

Molecular Simulation Studies for the Synthesis of Ni Nanowires in Zeolite Cancrinite

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ABSTRACT

Zeolites are promising materials to be used as templates in the synthesis of nanowires and other higher order nanostructures. Previous studies using molecular simulations with zeolites reported that there is a strong relation between the location of Al atoms in zeolites and the position of the metal atoms inside the zeolite framework structure; this reflects the importance of the Si/Al ratio in the selection of adequate zeolites for the templated synthesis of metal nanowires. In the present work, Metropolis Monte Carlo simulations were done to study the behavior of Ni at different loadings in zeolite cancrinite with Si/Al = 1 and Si/Al = ∞ . It was found that at Si/Al = 1, the positioning of Ni atoms at the larger one-dimensional pores was favored energetically and that higher loadings of Ni (19% w/w) promote the formation of one-dimensional Ni structures. These results suggest that it is possible to use zeolites with CAN structure and low Si/Al ratios as effective templates for the synthesis of Ni nanowires.

Keywords: molecular simulations, monte carlo, zeolites, cancrinite, nanowires.

1 INTRODUCTION

Metal nanowires are one-dimensional nanoparticles of special interest for the miniaturization of electrical circuits. These structures have especial characteristics because their electrons are quantum confined laterally, occupying different energy levels than the ones from other nanoparticles arrangements.[1] Nanowires' electrical and thermal conductance have discrete values because of the constraint on the number of electrons that can travel through their narrow diameter. Metal nanowires can be used in many practical applications such as nanoscale magnetic sensors and high-density magnetic recordings.

There are several techniques to synthesize nanowires, which include methods such as arc discharge, laser ablation, and aerosol synthesis.[2] A promising and convenient technique for the manufacture of nanoparticles is the templated method, which consists of the use of porous structures to synthesize the desired material inside their pores.[3] In this manner, the pores are used as casts in

which nanoparticles are formed. When compared with other techniques, templated synthesis has the advantage of allowing better control over final size and shape of particles being synthesized. A review of the template methods used for nanowires synthesis is available elsewhere.[4]

Zeolites are aluminosilicate crystal structures that are very promising materials to be used as templates for the synthesis of quantum sized nanoparticles. Typically, zeolites are composed of Si, Al and O atoms. The ratio of Si atoms to Al atoms (Si/Al) can vary from infinite to one, depending on the zeolite structure and the synthesis process. Zeolites, which have pore diameters ranging between 0.4 to 1.3 nm, are used in many commercial applications such as ion exchange, water adsorption, and catalytic cracking. Some zeolites, like cancrinite (CAN), have one-dimensional pore structures (main pore channels) that theoretically can be used in the templated synthesis of metal nanowires (see Figure 1).

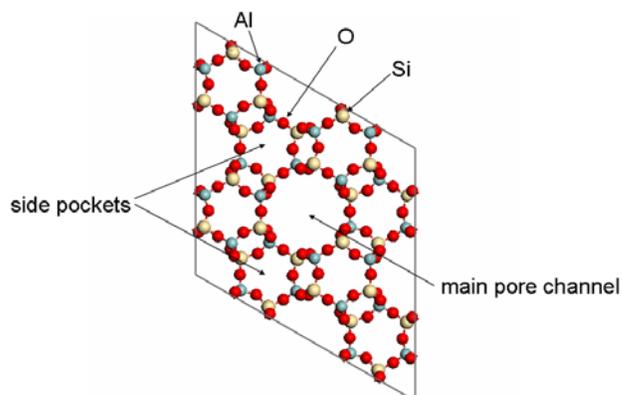


FIGURE 1: Cancrinite (CAN) basic cell structure.

The use of zeolites for the synthesis of metal nanoparticles has been studied and promising results have been obtained for 0D clusters.[5-7] However, there is a lack of relevant literature referent to the use of zeolites as templates for synthesis of metal nanowires and other higher dimension nanoparticles.

