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UNITÉ DE CATALYSE
ET CHIMIE DU SOLIDE

Synthesis of alternative fuels and chemicals from fossil and renewable feedstocks

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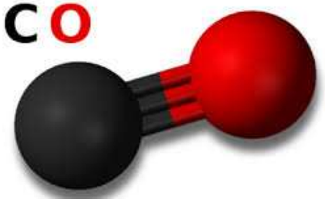
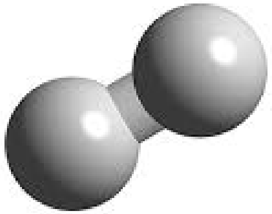
SYNGAS
important intermediate can be produced from all fossil and renewable feedstocks

Major components

CO

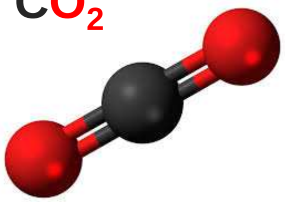


H_2



Minor components

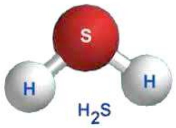
CO_2



CH_4

Impurities

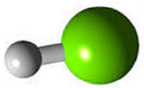
H_2S



NH_3

HCN

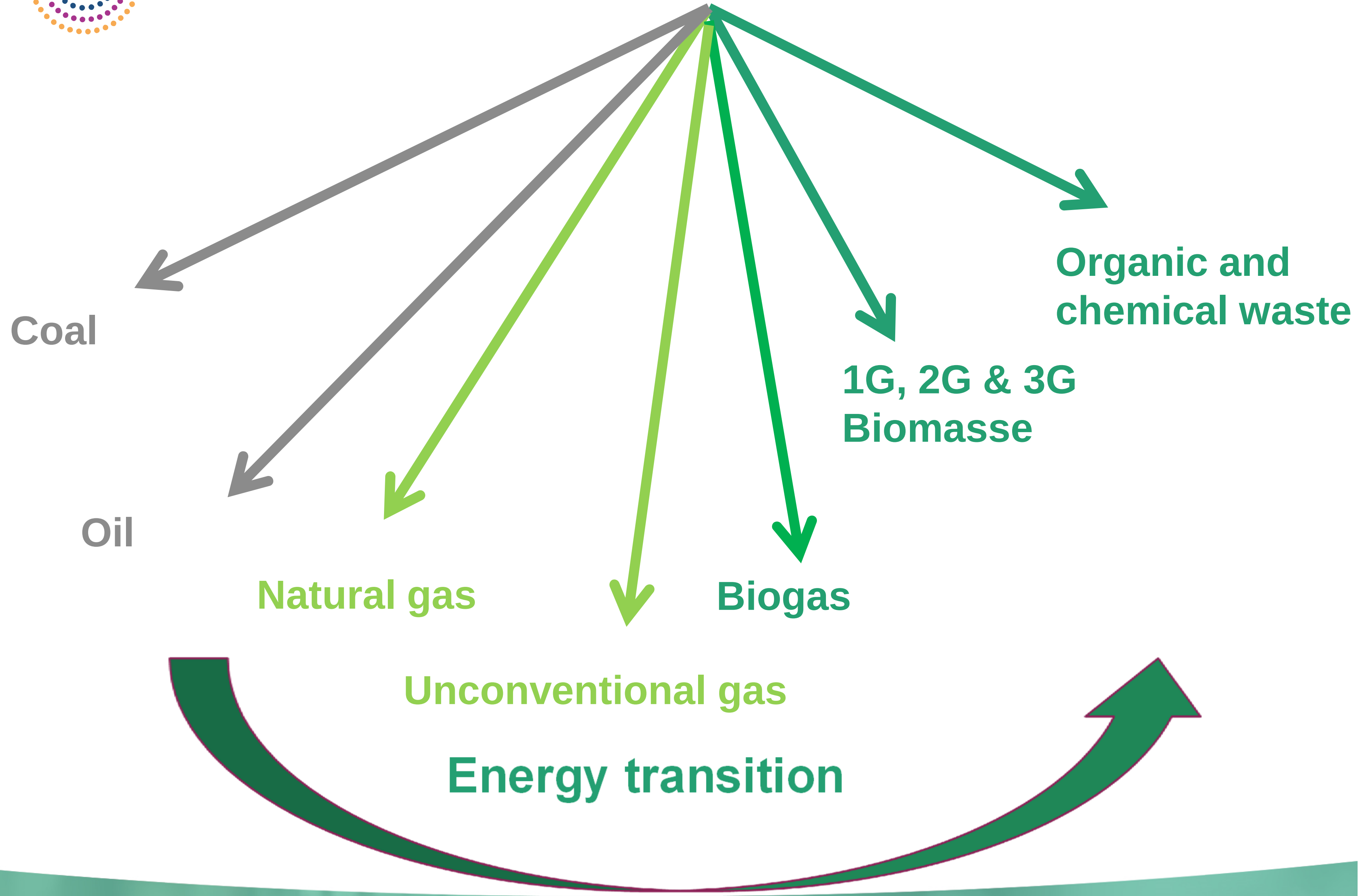
HCl



Tar

Which feedstocks to produce syngas?

Energy and Chemical Feedstocks



Coal

Oil

Natural gas

Unconventional gas

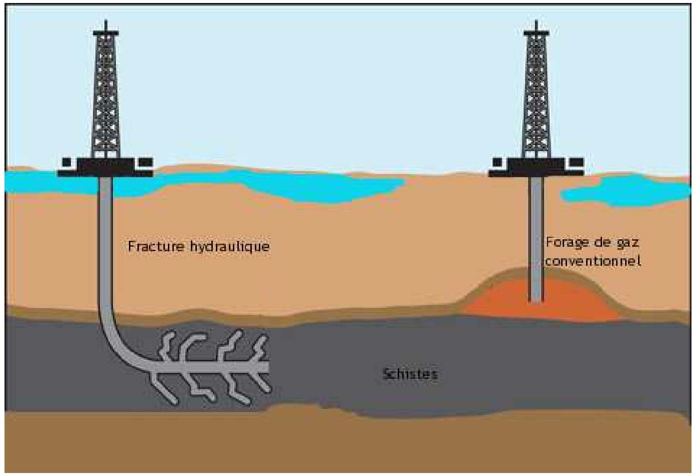
Biogas

1G, 2G & 3G Biomasse

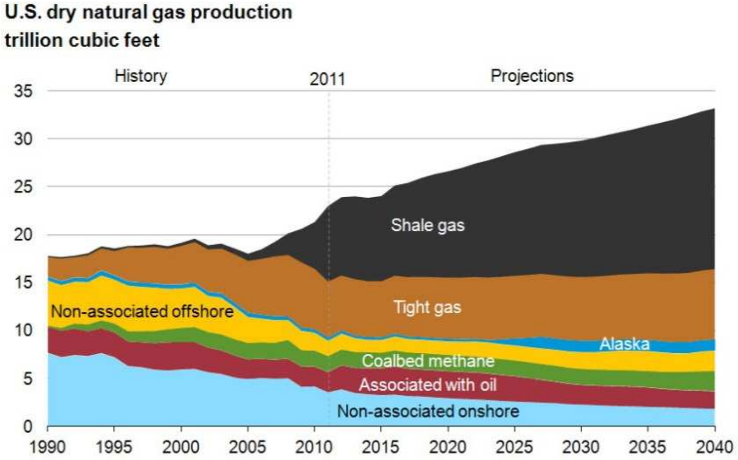
Organic and chemical waste

Energy transition

“New” raw materials: shale gas (USA)



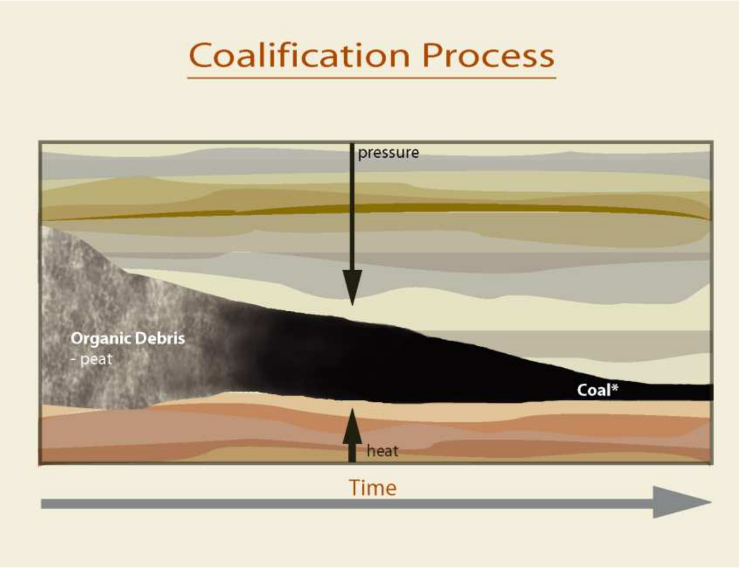
Shale gas and shale oil are hydrocarbons in argillaceous sedimentary rocks, located between 1 and 3 km from depth, which are both compact and waterproof



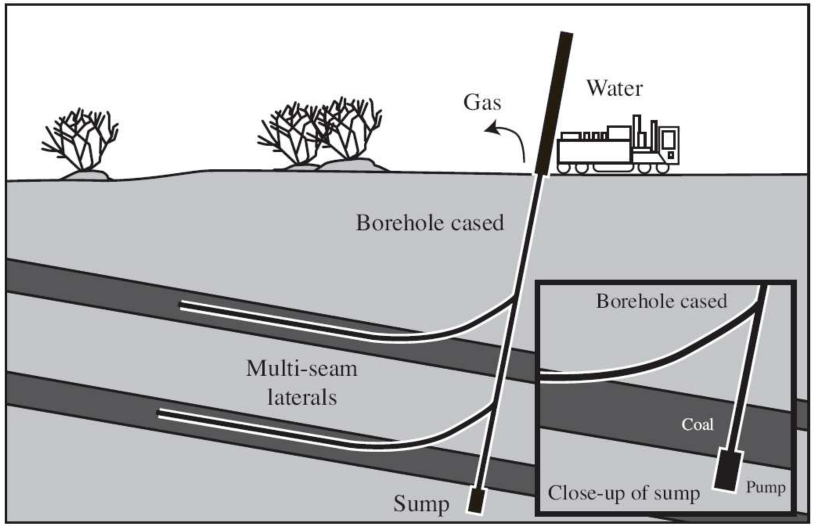
Source: U.S. Energy Information Administration, *Annual Energy Outlook 2013 Early Release*

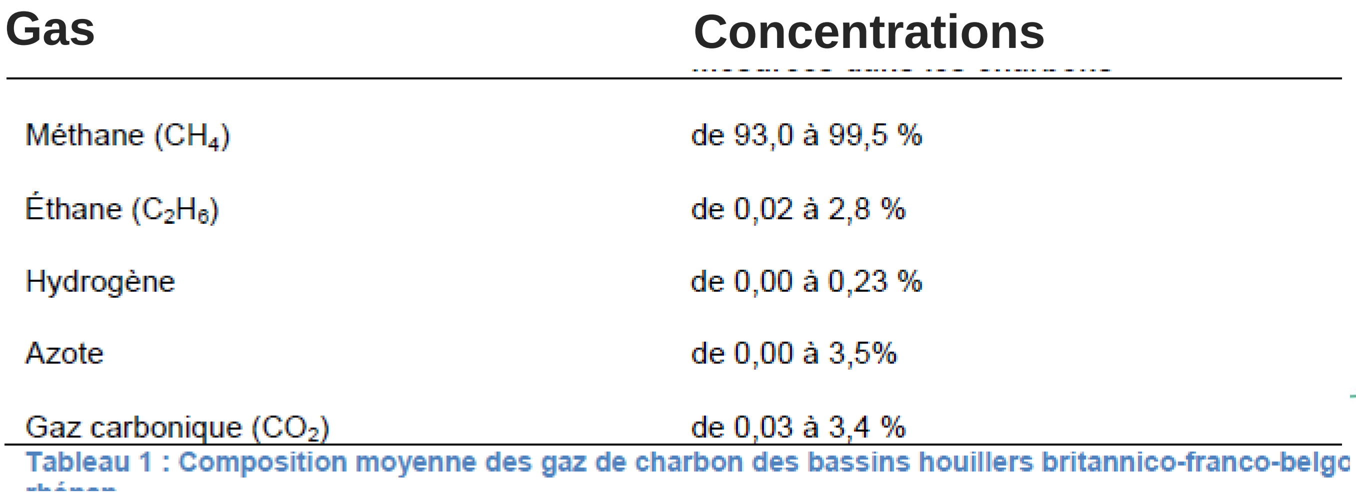
20-30% of gas production in 2015 in the USA compared to only 1% in 2000.

“New” raw materials: coalbed gas: relation between coal and gas



Gas extraction by pumping

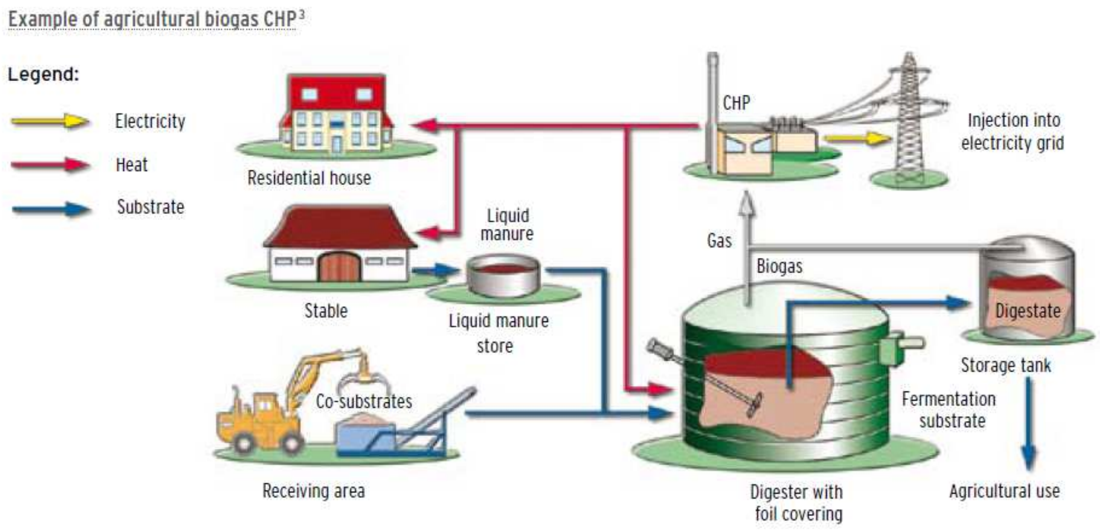




Gas	Concentrations
Méthane (CH_4)	de 93,0 à 99,5 %
Éthane (C_2H_6)	de 0,02 à 2,8 %
Hydrogène	de 0,00 à 0,23 %
Azote	de 0,00 à 3,5%
Gaz carbonique (CO_2)	de 0,03 à 3,4 %

Tableau 1 : Composition moyenne des gaz de charbon des bassins houillers britannico-franco-belgo

“New” energy feedstocks: Biogas


Example of agricultural biogas CHP[3]

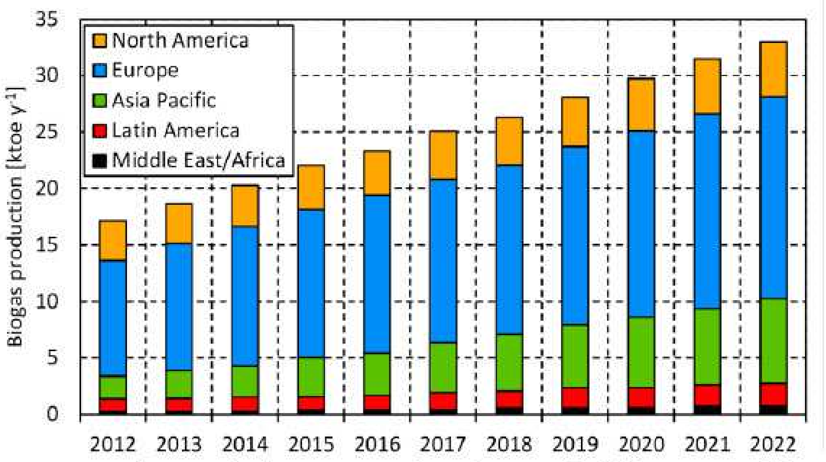


Figure 1. Biogas production at 2012 and trend to 2022 in different areas of the world (Pike Research, 2012).

