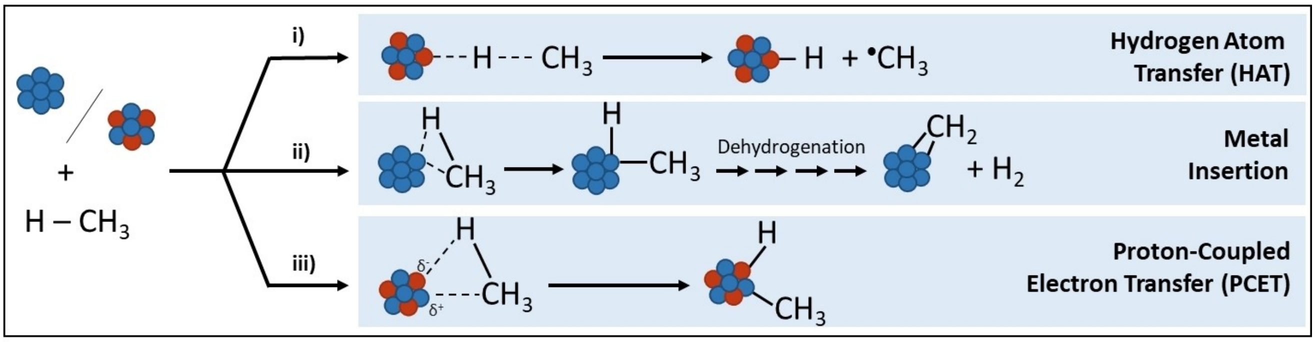

**Figure 3.** Different activation mechanisms of $CH_4$ on tantalum(oxide) clusters. i) shows the interaction of $Ta_nO_m^+$ with primarily one hydrogen atom. This interaction is followed by a hydrogen atom transfer, which results in the cleavage of the C–H bond. In ii), one atom of the catalyst inserts into one C–H bond. This reaction may be followed by consecutive insertion steps and the dehydrogenation of methane. Mechanism iii) involves two atoms of the cluster, acting as a Lewis acid-base pair. After an electron transfer, which is coupled with the transfer of a proton, the cleavage of the molecule is achieved. Oxygen atoms are given in red, tantalum ones in blue.

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doi.org/10.1002/cphc.202400513

Lewis acid-base pairs exist simultaneously on the metal oxide compound.[36] Instead, the formation of $\eta_2$-complexes, which was calculated to give rise to the most stable configuration of $CH_4$ interacting with neutral Pd,[37] does not seem to play an equally important role as the three other processes. For the reaction of consecutive methane molecules in particular, another pathway may become relevant, which occurs via a (possible hidden) transfer of hydrides. Here, a highly electrophilic carbon atom inserts into one of the C–H bonds of $CH_4$. This either happens in a stepwise (as found for the reaction with $AuC^+$)[38] or concerted process (found for $CuC^+$),[39] eventually leading to the formation of C–C bonds.

When looking at atomic cations, several elements were found to react with methane, but only some of them enable the dehydrogenation of the molecule at room temperature. First, Irikura and Beauchamp identified five cations, which enable the release of $H_2$.[40] Later, Shayesteh et al. added another two.[41] While the reaction was eventually found to be endothermic with $Nb^+$,[42] $Ta^+$ was among the elements enabling methane dehydrogenation in both studies.[40,41] One origin of this peculiar reactivity may lie in the strength of the metal-carbon bond supplying the driving force for the dehydrogenation reaction.[43] Relativistic effects further explain why in particular heavier elements and none of the elements with 3d configuration enable this reaction.[44]

The reaction of $Ta^+$ with methane has been investigated thoroughly by different groups. Buckner et al. were the first to report the dehydrogenation reaction,[45] followed by Irikura and Beauchamp,[46] who added considerations of different electronic properties to explain the reactivity. In the following, theoretical studies were conducted to understand the reaction and the origins of the reactivity in detail.[47–49] First, Sändig and Koch,[48] but later also Parke et al.,[49] performed DFT calculations to comprehensively map the potential energy surface of the reaction of $Ta^+$ with a single $CH_4$ molecule. Parke et al. further performed guided beam experiments and obtained dissociation energies for different species.[49] Eventually, these results were compared to the reactions of $CH_4$ with other 5d transition metals.[50] The structure of the reaction product $[TaCH_2]^+$ was investigated by IRMPD spectroscopy. In two different studies, a good agreement between the spectra and results from DFT calculations was achieved.[51,52]

Consequently, the reaction is finally comprehensively understood[48,49] (see Figure 4). First, methane adsorbs on $Ta^+$, which is energetically favored by about half an eV. The reaction then proceeds via two consecutive C–H bond cleavages, with the first one being caused by an insertion of the tantalum cation into the respective bond. The splitting of the first bond also requires a change in the spin states for thermodynamics to be favorable, which may originate from an intersystem crossing from the quintet to the triplet surface. The as-created hydrides can then recombine to form $H_2$, which can leave the cationic compound.[48,49] In an alternative, energetically likely even more favorable pathway,[49] $H_2$ is instead created by the interaction of the first hydride with the methyl group, while the insertion of $Ta^+$ into the second C–H bond is not required. In both cases, the resulting cationic compound is a tantalum carbene, whose structure has been confirmed in IRMPD measurements by Armentrout and co-workers.[51,52]

