

Monte Carlo Studies of the Effect of Temperature, Si/Al, and Metal Loading on the Templated Synthesis of Pt Nanowires in MOR-type Zeolites

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ABSTRACT

Molecular simulations were done to study the feasibility of synthesizing Pt nanowires inside the pores of MOR-type zeolites. Metropolis Monte Carlo (MMC) simulations show the effect of temperature, the zeolite's silicon to aluminum ratio (Si/Al) and metal loading on the positioning of Pt atoms inside the mordenite framework. It was found that low Si/Al and high temperatures promote the positioning of Pt atoms inside the main pore channels, which are the places where metal nanowires could be formed. On the other hand, high Si/Al and low temperatures promote the positioning of Pt atoms in the side pockets of the MOR structure at loadings of 10% w/w. For Pt loadings of 21% w/w, the guest metal atoms are positioned in the main pore channels, for all conditions studied. This suggests that there are in fact optimal conditions for the formation of subnanometer wires in zeolites.

Keywords: Molecular simulations, platinum, zeolites, mordenite, nanowires

1 INTRODUCTION

Zeolites are aluminosilicate crystalline materials that traditionally have been used in a wide variety of applications such as ion exchange in water purification, separation by adsorption of specific molecules, and catalytic reactions in the petrochemical industry. With the advent of nanotechnology, these materials have gained interest for the potential use of their pores as templates in the synthesis of quantum sized nanostructures. Depending on the framework type, zeolite pores can form channels in one, two, or three dimensions with diameters ranging between 0.4 to 1.3 nm. Zeolites with the same framework can have different ratios of Si atoms to Al atoms (Si/Al) which can range from infinite to one.

Mordenite (with MOR structural framework) is an example of a zeolite with one-dimensional pore channels (see Figure 1). The MOR type zeolites have a general molecular formula of $Al_nSi_{48-n}O_{96}$. In the particular case of mordenite with Si/Al = 5, $n = 8$ the molecular formula is $Al_8Si_{40}O_{96}$. The smallest distance between two opposed oxygen atoms in the main pore channels of MOR is 6.5 Å. These main pore channels have rings of 12 oxygen atoms

surrounded by smaller pores called side pockets. The windows to these side pockets are made by rings that have between four to eight oxygen atoms. The minimum distance between two opposed oxygen atoms in the largest rings of the pockets is ~ 3.4 Å.

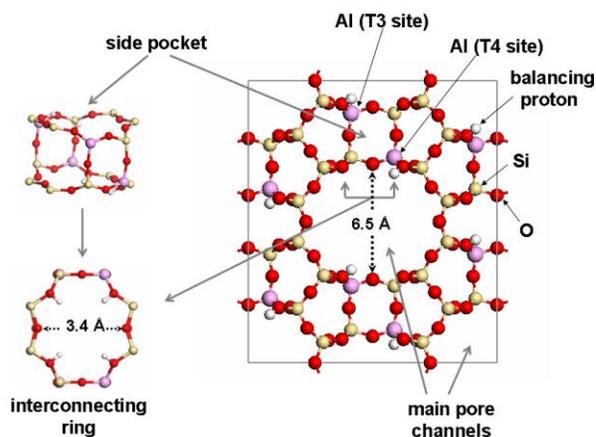


Figure 1: Mordenite framework with Si/Al = 5

There are several reports about successful templated synthesis of 0D metal clusters in zeolites [1-4] and some reports are available about trials for 1D nanostructures.[5-8] The later include trials of silica and silver nanowires, where the wires grew inside and outside the pores and had dimensions larger than the original pore size.[5,6] Similar results were obtained in studies that used an electron beam to irradiate a copper containing zeolite for the production of single crystal copper wires.[7] Another report of Pt nanowire growth in zeolite mordenite has been recently published by our group using a solid state reduction method.[8] However, in all these studies, the diameter of the reported nanowires was larger than the size of the pores evidencing a limitation in terms of the effective use of the zeolite as a template.

The lack of literature about the effective use of zeolites as templates for the synthesis of metal nanowires and other higher dimension nanostructures can be explained by the complexity of a process which is affected by many variables. Among others, these variables include the structural characteristics of the zeolite framework, zeolite composition, and temperature of the synthesis process.

Molecular simulations are a viable and cost effective way to study the effect of the variables mentioned above on the synthesis of metal nanowires. This type of theoretical studies can serve as a guide to focus experimental work for the development of templated synthesis procedures of metal nanowires and other higher dimension structures.

