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Developing Self-Supported Metal Oxide Nanowire Catalysts for the Oxidative Coupling of Methane

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Progress of the research

The major goal of the proposed research is to elucidate the synergy between MnO_x and WO_x species in the oxidative coupling of methane (OCM). Our strategy involves the synthesis of MnO_x and WO_x nanowires (NWs) and further grafting of WO_x and MnO_x species via atomic layer deposition (ALD), Surface Organometallic Chemistry (SOMC), or other surface chemistry approaches.

During the last year, one graduate student (10 months) was assigned to this project. We attempted to follow the protocols described in literature for the synthesis of MnO_x and WO_x NWs. However, most of these synthesis protocols showed poor reproducibilities. To this end, we developed new protocols to achieve the targeted thin NWs with relatively large scales. Further modification of these NWs, structural characterizations, and catalytic tests are currently in progress.

Synthesis of MnO_x NWs. Most reported recipes for the synthesis of MnO_x NWs typically yield a few hundreds of mg of product per batch, which is not sufficient for our proposed work. 200-300 mg of catalyst is needed for each catalytic test. Therefore, nearly a gram of sample should be synthesized in each batch. We initially attempted to reproduce the reported method by mixing $KMnO_4$ solution with $MnCl_2$ solution followed by hydrothermal treatment at 120°C (*CrystEngComm 2014, 16, 9999-10005*). This synthesis should result in ~0.7 g of ultrathin MnO_x NWs per batch. However, we observed a mixture of NWs and nanoplates (Figure 1). We have optimized the concentration, $KMnO_4/MnCl_2$ ratio, reaction temperature, and reaction time, the yield of NWs is still rather limited. Recently we developed a new synthesis protocol by replacing $KMnO_4$ with K_2MnO_4. When mixing K_2MnO_4 and $MnCl_2$ solutions at room temperature, precipitates are quickly formed. These amorphous precipitates can be converted to MnO_2 NWs upon hydrothermal treatment for a short period of time (Figure 1). In this way, we have successfully synthesized MnO_2 NWs with a large scale (2~3 g per batch).

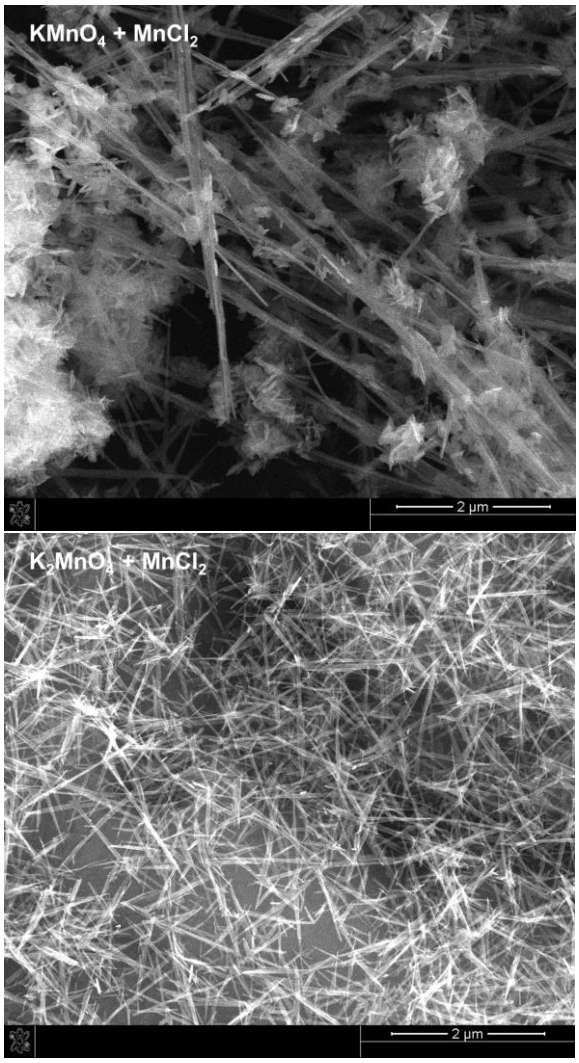

Figure 1. Scanning Electron Microscopic images of MnO_x synthesized based on the recipe reported in the literature (top) and our newly developed recipe (bottom).

