Direct CO_2 conversion into higher hydrocarbons: Catalyst development and mechanistic aspects

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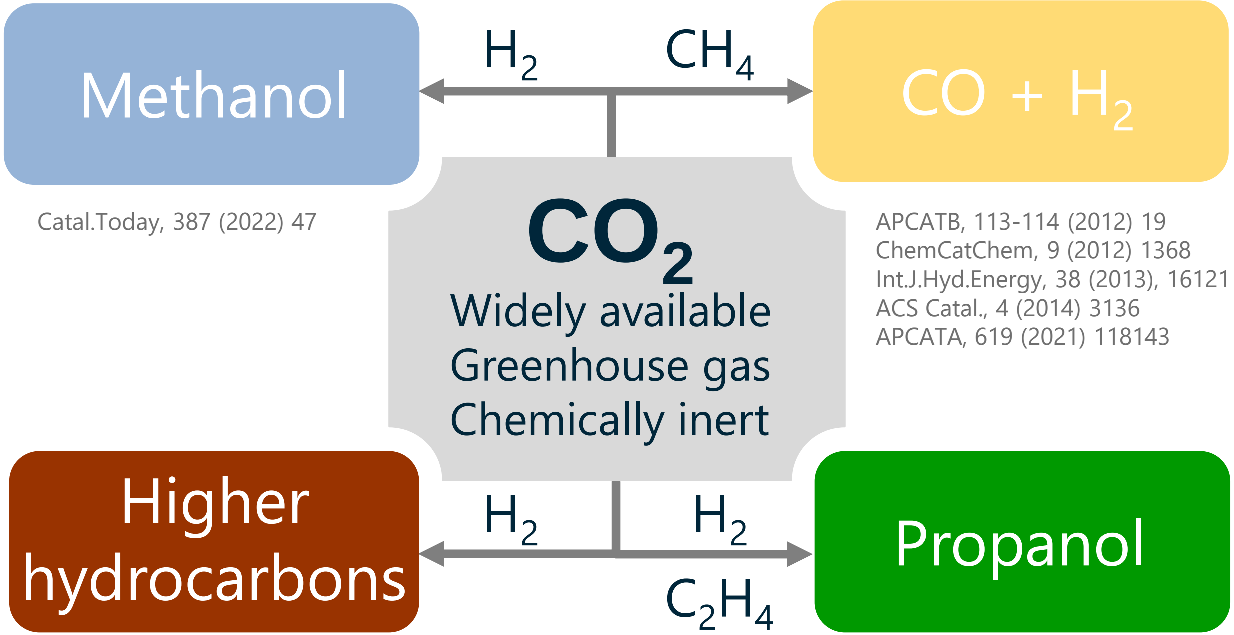
Our CO_2-related research areas and mission



Catal.Today, 387 (2022) 47

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ChemSusChem, 12 (2019) 651

Mission

- Elucidation of reaction mechanism on the level as elementary as possible
- Identification of active sites/species/phase and factors affecting their formation
- Determination of kinetics of product formation

Fundamentals for purposeful catalyst design and preparation

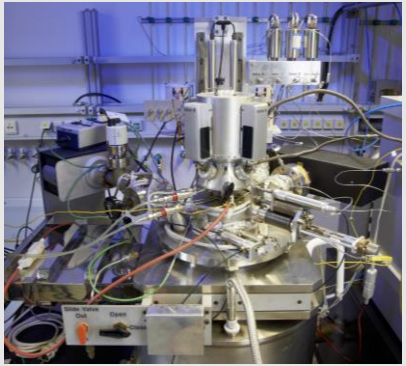
Our approach in CO_2 hydrogenation over Fe-based catalysts

Well-defined	Carefully investigated	Deeply understood	Optimally carried out
Catalysts	**Steady-state tests**	**Mechanism/kinetics**	**Reactors**

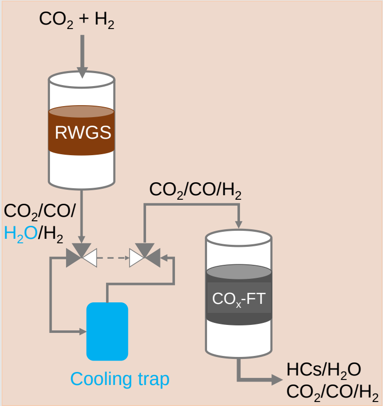
- α-Fe_2O_3, γ-Fe_2O_3 or their mixtures
- defined $Fe_xC_yO_z$ compositions
- promoted iron oxides or $Fe_xC_yO_z$
- supported materials
- **big-data analysis**

