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# PSYCHE

**Avec le soutien du Fonds européen de développement régional**
**Met steun van het Europees Fonds voor Regionale Ontwikkeling**

# From $CO_x$ to Light Olefins:

# Computer-Aided Catalyst Design

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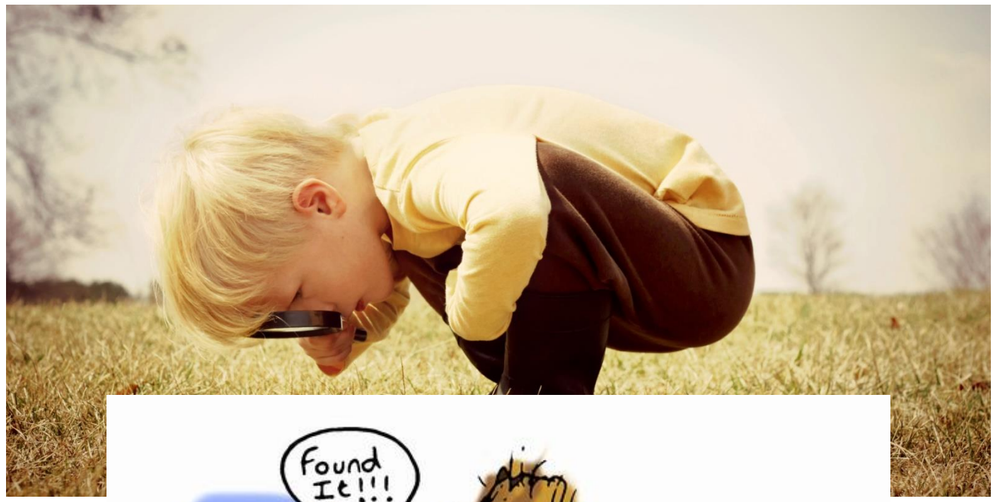
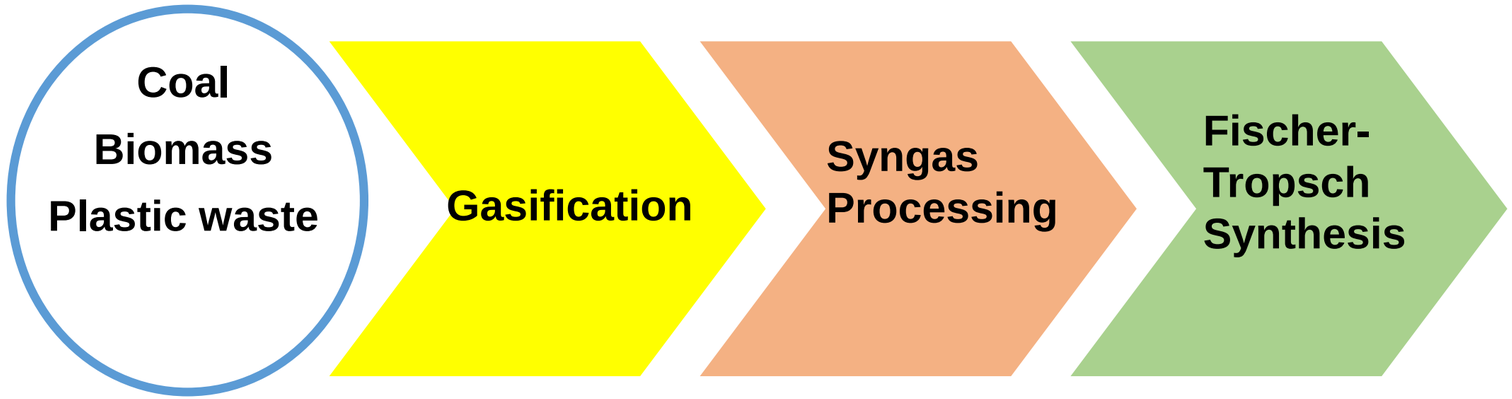
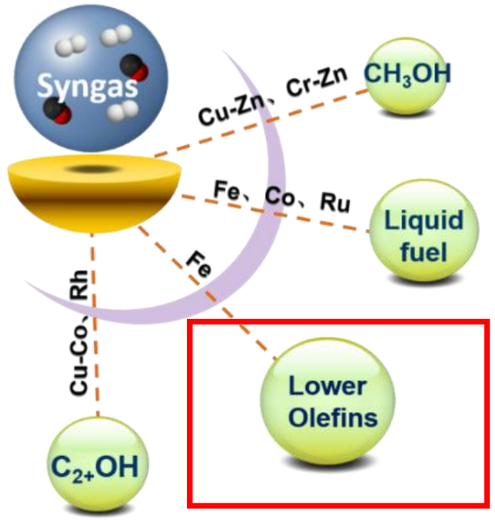
# ideal catalyst: needle in a haystack




# Fischer Tropsch Synthesis

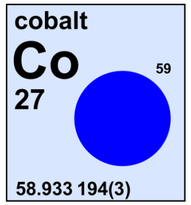


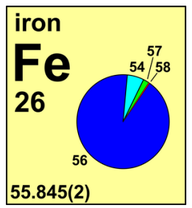

- carbon monoxide (CO) and hydrogen (H2), (syngas) conversion into hydrocarbons.

  $(2n+1)\ H_2 + n\ CO \rightarrow C_n\ H_{(2n+2)} + n\ H_2O$

  $CO + H_2O \rightarrow H_2 + CO_2$




- insight in reaction chemistry and process via modelling:
  - ✓ elementary steps
  - ✓ machine learning



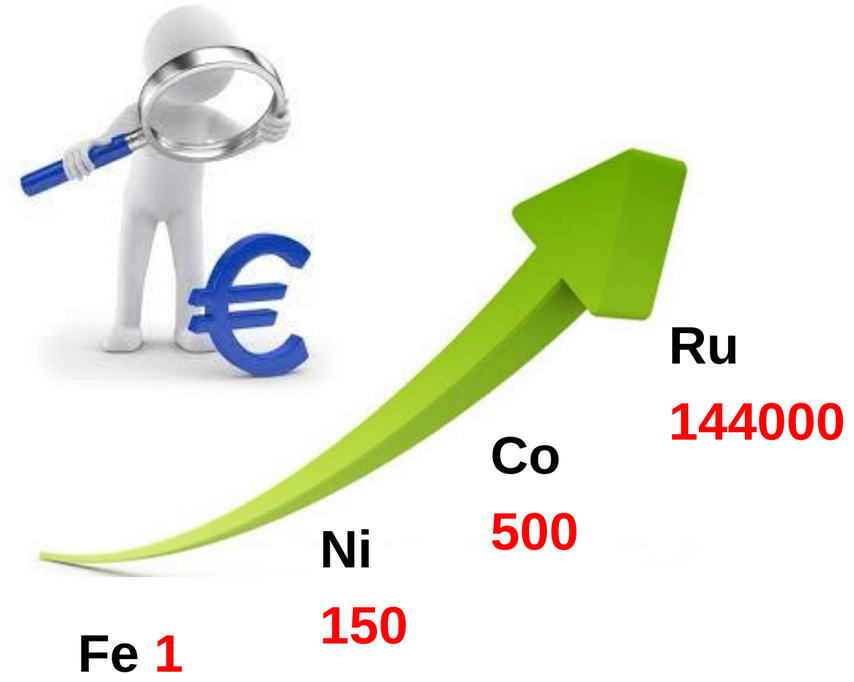
# choice of active metal

**Metals of VIII group of Periodic Table**

***CO dissociation = hydrocarbons***

| | | | | | |
|---|---|---|---|---|---|
| Cr | Mn | **Fe** | **Co** | **Ni** | **Cu** |
| Mo | Tc | **Ru** | **Rh** | **Pd** | **Ag** |
| W | Re | Os | **Ir** | **Pt** | **Au** |

***no CO dissociation = methanol***




| | |
|---|---|
| **Fe** | **gasoline range, olefins** |
| **Co** | **diesel and waxes** |
| **Ru** | **too expensive and difficult too handle** |
| **Ni** | **methanation** |
| **Rh** | **ethanol, $C_2$ oxygenates** |
| **Pd** | **methanol** |
| **Cu** | **methanol** |

***Cheap and abundant metal!***

Prices consulted on 02/12/21
https://www.londonstockexchange.com/

# choice of promoters

✓***Promoters selection*** **is an important point in the design of efficient catalysts**

✓**Different elements were chosen as promoters for CO and $CO_2$ hydrogenation**

| Soldering promoters | | | |
|---|---|---|---|
| Bi | Pb | Sb | Sn |

| Basic promoters | | | | |
|---|---|---|---|---|
| K | Cs | Mg | Ba | Ca |

| Multiple oxidation states | | | | | |
|---|---|---|---|---|---|
| Mo | Cr | W | Ce | V | Mn |

| Other metallic promoters | | | | |
|---|---|---|---|---|
| In | Zn | Ga | Nb | Cu |

