

0700295

SYNTHESIS AND CHARACTERIZATION
OF NANOSTRUCTURED IRON OXIDE
IN ZEOLITE MATRICES

YEE SWEE LI, MAXINE

A DISSERTATION SUBMITTED AS PART FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF TECHNOLOGY (MATERIALS SCIENCE)

INSTITUTE OF POSTGRADUATE STUDIES AND RESEARCH
UNIVERSITY MALAYA
KUALA LUMPUR

FEBRUARY 2004

Perpustakaan Universiti Malaya



A511706120

ABSTRACT

The formation of iron oxide nanoparticles within the sodalite cages and supercages of Na-Y zeolites was investigated. Ferrous ions were introduced as guest cations into the host zeolite through a vacuum-assisted ion exchange procedure. The formation of zeolite-iron oxide (ZIO) system was facilitated by addition of differing concentrations of NaOH, and accelerated by heating at 60°C and addition of hydrogen peroxide. Energy dispersive X-ray spectroscopy (EDS) studies showed a significant amount of iron in the exchanged samples. X-ray diffraction (XRD) results showed the gradual phase change to iron oxide as well as diminishing zeolite peaks at increasing concentrations of NaOH. At lower concentrations of NaOH solution, the zeolite matrix was retained but the precipitated iron oxide was too small to be detected. Several peaks were identified in the product, which corresponded to maghemite, as well as hematite, indicating that the product is a mixed oxide of iron. Calculation of the crystallite size using Scherrer's equation yielded an average diameter of 13.4 nm. Under scanning electron microscopy (SEM), the ZIO particles have a cluster-like appearance, different from the acicular particles obtained from free precipitation. Transmission electron microscopy (TEM) images of the ZIO specimens showed the particles to be less than 50 nm. The adsorption isotherm of the ZIO products is characteristic of materials with a high specific surface area, with a specific surface area of 785 m²/g, determined using the B.E.T. method. The mean pore diameter of pure zeolite was calculated to be 7.4 nm, using the BJH method, while the size of iron oxide particles precipitated within the internal pores of zeolite is estimated to be 7.1 nm. Magnetic response measurements obtained from an alternating gradient magnetometer (AGM) shows magnetization values up to 10.2 emu/g at the maximum applied field of 10 kOe. The absence of hysteresis loops indicates superparamagnetism.

ACKNOWLEDGEMENTS

I am indebted to the many wonderful people who have helped me in so many ways throughout the course of completing this dissertation. I am especially grateful to Associate Professor Dr. Iskandar Idris Yaacob for his expert guidance, support and enthusiasm. His help in conducting the XRD, AGM and gas adsorption desorption analyses was especially invaluable.

A special note of thanks also goes out to the technical staff at the Mechanical Engineering Dept: Encik Mohd. Said Sakat (Microcontrol laboratory) and Encik Ismail Jaafar (SEM laboratory); and Mr. T. Ragunathan from the TEM laboratory at the Institute of Postgraduate Studies and Research, University Malaya. I also thank Professor Dr. Hamzah Mohamad from the Geology Dept of Universiti Kebangsaan Malaysia for his help in the XRF analyses. Thanks also to Abdul Hadi for help in the gas adsorption analysis.

To my colleagues at University Malaya: J.C. Hoh, for your helpful comments in theoretical matters and use of photographs; and Roslina Ismail for your support during stressful times, a big thank you. The continuous encouragement and support of my family, especially my parents and husband, is deeply and sincerely appreciated.

I am also grateful for the financial support of University Malaya's tutorship scheme for the past three years, and Vote F Grant No. F0175/2001D.

Apologies to people whose contributions I have overlooked, but have been priceless to me. Thank you very much, I could not have done this without any of you!

TABLE OF CONTENTS

| | |
|--|------------|
| ABSTRACT | ii |
| ACKNOWLEDGEMENTS | iii |
| TABLE OF CONTENTS | iv |
| LIST OF FIGURES | vii |
| LIST OF TABLES | ix |
| | |
| CHAPTER 1: INTRODUCTION | 1 |
| 1.1 General | 1 |
| 1.2 Objectives | 2 |
| 1.3 Experimental Approach | 2 |
| 1.4 Conclusion | 3 |
| | |
| CHAPTER 2: LITERATURE REVIEW | 5 |
| 2.1 Zeolites | 5 |
| 2.2 Iron Oxides | 7 |
| 2.3 Magnetic Properties | 8 |
| 2.4 Synthesis of Iron Oxide Particles | 13 |
| 2.5 Matrix Supported Synthesis | 15 |
| 2.5.1 Synthesis of Nanoparticles Supported in Zeolite Matrices | 16 |
| 2.5.2 Synthesis of Nanoparticles Supported in Polymer Matrices | 17 |
| 2.5.3 Synthesis of Nanoparticles Supported in Silica Matrices | 18 |
| | |
| CHAPTER 3: EXPERIMENTAL PROCEDURES | 19 |
| 3.1 Raw Materials | 19 |
| 3.2 Apparatus | 19 |
| 3.3 Preparation of Reacting Solutions | 20 |
| 3.4 Preparation of Zeolite-Iron Oxide (ZIO) Systems | 21 |

