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From CO_x to Light Olefins:

Computer-Aided Catalyst Design

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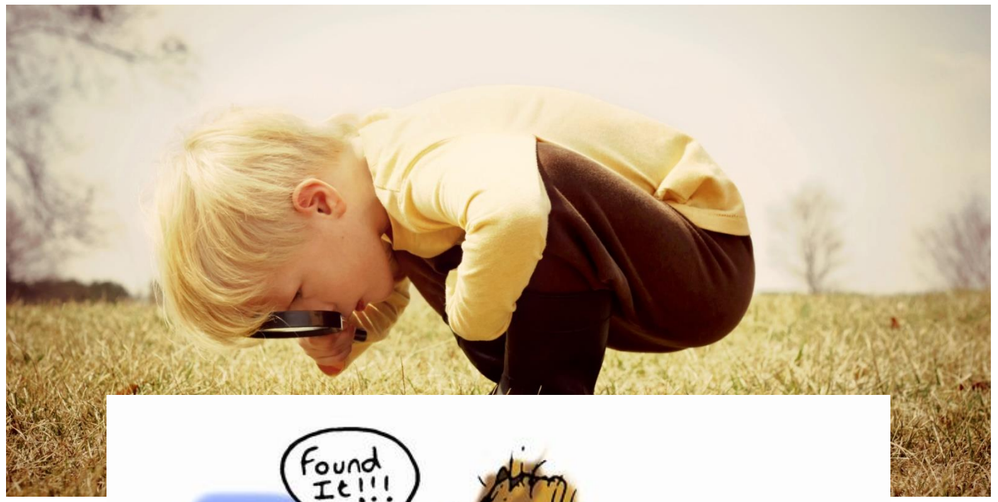
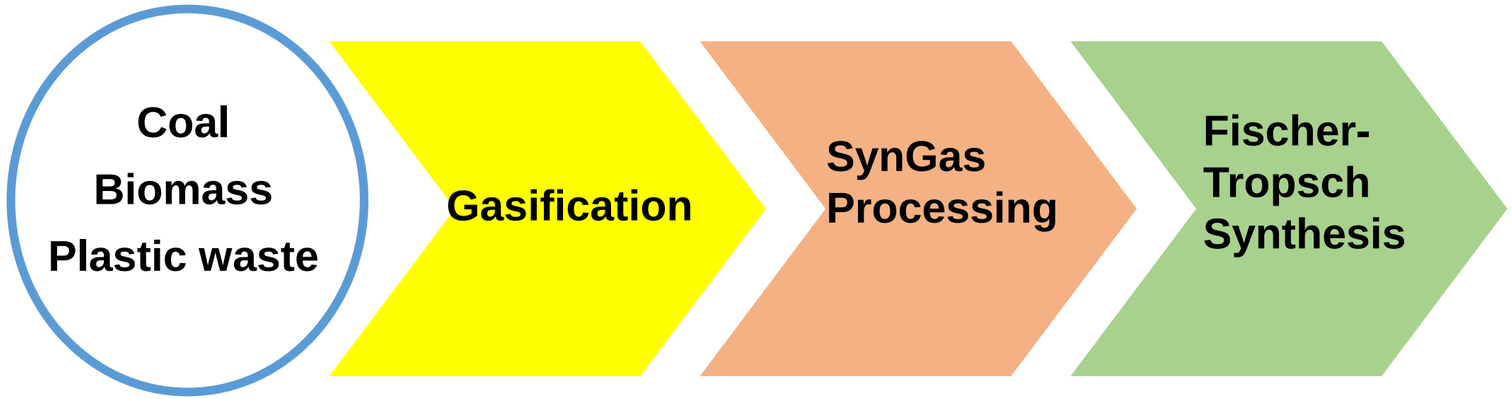
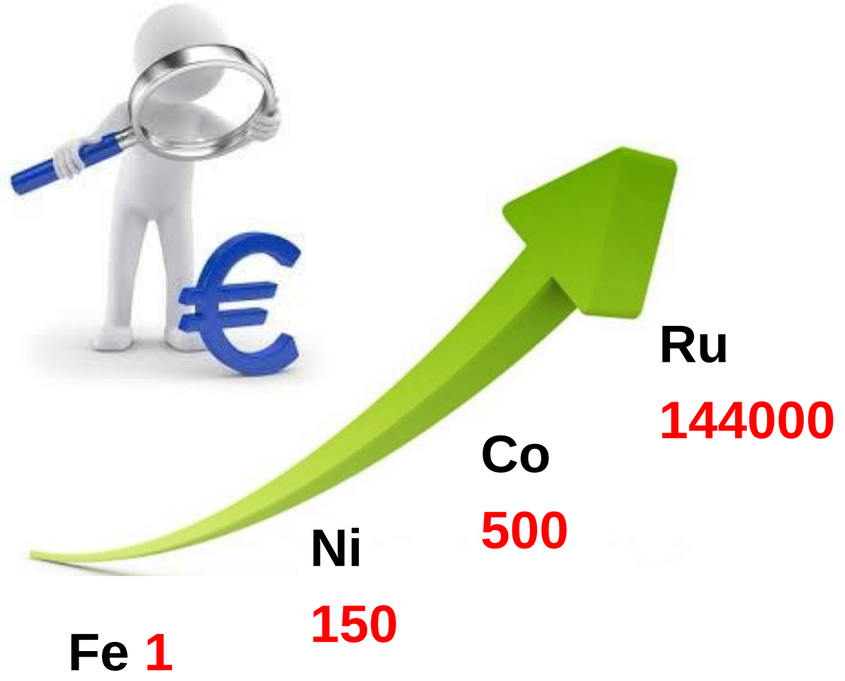
ideal catalyst: needle in a haystack



Fischer Tropsch Synthesis





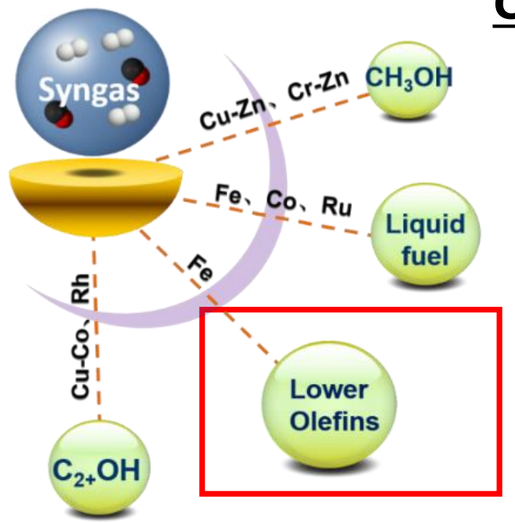
- carbon monoxide (CO) (or carbon dioxide (CO_2)) and hydrogen (H2), conversion into hydrocarbons.