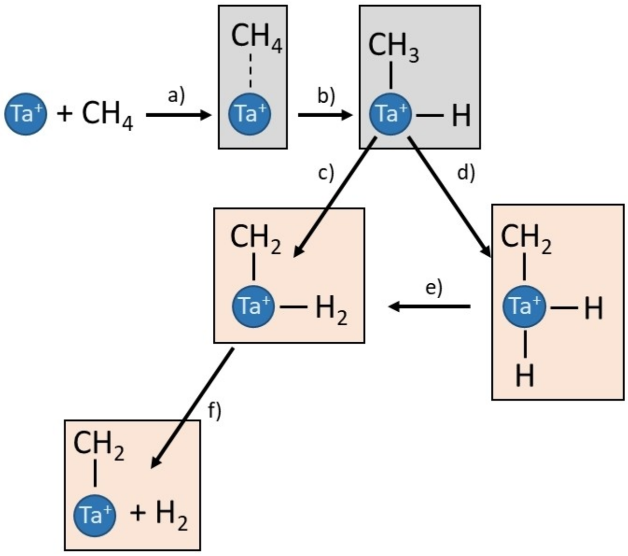


**Figure 4.** Activation of a methane molecule on $Ta^+$. a) shows the adsorption of the molecule, followed by the tantalum atom inserting into one C–H bond b). This leads to the splitting of the bond. After this, the hydride can either interact with the methyl group forming molecular hydrogen c) or the tantalum atom inserts again into a second C–H bond d). In the latter case, dihydrogen formation takes place when the two hydrides interact with each other e). This is followed by the desorption of the molecular hydrogen f), leaving behind a cationic tantalum carbene.

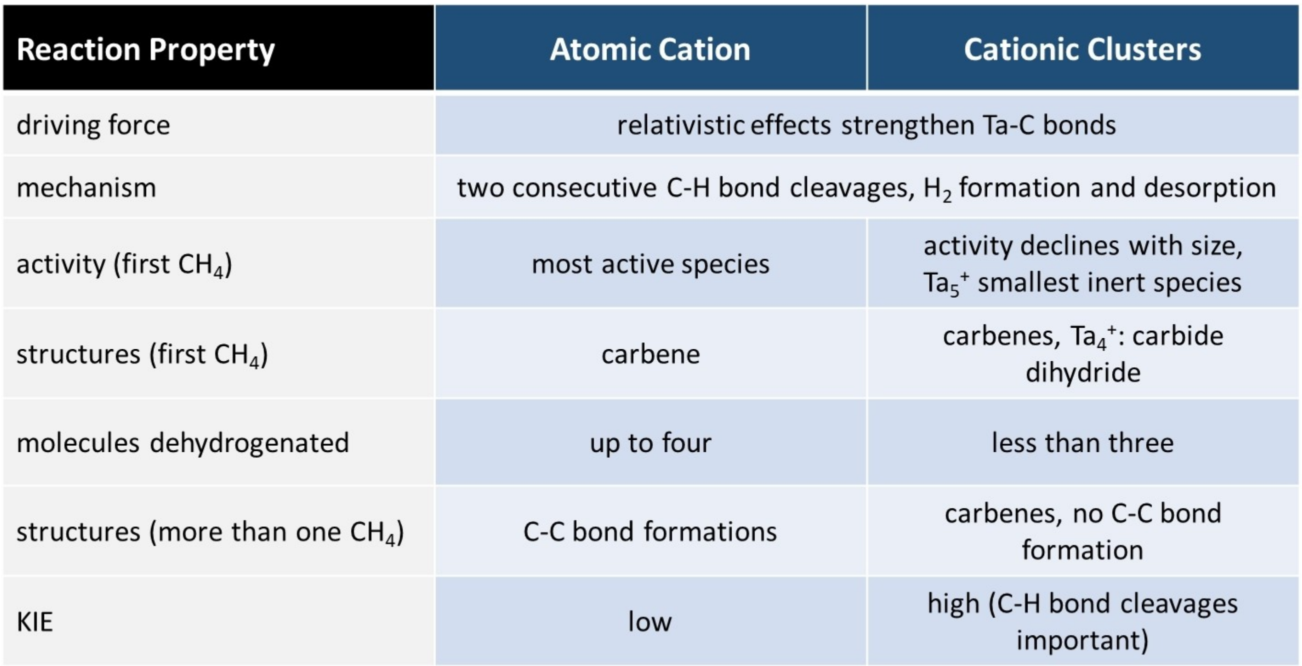
The entire reaction is slightly exothermic, with no significant barriers above the entrance channel of $Ta^+ + CH_4$. While the global minimum of the potential energy surface is H-$Ta^+$-$CH_3$, this species is not observed in experiments. A facile thermalization by the desorption of $H_2$ may be the main reason for this effect, while other relaxation pathways, such as the thermalization by collision with the buffer gas under multi-collision conditions,[41,53] are too sluggish to stabilize the species and avoid $H_2$ evaporation.

