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Short communication

Reactions of free gold cluster cations with H_2O, CH_3Cl, and mixtures thereof

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ABSTRACT

The reactions of the mass-selected gas-phase gold cluster cations Au_3^+ and Au_5^+ with H_2O, CH_3Cl, and mixtures of these reactants were studied under well-defined multi-collision conditions in an octopole ion trap. The reaction of CH_3Cl with the gold cations was found to proceed fast at room temperature, leading to the adsorption of one CH_3Cl molecule at each 'corner' atom of the cluster ion. This strong adsorption hindered the coadsorption of other reactants like H_2O. However, a considerable reduction of the CH_3Cl partial pressure led to distinct patterns of H_2O/CH_3Cl coadsorption products. Furthermore, the mass spectra indicated the loss of hydrogen after the reaction of CH_3Cl with Au_3^+.

1. Introduction

Extensive research has been concerned with the synthesis of methanol considering a variety of catalytic materials [1,2]. In this context, we currently aim to evaluate the potential of small mass-selected gold cluster cations as catalytic model systems.

Industrially, methanol is almost exclusively produced from syngas, a mixture of hydrogen, carbon monoxide, and carbon dioxide. However, the production of methanol may also be achieved via the direct oxidation of methane or by the reaction of methyl halogenides [2].

The conversion of methanol to methyl chloride via reaction with hydrogen chloride in the gas or liquid phase is a well known process that is utilized industrially. The reverse reaction to produce methanol according to

$$CH_3Cl + H_2O \rightarrow CH_3OH + HCl \quad (1)$$

was considered by Olah et al. for the methanol synthesis [2]. In these experiments, methanol was successfully produced via the selective catalytic monohalogenation of methane to methyl chloride combined with the subsequent catalytic hydrolysis on a $ZnO/Al(OH)_3/\gamma\text{-}Al_2O$ catalyst according to reaction (1). The reaction took place at temperatures between 200 °C and 400 °C and the highest achieved methyl chloride conversion amounted to 25% [2,3]. This process represents a useful approach to convert methane into methanol without producing syn-gas and it avoids the further oxidation of CH_3OH to formaldehyde and CO that presently limits the application of the direct methane oxidation [1,3].

We investigated reaction (1) employing small gold cluster cations, Au_3^+ and Au_5^+, as catalytic model systems. In this letter, we present the first experimental investigation of the reaction behavior of gold cluster cations toward water, methyl chloride, and mixtures of these gases.

2. Experimental

The experimental setup to study metal cluster ion reactions consists of a variable temperature radio frequency (rf) octopole ion trap inserted into a tandem quadrupole mass spectrometer. The general experimental layout is described in detail elsewhere and will only be outlined briefly [4].

The metal cluster cations are produced by a CORDIS (cold reflex discharge ion source) [5] sputtering ion source. Clusters are mass-selected in a first quadrupole filter. The cluster ion beam containing only clusters of one specific mass then enters the octopole ion trap, which is prefilled with about 1 Pa total pressure of helium and small amounts of the reactants (H_2O and CH_3Cl). The absolute pressure inside the trap is measured by a Baratron gauge (MKS, Typ 627B). The ion trap was held at room temperature in the experiments presented here. After a chosen reaction time t_R, all ions, intermediates and products, are extracted from the ion trap. The ion distribution is subsequently analyzed by a second quadrupole mass filter. To account for a slightly asymmetric mass peak shape occurring at very low ion intensities in our apparatus, the raw data have been deconvoluted with a constant apparatus function to yield the shown mass spectra [6,7].

To gain insight into the reaction behavior of the gold cations, we recorded ion mass distributions while changing three parameters: (i) the cluster size (Au_x^+, $x = 3, 5$), (ii) the reaction time t_R (0.1 s

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up to 2 s), and (iii) the reactant gas composition (H_2O, CH_3Cl, and H_2O/CH_3Cl).

3. Results and discussion

So far only few studies on the water adsorption on gas-phase gold clusters have been performed. *Anionic* gold clusters Au_x^- ($x = 2–5$) were reported to adsorb one water molecule at room temperature and several H_2O molecules at lower temperatures [8]. Under single collision conditions [9] the *cationic* gold atom reacted with one water molecule, while in a supersonic expansion large complexes $Au(H_2O)_y^+$ with up to 10 adsorbed water molecules were formed [10].

