

## Annual Report 2019

March 2020



Synfuels China's General Manager and company visit Syngaschem BV in September



Syngaschem BV is Research Partner of SynCat@Beijing; it receives base funding from Synfuels China Technology Co., Ltd, Beijing-Huairou.

## Syngaschem BV synthesis gas chemistry fundamental research projects

# Annual Report 2019

March 2020

## Highlights

- **EU Program successfully completed:** the Horizon 2020 CritCat Program with 9 European partners, funded by the EU-H2020 program finished in 2019.
- SynCat@DIFFER Major Research Program: the NWO-sponsored CHIPP project together with the DIFFER Institute and the TU/e, with 50/50% co-funding by NWO and Syngaschem BV, enabled by base funding from Synfuels China, is in its 4<sup>th</sup> year, and is generating many interesting results, with a paper in Nature Communications published in early 2020.
- **13** Publications: 4 papers on Syngaschem-based or initiated research, 4 in collaboration with SynCat@Beijing, 5 published in 2020, and 4 more in preparation
- 21 Scientific Presentations: Syngaschem staff gave 17 oral presentations at international conferences, workshops and universities in the Germany, Poland, Turkey, Denmark, Sweden, Belgium, Wales, South Africa, China, USA, and The Netherlands; the PhD students presented 4 posters at conferences.
- 6 staff-visits to Beijing: Syngaschem's Director and Deputy Director each visited SynCat@Beijing for three times a week, while the General Manager of Synfuels China visited SynCat@DIFFER in Eindhoven.
- Certainty on the next few years: Synfuels China Technology and Syngaschem BV agreed to extend their cooperation through 2023.

## Contents

1. Introduction: What is Syngaschem BV?	4
2. Vision and Mission: Energy Storage and CO <sub>2</sub> Avoidance	4
3. Research Program in 2019	5
4. Syngaschem Staff and Students in 2019	5
5. Research 2019	6
5.1 Fundamentals of the Fischer-Tropsch reaction (Dr. Kees-Jan Weststrate)	6
5.2 Water electrolysis with non-precious electrocatalysts (Dr Foteini Sapountzi)	8
5.3 Model catalysts and micro reactors for syngas research (Dr Hans Fredriksson)	10
6. International Projects Sponsored by Syngaschem BV	12
6.1 University of the Free State, Bloemfontein	12
6.2 University of Cape Town, c*change program	13
7. Collaboration and interaction with SynCat@Beijing in 2019	15
8 Output 2019: Publications, Presentations and Posters	15
8.1 Publications	15
8.2 Oral Contributions at Conferences, Summer Schools, Workshops; Seminars at Institutions	17
8.3 Posters at Conferences	18
8.4 SynCat Ac@demy Scientific Leadership Presentations	18
9. Sponsorships in 2019	18
10. Outlook 2020 and beyond: organizational changes	

## 1. Introduction: What is Syngaschem BV?

Syngaschem BV is a Dutch private research enterprise founded in collaboration with Synfuels China Technology Co. Ltd. in China. Together they established a laboratory for fundamental research, entitled SynCat@Beijing, which took off in 2015. Syngaschem was founded in 2013 to take care of recruitment of staff and planning of research programs and infrastructure, in close collaboration with the executive leadership of Synfuels China. In addition, Syngaschem serves as the Dutch branch of SynCat@Beijing, with its own research program, under the name SynCat@DIFFER, and located at the Dutch Institute for Fundamental Energy Research at Eindhoven. Syngaschem employs three research scientists and accommodates several students, while it is also active in providing scientific leadership training.

## 2. Vision and Mission: Energy Storage and CO<sub>2</sub> Avoidance

Syngaschem's research program is based on the vision that hydrogen and synthesis gas  $(CO + xH_2)$  are crucial intermediates in clean energy technologies for the future, in many parts of the world. Synthesis gas – or in short 'syngas' – can be obtained from traditional fossil sources, as well as from biomass and from electricity in combination with water and sources of carbon, see the scheme below. With the advent of renewable electricity from wind and solar energy, which is inherently intermittent, syngas is the intermediate to high-energy density fuels that serve to store energy. In the context of Coal-to-Liquids Technology in China, such renewable sources of electricity can be applied to decompose water in hydrogen, to supplement the syngas, and oxygen, to be used in the gasification step. In this manner, renewable electricity has the potential to significantly reduce the by-production of  $CO_2$  that presently accompanies the use of coal, even more so if all electric power used in the process itself would come from renewable sources as well.



The mission of Syngaschem BV is to obtain fundamental understanding behind the production of syngas by renewable energy and its utilization to produce synthetic fuels for the storage of energy. It therefore concentrates on electrochemistry for water and  $CO_2$  electrolysis, and on surface science and spectroscopy for understanding of CO hydrogenation reactions, often in combination with molecular modeling.

Syngaschem's Research program is not only carried out in SynCat@DIFFER in Eindhoven, but also in sponsored projects at the University of Cape Town (2 projects), and the University of the Free State (3 projects) in South Africa. In addition, Syngaschem sponsors two projects via the Netherlands Organization for Research (NWO).

## 3. Research Program in 2019

As a result of the generous base funding by Synfuels China and the additional subsidies (see Text Box), the research program continued to consist of three major subjects in 2018:

Fischer-Tropsch Chemistry, led by Dr. Kees-Jan Weststrate, in collaboration with SynCat@Beijing, and with the DIFFER institute. Emphasis of the work is on understanding the mechanism, in particular in relation to selectivity patterns. An external collaboration with the University of Cape Town (Prof Michael Claeys and Dr Nico Fischer) focuses on the selectivity of FTS Catalysts for special products, and the stability of catalysts over time, and it has been running successfully in 2019. We will continue to fund these projects in 2020 as well.

