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An ab Initio MO Study on Gas-Phase Adsorptive Interactions of Aromatic Compounds onto the Surface of Silica Gel

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Microscopic features of gas-phase adsorption phenomena of a few aromatic compounds on the surface of silica gel have been investigated by ab initio molecular orbital (MO) calculations. The interaction energies and the structures of the adsorbate-adsorbent systems have been discussed. It has been found that interactions between the substituent groups of the aromatic compounds and silanol groups of silica gel contribute much to the adsorption.

Silica gel is a very popular material often used as adsorbent. A lot of studies for adsorption phenomena and adsorptive interactions between adsorbates and silica surface have been reported in many years.[1-6] In particular in the past several years many theoretical studies[4-6] have been done, and microscopic information has been obtained as to the adsorption phenomena on silica surface, such as adsorption energies, orientations of adsorbates to adsorption sites or structures of adsorbate-adsorbent systems, and relations between structures of adsorption sites and adsorption energies. These works illustrate that by executing ab initio MO calculation we can get the knowledge that will help us to make the strategy for modification and design of adsorbents having desirable characters. In this point we are very interested in such theoretical studies, and the motivation of the present study is to dedicate to obtain and accumulate more information for adsorption phenomena.

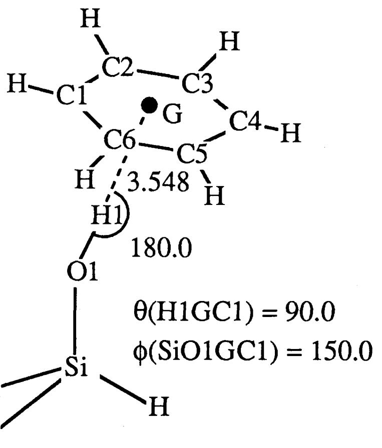

Fig. 1. Molecular model for adsorption of benzene onto silica gel. Center of mass of benzene is described as G. Symmetry is *Cs*.

In the present study we discuss gas-phase adsorption of a few aromatic compounds on the surface of silica gel. The adsorbates treated in this study are benzene, phenol, aniline, and nitrobenzene, that are very familiar in chemistry and chemical engineering. However, ab initio MO studies have not been reported concerning the adsorption of aromatic compounds on the surface of silica gel as far as we know. This paper might be the first one for such adsorbates.

It is known that in most cases silanol groups act as adsorption sites of silica gel.[1)] Hence we have studied interactions between the adsorbates and silanol groups on the surface of silica gel. The molecular model of adsorption sites used in this

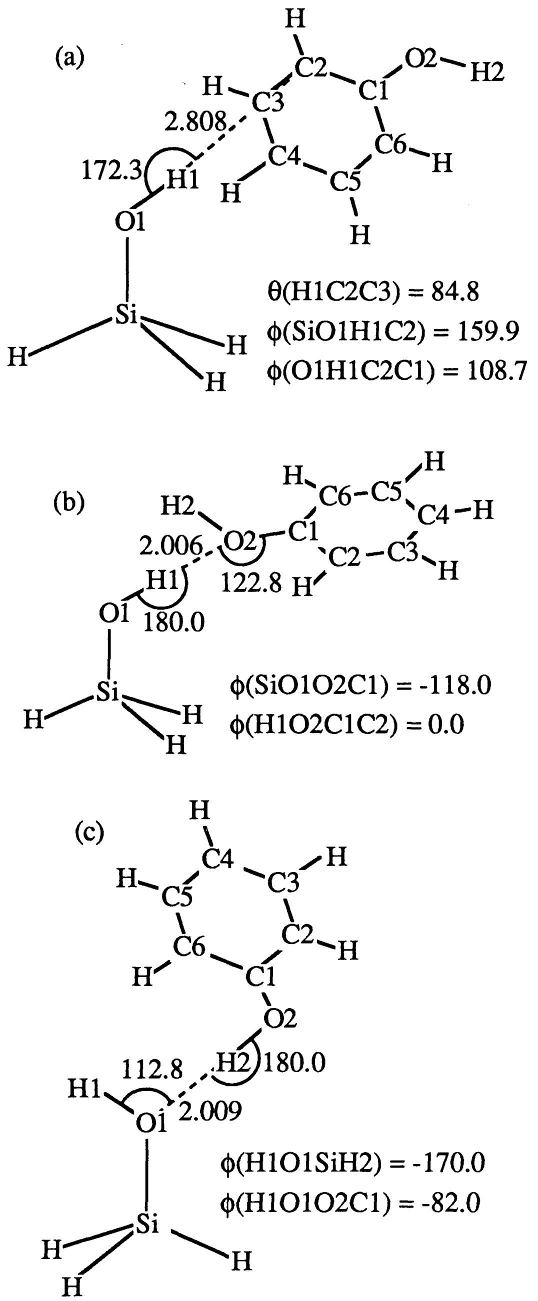

Fig. 2. Molecular models for adsorption of phenol onto silica gel. In each case adsorption is caused by (a) π-H, (b) O-H, and (c) H-O interactions, respectively. Symmetry is *C*1 for the all cases.

