Contents lists available at ScienceDirect

Surface Science



Interaction of silica-supported small silver clusters with molecular oxygen. A computational study

Aleksey M. Shor^a, Svetlana S. Laletina^a, Elena A. Ivanova Shor^{a,b}, Vladimir A. Nasluzov^a,

Valery I. Bukhtiyarov ^c, Notker Rösch ^{d,e,*}

^a Institute of Chemistry and Chemical Technology, Russian Academy of Sciences, 660036 Krasnoyarsk, Russian Federation

^b Siberian Federal University, 660041 Krasnoyarsk, Russian Federation

^c Boreskov Institute of Catalysis, Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation

^d Department Chemie and Catalysis Research Center, Technische Universität München, 85747 Garching, Germany

^e Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore

ARTICLE INFO

Article history: Received 2 April 2014 Accepted 18 August 2014 Available online 27 August 2014

Keywords: Silver clusters Oxygen activation Silica support Density functional calculations

1. Introduction

Ag clusters of nanometer and sub-nanometer size have attracted considerable attention due to their outstanding physico-chemical properties. Besides traditional application as a catalyst, e.g., for the epoxidation of ethylene [1] and the oxidation of methanol to formaldehyde [2], silver clusters have been used in various areas, such as photography [3], biological sensors [4], and optoelectronics [5]. The strong toxicity of silver particles for a wide range of microorganisms has extensively been exploited in many applications [6]. This large variety of applications has inspired extensive studies on small silver clusters and, in particular, their oxidation properties. The ability of silver to activate oxygen is the key factor determining its catalytic activity in oxidation reactions. On the other hand, oxidation can significantly decrease the strong fluorescence of Ag clusters [7,8].

The oxidation properties of silver clusters have extensively been studied experimentally and theoretically [9–25]. On silver particles with diameters above 5 nm, various atomic oxygen centers form the main active species [22–24]. However, on smaller particles, oxygen is preferentially stabilized in molecular form [25]. The main characteristics of O_2 adsorption complexes on silver clusters of less than a dozen atoms

ABSTRACT

The effect of nonbridging oxygen centers (NBOs) of a silica surface on the interaction of O_2 with small Ag_n clusters (n = 3,4) has been studied computationally, using a scalar relativistic density functional method and embedding in an elastic polarizable environment described by molecular mechanics. Two types of O_2 adsorption, molecular and dissociative, were analyzed. The electrostatic interaction of the metal clusters with the silica surface stabilizes adsorbed oxygen species, particularly those obtained via dissociative adsorption. O_2 dissociation seems feasible on both silver clusters, Ag_3 and Ag_4 , but relatively high activation barriers render O_2 dissociation less probable than O_2 desorption.

© 2014 Elsevier B.V. All rights reserved.

were shown to be quite sensitive to the size and charge of the metal cluster [11,15]. On anionic and neutral clusters, O_2 binding energies usually are larger than on cationic clusters [9,21]. These energies show odd–even alterations with the number of valence electrons of the silver clusters [9,18,21]. Binding is also accompanied by electron density transfer from the silver clusters to O_2 , resulting in the formation of doubly bonded superoxo-like O_2^- species [9,11,13,14,18].

For practical use and to avoid aggregation, metal clusters are immobilized [26,27]. Oxide surfaces as support offer various lowcoordinated sites, defects, and surface functional groups which affect the physical and chemical properties of the supported metal clusters [28], e.g., as observed for very small silver clusters supported on alumina, silica, or zeolites [29–32]. Specifically for supported Ag clusters, at conditions of catalysts preparation, the presence of O_2 can significantly affect the growth of metals and their size distribution, as may be rationalized by oxidized metal particles that are involved in the agglomeration process [26,33]. However, detailed investigations on the interaction of oxygen with small supported Ag clusters are still rare.

