A density functional study of CO adsorption on three- and five-coordinate Al in oxide systems

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Received 28 March 1996; accepted 14 May 1996

Conventional cluster models of strong and medium strength Lewis acid sites in alumina and zeolites, three-coordinate [Al(OH)3] and five-coordinate [Al(OH)3(OH2)2] respectively, are studied with the help of a density functional method. A constraint space orbital variation analysis reveals that the charge transfer from probe CO molecules adsorbed on cationic Al centre and the CO polarization comprise essential contributions to the adsorption energy \( D_a \). An analysis of the adsorption-induced C-O frequency shift \( \Delta \omega (C-O) \) is also provided. Structural modifications of the Lewis acid sites are considered with respect to their influence on \( D_a \) and \( \Delta \omega (C-O) \). A comparison of the measured and calculated C-O frequency shifts supports a hypothesis on the existence of Lewis acid sites in oxides in the form of four-coordinate Al cations.

Keywords: coordinatively unsaturated Al ions; Lewis acidity; CO probe; adsorption-induced frequency shifts; cluster models; density functional calculations

1. Introduction

When considering the Lewis acidic strength of aluminas (Al2O3) and of zeolites it is common to differentiate between strong and medium power Lewis acid sites (LAS). These two kinds of LAS can be identified using vibrational spectra of adsorption complexes with probe molecules, e.g. with CO [1-4]. Based on the spinel structure of \( \gamma\)-Al2O3, the strong LAS are assigned to three-coordinate Al ions, Al3c; precursors are Al ions located at the tetrahedral spinel positions. The LAS of medium strength are ascribed to five-coordinate Al ions, Al5c, with the prototype Al species placed in the octahedral spinel sites. This assignment was supported by quantum chemical calculations [5-8]. The theoretical quantification of the relative strength of these LAS was based either on the analysis of their electronic structure [5,7] or on the computed interaction energy with adsorbates [5-7]. Less efforts have been focused so far on rationalizing the difference in the strength of the Al3c and Al5c LAS with the help of calculated vibrational parameters of the adsorbed probe molecules. In this way a direct comparison to the measured spectroscopic data is possible. For example, a comparative analysis of the experimental and calculated adsorption-induced shifts of the C-N stretching vibrational band of acetonitrile interacting with Al3c and Al5c centres [8] allowed to delineate dissimilarities between the LAS in HY and ZSM-5 zeolites. Despite the fact that CO molecules belong to the most efficient probes of the Lewis acidic strength (ref. [1] and references therein), only a few papers deal with first-principles calculations of the C-O frequency shift induced by the adsorption of CO molecules at Lewis centres of coordinatively unsaturated (CUS) aluminium in oxide matrices; among them are communications [4,9] devoted to analysing the vibration of CO on Al13c.

The present model cluster density functional (DF) studies of bonding and vibration of CO molecule adsorbed on three- and five-coordinate Al centres (Al13c) in oxides address the following topics: (i) intrinsic uncertainties of the design of cluster models of the Al13c LAS \((n = 3, 5)\); (ii) the mechanism of CO interaction with Al13c LAS in dependence on the coordination number \( n \); (iii) various contributions to the C-O frequency shift in the Al13c-CO adsorption complexes.

A conventional cluster model of the Al13c LAS is Al(OH)3. Of special interest here is the dependence of the adsorption properties of the Al13c centre represented by the Al(OH)3 moiety on the position of the Al cation relative to the plane of the three surrounding oxygen anions, i.e. on the height of the AlO3 pyramid [10]. A widely used procedure to create Al13c centres from tetrahedrally coordinate Al species is to treat the oxide under thermovacuum conditions causing elimination of the hydroxyl groups [11]. One may speculate that the deformation of AlO3 fragments induced by the removal of an OH group from the tetrahedrally coordinate Al is of negligible importance due to the limited mobility of the oxygen atoms surrounding the Al species in the rigid oxide matrix [9]. Another approach would consist of a full geometry relaxation of the Al(OH)3 subsystem [8] which is based on the hypothesis of a rather flexible lattice of
the oxides. Finally, an intermediate procedure corresponds to a change of only the height of the Al atom above the plane of three O atoms, keeping the latter fixed in a position either taken from the experimental bulk structure [6] or determined by results of band structure calculations of the solid [7]. None of the mentioned strategies of the model cluster design seems to have indisputable advantages over the other two approaches. Thus, it is reasonable to evaluate how important the unavoidable variations of the cluster structures are for chemically meaningful features, like adsorption properties. In order to study the dependence of the results calculated for adsorption complexes on the substrate cluster geometry varied within the outlined uncertainty margins, the following three structures of the model cluster Al(OH)$_3$ are considered: a tetrahedral structure (3a, with the O-Al-O angle of 109.5°), a planar (3c, $\angle$ (O-Al-O) = 120°) and an intermediate one between the former two, 3b, $\angle$ (O-Al-O) = 117.1°, where the Al-O bonds form the angle of 100° with the vertical axis z.