The reaction of methane occurs in a very similar pathway on cationic tantalum clusters. (Note that for sake of simplicity, all species with more than one tantalum atom will be referred to as "clusters" in the following.) It also proceeds via the subsequent abstraction of two hydrogen atoms from $CH_4$ and the consecutive formation and desorption of $H_2$, as it can be seen for the reaction on $Ta_4{}^+$.[53] However, there are notable differences between the reaction of clusters and the atomic cation. The most significant deviation lies in the activity and its decline with an increasing number of atoms in the cluster. While the dimer, trimer and tetramer still enable methane dehydrogenation but with a reduced rate compared to the reaction of $Ta^+$, this reaction is not enabled anymore on $Ta_5{}^+$, a particularly inert size, and larger clusters.[25] The origin of this phenomenon is not yet fully understood but has recently been assigned to the presence of localized σ-bonding orbitals in the clusters.[54] In $Ta_5{}^+$ this causes a significant increase in the energy of the transition state of the C–H bond insertion by one of the tantalum atoms, as well as a higher energy demand for the evaporation of $H_2$ according to DFT calculations.[53]

The importance of the insertion into the C–H bond is also reflected in the kinetic isotope effect (KIE) of the reaction for the clusters enabling methane dehydrogenation. The KIE is a tool for identifying rate-determining reaction steps[55] and elucidating the role of certain bond cleavages in the rate of the reaction by isotopic substitution. For clusters, the reaction with $CD_4$ is considerably slower than the reaction with $CH_4$, giving rise to large KIE values (here, calculated using the ratio of the rate constants for the reaction with $CH_4$ and $CD_4$) of six and higher.[25] In contrast, the atomic cation only exhibits a KIE value of about two and lower.[25,49] Consequently, the contribution of C–H bond cleavages to the rate-determining reaction step is much more significant in the reaction of the clusters.

While the atomic cation is the most reactive size, it also enables the dehydrogenation of the highest number of methane molecules. In contrast to $Ta_2^+$, $Ta_3^+$ and $Ta_4^+$, which only release $H_2$ for the reaction with one or two $CH_4$ molecules,[25] $Ta^+$ dehydrogenates four methane molecules in consecutive reactions followed by the adsorption of an entire $CH_4$ molecule.[25,41] Even more significantly, the atomic cation is the only size of bare tantalum cations that enables a C–C coupling reaction according to DFT calculations.[25] The reason for this peculiar reactivity may lie in the absence of further tantalum atoms. In larger compounds, carbenes can adopt a state of lower energy by forming a bond to another tantalum atom adjacent to the one that has cleaved the C–H bond of the methane molecule. As such an additional bond formation is precluded in atomic cations, it may be energetically advantageous to form C–C bonds instead. Figure 5 summarizes the most important results and compares the reactivity of the atomic cation with that of bare metal cluster cations.

The oxidation of tantalum cluster cations changes their reactivity. The dioxide and trioxide of the atomic cation (i.e., $TaO_2^+$ and $TaO_3^+$) both enable the reaction with $CH_4$. Three different pathways are observed for $TaO_3^+$ under single-collision conditions.[56] While the main reaction channel involves the release of $CH_2$, the other two side reactions yield cationic products, which require the concomitant formation of neutral products with formaldehyde and methanol stoichiometry. In contrast to $TaO_3^+$, $TaO_2^+$ only enables the adsorption of an entire $CH_4$ molecules without the desorption of any neutral products.[57] However, DFT calculations suggest that a C–H bond cleavage takes place.[57] Similar to the reaction of the trioxide, the reaction proceeds via an entrance channel, in which the methane molecule approaches the tantalum atom with the carbon. The C–H bond cleavage is then facilitated by an oxygen atom adjacent to tantalum, eventually forming a hydroxide moiety. Such a scheme may be representative for higher degrees of oxidation. Instead, the addition of only one oxygen atom to the cationic tantalum tetramer and pentamer increases the reactivity (in case of $Ta_5O^+$, the inert $Ta_5^+$ becomes highly reactive for methane dehydrogenation), but does not change the reaction mechanism. This is also reflected in similar high KIE values as in the reaction of bare tantalum cluster cations.[53] Furthermore, the oxygen atoms do not actively take place in the reaction by bond formation or cleavages and hydroxide formation is energetically unfavorable according to DFT calculations. Such a reaction behavior may be representative for low oxidation states, in which the oxidation modifies the electronic properties of the clusters but maintains the typical characteristics of the reactivity. In agreement with this interpretation, Li et al. showed that the addition of an oxygen atom to the cationic tantalum clusters modifies the σ-orbitals of the metal bonds and their localization, which then



| Reaction Property | Atomic Cation | Cationic Clusters |
|---|---|---|
| driving force | relativistic effects strengthen Ta-C bonds | |
| mechanism | two consecutive C-H bond cleavages, $H_2$ formation and desorption | |
| activity (first $CH_4$) | most active species | activity declines with size, $Ta_5^+$ smallest inert species |
| structures (first $CH_4$) | carbene | carbenes, $Ta_4^+$: carbide dihydride |
| molecules dehydrogenated | up to four | less than three |
| structures (more than one $CH_4$) | C-C bond formations | carbenes, no C-C bond formation |
| KIE | low | high (C-H bond cleavages important) |

**Figure 5.** Comparison of the reactivity of $Ta^+$ with the reaction on Ta cluster cations in the activation of methane.

