

실리카 및 제올라이트의 전자구조에 대한 CNDO/2 분자궤도론적 계산 I. CO 흡착

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CNDO/2 MO Calculations for the Electronic Structure of Silicas and Zeolites I. Adsorbed Carbon Monoxide

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요약. 실리카 및 제올라이트의 OH기 또는 교환된 양이온과 CO 분자간의 상호작용과 전자구조를 살펴보기 위하여 CNDO/2 계산을 행하였다. 실리카의 OH기와 CO 분자간의 상호작용에너지는 약 12kcal/mol 이었고, 그 결합거리, $R(O-H\cdots C)$ 는 2.6Å 이었다. 여러가지의 양이온과 CO 분자와의 결합강도는 $H^+ < Na^+ < Li^+$ 의 순이었는데, 그것은 양이온의 정전기적 장의 세기와 일치하였다. 또한 OH기나 양이온과 결합하고 있는 CO 분자의 결합차수는 OH-CO type의 경우를 제외하고는 모두 증가하였다. 제올라이트에 있는 양이온을 떼어내는데 필요한 에너지는 $H^+ > Li^+ > Na^+$ 의 순이었으며, 이것은 제올라이트의 골격으로부터 양이온으로 이동되는 전하의 양과 관계가 있다.

ABSTRACT. The CNDO/2 method has been used to calculate the electronic structure of the zeolites and silicas, and to investigate the interaction of CO molecules with the OH groups or the exchanged cation in the zeolites. The interaction energies of CO molecules with OH groups in silica were ca. 12kcal/mol, the bond distance, $R(O-H\cdots C)$ was 2.6Å. The strength of bond between CO molecules and various types of cations in the zeolites was in the following order: $H^+ < Na^+ < Li^+$, *i. e.*, this increased with increasing electrostatic field of cations. The bond orders of CO molecules interacting with the OH groups or the cations increased but for the OH-OC type interaction. The theoretical decationization energies of exchanged cations in the zeolites decreased in the order: $H^+ > Li^+ > Na^+$. And these energies depended on the amount of charge density transferred from the skeleton to the cations in order to compensate its negative charge.

1. INTRODUCTION

Because their adsorption characteristics and catalytic properties are important, silicas and zeolites have been intensively studied in many years.^{1,2} And their surface hydroxyl groups or

exchanged cations play an important role as active sites in catalytic or adsorption processes.

Various experimental methods³⁻⁵ (primarily ir spectroscopy) have been used to determine the active sites, and to investigate the effect of these active sites in the zeolites on the interacting

molecules. In recent years, quantum chemical calculations on cluster models of zeolites have been carried out.⁶⁻⁸ Although these calculations are often qualitative, they can provide good deal of informations on the properties of zeolitic surface those often cannot be obtained experimentally.⁹

This work was carried out to obtain the electronic structures of the simplified models of silicas and zeolites, and to investigate the physicochemical characteristics of zeolites and silicas and their interactions with CO molecules using CNDO/2 methods.

2. MODEL AND CALCULATIONS

The orthosilicic acid, $\text{Si}(\text{OH})_4$, and simplified silica models, $\text{Si}_2\text{O}(\text{OH})_6$, consisting of two SiO_4 tetrahedra sharing a bridging oxygen atom, were used for the calculations. And $\text{SiAlO}(\text{OH})_6\text{X}$ (where X is H^+ , Li^+ or Na^+) zeolite skeletal model was used. In this model, the isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral network of zeolite necessitates the presence of extraframework cation to compensate the charge excess of the zeolite skeleton.

The physicochemical properties of zeolites can be carried out quantum chemically only by using a model of zeolite containing limited number of atoms because of computational difficulty. It, however, has been found that the quantum chemical calculations on such a model can provide qualitative informations about the electronic structures of zeolites.¹⁰

The geometries of silica and zeolite framework were obtained from X-ray data,¹¹ *i.e.*, $\text{SiO}=1.61\text{\AA}$, $\text{AlO}=1.75\text{\AA}$ and $\angle\text{O-T-O}=109.47^\circ$ (where T designates a Si or Al atom), and these were accounted as consistent throughout the calculations. The other bond lengths and angles were changed until the most stable state was obtained. The final skeletons were

shown in Fig. 1, 3 and 5.

Pople's CNDO/2 method¹² was used for the calculations of the electronic structures of silicas and zeolites, and sp basis for Na, Si and Al atoms to get rid of convergence problems.

All the results in this work were obtained without the inclusions of 3d orbitals, *i.e.*, sp basis. And the convergence limit on the electronic energy was set equal to $1.0 \times 10^{-6}\text{au}$. The calculations yielded qualitatively identical results with the case of the spd basis.^{13,14}

The CNDO/2 program, and COORD program which is to calculate the atomic cartesian coordinates of the molecules were QCPE(Quantum Chemistry Program Exchange) NO.261 and NO.226 respectively. These calculations were carried out by means of IBM-PC/XT-16. The results calculated with this computer were in good agreement down to four decimal places with those calculated by means of CYBER 6000 computer.

