

# Adsorption of NO on Au atoms and dimers supported on MgO(100): DFT studies

Silvia A. Fuente<sup>a</sup>, Patricia G. Belelli<sup>a</sup>, Ricardo M. Ferullo<sup>a,b,\*</sup>, Norberto J. Castellani<sup>a</sup>

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

<sup>b</sup> Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

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## ABSTRACT

The adsorption of NO on single gold atoms and Au<sub>2</sub> dimers deposited on regular O<sup>2-</sup> sites and neutral oxygen vacancies (F<sub>s</sub> sites) of the MgO(100) surface have been studied by means of DFT calculations. For Au<sub>1</sub>/MgO the adsorption of NO is stronger when the Au atom is supported on an anionic site than when it is on a F<sub>s</sub> site, with adsorption binding energies of 1.1 and 0.5 eV, respectively. In the first case the spin density is mainly concentrated on the metal atom and protruding from the surface. In such a way, an active site against radicals such as NO is generated. On the F<sub>s</sub> site, the presence of the vacancy delocalizes the spin into the substrate, weakening its coupling with NO. For Au<sub>2</sub>/MgO, as this system has a closed-shell configuration, the NO molecules bonds weakly with Au<sub>2</sub>. Regarding the N–O stretching frequencies, a very strong shift of ~340–400 cm<sup>-1</sup> to lower frequencies is observed for Au<sub>1</sub>/MgO in comparison with free NO.

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## 1. Introduction

In heterogeneous catalysis the reactive properties of supported metal particles depend on the cluster size and on the specific site of the support where the particle is anchored. When an oxide is used as support, the metal aggregates interact preferentially with surface oxygen vacancies [1,2]. In particular, on MgO these vacancies comprise several different types of surface defects such as F<sub>s</sub>, F<sub>s</sub><sup>+</sup> and F<sub>s</sub><sup>2+</sup>, depending on removal of a neutral O atom, an O<sup>-</sup> anion and an O<sup>2-</sup> anion, respectively. The interaction of transition metal atoms with both regular and defective MgO was investigated using quantum chemical approaches. It was observed that the adhesion is stronger on F<sub>s</sub> sites than on regular anionic sites [3].

The activity and selectivity of supported Au aggregates was intensively studied during the last years. They show an extraordinary activity to catalyze different reactions at low operating temperatures, such as the oxidation of CO, the selective oxidation of propene and the reduction of NO<sub>x</sub> [4]. In experiments, TiO<sub>2</sub> is used as the typical support, but other oxides like MgO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were also considered [5–7].

Recently, experiments were performed in order to clarify the importance of F<sub>s</sub> sites of MgO in the adhesion of gold. It was found a correlation between the catalytic activity of the supported Au

particles and the concentration of F<sub>s</sub> centers on MgO. Thus, these surface defects play a direct role in the activation of supported Au catalysts [1]. In another recent work, the electron paramagnetic resonance (EPR) and scanning tunnelling microscopy (STM) techniques were combined to verify the existence of surface defects as well as the nucleation of Au onto these defects [2]. Moreover, by using infrared (IR) spectroscopy of adsorbed CO, two bands were observed: one at 2120 cm<sup>-1</sup> and a broad one around 2070 cm<sup>-1</sup>. While the former was assigned to CO adsorbed on small neutral Au clusters deposited on regular anionic sites, the broad band was assigned to CO on negatively charged Au clusters. These charged particles are predicted to be produced by the adsorption of Au on defect sites of MgO. The larger red-shift is attributed to a greater π-backdonation from the negatively charged Au in comparison with that of neutral Au.

The deposition of Au atoms and clusters on regular five-coordinated O<sup>2-</sup> sites and on F<sub>s</sub> centers of the MgO(100) surface was recently studied from periodic DFT calculations [8–13]. It was observed that the presence of the vacancy enhances the metal–oxide interaction. Thus, these centers are essential to trap the diffusing Au atoms or clusters [9].

In the past, NO was used as a probe molecule to study the metal surface reactivity [14]. Besides, the bonding of NO to transition metal surfaces is of interest in relation to the catalytic reduction for pollution control. At ultrahigh vacuum (UHV) conditions, NO adsorbs weakly on Au(111) [15] but it decomposes on Au(310) giving N<sub>2</sub>O and atomic O on this stepped surface [16]. Gold supported on several metal oxides shows good catalytic performance for the

\* Corresponding author. Address: 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](mailto:caferull@criba.edu.ar) (R.M. Ferullo).

reduction of nitric oxide by hydrocarbons [7]. In these cases, the addition of CO and H<sub>2</sub> to the reactant gas improves the conversion of NO to N<sub>2</sub>. The NO + CO reaction was also studied for Au supported on MgO, TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [5]. These systems catalyze the reaction above 573 K yielding surface NCO.

The interaction of NO with isolated Au atoms was object of recent studies. Laser-ablated Au atoms interact with NO yielding neutral nitrosyl complexes AuNO and Au(NO)<sub>2</sub> [17]. For AuNO, the N–O and Au–N stretching modes are observed at about 1700 and 520 cm<sup>-1</sup>, respectively. On the other hand, the reaction of NO with free neutral Au<sub>x</sub> clusters (x = 1–6) was studied from DFT [18]. The NO + Au<sub>x</sub> reaction is exothermic, releasing 0.2–0.8 eV. The bond between NO and Au is accompanied by an electron transfer from the metal cluster to the NO molecule.

The first objective of this work is to analyze the deposition of one Au atom and the Au<sub>2</sub> dimer on anionic regular sites and on F<sub>s</sub> centers of the MgO(100) surface by employing an embedded cluster approach. The results are compared with recent periodic calculations [8–13]. While the Au–MgO interface was thoroughly studied, the adsorption properties of supported Au particles received relatively less attention. Specifically, in this work we are interested to study the adsorption of NO on supported gold which constitutes a valuable reference for other researchers. The corresponding results are compared with the reaction of NO with free Au particles in order to study the effect of the support on the adsorption capability of supported Au.

