Characterization of Different Surfaces Morphology in Heterogeneous Catalyst

Rajib Mukherjee*, Ahmet Palazoglu** and Jose A. Romagnoli*

* Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA, jose@lsu.edu
**Dept. of Chemical Engineering and Materials Science, UC Davis, Davis, CA 95616, USA, anpalazoglu@ucdavis.edu

ABSTRACT

Structures and property of surfaces are very important in different chemical, physical and biological processes. In the case of heterogeneous catalysis, reaction takes place at the surface of the active metal crystals (Pt, Rh, Ni etc) supported primarily on metal oxides. The interaction between the reactant molecules (adsorbate) and the surface are important in the performance of the catalyst. Surface has defects in terms of vacancies, dislocations and grain boundaries. The property of the surface depends on its crystal lattice structures and defects on them. This surface property influences the structure of the adsorbate on the surface. A first principle density functional theoretical (DFT) calculation is generally used to find the activation energy of different surface reaction on different catalysts [1]. In this paper we have simulated the energy of Ni (111) surface with and without defects. A fractal dimension of the crystal surface is found using wavelet transformation.

Keywords: crystal planes, surface energy, surface defects, wavelet transform

1 INTRODUCTION

The performance of various chemical, mechanical, biochemical and semiconductor products is governed by the characteristics of their surfaces. For example, the performance of heterogeneous catalysts is controlled by the characteristics of the molecular interfaces and nanostructure of their crystal surfaces. The surface structure of these crystals due to surface kinetics and surface diffusion governs the function of the material. The interaction of the reactant with the active centers and the support determine the performance of a catalyst. It is thus important to thoroughly characterize its surface properties to optimize its fabrication process. Understanding the surface characteristics at the microscopic level is essential in order to relate the surface characteristics to the performance of the product. To create an application of desired features, we first have to understand the surface characteristics in the microscopic level and then find the relation of product performance with the surface characteristic. This eventually will allow us to improve the product performance through optimizing the manufacturing process towards novel tailored nanostructures. Thus, the key to control fabrication of applications whose performance matrix is governed by its surface features is to characterize the surface. In this way we can optimize product performance.

The characterization of these nanostructured materials often involves surface imaging using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), high resolution electron microscopy (HREM) and several Scanning Probe Microscopy (SPM) methods such as Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). Those techniques can also reveal additional information about a catalyst (e.g., elemental surface composition, oxidation state, dispersion, acid/base properties). A high resolution electron microscopy (HREM) image of the catalyst surface can be used to obtain the crystal lattice structure of the active metal. The defects on the crystal surface of the crystal lattice structure can be found. The different crystal surface with or without defects has different property associated with them. While microscopy images can provide detailed, qualitative information about the features of a surface, for the applications mentioned above it is critical to obtain a quantitative description of the surface morphology.

In this paper, an estimation of the surface energy of Ni (111) with and without defects in terms of vacancies is made using CPMD [2] program. This surface energy of the catalyst is related to the absorption energy of the reactant molecules. Furthermore, the fractal dimension of the surface changes under the presence of defects. A regular surface will have a fractal dimension of two while a surface with defects in terms of vacancies will have fractal dimension between two and three. In this work, a fractal dimension of the crystal surface is found with and without defects using wavelet transformation.

2 SURFACE FREE ENERGY

The surface free energy $\sigma$ at a given temperature and pressure is given by the difference in Gibbs free energy of the surface and sum of the potential of each species in bulk.

$$\sigma(T, P) = \frac{1}{A} (G_s - \sum_i \mu_i N_i)$$

(1)
where \( G_s \) is the Gibbs free energy of the surface and \( \mu_i \) is the chemical potential of each species at the reference temperature and pressure and \( N_i \) is the number of atoms of specie \( i \) and \( A \) is the surface area [3]. The surface energy is thus a function of composition and configuration. For solid and single species say nickel and zero temperature the equation reduces to

\[
\sigma = \frac{1}{A} (E - e_{Ni}N_{Ni})
\]

where \( E \) is the internal energy of the surface and \( e_{Ni} \) is the energy per atom in the bulk nickel phase.

