Accelerated Communication

Rhenium oxide cluster anions in a molecular beam

Axel Pramann, Klaus Rademann*

Walther-Nernst-Institute of Physical and Theoretical Chemistry, Humboldt University Berlin, Bunsenstrasse 1, 10117 Berlin, Germany

Abstract

The formation of rhenium oxide cluster anions is studied in a pulsed molecular beam experiment as a function of source conditions and oxygen content (0.1–10%) in the carrier gas. $Re_nO_m^-$ clusters are formed directly in plasma reactions in the laser vaporization cluster source. With both increasing oxygen content and stagnation pressure, larger oxide clusters are formed ($m \geqq n$) and the distribution is dominated by certain mass peaks of high intensity indicating a high stability. At lower pressure and less oxygen content, a large variety of oxides is observed. Most stable clusters contain Re atoms with a formal oxidation state of +7 and oxygen in the −2 oxidation state. Oxygen rich clusters can be attributed to a series $(ReO_4)_l(Re_2O_7)_m(O)_n^-$ with $l=0–1$, $m=0–4$, and $n=0–1$. The results are explained by the nature of the Re–O bond which is important for the alkene metathesis reaction mechanism. (Int J Mass Spectrom 209 (2001) 1–4) © 2001 Elsevier Science B.V.

Keywords: Clusters; Transition metal oxides; Rhenium oxides; Mass spectrometry

1. Introduction

In recent years, transition metal oxide clusters have gained considerable importance due to applications as model systems in heterogeneous catalysis and materials science on a microscopic level [1,2]. Recently, a number of sophisticated studies concerning the electronic and geometric structures, and chemical reactivity of transition metal oxide clusters have been carried out (see [3–7]). Only few experimental studies concerning group VII transition metal oxide clusters have been performed [8–11].

In this Letter, we present a mass spectrometric investigation of oxygen-rich negatively charged rhenium oxide clusters ($Re_nO_m^-$) for the first time. Molecular-like rhenium oxide anions are known from the anions of hydrogen acids of Re like ReO_4^-, ReO_4^{2-}, ReO_5^{3-}, and ReO_6^{5-} [12]. Due to strong repulsive coulomb interactions, no gas-phase spectroscopic studies of these species have been performed. Supported rhenium clusters have shown important applications in alkene metathesis reactions in heterogeneous catalysis [13]. One of the most important and successful active phases in alkene metathesis are rhenium oxides of different stoichiometry, supported

---

* Corresponding author.
E-mail: ehlers@rad01.chemie.hu-berlin.de

on Al_2O_3 or SiO_2, because of the availability of d and f outer electrons. As is well known, selectivity and turnover frequencies depend strongly on the composition, which is related to the oxidation state of the metal. Not only rhenium in the $+7$ oxidation state, but also other oxidation states ($+5$, $+6$, ...) of Re are noticed to be very important during this process, stabilizing the active complex in the metathesis reaction. It still remains open, whether rhenium is able to form stable oxides in various oxidation states, which are not only intermediates with a short life time, but stable self consistent gas phase ions. Thus, gas phase mass spectrometry as applied in this study gives a detailed insight into formation criteria and stability of the respective ions. The present study is intended to screen the formation conditions and intensity distributions of $Re_nO_m^-$ clusters with the aid of mass spectrometric abundances to establish the criteria of formation and stability, and to determine the nature of bonding between Re and oxygen.

