Abstract:

Application of substitutional and intermetallic alloys to carbon dioxide hydrogenation by tandem catalysts

Co-supervisor 1: Prof. Dr. Aleksander Gurlo, TU Berlin

Co-supervisor 2: Prof. Dr. Reinhard Schomäcker, TU Berlin

Co-supervisor 3: Prof. Dr. Franziska Hess, TU Berlin

Carbon dioxide hydrogenation by tandem catalysis is a promising technology to help mitigating anthropogenic carbon emissions and minimize the negative impact of climate change. Metal alloys provide unprecedented electronic configurations that can open new reaction pathways and substitute expensive single-metal catalysts, and have proved their applicability to several reactions, including methanol synthesis and alkyne semihydrogenation. In this project, we aim to (i) select target bi-metallic alloys and synthesize tandem bi-functional catalysts, (ii) test the tandem catalysts for CO_2 hydrogenation to DME or olefins in a high-pressure plug-flow reactor, (iii) follow the crystal structure and alloy formation/segregation during synthesis and catalysis using in situ scattering and spectroscopic techniques combined with ab-initio thermodynamics; (iv) obtain theoretical values of adsorption and reaction energy barriers using DFT and finally (v) to establish the structure-activity correlations.

Extended description version of the project:

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1. Overall goal of the project

This project's goal is to investigate the applicability of alloy compounds (both substitutional and intermetallic) to CO_2 hydrogenation by tandem catalysts. These compounds provide modified electronic configurations compared to single metal-supported catalysts, altering adsorption and reaction energies and opening new reaction pathways. Bi-metallic alloys enable the placement of two different metal atoms in close vicinity, supplying unprecedented scaffolds for consecutive chemical reactions. In this project, we will select appropriate candidates for CO_2 hydrogenation by tandem catalysis, follow the structure of such compounds from synthesis to application to establish the structure-activity correlations by a combination of catalytic tests, in situ/operando methods and density functional theory calculations and ab-initio thermodynamics.

2. State of the art

Tandem catalysis aims to combine several chemical reactions in a single reactor in order to optimize reaction rates, product selectivity, avoid the handling of hazardous intermediates of reaction and minimize costs. Single-metal supported catalysts on specific ceramic supports and multi-metallic catalysts have already been investigated within UniSysCat with the focus on fundamental understanding of the size and sictance effect. Up to date, no project is dealing with applying substitutional or intermetallic alloys as catalysts for individual or combined functionalities, despite their potential. The amazing progress in computational chemistry of the past years has provided tools to formulate multi-metallic systems, which aim to provide new scaffolds for reaction and potentially substitute scarce and expensive metals. In this manner, different systems have been formulated, including the Pd-Ga [1] and Ni-Ga [2] systems for methanol synthesis, and Pd-intermetallic compounds for selective semihydrogenation reaction [3]. We have recently developed a measurement technique / instrument for time-resolved in situ transmission synchrotron XRD studies at elevated temperature and controllable gaseous atmospheres, which is used at beamline 12.2.2 of the Advanced Light Source (ALS) synchrotron of the LBNL (Berkeley, USA) and is under installition at PETRA III. Application of this technique to catalytic studies has enabled the in-situ observation of metallic particle behaviour and crystallographic phase composition of a 5% Ni/MnO catalyst under dry reformation of methane (DRM) reaction conditions, allowing determination of reaction intermediates and deactivation phenomena. We studied the structural and chemical consequences of reactive metal-support interaction (RMSI) effects occurring under hydrogen reduction in the Pd/rh-In_2O_3 system as well as for a Pd-Ce catalyst for the Steam Reforming of Methane (SRM).

