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QUANTUM CHEMICAL CONSIDERATION OF CO ADSORPTION OVER CATION EXCHANGED FAUJASITE

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Abstract—CNDO/2 calculation for atomic charges, Wiberg bond orders and adsorption energies of CO molecules on the cluster model whose Si/Al ratio varied were carried out.

The data for the normal cluster and dealuminated cluster were compared. Decationization energies of the cations increased with the charge densities of cation and number of aluminum involved. Adsorption process of CO on the monovalent cations such as H^+, Li^+, Na^+ and divalent cations, Be^{2+}, Ca^{2+}, and Mg^{2+} was supposed to be occurring by the donation of non-bonded electrons from CO. The decationization energies of cations obviously decreased by the dealumination process. Adsorption energies of CO on the cations generally decreased as the dealumination took place except the case of H^+ and Na^+.

INTRODUCTION

In order to have a better understanding of the modification made by the dealumination on the catalytic activities and the adsorption capacities of X and Y zeolites, CNDO/2 calculations, recently, have been made on a cluster model representing the faujasite structure [1-3]. An attempt to rationalize the acid attack mechanism of dealumination in the cation exchanging reaction of faujasite was made [4]. The calculated net charges of cations located on the mineral, interaction energies and bond orders of the atoms within the structure gave us a good information to understand the mechanism of adsorption of gases on zeolites.

The influence of Si/Al ratio on the acidity and site selectivity of cations in faujasite-type zeolite was explained by using calculated atomic net charges and cation-bonding energies [5]. The distribution of cations in model compounds is determined by calculating the binding energies for several possible cation arrangement.

Using the assumption of complete ionicity, Madelung potentials for the monovalent and divalent cations in ordered models of X and Y faujasites have been calculated. And results of the calculations for monovalent zeolites agreed well with ionic distributions found from X-ray studies [6]. And it was found also that site I is filled first to 100% occupancy and site II is filled next, to the extent of ions are available.

It is suggested that the role of electronegativities of the cations or of the T atoms in the zeolite structure is most important for the intensity of pyrole adsorption on zeolites [7].

Five adsorption models of CO on the cations supported on materials such as silica and alumina were suggested [8]. And a linear structure model with a double bond between the cation and carbon was proposed as one of the most favourable structure. An experimental facts show that adsorbed CO molecules stand perpendicularly to the transition metal surface with C in direct contact to the metal [9].

This work was carried out in order to obtain geometric structure and atomic charges of cations and stabilities of the faujasite and to understand the effect of dealumination of faujasite on the adsorption behaviours of CO.

EXPERIMENTAL AND CALCULATION

CNDO/2 calculations have been made on a small atomic cluster, $T_6O_6(OH)_6$ model, representing portions of the Faujasite structure [1-5]. The CNDO/2 program and COORD program employed here were QCPE No. 261 and No. 226, respectively. All the quantum-chemical calculations were accomplished taking into account only the orbitals lower in energy than 3d, i.e., the sp basis. Convergence limits on the electronic energies were set equal to 1×10^{-6} a.u. As a result of Loewensteins rule, the first coordination sphere of

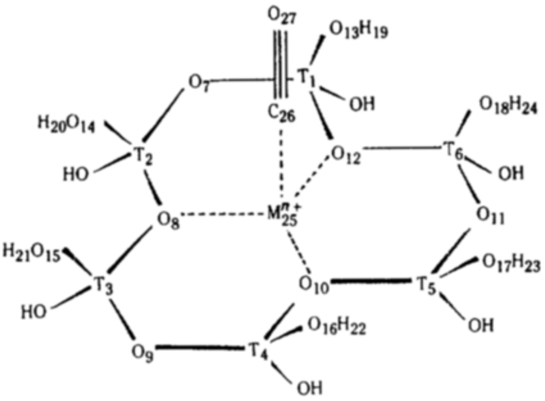

Fig. 1. Atomic arrangement of zeolite cluster model and carbon monoxide adsorbed, Al locations according to the Si/Al ratio are T_2, T_4, T_6 for 1 (Si/Al), T_3, T_6 for 2 and T_6 for 5.

aluminum atoms are composed entirely of silicon atoms. Bond lengths of Si-O, Al-O and O-H for cluster geometry, 1.61A, 1.75A, 1.025A for Si-OH, 1.035A for Al-OH respectively taken from the X-ray data [10], were applied. X-ray data of 109.5 for the bond angle of O-T-O was also used.

