



Interaction of NO with Au nanoparticles supported on (100) terraces and topological defects of MgO

Silvia A. Fuente^{a,b}, Ricardo M. Ferullo^{a,b,*}, Nicolás F. Domancich^a, Norberto J. Castellani^a

^a Grupo de Materiales y Sistemas Catalíticos, Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

^b Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:

Received 16 July 2010

Accepted 1 October 2010

Available online 8 October 2010

Keywords:

Nitric oxide

Au/MgO

Model catalysts

NO adsorption

DFT

Cluster model

ABSTRACT

The adsorption of nitric oxide (NO) on Au_n (n = 1–3) particles deposited on anionic (O²⁻) sites of MgO has been studied using the DFT (Density Functional Theory) approach. The regular O²⁻ sites of MgO(100) and the sites in edge and corner topological defects with high symmetry of MgO were considered. The adhesion energy of Au_n to MgO is larger for Au₂ and Au₃ due to higher polarization effects. On the other hand, the interaction strength of NO with supported Au_n particles depends mainly on the electronic configuration (open or closed shell) of the particle; the Au particles with odd number of atoms show larger NO binding energies. A comparison was performed with the reactivity of free Au_n particles. From this, it is possible to conclude that the support enhances the NO–Au_n bonding strength for the monomer, weakens this interaction in the case of the dimer, and does not have an effect in the trimers. Besides, the NO–Au_n bonding is essentially insensitive to the coordination of the anionic site where the Au_n particle is linked. A large red-shift of the N–O stretching frequency was obtained, particularly for the Au particles with odd number of atoms, due to a negative charge transfer from Au to NO.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Supported Au nanoparticles present an extraordinary activity to catalyze different reactions at low operating temperatures, such as the oxidation of CO, the partial oxidation of hydrocarbons and the reduction of NO_x [1]. TiO₂ have been used as the typical support for Au particles, but other oxides like MgO, SiO₂ and Al₂O₃ were also considered [1–4].

Nitrogen oxides are air-pollutants produced by combustion engines. Therefore, the necessity to develop efficient catalytic converters for the post-processing of the exhaust gases has stimulated extensive investigations of the adsorption and decomposition of NO_x molecules on the surfaces of metallic catalysts (for reviews see, for example, Refs. [5,6]).

In particular, the catalytic reduction of nitrogen oxides towards N₂ and O₂ is one of the most important reactions that takes place in the three-way catalysts [7,8]. A highly practical and suitable method to remove NO_x seems to be the catalytic reduction using compounds such as CO, hydrogen and hydrocarbons contained in exhaust gases. Ueda and Haruta [4] found that Au catalysts supported in a variety of metallic oxides show a great catalytic activity in the reduction of NO with hydrocarbons such as propene, propane, ethene and ethane.

As one of the key factors to understand certain catalytic mechanisms, the adsorption of NO molecules on unsupported Au particles has been experimentally studied. For example, Citra et al. [9] analyzed the reaction of Au clusters with NO at very low temperatures producing neutral complexes like AuNO and Au(NO)₂ as principal products. On the other hand, Ding et al. [10] performed theoretical studies for the adsorption of NO on Au clusters with 1 to 6 atoms in neutral as well as in positively and negatively charged states. They found that all these Au aggregates are able to adsorb NO with greater adsorption energies for cationic clusters.

MgO is usually used as a model support due to its simple crystal structure and because it presents different types of defects which are relatively easy to be included in the simulations. The deposition of Au aggregates on the MgO(100) surface has been deeply studied using the DFT approach [11–19]. Most of the theoretical works dealing with the adsorptive and catalytic properties of Au/MgO have used CO as probe molecule. Basic aspects, such as the CO-induced modification of the Au–MgO interface [20], the vibrational properties of CO adsorbed on Au₁/MgO [21,22], and the paramagnetic behavior of CO/Au/MgO [23] were investigated. Besides, it was observed that three-dimensional and two-dimensional nanoclusters deposited on MgO [24–26] and MgO/Mo [27], respectively, show a remarkable activity for CO oxidation.

Among the very small Au particles, Au₁ and Au₃ present the highest NO adsorption energies [10]. Therefore, the study of the NO adsorption capability of these tiny particles in a supported state could be of great interest. In a previous work [28] we have presented a

* Corresponding author. Grupo de Materiales y Sistemas Catalíticos, Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina. Tel.: +54 291 4595141; fax: +54 291 4595142.

E-mail address: caferull@criba.edu.ar (R.M. Ferullo).

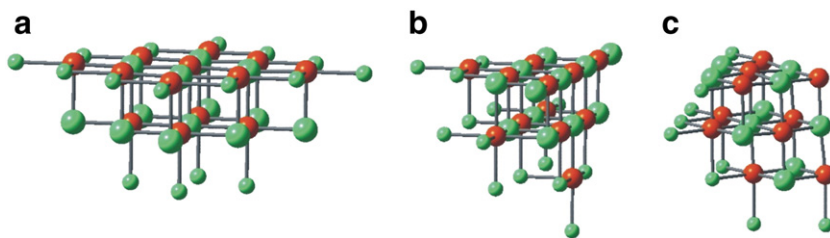


Fig. 1. a) $\text{Mg}_{13}\text{O}_{13}(\text{Mg-ECP})_{16}$ cluster used for modeling the $\text{MgO}(100)$ surface. b) $\text{Mg}_{12}\text{O}_{12}(\text{Mg-ECP})_{14}$ cluster used for modeling the edge topological defect of MgO due to the intersection of two $[100]$ and $[010]$ oriented planes. c) $\text{Mg}_{10}\text{O}_{10}(\text{Mg-ECP})_9$ cluster used for modeling the corner topological defect of MgO due to the intersection of three $[100]$, $[010]$ and $[001]$ oriented planes. Red spheres: O. Green spheres: Mg. Small green spheres: Mg-ECPs. Point charges are not shown.

