Microwave heated chemical looping ammonia synthesis over Fe and CoMo particles

Siobhan Brown[a.], Brandon Robinson[a.], Yuxin Wang[a.], Christina Wildfire[b.], Jianli Hu[a.]

[a.] Department of Chemical and Biomedical Engineering, Benjamin M. Statler College of Engineering and Mineral Resources, West Virginia University, 395 Evansdale Drive, Morgantown, WV 26505, United States of America.

Email: john.hu@mail.wvu.edu.

[b.] US Department of Energy-National Energy Technology Laboratory, Morgantown, WV, 26505, United States of America.

1.1 CLAS Materials Test Matrix

The exhaustive list of CLAS candidates is presented in Table 1 with operation notes and observations. Support and microwave sorbent materials were tested to confirm inactivity at CLAS conditions. Microwave materials were tested in the microwave reactor up to 3 kW power to heat to reaction temperatures, if microwave heating was not achieved this result was noted.

Table 1. Compiled reaction engineering observations for CLAS candidates.

CLAS Candidate	CLAS Experiment Notes
Mo^0	Mo is not an ideal candidate for nitrogen chemical looping; however, it holds historical and scientific importance to nitrogen fixation.
MoO_2	The low vapor pressure of MoO_3 causes some mass loss to reactor walls as a molybdenum film. The oxides do heat under microwave irradiation, but this effect decreases as the oxygen content is reduced.
Mn^0	Excellent candidate for nitrogen chemical looping as shown by the publication record, however, a distinct drawback is the massive loss of suffer area when metal particles sinter together during nitridation. This material heats poorly in the microwave.
MnO_2	The temperature required to fully reduce MnO_2 to Mn is above the range studied here, however, MnO still forms a limited nitride which can produce small amounts of ammonia. The Mn suboxide form can be easily observed by a pale green coloring and is easily re-oxidized. This material does not succumb to sintering like pure Mn metal

	does at ~700°C.
Co_3O_4	Cobalt oxides reduce at a low temperature but retain very small amounts of nitrogen alone.
Mg^0	The melting point of metallic Mg is within the range of efficient nitride synthesis, ~650°C, making this a difficult material to work with alone.
2.5% Co 2.5 % Mo/γ-Al_2O_3	Hydrodesulfurization catalyst shows some limited nitride formation despite low metal loading.
$CoMoO_4$	Can be observed to heat in microwave reactor but this effect is limited to changing oxidation states and thus does not last and is not repeatable. Like MoO_2, temperature ramp rate can create metallic films which indicate loss of MoO_3.
$MgFe_2O_4$	No ammonia detected.
$La_{0.6}Sr_{0.4}FeMnO$	No ammonia detected.
$CoMoO_4$ + SiC	Tested in microwave reactor.
$CoMoO_4$ + SiO_2	Did not heat in microwave reactor.
MoO_2 + SiC	Tested in microwave reactor.
MoO_2+ SiO_2	Did not heat in microwave reactor.
Mn + SiC	Did not heat in microwave reactor.
Mn + SiO_2	Did not heat in microwave reactor.
MnO_2 + SiC	Did not heat in microwave reactor.
MnO_2 + SiO_2	Did not heat in microwave reactor.
Mo + SiC	Did not heat in microwave reactor.
Mo + SiO_2	Did not heat in microwave reactor.
Ta_2O_5	No ammonia detected.
$CoMoO_4$:Al_2O_3	Ground with mortar and pestle the 1:1 ratio and calcined at 550°C, this material did heat effectively in the microwave for at least one cycle. Rapidly deactivated and lost performance afterward.
4% Ru 4% Cs/MgO	Model traditional catalyst used in this laboratory.

1% K 1% Ru/γ-Al₂O₃	Model traditional catalyst used in this laboratory.
C12A7	Did not heat in microwave reactor.
SiO₂	'Invisible' to microwave heating. Separates catalyst particles to allow heating and reduce electron conduction in the mass when homogeneously mixed.
SiC	Efficient absorber of microwave energy used to heat nearby particles when homogenously mixed.
Al⁰	The melting point of metallic Al is within the range of efficient nitride synthesis, ~650°C, also making this a difficult material to work with alone. The oxide is extremely stable.
Ti⁰	No ammonia detected.
TiMn₂	No ammonia detected.
γ-Al₂O₃	No ammonia detected.
MgO	No ammonia detected.
BaTiO₃	Does not heat, no ammonia detected.