Several experimental and theoretical studies on the $Au(H_2O)^+$ complex revealed binding energies in the range of 1.1–1.8 eV of H_2O to the positively charged gold *atom* [9,11,12]. In contrast, calculations on the neutral free and on MgO(1 0 0) supported *cluster* Au_8 yielded a relatively weak water adsorption energy between 0.2 eV and 0.6 eV [13]. These values are similar to the results of the only known theoretical study of free gold cluster cations, performed on the $Au_{10}(H_2O)^+$ complex [14]. DFT calculations revealed the coordination of the water molecule to the gold cluster through the more electronegative oxygen atom. The calculated Au_{10}^+-H_2O binding energy is 0.54 eV while a charge of 0.15 eV donated from H_2O to Au_{10}^+. In this complex, the bound water molecule was found not to change its geometry and the O–H bond length of 0.96 Å is only altered by less than 1%. Thus, the adsorption on the gold cluster does not weaken the O–H bond of the water molecule and does probably not activate the water molecule.

To our knowledge neither experimental nor theoretical studies on methyl chloride adsorption on free gold cations are available. However, since the chlorine atom exhibits the largest electronegativity in CH_3Cl, it can be assumed that methyl chloride coordinates to the cluster cations through the chlorine atom.

The reaction behavior of small cationic gold clusters, Au_3^+ and Au_5^+, toward H_2O and CH_3Cl as well as mixtures of these gases was investigated here experimentally for the first time. Fig. 1(a) shows a product ion mass distribution of the reaction of Au_3^+ in the presence of 0.02 Pa CH_3Cl. Already after a comparably short reaction time of 0.1 s the bare cluster ion signal has disappeared and the sole product $Au_3(CH_3Cl)_3^+$ is detected.

To unambiguously identify the stoichiometry of this product it is necessary to consider the isotope distribution of methyl chloride. The natural occurrence of ^{35}Cl and ^{37}Cl amounts to 75.77% and 24.23%, respectively, yielding the mass distribution for $Au_3(CH_3Cl)_3^+$ depicted as bars in Fig. 1(a). From these bar graphs it can be seen that the probability for the products $Au_3(CH_3{}^{35}Cl)_3^+$ and $Au_3(CH_3{}^{35}Cl)_2(CH_3{}^{37}Cl)^+$ is almost identical. Thus, the flattened peak shape of the $Au_3(CH_3Cl)_3^+$ ion signal is due to the isotope distribution. However, the mass peak is slightly more broadened at the low mass edge than expected from the isotope distribution of methyl chloride. This might indicate the loss of hydrogen, which is not clearly resolved by the mass resolution of the quadrupole filter.

The Au_3^+ minimum energy structure is a planar equilateral triangle (D_{3h} symmetry) [15–18] with three electronically equivalent 'corners' [19]. Thus, the maximum number of adsorbed CH_3Cl molecules equals the number of gold atoms, i.e., the number of corner sites in the corresponding ground state geometry. This leads to the conclusion that the gold trimer immediately adsorbs one CH_3Cl molecule at each Au atom. The adsorption of methyl chloride is fast (estimated lower limit for the termolecular rate constant under the given experimental conditions: $k^{(3)} \geq 2 \times 10^{-25}\ \mathrm{cm^6\ s^{-1}}$) and hinders the coadsorption of other molecules like, e.g., H_2 or H_2O, additionally introduced to the ion trap under the above CH_3Cl pressure conditions.