3. Specific aims and how they may be reached

The objectives of the present project are: (i) to select target bi-metallic alloys and synthesize tandem catalysts; (ii) to test the tandem catalysts for CO_2 hydrogenation in a plug-flow reactor; (iii) to follow the crystal structure and alloy formation/segregation during synthesis and catalysis using in situ techniques and computational ab-initio thermodynamics; (iv) to obtain theoretical values of adsorption and reaction energy barriers using DFT and (v) to establish the structure-activity correlations. The working packages (WPs) of the present project are:

WP 1. Synthesis and characterization of tandem catalysts for CO_2 hydrogenation. Within this project, two main routes for CO_2 hydrogenation by tandem catalysts will be studied. Firstly, the methanol-mediated route with later dehydration to form dimethyl ether: Nickel-based (*e.g.* Ni-Ga[2]) and In-based (*e.g.* In-Pd[4]) alloys will be applied as the first functionality combined with a zeolite acting as the second functionality. Secondly, the CO-mediated route, also using Ni-based systems like NiPt, combined with a typical Fischer-Tropsch synthesis catalyst based on cobalt. 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 3.1) will be applied to monitor and optimize conditions. Later, the effect of weight ratio and distance between active sites will be studied by careful catalyst design and the use of inert separating layers, *e.g.* porous SiO_2 in core-shell structures.

WP 2. Catalytic tests. Catalytic tests will be performed in a high-pressure plug-flow fixed-bed reactor within research unit A of UniSysCat. CO_2 reaction rates and desired product selectivity will be monitored at different temperatures and reactant ratios to select the best candidates. Later, long-term experiments will be conducted to determine catalyst stability.

WP 3. Generation of structure-activity correlations. 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.

WP 3.1. In situ/operando characterization. Selected catalysts generated in WP 1 and tested in WP 2 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.

WP 3.2. Surface stability and activity by Density Functional Theory (DFT) calulations. DFT calculations will be applied to develop a deeper understanding of the surfaces of bimetallic compounds under synthesis and operating conditions employing an ab-initio thermodynamics approach. This enables the computation of surface free energies with different metals exposed at the surface under defined gas atmosphere and can help explain surface segregation phenomena and suggest changes in the synthesis protocol to target specific surface compositions. For the as-prepared surfaces obtained by characterization techniques in WP 3.1, adsorption and reaction energy barriers of the kinetically relevant reaction steps on the metal surfaces will be computed. This tool can provide insight into the reaction mechanisms and further help in elucidating the structure-activity correlations.

The objectives and WPs described here can be accomplished with the equipment and knowledge available in the proposer's groups. The research unit A of UniSysCat has already created synergies that facilitate cooperative research, exemplified by the on-going projects of Bischoff (EC2-2019, Gurlo), the in situ synchrotron and lab-based XRD and XAS technique (Schomäcker/Gurlo/Kanngießer), etc. The current project would be embedded in such framework, feeding on the available knowledge for catalyst synthesis, the availability of a high-pressure plug-flow reactor (Schomäcker group), and other characterization techniques, including TEM/STEM (ZELMI). Expertise in the area of DFT calculations for bi-metallic compounds will be provided by the Hess group. Further possible collaborations of the current project are electrochemical investigations with Strasser group (Unit D), as intermetallic compounds of Ni have found great success in electrochemical CO_2 activation[5].

Project-relevant literature (max 5):

(1) Armbrüster, M.; Kovnir, K.; Behrens, M.; Teschner, D.; Grin, Y.; Schlögl, R. Pd-Ga intermetallic compounds as highly selective semihydrogenation catalysts. *J. Am. Chem. Soc.* **2010**, *132* (42), 14745–14747.

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(3) Armbrüster, M.; Grin, Y. Intermetallic compounds in heterogeneous catalysis. *Science and Technology of Advanced Materials* **2020**, *21* (1), 767.

(4) Snider, J. L.; Streibel, V.; Hubert, M. A.; Choksi, T. S.; Valle, E.; Upham, D. C.; Schumann, J.; Duyar, M. S.; Gallo, A.; Abild-Pedersen, F.; Jaramillo, T. F. Revealing the Synergy between Oxide and Alloy Phases on the Performance of Bimetallic In–Pd Catalysts for CO_2 Hydrogenation to Methanol. *ACS Catal.* **2019**, *9* (4), 3399–3412.

(5) Torelli, D. A.; Francis, S. A.; Crompton, J. C.; Javier, A.; Thompson, J. R.; Brunschwig, B. S.; Soriaga, M. P.; Lewis, N. S. Nickel–Gallium-Catalyzed Electrochemical Reduction of CO_2 to Highly Reduced Products at Low Overpotentials. *ACS Catal.* **2016**, *6* (3), 2100–2104