1.2 FLIR Imagery

Still images of the fixed bed reactor were taken using a FLIR camera after it reached a temperature set point, each pixel was then assigned a temperature. This allowed an independent measurement of the temperature of the microwave reactor fixed bed, in-situ. Figure 1 and Figure 2 contain the results from both the Fe and the CoMo nitridation and hydrogenation reactions. These pixel counts were used to develop descriptive statistics on bed temperature.
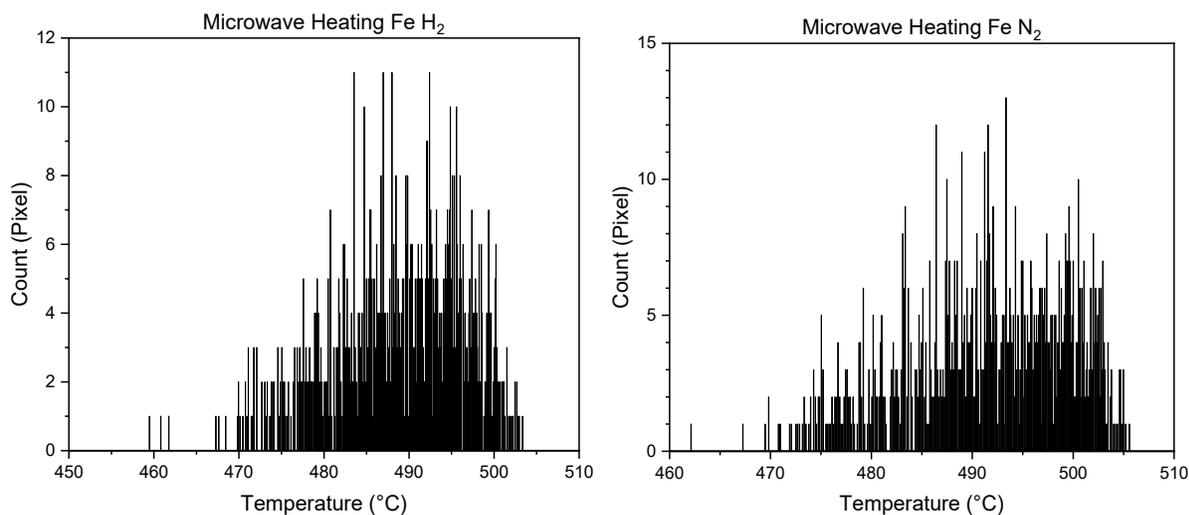
Figure 1. Histograms of the temperature distributions under of Fe under both N_2 and H_2. The temperature set point was 450 °C for both reactions.
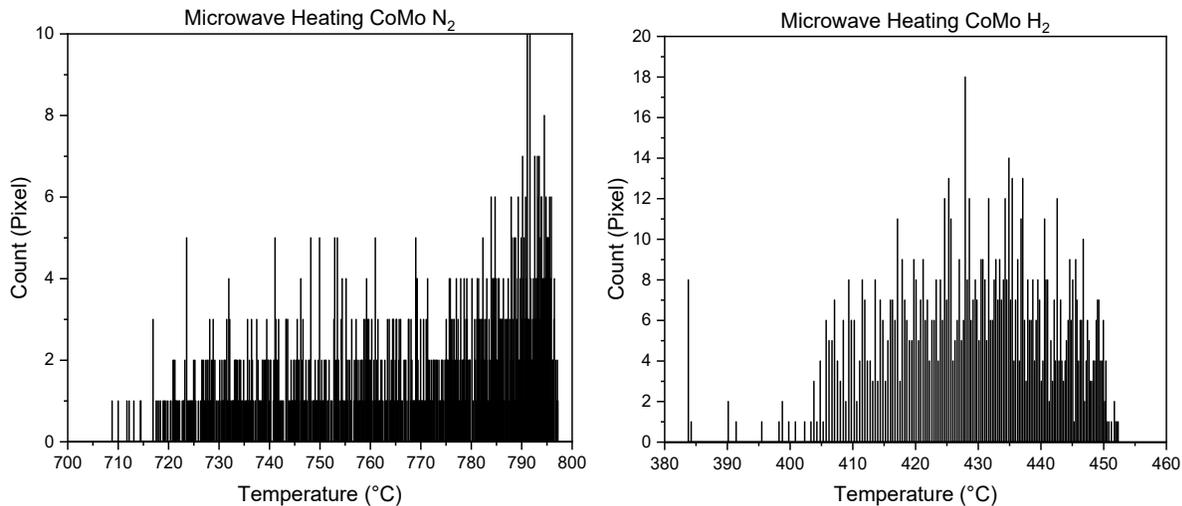
Figure 2. Histograms of the temperature distributions under of CoMo under both N_2 and H_2. The temperature set points were 750 °C and 450 °C, respectively.