Biogas composition

Constituants	% volume
CH_4	55-75
CO_2	25-45
H_2S	0-1.5
NH_3	0,05

“New” raw materials:
2G biomass, ligno-celullose

Waste, the wheat, corn stalks, wood, fibrous biomass (e.g. miscanthus) or macro-algae cultures.

Fire-wood

50% of wood production is intended for energy, 50% industrial use

Residue or agricultural waste

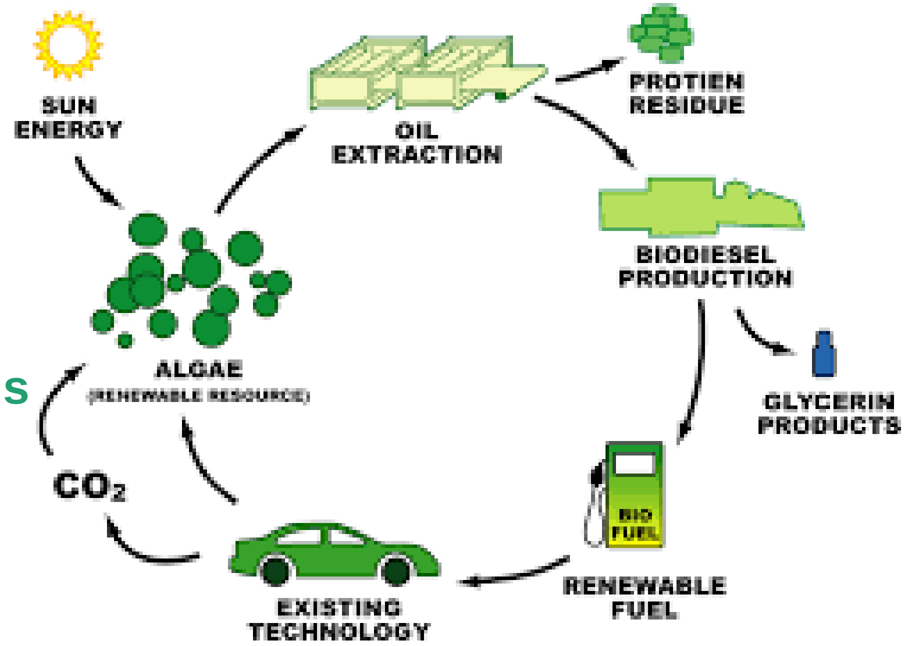
Dedicated crops

Crops with short rotation (annual species crops)
Perennial undergrowth off wood (miscanthus...)

“New” raw materials: 3 G biomass

Photobioreactors

Open ponds or closed-loop systems



3rd generation biofuels differ from the 2nd generation by the type of biomass used.

- Microalgae and macroalgae in autotrophic condition (capacity to synthesize organic matters from mineral matter).
- In addition to microalgae, 3rd generation include all biofuels which are produced using biomass from water resources

History of syngas

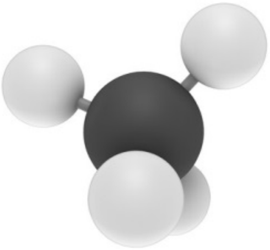
- 17th century first experiments with syngas Thomas Shirley, Dean Clayton
- 1840 First commercially used gasifier in France
- 1850 Streets of London lighted with syngas
- 1878 Gasifiers were successfully used with engines for power generation
- 1901 Passenger vehicle with syngas
- 1940-1945 1 000 000 gasifiers, several 10^5 cars and tractors

London gas lighting

Renault AFVH with a Gasifier Imbert [1941-45]. This tractor was started with gasoline.

Syngas from conventional and nonconventional gas

Methane, Lighter alkanes



Steam reforming endothermic

$CH_4+H_2O=CO+3H_2$

Partial oxidation exothermic

$2CH_4+O_2=2CO+4H_2$

Autothermic reforming

Dry reforming endothermic

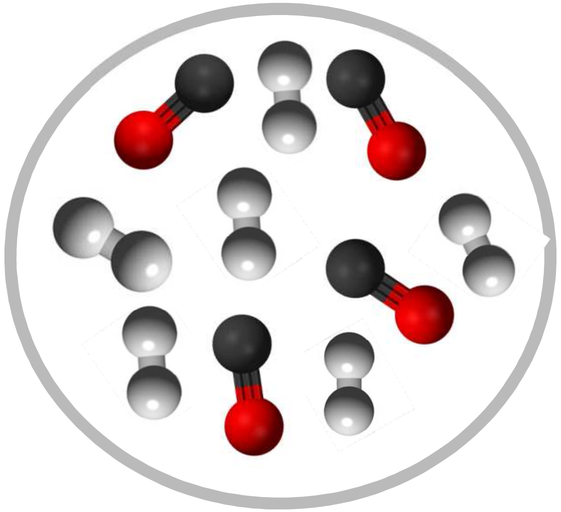
$CH_4+CO_2=2CO+2H_2$

Water gas shift reaction

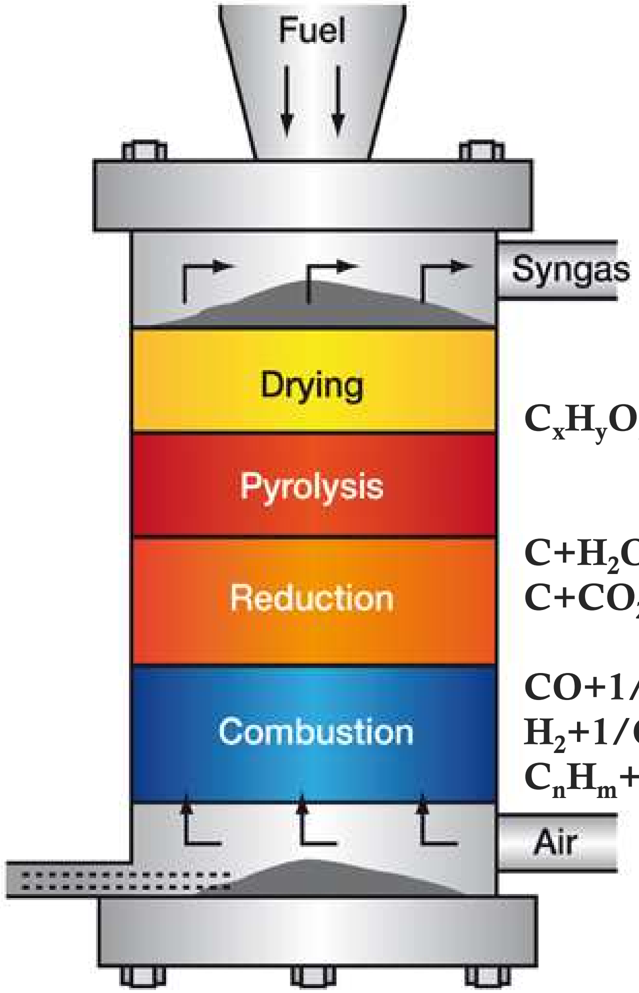
$CO+H_2O=CO_2+H_2$

Tubular reactor
700-1100°C, 3-25 bars
Ni, Rh, Pt, Pd, Ir, Ru
Non-catalytic PO

Hydrogen, carbon monoxide, carbon dioxide and impurities



Syngas from biomass and coal gasification



$C_xH_yO_z=CH_s+CO/CO_2+C_kH_lO_m$

$C+H_2O=CO+H_2$
$C+CO_2=2CO$

$CO+1/2O_2=CO_2$
$H_2+1/O_2=H_2O$
$C_nH_m+xO_2=nCO_2+m/2\ H_2O$

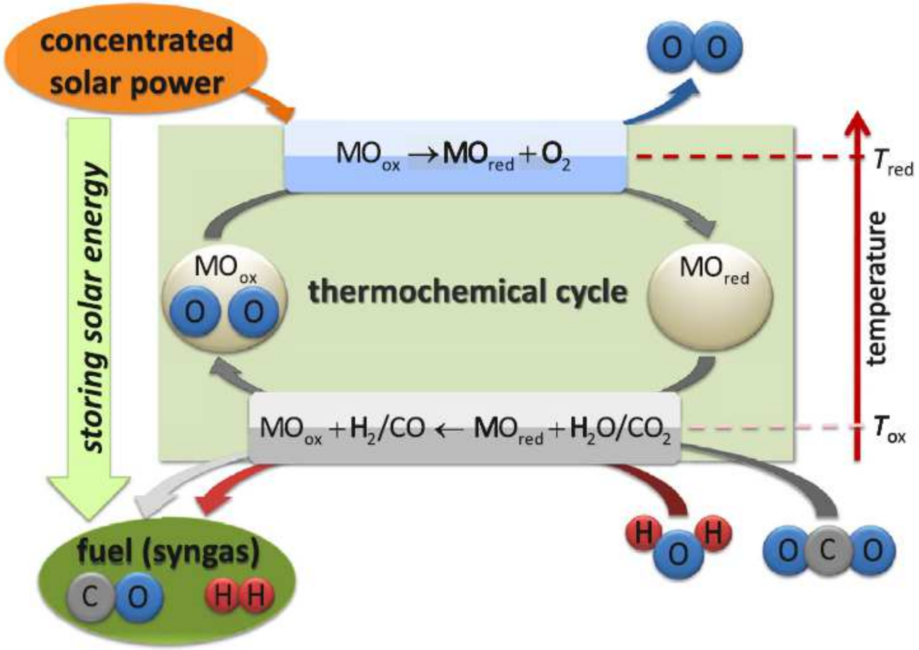
Wabash River Clean Coal Power Plant in USA

Gussing (Austria) biomass gasification plant

Other technologies of syngas production

- Biomass catalytic partial oxidation

- Solar upload (thermochemical cycle)



- Photochemistry

Use of Syngas as Fuel

Combustion, Combined Heat & Power (Gas turbine, electricity generation)

Heavy pollution because of traditional coal combustion in China

Better than coal!

Environmental Benefits

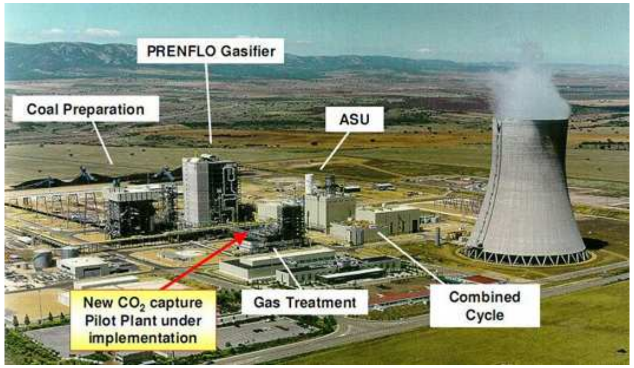
Extremely low SO_x, NO_x and particulate emissions from burning coal-derived gases.

Carbon dioxide in concentrated gas stream can be captured and sequestered more easily and at lower costs.

Efficiency Benefits

35% typical plant efficiency of conventional subcritical pulverized coal (PC) power plant

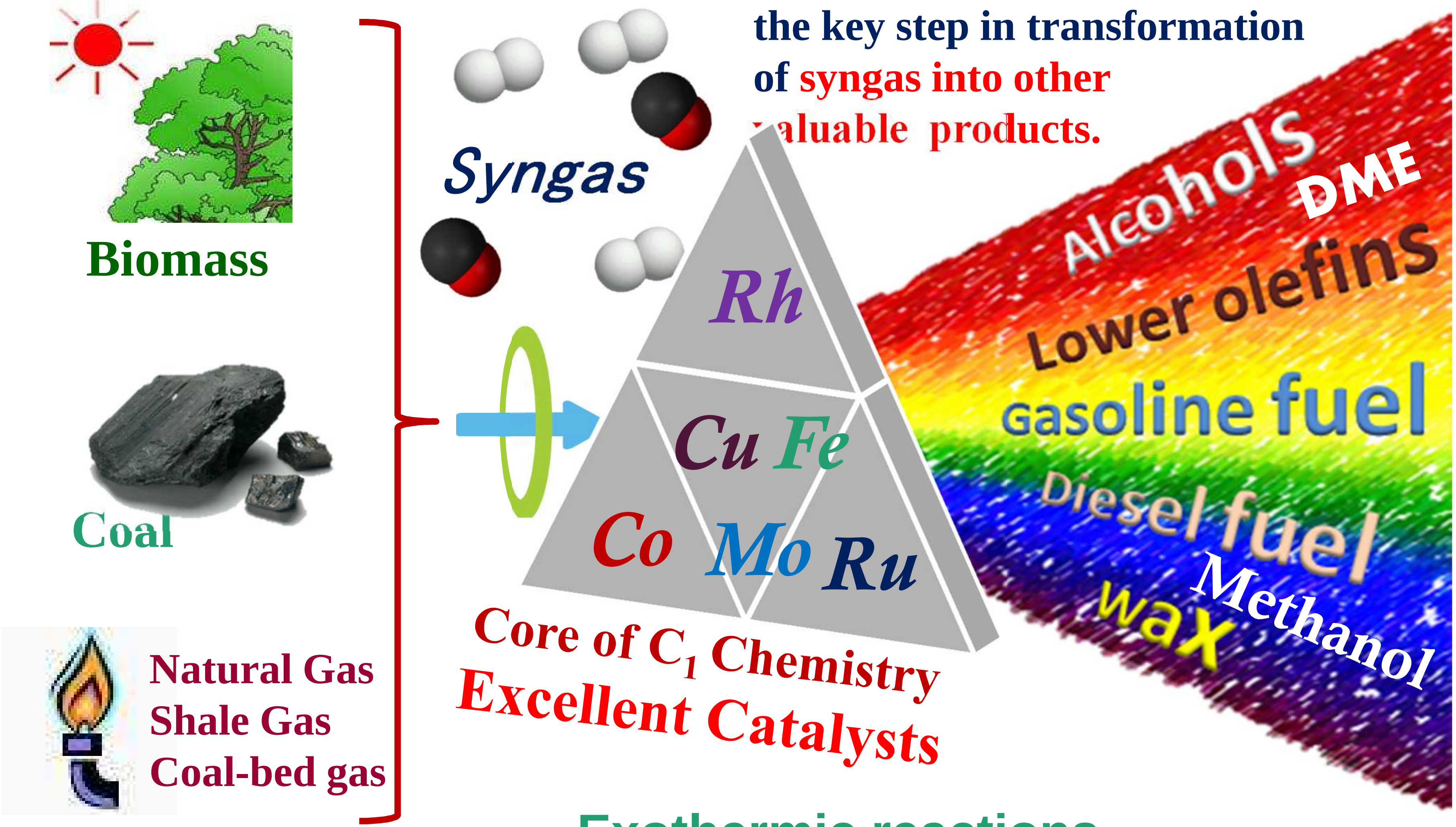
> 50% fuel efficiency of coal gasification plants



Puertollano integrated gasification combined cycle (IGCC) Plant

Syngas is an important intermediate for fuels and chemicals

Fischer-Tropsch (FT) synthesis is the key step in transformation of syngas into other valuable products.