governs the reactivity of the clusters.[54] Finally, the proper degree of oxidation may enable a catalytic behavior of the tantalum compound, as we have shown for the reaction of methane on $Ta_2O_8^+$.[58] Here, the temperature-dependent reactivity suggests a reaction of two $CH_4$ molecules to ethane and $H_2$, following the NOCM. Similarly, this reaction was observed for a silica-supported tantalum hydride in heterogeneous catalysis.[4] Thermodynamics of this reaction dictate that the equilibrium concentrations are strongly on the side of the reactants at room temperature, which makes studies in heterogeneous catalysis difficult. In turn, but at the costs of a precluded detection of neutral products, the sensitive detection of charged reaction products in gas phase studies at very low conversions facilitates the analysis of such reactions. The NOCM on tantalum may benefit from the modest energy gain by less than 1 eV in the dehydrogenation of methane by tantalum clusters and oxides,[25,53,54] which enables the conversion of products in consecutive reactions. However, in oxidation reactions, the oxophilicity of tantalum may lead to unwanted oxidation of the tantalum-based catalysts and, thus, to their deactivation. This may be avoided when reactions are conducted under anaerobic conditions as in the NOCM.

While also $[TaOH]^+$ and $[HTaO]^+$ have been described to react with $CH_4$,[59] and the reaction with doubly-charged $Ta^{2+}$ led to a variety of different products,[60] only few anionic systems have been reported so far to activate methane. Usually, active systems contain heteroatoms, as in the cases of $[Ta_2C_4]^-$[61] and $[Ta_2N_3]^-$.[62] In general, this suggests an inferior reactivity of anionic tantalum compounds in comparison to cationic systems.

## 4. Tantalum Reactivity with Ammonia

$NH_3$ as an energy carrier is a popular choice in sustainable energy research, since it has various advantages over the thoroughly investigated hydrocarbon options. On the one hand, the technically comparatively simple ammonia liquefaction process is comprehensively studied and enables the transportation of the molecule in its liquid form,[63] which is usually preferred over the shipment of gases. For most suitable hydrocarbons (e.g., for methane or natural gas, respectively),[64] this process is much more challenging. On the other hand, ammonia can be used for the sustainable storage of energy and $H_2$. While the release of hydrogen from carbonaceous species is usually coupled to the formation of CO and $CO_2$, which comes with environmental strain,[65] similar reactions with $NH_3$ as a carbon-free energy carrier will only yield $N_2$ as a non-hazardous by-product.[66] Besides these advantages, a big concern when working with ammonia is its health hazard and the environmental danger, e.g., for aquatic life. Because of that, significant research efforts focus on the so-called "ammonia slip catalysis"; an efficient way to convert the hazardous ammonia "slipping" through the process to the safer compound nitrogen.[12] While in these applications, the oxidation is performed to yield $N_2$,[67] it can also be conducted with the goal of NO production for synthetic purposes.[68] Nevertheless, for ammonia as a fuel source, the reaction should usually be carried out with a high selectivity toward $N_2$ to avoid the generation of nitrous gases, which are a well-known health risk.[69] In order to achieve high conversion rates, which are mandatory for a good ammonia slip catalyst, and the required high selectivity toward $N_2$, the activation of the $NH_3$ molecule is a crucial point. Here, isolated metal clusters in the gas phase can again serve as a suitable model catalyst to investigate the adsorption and activation processes of $NH_3$, which have been shown to be critical steps in heterogeneously catalyzed reactions.[70]

As reported for different atomic cations,[71,72] the adsorption of ammonia can take place via two different mechanisms. The molecule can either i) adsorb molecularly via ligation or ii) eliminate $H_2$ while forming an imide bond (see Figure 6).

For atomic cations, the transition metal determines which of these pathways is followed in the reaction with $NH_3$.[71] Concerning the adsorption of the first ammonia molecule, the imide-formation mainly occurs for early transition metals, while the $NH_3$ ligation is predominant for late transition metals. In addition, the probability of imide formation increases as one moves down within a group of the periodic table.[71,73] For most transition metal cations, only one particular pathway takes place in the reaction with the first ammonia molecule. The exception is $Ir^+$, which enables both reaction types.[71] Concerning the adsorption of the second $NH_3$ molecule, an ensuing ligation reaction occurs for all transition metals except for elements in the 3rd row (i.e., $Ta^+$, $W^+$ and $Os^+$ cations), which enable a second imide-bond formation via $H_2$ elimination. All reactions with further $NH_3$ molecules result only in ligand formations.

The mechanism of the ammonia dehydrogenation (reaction type ii) proceeds via the insertion of the metal cation into the ammonia molecule,[71] achieving the cleavage of the first N–H bond. This way, a bond from the hydrogen atom to the metal is established. Then, the adsorbed $NH_2$ undergoes subsequent cleavage of a further N–H bond through a mechanistically identical insertion process. Here, $H_2$ is eliminated, which results in an imide bond to the metal atom.[74] After this reaction, either dissociative adsorption of further $NH_3$ molecules following the same reaction path can take place or ligation occurs with the adsorption of entire $NH_3$ molecules. Once ligation has started, no further ammonia molecules will adsorb dissociatively on the

