Tuning the Dissociative Action of Rh clusters towards NO by substituting a Single Ta Atom

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ABSTRACT: The modification of Rh chemical activity for decomposition of NO by alloying with Ta was studied by vibrational spectroscopy of gas phase clusters, where one single Rh atom was substituted by Ta, with NO adsorbed. While NO adsorbs molecularly on pure Rh clusters, it was found to adsorb dissociatively on RhₙTa⁺ (n = 2–8) with the O bound to the Ta on-top site. A reaction path for NO decomposition obtained by DFT calculations for octahedral Rh₅Ta⁺ and Rh₆⁺ suggests that the Ta oxygen affinity strongly reduces the energy barrier right before bond cleavage, facilitating NO dissociation. The trend is consistent with the Bell-Evans-Polanyi principle. The addition of other, slightly less oxophilic dopant atoms is expected to enhance catalytic reactivity of Rh.
1. Introduction

The continuous increase in emission of combustion products harmful to the human respiratory system or the planet’s heat balance poses a prime challenge for the natural sciences. Mitigation of such detrimental side-effects of economic growth can be promoted by the development of efficient catalysts that can convert harmful emission products into harmless omnipresent atmospheric molecules as N₂ and O₂. The recent issue involving NOₓ emission fraud in the automobile industry serves to underline the need for efficient catalysts for NO reduction. Such catalysts can either be found using screening techniques, or through targeted development based on a thorough understanding of the underlying reaction mechanism, often obtained through careful, controlled reactivity experiments, complemented by quantum-chemical calculations to characterize the energetics of the reaction path. In this work, we present a combined experimental and theoretical study of the adsorption reaction of NO onto isolated clusters of rhodium that are modified through substitution of one single Rh atom by a Ta. The substitution dramatically reduces the activation barrier towards NO dissociation, promising a route towards developing more efficient rhodium catalysts.

Rhodium is widely used in catalysts of the three-way converter of automobiles for after-treatment of engine exhaust to reduce NO to N₂.¹ The key step in this process is the dissociative adsorption of NO on the Rh surface, with an activation energy required for the NO bond rupture.² As a consequence, the catalysts are in practice used at temperatures exceeding 600 K. At lower temperatures, NO only adsorbs molecularly on the Rh surface.³–⁶ An important topic of research is thus to find a method to enhance catalyst reactivity allowing it to function at lower temperature.
Gas phase clusters are a useful model system for nano-catalysts. Reaction mechanisms can be elucidated on the atomic and molecular level, as the reactions can be examined with atomic resolution using mass spectrometry. Three independent studies carried out under collision-free conditions found that, upon reacting two NO molecules with cationic rhodium clusters, N\textsubscript{2} is released, leaving Rh\textsubscript{n}\textsuperscript{+}O\textsubscript{2} behind. These observations were interpreted as resulting from the dissociative adsorption of NO, generating N atoms that can migrate on the surface of the cluster. However, under thermalized conditions at 300 K, no decomposition of NO was observed, and release of N\textsubscript{2} only takes place at higher temperatures (>700 K), suggesting that the collision-free reaction was driven by heat generated upon NO adsorption; under thermal reaction conditions, this heat is rapidly dissipated by collisions, and the reaction is throttled.

This throttling was confirmed in our recent study, where we recorded the vibrational spectra of Rh\textsubscript{n}\textsuperscript{+}NO (n = 6−16) under near-thermal conditions at 223 K, using infrared multiple-photon dissociation (IRMPD) spectroscopy. A vibrational spectrum is a fingerprint for a molecule or ion, and for Rh\textsubscript{n}\textsuperscript{+}NO it can serve to identify the adsorption form of NO. All clusters studied exhibited intense vibrational bands around 1800 cm\textsuperscript{-1}, characteristic for molecularly adsorbed NO. Concurrent DFT calculations suggested that dissociation of NO on Rh\textsubscript{n}\textsuperscript{+} is energetically as stable as molecular adsorption, pointing to the presence of a substantial activation barrier for the NO molecule towards dissociation on Rh\textsubscript{n}\textsuperscript{+}. From these experiments it was concluded that for all Rh clusters studied, the first NO molecule adsorbs in molecular form at 223 K.