Here we describe theoretical studies on how a silica support affects the ability of small silver clusters to bind and activate an oxygen molecule. The clean dehydroxylated regular surface of crystalline silica or a silica film is rather inert toward the adsorption of small coinage metal clusters; binding energies were calculated not to exceed a few kJ·mol⁻¹ [34–37]. Surfaces of amorphous silica are hydroxylated under common experimental conditions [38], but calculations showed that hydroxyl groups also do not bind coinage metal atoms [39].





CrossMark

^{*} Corresponding author at: Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore. Tel.: +49 89 2891 3620; fax: +49 89 2891 3468.

E-mail address: roesch@mytum.de (N. Rösch).

However, point defects on a SiO₂ surface, e.g., nonbridging oxygen centers, \equiv Si–O• (NBO), or silicon dangling bonds, \equiv Si• (E'), can efficiently trap coinage metal atoms and clusters [34,35,37,40,41]. Both types of defects are present in abundance (~2 × 10⁻² per nm² [42]) on the surfaces of mechanically or/and thermochemically treated SiO₂ and define their chemical properties [42]. On a hydroxylated silica surface, OH groups can be transformed into NBO centers by radiolysis [43]. Metal clusters on an oxide surface typically are synthesized by reacting mononuclear organometallic complexes or metal carbonyl clusters with surface oxygen centers or hydroxyl groups where metal–oxygen bonds are formed [44].

Previously, we studied computationally the adsorption and the growth mechanism of Ag_n clusters (n = 1-4) on such surface defect centers of SiO₂ [34]. In the work reported here, we focus on how electronic properties of NBO adsorption sites of a SiO₂ surface affect the interaction of O₂ with small Ag_3 and Ag_4 clusters attached to these centers. As in our previous work [34], these complex systems of silica-supported metal clusters were modeled by applying a highly accurate quantum mechanics/molecular mechanics (QM/MM) hybrid approach where a QM partition of the system, described at the DFT level, is embedded in a flexible and polarizable lattice environment, described at the MM level [45].

2. Computational approach

The QM calculations were carried out with the all-electron scalar relativistic Douglas-Kroll-Hess variant [46–48] of the linear combination of Gaussian-type orbitals fitting-function density functional (LCGTO-FF-DF) method [49] as implemented in the parallel program ParaGauss [50,51]. All computational aspects were taken as in our previous work [34], in particular the gradient-corrected exchange-correlation functional as suggested by Becke and Perdew (BP) [52,53], the Gaussiantype basis sets to represent the one-electron wave functions and the auxiliary (fitting) function to represent the electron charge density when calculating the Hartree contribution of electron–electron interaction.

Energies and geometries of transition state (TS) structures were determined by a two-step strategy. First, the minimum energy pathway between two $O_2/Ag_n/SiO_2$ equilibrium structures, the molecular one and that formed after O_2 dissociation, was approximated by a set of 18 beads of the growing string method [54]. Then, the "spline and polynomial" approach [55] was used to estimate the TS along the calculated reaction path. This estimate was further refined with the dimer method [56] to locate a saddle point. For both searching procedures the utility package ParaTools [57,58] was applied. For structure optimizations, the convergence threshold of the largest component of the displacement gradients and the length of the update step were set to 10^{-6} a.u.

The binding energies of atomic and molecular oxygen to silver clusters, $E_b = E(Ag_n) + E(O_2) - E(O_2 / Ag_n)$, were approximately corrected for the basis set superposition error by invoking the counterpoise method [59] in single-point fashion at the equilibrium geometry of the adsorption complexes. This correction changed the binding energy at most by ~15 kJ·mol⁻¹.

The charge transfer between supported silver clusters and adsorbed O_2 species and the spin density distribution of the adsorption complexes were evaluated using Mulliken populations. This approach is justified as it assures consistency between the QM and MM partitions. In the QM/MM scheme used, the electrostatic potential of the MM region is represented by centers carrying potential-derived charges (PDCs). Mulliken and PDC procedures give quite similar charge values on atoms of silica support as well as adsorbed species, Ag and O_2 (see Supplementary data).

