

**SPECTROSCOPIC CHARACTERIZATION OF THE METAL  
CATION SITING AND THE ADSORBATE–CATION  
INTERACTIONS IN Cu (II) AND Co (II)  
EXCHANGED FAUJASITE-X  
ZEOLITE**

**BY**

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**DISSERTATION**

**Submitted in partial fulfillment of the requirements for the  
degree of Doctor of Philosophy in Chemistry  
in the Graduate School of  
Binghamton University  
State University of New York  
2006**

UMI Number: 3220349

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**Accepted in partial fulfillment of the requirements for  
the degree of Doctor of Philosophy in Chemistry  
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Binghamton University  
State University of New York  
2006**

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## Abstract

Toxic chemicals are abundant in the environment and their detection often requires very costly and time consuming methods. Where such molecules are able to interact with the transition metal cations, their characteristic electronic transitions are identifiable by spectroscopic methods and provide a potential means of simple identification.

Zeolites offer a very porous and polar solid-state environment that attracts molecules and stabilizes cations, hence enabling complexes to form in it.

In this work, the  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  complexes of ammonia, pyridine, acetone, water and sulfur dioxide in zeolite-X were characterized by UV-Vis reflectance, electron paramagnetic resonance, infrared and nuclear magnetic resonance spectroscopic methods. At lower concentrations (such as at 1 copper per unit cell (1 Cu/UC), the cations were found to bind the framework oxygens at the  $\text{Si}(\text{OAl})_4$  tetrahedra. The exchanged cations at low concentrations reside in site I' where two  $\text{Cu}^{2+}$  species (I and II) are seen to emerge, as a result of different local charges. Apart from water, other adsorbates do not interact with the exchanged cations at low concentration (1 Cu/UC). Higher exchange levels of the cations are found to occupy supercage sites of II' and possibly III. As the concentration of the cations increases to ca. 8 Cu/UC, dynamic spin-spin averaging begins to take place. Thus, at  $\geq 8$  Cu/UC, CuX continuous-wave EPR (CW-EPR) spectra have contributions from both the dynamic spin-spin averaging and some residual static powder pattern spectrum of isolated  $\text{Cu}^{2+}$ .

In the supercage accessible cation sites, ammonia and pyridine showed interactions with cations at single four-ring site III (S4R (III)), whereas acetone and water coordinate the cations at single six-ring site II' (S6R (II')). Sulfur dioxide showed little evidence of reaching the cations at any cation exchange levels. The presence of the adsorbates in the highly  $\text{Cu}^{2+}$  exchanged samples did not eliminate the occurrence of dynamic spin-spin averaging among the proximate  $\text{Cu}^{2+}$  ions. This broad range of results gives us a characteristic ordering of ligand field strengths of ammonia > pyridine >  $\text{O}_{\text{zeo}} \geq$  acetone  $\approx$  water > sulfur dioxide.

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## Dedication

To

My

Wife, Caren

Our children Robert,

Edna and

Sandra.

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## Acknowledgements

This work is a testimony of the huge debt, both academic and social, I owe to many. I wish to sincerely thank the following people and organizations for either directly or indirectly enabling this work to be in the present form.

Prof. David C. Doetschman of Binghamton University for introducing me to the intricate world of zeolites and for being more than an academic advisor to me - in fact a mentor. I equally thank Prof. Doetschman for the research assistantships and generous financial summer supports during my PhD studies at the Binghamton University (BU).

Chemistry Department of BU is acknowledged for the assistantships, research grants and financial summer supports in order that I could undertake this study. The Faculty/Professors of BU for the gift of knowledge, fellow students at BU for sharing the knowledge and the jokes and to the non-teaching staff, for their support and understanding. Special thanks go to Mr. Bob Gonzalez for never tiring to repair the electronic research instruments in our laboratories, Dr. Jurgen Shulte for his help with NMR data, and Dr. A. Silva for her timely guidance and counseling with the teaching laboratories. Further, Dr. Ralph T. Weber of Bruker Corporation is saluted for his technical help with EPR work.

Prof. D. C. Doetschman's group members, both past, Dr. A. Meenakshi, and Dr. R. Mehlenbecher, and present, Dr. S. Yang, Dr. J. Fox, B. Jones, C. Kanyi, J. DeCoste, J.



Sambur, K. Yan, and M. Lee, are all sincerely thanked for their valued academic contributions and the friendship they accorded me during my student days at Binghamton University. This work owes a lot to them.

My life at Binghamton could not have been more bearable without the social buffers provided by the members of the graduate students organization, graduate African students organization, the East African community of Binghamton, Shotokan Karate club of Binghamton and Appalachin and members of both St. Patrick and St. James Catholic churches of Binghamton and Johnson city.

My parents, relatives and friends are equally acknowledged for their constant encouragements and pushing in order to accomplish this goal.

Finally, I duly appreciate and acknowledge the understanding, encouragements, and forbearance from my wife, Caren, during these long times of ‘separations’ in order that this work be done. Our beloved children; Robert, Edna, and Sandra are sincerely thanked and appreciated for putting up with a telephone father for the period of this study, and consequently, this work is dedicated to them.

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## List of Abbreviations

Abbreviation	Meaning
Acet.	Acetone
Antisym.	Antisymmetric
CoX	Cobalt exchanged Faujasite – X
Co/UC	Cobalt per unit cell
23 Co/UC	23 Moles of cobalt (II) per unit cell of zeolite
Co/UC + NH <sub>3</sub>	Cobalt per unit cell exposed to maximal ammonia
Co/UC + 3 NH <sub>3</sub>	Co/UC exposed to three moles of ammonia
CuX	Copper exchanged Faujasite –X
CW-EPR	Continuous wave electron paramagnetic resonance
D6R	Double six ring structure of the zeolite framework
Dehy.	Dehydrated/evacuated
DRS	Diffuse reflectance spectroscopy
FAU-X	Faujasite-X
$g_{av}$	Averaged g-values
$g_{iso}$	Isotropic g-value
Hyd.	Hydrated
Kmu	Kubelka-Munk units
LMCT	Ligand to metal charge transfer
NaX	Sodium exchanged Faujasite-X
3 NH <sub>3</sub> /Cu/UC	Three moles of ammonia per mole of copper in the unit cell
O <sub>zeo.</sub>	Oxygen atoms of the zeolite framework
Pyr	Pyridine
S4R	Single four ring structures of the zeolite framework
S6R	Single six ring structure of the zeolite framework
Si/Al	Silicon to aluminum ratio
Str.	Stretching
Sym.	Symmetric

## List of Symbols

Symbol	Meaning
L	Ligand
$M^{n+}$	Metal cation
M-L	Metal-Ligand
$P_A$	Probability of finding aluminum at a particular tetrahedra
$P_S$	Probability of finding silicon at a particular tetrahedra
T	Al or Si atom in the tetrahedron/tetrahedral
UC	Unit cell

PREVIEW