24/7 operation mode

Time-resolved methods
In situ characterization

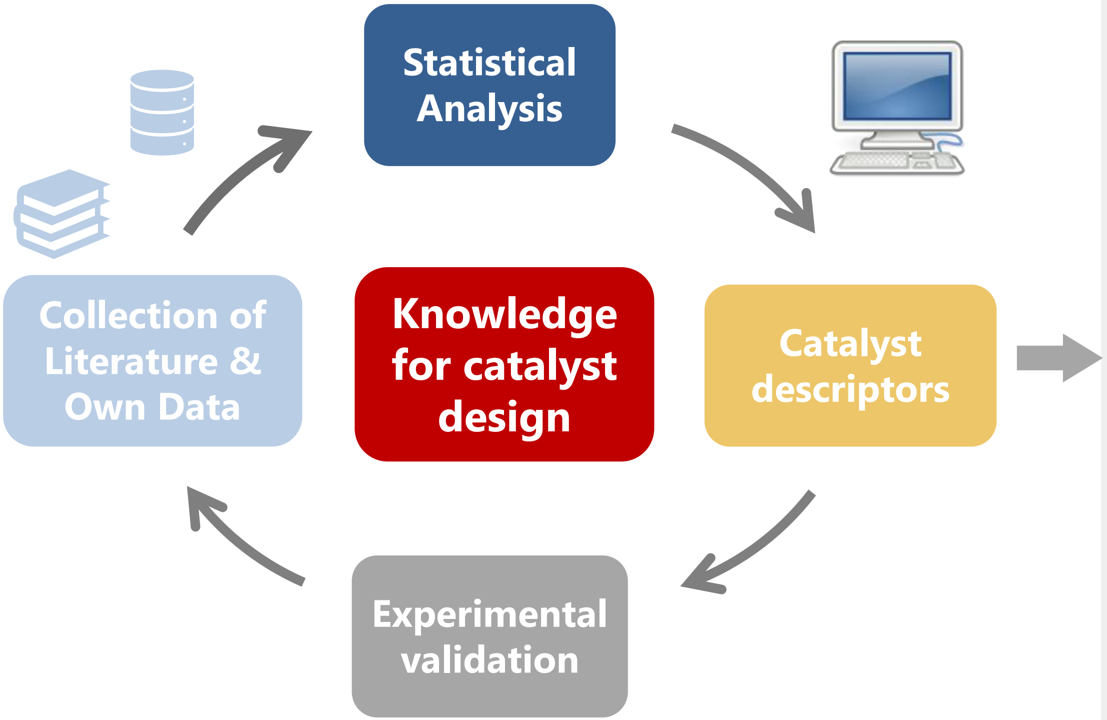


Unsteady-state operation
Coupling of reactions



Improved or new catalysts/processes

Machine learning for catalyst development



Q. Yang, ..., EVK, Appl. Catal. B, 2021, **282**, 119554.

The most vital descriptors for rate of CO_2 conversion:

- Total pressure
- Catalyst treatment duration
- Kind of iron source
- **K promoter**

selectivity to C_{2+} hydrocarbons:

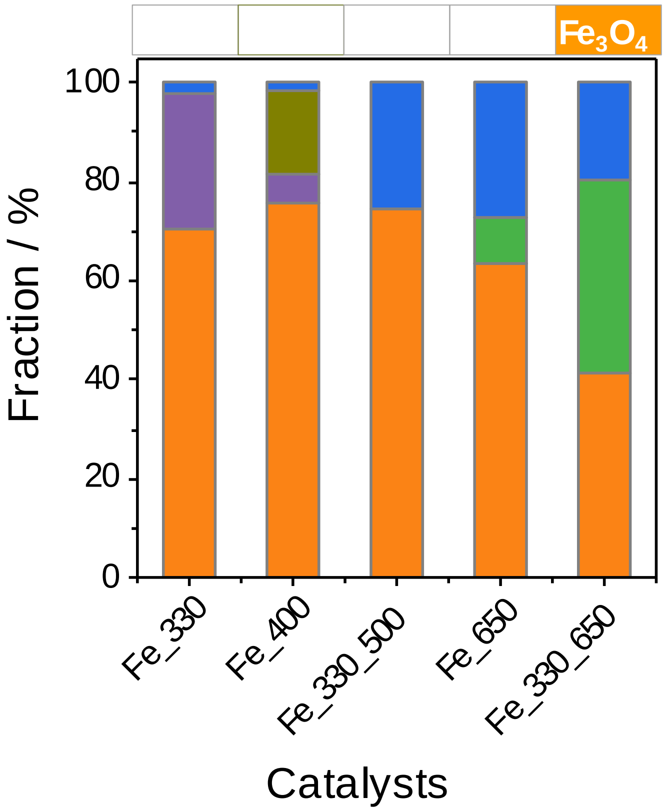
- **Bulk catalysts (promoted)**
- Total pressure
- Promoter/Fe>0.02
- K promoter in combination with transition metals
- **Promoter electronegativity**

olefin/paraffin ratio:

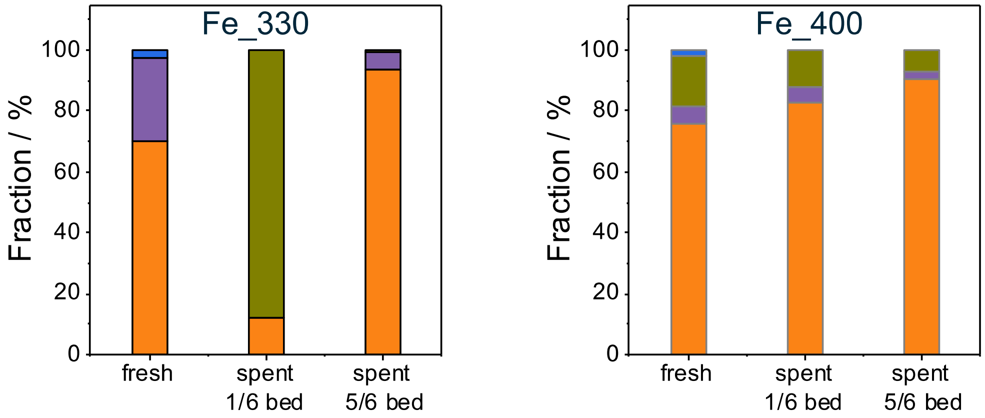
- Bulk catalysts (promoted)
- Kind of iron source
- K or Na promoter in combination with transition metals

