

# Formation of surface magnetite nanoparticles from iron-exchanged zeolite using microwave radiation

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**Abstract** Microwave radiation simplifies synthesis methods by reducing reaction times, requiring fewer materials, and also controlling reaction processes. We have successfully synthesized nanoparticles of iron oxide and zinc oxide coated on zeolite A using microwaves. The radiation assisted in displacing either ferrous or zinc ions from the pre-loaded zeolite network and increasing reaction speed with solution at the interface. Products were characterized by TEM, XRD, VSM, ICP-AES, and fluorescence. We demonstrate the ability of using cation-exchanged zeolites as microreactors to bias reactions onto the zeolite surface. Efficient structure-directed surface reactions are a potential route to making unique supported nanomaterials for applications such as sensors, environmental remediation, and chemical catalysis.

## Introduction

Many of the unique phenomena that nanomaterials exhibit are highly dependent not only on the chemical constituents, but also on the size and shape of the nanomaterial. Given that controlling the rate of nucleation is the key to

controlling size, and in some cases shape, it would be desirable to quickly and uniformly synthesize nanomaterials. One approach to obtaining this control is the use of microwave systems in synthesis. Besides the obvious advantage of reducing reaction times from days to minutes, the nucleation processes are better controlled under microwave conditions since the reaction is driven by the quick heat and pressure produced by the microwave system [1–3]. The resulting physical characteristics of the nanoparticles are controllable and more reproducible [4]. For example, microwave methods now exist to synthesize nanoparticles with high degrees of monodispersity [5]. An added advantage is that the amounts of reactants and solvents used in the synthesis are reduced, providing a “greener” synthesis route with fewer cleanups required.

Of particular importance to this report is that microwave synthesis of submicron-sized magnetite powders has been shown [4]. They reacted both ferrous and ferric salts together and the ferrous salt alone with sodium hydroxide in teflon digestion vessels in a high-powered (1,200 W) microwave. By using only two chemicals in the reaction, the conversion has few byproducts, resulting in a product with little impurity. The complement of microwave power facilitates rapid synthesis and relatively consistent heating within the vessel.

Solution-based nanoparticles are not always the optimal path of synthesis since the functionality of the particles can be realized only after removal of the solvent and placement of the particles in another media. For instance, some nanoparticle metal oxides are important in the development of industrial catalysts [6]. It would be ideal to synthesize the desired nanoparticles within the proper medium, thereby eliminating the transfer step. One widely-used catalyst is zeolite A, a white powder of aluminosilicate networks. Oliveria et al. used this zeolite not as a catalyst,

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but rather as an ion-extracting agent in water [7]. The group used solution-based synthesis to produce a magnetic zeolite by incorporating magnetite ( $\text{Fe}_3\text{O}_4$ ) about the zeolite particles. The zeolite framework remained open to extract cations from the solution and the attached magnetite allowed powder withdrawal by using a simple magnet.

As an extension of prior work, we are reporting a microwave synthesis method to yield submicron-sized magnetite and zinc oxide particles coated on zeolite A. Microwave radiation served to both rapidly displace ions from the zeolite matrix and position them at the zeolite/solution interface. After preloading a zeolite with selected cations, they were displaced from the framework to the solution interface where the appropriate chemical reactions took place. The significance is our method of employing microwaves to a chemical system yielding nanoparticles coated directly on the support matrix with little solution reaction competition. Minimal preparation and reaction time enhance the success of this method.

## Experimental procedure

Chemicals were used without additional purification unless otherwise noted. Ferrous sulfate, zinc nitrate, and sodium hydroxide were purchased from Aldrich. Valfor<sup>®</sup> 100 zeolite was donated by The PQ Corporation.

Zeolite was first preloaded with the desired cation by stirring 100 mL of 1 M ferrous sulfate or zinc nitrate solution with 8 g of zeolite. The suspension was allowed to equilibrate for at least 24 h to ion-exchange either iron or zinc, respectively. After sufficient mixing the slurry was filtered and thoroughly washed with deionized water, then diluted to 30 mL. Once the zeolite was loaded and washed it was ready for reaction in the microwave vessel.

