

## Supporting Information.

### *The Synthesis of Fe sulfides doped with W, Mo, and pyrrhotite-like-doped Fe sulfides.*

The synthesis of Fe sulfides, including ones doped with Mo and W, was carried out using the "dry" method. The synthesis of iron sulfides doped with Mo and W (dopant content up to 3 at%) was carried out by sintering thoroughly homogenized powders of iron sulfide and sulfides of molybdenum and tungsten in pre-vacuumed quartz ampoules followed by heating to a temperature of 850 °C for 48 hours. To obtain iron sulfides of Fe<sub>0.87</sub>S composition with the structure of pyrrhotite, an excess of sulfur was introduced before synthesis.

### *The Synthesis of a Ni<sub>3</sub>S<sub>2</sub> catalyst.*

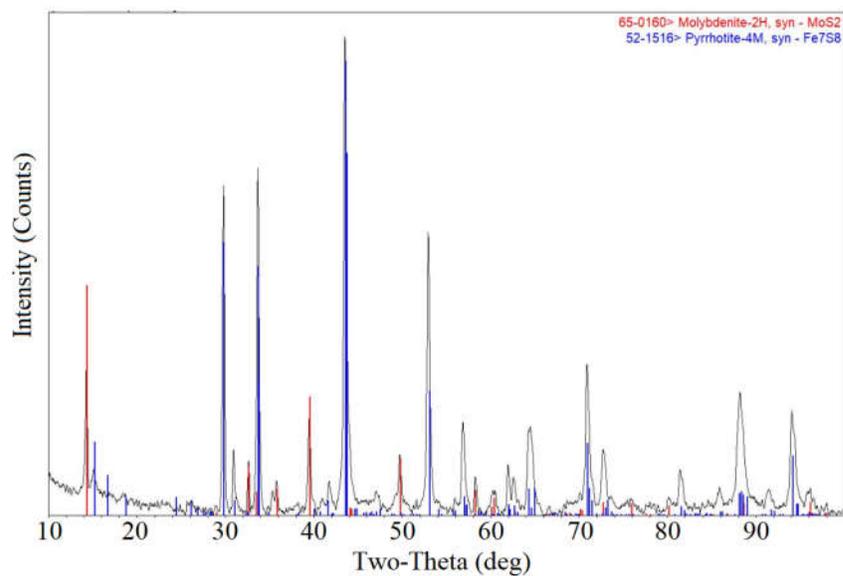
First, NiS powder was precipitated from a solution of Ni(NO<sub>3</sub>)<sub>2</sub> through a reaction with (NH<sub>4</sub>)<sub>2</sub>S. The resulting powder was filtered, dried, and loaded into a tubular reactor, where it was subjected to partial reduction at 300 °C for 8 hours in a flow of a H<sub>2</sub>-H<sub>2</sub>S mixture in a ratio of 1:0.15 by volume.

The synthesis of supported Ni<sub>3</sub>S<sub>2</sub> was carried out using the impregnation method. In a typical synthesis, per 10 g of AAO beads (AMK Grupp, grade K1, 3-5 mm diameter), impregnation was carried out with 4.57 g of Ni(NO<sub>3</sub>)<sub>2</sub> dissolved in water. After drying, the resulting Ni(NO<sub>3</sub>)<sub>2</sub>/AAO was treated with excess (NH<sub>4</sub>)<sub>2</sub>S solution to obtain NiS/AAO. The resulting material was then dried and loaded into a tubular reactor, where it was subjected to partial reduction at 300 °C for 8 hours in a flow of a H<sub>2</sub>-H<sub>2</sub>S mixture in a ratio of 1:0.15 by volume. As a result, a Ni<sub>3</sub>S<sub>2</sub>/AAO catalyst containing a 20 wt% active phase was obtained, confirmed by the ICP-AES using SHIMADZU ICPE-9000; the analyzed sample was pre-mineralized in a mixture of concentrated acids, namely H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> (1:2).

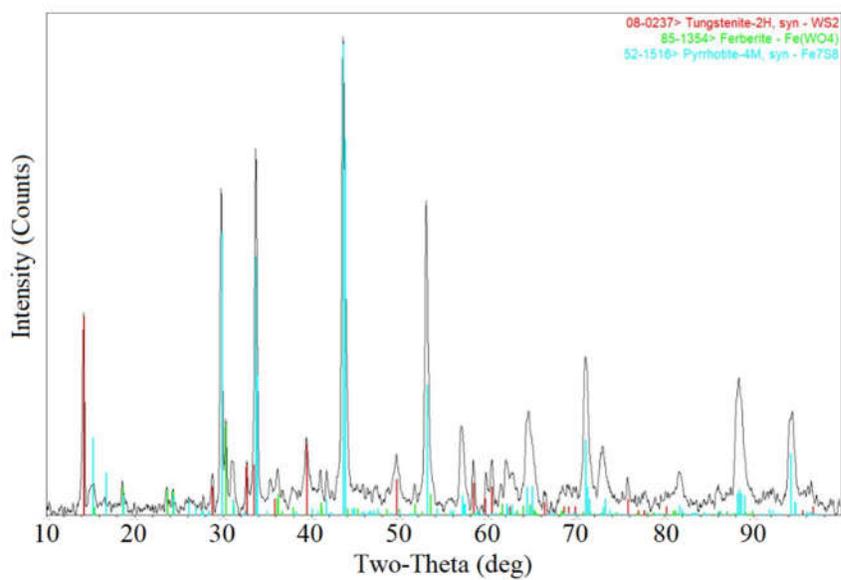
### *The Synthesis of hexaaluminate catalysts LaFe<sub>x</sub>Al<sub>12-x</sub>O<sub>19</sub> (x = 2, 4, 6).*