Spatial distribution of phase composition is important

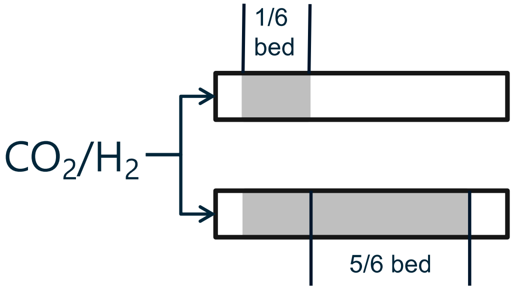
Phase composition of fresh samples



Phase composition of spent samples



Reactor loadings

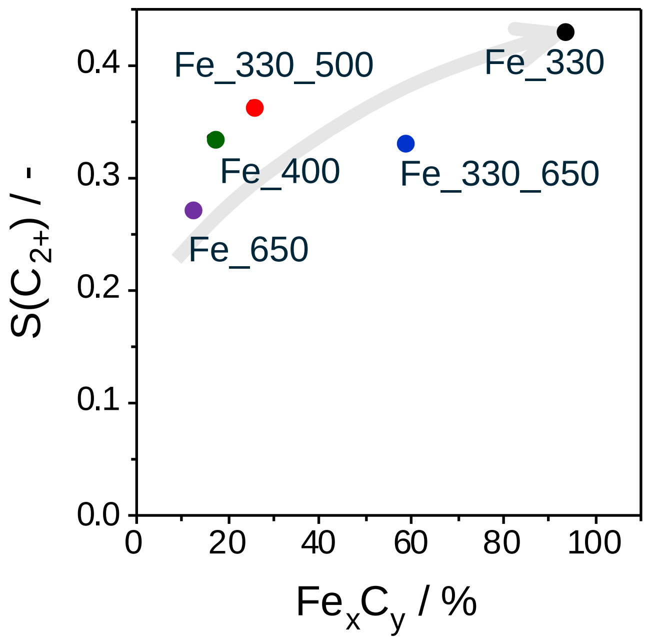


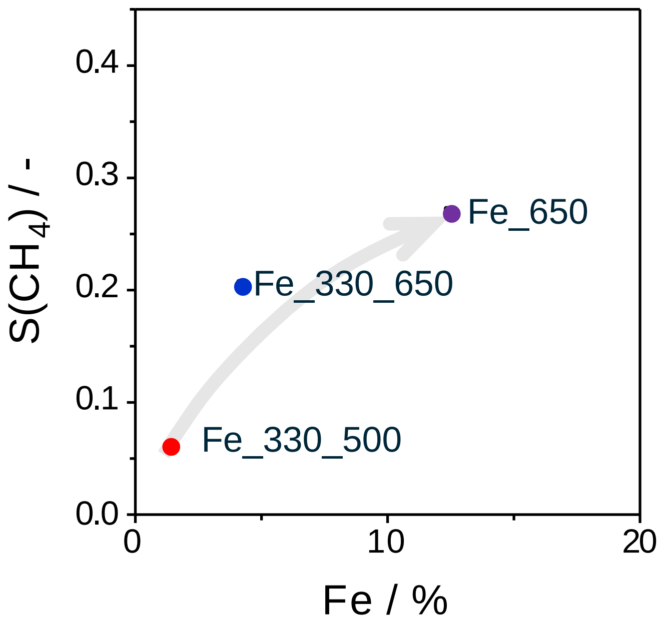
A.S. Skrypnik, ..., EVK., *Appl. Catal. B, 2021,* ***291****, 120121.*

Effect of steady-state composition on product selectivity

Reaction conditions: no treatment, CO_2:H_2=1:3, T=300°C, 15 bar.

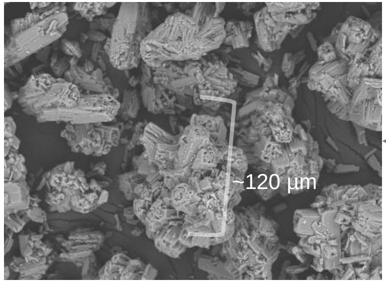
The amount of Fe_xC_y and Fe was determined in catalyst layer required to reach 20% X(CO_2)!

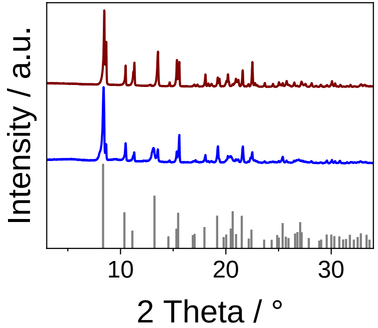


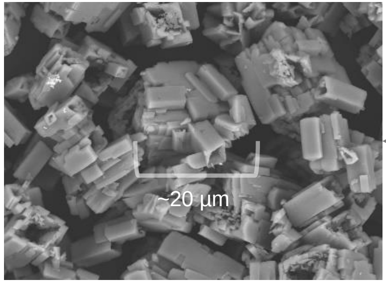


To selectively convert CO_2 into C_{2+}hydrocarbons, Fe_xC_y is required, while metallic Fe should be avoided.

A family of Fe_2O_3 materials







FeC_2O_4_c

Different morphology!

