

Size-dependent gas phase reactivity of tantalum cluster cations with small alcohols



K. Lange^a, B. Visser^a, D. Neuwirth^a, J.F. Eckhard^a, U. Boesl^a, M. Tschurl^{a,*},
K.H. Bowen^b, U. Heiz^a

^a Lehrstuhl für Physikalische Chemie & Catalysis Research Center, Chemistry Department, Technische Universität München, Lichtenbergstraße 4, Germany

^b Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA

ARTICLE INFO

Article history:

Received 27 August 2014

Received in revised form 8 October 2014

Accepted 14 October 2014

Available online 27 October 2014

Keywords:

TOFMS

Metal cluster cations

Tantalum

Cluster reactivity

Dehydrogenation

OH abstraction

ABSTRACT

Small tantalum cluster cations (Ta_{4-9}^+) were produced in the gas phase by laser vaporization. Various alcohols (methanol, ethanol, *n*-propanol and 2-propanol) were consecutively added to the cluster beam in a pulsed jet and allowed to react to an extent of conversion of approximately 50%. The charged reaction products were subsequently measured using time of flight mass spectrometry. Two distinct reaction pathways were observed, involving complete dehydrogenation or OH abstraction from the alcohol molecule. The relative total reaction yield was found to not vary significantly within the cluster size regime studied. The branching ratios for the reaction demonstrated a cluster-size dependence, with a minimum of OH abstraction occurring for Ta_7^+ .

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent decades it has been shown that typically non-reactive bulk metal species can be reactive for particle sizes in the non-scalable (cluster) size regime [1]. Furthermore, it has been discovered that the reactivity within this regime depends on particle size, can vary on a per atom basis [2–6], and can be isomer sensitive [7]. The study of gas phase reactions of metal clusters and metal containing systems has been shown to provide important information on reaction mechanics and remains a highly topical field [8–10]. While the application of nanoparticulate metal catalysts in industrial scale reactions is already well advanced, even smaller, size-selected clusters have been touted as potentially more efficient replacements [11]. Some examples of industrially important reactions are the activation and subsequent conversion of alkanes as well as the conversion of methanol to formaldehyde. Small tantalum and tantalum oxide clusters have been shown to activate alkanes [12,13] and theoretical studies show that the dehydrogenation of methanol by the atomic cation is energetically favorable [14].

In comparison to the precious metals often used as catalysts, tantalum is relatively inexpensive and abundant. It is then surprising that relatively few reactivity studies of small tantalum clusters have been performed. One of the few works in this field was performed by Cao et al. [14], who studied the gas phase reactions of the atomic Nb, V and Ta cations with methanol using Fourier Transform Ion Cyclotron Resonance mass spectrometry (FT-ICR). The reaction products found to be in common for reactions with all three metals were the formation of MO^+ and MOH^+ . For the atomic cations of Nb and V, $M(CH_3O)^+$ and $M(CH_2O)^+$ were also formed. While the dehydrogenation reaction was not observed in the case of Ta^+ , viz., $Ta(CH_3OH)^+ \rightarrow Ta(CH_2O)^+ + H_2$, it was calculated to be energetically favorable with an overall energy change of -78.5 kcal/mol [14]. Similar reaction products have also been found for the reaction of small alcohols with other metal and metal oxide cations [15,16].

The dehydrogenation reaction pathway was observed in the reaction of gas phase neutral tantalum clusters with unsaturated hydrocarbons by He et al. [17]. The unsaturated hydrocarbons were added via a pickup cell and the neutral reaction products were measured using laser ionization mass spectrometry. It was found that completely dehydrogenated association products for clusters larger than the trimer (e.g. Ta_nC_6 for the reaction of neutral tantalum clusters with benzene, where $n > 3$) were highly favored, with partial dehydrogenation products only observed in special cases.

* Corresponding author. Tel.: +49 08913414.

E-mail address: tschurl@tum.de (M. Tschurl).

