

Project title: Supporting Climate Protection – From Renewable Hydrogen and Aerobic CO₂ to Methanol

Project number: K308/2020

Executive Summary

The project comprised closely interlinked work packages focusing on the catalytic conversion of CO₂ to methanol. Various technological approaches were used, including heterogeneous and homogeneous catalysis, non-thermal plasma processes and chemical absorption systems. Particularly noteworthy are MOF-supported copper catalysts with high methanol yield, liquid-phase CuAu/ZnO systems with selective CO₂ conversion, and novel amino acid-based ionic liquids with high absorption and conversion performance. Homogeneous catalysis, in particular based on Ru complexes such as MACHO-BH in combination with amino acid-based ionic liquids, proved to be extremely efficient for the direct conversion of absorbed CO₂ into methanol under mild conditions at a high turnover number. In the plasma processes, targeted variation of flow profiles, pressure and reactor geometries resulted in significant efficiency increases and new insights into the coupling of plasma and catalyst. The carbides, Ce-based systems and model catalysts investigated showed high stability under practice-relevant conditions and provided mechanistic insights through in situ methods such as DRIFTS and EPR. In parallel, absorbers developed on a triethanolamine basis enabled CO₂ binding under mild conditions with subsequent material recycling. The results were published in several high-ranking journals and formed the basis for further scientific work.

1. Achievement of objectives and milestones

In this project, we aimed to develop non-classical ways for coupling the mining of CO₂ from air with its conversion to methanol by sustainable H₂. Methanol is one of the most important chemical commodities with an annual production of 100 million tons, yet the current synthesis process is based on syngas (CO/H₂ mixtures) and requires high temperatures and pressures (>250 °C, up to 100 bar).

We developed homogeneous and heterogeneous catalysts and processes that are able to couple both steps, uptake and hydrogenation of aerobic CO₂, within the same process at temperatures and pressures well below those of the industrial process. Rational approaches were developed that integrated material synthesis and testing, exploration of structure- reactivity relationships by operando spectroscopy as well as kinetic studies.

The main results of the individual sub-projects are briefly presented below.

WP 1. Ce_{1-x}M_xO₂ materials and Cu-based catalysts supported on a metal organic framework (MOF) with well-defined active sites were developed. Additionally to these catalysts, Cu_xAu_y/ZnO were successfully studied in a comparative approach for the CO₂ reduction toward methanol both at the gas/solid and liquid/solid interfaces. Moreover, new porous materials for direct air capture were developed. The collaboration on high-entropy alloys was continued with the group of Dr. Reichenberger (University of Duisburg-Essen). However, their materials showed a preference for activity in methanation.

WP 2. Cerium oxide layers could be produced using reactive sputtering (Ce in gas mixture Ar:N₂= 60:40 and subsequent oxidation in air). At INP, the reaction of CO₂ with H₂ was investigated using non-thermal plasmas, specifically in dielectric barrier discharges (DBD). Under the conditions studied, the conversion of CO₂ with H₂ yielded mainly CO. Therefore, the non-thermal plasma process can be considered as a precursor for the provision of CO for a conventional catalytic methanol production.

WP 3. Absorption systems for the capture of CO₂ at low CO₂ partial pressure and even from air have been achieved. The reduction of CO₂ utilizing the capture material was successful. However, the reduction product was not methanol but formate. The capture material could be directly used for the synthesis of cyclic carbonates from epoxides.

WP 4. Investigations with the aim of developing catalytic systems for non-classical low-temperature direct hydrogenation of CO₂ to MeOH were carried out as planned. By using suitable additives, e.g. amino acids and amino acid-based ionic liquids, both the CO₂ separation from different CO₂ sources (air, 2 bar and 20 bar CO₂) and the direct hydrogenation of the adsorbates to methanol were successfully combined. Direct CO₂ capture from air was also possible, although at lower captured CO₂ / TBA·Arg ratio.