Biomass

Coal

Natural Gas
Shale Gas
Coal-bed gas

Syngas

Rh

Cu Fe

Co Mo Ru

Core of C_1 Chemistry

Excellent Catalysts

Alcohols

DME

Lower olefins

Gasoline fuel

Diesel fuel

wax

Methanol

Exothermic reactions

Gas-To-Liquids, Coal-To-Liquids, Biomass –To Liquids : GTL industrial reality

Natural gas (CH_4)

Syngas
H_2 + CO

Natural gas

≈ 1100 billon barrels eq. crude oil

Syngas Production

Steam reforming
- *Partial oxidation*
- *Autothermal reforming*

Fischer-Tropsch process

Syngas conversion into hydrocarbons (LT-FT)

Final products

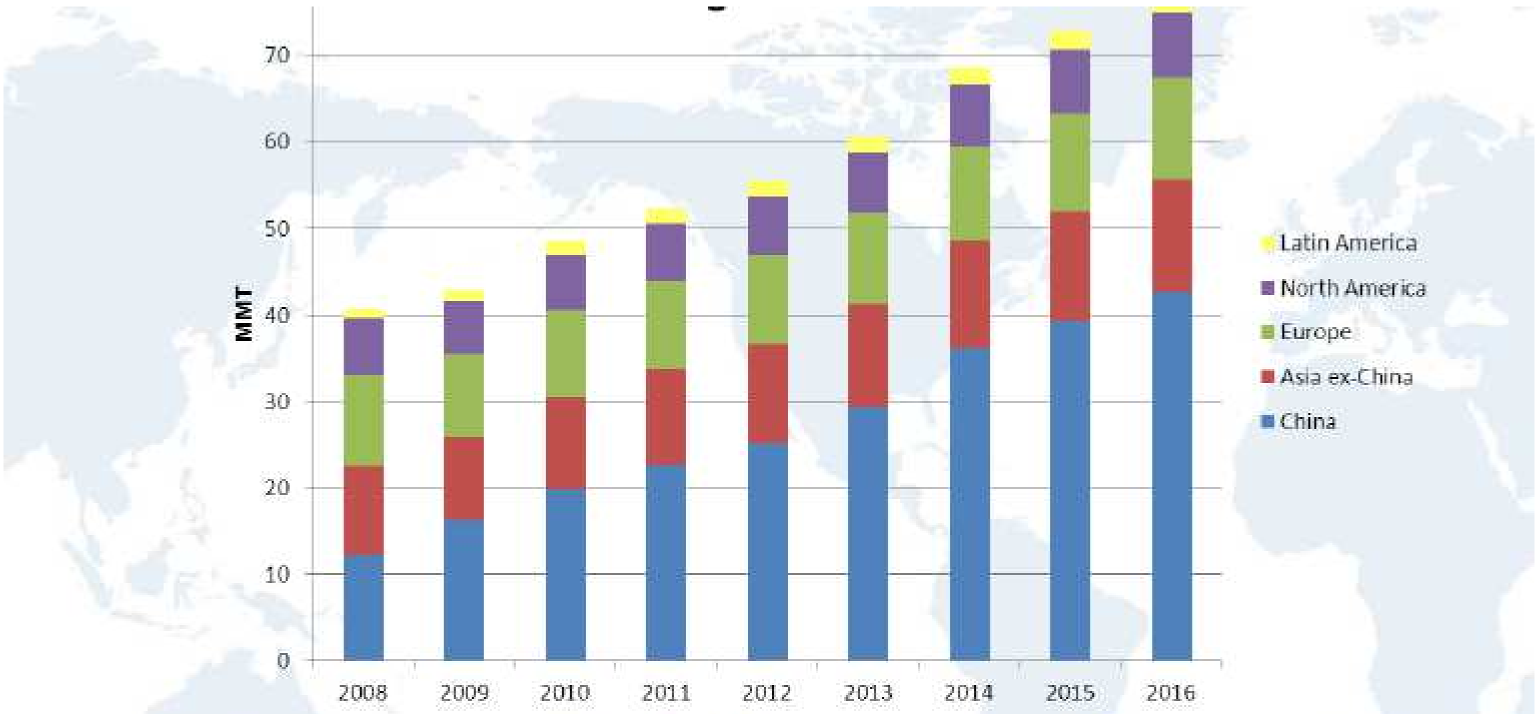
-Hydrocracking
-Hydroisomerisation

AN INDUSTRIALLY FEASIBLE SUPPORTED COBALT SLURRY PHASE FISCHER-TROPSCH SYNTHESIS (FTS) CATALYST WAS DEVELOPED AND COMMERCIALIZED AT THE ORYX GTL PLANT

Two slurry phase FTS reactors
(Height = 60m; Diameter = 10m)

- Plant was inaugurated on 6 June 2006

Methanol demand
Capacity 100 million tons per year



- China represents ~ 80% of global demand growth 2016 versus 2011
- Asia ~ 70% of global demand by 2016
- More moderate Atlantic growth projected

Source: CMAI, August 2012 (excludes integrated MTO demand)

Methanol Synthesis from Syngas

$CO+2H_2=CH_3OH$ exothermic

$CO_2+3H_2= CH_3OH + H_2O$ exothermic

$CO+H_2O=CO+H_2$ exothermic

Catalyst: $Cu/Zn/Al_2O_3$

T=240-270°C (thermodynamic limitations)
P=50-100 bars

3000-5000 t/j
ICI, Lurgi, Topsoe

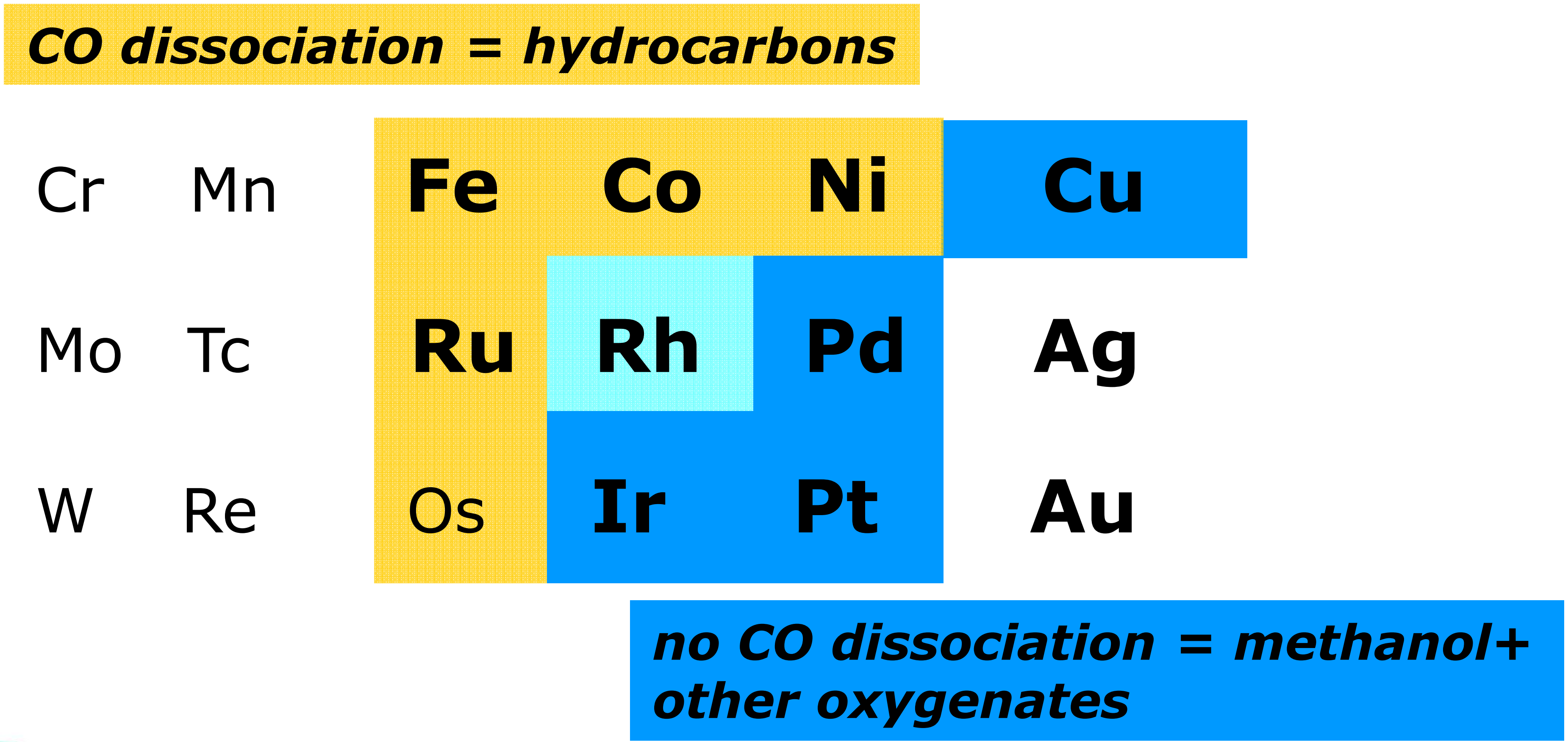
Catalysts for syngas conversion: metals, sulfides and carbides

Catalyst	Products
Fe/Fe_xC_y	gasoline, olefins, oxygenates
Co	diesel and waxes
Ru	too expensive and volatile
Ni	methanation
Rh	ethanol, C_{2+} oxygenates
Pd	methanol
Cu	methanol
MoS_2/Mo_2C	alcohols, olefins

Selectivity?

Selectivity challenge in syngas conversion

Hydrocarbons or oxygenates?



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+ other oxygenates

From J W (Hans) Niemantsverdriet

Model of linear polymerization (Schulz, Flory 1935-1936) adapted by Anderson

$$\alpha = \frac{v_p}{v_p + v_t}$$

α is the probability of chain growth,

v_p and v_t propagation and termination rates

$$S_n = \frac{n\alpha^n (1-\alpha)^2}{\alpha}$$

Mass fraction of C_n hydrocarbon

Broad Anderson-Schulz-Flory (ASF) distribution

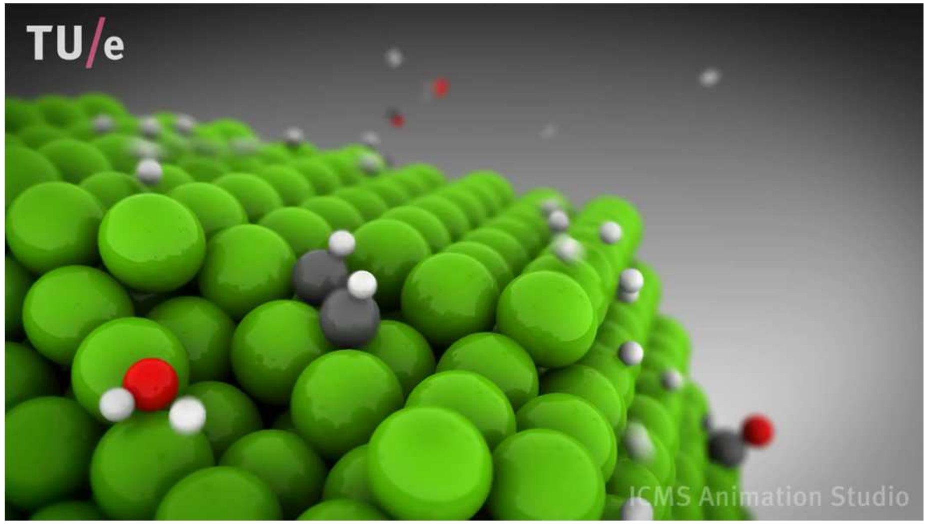
Main reactions:

$H_2 + CO \rightarrow C_nH_{2n+2}$ (Paraffins)

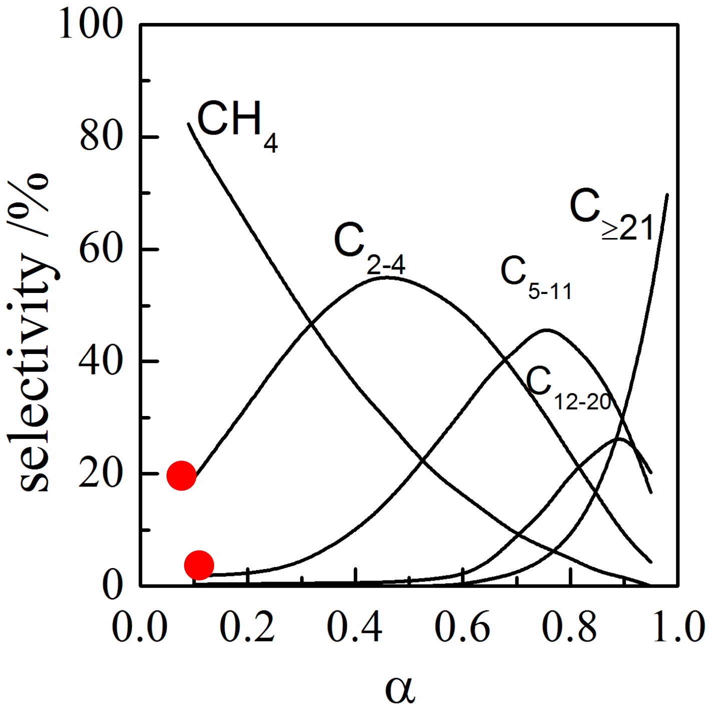
$H_2 + CO \rightarrow C_nH_{2n}$ (Olefins)

$H_2 + CO \rightarrow C_nH_{2n+1}OH$ (Oxygenates)

The mechanism of polymerization
Anderson-Schulz-Flory(ASF)



Video from ICMS, Eindhoven University of Technology



Chain growth factor α

Challenge: increasing the $C_{2-4}^{=}$, C_{5-11} and C_{12}-C_{20} selectivities

Production of water and carbon dioxide in syngas conversion

Water gas shift reaction

$CO+H_2O \leftrightarrow CO_2+H_2$

CO_2 is thermodynamically favored at FT reaction temperatures (200-300°C)

- **$CO+2H_2$=-CH_2-+ H_2O**

Cobalt, ruthenium catalysts

- **$2CO+H_2$=-CH_2-+CO_2**

Iron, molybdenum sulphide catalysts….