FeC_2O_4 _h

Single phase α-Fe_2O_3

- Fe_c_10nm
- Fe_c_14nm
- Fe_c_19nm
- Fe_c_26nm
- Fe_h_31nm

Size of α-Fe_2O_3 crystallites

Mixed phase α-Fe_2O_3&γ-Fe_2O_3

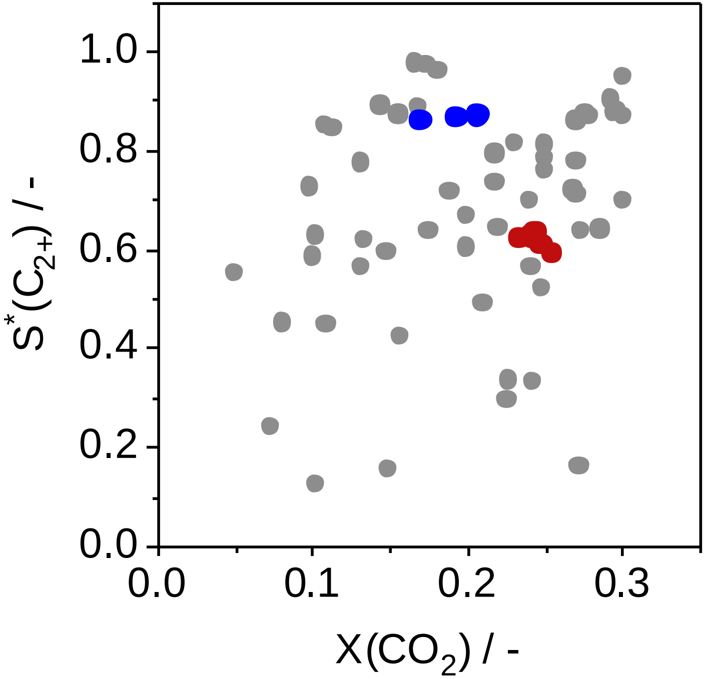
- Fe_h_23%
- Fe_c_53%
- Fe_c_64%
- Fe_c_am
- Fe_h_82%

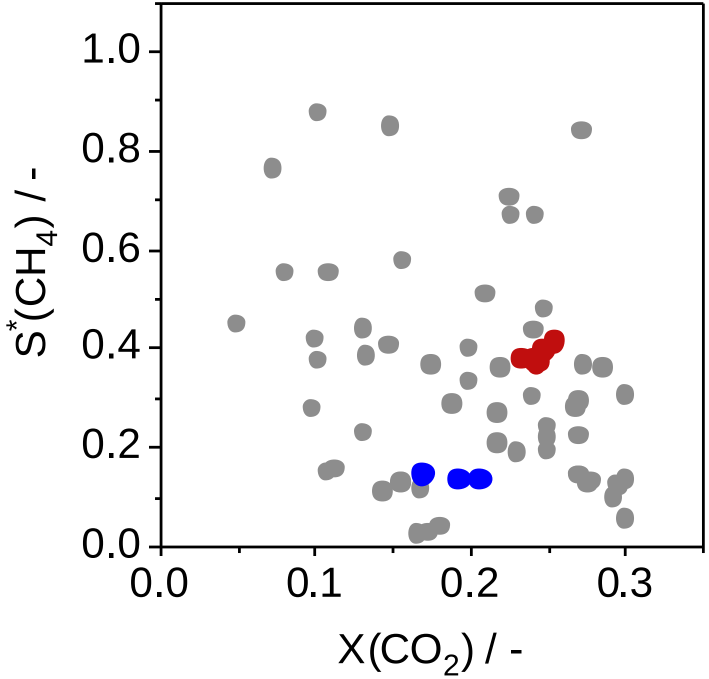
Fraction of α-Fe_2O_3

A.S. Skrypnik, …, EVK., *under review.*

Catalyst performance: benchmarking

Grey symbols stand for best-performing catalysts reported in literature.
Blue and **red** symbols represent the developed Fe_2O_3 catalysts.



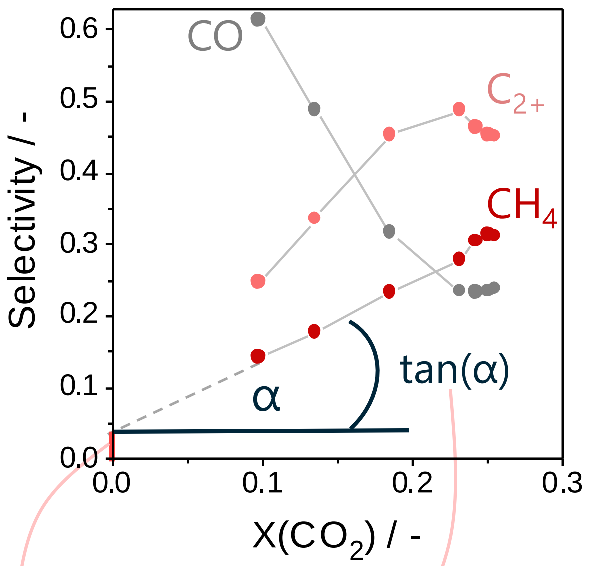


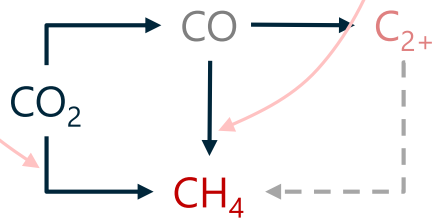
Our unpromoted catalysts perform similar or superior to the state-of-the-art materials.
Why do they differ in their performance?

