FTMS Studies of Sputtered Metal Cluster Ions: (II) The Chemistry of Ni_n^+ with C_2H_4 and CH_4 at Long Timescales

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Nickel cluster cations, generated in an external source by sputtering with 20 keV Xe^+ were transferred to the ICR cell of a Fourier transform mass spectrometer (FTMS), collisionally cooled, and trapped for long time periods. During storage, the chemistry of Ni_n^+ was studied with ethylene and methane in the range $n = 1 \ldots 20$. Rather than undergoing adsorption as an intact unit, C_2H_4 was dehydrogenated in the 1,2-position to yield HCCH adducts $Ni_n(C_2H_2)_m^+$ with a dramatic size-specificity: Whereas Ni_n^+ ions proved absolutely inert for $n = 1, 3, 4$, they were found highly reactive from $n = 5$ on. Cyclotroning in the presence of C_2H_4 for up to 40 s, Ni_5^+ was found to add on a maximum of nine C_2H_2 ligands. A second "hidden" size-specific effect was discovered between $n = 11$ and $n = 12$, where dehydrogenation intensifies to yield $Ni_nC_6^+$ as final products. These are being discussed in terms of close-packed lattice structures. Finally, the threshold for methane activation by Ni_5^+ leading to Ni_5C^+ was determined to be 2.0 ± 0.5 eV.

1. Introduction

In order to get a more profound understanding of heterogeneous catalysis, it will be helpful to study the chemistry of bare metal clusters in the gas phase as a function of size. Unlike solvated or supported clusters they are undisturbed by matrix effects and allow a closer simulation of the active surface centers. We recently described a new procedure for the investigation of the chemistry of naked size-selected thermal metal cluster ions [1,2 (= I in this series), 3]. A combination of Fourier transform mass spectrometry (FTMS) with cluster generation by Xe^+ ion bombardment of nearly all metal targets avoids undesired fragmentation phenomena and allows clear identification of reactants and products. In certain cases, the available option for high mass resolution is essential for a clear identification of reaction pathways. Thus, the newly introduced method can serve as a powerful alternative to the molecular beam technique still practiced by a vast majority of researchers in the field. It involves cluster synthesis by laser vaporization, transfer to a flow reactor and subsequent photoionization for mass spectral analysis, see for example, Refs. [7, 8, 13, 15–18, 21, 22].

Preliminary results on nickel cluster ions [3] convinced us of their extremely rich and varied chemistry that would merit a more thorough study. We here report on the dehydrogenation of ethylene and methane by long-time stored, size-selected Ni_n^+ cluster ions. With ethylene, chemisorption is a facile process that is characterized by two dramatic size-specific effects. The reaction with methane is found endothermic and thus requires reactant cluster ions to be excited above their thermal energy content.

2. Experimental

As the experimental procedure has already been described in full detail [3], only a brief review is given here: Metal cluster ions are generated in a differentially pumped chamber by bombardment of the appropriate metal target with a 20 keV Xe^+ beam. Through an electrostatic lens arrangement they are transferred to the ion cyclotron resonance (ICR) cell of a home-built Fourier transform mass spectrometer (FTMS), where they are stored for diverse amounts of time. To aid in trapping and thermalization of the injected ions, neon is pulsed in up to about 10^{-5} mbar via a fast piezoelectric valve close to the ICR cell. After frequency-sweep ejection of unwanted ions, only those of a predetermined mass are left over in the cell for further study. It has been demonstrated that the so-isolated ions are characterized by a temperature low enough to allow the study of thermal reactions: Cu_n^+ clusters, for example, were found unable to react with admitted oxygen, unless additionally activated [2].