CHALLENGE: DEACTIVATION OF CATALYSTS FOR SYNGAS CONVERSION

- Deactivation as a major challenge
  - Higher operational cost
  - Lower catalyst productivity
- Several possible mechanisms

Sintering

Carbon Deposition

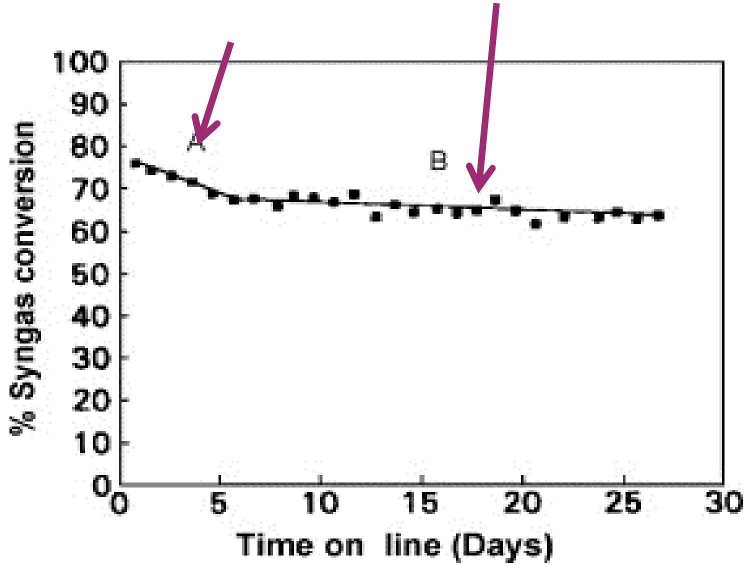
Cobalt Loss

Oxidation

Metal-Support Compounds

Poisoning

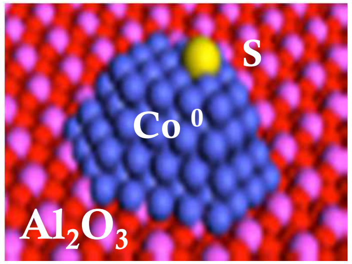
Catalyst and reactor effects



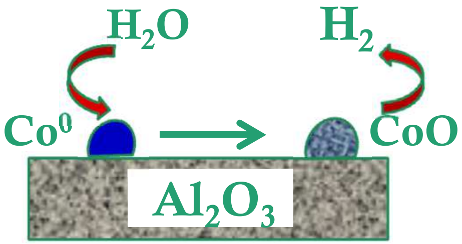
Two-step catalysts deactivation process in demonstration plants for both cobalt and iron based catalysts (van Berge and Everson, 1997)

Deactivation mechanisms

(1) Poisoning



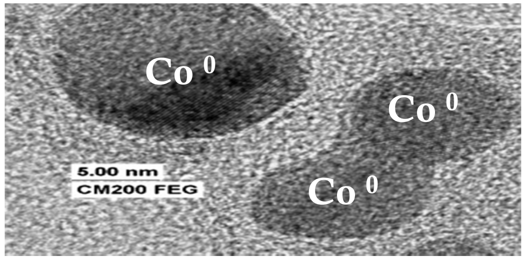
(2) Metal re-oxidation



(3) Mixed compounds

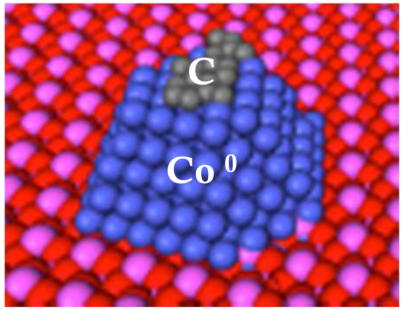
$Co^0 \xrightarrow{\text{oxidation}} CoO \xrightarrow{\text{diffusion}} CoAl_2O_4$

(4) Sintering

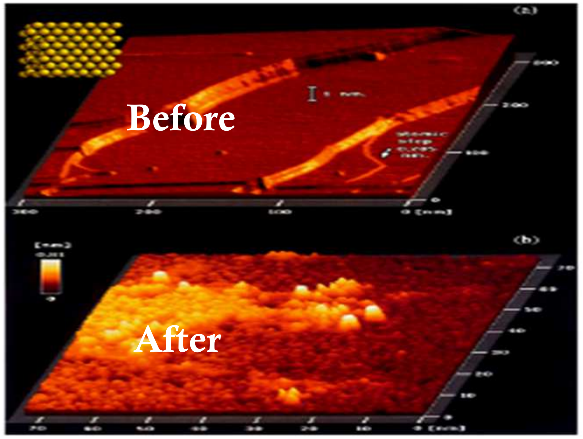


S. Soled, et al, Proc. 11th Int. Symp. 21st North American Meeting 2009

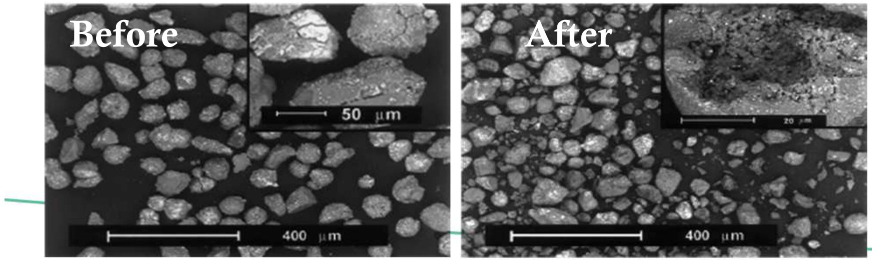
(5) Carbon deposition



(6) Surface reconstruction



J. Wilson, C. de Groot, J. Phys. Chem. 99 (1995) 7860–7866



R. Zhao et al. Applied Catalysis A: General 189 (1999) 99–116

(7) Catalyst attrition (catalyst loss in slurry reactor)

Crucial challenges in syngas conversion

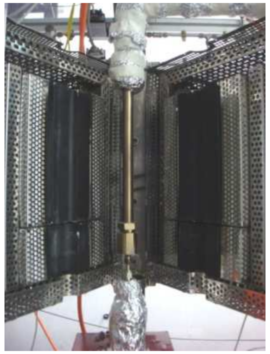
Selectivity and catalyst stability

Which are the important parameters which influence the selectivity and stability?

Examples

Tools: Laboratory Reactors for Syngas Conversion

Centimetric fixed bed



ID = 1.3 cm
L = 5 cm
m_{cat} = 1 g
SiC/Cat = 5:1
Electrical heating

Milli-fixed bed

ID = 0.14 cm
L = 32 cm
m_{cat} = 0.5 g
No SiC dilution
Double-shell heat exchanger

Slurry stirred tank reactor

Mechanically stirred (100 mL)
m_{cat} = 5 g
Catalyst suspended in wax

High Throughput Flowrence Unit from Avantium

16 parallel reactors

A High Throughput Technologies REALCAT Platform: Catalyst Synthesis, Characterization and Test

How to control the selectivity in Fischer-Tropsch synthesis?

- **Using the two stage process =Two catalysts and two reactors**

Fischer-Tropsch synthesis+Hydrocracking

Industry (Oryx, Pearl Qatar)

- **Bifunctional catalysts**

Well-dispersed metal particles + Mordenite, Beta and ZSM-5 zeolite

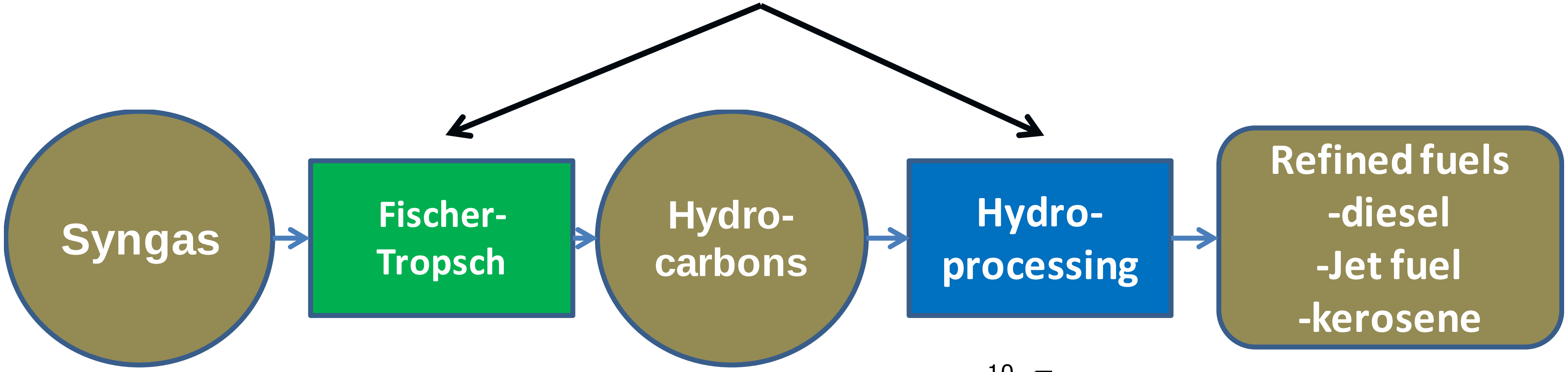
- **Nanoreactors**

Metal particle encapsulation, steric effects on chain growth

- **Promotion (Iron catalysts)**

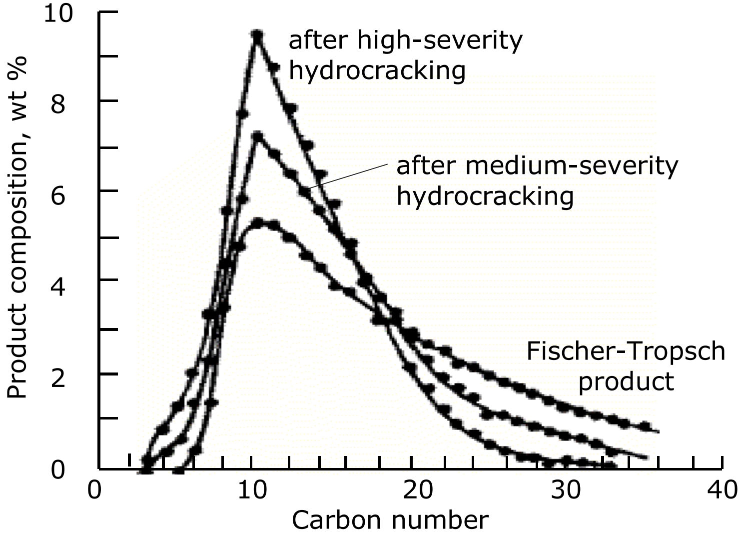
Selectivity to olefins and alcohols to olefins, alkanes and alcohols

Two stage process =Two catalysts and two reactors



Syngas → Fischer-Tropsch → Hydrocarbons → Hydroprocessing → Refined fuels
-diesel
-Jet fuel
-kerosene

Sasol-Qatar Petroleum Oryx Plant Qatar

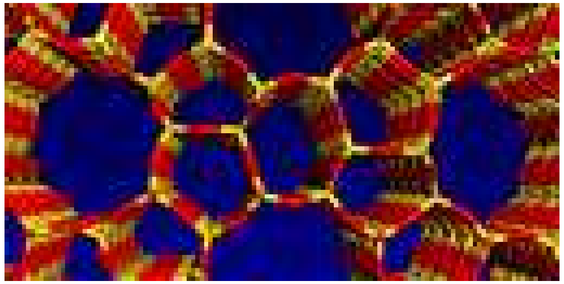


Hydrocarbon distribution of the Fischer-Tropsch products over cobalt-based catalysts and by additional hydrocracking (adapted from Sie and Senden)

Bifunctional catalysts
Co/Zeolite

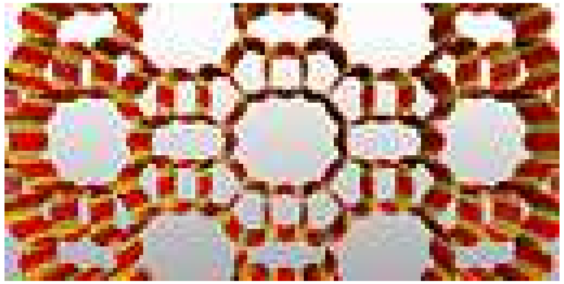
Two reactions (Fischer-Tropsch and cracking/isomerisation) on the same catalyst

ZSM-5



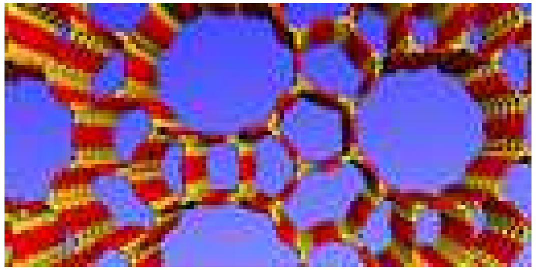
Pore diameter = 5.5 Å

Mordenite



Pore diameter = 6.5 Å

Beta



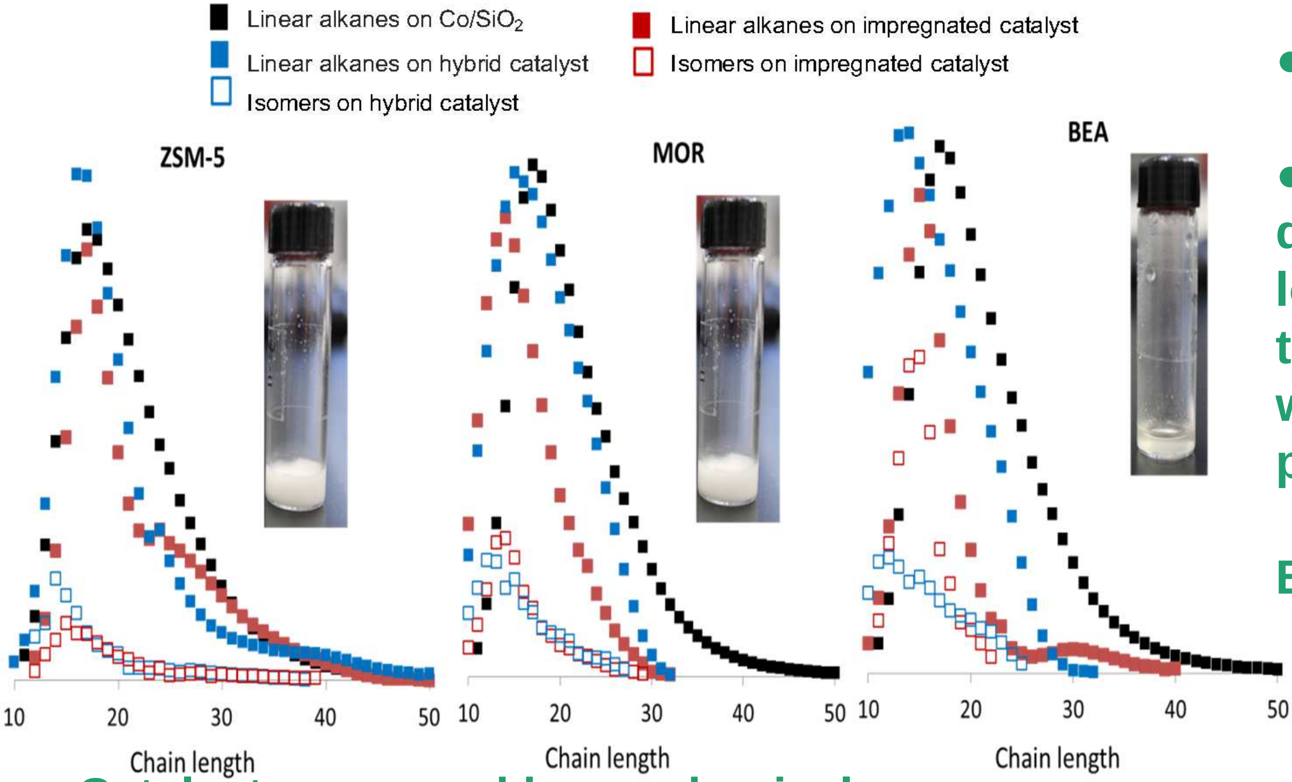
Pore diameter = 7.6x6.4 Å

Pore diameter →

"Small sizes of the pore is a handicap for the ZSM-5 zeolite…"
C. Marcilly, Zeolites in the Petroleum Chemistry

C_{10}-C_{20}

Bifunctional catalysts: Hydrocarbon distribution in heavier products



Catalysts prepared by mechanical mixing and by impregnation

- Zeolite porous structure

- The most significant decrease in the fraction of long chain hydrocarbons or the BEA based catalysts, which have the most open pore system.