# experimental search for  best catalysts

***Determination of active species (XAS,Mössbauer, NAP-XPS, etc)***

**Characterization**

***Under optimized conditions***

***FINAL GOAL!***

***Activity***
***Selectivity***
***Stability***

**Promoters**

**Fe-based catalysts**

**Direct olefins production**

***Right support for CO and $CO_2$ reaction***

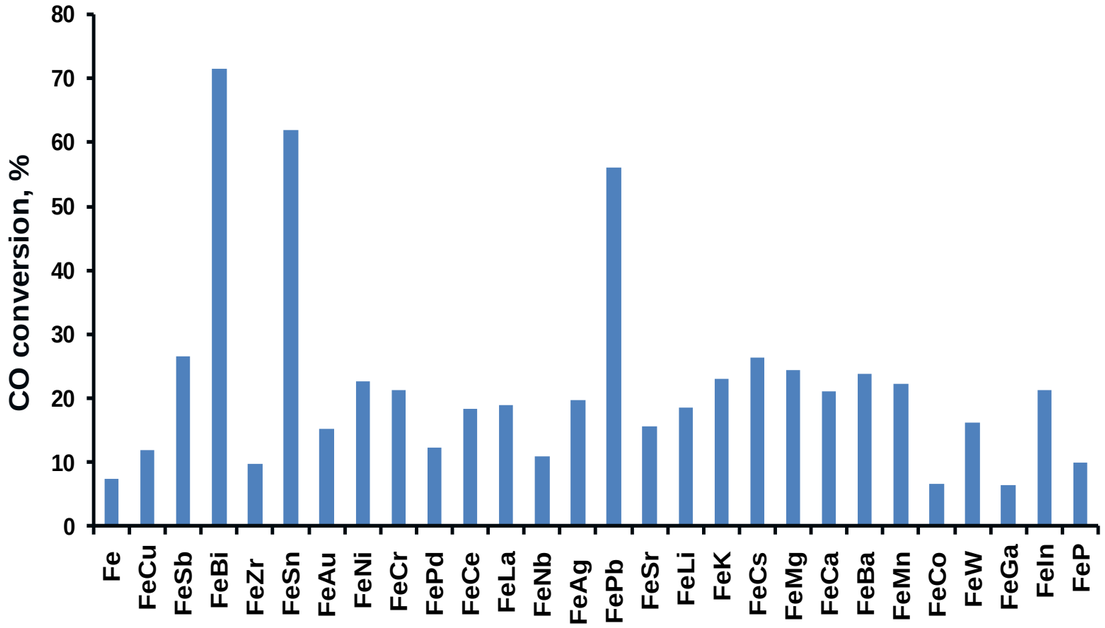
**Support**

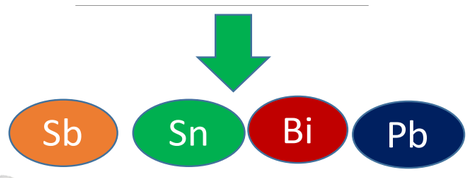

Avantium Flowrence
High throughput test
16 parallel reactors

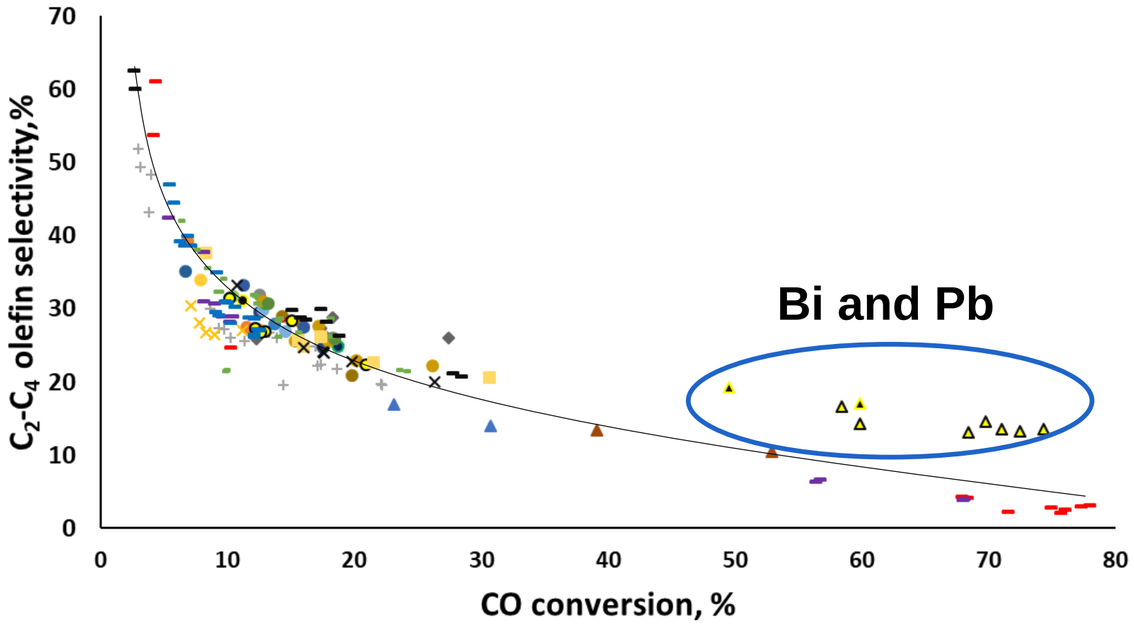
# light olefin synthesis from CO

- **Fe/$SiO_2$ catalyst was used as reference**
- **HTE used to evaluate 27 promoters**

**T= 350 °C, $H_2$/CO= 1, P= 10 bar**




- **Maximum olefins selectivity was obtained a lower CO conversion**
- **Bi and Pb show higher olefin conversion at similar conversion levels compared to other promoters**

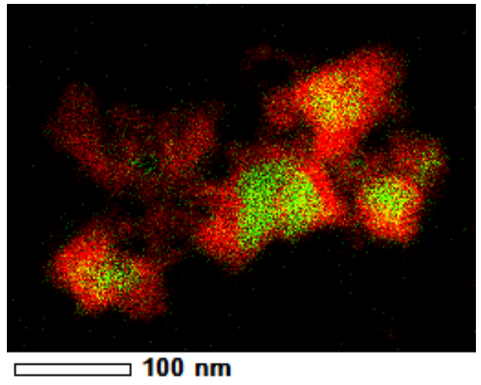
Barrios A., Bang G., Yuan L., Peron D., Petr. A., Virginie M., Wojcieszak R., Thybaut J., Ordomsky V.., Khodakov A. *Identification of efficient promoters and selectivity trends in high temperature Fischer-Tropsch synthesis over supported iron catalysts*. Appplied Catalyisis B: Environmental, 2020, 273.

# summary: light olefin synthesis from CO

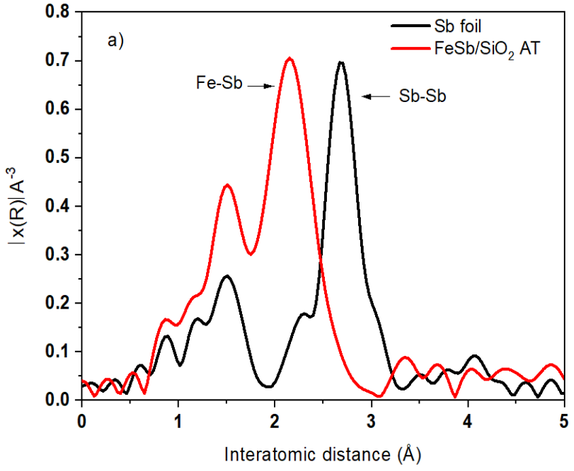
- **Promotion with soldering metals (Sn, Sb and Bi)**
- **Diffusion on catalyst surface**
- **Strong Fe-promoter interaction**

**Iron carbides formation was systematically observed by different techniques (XRD, Mössbauer, NAP(XPS) and Magnetization**

