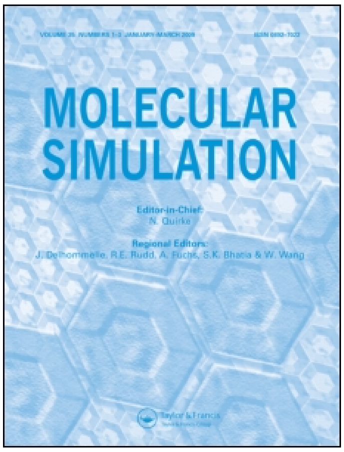

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Si/Al and metal loading effects on the templated synthesis of Ni nanowires in CAN and MOR zeolite frameworks

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Si/Al and metal loading effects on the templated synthesis of Ni nanowires in CAN and MOR zeolite frameworks

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Zeolites with 1D pore channels, such as cancrinite (CAN) and mordenite (MOR), have the potential to be used as templates in the synthesis of subnanometre metal nanowires. Previous studies show a strong correlation between the location of Al atoms in zeolites and the positioning of the metal atoms inside the zeolite framework. Thus, Metropolis Monte Carlo simulations were used here to study the behaviour of Ni atoms within the CAN- and MOR-type zeolites at different Si/Al ratios and Ni loadings. It was found for both zeolite frameworks that a lower Si/Al ratio favoured energetically the positioning of Ni atoms in the 1D pore channels and that higher loadings of Ni promote the formation of 1D Ni structures. These results suggest that it is possible to use zeolites with the CAN and MOR frameworks and low Si/Al ratio as effective templates for the synthesis of metal nanowires.

Keywords: Monte Carlo; zeolites; cancrinite; mordenite; nanowires

1. Introduction

Nanoparticles have received great attention because of their interesting physical properties, which usually differ from the ones of bulk materials of the same chemical composition. The size-dependent properties of nanoparticles include quantum confinement, surface plasmon resonance and superparamagnetism [1]. Because of the relation between nanoparticles' size and their uncommon properties, the next logical step is to study their properties when they reach a subnanometre size.

Metal nanowires are 1D nanoparticles of special interest for the miniaturisation of electrical circuits. Their electrical and thermal conductances 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.

An effective and convenient technique for the manufacture of nanowires is the templated method, which consists of the use of porous structures as casts in which nanowires are formed [2]. When compared with other techniques, templated synthesis has the advantage of allowing better control over final size and shape of particles being synthesised. A review of the methods for the templated synthesis of nanowires and other nanoparticle structures is available elsewhere [3].

Zeolites are aluminosilicate crystalline structures that are promising materials as templates for the synthesis of quantum-sized nanowires. The ratio of Si–Al atoms (Si/Al) can vary from infinite to one, depending on the zeolite structure and the synthesis process. Zeolites, which have effective pore openings ranging between 0.4 and 1.3 nm, are used in many commercial applications such as ion exchange, water adsorption and catalytic cracking. Some zeolites such as cancrinite and mordenite (with CAN and MOR structural frameworks, respectively) have 1D main pore channels that could theoretically be used in the templated synthesis of metal nanowires (see Figure 1).

The main pore channels of CAN-type zeolites have a diameter of 5.9 Å (measured between two opposed oxygen atoms). The rings that form these main pore channels have 12 oxygen atoms. These main pore channels are surrounded by side pockets with rings formed by four and six oxygen atoms. The interconnecting rings between the main pore channels and the side pockets of the CAN framework have an effective diameter of ~1.5 Å.

In the case of the MOR framework, the smallest distance between two opposite oxygen atoms in the main pore channel is 6.5 Å. These channels have rings of 12 oxygen atoms and are surrounded by different side pockets with windows that have between 4 and 8 oxygen atoms. For the larger windows, the minimum distance between two opposed oxygen atoms is ~3.4 Å.