BEA>MOR>ZSM-5

Wax over Co/BEA is liquid in comparison with solid wax formed over Co/ZSM-5 and Co/MOR!

Nanoreactors: Shape Selectivity Concept

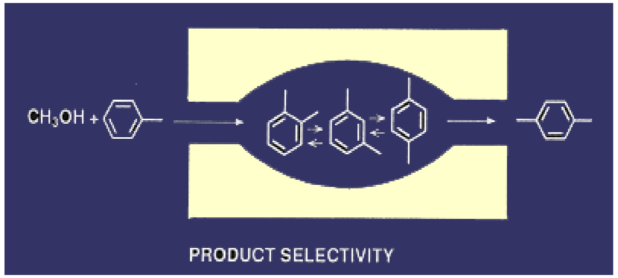
The shape selectivity concept suggests that “the transformation of reactants into products depends on how the processed molecules fit the active site of the catalyst” [B. Smit, T. L. M. Maesen, Nature 2008].

commonly used for zeolites

Reactant

Transition state

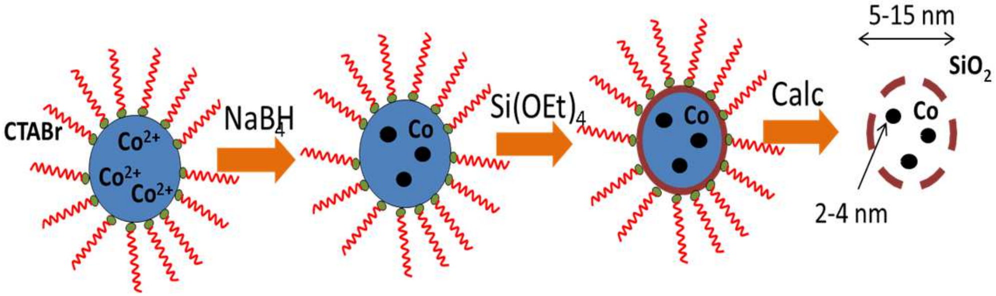
Products



Shape selectivity concept for Fischer-Tropsch synthesis

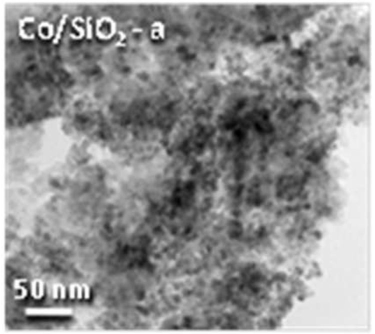
Developed with Dr. V. Ordomsky (UCCS)

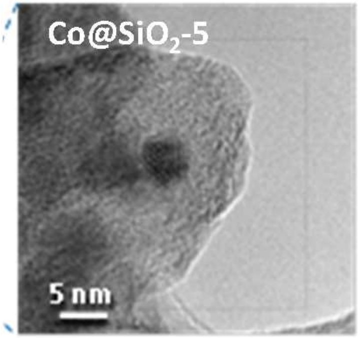
Nanoreactors: Synthesis

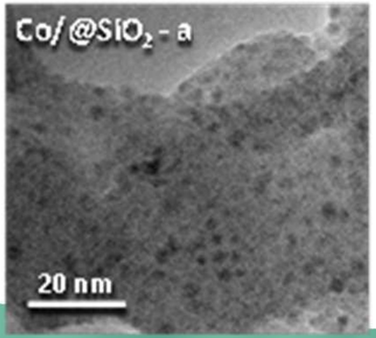


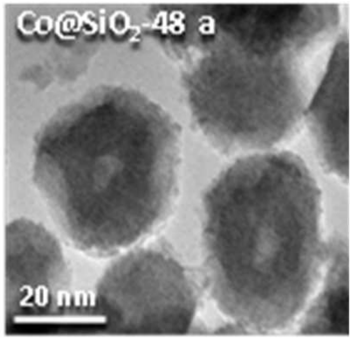
Impregnated samples

Nanoreactors







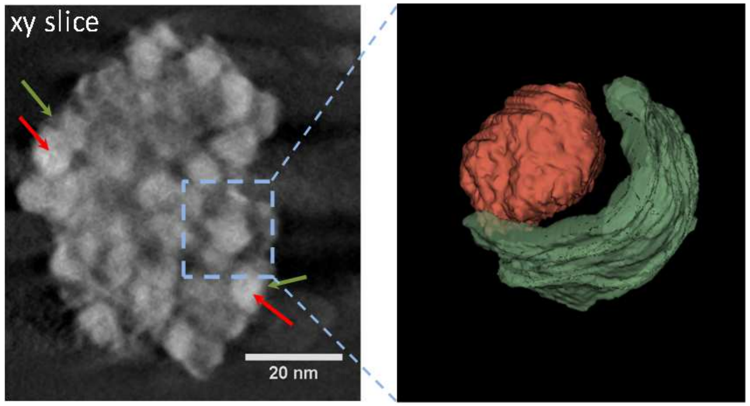


- Surfactant (CTAB) dispersed in hexanol
- addition of Co $(NO_3)_2.6H_2O$
- Clear emulsion was mixed with $NaBH_4$.
- After stirring the appropriate amount (to obtain 90 wt.% of SiO_2) of TEOS was added and allowed to hydrolyze during 5 h for $Co@SiO_2$-5 or 48 h for $Co@SiO_2$-48.
- The metal nanoparticles coated with silica were washed thoroughly using ethanol and water, dried and calcined.
- Co/SiO_2 prepared using nitrate impregnation

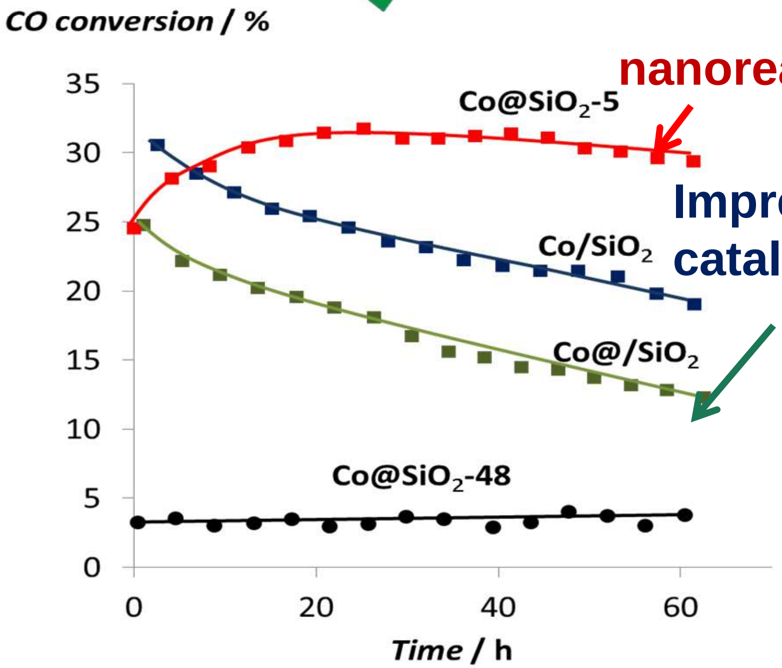
$Co@SiO_2$ prepared via impregnation with cobalt nanoparticles

Nanoreactors: Catalytic performance in Fischer-Tropsch synthesis

GHSV takes into account different cobalt loading



Slices redrawn from the volume reconstructed from the electron tomography analysis under STEM-HAADF
(S. Moldovan and O. Ersen).



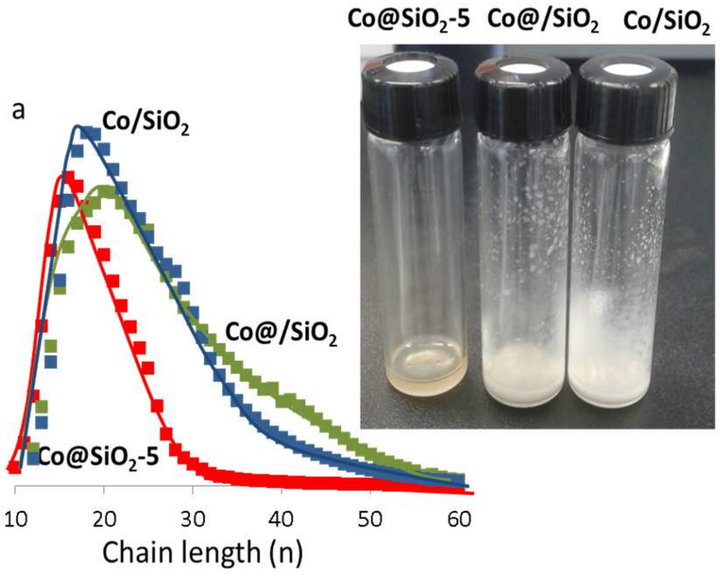
nanoreactors

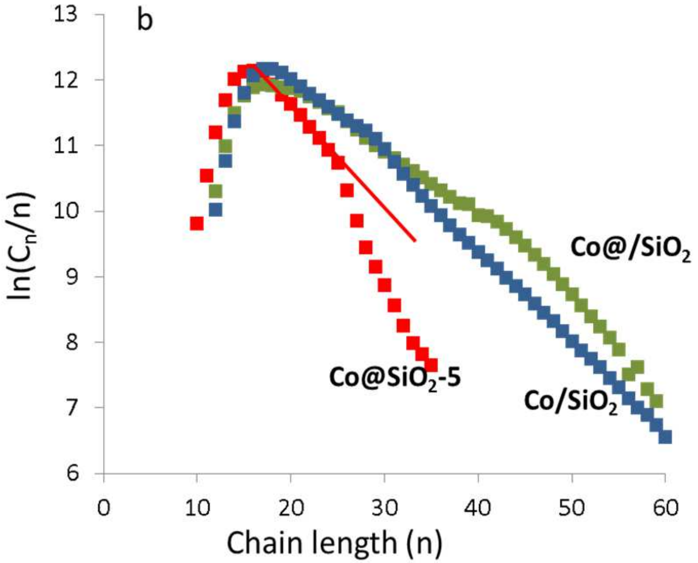
Impregnatec catalysts

240°C, 20 bar, H_2/CO= 2, GHSV of 67 L/g_{Co}·h

High activity per cobalt and better stability

Nanoreactors: Hydrocarbon selectivity





ASF distribution for both the Co/SiO_2 and $Co@/SiO_2$ catalysts prepared by impregnation.

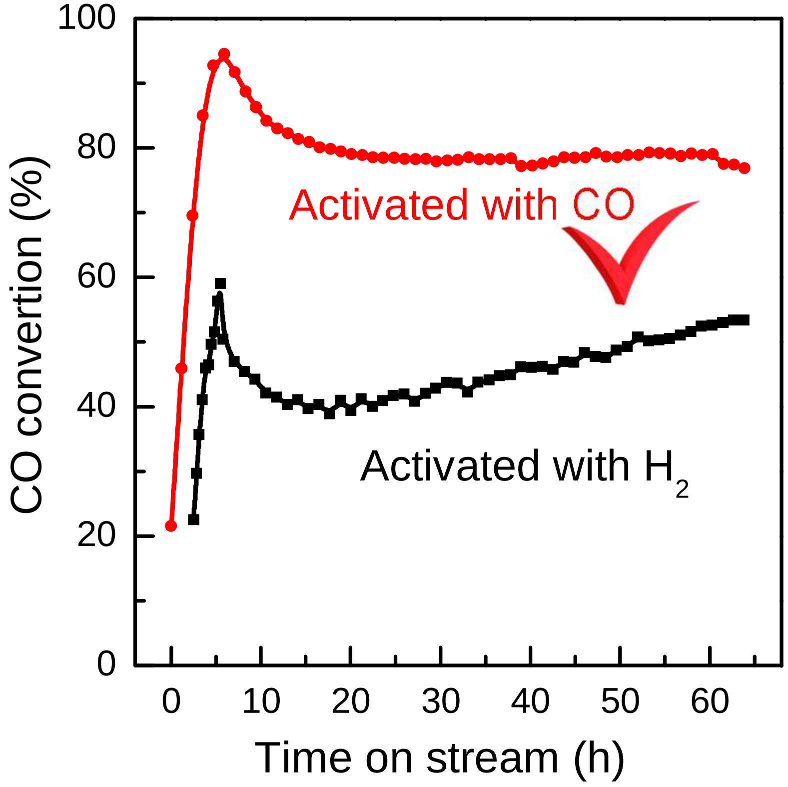
Significant deviations from the ASF distribution for $Co@SiO_2$-5.

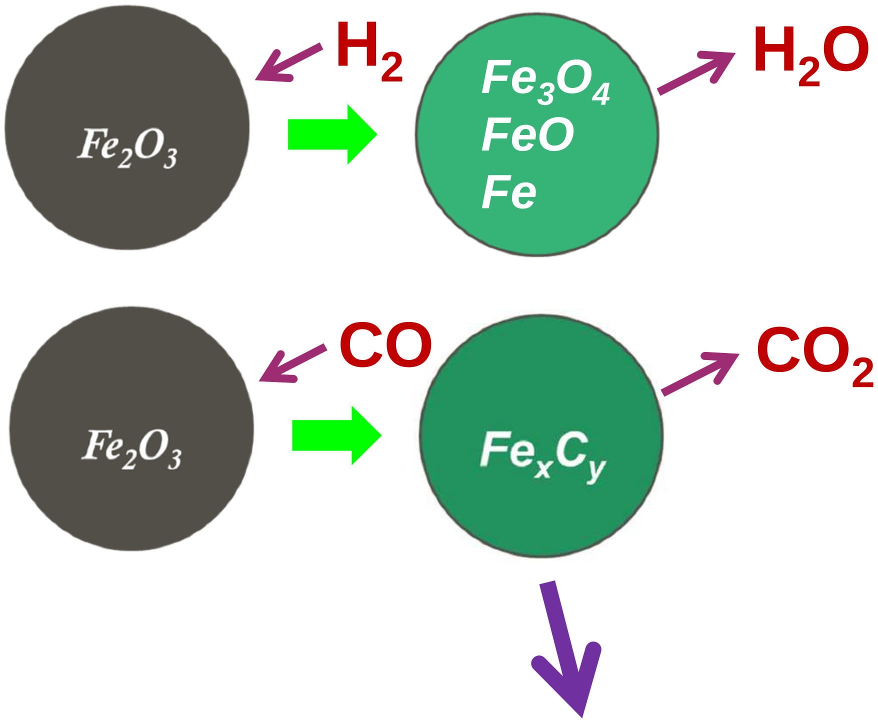
Lower selectivities to heavier hydrocarbons than could be expected from the ASF model.