A possible route towards a more efficient catalyst is to tune its reactivity by
tailoring its elemental composition to reduce this activation energy barrier. In an earlier work, we proposed the addition of Ta, as it has a strong affinity to both N and O.\textsuperscript{13} To investigate the effect of Ta on the adsorption process, we recorded IRMPD spectra for Rh\textsubscript{n}Ta\textsuperscript{+}NO (\(n = 2\textendash 8\)) under the same conditions as the previous work on Rh\textsubscript{n}\textsuperscript{+}NO where NO was observed to adsorb intactly.\textsuperscript{12}

2. Experimental methods

We conducted IRMPD spectroscopic characterization of Rh\textsubscript{n}Ta\textsuperscript{+}NO in a molecular beam environment using the free electron laser for infrared experiments (FELIX) to determine their geometrical structures. As the details of the molecular beam apparatus at FELIX have been described elsewhere,\textsuperscript{14} we limit ourselves to the experimental conditions relevant to the present study.

Gas phase Rh\textsubscript{n}Ta\textsuperscript{+} clusters were produced by laser ablation at 532 nm of an alloyed metal rod composed of 90\% Rh and 10\% Ta, (manufactured by Furuya metal Co. upon request), in the presence of a Ar:He mixture (0.33-0.5 \% Ar) injected into a clustering channel through a pulsed valve at a stagnation pressure 0.8 MPa. Downstream from the ablation site, the clusters formed interacted with a NO:He mixture (0.48 \%) pulsed in at 0.1 MPa stagnation pressure through a second valve, forming the Rh\textsubscript{n}Ta\textsuperscript{+}NO product. In the present work, IRMPD spectra of Rh\textsubscript{n}Ta\textsuperscript{+}NO were recorded through photodissociation of Rh\textsubscript{n}Ta\textsuperscript{+}NO-Ar complexes, because the IR induced detachment of Ar from Rh\textsubscript{n}Ta\textsuperscript{+}NO-Ar is more facile than NO from Rh\textsubscript{n}Ta\textsuperscript{+}NO, reducing spectral broadening and other multiple photon effects. The Rh\textsubscript{n}Ta\textsuperscript{+}NO-Ar complexes were formed in the expansion of the reactive mixture into vacuum, and was enhanced by cooling the clustering region to temperatures of \(\sim 200\) K using liquid N\textsubscript{2}. Pressures and concentrations
of the gases were regulated by Bronkhorst pressure and mass flow controllers for tuning the optimized condition in the series of the experiments. A residual gas analyzer also monitored partial pressures of He, Ar, and NO gases inside of the cluster source chamber.

3. Computational methods

To elucidate geometrical structures of Rh$_n$Ta$^+$NO ($n = 2$–$8$), density functional theory (DFT) calculations were performed using the Gaussian09 program.$^{15}$ Computational steps were almost the same as the previous studies.$^{12}$ For Rh$_5$Ta$^+$NO, more than one hundred initial geometries, prepared randomly, were calculated using Becke's three-parameter hybrid density functional with the Lee-Yang-Parr correlation functional (B3LYP). As basis set for the search, the LANL2DZ basis set and effective core potential (ECP) for Rh and Ta and 6-31G(d) basis sets for N and O atoms were used. Selected obtained lower energy isomers were further re-optimized using SDD basis sets and ECP for Rh and Ta, and 6-311+G(d) basis sets for N and O; at the same level, harmonic frequencies were calculated.

Vibrational spectra were constructed by convoluting the (unscaled) harmonic frequencies and intensities with a Gaussian line shape functions. To reflect the changing bandwidth of the FEL, the spectral width (FWHM) was chosen 5 cm$^{-1}$ in the range below 300 cm$^{-1}$, and 20 cm$^{-1}$ above. For the calculation of the reaction paths, LANL2DZ for Rh and Ta and 6-31G(d) for N and O were applied. Transition states and the energy barriers were calculated using the quadratic synchronous transit-guided quasi-Newton (STQN) method.$^{21,22}$

B3LYP is known to provide reasonable results at low calculational costs.$^{16}$ Harding and coworkers used the Perdew, Burke, and Ernzerhof functional (PBE1) with
the Stuttgart/Dresden (SDD) basis set with ECP for the Rh$_6^+$ clusters and LANL2DZ for larger Rh$_n^+$ clusters as basis set and ECP. We compared vibrational spectra obtained using B3LYP and PBE1 (Figures S2-S5). Interestingly, the differences in spectra calculated using the two methods are most pronounced for the bare clusters (Figures S6 and S7); for the structures with NO adsorbed, we find that there are no significant differences depending on the functional (Figures S2-S5). We conclude that the current method is sufficient for structure determination of our systems of interest.

