

tion was washed with  $\text{CHCl}_3$  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 ml) and solution of nuclease PI (3.5  $\mu\text{g}$ ) in the same buffer (0.02 ml) were added to a solution of the diastereomer (0.2 mg) in water (0.01 ml). The resulting solution was maintained for 2 h at 37°C. 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 $\text{AlPO}_4\text{-5}$ Molecular Sieves

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In order to determine the cobalt substituting site in  $\text{AlPO}_4\text{-5}$  framework, ASED-MO theory has been used. The substitution of cobalt for aluminum is energetically more favorable than that for phosphorous. 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  $\text{AlPO}_4\text{-5}$  and  $\text{CoAlPO}_4\text{-5}$  systems. Then, we 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 ( $\text{A}^{\text{III}}\text{B}^{\text{V}}\text{O}_4$ ) are industrially important as acid site, reagent for separation, ion exchanger, catalyst and catalyst support.<sup>1,2</sup>

Aluminophosphate frameworks<sup>3-6</sup> 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,<sup>7</sup> Shiralkar and coworkers<sup>8</sup> studied on some of the porous aluminophosphates that contain isomorphous substitution in framework of  $\text{M}^{2+}$  for  $\text{Al}^{3+}$ .  $\text{AlPO}_4\text{-5}$  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-oxygen ring system. It possesses a hexagonal crystal symmetry with  $a \approx 13.7$  Å and  $c \approx 8.5$  Å.

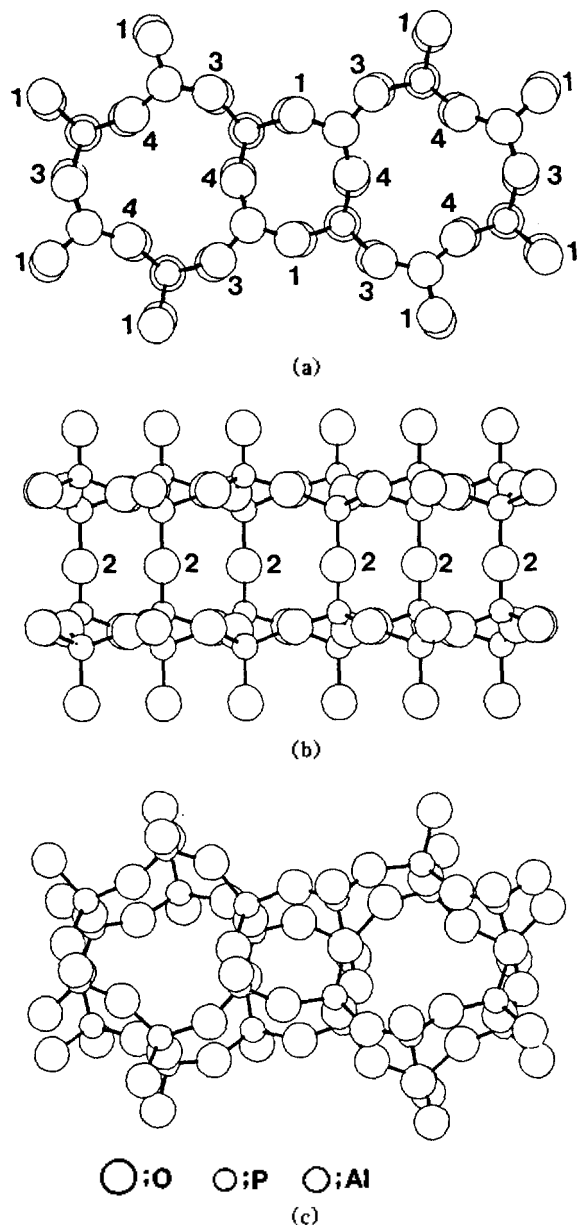
The isomorphous substitution<sup>8</sup> in  $\text{AlPO}_4\text{-5}$  framework inve-

stigated 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.<sup>8</sup>

This paper investigates the substituting site of Co for Al or P and calculate the net charge of Al, P, Co, and O in  $\text{AlPO}_4\text{-5}$  and  $\text{CoAlPO}_4\text{-5}$  framework. The net charge were calculated using the atom superposition and electron delocalization molecular orbital (ASED-MO) theory<sup>10-15</sup> and backbone model.

