

L-IV | Application of Prussian Blue Analogue-Derived Mn-Co Catalysts in the Hydrogenation of CO to Higher Alcohols

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Higher alcohol synthesis (HAS) offers the possibility to obtain various valuable chemicals such as higher alcohols and olefins in a single process. A new class of HAS catalysts based on $Mn_xCo_{3-x}[Co(CN)_6]_2$ prussian blue analogues (PBAs) with different Mn:Co ratios was investigated in this study.^[1] Pyrolysis of the K-promoted PBAs resulted in the metal atoms being embedded in a unique functionalized carbon matrix. The obtained multifunctional catalysts were found to enable a unique reaction network bridging the gap between heterogeneous and homogeneous catalysis.

Synthesis of PBA-derived Mn-Co catalysts and their performance in HAS

Co-, Mn-, and K-containing PBAs were obtained using a microemulsion-assisted co-precipitation. The precursors were pyrolyzed leading to the collapse of the well-defined PBA structure. This was the key step in the formation of a unique N- and O- functionalized carbon matrix with embedded metal nanoparticles. Thereby, the formation of Co_2C during CO hydrogenation was favored, which is crucial for HAS.^[2] Decreasing the Mn:Co ratio resulted in an almost linear increase of CO conversion up to 10.6 % for the Mn_1Co_{11} catalyst. However, completely removing Mn significantly reduced CO conversion, thereby demonstrating the importance of Mn as a promoter for HAS catalysts. A broad product distribution of primary and secondary alcohols was obtained with all catalysts. However, a CO_2 selectivity between 27–36 % was observed although a Cu-free catalyst was investigated, which was ascribed to Co_2C promoted with K being active for the water-gas shift reaction^[3] and solid-state reactions involving Co_2C resulting in the formation of CO_2 .^[4]

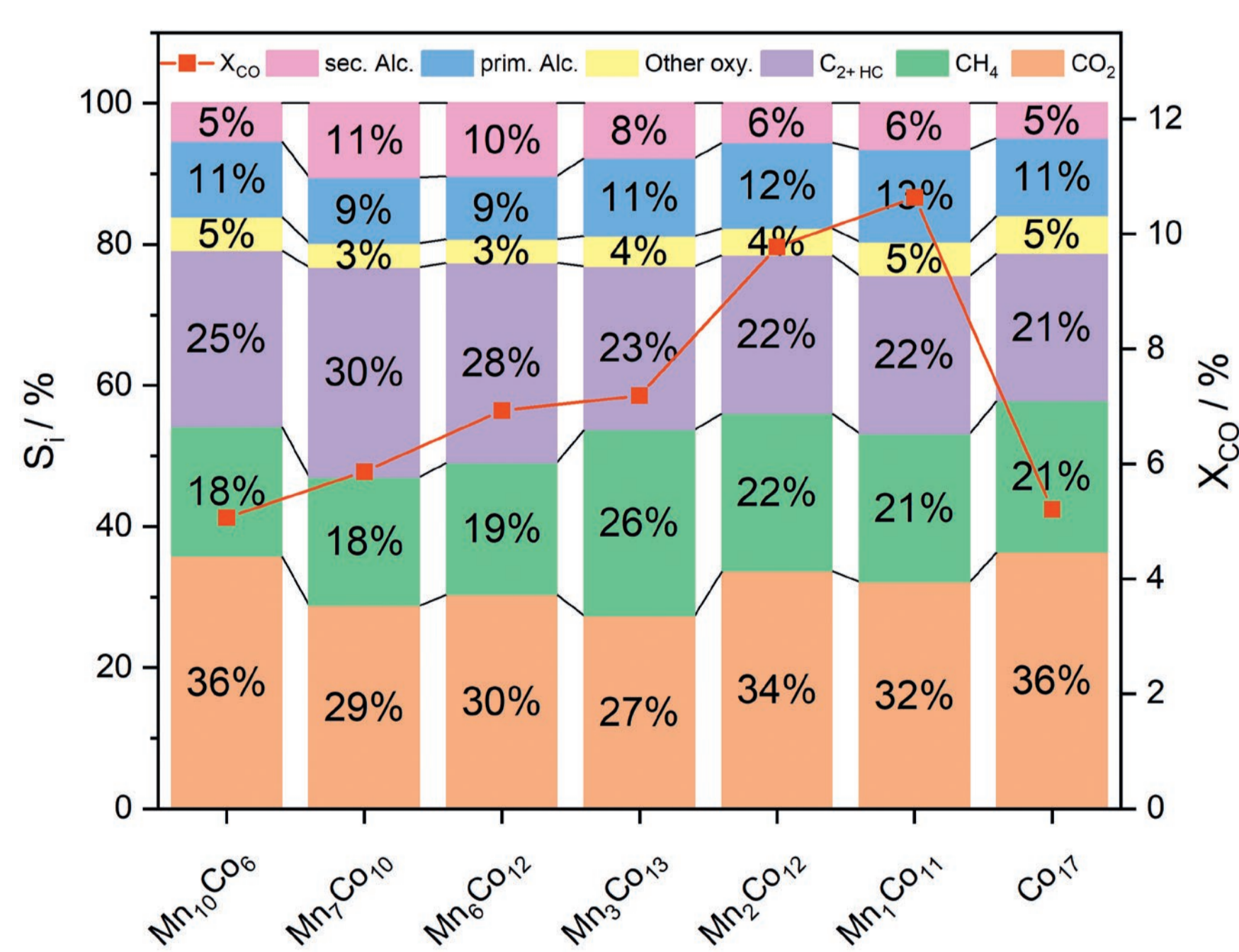


Figure 1: Conversion and selectivities of the catalysts with different Mn:Co ratios after 72 h TOS at 260 °C, 60 bar, a H_2/CO ratio of 1 and a GHSV of $12000 \text{ cm}^3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$. The red line is intended to guide the eye.