The "embedded cluster" calculations were carried out with the hybrid QM/MM scheme covEPE [45], a variant of the elastic polarizable environment [60] for such covalent materials as silicates and zeolites. Relying on the successful examples of our previous study [34], silicate

surfaces were modeled by the idealized structure of the walls that form the hexagonal channels of MCM-41 mesoporous silicalite [61]. The QM partition was represented by a model cluster of 7T centers with an extended border region to provide adequate boundary conditions [45b]. The atoms of this QM partition, located at the "top" layer of the two-layer slab, form a complete six-member ring which comprises all crystallographic positions up to the third coordination shell of an NBO center (Fig. 1). In this way, one is able to avoid interaction artifacts of adsorbed cluster species with centers of the border region of the QM partition.

In the following, we designate adsorption complexes of an Ag trimer or tetramer attached to an NBO defect of SiO₂ surface as Ag_n/O_N, while O₂/Ag_n/O_N generically refers to any type of O₂ (or two O atoms) adsorbed complexes on supported silver clusters. Terminal and bridging molecular and dissociative complexes of O₂ adsorbed on silver clusters are designated as Ag_nO₂, Ag_nOO and OAg_nO, respectively. As the interaction of O₂ with Ag₄ is more diverse and can be accompanied by a 2D \rightarrow 3D transformation of the silver cluster, four additional upper indexes were used to indicate the structure of the oxygen–metal moiety. We discriminate O₂ attached to a metal center at an obtuse (O) or an acute (A) angle of the rhombus, or at a rhombohedral-like (R) and tetrahedral-like (T) configuration of the Ag tetramer.

3. Results and discussion

3.1. Bare supported Ag clusters

Our current and previous scalar relativistic QM calculations [34,62] showed that in its ground-state, a free Ag₃ cluster has a doublet electronic configuration and the structure of an isosceles triangle (C_{2v} symmetry) with an angle of 70° between the two Ag – Ag bonds, 264 pm, which make up the short edges of the triangle. A free Ag₄ cluster has a singlet electronic ground-state and a planar rhombus structure of D_{2h} symmetry which edges of 275 pm and a short diagonal of 261 pm.

To provide a convenient reference, we briefly recall computational results obtained for the interaction of Ag_n clusters (n = 3, 4) with NBO centers of the SiO₂ support. Note that in the present model, the QM partition of the SiO₂ support (Fig. 1) is somewhat smaller than that used previously [34]; yet the present results (Table 1, Fig. 2) are essentially the same. Silver clusters interacting with the unpaired electron of the NBO center donate electron density to the defect, thus forming polar bonds Ag1–O_N of 211 pm (Fig. 2). The amounts of charge donated are similar for the complexes Ag_n/O_N studied, 0.46 e (n = 3) and 0.42 e (n = 4), Table 1. Both metal clusters interact in addition to bridging oxygen centers O_S of SiO₂ surface, as demonstrated by relatively short Ag–O_S distances, 246 pm (Ag₃) and 266 pm (Ag₄); see Fig. 2 and Table 1. The complex Ag_3/O_N features a singlet ground state while the complex Ag_4/O_N has a doublet ground state with 96% of the total spin density localized on the metal moiety (Table 1). Thus, the spin states



Fig. 1. Embedded cluster model describing a nonbridging oxygen defect O_N (NBO, \equiv Si-O•) at a SiO₂ surface. Atomic centers treated at the full QM level are rendered as balls (Si, O). Oxygen centers O* at the border of the QM region and silicon centers Sipp* at the border of the MM region are rendered as sticks only; they are described by specially designed pseudopotentials; see Ref.45b.

Download English Version:

https://daneshyari.com/en/article/5422049

Download Persian Version:

https://daneshyari.com/article/5422049

Daneshyari.com