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Molecular Structure of a Surface Superoxide Radical Anion on MgO

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Using the MINDO/3 method the coadsorption of dihydrogen and dioxygen molecules on dehydroxylated magnesium oxide is considered and a molecular model for the adsorbed superoxide radical anion O_2^- is proposed on the basis of the results obtained; both the optimized geometrical characteristics and the calculated set of hyperfine coupling tensor (***B***) data are in good agreement with the experimental set.

It is well known that the superoxide radical anion O_2^- can be stabilised on the surface of many oxide catalysts, with the cations of the oxide lattice localised at the site of adsorbed O_2^-.[1,2] It is interesting to analyse the detailed molecular structure of the chemisorption complexes of O_2^- and, in particular, to consider their chemical activity. Unfortunately, the possibilities of using spectroscopic methods, including the most informative EPR method, for this task are severely limited. As a rule, they only allow a distinction between a π- or σ-structure of the complexes. A recent paper[3] details the observation in an EPR spectrum of O_2^- on MgO of hyperfine structure due to weak dipole–dipole interaction with a nearby hydroxy group. These results allowed the authors[3] to suggest a possible molecular structure for the chemisorption complex. It is interesting to compare this molecular model of O_2^- on MgO with the results of direct quantum-chemical calculations.

Cluster quantum-chemical calculations have been carried out within the framework of the MINDO/3 method, with

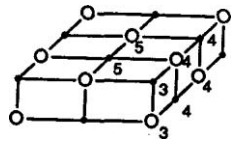

Fig. 1 Structure of the model molecular cluster $Mg_{12}O_{12}$ with coordination numbers (nC) marked as 3, 4, 5, respectively

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parameterization extended in order to consider the geometry and energetics of various chemisorption structures on a magnesium oxide surface.[4,5] The latter was modelled by a molecular cluster of $Mg_{12}O_{12}$ (Fig. 1) containing all the possible types of chemically active low-coordinated magnesium and oxygen ions (Mg_{nC}^{2+} and O_{nC}^{2-}) (n = coordination number). In the calculations full optimization of the geometry of both the initial cluster and the adsorbate molecules and various chemisorption complexes up to the total energy minimum was carried out, *i.e.* taking into account structural relaxation at the active centres (AC) of the oxide surface.

It has been noted previously[3] that two different methods are possible for the generation of superoxide radical anion $O_2^{\bullet-}$ on MgO. According to the first one, an outgassed sample of MgO is first γ- or UV-irradiated in an H_2 or D_2 atmosphere and then treated with molecular dioxygen. According to the second method, the desired particle $O_2^{\bullet-}$ is obtained *via* the reaction of a slightly acidic hydrogen-containing molecule HX with $O_2^{\bullet-}$ at the surface. As HX, for example,[2] benzene, ethylene, ammonia, toluene, propene, acetylene and dihydrogen were used. In both cases, in order to stabilize the surface $O_2^{\bullet-}$, the prior formation of surface hydroxy groups is necessary. Taking into account these circumstances, let us now consider the possibility of formation of the superoxide anion-radical during successive adsorption of dihydrogen and dioxygen on a dehydroxylated MgO surface. As shown previously using the MINDO/3 method,[4,5] dissociative chemisorption of a dihydrogen molecule on an MgO surface proceeds on either O_{3C}^{2-}—Mg_{4C}^{2+} or Mg_{3C}^{2+}—O_{4C}^{2-} pairs of acid–base centres. Molecular adsorption of dioxygen on pure MgO leads to stabilization of the π-complex only in the case of participation by three-coordinate Mg_{3C}^{2+}. The energy of formation of the latter is 9.4 kcal mol^{-1}† relative to that of a noninteracting cluster and a free dioxygen molecule. However, because of its geometry and electronic characteristics it cannot be ascribed to the superoxide anion-radical. In such a surface π-complex the O—O bond length is slightly perturbed, *i.e.* its lengthening in comparison with that of a noninteracting dioxygen molecule is only 0.5%. The distance from the centre of gravity of the adsorbed dioxygen molecule to the adsorption site (the three-coordinate magnesium cation) is 2.254 Å. The charge transfer from the dioxygen molecule to Mg_{3C}^{2+} is 0.17 e. This result is in good agreement with the commonly accepted idea that dioxygen adsorption on a pure MgO surface cannot lead to the formation of superoxide radical anions owing to the lack of electron-donor defects on the oxide surface.[2]

Let us now consider the situation whereby the dihydrogen molecule chemisorbs first on a M_{3C}^{2+}—O_{4C}^{2-} pair. In terms of energetics, this process requires only a slight increase of the interaction temperature of the whole system.[4] Then, on the interaction of such an initial state with a dioxygen molecule one can expect abstraction of the hydrogen atom bonded to the three-coordinate magnesium cation, resulting in the formation of a surface radical structure. This assumption is based on the bond energies of a hydrogen atom both with lattice Mg_{3C}^{2+} and with a dioxygen molecule. These two values are of approximately the same order. Thus, for example, the Mg_{3C}^{2+}—H bond energy calculated using the MINDO/3 method is 52 kcal mol^{-1} (ref. 4) and for the peroxide radical H—$O_2^{\bullet-}$ 47 kcal mol^{-1}. Another dioxygen molecule can then interact with this surface radical centre and, according to our calculations, coordination to either three- or four-coordinate neighbouring magnesium cations is possible for $O_2^{\bullet-}$. Coordination to Mg_{3C}^{2+} is more profitable energetically (the energy of formation of such a complex is 79 kcal mol^{-1} relative to that of a noninteracting hydrogen-containing surface radical centre and a dioxygen molecule, compared with the corresponding value for Mg_{4C}^{2+} of 38 kcal mol^{-1}). In both cases the dioxygen molecule is chemisorbed as a π-complex on the selected surface

† 1 cal = 4.184 J.