In the interaction of CO molecules with the hydroxyl groups of silica surface or the exchanged cations on the zeolites, the calculations were carried out with the CO bond length of 1.191\AA which was optimized by CNDO/2 method, and was supposed to be consistent even on the interaction with active sites. The interaction energy, ΔE , is determined as the difference between the energy of the complex, (E_{AB}), and the sum of the energies of each isolated molecules, ($E_A + E_B$), in their optimized geometries:

$$\Delta E = E_{AB} - (E_A + E_B) \quad (1)$$

The decationization energies for the exchanged cations located in the zeolites was obtained. And it is defined as the difference between the total energy [of zeolites with and without a cation:

$$E_D = E_{\text{SiAlO}(\text{OH})_6\text{X}} - E_{\text{SiAlO}(\text{OH})_6} \quad (2)$$

3. RESULTS AND DISCUSSION

The schematic diagrams of orthosilicic acid, $\text{Si}(\text{OH})_4$, and each atoms were specified as shown in Fig. 1.

At first, the total energy of the system A was obtained as a function of the O-H bond length with the fixed Si-O bond length and the angle SiOH as 1.61\AA and 137.5° respectively. The most stable state of molecule A was found at the O-H distance of 1.025\AA , slightly longer than the ordinary bond length of 0.96\AA . And then, the angle of SiOH was varied next the fixed O-H bond length as 1.025\AA . The total energy of the system dropped to its lowest value at the angle of 122° , and then rose up again. This value was lower than that of calculated by Takahashi¹⁵ and larger than that of experimentally obtained by Peri.¹⁶

Beran^{6,9,13,17} calculated the electronic structures of faujasite with T-O-H type (where T designates a Si or Al atom) lying on a straight line with the angle of 180° and OH bond length of 1.08\AA . Mortier¹⁸ carried out similar calculations with the OH bond length of 0.96\AA .

The calculation for system B were performed with the values found for the system A. At this time, the dihedral angle defined as the angle between the planes those involve the atomic sets of $\text{O}_3, \text{Si}, \text{O}_2$ and $\text{Si}, \text{O}_2, \text{H}_2$, was varied with the fixed bond length and bond angle of OH and SiOH, 1.025\AA , 122° , respectively. The dihedral angle, ϕ , is always selected within the

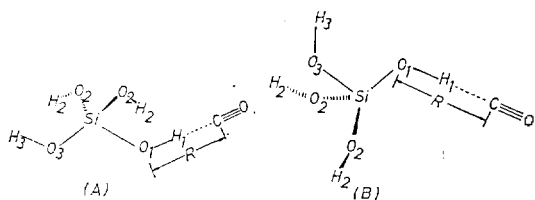


Fig. 1. Schematic diagrams of orthosilicic acid, $\text{Si}(\text{OH})_4$, with their numbering.

limit of $0^\circ < \phi < 180^\circ$. The most optimum angle of the system B was 17° to have the most stable form. The system B was energetically more stable than system A as an extent of ca. 2kcal/mol .

The interaction of CO molecules with the H atom of the hydroxyl group ($\text{O}_1\text{-H}_1$) was investigated for the system A and B. Three types of interaction of CO molecules with the hydroxyl groups are considered: OH-CO, OH-OC and O-CO type interactions. However, semi-empirical calculations did show little interaction of CO molecules with the skeletal oxygen atoms as an example of van der Waals interaction. Consequently, this type of interaction was not included in the calculations.

The interaction energy, ΔE , of CO molecules interacting with H atom of the $\text{A-O}_1\text{-H}_1$ where A represents system A was approximately similar to that of system B. Accordingly, the energies, ΔE , of the OH-CO and OH-OC type interaction of system B were plotted as a function of the distance, $R(\text{O-H}\cdots\text{C or O})$, as shown in Fig. 2.

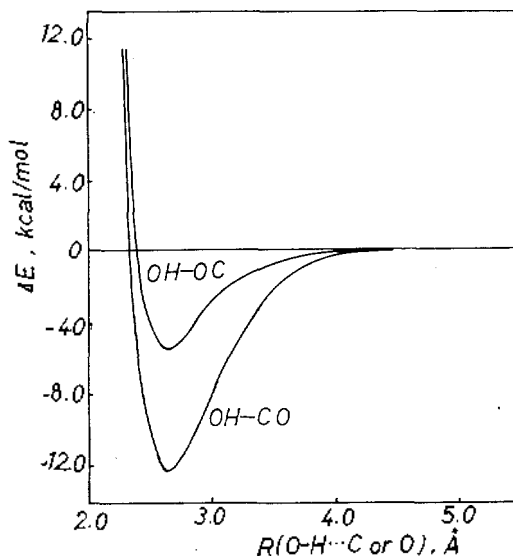


Fig. 2. Plot of the interaction energy, $\Delta E(\text{kcal/mol})$, as a function of the distance, $R(\text{O-H}\cdots\text{C or O})$, between the C(O) atom of CO and the H atom in interactions of CO with the OH groups in orthosilicic acid, $\text{Si}(\text{OH})_4$, (cf. Fig. 1).

