BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL ALUMINOSILICATES

Technical Progress Report for the Period

June 1991-August 1991

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September 1991

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-FG22-89PC89784

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OBJECTIVE AND SCOPE OF WORK

The objective of this research is to provide the scientific understanding of processes that actively and selectively reduce NO in dilute exhaust streams, as well as in concentrated streams, to N₂. Experimental studies of NO chemistry in transition metal-containing aluminosilicate catalysts are being carried out with the aim of determining the chemical rules for NO reduction on non-precious metals.

The catalyst supports chosen for this investigation are A and Y zeolites, mordenite, and monoliths based on cordierite. The supported transition metal cations that will be examined are principally the first row redox metals, e.g. Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Cu(I). The reactions of interest are the reductions of NO by H₂, CO, and CH₄, as well as the disproportionation of NO.

In order to stabilize the transition metal cations in accessible sites and with desired oxidation states so that the resultant activity and selectivity to NO reduction are increased, rare earth cations that possess redox properties will be placed in the more shielded sites, e.g. Site I in Y zeolite, prior to or simultaneously with the exchange procedure with the transition metal cations. The rare earth redox couples that can be utilized include Ce(III)/Ce(IV), Eu(II)/Eu(III), Sm(II)/Sm(III), and Pr(III)/Pr(IV). The prepared catalysts will be tested in batch, pulsed, recycle, and continuous flow reactors with in-line gas chromatographic or mass spectrometric analyses, and they will be fully characterized before and after catalytic testing.

To provide insight into the functioning of the redox cations and guidance in choosing the best transition metal/rare earth combination for the dissociative chemisorption of NO, theoretical calculations of the electronic structure of the transition metal cations in zeolitic sites will be carried out by *ab initio* methods, such as the scattered wave X_α and Gaussian 86 or 90 packages. The aim of this part of the research is to find the best match between the metal-based antibonding orbitals and the antibonding orbitals of the NO molecule such that the N-O bond is weakened and is readily broken.

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SUMMARY OF TECHNICAL PROGRESS

Preliminary extended Huckel calculations of the electronic structure of transition-metal ions in zeolites are reported. The calculations have been performed on the basis of a $M[Si_3Al_3O_6(OH)_{12}]$ cluster ($M = Na^{1+}, Ca^{2+}, Co^{2+}$) to model the favored sorption site (the S I cation site) in zeolite A. Evaluation of the electronic structure gave several separated energy bands. The 3d level of Co is found to be on the top of the valance band, which confirmed the ESCA results. The CO molecule has been chosen to be studied in the adsorbed state on the cations in zeolite A in order to test the calculation method. The NO-M complexes in zeolite A will subsequently be studied by this computational method.

TECHNICAL PROGRESS

Introduction

The electronic properties of zeolite A containing transition metal cation are reported to be catalytically important for various chemical reactions. One of our interests in this project is to study the binding in terms of electronic interaction between NO and those transition metal cations. The electronic structure of the cations has been determined theoretically by applying the ligand field or the scattered-wave X_α (SW X_α) method of computation. The ligand field model has been successful, but it requires the use of empirical parameters representing the ligand field strength and the electron-electron repulsion. The SW X_α calculations are *ab-initio*, but they were found to be size inconsistent for clusters modelling a Cu^{2+} ion located in the hexagonal window of A- or Y-type zeolites. The preliminary state-of-the-art *ab-initio* calculations using the Gaussian 86 package have been performed in this research group before. By using $\text{Cu}(\text{H}_2\text{O})_3^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_3^{2+}$ as models of the zeolite site, unsatisfactory results were obtained. More effort is required in this direction, and this involves using larger basis sets, larger clusters, and more computation time.

During this quarter of research, the electronic states of the cations have been investigated by a semiempirical molecular orbital calculation method, i. e. the extended Huckel method. The size of the models in the calculations in terms of number of atoms and orbitals forced us to use a semiempirical method. The extended Huckel theory, developed by Hoffmann (1), suited our objectives. Besides the computational efficiency and feasibility, the method has been used extensively in the past for the successful study of transition metal systems.

Calculation procedure

The calculations were performed on the Lehigh Vax 8350 computer using the Extended Huckel Molecular, Crystal and Properties Package (version 1.0) written by Whangbo et al. (2).

Parameters

For the diagonal elements H_{rr} of the Hamiltonian H of H, O, Si, Al, Na, and Ca, the valence-state ionization potentials with charge $q = 0$, calculated by Basch, Viste, and Gary (3), were taken as derived from spectroscopic data (4). For Co, which has d orbitals, the diagonal terms are those determined by Baetzold (5). The off-diagonal terms H_{rs} are calculated with the Wolfsberg-Helmholtz expression (6),

$$H_{rs} = (K/2)(H_{rr} + H_{ss})S_{rs},$$

with constant $K = 1.75$ and where S_{rs} is the overlap integral calculated on the Slater basis.

