

Abstract:**Title of Project: Electrospun Co-Pt-based tandem catalysts for the CO₂ hydrogenation to olefins****Co-supervisor 1: Prof. Dr. Aleksander Gurlo, TU Berlin****Co-supervisor 2: Prof. Dr. Jens-Uwe Repke, TU Berlin**

CO₂ utilization by tandem catalysis is a promising technological approach to reducing the negative impact of CO₂ on global warming and climate change. Combining Pt as a reverse water gas shift catalyst with Co as a catalyst for subsequent Fischer-Tropsch synthesis is a promising approach towards CO₂ hydrogenation to olefins. However, applying a well-defined nanostructured tandem catalyst with a fixed spatial separation between Pt and Co nanoparticles is a crucial factor for producing the desired hydrocarbons. In this project, we aim to (i) simulate target Co-Pt tandem catalysts on inert (e.g., SiO₂) and active (e.g., CeO₂) supports by numerical simulations, (ii) synthesize these catalytic systems by electrospinning technique with varying metal loadings; (iii) test the tandem catalysts for CO₂ hydrogenation to olefins; (iv) follow the crystal structure changes during synthesis and catalysis using in situ XRD techniques; and (v) establish the structure-activity correlations.

Extended description version of the project:

Title of Project: Electrospun Co-Pt-based tandem catalysts for the CO₂ hydrogenation to olefins

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1. Overall goal of the project

This project's goal is to investigate the applicability of the Co-Pt catalytic system for the tandem CO₂ hydrogenation to olefins by tandem catalysts. These bi-metallic compounds provide modified electronic configurations compared to single metal-supported catalysts, altering adsorption and reaction energies and opening new reaction pathways for consecutive chemical reactions. This research will be conducted in four consecutive work packages: (I) numerical simulations to find the best set of parameters, such as distance of active sites and catalyst loading of different functionalities, (II) validation of the model by manufacturing bifunctional catalysts by electrospinning where catalyst loading and active site distance can be adjusted precisely, (III) in-situ investigation of the support modifications (i.e., use of inert and active supports) and microstructure architectures, e.g. supports with bi-modal pore distribution, to minimize or eliminate catalyst deactivation and (IV) fine-tuning of the catalytic properties by doping of the support - e.g. doping of CeO₂ with Sm or La for an enhanced oxygen ion conductivity. This project aims to elucidate the fundamental reaction and deactivation mechanisms that control two or more size- and distance-controlled catalytic sites by combining catalytic tests, in situ/operando synchrotron X-ray diffraction and numerical optimization/simulation.

2. State of the art

The coupling of catalytic reactions in a single reactor using more than one catalyst is called *orthogonal tandem catalysis*. Reaction coupling yields the advantage of reducing separation and purification steps compared to separate single reactions and consequently minimizes energy demands and waste production. The combination of Pt as a reverse water gas shift catalyst and Co as a catalyst for subsequent Fischer-Tropsch synthesis has already proved to be a promising catalyst for the tandem CO₂ hydrogenation to olefins. The application of a well-defined nanostructured tandem catalyst with a fixed spatial separation between Pt and Co nano-particles has been revealed as a crucial factor for the production of the desired hydrocarbons.^{1,2} However, complex synthesis routes and low conversion limit the applicability of such catalysts. Thus, a deeper understanding of the fundamental mechanisms of interaction and deactivation in the Co-Pt catalytic systems is required to further its industrial applicability. Therefore, the main goal of our work is to study the catalytic Co-Pt material system for the tandem CO₂ hydrogenation to olefins with different metal loadings, loaded onto several ceramic supports via electrospinning technique to obtain information about its catalytic and deactivation mechanisms. Electrospinning has been chosen for this work because it will allow us to obtain catalytic fibre materials with controllable diameters ranging from the nano- to micron-meter scale in a continuous way for scaling-up potential. Moreover, several recent studies showed that metal nanoparticles (e.g., Ni, Co) could be in situ formed and uniformly distributed inside the electrospun nanofibers supports.^{3,4} This proposed work contributes to the elucidation of the mechanisms and dynamics of the Co-Pt system in particular and spatio-temporally coupled multi-metallic catalytic systems in general. By in situ XRD characterization under reaction conditions and combined with multiple other methods, we will provide insight into the cause-effect relationships between reaction and deactivation mechanisms of catalytic systems. From the model system to the performance-optimized catalyst, we expect to contribute to the development of unprecedented synthesis routes and system optimization. We expect to decisively contribute to the development of new energy- and material-efficient catalytic routes by studying this specific catalytic system.