### **Overview Funding Sources**

- Base funding from Synfuels China Technology Co. Ltd.
- NWO CHIPP Subsidy for a 4-years research program together with the DIFFER Institute and TU/e (total budget approximately 1.6 M€)
- European Union Horizon 2020 funding for the CritCat program (total amount 535 k€ for 2016-2019)
- Annual subsidy on labour cost in tax deductions from the Ministry of Economic Affairs (WBSO-subsidy)
- Electrolysis of Water, Alcohols and CO<sub>2</sub> led by dr Foteini Sapountzi, with support from Dr Hans Fredriksson. This program is carried out in collaboration with DIFFER and has its main focus zero-gap configuration electrolysis, using both proton and anion exchange membranes (collaboration with Prof Hristo Penchev, Bulgarian Academy of Sciences, Sofia). Within the CritCat consortium the emphasis was on testing novel formulations based on computational predictions for H<sub>2</sub> evolution, in particular with the Nanochemistry Research Group at the International Iberian Nanotechnology Laboratory (INL) in Braga, Portugal. In a collaboration with the University of the Free State in South Africa (Dr Blener Buitendach and Prof Jannie Swarts), we study cluster derived iridium-ruthenium systems for oxygen evolution reactions.
- Model Catalysts and Micro Reactors for in situ studies led by dr Hans Fredriksson. Focus of the work has been to study Cu-based catalysts for CO<sub>2</sub> activation with optical plasmon resonance techniques inside microreactors. In the framework of the CritCat Project, catalysts have been tested for H<sub>2</sub> formation by ammonia decomposition and for decomposition of volatile organic compounds. Within this project, a PhD thesis on pulsed operation in microreactors (collaboration with Prof. Dr. Ton Backx, TU/e) was completed in 2019 by Mr Zhenghang Zhu and will be defended in 2020.

Name	Major Activities	Project Funding
Dr Hans Fredriksson (0.9 fte)	In situ spectroscopy, micro reactors, CO2	EU; SynCat@DIFFER
Dr Foteini Sapountzi (0.8 fte)	Electrochemistry; electrolysis	EU; SynCat@DIFFER
Dr Kees-Jan Weststrate (0.9 fte)	Surface Science; Fischer-Tropsch Chemistry	SynCat@DIFFER
Mr Antonio Vaccaro (0.1 fte)	Administration	
Ir Jan Karel Felderhof (0.1 fte)	Director Strategy, Organisation, HR Development; SynCat Ac@demy	
Prof dr Hans Niemantsverdriet (0.6 fte)*	Director Syngaschem BV	
Students and funding programme		
Ms Devyani Sharma (NWO)	PhD student, SynCat@DIFFER research progra	mme
Mr Daniel Garcia Rodriguez (NWO)	PhD student, SynCat@DIFFER research programme	
Mr Yannick Bannink (Fontys*)	BSc student; EU-CritCat project	
Mr Dave Leurs (Fontys*)	BSc student; EU-CritCat project	
Mr Kees Buiter (Fontys*)	BSc student; SynCat@DIFFER program	
Mr Bjorn Koevoet (Fontys*)	BSc student; SynCat@DIFFER program	
Mr Tom Vroomen (Fontys*)	BSc student; SynCat@DIFFER program	

## 4. Syngaschem Staff and Students in 2019

\* Fontys University of Applied Sciences, Eindhoven

#### 5. Research 2019

#### 5.1 Fundamentals of the Fischer-Tropsch reaction (Dr. Kees-Jan Weststrate)

Two projects are performed in the Syngaschem Laboratories in the context of the SynCat@DIFFER program.

In Project 1 we use single crystal surfaces of cobalt to study elementary steps of FTS chain growth. Our earlier high resolution XPS studies in ultrahigh vacuum (2018 annual report) showed that the reactivity of C<sub>x</sub>H<sub>y</sub> intermediates on Co(0001) is strongly affected by the presence of CO spectators. In 2019 we further explored this by using the HIPPIE beamline of MAX IV which allows XPS measurements at near-ambient pressure. Acetylene was used as a precursor molecule to study how  $C_x H_v$ species react under high pressure conditions. Figure 1 shows a series of C1s spectra recorded during an isothermal experiment at 313 K in which a 0.08 ML acetylene-covered Co(0001) surface (prepared by dosing ethylene at 313 K) was exposed to an increasingly high H<sub>2</sub> pressure. A H<sub>2</sub> pressure of  $\sim 10^{-5}$  mbar would be sufficient to create a high hydrogen coverage at 313 K, but the spectra shape shows that co-adsorbed hydrogen did not cause the acetylene to react.

A CO contamination in the gas led to the appearance of  $CO_{ad}$  when the hydrogen pressure was increased to  $1 \times 10^{-2}$  mbar. The appearance of  $CO_{ad}$  coincides with the conversion of acetylene to ethylidyne, the temporary formation of the latter being evident from the transient peaks at 282.9 eV and 283.8 eV. The  $CO_{hollow}$  peak (285.2 eV) comes and goes together with the ethylidyne-related peaks, consistent with the RAIRS results which show that  $CO_{hollow}$  is associated with ethylidyne. Ethylidyne reacts further to produce 2-butyne, evident from a peak at 283.4 eV due to the two central carbon atoms and at 284.1 eV due to the two methyl groups. Acetylene conversion reached completion after 400 s in  $1 \times 10^{-2}$  mbar H<sub>2</sub>, and a pressure increase to  $1 \times 10^{-1}$  mbar H<sub>2</sub> did not affect 2-butyne at all.

These results confirm that CO has a profound influence on the reactivity of  $C_xH_y$  adsorbates on a Cobalt catalyst surface. We find that it stabilizes them in the alkylidyne form, which readily reacts to form new C-C bonds. Their



Figure 1: XPS at near-ambient pressures. C1s spectra recorded during exposure of an acetylene-covered Co(0001) surface to increasingly high H<sub>2</sub> pressures at T=313 K. The time evolution of the C1s spectra is shown in the lower panel, whereas the top view shows the spectra at specific stages of the experiment (hv = 420 eV). Note that the signal intensity of the acetylene spectrum in the upper panel was divided by 2 to facilitate comparison.

high reactivity for chain growth, combined with a high resistance towards termination reactions, makes the alkylidyne intermediate a feasible candidate as the principal chain growth intermediate on cobalt-catalyzed FTS. This study was accepted for publication in Nature Communications and appeared in February 2020<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup> Kees-Jan Weststrate, Devyani Sharma, Daniel Garcia Rodriguez, Michael Gleeson, Hans Fredriksson, Hans Niemantsverdriet, *Mechanistic insight into Carbon-Carbon bond formation on Cobalt under simulated Fischer-Tropsch Synthesis conditions*, Nature Communications 11 (2020) 750

In Project 2 with PhD student Daniel Garcia, we aim to prepare iron carbide model catalysts by evaporation of iron onto a copper (100) substrate, followed by ethylene treatments to carburize the sample. We used a combination of TPD, STM and low energy electron diffraction to characterize the carbide morphology as a function of Fe film thickness. After evaporating different amounts of Fe onto our Cu(100) held at room temperature we cooled the sample to 100 K and saturated the surface with ethylene. The amount of carbon deposited during subsequent heating was deduced from the H<sub>2</sub> desorption spectrum shown in Figure 2 (left). We found that the quantity of carbon deposited is independent on the amount of Fe present on the surface, which means that the C/Fe ratio decreases with increasing Fe thickness. STM measurements combined with LEED show that carbon reconstructs the surface into the so-called clock-reconstruction which has a local coverage of 0.5 ML.