In order to simulate the cations localized in the S_{II} and $S_{I'}$, cationic positions of zeolite cavities, cations were positioned in somewhere about the center of the cluster to meet most stable energy state. The presence of one M^{n+} ion per unit cluster has no substantial effects on the perfect charge saturation within the skeleton. All the calculations were done only taking into account of the orbitals up to 3d. The calculation provided results is qualitatively identical with those previously reported [4].

The decationization energies, E_d, were obtained from the difference between two total energies with and without cations.

$$E_d = E[T_6O_6(OH)_6M]-E[T_6O_6(OH)_6^{\,n-}]$$

Adsorption energies, E_{ad}, of CO on cation supported cluster were calculated from the equation.

$$E_{ad} = E[T_6O_6(OH)_6M\text{-}CO]-E[T_6O_6(OH)_6M]\text{-}E(CO)$$

RESULT AND DISCUSSION

The bond length of the cation to the closest oxygen located along three fold axes in the plane of the 6-oxygen ring varied according to the size of the cations. Medium size cations such as Li^+, Be^{2+}, Mg^{2+} located almost in the center of the plane whereas small cation such as H^+ shifted toward the O_{12} to satisfy most favourable energy state. Large size cations, Ca^{2+} and Na^+, localized in the position lifted above the oxygen plane to meet good agreement with the X-ray data [11,12]. Interaction energies of cations, illustrated in terms of decationization energies in Table 2, depended primarily on the charge densities of the cation and number of aluminum involved. This is simply attributed to the Coulomb interaction between the cations and the charge deficient cluster.

Table 1. Bond length of cation-oxygen of zeolite, cluster, $T_6O_6(OH)_6M$

Cation	Si/Al	R(M-O_8)	R(M-O_{10})	R(M-O_{12})
H^+	1	2.66	2.61	1.03
	2	2.44	2.63	1.03
	5	2.68	2.76	1.03
Li^+	1	2.14	1.99	1.98
	2	1.98	2.02	1.98
	5	2.10	2.16	1.98
Na^+	1	2.81	2.81	2.81
	2	2.78	2.81	2.81
	5	2.72	2.83	2.81
Be^{2+}	1	2.17	2.03	1.91
	2	2.00	2.06	1.91
	5	2.14	2.20	1.91
Mg^{2+}	1	2.14	1.99	1.98
	2	1.98	2.02	1.98
	5	2.07	2.16	1.98
Ca^{2+}	1	2.81	2.81	2.83
	2	2.78	2.82	2.83
	5	2.72	2.83	2.83
Co^{2+}	1	2.30	2.30	2.30
	2	2.00	2.11	2.12
	5	—	—	—

Table 2. Decationization energies of cations, ΔE_D (kcal/mol), on the zeolite cluster

Si/Al	H^+	Li^+	Na^+	Be^{2+}	Mg^{2+}	Ca^{2+}	Co^{2+}
1	601	491	261	1217	377	169	2749
2	510	402	173	1050	345	154	704
5	446	320	121	873	295	131	—

Charges of cations in the cluster is shown in Table 3 are significantly different from the expected formal charges due to the charge transfer from the skeleton. Charge transfer, the difference from 0.0779 for carbon and -0.0779 for oxygen of isolated CO molecule, created on the process of bond formation with cation increased with the number of aluminum in the cluster and the charge densities of the cation. An attempt has

Table 3. Charges of cations, q(M), on the zeolite cluster

Si/Al	H^+	Li^+	Na^+	Be^{2+}	Mg^{2+}	Ca^{2+}	Co^{2+}
1	0.1240	0.1562	0.4156	0.3919	0.8921	1.3987	2.2083
2	0.1301	0.1703	0.4667	0.4356	0.9209	1.4943	2.4198
5	0.1429	0.1928	0.4760	0.5009	0.9610	1.5053	—