1.3 X-ray Diffraction

1.3.1 Mn Systems

Fresh Mn powder was nitrided under pure N_2 for 3 h and 5 h for Nitride 1 and Nitride 2, respectively. The fresh Mn powder corresponds best with alpha phase Mn, the intermediate nitride is found to contain beta phase Mn, Mn_2N, the 5 h nitride samples is completely the Mn_4N phase.
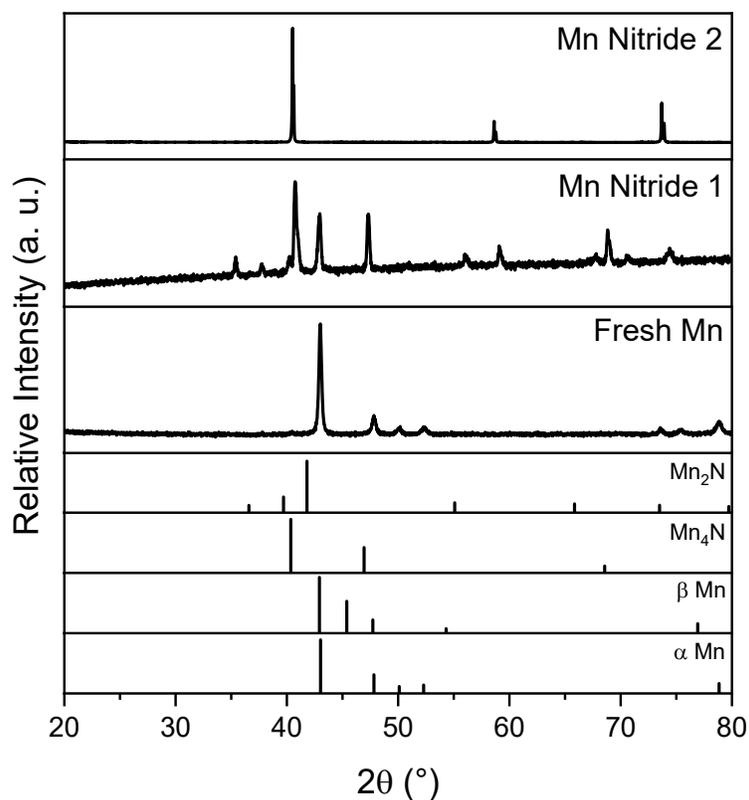
Figure 3. Fresh Mn, and 3 h (Mn Nitride 1) and 5 h (Mn Nitride 2) nitrided under N_2 samples.