In synthesis trials of silica and silver nanowires using zeolites, wires grew inside and outside the pores; also, the dimensions of the obtained nanowires were larger than the original pore size, somewhat limiting the effective use of the zeolite as a template.[8,9] Similar results were obtained in studies that used an electron beam to irradiate copper

containing zeolite, for the production of single crystal copper wires.[10] As opposed to metal nanowires, successful trials has been obtained in the synthesis of single walled and multiwalled carbon nanotubes. [11-12]

Molecular simulations are a convenient way to gain insight of the behavior of molecular structures. It can be used as a guide to focus experimental work that will serve to develop procedures for synthesizing metal nanowires using zeolites as templates. There are many publications that deal with molecular simulations involving zeolites, mainly because of the generalized industrial applications that these aluminosilicate materials have. Many of these reports are focused on the adsorption of chemical compounds related to commercial applications.[13-16] Other subject commonly studied with molecular simulations is the diffusion of chemical compounds inside the zeolite pores.[17-21] However, to the best of our knowledge, there is no relevant literature about molecular simulations that directly address the synthesis of metal nanowires inside zeolite pores.

Grillo et. al. published a molecular simulation study on the stability of metal particles inside zeolites.[22] In this work, lattice energy minimizations were done to study the effects of different Al positions in acidic mordenite (MOR) framework on the location and stability of monoatomic Pt particles. For this purpose, two Al atoms were positioned at different T sites of the MOR basic cell (see Figure 2).

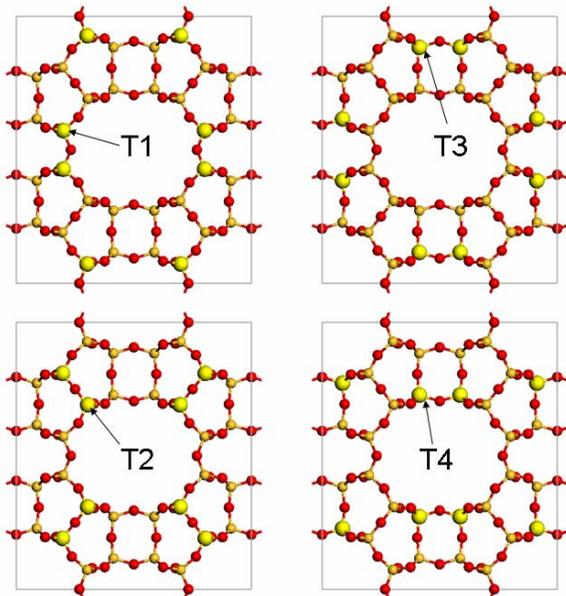


FIGURE 2: Position of the T sites in mordenite basic cell (identified by the bigger spheres)

Based on the lattice energy of the systems studied, the authors found that the stable sites of single Pt atoms in acidic MOR are highly influenced by the specific location of the Al atoms in the lattice. When the Al atoms were placed on the T1-T4, T3-T4, or T2-T4 sites of MOR, energy minimizations favored the position of the Pt atoms inside the side pockets of MOR; meanwhile, the main pore

channels were favored as the most stable places for Pt atoms with the T1-T3, T1-T2, or T3-T2 configurations. Taking into account the expected percent of Al with respect to each tetrahedral site of mordenite, the authors concluded that the side pockets are favored energetically to host Pt atoms in acidic MOR.

These results illustrate the importance of the location of the Al atoms for the synthesis of metal nanowires, as they influence the position of the host metal atoms inside the zeolite structure. During the final steps of the templated synthesis (i.e. the formation of the nanowires structure), metal particles alone are expected to be inside the one-dimensional main pores of the zeolite. In order to form nanowires, it is desired that the majority of metal particles remain in the main pores. The impregnation of adequate sized precursor molecules promotes the introduction of metal atoms inside the main pore channels. The migration of metal atoms to the side pockets during the final steps of the synthesis process will be detrimental in the formation of the nanowires structure.

For the actual synthesis process of zeolites, the Si/Al ratio and not the location of Al atoms can be controlled. However for zeolites that can reach the minimal Si/Al = 1, like cancrinite (CAN), the location of Al atoms is already fixed. Thus, theoretical studies using molecular simulations can be performed with both Si/Al = 1 and Si/Al = ∞ to describe the effect of the Al atoms in the positioning of metal atoms during the synthesis process of metal nanowires. Based on these facts, the present work was focused on the effect of Si/Al ratio and the magnitude of the metal loading on the displacement of Ni particles inside the pores of zeolites with a CAN framework.

