

## ***In-situ* Time-resolved Characterization of Catalysts: Nickel-molybdate and the Water-gas shift Reaction**

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### **Introduction:**

Recently, a novel and highly active Cu-MoO<sub>2</sub> catalyst was synthesized by partial reduction of a precursor CuMoO<sub>4</sub> mixed-metal oxide with CO or H<sub>2</sub> at 200-250 °C [1]. Significant water-gas shift catalytic activity was observed with relatively stable plateaus in product formation 350, 400 and 500 °C. The interfacial interactions between Cu clusters and MoO<sub>2</sub> increased the water-gas shift catalytic activities at 350 and 400 °C.

In this work, we investigate the water-gas shift activity of Ni clusters supported on MoO<sub>2</sub> that are prepared via reduction of a NiMoO<sub>4</sub>·nH<sub>2</sub>O in a H<sub>2</sub> gas stream at 700 °C. *In situ* TR-XRD is employed to correlate the water-gas shift activity with the structural transformations of the catalysts.

### **Experimental:**

The *in situ* time-resolved X-ray diffraction patterns were obtained at beam line X7B ( $\lambda=0.922$  Å) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory [1,2].

The NiMoO<sub>4</sub>·nH<sub>2</sub>O was synthesized by coprecipitation from aqueous solutions of Ni nitrate and ammonium heptamolybdate [3].

For the reduction of NiMoO<sub>4</sub>·nH<sub>2</sub>O and the water-gas shift reaction, the sample (3-4 mg) was loaded into a sapphire capillary tube, which was attached to a flow system [1,2]. The capillary was heated using a small resistance heater that was wrapped around the capillary and a 1 mm chromel-alumel thermocouple placed inside the capillary was used to measure the temperature.

The water-gas shift reaction was carried out isothermally at 350, 400 and 500 °C, with a flow of 5% CO/He gas mixture saturated with water by flowing through a bubbler at a rate of ~10 ml/min. At each temperature, the water-gas shift reaction was monitored for a period of three hours.

### **Results and Discussion:**

Figure 1 shows *in situ* XRD patterns collected during reduction of NiMoO<sub>4</sub>·nH<sub>2</sub>O with pure hydrogen. Around 350 °C, the diffraction peaks of NiMoO<sub>4</sub>·nH<sub>2</sub>O disappeared and the reduced catalyst consisted of a mixture of NiO, amorphous molybdenum oxide and Ni-Mo alloy, which showed broad (particle size

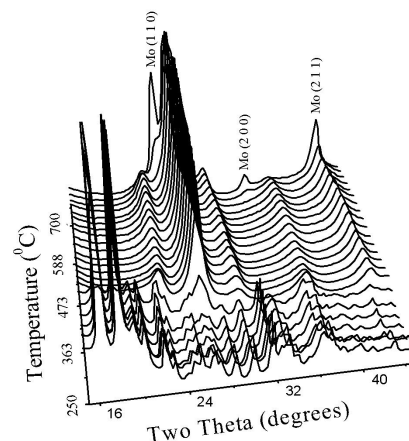


Figure 1. TR-XRD patterns for the reduction of NiMoO<sub>4</sub> hydrate

observed that Mo metal was oxidized to MoO<sub>2</sub> around 500 °C while Ni metal (lattice parameter of 3.52 Å) appeared, which had a particle size of 23 nm. The catalyst was not activated until 500 °C and the catalytic activity increased when the reaction was held at 500 °C for 3 hours, while the concentration of Ni and MoO<sub>2</sub> also increased. No catalytic activity was observed at lower temperature regions, such as 350 and 400 °C.

During the second pass of the water-gas shift reaction, stable catalytic activity was observed at 350, 400 and 500 °C, which was significantly larger than the catalytic activity of Ni or MoO<sub>2</sub> under the same conditions. TR-XRD data showed that two phases, Ni and MoO<sub>2</sub>, co-existed and the catalyst remained unchanged.

### **Acknowledgements:**

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### **Reference:**

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around 6 nm) and shifted diffraction peaks (lattice parameter of 3.62 Å) compared with those of the Ni metal (particle size 23 nm; lattice parameter 3.52 Å). Similar diffraction pattern observed under milder conditions in the reduction of alpha-NiMoO<sub>4</sub> resulted in a mixture of Ni<sub>4</sub>Mo, Ni and NiO [2]. Around 700 °C, diffraction peaks (as marked in Figure 1) that could be assigned to those of the Mo metal appeared and NiO was further reduced to Ni, which formed alloy with Mo.

Figure 2 shows *in situ* XRD patterns collected during the first pass of the water-gas shift reaction using the catalyst synthesized in figure 1. It was

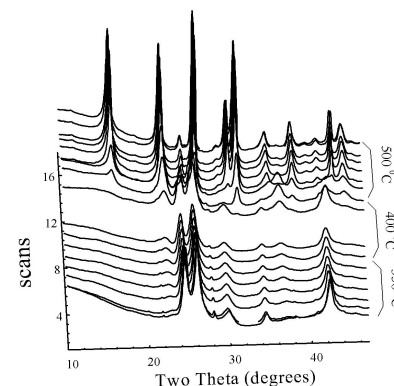


Figure 2. TR-XRD patterns during the first pass of the WGS reaction using NiMoO<sub>4</sub>·nH<sub>2</sub>O reduced at 700 °C as catalyst (see Fig. 1).