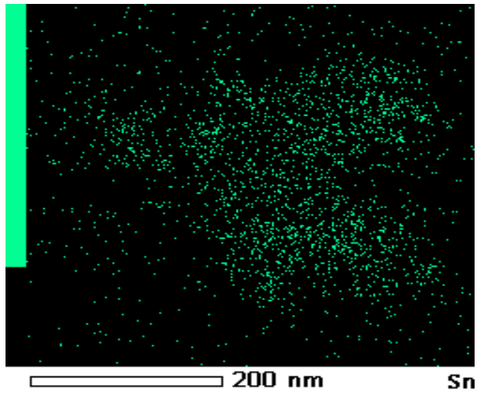
**core-shell structures**



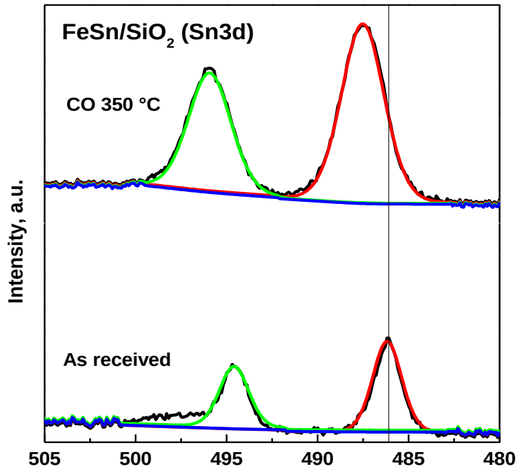

**Alloy formation**




**Close to FeNPs**

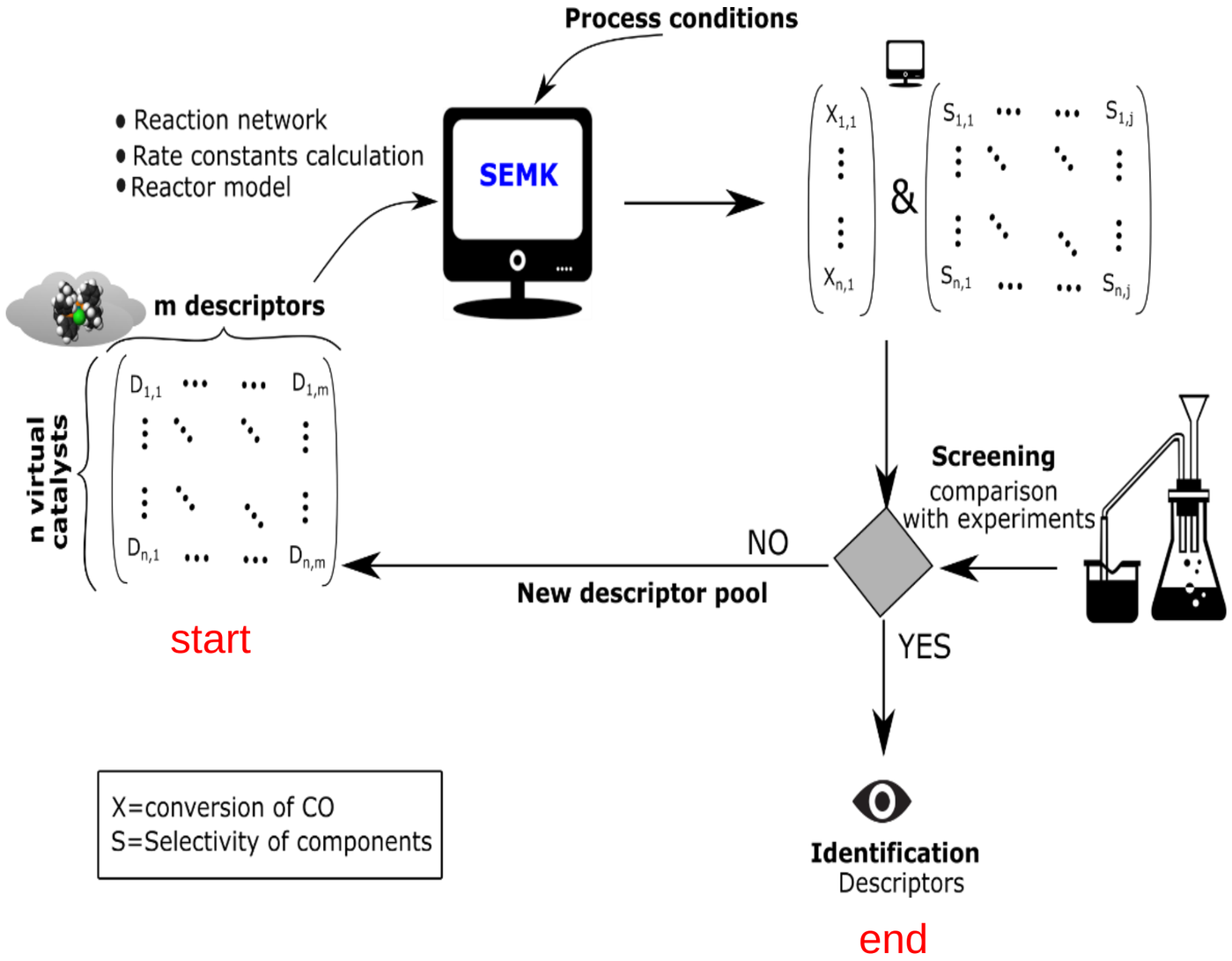



**redispersion**




**TOF increases because of close interaction of active sites with the promoters**

# virtual catalyst design




**SEMK framework :**

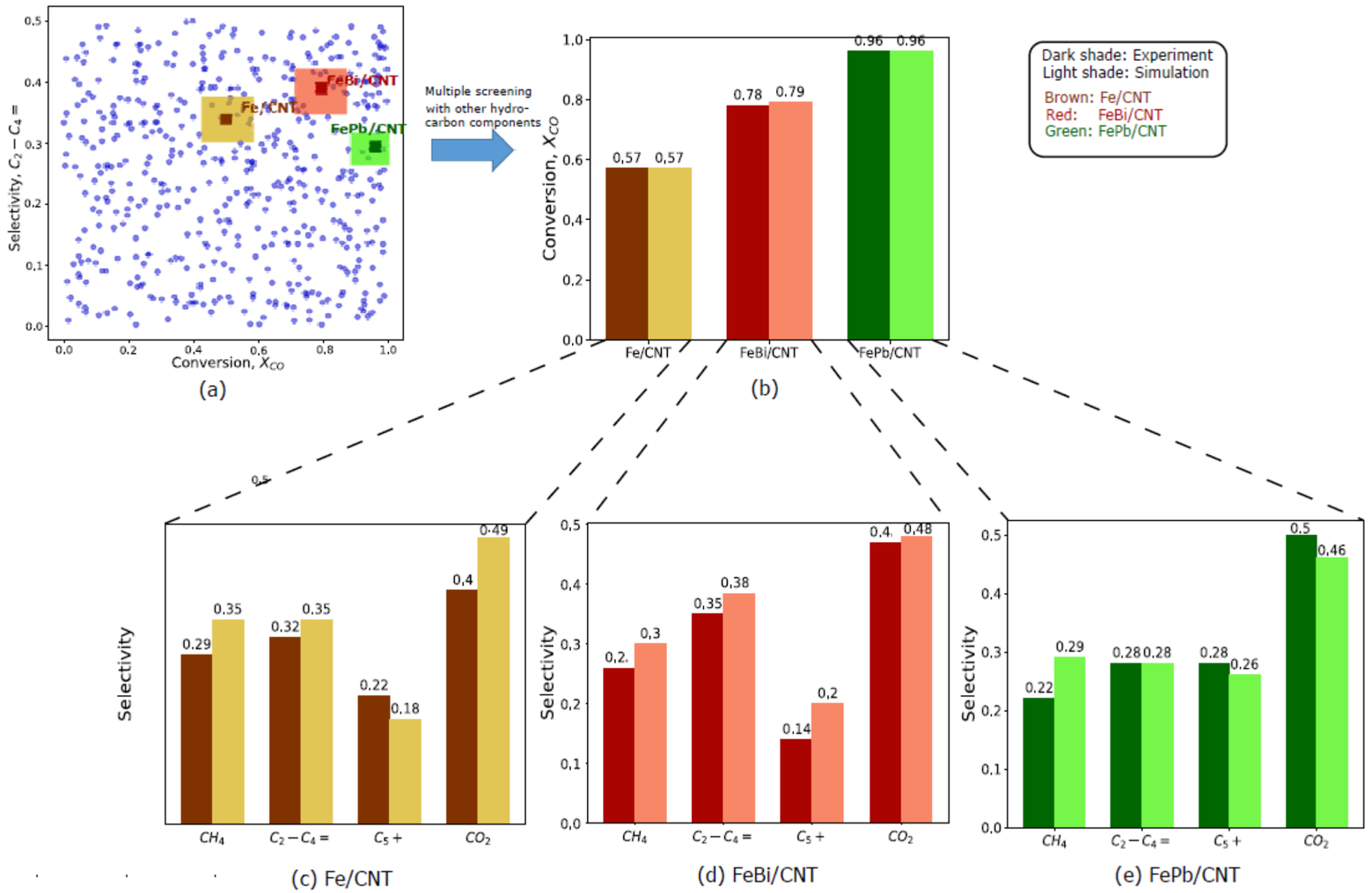
- network generation for FTS
- kinetic and catalyst descriptors.

**virtual catalyst design :**

- generation of virtual catalyst library.
- numerical simulation using SEMK.
- comparison and screening with experimental results (iterative process).

*Pirro et al. Catalysis Science & Technology **9** 3109 (2019)*

# identification of descriptors




| *Reaction family/elementary reaction* | $E_a^{for}$ (kJ/mol) |
|---|---|
| *Reactant adsorption* | |
| 1. $H_2 + 2M \rightleftharpoons 2MH$ | 0 |
| 2. $CO + 2M \rightleftharpoons MMCO$ | 0 |
| *Initiation reactions* | |
| 3. $MMCO + 3M \rightleftharpoons MMMC + MMO$ | $56.81 \pm 0.53$ |
| 4. $MMMC + MH \rightleftharpoons MMMCH + M$ | $77.66 \pm 0.70$ |
| 5. $MMMCH + MH \rightleftharpoons MMCH_2 + 2M$ | $11.94 \pm 0.10$ |
| 6. $MMCH_2 + MH \rightleftharpoons MCH_3 + 2M$ | $61.88 \pm 0.50$ |
| *Chain growth* | |
| 7. $MC_nH_{2n+1} + MMCH_2 \rightleftharpoons MC_{n+1}H_{2n+3} + 2M$ | $44.79 \pm 0.43$ |
| *Formation of alkanes* | |
| 8. $MC_nH_{2n+1} + MH \rightleftharpoons C_nH_{2n+2} + 2M$ | $117.75 \pm 0.67$ |
| *Formation of metal alkenes* | |
| 9. $MC_nH_{2n+1} + M \rightleftharpoons MC_nH_{2n} + MH$ | $96.27 \pm 0.50$ |
| *Alkene desorption* | |
| 10. $MC_nH_{2n} \rightleftharpoons C_nH_{2n} + M$ | 62.09 (n=2)<br>59.08 (n=3-10) |
| *Formation of carbon dioxide* | |
| 11. $O-CHO-M + M-OH + O \rightleftharpoons O-COOH-M + O-H + M$ | $138.95 \pm 1.15$ |
| *Water formation* | |
| 12. $MMO + MH \rightleftharpoons MOH + 2M$ | $103.80 \pm 0.96$ |
| 13. $MOH + MH \rightleftharpoons H2O + 2M$ | $86.22 \pm 0.62$ |

| Atomic Chemisorption enthalpies | Fe/CNT (kJ/mol) | FeBi/CNT (kJ/mol) | FePb/CNT (kJ/mol) |
|---|---|---|---|
| $Q_H$ $(Fe_xC-H)$ | 249.5 | 247.7 | 248.4 |
| $Q_C$ $(Fe_xC-C)$ | 644.1 | 632.1 | 641.5 |
| $Q_O$ $(Fe_xC-O)$ | 601.0 | 589.1 | 577.1 |