In order to assess the chemical reactions of cluster ions as a function of size, we can select different kinds of experiments: As outlined above, ions of a specific mass may be isolated in the ICR cell and the reactive gas be admitted via a pulsed valve. This has the advantage of detecting the ions when pressure is low and resolution is high again. Deviating from this general scheme, we may as well renounce mass preselection and continuously admit the reactive gas to the whole ion ensemble trapped in the cell. The resulting difference in mass spectra may be considerable, especially in high-mass regions, where peaks tend to become utterly crowded. To ultimately elucidate the origin of products one must receed to single-mass experiments. In both cases described, we have dealt with spontaneous reactions that may be studied as a function of "contact" time. Endothermic reactions that do not proceed at thermal energies become accessible via acceleration of the stored ions to larger orbits, thereby endowing them with additional energy. The procedure is to again preselect a given ion mass and admit the reactive gas continuously. In the following, we shall apply each one of these methods in turn.

3. Results

Ni_n^+ cluster ions generated and transferred to the ICR cell as described above have been detected up to $n = 25$ [3]. Fig. 1 shows the first part of the complete spectrum, mass-linearized up to $n = 15$. The characteristic isotope patterns are easy to recognize. Note, how clean the area between different cluster sizes is, i.e. there is no contamination by oxides, carbides or nitrides, as was observed in a previous SIMS study [4]. (However, the ion Ni_2H^+ was formed inadvertantly. As it turned out to be extremely stable, it was not separately ejected for the following experiments.)

(A) Ethylene

To get a rough idea of the kind of chemistry to expect, we began by continuously admitting ethylene to the whole series of trapped nickel cluster ions. The gas pressure was chosen such that the estimated number of collisions would stay below about 10 s^{-1}. At this value (ca. $1 \cdot 10^{-7}$ mbar) and at an exemplary reaction time of 4 s, the metal clusters have not yet completely reacted away, as evident from the mass spectrum in Fig. 2. Comparing this with the blank spectrum of Fig. 1, a pronounced size effect becomes evident:

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While most sizes react readily by a combination of C_2H_4 addition and dehydrogenation, Ni^+, Ni_3^+ and Ni_4^+ show no trace of a reaction at all! Ni_2^+ yields solely the product $Ni_2(C_2H_2)^+$, but all clusters from Ni_5^+ on are found capable of binding several C_2H_2 units.

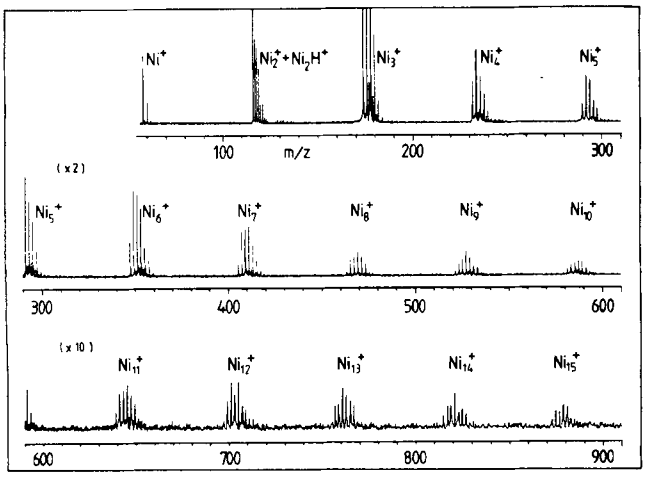

Fig. 1
Overview mass spectrum of pure nickel cluster ions, sputtered by 20 keV Xe^+, cooled by Ne pulses (max. $1 \cdot 10^{-5}$ mbar) and trapped at 7 T. Each isotope pattern is marked by the overall symbol Ni_n^+

