Supplemental Information

Tailoring High Entropy Borides for Hydrogenation: Crystal Morphology and Catalytic Pathways

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Experimental Methods

Materials

Acetone (Fisher Scientific), aluminum (Thermo Scientific, 99.97%, 100 + 325 mesh), deionized water (obtained from Purelab Flex unit at a resistance of 18.2 MΩ), methanol (Fisher Scientific), niobium (Beantown Chemical Inc., 99.99%, 325 mesh), Pelco® conductive carbon glue (Ted Pella Inc.), platinum (Strem Chemicals Inc., 99.00%), sodium hydroxide (Fisher Scientific), tantalum (Beantown Chemical Inc., 99.95%), 2,2,6,6-tetramethyl-1-piperidinyloxyl ("TEMPO", TCI, 98%), titanium (Alfa Aesar, 99.40%, 100 mesh), tungsten trioxide (Beantown Chemical, 99.5%).

Catalyst Preparation Flux Growth

The high entropy boride (HEB) of Al_{0.2}Nb_{0.2}Pt_{0.2}Ta_{0.2}Ti_{0.2}B₂ was synthesized using an aluminum molten flux growth. Pure elemental powders were combined with an additional 10 mmol of aluminum powder, which acted as the flux (typical loading values are listed in **Table S1**). The powders were stoichiometrically ground in an agate mortar and pestle and mixed uniformly with acetone. After the acetone evaporated, the resulting mixture was pressed into a 10 mm diameter pellet and placed in an alumina boat. The alumina boat was then introduced into a Lindberg Blue tube furnace capable of reaching 1000°C. A titanium rod was positioned upstream in the furnace to act as an oxygen getter at high temperatures, thereby further protecting the sample from oxidation. Throughout the entire heating process, a constant, slow flow of argon was maintained to create an inert atmosphere for the duration of the heating cycle. The thermal treatment followed the profile: an initial 6-hour room temperature purge to eliminate adsorbed water and oxygen, heating to 1000°C at a rate of 5°C/min, a 24-hour hold at 1000°C, and finally, cooling back to room temperature at a rate of 5°C/min.

At the conclusion of the heating cycle in the tube furnace, the pellet was etched by immersing the pellet in 6 M NaOH in an ice bath for 48-hours to remove the aluminum flux. Following this, the sample was centrifuged at 4000 RPM for 3 minutes, and the top 25 mL layer was discarded. The sample was replenished to 30 mL with deionized water, this washing step was repeated three times. Next, the sample underwent three additional washed with 15 mL of acetone each time to ensure the removal of any remaining aqueous residue. Finally, the sample was placed in a vacuum oven and dried for four hours to ensure complete removal of moisture.

Arc Melt HEB Synthesizing

Pure elemental powders were stoichiometrically ground in an agate mortar and pestle and mixed uniformly with acetone (typical loadings in **Table S2**). After the acetone evaporated, the resulting mixture was pressed into a 10 mm diameter pellet and placed in an alumina boat. The alumina boat was then introduced into a Lindberg Blue tube furnace capable of reaching 1000°C. A titanium rod was positioned upstream in the furnace to act as an oxygen getter at high temperatures, thereby further protecting the sample from oxidation. Throughout the entire heating process, a constant, slow flow of argon was maintained to create an inert atmosphere for the duration of the heating cycle. The thermal treatment followed the profile: an initial 6-hour room temperature purge to eliminate adsorbed water and oxygen, heating to 1000°C at a rate of 5°C/min, a 24-hour hold at 1000°C, and finally, cooling back to room temperature at a rate of 5°C/min.

The pellet was placed in an Edmund Bühler GmbH MAM 1 arc melter along with a zirconium slug as an oxygen getter at high temperatures to further protect the sample from oxidation. The chamber was purged and refilled with argon to ambient pressure, and this process was repeated three times. First, the zirconium slug was arced, the melting flame would then be placed onto the unreacted pellet where the flame would go in circular motions around the pellet to uniformly heat the sample. The pellet would be removed from the arc melter and flipped. The sample would then be flipped additional times until the pellet melted into an ingot. The sample was then hit with a stainless-steel high-impact mortar and pestle to break the sample into smaller pieces. The pieces were then transferred to a synthetic sapphire mortar and pestle where the HEB was ground into a fine powder with acetone.

