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ABNORMALLY LARGE DEUTERIUM UPTAKE ON SMALL TRANSITION METAL CLUSTERS

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Deuterium uptake experiments on gas phase transition metal cluster cations of Ni, Pt and Rh show that the small (< 10 Å dia.) clusters can bind many (up to 8) deuterium atoms per metal atom in the cluster, in contast to $(H(D)/M)_{max}$ ratios near unity typically reported for single crystal metal surfaces and in previous uptake experiments on nickel and iron clusters [11]. Abnormally large $(H(D)/M)_{max}$ ratios appear to be the rule rather than the exception for small transition metal clusters, an effect which has strong implications in chemical and catalytic processes involving hydrogen chemisorption.

Hydrogen chemisorption and activation are important for many industrial processes involving hydrogenation/dehydrogenation steps. Hydrogen chemisorption is also one of the primary means used to estimate the degree of metal dispersion, i.e. the number of exposed metal surface atoms and thus the metal particle size [1]. In order for such measurements to be meaningful, one must know (or measure) the maximum number of hydrogen atoms which can be adsorbed per metal (surface) atom $(H/M)_{max}$, i.e. the hydrogen to metal stoichiometry. If $(H/M)_{max}$ is known, then a simple titration experiment [2] allows the number of surface metal atoms to be determined. If $(H/M)_{max}$ is unknown, a value of 1 is typically assumed since this stoichiometry is measured for many metallic single crystal surfaces [3]. Recent data is challenging these assumptions. Christmann's group recently reported $(H/M)_{max} = 2$ for the Rh(110) [4] and Ru(1010) [5] surfaces and a value of 1.5 has been reported for the Ni(110) surface [6]. Similarly in several studies of highly dispersed supported metal catalysts $(H/M)_{max}$ values greater than one have been observed [7]. The origin of the large H/M values have been attributed to a variety of different effects; (a) hydrogen spillover [8], in which hydrogen dissociatively chemisorbs on the metal but hydrogen atoms subsequently diffuse (spillover) onto the substrate, (b) an increased stoichiometry for corner or edge metal atoms [9] compared to that for more highly coordinated atoms, or (c) subsurface hydrogen i.e. incorporation of H into the bulk as well as on the surface [10].

Chemisorption of hydrogen on gas phase metal clusters offers an approach free of support contributions to measure the hydrogen uptake upon saturation and establish H/M stoichiometry as a function of the number of constituent atoms. In an attempt to better understand the effect of particle size on hydrogen(deuterium) chemisorption we have measured deuterium uptake as function of cluster size for gas phase Pt, Ni and Rh cationic clusters and Pd neutral clusters containing less than 50 metal atoms. We find that these small transition metal clusters are "hydrogen rich" and can bond a large number of D atoms per metal cluster atom with $(D/M)_{max}$ values as high as 8 for Rh_n^+ and 5 for Pt_n^+ and Ni_n^+, and 3 for Pd_n. These results are in strong contrast to earlier studies of hydrogen uptake on gas phase clusters of iron [11] and nickel [12], where $(H(D)/M)_{max}$ ratios near unity were reported for the different size clusters.

Since the experimental techniques are described in detail elsewhere [13] only a short description will be given here. Metal clusters are generated by condensation of atomic metal vapor produced by pulsed laser vaporization of a metal rod installed in the throat of a high pressure pulsed nozzle. Clusters are formed during passage through a narrow (0.2 cm dia by 4.5 cm long) tube after which the cluster beam passes into a larger diameter (1 cm) reactor tube. Two types of deuterium injection can be used. In one the D_2/He mixture is injected into the reactor and new mass peaks corresponding to Pd_nD_m (m even) are observed. In the second, D_2 is mixed directly with the primary helium carrier gas. In this instance some D_2 is decomposed during the vaporization process and new mass peaks containing an odd as well as even number of D atoms are detected. The maximum deuterium uptake, however, typically differs only by one D atom [11] and thus has little effect on the value of $(D/M)_{max}$.

Bare clusters and clusters containing reaction products are detected using a time-of-flight mass spectrometer TOFMS where either the cluster ions are directly extracted from the beam by pulsing on the extractor voltages or are produced by photoionizing the neutral clusters when they pass between the extractor plates of the TOFMS. Figure 1 shows the results of deuterium uptake on platinum, nickel, and rhodium cluster cations as a function of size (total number of metal atoms in the cluster) and fig. 2 presents similar results of deuterium uptake measurements on neutral palladium clusters.