Scheme of product formation in the course of CO_2 hydrogenation

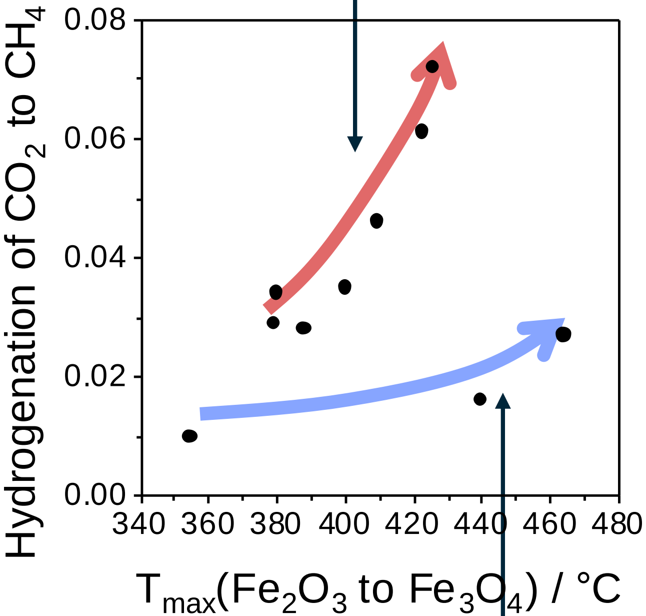
Fe_c_10nm

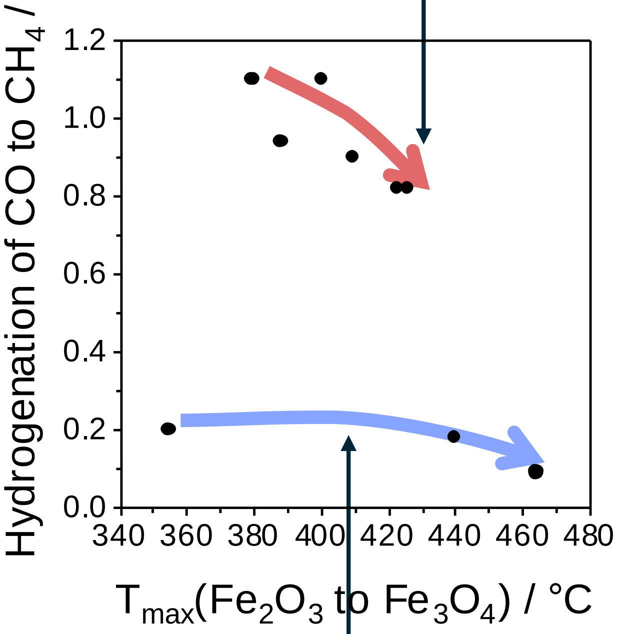
$H_2/CO_2/N_2$=3:1:0.3, 15 bar, 300°C





Prepared from FeC_2O_4_c

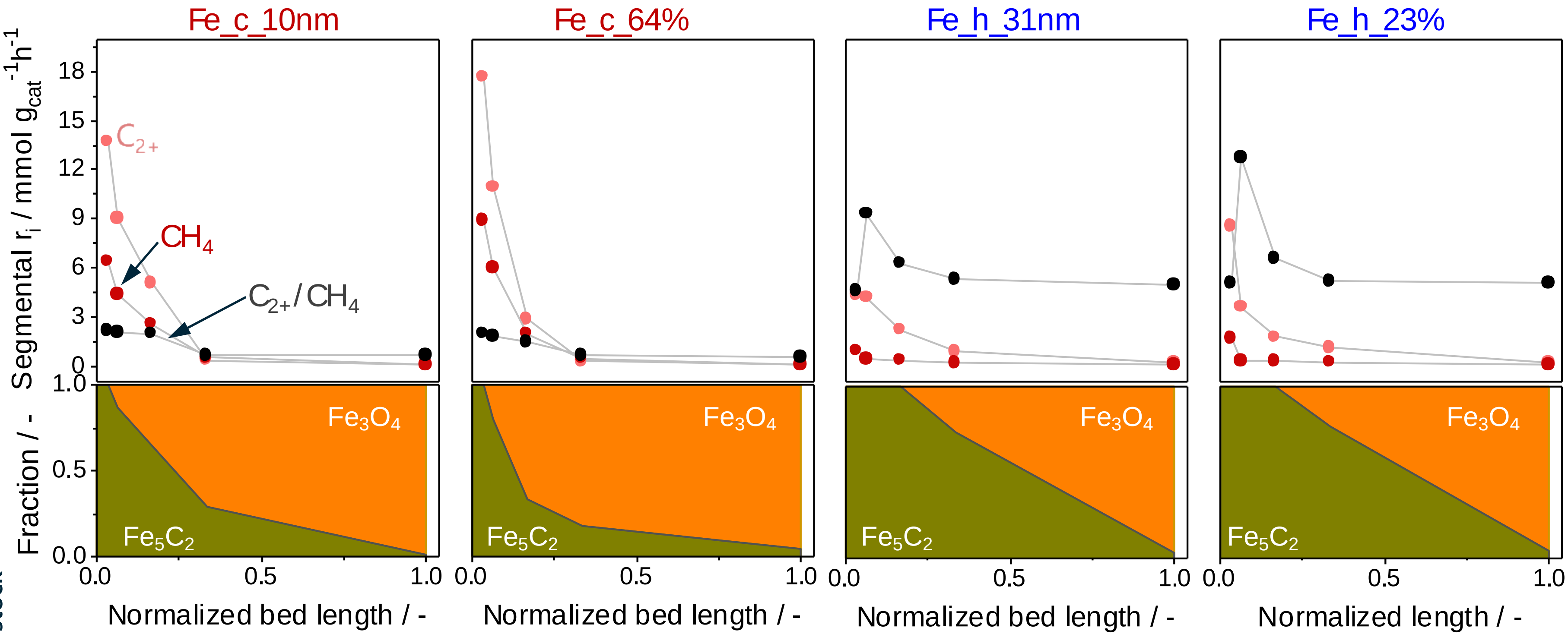




FeC_2O_4 _h

Valid for all catalysts

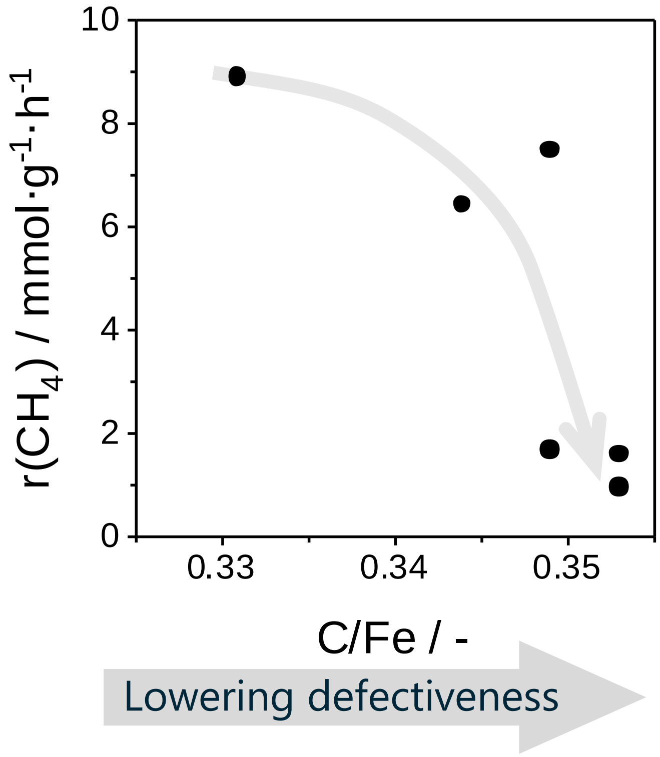