WP 5. All heterogeneous materials developed were tested in this WP. Moreover, Mo carbide supported Cu catalysts, which recently showed promising results in liquid-phase methanol synthesis, were included in the test program under gas-phase conditions. Particular attention was paid to the product formation

pathways on all catalysts. To this end, intensive kinetic studies were carried out and, in one case, kinetic isotope experiments were also conducted. Results are now available for very different material classes for the heterogeneously catalyzed conversion of CO₂ to methanol.

WP 6. In this WP, infrared spectroscopic measurements using DRIFTS have shown that not all materials are suitable for this method of investigation. Commercial zinc oxide shows complete absorption of infrared radiation, a phenomenon known as “IR blackening” of ZnO, which is caused by the photodesorption of oxygen. In the investigations of cerium zirconium oxides, a photothermal effect was observed. In this case, the desorption processes at the surface are not directly caused by light, but result from the secondary effect of heating caused by light incidence.

WP 7. This WP aimed to elucidate reaction pathways, intermediates, and active centers in CO₂ adsorption and reduction on homogeneous and heterogeneous catalysts using various in situ/operando methods. IR spectroscopy was used to identify reaction intermediates and analyze acid-base properties and exposed metal centers via adsorbed probe molecules. Additionally, operando EPR (for paramagnetic transition metal ions like Cu²⁺), in situ NAP-XPS (for surface composition and valence states), and operando Raman spectroscopy (for nanocrystalline phases and oxygen vacancies in Ce_{1-x}M_xO₂ materials) have been foreseen.

WP 8. The determination of the requirements for the MeOH synthesis using renewable energies was successful.

The following milestones were achieved

- Suitable synthesis protocols for Ce_{1-x}M_xO₂ and mesoporous HEA identified
- Co-sputtering protocol for NP deposition on Ce_{1-x}M_xO₂ established
- 1st generation homogeneous absorption system developed and tested
- Test of 1st gen. homo- and heterogen. catalysts completed
- Mechanistic studies on 1st gen. solid catalysts completed
- Based on mechanistic & kinetic studies (also under photoexcitation), a 2nd gen. system for DAC at low CO₂ concentrations of 400 ppm is developed)
- An optimized and finetuned absorption system for CO₂ capture from air and direct conversion to MeOH at low temperatures is developed

2. Activities and obstacles

WP 1. Ce-based materials containing Pd as active metal were first tested in DAC and later in the methanol synthesis in gas phase in WP5. Depending on the used modifiers (Zn, Cu), clear differences between Pd-only and CuZnPd catalysts became evident. Pd-based catalysts convert CO₂ to CO, which readsorbs and is hydrogenated to methanol following the known formate mechanism, whereas the modifiers Cu and Zn affect the electronic and structural properties of Pd and form CuZnPd alloys that suppress CO formation but enhance methanol decomposition. Through collaboration with an external partner (University of Duisburg-Essen), alternative HEA materials have been made available. Instead of high-temperature dealumination (up to 1000 °C), liquid phase pulsed laser ablation was applied. These materials showed indeed activity in conversion of CO₂ at elevated temperature, but instead of desired methanol mostly methane was formed. Obviously, the obtained high-entropy alloys with strong metallic character are not suited to mimic typical methanol catalysts which contain small Cu clusters and metal-support interfaces, and consequently, HEA failed as catalysts for methanol synthesis. New and other successfully synthesised and tested catalyst systems were a metal-organic framework (MOF) UiO-66 to support Cu and Cu_xAu_y/ZnO catalysts.

WP 2. At INP, non-thermal plasmas, specifically dielectric barrier discharges (DBD) were investigated. Two strategies for the reaction of CO₂ with H₂ were pursued: 1) the effect of the flow fields on the plasma chemistry for the CO₂ splitting studies was investigated using CFD simulations for the CO₂ conversion studies on the planar DBD reactors. For this purpose, CO₂ splitting was explored as a key step for reduction. These reactors were manufactured using 3D printing. 2) In a coaxial DBD, CO₂ splitting and the reaction with H₂ were studied in the pressure range 1-3 bar. Both empty and catalyst fixed bed reactors were studied. Regarding 1) The flow dynamics play an important role here. The reactor with the most uniform flow field shows the highest yields with about 30 g/kWh for CO. Regarding 2), the electrical and chemical characterization of coaxial DBD reactors shows a tripling of the CO₂ conversion and the energy efficiency of CO formation with an increase in operating pressure from 1 to 2 bar. The positive effect of pressure increase of the CO formation is demonstrated for the first time.