Figure 2: Examples from the iron carbide model catalyst research: (left) H<sub>2</sub> TPD shows that ethylene decomposition deposits 0.5 ML carbon on an iron surface; (center) STM images show the formation of a clock-reconstructed Fe<sub>2</sub>C layer, consistent with the LEED pattern (right). We conclude that on thick Fe films the carbon from ethylene decomposition remains adsorbed in the outermost layer to form thin carbide layer with Fe<sub>2</sub>C composition and forming the clock reconstruction.

We conclude that the surface carbon that forms during ethylene decomposition remains adsorbed on the Fe surface and does not diffuse into the bulk. This is attributed to the high stability of the clock-reconstruction. Reactivity measurements show that the saturated Fe<sub>2</sub>C carbide is inert. It was found that the dissociative adsorption of H<sub>2</sub> on the Fe<sub>2</sub>C surface is much more difficult than on Fe films. Moreover, adsorption of both CO and H<sub>ad</sub> is weaker on Fe<sub>2</sub>C, and dissociation of CO is inhibited. The inert nature of this saturated, carbon-rich iron carbide surface indicates that carbon-lean carbide surfaces and carbon vacancies are important for the dissociation of H<sub>2</sub> and CO, important elementary reaction steps in FTS.



PhD student Devyani Sharma studies the adsorption and dissociation of carbon monoxide on cobalt surfaces of different structure, the idea being that realistic catalyst particles are terminated by a variety of different surfaces. The XPS spectra of carbon, taken at a synchrotron, reveal small changes in the binding energy, which reflect minute changes in the adsorption modes of CO on surface sites of different structure, see Figure 3

Figure 3: X-ray photoelectron spectra taken at a synchrotron reveal small changes in the way CO binds to cobalt configurations as present on different single crystal surfaces

#### 5.2 Water electrolysis with non-precious electrocatalysts (Dr Foteini Sapountzi)

Our activities on water electrolysis are focused on the specific case of polymer electrolyte membranes with protonic conductivity (proton exchange membranes, PEM) and hydroxyl ion conductivity (anion exchange membranes, AEM). The development of non-precious electrocatalysts for PEM water electrolysis is expected to represent a true milestone for the commercialization of PEM water electrolysis, which currently relies on the rare and expensive platinum-group metals. On the other hand, AEM is an alternative water electrolysis technology which lately has received lot of interest by the scientific community since it combines the advantages of alkaline electrolysis (cheap electrocatalysts) and PEM electrolysis (zero-gap design). The main hurdles in AEM technology are the limited efficiency (and thus need for new electrocatalysts) and the poor stability/conductivity of the AEM membranes (thus need for new polymers).

Many studies exist in literature on the identification of promising alternative electrocatalysts which can be both acid-stable and active towards the hydrogen evolution reaction (HER), to be used as cathodes in PEM water electrolysis. These studies have already identified transition metal phosphides and sulfides as potential replacements for the currently used Pt cathodes. However, typical literature studies report electrocatalytic activity using half-cell measurements and studies on industrially relevant PEM water electrolysis remain scarce. Testing emerging electrocatalysts in full-cell configurations is of particular interest, since deviations can be expected from half-cell measurements where mass and ion transfer phenomena are less complex.

The few reported attempts on integrating non-precious metal HER electrocatalysts into full-cell PEM water electrolysis devices, deal mainly with the case of transition metal sulphides, see Figure 4. Together with our collaborators from INL (Portugal) and Iowa State University and the U.S. Department of Energy (USA), we pioneered in this direction, by demonstrating the successful implementation of transition metal phosphides in a PEM water electrolyser. In essence, our electrolyser operated in electrolysis of water vapors, with a NiP<sub>2</sub> cathode and 48 h durability was demonstrated. This work was published within this year in the well-esteemed ACS journal Chemistry of Materials (IF: 10.16).



Figure 4: Performance of various PEM water electrolysers with non-precious cathodic electrocatalysts, under 2 V polarization. The case of NiP<sub>2</sub> and FeP corresponds to our studies. Data for other non-precious materials are from the literature. Note that the yellow, red and orange data all have been obtained at higher temperatures, while the data in blue are valid for ambient temperatures

Our study on NiP<sub>2</sub>, revealed two additional interesting aspects, which will be our main focus for the next year. First, we showed that the performance of the PEM water electrolyser can be greatly affected by the design of the electrode. This will be the main subject for research in the next year, where cubic NiP<sub>2</sub> will be used as the showcase to systematically investigate the electrochemical engineering of membrane electrode assemblies in

terms of catalyst loading, ionomer loading, kind of gas diffusion layer, hot-press conditions, and so on. Second, fundamental investigations in half-cell measurements revealed high activity of NiP<sub>2</sub> towards the oxygen evolution reaction (OER) in alkaline media. Our target within 2020 is to develop, together with our collaborators, advanced AEM water electrolysers, where transition metal phosphides (Iowa State University, US Department of Energy, and INL, Braga, Portugal) will be combined with KOH-doped PBI membranes (BAS).

Apart from NiP<sub>2</sub>, our activities within 2019 have been also directed to the use of FeP as alternative cathodic electrocatalyst in PEM water electrolysis. FeP/C catalysts were synthesized by our colleagues in INL and we implemented them into membrane electrode assemblies. PEM water electrolysis in liquid phase operation took place at ambient conditions and we observed better performance with FeP/C compared to NiP<sub>2</sub>. In collaboration with DIFFER we confirmed and quantitatively measured the produced hydrogen, thus providing evidence that our water electrolyser with FePcathode operates with 84-100% Faradaic efficiencies and with an 4.1 kWh/Nm<sup>3</sup> energy consumption. The durability of our cathodes was demonstrated upon 100 h of continuous operation, see Figure 4a. Moreover, our cathodes showed excellent suitability to the intermittent operation of renewables, as confirmed with stability test upon variable power input, see Figure 4b. These results will be submitted for publication in early 2020.



