Molecular Modeling of Raney Nickel Catalytic Systems


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ABSTRACT

We will present computational studies on Raney Nickel, a porous catalyst whose precursor is a nickel aluminum alloy and which is typically used for hydration reactions of complex molecules. Since catalyst structure is a fundamental property and influences other material properties, we will present a generally applicable workflow which we have developed for creating realistic models of amorphous nanoporous material using molecular dynamics simulations. In addition we will present the influence of alloy composition, the initial structure of the precursor, and the composition of the final catalyst on the structural properties which has been systematically investigated. Our results suggest a stabilizing influence of remaining aluminum in the final precursor. The catalytic system has been further characterized by thermodynamic modeling. The solubility of hydrogen in the reactant mixture was studied for gaining information about the best possible reaction conditions.

Keywords: Nanoporous material, catalysis, alloys, thermodynamic modeling, molecular modeling

1 INTRODUCTION

In many industrial relevant areas, porous materials play a crucial role. Typical applications of porous materials are as catalysts or as storage medium for small molecules, e.g., for hydrogen or methane. Porous solids are also used as molecular sieves. Owing to their specific properties, they are becoming exceedingly interesting for other fields and are used, for instance, in biomedical applications or as advanced electrode material.

A common porous catalyst for reduction reactions is Raney Nickel (Ni). Due to its stability and efficiency, Raney Ni is used in a variety of industrial processes as well as in laboratory syntheses. One prominent application is the hydrogenation of benzene to cyclohexane.

In its active form, Raney Ni is a nanostructured porous solid. The precursor is a NiAl alloy which is prepared by quenching a molten mixture of Nickel and Aluminum. In the quenched alloy, different NiAl phases exist. From the phases NiAl3 and Ni3Al, Al is leached out, while in the NiAl phase the Aluminum remains. The latter is responsible for the thermal and structural stability of the catalyst. The activity of the catalyst depends on its structure which in turn depends on the catalyst and precursor composition.

In the following sections we will present a modeling workflow which we have developed for modeling realistic structure of amorphous porous materials. The workflow is generally applicable and is based on molecular dynamics simulations. The influence of the initial alloy composition, the NiAl phase, and the amount of remaining Al in the active form of the catalyst on the structural properties of the final catalyst will be discussed. In addition, we will show thermodynamic modeling studies on the reaction conditions for the hydrogenation reaction of benzene to cyclohexane.

2 RESULTS AND DISCUSSION

2.1 Workflow for modeling nanoporous Raney Nickel

In order to model the porous structure of Raney Ni, we followed a pseudo mimetic approach using quenched molecular dynamics. A supercell of NiAl3 was used as the structural basis in which Al atoms were randomly replaced to achieve a weight fraction of 50 wt% Al and 50 wt% Ni. Based on this model structure a sufficiently large supercell was created and subjected to a set of molecular dynamics (MD) simulations which are summarized in Figure 1.

![Figure 1: Schematic representation of the simulation workflow.](image-url)
More details are provided in the Computational Details section and in Ref. 1. In order to rule out artifacts, the simulation workflow has been applied on five different model structures generated as described above. For the quenched alloy structures we found a mean density of 4.1 g/cm$^3$. The structural properties after the final equilibration have been analyzed with respect to the porosity. With an average maximum pore diameter of 43 Å and an average free surface and volume of 134 m$^2$/g and 0.128 cm$^3$/g, respectively, the results agree nicely with experimental data as illustrated in Ref. 1 which demonstrates the validity of the simulation strategy.

2.2 Influence of the initial and final composition

In order to analyze how the structural properties depend on the precursor and final catalyst composition, simulations were performed for four different precursor compositions corresponding to 60/50/40/30 wt% Al. The density of the precursor ranges between 3.9 and 5.9 g/cm$^3$ depending on the composition which is consistent with literature data of NiAl$_2$ and Ni$_2$Al$_3$ phases [2]. For each precursor composition, three final compositions were considered. The final structures contained 0, 5, or 10 % Al. After leaching, i.e. removing the Al, the structures were equilibrated over 10 ns using NVT conditions to allow for pore formation. Following this step, the cells were equilibrated over 15 ns using NPT MD simulations. The densities of the final structures are summarized in Figure 2.

![Figure 2: Densities of final structures in dependence of the composition.](image)

In general, the densities decrease with increasing aluminum content with respect to both the precursor and final catalyst composition. Only the densities of the models with an initial composition of 60 wt% Al are not fully in line with the overall trend. For this initial composition, the density of the 0 % Al structure is almost the same as the density of the corresponding 0 % Al structure with initial 50 wt% Al composition. For the 60 wt% Al structure, the density of the 5 % Al structure is slightly smaller than the density of the 10 % Al structure, but is smaller than for the corresponding models with decreasing initial Al content and fits thus the overall trend. Overall, the analysis of the densities indicates a stabilizing influence of Al. The diameter of the largest pores was found to range between 32 and 77 Å depending on the initial precursor and final catalyst composition. The results are illustrated in Figure 3.