No increase in methane selectivity (S_{CH4}=2-4%)

Growth of hydrocarbon chain restricted by the nanoreactor volume ($C_{30}H_{62}$, d=3.5 nm).

Selectivity control on iron catalysts : Active phase in iron carbide catalysts





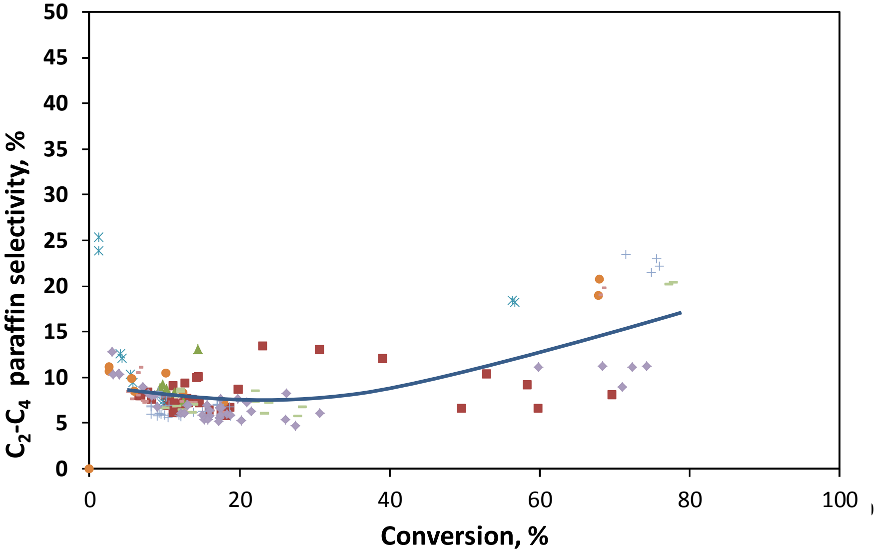
Supposed to be active phase for FTS.

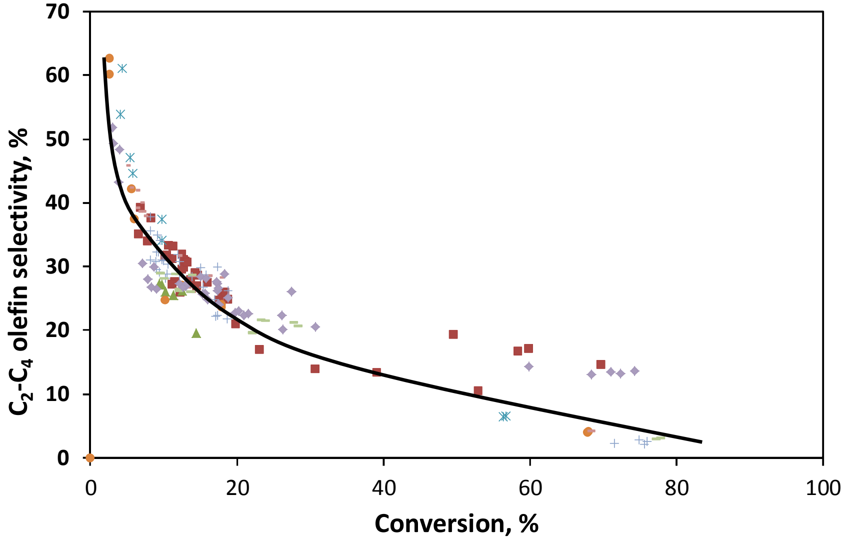
Results based on Fe/SiO_2 (Commericial silica)

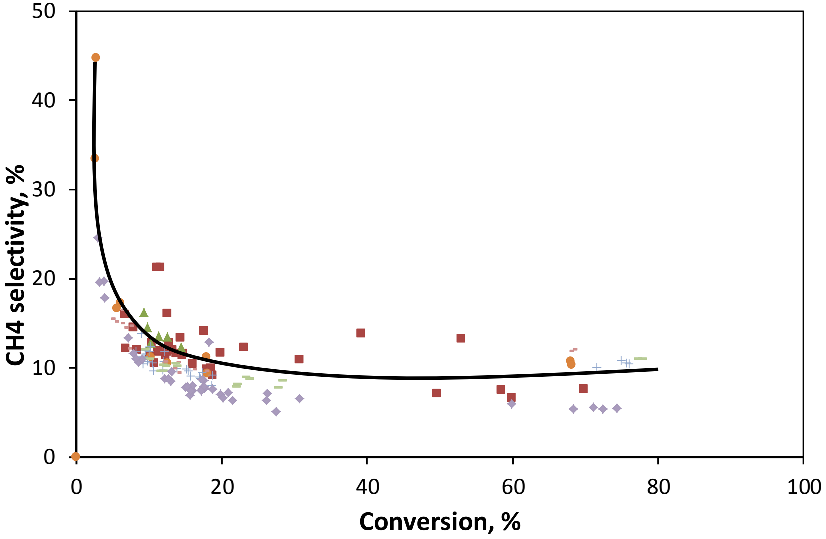
Activation conditions: H_2 or CO flow at 623 K for 10 h.
Reaction conditions: catalyst, 1.0 g; $H_2/CO = 2.1$; GHSV, 3.6 NL $g^{-1}h^{-1}$; temperature, 573 K; pressure, 20 bar; time on stream, 60 h.

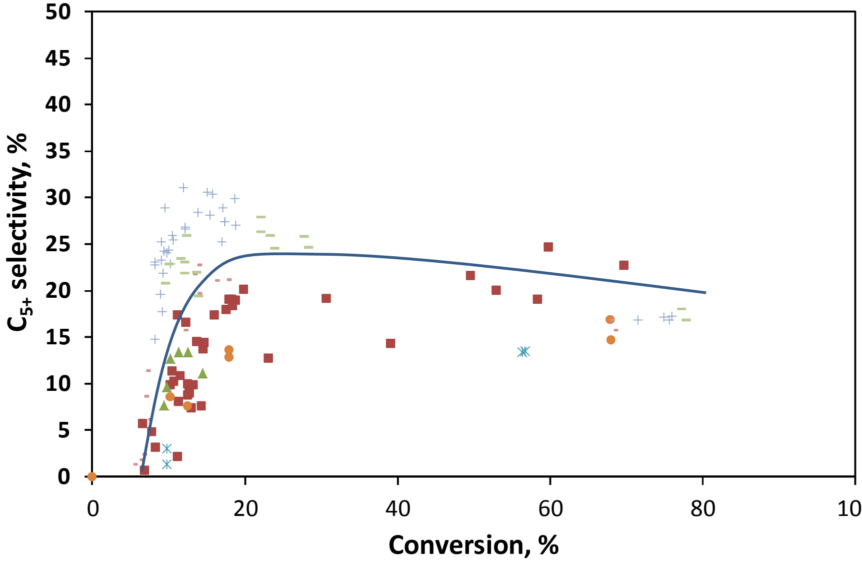
General trends in CO hydrogenation on iron catalysts – HTE Results UCCS

(series of mildly promoted Fe/SiO_2, Fe/P=100:2, H_2/CO=1, p=10 bar)



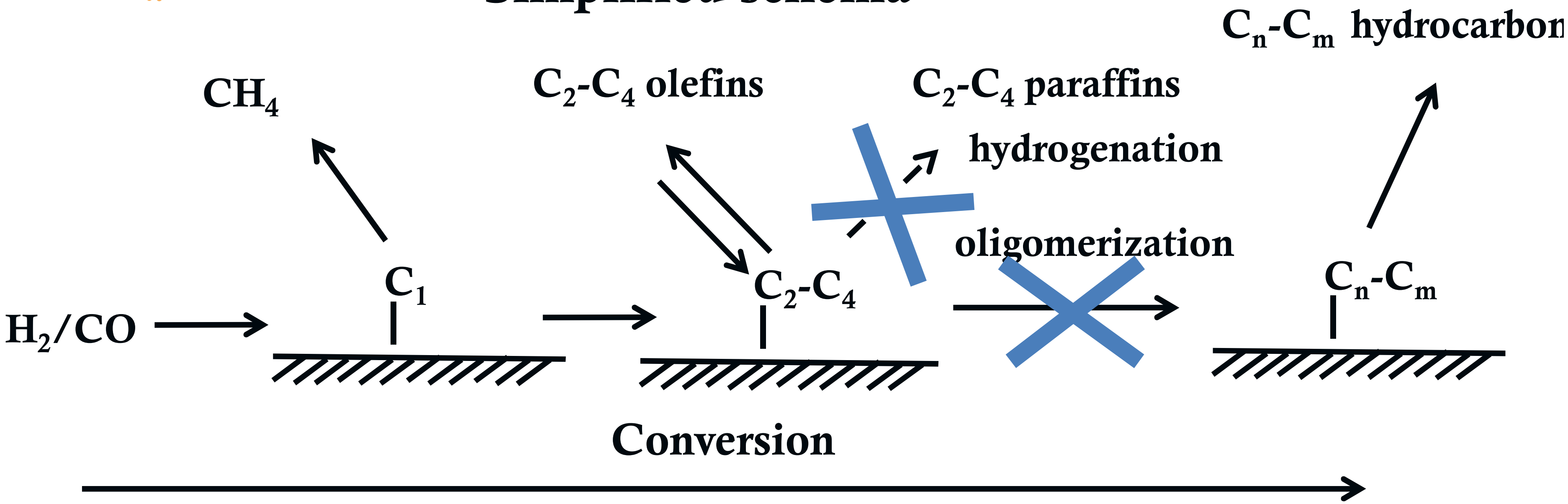






Trends in CO hydrogenation on Fe/SiO_2

Simplified schema

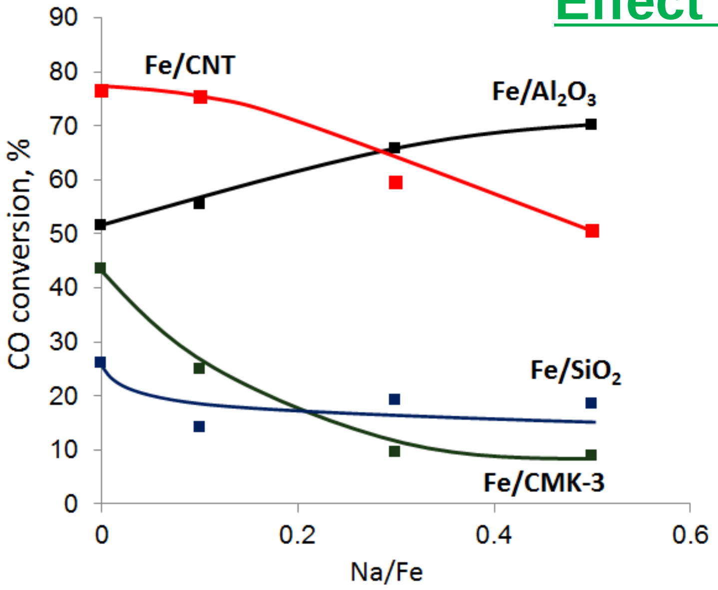


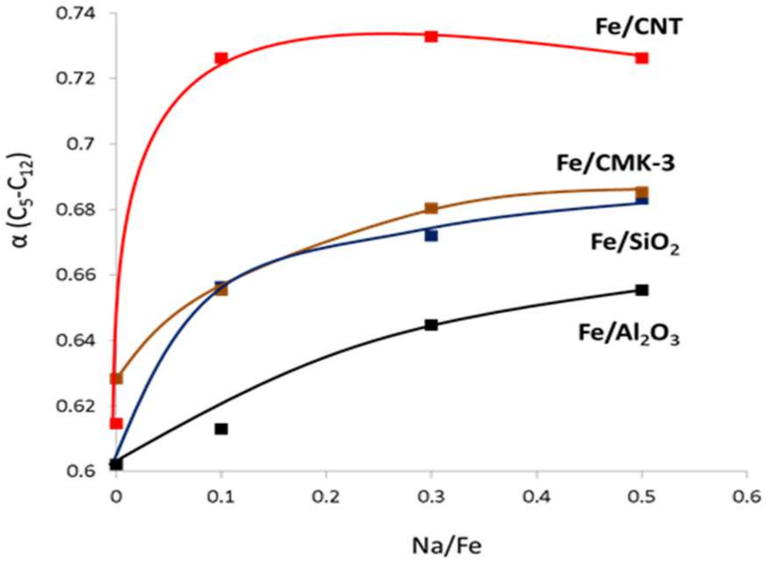
How to improve selectivity to light olefins?