Typically, to prepare LaFe<sub>2</sub>Al<sub>10</sub>O<sub>19</sub>, La(NO<sub>3</sub>)<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved individually in 60 °C deionized water in a proportion relevant to the desired structure (desired x). Except for aluminum nitrate, metal nitrates were first mixed to form clear solutions, followed by adjusting the pH = 1 with nitric acid. Then, the aluminum nitrate solution was added into the metal nitrate mixture. This mixed solution was poured under a vigorous stirring condition into a saturated (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution heated at 60 °C to form a precursor precipitate. During the precipitation process, the pH value of the solution was maintained between 7.5 and 8.0. After continuous stirring at 60 °C for 4 h and aging for 3 h, the precipitate was filtered, washed, and dried at 120 °C overnight. The obtained precursor materials were calcined at 1200 °C for 6 h.

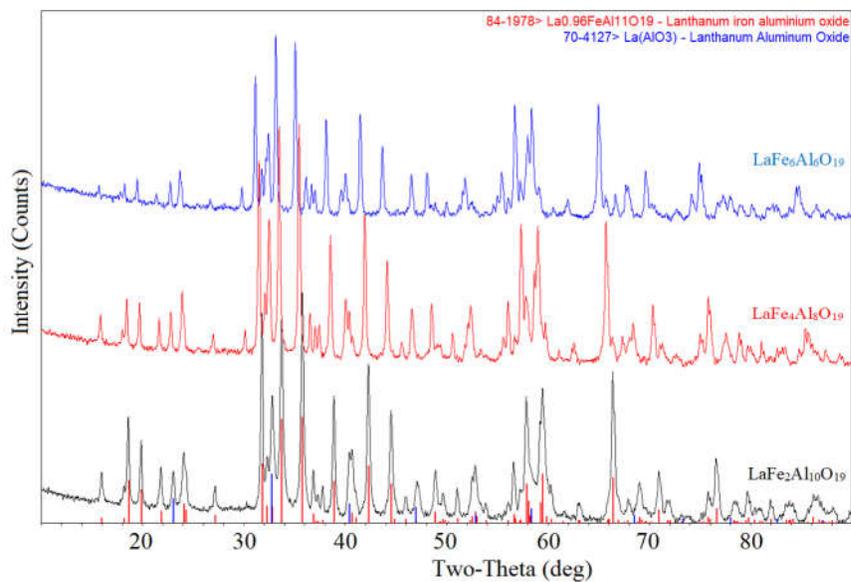
*Characterization of catalysts*



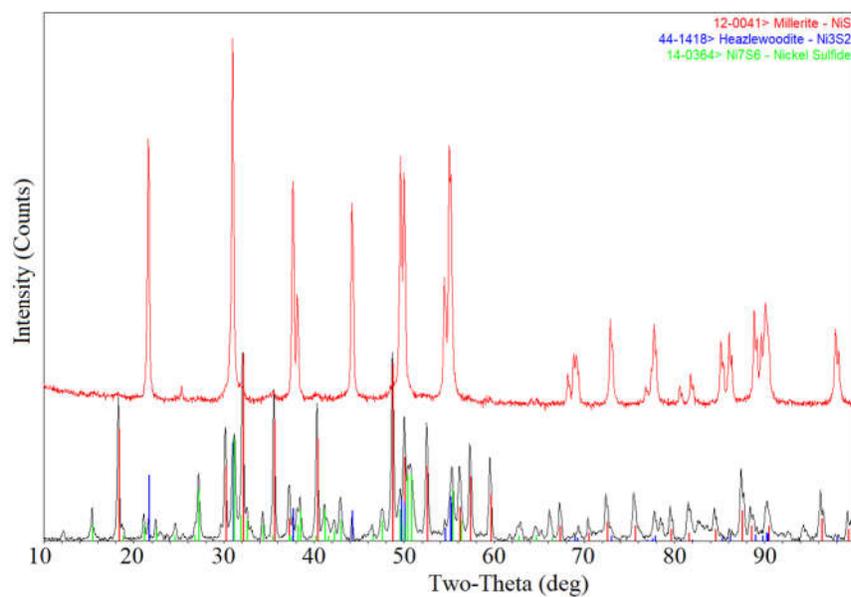
**Figure S1.** Typical XRD pattern of the troilite series catalysts  $\text{Fe}_{1-x}\text{Mo}_x\text{S}$  after catalysis.



