Data-Driven Development of High-Entropy Spinel Oxide Catalysts for CO_2 Utilization

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High-entropy spinel oxides (HESOs) represent an innovative class of heterogeneous catalyst in CO_2 utilization, particular for processes such as methanation or the reverse water-gas shift (RWGS) reaction. Unlike conventional spinel oxides, HESOs incorporate five or more transition metals in various ratios.[1] This compositional complexity generates vast chemical spaces that cannot be efficiently explored through traditional trial-and-error approaches.

Therefore, to navigate this high-dimensional parameter space and identify optimal catalyst compositions we are adopting modern machine learning tools, such as Bayesian optimization (BO). This data-driven methodology offers an efficient strategy to accelerate catalyst discovery and map structure-activity relationships, guiding empirical catalyst screening into a rational design process.[2]

For the initial phase of the project, systematic synthesis and characterization protocols were established for six-metal HESOs containing equimolar amounts of Sn, Co, Fe, Ni, Mn, Cr, and Zn. Four different methods based on coprecipitation and one on nanocasting were screened.

XRD analysis revealed that a single crystalline spinel phase form at calcination temperatures above 500 °C, with optimal crystallinity achieved at 650-800 °C. Figure 1 shows an example of the characteristic XRD patterns of a spinel catalyst calcined at 650 °C.

XPS confirmed the presence of all six transition metals at the catalyst surface in oxidation states of +2/+3 consistent with the archetypal AB_2O_4 spinel stoichiometry, shown in Figure 2.

The catalytic tests were performed in a quartz fixed-bed reactor equipped with an online non-dispersive infrared detector to quantify the concentration of CO_2, CO and CH_4. The fractionated catalysts were diluted with quartz, reduced under H_2 and then heated up to 500 °C under a flow of H_2 and CO_2. All catalytic tests were performed using a H_2:CO_2 ratio of 4:1 at a weight hourly space velocity of 15,000 $mL \cdot h^{-1} \cdot g^{-1}$. Under these conditions, the CO_2 conversion reached up to 69%, closely approaching the thermodynamic equilibrium at 500°C.[3]

Figure 3 shows conversion and selectivity from the first generation of tested catalysts. The initial data indicate a strong trend related to the content of Sn and Co. Although the presence of Co promotes CO_2 activation, it strongly favors methanation, leaving the CO selectivity below 14%. In contrast, Sn increases the selectivity toward CO.

Citric acid/urea-derived Sn-based samples (MMA-11, MMA-12) exhibited near-complete CO selectivity (>97%) but very low CO_2 conversions (6-11%), suggesting that this precipitation route produces insufficient active surface area or reducible site density for effective CO_2 activation at these calcination temperatures. Triammonium citrate/urea-derived Sn-based samples (MMA-5) showed improved conversions (46-52%) while retaining >97% CO selectivity, highlighting the critical role of the precipitating agent.

So far, the best results were obtained for the ordered mesoporous sample MMA-13, synthesized using nanocasting. The hard KIT-6 silica template exhibited a BET surface area of 522 $m^2\ g^{-1}$ and a total pore volume of 1.13 $cm^3\ g^{-1}$, consistent with its well-ordered cubic $Ia\bar{3}d$ mesoporous structure.[4] After impregnation, calcination and removal of the template, the replica resulted in 54.3% CO_2 conversion and 99.3% CO selectivity, yielding the highest site-time yield in the dataset (STY = 1,100 $\mu mol_{CO}\ min^{-1}\ g^{-1}$).

These initial data are currently used as training set for a Bayesian optimization workflow using the EDBO framework.[5] Building on the identified structure-selectivity trends in Sn and Co, EDBO will be employed to iteratively propose new multicomponent compositions and synthesis conditions that balance exploration and exploitation. To efficiently execute these suggested experiments, the synthesis protocols will be transferred onto a robotic platform capable of automated precursor dosing, precipitation, calcination, and catalyst conditioning. Closed-loop integration of the robotic synthesis platform, high-throughput RWGS testing, and EDBO-driven design will refine our understanding of underlying structure-activity relationships and accelerate the discovery of HESOs with optimal performance.

References

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FIGURES

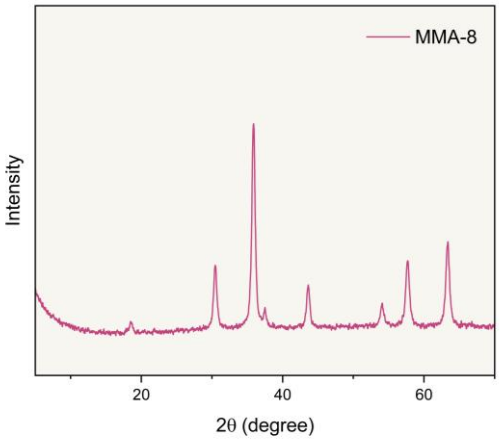

Figure 1. Powder XRD pattern of high-entropy spinel catalyst (MMA-8), synthesized with Triammonium Citrate and Urea as coprecipitant agents and calcined at 650 °C.

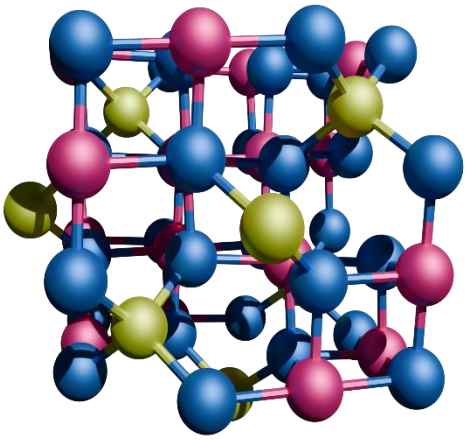

Figure 2. Spinel structure showing octahedral positions (pink) and tetrahedral positions (green).

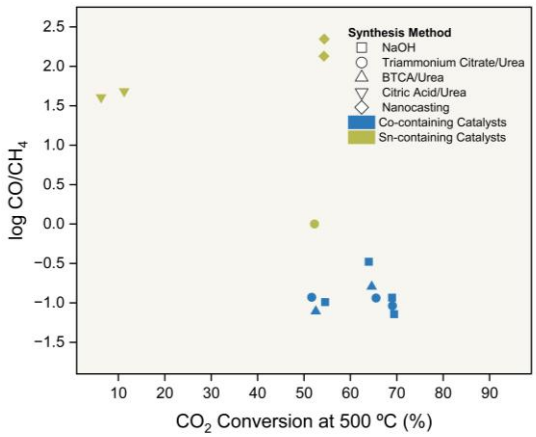

Figure 3. CO_2 Conversion and selectivity of Sn- and Co-containing high-entropy spinel oxides in the RWGS reaction at 500 °C.