4. Results and discussion

4.1 Adsorption of NO on Rh$_5$Ta$^+$

Figure 1 shows the IRMPD spectrum for Rh$_5$Ta$^+$NO. The spectrum shows several clear and well-resolved bands in the 100-300 cm$^{-1}$ spectral range, and three further bands at 482.5, 710.0 and 940.0 cm$^{-1}$. Note that the spectrum above 800 cm$^{-1}$ was recorded at substantially reduced laser intensity, to avoid saturation. Crucially, no band is observed in the region between 1600 and 1950 cm$^{-1}$, the spectral range indicative for intact NO, be it on-top, bridge or hollow bound. This lack of a band is strong evidence for Rh$_5$Ta$^+$NO having NO bound dissociatively.

DFT calculations confirm that finding an intactely adsorbed NO is unlikely. Above the experimental spectrum, Figure 1 shows calculated vibrational spectra of stable isomers with their relative energies and spin multiplicities. On three of these, NO has dissociated and N and O atoms are separately bound to the cluster. Only one isomer displayed has NO as an intact molecule, and its energy is an enormous 1.72 eV higher than the most stable dissociative complex.
The experimental spectrum agrees quite well with the spectrum of 5,1A, which is also calculated to be most stable (Figure 1(b)): The two bands at 635 and 703 cm\(^{-1}\) are associated to motions of the N atom parallel to the plane that three Rh atoms form, while the band at 478 cm\(^{-1}\) corresponds to the vibration where the N atom moves perpendicularly to the plane. The strong band at 938 cm\(^{-1}\) is due to the stretching vibration of the Ta-O bond. Finally, all bands below 300 cm\(^{-1}\) correspond to vibrations of the Rh\(_5\)Ta\(^+\) skeleton. The match between observed and calculated spectra, both in line positions and IR intensities, undoubtedly suggests that spectrum recorded is that for an octahedral Rh\(_5\)Ta\(^+\) cluster with the O atom adsorbed on the Ta on-top site and the N atom on one of the Rh hollow sites.

4.2 IR spectra of Rh\(_n\)Ta\(^+\)NO (n = 2–8)

To investigate if the dissociative adsorption of NO is common to Rh\(_n\)Ta\(^+\), we examined the spectra of other Rh clusters containing a single Ta atom, Rh\(_n\)Ta\(^+\) (n = 2–8) with one NO adsorbed (Figure 2). Evidently, the spectra are quite similar to that for Rh\(_5\)Ta\(^+\): no band appears above 1000 cm\(^{-1}\), indicating that NO adsorbs dissociatively on all cluster sizes examined. Indeed, in each spectrum one intense band appear in the 950–1000 cm\(^{-1}\) range, very likely assignable to the Ta-O stretch vibration. The appearance of the intense band is consistent to the dissociative adsorption of NO. Examining the size dependence closely, it was found that the band is slightly blueshifted by ~50 cm\(^{-1}\) going from n = 2 to 3, but remains essentially unchanged for n \(\geq\) 3 (Figure S1). The slight shift in frequency is due to a change in the Ta-O bond strength, manifested by the Wiberg bond index (1.97 and 1.86 for n = 2 and 3, respectively).
Bands relating to motion of the Rh-N-Rh atom also appear around 635 cm\(^{-1}\) in the spectra, which are relatively stable in frequency for \(n = 2–4\), but exhibit a redshift by \(-140\) cm\(^{-1}\) going from \(n = 4\) to \(n = 5\), suggesting a possible structural change (see Figure S1). Comparison of DFT calculated spectra with the observed IRMPD spectra for \(n = 2–8\) (Figures S2–S5) indicates that the O atom always adsorbs on the on-top site of Ta, and that the N atom adsorbs on a bridge site between two Rh atoms for \(n = 2\) and 3, and on a hollow site of Rh atoms for \(n \geq 5\) (Figure 3). For \(n = 4\), a transitional structure is found: based on the bond lengths between N and three Rh atoms alone, the N atom is considered to adsorb on the bridge site; visual inspection suggests it is approaching adsorption on the hollow site. Thus, the observed size dependence appears to indicate that the N atom favours a hollow site formed by three Rh atoms. As no such hollow site exists below \(n = 4\), the N atom adsorbs on the bridge site. DFT calculations for Rh\(_5\)Ta\(^+\) further suggest that adsorption of the N atom on bridge and on-top sites would be less favorable by +0.65 and +1.72 eV, respectively (see Figure 1). In our previous work, we also found a preference of the N atom for a hollow site on Rh\(_n\)\(^+\) \((n = 6, 8–10)\).\(^{12}\)