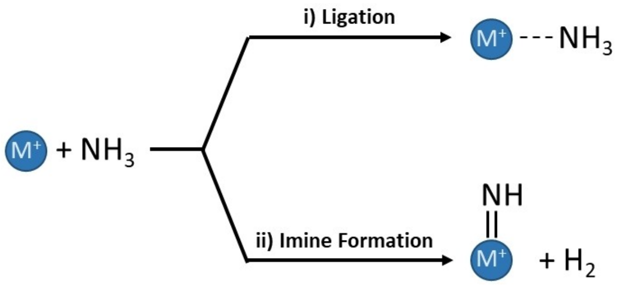


**Figure 6.** Reaction of ammonia with metal cations. Depending on the metal, the reaction can either take place via ligation i) or the molecule can be activated ii), forming an imide bond between the nitrogen and the metal atom while releasing $H_2$.

cationic species anymore.[71] The maximum number of $NH_3$ molecules adsorbing on the atomic cation depends on its electronic properties and, therefore, on the element. The electrons of the lone pair in the $NH_3$ molecule can bind to the empty d-orbital in the transition metal, resulting in a fast ligand addition. Once these d-orbitals are completely filled, further addition is possible through the interaction with the metal's p-orbital. This reaction pathway occurs, however, significantly slower.[71,75] When the p-orbitals are also filled, no more ammonia molecules can adsorb on the species anymore. For tantalum cations, this means that after two imide formations, four additional ammonia molecules can be added as ligands to the atomic cation.[71]

The reactions of cationic tantalum clusters with ammonia proceed in a similar way as the reaction of the atomic cation. Arakawa et al. studied those reactions with cations up to a size of 10 Ta atoms.[23] For all sizes including the atomic cation, the reaction with the first $NH_3$ is the dehydrogenation of the molecule, resulting in the formation of an imine. The rate constant of this reaction increases linearly with the cluster size until it levels off at $Ta_7^+$, reaching a plateau for the last four sizes.[23] While the reaction of the second ammonia molecule with the atomic cation yields a diimine, all other sizes of tantalum cluster cations enable a second dehydrogenation reaction, leading to the formation of a dinitride.[23] Generally, if the evolution of an additional $H_2$ is stochiometrically possible, it can enable the formation of a nitride. When it is not possible, an imine is formed as an intermediate species. The reaction with a further $NH_3$ molecule can then enable the evolution of two hydrogen molecules and the formation of a dinitride (see Figure 7). This sequence can be repeated serval times, depending on the size of the tantalum cluster.[23] Aided by DFT calculations of the atomic cation, the dimer, and the trimer, the authors found that at a certain number of dehydrogenated ammonia molecules, the additional dehydrogenation is energetically not favorable anymore so that the reaction stops at the diimine structure.[23] While this compound may still enable the adsorption of an entire $NH_3$ molecule – a reaction which sometimes also occurs in parallel to the dehydrogenation –, the formation of nitrides is instead not observed anymore. The change in the reaction is here correlated with the oxidation state of tantalum. As soon as all tantalum atoms significantly exceed the atom's maximal oxidation state of $+5$, the reaction behavior changes and prevents the liberation of another $H_2$ molecule. The authors assign this to the unfavorable oxidation state of the nitrogen atoms.[23] When $H_2$ is liberated and all tantalum atoms have lost their capability of donating electrons, the additional nitrogen atoms cannot reach the favorable oxidation state of around $-1$ and remain in a higher oxidized form, leading to a compound of higher energy.

While the anionic charge state has not been investigated yet, the interaction of ammonia molecules has also been studied for some neutral tantalum oxide compounds.[76] Mass spectroscopy studies were performed on $Ta_nO_m$ with $n=1$ and $m=0-4$ and $n=2$ and $m=1-6$, respectively. For highly oxidized species, reported association reactions take place preferably compared to pure metal clusters. Namely for TaO, $TaO_2$, $TaO_3$ and $Ta_2O_3$, $Ta_2O_4$, $Ta_2O_5$ and $Ta_2O_6$, the activation of the ammonia molecule within this association reaction is assumed. Here, a $NH_2$ moiety is formed and the hydrogen atom is transferred to the oxygen atom of the respective $Ta_nO_m$ species (see Figure 8).[76]