2. Experimental

An early stage of the experimental setup has been described in a previous paper [11], but is modified to enhance the resolution $m/\Delta m = 100$ of the in-line time-of-flight mass spectrometer (TOF-MS) and the overall transmittance of our new four stage linear molecular beam machine. Oxide clusters are generated in a pulsed laser vaporization cluster source. A focused beam of 532 nm photons of a Q-switched Nd:yttrium-aluminum-garnet laser (10 Hz repetition rate; pulse energy: 5–25 mJ) hits a set of rotating/translating rhenium wires (each 1 mm in diameter; 99.5%, Goodfellow). The resulting plasma is cooled with a high-pressure pulse of the carrier gas (0.1–10% O_2 diluted in helium, 99.999%, Messer Griesheim) which enters the cluster source via a pulsed solenoid valve. The clusters undergo an adiabatic supersonic beam expansion resulting in translationally cold beam bunches. After passing two skimmers and ion optics, the negatively charged clusters are mass analyzed with the TOF-MS.
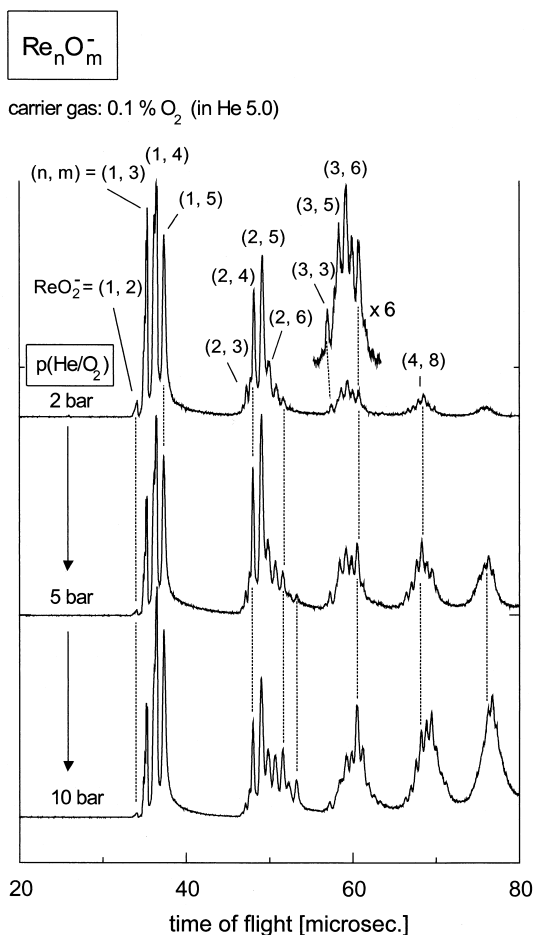

Fig. 1. Time-of-flight mass spectra of $Re_nO_m^-$ clusters obtained with a carrier gas containing 0.1% O_2 in helium. Spectra from the top to the bottom are recorded with increasing stagnation pressure of the carrier gas. In the same order larger clusters are formed. For each number n of Re atoms per cluster a multiple of oxide series is observed.

3. Results and discussion

Figs. 1–3 show time-of-flight mass spectra of $Re_nO_m^-$ clusters of different stoichiometries with high oxygen content. $Re_nO_m^-$ clusters are prepared as a function of both O_2 concentration in the carrier gas and source pressure. Changing the laser fluence does not affect the cluster distributions.

At 0.1% oxygen concentration in the carrier gas (Fig. 1) a large variety of small (n = 1–5) $Re_nO_m^-$ clusters are formed. Even when using small traces of
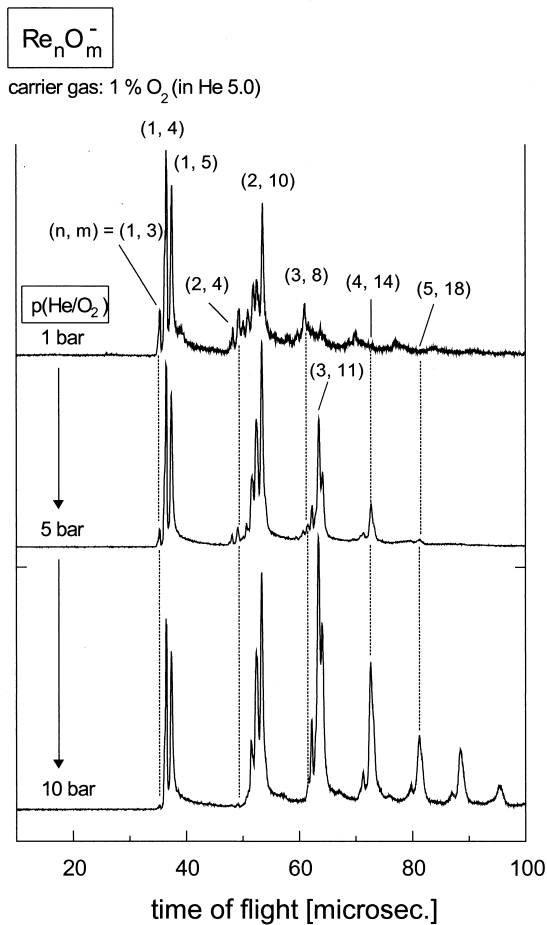
Fig. 2. Time-of-flight mass spectra of $Re_nO_m^-$ clusters obtained with a carrier gas containing 1% O_2 in helium. Spectra from the top to the bottom are recorded with increasing stagnation pressure of the carrier gas. In the same order larger clusters are formed. For each number n of Re atoms per cluster a multiple of oxide series is observed.
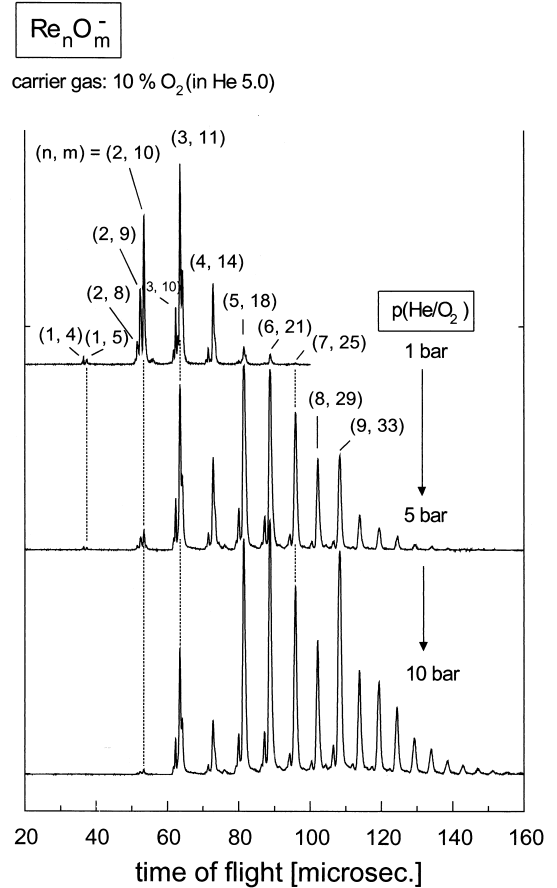