Proposed reaction network enabled by multiple Co-based active sites

Comparing the chain growth probabilities and the distribution of the primary alcohols and hydrocarbons showed that the values differ strongly, indicating the presence of various reaction mechanisms for oxygenate formation. Additionally, acetic acid and propionaldehyde were detected as intermediates in the chromatograms. Consequently, it was proposed that PBA-derived catalysts were not only active in the carbide-based reaction pathway to higher alcohols and olefins, but also in the reductive hydroformylation, the reductive carbonylation of primary alcohols and olefin hydration. The interplay between all reactions is shown in Figure 2. While it is known that the carbide-based mechanism is enabled by the Co^0/Co_2C interface, additional active sites are required for the other reaction mechanisms. It was therefore proposed that a molecular $Co-N-C$ site anchored by the carbon matrix enables the reductive carbonylation, which is remarkable since it usually is homogeneously catalyzed.^[5]

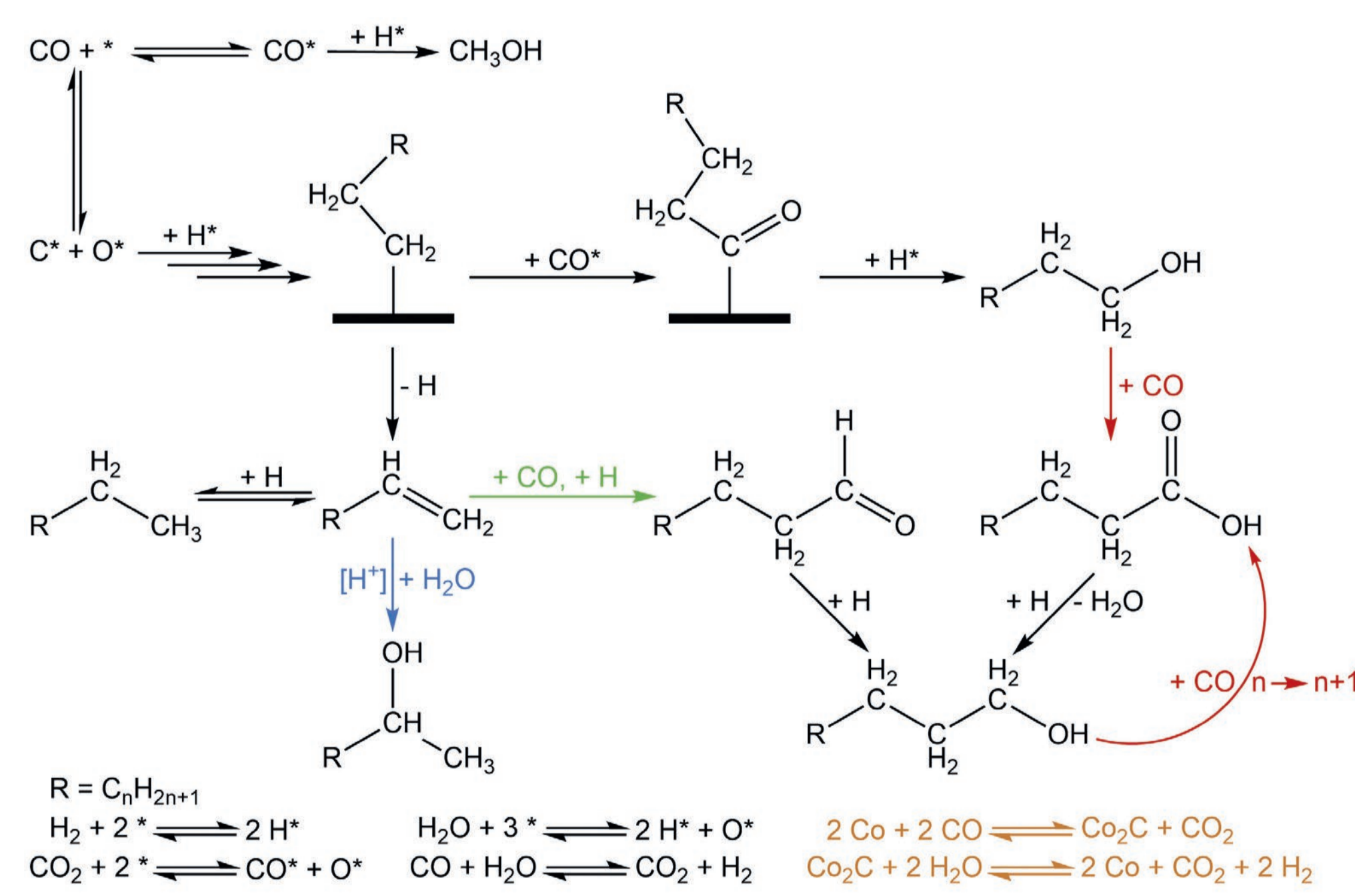


Figure 2: Proposed schematic reaction network for HAS over catalysts derived from PBA-based precursors.

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