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Iron-based catalysts for sustainable valorisation of CO_2, CH_4 and N_2
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Inhalt

1. Zielerreichung und Umsetzung der Meilensteine

The main objective of this project was to elucidate the potential of Fe-based catalysts for CO_2 hydrogenation to higher hydrocarbons (preferably C_2-C_5 olefins) or CO/formates, CH_4 conversion into C_2-C_3 olefins, and N_2 hydrogenation to NH_3 or amines. From a fundamental viewpoint, the focus was put on establishing structure-reactivity-selectivity relationships. To this end, eight groups (WG) from LIKAT were involved in this project (Figure 1). The work plan was generally fulfilled b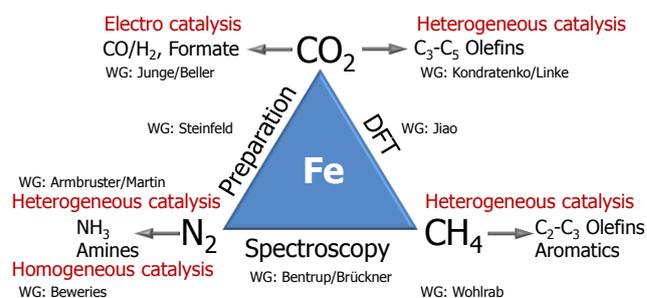oth in terms of content and time. Specifically, in the WG Junge/Beller, a co-electrolysis cell and setting up the necessary analytics for the products were built in 2017. The synthesis and testing of homogeneous and heterogeneous Fe-based catalysts of the 1st generation were fruitfully completed in 2018. In 2019, the development of the 2nd catalyst generation and design/construction of an electrolysis cell for continuous operation took place.

Figure 1 Project structure, reactions, and working groups (WG).

The WG Beweries prepared literature-known as well as novel Fe-PCP, PNP and PNN pincer halide complexes and elucidated their application potential for formation of dinitrogen complexes and electrocatalytic studies in the presence of olefins.

In the WG Armbruster/Martin, several alternative approaches were applied to synthesize heterogeneous catalysts with iron nanoparticles. The focus was set on immobilisation and controlled dispersion of iron particles and to check their impact on NH_3 synthesis.

Owing to the development of well-defined Fe-based bulk catalysts in the WG Kondratenko/Linke and WG Steinfeldt as well as to thorough catalytic tests (WG Kondratenko/Linke) and catalyst characterisation (WG Bentrup/Brückner), it was possible to establish selectivity-activity-relationships in the CO_2-hydrogenation to higher hydrocarbons.

The results of theoretical calculations rationalized the experimental results and provided constructive suggestions for optimizing reaction conditions and catalyst development.

The WG Wohlrab tried to check the potential of CH_4 conversion into C_2-C_3 olefins over single site Fe-based catalysts according to Ref. [X. Guo, et al., Science 344 (2014) 616]. The claimed performance could not be reproduced. Thus, it was decided to not continue studies with such materials but to develop alternative Fe-based catalysts for CH_4 or N_2 conversions.

2. Aktivitäten und Hindernisse

A new FTIR transmission cell was developed (Figure 2(a)), which enables operation at elevated pressure up to 30. Thus, the formation of ads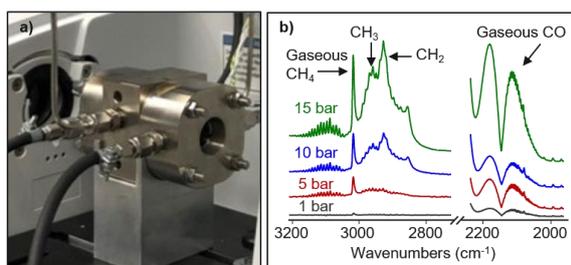orbates and reaction products in CO_2 conversion into valuable products was studied. Fe_3O_4 operating at 1 bar reduces CO_2 to CO (Figure 2(b)). Starting from 5 bar, the formation of methane is clearly seen (the main band at 3016 cm^{-1}). The formation of higher hydrocarbons starts at pressures above 10 bar as concluded from the appearance of bands at 2959/2854 and 2927 cm^{-1} characteristic for surface CH_3 and CH_2 fragments. The intensity ratio of these bands increases with a further increase in pressure, too. This is an indication of chain growth. While DRIFT

Figure 2. a) In house developed heatable, high pressure FTIR reaction cell. b) FTIR-spectra recorded after 60 min exposure of Fe_3O_4 to the CO_2/H_2/He/Ne-feed (20/60/18/2; 50 ml/min) at different pressures.

spectroscopy is suitable for examining adsorbates, measurements being performed in

transmission mode are particularly well suited to analyze gaseous and adsorbates simultaneously. However, dark samples lead to very weak signals, so that especially some of the Fe_3O_4-catalysts, active for the CO_2-FT-reaction, could not be investigated.