WP 3. A system using triethanolamine in combination with alkali metal halides as absorber was developed. At room temperature and under the pressure of 1 bar, the phase-transfer behavior was observed, and a

stable solid was obtained after simple filtration. Under optimized conditions the capture of atmospheric pressure was also achieved. ^{13}C NMR and elemental analysis confirm that the product is bicarbonate. The CO_2 uptake for the different alkali metal halide systems was determined by NMR spectroscopy. The NaBr system absorbed the highest amount of CO_2 at 0.82 mol CO_2 per mol TEA, the equilibrium was reached within 6 hours. When the pressure was reduced to 0.2 bar for a longer time, the uptake of CO_2 was 0.64 mol per mol TEA. Without THF, the uptake of CO_2 is comparable, but no solid phase is observed, which shows that THF only contributes to the solid phase forming. The CO_2 desorption properties of the materials were investigated. The CO_2 desorption and thus the uptake capacity was analyzed by thermogravimetric measurements and quadrupole mass spectrometry. Particularly noteworthy is the low desorption temperature of approx. 60 °C, low energy requirement for desorption and the recyclability of the mixture (in collaboration with Strunk and Wohlrab/ WP1 & 6). Hydrogenation reactions utilizing the CO_2 loaded capture material was also successful. Hydrogenation utilizing the pincer-type catalyst Ru-MACHO-BH₃ led to the corresponding formate in moderate yields (in collaboration with Junge/WP4). The uncatalyzed cycloaddition reaction of CO_2 to epoxides yielding cyclic carbonates was also successful. Notably, the solid phase [TEA.Br][K HCO_3] directly reacted with 12 epoxides yielding the corresponding cyclic carbonates.

WP 4. The first work focused on the development of a novel reaction system based on amino acids (AAs) for the capture and utilisation of CO_2 and its hydrogenation. In the presence of the naturally occurring amino acid L-lysine and using a specific ruthenium-based catalyst system, the hydrogenation of absorbed CO_2 initially took place with high activity and excellent productivity to form the formate. We then further improved the catalytic system. Based on our previous work on CO_2 hydrogenation to formates, we developed a new class of ionic liquids (ILs) based on amino acids (AA-ILs) for use in the capture and in situ hydrogenation of CO_2 to formates. Compared to our previous work, the present AA-ILs absorbents showed a significantly higher maximum CO_2 absorption capacity, and a ratio of up to 1.94 mmol CO_2 per AA-ILs was achieved, instead of 0.73. Such a high ratio has rarely been achieved for ILs or amines for combined CO_2 absorption and hydrogenation. Furthermore, the CO_2 hydrogenation in the recent work was carried out under milder conditions ($T = 80$ °C). It is noteworthy that the low vapor pressure, non-toxicity and high reactivity of amino acid-based ionic liquids towards CO_2 make them ideal for absorbing CO_2 , even from ambient air, and converting it into downstream products. Additionally, we found that formamides form at temperatures above 80 °C. Since the formation of formamide is essential for further hydrogenation to methanol, further investigations were carried out by varying the process parameters. These led to the formation of the target compound methanol at a temperature of 165°C (TON = 200). Further activities aimed at defining suitable conditions for increased stability of CO_2 absorbents and catalysts allowing for methanol generation. As heterogeneous catalysts were not as successful as the homogeneous ones, the focus laid on the development of a combined CO_2 absorption and hydrogenation to methanol based on homogeneous catalysts. This was done combining the ionic liquid tetrabutylammonium L-argininate (TBA-Arg) with the ruthenium-MACHO-BH complex, that allowed achieving significant yields of methanol up to 5.8 mmol as well as a turnover number (TON) up to 700 at a temperature of 150°C.