- Slow down surface polymerization
- Decrease the catalyst hydrogenation activity

Na promotion: Decrease in hydrogenating activity, enhancement of chain growth

Effect of the support





CO conversion and ole/para ratio in C_2-C_4 products depending on Na/Fe ratio

(P = 2 MPa, H_2/CO=2.1, GHSV=16 L h^{-1} g^{-1}, T = 573 K)

Different effect of Na on the catalytic performance depending on the support

Na addition causes activity decreasing for Fe/CNT, Fe/SiO$_2$, and Fe/CMK-3

Increase in the activity of Fe/Al$_2$O$_3$

Increase in ole/paraffin ratio after promotion with Na

Increase in chain growth probability

Another way to FT control selectivity: iron-zeolite bifunctional catalysts

FT synthesis

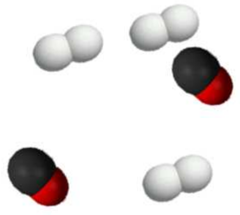
Iron carbide

ASF Hydrocarbons

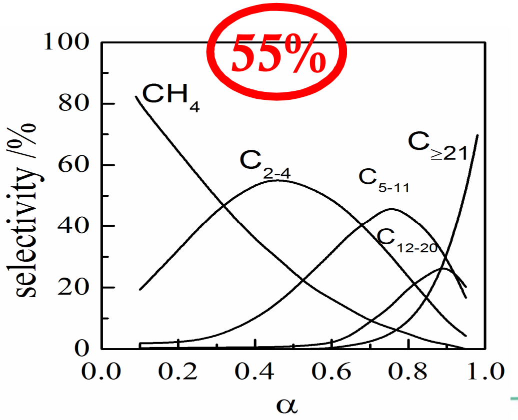
Zeolite

Cracking/ isomerisation

Non ASF Hydrocarbons



Syngas



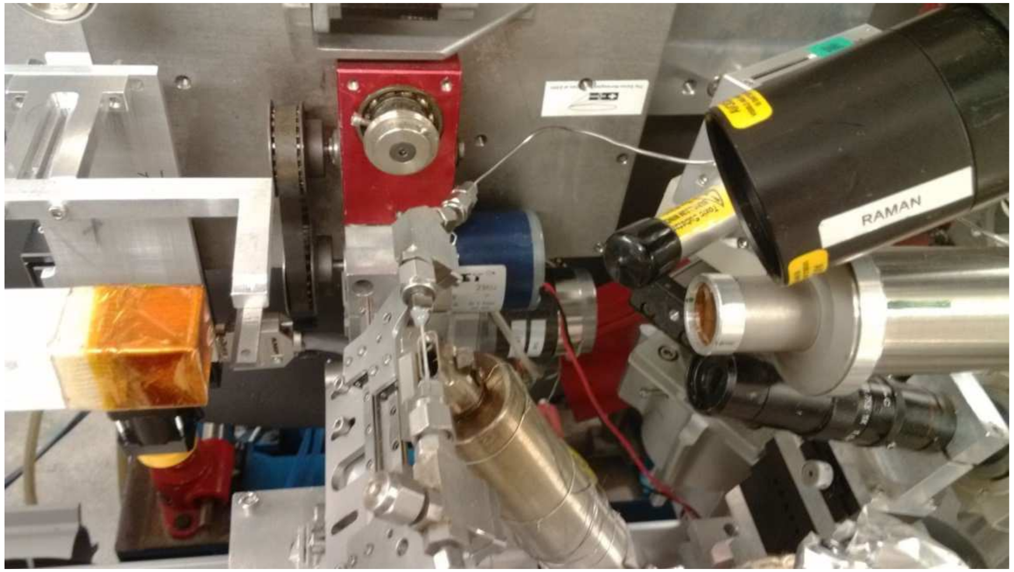
Chain growth

- Suitable to reduce the hydrocarbon chain
- Not suitable for olefin synthesis because of strong zeolite hydrogenation activity

Challenges in synthesis of fuels and chemicals: Catalyst deactivation

Identification of initial deactivation mechanisms using operando techniques

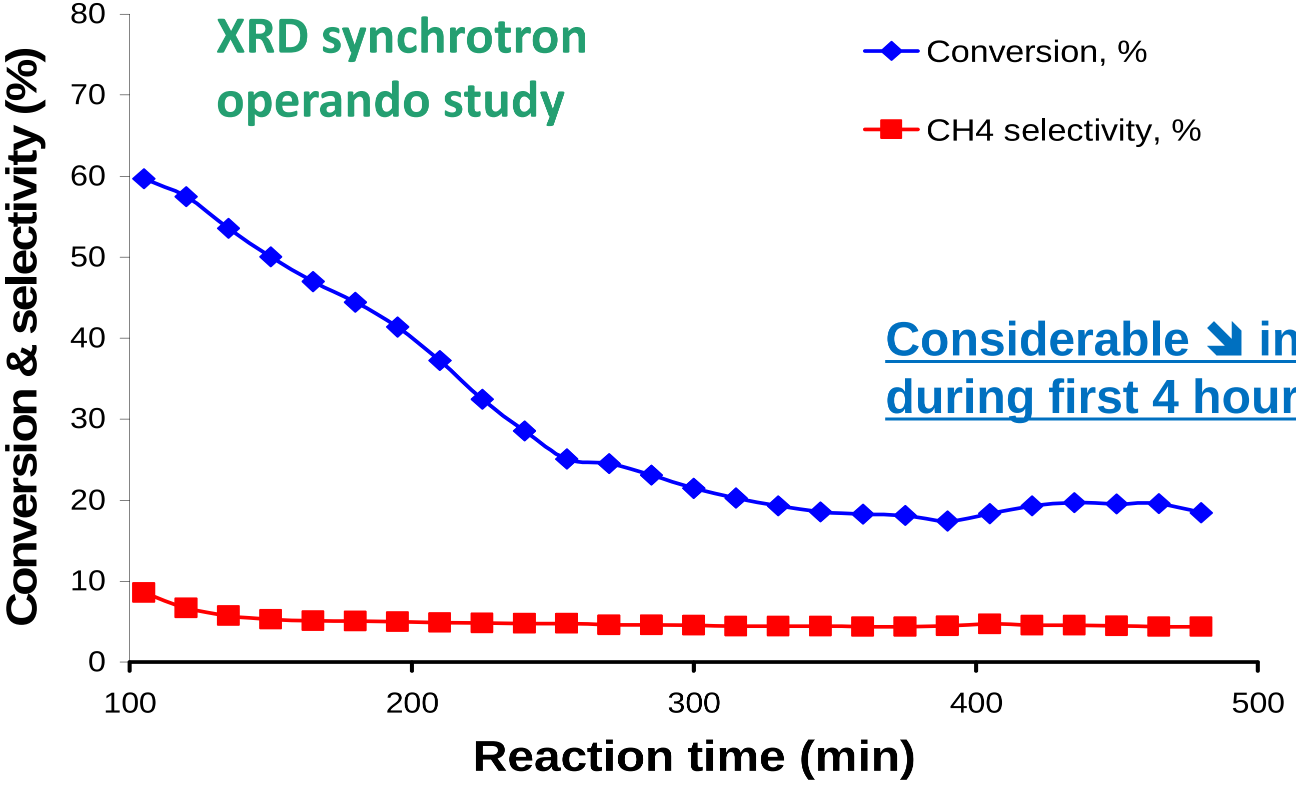
Reactor and setup for in-situ synchrotron based XRD/XAS/Raman measurements



- Real plug flow reactor (20 bar, 200-300° C) with comparable GHSV with lab-scale reactor
- Possibility to follow each step (from the reduction to the reaction)
- XRD and EXAFS/XANES operando measurements

BM01B (SNBL) beamline (ESRF, Grenoble,France)

25%Co0.1%Pt/Al_2O_3 catalyst: Catalytic performance under realistic conditions



XRD synchrotron operando study

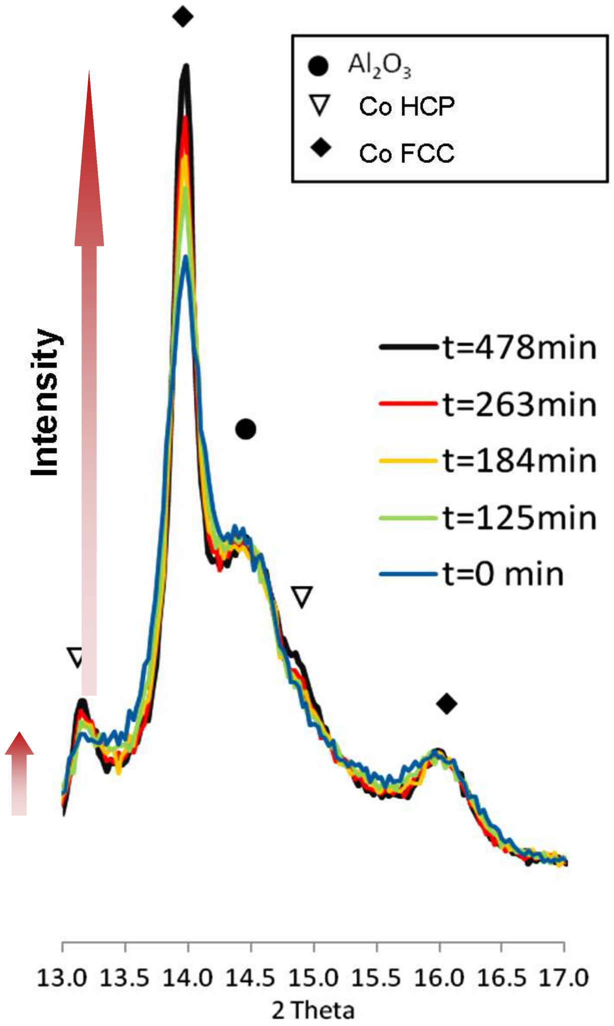
Considerable ↘ in the activity during first 4 hours of reaction

Steady state

P=20 bar, T=220° C, GHSV= 25000 $Nml.h^{-1}/g_{cat}$

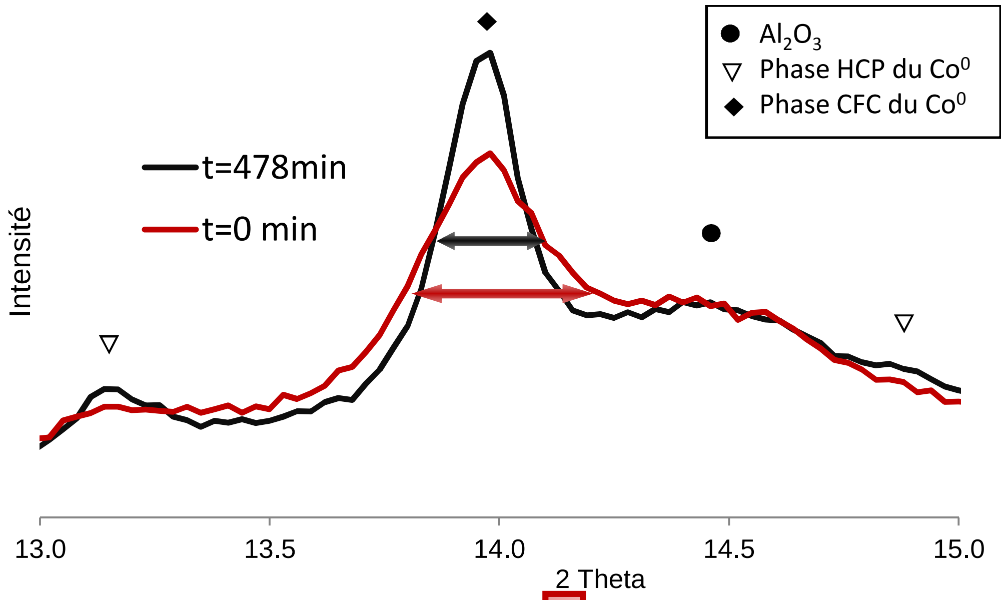
X_{CO} = 19% and S_{CH4} = 4.5%

Evolution of cobalt phases under standard reaction conditions



Changes of XRD patterns

Narrowing XRD patterns

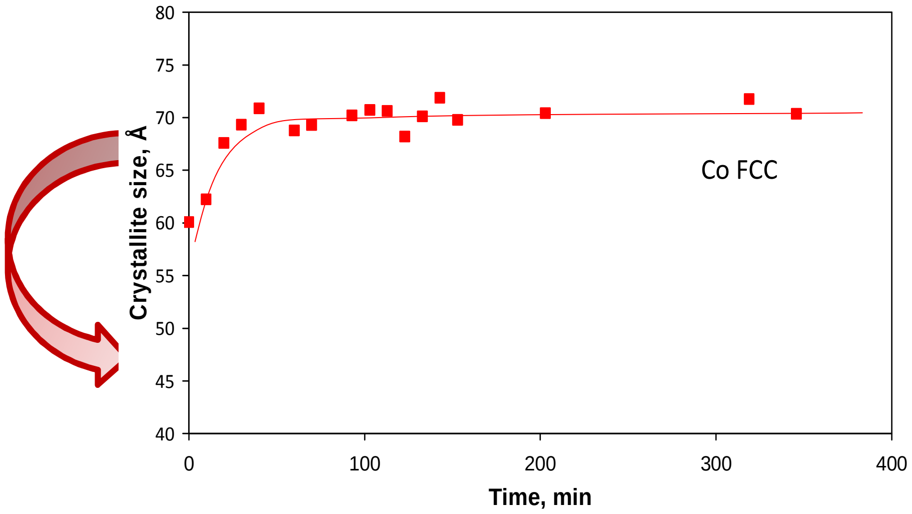


Sintering of cobalt particles, traces of cobalt carbide

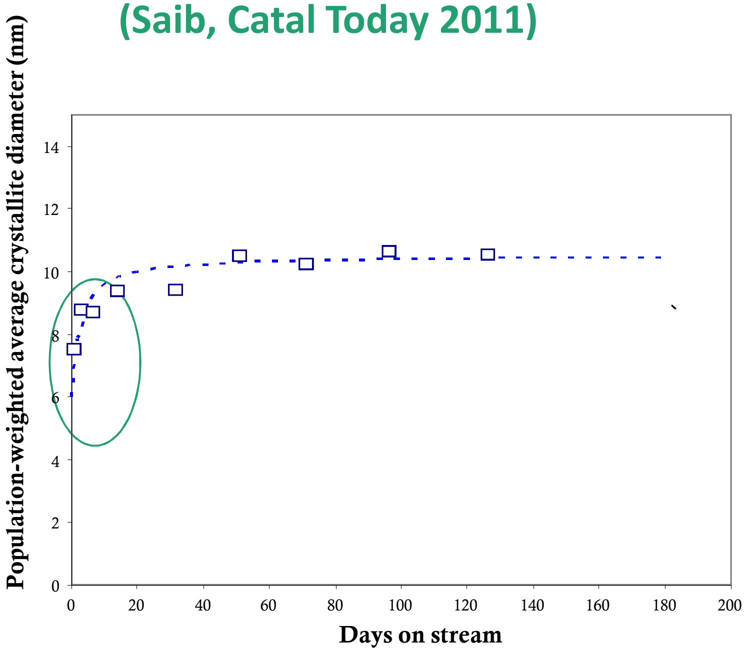
Evolution of cobalt particle size during the reaction under standard conditions

Modeling operando XRD data using « Whole Pattern Matching »

Karaca, Sadeqzadeh, 2011



TEM data with spent CoPt/Al_2O_3 catalyst from slurry pilot plant (Saib, Catal Today 2011)

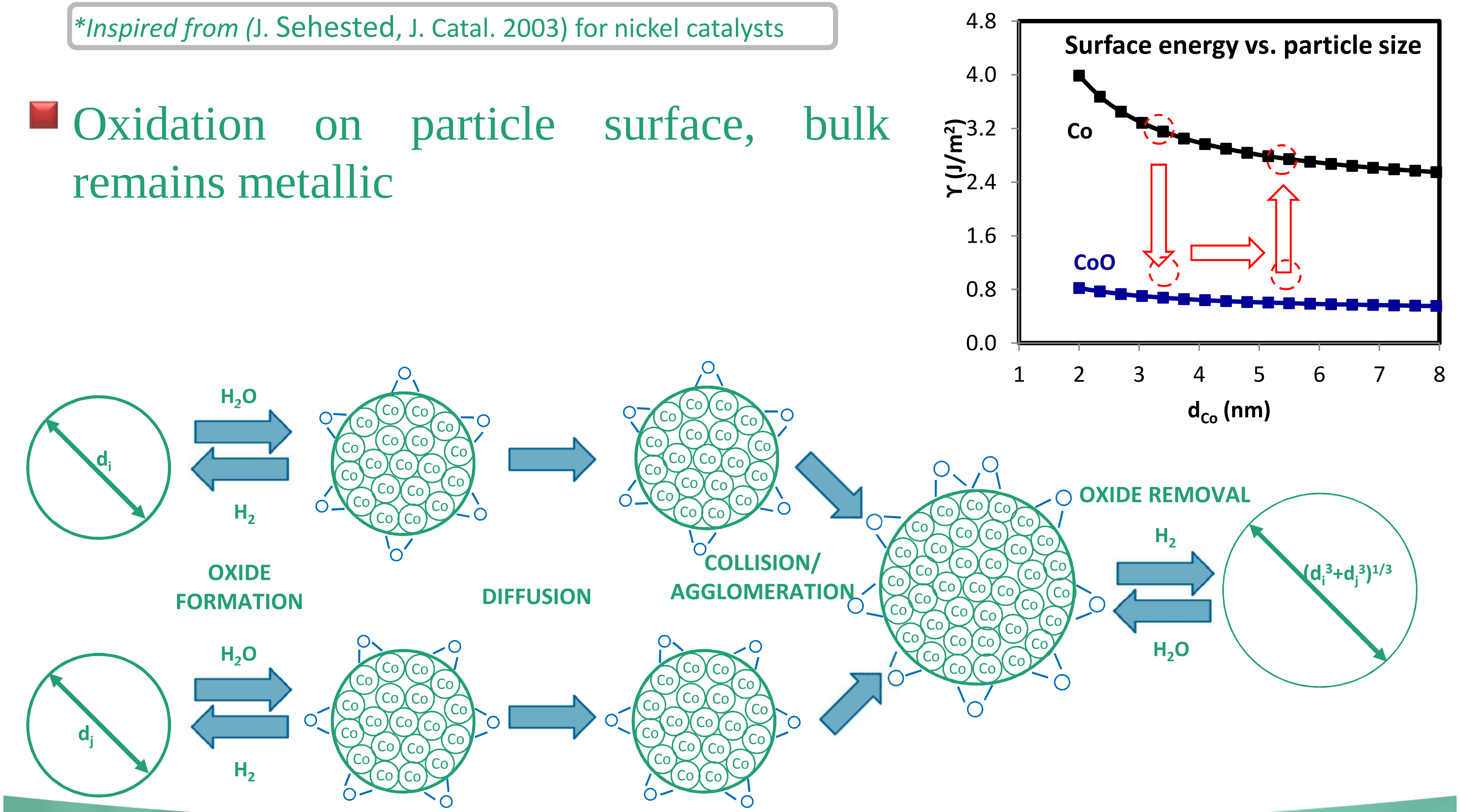


Few hours of the reaction in fixed bed, longer sintering time in slurry reactor?

