tion was washed with $CHCl_3$ and ether. The aqueous layer was evaporated. The unblocked material was passed through a Sephadex G-15 and was chromatographed on DEAE-Sephadex A-25. The Column was eluted with TEAB buffer (pH 7.5, linear gradient 0.001-1.0 M). Analytical details are given in Table 1.

Enzymatic hydrolysis. 0.025 M Tris-HCl buffer (pH 7.0, 0.2 m*l*) and solution of nuclease Pl (3.5 μg) in the same buffer (0.02 m*l*) were added to a solution of the diastereomer (0.2 mg) in water (0.01 m*l*). The resulting solution was maintained for 2 h at 37℃. The products were analyzed by reversed-phase HPLC (gradient II).

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Theoretical Study of the Cobalt Substituting Site in the Framework of $AlPO_4$-5 Molecular Sieves

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In order to determine the cobalt substituting site in $AlPO_4$-5 framework, ASED-MO theory has been used. The substitution of cobalt for aluminum is energetically more favorable than that for phasphorous. The stabilized energy of the former is 51 eV lower than that of the latter. The calculated net charge was +1.27 for Al, +0.85 for P, and +1.56 for Co, respectively. The valence electron population (VEP), reduced overlap population (ROP) and net charge for the charged cluster models were compared for $AlPO_4$-5 and $CoAlPO_4$-5 systems. Then, twe find that the covalency of P-O bond was greater than that of Al-O bond.

Introduction

The crystalline molecular sieves having porous frameworks of zeolite type ($A^{III}B^{V}O_4$) are industrially important as acid site, reagent for separation, ion exchanger, catalyst and catalyst support.[1,2]

Aluminophosphate frameworks[3-6] were synthesized by Wilson and coworkers. They thought that their frameworks are strict alternation of phosphorus and aluminum tetrahedra. Since many of the industrially important hydrocarbon conversion reactions require acidic catalysts,[7] Shiralkar and coworkers[8] studied on some of the porous aluminophosphates that contain isomorphous substitution in framework of M^{2+} for Al^{3+}. $AlPO_4$-5 structure identified among aluminophosphate molecular sieves has a unidirectional pore system consisting of cylindrical channels with large pore opening of 8 Å, bounded by a 12 membered-oxigen ring system. It possesses a hexagonal crystal symmetry with $a \simeq 13.7$ Å and $c \simeq 8.5$ Å.

The isomorphous substitution[8] in $AlPO_4$-5 framework investigated by X-ray diffraction, scanning electron microscopy, Mössbauer spectroscopy and Fourier transform infrared spectroscopy. However, it is uncertain whether the substitution of cobalt takes place in aluminum or phosphorus site.[8]

This paper investigates the substituting site of Co for Al or P and calculate the net charge of Al, P, Co, and O in $AlPO_4$-5 and $CoAlPO_4$-5 framework. The net charge were calculated using the atom superposition and electron delocalization molecular orbital (ASED-MO) theory[10-15] and backbone model.

Theoretical Method

The atom superposition and electron delocalization molecular orbital theory (ASED-MO) used in past studies[10-15] is a semi-empirical theory for deriving molecular structures, force constants, bond strengths, electronic spectra and orbitals starting with experimental atomic valence ionization potentials and corresponding Slater orbitals. This theory identifies two energy components for the chemical bond formation.