Sodium hydroxide solution was used for both syntheses as the other reactant. A 4.8 mL aliquot of 0.25 M NaOH (reaction concentration of 0.2 M) was combined with 1.2 mL of loaded zeolite suspension in a glass reaction vessel and capped with a pressure-sensitive lid. Identical samples were also left to sit overnight without being exposed to radiation to observe unassisted reactions. Solution reactions without zeolite present were synthesized by combining 1.2 mL of either 0.2 M ferrous sulfate or zinc nitrate solutions with 4.8 mL of 0.25 M NaOH. The reaction tubes were exposed to microwave irradiation in a CEM Discover<sup>®</sup> unit using the following parameters: Power—300 W; Ramp time—10 s; Hold time—10 min; Max temperature—150 °C; Max pressure—200 PSI; Stirring and powerMax—On.

Products were investigated with transmission electron microscopy (TEM), X-ray diffraction (XRD), vibrating sample magnetometry (VSM), fluorescence spectropho-

tometry (zinc synthesis only), and inductively coupled plasma (ICP) emission spectroscopy. The specifications are as follow. TEM pictures were obtained using a Zeiss 10C operated at 100 KeV with the images being captured on Kodak 4489 film and scanned in on an Agfa Duoscan at 1000PPI. XRD patterns were obtained using a Scintag X1 powder X-ray diffractometer. VSM measurements were made on a home-assembled apparatus utilizing the Faraday Law to detect induced voltage in the pick-up coils by the vibration of the measured magnetic sample in the magnetic field. The frequency used for the vibrator is about 48 Hz and the system was calibrated using a standard Pd sample with known moment. This VSM system has a moment of sensitivity of about 10 micro-emu. Fluorescence data was obtained on a Horiba Jobin Yvon Fluorolog-3 FL3-22 spectrophotometer. ICP emission data was obtained on a Varian Liberty 150 spectrometer.

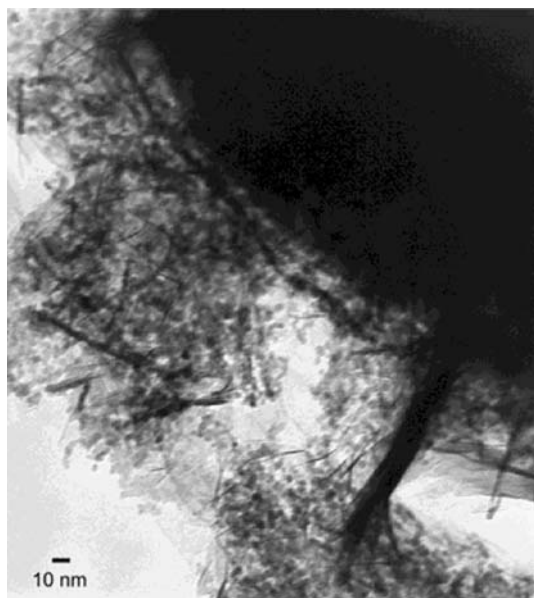
Glycerin (60% v/v) was added to a ferrous ion/zeolite/hydroxide solution to increase the solution viscosity and affect magnetite particle nucleation and growth. It was hypothesized that different solvent properties would affect formation of the iron oxide particles. Microwave conditions and ion concentrations remained unchanged from the previous experiments.

Since zeolite is often used as a cation-exchange medium, the exchange capability was tested using calcium ions. After the products were obtained, filtered, and rinsed, saturated calcium solutions were added. They were allowed to equilibrate for at least 24 h. The filtered solids were dried under ambient conditions and digested with hydrochloric acid. The resulting solution was analyzed using ICP emission spectroscopy.

## Results and discussion

The results obtained clearly demonstrate the hypothesized interface-directed nanoparticle syntheses. Both iron oxide and zinc oxide nanoparticles were synthesized about the zeolite surface after exposure to microwave radiation. Samples not exposed to microwave radiation took hours to react and the particles were of micrometer size. The reaction did not appear to go to completion after 24 h. However, under microwave radiation conditions, small, more desirable nanoparticles were synthesized rapidly.

A representative TEM picture of the iron oxide/zeolite product is given by Fig. 1. Glycerin was added to the same reaction mixture as the typical ferrous ion/zeolite mix. A TEM image (not shown due to rapid decomposition under the electron beam) of the glycerin samples shows a significantly narrower size distribution relative to the water-only syntheses. Particles about the zeolite were between one to three nanometers and showed a high degree of uniformity.



**Fig. 1** TEM image of the magnetite/zeolite product

The same product shown in Fig. 1 was investigated using XRD to determine the form of iron oxide present. As can be seen by Fig. 2, the zeolite peaks dominate the spectrum, obscuring iron oxide peaks. This indicates the zeolite remained intact after microwave exposure but gives no data regarding the iron oxide species formed.