### Theoretical Method

The atom superposition and electron delocalization molecular orbital theory (ASED-MO) used in past studies<sup>10-15</sup> 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.**  $\text{Al}_{12}\text{P}_{12}\text{O}_{62}$  cluster model of hexagonal crystal symmetry; oxygen atom positions expressed as  $\text{O}_1$ ,  $\text{O}_2$ ,  $\text{O}_3$ , and  $\text{O}_4$ . (a) The top view of  $\text{Al}_{12}\text{P}_{12}\text{O}_{62}$  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:

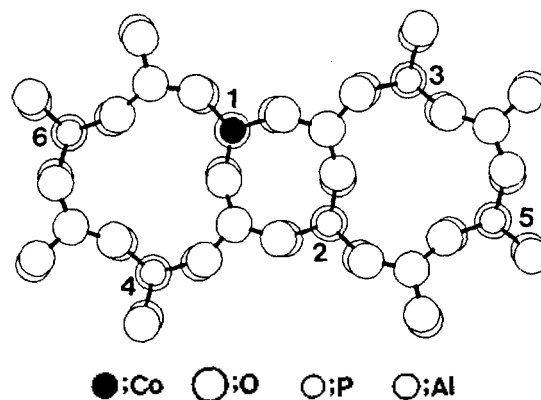
$$E \approx E_R + E_{MO} \quad (1)$$

The calculated unit of  $\text{AlPO}_4$ -5 that has a hexagonal crystal symmetry is modeled by  $\text{Al}_{12}\text{P}_{12}\text{O}_{62}$  cluster shown in Figure 1. Top view of  $\text{Al}_{12}\text{P}_{12}\text{O}_{62}$  cluster is shown in Figure 1(a). The side views rotated in  $90^\circ$  and  $20^\circ$  from  $z$ -axis are shown in Figure 1(b) and (c), respectively. For Figure 1(a), oxygen

**Table 1.** Interatomic Distance ( $\text{\AA}$ ) and Angles( $^\circ$ ) of  $\text{AlPO}_4$ -5

Distance <sup>a</sup>		Angles <sup>a</sup>	
P-O <sub>(1)</sub>	1.472	O <sub>(1)</sub> -P-O <sub>(2)</sub>	108.1
O <sub>(2)</sub>	1.456	O <sub>(3)</sub>	110.9
O <sub>(3)</sub>	1.492	O <sub>(4)</sub>	110.1
O <sub>(4)</sub>	1.526	O <sub>(2)</sub> -P-O <sub>(3)</sub>	107.9
mean	1.486	O <sub>(4)</sub>	109.3
Al-O <sub>(1)</sub>	1.729	O <sub>(3)</sub> -P-O <sub>(4)</sub>	110.5
O <sub>(2)</sub>	1.700	O <sub>(1)</sub> -Al-O <sub>(2)</sub>	109.8
O <sub>(3)</sub>	1.726	O <sub>(3)</sub>	104.2
O <sub>(4)</sub>	1.683	O <sub>(4)</sub>	108.6
mean	1.710	O <sub>(2)</sub> -Al-O <sub>(3)</sub>	112.8
		O <sub>(4)</sub>	110.3
		O <sub>(3)</sub> -Al-O <sub>(4)</sub>	111.0
		P-O <sub>(1)</sub> -Al	150.2
		O <sub>(2)</sub>	178.1
		O <sub>(3)</sub>	148.8
		O <sub>(4)</sub>	151.0

<sup>a</sup>Ref. 16.



**Figure 2.** The top view of  $\text{CoAl}_{11}\text{P}_{12}\text{O}_{62}$  cluster model of hexagonal crystal symmetry; numbers are aluminium site to be substituted by  $\text{Co}^{2+}$ .

$1(\text{O}_1)$  is in four membered ring and twelve membered ring that composes the internal surface of  $\text{AlPO}_4$ -5 framework. Oxygen  $3(\text{O}_3)$  is in six membered ring and twelve membered ring, and oxygen  $4(\text{O}_4)$  is in four membered ring and six membered ring. For Figure 1(b), oxygen  $2(\text{O}_2)$  in twelve membered ring links upper layer with lower layer.