In previous studies using Monte Carlo simulations with Ni in the CAN framework at $T = 298\text{K}$, it was found that the small diameter of the interconnecting rings (1.5 \AA) prevented the displacement of Ni between pore channels and the side pockets.[9] In the case of the MOR framework, such displacement is permitted due to its larger sized side pocket windows. This fact can have a detrimental effect on the synthesis of metal nanowires because of the desirability of maintaining the metal atoms in the main pore channels, which are the places where subnanometer wires can be formed.[10]

Pt nanowires are interesting because of their potential high electrical conductivity, catalytic properties, and use in electrical circuits.

Many of the templated synthesis processes of metal nanostructures require the use high temperatures. Thus, the present work is focused on the effect of temperature, Si/Al and metal concentration on the positioning of Pt atoms in the MOR framework.

2 SIMULATION METHODOLOGY

The Metropolis Monte Carlo (MMC) simulations described here were done using the Sorption module of Materials Studio Software™, Version 4.0 (Accelrys, Inc.). Geometric minimizations were performed with the Forcite module of the same software. The MMC simulations were done using a canonical ensemble with 2×10^6 equilibration steps, 1×10^7 processing steps, and a cut off ratio of 18.5\AA . The energy computations were done using the *pcff* forcefield, which was developed by Sun et al.[11]. This forcefield is parameterized for zeolites as well as 20 inorganic metals (including Pt), and accounts for the interaction between metal atoms and the ones found in the zeolite framework.[12]

The MMC simulations were done using the MOR framework with $\text{Si/Al} = \infty$ and $\text{Si/Al} = 5$ and a supercell composed of $1 \times 1 \times 6$ unit cells. The relative position of the atoms in each framework was fixed during the simulation processes and determined previously from crystallographic data. For MOR with $\text{Si/Al} = 5$, the positioning of the eight Al atoms per unit cell was selected using a similar criteria to the one used by Demuth et al.;[13] the Al atoms were preferentially positioned at the T3 sites and secondly at the T4 sites (shown in Figure 1), which are the preferred T-sites for Al atoms in zeolite mordenite. Also, the empirical Löwenstein rule was applied. To establish the position of the charge-balancing protons, geometric optimizations were done for the several

configurations selecting the ones that resulted in a lower total energy.

In order to study the combined effect of Si/Al and temperature on the positioning of Pt inside MOR, MMC simulations were done with a loading of one Pt atom at 298 K and 623 K. These temperatures are common in many synthesis processes found in literature. Also Pt loadings equivalent to 10, 16, and 21 % w/w were studied at the same conditions of Si/Al and temperature.

3 RESULTS AND DISCUSSION

The frequency plots from the MMC simulations with one Pt atom are presented in Figures 2a to 2d. When the $\text{Si/Al} = \infty$, the path of the Pt atom suggests that the presence of this metal in the side pockets of MOR is favored. On the other hand, when $\text{Si/Al} = 5$ the preferred position of the Pt atom is shifted from the side pockets to the main pore channels of the structure. This is consistent with previous results obtained for Ni.[10] The obtained results also suggest that there is an energetic barrier that reduces the ability of Pt to pass through the interconnecting ring between the side pockets and the main pore channels. This energetic barrier is easily explained by the fact that the diameter of the interconnecting ring is about the same magnitude of the Van der Waals diameter of the Pt atom (3.5\AA). At 623 K, the acceptance of the random walk through the interconnecting ring by the MMC scheme is greater than the observed at 298 K, making possible for the Pt atom to visit more frequently the less energetically favored places.

Figure 3 shows the results for the canonical MMC simulations at Pt loadings of 10% (w/w). These schematics present the snapshots of the lowest energy configurations obtained during the simulation. Notice that for the lower temperature, the behavior of the positioning of Pt is quite similar to the one obtained at the same temperature for the one atom simulation. For $\text{Si/Al} = \infty$ and $T = 298 \text{ K}$, the Pt atoms are positioned at the side pockets of the framework. Meanwhile for $\text{Si/Al} = 5$ and $T = 298 \text{ K}$, the Pt atoms were positioned at the main pore channel of the structure. For Pt at these concentrations, the small number of atoms allows them to remain dispersed through the zeolite framework. When the temperature of the simulation was fixed to 632 K, the new condition promoted the acceptance of the path of Pt through the interconnecting ring by the MMC simulation scheme. As a result, Pt atoms gain access to both, the pore channels and the side pockets of MOR. The agglomeration of the Pt atoms in the main pore channels can be attributed by the interaction of these guest atoms (when they gain access to the main pore channels) and the greater energetic stability that resulted from their cohesive forces. The size of the clusters formed does not allow their inclusion in the side pockets of MOR.