Table 4. Atomic charge of exchanged cation and carbon monoxide

Si/Al = 1	(Z) — M	(Z) —— M	—— C	—— O
H^+	0.1240	0.2373	0.0983	-0.0637
Li^+	0.1562	-0.1460	0.3740	-0.1056
Na^+	0.4156	0.3158	0.2014	-0.1032
Be^{2+}	0.3999	0.1210	0.3792	0.0262
Mg^{2+}	0.8921	0.7973	0.2023	-0.0136
Ca^{2+}	1.3987	1.4081	0.1024	-0.0689
Co^{2+}	2.2083	2.2138	0.0364	-0.0364
Si/Al = 2	**(Z) — M**	**(Z) —— M**	**—— C**	**—— O**
H^+	0.1301	0.2594	0.0784	-0.0243
Li^+	0.1703	-0.1397	0.2574	0.0150
Na^+	0.4677	0.3613	0.1244	-0.0167
Be^{2+}	0.4356	0.1396	0.3819	0.0361
Mg^{2+}	0.9209	0.8011	0.1698	0.0222
Ca^{2+}	1.4943	1.4527	0.0880	-0.0480
Co^{2+}	2.4198	2.4452	0.0182	-0.0181
Si/Al = 5	**(Z) — M**	**(Z) —— M**	**—— C**	**—— O**
H^+	0.1429	0.2339	0.0152	-0.0169
Li^+	0.1928	-0.1162	0.3394	0.0386
Na^+	0.4760	0.3064	0.1679	-0.0102
Be^{2+}	0.5009	0.3254	0.3734	0.0824
Mg^{2+}	0.9610	0.9070	0.1649	0.0511
Ca^{2+}	1.5053	1.4598	0.1045	-0.0278
Co^{2+}	—	—	—	—

been made to relate the calculated partial charges transferred from the cluster to the protons and decationization energies of the cations.

Decationization energy generally increased along with the charges transferred from the cluster to the cations. Although the increasing rate of monovalent cations was not same as that of divalent cations.

Decationization energies is considered to be a measure of the electron acceptor ability for the nontransition metal cation but the case of Co^{2+} indicated a possibility of d-π^* back donation lowering positive charge of carbon and promoting C-O bond order as well.

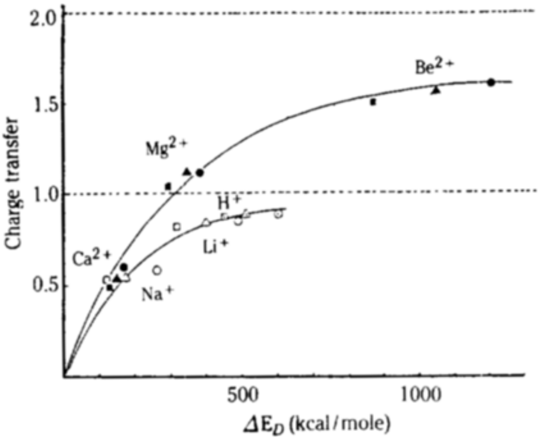

Fig. 2. Decationization energies (kcal/mole) of the cations and charge transferred from the cluster.

Circle, triangle and square indicate 1, 2, 5 of Si/Al ratio respectively.

The bond order between carbon and oxygen in Table 5 to represent the intensities of CO adsorption increased after the adsorption process took place as much as the difference from 2.5766 of isolated CO molecule. Correlation between the vibrational frequencies, ν_1 of CO interacting with the cations of zeolites and the Wiberg bond orders calculated for the corresponding interaction complexes of CO were reported [13-15]. Nevertheless, it is clear that neither the increase in CO bond order nor the stretching vibration bond force constant of CO is directly related with the intensities of adsorption.

The adsorption energies in Table 6 and the bond order increase of CO adsorbed on monovalent and divalent cations in Table 5 can be hardly explained by Clark's back donation theory [8]. CO molecule adsorbed on those cations are able to donate the lone pair on carbon to the vacant orbitals of cations and back donate electrons from filled d or p orbitals of cations to the vacant antibonding π^* orbitals on CO to promote the C-O bond order. However, the C-O bond order increase due to back donation from those, mono and divalent cations, particularly, H^+, Li^+ and Be^{2+}, are impossible. On the other hand, it thus seems highly probable that the donation of nonbonded pairs of