The use of zeolites for the synthesis of metal nanoparticles has been studied due to its catalytic applications [4,5]. However, there is a lack of literature relevant 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

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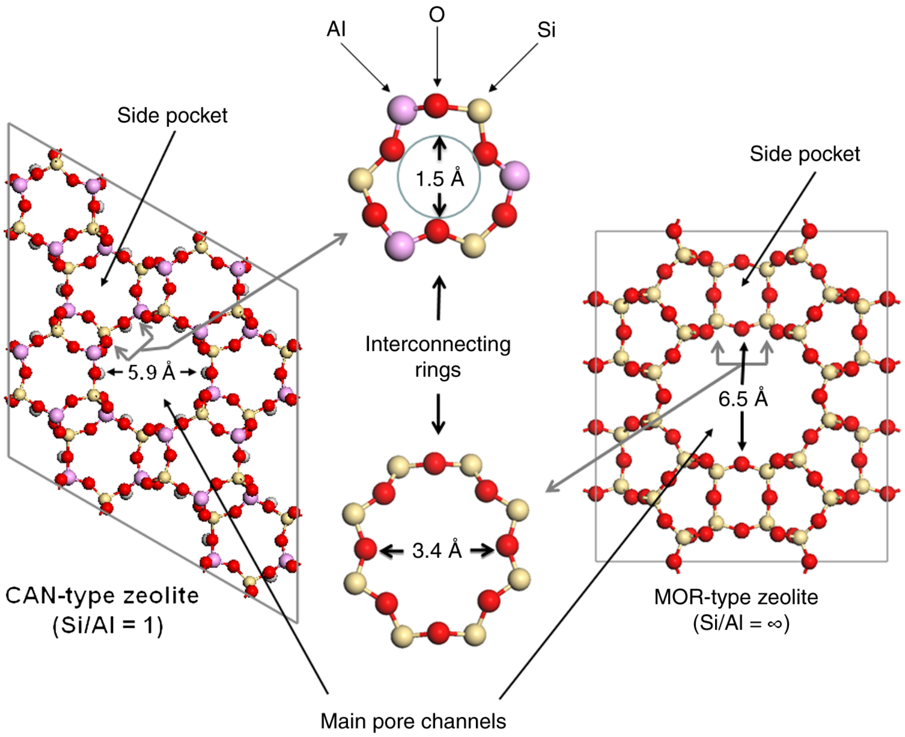

Figure 1. CAN and MOR frameworks.

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 [6,7]. 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 [8]. As opposed to metal nanowires, successful trials have been reported for the synthesis of single-walled and multiwalled carbon nanotubes [9,10].

Molecular simulations can be used to guide experimental work focused on the development of synthetic procedures to obtain metal nanowires using zeolites as templates. There are many published molecular simulation studies involving zeolites, mainly because of the generalised industrial applications that these aluminosilicate materials have, e.g. adsorption and ion exchange and catalysis [11–21]. 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 and Ramírez de Agudelo [22] published a molecular simulation study on the stability of metal particles inside zeolites. In this work, lattice energy minimisations were done to study the effects of different Al positions in the acidic MOR-type zeolite on the location and stability of monoatomic Pt particles. For this purpose, two Al atoms were positioned at different tetrahedral (T) sites of the MOR framework unit cell. On the basis of the lattice energy of the systems studied, the authors found that the stable sites of single Pt atoms in acidic MOR-type zeolite are highly influenced by the specific location of the Al atoms in the lattice. Taking into account the expected per cent of Al with respect to each tetrahedral site of MOR, the authors concluded that the side pockets are favoured energetically to guest Pt atoms in MOR. These results illustrate the importance of the location of the Al atoms for the templated synthesis of metal nanowires, as they influence the position of the guest metal atoms inside the zeolite structure.

In the final step of a templated synthesis, it is desired that most of the guest metal particles remain in the main pore channels to promote the formation of the nanowires structure, as the migration of metal atoms to the side pockets will be detrimental to their formation. The molecular simulation studies presented here address the influence of the Al sites and metal loading in the positioning of guest metal atoms during the final step of the synthesis process.

For the actual synthesis process of zeolites, the Si–Al ratio and not the location of Al atoms can be controlled. Thus, theoretical studies can be accurately performed only with zeolites where the positioning of the Al atoms can be uniquely identified. On the basis of this, we selected the CAN framework with Si/Al = 1 and Si/Al = ∞, and the MOR framework with Si/Al = 5 and Si/Al = ∞ as study cases.

2. Simulation methodology

Molecular simulations and geometric optimisations described in the following paragraphs were performed using the Sorption and Forcite modules of Material Studio Software™, Version 4.0 (Accelrys Inc. San Diego, CA, USA). Wherever the Metropolis Monte Carlo (MMC) scheme was performed, the canonical ensemble was used with 2×10^6 equilibration steps, 1×10^7 processing steps and a cut-off ratio of 18.5 Å. For these MMC simulations, the temperature was set to 298 K.

