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Molecular modeling and simulation of Raney Nickel: From alloy precursor to the final porous catalyst

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ABSTRACT

Raney Nickel is a nanostructured catalyst which is used in a variety of industrial processes. It has a characteristic porous, amorphous structure. Since the structure of both the precursor alloy and the active form of Raney Nickel is determining the catalytic activity and performance, it is crucial to use realistic porous structures for simulating the catalytic reaction. The simulation protocol for the formation of porous Raney Nickel is shown in this study. The structures are then characterized in silico by means of typical characteristics such as the pore size, pore size distribution, density, free volume and free surface. In addition to this, the influence of the Aluminum content in the final form of the catalyst after pore formation is investigated. Furthermore, the cell size of the unit cell was doubled in *x*, *y*, and *z* directions to elucidate the influence of the impact of the cell size on the pore size.

1. Introduction

Metal catalysts play an important role in many industrial applications. A major challenge is to improve the catalyst performance and typically, trial-and-error experimentation, high-throughput experimentation, and analytical characterization are used routinely for this purpose. In order to remain competitive and cost effective, more insights on these complex catalysis systems are needed at the nano scale. In the last 20 years, catalysis industry has leveraged molecular modeling and simulation technology to help answer key questions and thus enable more focused and efficient experimental designs.

Raney Nickel (Ni) [1] is a nanostructured catalyst which is used in a variety of industrial processes and organic syntheses such as hydrogenation reactions. Due to its catalytic activity at room temperature, it is used for reduction of benzene, conversion of nitro compounds to amines, and for desulfurization of thioacetals to hydrocarbons.

The initial form of Raney Nickel is a Ni–Al alloy which is transformed into the active form by leaching out aluminum which leads to the characteristic porous structure of the final catalyst. The porosity depends on the initial composition of the Ni–Al alloy which is typically prepared by melting nickel together with aluminum and subsequent quenching. The quenching process induces the formation of different Ni–Al phases [2] and thus affects the pore formation in the final catalyst. Experimental studies indicate that the sponge-type structure of Raney Nickel grains is formed by a collection of crystallites adhering together [3]. Since the structure of both the precursor alloy and the active form of Raney Nickel determines the catalytic activity and performance, it is crucial to gain a detailed understanding of the structural properties at the atomistic level. The ultimate goal of this work is to leverage molecular modeling to provide critical insights into how the composition of the precursor alloy affects the porosity and thus the catalytic activity of Raney Nickel.

The initial Ni–Al alloy compositions can range from 40 to 70 wt% Al [2,4,5]. Freel et al. [2] determined the mean pore diameter to be in a range between 2.5 and 10 nm. The basis for approaching the structure of the active form are the characterization studies of Raney Nickel [2,6–8] by Anderson's group and others which yield a qualitative picture of Raney Nickel. The void volume of these particles ranges from 0.05 to 0.15 cm^3/g [1]. X-ray diffraction [3] and X-ray Absorption Spectra [4] show that local structure of Raney Ni is similar to FCC Ni. Fouilloux et al. [3] gave a qualitative description of Raney Nickel as a spongy material composed of 100 nm nano-agglomerates of smaller than 2.5–15 nm nanocrystals. Several modeling studies of grain boundaries use molecular dynamics (MD) to generate structures. Van Swygenhoven and Caro [9] used a stochastic procedure that starts with randomly placed seed particles with the rest of the space

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filled with a Voroni construction. Keblinski et al. [10] randomly placed seed particles in a liquid metal and then quenched the melt to generate a model crystal with grain boundaries. These procedures yield a model of a solid composed of nanocrystalline grains.

These studies focus on modeling the structure of the final catalyst. Since a critical question is, how the initial alloy composition influences the final catalyst performance, we, therefore, pursued a different approach. The aim of the present work is to demonstrate how a porous structure of Raney Ni can be modeled with random pore distribution while taking the initial precursor composition into account. We will discuss our computational approach based on the example of an industrially accepted and widely used alloy precursor consisting of 50 wt% Al and 50 wt% Ni. For the catalyst in its active form, the influence of the remaining percentage of aluminum on the nature and stability of the created pores will be analyzed. We will show that our simulation protocol allows creating realistic models of Raney Ni with characteristics comparable to the experimentally measured ones. This work involved fairly long molecular dynamics simulations on large alloy models enabled by access to high performance compute power (HPC) at Argonne National Lab (ANL).

2. Methodology

For building the structures, setting up the simulations, and analyzing the results, Scienomics MAPS platform was used [11]. In addition, the program package Zeo++ [12,13] was used for parts of the analysis. The calculations were performed at the ANL Laboratory Computing Resource Center (LCRC) using the software package LAMMPS [14]. An overview of the work flow for obtaining and analyzing the porous model structures of the Raney Nickel catalyst is illustrated in Fig. 1.

