

Analysis of the Promoter-Catalyst interaction between Mn and Rh by Transmission Electron Microscopy

B. Graham

Department of Materials Science and Engineering, University of Alabama at Birmingham

R.F. Klie, PhD

Department of Physics, University of Illinois at Chicago

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Abstract

In the hope of optimizing the Fischer-Tropsch mechanism to produce cleaner ethanol, the catalyst- promoter interaction between rhodium and manganese was examined by transmission electron microscopy. Three samples were analyzed on a carbon nanotube (CNT) substrate with 3 wt% rhodium (3%Rh/CNT), 1% manganese with 3 wt% rhodium (1%Mn/3%Rh/CNT), and 2% manganese with 3 wt% rhodium (2% Mn/3% Rh/CNT). The average particle size were found to be (1.9 ± 0.6) nm, (2.1 ± 0.5) nm, and (3.2 ± 0.6) nm respectively. An increase in particle size indicates that the rhodium and manganese are interacting, and the distributions were Gaussian conforming they are statistically sound. The lattice parameters were also determined to be (4.1 ± 0.1) Å, (4.2 ± 0.1) Å, and (3.8 ± 0.1) Å again respectively. The decrease in lattice parameter in the 2%Mn/3%Rh/CNT sample is due to a shift in the crystal structure of the rhodium particles.

Introduction

Finding a reliable source of energy is a major topic of research interest in the world today. We will discuss the potential of using the Fischer-Tropsch process to obtain higher octane fuels.¹ This is achieved through a mechanism of converting syngas, a CO and H₂ mixture, to ethanol. Ethanol is a simple hydrocarbon that has a wide range of industrial uses, and is being looked into as a potentially cleaner source of energy. However, traditional fermentation routes to produce alcohols are often slow and inefficient. In addition, using crops for fuel grade alcohol production is controversial due to doubts about its overall energy efficiency and its effect on food prices.

Catalysts are used to increase the selectivity and activity of reaction. Catalysts are often paired with promoters, which are species not involved in the chemical reaction but increase the activity and selectivity of the active catalyst particles. While the large scale benefits of catalyst and promoters are easy to see, the intricate interactions at the nano-scale level are not as well understood. By examining the fundamental interactions between rhodium and manganese, we hope to better implement them in the conversion of syngas.

In heterogeneous catalysis, metal catalysts are of special interest.²⁻⁴ Rhodium is an example that has been extensively studied for its properties as a catalyst.⁵⁻⁷ Among the transition metal catalysts, rhodium has a high selectivity to produce alcohols in the syngas conversion.⁵ The drawback to rhodium is its selectivity to methanol.⁵⁻⁶ It has been shown that when promoted with manganese, there is an increase in the selectivity towards ethanol.⁵ This catalyst promoter pairing of rhodium and manganese has great potential to make the syngas conversion a viable option.

A transmission electron microscope (TEM) will be used to examine the interactions between rhodium and manganese. When the electrons from the electron source interact with the specimen many different signals are produced, as seen in Fig. 1. The elastically scattered electrons transmitted

through the specimen in the TEM allow for the bright field imaging of a specimen at the atomic scale.⁸ Bright field images composed of phase and mass contrast. In this study, the rhodium and manganese will be loaded on carbon nanotubes, which will provide better support when being imaged in the TEM.⁹¹⁰ This will allow for better resolution at higher magnifications.

Some prior work done on analyzing this catalyst and promoter pair of rhodium and manganese can be seen in Fig. 2,⁵ in which an electron energy loss spectrometry (EELS) was taken from a silicon dioxide supported catalyst sample. There is evident overlapping in the mapping between the rhodium and manganese as seen in Fig. 2. EELS collects the in-elastically scattered electrons that are transmitted through the sample and yields chemical bonding information.

Material and Methods

The three powder samples obtained included a 3 wt% rhodium carbon nanotube (Rh/CNT), a 1% manganese and 3wt% rhodium on carbon nanotube (1%Mn/Rh/CNT), and a 2% manganese and 3wt% rhodium on carbon nanotube (2%Mn/Rh/CNT). These samples were prepared as previously described by Liu et al.¹¹ and is briefly summarized below.