Spillover of WO₃

The platinum catalyst (2.0 mg, 0.67% w/w) or the HEB catalyst (7.5 mg – 2.5% w/w) was ground in a mortar and pestle with 300 mg of WO₃. Then, placed in 5 mL of methanol within a 25 mL round bottom flask along with a small magnetic stir bar, equipped with a septum and sealed with parafilm. The flask was then vacuumed and repressurized with hydrogen gas to 1 atm. This purging and pressurizing process was repeated three times. The flask was then placed on a magnetic stir plate set to 800 RPM and agitated for 48-hours while maintaining a hydrogen pressure of 1 atm.

Spillover of TEMPO

The platinum catalyst (2.0 mg, 0.67% w/w) or the HEB catalyst (7.5 mg, 2.5% w/w) was ground in a mortar and pestle. Then, placed into a 25 mL round bottom flask along with 300 mg of TEMPO, 5 mL of methanol, and a small magnetic stir bar. Equipped with a septum and sealed with parafilm. The flask was then vacuumed and repressurized with hydrogen gas to 1 atm. This purging and pressurizing process was repeated three times. The flask was then placed on a magnetic stir plate set to 800 RPM and stirred for 48-hours while maintaining a hydrogen pressure of 1 atm.

Sample Characterization Instrumentation

Sample characterization was performed using powder X-ray diffraction (Rigaku Miniflex 6T), scanning electron microscope (Regulus 8100 Scanning Electron Microscope) coupled with energy-dispersive X-ray spectroscopy (Octane Elect EDS), and Fourier Transform Infrared Spectrophotometer (Shimadzu IRTracer-100).



Figure S1. EDX mapping for the flux growth HEB: $AI_{0.2}Nb_{0.2}Pt_{0.2}Ta_{0.2}Ti_{0.2}B_2$, showing fairly homogeneous distribution of metals across a single crystal. Note, the dark spot in the top-right corner is likely attributed to the shadow from the height of material as seen from the SEM image (top).



Figure S2. EDX mapping for the arc melted HEB: $AI_{0.2}Nb_{0.2}Pt_{0.2}Ta_{0.2}Ti_{0.2}B_2$, showing homogeneous distribution of transition metals across a single crystal. There is some inhomogeneity with the aluminum which may be due to the lower melting point.



Figure S3. EDX mapping for the flux growth HEB: $AI_{0.25}Nb_{0.25}Ta_{0.25}Ti_{0.25}B_2$, showing fairly homogeneous distribution of metals across a single crystal.



Figure S4. FTIR spectra for $AI_{0.2}Nb_{0.2}Pt_{0.2}Ta_{0.2}Ti_{0.2}B_2$ HEB after exposure to 1 atm H₂ after 24hours. This shows no B-H stretching frequency around 2500 cm⁻¹, suggesting that the no boronhydrogen bond forms.



Figure S5. A) pXRD pattern of unreacted WO₃. **B)** pXRD pattern of WO₃ after catalysis with platinum, resulting in a mixture of $H_{0.23}WO_3$ and $H_{0.5}WO_3$. **C)** pXRD pattern of WO₃ after catalysis with the Al_{0.2}Nb_{0.2}Pt_{0.2}Ta_{0.2}Ti_{0.2}B₂ HEB catalyst resulting in a reduction to $H_{0.23}WO_3$.



Figure S6. pXRD pattern for HEB: $AI_{0.25}Nb_{0.25}Ta_{0.25}Ti_{0.25}B_2$.

Element	mmol	Mass (mg)
AI	10.0	275.30
Nb	0.2	18.59
Pt	0.2	39.02
Та	0.2	36.18
Ti	0.2	9.60
В	2.0	21.63

Table S1. Starting Material and Typical Loadings – Flux Growth

Element	mmol	Mass (mg)
Al	0.8	21.59
Nb	0.8	74.33
Pt	0.8	156.07
Та	0.8	144.76
Ti	0.8	38.29
В	8.0	86.48

Table S2. Starting Material and Typical Loadings – Arc Melting