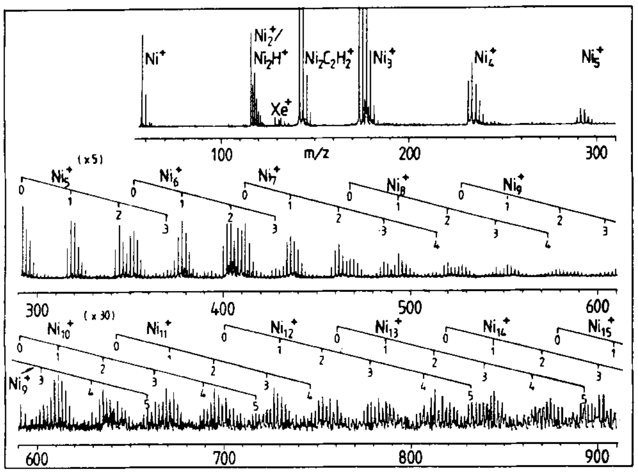

Fig. 2
Overview mass spectrum of pure nickel cluster ions (conditions as in Fig. 1) and product ions, when C_2H_4 is continuously admitted to the storage cell at about $1 \cdot 10^{-7}$ mbar. Each isotope pattern represents a product $Ni_n(C_2H_2)_m^+$, marked by the overall symbol Ni_n^+ with the observed sequence of numbers m indicated below

For a closer investigation of those effects, different specific-sized cluster ions were sequentially isolated in the ICR cell and exposed to ethylene at the same concentration as before, but now for varying time periods. These single-mass experiments served to confirm and clarify the global picture obtained above.

Ni_2^+:

In the case of the dimer ion, it was verified that $Ni_2(C_2H_2)_1^+$ was the only product formed, even after a reaction time of 32 s.

Ni_3^+ and Ni_4^+:

As these clusters below $n = 5$ proved unreactive, at a storage time of 4 s each kind was separately accelerated to kinetic energies up to 50 eV (center-of-mass), to check whether this would eventually induce a chemical change. The only effect was collision-induced dissociation (CID) to lower mass ions, preferentially to the monomer and in small amounts to Ni_2^+ or Ni_3^+ respectively.

In another experiment, Ni_3^+ was isolated and under otherwise identical conditions accelerated to a constant energy of about 13.5 eV (center-of-mass), now with an increasing time delay between activation and detection pulses. First, Ni_2^+ formed in larger amounts, at a later time, Ni^+ appeared as well and finally, with a delay between 4 and 16 s, $Ni_2(C_2H_2)^+$. Thus, it is certain that this ion is not produced through fragmentation from higher clusters, but only by long-time reaction of Ni_2^+ with C_2H_4.

Ni_5^+:

The nickel pentamers demonstrated extraordinary reactivity, as expressed in the stacked mass spectra of Fig. 3, where the parameter is the reaction period. With increasing time, the cluster adds on more and more C_2H_4 units which are instantaneously dehydrogenated to C_2H_2 ligands. This process seems to work for the Ni_5^+ cluster up until nine ligands have been attached to it, finally yielding $Ni_5(C_2H_2)_9^+$. Simultaneously, CID is occurring to Ni_4^+, with increasing time also to Ni_3^+ and to Ni_2^+. As confirmed above, the latter may continue reaction with C_2H_4 to $Ni_2(C_2H_2)^+$.

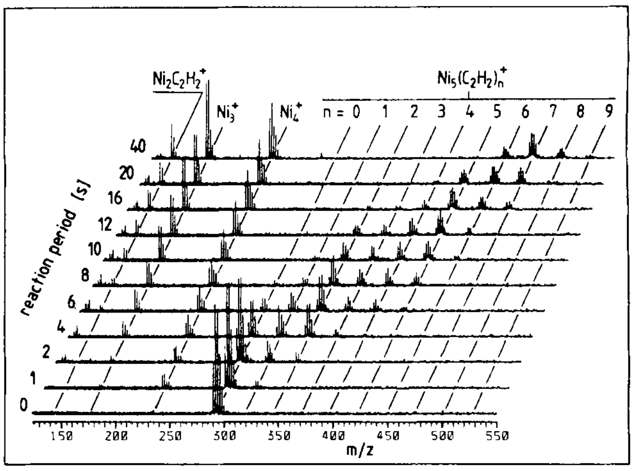

Fig. 3
Stacked mass spectra of ions obtained from isolated Ni_5^+ clusters, stored for various time periods in C_2H_4 at ca. $1 \cdot 10^{-7}$ mbar

It should be remarked that to yield the last spectrum, cluster ions have been stored in the ICR cell for up to 40 seconds! We do not know of any other successful trapping of externally generated cluster ions for such a long time. The sum over all ion peak heights after 40 s is still about 75% of the original intensity (summed over the complete Ni_5^+ isotope pattern). This tells us our ion trap must be functioning efficiently.