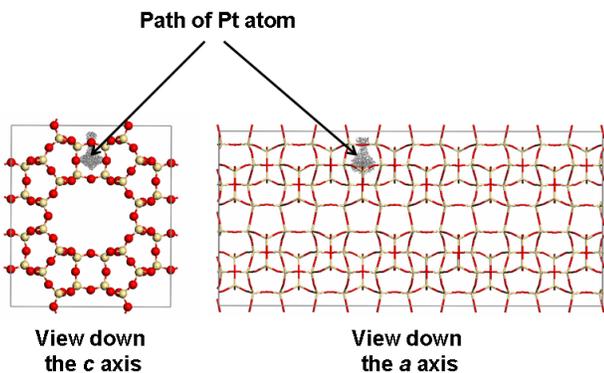


Figure 2a: One Pt atom simulation - $\text{Si/Al} = \infty$ and $T=298\text{K}$

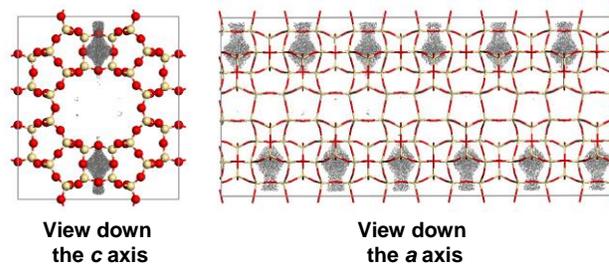


Figure 2c: One atom Pt simulation - $\text{Si/Al} = \infty$ and $T=623\text{K}$

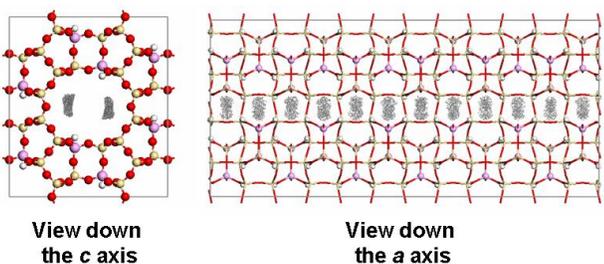


Figure 2b: One Pt atom simulation - $\text{Si/Al} = 5$ and $T=298\text{K}$

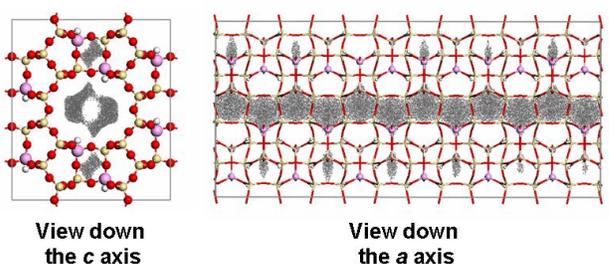


Figure 2d: One atom Pt simulation - $\text{Si/Al} = 5$ and $T=623\text{K}$

Results for the MMC simulations at Pt loadings of 16% w/w are presented in Figure 4. For $\text{Si/Al} = 5$, the same trend of previous simulations is observed; the location of the Pt atoms is in the main pore channels and not on the side pockets. For the conditions of MOR with $\text{Si/Al} = \infty$ and $T = 632\text{ K}$, the results are similar to those at a Pt concentration of 10% w/w. However, for MOR with $\text{Si/Al} = \infty$ and $T = 298\text{ K}$, Pt atoms are observed in both, the main pore channels and the side pockets of the structure.