2.1 Energy computations

The *pcff* force field was used for the energy computations required in both the geometric optimisations and MMC simulations presented here. *Pcff* is the well known and extensively used force field developed by Sun et al. and it is based on the *cff* force field [23–25]. *Pcff* was parameterised 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 frameworks. The parameterisation 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 (Literature provided by Accelrys in Material Studio Software (Version 4.0)).

2.2 Supercell definition and the positioning of the Al atoms in the zeolite frameworks

The molecular simulations presented here were performed using the CAN-type zeolites with Si/Al $= \infty$ and Si/Al $= 1$, and the MOR-type zeolites with Si/Al $= \infty$ and Si/Al $= 5$. For CAN-type zeolites, a supercell composed of $2 \times 2 \times 16$ basic unit cells (2304 atoms) was used. In the case of MOR-type zeolites, the supercell used was composed of $1 \times 1 \times 16$ basic unit cells (also 2304 atoms).

The relative position of the atoms in the frameworks used was fixed during simulation processes and determined previously from crystallographic data. The positioning of the Al atoms for CAN framework with Si/Al $= 1$ is easily obtained with the Löwenstein rule.

For the MOR-type zeolite with 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. [26]; 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 MOR. The empirical Löwenstein rule was also applied, which states that the presence of two Al atoms bonded to the same oxygen atom is highly unlikely. There are eight T3 sites in the MOR framework basic unit cell; the Löwenstein rule only permits the positioning of a maximum of four Al atoms in them. The same is true for the T4 sites, thus the eight Al atoms can be positioned in the T3 and T4 sites, occupying completely the available positions for those two sites in the basic unit cell of MOR-type zeolite. To establish the position of the charge-balancing protons in the alumina-rich CAN- and MOR-type zeolites, we performed geometric optimisations for the several configurations selecting the ones that resulted in a lower total energy.

2.3 One Ni-atom simulations for CAN- and MOR-type zeolites

In order to study the interaction between Ni and the different zeolite framework, we performed MMC simulations with a loading of one Ni atom. These simulations were performed for the CAN framework with Si/Al $= \infty$ and Si/Al $= 1$ as well as for the MOR framework with Si/Al $= \infty$ and Si/Al $= 5$. The purpose was to establish the conditions that promote the displacement of Ni within the 1D main pore channels for each framework, by avoiding diffusion to the side pockets. In these simulations, the path of a single Ni atom through the framework was used to generate frequency plots. The resulting plots help visualise the effect of the zeolite framework structure and composition (Si/Al) over the Ni-preferred positions, when considering only the interaction between the guest metal and zeolite atoms.

2.4 Energy minimisations for one Ni atom inside CAN- and MOR-type zeolites

Geometric optimisations were done with one Ni atom to find local energy minima for the positioning of Ni in the main pore channels and in the side pockets of CAN- and MOR-type zeolites at different Si/Al ratios. For these minimisations, the relative position of the zeolite atoms was fixed. To find the local minima, the Ni atom was placed initially at both the geometrical centre of each structure and near the positions with the lowest energy obtained with MMC simulations. The minimisations were done using the conjugate gradient algorithm and conversion was reached at tolerances of 2.0×10^{-5} kcal/mol for energy, 1.0×10^{-3} kcal/(mol Å) for force and 1.0×10^{-5} Å for displacement.

2.5 MMC simulations for zeolite frameworks at different Si/Al ratios and Ni loadings

Evaluation of the spatial distribution of Ni atoms within the CAN and MOR frameworks with different Si/Al ratios was done using MMC simulations at Ni loadings equivalent to 5, 10, 15 and 19% w/w. These simulations were done to obtain the relative position of Ni atoms at the most stable energetic conditions (minimal energy configurations). The simulations were conducted in order