The outcome of the long-time reaction of isolated Ni_5^+ with C_2H_4 can also be evaluated in a different manner to yield a time plot: In Fig. 4, the abundances of all participating ions (integrated over the corresponding isotope patterns) are displayed as a function of the reaction interval. With increasing time, parent ion intensity drops exponentially until reaching a value near zero after about 10 s. We recognize the picture typical of consecutive reactions: All products $Ni_5(C_2H_2)_n^+$ with $n = 1 \ldots 6$ traverse maxima and thus indicate their continuing reaction with C_2H_4 to the next higher C_2H_2 adduct. Those with $n = 2, 5, 7$ surpass the others in intensity, whereas the products following them ($n = 3, 6, 8$) only start to appear after a notable delay. The ions with $n = 7, 8, 9$ look as though they were final products, but since the experiment was terminated after 40 s, this does not need to be true. Therefore, we cannot state with absolute certainty that $Ni_5(C_2H_2)_9^+$ is indeed the end product of the Ni_5^+ cluster long-time reaction chain with C_2H_4, even though there is strong evidence for this.

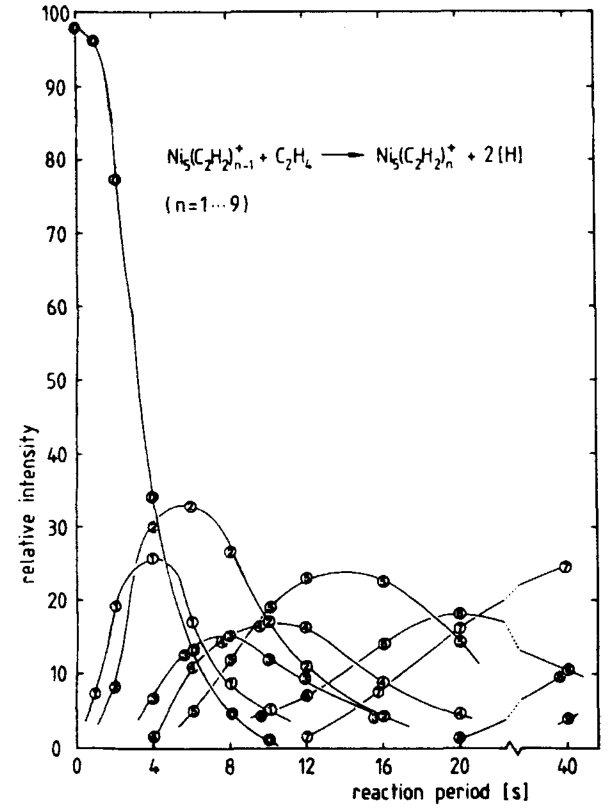

Fig. 4
Abundances of product ions as a function of time from the reaction of isolated Ni_5^+ clusters with C_2H_4 at ca. $1 \cdot 10^{-7}$ mbar