As shown in Figure 4, our FeP-based cathode outperforms others with non-precious metal electrocatalysts operated at similar conditions. Even though FeP-based cathodes showed somewhat lower activity compared to commercial Pt cathodes, which result in higher energy needs, a preliminary cost analysis has nonetheless revealed their viability for practical application owing to their significantly lower cost. In essence, catalyst costs for the cathode have been calculated as of 0.15 Euros/cm<sup>2</sup> for Pt and <0.002 Euros/cm<sup>2</sup> for FeP respectively. On the other hand, the electricity cost required to drive water electrolysis at 0.2 A/cm<sup>2</sup> for a typical system lifetime of 10,000 hours is of 0.21-0.58 Euros/cm<sup>2</sup> and 0.25-0.70 Euros/cm<sup>2</sup> for Pt and FeP respectively (based on current electricity costs in EU). Thus, the cost increase due to the higher energy penalty for FeP is much lower than the savings in capital cost, thus showing the potential practical importance of FeP. Even more, with appropriate electrochemical engineering of FeP-based cathodes, we aim within 2020 to further improve the performance of FeP cathodes and thus even further decrease the energy penalty for enabling water electrolysis.

#### 5.3 Model catalysts and micro reactors for syngas research (Dr Hans Fredriksson)

The overall activities during 2019 have been focused on three main topics: i) Further development of micro reactors for simultaneous, in-situ characterization of model catalysts with UV-vis and mass spectrometry, ii) fundamental aspects of Cobalt catalysts and iii) rounding up the CritCat project.

#### Micro reactor for nanoparticles and foils

Supported/promoted catalyst are the most frequently used type in heterogenous catalysis. The in-house developed micro reactor with in-situ UV-vis spectroscopy (Figure 6) has been further improved. Previously been used for characterization of both flat model catalysts and powder catalysts in reactions like H<sub>2</sub>, and CO oxidation as well as the water gas shift reaction and ammonia decomposition. During 2019, it has been used

to test, nanoparticles, thin films and metal foils. Optical characterization in both transmission and reflection mode has been accomplished. The latter configuration has been developed and tested thoroughly. With the addition of reflection measurements, in-situ optical characterization of foils and thick films are also possible. This opens for the possibility to investigate deeper oxidation and reduction of surfaces as well as build-up of thicker layers of carbonaceous species. In addition to this, a microreactor dedicated to in-situ measurements and treatments of TEM-compatible samples has been developed.



#### NH<sub>3</sub> decomposition

The fundamental aspects of catalytic NH<sub>3</sub> decomposition have been studied in a joint project between Syngaschem and the universities of Jyväskylä and Tampere (Finland) and Trondheim (Norway) within the EU-CritCat Project. The study includes DFT calculations of the NH<sub>3</sub> decomposition on small Ru-clusters and Rusurfaces, simulations of the reaction kinetics and experimental verifications. A novel mechanism involving NH<sub>2</sub> and N<sub>2</sub>H coupling to form N<sub>2</sub> has been identified, resulting in significantly lower activation barriers for NH<sub>3</sub> decomposition. The work has been written up for publication and is due for submission shortly.

#### Flat model catalysts: foils and nanoparticles prepared by ALD and PVD with focus on Cobalt

Flat model catalyst deposited by various techniques can already be routinely tested in the in-house micro reactor (Figure 7, left and middle). In order to extend the range even further, experiments have been performed to use ALD for making three dimensional "flat" samples. These consist of a nano or micro structured surface, homogeneously covered with Co nanoparticles (Figure 7, right). With these types of samples, slower reactions can be tested, due to the higher content of active surface area, while the high definition of 2D-samples is maintained and characterization techniques such as AFM/STM, TEM and XPS can still be used in an efficient manner. These experiments have been written up in a manuscript intended for publication during early 2020.

The foils experiments have shown interesting results. Not only is the signal intensity for the mass spectrometer strong and easy to detect, the samples simple to prepare and analyze, but the optical reflectance measurements also reveal the formation of interference fringes during oxidation and reduction of Cobalt. This is due to formation of the transparent cobalt oxide CoO and allows for investigation of the diffusion of oxygen and cobalt ions through the oxide at low temperatures. These processes are important, not only during activation/deactivation of cobalt catalysts but also in other fields, including oxygen conducting electrolysers and Li-ion batteries.



Figure 7: Cobalt model catalysts; Co-foils, Co deposited by evaporation, by ALD on flat surfaces and on nanowires

#### CritCat Project: Critical Materials Replacement

The European union funded research project CritCat focusing on research to replace critical materials such as Platinum group metals for heterogeneous and electro catalysis has been successfully finished. All deliverables assigned to Syngaschem has been duly met and reported at the final revision meeting in Milan. Apart from the scientific achievements in the fields of heterogeneous and electro catalysis, the CritCat project has led to the establishment of good, lasting contacts with top level research groups in Germany, Finland, Norway, UK and Portugal.

### 6. International Projects Sponsored by Syngaschem BV

#### 6.1 University of the Free State, Bloemfontein

Under direction of Prof J.C. Swarts, Dr Buitendach has performed very interesting research on the synthesis and characterization of Ir-Ru multinuclear clusters, in a project that has been sponsored by Syngaschem BV for several years. Our interest is to use these elegant complexes as precursors for precision catalysts on the



Figure 8: Five Ir-based complexes with Fe or Ru in the ligands; Fc stands for ferrocenyl, Rc for ruthenocenyl; hence complex 1 represents a bimetallic cluster with Ir and Fe, complex 2 has Ir + 2 Fe, and complex 5 is a trimetallic structure with Ir-Ru-Fe. Electrochemical characterization successfully reveals communication between the metal centers. model scale. The work has so far led to 3 publications on Mn-Fe complexes in earlier years, and one on bi- and multinuclear Ir-Ru complexes as precursors for oxygen evolution catalysts in 2019, see Figure 8. The complexes have been used as precursors for Ir-Ru electrodes for oxygen evolution and preliminary results indicate that the noble and unabundant Ir can be used in a very economic fashion in this manner.