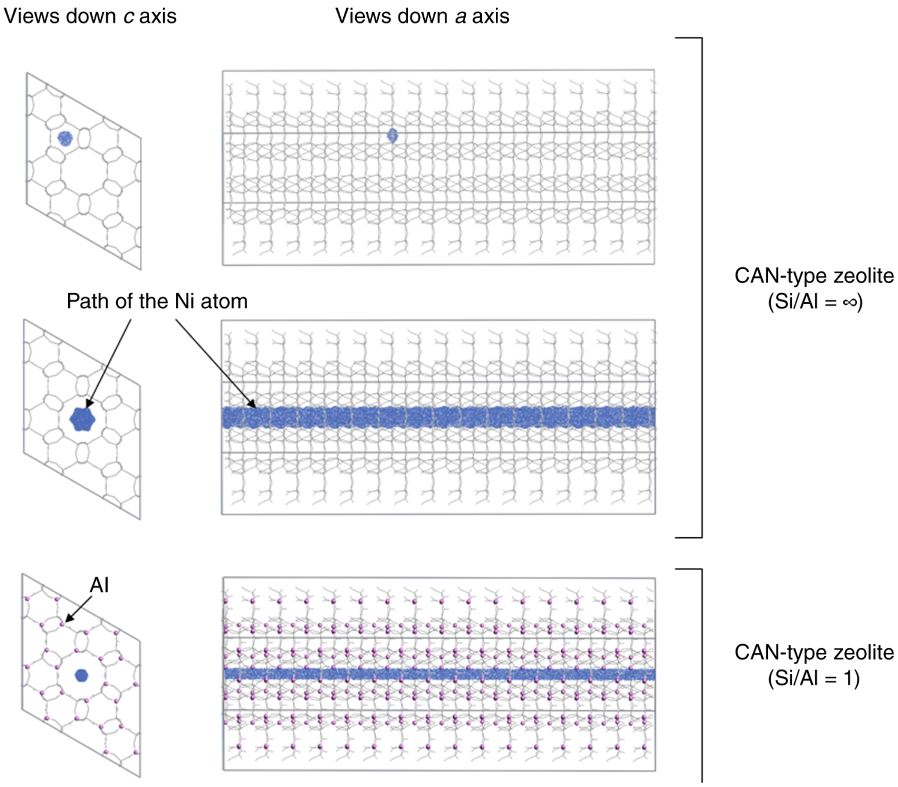

Figure 2. MMC simulation results of one Ni atom in the CAN framework. Parts of the figure are reproduced with permission from J. A. Huertas-Miranda and M.M. Martínez-Iñesta. Sens. Transducers 7 (2009), pp. 116–124. Copyright (2009) by IFSA.

to determine the conditions that promote the formation of 1D nanostructures inside the main pore channels.

3. Results and discussion

Figure 2 presents the results of one Ni-atom simulations for CAN-type zeolites with Si/Al = ∞ and Si/Al = 1.

Figure 3 presents the equivalent results for MOR-type zeolites with Si/Al = ∞ and Si/Al = 5. In these figures, the trace of the centre of the Ni atom is plotted for the movements generated by the MMC algorithm. In repeated MMC simulations of CAN-type zeolite with Si/Al = 1 and loadings of one atom, the side pockets of the zeolite were not a preferred location for Ni. In MMC simulations of

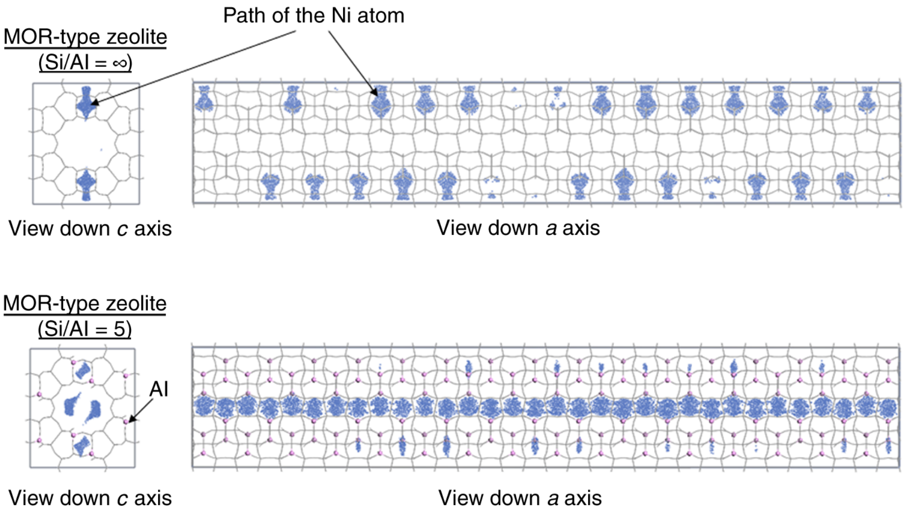

Figure 3. MMC simulation results of one Ni atom in the MOR framework. Parts of the figure are reproduced with permission from J. A. Huertas-Miranda and M.M. Martínez-Iñesta. Sens. Transducers 7 (2009), pp. 116–124. Copyright (2009) by IFSA.