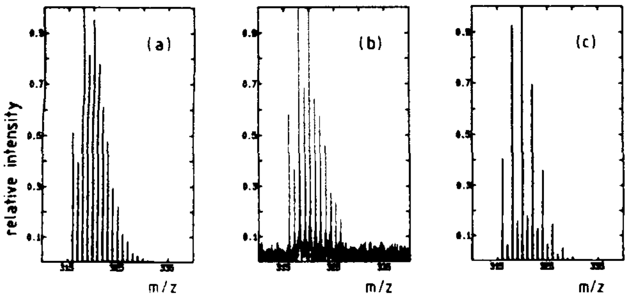

Fig. 5
Isotope patterns of $Ni_5(C_2X_2)^+$ product ions (X = H, D) from the reaction of isolated Ni_5^+ clusters with a mixture of deuterated ethylenes (40% 1.1-$C_2D_2H_2$, 25% C_2DH_3, 35% C_2H_4), as:
a) computer-simulated for an assumed 1.2-elimination of X_2;
b) experimentally measured;
c) computer-simulated for an assumed 1.1-elimination of X_2

In this context, interesting questions may be asked as to the detailed nature of the dehydrogenation process. The loss of two hydrogens may occur from the 1.1- or the 1.2-positions of ethylene and the identity of the C_2H_2 ligands remains unclear. An approach to finding the answers would be to repeat the reaction with isotopically substituted ethylenes. So, by dehydration of the alcohol D_3CCH_2OH we prepared a mixture of about 40% 1.1-$C_2D_2H_2$, 25% C_2DH_3 and 35% ordinary C_2H_4. When isolated Ni_5^+ cluster ions are treated with this mixture, the mass spectra naturally come out rather complex, due to the interfering isotope patterns of the reactant ions and the ethylene mixture. For the special case of reaction to the simple adduct $Ni_5(C_2H_2)^+$, Fig. 5 demonstrates how it is still possible to extract the desired information: mass spectra simulated by statistical analysis for the two cases to be distinguished look totally different from each other. The experimental result clearly resembles the simulated elimination from the 1.2-position. This has been verified for adducts with a larger number of C_2H_2 units, as well as for higher Ni_n^+ cluster compounds. We thus conclude that ethylene is adsorbed with its double bond parallel to the cluster "surface". The product of the ensueing dehydrogenation is therefore determined as HCCH, probably a rehybridized acetylene variation.

Ni_6^+, Ni_7^+, Ni_8^+ and Ni_{10}^+:

From the total of the reactive Ni_n^+ cluster ions, the above-quoted sizes were studied in an exemplary fashion. The highest adducts formed were $Ni_6(C_2H_2)_4^+$ after 15 s reaction time, $Ni_7(C_2H_2)_7^+$ after 36 s, $Ni_8(C_2H_2)_3^+$ after 8 s and $Ni_{10}(C_2H_2)_3^+$ after 4 s, respectively. Again, we do not claim the indicated compounds to be the actual final products in the corresponding reaction sequences.

$Ni_{11...20}^+$:

Working with the deuterated ethylenes, we accidentally came across a second important and "well-hidden" size-specific effect: From $n = 12$ on, carbides of the form $Ni_nC_6^+$ start appearing. These are stable end products, even though $Ni_nC_2^+$ and $Ni_nC_4^+$ are also present in minor amounts. These carbides had always been formed, but were just not identified before since we did not expect them. To illustrate the situation through an example, different isotopes of $Ni_{12}(C_2H_2)_5^+$ and $Ni_{13}C_6^+$ have the same nominal mass and can only be distinguished by performing a narrow-band RF excitation over a small mass window. Of course, this procedure is not regularly applied to all signals detected in a wide-band mass scan, but is normally reserved for "unclear" cases. With the deuterated ethylenes, however, mass deviations were reinforced by the C_6 unit so that a definite search finally revealed the facts. This demonstrates how important high mass resolution can be for elucidating the details of metal cluster chemistry.

This second size-specific effect occurs between $n = 11$ and $n = 12$. When C_2H_4 was continuously added to the complete Ni_n^+ ensemble, the carbides $Ni_nC_6^+$ could be observed up to $n = 18$, with most stable ones at n = 13, 14, 15. (It was also possible to isolate Ni_{12}^+ in the cell and after reaction with ethylene for 1 s detect $Ni_{12}C_6^+$.) At shorter times (0.5 s), the intermediates $Ni_nC_2^+$ and $Ni_nC_4^+$ were seen as well. Ni_{11}^+ was found absolutely unreactive with respect to carbide formation. Of course, the C_2H_2 adducts reported above were still present for the higher Ni_n^+ clusters, including Ni_{11}^+.