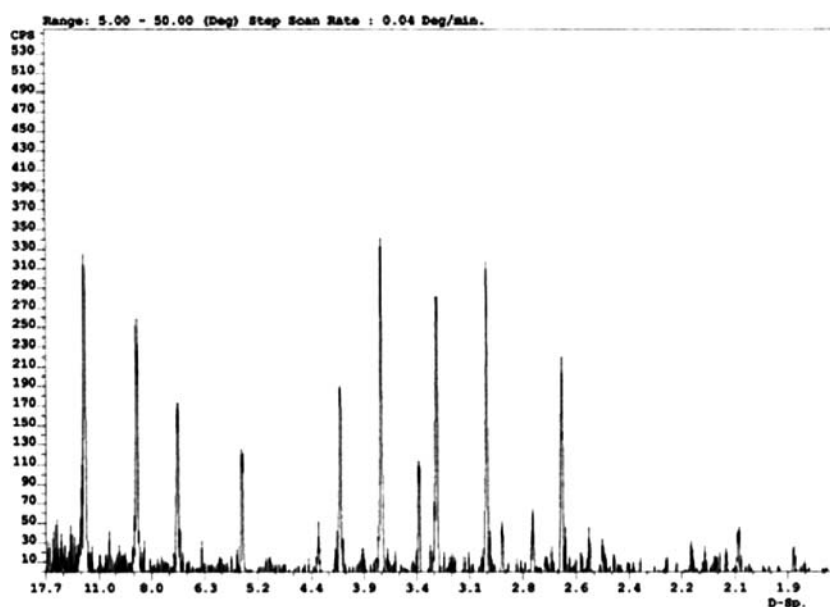
In order to determine what form of iron oxide was likely synthesized, we obtained an XRD diffractogram for the solution reaction product in the absence of zeolite. The XRD pattern of our iron oxide is shown in Fig. 3; black arrows indicate experimental peaks that align with literature peaks for magnetite. Although the peaks are weak in

intensity, they align well to the literature diffraction pattern of magnetite. Small particle sizes or the presence of amorphous material may be responsible for these weak signals. This result indicates the crystalline product is magnetite, as opposed to other ferrous/ferric oxides/hydroxides, was the dominant product. Since we did not obtain an XRD pattern containing peaks for both zeolite and magnetite species, the iron oxide in the zeolite reaction may not be entirely magnetite. However, the magnetization results support magnetite formation.

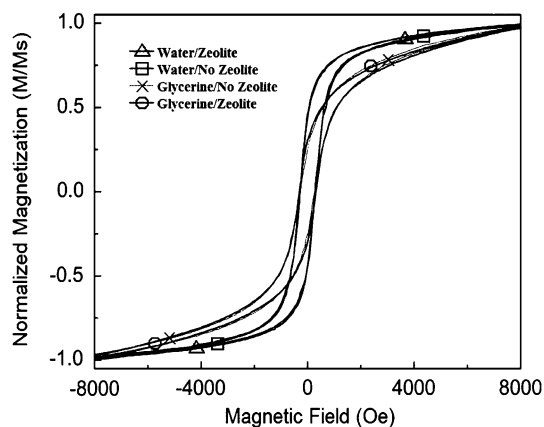
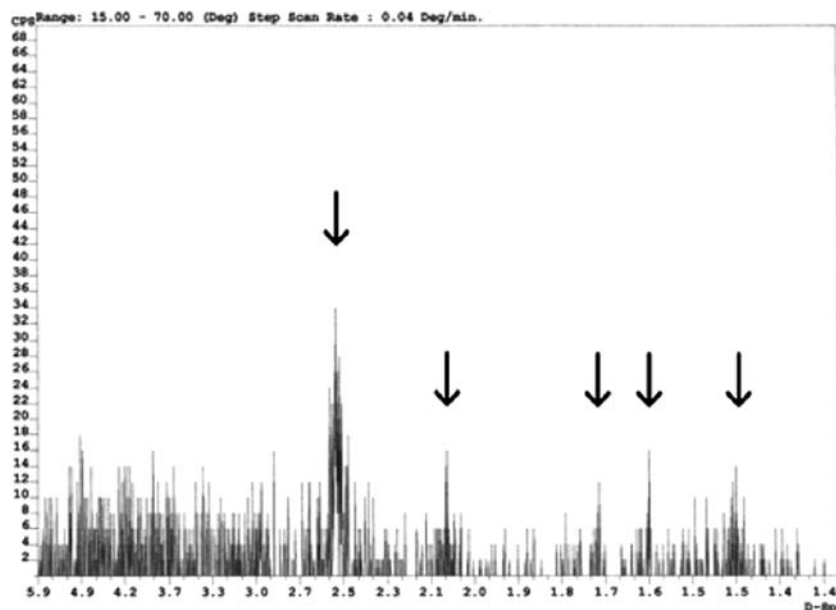
A further investigation into the magnetism of the iron oxide products gave an interesting result. VSM loops were obtained for four samples: magnetite from ferrous ions and hydroxide; ferrous ions, hydroxide, and glycerin; ferrous ions, zeolite, and hydroxide; and ferrous ions, zeolite, hydroxide, and glycerin. Figure 4 shows the normalized magnetization loops, indicating that solution conditions influence the magnetic properties of the synthesized products. The samples with the presence of glycerin have lower remanence and higher saturation field, compared to the water-only products, regardless of the zeolite presence. However, zeolite presence slightly increases the coercivity of the products from about 270–300 Oe. All samples do not saturate within 8 kOe available for these measurements. The shape of the hysteresis loops suggests a coexistence of superparamagnetism and ferromagnetism of the magnetic particles due to a size distribution.