3. Specific aims and how they may be reached:

The objectives of the present project are: (i) to simulate target Co-Pt tandem catalysts on inert (e.g., SiO₂) and active (e.g., CeO₂) supports by numerical simulations, (ii) to synthesize these catalytic systems by electrospinning technique and with varying metal loadings; (iii) to test the tandem catalysts for CO₂ hydrogenation olefins in a Berty and FBR reactor; (iv) to follow the crystal structure and alloy formation/segregation during synthesis and catalysis using in situ XRD techniques; and (v) to establish the structure-activity correlations. The working packages (WPs) of the this project are:

WP 1. Numerical simulations (J. Repke)

Numerical optimization will be first carried out to find the best set of parameters, such as the distance of active sites and catalyst loading of different functionalities. For that, a fast computing model for tandem core-shell catalyst particles was developed⁵ which needs to be adapted for the Fischer-Tropsch synthesis with kinetics from literature. Using advanced numerical optimization algorithms (e.g. ipopt) a best set of parameters for the design of the catalyst will be identified. Moreover, for a fixed design the best set of operatin conditions, i.e. temperature, pressure and feed composition, can be identified as well.

WP 2. Synthesis and characterization of tandem catalysts (A. Gurlo)

For validation of the method, we will synthesize these bifunctional catalysts by electrospinning where catalyst loading and active site distance can be adjusted precisely. Pt-Co supported on amorphous SiO₂ and CeO₂ will be prepared in situ during electrospinning or by different impregnation methods and with varying metal loadings. The synthesis of the tandem systems will be demonstrated using XRD, ICP, and microscopic techniques such as SEM and TEM. The synthesis of these compounds is not trivial, and in situ techniques (WP 4) will be applied to monitor and optimize conditions.

WP 3. Catalytic tests (J. Repke)

Catalytic tests will be tested in suitable reactors (Berty and FBR, in Repke's, INGA setup in Schomäcker's) to obtain kinetic data, selectivity and yield profiles with respect to temperature and pressure, and stability measurements.

WP 4. Generation of structure-activity correlations (A. Gurlo)

The generation of such correlations is necessary for proper catalyst design and is based on a deep understanding of the catalyst structure under reaction conditions. Selected catalysts simulated in WP 1, synthesized in WP 2 and tested in WP 3 will be monitored in situ/operando using synchrotron (at PETRA III - Deutsches Elektronen-Synchrotron DESY in Hamburg and the Advanced Light Source at Lawrence Berkeley National Laboratory in Berkeley) and lab-based techniques available within our collaboration network: XRD, XAS and XPS. Moreover, the morphology and phase composition of the catalysts before and after reaction will be compared using HR-TEM. Using this combination of techniques, the crystal structure, crystallite and particle size, bond distance, and bulk and surface composition of the catalysts can be determined before, under, and after reaction conditions. Moreover, the formation of alloys and intermediate phases, metal segregation, etc., can also be determined, and active sites/reaction mechanisms will be elucidated.

Project-relevant literature (max 5):

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3. Wen, S.; Liang, M.; Zou, J.; Wang, S.; Zhu, X.; Liuab, L.; Wang, Z., Synthesis of a SiO₂ nanofibre confined Ni catalyst by electrospinning for the CO₂ reforming of methane. *J. Mater. Chem. A* 3 (2015) 13299-13307
4. Zhang, Z.; Zhao, Y.; Li, Z.; Zhang, L.; Liu, Z.; Long, Z.; Li, Y.; Liu, Y.; Fan, R.; Sun, K.; Zhang, Z., Synthesis of carbon/SiO₂ core-sheath nanofibers with Co-Fe nanoparticles embedded in via electrospinning for high-performance microwave absorption. *Advanced Composites and Hybrid Materials* 5 (2022) 513-524
5. Brösigke, G.; Repke, J.-U.; Schomäcker, R.; Matera, S.; The closer the better? Theoretical assessment of the impact of catalytic site separation for bifunctional core-shell catalyst particles, *Chem Eng J*, 446, 1, (2022), 136891