(B) Methane

With methane continuously admitted to the whole thermalized Ni_n^+ distribution no reaction at all was observed, even at the highest pressures (ca. $1 \cdot 10^{-6}$ mbar). The situation was clearly similar to the one encountered during our study of copper cluster ion oxidation where distinct thresholds had to be overcome as well, before the endoergic reactions would set in [2]. Reaction of size-selected nickel cluster ions trapped in a uniform methane environment (again at about $1 \cdot 10^{-6}$ mbar) could be induced only through additional excitation to kinetic energies above definite thresholds. For the exemplary case of Ni_5^+ parent ions, Fig. 6 contains a graph of ion abundances measured while increasing the relative kinetic energy. Ni_5^+ intensity is seen to decrease linearly, with products starting to arise that identify the main process as CID to lower mass cluster ions. It is accompanied to a lower extent by CH_4 addition/dehydrogenation yielding the simple carbides Ni_nC^+, in the special case of $n = 3$ together with an equal amount of Ni_3CH^+. A more quantitative statement is to be made for the example of Ni_5C^+ formation, which obviously requires a minimum collision energy of the order of 2.0 ± 0.5 eV (center-of-mass).

Due to its inertness and high ionization energy, we generally add neon to support trapping and cooling of the cluster beam during injection into the ICR cell [3], although Ne atoms are certainly not the most effective collision partners. CH_4 molecules with their larger number of internal degrees of freedom, on the other hand, should be more suitable for this purpose. We confirmed in a separate experiment that methane may indeed replace the neon, yielding a spectrum of pure Ni_n^+ clusters, like Fig. 1.

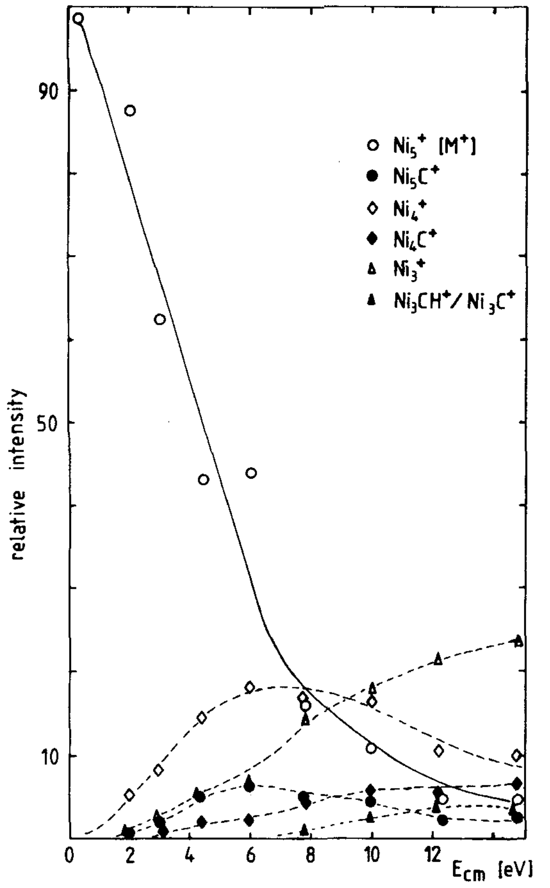

Fig. 6
Breakdown graph for isolated Ni_5^+ cluster ions excited to diverse kinetic energies in the presence of CH_4 (ca. $1 \cdot 10^{-6}$ mbar)

4. Discussion

(A) Ethylene

The observation of ethylene dehydrogenation to some kind of a "pseudo acetylene" (HCCH) by thermalized Ni_n^+ clusters agrees well with the results from adsorption studies onto solid Ni surfaces. At low temperature, ethylene is found to adsorb with the double bond parallel to the metal surface. The MOs are rehybridized to give a di-sigma-bonded complex. At elevated temperature, it desorbs via acetylene-like intermediates to yield hydrogen and surface carbon [5, 6].

