

Experiment Report Form



	Experiment title: Operando XRD and PDF analysis of novel Co-CeO ₂ catalysts for direct hydrogenation of CO ₂ to C ₂ + hydrocarbons	Experiment number: CH6391
Beamline: ID15A	Date of experiment: from: 29/08/2022 to: 05/09/2022	Date of report: 08/09/2023
Shifts: 15	Local contact(s): Gavin Vaughan	<i>Received at ESRF:</i> 08/09/2023
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Report:

Overview

In the recent years the catalytic hydrogenation of CO₂ has great potential to reduce an enormous amount of CO₂ by converting CO₂ into value-added products such as hydrocarbons and CH₃OH. To develop highly efficient catalysts for the catalytic hydrogenation of CO₂, understanding of chemical phenomena underlying the metal-support interactions is crucial to design the next generation of catalysts for many industrially relevant processes.

In order to study the changes in phase or structures of cobalt and ceria we turned to synchrotron based XRD. The measurements under operation condition with high resolution detectors allowed us to demonstrate the formation of metallic cobalt after reduction and minor changes of its oxidation states under CO₂ methanation conditions.

Quality of measurement/data

First experiment on this beam line showed that beam worked properly. The interface of program was user-friendly. Obtained data was high quality and used further.

Status and progress of evaluation

Manuscript is in preparation. PDF analysis is in discussion with beam scientist.

Results

Synchrotron-based XRD measurements allowed us to detect the changes in the unit cell and reduction of Co supported on ceria for the samples with high cobalt loading. As shown on diffractograms obtained during the reduction of 10CoCeFSP full reduction Co₃O₄ to metallic Co occurred at 300°C (Fig 1a). In turn, the reduction of samples with low loading of Co did not show the segregation of formation of metallic cobalt during the reduction, probably due to high dispersion of Co on the surface or stabilization of Co-O-Ce interfaces (Fig 1b). The refined unit cell of doped CoCeFSP showed that that the doping Co into the CeO₂ leads to a significant

expansion of the unit cell during the ramp of the temperature. Moreover, the stabilization of the unit cell happens faster for CoCeFSP than for CeFSP. In turn, 2.5CoFSP demonstrated bigger unit cell parameter after reduction than catalysts with higher Co loadings probably due to stabilization of Co-O-Ce interfaces into material after the reduction. Switch of reduction mixture to reaction conditions lead to increase of unit cell for all samples, that could be correlated with re-filling of CeO₂ vacancies with O from CO₂ during dissociative adsorption of CO₂. Refined particle sized of CeO₂ for all doped CoCeFSP and CeFSP demonstrated the same trend during reduction and switch to reaction mixture. Interesting to note, that sample with low loadings of Co showed first increase in particle size and then slight decrease, that probably could be explained by structural changes or re-organisation of Co-O-Ce centers in the material.

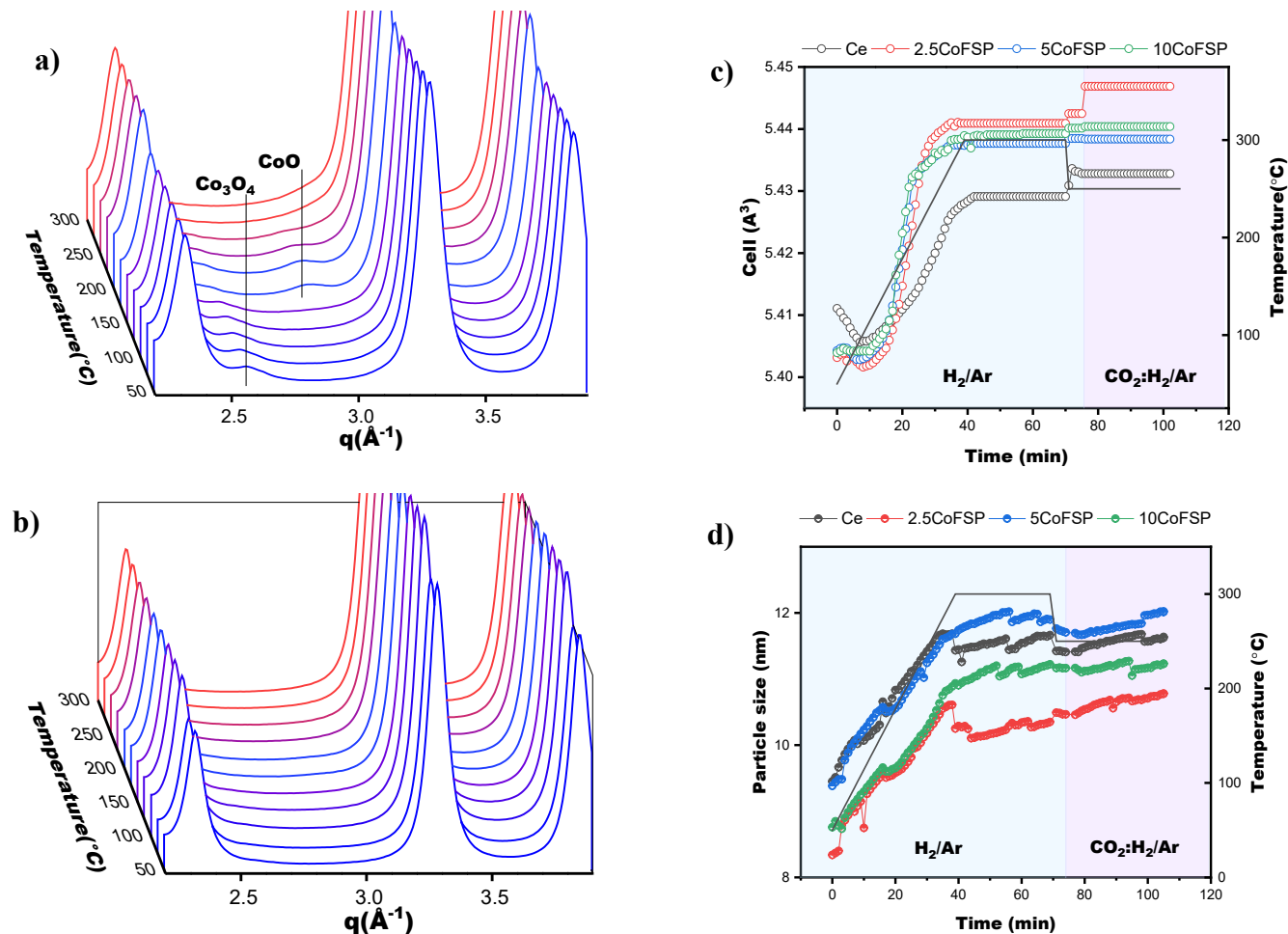


Figure 1. Diffractograms of 10CoCeFSP during the reduction(a). Diffractogram of 2.5CoCeFSP during the reduction(b). Unit cell of CoFSP (Co loadings= 2.5, 5, 10 mol %) and CeFSP during reduction in 20% H₂ in Ar at 300°C and CO₂ methanation. Experimental conditions: 25 mg of catalyst, 50 mL/min, 5 vol.% CO₂, 20 vol.% H₂, 25 vol.% Ar, 250°C, 1 bar.(c). Refined particles size of CoFSP (Co loadings= 2.5, 5, 10 mol %) and CeFSP during reduction in 20% H₂ in Ar at 300°C and CO₂ methanation. Experimental conditions: 25 mg of catalyst, 50 mL/min, 5 vol.% CO₂, 20 vol.% H₂, 25 vol.% Ar, 250°C, 1 bar. (d).