Fig. 3. Time-of-flight mass spectra of $Re_nO_m^-$ clusters obtained with a carrier gas containing 10% O_2 in helium. Spectra from the top to the bottom are recorded with increasing stagnation pressure of the carrier gas. In the same order larger clusters are formed. For each number n of Re atoms per cluster a multiple of oxide series is observed.

oxygen in the carrier gas, no pure Re_n^- clusters are observed as a result of the strong Re–O binding energy (D_0(Re–O)=626.8 kJ/mole [14]). At lower stagnation pressures (up to 5 bar) the most prominent oxides are ReO_{3-5}^-, $Re_2O_4^-$, $Re_2O_5^-$, $Re_3O_6^-$, and $Re_4O_8^-$. Increasing the stagnation pressure at constant oxygen concentration, the intensity distribution is shifted slightly towards higher masses. In the 10 bar regime, ReO_4^-, ReO_5^-, $Re_2O_4^-$, $Re_2O_5^-$, $Re_3O_8^-$, and $Re_4O_{10}^-$ appear with highest abundances.

Using an oxygen concentration of 1% (Fig. 2) the

cluster distribution is changing systematically towards oxygen rich components. Here, the spectra are dominated by ReO_4^-, ReO_5^-, $Re_2O_{10}^-$, $Re_3O_{11}^-$, $Re_4O_{14}^-$, and larger, less resolved oxides. Especially, $Re_2O_{10}^-$ and $Re_3O_{11}^-$ have particularly high intensities. This can be explained using simple bonding considerations of oxidation states. Due to the presence of f-orbitals rhenium is able to take on a large coordination sphere. Therefore, oxide clusters have compositions of m≧n. Additionally, the most stable oxide clusters will achieve the highest oxidation state for the Re atoms: In $Re_3O_{11}^-$ rhenium has the oxidation state of +7.

This evolution is evident when increasing the oxygen content up to 10% (see Fig. 3). When the stagnation pressure is enhanced, the mass distribution is shifted towards larger clusters. At each number of Re atoms per cluster only a few very intense oxygen rich clusters appear: $Re_3O_{11}^-$, $Re_4O_{14}^-$, $Re_5O_{18}^-$, $Re_6O_{21}^-$, $Re_7O_{25}^-$, $Re_8O_{29}^-$, and $Re_9O_{33}^-$.