3 SURFACE FRACTALS FROM WAVELET VARIANCE

A surface is generally characterized by its fractal dimension. Fractal dimension can be obtained from the variance of wavelet coefficients. In wavelet transformation, a wavelike function called wavelets \( \psi_{a,b} \) is used to transform a function \( f(x) \) in space or time into another form by convolution. The normalized unidirectional wavelet function is often written as:

\[
\psi_{a,b}(x) = \frac{1}{\sqrt{a}} \psi\left(\frac{x-b}{a}\right)
\]

where \( a \) is the dilation parameter (also called scale, inverse of resolution) and \( b \) is the translation parameter [4]. The transformation integral is written as:

\[
T(a,b) = \int_{-\infty}^{\infty} f(x) \psi^*_a(x) dx
\]

The asterisk is because the complex conjugate of the wavelet function is used for transformation.

Self affinity is defined as: when \( x \) changes to \( \lambda x \) then the function \( f(x) \) changes to \( \lambda^H f(x) \) where \( H \) is the Hurst exponent also known as roughness exponent. Thus we can write:

\[
f(x) = \lambda^{-H} f(\lambda x)
\]

Taking wavelet transformation on both sides with dilation parameter \( a \) and translation parameter \( b \) we get

\[
T[f(x)](a,b) = T[\lambda^{-H} f(\lambda x)](a,b)
\]

When \( f(\overline{x}) \) happens to be a function of two variables (a plane, \( \overline{x} \) is a vector \( x_1, x_2 \)) then the location parameter \( \overline{b} \) must also be a vector with two variables \( \overline{b} (b_1, b_2) \). The wavelet transformation is given by

\[
= \frac{1}{a} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \lambda^{-H} f(\lambda \overline{x}) \psi\left(\frac{\overline{x}-\overline{b}}{a}\right) dx_1 dx_2
\]

Taking \( \lambda \overline{x} = \overline{x}' \) i.e. \( \lambda x_1 = x'_1 \) and \( \lambda x_2 = x'_2 \) we can write

\[
= \lambda^{-H-1} \frac{1}{\lambda a} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\overline{x}) \psi\left(\frac{\overline{x} - \lambda \overline{b}}{\lambda a}\right) dx'_1 dx'_2
\]

\[
= \lambda^{-H-1} T[f(\overline{x})]\left(\lambda a, \lambda \overline{b}\right)
\]

And thus we can write wavelet transformation as

\[
T[f(\overline{x})]\left(\lambda a, \lambda \overline{b}\right) = \lambda^{H+1} T[f(\overline{x})]\left(a, \overline{b}\right)
\]

This for a dyadic grid \( \lambda = 2^m \) and taking square becomes:

\[
T^{2}[f(\overline{x})]\left(\lambda a, \lambda \overline{b}\right) = 2^{m(2H+2)} T^2[f(\overline{x})]\left(a, \overline{b}\right)
\]

When we plot log base 2 of the wavelet coefficient variance at different scale index \( m \) for a rough 2D plane, the slope \( s \) is related to the Hurst exponent as

\[
H = \frac{s-2}{2}
\]

For a surface the roughness or Hurst exponent is related to the fractal dimension \( D \) through

\[
D = 3 - H
\]

4 COMPUTATIONAL DETAILS

In this paper we have worked with a Ni(111) surface. A DFT estimation of the surface energy is made for both regular surface as well as surface with defects using CPMD program. The wave function was expanded on a basis set of plane wave with cutoff of 70 Ry. We have used a norm conserving pseudo potential of Trouiller-Martins with Becke-Lee-Yang-Parr functional and non linear core correction (NLCC). Geometry optimization is done for the nickel face centered cubic (fcc) structure and Ni(111) surfaces. The fcc structure is simulated with periodic boundary condition (PBC) and different surfaces are simulated with PBC in two dimensions (x-y plane). In order to obtain the energy per atom in the bulk, the number of unit cell is increased until a constant energy per atom is obtained. The surface free energy is obtained from the difference of energies of surface structure and similar number of atoms from the bulk fcc structure. In this paper...
we have calculated the surface free energy of a Ni(111) plane using equation 2. A change in average surface energy is calculated for surface with defects like vacancies.