Dr Lizette Erasmus works on a project aimed at  $CO_2$  capture by Frustrated Lewis Pairs. These are complexes of acids and bases in which steric constraints prevent them to form close bonds.

As a result, they leave space and 'open charges' where CO<sub>2</sub> can bind and possibly also react. Dr Erasmus successfully anchored such complexes to a silica support and demonstrated their activity for (a) CO<sub>2</sub> capture at dry ice temperature, (b) CO<sub>2</sub> release at room temperature, and (c) the reaction to formic acid. The work will be published in 2020.



Frustrated Lewis Pair (FLP)



Dr Ernie Langner uses metal organic frameworks of the Zeolitic Imidazolic Framework type, ZIF-8, for capturing CO<sub>2</sub>. By sensitizing the Zn-based ZIFs by means of solvent-assisted ligand exchange, the already appreciable CO<sub>2</sub> sorption

capacity of ZIF-8 is substantially enhanced<sup>2</sup>. Further optimization lies ahead by varying the metal ions in the framework, and in this sense cobalt appears attractive. The work has been extended by molecular modeling to obtain leads for further improvement of the metal organic frameworks for CO<sub>2</sub> capture, storage and release.

Progress meetings with the Bloemfontein team were held on November 14 and 15, 2019, while Prof Swarts stayed in Eindhoven for three weeks to work on joint papers in May 2019.

UNIVERSITY OF THE FREE STATE UNIVERSITEIT VAN DIE VRYSTAAT YUNIVESITHI YA FREISTATA



<sup>&</sup>lt;sup>2</sup> Tsai, C. W., Niemantsverdriet, J. W., Langner, E. H. G., *Enhanced CO*<sub>2</sub> adsorption in nano-ZIF-8 modified by solvent assisted ligand exchange, Microporous and Mesoporous Materials 262 (2018) 98-105.

#### 6.2 University of Cape Town, c\*change program

Syngaschem BV also sponsors collaborative projects in the Research Group of Prof Michael Claeys and Dr Nico Fischer at the University of Cape Town, on the subject of catalyst behavior in the Fischer-Tropsch reaction as studied by magnetic methods and X-ray diffraction, and on FTS product selectivity with a focus on specialty chemicals, see Figure 9.



Figure 9: Detailed product analysis (GCxGC) of iron-based bimetallic Fischer-Tropsch catalysts at 20 bar,  $H_2/CO = 2$  and 280°C; (a) Fe; (b) CoFe; (c) NiFe; (d) CoNiFe. In the smaller graphs paraffins are labeled as (1), olefins as (2), aldehydes/ketones as (3), alcohols as (4), and acids as (5), while enlarged sections highlight linear and branched alcohols (experiments by Muhamed Fadlala, UCT).

Progress meetings were held, in Aachen (August 2019) and in Cape Town (November 2019). In 2020 the focus will be on publishing the work done in 2016-2019.



synthesis gas chemistry

DIFFER

#### CO dissociation on iron carbide thin films supported on Cu(100) as a Fischer-Tropsch synthesis (FTS) model catalyst

Daniel Garcia Rodríguez<sup>1,2</sup>, Michael Gleeson<sup>2</sup>, Devyani Sharma<sup>1,2</sup>, J.W.Niemantsverdriet<sup>1,3</sup> and C.J. Weststrate<sup>1</sup>

- 1. SynCat@DIFFER, Syngaschem BV, 5600HH Eindhoven, The Netherlands
- DIFFER (Dutch Institute for fundamental energy research). Eindhoven, The Netherlands.
  SynCat@Beiiing, Synfuels China Technology Co., Ltd., Huairou, Beiiing 101407, PR China



#### Objective

Fischer-Tropsch synthesis is a surface polymerization reaction of CO + H<sub>2</sub>which produces a distribution of hydrocarbon products. Iron-based catalysts are widely used in the industry, but the complexity of an industrial catalyst makes it very difficult to get atomic level insights into the reaction mechanism. During FTS conditions metallic iron, iron carbide, and iron oxides coexist. To reduce the complexity of real catalysts we make our own FeC<sub>x</sub> surfaces using ethylene, an oxygen free molecule, as carbon precursor to obtain detailed information on elementary reaction steps relevant to Fischer-Tropsch synthesis. In this poster, we provide details about the composition and structure of our FeC<sub>x</sub> model catalyst and explore how CO dissociation is affected by the carbon concentration on FeC<sub>x</sub> surfaces.



[1] J. van Loosdrecht et.al. , Surface Inorganic Chemistry and Heterogeneous Catalysis; Vol. 7.20). Elsevier Chemistry (2013) [2] Y. Gauthier, R. Baudoing-Savois, K. Heinz, H. Landskron. Structure determination of p4g Ni(100)-(2x2)C by LEED. Surf.Sci. 251-252, 493-497 (1991) [3] S. Zhao, X. Liu, C. Huo, Y. Li, J. Wang, H. Jiao. Determining surface structure and stability of different Fe<sub>x</sub>C phases under carburization environment from combined DFT and atomistic thermodynamic studies. Catal. Struct. React. 1, 44-59 (2015) This work has carried out as part of the SynCat@DIFFER programme between the Dutch institute for fundamental energy research (DIFFER), Eindhoven university of Technology (TU/e) and Syngaschem BV and is funded jointly by the Netherlands Organization for Scientific Research (NWO) and Syngaschem BV. We acknowledge ASTRID2, Synchrotron light source in Aarhus, Denmark (proposal ISA-19-1007) for provision of beamtime and the staff for their excellent support. DUtch Institute for

Fundamental Energy Research

Poster presented by PhD student Daniel Garcia at the Netherlands Catalysis and Chemistry Conference in Noordwijkerhout, NL

## 7. Collaboration and interaction with SynCat@Beijing in 2019

Frequent interaction exists between the two SynCat laboratories, with Drs Kees-Jan Weststrate and Prof Hans Niemantsverdriet each visiting three times in 2019, while Prof Yong-Wang Li visited SynCat@DIFFER in September. The Table below gives a summary. Several joint publications appeared, in the area of mechanistic Fischer-Tropsch research, and on photochemistry.