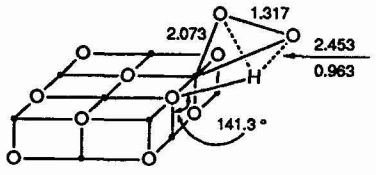

Fig. 2 Surface superoxide anion-radical on Mg_{4C}^{2+} interacting with the proton of a neighbouring hydroxy group; bond lengths in Å

adsorption site. In the former case, however, the position of the oxygen atoms of the adsorbed O_2 molecule is strongly unsymmetrical relative to the neighbouring hydrogen atom of the O_{4C}^{2-}—H group. Hence, in such a complex the effective charges on the oxygen atoms of adsorbed dioxygen are different: −0.304 e and −0.326 e, respectively. In this respect the Mg_{4C}^{2+} surface complex (Fig.2) is more interesting, since the position of the oxygen atoms of the adsorbed O_2 is strictly symmetrical with respect to both Mg_{4C}^{2+} and the hydrogen atom of O_{4C}^{2-}—H group (Fig. 3). The optimized geometrical characteristics of this complex are in good agreement with analogous data.[3] In ref. 3 the geometry of the surface superoxide radical anion $O_2^{\bullet-}$ was obtained from the conditions required for optimal conformity of both the experimental and calculated components of the principal values of the proton hyperfine coupling tensor ***B***. It should be noted that in ref. 3 the O—O and O_{4C}^{2-}—H bond lengths were not optimized (they were fixed at 1.35 Å and 1.0 Å, respectively), the best results being obtained with $R_{Mg\cdots O} = 2.07$ Å and $R_{O\cdots H} = 2.41$ Å (*cf.* our results in Fig. 2)).

The calculated value of the total effective charge on $O_2^{\bullet-}$ is −0.63 e, the spin density being practically fully localized on the 2p orbitals of the two oxygen atoms.

Let us now move on to analyse the components of the tensor ***B*** in the EPR spectra of this superoxide radical anion. Starting from the same assumptions as ref. 3, namely that (*i*) the ***g*** and ***B*** tensors have the same principal directions; (*ii*) the proton is perpendicular to a 2p orbital containing an unpaired electron; (*iii*) the perturbation produced by the hyperfine interaction is small compared to the external magnetic field, we can write the energy of the dipole–dipole coupling between the electron-spin and nuclear-spin moments (in magnetic field units) as eqn. (1).

$$B(\theta) = g_N \beta_N (3\cos^2\theta - 1)/r^3 = B'(3\cos^2\theta - 1) \qquad (1)$$

The components of the dipolar ***B*** tensor are given by eqns. (2) (Fig. 3).

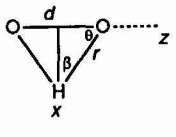

Fig. 3 Schematic representation of a T-shaped symmetrical superoxide radical anion interacting with the proton of a neighbouring hydroxy group

$$B_x = B'(3\cos^2\beta - 1); \quad B_y = -B'; \quad B_z = B'(3\cos^2\theta - 1)$$
$$\theta = \cos^{-1}(d/2r); \quad \beta = \pi/2 - \theta \qquad (2)$$

Substituting into expression (2) the MINDO/3-optimized geometrical characteristics ($R_{O\cdots H} = r = 2.4528$ Å; $R_{O-O} = d = 1.317$ Å; $R_{Mg\cdots O} = 2.073$ Å) of the surface complex produces the following coordinates: $B_x = 0.34$ mT, $B_y = -0.19$ mT and $B_z = -0.15$ mT. These results are in good agreement with the experimental data ($B_x = \pm 0.37$ mT, $B_y = \pm 0.21$ mT and $B_z = \pm 0.10$ mT)[3] and they can be considered as additional theoretical confirmation of the proposed molecular structure of the surface superoxide radical anion $O_2^{\bullet-}$ on MgO.[3]

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References

1 M. Che and A. J. Tench, *Adv. Catal.*, 1983, **32**, 1.
2 E. Giamello, P. Ugliengo and E. Garrone, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1373.
3 E. Giamello, E. Garrone, P. Ugliengo, M. Che and A. J. Tench, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 3987.
4 N. U. Zhanpeisov, A. G. Pelmenschikov and G. M. Zhidomirov, *Kinet. Katal.*, 1990, **31**, 564; *Kinet. Catal. (Engl. Transl.)*, 1990, **31**, 491.
5 N. U. Zhanpeisov, A. G. Pelmenschikov and G. M. Zhidomirov, in *Proceedings of the 5th International Symposium on Small Particles and Inorganic Clusters*, University of Konstanz, Germany, 1990, p. 139.

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