Synthesis of WO_x NWs. Two papers were published on WO_x NW synthesis by dissolving WCl_6 in absolute ethanol and followed by solvothermal treatment at 160-180°C (*J. Am. Chem. Soc. 2012, 134, 6508-6511; Angew. Chem. Int. Ed. 2012, 51, 2395-2399*). Following these recipes, we obtained ultrathin WO_x NWs together with aggregates of nanoparticles (Figure 2). We then modified the recipe by prolonging the reaction time and introducing surfactants. The morphological purity of NWs were improved but a small quantity of aggregates were still present. We also explored other synthetic

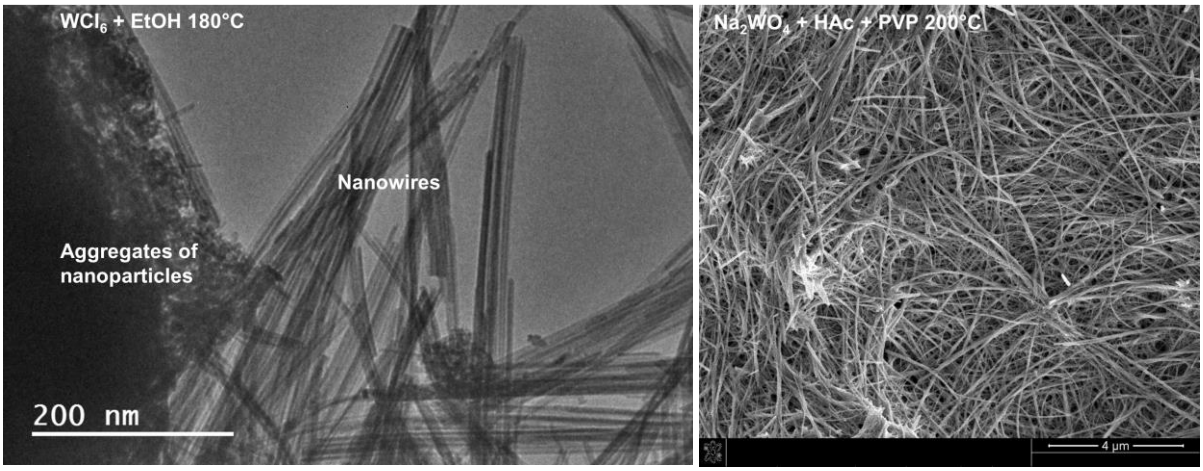

Figure 2. (Left) Transmission Electron Microscopic image of WO_x synthesized based on the recipe reported in the literature (*J. Am. Chem. Soc. 2012, 134, 6508-6511*). (Right) Scanning Electron Microscopic images of WO_x synthesized based on the recipe reported in the literature (*J. Am. Chem. Soc. 2018, 140, 9078-9082*).

protocols and managed to obtain WO_x NWs with high morphological purity (Figure 2) following another literature work (*J. Am. Chem. Soc. 2018, 140, 9078-9082*). However, the product yield was quite low (less than 100 mg per batch). Further work is needed to achieve WO_x NWs with desired quantity and structural uniformity.

Impact of the research on PI's career

During the funding period, the PI was invited to give a talk at SABIC to discuss our research on natural gas catalytic conversions. The PI also visited Oak Ridge National Lab for a few times to carry out advanced microscopy studies on the catalysts, in collaboration with scientists at ORNL. The PI attended North American Catalysis Society meeting in Chicago and chaired two sessions. These activities has strengthened the PI's connections with other scientists in the field.