To confirm our synthesis method was general and not unique to iron oxide, we carried out the synthesis with zinc ions in place of iron ions. As in the iron reaction, we again observed nanoparticles, here as zinc oxide draped about the zeolite surface. The TEM image of the product, Fig. 5, shows this; the zinc oxide coverage, however, is not as

**Fig. 2** XRD pattern of ferrous ion-loaded zeolite A after microwave exposure



**Fig. 3** XRD pattern of iron oxide powder

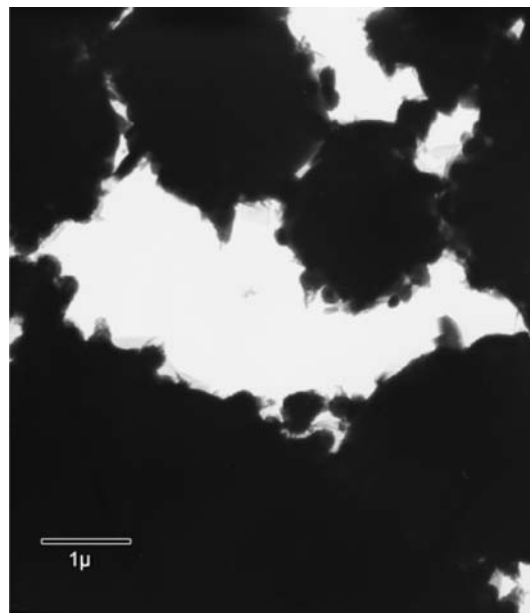


**Fig. 4** VSM loops of magnetite/zeolite products

extensive as the coverage by the magnetite about the zeolite. Explanations for the observed coverage differences are being pursued.

Zinc oxide growth composition about the zeolite was more varied in comparison with the iron oxide. Cones, large clusters, and flat sheets of zinc oxide were observed. The implication is the zinc oxide nucleated and grew via multiple mechanistic pathways.

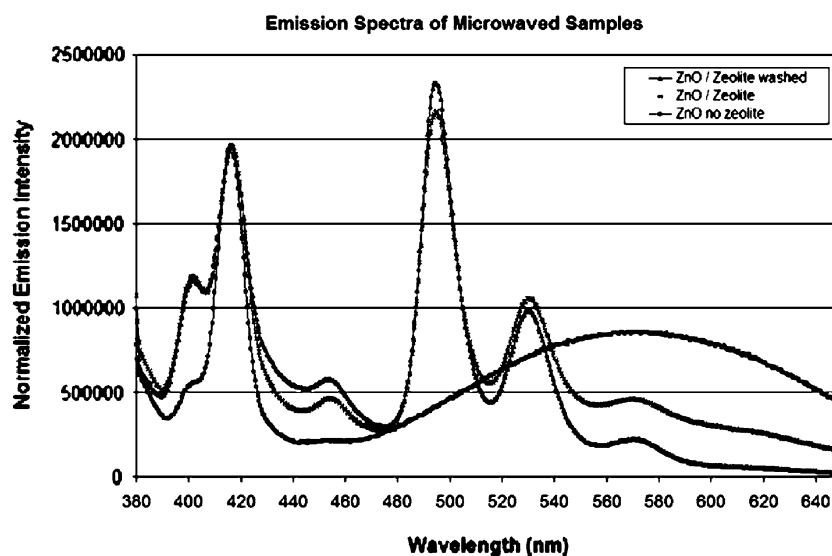
Because zinc oxide is a known fluorophore, fluorescence spectra were obtained to compare the zinc oxide solution and zeolite interface-directed synthesis products. Spectra were normalized at the 416 nm peak for comparison. The spectra given in Fig. 6, collected with an excitation wavelength of 365 nm, show highly resolved vibrational structure for zinc oxide on zeolite. Comparing the zinc-exchanged and washed zeolite reaction spectrum (labeled “ZnO/Zeolite washed”) with the zinc-exchanged zeolite



