CO Disproportionation on a Nanosized Iron Cluster

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Received: May 5, 2009; Revised Manuscript Received: June 16, 2009

First-principles electronic structure calculations, fully incorporating the effects of spin polarization and noncollinear magnetic moments, have been used to investigate CO disproportionation on an isolated Fe cluster. After CO dissociation, which occurs on a vertex between the facets, O atoms remain on the surface while C atoms move into the cluster as the initial step toward carbide formation. The lowest CO dissociation barrier found (0.77 eV) is lower than that on most of the studied Fe surfaces. Several possible paths for CO₂ formation were identified. The lowest reaction barrier was 1.08 eV.

The carbon nanotubes (CNTs) are of great interest since they exhibit unique and useful chemical and physical properties related to toughness, electrical/thermal conductivity, and magnetism.¹ The chemical vapor deposition (CVD) methods are widely used as a CNTs synthesis method since they open a way to highly controlled and continuous CNT production.²⁻⁵ In these processes, metal nanoparticles are produced in a mixed flow of carbon precursors and other gases (e.g., hydrogen), and the growth process is driven by cleaving the carbon atoms from the precursors, and these atoms will form carbon structures on the nanoparticles’ surface. All properties, like diameter and chirality, of the nanotube are determined by the metal particle. In addition to the CNT synthesis, the metal nanoclusters with a size of less than 10 nm have attracted a great deal of attention due to their applications in magnetism,⁶ electronics,⁷ and catalysts.⁸ The metal nanoparticles are widely used in several real-world catalytic applications, including the car exhaust catalysts, where reactions happen on 3⁻⁸ nm size Pt group metal particles. Often, the good catalytic activity can be related to catalytic sites, like atomic size steps, on the cluster. Due to the high curvature of the clusters, the special site density and distribution is much higher than that on almost flat surfaces. Furthermore, the real nanoclusters have several unique active sites like facets and vertexes between the facets, which can have catalytic properties that differ drastically from the ones of almost flat surfaces. The research related to the active sites is mainly limited to atomic steps, and the nanosized clusters have received much less attention.⁹ Experimentally, many investigators have studied metal nanostructures using a wide range of surface science techniques, but these studies were done with rather a arbitrary size of clusters because it is very difficult to prepare fixed size clusters.⁹ If we want to understand the active sites on clusters, we have to know which cluster we are studying. Even then, each cluster has several different active sites, and it is very difficult to know which of them is the most active one. For this reason, the computational approach, where precise sites can be studied, is very attractive.

The present study is addressing the CO disproportionation \( \text{CO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{C} \) on an iron nanocluster during the CVD method for the synthesis of single-walled carbon nanotubes (SWCNTs).²⁻¹⁰ The chemistry on the surface of SWCNT catalyst transition-metal nanoparticles is largely unknown, but it is believed that the adsorbed CO first dissociates, \( \text{CO}(\text{s}) \rightarrow \text{C}(\text{s}) + \text{O}(\text{s}) \), and the O will react with an undissociated \( \text{CO}_2(\text{g}) \) to form surface \( \text{CO}_2(\text{s}) \) (Figure 1).¹²⁻¹³

In order to understand the role of the cluster in this reaction, we have used first-principle calculations to study the steps of this reaction on a 55 atom nanocluster. There are only a few ab initio studies of nanosized clusters,¹⁴⁻¹⁵ but these works do not address any chemical reactions. The computational work is combined with experimental investigations of the same reaction on larger nanoclusters.

A gas-phase process of SWCNTs formation, based on thermal decomposition of ferrocene in the presence of carbon monoxide (CO), was investigated in ambient pressure laminar flow reactors in the temperature range of 600⁻¹300 °C.¹⁰ In situ sampling carried out at 1000 °C showed that the SWCNT’s growth occurred from individual metal particles in the heating section of the furnace in the temperature range of 891⁻⁹28 °C, in which the growth rate was estimated to exceed 2 μm/s.¹⁶ Kinetic investigations of the CO disproportionation reaction were performed in a horizontal quartz tube at a heating rate of 5 °C/min from room temperature. A silica substrate with deposited 15 nm sized iron particles was placed inside of the tube. Investigations show appreciable reaction rates in the temperature interval from 470 to 820 °C, with a maximum rate at about 625 °C. The region of the CO₂ concentration increase from about 325 to about 600 °C is the kinetic region where the rate of the CO disproportionation reaction can be measured. By plotting the kinetic region in the coordinates of \( \ln \frac{X_{\text{CO}_2}}{T} \) versus 1/T, one gets an Arrhenius dependence, \( X_{\text{CO}_2} = k_0 \exp(-E_a/RT) \), where \( X_{\text{CO}_2} \) is the carbon dioxide mole fraction, \( k_0 = 7.16091 \), and \( E_a \)