Of these two types of interaction investigated for CO molecules with the OH group, the OH-CO type of interaction was energetically about twice more favorable than the interaction of the OH-OC type. These results were in good agreement with the calculated values of CO molecules with hydroxyl groups on H-faujasite.¹⁹ The interaction between CO and hydrogen halides, HX (X=F⁻, Cl⁻, Br⁻) also known as the form of X-H...CO.²⁰ These are consistent with the experimentally determined dipole polarity of carbon monoxide, which is C⁻O⁺, and contrary to what would be expected from electronegativity considerations.^{21,22}

The calculated equilibrium distance of the CO molecules interacting with the hydroxyl groups, R(O-H...C) was 2.64Å for OH-CO, and R(O-H...O) was 2.60Å for OH-OC type interaction. When the CO molecule interacts with OH groups, the OH bond lengthening occurs. The

OH bond lengthened from 1.025Å to 1.053Å for OH-CO type and from 1.025Å to 1.04Å for OH-OC type interaction. And, the most stable molecular location of CO was in the straight line through O-H bond axis either for the OH-CO or the OH-OC type interaction. The electronic structures of system A, B and the state interacting with CO molecules were given in Table 1.

As shown in Table 1, when the CO molecule interacted with OH, the charge densities of O and H atoms on the O₁-H₁ became more negative and positive, respectively. The bond orders²³ of OH interacting with CO molecules decreased. On the contrary, those of neighboring Si-O increased due to the interaction of CO molecules. The bond order of H₁...O for OH-OC type was approximately a half of that for H₁...C, and about same value for the hydrogen bonding (H...O) in dimeric methyl alcohol.²⁴ In the

Table 1. CNDO/2 atomic charges, *q*, bond orders, *p*, equilibrium distances, R(O-H...C(O))^b, and interaction energies, Δ*E*(kcal/mol), for interaction of CO molecules with OH groups in orthosilicic acid, Si(OH)₄, (cf. Fig. 1)

	A	B	CO	AOH-CO	BOH-CO	BOH-OC
<i>q</i> (O ₁)	-0.5106	-0.4989	—	-0.5522	-0.5450	-0.5301
<i>q</i> (O ₂)	-0.5106	-0.5105	—	-0.5137	-0.5123	-0.5110
<i>q</i> (O ₃)	-0.5106	-0.5099	—	-0.5108	-0.5126	-0.5133
<i>q</i> (H ₁)	0.1144	0.1182	—	0.1420	0.1449	0.1466
<i>q</i> (H ₂)	0.1144	0.1113	—	0.1097	0.1095	0.1094
<i>q</i> (H ₃)	0.1144	0.1149	—	0.1093	0.1102	0.1109
<i>q</i> (C)	—	—	0.0779	0.1108	0.1111	0.1050
<i>q</i> (O)	—	—	-0.0779	-0.0567	-0.0569	-0.0785
<i>p</i> (O ₁ -H ₁)	0.9680	0.9692	—	0.8874	0.8887	0.9273
<i>p</i> (O ₂ -H ₂)	0.9680	0.9700	—	0.9691	0.9706	0.9704
<i>p</i> (O ₃ -H ₃)	0.9680	0.9697	—	0.9695	0.9709	0.9707
<i>p</i> (Si-O ₁)	0.8214	0.8419	—	0.8542	0.8676	0.8614
<i>p</i> (Si-O ₂)	0.8214	0.8183	—	0.8126	0.8140	0.8153
<i>p</i> (Si-O ₃)	0.8214	0.8250	—	0.8154	0.8173	0.8184
<i>p</i> (H ₁ -C)	—	—	—	0.0727	0.0730	0.0340
<i>p</i> (C-O)	—	—	2.5766	2.5853	2.5851	2.5501
R(O-H...C(O))	—	—	—	2.64	2.64	2.60
Δ <i>E</i> (kcal/mol)	—	—	—	12.2	12.1	5.2

^a see reference 23. ^b Å unit

OH-CO interaction, the bond orders of CO molecules interacting with hydroxyl groups were higher than that of isolated CO molecules. But in the OH-OC type interaction, they were lower than that of isolated ones. It was attributed to the CO bond strengthening in the OH-CO type interaction due to the transfer of electron from the CO molecule to the hydroxyl group on silica. This transfer leads to localization of a positive charge on the CO molecule. Thus the negative charge densities of O atoms on CO molecule decrease, in the end, the CO molecule come into CO^+ ion. It is assumed that the increased positive charge on the CO molecule will probably cause an increase in its vibrational frequency. This phenomenon will occur more obviously in the change of the CO molecule into the CO^+ ion. On the contrary, in the case of interaction of CO molecules with transition-metal cations the C-O bond weakening occurs resulting from backdonation²⁵ of electrons from the d atomic orbitals of the cation to the π^* MO of the CO molecules.