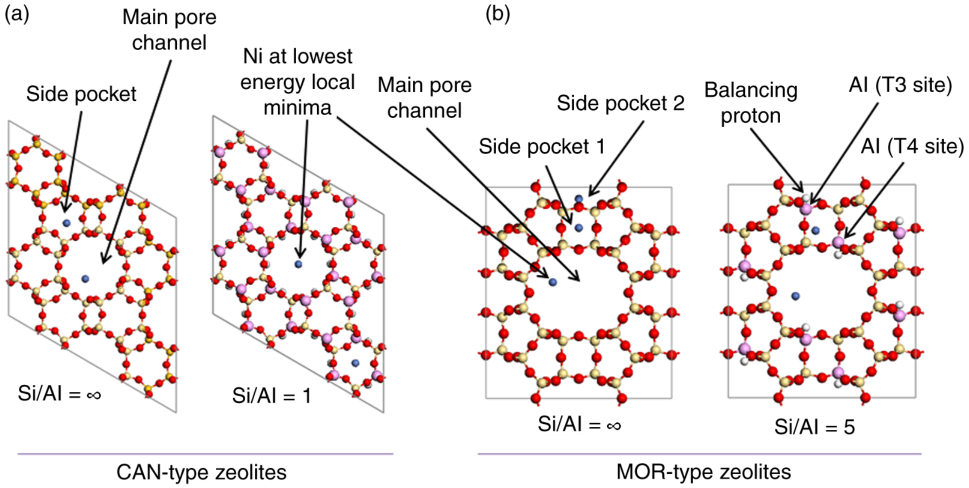

Figure 4. Positions after local energy minimisations of one Ni atom in the CAN and MOR frameworks (see Tables 1 and 2 for values of energy).

CAN-type zeolite with Si/Al = ∞ and one Ni atom, Ni was positioned in either the side pockets or the main pore channels. We observed that the path generated suggested that a Ni atom initially positioned at the main pore channels would not pass through the interconnecting ring to the side pockets and vice versa. On the other hand, one Ni-atom simulations in MOR-type zeolites (Si/Al = ∞ and Si/Al = 5) suggest that this behaviour is different; the Ni atom passed through the interconnecting ring from the main pore channel to the side pockets and vice versa.

These differences can be explained by the diameter of the larger interconnecting rings of these two frameworks, which is ~1.5 Å for CAN and ~3.4 Å for MOR (see Figure 1). With a van der Waals atom diameter of 3.26 Å, Ni atoms are hindered to pass through the CAN-type zeolite interconnecting rings. In this respect, CAN-type zeolites result in a better alternative than MOR-type zeolites for the templated synthesis process of Ni nanowires.

The inability of Ni to pass through the interconnecting rings in the CAN framework and its absence from the side pockets for the zeolite with Si/Al = 1 suggest that these are not an energetically favourable sites for the guest metal atoms. This was confirmed by energy minimisations of one Ni atom in the side pockets and in the main pore channels for the CAN-type zeolites with Si/Al = 1 and Si/Al = ∞. The results of these energy minimisations are presented in Figure 4(a) and Table 1. The ΔE is positive for one Ni atom in the side pocket of the CAN-type zeolite with Si/Al = 1 (suggesting that the positioning of Ni in this place is not favoured at these conditions).

The plots of the MMC simulations in Figure 3 reflect that for the MOR framework with Si/Al = ∞, the positioning of Ni in the side pockets is favoured; meanwhile the positioning of Ni in the main pore channel is more significant for the MOR-type zeolite with Si/Al = 5. These results are consistent with the energy minimisations of one Ni atom inside the side pockets and the main pore channels of MOR-type zeolites with Si/Al = 1 and Si/Al = 5 (see Figure 4(b) and Table 2).

