Computational Study of Small Vanadium and Chromium Oxide Clusters: Effect of Hydrogenation

Ankur Chahal1 and Haider Abbas1

1Department of Physics, Manav Rachna University, Faridabad, Haryana, India.
Email: haiderabbasphy@gmail.com

Abstract. In the present work we report the effect of hydrogenation on small vanadium oxide (V₂O₄, V₂O₆ and V₄O₁₀) and chromium oxide (Cr₂O₄, Cr₂O₆ and Cr₄O₁₀) clusters, within the framework of density functional theory. Comparison between dehydrogenated and hydrogenated cluster suggests that hydrogenation of these clusters changes the HOMO-LUMO position and their gap. A considerable enhancement in dipole moment is also observed. It is found that hydrogenation enhances the occupancy of the metal in these clusters and therefore, the metallicity increases. The observed mechanism of charge transfer due to hydrogenation is in good agreement with the reported experimental and theoretical results.

1. Introduction:
Transition-metal oxides, carbides, nitrides, and silicides have been a subject of increasing scientific scrutiny due to their importance not only from a fundamental standpoint but also their use in industrial processes. Involvement of d orbitals in bonding make the chemistry of transition metal oxides diverse which leads to a range of technological applications e.g. vanadium and chromium oxide catalysts are widely used in chemical industries. A major impediment in creating nanoscale materials with useful electronic and magnetic properties have been the identification and production of classes of clusters. The size and composition dependence of structural, electronic, and magnetic properties of these oxide clusters may offer opportunities to tailor the chemical and physical properties for future applications. Despite the abundance of experimental and theoretical studies on transition metal oxide clusters, the study on hydrogenated clusters of vanadium and chromium oxides have not been reported yet. In this letter, we report the effect of hydrogenation on two important transition metal oxide clusters namely vanadium and chromium oxide.

2. Computational Details
All calculations have been performed with the GAMESS package [1]. The ground state geometries (shown in Fig.1) were obtained from optimization in C1 symmetry using the density functional theory (DFT/B3LYP) with the 6-31G (d, p) basis. All the clusters shown in the figure have singlet spin multiplicity and paired electrons.

3. Results and Discussion:
3.1. Vanadium oxide
Vanadium oxide is widely used as a component of oxidation catalysts [2-5] and optical materials [6]. Due to these diverse applications, numerous experimental investigations have been reported: using mass spectroscopy [7-11], matrix isolation [12], electron spin resonance spectroscopy [13], infrared photo dissociation [14], and anion photoelectron spectroscopy [15-18]. A number of theoretical studies have also been carried out to investigate the structure and the bonding characteristics of vanadium oxide [19-22]. Further, an interesting and intriguing aspect is the transition from metal to insulator and semiconductor to metal which depends upon the change of external parameters, such as temperature. Recent theoretical and experimental studies [23] show that the metal-insulator transition in nanoscale
beams of vanadium dioxide can be strongly modified by atomic hydrogen doping. To understand this phenomenon at the microscopic level, small clusters of hydrogenated vanadium oxide can be considered as a good model.

The optimized geometries of the hydrogenated vanadium oxide with DFT calculations are presented in Fig.1. In V2O4, HOMO is localized on both the vanadium atoms and LUMO consists of both the vanadium atoms as well as a little contribution of all the oxygen atoms. On hydrogenation, HOMO is localized on one vanadium atom while LUMO is located mainly on the other vanadium atom. In V2O6, HOMO is found to delocalize over all the six oxygen atoms with a larger contribution from the terminal oxoligands. The nearly same result is observed for the LUMO with slightly increased density on the ring's oxygen. When this cluster is hydrogenated, HOMO is found on both vanadium atoms as well as on the ring's oxygen atoms while LUMO is situated on both vanadium atoms and slightly on the terminal oxygen atoms. In the case of V4O10 cluster, HOMO is found on all oxygen atoms while LUMO is located on all vanadium atoms. In hydrogenated V4O10 cluster, the position of HOMO is completely reversed and found on all vanadium atoms. However, in LUMO a slight contribution from a few oxygen atoms is observed. HOMO-LUMO gap in all clusters, except V2O6, is found decreasing with the addition of hydrogen but an enhancement in dipole moment is observed.

Bond distance analysis in hydrogenated clusters shows a strong H-O bond with distance lying in the range 0.959 Å to 0.967 Å. The gross DFT Mulliken population analysis shows that charge transfer occurs from hydrogen to oxygen, thus the electronegativity of the latter reduces. Consequently, oxygen atoms draw less charge from the vanadium atoms in comparison to dehydrogenated vanadium oxide clusters. Therefore, hydrogenation increases the charge of metal atoms. In recent experimental and theoretical investigations, the same mechanism was presented in order to explain the metallicity in hydrogenated VO2 [23]. Thus, our results provide a good picture of the electronic structures of the hydrogenated vanadium oxide clusters.

3.2. Chromium oxide
Chromium oxide has a significant current interest, due to its broad applications in catalysts, spintronic, and magnetic recording tapes. In recent years, there have been a number of gas-phase experimental [24-29] and theoretical [30-35] studies on small chromium oxide clusters. The simple metal oxide clusters serve as model systems to obtain molecular-level information for surface and catalytic processes.

The optimized geometries of hydrogenated chromium oxide with DFT calculations are presented in Fig.1. In Cr2O4, HOMO is the same as that of V2O4, and LUMO consists mainly of both the chromium atoms with very little contribution from terminal oxygen atoms. On hydrogenation, HOMO is found mainly on one chromium atom with a little contribution from another chromium atom as well as both the ring's oxygen atoms. The position of LUMO is symmetrical to HOMO except for some more contribution from the other chromium atom. The position of HOMO in Cr2O6 is similar to the position of HOMO in V2O6 but LUMO is located mainly on both the chromium atoms and partially on all the six oxygen atoms. When Cr2O6 is hydrogenated, HOMO is found on both the chromium atoms with a little contribution from the terminal oxygen atoms, while LUMO is situated on both the chromium atoms as well as on the ring's oxygen atoms. In case of Cr4O10 cluster, HOMO is on all chromium atoms and LUMO is found to delocalize nearly overall oxygen and chromium atoms. On hydrogenation, HOMO is found on the three chromium atoms and partially on oxygen atoms, except two of them while all chromium atoms contribute to the LUMO. HOMO-LUMO gap in all the clusters, except for Cr2O4, is found decreasing with the addition of hydrogen but dipole moment
increases in general. The H-O bond distance in hydrogenated chromium oxide clusters are found lying in the range of 0.962 Å to 0.973 Å. The enhanced metallicity of the chromium oxide clusters after hydrogenation is found to be originated by the same mechanism of charge transfer as that of hydrogenated vanadium oxide clusters.

Fig. 1. Optimized geometries of the hydrogenated clusters.

4. Conclusion
In order to understand the charge transfer mechanism in hydrogenated metal oxide clusters, we have conducted a comparative study of small clusters of dehydrogenated and hydrogenated vanadium and chromium oxide. DFT/B3LYP calculations are performed to locate the ground state of these clusters. It is observed that hydrogenation increases the metallic character of these clusters by increasing the occupancy of the metal atoms. The current theoretical data support the performance of DFT to understand the charge transfer mechanism in vanadium and chromium oxide nanomaterials and are in good agreement with recent experimental and theoretical results. In general, hydrogenation of these clusters enhances the dipole moment but decreases the HOMO-LUMO gap.
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