

Revealing the Reaction Behavior of $\text{Co}_{0.86}\text{Mn}_{0.14}\text{O}$ under H_2 using *in situ* Closed-Cell Gas Reaction S/TEM

Kinga A. Unocic^{1*}, Nicole LiBretto², Anh T. To², Jeremy A. Kropf³, Daniel A. Ruddy², Theodore R. Krause³, Lawrence F. Allard⁴ and Susan E. Habas²

- ¹. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA.
 - ². National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO, USA.
 - ³. Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL, USA.
 - ⁴. Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA.
- * Corresponding author: unocicka@ornl.gov

CO_2 hydrogenation is an attractive pathway for converting CO_2 into long chain hydrocarbons, which can be used as transportation fuels [1]. Co catalysts modified with Mn oxides are attractive catalyst candidates since they exhibit high C-C coupling activity in similar CO hydrogenation reactions [2]. In general, CoO reduction under H_2 occurs at $\sim 400^\circ\text{C}$. However, the addition of Mn can shift the CoO reduction to higher temperatures allowing for controlled Co speciation with Mn concentration and reduction temperature. Therefore, an investigation of the Co species in Co-Mn oxide system is appealing.

In this study, we supported the $\text{Co}_{0.86}\text{Mn}_{0.14}\text{O}$ (5.63Co-0.859Mn wt.%; Co/Mn molar ratio of 6.1) catalyst on SiO_2 with a target of 10% active phase. The catalyst was prepared by a solution synthesis method using the thermal decomposition of $\text{Co}(\text{acac})_2$ and $\text{Mn}(\text{acac})_3$ to a mixed oxide phase with a cubic crystal structure. The $\text{Co}_{0.86}\text{Mn}_{0.14}\text{O}$ catalyst was supported on SiO_2 in chloroform to obtain dispersed catalyst particle aggregates. A JEOL 2200FS scanning transmission electron microscope (S/TEM), equipped with Bruker-AXS silicon-drift detector for energy dispersive x-ray spectroscopy (EDS), and an FEI Titan (60-300kV) equipped with a Gatan Quantum electron energy loss (EEL) spectrometer was used to monitor the *in situ* reduction of $\text{Co}_{0.86}\text{Mn}_{0.14}\text{O}$ in H_2 . Both microscopes are equipped with CEOS GmbH (Heidelberg, Ger) aberration correctors on the probe forming lenses, MEMS-based closed-cell gas reaction (CCGR) systems (Protochips *Atmosphere*TM), and an integrated residual gas analyzer (RGA) on the gas outlet side [3,4]. The gas-cell was purged two times with nitrogen from 100 to 0.1 Torr to remove residual O_2 , and with a final purging step of 100 to 0.001 Torr. The gas cell was filled with 100% H_2 at 760 Torr at room temperature (RT) and the catalyst was heated at $10^\circ\text{C}/\text{min}$ to 410°C under flowing H_2 and held for 2 hours. Because the reaction was performed under flowing H_2 there was a drop in the H_2 total pressure, which was accommodated by refilling the supply tank as needed.

Figure 1 shows time-lapsed bright-field (BF-STEM) images of the catalyst evolution during exposure to flowing H_2 . Figure 2A-C highlights a final stage of heating at the indicated total pressures. Figure 1A includes the outline of the catalyst at 401°C to help visualize the changes in subsequent stages. After reaching 410°C (Fig. 1C) the morphological changes have been already initiated. Additionally, catalyst restructuring and channeling (visible lines within the $\text{Co}_{0.86}\text{Mn}_{0.14}\text{O}$ particles) has been observed which suggests interaction of the catalyst with hydrogen. After reaching 410°C (Fig. 1D), the catalyst slightly consolidated, which was followed by formation of small spherical particles on the surface of the large $\text{Co}_{0.86}\text{Mn}_{0.14}\text{O}$ that eventually became individual particles after reaching a certain size. The formation of the small spherical particles was already observed after 8 min of exposure at 410°C . Their formation

density increased even further after 24 min. The final stage of the reaction, around 110 min of exposure (Fig. 1G), showed well defined spherical particles that still were forming at the final stage after 120 min (Fig. 1H-I). Throughout the exposure at 410°C visible channels within the catalyst were observed which most likely help to assist with the formation of spherical particles by acting as diffusion pathways to accommodate Co transport to the surface (this still requires additional study). A computed fast Fourier transform of the smaller particle suggested the presence of metallic Co with a hexagonal structure and a space group of P 63 m c (186)), which agrees with XANES data. Further, post STEM-EELS analysis performed at room temperature confirmed the existence of metallic Co particles (inset in Fig. 1I). *In situ* CCGR STEM gas-composition measurements were also performed. This was an important part of the experiment/study to use an RGA system incorporated into the experimental geometry. The RGA system confirmed reducing conditions (presence of H₂) within the cell.