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

  $CO + H_2O \rightarrow H_2 + CO_2$

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

Cheap and abundant metal!



experimental search for best catalysts

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

Characterization

Activity
Selectivity
Stability

Promoters

Fe-based catalysts

Under optimized conditions

Direct olefins production

FINAL GOAL!

Right support for CO and CO_2 reaction

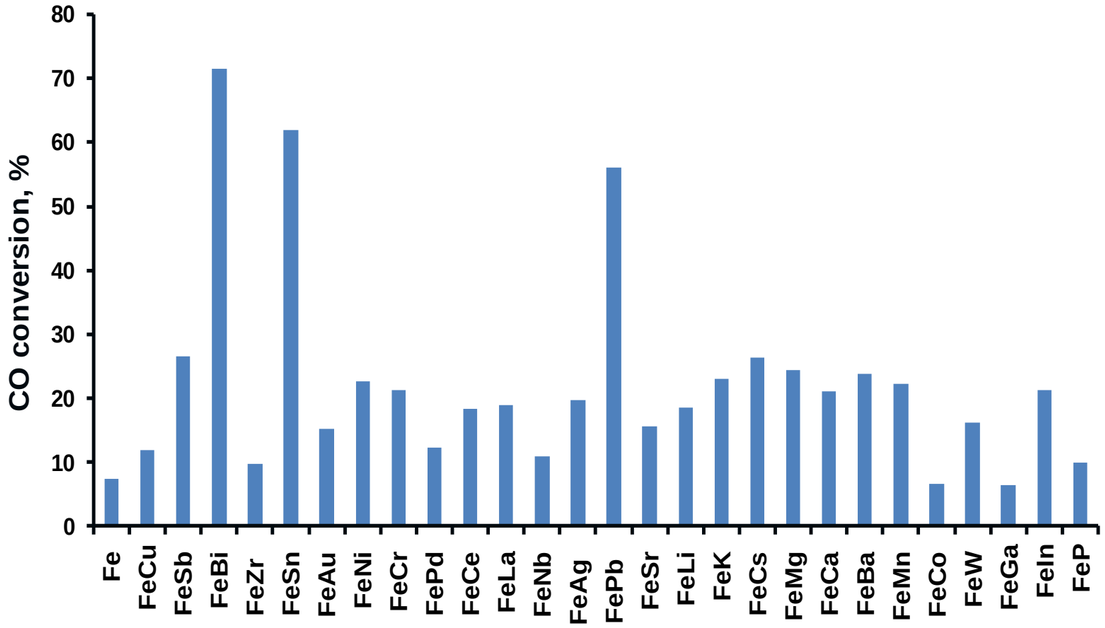
Support

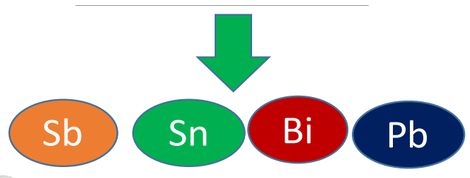
Avantium Flowrence
High throughput test
16 parallel reactors

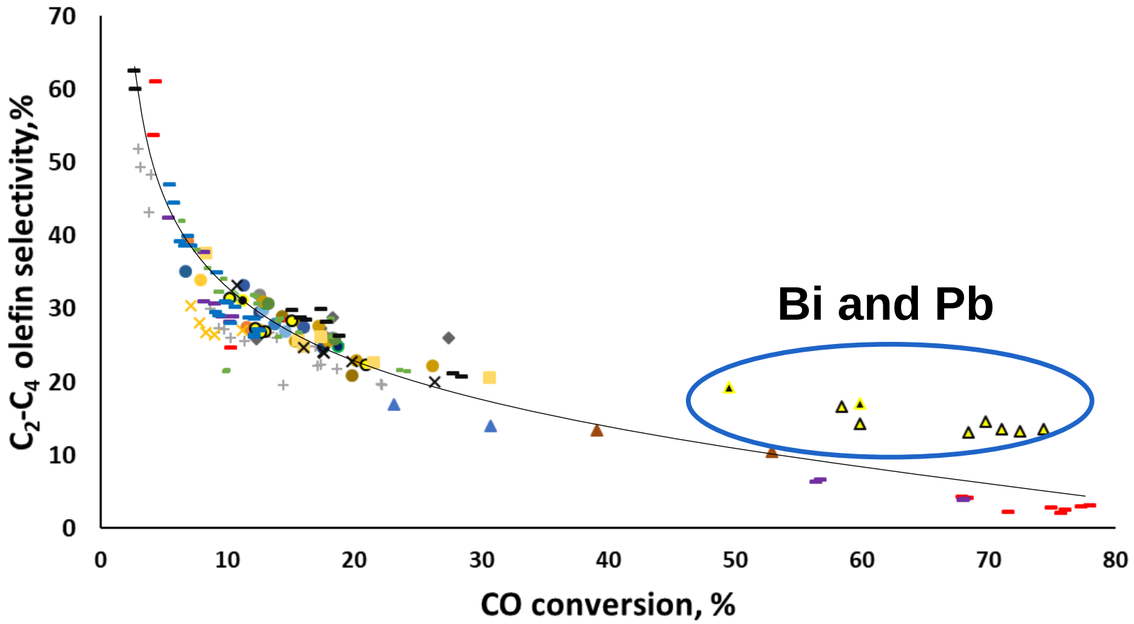
light olefin synthesis from CO

- **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**

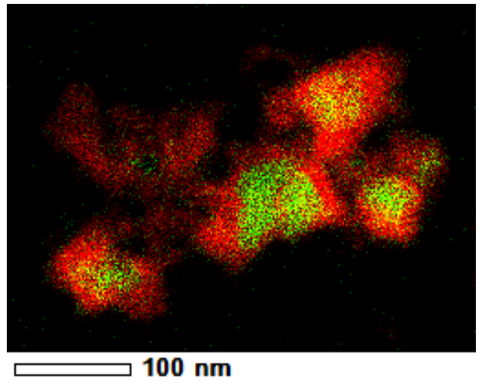
Barrios A., Bang G., Yuan L., Peron D., Petr. A., Virginie M., Wojcieszak R., Thybaut J., Ordomsky V.., Khodakov A. *Identification of efficient promoters and selectivity trends in high temperature Fischer-Tropsch synthesis over supported iron catalysts*. Appplied Catalyisis B: Environmental, 2020, 273.