![Figure 3: Largest pores size after 10 ns NVT and 15 ns NPT equilibration.](image)

While for the final 0% and 5% Al structures the largest pore size diameter tends to decrease with decreasing initial Al content, the 10 % Al structures show a slight increase in the pore size diameter from initial 50 wt% Al to 30 wt% Al. Experimentally, there is also no uniform trend [3,4]. Overall, the results show that the dependence of the pore size is a complex balance between initial and final composition.

2.3 Influence of the initial NiAl phase

In order to investigate the influence of the initial NiAl phase on the structural properties, we performed additional simulations for model systems starting from a Ni$_2$Al$_3$ unit cell. Atoms were replaced to achieve a weight fraction of 50 wt% Al. For the activated catalyst 0, 5, and 10 % Al structure were considered. The densities of the final structures range between 3.1 and 6.0 g/cm$^3$ depending on the Al content. The largest pore size diameters are listed in Table 1. Except for the 0 % Al structure, the pore size diameters are in the same range for both initial NiAl phases. While after NVT equilibration the largest pore size diameters for the Ni$_2$Al$_3$ models are similar and range
between 56 and 58 Å, the pore size after 10 ns NPT equilibration of the 0 % Al is smaller compared to the other models. A possible explanation for the high density and small size of the largest pore of the 0 % Al structure could indeed be due to the different initial unit cell structure and the large void volume when the entire Al is removed. This indicates as well a stabilizing influence of Al on the structural properties of the final catalyst.

<table>
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<tr>
<th></th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
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<tbody>
<tr>
<td>NiAl₃</td>
<td>43.6</td>
<td>49.9</td>
<td>42.5</td>
</tr>
<tr>
<td>Ni₂Al₃</td>
<td>29.1</td>
<td>48.9</td>
<td>40.0</td>
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Table 1: Largest pore size diameter in Å for initial NiAl₃ and Ni₂Al₃ simulations cells.

2.4 Influence of the cell size

In order to study size effects on the structural properties, we have performed additional simulations for 50 wt% composition. 2x2x2 supercells were build and equilibrated over 10 ns in the NVT ensemble followed by 10 ns in the NPT ensemble. The final conformation of the 10 % Al structure is shown in Figure 4.

The largest pore size diameters were 87.4, 68.5, and 70.6 Å for the 0, 5, and 10 % Al structure, respectively. The largest pore size is thus somewhat larger compared to the original cell, but is still in the same magnitude.

2.5 Modeling of the reaction mixture of benzene hydrogenation

In addition to the studies on the catalyst and its structural properties, thermodynamic modeling has been carried out to study the conditions for the catalytic reaction. For this purpose, we used PC-SAFT to calculate the solubility of hydrogen in benzene and in a reaction mixture of benzene and cyclohexane. Details on the simulations can be found in Ref. 1. We found that an increase in pressure results in a higher solubility, as expected. For a pressure of 50 bar we found the highest solubility at 475 K. With decreasing pressure, lower temperatures for the highest solubility are observed. Our results also show that the presence of cyclohexane in the reaction mixture leads to an increased solubility of hydrogen.

3 COMPUTATIONAL DETAILS

Scienomics MAPS software platform [5] was used for building models and manipulating the model structures, setting up simulations to mimic the process, and analyzing the trajectories to understand and interpret the properties. Additional analysis was carried out using Zeo++ [6]. A detailed description of the simulation set-ups and protocols can be found in Ref. 1 and 7. For the simulations of the Ni₂Al₃-based models, cell parameters for the unit cell of Ni₂Al₃ were taken from literature [2]. A 3x3x3 supercell was created and 12 Ni atoms were randomly replaced with Al to obtain a composition of 50 wt% Ni/Al. Based on this, an 8x8x8 supercell was build containing 69120 atoms which roughly corresponds to the system size of the corresponding system based on NiAl₃. The simulation cell was equilibrated over 50 ps at room temperature using NVT conditions. After heating at 2000 K over 200 ps using NPT MD simulation, the structure was quenched to 300 K over 1 ns. Aluminum was removed and three models were created containing 0, 5, and 10 % Al. Then, a NVT simulation at room temperature over 10 ns was performed, before finally equilibration the structure over 10 ns in the NPT ensemble.

4 CONCLUSION

We have presented computational studies on the dependence of the structural properties of Raney Ni catalytic systems on the initial precursor and final catalyst composition. The results suggest that the porosity depends on the composition and that aluminum has a stabilizing influence on the porous structure.
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REFERENCES