Table 5. Wiberg bond order, M-O, M-C and C-O

		Si/Al = 1				Si/Al = 2				Si/Al = 5			
		Z — M	Z —— M	—— C	—— O	Z — M	Z —— M	—— C	—— O	Z — M	Z —— M	—— C	—— O
H^+	(O_{12}^-)	0.9539	0.8204	0.0794	2.5999	0.9458	0.8142	0.0819	2.6124	0.9396	0.8399	0.0864	2.6157
Li^+	(O_8^-)	0.3941	0.2769			0.4284	0.3737			0.3023	0.2546		
	(O_{10}^-)	0.4135	0.3767			0.3124	0.2851			0.2891	0.2598		
	(O_{12}^-)	0.4210	0.3850	0.4306	2.6032	0.4229	0.3631	0.4339	2.6132	0.4164	0.3762	0.4784	2.6165
Na^+	(O_8^-)	0.1254	0.1278			0.1203	0.1181			0.0840	0.0831		
	(O_{10}^-)	0.1250	0.1273			0.0853	0.0818			0.1068	0.1066		
	(O_{12}^-)	0.1265	0.1287	0.1794	2.6078	0.1174	0.1150	0.1956	2.6144	0.1388	0.1337	0.2123	2.6157
Be^{2+}	(O_8^-)	0.4601	0.4089			0.7948	0.6866			0.5097	0.4339		
	(O_{10}^-)	0.7882	0.6750			0.4466	0.3945	0.4739	0.2841				
	(O_{12}^-)	0.8080	0.6889	0.6853	2.6020	0.7849	0.6778	0.6908	2.6151	0.9014	0.8122	0.7285	2.6285
Mg^{2+}	(O_8^-)	0.3998	0.3295			0.4057	0.3664			0.2975	0.2636		
	(O_{10}^-)	0.4006	0.3291			0.3167	0.2942			0.2977	0.2732		
	(O_{12}^-)	0 4010	0.3287	0.3088	2.6478	0.3960	0.3575	0.3111	2.6764	0.4338	0.4071	0.3528	2.6875
Ca^{2+}	(O_8^-)	0.0925	0.0901			0.0843	0.0873			0.0597	0.0595		
	(O_{10}^-)	0.0919	0.0894			0.0559	0.0541			0.0556	0.0554		
	(O_{12}^-)	0.0928	0.0908	0.0635	2.6274	0.0806	0.0833	0.0757	2.6314	0.0908	0.0906	0.0879	2.6387
Co^{2+}	(O_8^-)	0.3030	0.3096			0.2863	0.2884			—	—		
	(O_{10}^-)	0.3028	0.3094			0.1827	0.1827			—	—		
	(O_{12}^-)	0.3027	0.3092	0.0001	2.6101	0.2291	0.2221	0.0001	2.6239	—	—	—	—

Table 6. Adsorption energies, ΔE_{ad} (kcal/mol), of CO on the cation in the zeolite cluster

Si/Al	H^+	Li^+	Na^+	Be^{2+}	Mg^{2+}	Ca^{2+}	Co^{2+}
1	18.5	92.6	18.5	195.1	183.3	23.0	0.00
2	21.1	96.7	24.8	199.0	191.0	28.1	-7.15
5	24.4	123.6	28.9	207.0	196.0	33.4	—

Table 7. Bond length (Å) of cation-oxygen in the dealuminated Z-cluster

Cation	(Si:Al)	R(M-O_8)	R(M-O_{10})	R(M-O_{12})
H^+	3:2	1.03	2.55	2.71
	4:1	1.03	2.64	2.44
	5:0	1.03	2.59	2.74
Li^+	3:2	1.98	1.99	2.10
	4:1	1.99	1.96	2.07
	5:0	1.98	2.09	2.14
Na^+	3:2	2.81	2.97	2.77
	4:1	2.81	2.93	2.52
	5:0	2.81	2.96	2.77
Be^{2+}	3:2	1.91	2.12	2.17
	4:1	1.90	1.98	2.12
	5:0	1.90	2.10	2.06
Mg^{2+}	3:2	1.98	2.05	2.02
	4:1	1.99	2.04	1.98
	5:0	2.02	2.07	2.11
Ca^{2+}	3:2	2.83	3.06	2.75
	4:1	2.83	3.02	2.49
	5:0	2.83	3.09	2.74

electron from the carbon to cations and oxygen to carbon possibly exert a synergistic induction effect enhancing each other. This is supported by the charge increase on oxygen in due course of the adsorption process. Bonding between the cations and the cluster became weakened for the sake of the new bond formation, M-C, on the process of CO adsorption. It was reported that the most of the bonding between metal clusters and atoms of adsorbed CO is primarily sp character and d-π^* back donation is generally small [16].

The electron acceptor abilities of these cation zeolites exhibit the following trend: H^+->Na^+->Ca^{2+}->Li^+->Mg^{2+}->Be^{2+}-. The binding energies of cations decreased with a decrease of aluminum content to meet well consistence with the work of others [5].