“Multi-walled carbon nanotubes (CNTs) were purchased from Cheap Tube Inc., raw CNTs were refluxed in concentrated HNO₃, for 10 hours at 120°C in a heating mantle while the magnetic stirring continued, then the mixture was filtered and washed with deionized water 8 times, followed by drying at 80 °C for 8 hours. The supported Rh₂O₃ on CNTs was synthesized via Incipient Wetness Impregnation (IWI) using rhodium nitrate, Rh(NO₃)₃. The precursor was dissolved in deionized water, and then added drop wise to impregnate the support. The weight loading of Rh was controlled at 3wt%. The catalyst was dried in air in room temperature for 24 hours followed by calcination at 280°C for 4 hours (5°C /min ramp) to convert the rhodium nitrate into rhodium oxide, Rh₂O₃.”¹¹

In order to prepare these samples for the TEM, the powder needed to be crushed to the smallest size possible in order to best observe them on the nano-scale level. To achieve this, a small amount of the powder was processed in the mortar and pestle. Next, the powder was placed vial before being suspended in 2-propanol. This solution was then placed in the super-sonic shaker for fifteen minutes. A drop of this solution was then extracted and placed on a lacey carbon film, which could then be placed in the TEM. Once the TEM was properly aligned and loaded with the specimen, the average particle size for each specimen was measured. Additionally, atomic resolution images were obtained to observe and characterize the morphology of the catalyst samples. The d-spacing, or distance between atomic planes was measured, and by using Eq. 1 the lattice parameters were calculated for all three samples. In Eq. 1, a is the lattice parameter, d_{hkl} is the measured d-spacings, and h , k , and l are the corresponding miller indices.

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (1)$$

Results

Fig. 3 shows an example of a TEM image taken at three hundred thousand times magnification, which shows several different rhodium particles. This image is ideal for measuring the average particle size as it includes multiple particles, maximizing the efficiency of picture taking. Fig. 4 shows an example TEM image taken at six hundred thousand times magnification. Atomic resolution of the manganese and rhodium particle can be seen, as the ordered rows or atomic fringes in the middle of the image. By measuring the spacing between these fringes, the d-spacing, or the distance between atomic planes in a crystal lattice, was obtained and was found to be 2.19 Å which corresponds to the (111) plane in a rhodium face-centered cubic lattice. Table 1 has the average particle sizes measurements that were taken from one hundred particles for the 3%Rh/CNT, 1%Mn/3%Rh/CNT, and 2%Mn/3%Rh/CNT samples and their standard deviations. Also in Table 1 are the average lattice parameters that were

experimentally calculated. Lattice parameter is the distance of one unit cell. There was a noticeable increase in particle size from the 3%Rh/CNT to the 2%Mn/3%Rh/CNT samples. Figures 5, 6, and 7 shows the distribution of the average particle size for these three samples to be Gaussian, which indicates that these results are statistically sound.

Discussion

The increase in size of the particles in the 3%Rh/CNT and 1%Mn/3%Rh/CNT samples to the 2% Mn/3%Rh/CNT samples would indicate that there is an interaction between the manganese and rhodium atoms. The TEM bright field images that were taken to make these measurements are composed of phase and mass contrast. Therefore, the increase in particle size is most likely due to a coating of manganese around the rhodium, as shown schematically in Figure 6. This interaction between rhodium and manganese is due to the surface energy acting as a driving force to keep the particles together.

The decrease for the lattice parameter in the 2%Mn/3%Rh/CNT would indicate a shift in the crystal lattice. As the manganese concentration increases, this might result in the oxidization of rhodium shifting the face centered cubic structure to an orthorhombic. However, this will require further measurements to determine if this is the cause of the change in the lattice parameter. From the current results, the exact nature of the interaction between the manganese and rhodium cannot be identified. However, this confirms that there is an observable interaction between the two particles.

Conclusions

To better implement the Fischer-Tropsch mechanism to produce higher octane fuels cleanly, the catalytic and promoter interaction of rhodium and manganese was analyzed using transmission electron microscopy. The average particle size for the 3%Rh/CNT, 1% Mn/3%Rh/CNT, and 2% Mn/3%Rh/CNT samples were (1.9 ± 0.6) nm, (2.1 ± 0.6) nm, and (3.2 ± 0.6) nm respectively. The average particle size for

both samples had a Gaussian distribution which indicates that these results are statistically sound. This increase in particle size could be due to the interaction between the manganese and rhodium atoms, as the surface energy acts as a driving force to keep them together rather than dissociate. Additionally the decrease in lattice parameter for the 2% Mn/3%Rh/CNT sample is likely due to a crystal structure shift in the rhodium lattice. More analysis is required to better characterize the morphology of this interaction.