The MMC results at Pt loadings of 21% w/w are presented in Figure 5. Notice that for all the conditions at this concentration, the positioning of Pt is in the main pore channels of MOR. These results suggest that higher concentrations of Pt have a predominant effect on the positioning of the guest metal atoms in the framework of MOR, diminishing the effect of the other variables considered in this study. The fact that at this loading the $\text{Si/Al} = \infty$ has no effect on the positioning of the guest metal atoms, when $T = 298\text{ K}$, seems to be related to the number of Pt atoms and their strong cohesive forces. A larger number of Pt atoms promote larger size of clusters. When clusters reach a certain size, it is reasonable to expect that the resultant force over each Pt atom in vicinity of this particle is redirected to the center of the cluster. While these forces are not considered by the MMC scheme, they have an important effect on the parameterization of the forcefield used to estimate potential energy. Thus, the behavior observed by Pt atoms in MOR can ultimately be

explained in terms of the overall energetic stability of the system.

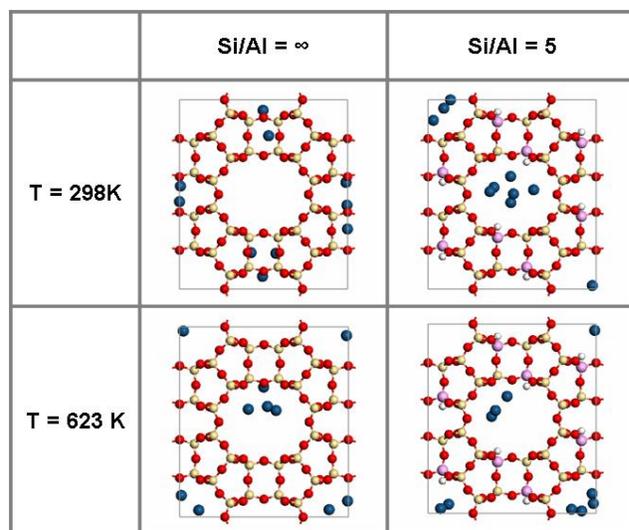


Figure 3: MMC results for MOR Pt loadings of 10% (w/w)

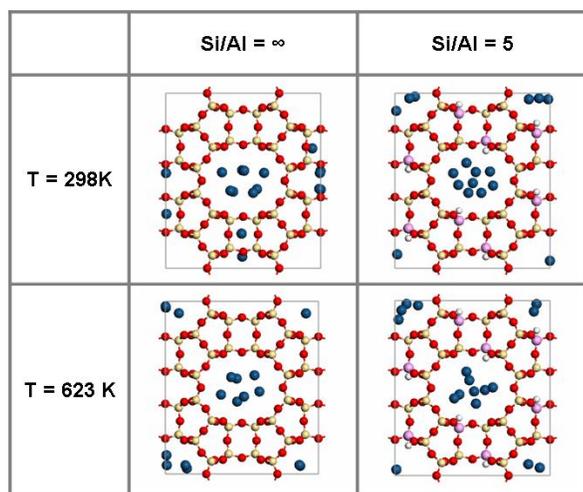


Figure 4: MMC results for MOR
Pt loadings of 16% (w/w)

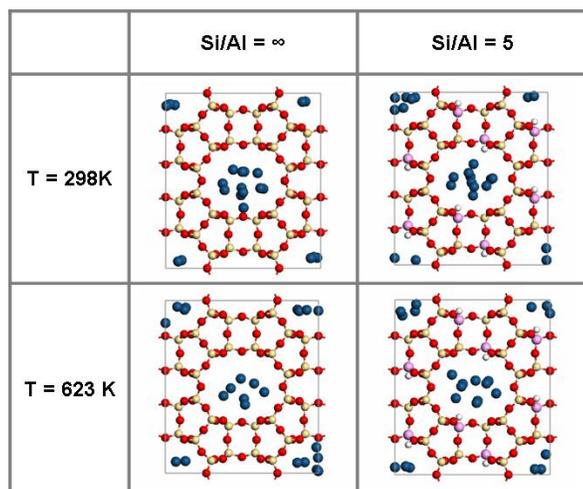


Figure 5: MMC results for MOR
Pt loadings of 21% (w/w)

CONCLUSIONS

The results presented here show the importance of temperature, Si/Al and metal concentration on the synthesis of Pt nanostructures within MOR type zeolites. Through the careful use of these parameters, the displacement of Pt atoms to the side pockets or the main pore channels can be controlled. Our results indicate that high temperature (632 K), low Si/Al and high Pt loading (20% w/w) promote the displacement of Pt atoms to the main pore channels of the MOR framework, where nanowires can be formed. This suggests that there are in fact optimal conditions for the formation of subnanometer Pt nanowires in zeolites.

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