Spatial profiles of reaction rates and catalyst composition

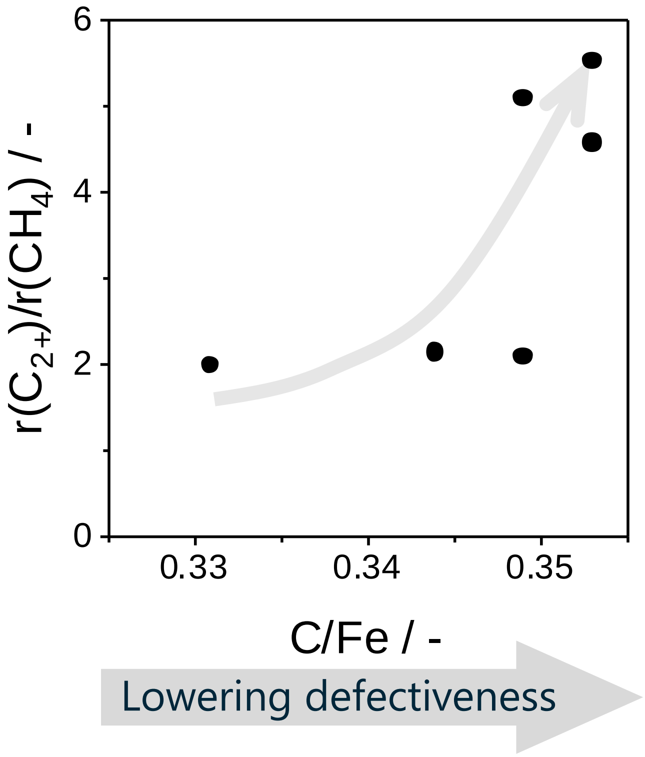


Redox properties of Fe_2O_3 are decisive for the distribution of in situ formed Fe_5C_2 along the catalyst bed.

Defectiveness of Fe_5C_2 and its consequence for product formation

C/Fe ratio in Fe_5C_2 represents its defectiveness.