2 SIMULATION METHODOLOGY

Evaluation of the spatial distribution of Ni metal atoms inside the zeolite framework was done using molecular simulations for CAN at two Si/Al ratios (Si/Al = 1 and Si/Al = ∞), and at four Ni loadings equivalent to 5%, 10%, 15%, and 19% w/w. Also, one Ni atom simulations were done for CAN with the same Si/Al ratios and compared with a similar simulation with MOR (Si/Al = ∞). These simulations were done at room temperature (298 K) to obtain the relative position of Ni atoms at the most stable energetic conditions. The idea here was to establish the conditions that promote the displacement of Ni inside the one-dimensional main pores channels and not inside of the pockets of the zeolite structure. The simulations were performed using Sorption from Material Studio 4.0 (Accelrys, Inc.). For each simulation, the Metropolis Monte Carlo (MMC) scheme was used in the canonical ensemble, with 2×10^6 equilibration steps, 1×10^7 processing steps, and a cut off ratio of 18.5 \AA . A supercell composed of $2 \times 2 \times 16$ primitive cells (2304 atoms) was used for CAN. The relative position of the atoms in the zeolite structure was fixed during the simulation process and determined

previously from crystallographic data. To determine the position of the balancing protons in the CAN acidic zeolite, energy minimizations were done with several configurations for the bounding of the balancing protons and selected the one that resulted in lower total energy.

The *pcff* forcefield was used in these energy minimizations as well as in the MMC simulations. *Pcff* is well known and extensively used forcefield developed by Sun and other researchers and its based on the *cff* forcefield.[23] *Pcff* was parameterized using *ab-initio* methods and includes parameters for zeolites as well as 20 inorganic metals (including Ni), accounting for the interaction between metal atoms and the ones found in the zeolite framework. The parameterization of the *pcff* for the metal-metal interactions is based on the 9/6 form of the Lennard-Jones potential and was obtained by fitting parameters to crystal structures and elastic constants of the selected metals.[24]

3 RESULTS AND DISCUSSION

Figure 3 presents views down the C axis of the minimum energy configurations obtained from the MMC simulations for CAN at Si/Al = 1 and Si/Al = ∞ with loadings of Ni equivalent to 10% w/w. In these drawings, it is easily observed that Ni is present only in the main channels of CAN at Si/Al = 1, while metal atoms are present also in the site pockets of CAN at Si/Al = ∞. This behavior was consistently observed in almost all the simulations performed at different loadings of Ni; it was not until the number of Ni atoms reached the maximum possible loading (in the simulation) that single Ni atoms were observed at the pocket sites of CAN with Si/Al = 1.

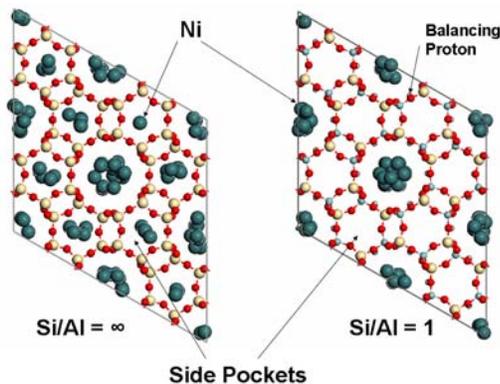


FIGURE 3: View of CAN with Ni loading of 10% w/w

In repeated MCC simulations of CAN with Si/Al = 1 and a loading of one atom, Ni never was positioned in the side pockets of the zeolite. When MMC simulations were performed for CAN with Si/Al = ∞ and Ni loadings of one atom, we observed that the path generated by the algorithm suggested a non-ergodic behavior for Ni, i.e. the Ni atom initially positioned at the main pore channel did not pass

through the interconnecting rings to the side pockets (and vice versa). Preliminary simulations with MOR (Si/Al = ∞) suggest that this behavior is different in that structure, i.e. the Ni atom can pass through the interconnecting rings from the main pore channel to the side pockets and vice versa. These differences can be explained by the diameter of the interconnecting rings, which is about 2.8Å for CAN and 4.6Å for MOR (see Figure 4). With a Van der Waals atom diameter of 3.58Å, Ni atoms are not expected to pass through the CAN interconnecting rings. This fact makes CAN a better alternative than MOR for the templated synthesis process of Ni nanowires.