1.3.2 CoMo Systems

The samples of CoMo:SiC were subjected to powdered x-ray diffraction on cycle 1 and cycle 2 of the chemical looping ammonia synthesis process. Post nitridation samples were collected after treatment in the MWFB and the CTFB and compared for the existence of active phases.
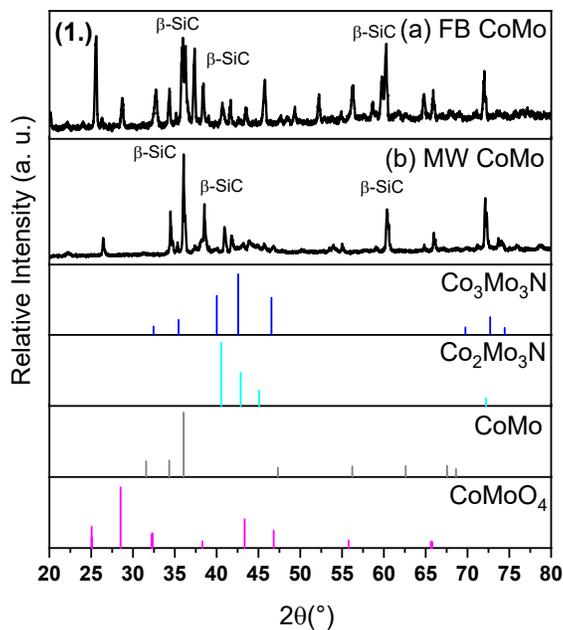
Figure 4. First CLAS cycle XRD results for the CoMo system. Sample (a) was taken post-nitridation in the conventional fixed bed, (b) was taken post-nitridation in the microwave fixed bed.
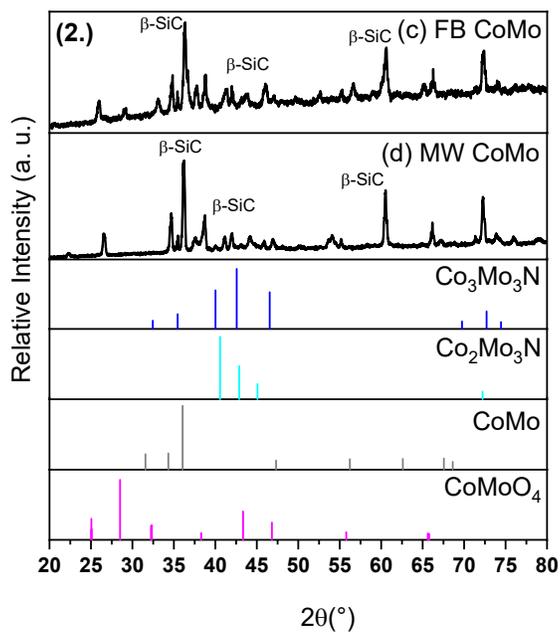
Figure 5. Second CLAS cycle XRD results for the CoMo system. Sample (a) was taken post-nitridation in the conventional fixed bed, (b) was taken post-nitridation in the microwave fixed bed.

The results in Figures 4 and 5 for the first and second CLAS cycles indicate that the fixed bed systems appear to have more varied phases present, this is likely due to the methods of heating. Where the microwave process has some heat variations which may lead to slower phase change kinetics for deactivation processes. Additionally in Figure 4 (a) the first cycle fixed

bed result shows the presence of the less active precursor Co2Mo3N to the more active Co_3Mo_3N phase. We believe that this likely is the cause of the observed induction period in the first FB cycle.

1.4 Mn Time on Stream Results

Manganese is a well-studied material for CLAS processes and is thermodynamically favorable to form nitrides. The material was tested under identical conditions to the CoMo system in both CTFB and the MWFB, but the material proved very difficult to heat in the microwave.

The results of the three-cycle CLAS experiment in the thermal fixed bed are shown in Figure 4 below. The Mn powders were found to deactivate quickly after two cycles and produce no significant ammonia on the third cycle. Additionally, interest was focused on the Fe and CoMo samples because the production of ammonia from the Mn samples was low, and the kinetics were found to be slower.
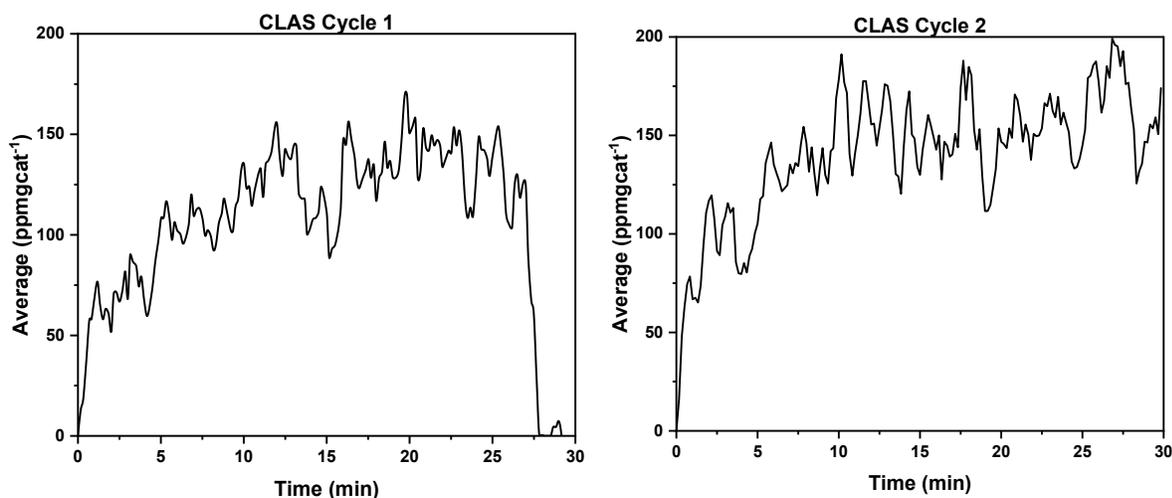
Figure 6. Ammonia produced for time on stream experiments over Mn samples under CLAS conditions, 750 °C nitridation under N_2 for 3 h followed by 450 °C hydrogenation under H_2.