The orbital exponents of the radial part of the atomic orbitals (STO), calculated by Burns (7), are taken rather than those of Slater since they account for the outer electrons as well as for the inner electrons. Table 1 gives the list of orbital exponents for the different elements used in our extended Huckel molecular orbital (EHMO) calculations.

The d atomic orbitals of Co are built up as a linear combination of two Slater-type functions because this is a better approximation of the d orbital shape.

Table 1. Parameters used in the EHMO Calculations

orbital		H _{rr} (eV)	e1	e2	c1	c2
H	1s	-13.60	1.3			
O	2s	-32.3	2.2			
	2p	-14.8	1.975			
Si	3s	-17.3	1.533			
	3p	-9.2	1.083			
Al	3s	-12.3	1.317			
	3p	-6.5	0.867			
Na	3s	-5.1	0.9			
	3p	-3.0	0.533			
Ca	4s	-7.0	1.2			
	4p	-4.0	1.2			
Co	4s	-9.21	2.0			
	4p	-5.29	2.0			
	3d	-13.18	5.55	2.10	0.56786	0.60586

Models

For the model cluster chosen for the computations, preferential adsorption is assumed to occur on the metal cation located on Site I of zeolite A, which is located in front of the plane of the six-ring opening interconnecting the α and β cages. In Figure 1, the zeolite A unit cell is shown together with the cluster, inserted in the lower right corner of the drawing as dots, that was used for the calculations. The cluster is limited to the 37 atoms. The oxygen atoms are terminated by H with an O-H distance of 1.08 Å in order to get a closed-shell configuration. The cluster under consideration is introduced into the calculations with C_{3v} symmetry, and all the geometry parameters for the Na complex are taken from Reference 8 and

without the change applied to the Ca complex. The Co complex parameters are taken from Reference 9. The ionic charge of the $M[Si_3Al_3O_6(OH)_{12}]$ clusters is -2, -1, and -1 for $M = Na, Ca,$ and $Co,$ respectively. The spin multiplicity of Na and Ca is singlet, while that of Co is forced to be quartet. When considering CO adsorption, the direction of the Na-CO and Ca-CO bond coincides with the threefold axis of the model cluster pointing towards the center of the large cavity. The C-O bond length is chosen as the free gas molecule of 1.128 Å. The Ca-C bond length is chosen as 2.7 Å, in agreement with that obtained from a classical interaction calculation. The number of atoms in the cluster + CO complex comprises 39 atoms, as shown in Figure 2.

Results and Discussion

First, the electronic structures of the bare transition metal-zeolite model clusters (NaA, CaA, and CoA) without any adsorbed molecules are described. In each case, the general feature is the splitting of the energy spectrum into several distinct regions or bands shown in Figure 3. More specific features of these calculations, with reference to the diagrams shown in Figure 3, include:

- (1) The "O(2s)-region" with a total of 18 (doubly occupied) levels was obtained as expected from the 18 oxygen atoms of the cluster covering the interval between -35.31 and -32.80 eV. The lowest three levels also contain considerable 3s admixtures from Al and Si (up to 14% per atom), and in this sense they form a s-bonding subband.
- (2) The "Si-O-Al bonding region" also constitutes 18 electronic energy levels between -18.40 to -15.31 eV. These states are in general completely delocalized with typical contributions of 5-10% per

atom; in other words, these molecular orbitals cannot be assigned definitely to one of the types of the constituent atoms.

- (3) The "O 2p lone-pair region" consists of 36 levels and extends from -15.14 to -14.09 eV, which is the energy of the HOMO. These states have almost pure oxygen character and do not take part in the bonding to Al or Si.
- (4) In the case of the Co A zeolite cluster, the d levels of the Co cation fall in the band gap region and form two doubly degenerate states of -12.93 eV and -12.26 eV with a single state between them at -12.92 eV. These Co d level are sitting on the top of the O 2p region.
- (5) The energies of the lowest unoccupied molecular orbitals (LUMO) of NaA, CaA and CoA are -1.99, -3.73, and -5.32 eV, respectively. These LUMOs consist of 98% contribution from s and p orbitals of Na, Ca, and Co. Since the energies of the LUMOs increase in the order of $\text{Co} < \text{Ca} < \text{Na}$, the ability to accept electrons, i.e. the Lewis acidity, increases in the order of $\text{Co} > \text{Ca} > \text{Na}$. Thus, Ca is a stronger center than Na, while Co is the strongest center for holding electrons.