summary: light olefin synthesis from CO

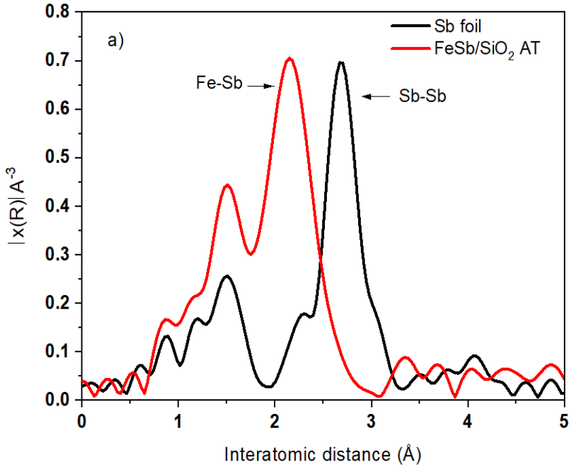
- **Promotion with soldering metals (Sn, Sb and Bi)**
- **Diffusion on catalyst surface**
- **Strong Fe-promoter interaction**

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

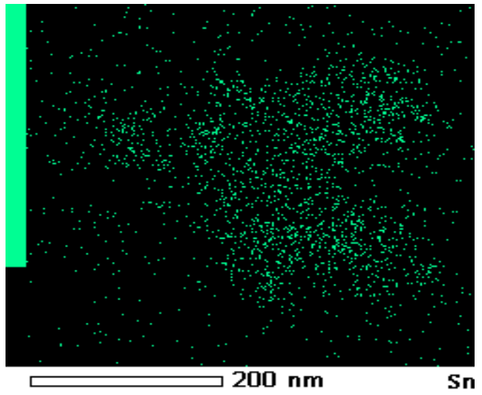
core-shell structures



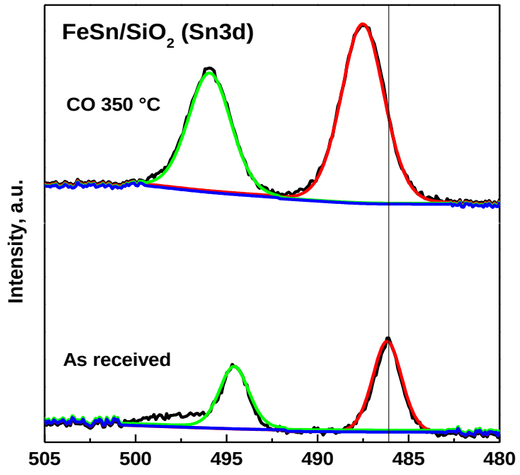
Alloy formation



Close to FeNPs

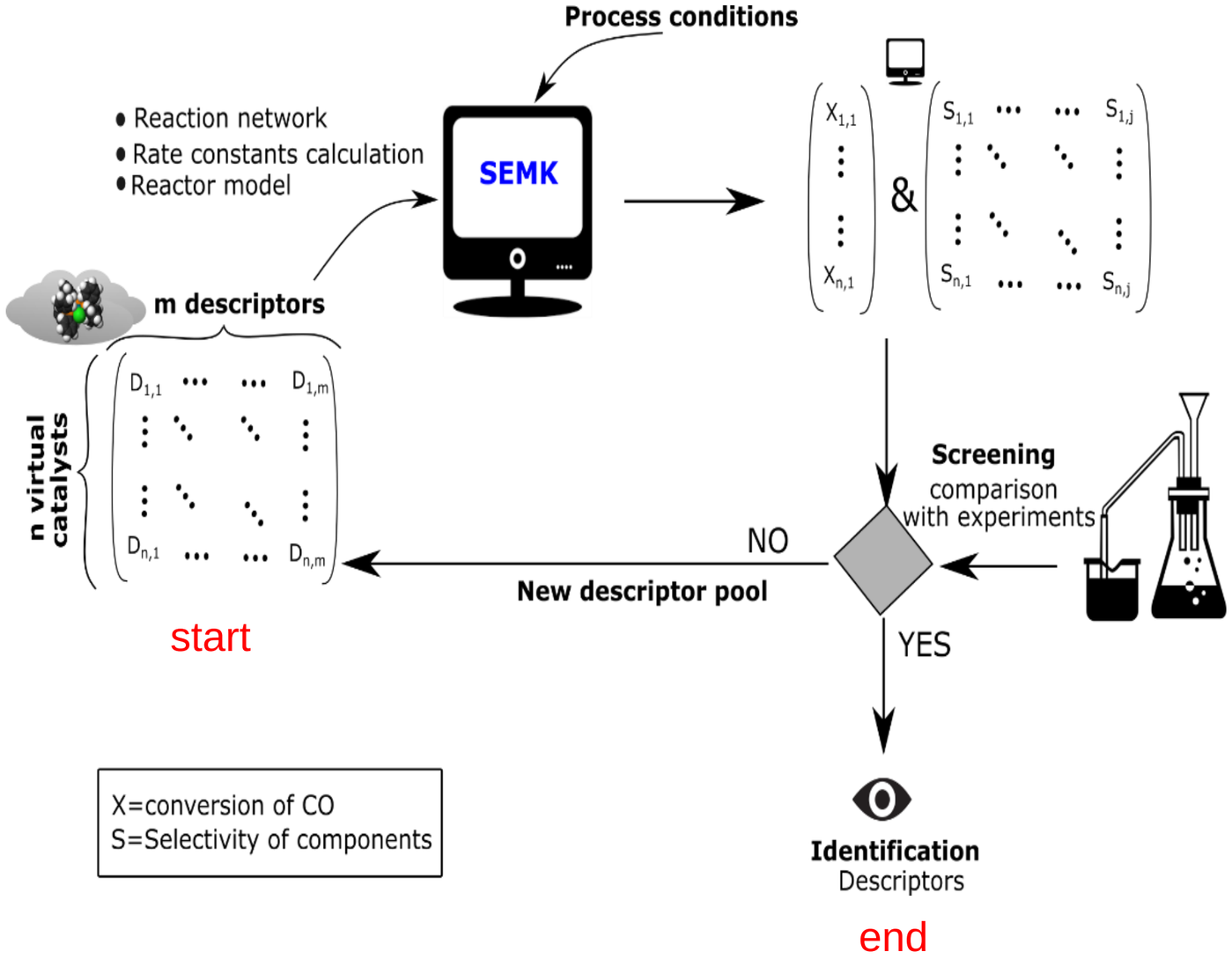


redispersion



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

virtual catalyst design



SEMK framework :

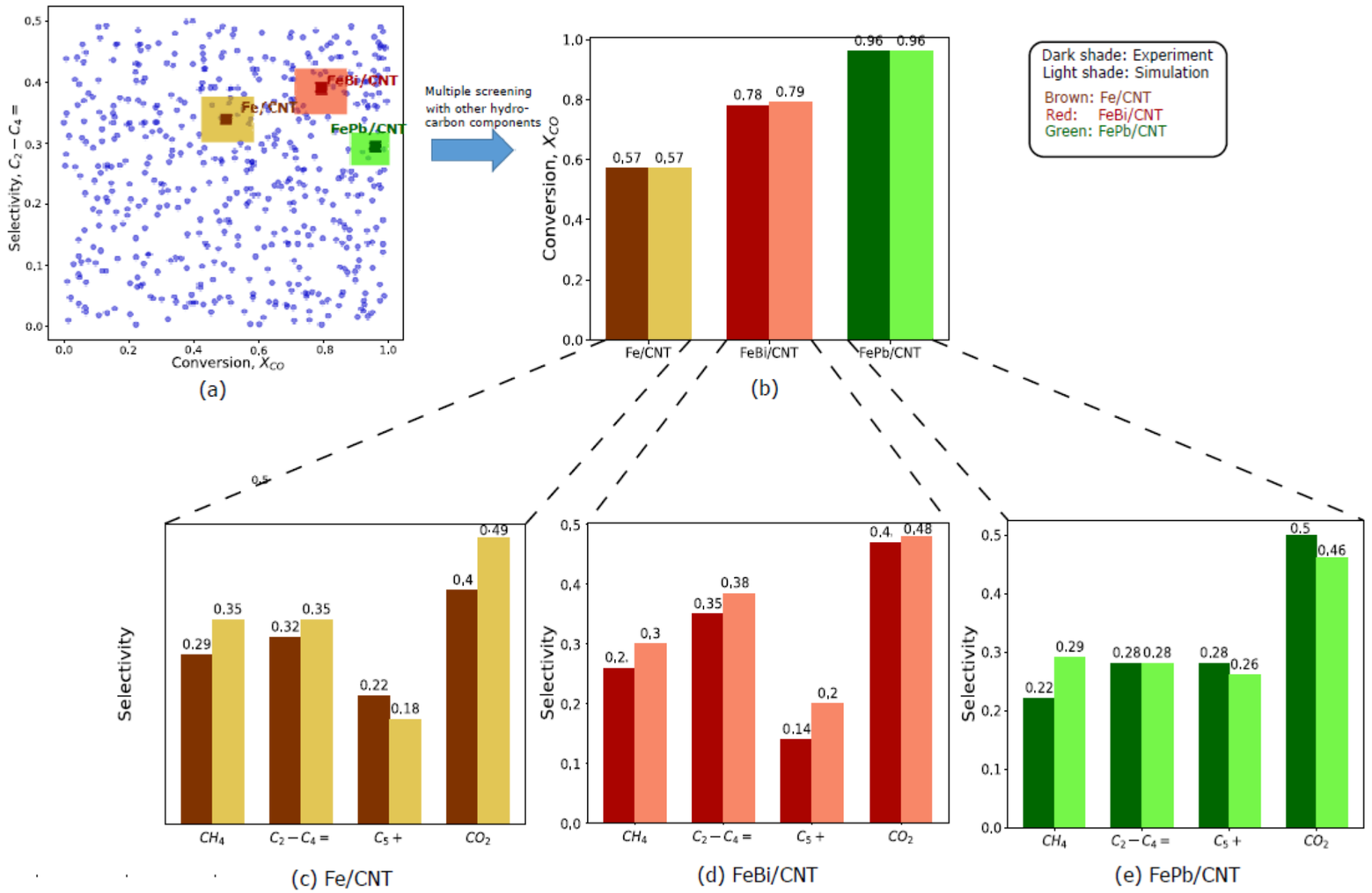
- network generation for FTS
- kinetic and catalyst descriptors.

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 ± 0.53
4. $MMMC + MH \rightleftharpoons MMMCH + M$	77.66 ± 0.70
5. $MMMCH + MH \rightleftharpoons MMCH_2 + 2M$	11.94 ± 0.10
6. $MMCH_2 + MH \rightleftharpoons MCH_3 + 2M$	61.88 ± 0.50
Chain growth	
7. $MC_nH_{2n+1} + MMCH_2 \rightleftharpoons MC_{n+1}H_{2n+3} + 2M$	44.79 ± 0.43
Formation of alkanes	
8. $MC_nH_{2n+1} + MH \rightleftharpoons C_nH_{2n+2} + 2M$	117.75 ± 0.67
Formation of metal alkenes	
9. $MC_nH_{2n+1} + M \rightleftharpoons MC_nH_{2n} + MH$	96.27 ± 0.50
Alkene desorption	
10. $MC_nH_{2n} \rightleftharpoons C_nH_{2n} + M$	62.09 (n=2) 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 ± 1.15
Water formation	
12. $MMO + MH \rightleftharpoons MOH + 2M$	103.80 ± 0.96
13. $MOH + MH \rightleftharpoons H2O + 2M$	86.22 ± 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

