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Quantum-Chemical Study of the Nature of Hydroxy Groups on an MgO Surface

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It has been shown that the O—H stretching frequencies of six kinds of hydroxy groups on MgO and their local structures, calculated by a harmonic oscillator approach using the MINDO/3 method, are in good agreement with available experimental data; on the basis of the obtained theoretical results the nature of the surface OH-groups are discussed.

Surface hydroxy groups play an important role in the catalytic activity of magnesium oxide and behave as active centres for many catalytic reactions. Information on the nature of these OH-groups is usually obtained by means of IR spectroscopy. Various correlations such as the dependence of the O—H stretching frequency ν_{OH} on the bond order P_{OH}, on the Wiberg index of this bond, on the H atom electronic charge or on the resonance component of the two-centre bond energy E^{R}_{OH}, *etc.* (see, for example, refs. 1 and 2), calculated by some quantum-chemical method, are usually employed for theoretical studies. Direct calculations of the O—H stretching frequency ν_{OH} on MgO using an optimized geometry within the framework of some quantum-chemical method are not, as far as we know, available in the literature. Quite recently an interesting experiment[3] has been performed whereby high-temperature IR spectroscopic techniques have been used to study the deuterium exchange reaction of surface OD-groups with H_2 on MgO. It was found that the OD-groups on an Mg atom are composed of three types, exhibiting different vibrations at 2771, 2765 and 2756 cm^{-1}. In addition to these 'on-top' OD-groups, three different kinds of multiply bridged OD-groups are also observed at 2710, 2680 and 2600 cm^{-1}. On the basis of the usual electrostatic model, these bands were ascribed to the corresponding local structures. In this connection it is interesting to find out how these experimental bands can be described within the framework of the MINDO/3 method. In our opinion, such direct calculations of the band frequencies for surface OH-groups will prove useful in interpreting the available experimental data. On the basis of the results obtained from such calculations the nature of the surface OH-groups and other questions are discussed here.

Cluster quantum-chemical calculations may be carried out using the MINDO/3 method, whose parametrization has also been extended to consider magnesium compounds.[4] The surface of dehydroxylated magnesium oxide is modelled by clusters of Mg_9O_9, $Mg_{12}O_{12}$ and $Mg_{32}O_{32}$ representing two- and four-layer molecular structures and containing the most chemically active low-coordinate magnesium and oxygen ions (Mg_{LC}^{2+} and O_{LC}^{2-}) in various surface irregularities: faces, edges, corners, *etc.* (Fig. 1). In these calculations,[4] a full optimization of geometry of both the initial clusters and the chemisorption complexes was carried out. Calculations of the O—H stretching frequencies ν_{OH} of various surface OH-groups on MgO were carried out on the basis of a harmonic oscillator approach in the locality of the total energy minimum represented by a parabola at the optimized distance R_{OH} and at $R_{OH} \pm 0.005$ Å. These OH-groups are formed *via* dissociative chemisorption of water molecules on MgO and differ from each other in the degree of coordination of hydroxy group by metal atoms in the first and by oxygen atoms in the second coordination spheres [Fig. 1(*c*)]. Table 1 shows the optimized geometries of various OH groups on MgO and their bond order P_{OH} and Table 2 shows the calculated results $\nu_{OH}^{calc.}$ using a scaling factor $f = 0.924$. The second column of Table 2 shows the calculated O—D stretching frequency of the OD-group using the well-known correlation $\nu_{OH}/\nu_{OD} = 1.35$.[5]

We can draw the following conclusions from the data in Table 2. First, in accordance with general ideas[2,6] the formation of a dative bond decreases the O—H stretching frequency, *i.e.* the OH group with a higher degree of coordination by metal atoms (the number of Mg atoms bonded with OH groups in the first coordination sphere) has the lowest band frequency. This is due to the fact that increasing the coordination number of the OH group by Mg atoms reduces the strength of the bond (bond order P_{OH}, Table 1) and leads to a lengthening of the OH bond (Table 1). The latter results in a decrease in the electron density on the OH bond. Second, changing the coordination number of

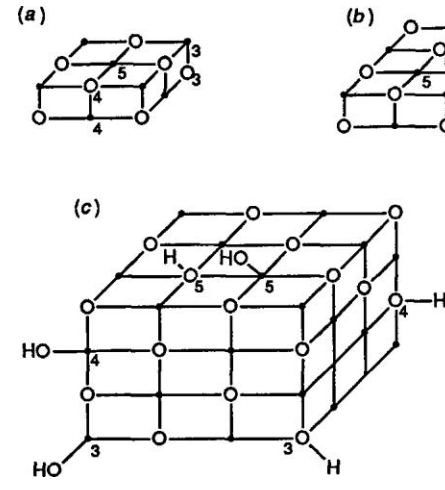

Fig. 1 Molecular clusters modelling a magnesium oxide surface: (*a*) Mg_9O_9, (*b*) $Mg_{12}O_{12}$, (*c*) $Mg_{32}O_{32}$, with various types of surface hydroxy groups. The numerals correspond to the degree of coordination *n* of various centres: ○ O_{nC}^{2-}, · Mg_{nC}^{2+}