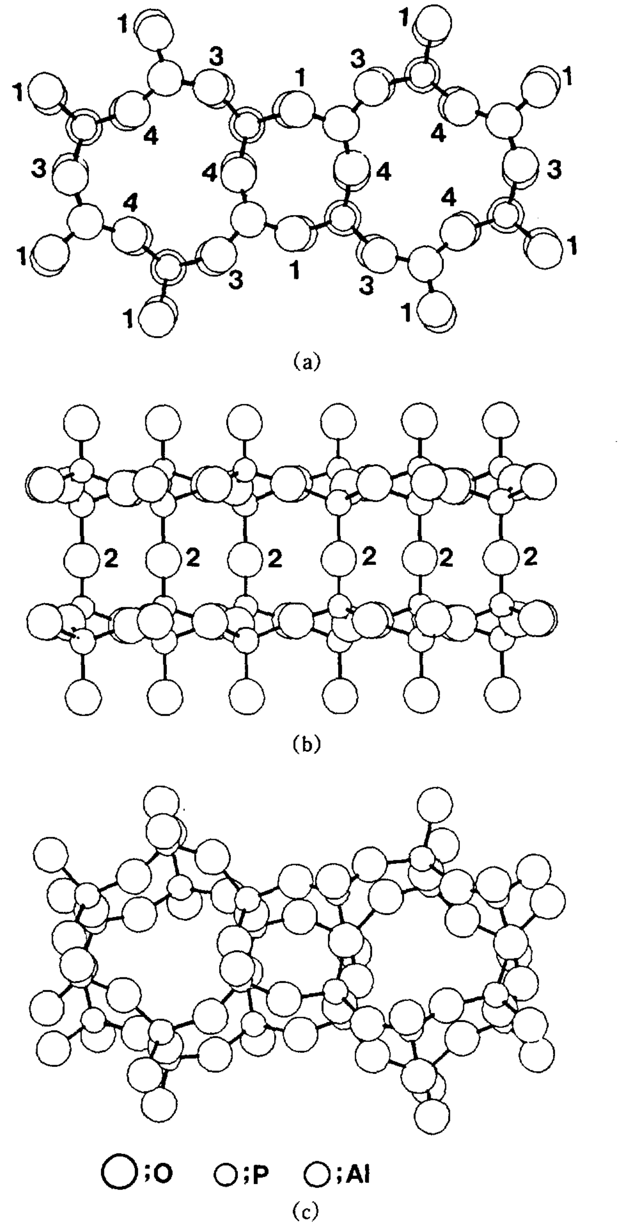

Figure 1. $Al_{12}P_{12}O_{62}$ cluster models of hexagonal crystal symmetry; oxygen atom positions expressed as O_1, O_2, O_3, and O_4. (a) The top view of $Al_{12}P_{12}O_{62}$ cluster model. (b) the side view rotated in 90 degree from *z*-axis, and (c) the side view rotated in 20 degree from *z*-axis.

One is a pair wise atom-atom repulsion energy called E_R. The other is an attractive energy due to the electron delocalization and bond formation. This energy is approximated by a one-electron molecular orbital energy, E_{MO}, obtained by diagonalizing a Hamiltonian similar to the extended Hückel Hamiltonian:

$$E \simeq E_R + E_{MO} \tag{1}$$

Table 1. Interatomic Distance (Å) and Angles(°) of $AlPO_4$-5

Distance[a]		Angles[a]	
P-$O_{(1)}$	1.472	$O_{(1)}$-P-$O_{(2)}$	108.1
$O_{(2)}$	1.456	$O_{(3)}$	110.9
$O_{(3)}$	1.492	$O_{(4)}$	110.1
$O_{(4)}$	1.526		
mean	1.486	$O_{(2)}$-P-$O_{(3)}$	107.9
		$O_{(4)}$	109.3
Al-$O_{(1)}$	1.729		
$O_{(2)}$	1.700	$O_{(3)}$-P-$O_{(4)}$	110.5
$O_{(3)}$	1.726		
$O_{(4)}$	1.683	$O_{(1)}$-Al-$O_{(2)}$	109.8
mean	1.710	$O_{(3)}$	104.2
		$O_{(4)}$	108.6
		$O_{(2)}$-Al-$O_{(3)}$	112.8
		$O_{(4)}$	110.3
		$O_{(3)}$-Al-$O_{(4)}$	111.0
		P-$O_{(1)}$-Al	150.2
		$O_{(2)}$	178.1
		$O_{(3)}$	148.8
		$O_{(4)}$	151.0

[a] Ref. 16.