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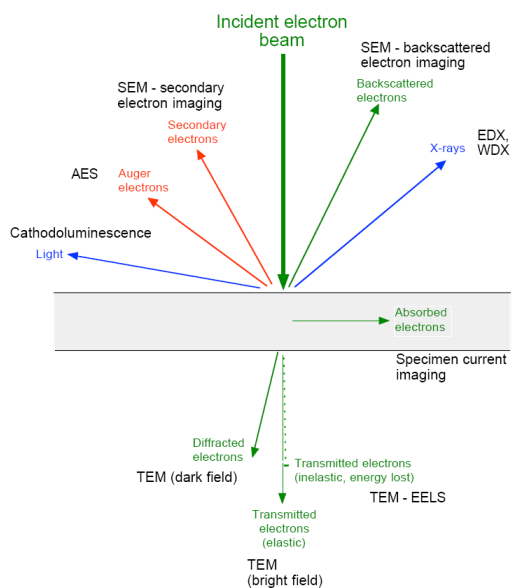


Figure 1: When electrons interact with a specimen, several signals are produced that can provide information for the characterization of the specimen.

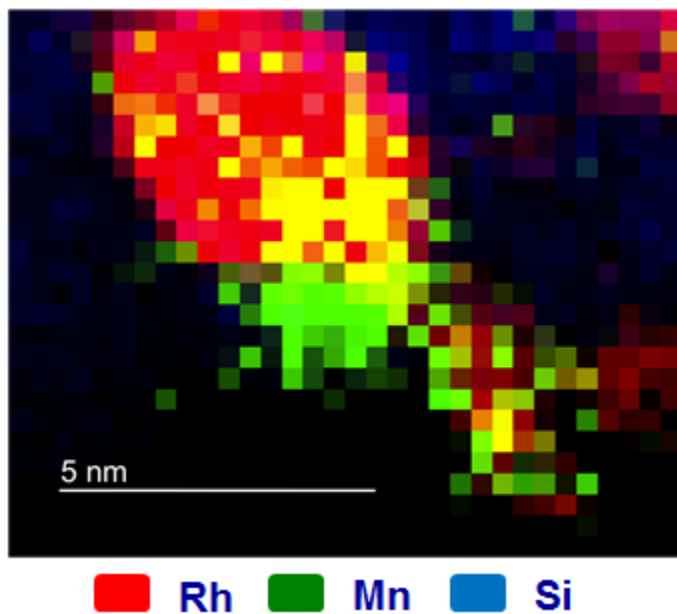


Figure 2: EELS mapping of rhodium and manganese interaction supported by a SiO₂ substrate. EELS performed in a scanning transmission electron microscope (STEM).

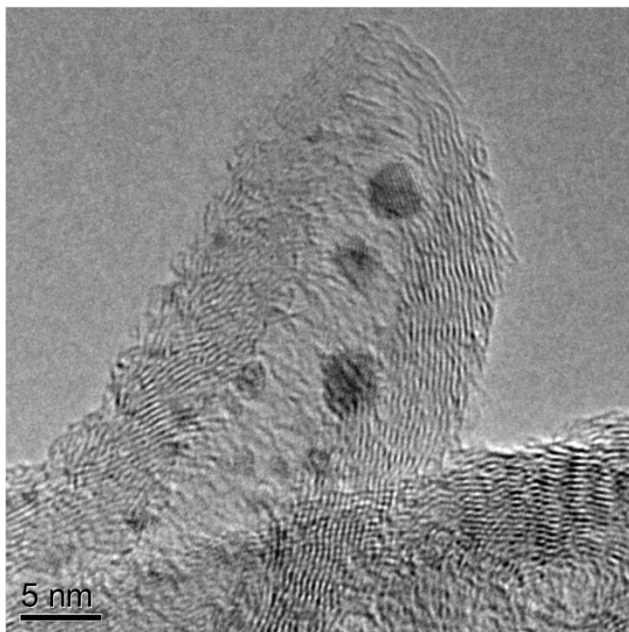


Figure 3: TEM Image of Rh/CNT sample at 300Kx, numerous Rh particles are visible ideal for particle size sampling.