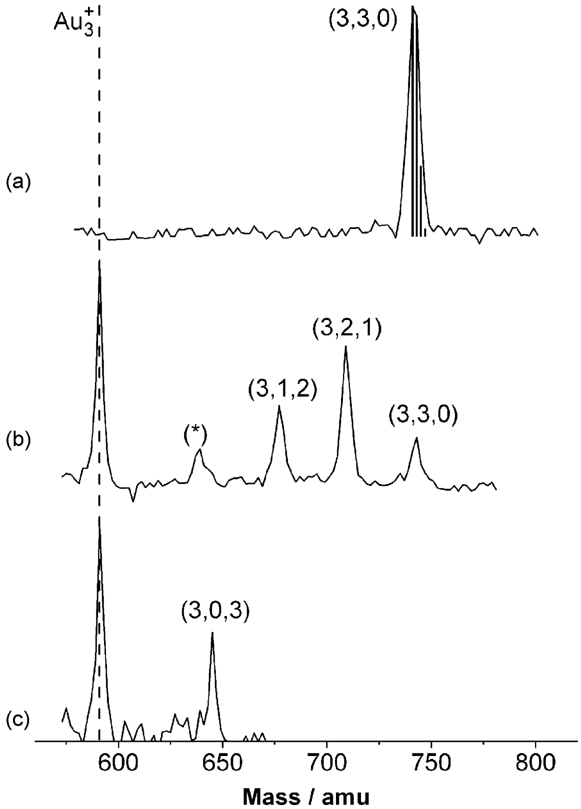

Fig. 1. CH_3Cl pressure dependent ion mass distributions of Au_3^+ at $T_R = 300$ K and $t_R = 0.1$ s in the presence of (a) $p(CH_3Cl) = 0.02$ Pa; (b) $p(CH_3Cl) < 0.01$ Pa and $p(H_2O)$ determined by the vapor pressure of water in the reservoir recipient at room temperature; (c) no CH_3Cl and $p(H_2O)$ determined by the vapor pressure of water in the reservoir recipient at room temperature. The mass peaks are denoted with (x,y,z) and correspond to complexes of the stoichiometry $Au_x(CH_3Cl)_y(H_2O)_z^+$. The peak assigned with an asterisk corresponds to the stoichiometry Au_3CHCl^+. The bars represent the calculated mass distribution of $Au_3(CH_3Cl)_3^+$ derived from the natural occurrence of the Cl isotopes.

However, adding small amounts of water (determined by the vapor pressure of water in the reservoir recipient at room temperature) and considerably reducing the partial pressure of CH_3Cl below the Baratron detection limit of 0.01 Pa leads to a distinct pattern of coadsorption products as displayed in Fig. 1(b). Besides the pure cluster ion signal the products $Au_3(CH_3Cl)(H_2O)_2^+$, $Au_3(CH_3Cl)_2(H_2O)^+$, and $Au_3(CH_3Cl)_3^+$ are discovered. For longer reaction times of up to 1.0 s (not shown here) the pure cluster ion signal disappears but the product distribution and also the relative intensities of the products remain constant. The number of adsorbate molecules never exceeds the number of 'corner' gold atoms. These findings point toward a competing displacement reaction of CH_3Cl and H_2O at equilibrium conditions as the main reaction channel [8,20]. In contrast, the mass peak assigned with an asterisk in Fig. 1(b) does not correspond to any H_2O/CH_3Cl coadsorption product but can be assigned to the stoichiometry Au_3CHCl^+. This indicates an additional minor reaction channel that involves the dissociation of the adsorbed methyl chloride molecule and the elimination of H_2.

Without CH_3Cl but only H_2O in the ion trap finally the ion mass distribution shown in Fig. 1(c) is obtained. The only observed reaction product is $Au_3(H_2O)_3^+$ with probably one water molecule adsorbed at each atom of the gold cluster. No intermediates of the stoichiometry $Au_3(H_2O)^+$ and $Au_3(H_2O)_2^+$ are detected, indicating that the adsorption of the first H_2O is the rate determining reaction step and that the subsequent sequential H_2O adsorption steps are very fast on the timescale of our experiment. No further product ions are observed at longer reaction times.

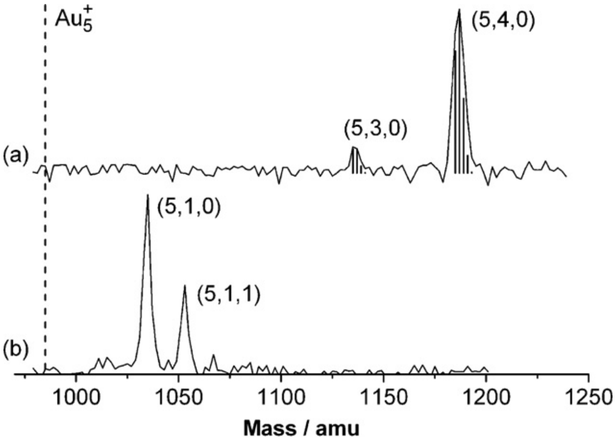

Fig. 2. CH_3Cl pressure dependent ion mass distributions of Au_5^+ at $T_R = 300$ K and $t_R = 0.1$ s in the presence of (a) $p(CH_3Cl) = 0.02$ Pa and $p(H_2) = 0.07$ Pa; (b) $p(CH_3Cl) < 0.01$ Pa and $p(H_2O)$ determined by the vapor pressure of water in the reservoir recipient at room temperature. The mass peaks are denoted with (x,y,z) and correspond to complexes of the stoichiometry $Au_x(CH_3Cl)_y(H_2O)_z^+$. The bars represent the calculated mass distributions of $Au_5(CH_3Cl)_3^+$ and $Au_5(CH_3Cl)_4^+$ derived from the natural occurrence of the Cl isotopes.