DFT calculations provided mechanistic insights into CO, H_2, CO_2, CH_4 and N_2 activation on Fe-based catalysts. The flat Fe(110) surface favors H-assisted CO activation, while the stepped Fe(710) surface prefers direct CO activation. Both, methanation and chain growth over the Fe(110) surface have the same rate-determining step as CHO dissociation. Coverage-dependent chain initiation and propagation mechanisms with methylidyne and alkylidyne as intermediates were proposed. These high coverage results explain the experimentally observed formation of methane and higher hydrocarbons from CO and H_2. On the $Fe_3C(010)$ surface, mixed Fe/C termination prefers H-assisted CO activation and Fe-termination prefers direct CO activation. We also computed the electrochemical N_2 activation and rationalized the remarkable role of doping carbon atoms into oxygen vacancies on TiO_2 forming Ti-C bonds as the active sites for NH_3 synthesis.

To develop heterogeneous catalysts for CO_2 hydrogenation to higher hydrocarbons, we followed two approaches: (i) machine learning for identifying activity/selectivity relevant descriptors and (ii) preparation of well-defined structures. In the first approach, we created a database using the available published studies on the target reaction. The database includes catalyst activity and selectivity as well as various descriptors, which are elemental catalyst composition, the kind of promoter, support material, alkali metal to Fe ratio, iron precursor, catalyst preparation method, treatment, reaction conditions and feed composition. Based on statistical analysis of the collected data, total pressure, catalyst treatment and reaction temperature are the most decisive parameters for CO_2 conversion and formation of higher hydrocarbons. With respect to catalyst design, the Pauling electronegativity of metal dopant for Fe_2O_3 is an appropriate descriptor affecting the rate of CO_2 conversion and CH_4 selectivity. The selectivity to higher hydrocarbons and the olefin/paraffin ratio are improved when combining promoters based on oxides of alkali and transition metals. On this basis, we developed a K-Mn/Fe_2O_3 catalyst with the selectivity to higher hydrocarbons of 83% at CO_2 conversion of 42%. A correlation between product selectivity and the steady-state composition was established. The higher the fraction of iron carbides, the higher the selectivity to higher hydrocarbons is. The presence of metallic Fe and Fe_3O_4 is relevant for CO hydrogenation to CH_4. Iron carbides also produce CH_4 through direct CO_2 hydrogenation and hydrogenolysis of higher hydrocarbons but with significantly lower rates than the rate of CO hydrogenation to higher hydrocarbons.

Homogeneous and heterogeneous Fe-containing catalysts were developed for electrocatalytic CO_2 conversion into CO/formic acid (WG Junge/Beller). The best performing catalysts show Faraday efficiencies greater than 90%. Knölker cyclopentadienone Fe(0) complexes developed for the photocatalytic reduction of CO_2 to CO were also used as electrocatalysts. During electrolysis at constant applied voltage without addition of a Brønsted acid, CO was selectively formed with a Faraday efficiency of 96%. The system also shows high catalytic currents and good long-term stability. A FeN_xC material was initially selected as a potential heterogeneous material. It was produced from phenanthroline and Fe(II)acetate with subsequent deposition on a carbon black followed by treatment in Ar at 800°C. However, this material catalyzed H_2 formation in addition to CO due to water reduction. To increase Faraday's efficiency regarding CO, an Fe-containing complex, hemin, was used as a precursor. The resulting catalyst contains many iron single atom centers (SAC) favoring the reduction of CO_2 to CO. In the case of iron(II)acetate, nanoparticles are mainly present and catalyze water reduction. Despite the very good selectivity of SAC, the turnover of CO_2 is still very low. The use of freeze-drying and the synthesis of carbon aerogels helps to increase catalyst surface area and to positively influence the formation of SAC.

For NH_3 synthesis from N_2 and H_2, more than 50 materials were prepared using wet chemical preparation, mechanochemical and decomposition/pyrolysis routes. Their intensive characterization was only partly successful, as many of the available techniques, although

using high-end equipment, did not provide satisfactory hints on the nature of supported iron. This concerns mostly the available techniques for determination of metallic iron dispersion. The prepared catalysts were tested in NH_3 synthesis under kinetically controlled conditions at 250-450 °C and pressures up to 150 bar using a test rig also applied for evaluation of commercial catalysts. The latter are available as benchmark and used for control runs. Our results do not show any beneficial effects of iron nanoparticles as reported in literature. The home-made catalysts reveal Fe-related activities comparable to commercial materials although the observed optimum iron metal cluster size on supports was 5-10 times larger than known for commercial samples. This was surprising as activity is expected to decrease for larger particles. Furthermore, supported iron catalysts prepared in WG Wohlrab through photodecomposition of suited Fe bipyridinyl complex precursors were competitive in NH_3 synthesis although no promotors were used as in commercial materials.