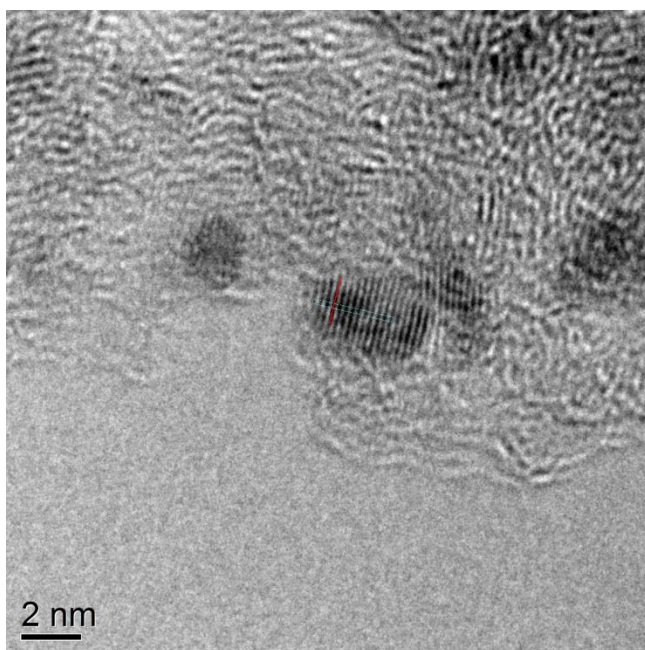
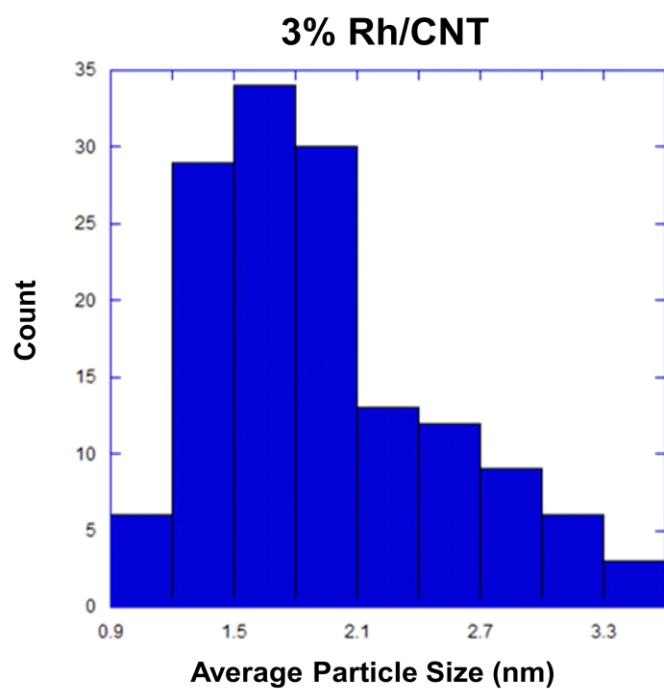


Figure 4: TEM bright field image of 2% Mn/Rh/CNT sample at 600Kx, showing the atomic resolution of the Mn/Rh particle making it possible to determine the crystallographic orientation of the particle.

Table 1: Average particle size for the three samples along with the standard deviations.

Catalyst	Average Particle Size (nm)	Lattice Parameter (Å)
3%Rh/CNT	1.9 ±0.6	4.1±0.1
1%Mn/3%Rh/CNT	2.1 ±0.5	4.2±0.1
2%Mn/3%Rh/CNT	3.2 ±0.6	3.8±0.1