1.5 SEM Imagery

SEM images were collected for fresh and nitrided Mn particles showing some evidence of sintering post-nitridation.
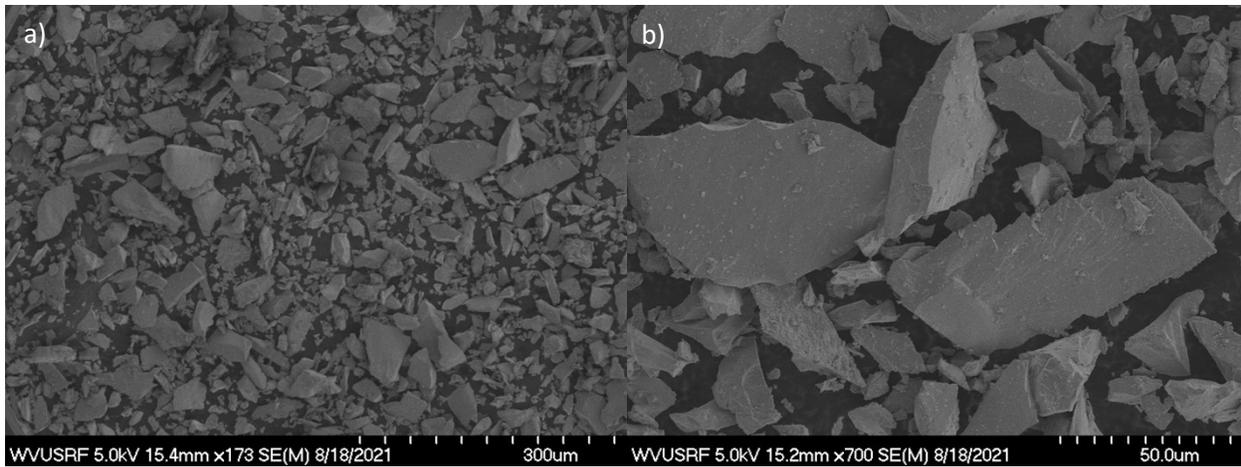
Figure 7. Fresh Mn powders at low (a) and high (b) magnification.
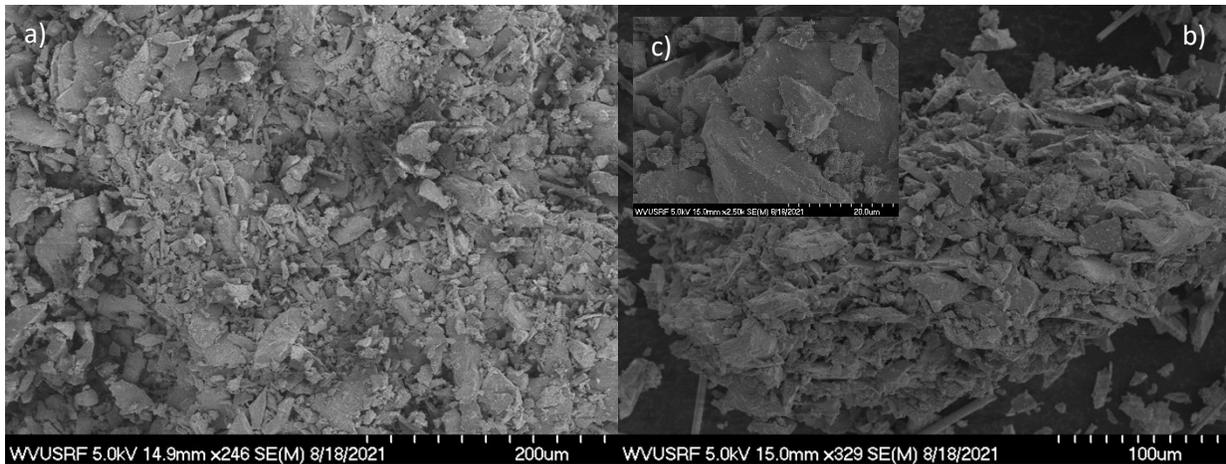
Figure 8. Nitrided Mn powders with N_2 gas for 3 h at low (a), medium (b), and high (c) magnification.