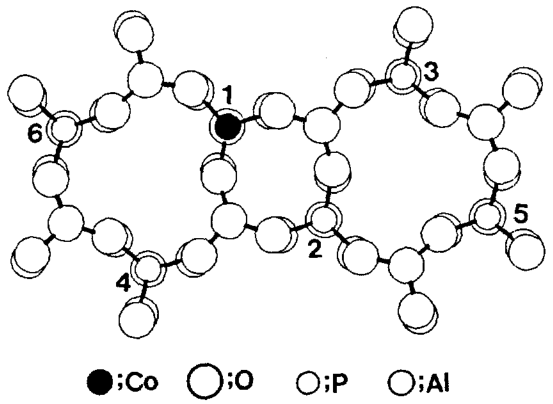

Figure 2. The top view of $CoAl_{11}P_{12}O_{62}$ cluster model of hexagonal crystal symmetry; numbers are aluminium site to be substituted by Co^{2+}.

The calculated unit of $AlPO_4$-5 that has a hexagonal crystal symmetry is modeled by $Al_{12}P_{12}O_{62}$ cluster shown in Figure 1. Top view of $Al_{12}P_{12}O_{62}$ cluster is shown in Figure 1(a). The side views rotated in 90° and 20° from *z*-axis are shown in Figure 1(b) and (c), respectively. For Figure 1(a), oxygen 1(O_1) is in four membered ring and twelve membered ring that composes the internal surface of $AlPO_4$-5 framework. Oxygen 3(O_3) is in six membered ring and twelve membered ring, and oxygen 4(O_4) is in four membered ring and six membered ring. For Figure 1(b), oxygen 2(O_2) in twelve membered ring links upper layer with lower layer.

The average bond length (Å) and bond angle (°) in $AlPO_4$-5 framework are 1.49 Å (P-O), 1.71 Å (Al-O), 109.5° (O-P-O) and 109.5° (O-Al-O), respectively.[16] The Al-O-P angles except for Al-$O_{(2)}$-P (178.1°) are near 150°. The experimental values used in this calculation are given in Table 1. Figure 2 illustrates the top view of $CoAl_{11}P_{12}O_{62}$ cluster model to describe the substituting site of Co for Al. The numbers in figure are aluminum site to be substituted by Co. The unshifted basic parameters (the ionization potentials and Slater orbital exponents) is shown in Table 2, and the shifted

Table 2. Unshifted Atomic Parameters; Principal Quantum Number, *n*, Ionization Potential, Ip (eV), and Slater Orbital Exponent, ε (au)

Atom	*s*			*p*			*d*			
	n	Ip	ε	*n*	Ip	ε	*n*	Ip	ε	*c*
Co^a	4	7.86	1.750	4	4.93	1.450	3	9.00	5.550	0.555
									1.900	0.646
Al^b	3	10.62	1.372	3	5.99	1.355				
P^b	3	16.15	1.880	3	10.49	1.628				
O^a	2	28.48	2.246	2	13.62	2.227				

^{a}Ref. 18(b). ^{b}Ref. 18(a).

Table 3. Calculated Net Charge for Ip Shifts of Cobalt. Aluminum and Phosphorous with Variation of the Oxygen Exponents, Δε

	ΔIp (eV)			Δε (au)	Net Charge				
					Calc.			Exp.^{e}	
	Co^a	Al^b	P^c	O^d	Co	Al	P	Al	P
AlPO$_4$-5		−1.4	+2.0	−0.3		1.0	1.8	1.4	1.0
		−1.7	+4.0	−0.4		1.1	1.5		
		−2.0	+6.0	−0.5		1.2	1.2		
		−2.3	+8.0	−0.6		1.3	0.9		
CoAlPO$_4$-5	+1.3	−1.7	+4.0	−0.4	1.9	1.2	1.5		
	+1.4	−2.0	+6.0	−0.5	1.8	1.3	1.2		
	+1.5	−2.3	+8.0	−0.6	1.6	1.4	0.8		

^{a}Ref. 18(b). ^{b,c}Estimated value for net charge. ^{d}Ref. 18(b). ^{e}Ref. 9.

atomic parameter details to the calculate net charges are shown in Table 3. Although the parameters were shifted to net charges, all of oxygen for AlPO$_4$-5 and CoAlPO$_4$-5 were used the same VSIP (valence state Slater orbital exponent[17] and ionization potential[18]) values, and P and Al also treated with the same way.