This study shows the effect of the environment on structure and morphology of the catalytic species, using *operando* CCGR STEM capabilities to reveal catalytic species behavior and mechanism of CoO_x reduction by performing a reaction sequence. Further, the CCGR system with an integrated RGA allows to confirm the environmental conditions during examination/testing [6].

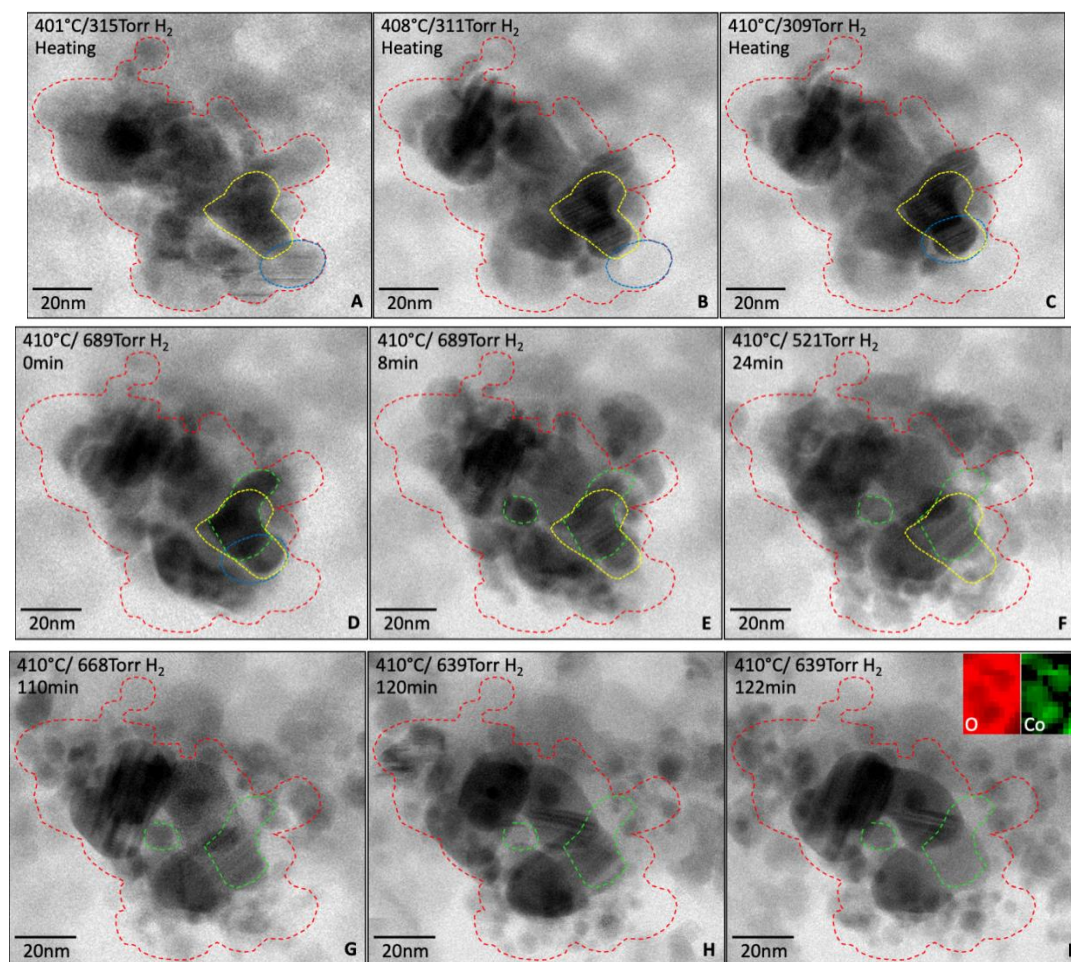


Figure 1. BF-STEM images of Co_{0.86}Mn_{0.14}O catalyst acquired under series of reaction conditions under flowing H₂. (A-C) During final stage of heating; (D- I) After different times at 410°C.

References:

- [1] IC Have et al., *Nature Com.* **13** (2022) p. 324.
- [2] J. Loosdrecht, et al., *Compreh. Inorg. Chem. II* **7** (2013) p. 525.
- [3] KA Unocic et al., *Oxid. Metals* **88** (2017) p.495.
- [4] KA Unocic et al., *Microscopy and Microanalysis* **26** (2020) p. 229.
- [6] Work performed in collaboration with ChemCatBio, a member of the Energy Materials Network (EMN) and supported by the U.S. Department of Energy (DOE) Bioenergy Technology Office under Contract DE-AC05-00OR22725 (ORNL), Contract DE-AC36-08-GO28308 (NREL), and Contract DE-AC02-06CH11357 (ANL). Microscopy performed as part of a user project at the Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.