	PERIOD	MAJOR ACTIVITIES
1	January 20-29	Hans Niemantsverdriet visited SynCat@Beijing and had meetings with the executive management (Profs Yongwang Li, Yong Yang, Xiaoding Wen, Jian Xu) and with all SynCat staff, including Drs Ren Su and Xi Liu.
2	February 25 - March 2	Kees-Jan Weststrate had project meetings with all SynCat Staff in surface science, with Dr Jian Xu and Dr Xiaodong Wen, and worked on updating the TPD equipment
3	April 21-28	Hans Niemantsverdriet visited and had meetings with all SynCat staff members, with Prof James Lewis, and with Dr Jian Xu and Dr Xiaodong Wen.
4	June 24-29	Kees-Jan Weststrate visited SynCat@Beijing and had project meetings with the SynCat surface science staff, and met with Prof Li, Dr Xu and Dr Wen. He also worked on the manipulator of the TPD setup.
5	Augustus 12-22	Hans Niemantsverdriet visited SynCat and met with Prof Yongwang Li, Jian Xu and Xiaodong Wen, and all staff members; he also visited the Institute of Coal Chemistry for the International Advisory Board Meeting of the State Key Laboratory for Coal Conversion (SKLCC) in Taiyuan and presented a lecture in the associated conference.
6	September 27	Prof Li and company visited DIFFER, and met with staff and students. Director Richard van de Sanden presented the DIFFER Institute, and SynCat@DIFFER staff and PhD students presented their work. Jan-Karel Felderhof presented an update on the leadership programs. A Laboratory tour completed the visit.
7	November 11-16	Kees-Jan Weststrate visited SynCat@Beijing and had project meetings with all SynCat Staff in surface science, and with Dr Xu.

## 8 Output 2019: Publications, Presentations and Posters

#### 8.1 Publications

- 1. Overpotential analysis of alkaline and acidic alcohol electrolysers and optimized membrane-electrode assemblies; Sapountzi, FM; Di Palma, V; Zafeiropoulos, G; Penchev, H; Verheijen, MA; Creatore, M; Ublekov, F; Sinigersky, V; Bik, WM; Fredriksson, HOA; Tsampas, MN; Niemantsverdriet, JW; INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 44 (2019) 10163-10173
- 2. NiP<sub>2</sub>: A Story of Two Divergent Polymorphic Multifunctional Materials; Owens-Baird, B; Xu, J; Petrovykh, DY; Bondarchuk, O; Ziouani, Y; Gonzalez, N; Yox, P; Sapountzi, FM; Niemantsverdriet, JW; Kolen'ko, YV; Kovnir, K; CHEMISTRY OF MATERIALS 31 (2019) 3407-3418
- Synthesis, Spectroscopy and Electro chemistry in Relation to DFT Computed Energies of Ferrocene- and Rutheno-cene-Containing beta-Diketonato Iridium(III) Complexes; Buitendach, BE; Conradie, J; Malan, FP; Niemantsverdriet, JW; Swarts, JC; MOLECULES 24 (2019) 3923-3952
- **4.** Effect of ammonia on cobalt Fischer-Tropsch synthesis catalysts: a surface science approach; Kizilkaya, AC; Niemantsverdriet, JW; Weststrate, CJ; CATALYSIS SCIENCE & TECHNOLOGY 9 (2019) 702-710

#### Papers with SynCat@Beijing in the affiliation where Syngaschem BV staff contributed:

- **5.** Atomically Defined Iron Carbide Surface for Fischer-Tropsch Synthesis Catalysis;Li, Yijia; Li, ; Ahsen, A; Lammich, L; Mannie, GJA; Niemantsverdriet, JW; Lauritsen, JV; ACS CATALYSIS 9 (2019) 1264-1273
- 6. Solid Base Bi<sub>24</sub>O<sub>31</sub>Br<sub>10</sub>(OH) with Active Lattice Oxygen for the Efficient Photo-Oxidation of Primary Alcohols to Aldehydes; Dai, Yitao; Ren, Pengju; Li, Yaru; Lv, Dongdong; Shen, Yanbin; Li, Yongwang; Niemantsverdriet, JW; Besenbacher, F; Xiang, Hongwei; Hao, Weichang; Lock, N; Wen, Xiaodong; Lewis, JP; Su, Ren; ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 58 (2019) 6265-6270
- 7. Promotion Mechanisms of Au Supported on TiO₂ in Thermal- and Photocatalytic Glycerol Conversion; Shen, Yanbin; Mamakhel, A; Liu, Xi; Hansen, TW; Tabanelli, T; Bonincontro, D; Iversen, BB.; Prati, L; Li, Yongwang; Niemantsverdriet, JW; Hutchings, G; Dimitratos, N; Villa, A; Su, Ren; JOURNAL OF PHYSICAL CHEMISTRY C 123 (2019) 19734-19741
- 8. Boosting Photocatalytic Hydrogen Production by Modulating Recombination Modes and Proton Adsorption Energy; Dai, Yitao; Bu, Qijing; Sooriyagoda, R; Tavadze, P; Pavlic, O; Lim, T; Shen, Yanbin; Mamakhel, A; Wang, Xiaoping; Li, Yong-wang; Niemantsverdriet, JW; Iversen, BB; Besenbacher, F; Xie, Tengfeng; Lewis, JP; Bristow, AD; Lock, N; Su, Ren; JOURNAL OF PHYSICAL CHEMISTRY LETTERS 10 (2019) 5381-5386

#### Papers published in 2020:

- 9. Interaction of hydrogen with flat and corrugated cobalt surfaces; Weststrate, CJ; Mahmoodinia, M; Farstad, MH; Svenum, I-H; Stromsheim, MD; Niemantsverdriet, JW; Venvik, HJ; CATALYSIS TODAY 342 (2020) 124-130
- **10.** Sintering of cobalt during FTS: Insights from industrial and model systems; Moodley, D; Claeys, M; van Steen, E; van Helden, P; Kistamurthy, D; Weststrate, CJ; Niemantsverdriet, JW; Saib, AM; Erasmus, W; van de Loosdrecht, J; CATALYSIS TODAY 342 (2020) 59-70
- **11. Editorial: 3rd Syngas Convention, Cape Town 2018**; Van Steen, E; Niemantsverdriet, JW; Hutchings, GJ; Claeys, M; Fischer, N; CATALYSIS TODAY 342 (2020) 1-3
- 12. Mechanistic insight into Carbon-Carbon bond formation on Cobalt under simulated Fischer-Tropsch Synthesis conditions; Weststrate, CJ; Sharma, D; Garcia Rodriguez, D; Gleeson, M; Fredriksson, HOA; Niemantsverdriet, JW; NATURE COMMUNICATIONS 11 (2020) 750-759
- 13. Relevance of Chemical vs. Electrochemical Oxidation of Tunable Carbene Iridium Complexes for Catalytic Water Oxidation; Olivares M; vd Ham CJ; Mdluli V; Schmidtendorf M; Müller-Bunz H; Verhoeven MWGM; Li M; Niemantsverdriet JW; Hetterscheid DGH; Bernhard S; and Albrecht M; EUROPEAN JOURNAL OF INORGANIC CHEMISTRY 10 (2020) 801-812

