Melting Dramatically Enhances the Reactivity of Aluminum Nanoclusters

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Received December 5, 2008; E-mail: mfj@indiana.edu

Not much is known about the chemistry of liquid metal surfaces. The melting points of most metals are above the temperature where organic molecules pyrolyze, and so the chemistry is usually not very interesting. Small particles, however, have depressed melting temperatures,[1−6] and for nanoclusters with less than several hundred atoms, there are size-dependent fluctuations where changing the size by a single atom can cause a large drop in the melting temperature. Thus, the liquid state that usually requires exotically high temperatures for a bulk sample can become accessible at close to room temperature for some cluster sizes. For example, several aluminum clusters with less than 100 atoms have melting temperatures that are ∼450 K, well below the bulk melting temperature (934 K).[7,8]

The existence of low-temperature liquid metal nanoclusters raises an interesting question about their chemical properties. How does the reactivity and selectivity change when a metal nanocluster melts at low temperature? The change in surface structure may cause a change in the chemical properties, and the enhanced mobility of the liquid metal at the atomic level may facilitate the dissolution of adsorbates, enabling different chemical processes to occur.

Here we report studies of the chemisorption of N_2 on solid and liquid Al_{100}^+. We have performed heat capacity measurements for Al_{100}^+ to determine its melting temperature and used ion beam experiments to investigate the reaction between the Al_{100}^+ cluster and N_2. In the ion beam experiments we set the temperature of the Al_{100}^+ clusters and then collide them with N_2 gas at a well-defined collision energy. Both the collision energy and the cluster temperature can be independently varied over a wide range. The activation energy for chemisorption of N_2 is determined from measurements of the reaction cross section as a function of the collision energy. This measurement is then performed as a function of the cluster's temperature.

The experimental apparatus used for these studies has been described in detail elsewhere.[9,10] Briefly, aluminum nanoclusters are prepared by pulsed laser vaporization and then carried into a temperature variable extension where their temperature is set by collisions with a buffer gas. Clusters that exit the extension through a small aperture are focused into a quadrupole mass spectrometer set to transmit only Al_{100}^+. For heat capacity measurements the size selected clusters are focused into a high pressure collision cell containing 1.00 Torr of helium where multicollisional excitation causes the clusters to dissociate if their translational energy is high enough. Fragment ions and undissociated clusters are carried across the collision cell by a weak electric field and exit through a small aperture. The ions that exit are focused into a second quadrupole mass spectrometer where they are mass analyzed and then detected.

The Al_{100}^+ clusters dissociate by sequential loss of aluminum atoms. The fraction that dissociates is measured as a function of translational energy. A linear regression is then used to determine the translational energy required for 50% dissociation (TE50%D). TE50%D d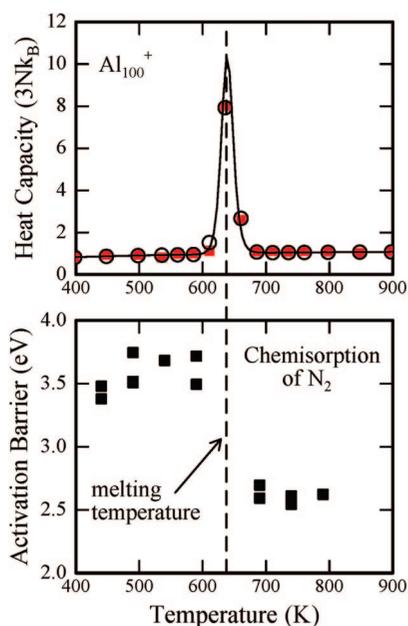ecreases as the temperature is raised and the cluster's internal energy increases. The derivative of TE50%D with respect to temperature is proportional to the heat capacity.

Figure 1. The upper plot shows heat capacities recorded for Al_{100}^+ as a function of temperature. The heat capacities are in units of the classical value $3Nk_B$ with $N = 3n − 6 + \frac{3}{2}$ (n is the number of atoms). The solid line and open circles show a fit to the measured heat capacities (red points) using a two-state model.[11] The lower plot shows the activation barrier for chemisorption of N_2 on Al_{100}^+ as a function of cluster temperature.

Heat capacities recorded for Al_{100}^+ are shown in the upper half of Figure 1. The red squares are the experimental measurements. We attribute the peak centered at ∼640 K to the melting transition. The open circles and solid line in the figure are the result of a fit to the measured points with a two-state model (see ref 11 for details). The two-state model includes only fully solid and fully liquid clusters. There are no long-lived partially melted clusters present, in agreement with computer simulations of cluster melting.[11,12] Unlike a bulk object which has a single melting point (and a sharp spike in the heat capacity) the solid and liquid clusters coexist over a range of temperatures. The peak in the heat capacity for Al_{100}^+ is a little over 40 K wide. The latent heat of melting for Al_{100}^+ (the area of the peak) is 5.85 eV (565 kJ/mol) which is just over half of the bulk value.