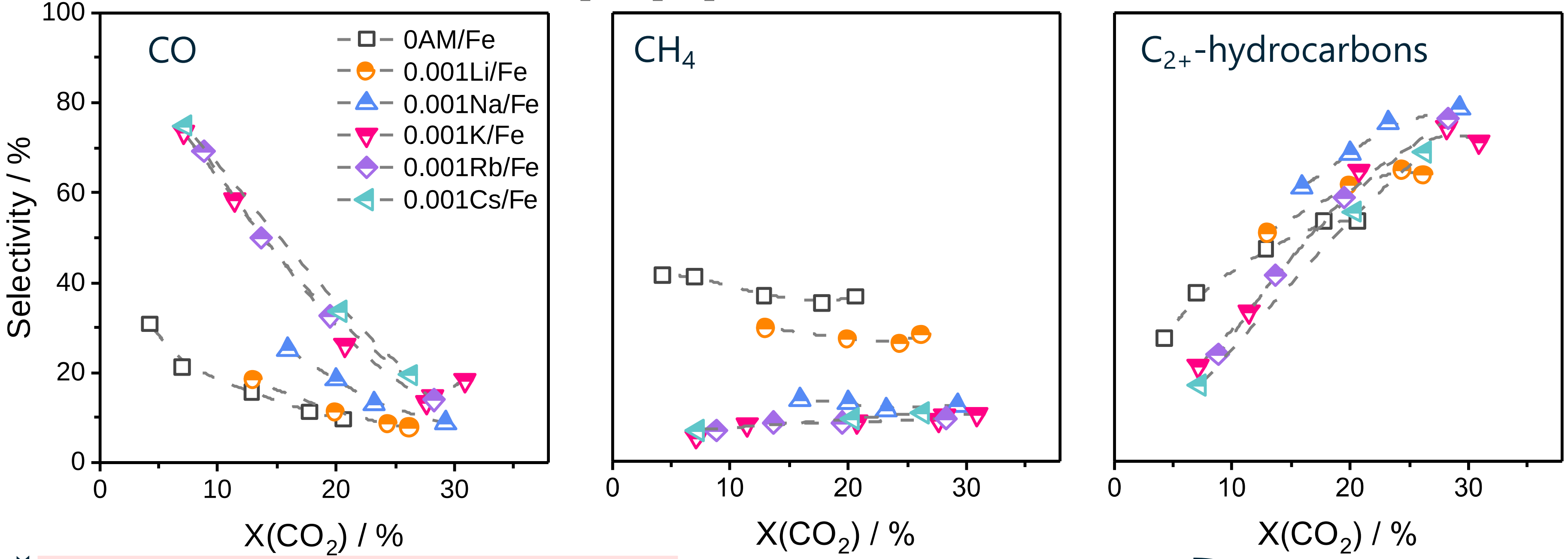


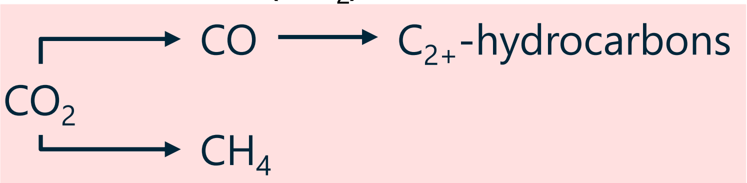


Low defectiveness of Fe_5C_2 is required for selective hydrogenation of CO_2 to higher hydrocarbons.

Selectivity-conversion dependence: effect of alkali metal promoter

$H_2/CO_2/N_2$=3:1:0.3, 15 bar, 300°C





Q. Yang, ..., EVK, AChIE, 2022, doi.org/10.1002/anie.202116517

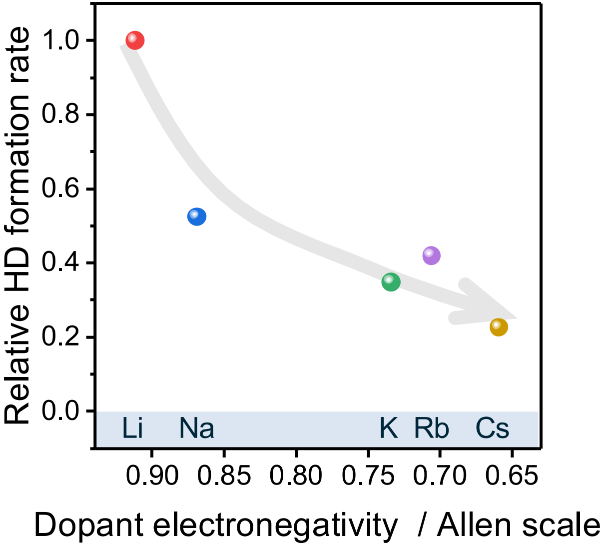
Alkali metals affect:
(i) CO_2 methanation
(ii) CO hydrogenation

Fundamentals behind these effects?

Effects of promoter electronegativity on $H_2/CO_2/CO$ activation

H_2 activation

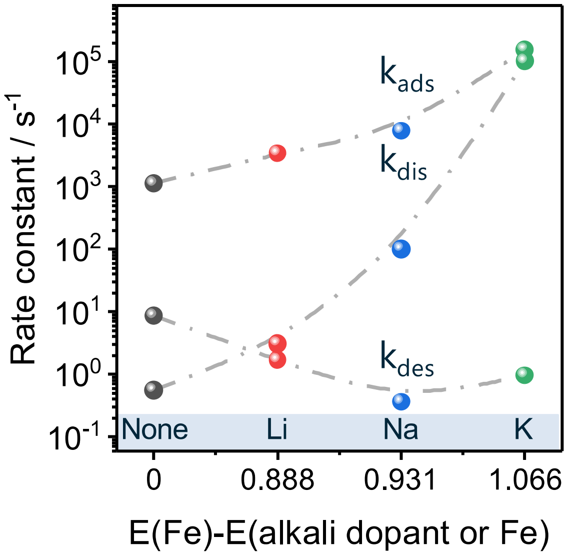
H/D exchange tests



CO_2 activation

$$CO_2 + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} *\text{-}CO_2$$

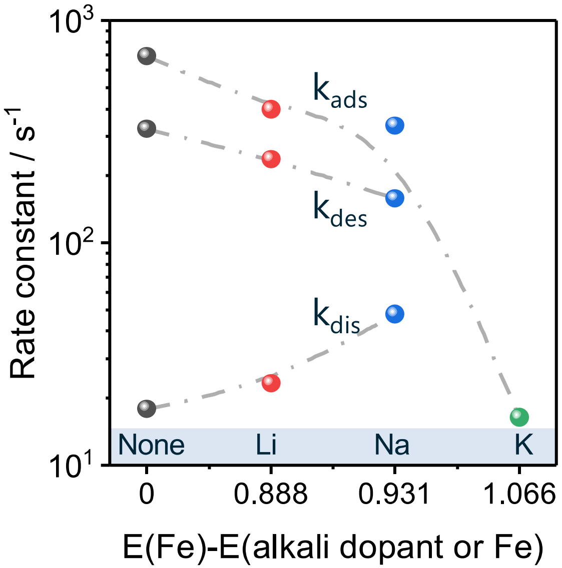
$$*\text{-}CO_2 + * \xrightarrow{k_{dis}} *\text{-}CO + *\text{-}O$$