Results and Discussion

The energy change due to substitution of cobalt for aluminum was 119 eV and that of phosphorus was 68 eV. From this results, the substitution of cobalt for aluminum is more favorable than that of phosphorus. The difference of stabilized energy change was 51 eV. As suggested in earlier experimental work,[8,19] this result supported the possibility to substitute Co^{2+} ion for aluminum. For the claculation of edge effects, we thought of only upper layer. Aluminum sites that can be substituted by Co^{2+} are shown in Figure 2 and the numbers indicate the substitution site. The energy changes of substitution of cobalt were 119.2 eV for the site 1 and 2, 118.6 eV for the site 3 and 4, and 118.8 eV for the site of 5 and 6. This results showed the small magnitude of edge effects. Because of the limitations of cluster model and approximation of ASED-MO thoery, the slight stability gain for substitution of Co^{2+} does not imply that the extended aluminophosphate-5 cluster should reorder.

Table 4. Valence Electron Population in AlPO$_4$-5 and CoAlPO$_4$-5

		s	*p*	d_{x2-y2}	d_{z2}	$t_{2g}{}^b$	Δ^a
AlPO$_4$-5	Al	0.179	1.547				1,273
	P	1.060	3.097				0.853
	O$_1$	1.571	4.980				−0.551
	O$_2$	1.556	4.861				−0.417
	O$_3$	1.574	5.223				−0.797
	O$_4$	1.583	5.049				−0.632
CoAlPO$_4$-5	Co	0.264	0.844	1.262	1.262	3.805	1.563
	P	1.070	3.119				0.811
	O$_1$	1.547	4.793				−0.340
	O$_2$	1.529	4.682				−0.211
	O$_3$	1.548	4.826				−0.374
	O$_4$	1.533	4.730				−0.263

^{a}The summation of VEP in free atom−the summation of VEP in AlPO$_4$-5 and CoAlPO$_4$-5. $^b d_{xy}+d_{xz}+d_{yz}$.

In order to calculate the net charge, oxygen VSIP shift established in earlier Anderson's work[18b] was used for Al-O, P-O, and Co-O bond in this study. For cobalt, ionization potentials of valence *3d*, *4s* and *4p* were increased in 0.1 increments.[18b] For phosphorus, IP's of valence *3s* and *3p* were increased in 2.0 increment to produce expected mean charge.[9] For aluminum, IP's of valence *3s* and *3p* were varied on −1.7, −2.0 and −2.3. All unshifted atom parameters are in Table 2. Table 3 shows the calculated net charges for shifts in IP's of Co, Al, and P with variation of the oxygen exponents. Table 4 shows the valence electron population (VEP) in *s* and *p* (p_x, p_y, and p_z) orbital of oxygen, aluminum, and phosphorous for AlPO$_4$-5 and in *s*, *p* and *d* orbital of cobalt for CoAlPO$_4$-5. For AlPO$_4$-5 cluster, the VEP's of tetrahedral aluminum site to be substituted by Co^{2+} in AlPO$_4$-5 framework were obtained. Δ is defined as the difference between summation of VEP in free atom and those in AlPO$_4$-5 and CoAlPO$_4$-5. The Δ values correspond to the degree of the electron transfer in AlPO$_4$-5 framework with respect to the free atom. Comparing the differences of VEP in Al with P, the results that the difference of VEP of Al is greater than that of P indicated that P-O bond has more covalency than Al-O bond. For CoAlPO$_4$-5 cluster, the VEP of substituting site by Co^{2+} was compared with the cobalt free atom. As the oxygens in the region of substituting site by Co^{2+} for CoAlPO$_4$-5 framework were compared with the oxygens for AlPO$_4$-5 framework, VEP of the oxygens for AlPO$_4$-5 was greater than that for CoAlP$_4$-5. That is, the oxygens of AlPO$_4$-5 drew more electron from metal and had more electron population than that of CoAlPO$_4$-5. From this results, the oxidation state of cobalt is 1.56 in an agreement with the experimental values[8] of Co approximately. Table 5 shows reduced overlap population (ROP) in AlPO$_4$-5 and CoAlPO$_4$-5. From this result, the ROP depends on bond length in Table 1. As the overlap of molecular orbital between two atoms is greater, the bond length shortens. The P-O$_4$ and Al-O$_2$ bond of AlPO$_4$-5 cluster do not have such tendency, because the tetrahedral angles of O$_2$ and O$_4$ atom in AlPO$_4$-