For building the alloy precursor, we started from a $NiAl_3$ unit cell, which is one of the Ni–Al phases formed during the experimental precursor preparation. The composition of the alloy precursor is rather complex and consists of $NiAl_3$, Ni_2Al_3 and an eutectic Al–Ni Al_3 phase.

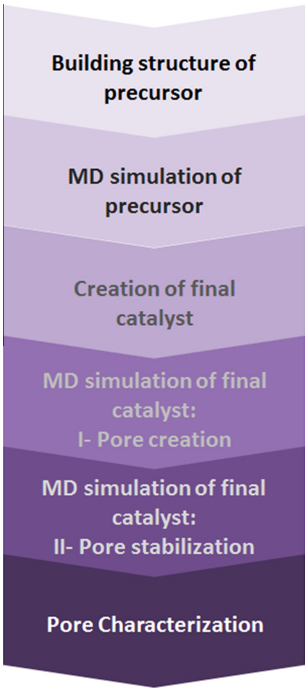

Fig. 1. Simulation workflow to obtain and analyze the Raney Nickel pores.

Since this work is focused on establishing a computational protocol for generating a reasonable model system, we have used only one phase as starting material and adjusted the Ni:Al ratio to the final composition of the precursor to keep the system size and thus the computational time reasonable. In future work, we will apply the simulation protocol developed here to other phases and to more advanced models. The cell parameters for the $NiAl_3$ unit cell were taken from Ref. [15]. Based on the $NiAl_3$ unit cell, a model structure with 50 wt% Al and 50 wt% Ni was created by generating a 2 × 2 × 2 super cell and randomly replacing Al in the corresponding weight fraction which is illustrated in Fig. 2.

In this way, five different initial models represented as m1, m2, ... to m5 were created to ensure a statistically relevant sampling and to rule out possible artifacts. Based on these model structures, 8 × 8 × 8 super cells with cell lengths between 7 and 12 nm and containing 65,536 atoms were built to ensure that the cell size is large enough to cover the experimental pore size which lies in a range between 2 and 10 nm. Molecular dynamics (MD) simulations were then performed using LAMMPS together with an alloy potential developed by Mishin [16] as obtained from the NIST Interatomic Potentials Repository [17]. A combination of constant volume–temperature (NVT) and constant pressure–temperature (NPT) molecular dynamics settings were used.

At the start, a 50 ps NVT equilibration at room temperature was performed to obtain the correct density, followed by a 200 ps NPT simulation at 2000 K, which is well above the melting temperature of the intermetallic Ni–Al phases. Then, the system was cooled down to room temperature during a 1 ns NPT simulation. For one model structure (m1), an additional NPT simulation of 1 ns at room temperature was performed to check the convergence of the density and the cell size. The procedure described above was used to ensure a decent equilibration at the elevated temperature of the system and to overcome local barriers of the potential energy surface in the spirit of a pseudo-mimetic approach attempting to capture the effect of disordering in the final structure by exploiting the metastable character of the material.

After quenching to room temperature, aluminum was removed. For studying the influence of the remaining amount of Al on the pore formation of the final catalyst, two percentages of remaining Al have been considered: (a) 0% and (b) 5% Al were left for modeling the active form of the catalyst. These structures were then optimized using 5000 steps Steepest Descent. A short 200 ps NVT simulation was performed from which the structures of 10 snapshots were extracted. These structures were optimized and used as starting points for 10 ns NVT MD simulations at 300 K. In order to ensure a statistically relevant sampling, initial velocities were randomly chosen for each system. Finally, a 20 ns NPT simulation was performed to allow the system to converge toward experimental conditions.

In order to study the influence of the system size on the size of the created pores, a 2 × 2 × 2 supercell was created after quenching for both the 0% and 5% Al structure containing 163,840 atoms and 181,856 atoms, respectively. For both systems, first a 10 ns NVT simulation was performed followed by a 10 ns NPT simulation.

To characterize the system as completely as possible, different characterization approaches were used. MAPS platform was used to study the evolution of the density, free volume, and free surface of the system along the NVT and NPT simulations. Zeo++ software [12,13] was used to estimate the size of the created nanopores as well as their distribution. This program performs geometry-based analysis of porous materials and their voids and allows the calculation of the diameter of the largest included sphere (in the following denoted as maximum pore diameter). The values of the different properties were computed and analyzed at different time steps of the simulations: At 200 ps, 500 ps, 1 ns, 2 ns, 5 ns and 10 ns for the NVT simulations and at 200 ps, 500 ps, 1 ns, 2 ns,