The bond distances of $\text{O}_1\text{-C}$ and $\text{O}_1\text{-O}$, 2.6\AA , were similar to that of linearly hydrogen bonded water dimer.²⁶

The schematic diagrams of $\text{Si}_2\text{O}(\text{OH})_6$ were used in the CNDO/2 calculation as shown in Fig. 3.

The total energy of system IA was plotted as a function of the SiOSi angle with the fixed Si-O, O-H bond length and the angle SiOH as 1.61\AA , 1.025\AA and 122° respectively. The most stable state was found at $\text{SiOSi}=136.5^\circ$. This value was slightly smaller than both observed²⁷ and calculated one from the ab initio method.²⁸ And then the dihedral angles defined as the angle between the planes those include atomic sets $\text{O}_1, \text{Si}_1, \text{O}_2$, and $\text{Si}_1, \text{O}_2, \text{H}_2$ (and between the planes of the atomic sets $\text{O}_1, \text{Si}_1, \text{O}_2$ and $\text{Si}_2, \text{O}_4, \text{H}_4$) were changed, with the angle $\text{SiOSi} =$

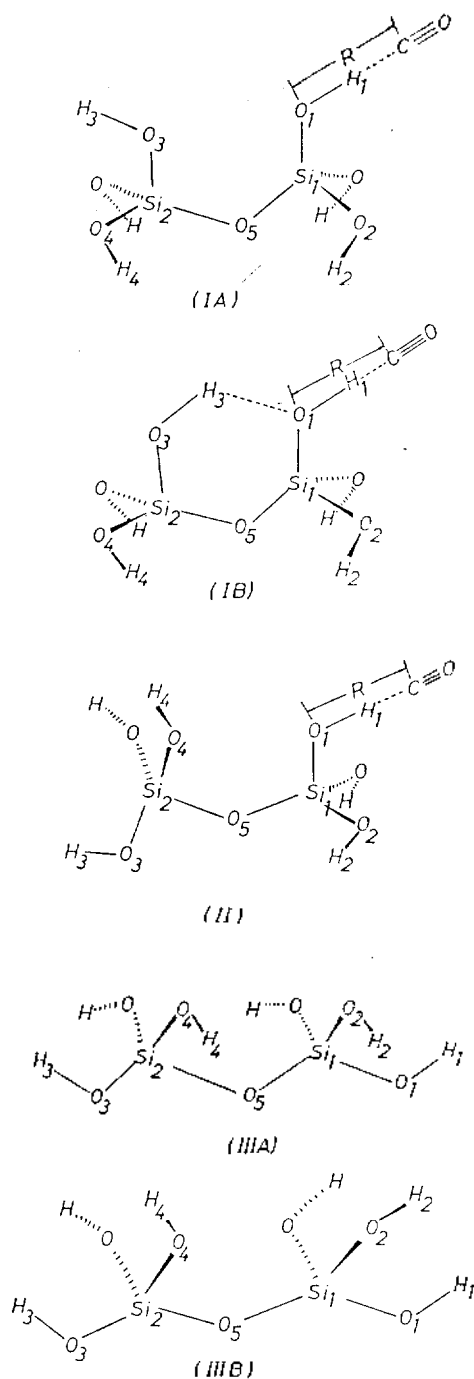


Fig. 3. Schematic diagrams of simplified silica models, $\text{Si}_2\text{O}(\text{OH})_6$, with their numbering.

136.5° , to get the lowest total energy at $168.^\circ$

For the system IB, H_3 atom put to form hy-

drogen bond with O_1 atom, at the most stable state indicated the angle $SiOSi$ also 136.5° . And the dihedral angle between the planes including the atomic sets O_5, Si_1, O_2 and Si_1, O_2, H_2 was 45° , and another dihedral angle between the planes of O_3, Si_2, O_4 and Si_2, O_4, H_4 was 54° at the lowest energy state. The other bond length and angles were not different from those of system IA. The system IIIA was more unstable than the others, therefore, the dihedral angle between the planes of O_1, Si_1, O_2 and O_2, Si_1, H_2 (also between the planes of O_2, Si_4, O_4

and Si_3, O_2, H_4) was 45° at the most stable state.

The physicochemical properties such as charge densities and bond orders etc. of these simplified silica model(system IA~IIIB) were listed in Table 2.