Table 5. Reduced Overlap Population[a] in $AlPO_4$-5 and $CoAlPO_4$-5

$AlPO_4$-5		$CoAlPO_4$-5	
Al-O_1	−0.812	Co-O_1	0.160
Al-O_2	−0.889	Co-O_2	0.189
Al-O_3	−0.713	Co-O_3	0.164
Al-O_4	−0.411	Co-O_4	0.285
P-O_1	0.841	P-O_1	0.869
P-O_2	0.850	P-O_2	0.930
P-O_3	0.777	P-O_3	0.784
P-O_4	0.943	P-O_4	0.967

[a] The ROP of each atom to be at substitution region in framework.

Table 6. Net Charge in $AlPO_4$ and $CoAlPO_4$-5

Atom	Net Charge (calc.)	Net Charge (exp.)[a]
$AlPO_4$-5		
Al	1.27	1.4
P	0.85	1.0
O_1	−0.55	
O_2	−0.42	
O_3	−0.80	
O_4	−0.63	
O(mean)	−0.60	−0.6
$CoAlPO_4$-5		
Co	1.56	
P	0.81	
O_1	−0.34	
O_2	−0.21	
O_3	−0.37	
O_4	−0.26	
O(mean)	−0.30	

[a] Ref. 9.

5 framework are strained out of 109.5°. For $AlPO_4$-5 and $CoAlPO_4$-5, it was found an interest that the ROP of bonds in the framework decreas as the following order; P-O>Co-O>Al-O. It has meaning that the site of aluminum in framework could substitute by cobalt and the substitution of cobalt prefers the aluminum site to the phosphorous one. This results were compatible with the results of stabilized energy change mentioned above. Table 6 shows the net charge for aluminum, cobalt, and phosphorous in $AlPO_4$-5 and $CoAlPO_4$-5, the net charge is +1.27 for Al, +0.85 for P and +1.56 for Co, respectively. Although we have not found an experimental value of $AlPO_4$-5, the net charges of $AlPO_4$-5 were calculated comparing with the experimental values of Quartz form $AlPO_4$ which have bond lengthes and bond angles similar $AlPO_4$-5.

In particular, net charges of $AlPO_4$-5 are deduced from $AlPO_4$ form of quartz by Pluth.[16] The formal net charges for Al, P and Co are +3, +5, and +2, but the calculated values are +1.27 for Al +0.85 for P and +1.56 for Co. Table 3 also indicated that the covalency of P-O bond is greater than that of Al-O bond.

Conclusion

The substitution of cobalt in the site of aluminum is more stable than that of phosphorous. The calculated net charge in $AlPO_4$-5 and $CoAlPO_4$-5 was +1.27 for Al, +0.85 for P, and +1.56 for Co. The P-O bond was more covalent than the Al-O bond.

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