A model Al(OH)$_3$(OH)$_2$ of the five-coordinate Al LAS has also been considered in two variants discussed in the literature: one with optimised equal Al-OH and Al-OH$_2$ distances (5a)[5–7] and another one obtained in the course of an independent variation of the two types of the Al-O bond lengths (5b)[8].

For the models 3b and 5a, which are most adequate from our viewpoint, a constraint space orbital variation (CSOV) analysis has been carried out for the energy of CO adsorption on Al$_{3c}$ and Al$_{5c}$ centres as well as for the adsorption induced shift of the C-O vibrational frequency.

### 2. Computational details

The first principles linear combination of Gaussian-type orbitals density functional (LCGTO-DF) cluster method [12] has been used with the parametrization of exchange–correlation interactions suggested by Vosko, Wilk, and Nusair (VWN) [13]. After achieving self-consistency, gradient corrections to the exchange [14] and to the correlation [15,16] energy functionals (BLYP) were computed using the VWN electron density to improve description of the cluster energetics. This "post-hoc" procedure to account for non-local contributions to the exchange–correlation functional has been found [17] to yield essentially the same results as the direct procedure where gradient-corrected potentials are employed self-consistently.

The orbital basis sets and the contraction coefficients for Al(12s9p2d) $\rightarrow$ [6s4p2d], C(9s5p2d) $\rightarrow$ [5s4p2d], O(9s5p2d) $\rightarrow$ [5s4p2d] and H(6s2p) $\rightarrow$ [3s2p] atoms have been taken from previous LCGTO-DF studies [18–20]. Generalized contractions based on atomic eigenvectors were employed throughout. The two auxiliary basis sets used in the LCGTO-DF method to represent the electron charge density and the exchange–correlation potential were constructed from the orbital exponents in a standard fashion [12].

A cyclic optimization of the Al-OH and O-H distances as well as of the angle Al–O–H was employed to search for the equilibrium geometry of the cluster Al(OH)$_3$ (model 3a) under C$_{3v}$ symmetry constraints. The optimised parameters of 1.739 Å, 0.975 Å and 112.8°, respectively, were used in calculations of the other Al(OH)$_3$ models 3b and 3c (C$_{3v}$ symmetry). For the models of the Al$_{3c}$ centres (C$_{3v}$ symmetry group, four oxygen atoms of the AlO$_3$ fragment are in the plane of the Al atom) only the Al–O distances were varied with the O–H bonds and Al–O–H angles fixed at the values as computed for model 3a; the H$_2$O parameters /$\langle$H–O–H$\rangle$/ of 103.8° and r(O–H) of 0.979 Å were taken from LCGTO-DF calculations of a free water molecule. This variation resulted in r(Al–O) of 1.862 Å for the distances with both OH and OH$_2$ ligands (model 5a) or in the r(Al–O) values of 1.795 Å and 2.043 Å, respectively (model 5b). The adsorbed CO molecule was assumed to be oriented upright along the symmetry axis (z axis) of the substrate cluster with the C-atom pointed to the Al cation (fig. 1). Al–CO and C–O distances were optimised in a cyclic fashion with no adsorption-induced change in the substrate cluster geometry taken into account. The Al$_{3c}^{1+}$–CO binding energy has been corrected for the basis set superposition error (BSSE) with the help of the counterpoise technique [21]. The normal modes of adsorption complexes have been approximated by the computed Al$_{3c}^{1+}$–CO or C–O internal modes. Anharmonic vibrational frequencies $\omega$ (energies of the 0 $\rightarrow$ 1 transition between the vibrational levels) were computed by fitting a polynomial to seven (C–O mode) or five (Al$_{3c}^{1+}$–CO mode) points near the minimum of the corresponding potential curve.

The nature of the Al$_{3c}^{1+}$–CO bonds has been analysed with the help of the CSOV procedure [22] originally proposed in the framework of the HF method and recently employed for the first time in combination with DF studies [18,20,23]. Relevant details of the CSOV procedure are given in section 3.