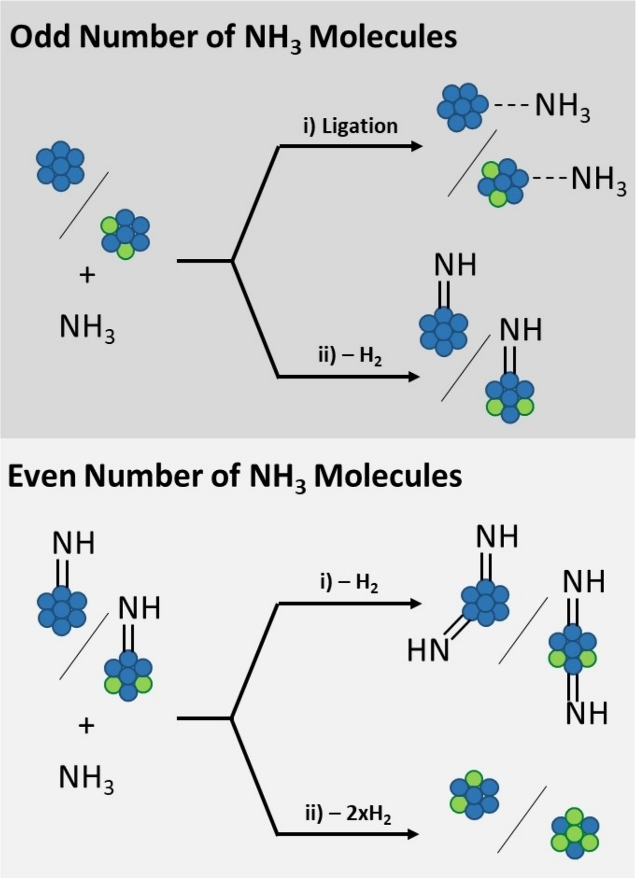


**Figure 7.** Product formation reactions of cationic tantalum clusters and nitrides including the atomic cations with a different number of $NH_3$ molecules. While reactions with an odd number of ammonia molecules lead to either a ligation reaction or imine formation, either a second $H_2$ molecule is released or a diimine is formed when the compound reacts with an even number of $NH_3$ molecules.[23] In addition, ligation, which is not included in the figure for the reaction with an even number of ammonia molecules, represents a third pathway that can start at any stage of the reaction sequence. Tantalum atoms are given in blue, nitrogen atoms in green.

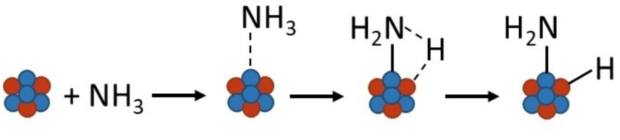


**Figure 8.** The activation of $NH_3$ on oxidized tantalum cations and tantalum oxide clusters. The reaction includes the formation of a $NH_2$ moiety resulting from the transfer of a hydrogen atom to oxygen. Tantalum atoms are shown in blue, oxygen atoms in red.

## 5. Activation of $N_2$ by Tantalum

While ammonia is seen as a potential sustainable fuel source, its production still proves to be a challenge.[13] Until the beginning of the 20th century, ammonia was obtained by mining limited deposits of sodium nitrate (so-called "Chile saltpeter"), mostly in South America. With the Haber-Bosch process, the first industrial process was developed.[77] Here, $N_2$ and $H_2$ are used to form $NH_3$ on an osmium catalyst. Since the osmium availability is limited, industry soon switched to the newly discovered iron-based catalyst. The biggest challenge of this reaction is the decrease in entropy toward product formation, therefore favoring low temperatures, while a certain energy is needed to overcome present barriers.[78] Therefore, the reaction is performed at high pressures and mild temperatures, but still considerably small conversion rates in the range of 15% are yielded even when a second-generation Ru-type catalyst is applied.[79] Research remains therefore focused on various ways to improve this conversion rate by either changing the reactor design or the catalyst material.[79] In order to find a suitable catalyst, a material is required which is able to efficiently activate $N_2$.

The interaction of nitrogen with a potential catalytic material can take place by two main pathways. The molecule may either adsorb molecularly or dissociatively onto the catalyst. The latter leads to the cleavage of the strong N–N triple bond so that the molecule may be converted in a consecutive reaction, for example with molecular hydrogen as discussed for the reaction with $Ta_2^+$.[80] Therefore, dissociative adsorption is a strong indication that the $N_2$ molecule has been activated. Mou et al. reviewed the literature on the activation of $N_2$ by different gas phase metal species.[81] In their work, it is shown that only ten metallic elements enable the dissociative adsorption of $N_2$ or the functionalization of nitrogen. Six of those do not require additional heteroatoms other than hydrogen or nitrogen, which are reactants used in the ammonia synthesis. One of these elements is tantalum, which even enables the dissociative adsorption of molecular nitrogen on bare metallic cations.

When $N_2$ adsorbs on tantalum clusters of different sizes, two main size regimes are observed, differing in the cluster's interaction with the nitrogen molecule (see Figure 9). According to DFT calculations and cryogenic infrared photon dissociation (IRPD) studies, the adsorption of the first $N_2$ leads to its dissociation on small clusters up to a size of $Ta_4^+$.[24,82] In case of $Ta_4^+$, the resulting dinitride is still capable to dissociate a second nitrogen molecule before intact adsorption is reported.[24,82] Similarly, the mononitride of $Ta_2^+$ (i.e., $Ta_2N^+$) also activates nitrogen, which was demonstrated by the exchange of the nitrogen atom in the reaction with $^{15}N_2$.[83] However, the capability of tantalum cluster cations enabling N–N bond scissions seems to vanish when their size increases to clusters with five or more tantalum atoms. Other than for their smaller counterparts, $Ta_{5\text{-}8}^+$ give IRPD spectra that point to end-on and side-on adsorption of $N_2$ rather than to the dissociation of the molecule, regardless of the number of nitrogen molecules adsorbed.[84] In turn, it was shown in thermal desorption studies that $N_2$ is strongly bound to $Ta_6^+$ once the barrier for N–N dissociation can be overcome, as two nitrogen atoms remained bound to the clusters even when they were heated to 1000 K.[85] The authors further concluded from the thermal behavior that the dissociation of the first $N_2$ molecule occurs rather readily while the dissociation barrier quickly increases for the adsorption of additional nitrogen molecules.