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0.77 eV. Here, we focus to the two lowest barrier paths, (MEPs) were calculated, and the obtained barriers vary between to the minimum-energy path. Several minimum-energy paths minimization of the forces acting on the images, brings the band images is added to ensure continuity of the path, thus mimicking point configurations. A harmonic interaction between adjacent images of the adsorbate system is generated between the end points. A more complex reaction path was found by taking CO_C_O_2 as the starting point, possible paths to CO2_C_1 can be easily conceived. The corresponding structures of all transition states and intermediates are depicted in Figure 4a together with the energy profile. The obtained formation energy is −0.37 eV with a barrier of 1.33 eV. This path presents an elementary rearrangement of atoms and molecules on the surface. A more complex reaction path was found by taking CO_C_O_2 as the starting point and CO2_C_2 as the final point of the path. This path has a formation energy of +0.88 eV and barrier of 1.08 eV.

We can also compare the calculated results with our experimental results reported in the initial part of this letter. The DFT results above show that CO disproportionation on a nanosized iron cluster is a multistep process in which the rate-limiting step is the formation of CO2 from O and CO. We studied different reaction channels, and the lowest-energy channel showed a barrier of 1.08 eV. This is consistent with the kinetic investigations that suggest a barrier of 0.65 eV for the overall process. The agreement is reasonable considering the difference in the size of the clusters and the unknown coverage in the experiments. The computed nanoparticle is very small and regular and, thus, it has only a few types of active sites. In this sense, it is probably rather unreactive as a nano-cluster. The larger clusters relevant in the experiments will have much more active sites, and some of them can have lower activation barriers. Also, our calculations are at 0 K; therefore, the Fe atom diffusion is not taken into account, whereas the experiments are at around 900 K where the Fe atoms are very mobile. The iron mobility can also cause new active sites that are very difficult to model with the static calculations. Even
the difference between the experimental and simulated cluster is rather large, and we wanted to emphasize that the calculations have given new information of the reactivity of nanoclusters and that the comparisons to real-world systems is more relevant at lower temperatures.

In summary, we have presented an ab initio study of the CO adsorption, dissociation, and CO2 formation on a small iron nanoparticle. To our knowledge, this is the first computational study of a chemical reaction on a real nanosized iron particle. Even more importantly, we have studied active sites that have not been studied before, the facets and vertexes. Overall, we see the small clusters as new and important model systems for nanocatalyst studies. They exhibit new active sites that complement the stepped surface calculations. When the computational capacity will permit, larger clusters can also be studied. Presently, detailed chemical reactions can be studied at clusters with a size of 50–100 atoms. Another novel aspect of our study is the use of the spin polarization with noncollinear magnetic moments.

In our calculations, the Fe55 cluster has high catalytic activity. We have observed one important effect, the increased reactivity of low-coordinated molecules on the vertexes. Such sites are particularly abundant on the small nanosized particles, and they very likely explain the catalytic activity of them.9 We have been able to show that the reaction barriers for both the CO dissociation and CO2 formation are relatively low, and an exothermic path for surface bound elemental carbon has been found. The carbon atom formation is the initial step for the CNT formation. Under the CVD conditions, the 1.5–2.5 nm size clusters are the CNT catalysts. These clusters probably have a
similar geometry to what we have studied here, and we believe that also in this case, the vertexes are the catalytically active sites.

In further studies, we will focus on carbon–carbon and nitrogen–carbon reactions on the nanoparticle since we are interested in the CNT formation. We need to include other chemicals, like H₂, in our study. Overall, the CNT formation chemistry on the iron particle is very challenging. It is not very difficult to model the full CNT growth process with ab initio methods, but we can model elementary reactions between small C fragments (at least up to approximately C₁₂) with C, O, and H. Such studies will give a lot of details of the chemistry on iron nanoparticles.

Acknowledgment. The authors would like to express their sincere thanks to Dr. A. S. Foster and Dr. A. V. Krasheninnikov for useful discussions. The proposed project has mainly used the existing computational facilities available at CSC (Center for Scientific Computing), Espoo. This work has been supported, in part, by the European Commission under the 6 Framework Programme (STREP project BNC Tubes, Contract Number NMP4-CT-2006-03350) and the Academy of Finland (Project Number 128445).

Supporting Information Available: Additional methods and results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


JP904200E