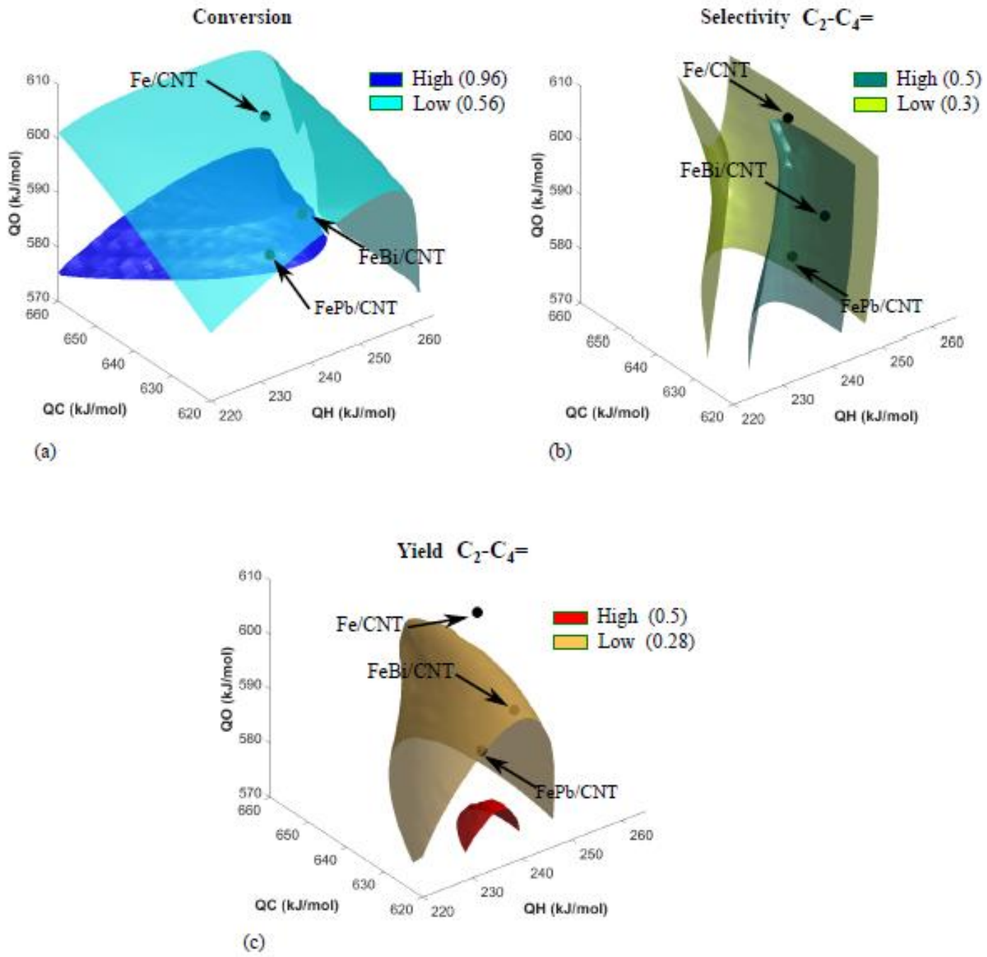


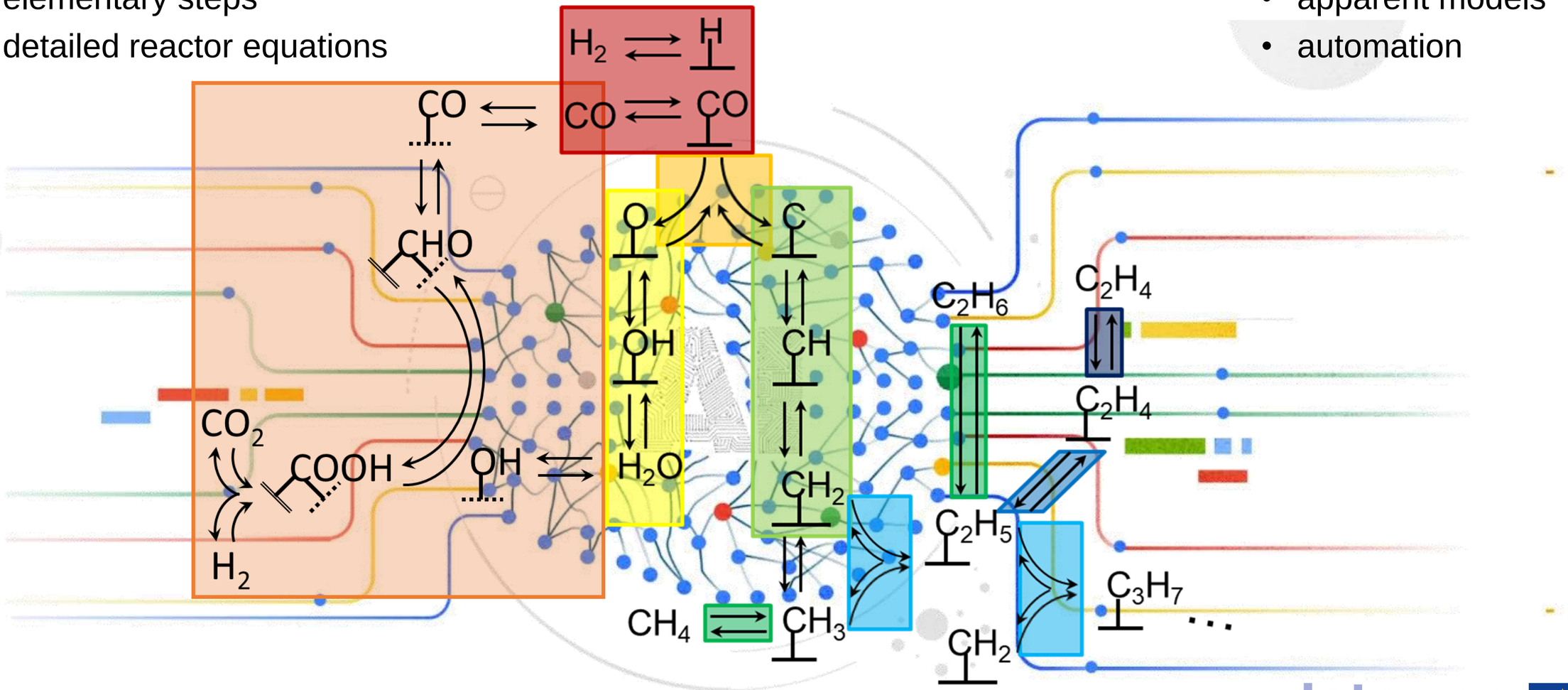
Fig: Iso-surfaces of conversion, light olefin selectivity and yield.