1.6 Lambda Microwave Reactor Time on Stream Experiments

The Lambda microwave reactor system was used to evaluate the CLAS:SiC samples for 1 CLAS cycle. The samples were subjected to identical conditions to those evaluated in the Sairem microwave and the conventional thermal fixed bed 3-cycle experiments. The only difference between the systems is that the Lambda system operates at a maximum power of 1 kW and 5.85 GHz. If the penetration depth equation is considered, the lower productivity can be explained by less efficient volumetric heating processes due to a higher frequency in the denominator.
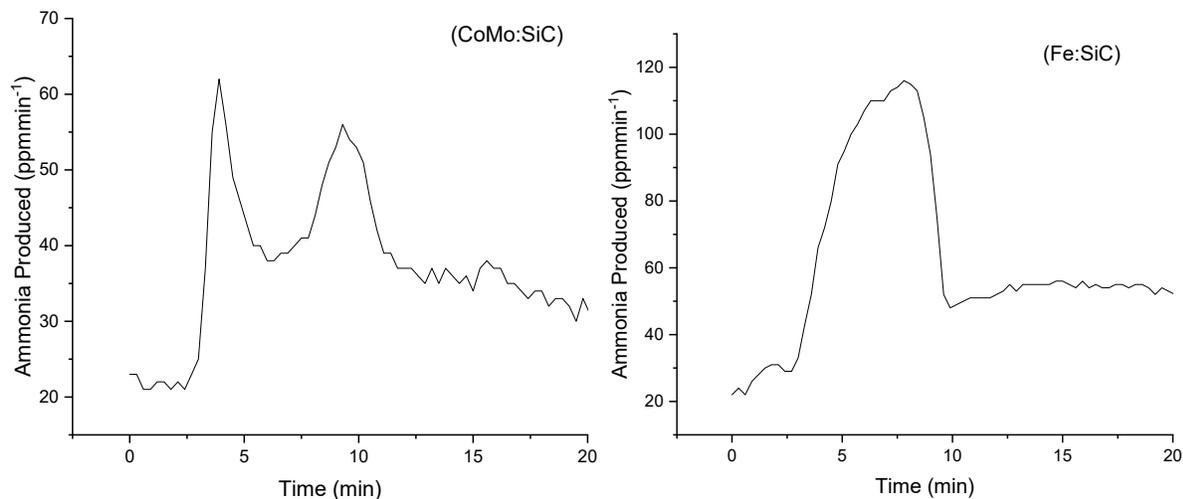
Figure 9. Hydrogenation of 1:1 SiC:CLAS materials nitrided at 750 °C and 450 °C under 50 mL/min N_2 for 1 h, followed by a 450 °C hydrogenation step under 50 mL/min H_2.

1.7 BET Surface Area Measurements

Additional surface area measurements were carried out to understand the CoMo system CLAS results. Samples were prepared at the nitridation stage using the MW and FB reactor systems for cycle 1 and cycle 2. There is a clear trend towards higher surface areas, but the increases between each cycle are quite low. The bulk surface areas of the samples increase with each cycle but the microstructure that originally provided the enhanced reaction rates is destroyed, and replaced with the mixed phases observed in the XRD results.

Table 2. BET surface area measurements for nitrided CoMo materials after cycle 1 and cycle 2 reactions.

BET Sample	Surface Area [m^2/g]
CoMo MW Cycle 1	0.28
CoMo MW Cycle 2	0.84
CoMo FB Cycle 1	0.60
CoMo FB Cycle 2	1.17
Fresh CoMoO$_4$	15.98