The results of CNDO/2 calculation for $Si_2O(OH)_6$ are generally similar to those of $Si(OH)_4$. The only difference between them is that the former has the siloxane linkage. The negative charge densities of bridging oxygen atoms were larger than those of terminal oxygen atoms. The changes of charge densities of nonneigh-

Table 2. CNDO/2 atomic charges, q , bond orders, p , equilibrium distances, $R(O-H\cdots C(O))$, and interaction energies, $\Delta E(\text{kcal/mol})$, for interaction of CO molecules with OH groups in simplified silica models. $Si_2O(OH)_6$ (cf. Fig. 3)

	IA	IAOH-CO	IB	IBOH-CO	II	IIOH-CO	IIIB
$q(O_1)$	-0.5041	-0.5457	-0.5140	-0.5563	-0.5087	-0.5505	-0.5097
$q(O_2)$	-0.5117	-0.5144	-0.5146	-0.5098	-0.5126	-0.5142	-0.5198
$q(O_3)$	-0.5041	-0.5041	-0.5168	-0.5186	-0.5108	-0.5115	-0.5097
$q(O_4)$	-0.5117	-0.5129	-0.5069	-0.5083	-0.5220	-0.5223	-0.5198
$q(O_5)$	-0.7220	-0.7223	-0.7354	-0.7357	-0.7035	-0.7036	-0.6846
$q(H_1)$	0.1158	0.1445	0.1177	0.1464	0.1187	0.1475	0.1073
$q(H_2)$	0.1068	0.1033	0.1079	0.1042	0.1103	0.1067	0.1064
$q(H_3)$	0.1158	0.1132	0.1288	0.1285	0.1056	0.1037	0.1073
$q(H_4)$	0.1068	0.1054	0.1091	0.1076	0.1044	0.1022	0.1064
$q(Si_1)$	1.5589	1.5408	1.5548	1.5373	1.5708	1.5525	1.5715
$q(Si_2)$	1.5589	1.5570	1.5683	1.5663	1.5622	1.5597	1.5715
$q(C)$	—	0.1116	—	0.1105	—	0.1111	—
$q(O)$	—	-0.0577	—	-0.0561	—	-0.0565	—
$p(O_1-H_1)$	0.9695	0.8891	0.9689	0.8879	0.9687	0.8872	0.9699
$p(O_2-H_2)$	0.9710	0.9721	0.9706	0.9718	0.9702	0.9713	0.9712
$p(O_3-H_3)$	0.9695	0.9702	0.9567	0.9566	0.9706	0.9711	0.9699
$p(O_4-H_4)$	0.9710	0.9713	0.9698	0.9702	0.9718	0.9724	0.9712
$p(Si-O_1)$	0.8270	0.8602	0.8138	0.8474	0.8253	0.8591	0.8111
$p(Si-O_2)$	0.8080	0.8015	0.8083	0.8016	0.8137	0.8071	0.7999
$p(Si-O_5)$	0.8443	0.8335	0.8589	0.8487	0.8272	0.8161	0.8669
$p(Si-O_3)$	0.8270	0.8247	0.8280	0.8264	0.8083	0.8060	0.8111
$p(Si-O_4)$	0.8080	0.8052	0.8148	0.8117	0.7959	0.7935	0.7999
$p(Si_2-O_5)$	0.8443	0.8527	0.8205	0.8299	0.8829	0.8918	0.8669
$p(H_3-O_1)$	—	—	0.0071	0.0074	—	—	—
$p(H-C)$	—	0.0728	—	0.0740	—	0.0736	—
$p(C-O)$	—	2.5845	—	2.5858	—	2.5854	—
$R(O-H\cdots C)$	—	2.64	—	2.64	—	2.64	—
$\Delta E(\text{kcal/mol})$	—	12.2	—	12.3	—	12.4	—

Table 3. CNDO/2 total energies (au.) and dipole moments (Debye) for various types of simplified silica models

Structure	IA	IB	II	IIIA	IIIB	IV ^a
Total energy au.	-138.147	-138.146	-138.147	-138.140	-138.144	-138.107
Dipole Moment (Debye)	2.71	6.24	3.88	2.73	4.24	—

^a See ref. 15.Table 4. CNDO/2 atomic charges, q , bond orders, p , equilibrium distances, $R(O-H\cdots C(O))$, and interaction energies, ΔE (kcal/mol), for interaction of CO molecules with H^+ , Li^+ , and Na^+ cations located in zeolites, $SiAlO(OH)_6X$ ($X=H^+$, Li^+ , and Na^+), (cf. Fig. 5)