After synthesizing a set of Fe pincer complexes, we attempted to generate dinitrogen complexes from these species. None of the attempts was however successful. The nature of the pincer ligand seems to play an important role for complexation of N_2. We also carried out electrocatalytic studies using Fe halide complexes in the presence of N_2 and acids. Unfortunately, NH_3 was not formed, while H_2 was the dominant product. As no complexes with activated N_2 ligands could be obtained, further studies with addition of olefins for further functionalisation could not be performed. Bes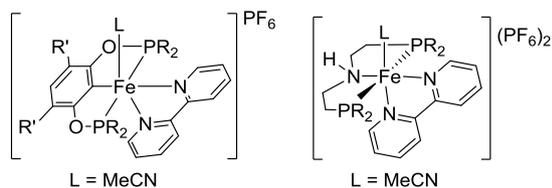ides, we tried to prepare Fe bipyridine complexes with pincer ligands (Figure 3). They, however, undergo disproportionation. Such systems are thus not applicable for our studies. A major challenge we experienced when reproducing literature data is the quantification of NH_3 produced (electro)catalytically. In literature, typically multistep indophenol method is used for this purpose.

Figure 3. Proposed Fe(II) pincer complexes with bipyridine ligands.

The high coke resistance of FeO_x/SiO_2 catalysts with isolated iron sites in the non-oxidative CH_4 conversion into C_2-C_3 hydrocarbons and aromatics as claimed in a previous study [X. Guo, et al., Science 344 (2014) 616] could not be reproduced in the present project. Even the walls of quartz reactors served as a surface for coke formation, resulting in a coke selectivity of about 50%. Thus, this type of catalysts was not further developed, while promising alternatives, albeit for another catalytic application, were prepared through deposition of individual metal atoms, first on carbonaceous supports, from photosensitive Fe-complexes. Graphene, graphene oxide, zeolites, SBA-15 and hydrotalcite were so used as alternative supports. Selected materials were examined for the activation of CH_4 or N_2. The CH_4 dehydroaromatization was not successful using 5wt% Fe on graphite. However, formaldehyde yield of 0.81% at 625 °C could be achieved over Fe(0.01 wt%)/SBA-15 in the partial oxidation of methane. This corresponds to an Fe-related formaldehyde formation rate of 2.0 mol_{CH2O} $mol_{Fe}^{-1}s^{-1}$, which is consistent with previous literature [Q. Zhang, et al., Appl. Catal. A Gen. 356 (2009) 103]. In NH_3 synthesis at 430 °C and 100 bar, Fe(0.9 wt%)/MgO-Al_2O_3 performed similarly to an industrial catalyst (Amomax) at high gas flows.

3. Ergebnisse und Erfolge

Electrocatalytic production of H_2 from reduction of the proton source was studied in more detail using a [(PNNH)FeBr$_2$] complex[1] and a related Ni pincer complex.[2] Design principles that were identified as promising for Fe systems could be transferred to a Ru catalyst, which shows promising activity for electrocatalytic CO_2 reduction. These studies were used to set up and benchmark our electrochemical equipment. Partick Hasche working as PhD student on this topic has successfully defended his PhD thesis at University Rostock (supervisor: PD Dr. Beweries).

Homogeneous and heterogeneous Fe-containing materials electrocatalytically reducing CO_2 to CO or formic acid with Faraday efficiencies greater than 90%containing were developed. Based on the results obtained, several articles have been published or are in

preparation.[3,4,5,6] Alonso Rosas-Hernández has defended his PhD thesis at University of Rostock (supervisors: Dr H. Junge and Prof. M. Beller). In addition, an external PhD student (Matteo Miola) from university Aarhus, Denmark worked as a guest in this project (01/17-04/17 and 02/18-04/18).

Heterogeneous Fe-based catalysts developed in the frame of this project for classical NH_3 synthesis show Fe-related specific activity comparable to commercial catalysts. The obtained results build the basis for a PhD thesis of Markus Vogt, who worked on this topic. The thesis will be submitted to University of Rostock in 2021 (supervisor; Dr. U. Armbruster).

Systematic DFT computation revealed the surface and coverage-dependent activation mechanisms of CO, H_2, CO_2 and CH_4 on different iron surface, differently terminated iron carbides surfaces,[7,8,9,10,11] and carbon atoms doped TiO_2 surface for NH_3 synthesis from electrochemical N_2 activation.[12] These results rationalize the experimentally observed phenomena and provide the basis for designing novel catalysts.