| | |
|---|-----------|
| CHAPTER 4: CHARACTERIZATION METHODS | 26 |
| 4.1 X-Ray Powder Diffractometry | 26 |
| 4.1.1 Introduction | 26 |
| 4.1.2 Principle | 26 |
| 4.1.3 Sample Preparation | 28 |
| 4.2 Alternating Gradient Magnetometry | 30 |
| 4.2.1 Introduction | 30 |
| 4.2.2 Principle | 30 |
| 4.2.3 Sample Preparation | 30 |
| 4.3 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry | 33 |
| 4.3.1 Introduction | 33 |
| 4.3.2 Principle | 33 |
| 4.3.3 Sample Preparation | 36 |
| 4.4 Transmission Electron Microscopy | 37 |
| 4.4.1 Introduction | 37 |
| 4.4.2 Principle | 38 |
| 4.4.3 Sample Preparation | 38 |
| 4.5 Gas Adsorption Desorption | 40 |
| 4.5.1 Introduction | 40 |
| 4.5.2 Principle | 40 |
| 4.5.3 Sample Preparation | 42 |
| | |
| CHAPTER 5: RESULTS AND DISCUSSION | 43 |
| 5.1 Physical Observations | 43 |
| 5.2 Elemental Composition | 45 |
| 5.3 Phase and Crystal Structure | 47 |
| 5.4 Particle Morphology | 52 |
| 5.5 Response to Magnetic Field | 58 |
| 5.6 Pore Size and Volume Distribution | 63 |
| | |
| CHAPTER 6: CONCLUSIONS | 65 |
| | |
| REFERENCES | 67 |

| | | |
|---------------------|--|------------|
| APPENDICES | 73 | |
| 1 | Certificate of XRF analysis of zeolite Na-Y | 74 |
| 2 A | X-ray data card for γ -Fe ₂ O ₃ | 78 |
| 2 B | X-ray data card for α -Fe ₂ O ₃ | 79 |
| 2 C | X-ray data card for γ -Fe ₂ O ₃ •H ₂ O | 80 |
| 3 A | X-ray report and diffractogram of zeolite Na-Y | 81 |
| 3 B | X-ray report and diffractogram of ZIO-1 | 84 |
| 3 C | X-ray report and diffractogram of ZIO-2 | 87 |
| 3 D | X-ray report and diffractogram of ZIO-3 | 90 |
| 3 E | X-ray report and diffractogram of ZIO-4 | 93 |
| 3 F | X-ray report and diffractogram of ZIO-5 | 95 |
| 4 | Profile Fit report for ZIO-5 | 97 |
| 5 A | Magnetization curve of ZIO-0 | 103 |
| 5 B | Magnetization curve of ZIO-1 | 104 |
| 5 C | Magnetization curve of ZIO-2 | 105 |
| 5 D | Magnetization curve of ZIO-3 | 106 |
| 5 E | Magnetization curve of ZIO-4 | 107 |
| 5 F | Magnetization curve of ZIO-5 | 108 |
| 6 A | Adsorption-desorption isotherm of zeolite Na-Y | 109 |
| 6 B | Adsorption-desorption isotherm of Fe(II)-exchanged zeolite | 110 |
| 6 C | Adsorption-desorption isotherm of ZIO-2 | 111 |
| 7 A | EDS results of zeolite Na-Y | 112 |
| 7 B | EDS results of Fe(II)-exchanged zeolite Na-Y | 113 |
| 7 C | EDS results of ZIO-0 | 114 |
| 7 D | EDS results of ZIO-1 | 115 |
| 7 E | EDS results of ZIO-2 | 116 |
| 7 F | EDS results of ZIO-3 | 117 |
| 7 G | EDS results of ZIO-4 | 118 |
| 7 H | EDS results of ZIO-5 | 119 |
| | | |
| PUBLICATIONS | | 120 |