molecular orbital study on the NO interaction with Au monomers and dimers anchored on the $\text{MgO}(100)$ surface. We found that when the Au atom is adsorbed on an anionic site it essentially retains its spin and for this reason it can couple efficiently with NO (a radical); conversely, when the Au atom is deposited on an O-vacancy the Au-NO bond is relatively weak because of the partial spin delocalization toward the cavity. In the present paper, we extend the study by considering O^{2-} sites at edge and corner topological defects of MgO and also including the gold trimer.

This work is divided in two sections: 1) adhesion of Au particles (1–3 atoms) in a O^{2-} site of the $\text{MgO}(100)$ surface (terrace site) as well as on O^{2-} sites at topological defects (edge and corner sites); and 2) adsorption of NO on Au particles supported on the same sites of MgO .

2. Computational details

Density Functional Theory (DFT) molecular orbital calculations were performed using the gradient corrected Becke's three parameters hybrid exchange functional in combination with the correlation functional of Lee, Yang and Parr (B3LYP) [29]. All the calculations have been carried out using the Gaussian-03 program package [30]. The terrace site at MgO

(100) surface was represented by a $\text{Mg}_{13}\text{O}_{13}$ cluster consisting of two layers (first layer: Mg_4O_9 ; second layer: Mg_9O_4). To take into account the Madelung field due to the rest of the extended surface, the cluster was embedded in an array of ± 2 point charges. Besides, the positive point charges at the interface between the cluster region and the region of point charges were replaced by effective core potentials (ECP) corresponding to the Mg^{2+} cation to account for its finite size and to avoid spurious charge polarization. The corresponding $\text{Mg}_{13}\text{O}_{13}(\text{Mg-ECP})_{16}$ cluster is represented in Fig. 1a. This embedding technique was used previously for the study of both bulk and surface properties giving results which are in good agreement with those obtained by periodic calculations [21,31–33]. For the topological defects, a similar modeling was used resulting in the following clusters: $\text{Mg}_{12}\text{O}_{12}(\text{Mg-ECP})_{14}$ (edge sites) and $\text{Mg}_{10}\text{O}_{10}(\text{Mg-ECP})_9$ (corner sites) (Fig. 1b and c, respectively).

While the atomic orbitals of the oxygen ion acting as the adsorption site and its nearest four O neighbors (three for corner site) were described by the 6–31+G(d) basis set, those of the exposed Mg ions (four for terrace and edge sites, three for corner site) directly bonded with the O adsorption site were expressed using the 6–31G(d) basis set; for the rest of the Mg and O ions of the cluster, the 6–31G basis set was used. The 6–31+G(d) basis set was employed for the

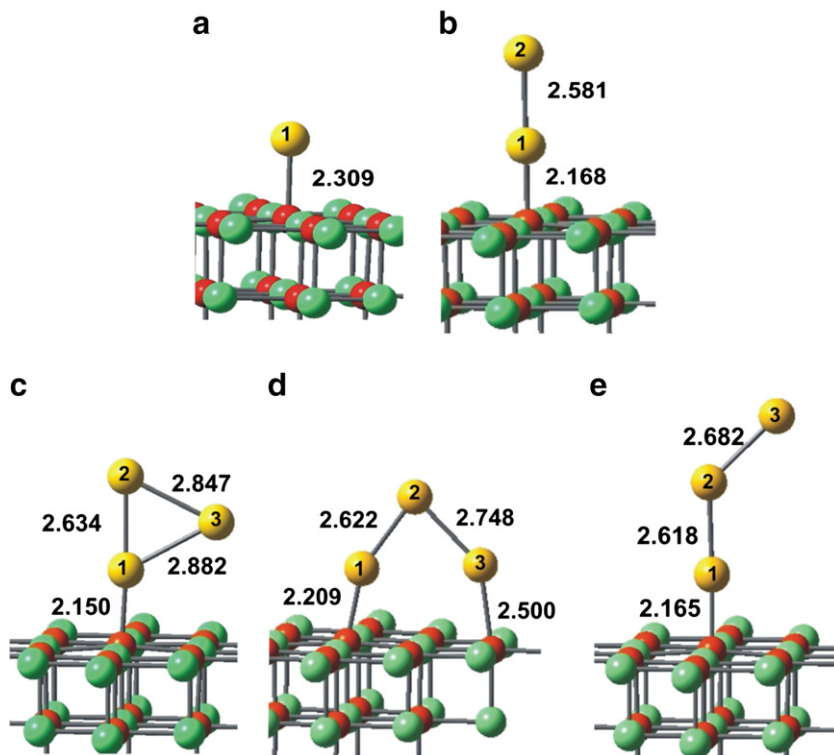


Fig. 2. Schematic representations of Au_n ($n = 1-3$) clusters deposited on a O^{2-} site of the $\text{MgO}(100)$ surface. a) Monomer; b) dimer; and c)–e) trimers. Red spheres: O. Green spheres: Mg (including Mg-ECPs). Yellow spheres: Au.

Download English Version:

<https://daneshyari.com/en/article/5423640>

Download Persian Version:

<https://daneshyari.com/article/5423640>

[Daneshyari.com](https://daneshyari.com)