

On the problem of differentiation of acetone adsorption species on the silica gel: molecular models of adsorption complexes

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Abstract

In the framework of the cluster approach ab initio calculations of the adsorption complexes of acetone molecule with an isolated terminal OH group of a silica gel (S1), with the fragment including hydrogen-bonded OH group (S2) and with two separated terminal OH groups simulating bifurcated acetone interaction (S3) were carried out. It is found that the difference between the stability of acetone complexes S1 and S2 is insignificant, and it is concluded that the bifurcated acetone interaction could result in a more stable adsorption form of acetone with the silica gel. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Silica gel surface; Acetone; Ab initio calculations

1. Introduction

IR-spectroscopy, including an application of probe-molecule (NH_3 , CO, NO, acetone, etc.), is widely used for analysis of the phase composition of supported systems, the determination of the active sites on the catalysis surface and estimation of their concentration. The acetone adsorption on the silica surface has been studied in a number of papers [1–3]. Two IR-absorption bands of stretching carbonyl vibrations were recorded after the acetone adsorption from a carbon tetrachloride solution on a fully hydroxylated silica gel surface [2]. One of these bands

was observed at low acetone concentration in the carbon tetrachloride solution and corresponded to a stronger adsorption complex. In the author's opinion [2], in this complex the acetone molecule is involved in hydrogen bonding with two adjacent hydroxyl groups (bifurcated structure). Another complex was assigned to the hydrogen-bonding interaction between an isolated terminal OH group and the acetone molecule. A later study of the acetone adsorption from the gas phase on the surface of silica gel [3] has confirmed the conclusion about two primary centres of the acetone adsorption on silica, as two bands of the CO stretching frequency of acetone were observed with 1695 cm^{-1} and 1705 cm^{-1} ($\omega_{\text{C=O}} = 1740\text{ cm}^{-1}$ for free acetone molecule in the gas phase).

The above mentioned experimental data formulate a problem of molecular modelling of the

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two types of the acetone adsorption complexes with silica gel surface hydroxyl groups.

According to numerous experimental studies, the hydroxyl coverage of silica gel surface is irregular, and its composition strongly depends on the preparation and thermovacuum treatment of a sample. As a rule, silica gel surface contains (a) isolated hydroxyl groups, (b) hydrogen-bonded hydroxyl groups, (c) different kinds of adjacent hydroxyl groups [4–6]. Experimental studies showed that the lower stable adsorption complex is the coordination of an acetone molecule by single hydroxyl group [2,3]. The second form of the complex could involve (a) interaction of an acetone molecule with a surface fragment containing hydrogen-bonded hydroxyl groups or (b) bifurcated coordination of an acetone molecule by two proper adjacent hydroxyl groups. This alternative is studied in the present paper on the base of simple cluster modelling of active sites of the surface.

2. Calculation details

Isolated hydroxyl groups of the silica surface were modelled by an H_3SiOH cluster structure. The approach of two interacting H_3SiOH groups (see Fig. 1) was chosen for simulating of hydrogen-bonded surface hydroxyl groups as it was earlier used in [7,8]. As to the two-coordinated complex, we looked for an optimal structure for such interaction in order to discuss the possibility of its realization on silica gel surface. So, the approach of the coordination of an acetone molecule by two isolated hydroxyl groups was chosen (see Fig. 2, S3).

Ab initio calculations of structures mentioned above were carried out by a density functional

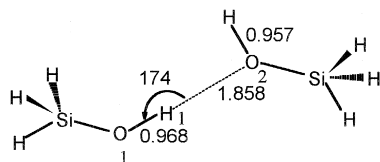


Fig. 1. The optimized geometry of the cluster with hydrogen-bonded terminal OH groups.