Table 1. Interaction energies

Adsorbate	Type of interaction	ΔE_{HF} kJ mol^{-1}	ΔE_{MP2} kJ mol^{-1}	E_{Coul} kJ mol^{-1}	E_{disp} kJ mol^{-1}
C_6H_6	π-H	12.34	20.65	7.54	8.31
C_6H_5OH	π-H	12.56	21.23	4.04	8.66
	O-H	21.57	31.27	17.61	9.71
	H-O	24.17	33.54	16.50	9.37
$C_6H_5NH_2$	π-H	14.02	22.61	5.87	8.59
	N-H	26.48	39.07	15.65	12.59
	H-O	8.52	12.72	4.60	4.20
$C_6H_5NO_2$	π-H	5.40	11.61	2.06	6.21
	O-H	22.24	31.51	9.18	9.27

study are in the following. The number of silanol group is, though it would be different for various kinds of silica gel, about 5 per 1nm^2.$^{3)}$ Hence, if one supposes that silanol groups locate homogeneously on the surface, the adsorbates treated in the present study would interact with one silanol group at a time. Therefore the adsorption site made by only one silanol group is treated in the present study. Previous studies$^{5)}$ treated this type of adsorption site, and used silanol as the molecular model of the adsorption site; we have treated the adsorption site in the same way.

We have carried out MP2/6-31G(p,d)//HF/6-31G(p,d) level calculations with GAUSSIAN92$^{7)}$ program. In previous studies$^{4-6)}$ results calculated by using valence double-ζ basis sets seem to be accurate enough to explain experimental results. Hence 6-31G(p,d)$^{8)}$ basis set has been adopted. Geometry optimization has been carried out in order to determine structures of the adsorption sites, the adsorbates, and the adsorbate-adsorbent systems. Electron correlation has been taken into account by MP2$^{9)}$ (frozen core) calculation. The energy of adsorbate (E1), that of adsorption site (E2), and that of adsorbate-adsorbent system (E3) have been determined, then the interaction energy ΔE is estimated by the following equation:

$$\Delta E = E1 + E2 - E3. \qquad (1)$$

We show the structures of the adsorbate-adsorbent systems in Figures 1-4. The interaction energies between the aromatic compounds and the silanol groups are listed in Table 1. There are two cases in the adsorption of aromatic compounds onto silica gel. The first case is caused by the interactions between the orbital of the conjugated systems in aromatic compounds and adsorption sites. The second case is caused by the hydrogen bond between the substituent group of the aromatic compounds and adsorption sites. In order to distinguish these two cases, the type of interaction is shown in

