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A reinvestigation of the CO vibration frequency as a probe to determine the species of Au in the Au/MOR catalyst

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ABSTRACT

ONIOM calculations have been carried out to determine geometries, adsorption energies and vibrational frequencies of CO on Au_2 and Au_4-exchanged mordenite catalysts (Au_2/MOR and Au_4/MOR) using DFT with the B3LYP and ωB97X-D functionals. We considered structures with two Al atoms, MOR(TT), with at least one of them at the preferential site T4. To investigate the CO adsorption on Au_2/MOR(TT) we examined three different situations: the adsorption of one single CO molecule bridged to two Au atoms (case I), one CO molecule adsorbed on a single Au atom (case II), and two molecules of CO absorbed on two Au atoms, one CO per Au atom (case III). From all the previous theoretically and experimentally proposed species of Au inside the MOR channels, including the ones considered in this work, only the μ_2-CO-Au_2/MOR configuration, with one CO adsorbed in a bridge form on two Au atoms, exhibits ν(CO) frequencies within the experimental range of 1949–2120 cm^{-1} (low frequencies). Increasing the size of the Au particles shifts the ν(CO) to higher frequencies. The values of ΔH_{ads} decrease when the number of adsorbed CO molecules increases, similarly to what is experimentally observed when CO is adsorbed on Au/TiO_2 and Au/Al_2O_3. Charge analysis shows that the Au_2 in the Au_2/MOR and the Au_4 cluster in the Au_4/MOR are cationic. Based on the present results we conclude that the use of ν(CO) as a probe to determine the Au species in the channels of MOR can only clearly identify $Au_2^{\delta+}$ species inasmuch as the μ_2-CO-Au_2/MOR configuration is the only one among several others to exhibit ν(CO) frequencies within the experimental low frequency region.

1. Introduction

Au has attracted attention in heterogeneous catalysis as well as in colloidal chemistry and nanoparticles systems. The discovery of the unique activity of gold nanoparticles in CO oxidation at low temperatures [1,2] has stimulated research on gold catalysts. Additionally, well-dispersed Au^+ species inside NaY and ZSM-5 zeolites exhibit catalytic activity in the NO reduction and CO oxidation [3,4].

Zeolites are interesting host materials due to their ability to disperse transition metals species inside their pores and the possibility of controlling the particle size [5]. The Au^+ in Au/KLTL, and Au^+-Au^0 species in Au/ZSM-5 and Au/MOR are considered responsible for the water-gas shift (WGS) reaction at low temperature [6,7].

Heterogeneous catalysis is a very complex process and involves several steps. In order to design a more efficient catalyst one has to understand how the specific process under study takes place, i.e., its mechanism. Once the mechanism is known it would be possible to envisage changes to make the catalyst more efficient for that specific process. The interplay between experiment and theory has proven to be a very efficient way of determining the mechanism of complex catalytic processes. On the other hand, any mechanistic study must start with a good characterization of the catalyst active site(s), which is exactly the ***focus*** of the present work.

The characterization of Au species inside zeolites is a challenging work. The results of several experimental works conducted to characterize the Au species dispersed inside ZSM-5 [3,6,8], Y [6,9,10] and MOR [6,11,12] zeolites suggested the presence of different Au clusters, varying in size and charge. For the specific

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case of MOR experiments using different techniques suggest the presence of Au^0, Au^+, $Au^{\delta+}$, Au^{3+}, $Au_n{}^{\delta+}$, and Au_n ($n \leq 8$). Simakov et al. [11], using CO adsorption and Fourier transform IR (FTIR) and UV–vis diffuse reflectance spectroscopy (DRS), proposed that the Au could be present in MOR as Au^+, $Au^{\delta+}$, Au^{3+} and Au^0. Tuzovskaya et al. [12], used UV–vis DRS, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and temperature programmed reduction (TPR) with hydrogen to characterize gold species in MOR and concluded that Au^{3+} and charged clusters ($Au_n{}^{\delta+}$ $n \leq 8$) could be found inside the zeolite channels. This scenario clearly indicates the uncertainties concerning the species present inside the pores.

To date, the CO vibrational frequency has been the main source of information to characterize Au species present in CO-Au/zeolites, but attempts at assigning these bands have been made in analogy to what is observed for CO adsorbed on metal Au surfaces as well as to CO coordinated to neutral and charged Au clusters. Nevertheless, the Au surface states can be quite different from the clusters ones and the geometry of the free clusters might differ substantially from the ones inside the zeolite.

For the CO-Au/MOR catalyst, the experimental results indicate a region of low frequencies, 1949–2120 cm^{-1}, and one of high frequencies, 2119–2210 cm^{-1}.The low frequencies, 1949–2120 cm^{-1}, have been attributed to CO adsorbed on Au^0 and metallic cluster of Au [11], in analogy to what is observed for CO adsorbed on a Au surface, as well as to CO coordinated to negatively charged Au clusters [13]. A broad band centred in 1949 cm^{-1} was also observed by Mohamed et al. [14] for CO adsorbed on Au/dealuminated H-MOR in the presence of residual water molecules. The authors attributed this band to a strongly held bridging carbonyl-Au species. In spite of these studies, the nature of the Au species responsible for the low frequencies remains unknown. The high frequency bands, 2119–2210 cm^{-1}, have been associated to CO adsorbed on positively charged Au species (Au^+, $Au^{\delta+}$ and Au^{3+}) [11,15]. However, as pointed out by Simakov et al. [11] the fact that bands of CO adsorbed on Brønstead and Lewis acid and base sites also occur in this region makes an exact interpretation of these bands more difficult.