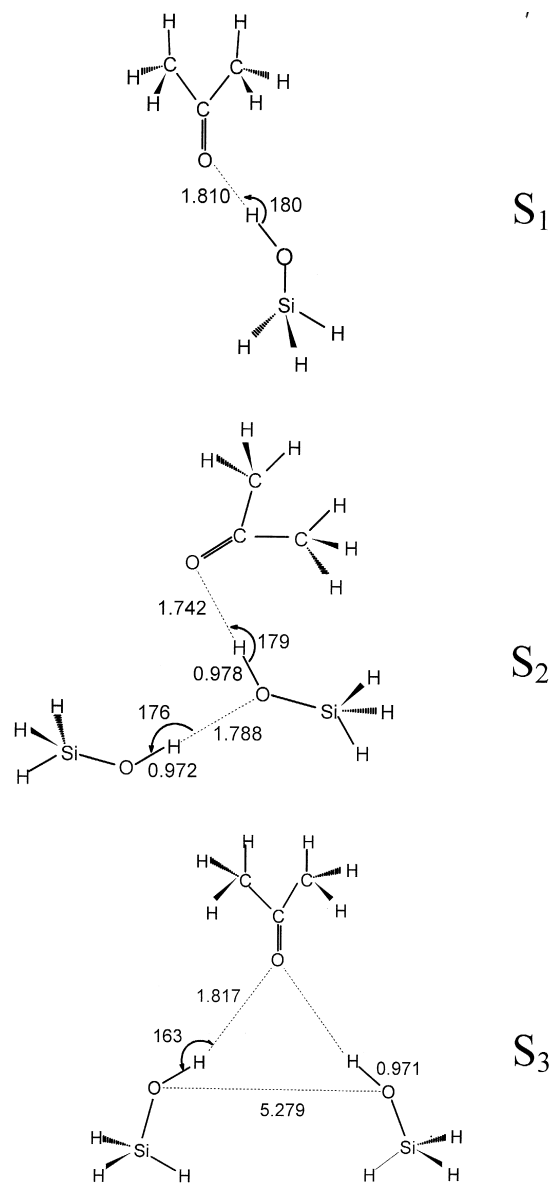


Fig. 2. The optimized geometry of the considered adsorption complexes: complex S_1 corresponds to the adsorption on a terminal hydroxyl; complex S_2 — to the adsorption on a hydrogen-bonded terminal OH groups; complex S_3 — bifurcated adsorption of acetone. The bond lengths are given in Å, angles are given in degrees.

method with the use of the Becke3P86 exchange-correlation functional [9,10]. For Si and H atoms of silica, the basis 3-21G was used. The basis 6-31G complemented by two sets of d-functions for atoms C and O, and extended by

two sets of the p-functions for hydrogen atoms of acetone and the OH groups of silica was used.

The adsorption energy was defined as a difference between the total energy of the adsorption complex and the sum of energies of the initial cluster and a free acetone molecule. The frequency shift was estimated as a difference between the CO stretching frequency for free acetone molecule and CO stretching frequency for the adsorption complex. The GAUSSIAN-92 program [11] was used for the calculations.

3. Results and discussion

The calculated geometry of the cluster simulating hydrogen-bonded hydroxyl groups is shown in Fig. 1. The length of the hydrogen bond is 1.858 Å and the corner $O_1H_1 \dots O_2$ is close to 180° . The shift of the O_1H_1 stretching frequency due to hydrogen-bond interaction is 217.2 cm^{-1} with respect to the frequency of the isolated OH group, whereas that for the O_2H group is 0.5 cm^{-1} .

Acetone interacting with the cluster gives the adsorption complex designated by S2, whose geometrical parameters are given in Fig. 2 together with the structures of the acetone adsorption complexes with isolated terminal OH group of the silica surface (S1), as well as with two separated terminal OH groups (so-called bifurcated complex S3). The adsorption energies and the shifts of the CO stretching frequency for the various acetone adsorption complexes are presented in Table 1. The formation of hydrogen

bonding in the initial cluster (Fig. 1) results in the reduction of the length of a hydrogen bond between a free OH group of the cluster and an acetone molecule by about 0.06 Å as compared with the S1 complex. Accordingly, the adsorption energy in the S2 complex is slightly larger (10.45 kcal/mol) than that in S1 (8.22 kcal/mol). It is interesting to note that the acetone adsorption on the fragment with the hydrogen bonding leads to an increase of interaction inside the cluster, so that the length of its hydrogen bond decreases from 1.858 to 1.788 Å for the S2 complex. The length of hydrogen bond in the S3 bifurcated complex is close to that in the S1 complex with isolated terminal OH group and is equal to 1.817 Å . As in the given structure two hydrogen bonds are formed, the acetone adsorption energy is essentially greater (16.9 kcal/mol). The full optimization of S3 resulted in a rather large distance between oxygen atoms of the OH groups -5.279 Å . The increase in the distance between oxygen atoms in the bifurcated complex influences not only the adsorption energy but also increases the shift of the CO group whose stretching frequency is 69 cm^{-1} , whereas the experimental value [3] of the frequency shift for strong acetone adsorption is measured to be 45 cm^{-1} . For the S1 and S2 adsorption complexes, the CO group frequency shifts are equal to 26 and 32 cm^{-1} , respectively, as compared with the experimental value of 35 cm^{-1} measured for a weak adsorption mode [3]. It is necessary to note that the calculated frequency depends to some extent on the calculation method and on the choice of the initial model cluster. As the difference between the shifts of the CO stretching frequency for S1 and S2 is within the accuracy of the calculation procedure (5 cm^{-1}), and the difference in the acetone heat of adsorption for these complexes is just 2.2 kcal/mol , it is reasonable to conclude that the structure with hydrogen-bonded hydroxyl groups does not result in other forms of adsorbed acetone different from those formed by acetone adsorption on isolated hydroxyl group. Apparently stronger forms of ace-

Table 1
Energies of adsorption and shifts of the C–O stretching frequency for different adsorption complexes of acetone on silica gel surface

Adsorption species	Adsorption energy (kcal/mol)	Shift of the C–O stretching frequency (cm^{-1})
S ₁	8.2	26
S ₂	10.5	32
S ₃	16.9	69

Table 2
Energies of adsorption and shifts of the C–O stretching frequency for different adsorption complexes of acetone on silica gel surface