WP 5. For investigation of the reaction pathways and mechanism, selected catalysts were tested by variation of T , p , contact time and feed composition (H_2 , CO_2 , CO , N_2) to establish selectivity-conversion relationships which can reveal reaction sequences, and partly by kinetic isotope experiments ($^{13}\text{CO}_2$, D_2). The inclusion of Mo carbides in the test program (WP5) was motivated by recently published work on liquid-phase methanol synthesis. Such carbides are not purchasable and preparation by carburization at harsh conditions (CH_4 , H_2 , 400 °C) is challenging. Thus, focus was first set on the impact of preparation conditions on catalytic performance, and a fixed-bed preparation method was developed for homogeneous samples of high quality. The obtained catalysts indeed showed appreciable selectivities for gas phase methanol synthesis at 160-200 °C. Unpromoted Mo_2C favoured hydrocarbon formation, while Cu/ Mo_2C showed enhanced methanol selectivity and was 3.75 times more active than Mo_2C at 160 °C. Kinetic studies at 20 and 50 bar revealed the influence of reaction conditions on methanol selectivity and its decomposition. These findings contribute to the rational design of carbide-based catalysts for efficient CO_2 -to-methanol conversion. Apart from the HEA, all selected catalyst systems showed significant methanol yields at temperatures of 160 - 200 °C, which corresponds to the overall project goal.

WP 6. A direct influence of irradiation could be observed for the commercial titanium oxide samples. Irradiation has a significant influence on the adsorption equilibrium of CO_2 on titanium oxide, causing the relative ratio of surface intermediates to change. For more in-depth experiments to identify the surface species, the two titanium oxides P25 and anatase were compared. During CO_2 adsorption under irradiation of anatase, four species could be identified: monodentate, bidentate, chelating bidentate carbonate species and stable bidentate bicarbonate species. In contrast, these compounds are hardly detectable during the

control measurement without light due to their very low band intensity. The formation of carboxylic acid functionalities was observed for P25 both in the light and in the dark. These species are thought to play a crucial role in photocatalytic CO₂ reduction, since the activity of CO₂ reduction decreases when sodium-modified P25 is used. In addition, formate and bicarbonate species are formed under the influence of light. These observations suggest that irradiation already has a significant influence on the first elementary steps and the adsorption equilibria of the reactants.

WP 7. Firstly, a CeO₂-ZrO₂ mixed oxide was used to investigate the extent to which the existing operando DRIFTS apparatus is suitable for detecting the adsorption of CO₂ in the atmospheric concentration range (approx. 400 ppm). Carbonate and bicarbonate species were identified and differences in stability were observed. It was shown that CO₂ adsorbs on Ce_{0.8}Zr_{0.2}O under conditions that are relevant for CO₂ extraction from the air. This proved that experiments under such conditions are feasible with our available DRIFTS setup and lead to usable results. This was followed by operando DRIFTS investigations of the hydrogenation of CO₂ to methanol at 20 bar on Cu-containing metal organic frameworks (Cu-MOFs) and corresponding investigations with CO as a probe molecule. Both materials were provided by the Wohlrab group. In addition to the MOF materials, supported Cu catalysts on Zn-containing oxides (ZnO, ZnO-ZrO₂, ZnO-CeO₂ and ZnO-ZrO₂-CeO₂) were investigated with regard to methanol formation using DRIFTS. The aim here was to find an alternative to the typical Cu/ZnO-Al₂O₃ methanol catalyst that uses less Cu and reduces the usual deactivation of the commercially available Cu/ZnO-Al₂O₃ by sintering ZnO. For comparison with the above-mentioned catalysts, model investigations were carried out using various operando methods (in particular DRIFTS, EPR) on the role of oxygen vacancies in the activation of CO₂ which, apart from CO₂ conversion to methanol, comprised also possible side reactions such as RWGS and methanation of CO₂. To this end, also supported Au and Ru catalysts have been included.

3. Results and successes

In the project, 6 doctorates have already been completed or are still being completed. 22 publications have resulted from the project. 2 press releases have been published. New national and international collaborations have been established. The wealth of experience generated by this project now serves as a basis for further projects and research work.