- 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)*

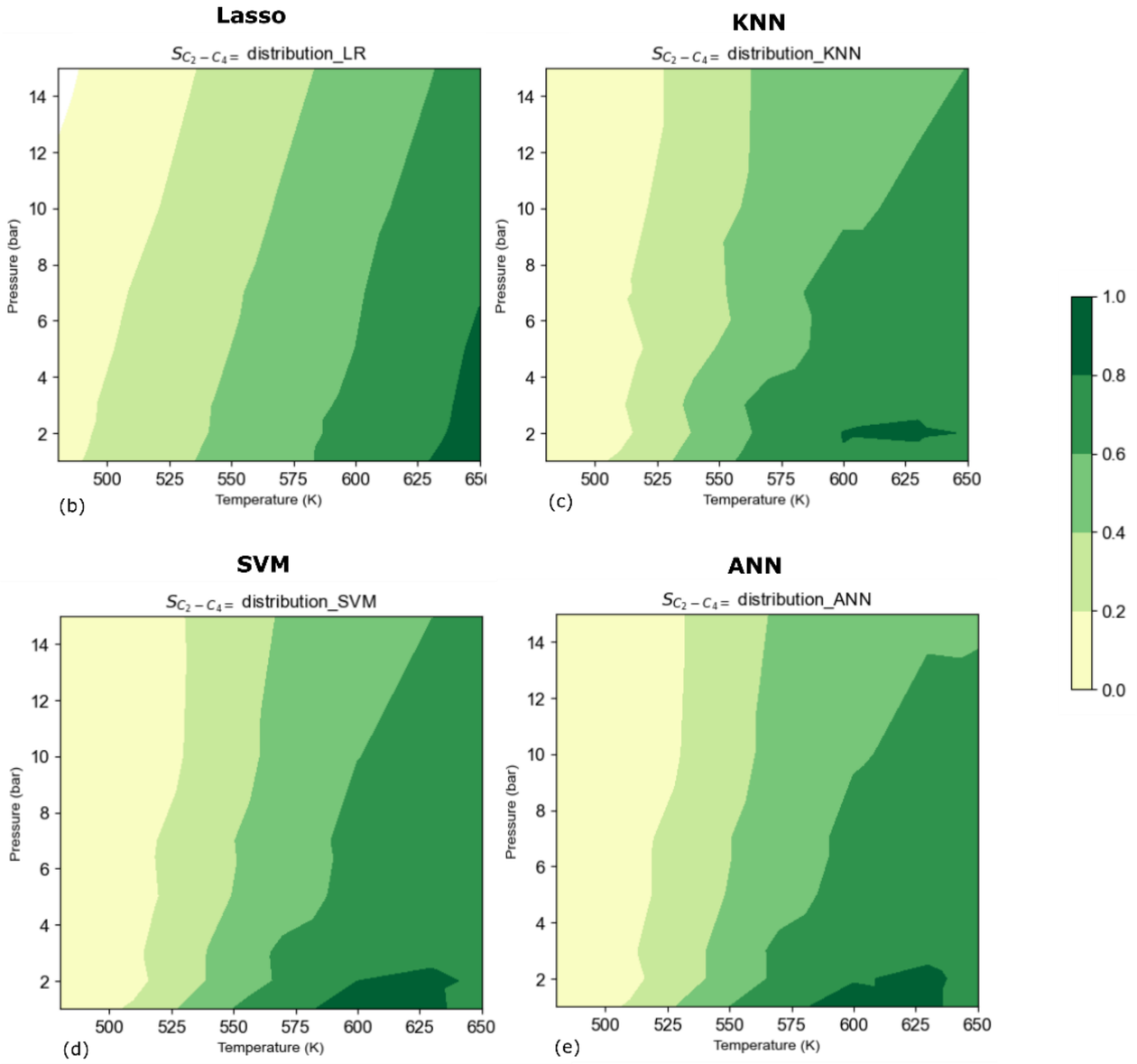
balance between effort and insight

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

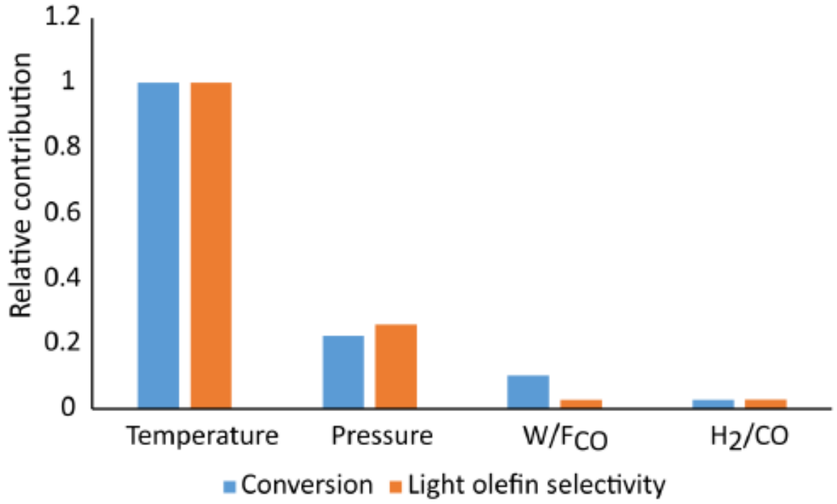


light olefin selectivity

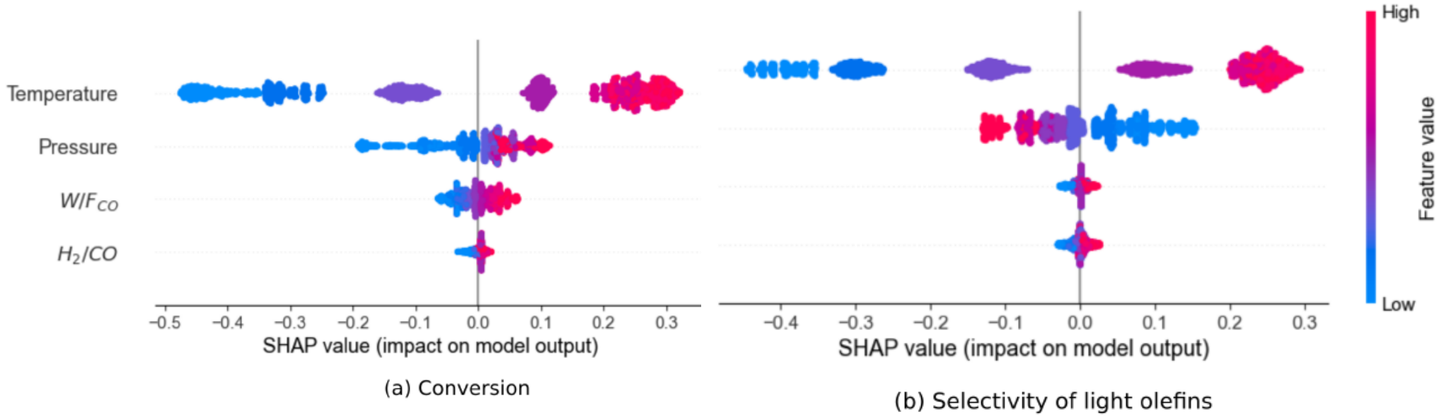
- light olefin selectivity more pronouncedly nonlinear with temperature and pressure
- lasso regression, but also kNN unable to capture these nonlinearities