*Gu et al. Applied Catalysis B: Environmental **234**, 153 (2018).*

*Chakkingal et al. Chemical Engineering Journal **419**, 129633 (2021)*

# identification of optimal catalyst descriptors

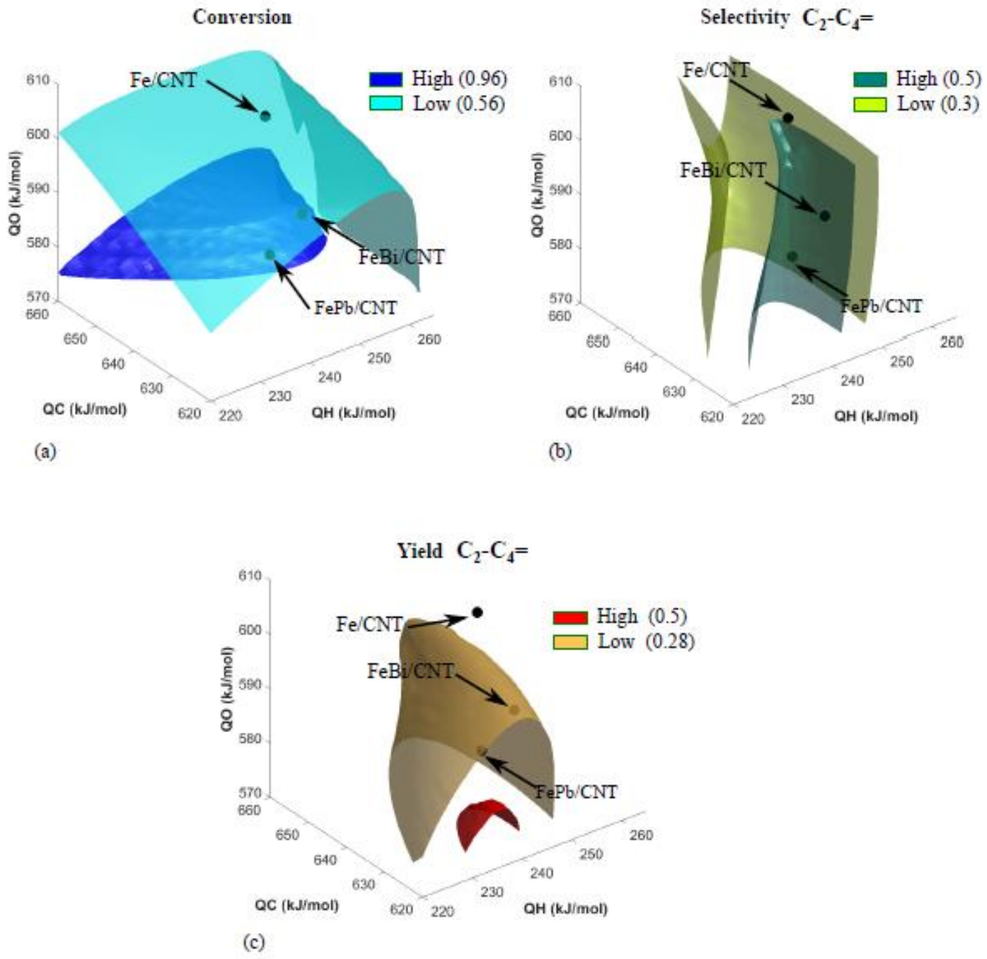


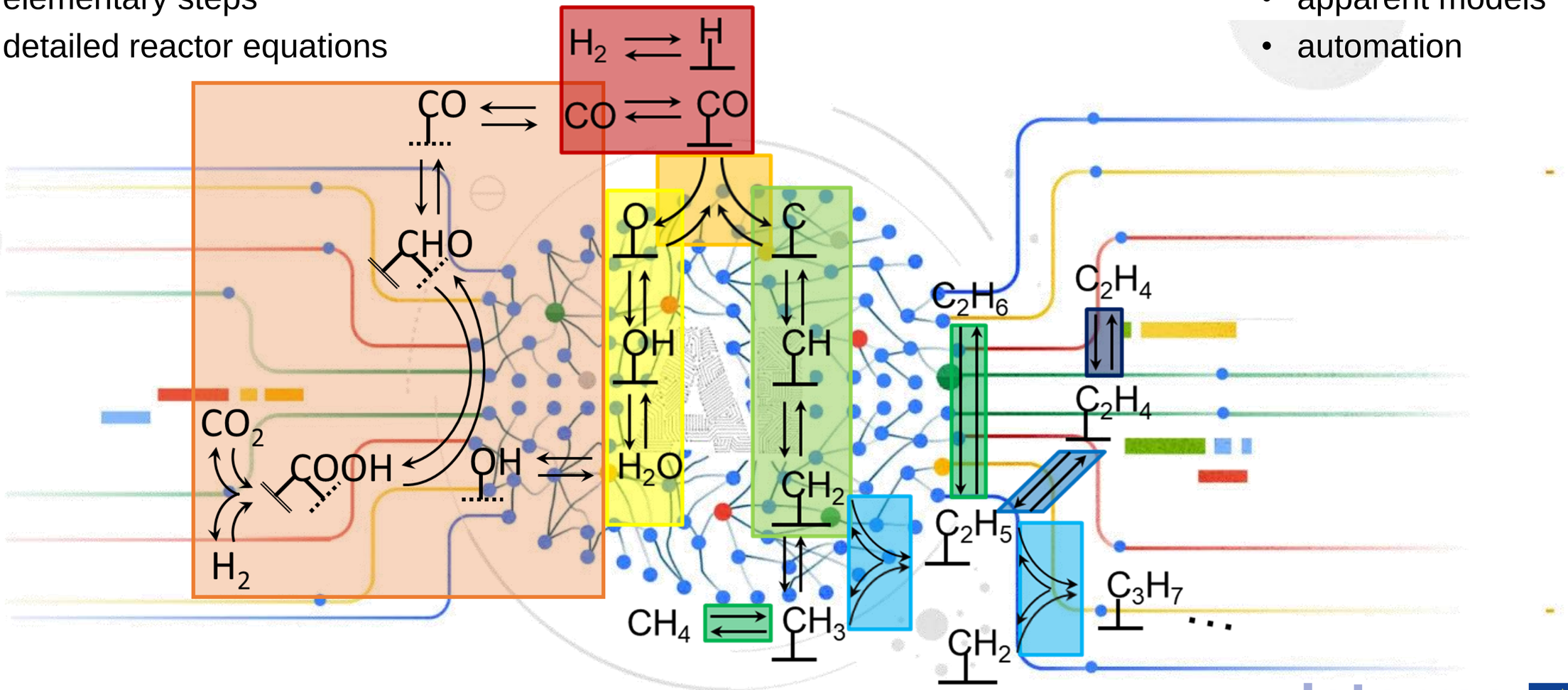

Fig: Iso-surfaces of conversion, light olefin selectivity and yield.

- 3D descriptor spaces representing conversion, selectivity & yield
- experimentally observed yields:
  - Fe/CNT: 20%
  - FeBi/CNT: 27%
  - FePb/CNT: 30%
- maximum achievable light olefin yield: 50%
  - $Q_H \approx 234$ kJ/mol
  - $Q_C \approx 622$ kJ/mol
  - $Q_O \approx 576$ kJ/mol

*Chakkingal et al. Chemical Engineering Journal **419**, 129633 (2021)*

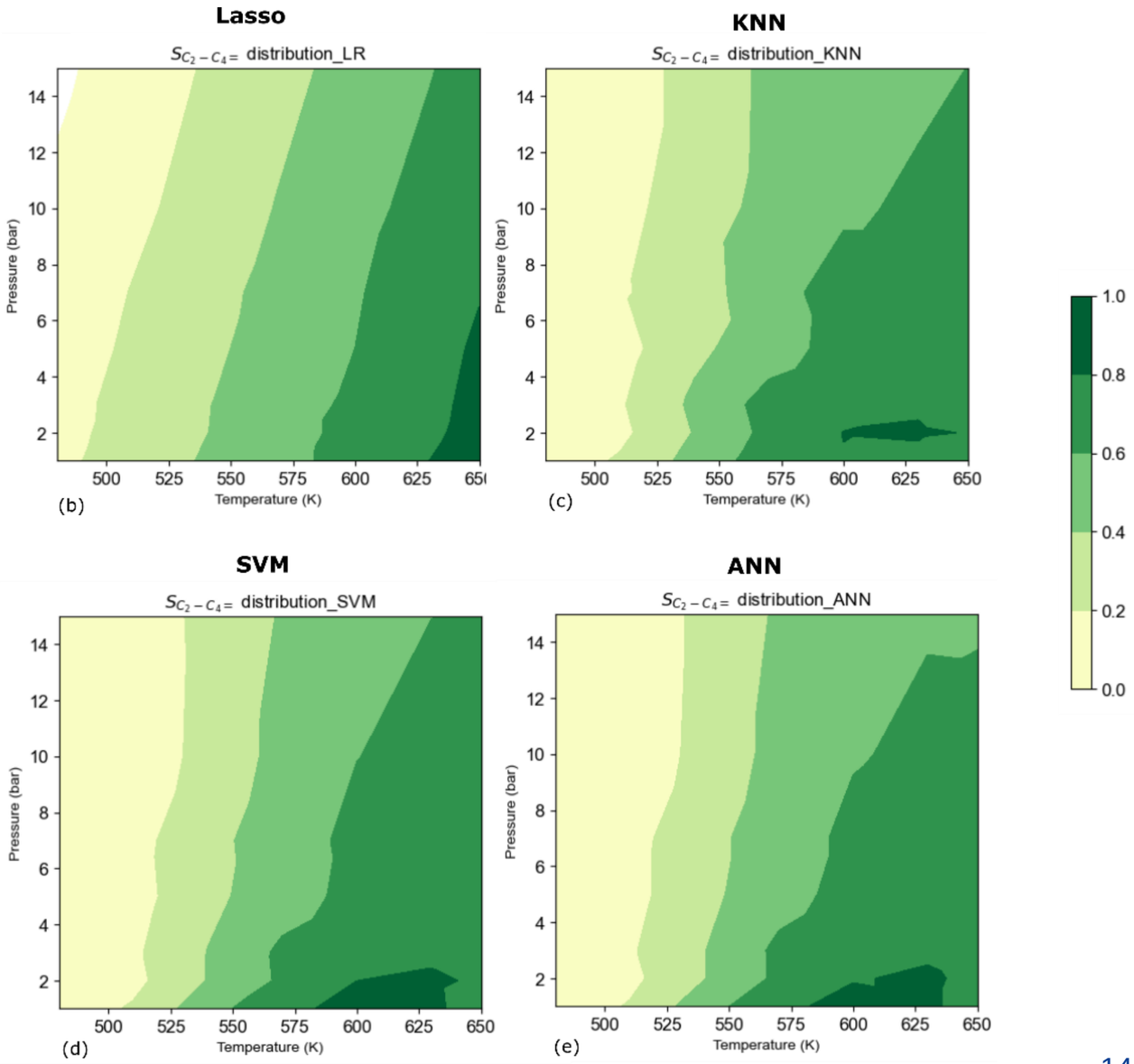
# balance between effort and insight

- microkinetic model
  - elementary steps
  - detailed reactor equations
- machine learning
  - apparent models
  - automation