Under these extreme oxidation conditions a general stoichiometry $(ReO_4)_l(Re_2O_7)_m(O)_n^-$, with $l=0–1$, $m=0–4$, and $n=0–1$ appears. The extraordinary stability of $Re_2O_{10}^-$ does not fit into this series. This can be explained by a very stable complex of composition $Re_2O_7 \cdot O_3^-$ with Re in an oxidation state of $+7$. The ozonide anion is attached onto this framework due to the high electron affinity of 2.10 eV [14]. $Re_2O_{10}^-$ diminishes strongly and $Re_3O_{11}^-$, $Re_5O_{18}^-$, $Re_6O_{21}^-$, and $Re_9O_{33}^-$ are the most prominent clusters. The explanation of stability due to high oxidation states is also evident, when positively charged rhenium oxides are generated. Beyer and coworkers [15] have studied $Re_nO_m^+$ clusters ($n=1$, $m=2–6$, 8) using collision induced dissociation and ligand exchange reactions. The most stable oxide is ReO_3^+ - again in the $+7$ state.

In a recent investigation, Zhou and coworkers [16] have performed infrared-matrix spectroscopy and additional discrete Fourier transform (DFT) calculations of small neutral and negatively charged rhenium oxide molecules. In that study, reaction mechanisms are presented and electron capture seems important.

These mass spectroscopic investigations are further supported by photoelectron spectroscopic studies of small $Re_nO_m^-$ clusters performed in our group [17]. These results are in good agreement with recent DFT calculations [16]. Briefly, the nature of Re–O bonding seems to appear covalent ionic due to the overlap between Re 5d orbitals and oxygen 2p orbitals. Additionally, the larger Re_nO_m clusters take on very high electron affinities.

4. Conclusion

We have reported on the formation and stability criteria of oxygen rich $Re_nO_m^-$ clusters as a function of cluster source conditions and oxygen concentration of the carrier gas for the first time. Very intense $Re_nO_m^-$ clusters appear each with rhenium in the oxidation state around $+7$. A general stoichiometry of $(ReO_4)_l(Re_2O_7)_m(O)_n^-$ with $l=0–1$, $m=0–4$, and $n=0–1$ is observed. For $Re_2O_{10}^-$ an ozonide complex $Re_2O_7 \cdot O_3^-$ is postulated. These findings provide insights into oxidation state dependences of $Re_nO_m^-$ as will be valuable for the basic understanding of alkene metathesis.

Acknowledgements

References

[1] D. Schröder, H. Schwarz, Angew. Chem. Int. Ed. Engl. 34 (1995) 1973.

[2] R.G. Keesee, B. Chen, A.C. Harms, A.W. Castleman, Jr, Int. J. Mass Spectrom. Ion Processes 123 (1993) 225.

[3] H. Wu, L.-S. Wang, J. Chem. Phys. 107 (1997) 8221.

[4] H. Wu, L.-S. Wang, J. Chem. Phys. 108 (1998) 5310.

[5] H. Wu, L.-S. Wang, J. Phys. Chem. 102 (1998) 9129.

[6] W.D. Vann, R.L. Wagner, A.W. Castleman, Jr., J. Phys. Chem. A 102 (1998) 1708.

[7] W.D. Vann, R.L. Wagner, A.W. Castleman, Jr., J. Phys. Chem. A 102 (1998) 8804.

[8] P.J. Ziemann, A.W. Castleman, Jr,, Phys. Rev. B 46 (1992) 13480.

[9] P.B. Armentrout, S.K. Loh, K.M. Ervin, J. Am. Chem. Soc. 106 (1984) 1161.

[10] M.C. Oliveira, J. Marcalo, M.C. Vieira, M.A. Almoster Ferreira, Int. J. Mass Spectrom. 185–187 (1999) 825.

[11] A. Pramann, K. Rademann, Int. J. Mass Spectrom. 185–187 (1999) 673.

[12] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon, Oxford, 1984.

[13] G. Ertl, H. Knoezinger, J. Weitkamp (eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997, Vols. 2 and 5.

[14] D. R. Lide (ed.), CRC Handbook of Chemistry and Physics, 75th edition, CRC, Boca Raton, Florida, p.194.

[15] M. Beyer, C. Berg, G. Albert, U. Achatz, S. Joos, G. Niedner-Schatteburg, V. E. Bondybey, J. Am. Chem. Soc. 119 (1997) 1466.

[16] M. Zhou, A. Citra, B. Liang, L. Andrews, J. Phys. Chem. A 104 (2000) 3457.

[17] A. Pramann, K. Rademann (to be published).