To investigate the reactivity of the Al_{100}^+ cluster as a function of temperature, the high pressure collision cell is replaced by a low pressure reaction cell and N_2 gas is admitted to a pressure of <1 mTorr. The reaction cell and the N_2 are at room temperature (300 K). The cluster temperature is set in the temperature variable extension where the clusters are in a buffer gas and form a canonical ensemble. After the clusters exit the extension they are in vacuum and retain their internal energy distribution as they travel to the
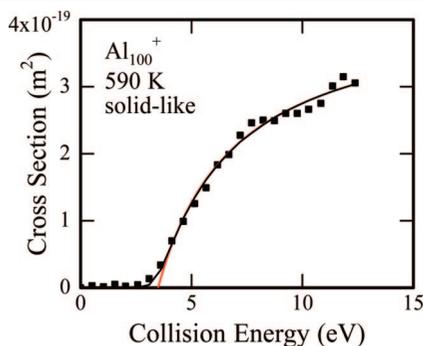
Figure 2. Plot of the reaction cross sections for chemisorption of N_2 on Al_{100}^+ (590 K) as a function of collision energy. The points are the experimental results. The black line is a fit (see text) using an assumed cross section function shown by the red line.

reaction cell. If significant radiative emission occurred on the time scale of our experiments, it would cause an artifact in heat capacities (a falloff at high temperatures) which we do not observe.

With center of mass collision energies ranging from 0.5 to 13.0 eV, the only product observed with significant abundance from $Al_{100}^+ - N_2$ collisions is $Al_{100}N_2^+$ (and a small amount of $Al_{100}(N_2)_2^+$ from two reactive collisions). Figure 2 shows a plot of the reaction cross section measured as a function of the $Al_{100}^+ - N_2$ center of mass collision energy for a cluster temperature of 590 K. The points are the measured cross sections. They are near zero at low center of mass collision energies, show a threshold at ~3 eV, and then increase with increasing collision energy. This behavior is characteristic of a reaction with an activation barrier.

To determine an accurate value for the activation barrier, it is necessary to account for the distribution of collision energies that result from the thermal velocity distribution of the N_2 molecules and the distribution of ion beam energies. We ignore the latter contribution because, with the ion beam energies used here, it is small compared to the former. To account for the broadening effects of the thermal velocity distribution of the neutral reagent, we fit the measured reaction cross sections with an assumed cross section function and explicitly account for the distribution of collision energies. For the cross section we employ the following widely used empirical function:[13]

$$\sigma = \sigma_0 \frac{(E - E_0)^n}{E} \tag{1}$$

where E is the center of mass collision energy, E_0 is the reaction threshold, and σ_0 is the cross section scaling factor. Good fits were obtained with $n = 1$. A least-squares procedure was used to fit the assumed cross section function to the measured cross sections. The solid line in Figure 2 shows the result of the fit while the red line shows the cross section function excluding the effects of the velocity distribution of the N_2 reagent. The best fit was obtained with $E_0 = 3.50$ eV (338 kJ/mol).

N_2 is known to physisorb on bulk aluminum surfaces at low temperatures.[14] The large activation energy for N_2 adsorption on Al_{100}^+ and the fact that the N_2 remains adsorbed despite the relatively high cluster temperature are both consistent with the idea that the N_2 molecule is chemisorbed on the Al_{100}^+ cluster.

The lower half of Figure 1 shows a plot of the activation barriers for N_2 chemisorption on Al_{100}^+ for cluster temperatures between 440 and 790 K. The vertical dashed line shows the center of the melting transition which occurs at 640 K. Below the melting transition, the activation barriers are almost independent of temperature, perhaps increasing slightly as the temperature is raised to

reach a value of ~3.6 eV. Above the melting temperature the barriers are essentially independent of temperature, averaging to ~2.6 eV. So when the clusters melt, the activation barrier drops by ~1 eV. This is a very large decrease. Assuming Arrhenius behavior, a decrease in the activation energy by 1 eV leads to a 10^8-fold increase in the reaction rate constant at the melting temperature.

Aluminum nitride, an important electronic material, is made by a direct reaction between aluminum and N_2 at high temperature and pressure. The aluminum is heated and ignited, and then the exothermicity drives the reaction to completion.[15,16] The combustion temperature is above the melting temperature of bulk aluminum. The importance of this process has motivated Romanowski et al. to perform theoretical studies of the reaction between N_2 and liquid aluminum.[17] They determined the activation barrier for dissociative chemisorption of N_2 on "liquid" aluminum to be 3.0 eV. But their "liquid" surface is really a frozen slab of Al(111), and so their studies cannot provide any insight into why the activation barrier is substantially lower for the liquid cluster than for the solid.

The decrease in the activation barrier is not just a consequence of the latent heat. At the melting temperature, the liquid and solid clusters have approximately the same internal energies. Their potential energies differ by the latent heat, but this energy is not available to drive the chemisorption reaction, unless the reaction causes the liquid cluster to freeze!

DFT calculations indicate that the ground-state structures for Al_n^+ prefer to display low energy Al(111) facets.[18] However, many of the surface atoms are not in a (111) environment; they are located at edges and other defect sites. The edges and corners should become less sharp and hence less reactive in the liquid clusters. In other words, the surface energy is expected to decrease when the cluster melts, and the lower surface energy should lead to a higher activation barrier for N_2 chemisorption. The activation barrier may decrease when the cluster melts because the atoms in the liquid are more mobile and better able to adjust to the incoming N_2 molecule. As the N_2 approaches, the atoms on the surface of the liquid cluster move to minimize their energy, lowering the activation barrier.

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JA809516H