4. Equal opportunities, career development and internationalisation

In WP 1, a coworker from Egypt and a PhD student from Mexico performed the research together.

In WP 2, in the INP the project finances a temporary PhD position for a candidate from Indonesia.

The WP 3 was handled by a female PhD student from Croatia. She was supported by a Chinese female student assistant who was co-financed by the institute.

In WP 4, 2 male (33%) and 4 female (67%) individuals have been involved in the subproject WP, of whom 50% come from abroad (China, Iran, Italy).

In WP 5, the work on reaction pathways was carried out by a Russian student as part of a doctoral thesis.

In WP 6 a PhD student from Croatia was employed.

In the WP 7, a PhD student from Colombia was hired.

There were other smaller contributions from other scientists.

5. Structures and collaboration

As planned, the project is being carried out in close collaboration with the groups at LIKAT, whose contributions were essential to the study. In Dr. Wohlrab and Prof. Strunk's group, experiments were conducted to assess the thermal stability and CO₂ loading capacity of the CO₂-loaded material. Meanwhile, in Dr. Junge's group, the CO₂-loaded material was successfully utilized in hydrogenation reactions to produce formate. In the group of Dr. Armbruster the catalytic evaluation of heterogeneous materials was carried out whereas Dr. Junge tested materials in batch. Prof. Werner established his adsorption methods with the materials scientists at LIKAT. Prof. Brückner supported and cooperated with all groups with her expertise and work on material characterization.

Due to technical problems that had already occurred in 2021 in the production of the high-entropic alloys at the project partner IWT Bremen, alternative solutions were sought at an early stage. A cooperation with

the research group of Dr. Reichenberger, University of Duisburg-Essen, was agreed. HEAs are produced there by different methods than at IWT. Jointly selected material compositions for the catalyst tests in 2022 were handed over to LIKAT and evaluated in methanol synthesis from CO₂.

An intensive cooperation of INP is reflected in the collaboration with the group of Sebastian Wohlrab (LIKAT) and in the supervision of PhD student Dimas by Prof. Dr. Sven Grundmann from University of Rostock. New collaborations in the subject area with national institutions and companies in the frame of two projects (PlasCO₂ – Plasmainduzierte Generierung von Kohlenmonoxid aus Kohlendioxid und dessen chemische Verwertung; 033RC030D BMBF and PLEKTRON - Plasmaunterstützte Elektrodenprozesse an elektrochemischen Zellen für die Energieumwandlung; 13N16754 BMBF) have emerged in the course of the project. Through funding from an EU cooperation project (Marie Skłodowska-Curie Research and Innovation Staff Exchange), a PhD student got the opportunity to spend a four-week research stay at the Instituto Tecnológico Metropolitano (Medellín) to learn a new catalyst synthesis method from the local cooperation partner.

6. Quality assurance

The principles of good scientific practice are explicitly defined in the statutes of LIKAT and were applied to this collaborative project. All important results and observations are recorded in laboratory journals and electronic measurement data are initially stored on the measuring computers and backed up daily on backup computers. The targeted processing of the work plan and the scientific progress of the work are reviewed in regular meetings and adjusted accordingly. Animal testing is not carried out.

7. Additional resources

The in-kind human resources provided by LIKAT are estimated to 9 person months for scientists (group members and institute staff) and for technical staff (4 person month).

At the INP, an own contribution was made by the management of the work package WP 2 by Volker Brüser, the co-supervision by Prof. Dr. Ronny Brandenburg and Dr. Milko Schiorlin and a INP co-funded PhD student Rezvan Hosseini Rad.

8. Outlook

The results obtained in the project open up new perspectives for the customized development of catalyst systems and materials for efficient CO₂ conversion under variable process conditions. The targeted combination of rational catalyst design, innovative material integration and in situ methodological expertise has created a solid base for future technological breakthroughs in the sustainable chemical research. Building on the knowledge gained, future research approaches to decarbonization can be derived that combine both experimental and model-based strategies and enable their transfer into industrial applications.