For all the metal cluster systems we have investigated here, we find that the D/M ratio is greatest for the smallest clusters, only gradually approaching unity as cluster size increases. As is seen in the figures, the smaller clusters have very large D/M ratios. For the larger sizes ($n > 25$) the D/M ratio for Pt and Ni clusters does drop below 1, but if only surface atoms are considered D/M_{surf} still remains equal to or somewhat greater than 1 [14]. For rhodium cations and palladium neutrals the D/M ratio remains above unity for clusters containing up to 54 and 23 atoms, respectively. Note also that, in general, for a fixed cluster size D/Ni < D/Pt < D/Rh.

Some discontinuities in saturated D_2 coverage are noted for the different transition metal cluster cations studied here, i.e. D/M does not decrease monotonically with increasing cluster size, especially for clusters containing fewer than 30 atoms. For example, nickel cations exhibit the largest size to size discontinuities in D uptake in the range $12 < n < 19$; platinum cations in the range $6 < n < 19$; and rhodium cations in the range $4 < n < 26$. Especially visible is the odd/even alternation for Ni_n^+ for $12 < n < 20$. Understanding the origin of such discontinuities will require further investigation, but we suspect that such effects are indicative of one or more of the following: (a) Structural transformation of the cluster upon addition of an additional metal atom or reagent molecule. (b) Alteration of the hydrogen chemisorption energetics, i.e. variation of hydrogen binding energies, number or type of binding sites and/or changes in hydrogen desorption energetics. (c) Changes in chemisorption kinetics (activation barriers). The above effects may be expected to vary not only as a function of cluster size but as a function of hydrogen coverage and metal type.

In contrast to studies of D_2 uptake on cations, studies of D_2 uptake on neutral Pd_n clusters show sharp discontinuities near $n = 13$–15 [15], similar to discontinuities reported by Riley et al. in studies of hydrogen, ammonia and water uptake on iron clusters [16]. Riley et al. suggested that such discontinuities are indicative of a structural transformation, e.g. an icosahedral to fcc transformation. Such

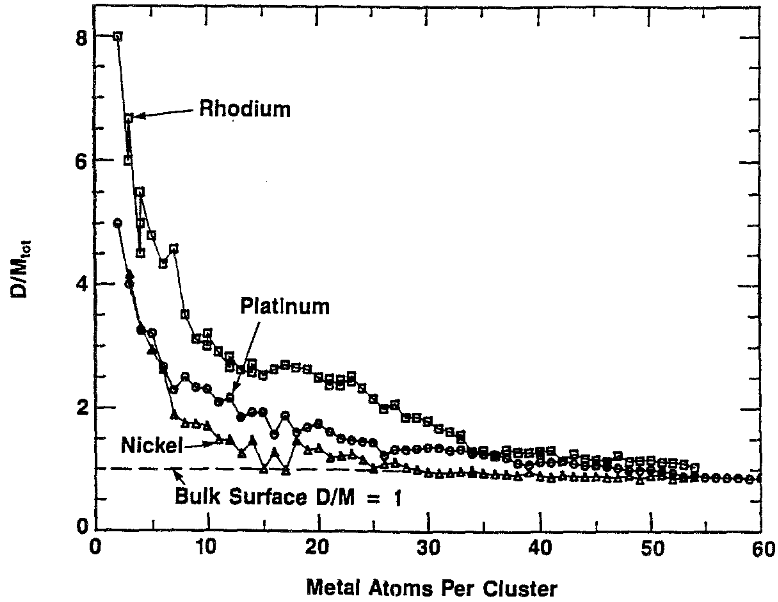

Fig. 1. The deuterium uptake ratio D/M_{tot} is plotted versus the total number of metal atoms in the cluster for cluster cations of Pt_n^+, Ni_n^+ and Rh_n^+. The dashed line is the value expected for a D/M_{surf} ratio of 1, where M_{surf} is the number of surface metal atoms. D_2 is added in the reactor.