Most remarkable in the present investigation of Ni_n^+ cluster ion chemistry with ethylene are the dramatic size effects observed. The fact that Ni_3^+, as well as Ni_4^+, appear totally inert provokes us to postulate that in these smaller clusters the atoms are still arranged in a two-dimensional configuration. For example, it is unproven that four Ni atoms (together with a positive charge) have to necessarily arrange in the shape of a tetrahedron. On the other hand, the sharp onset in reactivity from Ni_5^+ on suggests that at this size, clusters start to exhibit spatial structure.

There are not many investigations of nickel cluster reactivity in the literature. Without reference to their chemistry, Kaldor and coworkers studied photoionization of neutral Ni_n clusters ($n = 2 \dots 23$), generated by laser vaporization in a supersonic He beam [7]. Using a similar technique, Smalley and coworkers found D_2 chemisorption to vary smoothly with cluster size [8]. Michl and coworkers briefly report on the reactions of sputtered Ni_n^+ clusters ($n = 1 \dots 10$) with n-butane in a triple quadrupole. No spectacular size effects were seen, while the most important reactions seemed dehydrogenation and cracking by Ni^+ and Ni_2^+. It was noted that collisionally cooling the ions before reaction was necessary in order to detect any products [9].

With almost identical equipment but more detailed, Wöste has studied the reaction of sputtered Ni_n^+ clusters ($n = 2 \dots 13$) with carbon monoxide, where no distinct size effects were apparent either [10]. He found all clusters, even Ni_3^+ and Ni_4^+, to be reactive in adding some number of CO ligands. Ni_5^+, which is supposed to have trigonal bipyramidal structure, was observed to bind a maximum of 12 CO ligands. An attempt was made to correlate metal cluster behavior with electron counting rules for organometallic compounds [11]. The approach does not seem to be of general validity, however, as evident for the smaller clusters.

The trigonal bipyramid proposed for the structure of the pure Ni_5^+ cluster should provide for nine bridge positions. If the addition of C_2H_4 with subsequent dehydrogenation to C_2H_2 required such a bridge position for each molecule chemisorbed, our findings might become easily interpretable: Ni_5^+ would have the capacity to add up to 9 C_2H_2 ligands, while Ni_2^+ as the simplest "cluster" could provide only one such position and correspondingly bind just one C_2H_2 unit. This model would have worked, supposed the C_2H_2 group had indeed vinylidene structure ($=C=CH_2$), as observed in certain organometallic complexes [12]. To check for this eventuality, we conducted the experiment with the deuterated ethylenes to learn that indeed acetylene-like HCCH is attached to the cluster in a parallel configuration. Thus, the model sketched above has unfortunately proved not suited for our purpose, so that we are presently unable to explain our findings in a consistent manner.

Ethylene as a reactive gas has also been applied to vanadium and cobalt clusters in a conventional laser vaporization/ionization arrangement [13]. Under the single-collision conditions used, only one molecule per metal cluster was generally observed to undergo reaction. Neutral Co_n clusters behaved like our Ni_n^+ cluster ions, with the exception that physical adsorption to $Co_nC_2H_4$ was seen as well. Dehydrogenation to $Co_nC_2H_2$ was found to set in at the definite size of $n = 9$. The carbides Co_nC_2 appeared from $n = 12$ on. The size effect in dehydrogenation can obviously be understood as caused by the increasing Co_n diameter: If C_2H_4 is adsorbed horizontally, the H atoms will be far away from the cluster as long as it is small enough, but will come into closer contact with it from a certain size on. Then, C–H bond cleavage is facilitated, leading to dehydrogenation and H atom recombination.