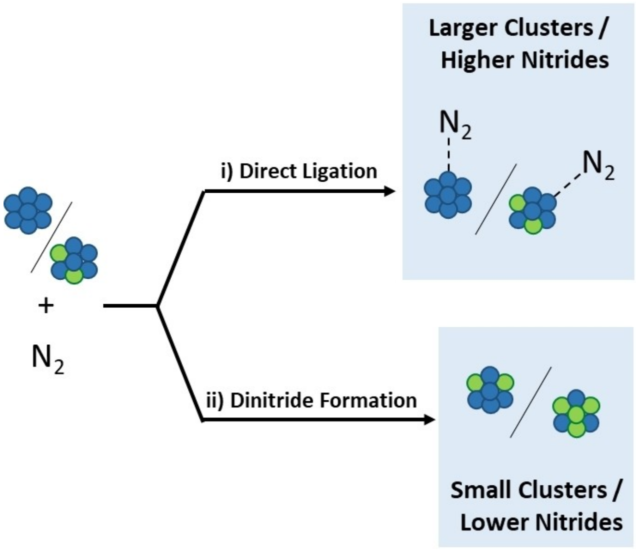


**Figure 9.** Reaction of cationic tantalum compounds with $N_2$. Depending on the number of tantalum and nitrogen atoms, the reaction can either lead to direct ligation or yield dinitrides by the cleavage of the N–N triple bond. Tantalum atoms are given in blue, nitrogen atoms in green.

Nevertheless, this behavior and, in particular, the reactivity of smaller clusters indicate that tantalum might be a suitable candidate for a catalytic conversion of $N_2$, as for the synthesis of ammonia. This hypothesis was tested by Geng et al.,[80] who investigated the activation of $N_2$ on $Ta_2^+$ clusters with the subsequent interaction with $H_2$. In a theoretical study supported by experimental observations, they outlined a possible catalytic reaction pathway for the coupling of $N_2$ and $H_2$ to $NH_3$ on $Ta_2^+$. However, the overall reaction has not been tested in a catalytic experiment yet.

Reactions of molecular nitrogen with tantalum clusters in other charge states than the cationic one are much less investigated. For small neutral clusters (i.e., $Ta_{1\text{-}4}$) DFT calculations predict a dissociative adsorption of $N_2$ for the structures of lowest energy.[81,86] Depending on the cluster size, the dissociated molecule parts are either end-on, solely interacting with one Ta metal center, or bridging between multiple Ta atoms. While these structural motifs usually differ strongly in the binding energies, different isomers of one motif may be formed in the reaction of $Ta_3$ and $Ta_4$ with $N_2$ according to the calculations.

Anionic systems are again much less investigated than cationic species. One work reports only weak adsorption of $N_2$ for rather large clusters with 14 atoms or more (i.e., $Ta_n^-$ with $n \geq 14$),[87] while the authors did not observe any adsorption for smaller sizes (i.e., $Ta_{5\text{-}13}^-$) at the experimental conditions of the study. This behavior may once again suggest an inferior reactivity of anionic clusters compared to cationic ones. In contrast, a theoretical study predicts that $Ta_3^-$ and $Ta_3N_2^-$ are actually capable of cleaving the N–N triple bond more efficiently than cationic compounds.[88] Furthermore, DFT calculations for $Ta_2N^+$ and $Ta_2N^-$ show that the reaction of $N_2$ could be very similar for both species, but with significantly lower energies of the transition states relative to the entrance channel for the anionic system .[83] The authors assign this effect to a π-backdonation weakening the N–N triple bond, which is facilitated for the anionic system due to the additional electrons. These findings may motivate future studies on anionic tantalum compounds. A first step toward the goal of performing the Haber-Bosch reaction with tantalum cluster anions was made by Cheng et al., who showed the activation of $N_2$ by $Ta_2^-$ cluster hydrides (more precisely $Ta_2D_2^-$ and $Ta_2D_4^-$), resulting in the presence of both reactants needed for ammonia synthesis in a dissociated state on the same cluster species.[89]

## 6. Conclusion and Outlook

The study of tantalum species in the gas phase demonstrates the capabilities of obtaining a fundamental understanding of the reaction of small molecules. Significant insights have been gained on the activation of methane. It was possible to identify relativistic effects as a crucial aspect for the driving force of methane dehydrogenation.[44] Mechanistically, the reaction occurs similar on all bare tantalum compounds with insertions of the metal into C–H bonds and the ensuing formation and desorption of $H_2$.[49,53] In the majority of reactions, carbenes are formed,[25,49,52] with only $Ta_4^+$ deviating from this general behavior.[41,90] The structural differences of the carbonaceous products help to explain the changes in the consecutive oxidation reactions.[91] Besides the similarities, the reaction of atomic cations and cationic clusters with methane exhibits notable differences. Most significantly, only atomic cations enable C–C coupling reactions, while consecutive methane dehydrogenation on cationic tantalum clusters only yields carbenes.[25] This behavior may result from the absence of bond formation options to adjacent tantalum atoms in the reaction of the atomic cation, making bond formation to other carbonaceous species thermodynamically favorable. Consequently, the application of either single-atom catalysts or clusters may be a tool to steer the reaction toward the product of interest.