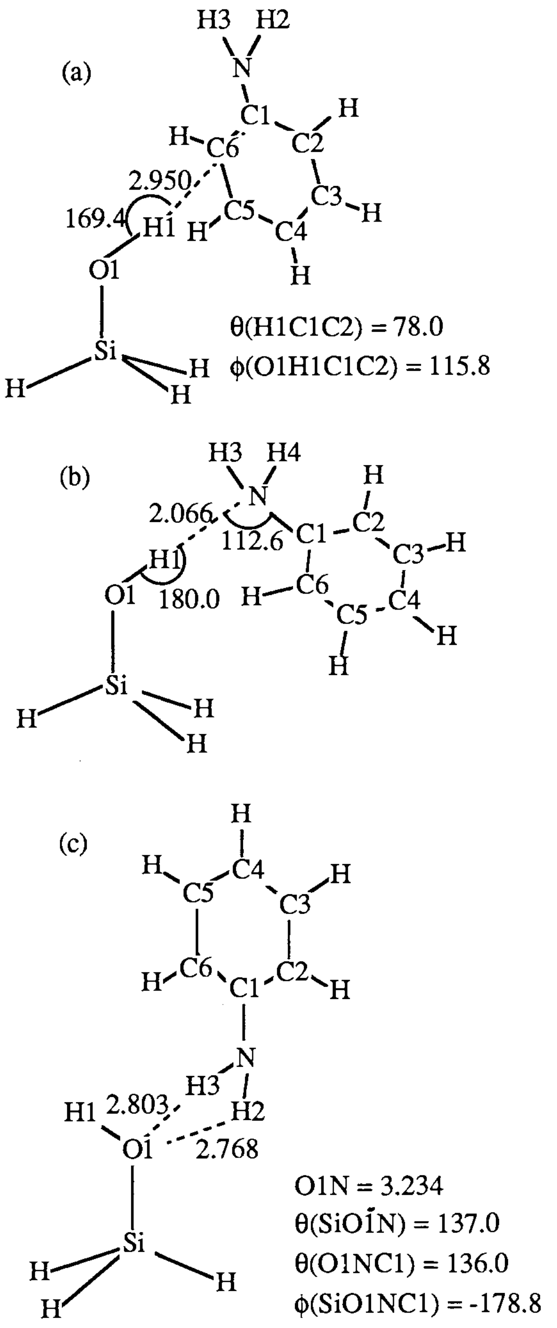

Fig. 3. Molecular models for adsorption of aniline onto silica gel. In each case adsorption is caused by (a) π-H, (b) N-H, and (c) H-O interactions, respectively. Symmetries are *Cs* for (a) and (b), and *C*1 for (c).

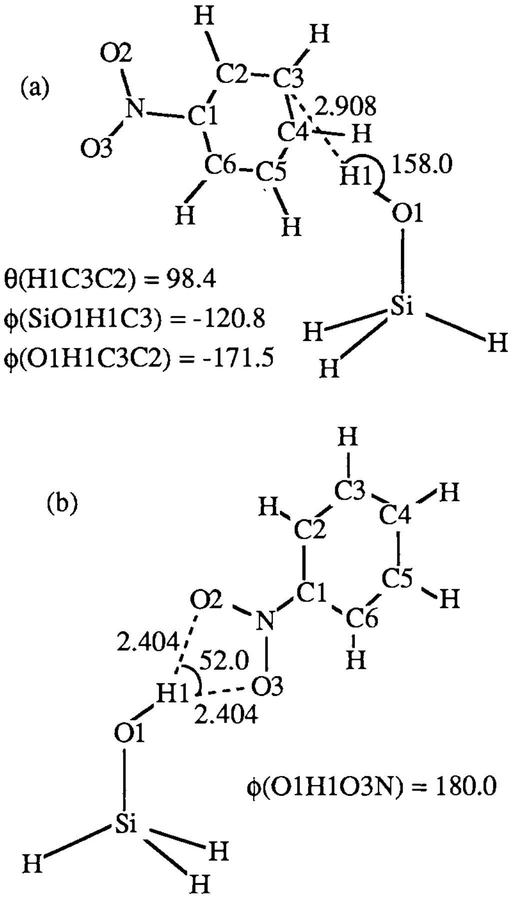

Fig. 4. Molecular models for adsorption of nitrobenzene onto silica gel. In each case adsorption is caused by (a) π-H and (b) O-H interactions, respectively. Symmetries of them are *C*1 and *Cs*, respectively.

Table 1. For the first case we have denoted the type of interactions as π-H. For the second case there are two types. One type is that the silanol group acts as a proton donor. The other type is that the silanol group acts as a proton acceptor. For example, in adsorption of phenol, the O atom of the hydroxyl group can act as both a proton acceptor and a proton donor for the silanol group. These interactions are denoted as O-H and H-O, respectively. For other molecules we have denoted the type of interactions in the same manner.

Let us discuss the first case. The interaction energy between benzene and silica gel is 20.65 kJ mol^{-1} at MP2 level calculation. Compared with the result, the interaction energies for phenol and aniline are 21.23 and 22.61 kJ mol^{-1}, and are slightly lager than the interaction energy for benzene. The interaction energy of nitrobenzene is 11.61 kJ mol^{-1}, and is less than that of benzene. The result seems to be reasonable because the hydroxyl group and the amino group are electron donating and the nitro group is electron withdrawing.

Concerning the second case, we have found that the interaction energies are bigger than those for the first case. Except for the case of H-O interactions of aniline, interaction energies are in between about 30 and 40 kJ mol^{-1}. From the present results, we can consider that the hydrogen bond between the substituent group and the adsorption site contributes to the gas-phase adsorption more than the interaction between the orbital of the conjugated system and the adsorption site.

Table 1 also shows Coulombic interaction energies E_{Coul} and dispersion energies. E_{Coul} is estimated by using Mulliken charges calculated by MP2/6-31G(d,p) level, and E_{disp} is estimated by the electron correlation energy, that is, ΔE_{MP2}-ΔE_{HF}.10) Comparing E_{Coul} with E_{disp}, one can see there is a tendency that E_{Coul} contributes more for hydrogen bonds and less for π-H type interactions.

Data of adsorption energies determined by experiments are available only for adsorption of benzene as far as we know. The energies are in between about 40 and 50 kJ mol^{-1}.11) We believe that the difference is mainly caused by the heterogeneity of the surface, because previous studies5) succeeded in explanation of experimental results by using the same model. If silanol groups distribute heterogeneously, the adsorption sites constructed by two or more silanol groups would exist. It is expected that for such adsorption sites the adsorption energies are bigger than the present cases. A study for such problem will be published elsewhere.

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