In the above-mentioned one Ni-atom MMC simulations, it is observed that the presence of Al in the zeolite structure promotes a separation of the Ni neutral atom from the wall surfaces of the zeolite structure. This behaviour suggests that van der Waals repulsion forces between Ni and the oxygen atoms bonded to Al atoms are stronger than the forces between Ni and the oxygen atoms bonded to Si atoms. The magnitude of these repulsion forces is usually associated with the interaction of the electron cores of the nearby atoms.

Figure 5 shows the views down the *c*-axis of MMC simulation results for CAN-type zeolites with Si/Al = ∞ and Si/Al = 1 at different Ni loadings. These views present the minimum energy configurations obtained with the MMC algorithm. In these schematics, it is observed that Ni is almost absent from the side pockets of the CAN-type zeolite with Si/Al = 1 at all loadings, meanwhile guest metal atoms are consistently present in the side

Table 1. Energy of one Ni atom in CAN framework pores (in kcal/mol)[a].

System	Total energy	Δ Energy
CAN-type zeolite (Si/Al = ∞)	−28009.9	0.0
+ Ni main channel	−28017.2	−7.3
+ Ni side pocket	−28020.3	−10.4
CAN-type zeolite (Si/Al = 1)	−90155.3	0.0
+ Ni main channel	−90158.3	−3.0
+ Ni side pocket	−90153.0	2.3

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Table 2. Energy of one Ni atom in MOR framework pores (in kcal/mol).

System	Total energy	Δ Energy
MOR-type zeolite (Si/Al = ∞)	−43011.3	0.0
+ Ni main channel	−43019.2	−7.9
+ Ni side pocket 1	−43020.8	−9.5
+ Ni side pocket 2	−43021.3	−10.0
MOR-type zeolite (Si/Al = 5)	−52891.8	0.0
+ Ni main channel	−52898.8	−7.0
+ Ni side pocket 1	−52897.7	−5.9
+ Ni side pocket 2	–	–

pockets of the CAN-type zeolite with Si/Al = ∞ at all loadings. For the CAN framework with Si/Al = 1, only at the highest metal loading studied (19% w/w), Ni atoms were observed in the side pockets. Positioning of the Ni atoms in the main pore channel follow a similar trend to that observed in the one Ni-atom simulations; the Ni atoms for CAN-type zeolite with Si/Al = 1 are more distanced from the zeolite walls than the corresponding Ni atoms in CAN-type zeolite with Si/Al = ∞, resulting in more compact Ni agglomerates. The consistency of this behaviour in simulations at different Ni loadings supports our prior observation that the presence of Al atoms promotes the repulsion of Ni atoms from the walls of the zeolite framework.

Figure 6 presents the results for MMC simulations of MOR-type zeolites with Si/Al = 5 and Si/Al = ∞ at different Ni loadings. Here, the pattern observed is similar to the one showed by the MMC simulations for the CAN framework; the simulations of MOR-type zeolite with the lower Si/Al ratio strongly favour the positioning of the metal atoms inside the main pore channels and higher Si/Al ratio promotes the displacement of Ni into the side pockets. This behaviour is consistent with the results observed in the one Ni-atom MMC simulations. However, the effect of Ni concentration on the positioning of the guest metal atoms is different in MOR-type zeolite than in CAN-type zeolite with Si/Al = ∞. For the MOR framework, loadings higher than 5% (w/w) seems to favour a displacement of the Ni atoms from the side pockets to the main pore channel. This behaviour seems to be related to the attraction forces that exist between the Ni metal atoms and the availability of a greater space in the main pore channels to accommodate them. In the case of CAN-type zeolite (Si/Al = ∞), as the Ni loading is increased, an increase of the number of guest metal atoms of both the main pore channels and the side pockets is observed. The latter behaviour can be attributed to the hindrance of Ni to pass through the interconnecting rings between the side pockets and the main pore channels after the aleatory positioning of metal atoms in the loading steps of the MMC algorithm.