	A-H	A-H-CO	A-Li	A-Li-CO	A-Na	A-Na-CO
$q(O_1)$	-0.5335	-0.5324	-0.5316	-0.5349	-0.5325	-0.5337
$q(O_2)$	-0.5251	-0.5271	-0.4997	-0.5020	-0.5134	-0.5142
$q(O_3)$	-0.4728	-0.4731	-0.4823	-0.4864	-0.4844	-0.4859
$q(O_4)$	-0.4964	-0.4992	-0.4944	-0.4969	-0.5067	-0.5077
$q(O_5)$	-0.4871	-0.5507	-0.6769	-0.6620	-0.7244	-0.7208
$q(H_1)$	0.0632	0.0605	0.0534	0.0477	0.0397	0.0380
$q(H_2)$	0.0284	0.0214	0.0355	0.0335	0.0044	0.0056
$q(H_3)$	0.1523	0.1467	0.1240	0.1174	0.1013	0.0994
$q(H_4)$	0.1293	0.1191	0.1024	0.1010	0.0647	0.0659
$q(Al)$	1.2578	1.2607	1.3017	1.3113	1.2807	1.2827
$q(Si)$	1.6064	1.5951	1.5581	1.5633	1.4723	1.4729
$q(X)$	0.1414	0.1791	0.3661	0.0434	0.7494	0.6308
$q(C)$	—	0.0980	—	0.3053	—	0.1381
$q(O(CO))$	—	-0.0123	—	0.0237	—	-0.0208
$p(O_1-H_1)$	0.9724	0.9733	0.9757	0.9765	0.9774	0.9776
$p(O_2-H_2)$	0.9805	0.9806	0.9335	0.9353	0.9558	0.9556
$p(O_3-H_3)$	0.9566	0.9590	0.9676	0.9692	0.9734	0.9738
$p(O_4-H_4)$	0.9660	0.9678	0.9322	0.9332	0.9589	0.9585
$p(Al-O_1)$	0.7748	0.7733	0.7619	0.7520	0.7492	0.7460
$p(Al-O_2)$	0.7484	0.7362	0.6361	0.6331	0.6459	0.6457
$p(Al-O_5)$	0.3204	0.3396	0.4536	0.4597	0.5252	0.5267
$p(Si-O_3)$	0.8906	0.8849	0.8503	0.8410	0.8309	0.8278
$p(Si-O_4)$	0.8528	0.8383	0.7281	0.7263	0.7220	0.7220
$p(Si-O_5)$	0.6303	0.6814	0.9080	0.9162	1.0273	1.0290
$p(O_5-X)$	0.9269	0.8247	0.4040	0.3985	0.1059	0.1049
$p(X-C)$	—	0.0960	—	0.5286	—	0.2130
$p(C-O)$	—	2.6124	—	2.6172	—	2.6143
$R(O_5-X)$	1.05	1.09	2.10	2.13	3.20	3.20
$R(X-C)$	—	1.55	—	2.15	—	3.10
ΔE (kcal/mol)	—	18.3	—	120.6	—	26.5

boring atoms on the atom interacting with CO molecule were trivial. The bond orders of bridging Si-O were also larger than those of terminal Si-O, and the former were very sensitive

to the geometrical structure, especially, to the position of H atoms. They increased with the approaching of H atoms. When the silica interacted with CO molecules, the bond orders were

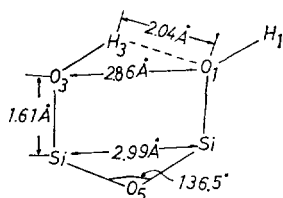


Fig. 4. Intramolecular hydrogen-bonded vicinal OH groups in silica, and their interatomic distances.

alternately changed, *i. e.*, the order of bond connecting with atom which interacted with CO molecules decreased, and that of the next bond increased, etc. The bond order, $\rho(O_1-H_3)$, for intramolecular hydrogen bonding was approximately equivalent to only one-tenth that of $H_1 \cdots C$ for OH-CO type interaction. It was seemed to be ascribed to a long distance of $H_3 \cdots O_1$ as 2.04 Å (*cf.* Fig. 4). This intramolecular hydrogen bonding facilitates the interaction of CO molecules with hydroxyl group (O_1-H_1).

The total energies and dipole moments for various types of $Si_2O(OH)_6$ are listed in Table 3.

The structure of system IV are very similar to that of system IB. It was the most stable state considered in ref 15. Although the formation of intrahydrogen bond in system IB, the total energy of system IB was negatively smaller than that of scheme IA. This was seemed to be ascribed to the larger polarity of system IB.

The schematic diagrams of the cation exchange aluminosilicates, $SiAlO(OH)_6X$, (where X is H^+ , Li^+ or Na^+) were used in the CNDO/2 calculations as shown in Fig. 5.