#### Papers in preparation:

- Elucidating reaction mechanisms of ammonia decomposition over Ru/γ-Al<sub>2</sub>O<sub>3</sub>(100) catalysts; Wang J; Melander M; Ma, L; Fredriksson HOA; and Akola J; manuscript in-preparation
- Plasma-Enhanced Atomic Layer Deposition of Cobalt Nanoparticles for CO Methanation; v Straaten G; Vos, M; Verheijen, M; Fredriksson HOA; Kessels E; Creatore A; manuscript in-preparation
- Enhanced oxygenates in Fischer-Tropsch Synthesis over Ni and/or Co containing Fe Alloys Characterisation and 2D Gas Chromatography Product Analysis; Fadlalla MI; Babu SG; Nyathi T; Weststrate CJ; Fischer N; Niemantsverdriet JW; Claeys M; manuscript in preparation.

#### 8.2 Oral Contributions at Conferences, Summer Schools, Workshops; Seminars at Institutions

- 1. <u>C.J. Weststrate</u>, "Fundamental insights into the Fischer-Tropsch synthesis reaction on Cobalt: taking the surface science approach", iNano, Aarhus, Denmark, May 10, 2019
- 2. <u>J.W. Niemantsverdriet</u>, "Electricity and Chemistry: Opportunities and Challenges for Solar Fuels", Cardiff Doctoral Training In Catalysis Conference, UK, June 5, 2019 *(invited lecture)*
- 3. <u>C.J. Weststrate</u>, "New Light on an Old Catalyst: Mechanisms of CO-induced Ethylene Dimerization and Fischer-Tropsch Chain Growth on Cobalt", Laboratory for Chemical Technology, Ghent University, Belgium, June 7, 2019
- 4. <u>F. Sapountzi</u>, "Zero-gap water electrolysers for storing electricity: current status and perspectives", ECCM Conference, The Hague, The Netherlands, June 21, 2019
- 5. <u>H.O.A. Fredriksson</u> et al., "CritCat WP4 "Model catalyst preparation and testing", CritCat 36-month progress meeting, Milan, Italy, June 25-26, 2019
- 6. <u>H.O.A. Fredriksson</u> et al., "CritCat WP5 Catalyst development and optimization", CritCat 36-month progress meeting, Milan, Italy, June 25-26, 2019
- 7. <u>F. Sapountzi</u>, "Ethanol electrolysis using different kinds of polymeric membranes and gas diffusion electrodes", European International Conference on Catalysis in Membrane Reactors (ICCMR-14), Eindhoven, The Netherlands, July 8-11, 2019
- J.W. Niemantsverdriet, "Opportunities and Challenges for Electrolysis and Syngas Chemistry in Solar Fuels: Highlights from the SynCat Laboratories at Beijing and Eindhoven", The 1<sup>st</sup> meeting of the International Advisory Board of the State Key Laboratory of Coal Conversion, Taiyuan, Shanxi, PR China, August 2019 (invited lecture)
- 9. <u>F. Sapountzi</u>, "Alcohol electrolysis using H<sup>+</sup> and OH<sup>-</sup> conducting polymer membranes and different electrode designs", EuropaCat 2019, Aachen, Germany, August 18-23, 2019
- 10. <u>H.O.A. Fredriksson</u>, "In situ UV-vis Characterization & Activity Testing of Flat Model Catalysts in Custom Built Micro Reactors", EuropaCat 2019, Aachen, Germany, August 18-23, 2019
- 11. <u>C.J. Weststrate</u>, D. Sharma, D. Garcia Rodriguez, M.A. Gleeson, H.O.A. Fredriksson, J.W. Niemantsverdriet, "Carbon-carbon coupling on a Cobalt surface: how CO spectators determine the selectivity of surfacecatalyzed reactions", EuropaCat 2019, Aachen, Germany, August 18-23, 2019
- 12. J.W. Niemantsverdriet, X. Zhou, T. Zhang, Y.W. Li, and C.J. Weststrate, "Surface Science in Catalysis: Singlecrystals and Two-dimensional Models of Supported Catalysts in Fischer-Tropsch Research", 5th Anatolian School of Catalysis, Izmir, Turkey, September 8-11, 2019
- 13. <u>F. Sapountzi</u>, "Emerging materials for acidic and alkaline zero-gap water electrolysis", European Materials Research Society (E-MRS) Fall meeting, Warsaw, Poland, September 16 -19, 2019 *(invited lecture)*
- J.W. Niemantsverdriet, "Hydrogen, Oxygen and Syngas for Storage of Energy and 'Greening' of Coal-based Fischer-Tropsch Technology", DGMK Symposium 'Circular Economy – A Fresh View on Petrochemistry', Dresden, Germany, October 9-11, 2019 *(invited lecture)*
- <u>C.J. Weststrate</u>, D. Sharma, D. Garcia Rodriguez, M.A. Gleeson, H.O.A. Fredriksson, J.W. Niemantsverdriet, "High Resolution XPS to Identify C<sub>x</sub>H<sub>y</sub> Surface Species on a Cobalt Model Catalyst: The Importance of Alkylidynes as Growth Intermediates in Fischer-Tropsch Synthesis", AVS 66<sup>th</sup> international symposium 7 exposition, Columbus (OH), USA, October 20-25, 2019
- 16. <u>J.W. Niemantsverdriet</u>, "Hydrogen, Oxygen and Syngas for Storage of Energy and 'Greening' of Coal-based Fischer-Tropsch Technology", Group Seminar Physical Chemistry, University of the Free State Bloemfontein, South Africa, November 14, 2019,
- <u>C.J. Weststrate</u>, D. Sharma, D. Garcia Rodriguez, M.A. Gleeson, H.O.A. Fredriksson, J.W. Niemantsverdriet, "Using high resolution XPS at low and near-ambient pressures to resolve mechanistic issues in cobaltcatalyzed Fischer-Tropsch synthesis", AP-XPS (ambient pressure XPS workshop), Lund, Sweden, December 12, 2019