- SVM and ANN predict the nonlinear relation accurately.



relative importance (Shap)

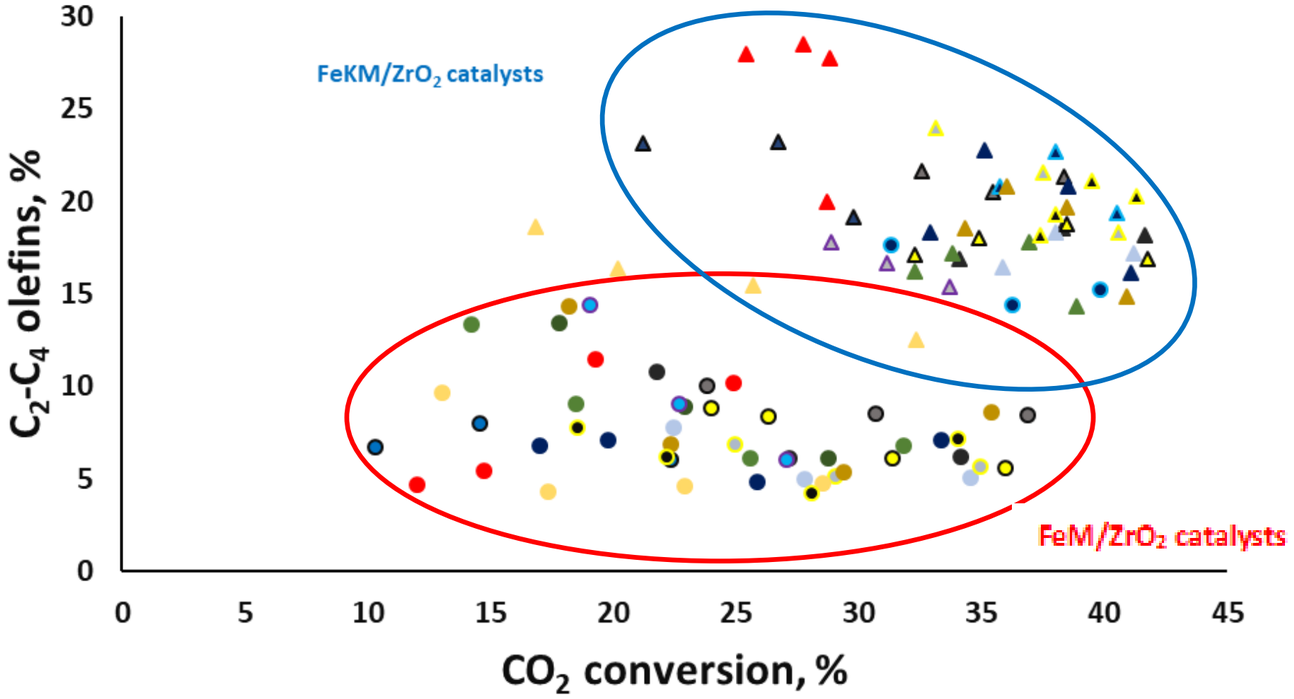


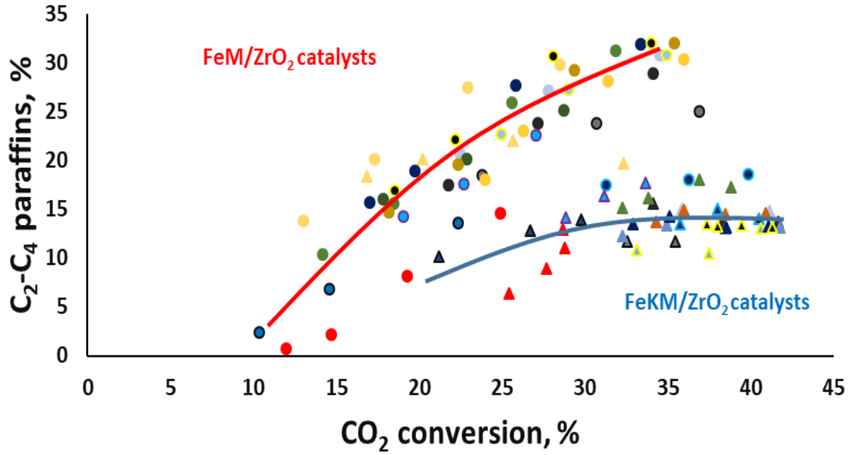
- temperature (1x) and pressure (0.22-0.26x) are most influential (both conversion and light olefin selectivity)
- conversion: space time (0.1x) over syngas ratio (0.03x).
- light olefin selectivity: syngas ratio (0.03x) and space-time (0.03x).

