Chemical Reaction of Metal-Carbon Binary Cluster Anions by FT-ICR Mass Spectrometer

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Generation mechanism of endohedral metal-fullerene and single walled carbon nanotubes are investigated through experimental studies of interaction of 'metal' atom and carbon clusters. Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer directly connected to the laser-vaporization cluster beam source shown in Fig. 1 was implemented (1) with the same basic design concept to our previous version at Rice University (2). We have shown that positive La-C, Y-C, Sc-C, Gd-C, and Ce-C binary clusters commonly showed strong MC_{2n}^+ signal in the range of $36 < 2n < 76$ with intense magic numbers at MC_{44}^+, MC_{50}^+ and MC_{60}^+ (1). Here, in order to probe the structure of clusters appearing in mass spectra, reactivity of negative carbon clusters and metal-carbon binary clusters to nitric oxide were measured.

As shown in Fig. 2, negative cluster ions injected, trapped, and mass-selected in the ICR cell were exposed to nitric oxide gas. In Fig. 2, almost half of C_{47}^- reacted with NO compared to C_{44}^-, which was only slightly reacted. Virtually no reaction was observed for LaC_{44}^-. Systematic experiments showed that odd-numbered empty carbon clusters were much more reactive than even-numbered clusters. Furthermore, carbon clusters with La atom such as LaC_{44}^- were very much unreactive to NO. The reactivity of clusters contaminated with a hydrogen atom was very curious. One hydrogen atom made odd-numbered clusters less reactive and even-numbered clusters more reactive. These experimental results were perfectly explained by a consideration of number of dangling bonds based on the random-raged geometric structure predicted by the molecular dynamics simulations (3,4). Proposed random caged structures of those small clusters are shown in Fig. 3. Since an odd-numbered carbon cluster has at least one atom with dangling bond, there is a reactive site that can be terminated by a hydrogen atom. Even-numbered carbon cage can be well annealed to non-dangling-bond caged structure that is not necessarily made of only pentagons and hexagons as in Fig. 3(b).

Similar chemical reaction experiments for Ni-Co and Ni-Y composite samples are now being performed to study the precursors of single walled nanotubes.

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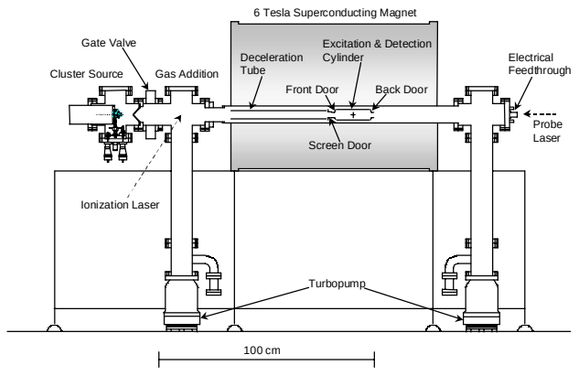


Fig. 1 FT-ICR mass spectrometer directly connected with laser-vaporization cluster beam source.

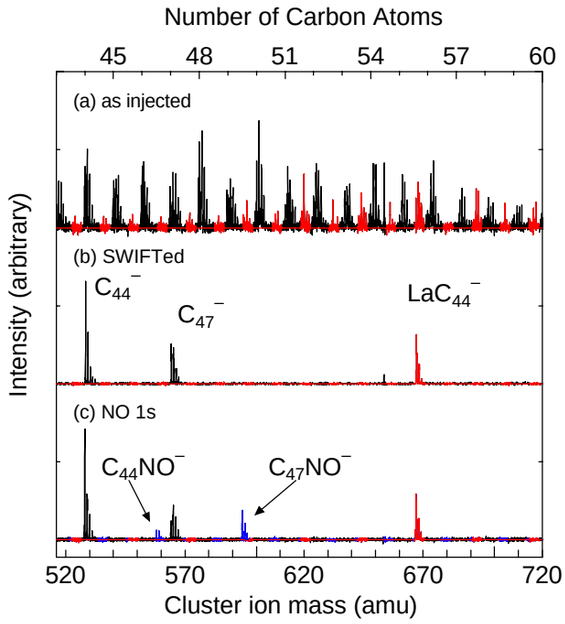
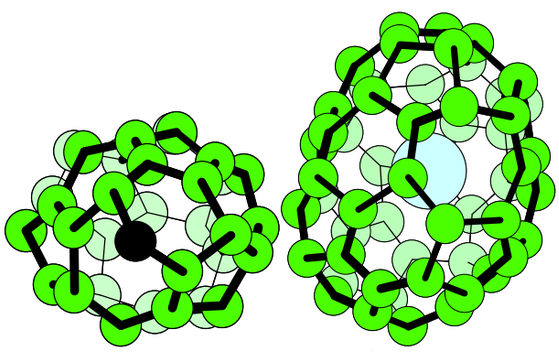


Fig. 2 Chemical reaction of selected clusters with NO. (a) Negative cluster ions injected from cluster beam source with a composite carbon sample disk with La (0.8 %). (b) C_{44}^-, C_{47}^-, LaC_{44}^- clusters were selected by over-exciting away all other ions by 'SWIFT' technique. (c) After reaction with NO at 10^{-5} Torr for 1 s.



(a) C_{33} (b) $La@C_{54}$

Fig. 3 Typical random-caged structures picked up from the molecular dynamics simulations. (a) Odd-numbered empty carbon cluster C_{33} with one dangling bond (in black atom). (b) Even-numbered carbon cluster with La atom inside: $La@C_{54}$. All carbon atoms have 3-coordinates bonding in spite of a 7-membered ring.