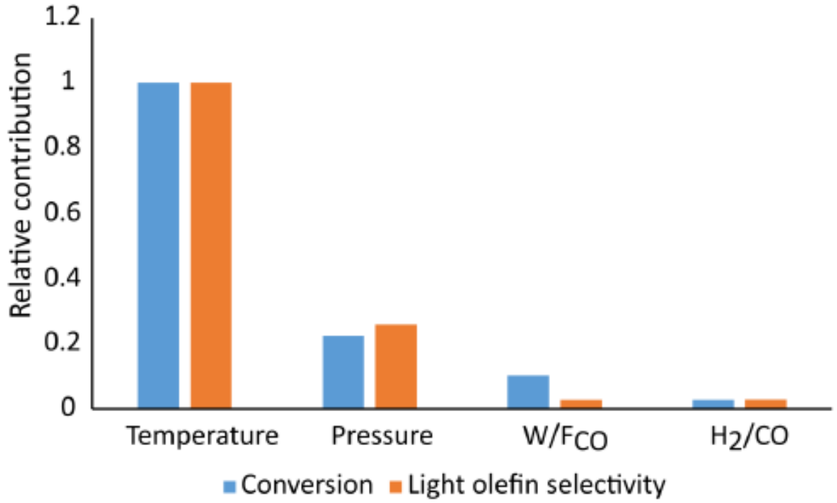


# light olefin selectivity

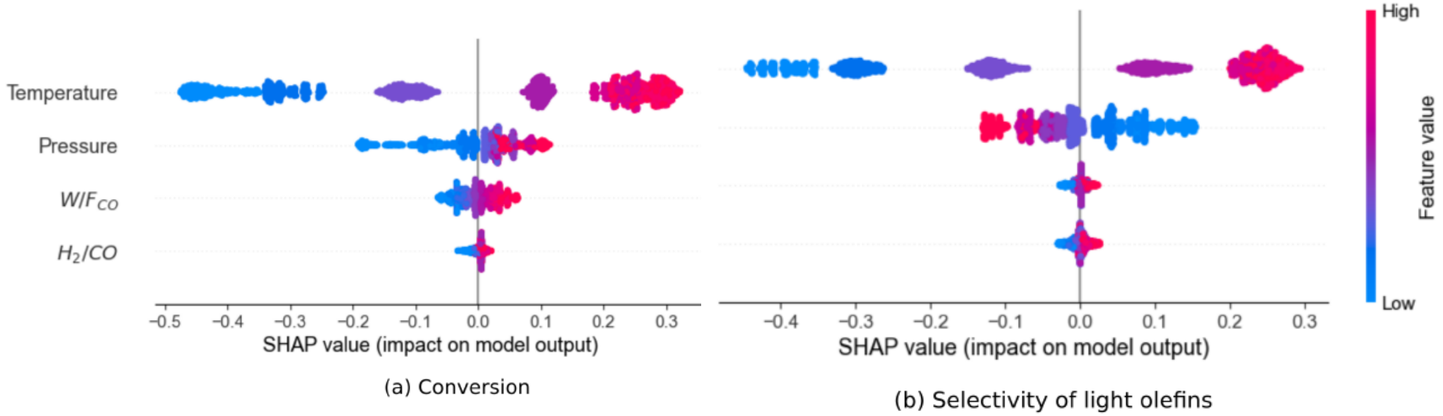
- light olefin selectivity more pronouncedly nonlinear with temperature and pressure
- lasso regression, but also kNN unable to capture these  nonlinearities
- SVM and ANN predict the nonlinear relation accurately.



# relative importance (Shap)

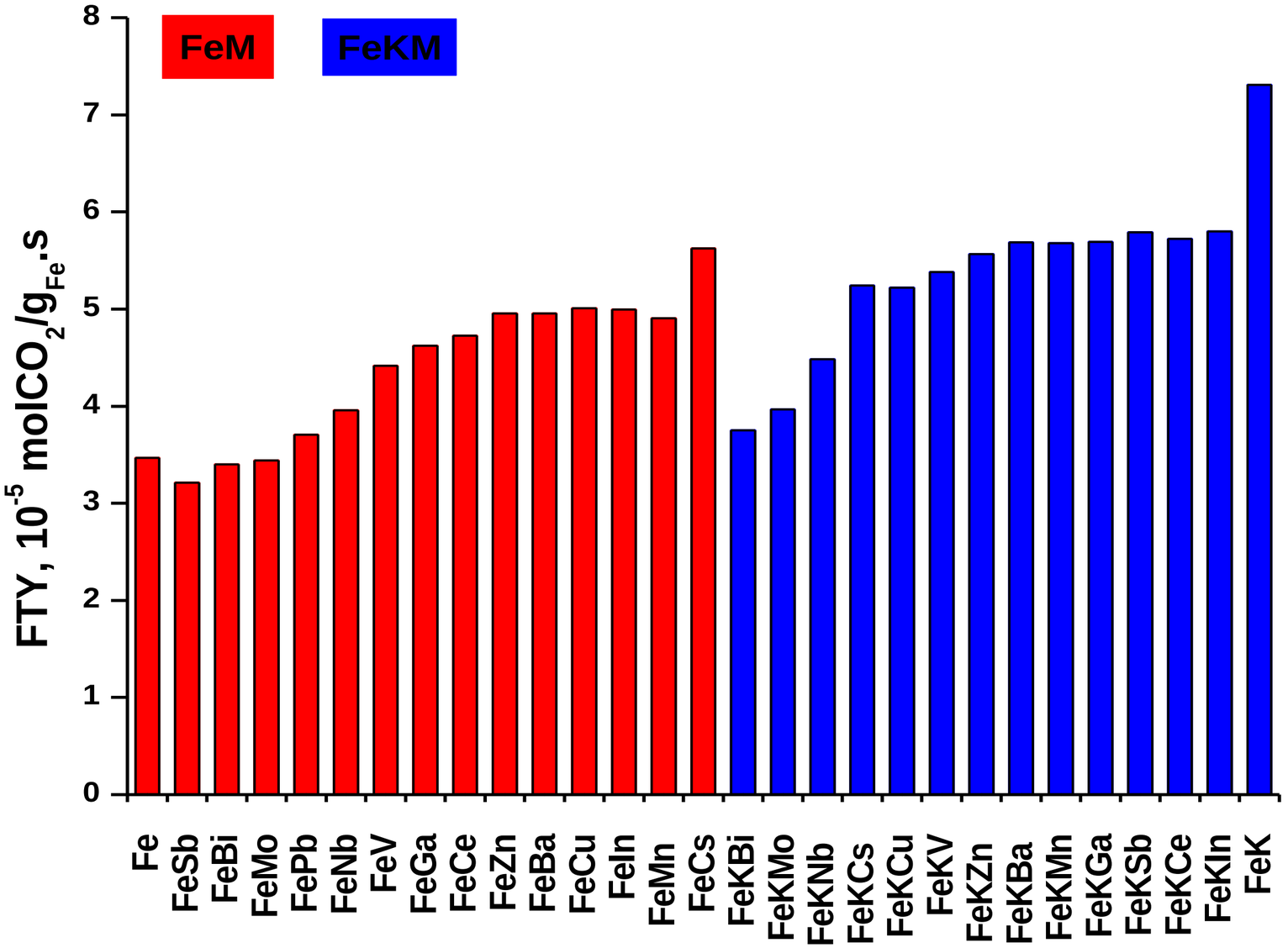



- temperature (1x) and pressure (0.22-0.26x) are most influential (both conversion and light olefin selectivity)
- conversion: space time (0.1x) over syngas ratio (0.03x).
- light olefin selectivity: syngas ratio (0.03x) and space-time (0.03x).




*Chakkingal et al. Chemical Engineering Journal revised version submitted (2022)*