Adsorption energies of CO increased with charge densities of cation with the exception such as transition metal cation. And the energies decreased with the cluster in which aluminum amount increased. CNDO/2 calculation was also carried out for the dealuminated system with the cluster as shown in Fig. 1 except eliminating one AlO_2 in the position of T_6. Bond lengths of

Table 8. Cation localization and total energies of dealuminated Z-cluster

Cation	(Si:Al)	R(M-O_8)	θ(T-O-M)	Et.(A.U.)	R^o(M-O_8)*
H^+	3:2	1.03	117.85	-312.62	2.66
	4:1	1.03	117.75	-314.35	2.44
	5:0	1.03	117.85	-315.93	2.68
Li^+	3:2	1.98	112.75	-312.41	2.14
	4:1	1.99	120.65	-314.11	1.98
	5:0	1.98	113.85	-315.74	2.10
Na^+	3:2	2.81	99.17	-312.04	2.81
	4:1	2.81	101.17	-313.72	2.78
	5:0	2.81	98.17	-315.37	2.72
Be^{2+}	3:2	1.90	110.25	-313.43	2.17
	4:1	1.90	121.75	-315.01	2.00
	5:0	1.91	113.75	-316.42	2.14
Mg^{2+}	3:2	1.98	110.25	-312.05	2.14
	4:1	1.99	117.75	-313.59	1.98
	5:0	2.02	113.75	-315.17	2.07
Ca^{2+}	3:2	2.83	97.17	-310.90	2.81
	4:1	2.83	99.17	-312.23	2.78
	5:0	2.83	95.17	-313.84	2.72

*R^o(M-O_8); M-O_8 Bond length of non-dealuminated Z.

Table 9. Bond length of M-C and CO and total energy of dealuminated Z-cluster

Cation	Si:Al	M-C	C-O	Energy(a.u.)
H^+	3:2	1.509	1.190	-337.72
	4:1	1.501	1.189	-339.45
	5:0	1.492	1.188	-341.01
Li^+	3:2	2.143	1.189	-337.58
	4:1	2.119	1.189	-339.28
	5:0	2.106	1.188	-340.92
Na^+	3:2	3.116	1.189	-337.14
	4:1	3.099	1.189	-338.82
	5:0	3.080	1.189	-340.48
Be^{2+}	3:2	1.846	1.186	-338.75
	4:1	1.837	1.186	-340.32
	5:0	1.820	1.184	-341.77
Mg^{2+}	3:2	2.510	1.183	-337.14
	4:1	2.507	1.182	-338.68
	5:0	2.493	1.180	-340.26
Ca^{2+}	3:2	4.312	1.189	-335.96
	4:1	4.296	1.187	-337.29
	5:0	4.276	1.186	-338.91

cation-oxygen in the dealuminated cluster are not significantly different from those of normal cluster. The dealumination process ultimately shifted the location of the cations closely toward the oxygen. O_8 instead of O_{12}. The bond angle of T_6-O_8-M in the Table 8 illustrates that Na^+ and Ca^{2+} ions are slightly lifted above the plane similarly and the rest of the cations are on the plane. The dealumination effects on the adsorption energies of CO, bond lengths of M-C and bond length of C-O are significant. The atomic charges of cations on the cluster as listed in the Table 10 increased more than those of normal cluster due to the elimination of aluminum. In order to have better understanding of this charge increase, it is necessary to consider the electron induction and transfer processes in the cation-zeolite interaction which is bothered by the decrease in charge difficiency. And the dealumination enhanced less the donation of electron pairs from CO proportionally. These have suggested that the frame work bonding of cation-cluster interaction and adsorption process are more covalent through out the entire molecule than had been assumed in ion to ion or atom to atom interaction.

Table 10. Atomic charge of exchanged cation and carbon monoxide on dealuminated cluster

Si/Al = 3:2	(Z) — M	(Z)——M——C——O		
H^+	0.1606	0.2363	0.0405	-0.0930
Li^+	-0.0088	-0.1233	0.1994	-0.0027
Na^+	0.4977	0.3945	0.1018	0.0027
Be^{2+}	0.4767	0.2857	0.2907	0.0091
Mg^{2+}	0.9684	0.8962	0.1402	0.0079
Ca^{2+}	1.4586	1.4138	0.1166	-0.0699
Si/Al = 4:1	(Z) — M	(Z)——M——C——O		
H^+	0.1664	0.2445	0.0853	-0.1347
Li^+	0.0301	-0.0927	0.2445	-0.0587
Na^+	0.5198	0.4037	0.1856	-0.0672
Be^{2+}	0.5103	0.3315	0.2152	0.0827
Mg^{2+}	1.0058	0.9354	0.1038	0.0423
Ca^{2+}	1.4958	1.4444	0.0288	0.0249
Si/Al = 5:0	(Z) — M	(Z)——M——C——O		
H^+	0.2002	0.2794	0.0728	-0.1084
Li^+	0.0922	-0.0513	0.2221	-0.0132
Na^+	0.5567	0.4253	0.1110	0.0210
Ba^{2+}	0.5926	0.3952	0.2097	0.1254
Mg^{2+}	1.0672	0.9918	0.0836	0.0802
Ca^{2+}	1.5352	1.4710	0.0241	0.0408