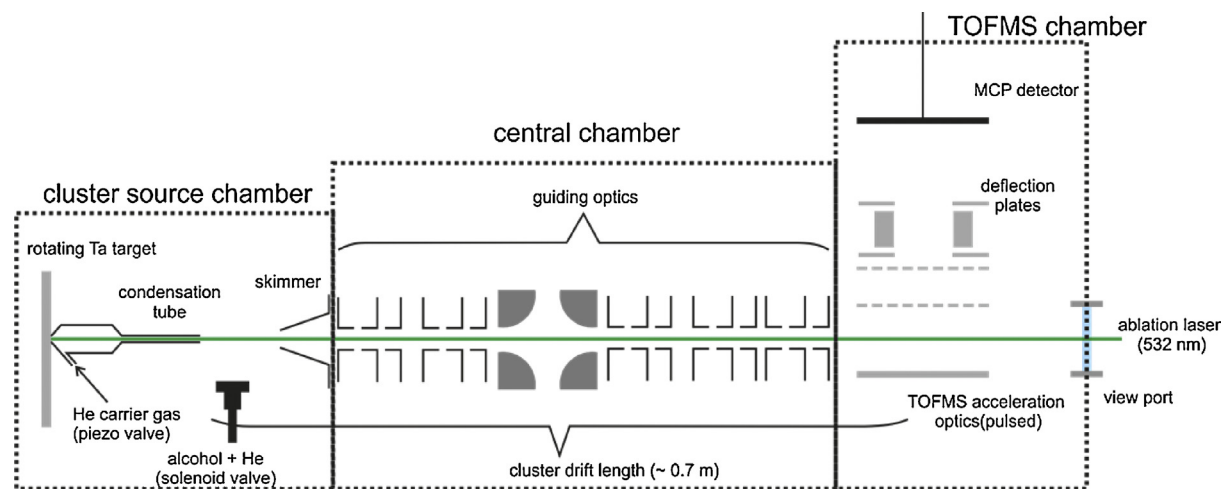


Fig. 1. Schematic of the experimental setup. Clusters are formed in a laser vaporization source and expanded into vacuum by a He gas pulse. Immediately after this expansion, alcohol molecules are introduced into the vacuum through a pulsed valve. The positively charged cluster and cluster-adsorbate species are then guided by numerous Einzel lenses to a TOFMS. Here, the ions are extracted perpendicularly by a high voltage pulse and detected with a microchannel plate detector (note that the quadrupole bender functions as a linear ion guide for this experiment).

Furthermore, reaction products resulting from the interaction of the Ta clusters with multiple hydrocarbon molecules were found in the form of carbon chain building and metcar (M_8C_{12}) formation.

The reactions of tantalum oxide clusters have been studied more thoroughly and in one such study Zemski et al. investigated the reactions of a number of small hydrocarbons with tantalum oxide cluster cations and anions in the gas phase [18–20]. The primary reaction mechanisms were identified as C–C insertion of the metal oxides, leading to carbon chain cracking.

Insights about the reactivity of niobium and niobium oxide clusters provide useful direction to studies involving tantalum clusters. Jackson et al. [21] exposed niobium oxide cluster anions to alcohol molecules in an FT-ICR mass spectrometer. The most important recurring mechanism was the initial attachment of the alcohol at a metal-oxygen double bond. The major reaction pathways were found to involve hydroxyl abstraction and alkyl fragment liberation, association and dehydration and, finally, oxidation. Dehydrogenation was only found to occur in special cases.

In this work we report the size-dependent reactivity of tantalum cluster cations with alcohol molecules in the gas phase. The results for cationic tantalum clusters Ta_n ($n = 4–9$) with several alcohols are shown and the size dependency of the observed reaction products is discussed.

2. Experimental

The experimental setup used in this study is described for the first time here and is accompanied by a schematic, which is shown in Fig. 1. Metal clusters were produced in a metal disc type laser vaporization cluster source that is similar to the source reported previously by Heiz et al. [22]. Vaporization of the metal target was performed with the second harmonic of a Nd:YAG laser (Innolas Spitlight DPSS), timed to coincide with a pulse of helium carrier gas (Westfalen AG, Helium 6.0). The cluster source condensation tube has a length of 60 mm and a diameter of 2 mm.

The alcohols were introduced into the vacuum in the cluster source chamber immediately after the cluster expansion using a pulsed solenoid valve (General valve, series 9) resulting in an average pressure of 1×10^{-2} mbar in the chamber. A stainless steel vessel was filled with the alcohol of interest and helium backing gas (Westfalen AG, Helium 5.0) was bubbled through the liquid alcohol. The general valve was pulsed and timed to coincide with the expansion of the cluster beam from the cluster source using a

delay generator (Stanford Research Systems, DG645). The cluster and alcohol beams were crossed perpendicularly within the source chamber.

Following skimming of the entrained metal cluster-alcohol beam, the nascent cationic species were guided to the time of flight mass spectrometer (TOFMS) using a number of Einzel lenses. The time of flight mass spectrometer utilized a homebuilt Wiley McLaren, two stage design and consists of annular plates constructed from stainless steel. The plates have an inner diameter of 40 mm, which are covered with mesh wherever changes in the electric field strengths occur. Deflection plates were mounted directly after the TOFMS electrodes and were used to steer the ion beam to the detector. The electrodes of the TOFMS were pulsed to high voltage using a pair of power supplies (FuG Elektronik GmbH, HCP 14-6500) connected to two high voltage pulsing units (homebuilt with HV switches from Behlke Power Electronics GmbH, ± 6.5 kV) at the arrival time of the ions. The ions were then extracted orthogonally into the 300 mm long drift region of the linear TOFMS. The ions were subsequently detected with a microchannel plate detector (Photonis, APD 2 MA 40/12/10/8 D60:1, chevron configuration). Spectra were visualized and recorded using an oscilloscope (LeCroy Waverunner, 44Xi-A). The mass resolution of the experimental setup was measured to be approximately 250. The presented spectra were created by averaging 1000 individual traces.

3. Results

Typical mass spectra of the reaction products of cationic tantalum clusters Ta_n ($n = 4–9$) with methanol, ethanol, *n*-propanol and 2-propanol are shown in Fig. 2. The major peaks in the spectra correspond to the bare metal clusters, but numerous reacted species are also observed. The major reaction product peaks are located at the parent metal cluster mass plus 17 and 28, 40 or 52 μ , depending upon the parent alcohol and are assigned to OH and dehydrogenated alcohols attached to the metal clusters, respectively. Example reaction schemes are given in Eqs. (1) and (2) below. The small peaks at masses larger than the reactant alcohol-cluster association mass were assigned to co-adsorbed products such as $(C_xO)(OH)$ originating from the reaction of one cluster with more than one alcohol molecule. Given the aforementioned low intensities, the 1:2 and higher cluster:alcohol stoichiometric products are not considered further in this work. The structural composition of the reaction products are as of yet unknown, though previous

Download English Version:

<https://daneshyari.com/en/article/1192122>

Download Persian Version:

<https://daneshyari.com/article/1192122>

[Daneshyari.com](https://daneshyari.com)