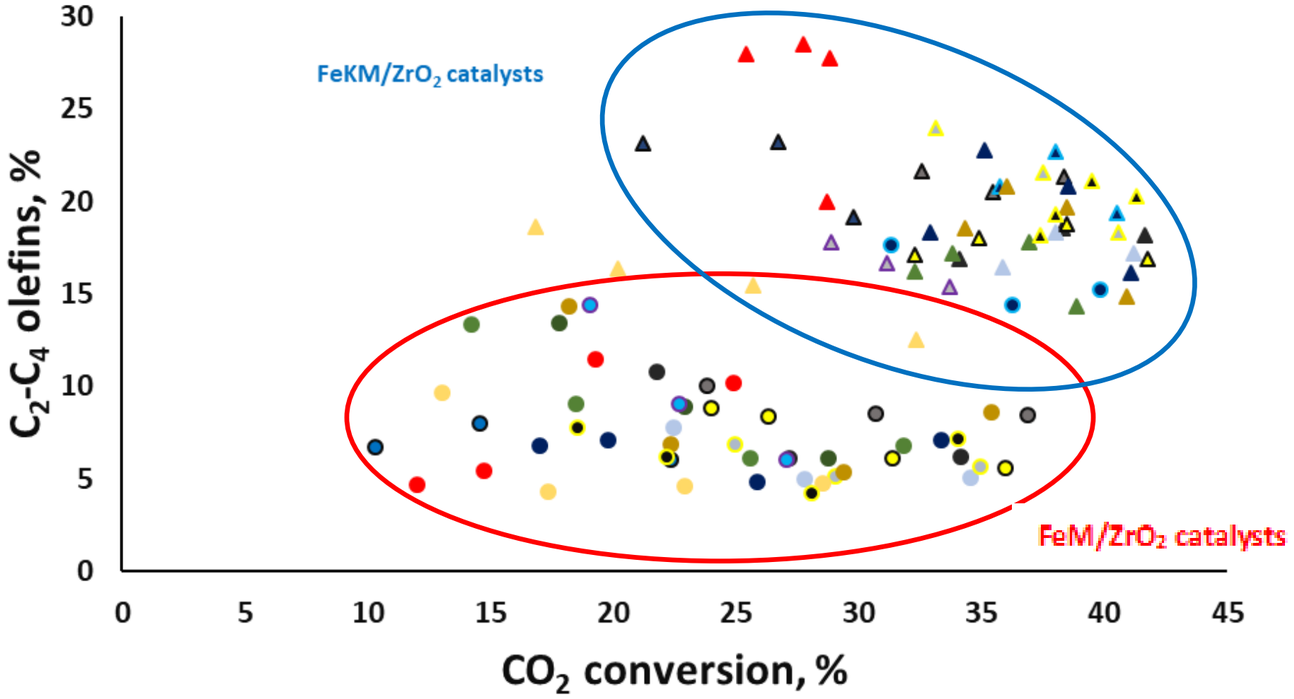
# light olefin synthesis from $CO_2$

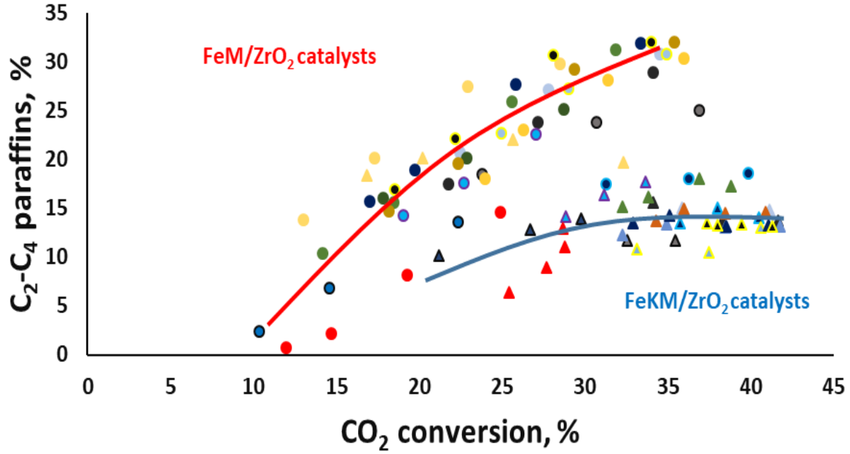


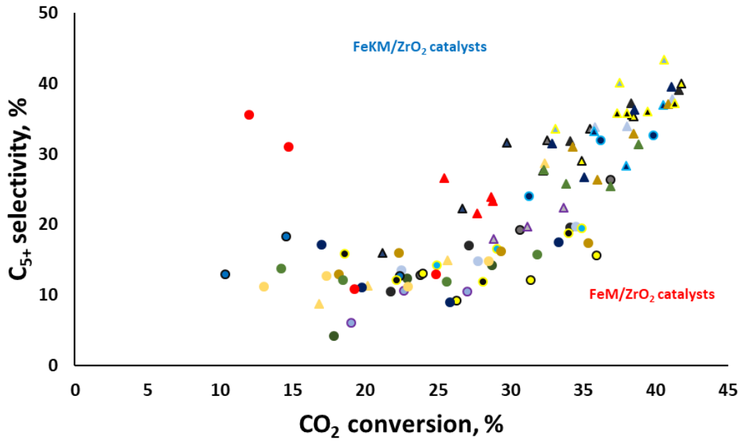

**T= 350 °C, $H_2$/CO= 3, P= 10 bar**

- **$Fe/ZrO_2$ was used as reference**
- **Promoted catalyst show higher activity than reference one**
- **More pronounced for the K promoted catalyst**

# light olefin synthesis from $CO_2$



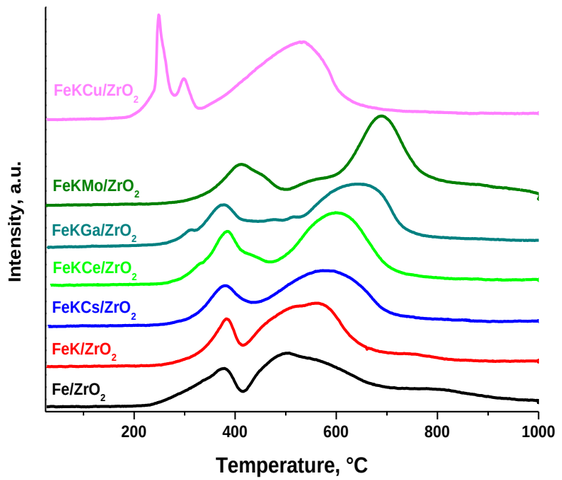




- **Catalysts promoted with K showed the highest olefin selectivities**
- **Most selective catalysts to lower olefins were selected to be further studied**

# summary: catalyst parameters for light olefin synthesis from $CO_2$

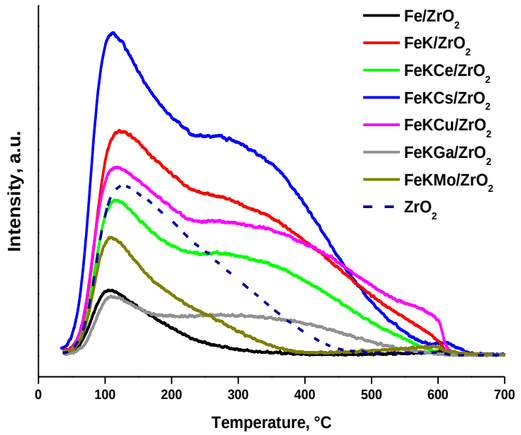
## Better Fe Reducibility



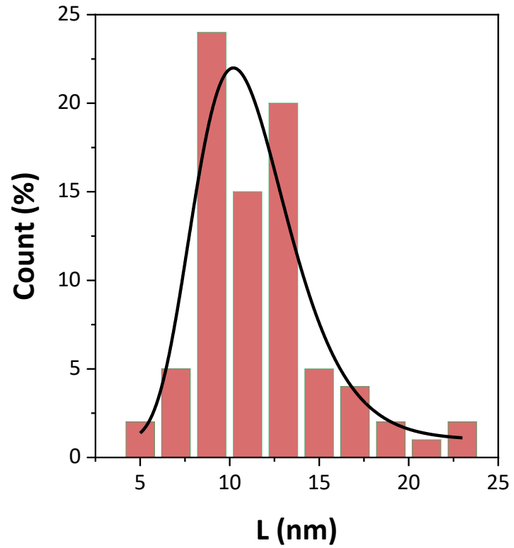

## Higher extent of iron carbidization

| Sample | Phase | Spectral contribution (%) |
|---|---|---|
| **$FeKMo/ZrO_2$** | $\chi$-$Fe_5C_2$ | 60 |
| | $\epsilon$'-$Fe_{2.2}C$ | 14 |
| | $Fe_xC$ (SPM) | 10 |
| | $Fe_{1-x}O$ (SPM) | 16 |

## Basicity




## Better Fe dispersion




**Best promoters are alkaline metals. Work better together with Cu, Mo, Ga and Ce**

# light olefin synthesis from CO or $CO_2$ ?

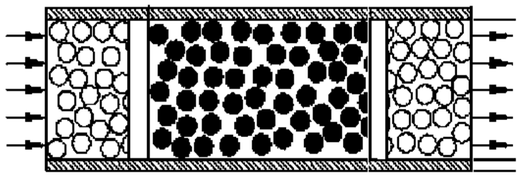
The best catalysts for hydrogenation of CO to light olefins are not good for hydrogenation of $CO_2$ and vice versa.

CO hydrogenation shows higher light olefin selectivity compared to $CO_2$ hydrogenation

Importance of sustainable hydrogen !

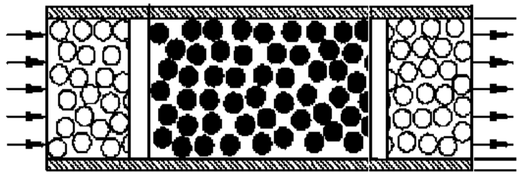
**RWGS**

**$CO_2$**

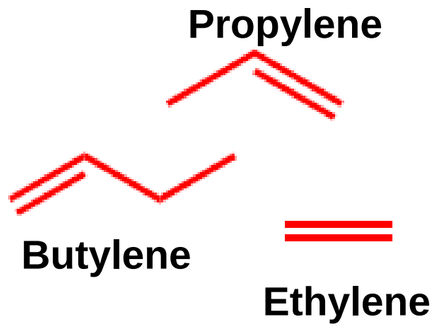


Catalyst

**CO**



Catalyst




Selectivity to CO close to 100%

Maximum selectivity to light olefins ~ 60%

# conclusions

- modeling provides crucial insights in how reaction performances relate to input and operating conditions
- balance between effort and insight is pursued
  - elementary step based modeling
  - machine learning

- Fischer Tropsch synthesis case study
  - SEMK virtual catalyst design identified descriptors for enhanced light olefin selectivity.
  - Machine Learning models for optimizing operating conditions (trained on SEMK data)
  - nonlinearities in chemical kinetics require ANN and SVR ML models over Lasso or kNN
  - interpretation techniques allow opening the black box ML models

# future perspectives

- linking modeling results back to experiments
- nr. of data points for training ML models
- use of ML for experimental design

# Q&A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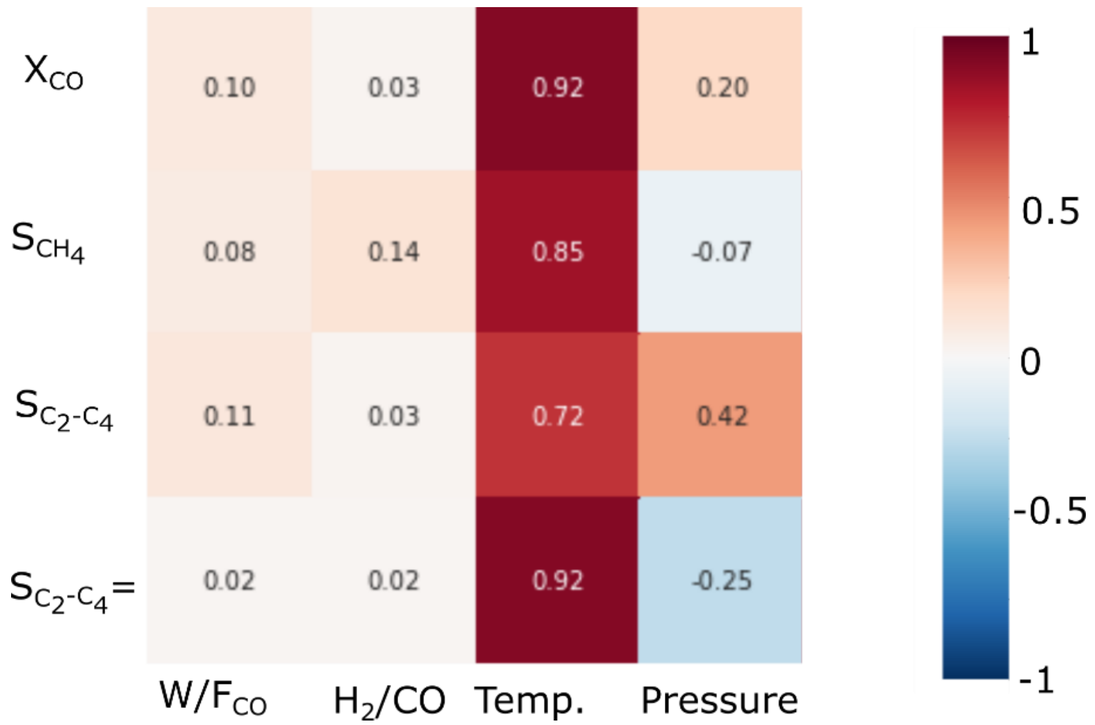
# Data analysis: Correlation coefficient