Low degrees of oxidation of the bare tantalum clusters change their activity, but not the overall reaction mechanism.[53] As the structure of the bare clusters is also largely preserved after such a process, this effect may mostly be assigned to changes in the clusters' electronic structure. Indeed, the localization of the Ta–Ta σ-bond, which can be tuned by oxidation, has been identified as the origin of the reactivity toward methane.[54] The additional oxygen atoms may further only function as ligands and do not actively participate in the reaction by bond formations or cleavages.[53]

In contrast, higher degrees of oxidation change the reactivity more significantly. On the one hand, the activity may decline, as the insertion of the metal into the C–H bond starts to exhibit higher barriers.[54] On the other hand, additional reaction pathways typical of oxide species (i.e., a HAT or PCET) may become accessible. This is shown in reactions of oxides of the atomic cation,[56,57] in which bond formations between hydrogen and oxygen atoms become possible. The change in reactivity of strongly oxidized clusters may thus be associated with structural differences and the absence of Ta–Ta bonds due to oxygen atoms bridging between two tantalum atoms,[26] with the compound then rather resembling an oxide than an oxidized metal cluster.

Due to the high oxophilicity and desire to avoid decomposition pathways by unwanted cluster oxidation, it may be advantageous to conduct anaerobic reactions with tantalum compounds rather than oxidation reactions with $O_2$. In this regard, it may be beneficial that methane dehydrogenation is largely isoenergetic, according to DFT calculations,[53,54] facilitating subsequent conversion reactions even when not being strongly thermodynamically favorable. Indeed, the reaction of $Ta_8O_2^+$ with methane suggests that the compound catalytically performs the NOCM,[58] similarly to a compound with single tantalum centers in heterogeneous catalysis.[4] While the low conversions at room temperature hamper studies in heterogeneous catalysis, the highly sensitive detection of reaction intermediates in gas phase studies allows overcoming conventional analytical limitations.

Much less research has been done on the activation of ammonia, but studies of clusters in the gas phase revealed that the activation of $NH_3$ mechanistically also occurs via metal insertion into an N–H bond.[71] As this insertion can occur twice, it similarly enables the dehydrogenation of the reactant with the release of $H_2$ and an imine formation on the tantalum compound. The reaction with a second $NH_3$ molecule then enables the formation of two additional hydrogen molecules so that a dinitride results.[23] However, the reaction depends on the stability of the dinitride with respect to the diimine and governs, which of the two species is eventually formed.[23]

The stability of nitrides is also defining the reaction with $N_2$. While small tantalum cations activate $N_2$ at low temperatures and result in the formation of dinitrides,[24] larger clusters with more than 5 Ta atoms likely have to overcome significant barriers.[84,85] A high stability of nitrides in the reaction of small clusters[24,85] will be detrimental for the conversion in subsequent reactions, as in the synthesis to ammonia with $H_2$ or for the formation of $N_2$ in the ammonia decomposition. While the interplay of different factors as the size of the tantalum compound or the degree of nitride formation may be delicate, gas phase studies can also demonstrate that such reactions may be possible as outlined for the reaction of $N_2$ and $H_2$ on $Ta_2^+$.[80]

While the study of tantalum compounds in the gas phase reveals the catalytic potential of the metal by the identification of fundamental effects beneficial for the activation of small molecules, they can also serve as a platform for studying the same or similar reactions for different elements. As Ta has only one stable isotope, mass spectrometric studies are strongly facilitated for larger clusters. The established methodology in the research on tantalum may thus open the door for investigations of large clusters with elements of a rather complex isotopic pattern, such as Pt, Ru or Pd.

In addition, gas phase methods may be further developed to address questions which can currently not be answered for the systems discussed in this work. Especially, the experimental investigation of consecutive reactions, the elucidation of the structure of reaction products and intermediates by spectroscopy and the study of truly catalytic reactions are at best in their infancies. Here, more complex setups featuring several reactors, as already suggested by Lang and Bernhard,[5] may facilitate deeper insights, in particular when being coupled to powerful spectroscopic techniques, using for example free electron lasers in the IR range[92] or different table-top systems.[93] Furthermore, other ways of conducting the reactions, as e.g., by crossed beam velocity imaging, used for the reaction of Ta$^+$ and $CO_2$[94], may also provide further insights into characteristics of the reaction pathways.

## Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through the project CRC 1441 (project number 426888090). Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interests

The authors declare no conflict of interest.

**Keywords:** C–H activation · Gas-phase reactions · N–H activation · N–N activation · Tantalum

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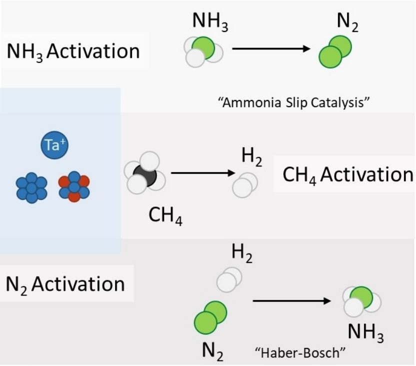
Manuscript received: May 3, 2024
Revised manuscript received: November 29, 2024
Accepted manuscript online: November 29, 2024
Version of record online: ■■, ■■

The results from the literature pertaining to the reaction of tantalum clusters with small molecules are reviewed. The work focuses on insights into the activation of methane, ammonia, and molecular nitrogen, which are important for a future sustainable chemistry. In particular, fundamental properties of the metal particles with potential relevance to applied systems are discussed.



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**Activation of $CH_4$, $NH_3$, and $N_2$ by Tantalum Ions, Clusters and Their Oxides: What Can Be Learnt from Studies of Ions in the Gas Phase**