LIST OF FIGURES

| Figure | | Page |
|--------|---|------|
| 1.1 | The flow-chart of the study. | 4 |
| 2.1 | A schematic representation of the tetrahedra of which zeolites are made up. T is either Si or Al. The tetrahedra join by sharing O at the corners and extend in three-dimensions infinitely to make up the aluminosilicate framework. | 6 |
| 2.2 | The zeolite Y structure in the dehydrated state. Positions occupied by metal ions within the structure are indicated by the spheres (taken from [5]). | 7 |
| 2.3 | Schematic representation of formation and transformation pathways of common iron oxides (taken from Cornell & Schwertmann [22]). | 14 |
| 3.1 | The ion-exchange procedure. | 23 |
| 3.2 | The iron oxide precipitation procedure. | 24 |
| 4.1 | Diffraction of x-ray beams by planes of atoms, as governed by Bragg's Law. | 27 |
| 4.2 | Diffraction patterns of a nanocrystalline material showing broadening because of particle size. | 28 |
| 4.3 | Sample chamber of XRD where the sample is subjected to X-rays. | 29 |
| 4.4 | The transducer probe on which the sample is mounted. | 31 |
| 4.5 | The set-up of the transducer probe within the magnetometer assembly. | 32 |
| 4.6 | Effects of electron-specimen interaction. | 34 |
| 4.7 | Production of characteristic X-rays for EDS. | 35 |
| 4.8 | The sampling chamber of the SEM. | 36 |
| 4.9 | The Philips TEM used for observation of specimens. | 37 |
| 4.10 | A schematic representation of the TEM and the location of the sample. | 39 |
| 4.11 | The Sorptomatic machine used for gas adsorption desorption measurements. | 42 |
| 5.1 | Diffraction spectra of the precipitated zeolite-iron oxide (ZIO) samples [patterns (b) to (f)] compared with the pattern of pure zeolite (a). | 47 |

| | | |
|--------|--|----|
| 5.2 | The diffraction patterns of (a) ZIO-4 and (b) ZIO-5, after subtracting the background contribution. | 49 |
| 5.3(a) | SEM image of pure zeolite powder. | 52 |
| 5.3(b) | SEM image of ZIO-1. | 53 |
| 5.3(c) | SEM image of ZIO-2. | 53 |
| 5.3(d) | SEM image of ZIO-3. | 54 |
| 5.3(e) | SEM image of ZIO-4. | 54 |
| 5.3(f) | SEM image of ZIO-5. | 55 |
| 5.4 | The surface morphology of ZIO-0 obtained from free precipitation without any zeolite constraining effect, as observed under SEM. | 55 |
| 5.5 | TEM images of the zeolite-iron oxide samples, (a) ZIO-3, (b) ZIO-5, (c) ZIO-1, (d) ZIO-2 and (e) ZIO-4. | 56 |
| 5.6 | The ZIO-5 system as seen under TEM. | 57 |
| 5.7 | The magnetization curves of (a) ZIO-1 and (b) ZIO-2. | 60 |
| 5.8 | Magnetization curves of (a) ZIO-3, (b) ZIO-4 and (c) ZIO-5. | 60 |
| 5.9 | The magnetization curve of ZIO-0. | 61 |
| 5.10 | Gas adsorption-desorption isotherm of pure zeolite Y powder. | 63 |
| 5.11 | Gas adsorption-desorption isotherm of (a) Fe(II)-exchanged zeolite Y and (b) ZIO-2. | 64 |

LIST OF TABLES

| Table | | Page |
|-------|--|------|
| 2.1 | A summary of the iron oxides and their general characteristics. | 8 |
| 3.1 | Weight of NaOH mini pearls required to prepare various concentrations of alkali solutions. | 20 |
| 3.2 | Sample preparation of zeolite-iron oxide (ZIO) systems. | 25 |
| 5.1 | Compilation of physical characteristics of samples before being subjected to further characterization. | 44 |
| 5.2 | Elemental composition and Si:Al molar ratio of various treated zeolite samples (wt. %). | 46 |
| 5.3 | Comparison of peak positions and d-spacings between standard reference materials and ZIO-5. | 49 |
| 5.4 | Estimation of crystallite size of zeolite-iron oxide from ZIO-5 calculated using Scherrer's equation. | 51 |
| 5.5 | Summary of magnetic properties of ZIO samples. | 58 |
| 5.6 | 'Magnetic' size of the particles. | 59 |