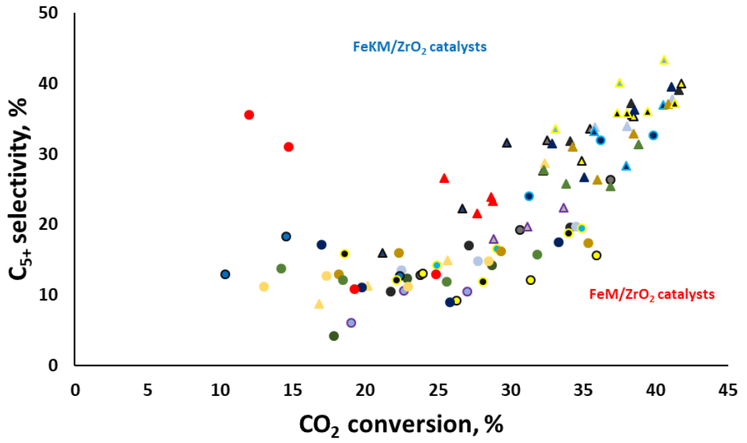


Chakkingal et al. Chemical Engineering Journal (2022)

light olefin synthesis from CO_2 over promoted Fe/ZrO_2 catalysts



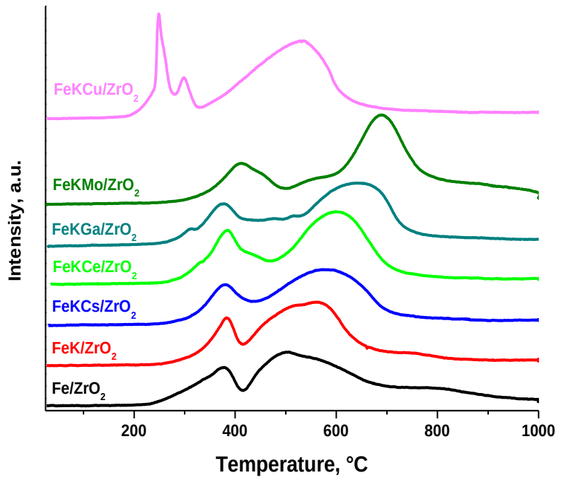




- **Catalysts promoted with K showed the highest olefin selectivities**
- **Most selective catalysts to lower olefins were selected to be further studied**

summary: catalyst parameters for light olefin synthesis from CO_2

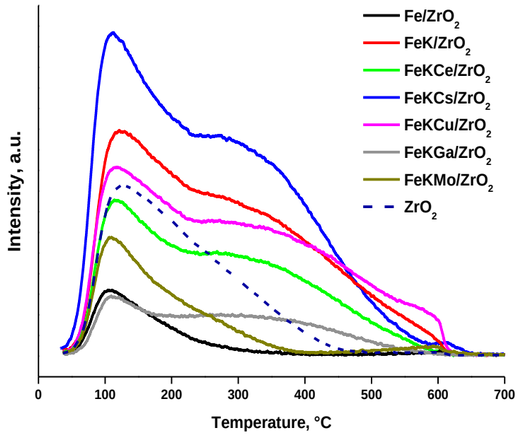
Better Fe Reducibility



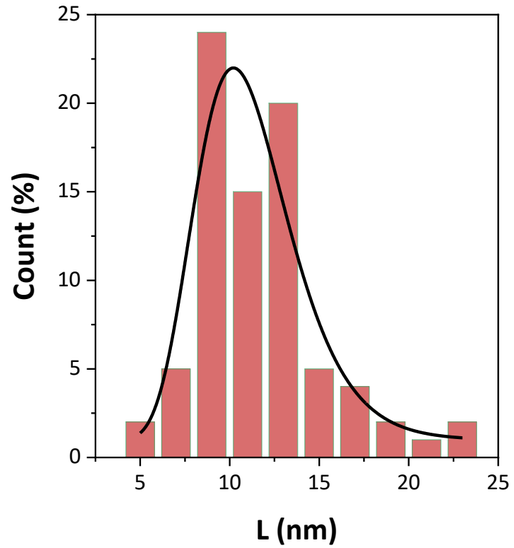
Higher extent of iron carbidization

Sample	Phase	Spectral contribution (%)
$FeKMo/ZrO_2$	χ-Fe_5C_2	60
	ϵ'-$Fe_{2.2}C$	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 ?

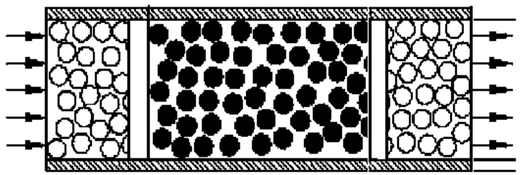
The best catalysts for hydrogenation of CO to light olefins are not good for hydrogenation of CO_2 and vice versa.

CO hydrogenation shows higher light olefin selectivity compared to CO_2 hydrogenation

Importance of sustainable hydrogen !

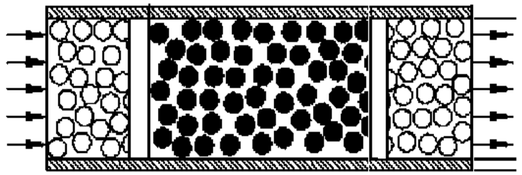
RWGS

CO_2

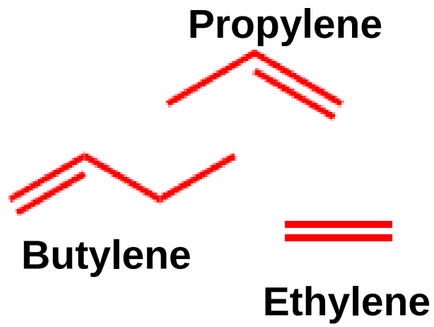


Catalyst

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

Q&A

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