In this calculations, first, putting that X for H with fixed $O_5 \cdots X$ bond length as 1.10 Å, the bond lengths of OH connecting with Al atom were varied with fixed angle of $SiOAl$ and $AlOH$ to 136.5° , 122° respectively. consequently, the lowest total energy of the system was obtained at the $OH=1.035 \text{ \AA}$. Next, the angle $SiOAl$ was changed until the lowest total energy was obtained. Therefore, the most stable state was

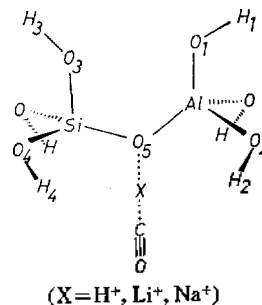


Fig. 5. Schematic diagrams of the cation exchanged aluminosilicates, $SiAlO(OH)_6X$ ($X=H^+$, Li^+ and Na^+).

at the angle $SiOAl=160^\circ$. This angle was less variable against the type of X and the interaction of CO molecules with the cations. And the other bond lengths and angles were used in the case of $Si_2O(OH)_6$. The bond lengths of O_5-X at the most stable state were 1.05, 2.10, and 3.20 Å for H^+ , Li^+ , and Na^+ respectively. CNDO/2 calculations were also performed for the interaction of CO molecules with the cations on the zeolites. These results are given in Table 4.

As shown in Table 4, the negative charge densities of the O atoms connecting with Al atom were larger than those of connecting with Si atom, and they were slightly varied by introducing the cations. The negative charge densities of bridging oxygen atom (O_5) in these system were generally smaller than those in $Si_2O(OH)_6$ system. And they increased in the order $H^+ < Li^+ < Na^+$; *i. e.*, they increased with decreasing electronegativity of the cation. The positive charge densities of H atoms on the hydroxyl groups connected to Al atom were near-zero. This is due to the difference of electronegativity between Al and Si atoms. The positive charge densities of the cation located on the skeleton increased in the order $H^+ < Li^+ < Na^+$. In all case, the bond strengths of Si-O were stronger than those of Al-O, since the mass of Al and Si were nearly the same, these

were ascribed to the longer bond length of Al-O and the smaller electronegativity of Al. The bond strengths of skeletal T-O (where T represents Si or Al atom) were weaker than those of terminal T-O. The formers had been greatly influenced by introducing cations. The effects of cations to the strengths of T-O was as the decreasing order of $H^+ > Li^+ > Na^+$. On the other hand, the strength of O_3-X decreased in the order: $H^+ > Li^+ > Na^+$. But also, the difference of Al-O bond strengths between Al-O₅ and Al-O₁ decreased in the order: $H^+ > Li^+ > Na^+$. It is possible to pre-estimate the frequency shifts of Al-O vibrations for the cation exchanged zeolites.

These trends were not particularly influenced by interaction of CO molecules with the cations on the skeleton. However, the changes due to interaction of CO molecule with the cations were fairly large in charge densities of cation and CO molecule. The extent of change was in the decreasing order of $Li^+ > Na^+ > H^+$. This trend was similar to those of bond orders of X-C and C-O. When the CO molecule interacted with Li cation-zeolite, eventually CO molecule partly ionized. Therefore, the vibrational frequency of CO molecule will be shifted to higher frequency than that of isolated one. Although the bond distance, $R(X-C)$, increased in the order $H^+ < Li^+ < Na^+$, the interaction energy of CO molecule with the cations increased in the order $H^+ < Na^+ < Li^+$. The interaction energy, ΔE , was plotted as a function of the distance, $R(X-C)$, between the C atom of CO and the cations, and it was as shown in Fig. 6.

In the interaction of CO molecules with the cations in the zeolites, especially, when the Li^+ cation is introduced into the skeletal oxygen atoms of zeolite, since it has a smaller size and larger electrostatic field than those of Na^+ cation, it will be more advantageous to be placed in

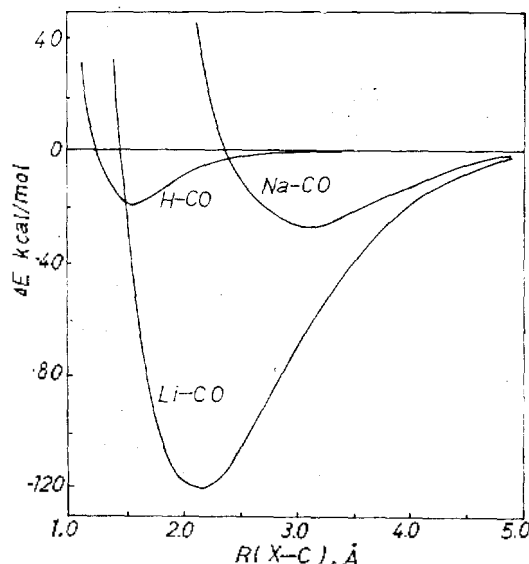


Fig. 6. Plot of the CNDO/2 interaction energies, ΔE (kcal/mol), as a function of the distance, $R(X-C)$, between the skeletal oxygen atom and the H^+ , Li^+ , and Na^+ cations in zeolites.

the oxygen cavity. (cf. Fig. 7).