The effects of various structures of Fe-based materials and reaction conditions including catalyst treatment procedures on activity and product selectivity in CO_2 hydrogenation were systematically investigated. The obtained results enabled us to derive fundamentals relevant for catalyst design and reactor operation.[13,14] Owing to the experience gained in this project, we applied for a DFG project in the frame of SPP 2080, which has been approved (2019-2021). In addition, an external PhD student (Andrey Skrypnik) from University of Novosibirsk, Russia contributed to this project as a guest supported by DAAD (09/19-07/20).

A method based on photosensitive Fe-complexes was developed and applied for preparation of supported Fe-based catalysts. They show attractive performance both in NH_3 synthesis and the partial oxidation of CH_4 to formaldehyde. Stefan Peters, who was a PhD student in this project, will submit his PhD thesis to University of Rostock in 2021 (supervisor: Dr. S. Wohlrab).

4. Chancengleichheit

Studies carried out in WG Beweries were conducted by a PhD student (MSc Patrick Hasche), supported by two female Indian postdocs, Dr. Hemlata Agarwala and Dr. Sandeep Kaur-Ghumaan. Dr. Jana Weis und Dr. Dr. Pragati Joshi worked in WG Bentrup/Brückner.

5. Qualitätssicherung

All raw data collected in the frame of this project are saved on servers of LIKAT for documentation. The results obtained within the project have been published in per-reviewed journal. Thus, their quality has been indirectly approved by independent reviewers. Two papers have been published in open-access journals.

As NH_3 tests were carried out low conversion degrees, long-term absorption of NH_3 in aqueous HCl followed by titration was used for quantification. This allowed highly reproducible measurements. Frequent control experiments with commercial standard catalyst ensured that measurement conditions were stable over the complete project.

6. Zusätzliche eigene Ressourcen

Valuable contributions for practically all working groups were provided by the central analytical service of LIKAT and colleagues from the department "Catalytic In Situ Studies" to characterize fresh and spent catalysts. The related resources (senior scientists and technicians) are estimated to cover 10 person months within three years. The maintenance shutdown of some essential equipment (TEM, XPS) led to some delay, and therefore samples were sent to external institutions to accomplish these measurements in due time (less than one person month). Catalyst characterisation by Mössbauer spectroscopy was also carried by an external partner (about one month of senior scientist).

N_2, air, O_2, He and Ar as well as liquid nitrogen and dry ice (solid CO_2), which are required for gas chromatographic analysis, catalytic tests and catalyst synthesis were provided by LIKAT.

Costs for the procurement of computing nodes and software were covered by LIKAT. The software and the hardware were provided by the IT and Media Centre University of Rostock.

7. Strukturen und Kooperation

In general, the groups involved in the project (Figure 1) successfully cooperated with each other according to the planned tasks. Specifically, WG Bentrup/Brückner was involved in ex situ and in situ characterization of catalysts used practically in all other working groups. A part of catalysts tested for CO_2-hydrogenation to higher hydrocarbons in WG Kondratenko/Linke were prepared in the WG Steinfeld. The groups Armbruster/Martin and Wohlrab developed a novel method for preparation of supported Fe-based catalysts, which were also tested in WG Armbruster/Martin. Theoretical calculations carried out in WG Jiao were relevant for interpreting experimental data and catalyst development in WG Kondratenko/Linke. For setting up the electrochemical equipment and for first tests, WG Beweries cooperated with Dr. A.-E. Surkus. The cooperation planned with WG Jiao was not possible due to the above-mentioned problems with preparative and catalytic studies.

8. Ausblick

Conversion of small and widely available molecules, like N_2, CO_2 and CH_4, will continue to play an important role in fundamental and industrially oriented projects both at LIKAT and worldwide. The results obtained in the frame of this project provide a basis for tailored design of catalysts for the above-mentioned reactions.

Although, (electro)catalytic activation and functionalization of N_2 with molecular Fe systems was not possible in this project, we have collected valuable data on ligand and catalyst design as well as electrochemical activation of small molecules that will be relevant to further individual and joint projects.

For heterogeneous N_2 conversion into NH_3, we have developed a method of preparation of supported catalysts at room temperature using photosensitive Fe-complexes. It offers room for further scientific findings because our promoter-free catalysts show a similar performance as industrial catalyst.

The established correlations between the Pauling electronegativity of metal dopant for Fe_2O_3 and methane selectivity as well as between the concentration of metallic Fe and CH_4 production can be used for developing selective CO_2-hydrogenation catalysts.

In addition to catalyst preparation, the developed cell for operando FTIR tests will be applied for providing mechanistic insights relevant for catalyst preparation and optimization of reaction conditions for improving catalyst activity and product selectivity.

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