#### 8.3 Posters at Conferences

- 1. <u>D. Sharma</u>, M. Gleeson, D. Garcia Rodriguez, J.W. Niemantsverdriet, C.J. Weststrate, "Influence of defects on CO adsorption and dissociation on Co surfaces", NCCC XX, Noordwijkerhout, The Netherlands, March 4-6, 2019
- D. García Rodríguez, J. Gracia, D. Sharma, J.W. Niemantsverdriet, C.J. Weststrate, "CO adsorption on iron carbide thin film supported on Cu(100) and Cu(111) as a Fischer-Tropsch synthesis (FTS) model catalyst", NCCC XX, Noordwijkerhout, The Netherlands, March 4-6, 2019
- 3. <u>D. García Rodríguez</u>, M.A. Gleeson, J.W. Niemantsverdriet, C.J. Weststrate, "CO adsorption on iron carbide thin films supported on Cu(100) as a Fischer-Tropsch synthesis (FTS) model catalyst", EuropaCat 2019, Aachen, Germany, August 18-23, 2019
- 4. <u>D. Sharma</u>, D. Garcia Rodriguez, M.A. Gleeson, J.W. Niemantsverdriet, C.J. Weststrate, "Molecular adsorption and dissociation of CO on a defect-rich Co surface", EuropaCat 2019, Aachen, Germany, August 18-23, 2019

#### 8.4 SynCat Ac@demy Scientific Leadership Presentations

- 1. G.J. Hutchings and J.W. Niemantsverdriet, "How to Give Efficient Oral Presentations", Cardiff Doctoral Training In Catalysis Conference, UK, June 6, 2019
- 2. J.K. Felderhof, M.C.M. van de Sanden, J.W. Niemantsverdriet, "Introduction to Scientific Leadership", DIFFER Institute, Eindhoven, The Netherlands, June 24, 2019
- 3. J.K. Felderhof, J.W. Niemantsverdriet, Full Day Meeting on Leadership DIFFER, Akademisch Genootschap, Eindhoven, The Netherlands, June 25, 2019
- 4. J.W. Niemantsverdriet, "Introduction to Scientific Leadership", 5th Anatolian School of Catalysis, Izmir, Turkey, September 8-11, 2019

## 9. Sponsorships in 2019

On a regular basis, Syngaschem BV supports the Vincentre, a museum dedicated to the Dutch painter Vincent van Gogh in Nuenen, and the Classical Symphony Orchestra, The Philharmony Zuid-Nederland.On occasion, we sponsor local cultural events, such as the Mierlo Jazz Festival of the JazzCape Big Band, July 6, 2019. In May 2019, we supported the National Sports Contest of the Dutch Chemistry Students, ONCS 2019. We also sponsored the E-MRS 2019 Fall Meeting, Warsaw, Poland – September 16 - 19, 2019.





philharmonie zuidnederland

## 10. Outlook 2020 and beyond: organizational changes

In 2020 we enter the final year of our funding contract with Synfuels China Technology. During the visit to SynCat@DIFFER and in meetings at Beijing in January 2020, the General Manager Prof Yong-Wang Li and his Deputy Director, Prof Yong Yang and Research Director Xiadong Wen have generously agreed to extend the contract for another three years, until ultimo 2023, implying that Syngaschem BV will continue to be involved in SynCat@Beijing, while at the same time it will be enabled to carry on with its research program at Eindhoven. Of course, Syngaschem BV feels honoured and highly grateful for this fantastic opportunity.

At the request of the present Director, Syngaschem staff have agreed to change the organizational structure per medio 2020. Our present Director Strategy, Organization and HR Development, Ir. Jan Karel Felderhof, will assume the role of Managing Director, and take final responsibility for the company. The present Director, Prof Hans Niemantsverdriet, will become Research Director, and Dr Kees-Jan Weststrate will be Deputy Director to both. Antonio Vaccaro will serve as Office Manager for 0.3 fte. We intend to continue with the ongoing research program, which is financially consolidated until medio 2024. Nevertheless, we strive to obtain additional funding by engaging in consortia for European funding, like the just completed CritCat program, when the opportunity arises.



Impressions from Syngaschem's End of the Year meeting in the Akademisch Genootschap on December 18, 2019, after agreeing on the new organization structure; from left to right: Jan Karel Felderhof, Kees-Jan Weststrate, Hans Niemantsverdriet, Kees-Jan, Hans Fredriksson, Antonio Vaccaro, Foteini Sapountzi.

Syngaschem Electrolysis Article hits 100 citations within 3 years A review article published in January 2017 by a team from Syngaschem Eindhoven and SynCat@Beijing, with Foteini Sapountzi as first and corresponding author has attracted 100 citations by the end of 2019, according to the ISI Web of Science. This notable achievement makes it officially a "Highly Cited Paper," meaning that it belongs to the top 1% best referenced articles in the engineering field. The paper appeared in the open access category of Elsevier's journal Progress in Energy and Combustion Science (Impact Factor 26.467) and is freely available for everyone who is interested, which may well have contributed to its popularity. We cordially congratulate Foteini and the other authors with the success of this apparently much appreciated review of electrocatalysts for water splitting





#### **Research Laboratory:**

Visiting address:SynCat@DIFFER, De Zaale 20, 5612 AJ Eindhoven, The NetherlandsPostal address:PO Box 6336, 5600 HH Eindhoven, The NetherlandsEmail addresses:info 'at' syngaschem.com; office 'at' syngaschem.comWebsite:www.syngaschem.com

Syngaschem BV is a private company with liability limited by shares and a subsidiary of CatPhysChem BV Syngaschem BV is registered at the Dutch Chamber of Commerce under 57986630 | BTW (VAT) nr: NL823738589B01 Registered Address: Valeriaanlaan 16, 5672 XD Nuenen, The Netherlands Bank accounts IBAN: NL40 INGB 0008 6625 64 or NL27 KNAB 0258 0851 85 of Syngaschem BV, Nuenen, The Netherlands