Upon insertion of the CO molecule into the electronic valence ground state configuration, the following features are obtained (see Figure 4):

- (1) A gross shift for all the CO orbital energies occurred compared with the free CO molecule values. This is due to a slight charge transfer from CO to the metal-zeolite, resulting in an effective charge of +0.22 eV for CO in the Ca zeolite and +0.14 eV for CO in the case of Na. Therefore, the first valence level of CO is lowered to -35.238 eV. Accordingly, the second orbital energy is

shifted down from the bonding region into the gap between the O 2s band and the Si-O-Al band. These two orbital states, as well as the 1 pi (π) state at -15.929 eV, are of almost pure CO character. The bonding of CO to the zeolite via the Ca cation takes place over the 3 sigma electrons only, where CO contributes about 84% and Ca also contributes with 4% to the molecular orbital.

- (2) The highest occupied molecular orbital (HOMO) is the top of the O 2P lone-pair band is a little lowered in comparison with the zeolite cluster itself, thus indicating a slight stabilization of the system due to the adsorption of CO.
- (3) The LUMO of the zeolite + CO system is an almost purely antibonding π^* orbital of CO, while in the bare zeolite the LUMO is mainly a Ca orbital. There is no back-donation taking place. In order to estimate the influence of the cation, comparative calculations were performed with Na instead of Ca located on Site 1 (see Table 2). The lower LUMO energy obtained in the Ca example demonstrates that Ca is the stronger center in comparison with Na.

Table 2. LUMO energies (eV)

	Cluster + CO	Bare cluster
Ca on site I	-8.11	-3.73
Na on site I	-8.10	-1.99

The charge distribution of the valence electrons according to Table 3 shall be discussed, where the calculated effective charges of C and O in the

free molecule, the charges of the CO free zeolite, and the respective values of the sorption system are compared to each other.

Table 3. Effective Charges (eV) from the EHMO Method

Charge	Cluster + CO	Bare Cluster	Free CO Molecule
q(Si)	2.298	2.301	
q(Al)	2.087	2.088	
q(O ₃)	-1.375	-1.374	
q(O ₂)	-1.418	-1.419	
q(O, outer shell ave.)	-1.033	-1.030	
q(Ca)	1.88	2.101	
q(C from CO)	0.5		0.23
q(O from CO)	-0.28		-0.23

From these values, it may be seen that most of the 0.22 eV transfer of CO electrons occurs from the CO molecule to the Ca ion. In minimizing the Coulomb repulsion, a charge reorganization throughout the whole cluster takes place affecting mainly its outer regions, the positive charges of Si and Al decrease slightly, and the negative charge of the outer oxygen shell increases. While the former effect of charge reduction at the cation sites seems to be realistic, the latter effect could be an artifact of the termination of the cluster at this shell of oxygen atoms, and it can be supposed that in reality the additional oxygen charge will spread over the next shell of Al and Si atoms. As for Ca, it should be noted that despite

the less positive character of the Ca ion in the CO adsorbed cluster, the bonding of Ca to the zeolite becomes slightly stronger in the adsorbed state, which follows from the corresponding overlap integrals and the bond order matrix elements.

Now consider the more interesting charge reorganization effects within the CO molecule. The electron transfer towards the cluster leads to changes in the electron density between C and O. The net effect of electron transfer in the CO-Ca-A zeolite model cluster is a slight increase of the overlap between C and O from 1.5361 to 1.5835 electrons, as well as the larger increase in electron overlap between C and Ca.

These calculations will also be carried out for the CoA + CO system, and it will be determined if there is any electron back-donation occurring because there are d orbitals in the system. Ni-, Fe-, and Cu-type clusters will also be calculated to compare the adsorption ability. Furthermore, NO has one more electron than CO, and it occupies an *antibonding orbital*. The binding between NO and transition metal cations in zeolites will be studied in the near-future to determine which metal ion-NO complexes exhibit the lowest electron density between the N and O atoms, i.e. weakest N-O bonds.

Conclusion

The results of the EHMO calculations include the electron energies, as well as the charge distributions for the metal ions and adsorbed molecules. These calculations indicate that the CO polarizing strength of zeolite A-held cations should increase in the order of $\text{Na} < \text{Ca} < \text{Co}$, and further EHMO calculations will contribute to a better understanding of the molecular adsorption and activation of CO and NO on metal ions located at the exposed Site I center of zeolite A.

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Figure 1. Secondary structure of type A zeolite. The cluster used for calculation is inserted in the drawing.

Figure 2. Drawing of the model cluster chosen for the computations.

Figure 3. MO diagram of the electronic energies calculated by the EHMO method for the NaA, CaA and CoA bare clusters.

Figure 4. MO diagram of the electronic energies calculated by the EHMO method for the free CO molecule, the bare CaA cluster and the CO-loaded cluster.

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