4.3 Reaction pathway for dissociation of NO on Rh\(_5\)Ta\(^+\)

Rh\(_6\)\(^+\) was previously found to have an octahedral geometry;\(^{17}\) the current experimental spectrum suggests that Rh\(_5\)Ta\(^+\) has the similar octahedral structure (see Figures S6 and S7), with one of the Rh atoms replaced by a Ta atom. What makes Rh\(_5\)Ta\(^+\) then more active than Rh\(_6\)\(^+\)? For this, we calculated possible reaction
paths for the dissociation of NO on Rh$_5$Ta$^+$ and compare them to the same reaction over Rh$_6^+$ (Figure 4).

For Rh$_5$Ta$^+$, the NO molecule is considered to initially adsorb on the Ta on-top site of the cluster through the N atom. N-bound on-top adsorption at the Ta atom is calculated to be favoured (binding energy 2.1 eV) over O-bound adsorption (1.6 eV): The orientation is common to the adsorption of small, N-containing molecules on metal surfaces.$^{23-27}$ According to the natural charges of atoms, the charge is mainly localized on the Ta atom (Natural charge +0.97 e) while Rh atoms are very slightly negatively charged except for the Rh atom that is located at the diametrical opposite side of the Ta atom (+0.15 e). Upon adsorption of NO, all Rh atoms become positively charged and the N (−0.15 e) and O (−0.10 e) atoms are negatively charged, suggesting that electron density is donated to the $\pi^*$ antibonding orbital of NO. Indeed, the NO bond is slightly elongated from 1.15 Å to 1.18 Å upon adsorption.

After adsorption, the NO molecule migrates to a hollow (IM2) and subsequently to a bridge site (IM3). NO leans towards the Ta (TS3) until the O atom is bound to it (IM4). The NO bond is ruptured after passing TS4 with the energy barrier of 0.69 eV, forming separate O and N atoms. The activation energies in the reaction path are low enough that Rh$_5$Ta$^+$NO can readily overcome the barriers, with the energy obtained upon adsorption of NO.

For Rh$_6^+$, a similar reaction path had previously been proposed (see Figure 4).$^9$ N-bound on-top adsorption on Rh$_6^+$ is exothermic by 1.55 eV. Subsequently, the NO molecule migrates to a bridge site, leaning toward a Rh atom until the O atom in NO binds to it. However, the transition state for bond cleavage is located quite high, forming a $^{+2.41}$
eV energy barrier relative to the entrance complex. This high activation barrier prevents NO from dissociating.

In contrast, for all reaction paths found for Rh₅Ta⁺ (Figures 4 and S8), adsorption of the O atom on the Ta on-top site is exothermic by more than 3 eV with respect to the reactants. This is due to higher oxygen affinities of Ta-containing clusters: Comparing binding energies, the binding energy of the O atom to Rh₅Ta⁺ on its on-top site of the Ta atom is higher by 3.0 eV than that to Rh₆⁺ (see S9). This strongly enhanced stabilization by the oxide binding lowers the activation barrier for dissociation of NO. This reaction thus forms a textbook example for the Bell-Evans-Polanyi principle, predicting reduction of the activation energy with the decrease in the formation energy of the product species. The current work thus convincingly demonstrates that the targeted elemental tailoring of Rh catalyst material is possible by substituting oxophilic elements, as Ta can strongly reduce the barrier for NO dissociation. It can of course be expected that Ta is too oxophilic, leading to catalyst poisoning, and that other less oxophilic elements provide a better balance between reduction of the barrier towards dissociation and O binding strength. Further studies of doped Rh cluster systems to investigate such and other effects, eventually aimed at elucidating full catalytic NO reduction cycle, are currently underway.