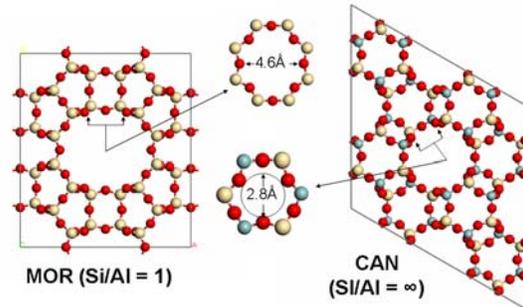


FIGURE 4 - Interconnecting rings of MOR and CAN

When considering the results for CAN (Si/Al = 1) with one Ni atom and the non-ergodic nature of this structure, MCC trials of positioning Ni inside the side pockets failed. This suggests that energetic conditions inside the side pockets when Si/Al = 1 do not promote the positioning of Ni atoms here. This was confirmed by energy minimizations for Ni atoms inside the side pockets and in the main pore channels for CAN with Si/Al = 1 and Si/Al = ∞. The results are presented in Table 1. Notice that ΔE for CAN with Si/Al = 1 and one atom of Ni in the side pocket is positive, which implies that the positioning of Ni in this place is not favored at these conditions.

System	Total Energy	Δ Energy
CAN Si/Al=∞	-28,010.0	0.0
+ Ni main channel	-28,015.2	-5.2
+ Ni side pocket	-28,020.2	-10.2
CAN Si/Al=1	-90,155.3	0.0
+ Ni main channel	-90,158.4	-3.1
+ Ni side pocket	-90,152.1	3.2

Table 1: Energy of one atom of Ni in CAN Pores (kcal/mol)

Figure 5 presents the positioning of Ni atoms along the supercell of CAN at Si/Al = ∞ and Si/Al = 1 for Ni loadings of 10% w/w; a view of CAN (Si/Al = 1) with 19% w/w Ni loading is also included. For the MCC simulations with lower Ni concentrations, the formation of Ni clusters was observed. The size of these agglomerations increased with Ni concentration in both cases. For CAN with Si/Al = 1, the observed size of the clusters at the main pore channels was greater than for CAN with Si/Al = ∞. As the metal concentration increased, the observed Ni agglomerates in

CAN (Si/Al = 1) increased in elongation. At 19% w/w Ni, the agglomerates form one-dimensional structures that resemble Ni nanowires, suggesting that a low Si/Al and high metal loadings will promote the formation of nanowires.

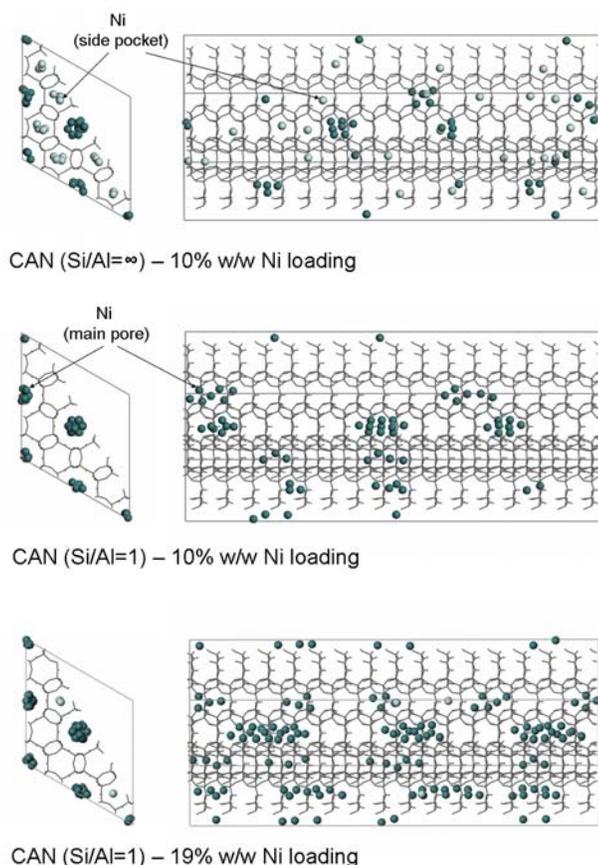


FIGURE 5: MMC simulations of Ni in CAN (*lighter colored Ni atoms are in the side pockets and darker colored Ni atoms are in the main pores*)

4 CONCLUSIONS

Our results illustrate importance of the Si/Al ratio and metal loading in the synthesis of metal nanowires using zeolite structures. For CAN, a Si/Al ratio of one favored energetically the positioning of Ni atoms inside the main pore channels. This suggests that lower Si/Al ratios can reduce the displacement of metal particles from main channels to side pockets in zeolites like mordenite, improving the usefulness of such zeolites in the templated synthesis of metal nanowires. In the case of CAN, the dimensions of the interconnecting rings prevent the migration of Ni and other metal atoms to the side pockets. This fact can be useful during the templated synthesis of metal nanowires if adequate size precursor molecules are used during impregnation, placing the metals atoms inside the main pore channels of the CAN structure.

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