Adsorption species	Adsorption energy (kcal/mol)		Shift of the C–O stretching frequency, cm^{-1}
	HF	MP2/HF	
a	9.1	11.7	31
b	4.1	6.0	13

tone adsorption might be treated as a bifurcated structure of the complex with participation of two space separated OH groups. It has been found that the calculated optimal distance R between oxygen atoms of the OH groups (5.28 Å) is close to the mutual arrangement of hydroxyl groups on fully hydroxylated (111) face of β -cristobalite (5 Å). The model of the silica surface including local fragments of (111) and (100) faces of cristobalite has been actively discussed in the literature [6]. The assumption that the bifurcated structure of acetone complexes correlated with (111) face of β -cristobalite does not contradict the experimental observation of strong adsorption form disappearance

when the silica gel was preliminary heated [3]. The dehydroxylation of this face is beginning under average temperatures of heating and the remaining isolated hydroxyl groups of (111) face and stable vicinal and geminal OH groups of (100) face [5,6] will be correlated with the weak form of adsorption. This brings a question about the possibility of two-point (bifurcated) adsorption of an acetone molecule on a vicinal group. We have performed the calculation of this adsorption form for the cluster model $(\text{HO})\text{H}_2\text{SiOSiH}_2(\text{OH})$ with the most typical for amorphous silica value of $\angle\text{SiOSi} = 135^\circ$ [12]. For comparison, the calculations of the single-point adsorption of an acetone molecule on the same cluster have been conducted as well. Ab initio Hartree–Fock calculations of the structure were carried out using the basis set described above. The electron correlation effects on the adsorption energy were calculated using the second-order Møller–Plesset perturbation theory for structures optimized at the HF level. Calculated adsorption energies and shifts of the CO group stretching frequency for the above mentioned adsorption complexes are presented in Table 2.

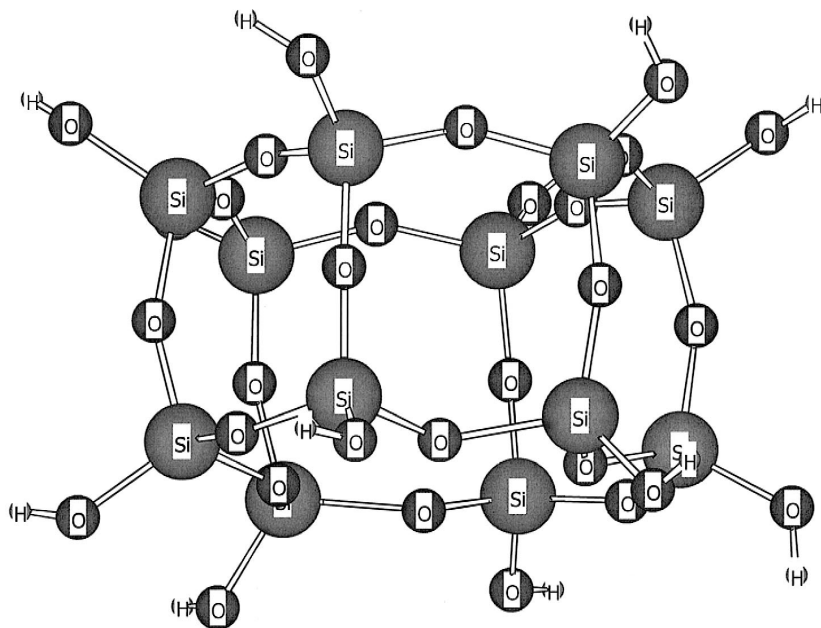


Fig. 3. Molecular model of the silica particle consisting of two interconnected 6-member rings.

The bifurcation interaction of acetone with two hydroxyl groups simultaneously (complex a) appeared to be relatively unfavourable. The adsorption energy and the shift of the CO vibrational frequency are significantly smaller than those for the adsorption on an isolated terminal hydroxyl group. This may result from the relatively short O–O distance in the vicinal fragment compared to that in S3 (see Fig. 2). The calculations showed that an increase of the SiOSi angle could stabilize the two point adsorption. The main reason here is the following increase of the O...O distance. At $\angle\text{SiOSi} \sim 180^\circ$ ($R_{\text{O}\dots\text{O}} = 4.4$) this adsorption form appears to be preferable in comparison with the single point adsorption. Probably, similar conformation of $(\text{HO})\text{H}_2\text{SiOSiH}_2(\text{OH})$ could be expected for rather small silica gel globules with the diameter 1 nm. One of the simplest molecular models of such silica gel particle is presented in Fig. 3 and consists of two interconnected 6-member rings. A molecular mechanics force field calculation of such structure by MM + method with full geometry optimization has been performed. Calculated distances between oxygen atoms of adjacent hydroxyl groups ranging from 3.94 to 5.17 Å are close to the corresponding values of effective bifurcated acetone interaction. Another interesting question is associated with the possibility of the hydrogen bond formation between vicinal hydroxyl groups. Our

calculations showed that this is possible only for the structure with $\angle\text{SiOSi} \leq 130^\circ$, and such conformation should be considered as defect.

Acknowledgements

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