speculations may indeed prove to be true but we note that for the neutral clusters such discontinuities might also arise, at least in part, from an experimental artifact, namely size selective dissociative ionization. Note that for both iron clusters [17] and palladium clusters [15] the cluster *IP* approaches a local maximum near $n = 15$. Thus it may be possible that the lower *IP* clusters undergo enhanced (relative to higher *IP* clusters) dissociative ionization, i.e. some deuterium is boiled off lower *IP* clusters by the ionization process. This may not be unreasonable if one accepts the hypothesis that for a given photon energy $E > IP$ a larger amount of excess energy might remain in a lower *IP* (e.g. Pd_{14}) cluster relative to the amount left in a higher *IP* cluster. Further experiments will be required to determine to what extent the UV ionization detection process perturbs the H(D)/M stoichiometry of the neutral Pd and Fe clusters.

We also point out that for certain size rhodium cluster cations, e.g. $n = 3$, 4, 10, 12, 21–23, more than one value of D/Rh is plotted. For these clusters more than

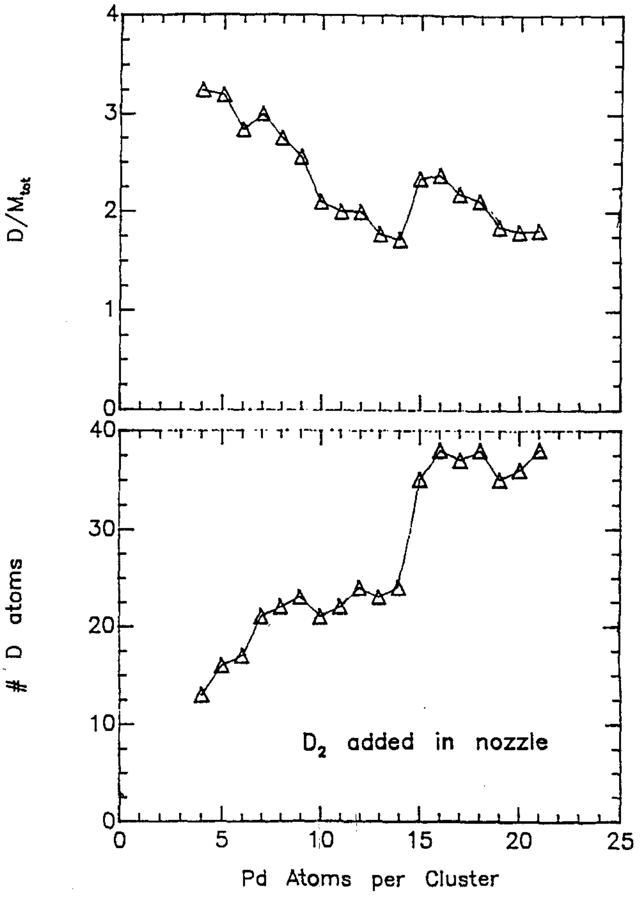

Fig. 2. The upper curve shows the D/M_{tot} results for neutral palladium clusters. The lower curve is the number of D atoms plotted versus the cluster size (the number of atoms). D_2 is added to the primary nozzle gas.

one strong deuterated product peak is detected. This behavior has previously been interpreted as indicating the presence of structural isomers which saturate at differing levels of hydrogen uptake [18–20].

It is interesting to compare our results with those of Kip et al. [21], who used a combination of hydrogen chemisorption and EXAFS to study highly dispersed Pt, Rh and Ir catalysts, and obtained $(H/M)_{max}$ of 1, 2 and 2.7 for lowest coordination number (presumably the smallest particles) Pt, Rh and Ir catalysts respectively. In addition, at a fixed coordination number they observed $H/Pt < H/Rh < H/Ir$, similar to our ordering $H/Ni < H/Pt < H/Rh$. Our observations support the conclusion that more than one hydrogen atom can be attached to a metal surface atom [21] or that some hydrogen also gets incorporated into the interior of a cluster as a result of chemisorption induced cluster reconstruction.