A comparable reaction behavior toward CH_3Cl and H_2O is also observed for the larger cluster Au_5^+ as depicted in Fig. 2. Introducing methyl chloride ($p(CH_3Cl) = 0.02$ Pa) to the ion trap yields the main product $Au_5(CH_3Cl)_4^+$ even in the presence of additional gases like H_2 (cf. Fig. 2(a)), which demonstrates the hindered coadsorption of other molecules, if CH_3Cl is pre-adsorbed. Besides, a low intensity mass peak corresponding to the complex $Au_5(CH_3Cl)_3^+$ is apparent. The bars, additionally shown in Fig. 2(a), represent the calculated mass distributions of $Au_5(CH_3Cl)_3^+$ and $Au_5(CH_3Cl)_4^+$ derived from the natural occurrence of the chlorine isotopes. From these bar graphs it an be seen that, in contrast to the $Au_3(CH_3Cl)_3^+$ mass peak, there is no indication for the loss of hydrogen in the case of $Au_5(CH_3Cl)_4^+$.

Au_5^+ exhibits an X-shaped (D_{2h} symmetry) ground state geometry [15,16,21] with four electronically equal 'corner' atoms and one central atom [19]. Thus, as discussed in the case of the gold trimer, also the product $Au_5(CH_3Cl)_4^+$ with four adsorbed CH_3Cl molecules corresponds to a complex with one CH_3Cl molecule bound to each 'corner' atom of the cluster.

Adding small amounts of water to the ion trap and considerably reducing the CH_3Cl partial pressure below the Baratron detection limit yields the ion mass distribution depicted in Fig. 2(b). Even at a short reaction time of 0.1 s the pure cluster ion signal of the pentamer vanishes immediately and the products $Au_5(CH_3Cl)^+$ and $Au_5(CH_3Cl)(H_2O)^+$ are formed. This product distribution and the relative intensities of the two products remain constant for all investigated reaction times of up to 2 s.

The presented mass spectra of Figs. 1 and 2 demonstrate that the H_2O/CH_3Cl coadsorption on the investigated gold cluster cations exhibits a strong CH_3Cl pressure dependence and is only possible in the presence of just small amounts of methyl chloride. Although for Au_3^+ a minor reaction channel is observed that involves the dissociation of methyl chloride, no product complexes with adsorbate stoichiometries corresponding to HCl or CH_3OH only (cf. reaction (1)) have been detected. This leads to the conclusion that water and methyl chloride are primarily simply coadsorbed on the cluster ions without undergoing reactions on the cluster surface that lead to the hydrolysis of CH_3Cl according to reaction (1).

For the reaction of methyl chloride and water on $ZnO/Al(OH)_3/\gamma$-Al_2O catalysts, performed by Olah et al. [3], it was proposed that H_2O interacts with ZnO yielding the complex $ZnO^{\delta+}\cdots H\cdots OH^{\delta-}$. Simultaneously, CH_3Cl should coordinate to an electron-deficient aluminum site of $Al(OH)_3$ to form a polarized intermediate $(HO)_3Al^{\delta-}\cdots Cl^{\delta+}–CH_3$. This intermediate then readily cleaves and forms CH_3OH with the OH group of ZnOHOH. As described above, the chlorine atom exhibits the largest electronegativity in CH_3Cl, thus it can be assumed that methyl chloride also coordinates to the investigated gold cluster cations through the chlorine atom yielding a complex that is similar to the intermediate $(HO)_3Al^{\delta-}\cdots Cl^{\delta+}–CH_3$. However, the water molecule is coordinated to the gold cations through the more electronegative oxygen atom without weakening of the O–H bond of the water molecule, instead of being coordinated through the H atom as in the complex $ZnO^{\delta+}\cdots H\cdots OH^{\delta-}$. This means that for the formation of methanol on the gold cations, not only the O–H bond should be broken but also the previously formed Au–O bond which requires additional energy. Thus, small free gold cations apparently represent a catalytic system too simple for the hydrolysis of CH_3Cl according to reaction (1). Probably a more complex catalytic material, like at least binary clusters, is necessary to simultaneously enable the activation of H_2O and CH_3Cl.

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