**Figure 5:** A Gaussian distribution of the average particle size of the 3%Rh/CNT sample

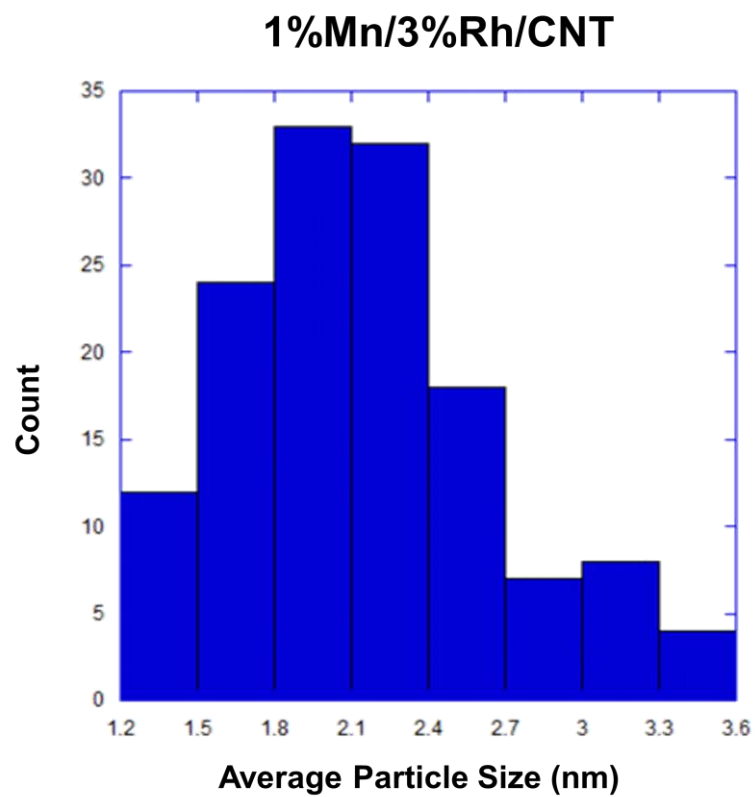


Figure 6: A Gaussian distribution of the average particle size of the 1%Mn/3%Rh/CNT sample

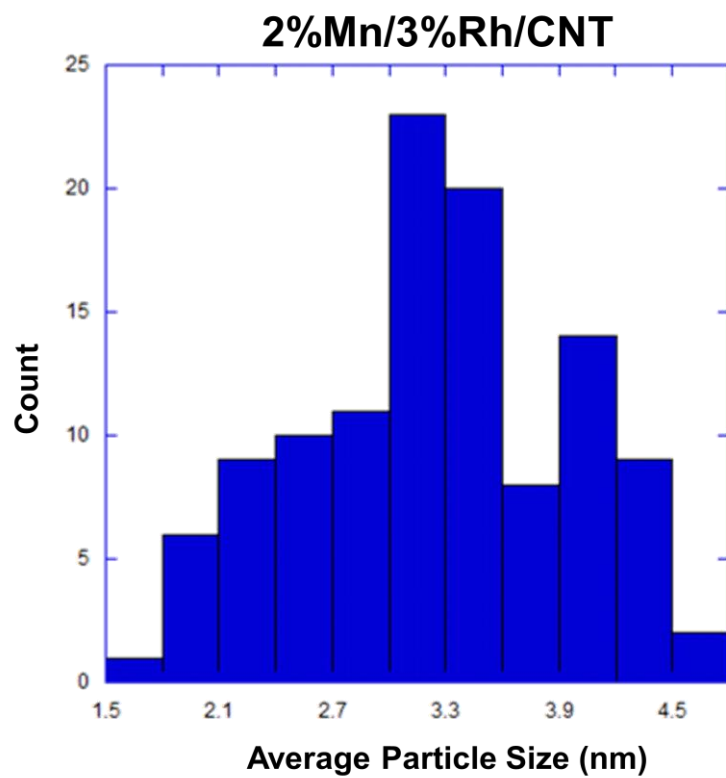


Figure 7: A Gaussian distribution of the average particle size of the 2%Mn/3%Rh/CNT sample

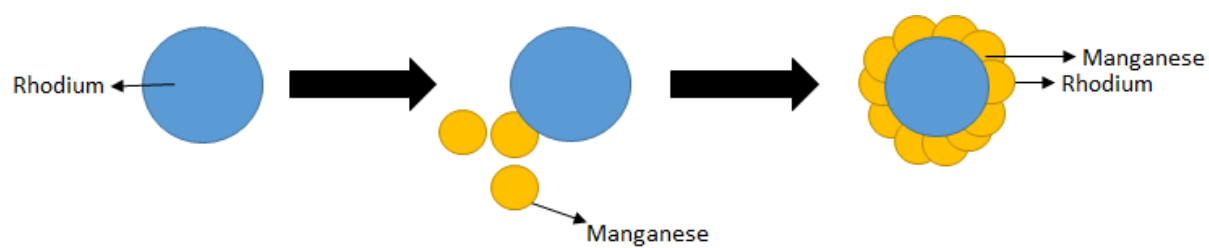


Figure 8: Schematic drawing of the qualitative interactions between the rhodium and manganese particles