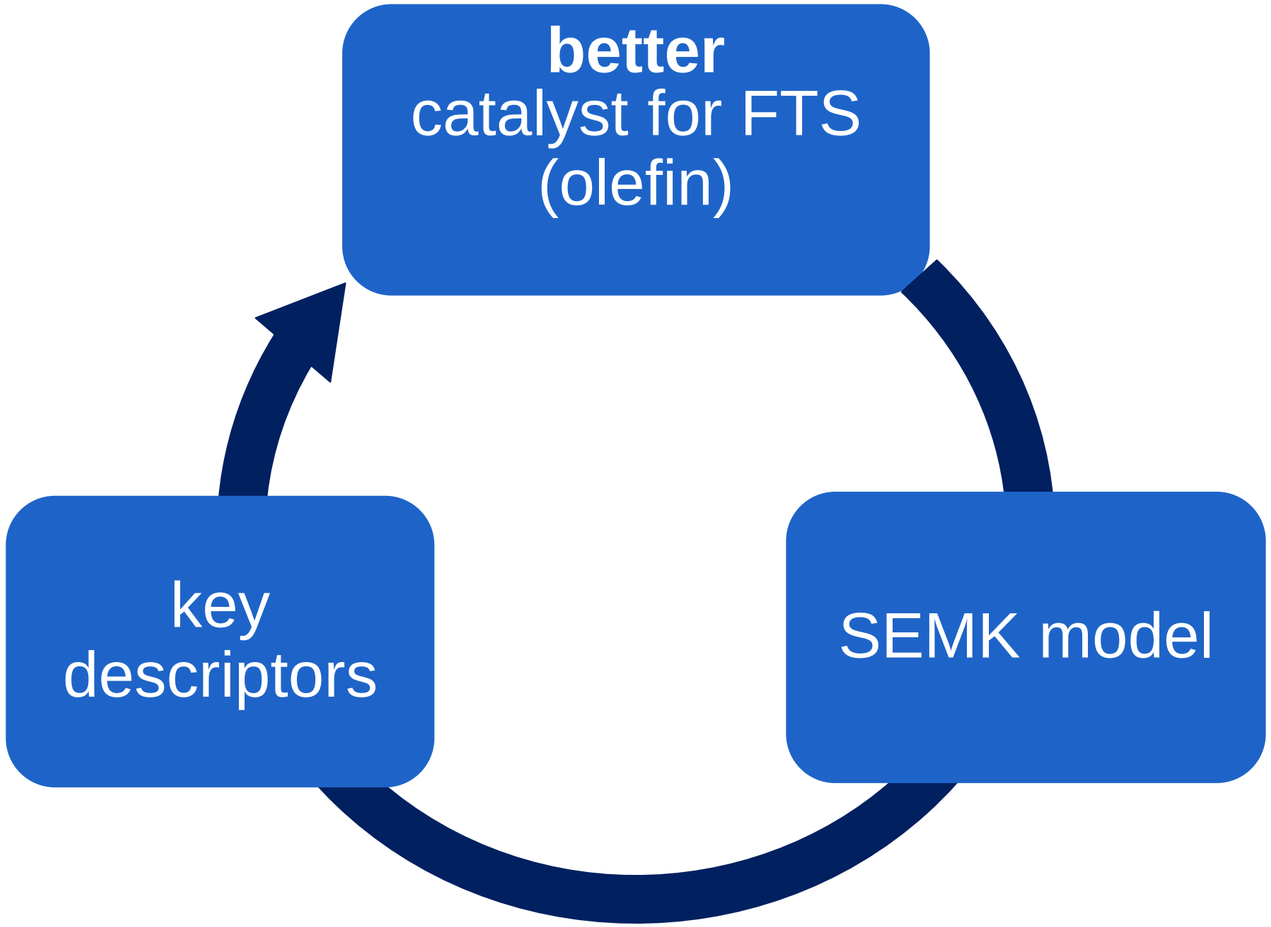



The Pearson correlation coefficient between a pair of variables( the predictor variables and the targeted FTS products.

$$r = \frac{\sum_{i=1}^{n}\left(X_i-\bar{X}\right)\left(Y_i-\bar{Y}\right)}{\sqrt{\sum_{i=1}^{n}\left(X_i-\bar{X}\right)^2}\sqrt{\sum_{i=1}^{n}\left(Y_i-\bar{Y}\right)^2}}$$

- If $r > 0$, there exists positive correlation between two variables.
- If $r < 0$, there exists the negative correlation.
- The absolute value of $r$ indicates the degree of correlation
- Temperature is most important process variable impacting the process.
- The impact of space time and syngas ratio is limited.

# catalyst performance optimisation



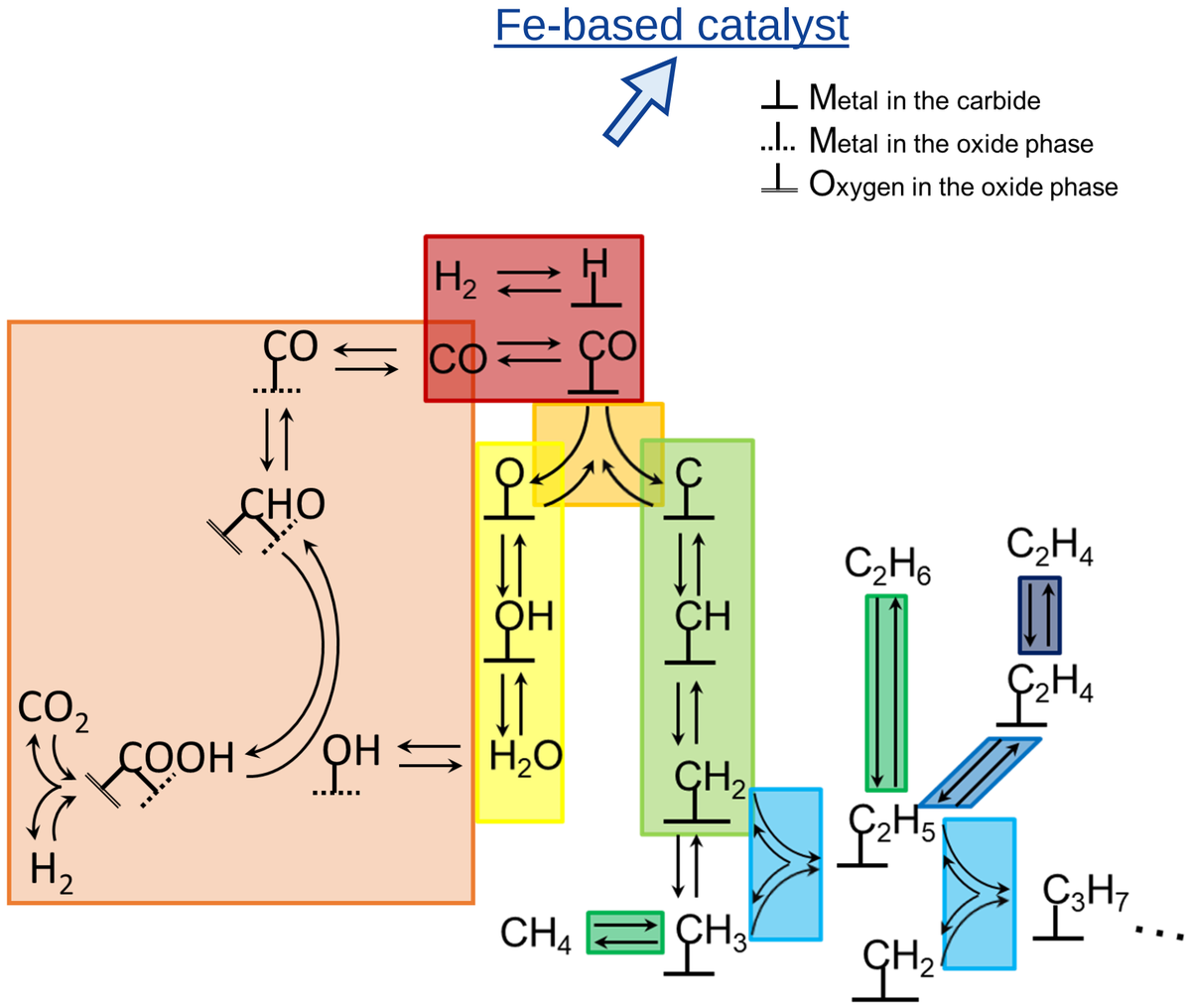

- elementary kinetic models provide fundamental insight in reaction chemistry
- Single-Event Micro Kinetic (SEMK) models particularly relevant for complex mixtures
- Fe-based FTS catalysts: low cost, selectivity to olefins
- light olefin selectivity can be enhanced with promoters, e.g. Pb, Bi promoters