Only a few measurements of hydrogen uptake on other gas phase transition metal clusters have been reported. The measured $(H/M)_{max}$ values vary from slightly above 1 for iron [11] and nickel [12], increasing up to near 1.4 and 1.6 for vanadium [19] and niobium [18–20], respectively. For palladium we note that $D/M \rightarrow 1$ as cluster size increases. This is consistent with the limiting stoichiometry of bulk PdD obtained for the β hydride phase of palladium with D atoms occupying the octahedral interstitial sites [22] as well as studies of hydrogen chemisorption on palladium metal [23–24]. For palladium particles supported on alumina, H/Pd values as large as 5 have been reported [25]. Such high H/M ratios for supported metal particles in many cases are attributed to hydrogen spillover. However our chemisorption measurements on the bare gas phase clusters suggest that high H(D)/M ratios may simply signify the presence of small (< 10 Å diameter) metal particles. Attributing large H(D)/M ratios to hydrogen spillover, without direct measure of the particle size distribution may have been erroneous. It could be argued that CO chemisorption has also been used to measure dispersion as well. While the range of data is limited, we note that CO chemisorption on Ni_n^+ also leads to large CO/M ratios (CO/M = 4.5 for Ni_2^+ dropping to only 1.7 for Ni_{12}^+) [26].

Interestingly, extended Huckel calculations [27] of hydrogen uptake on Pt_{1-13} clusters predict $(H/M)_{max}$ values ranging from 6 for Pt_2 dropping to only 2.6 for Pt_{13}, surprisingly close to our experimental values of 5 and 1.9, respectively. If one considers H_2 as a two electron donor similar to CO, the observed stoichiometries are reasonably consistent with electron counting rules for organometallic bonding to species with multi-metal cores.

The implications of these results on the mechanism of certain catalytic processes is also quite interesting. In recent studies of ethylene hydrogenation on specially prepared Pt/Al_2O_3 and Pt/SiO_2 catalysts Masson et al. [28] showed that the ethane turn-over-number TON exhibited a strong dependence on metal cluster size. For particle sizes larger than 20 Å diameter the TON was independent of particle size, but increased significantly as the particle size was reduced from about 20 Å to 6 Å, before dropping to near zero for very small platinum particles, possibly atomically dispersed platinum. First we note that the sharp drop off below 6 Å suggests a minimum cluster size (ensemble) is required for ethylene hydrogenation, consistent with the recent observation that ethylene hydrogenation does not occur on a catalyst consisting of platinum atoms deposited on alumina [29].

Next we point out that the particle size dependence of TON correlates well with the cluster size dependence of the hydrogen to metal stoichiometry shown in fig. 1. In particular, we see that not only does D/Pt remain near 1 for larger particles where the TON is constant, but the increase in TON with decreasing cluster size happens in the same size range where D/Pt becomes larger than 1. This suggests that hydrogen "rich" clusters are more efficient hydrogenators. In addition to the fact that more chemisorbed hydrogen is available per metal atom for the smaller clusters, we speculate that at least two other effects could contribute to the enhanced hydrogenation activity of small clusters. (a) The metal-hydrogen binding energy may be lower for the smaller, more hydrogen "rich" clusters ($H/M \gg 1$) compared to that for the larger but less hydrogen "rich" ones ($H/M = 1$). (b) The ethane desorption energy may vary with cluster size and/or hydrogen coverage, i.e. it is lowest for the smallest, most hydrogen "rich" clusters. The suggestion that clusters possess different hydrogen binding sites is consistent with observations of multiple hydrogen bonding sites on metal surfaces [4,6]. We have no direct evidence that the ethane desorption energy may vary with cluster size, but we do know that the ethane chemisorption rate on metal clusters is significantly lower than that for hydrogen or ethylene [15]. Experiments are now being designed to allow us to probe both hydrogen and ethane desorption energetics as a function of cluster size and coverage.

Similarly small hydrogen "rich" clusters could hinder multiple C-H bond splitting [30], i.e. dehydrogenation of methane all the way to carbon, not only because they are hydrogen "rich" but also because of lower hydrogen desorption energies for these hydrogen saturated clusters.

Chemisorption studies show that the $(H(D)/M)_{max}$ or $(CO/M)_{max}$ stoichiometry is (typically) greater than 1 for small gas phase transition metal metal clusters is now well established. Such results have important implications in instances where H_2 or CO chemisorption/desorption occurs [1,2,7,8,31]. Since it is now feasible to mass select and deposit individual sized clusters onto supports [32], we plan to study hydrogen and CO chemisorption for deposited, monodispersed, mass selected clusters as a function of size and substrate.

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