Despite the technological importance of the Au-exchanged zeolites, a very small number of theoretical papers has been dedicated to the characterization of the Au species related to the distinct ν(CO) in CO-Au/zeolite systems. Deka et al. [16–18], using a nine tetrahedral faujasite (FAU) model with a Si/Al ratio (SAR) = 3 [16,17], and six tetrahedral FAU, with no Al atoms, and SAR = 1 and 5 [18], studied the CO-Au^{+p}/FAU system (p = 0, 1, 3). From these studies, the authors concluded that the ν(CO) shows a blue shift on going to higher oxidation states. In our previous work [15] we studied the adsorption of one to three CO molecules on Au^+/MOR and $Au_3{}^+$/MOR structures, using a ten tetrahedral model of the zeolite with one Al atom and the ONIOM methodology. Even though the calculated frequencies are in agreement with the experimental results for high frequencies, none of the ν(CO) obtained match with the experimental low frequencies. The fact that the previous calculations were not able to explain the nature of the lower frequencies is an indication that perhaps not all the species that might be present inside the MOR channels have been considered. The proper characterization of the Au species is of utmost importance to understand the nature of the active catalytic sites and, in particular, how they interact with CO.

The characterization of zeolite properties by molecular modelling requires the use of large clusters in order to take into account the confinement effects [19]. Notwithstanding the relative success of cluster calculations [20] in studies of catalysis by zeolites, they involve high computational costs. Alternatively, hybrid methods (QM/MM), which combine quantum and classical mechanics, can be used to model large systems at moderate computational costs. ONIOM [21] is a type of hybrid method that has been used successfully in studies of NH_3 and H_2O adsorption on acid chabatize [22], and amines adsorption on Li-MOR and Na-MOR [23]. Recently, using the ONIOM approach, we studied the effect of SAR on the NH_3 adsorption in MOR [24].

In this work a series of Au species is investigated in order to provide assignments of the vibrational frequencies of CO adsorbed on the Au_2/MOR and Au_4/MOR zeolites and to identify the possible Au species responsible for the bands in the lower frequency region. In addition, we report the adsorption energies, enthalpies and Gibbs free energy for all the species considered. To the best of our knowledge there are neither experimental nor theoretical results reported for these systems and this data can be extremely useful for interpreting calorimetric and TPD experimental studies in the future.

2. Computational details and models

The MOR unit cell contains four different tetrahedron (T) sites, namely, T1, T2, T3, and T4. A model of MOR which contains the four tetrahedron sites with 1011 atoms (Fig. S1 of the Supplementary material) was employed to perform the two-layer ONIOM calculations. The valence of the most external Si atoms was saturated with H atoms. This model contains 41 tetrahedron centres (41T) in the high-level and 223 tetrahedron centres (223T) in the low-level regions, respectively. High-level implies that the atoms therein are being treated at a high quantum-mechanical level of theory as opposed to the low-level ones, treated by classical mechanics or at a lower quantum-mechanical level. For the high-level region, the functionals B3LYP and ωB97X-D [25] were used, while the low-level atoms were treated by the Universal Force Field (UFF). During the optimization procedure, the atoms belonging to the low-level regions were fixed to maintain the MOR structure. All calculations were done in the Gaussian-03/09 program (G03, version RevD.02; and G09, version RevC.01) [26].

The Hay and Wadt pseudopotential [27] with its corresponding basis sets was used for H, Si, Al, and O atoms belonging to MOR. The re-adjusted small-core relativistic compact effective potential ACEP-121 [15] with its corresponding basis set was employed for Au. For CO the full electron 6–31 + G basis with two polarization functions $\zeta_d(C) = 0.335884$ and $\zeta_d(C) = 0.535903$ was used [28]. Frequencies calculations at 1 atm and 298.15 K were performed to show that the structures are minima on the potential energy surface. The zero-point vibration energy (ZPVE), the internal thermal energy and the basis set superposition error (BSSE) were determined from the final ONIOM high-level optimized structures, in order to correct the values of the electronic energy, E, enthalpy, H, and Gibss free energy, G. Additionally, the Grimme et al. [29] dispersion (D3) correction was included in the high-level energies from the ONIOM calculations at the B3LYP level.

The Brønsted sites in the acidic MOR structure (H-MOR) are created by replacing a Si atom by an Al atom at the four different T sites and adding a proton to one of the crystallographically distinct O atoms to compensate the negative charge. A cationic Au (Au^+) replaces the H acidic in the H-MOR. Even though the MOR synthesis process could affect the Al distribution, various works have shown that the acid Brønsted site is located preferentially at T4 [30–32] followed by T2 > T1 > T3 [31,32]. We considered two types of structures with two Al atoms MOR(TT), with at least one of them at the preferential T4 site: MOR[Al(T2)Al(T4)], and MOR[Al(T4)Al(T4′)]. Moreover, the relative position of the Al atoms was varied to produce the four structures shown in Fig. 1a–d. These structures are labelled as: near-MOR(T2T4), far-MOR(T2T4), near-MOR(T4T4′), and far-MOR(T4T4′), where near- and far- refers to the distance between the two Al atoms in the MOR cluster model.