5. Conclusions

Adsorption forms of a single NO molecule on gas phase metal cluster cations, RhₙTa⁺ (n = 2–8), were investigated by vibrational spectroscopy based on infrared multiple-photon dissociation using a IR free-electron laser. Rh, commonly used as a
reducing catalyst of NO in a three-way catalyst, is found to be activated for decomposition of NO by addition of a single Ta atom: while NO adsorbs molecularly on pure Rh clusters, it was found to adsorb dissociatively on Rh$_n$Ta$^+$ ($n = 2–8$) with the O atom on the on-top site of the Ta atom. The bands relating to motion of the N atom also appear in the spectra, indicating that the N atom adsorbs on a bridge site between two Rh atoms for $n = 2$ and 3, and on a hollow site of Rh atoms for $n \geq 5$.

Reaction pathways for NO decomposition were calculated for Rh$_5$Ta$^+$ and Rh$_6^+$ to understand what makes Rh$_5$Ta$^+$ more active than Rh$_6^+$. For Rh$_6^+$, the transition state for bond cleavage is located quite high, forming a +2.41 eV energy barrier relative to the entrance complex. This high activation barrier prevents NO from dissociating. In contrast, for Rh$_5$Ta$^+$NO, the activation energies in the reaction path are low enough that Rh$_5$Ta$^+$NO can readily overcome the barriers, with the energy gained upon adsorption of NO. Ta oxygen affinity strongly reduces the energy barrier right before bond cleavage, facilitating NO dissociation. The trend is consistent to the Bell-Evans-Polanyi principle. Addition of oxophilic dopant atoms is expected to enhance catalytic reactivity of Rh.

**ASSOCIATED CONTENT**

**Supporting Information**

The supporting information is available free of charge on the ACS Publication website at DOI: The wavenumbers of vibrations involving O and N atoms in Rh$_n$Ta$^+$NO as a function of the cluster size, $n$; IRMPD spectra of Rh$_n$Ta$^+$NO ($n = 2–8$) and their vibrational spectra obtained by DFT calculations using B3LYP and PEB1; IRMPD spectra of Rh$_6^+$ and Rh$_5$Ta$^+$ and their vibrational spectra obtained by DFT calculations; A reaction path of NO decomposition on Rh$_5$Ta$^+$. 
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Notes

The authors declare no competing financial interest.

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Figure captions

Figure 1.
(a) IR spectrum for Rh$_5$Ta$^+$NO and (b–e) DFT calculated vibrational spectra of the stable isomers of Rh$_5$Ta$^+$NO using B3LYP. The peak heights in panels (b–e) correspond to the IR spectral intensity given by the DFT calculations. The relative formation energy and spin multiplicity are shown in parentheses for each structure. Blue, red, dark-cyan and light blue balls represent N, O, Rh, and Ta atoms, respectively.

Figure 2.
Observed IRMPD spectra of Rh$_n$Ta$^+$NO ($n = 2–8$) with single NO adsorbed.

Figure 3.
Geometrical structures of Rh$_n$Ta$^+$NO ($n = 2–8$) determined based on the IRMPD spectroscopy and DFT calculations. Green, pink, blue and red balls represent Rh, Ta, N and O atoms, respectively.

Figure 4.
A reaction path for the dissociation of NO on Rh$_5$Ta$^+$ (black) and on Rh$_6^+$ (red). The reaction crosses from the septet to the triplet surface after IM1.
Figure 1
Figure 2

![Graph showing spectral data with x10 and x5 zoom factors.](image)

Figure 3

![Another graph related to spectral analysis.](image)
Figure 4

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