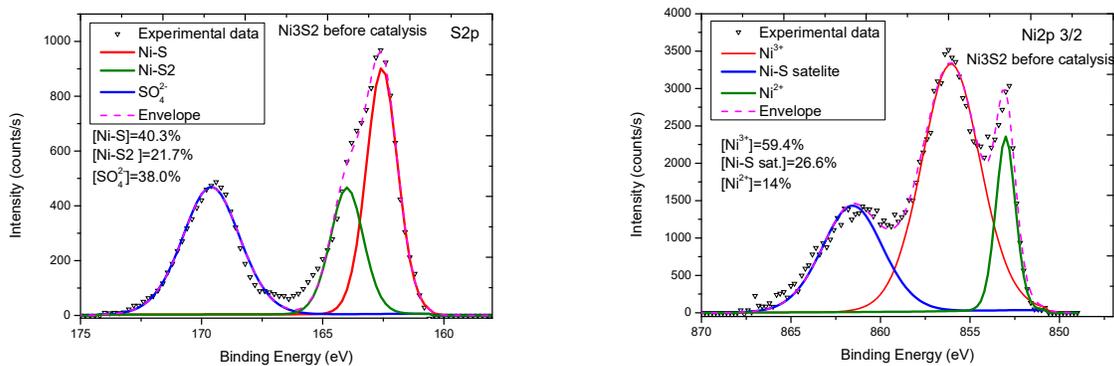
**Figure S2.** Typical XRD pattern of the troilite series catalysts  $\text{Fe}_{1-x}\text{W}_x\text{S}$  after catalysis.



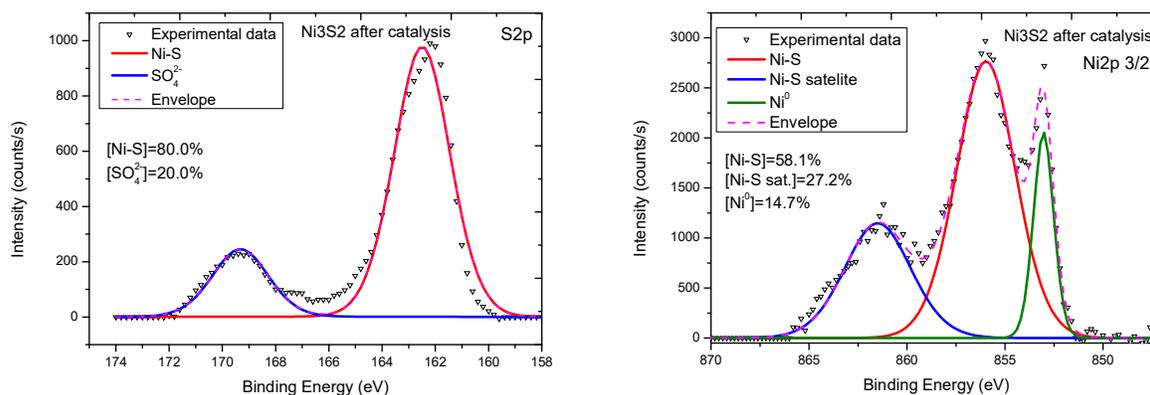
**Figure S3.** XRD spectra comparison of LaFe<sub>x</sub>Al<sub>12-x</sub>O<sub>19</sub> hexaaluminate catalysts after catalysis.



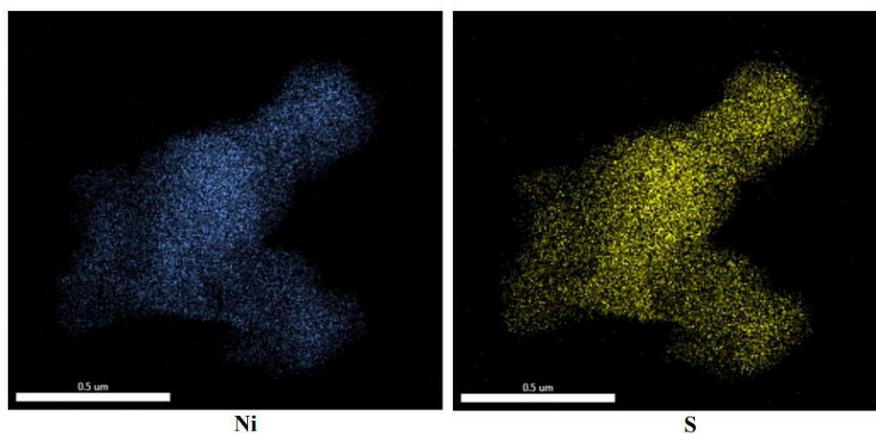
**Figure S4.** XRD spectra comparison for the Ni<sub>3</sub>S<sub>2</sub> original catalyst (red spectrum above) and after catalysis (black spectrum below).



**Figure S5.** XPS data on the Ni<sub>3</sub>S<sub>2</sub> catalyst before catalysis.



**Figure S6.** XPS data on the Ni<sub>3</sub>S<sub>2</sub> catalyst after catalysis.



**Figure S7.** STEM elemental distribution maps for Ni<sub>3</sub>S<sub>2</sub> after catalysis.