Figure 7 shows the MMC Ni positioning results in views down the *a*-axis along the supercells of MOR-type zeolites with Si/Al = ∞ and Si/Al = 5 and at Ni loadings of 10% w/w. A view of MOR-type zeolite (Si/Al = 5) with 19%

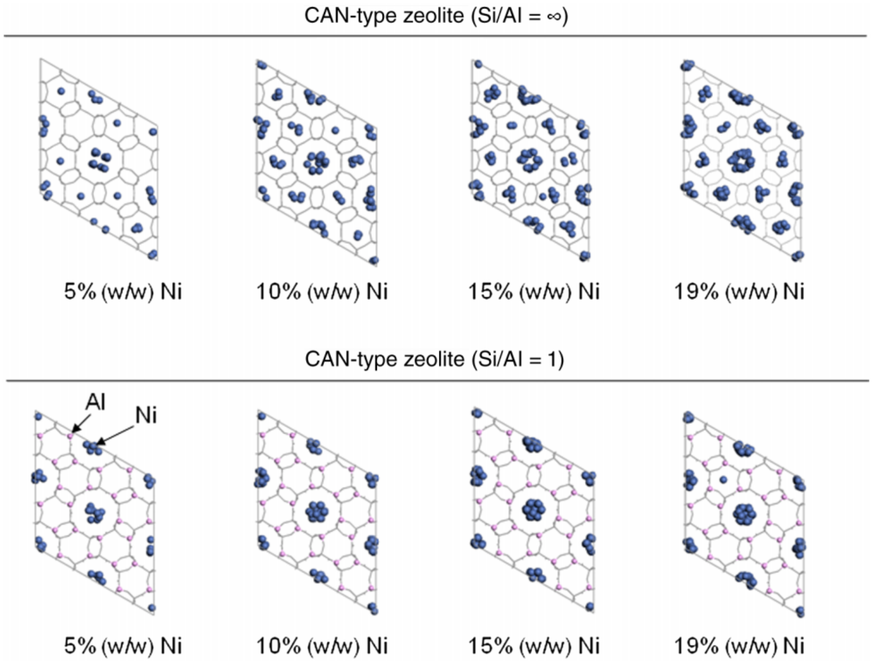
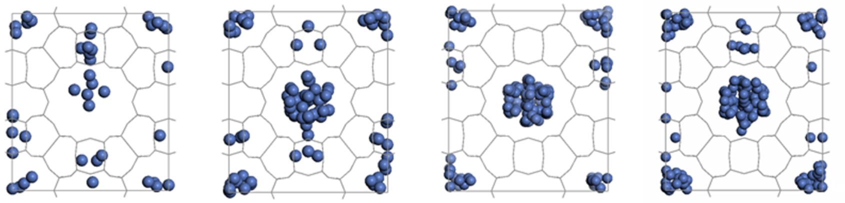


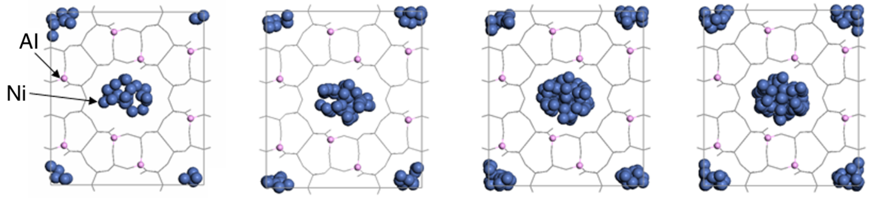
Figure 5. MMC simulation results of the CAN framework at different Ni loadings. Parts of the figure reproduced with permission from J.A. Huertas-Miranda and M.M. Martínez-Iñesta. Sens. Transducers 7 (2009), pp. 116–124. Copyright (2009) by IFSA.

MOR-type zeolite (Si/Al = ∞)



5% (w/w) Ni 10% (w/w) Ni 15% (w/w) Ni 19% (w/w) Ni

MOR-type zeolite (Si/Al = 5)