In our case, Ni_n^+ cluster ions from the smallest sizes on do not simply adsorb intact C_2H_4 molecules, but – appearing to have the appropriate sites – immediately dehydrogenate them in an exoergic reaction to C_2H_2 ligands. (This behavior seems typical for charged clusters, as it has not been observed with neutral Co_n, but persists also with Co_n^+ [14]). For the following reaction sequence that yields $Ni_nC_2^+$ and $Ni_nC_4^+$, with $Ni_nC_6^+$ as the final product, it appears reasonable to employ a mechanism like the one quoted above. So to explain our second size-specific effect, we would argue: As soon as the Ni_n^+ diameter becomes large enough ($n = 12$), the H atoms are in such close contact to the cluster ion surface that dehydrogenation goes on to the next stable product $Ni_nC_6^+$.

Dehydrogenation has been found earlier to occur with benzene in the presence of neutral Pt_n [15] and Nb_n [16–18] clusters. In the latter case, it may proceed all the way down to Nb_nC_6. Seemingly, the observations can best be explained by considering the relative stabilities of reactants and products, allowing the conclusion that maximization of metal-carbon bonds is the driving force for the reaction [17]. However, in these experiments where neutral clusters are first reacted and later ionized by UV laser radiation, it is extremely difficult to separate thermal effects from photoinduced contributions, making necessary a host of assumptions [16, 18]. It is much safer to follow our procedure and place the ionization step before chemical reaction. In any way, the cluster ion $Nb_nC_6^+$ was found extremely stable, in analogy to our dehydrogenation product $Ni_nC_6^+$.

What could the C_6 group of this compound look like? Unfortunately, the structure of the bare Ni_n^+ clusters is not well known. For the shape of Ni_{12}^+ or Ni_{13}^+, we may take the fundamental coordination unit of a hexagonal close-packed lattice (no. 42 of Ref. [11]) with the center position empty or occupied, respectively. This structure possesses two distinguished triangular faces, in the center of which a Ni atom might be placed to even yield the clusters Ni_{14}^+ or Ni_{15}^+. Further, it is characterized by three pairs of square planes that could incorporate altogether 3 C_2 groups adding up to our C_6 unit. Of course, the authors realize that all this is mere speculation, but as it agrees so well with the experimental findings they did not want to withhold it from the readers. To obtain deeper understanding of the general chemical behavior of Ni_n^+ cluster ions, we have also studied their chemical reactions with gaseous benzene at long storage times [19]. The results will allow interesting comparisons with the already known neutral cluster chemistry [15–18].

(B) Methane

The fact that methane is not easily activated by thermal Ni_n^+ clusters is not all too surprising. Neutral Fe_n [20], Al_n [21] and Rh_n [22] clusters have also been found inert towards methane. Although a Ni surface at high pressure and temperature will catalyze the steam reformation process ($CH_4 + H_2O \rightarrow CO + 3\,H_2$), it is much less reactive towards methane under UHV conditions. This so-called "pressure gap in heterogeneous catalysis" is caused by a very low adsorption probability at the low pressures. By making use of a molecular beam technique, Lee et al. demonstrated the existence of a barrier to the dissociative chemisorption of CH_4 on Ni(111), which may be overcome by supplying the methane with translational energy. The species adsorbed was identified as $CH_3\bullet$ radical, the activation process as C–H dissociation [23].

Also we have surmounted such barriers by translationally exciting one reactant, in this case the Ni_n^+ ions. Ni(100) and Ni(110) surfaces as well have been found to exhibit activation energies to CH_4 decomposition [24]. These thresholds of the order of 0.5 eV are much lower compared to our value of 2.0 eV. Obviously, the behavior of clusters does not lend itself easily to comparison with that of a solid surface. In our case, the relatively high energy is mostly needed to activate the first C–H bond. Once this has happened, the energy gained upon $Ni_n^+ - CH_3$ bond formation is probably sufficient to expel the remaining H atoms.

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