The average bond length ( $\text{\AA}$ ) and bond angle ( $^\circ$ ) in  $\text{AlPO}_4$ -5 framework are  $1.49 \text{\AA}$  (P-O),  $1.71 \text{\AA}$  (Al-O),  $109.5^\circ$  (O-P-O) and  $109.5^\circ$  (O-Al-O), respectively.<sup>16</sup> The Al-O-P angles except for Al-O<sub>(2)</sub>-P ( $178.1^\circ$ ) are near  $150^\circ$ . The experimental values used in this calculation are given in Table 1. Figure 2 illustrates the top view of  $\text{CoAl}_{11}\text{P}_{12}\text{O}_{62}$  cluster model to describe the substituting site of Co for Al. The numbers in figure are aluminium 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,  $I_p$  (eV), and Slater Orbital Exponent,  $\epsilon$  (au)

Atom	$s$			$p$			$d$				
	$n$	$I_p$	$\epsilon$	$n$	$I_p$	$\epsilon$	$n$	$I_p$	$\epsilon$	$c$	
$\text{Co}^0$	4	7.86	1.750	4	4.93	1.450	3	9.00	5.550	0.555	1.900 0.646
$\text{Al}^0$	3	10.62	1.372	3	5.99	1.355					
$\text{P}^0$	3	16.15	1.880	3	10.49	1.628					
$\text{O}^0$	2	28.48	2.246	2	13.62	2.227					

<sup>a</sup>Ref. 18(b). <sup>b</sup>Ref. 18(a).**Table 3.** Calculated Net Charge for  $I_p$  Shifts of Cobalt, Aluminum and Phosphorous with Variation of the Oxygen Exponents,  $\Delta\epsilon$ 

	$\Delta I_p$ (eV)				$\Delta\epsilon$ (au)				Net Charge				
	$\text{Co}^0$	$\text{Al}^0$	$\text{P}^0$	$\text{O}^0$	Calc.			Exp. <sup>c</sup>					
					Co	Al	P	Al	P				
$\text{AlPO}_4\text{-5}$		-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							
$\text{CoAlPO}_4\text{-5}$	+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						

<sup>a</sup>Ref. 18(b). <sup>b</sup>Estimated value for net charge. <sup>c</sup>Ref. 18(b). <sup>d</sup>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  $\text{AlPO}_4\text{-5}$  and  $\text{CoAlPO}_4\text{-5}$  were used the same VSIP (valence state Slater orbital exponent<sup>17</sup> and ionization potential<sup>18</sup>) 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,<sup>8,19</sup> this result supported the possibility to substitute  $\text{Co}^{2+}$  ion for aluminum. For the calculation of edge effects, we thought of only upper layer. Aluminum sites that can be substituted by  $\text{Co}^{2+}$  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 theory, the slight stability gain for substitution of  $\text{Co}^{2+}$  does not imply that the extended alu-

**Table 4.** Valence Electron Population in  $\text{AlPO}_4\text{-5}$  and  $\text{CoAlPO}_4\text{-5}$ 

		$s$	$p$	$d_{z^2-r^2}$	$d_{z^2}$	$t_{2g}^b$	$\Delta^c$
$\text{AlPO}_4\text{-5}$	Al	0.179	1.547				1.273
	P	1.060	3.097				0.853
	$\text{O}_1$	1.571	4.980				-0.551
	$\text{O}_2$	1.556	4.861				-0.417
	$\text{O}_3$	1.574	5.223				-0.797
$\text{CoAlPO}_4\text{-5}$	$\text{O}_4$	1.583	5.049				-0.632
	Co	0.264	0.844	1.262	1.262	3.805	1.563
	P	1.070	3.119				0.811
	$\text{O}_1$	1.547	4.793				-0.340
	$\text{O}_2$	1.529	4.682				-0.211
	$\text{O}_3$	1.548	4.826				-0.374
	$\text{O}_4$	1.533	4.730				-0.263

<sup>a</sup>The summation of VEP in free atom—the summation of VEP in  $\text{AlPO}_4\text{-5}$  and  $\text{CoAlPO}_4\text{-5}$ . <sup>b</sup> $d_{xy} + d_{xz} + d_{yz}$ .

minophosphate-5 cluster should reorder.