Comparing bond orders of Z-M in Table 11 and the data in Table 5, the interaction of cations with the dealuminated zeolites are slightly less favourable because of lowering in charge deficiency. The increas-

Table 11. Wiberg bond order, M-O, M-C and C-O on dealuminated cluster

		Si/Al = 3:2				Si/Al = 4:1				Si/Al = 5:0			
		Z — M	Z——M——C——O			Z — M	Z——M——C——O			Z — M	Z——M——C——O		
H^+	(O_8^-)	0.9388	0.8497	0.0637	2.4142	0.9358	0.8389	0.0692	2.3875	0.9264	0.8052	0.0878	2.4157
Li^+	(O_8^-)	0.4517	0.3966			0.4253	0.3912			0.3516	0.3197		
	(O_{10}^-)	0.4070	0.3358	0.3546	2.5743	0.3485	0.2851	0.3622	2.5231	0.3284	0.2721	0.3879	2.5608
	(O_{12}^-)	0.2907	0.2472			0.3003	0.2478			0.3084	0.2586		
Na^+	(O_8^-)	0.1339	0.1328			0.1293	0.1293			0.0918	0.0924		
	(O_{10}^-)	0.1058	0.1032	0.1901	2.6315	0.0788	0.0780	0.2139	2.5820	0.0839	0.0843	0.2364	2.6442
	(O_{12}^-)	0.0911	0.0910			0.1106	0.1095			0.0987	0.0982		
Be^{2+}	(O_8^-)	0.8057	0.7295			0.8407	0.7563			0.7276	0.6464		
	(O_{10}^-)	0.6784	0.5539	0.6245	2.5249	0.6263	0.4837	0.6285	2.5588	0.6157	0.4692	0.6686	2.5904
	(O_{12}^-)	0.5220	0.4110			0.4834	0.3716			0.5248	0.4102		
Mg^{2+}	(O_8^-)	0.3937	0.3810			0.4169	0.3922			0.3464	0.3031		
	(O_{10}^-)	0.3790	0.3416	0.2463	2.6204	0.2956	0.2627	0.2513	2.6400	0.3502	0.2858	0.2776	2.6652
	(O_{12}^-)	0.2766	0.2446			0.2950	0.2560			0.2924	0.2607		
Ca^{2+}	(O_8^-)	0.1056	0.1050			0.0968	0.0971			0.0718	0.0719		
	(O_{10}^-)	0.0909	0.0903	0.0875	2.5841	0.0649	0.0674	0.1000	2.6520	0.0685	0.0685	0.1200	2.6630
	(O_{12}^-)	0.0704	0.0699			0.0772	0.0764			0.0771	0.0768		

Table 12. Adsorption energy of CO with cation on dealuminated zeolite (kcal/mol)

Cation / Si:Al	H^+	Li^+	Na^+	Be^{2+}	Mg^{2+}	Ca^{2+}
3:2	28.10	71.82	22.58	169.49	23.08	1.82
4:1	26.28	74.96	27.10	161.02	19.07	3.45
5:0	24.15	80.04	31.36	176.33	25.53	8.78

ing tendency of M-C and C-O bond order along with Si/Al ratio for the dealuminated cluster are not essentially different from those of normal cluster. The adsorption energies of CO on H^+- and Na^+-dealuminated cluster increased than the case of normal cluster but decreased on the rest of the cations-dealuminated system.

CONCLUSION

The interaction of cations with the zeolites and carbon monoxide, particularly in the case of non-transition metal cation, depend primarily on the charge densities of the cation and the number of aluminum involved in the zeolite cluster. The electron acceptabilities of the cation zeolites exhibit the following trend, $H^+ > Na^+ > Ca^{2+} > Li^+ > Mg^{2+} > Be^{2+}$. The dealumination enhanced CO less donation of electron pairs. The adsorption energies of CO on the H^+- and Na^+-dealuminated cluster turned out to be more than the case of equivalent cation supported normal cluster. Likewise, the adsorption energies of CO on the Li^+- and Be^{2+}-dealuminated cluster were less than the case of normal cluster.

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