CO activation

$$CO + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} *\text{-}CO$$

$$*\text{-}CO + * \xrightarrow{k_{dis}} *\text{-}C + *\text{-}O$$



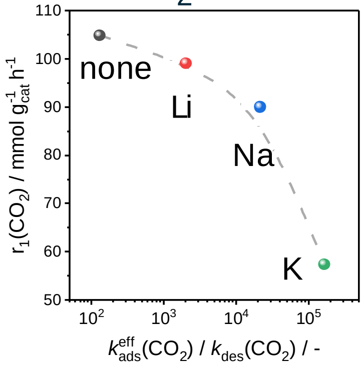
Alkali metal promoters affect electronic properties of iron in iron carbides and accordingly $H_2/CO_2/CO$ activation.

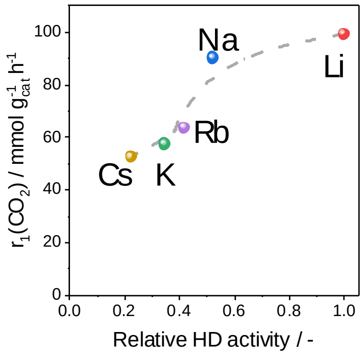
Descriptors affecting CO_2 hydrogenation to higher hydrocarbons

CO/CO_2 activation

H_2 activation

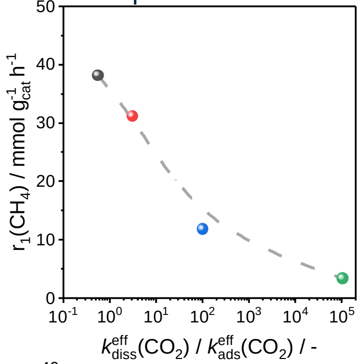
Overall CO_2 conversion

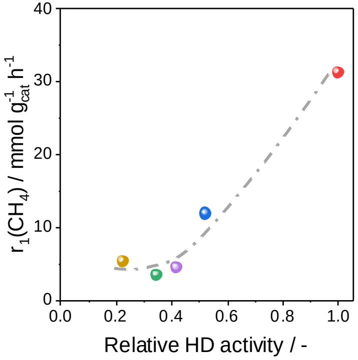




Strong CO_2 adsorption and low ability to activate H_2 are detrimental.

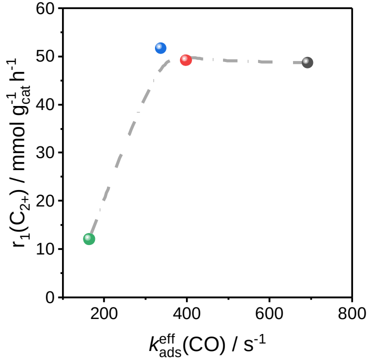
CH_4 formation

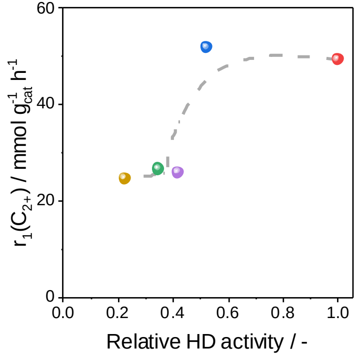




Low ability to split CO_2 and to activate H_2 is required to hinder CH_4 formation.

C_{2+} formation





For C_{2+} formation, an optimal ability for CO and H_2 activation is required.

Summary

- Reducibility of iron oxides is relevant for the formation of Fe_xC_y with certain properties for $H_2/CO/CO_2$ activation, which are relevant for product selectivity.

- The selectivity to C_{2+}-hydrocarbons over unpromoted Fe-based catalysts correlates with iron carbides fraction. Metallic Fe should be avoided.

- Alkali metal promoters for Fe_2O_3 affect electronic properties of Fe in Fe_5C_2, which are important for $CO/CO_2/H_2$ activation and for product selectivity in CO_2 hydrogenation.

Acknowledgement

Former and present members of CO_2 team

- Dr. S. Ahlers
- Dr. D. Heyl
- Dr. V. Kondratenko
- Dr. S. Mavlyankariev
- Dr. D. Zhao
- A. Skrypnik
- D. Troung
- Q. Yang
- L. Kraußer
- N. Ortner

Cooperation partners on CO_2 research

- LIKAT departments: “Analytics”, “Catalytic in situ studies”, “Heterogeneous Catalytic Processes”, “Catalyst Discovery and Reaction Engineering”
- Prof. J.-D. Grunwaldt, KIT
- Prof. M. Behrens, University of Kiel
- Dr. A. Matvienko and S. Petrov, Institute of Solid-State Chemistry and Mechanochemistry
- Dr. V. Bychkov, Semenov Institute of Chemical Physics

Financial support

- **DFG (German research foundation) SPP2080**
- DAAD (German Academic Exchange Service)
- BMBF (Hythanol eCO_2)
- Leibniz Society
- The Land of Mecklenburg-West Pomerania