In order to calculate the net charge, oxygen VSIP shift established in earlier Anderson's work<sup>18b</sup> 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.<sup>18b</sup> For phosphorus, IP's of valence  $3s$  and  $3p$  were increased in 2.0 increment to produce expected mean charge.<sup>9</sup> 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  $\text{AlPO}_4\text{-5}$  and in  $s$ ,  $p$  and  $d$  orbital of cobalt for  $\text{CoAlPO}_4\text{-5}$ . For  $\text{AlPO}_4\text{-5}$  cluster, the VEP's of tetrahedral aluminum site to be substituted by  $\text{Co}^{2+}$  in  $\text{AlPO}_4\text{-5}$  framework were obtained.  $\Delta$  is defined as the difference between summation of VEP in free atom and those in  $\text{AlPO}_4\text{-5}$  and  $\text{CoAlPO}_4\text{-5}$ . The  $\Delta$  values correspond to the degree of the electron transfer in  $\text{AlPO}_4\text{-5}$  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  $\text{CoAlPO}_4\text{-5}$  cluster, the VEP of substituting site by  $\text{Co}^{2+}$  was compared with the cobalt free atom. As the oxygens in the region of substituting site by  $\text{Co}^{2+}$  for  $\text{CoAlPO}_4\text{-5}$  framework were compared with the oxygens for  $\text{AlPO}_4\text{-5}$  framework, VEP of the oxygens for  $\text{AlPO}_4\text{-5}$  was greater than that for  $\text{CoAlPO}_4\text{-5}$ . That is, the oxygens of  $\text{AlPO}_4\text{-5}$  drew more electron from metal and had more electron population than that of  $\text{CoAlPO}_4\text{-5}$ . From this results, the oxidation state of cobalt is 1.56 in an agreement with the experimental values<sup>8</sup> of Co approximately. Table 5 shows reduced overlap population (ROP) in  $\text{AlPO}_4\text{-5}$  and  $\text{CoAlPO}_4\text{-5}$ . 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<sub>4</sub> and Al-O<sub>2</sub> bond of  $\text{AlPO}_4\text{-5}$  cluster do not have such tendency, because the tetrahedral angles of  $\text{O}_2$  and  $\text{O}_4$  atom in  $\text{AlPO}_4\text{-5}$

**Table 5.** Reduced Overlap Population<sup>a</sup> in AlPO<sub>4</sub>-5 and CoAlPO<sub>4</sub>-5

AlPO <sub>4</sub> -5		CoAlPO <sub>4</sub> -5	
Al-O <sub>1</sub>	-0.812	Co-O <sub>1</sub>	0.160
Al-O <sub>2</sub>	-0.889	Co-O <sub>2</sub>	0.189
Al-O <sub>3</sub>	-0.713	Co-O <sub>3</sub>	0.164
Al-O <sub>4</sub>	-0.411	Co-O <sub>4</sub>	0.285
P-O <sub>1</sub>	0.841	P-O <sub>1</sub>	0.869
P-O <sub>2</sub>	0.850	P-O <sub>2</sub>	0.930
P-O <sub>3</sub>	0.777	P-O <sub>3</sub>	0.784
P-O <sub>4</sub>	0.943	P-O <sub>4</sub>	0.967

<sup>a</sup>The ROP of each atom to be at substitution region in framework.

**Table 6.** Net Charge in AlPO<sub>4</sub> and CoAlPO<sub>4</sub>-5

Atom	Net Charge (calc.)	Net Charge (exp.) <sup>a</sup>
AlPO <sub>4</sub> -5		
Al	1.27	1.4
P	0.85	1.0
O <sub>1</sub>	-0.55	
O <sub>2</sub>	-0.42	
O <sub>3</sub>	-0.80	
O <sub>4</sub>	-0.63	
O(mean)	-0.60	-0.6
CoAlPO <sub>4</sub> -5		
Co	1.56	
P	0.81	
O <sub>1</sub>	-0.34	
O <sub>2</sub>	-0.21	
O <sub>3</sub>	-0.37	
O <sub>4</sub>	-0.26	
O(mean)	-0.30	

<sup>a</sup>Ref. 9.

5 framework are strained out of 109.5°. For AlPO<sub>4</sub>-5 and CoAlPO<sub>4</sub>-5, it was found an interest that the ROP of bonds in the framework decreases 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<sub>4</sub>-5 and CoAlPO<sub>4</sub>-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<sub>4</sub>-5, the net charges of AlPO<sub>4</sub>-5 were calculated comparing with the experimental values of Quartz form AlPO<sub>4</sub> which have bond lengths and bond angles similar AlPO<sub>4</sub>-5.

In particular, net charges of AlPO<sub>4</sub>-5 are deduced from AlPO<sub>4</sub> form of quartz by Pluth.<sup>16</sup> 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<sub>4</sub>-5 and CoAlPO<sub>4</sub>-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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