Because the coordination number of Al is higher than its valence, the $[AlO_4]^-$ tetrahedron unit has a negative charge which is not concentrated at any single point on the periphery of the complex anion but distributed along its inner bond O-Al,²⁹ while the compensating positive charge is concentrated in the exchanged cations which usually have a much smaller radius. Accordingly, the Li^+ cation interacts with also many other atoms in the zeolites. As shown in Fig. 7 the Li^+ cation interacted with four oxygen atoms (O_2, O_3), and each interaction was approximately same and the interaction with CO was stronger than the that of the OH-CO type. It seems as if the Li^+ cation is located on the entrance to a cavity of 5.4 Å in diameter (cf. Fig. 7b).

The decationization energies were obtained in order to investigate the stabilities of the exchanged cations located on the skeleton, and they

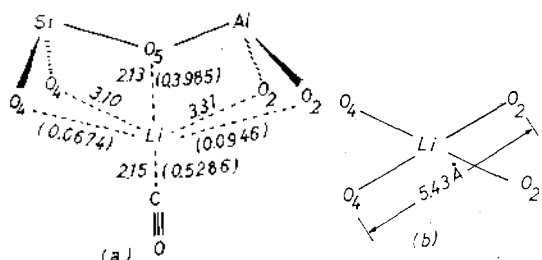


Fig. 7. Schematic diagram for interaction of Li^+ cation with the oxygen atoms in the zeolites: (a) bond orders between the Li^+ cation and oxygen atoms (bond distance); (b) bond distance.

Table 5. CNDO/2 decationization energies, E_D (kcal/mol), bond orders, $p(\text{O}_5\text{-X})$, between the cations and the skeletal oxygen atom, and charges on the cations, $q(\text{X})$, calculated for zeolites, $\text{SiAlO}(\text{OH})_6\text{X}$ ($\text{X}=\text{H}^+$, Li^+ , and Na^+).

	Cation type		
	H^+	Li^+	Na^+
E_D (kcal/mol)	449	281	122
$p(\text{O}_5\text{-X})$	0.9269	0.4040	0.1059
$q(\text{X})$	0.1414	0.3661	0.7494

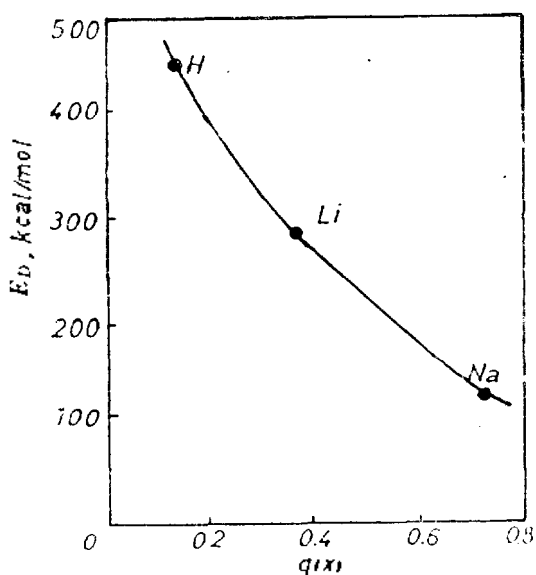


Fig. 8. Correlation between the decationization energies of the exchanged cations in the zeolites and the charges on the cations.

are given in Table 5.

The correlation between the cation charge and decationization energies of the exchanged cations were depicted in Fig. 8. These energies decreased in the order $\text{H}^+ > \text{Li}^+ > \text{Na}^+$. Thus these energies depended on the amount of charge density transferred from the skeleton to the cations compensating its negative charge.

4. CONCLUSIONS

From the above results, it was found that the interaction energy of CO molecules with the hydroxyl groups on silica was ca. 12 kcal/mol, and the bond distance, $R(\text{O}-\text{H}\cdots\text{C})$, was 2.64 Å. The bond distances between CO molecule and the various cations in the zeolites were in the following order: $\text{H}^+ < \text{Li}^+ < \text{Na}^+$. And their bond strengths between them were in the decreasing order: $\text{Li}^+ > \text{Na}^+ > \text{H}^+$, and increased with increasing electrostatic field of the cations. The bond orders of CO molecules interacting with either the OH groups on the silica or the cations in the zeolites increased but for the OH-OC type interaction. This phenomenon is due to the electron transfer from the CO molecule to OH groups or to the cations. The decationization energies of the exchanged cations in the zeolites decreased in the order: $\text{H}^+ > \text{Li}^+ > \text{Na}^+$, and these energies depended on the amount of charge density transferred from the skeleton to the cations in order to compensate its negative charge.

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