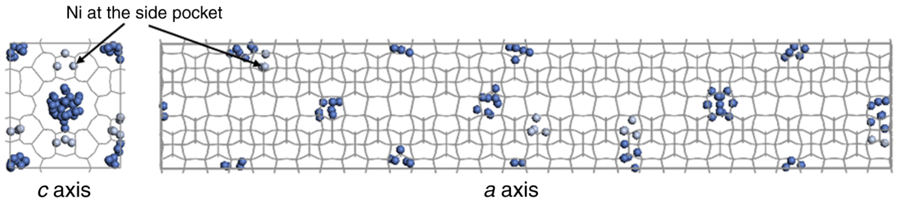


5% (w/w) Ni 10% (w/w) Ni 15% (w/w) Ni 19% (w/w) Ni

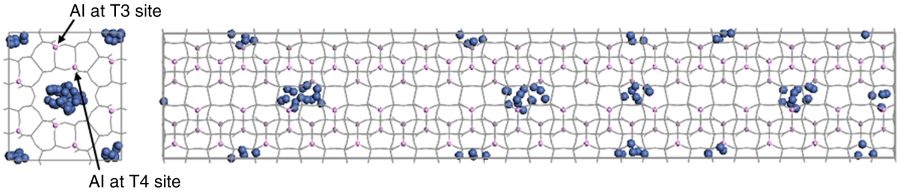
Figure 6. MMC simulation results of the MOR framework at different Ni loadings.

w/w Ni loading is also included. In the MMC simulations of MOR-type zeolite at lower Ni loadings, the formation of Ni clusters was observed. At higher Ni loadings with Si/Al = 5, the observed size of the clusters at the main pore channels was generally greater than for MOR-type zeolite at Si/Al = ∞. As the metal concentration increased, the observed Ni agglomerates in MOR framework (Si/Al = 5) elongated as observed in Figure 7(c). These patterns were also observed for the MMC simulations of the CAN framework. These results suggest that a low Si/Al ratio and high metal loadings promote the formation of metal nanowires.

(a) MOR-type zeolite (Si/Al = ∞) - 10 (w/w)% Ni



(b) MOR-type zeolite (Si/Al = 5) - 10 (w/w)% Ni



(c) MOR-type zeolite (Si/Al = 5) - 19 (w/w)% Ni

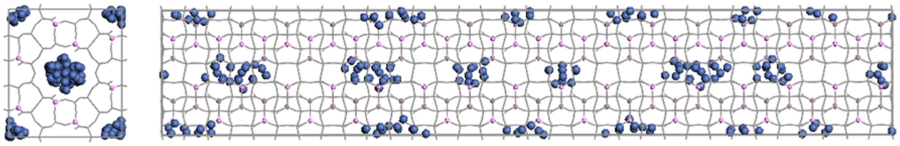


Figure 7. MCC simulation results of the MOR framework with views down the *a*-axis (lighter spheres represent Ni atoms in the side pockets).

4. Conclusions

Our results illustrate the importance of the zeolite framework, Si/Al ratio and metal loading in promoting the synthesis of metal nanowires using zeolite structures. For CAN and MOR frameworks, a low Si/Al ratio favoured energetically the positioning of Ni atoms inside the main pore channels. This suggests that lower Si/Al ratio can reduce the displacement of metal guest atoms from the main channels to the side pockets, improving the potential of such frameworks to be used in the templated synthesis of metal nanowires. In frameworks such as CAN, the small dimensions of the interconnecting rings prevent the migration of Ni and other metal atoms from the main pore channels 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, to place the metals atoms initially inside the main pore channels of the zeolite framework.

In the case of the MOR framework, the effect of lower Si/Al ratio acquires more relevance for the templated synthesis process because the greater size of the interconnecting rings allows the displacement of the metal atoms between the main pore channels and the side pockets. This can have a detrimental effect for the synthesis of metal nanowires; however, based on the results obtained in the MMC simulations presented here, the migration of metal atoms from the main pore channel to the side pockets can be highly reduced if low Si/Al ratio and high metal loadings are used.

In general, higher Ni loadings were necessary for the formation of elongated structures whereas smaller rounded clusters were favoured at lower Ni loadings. In the case of MOR-type zeolites, the combination of high Ni loadings and low Si/Al ratios promotes the formation of elongated structures and, therefore, seem to be the suitable combination for the synthesis of Ni nanowires.

When comparing the results obtained with CAN- and MOR-type zeolites, the CAN frameworks seem to be a better option than MOR frameworks for the synthesis of metal nanowires. However, there are several practical considerations that must be taken into consideration when evaluating these frameworks for their use as templates. For example, the zeolite CAN (which has a CAN framework with Si/Al = 1) presents several problems related to the commercial availability of the zeolite and the removal of the template compounds used to synthesise it; meanwhile, zeolites with the MOR framework such as MOR are easier to manage and are available commercially.

The results presented here illustrate the influence of the structure of the zeolite in the minimum energy locations of the Ni atoms inside the pores. This suggests that there is a set of optimum zeolite framework characteristics for the formation of nanowires.

Acknowledgements

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