5 RESULTS AND DISCUSSIONS

An fcc structure of nickel is created using CPMD program to obtain the energy of bulk nickel atom. A periodic boundary condition (PBC) is used. The number of crystal unit cell is increased until a constant energy per atom is obtained. The lattice parameter of nickel is found to be 6.66 au, or 3.52 angstrom. This is close to experimental value of 6.659 au [3]. Its structure is shown in figure 1.

![FCC Nickel crystal structure](image1)

Figure 1: FCC Nickel crystal structure.

A nickel (111) surface is created using CPMD program to obtain the energy of the nickel atom forming a surface. A periodic boundary condition is applied in two dimensions (x and y). Due to lattice relaxation at the metal surface the distance between the (111) planes at the surface is taken to be 4.014 au instead of 3.845 as found in the bulk. It is calculated from the 4.4% relaxation of the nickel (111) surface [5]. The number of atoms in a layer is increased until a constant energy per atom is obtained. It is shown in figure 2. The number of layers is increased till a constant surface energy is obtained. The energy is found to be same for a two and three layer slab. So the modeling is done with a two layer slab to represent the surface.

![Ni (111) surface without defects](image2)

Figure 2: Ni (111) surface without defects.

The (111) plane of fcc structure is modeled with a surface area of 0.994e-18 m². Equation 2 is used to calculate the surface energy. It is found to be 2.19 J/m². This is in agreement with the values of 2.01 J/m² to 2.45 J/m² reported in different literatures [6, 7].

When we introduce defects in the surface in terms of vacancies, a significant change in the surface energy occurs. A nickel (111) surface is created with few vacancies as shown in figure 3.

![Ni (111) surface with defects in terms of vacancies](image3)

Figure 3: Ni (111) surface with defects in terms of vacancies (1).

The average energy per atom is found to be higher in a surface with vacancies. The surface energy is found to be 2.49 J/m². This higher energy gives an enhanced reactivity of the surface. Vacancies created in another pattern are shown in figure 4.

![Ni (111) surface with defects in terms of vacancies](image4)

Figure 4: Ni (111) surface with defects in terms of vacancies (2).

The surface energy in this case is found to be 2.74 J/m². This indicates that along with the number of vacancies, the location of the vacant sites influences the energy of the surface.

In order to obtain a fractal dimension of the surface we need to create a surface with dyadic \(2^n\) number of atoms. A fractal dimension of the surface is created by simulating the same surface in a periodic manner. This will keep the fractal dimension same as it is based on the self affine nature of the surface. A simulated surface with fractal dimension estimation using wavelet variance is shown in figure 5 and 6 respectively.
The fractal dimension is calculated from the slope of the line in figure 6 using equation 12 and 13. For a regular surface the fractal dimension is found to be 2. Surface with similar vacancies as shown in figure 3 are simulated (shown in figure 7) and the fractal dimension are found from the slope of the wavelet variances shown in figure 8 as before. It was found to be 2.417. Similarly, the fractal dimension of the surface shown in figure 4 is found to be 2.035. Because of the regular nature of defect in the surface of figure 4 it has a lower fractal dimension.

**CONCLUSIONS**

Surfaces with defects have higher energies than regular surfaces and they are more reactive in nature. In this paper, using the pseudo potentials of the elements, the average surface properties for regular surface as well as for surface with defects were estimated using ab initio density functional theory simulation. We have shown how defects in the surface in terms of vacancies increased the surface energy. Furthermore, it was shown that a fractal dimension of the surface can be estimated using wavelet transform and it can be used to characterize the surface properties. Similar studies can be made with different surface planes of different active metals. Defects in terms of dislocations and grain boundaries can also be studied.

**REFERENCES**