**Fig. 5** TEM image of the zinc oxide/zeolite product

reaction in the presence of solution zinc ions (labeled “ZnO/Zeolite”) spectrum indicates the surface reaction is favored. The spectrum of zinc oxide solution reaction with no zeolite (labeled “ZnO no zeolite”) has a strong emission peak at 416 nm and a broad emission at 572 nm. The competitive solution product formation of the ZnO/zeolite product is most clearly seen in the higher fluorescence intensity at 572 nm versus the ZnO/Zeolite washed spectrum. The observed fine structure and limited elevated fluorescence between 510 nm and 620 nm indicates the reaction is highly weighted toward zinc oxide nucleation

**Fig. 6** Fluorescence spectra of zinc oxide and zinc oxide/zeolite products



on the zeolite. Had the solution-synthesized zinc oxide reaction dominated we would not have seen the predominant spectral fine structure between 480 nm and 550 nm; the broad fluorescence between 510 nm and 620 nm would have been more prominent.

The exchange capacities of the following solids were investigated: magnetite on zeolite, zinc oxide on zeolite, microwaved zeolite, and zeolite. Results from the acid digestion and subsequent ICP analysis indicate that no exchange capacity was lost when compared to the reagent zeolite sample, given in Table 1. An interesting point is that the microwaved zeolite control had a somewhat higher degree of exchange capacity, possibly attributed to the radiation increasing cavity activity compared with the untreated commercial product. The magnetite also shows a higher level of exchange, but this value may be enhanced by calcium adsorption on the magnetite. Magnetic zeolite has previously been shown to be a more efficient cation extractor than zeolite alone [7].

Also listed in Table 1 are the theoretical maximum percentages of product expected based on the ICP values obtained and the 5.5 milliequivalent per gram exchange capacity of zeolite A [8]. The data we obtained are slightly lower than the maximum values mainly due to inefficient exchange and incomplete cation reaction at the zeolite interface. Some metal oxide product formed may not have

bound to the zeolite. Despite this, the numbers confirm the majority of the metal oxide reacts at the zeolite/solution interface.

## Conclusions

We have demonstrated a zeolite interface-directed metal oxide nanoparticle synthesis method potentially useful in making catalysts, sensors, and a new approach to making nanostructured interfaces. These experiments show the ability of using zeolite ion-exchange as a means of delivering cations in reactions where the zeolite serves as a microreactor. Microwave radiation increases the ion exchange rate in a controlled manner to displace ions from the zeolite network to form magnetite or zinc oxide by reactions of simple ferrous or zinc salts with hydroxide. Cation delivery from the zeolite adds the ability to control nanoparticle growth and nucleation at the zeolite interface. Nucleation control at the interface and solvent effects provide a pathway to synthesize new nanostructured interfaces.

Future work in our laboratory is directed towards establishing microwave solution reaction conditions to control nanoparticle shape and size. Nanoparticle microwave synthesis provides a significant opportunity for time-efficient (less than 10 min) and green synthesis of unique interfaces with potential applications in catalysis, chemical analysis, electronic devices, and sensors.

**Table 1** Calcium exchange data and oxide percent values, both theoretical and experimental

	meq/g Ca <sup>2+</sup>	% Oxide	Theoret. %
Magnetite/zeolite	4.7 ± 0.3	17.2 ± 1.6	17.5
Zinc oxide/zeolite	4.1 ± 0.3	14.5 ± 0.6	18.3
Microwaved zeolite	5.3 ± 0.1	–	–
Zeolite	4.1 ± 0.2	–	–

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