*Gu et al. Applied Catalysis B: Environmental **234**, 153 (2018)*

# reaction network

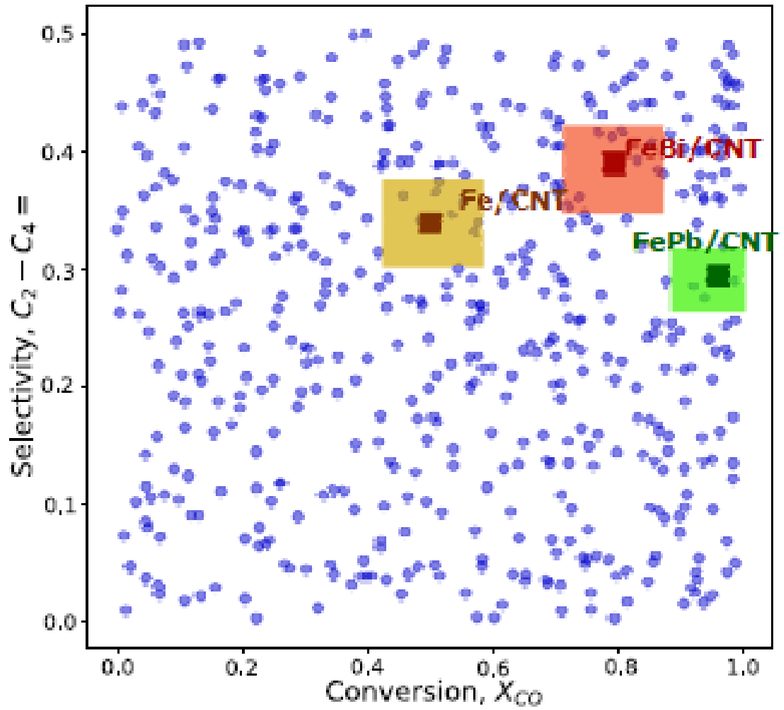
Reactions considered:

- Reactants chemisorption
- Direct CO dissociation
- Water removal by consecutive hydrogenation
- Monomer formation by consecutive hydrogenation
- Chain growth by $CH_2$ insertion
- Alkanes formation by hydrogenation
- Metal alkenes formation by hydrogen abstraction
- Alkenes chemisorption
- **Water Gas Shift**




the reaction network is considered till $C_{10}$ to avoid end of chain effects.

# virtual catalyst screening

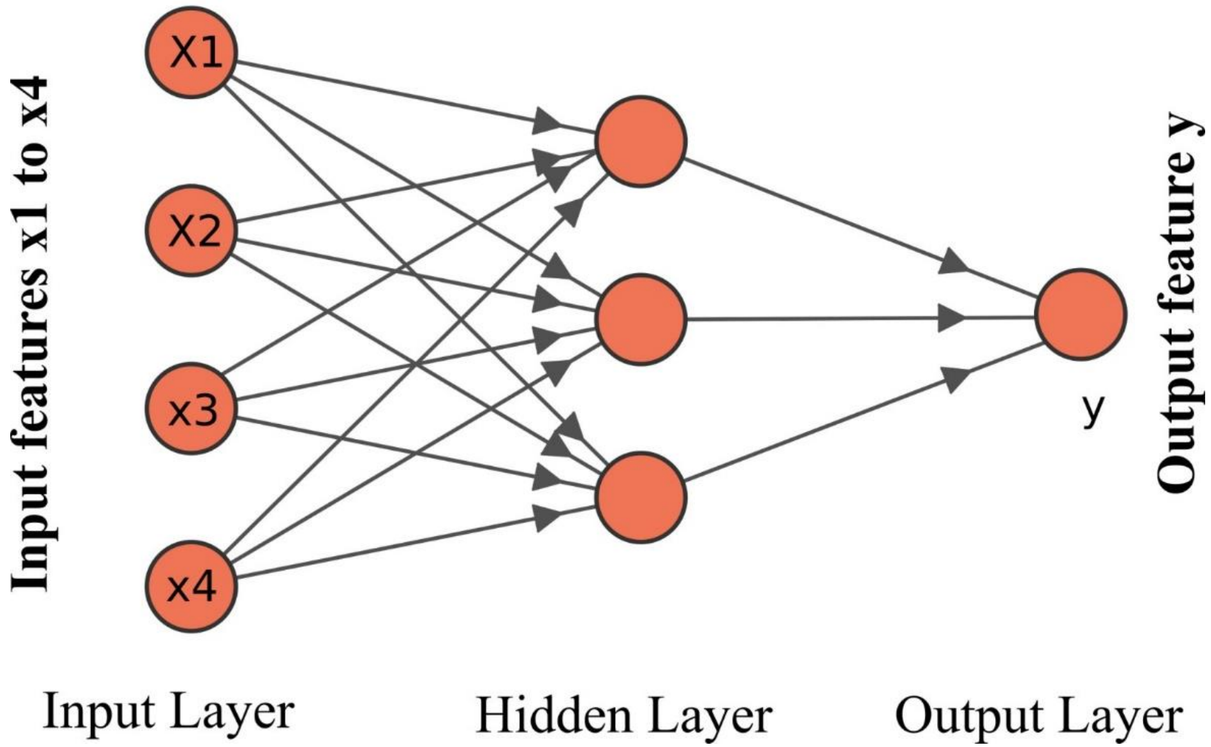



performance results for Bi and Pb promoted Fe catalyst, 623 K, 10 bar, GHSV =3.4 $Lg^{-1}h^{-1}$,$W_{cat}$=0.2 g

*Gu et al. Applied Catalysis B: Environmental **234**, 153 (2018)*

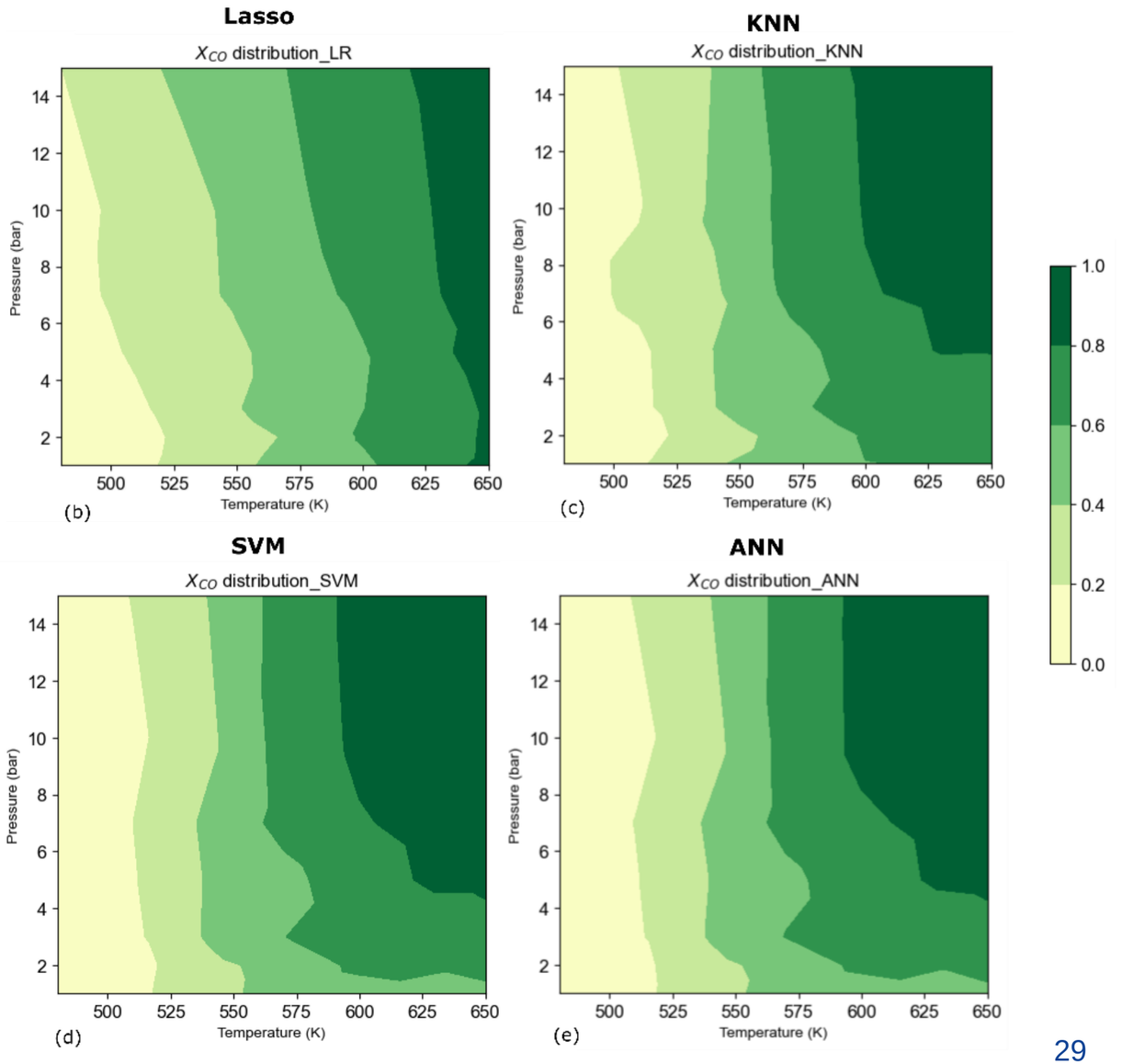
- entire catalyst descriptor space is sampled
- identification of virtual catalyst matching the experimental results.
- various performance indicators are considered:
  - light olefin selectivity (left)
  - methane production
  - heavy fraction
  - $CO_2$

# multi-response ML model: artificial neural network



# CO conversion

- conversion behaves non-linearly with temperature and pressure
- lasso regression unable to capture the nonlinear relations
- KNN, and particularly SVM and ANN more accurately



# interpretability: opening the black box model

**what about black box models (ANN)?**

- complex models like ANN are hard to interpret.
- interpretability techniques allow usage of more complex models without losing all interpretation power.

**does the ML model interpret the process variables as interpreted by the kinetic models?**

- interpretation process helps in ranking the process variables based on their impact on output.
- combined effects and correlation of different input features could also be identified.