## 2. Computational details

Density functional theory (DFT) molecular orbital calculations were carried out using the gradient corrected Becke's three parameters hybrid exchange functional in combination with the correlation functional of Lee, Yang and Parr (B3LYP) [19]. This method was widely used in the past to study adsorption processes yielding reliable results both on oxides and metal clusters.

The MgO(100) surface was represented by clusters of 26 atoms, Mg<sub>13</sub>O<sub>13</sub>, consisting of two layers (first layer: Mg<sub>4</sub>O<sub>9</sub>; second layer: Mg<sub>9</sub>O<sub>4</sub>). 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. Moreover, the positive point charges at the interface were replaced by effective core potentials (ECP) corresponding to Mg<sup>2+</sup> to account for the finite size of the cations and to avoid spurious charge polarization. The Mg<sub>13</sub>O<sub>13</sub> cluster plus the 16 Mg–ECP's is represented in Fig. 1. This methodology was widely used by the group of Pacchioni and other authors [20], giving results which are in good agreement with those obtained by periodic calculations. For example, if the embedded cluster model and the slab

approach are compared, the energy for creating an oxygen vacancy is only 1% different [21,22].

The 6-31+G(d) basis set was employed for the atoms of the NO molecule and the O atoms in the first layer of Mg<sub>13</sub>O<sub>13</sub> cluster, except the terminal ones. The atomic orbitals of the four Mg atoms in the first layer were described by the 6-31G(d) basis set, while those of the terminal O atoms and those of Mg and O atoms at the second layer, by the 6-31G basis set. For Au, the LANL2DZ basis set was used, which describes the 60 core electrons with a pseudopotential and the 19 valence 5s<sup>2</sup>5p<sup>6</sup>5d<sup>10</sup>6s<sup>1</sup> electrons with a [5s,6p,4d/3s,3p,2d] basis set [23,24]. Previously, the suitability of this basis set for the Au–NO interaction was examined by considering the isolated Au<sub>1</sub>NO molecule. For that purpose, the results of calculation using the LANL2DZ basis set was compared with that obtained with a larger one such as the SDD (Stuttgart–Dresden) [25]. The last describes the 19 valence electrons with a [8s,7p,6d/6s,5p,3d] basis set. The resultant distances, angles and frequencies values are very similar using both descriptions.

During the geometrical optimization procedure, the coordinates of atoms belonging to the adsorbed NO molecule and the metal particle, and those of the five central atoms in the first layer of Mg<sub>13</sub>O<sub>13</sub> cluster (the central O and its four Mg atoms directly bonded to it) were fully optimized without imposing geometric constrains. The geometries studied in this work were selected taking into account previous theoretical results [9–13]. With respect to the gold monomer deposited on the regular surface, only the adsorption on the anionic site was studied because it is well known that this is the preferred adsorption site for most transition metal atoms [26]. For the Au dimers on the perfect surface, the on-top geometry on one anionic site was considered following the results obtained in Ref. [12]. Regarding the defective surface several starting orientations for Au<sub>2</sub> were taken into account.

A neutral O vacancy was represented by Mg<sub>13</sub>O<sub>12</sub> cluster, with the vacancy localized in the center of the first layer. In this case, the geometrical optimization included the four central Mg atoms of first layer.

We define the binding energy of the Au<sub>x</sub> particle on MgO as  $E_B(\text{Au}_x) = -[E(\text{Au}_x/\text{MgO, site}) - E(\text{Au}_x) - E(\text{MgO, site})]$ , with x = 1, 2, and site = O<sup>2-</sup> or F<sub>s</sub>. Besides, we define the binding energy of NO molecule on Au<sub>x</sub>/MgO as  $E_B(\text{NO}) = -[E(\text{NO}/\text{Au}_x/\text{MgO, site}) - E(\text{Au}_x/\text{MgO, site}) - E(\text{NO})]$ . In both cases, positive values correspond to exothermic processes. The reactions energies were corrected by considering the basis set superposition error (BSSE), calculated according to the counter-poise correction [27]. The frequency values were scaled according to the factor of 0.9465, calculated as the ratio between the empirical and the calculated frequency values of free NO (1876/1982).

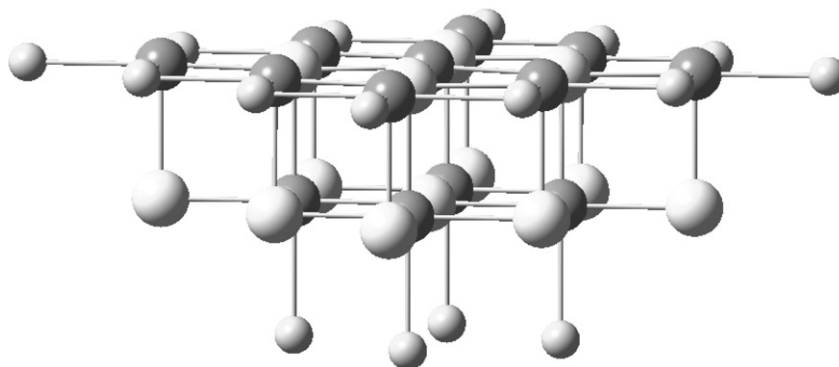


Fig. 1. Mg<sub>13</sub>O<sub>13</sub> cluster plus the 16 Mg–ECP used for modeling the MgO(100) surface. Dark grey spheres: O. Light grey spheres: Mg. Small spheres represent the Mg–ECP's. Point charges are not shown.

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