Table 1 Geometries of various types of OH groups on MgO and their bond order, calculated using the MINDO/3 method

Type of OH bond	Geometry: bond length/Å bond angle (°)	Bond order P_{OH}
$Mg_{5C}—O_1H$	OH, 0.9311; MgOH, 175.53	0.9431
$Mg_{4C}—O_1H$	OH, 0.9309; MgOH, 159.75	0.9435
$Mg_{3C}—O_1H$	OH, 0.9293; MgOH, 166.30	0.9454
$O_{3C}H$	OH, 0.9453; MgOH, 167.54	0.9175
$O_{4C}H$	OH, 0.9540; MgOH, 176.30	0.9112
$O_{5C}H$	OH, 0.9622; MgOH, 168.26	0.8951

Table 2 Calculated (MINDO/3) and experimental O—H stretching frequencies of hydroxy groups on MgO

Type of OH group	$\nu_{OH}^{(calc.)}$	$\nu_{OD}^{(calc.)}$	$\nu_{OD}^{(exp.)}$	$\nu_{OD}^{(exp.)a}$
$Mg_{5C}—O_1H$	3730	2763	2756	2771
$Mg_{4C}—O_1H$	3732	2765	2765	2765
$Mg_{3C}—O_1H$	3751	2779	2771	2756
$O_{3C}H$	3644	2699	2710	2710
$O_{4C}H$	3557	2635	2680	2680
$O_{5C}H$	3488	2584	2600	2600

[a] Experimental values $\nu_{OD}^{(exp.)}$ are taken from ref.3. The ruling box denotes the experimental band frequencies[3] that are not in agreement with those calculated by the MINDO/3 method. The third column corresponds to experimental $\nu_{OD}^{(exp.)}$ determined by us.

the Mg atom affects the ν_{O_IH} band frequency relatively weakly. Here, in contrast to ref. 3 but in accordance with ref. 7, the reverse dependence of ν_{O_IH} on the coordination number of the Mg atom is observed, *i.e.* upon increasing the number of O atoms in the second coordination sphere the ν_{O_IH} band frequency decreases. Accordingly, P_{OH} decreases and the corresponding OH bond length increases (Table 1), leading to an increase in the electron density on the OH bond. Third, as previously observed,[4] dissociative chemisorption of methane on MgO requires an increasing of the interaction temperature up to 573 K,[8,9] when a band appears at 3650 cm^{-1} in the IR spectrum.[9] Thus,[4] in this case O_{3C}^{2-}–Mg_{4C}^{2+} acid–base pairs, leading to the formation of a CH_3^- fragment stabilized on Mg_{4C}^{2+} and $O_{3C}H$ groups, may be activation centres for the methane molecule. An additional argument in favour of this proposal may also be the low-temperature adsorption of CO on MgO[10] (at 77 K) when two bands at *ca.* 3750 and 3640 cm^{-1} can be observed in the IR spectrum. The latter is ascribed to OH groups one- and three-coordinated by metal atoms, respectively. These results are in good agreement with data,[4] according to which the formation of O_IH and $O_{3C}H$ groups is energetically more favourable on chemisorption of water molecules on MgO. The number of these OH groups increases with increase in the interaction temperature owing to the participation of less reactive active centres of MgO in the dissociative chemisorption process. Our results make an essential correction to the early empirical ideas about the ν_{OH} dependence of the surface OH groups on their neighbouring chemical environment.

References

1 E. P. Smirnov and A. A. Tsyganenko, *React. Kinet. Catal. Lett.*, 1977, **7**, 425.
2 A. A. Tsyganenko and V. N. Felimonov, *J. Mol. Struct.*, 1973, **19**, 579.
3 T. Shido, K. Asakura and Y. Iwasa, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 441.
4 N. U. Zhanpeisov, A. G. Pel'menshchikov and G. M. Zhidomirov, *Kinet. Katal.*, 1990, **31**, 561 [*Kinet. Catal. (Engl. Transl.)*, 1990, **31**, 491].
5 B. Henderson and W. A. Sibley, *J. Chem. Phys.*, 1971, **55**, 1274.
6 A. A. Davydov, *IK spektroskopiya v khimii poverkhnostnykh okislov* (IR spectroscopy in oxide surface chemistry), *Nauka, Novosibirsk*, 1984 (in Russian).
7 A. G. Pel'menshchikov and G. M. Zhidomirov, *React. Kinet. Catal. Lett.*, 1986, **31**, 85.
8 M. Utijama, H. Hattori and K. Tanabe, *J. Catal.*, 1978, **53**, 237.
9 A. A. Davydov, A. A. Budneva, S. M. Aliev and V. D. Sokolovskii, *React. Kinet. Catal. Lett.*, 1988, **36**, 491.
10 M. I. Zaki and H. Knozinger, *Mater. Chem. Phys.*, 1987, **17**, 201.

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