



Synthesis and Characterization of Mesoporous Molybdenum Oxide

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Abstract

In this work, a “one-pot” synthetic approach was developed for the synthesis of mesoporous molybdenum oxide (MoO_3). Two different MoO_3 precursors were explored. Mesoporous MoO_3 synthesis starting with ammonium molybdate tetrahydrate was unsuccessful; it is insoluble at the low water levels typically used for the one-pot approach and did not react when water levels were increased to improve solubility. Experiments using molybdenum (V) chloride were more promising. By adjusting the solvent system used for the one pot synthesis to a mixture of methanol and butanol, MoO_3 was successfully synthesized, though further analysis is needed to determine if the material is mesoporous.

Introduction

The synthesis of mesoporous materials is an emerging field due to the application of these materials in catalysis, sorption, optics, sensing and ion exchange. These materials have high surface areas, nanocrystalline walls, and nanoparticle pore sizes ranging from 2 – 50 nm that make them useful in these applications. An inverse micelle, “one-pot” approach, modeled after a synthesis used for other transitional metal oxides, was explored. This approach uses P-123 (a polyethylene oxide polypropylene oxide block co-polymer) as a surfactant to direct the mesoporous structure formation. The MoCl_5 was first reacted with methanol to form the metal alkoxide, then combined with the P-123, solvent and nitric acid for further conversion of the molybdenum alkoxide to the oxide. The synthesis of the MoO_3 in the presence of the inverse micelle occurs via a sol-gel mechanism. First, the molybdenum alkoxide undergoes a hydrolysis reaction with any water present to form molybdenum hydroxide. The molybdenum hydroxide molecules then react with one another via condensation reactions to form the MoO_3 network.

Method and Materials

Molybdenum (V) Chloride (0.01 mol) was dissolved in methanol under nitrogen, then added to a 1-butanol solution containing HNO_3 and P123 in a 150-ml beaker at room temperature (RT) and under magnetic stirring. The obtained forest green solution was placed in an oven at 120 °C for 4-6h until a spongy, black solid was obtained. The resulting material was washed several times with excess ethanol, centrifuged and dried in a fume hood overnight. The dried black powder was heat treated to 150 °C for 12h, 250 °C for 4h, 350 °C for 3h, and 450 °C for 2h under air. After each heat treatment, the material was characterized by X-ray diffraction (XRD) and infrared spectroscopy (ATR-FTIR). XRD analyses were performed on a Rigaku MiniFlex diffractometer with an operating voltage of 30 kV and a current of 15mA. ATR-FTIR spectra of the powder were collected by Thermoscientific Nicolet FT-IR spectrometer.

Results

The XRD and ATR-FTIR results were used to characterize the chemical changes that occurred after each heating cycles. The ATR-FTIR spectrum show the presence of terminal Mo=O (1000 cm^{-1}) groups as well as Mo-O-Mo (960 and 840 cm^{-1}) bridging groups. The XRD data shows the material is amorphous following synthesis, but crystallizes to orthorhombic $\alpha\text{-MoO}_3$ at higher temperatures.

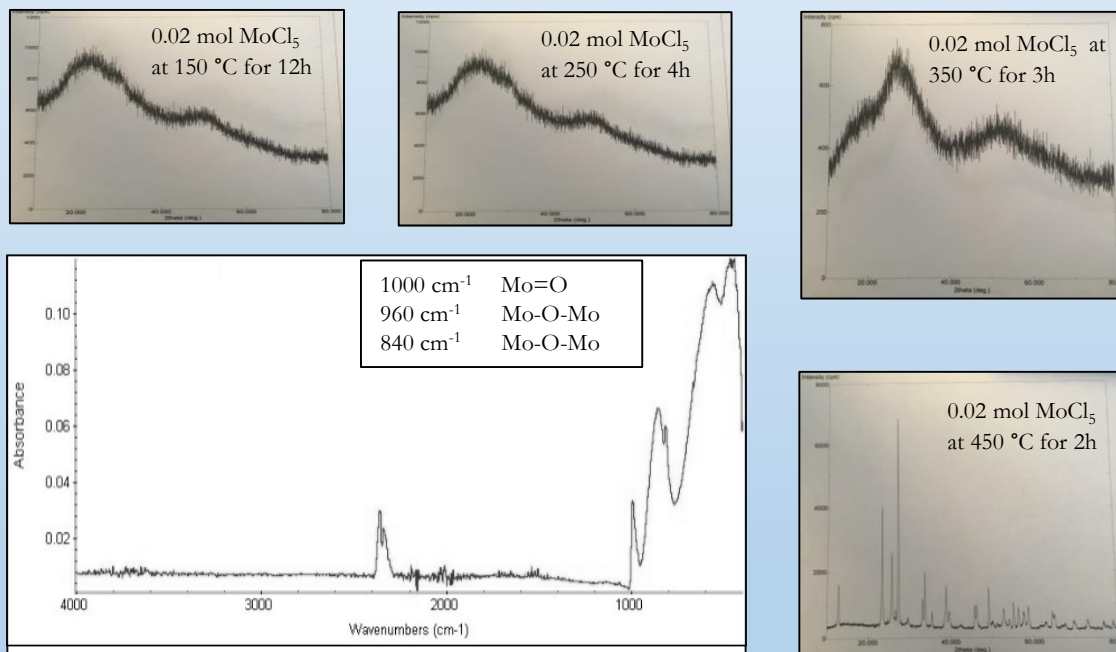


Figure 1: ATR-FTIR Spectrum of 0.02 mol MoCl_5

Conclusion and Future Work

Both the ATR-FTIR and XRD analyses indicate that MoO_3 has been synthesized from the MoCl_5 precursor using the “one-pot” approach. In the ATR-FTIR spectra, the Mo-O-Mo absorbance bands show are consistent with that expected for sol-gel MoO_3 synthesis. The Mo=O bands are terminal groups; the presence of these groups in the structure favors the formation of a solid (precipitate.) The XRD indicates that the material is amorphous following synthesis and low temperature heat treatments, but it crystallizes to the orthorhombic $\alpha\text{-MoO}_3$ phase at higher temperatures. Additional analysis is needed to determine if the material is mesoporous. This will be done by low-angle XRD with the new X-Ray diffractometer installed in the Department Chemistry and Chemical Engineering. Thermal gravimetric analysis (TGA) and Temperature-programmed desorption (TPD) will be used to determine the evaporation rate of nitrate and the surfactant and to monitor the removal of the nitrate and carboxyl groups, respectfully. If the material is mesoporous, it will be studied as a gas sensing material.

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