

Environmental TEM Studies of CoMn nanoalloys as Model Fischer-Tropsch Catalysts

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Fischer-Tropsch(FT) reaction involves the hydrogenation of carbon monoxide to hydrocarbons typically by group VIII metals [1]. Cobalt is one of the first metals used as FT catalyst and is typically mixed with Mn to promote carbon monoxide conversion to more valuable higher (C₅₊) hydrocarbons and olefins. The properties of metal catalysts can be controlled by fine-tuning chemical composition, surface oxidation, structure and dimension[2,3]. However, the performance of FT catalysts is strongly affected by oxidizing and reducing pre-treatments[1]. In this case, well-defined size and compositions of CoMn nanoalloys were synthesized and studied in oxidizing and reducing conditions as necessary for its viability as FT catalyst. Here *in situ* TEM was performed to determine the elemental distributions and morphological changes in the CoMn nanoalloys upon exposure to oxidizing and reducing environments to elucidate the observed nanoalloys' catalytic properties.

Environmental transmission electron microscope (ETEM) experiments of 1 cycle of oxidation and reduction at 0.1 mTorr in O₂ and H₂ gas at 300°C of the CoMn nanoalloys were performed. These nanoalloys (diameter of 3-6 nm) were dispersed in hexane and drop-casted on SiN grids for the *in situ* studies. A Hitachi H-9500 LaB₆ ETEM microscope operated at 200 KV was used for simultaneous acquisitions of videos and high resolution TEM (HRTEM) images. The elemental distributions of Co and Mn within the particle were obtained through the analysis of the HRTEM image's fast Fourier transform (FFT) by application of annular mask on a given lattice spot on the FFT [4].

Figure 1a shows a HRTEM image of a single NP at room temperature (RT) with the Co and Mn lattice spots separately masked in b. After masking the specific spots and inverting the FFT, the elemental distribution of Co and Mn were obtained and superimposed on initial HRTEM image (Figure 1c). Formation of Co and Mn oxides were detected after the oxidation cycle (Figure 2a). During oxidation, MnO is readily formed and appeared to cover the CoO (light blue areas in Figure 2a). Such results can be attributed to the faster oxidation rates for Mn versus Co resulting to Mn³⁺ doping of CoO [5]. Further reduction resulted to Co being reduced to its metallic phase and Mn remained as oxide. During the reduction cycle, both Co and Mn were equally distributed within the NP (elemental map in Figure 2b).

Additional ETEM experiments with longer exposure times of the reaction cycles are underway with more acquired HRTEM images during the reaction cycles for a quantitative analysis of the nanoalloy's reconstruction. Furthermore, correlation of the nanoalloy's reconstruction from the ETEM studies to ambient pressure X-ray photoelectron spectroscopy (AP-XPS) study of similar experimental conditions along with the catalyst activity experiments will be provided to obtain the optimum reaction conditions of these CoMn nanoalloys as model FT catalysts [6].

References:

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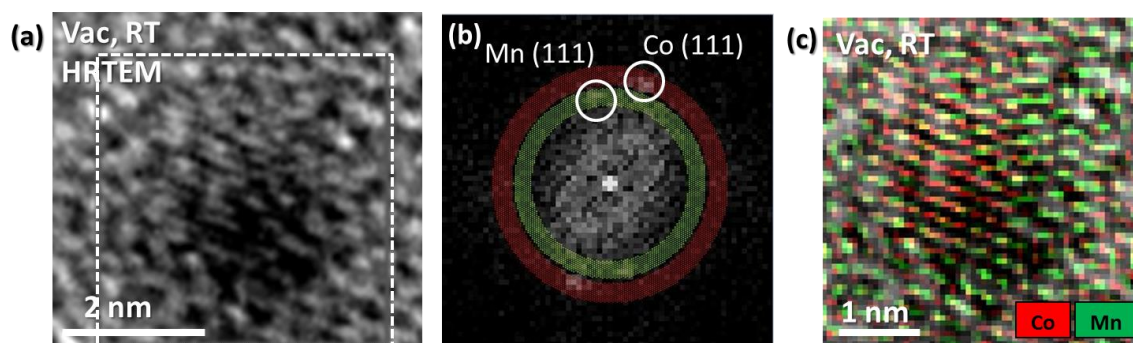


Figure 1. (a) HRTEM image of a single CoMn nanoalloy at room temperature before gas exposure. (b) shows the identified Co(111) and Mn(111) spots with applied annular masks on the FFT acquired from the selected area in a. (c) is image (a) with the colored areas of Co (red) and Mn (green) superimposed.

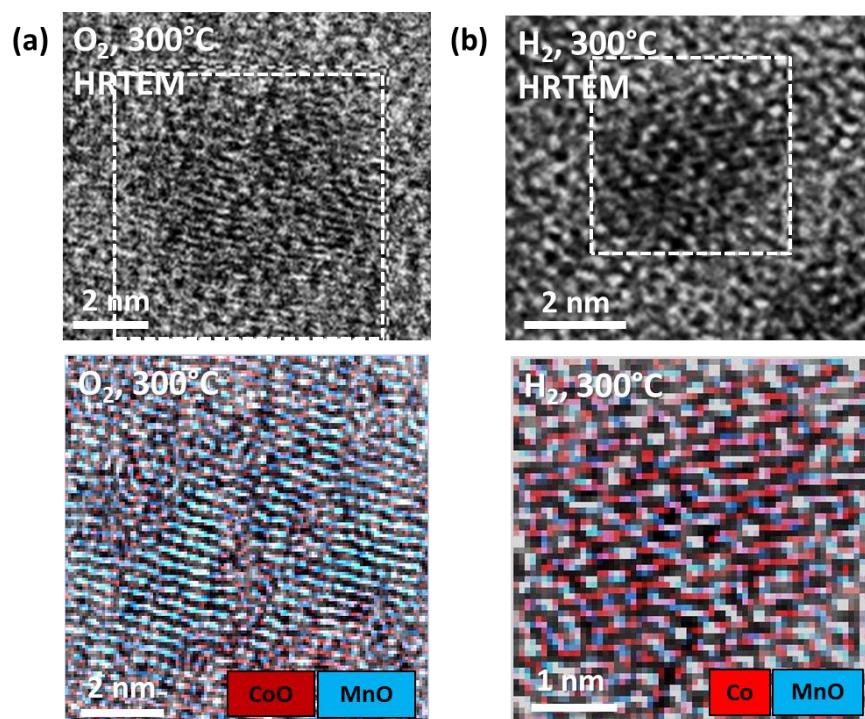


Figure 2. (a) HRTEM image of a single CoMn nanoalloy under O₂ exposure at 300°C identified with areas of CoO(maroon) and MnO(blue). Exposure to H₂ at 300°C(b) resulted to reduction of CoO to Co (red) and intermixing with MnO(blue).