Sintering mechanism: our concept

*Inspired from (J. Sehested, J. Catal. 2003) for nickel catalysts

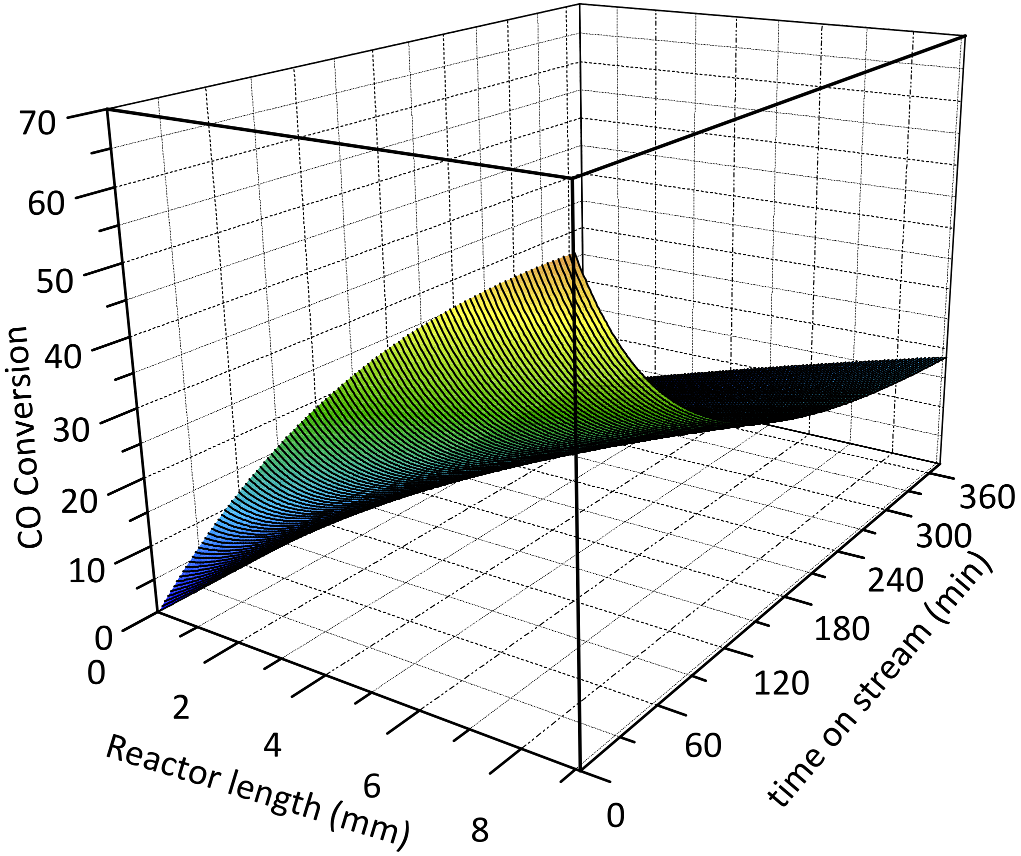
- Oxidation on particle surface, bulk remains metallic

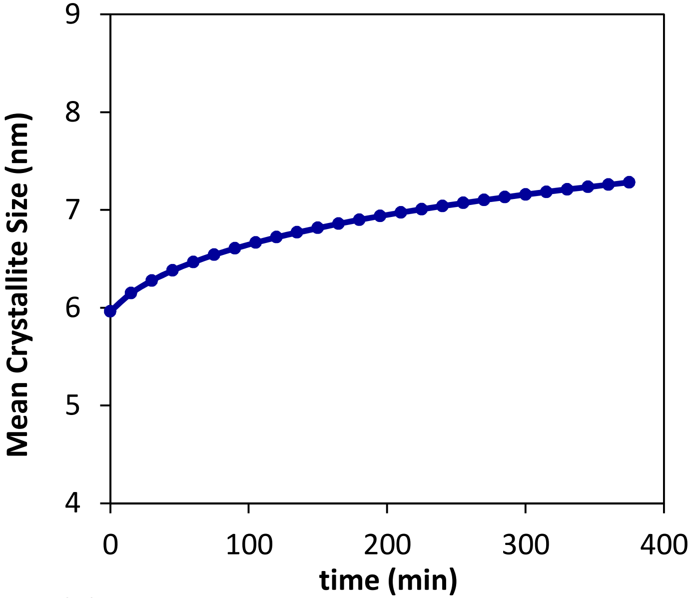


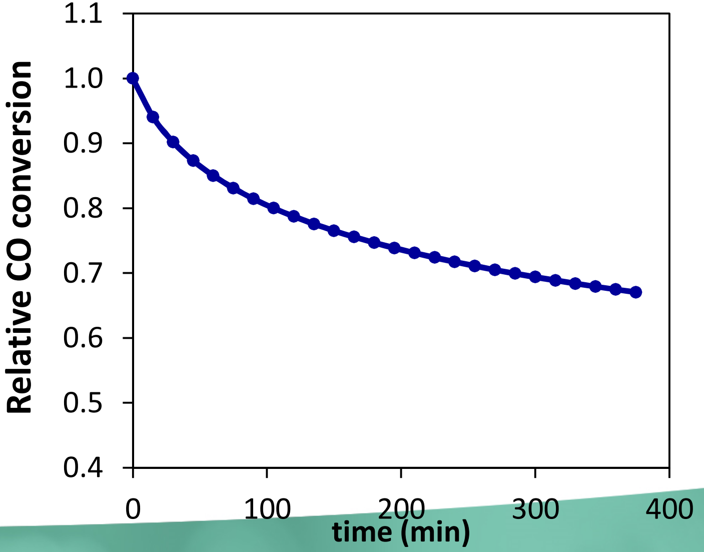
Fixed Bed Reactor Modeling

- Typical Simulation Results

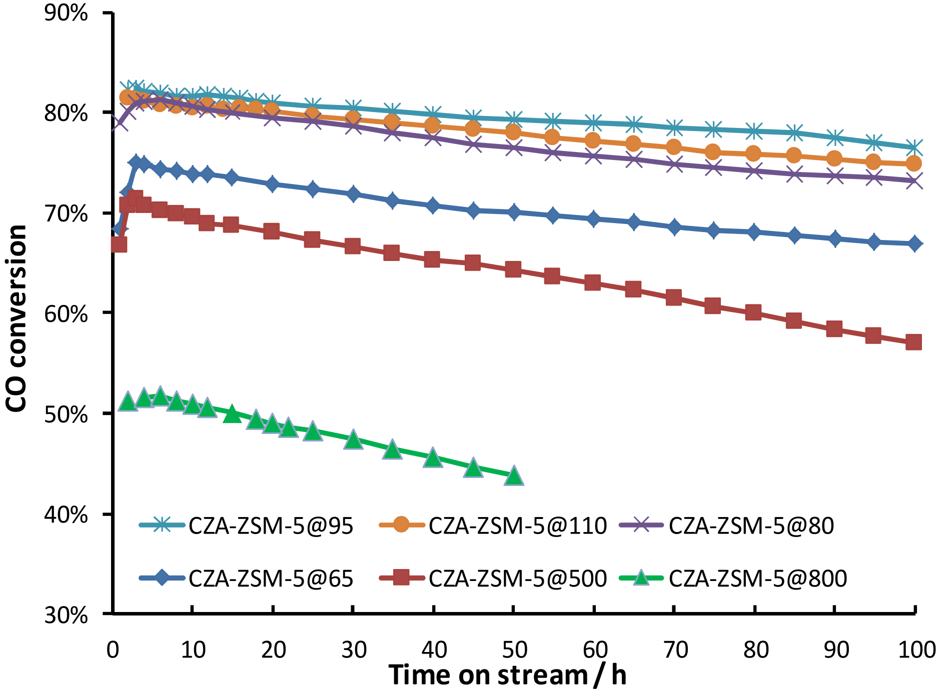
Effect of sintering on the catalytic activity (gPROMS model)

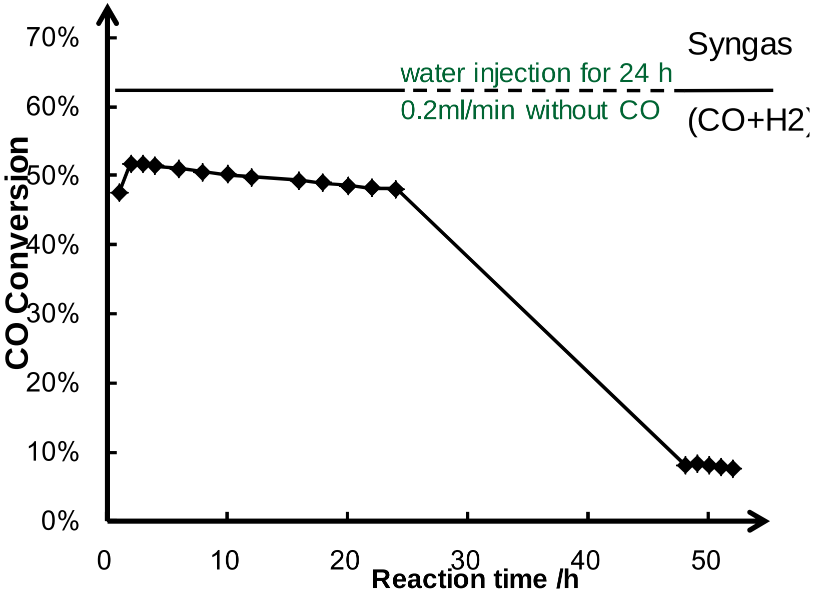






Deactivation of Copper-ZSM-5 catalysts for direct DME synthesis from syngas



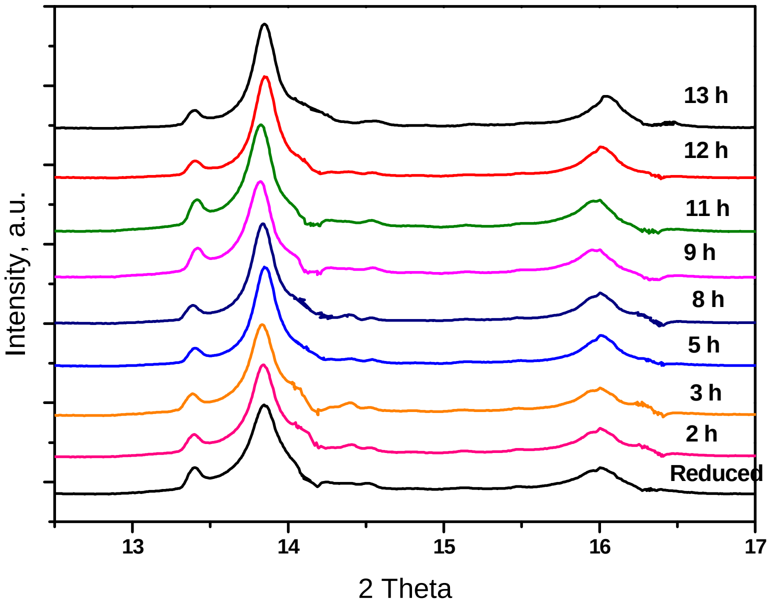


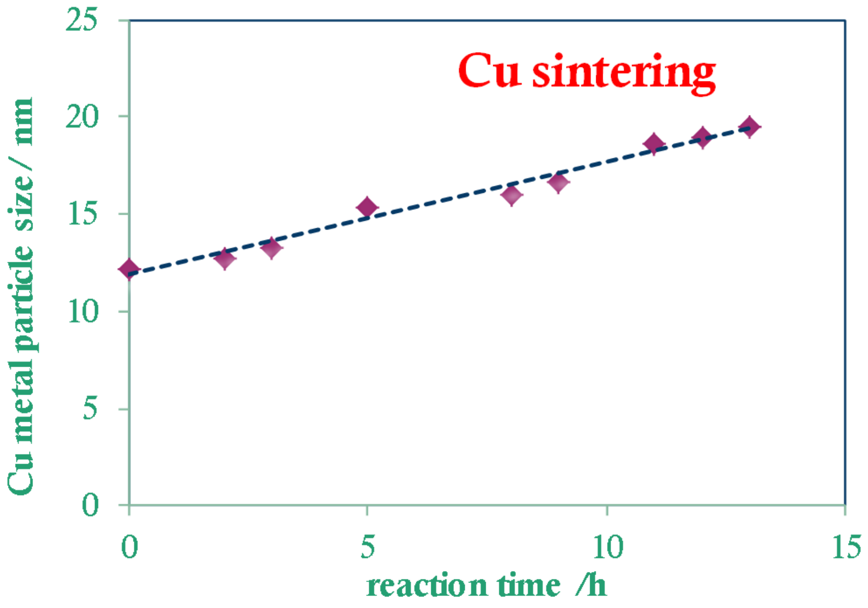
T=260 °C, P=20 bar, GHSV=3600 cm^3/g_{cat} h

Hybrid bifunctional catalysts showed noticeable deactivation

Water injection leads to a major drop in the activity

Copper sintering under the reaction conditions: in-situ XRD



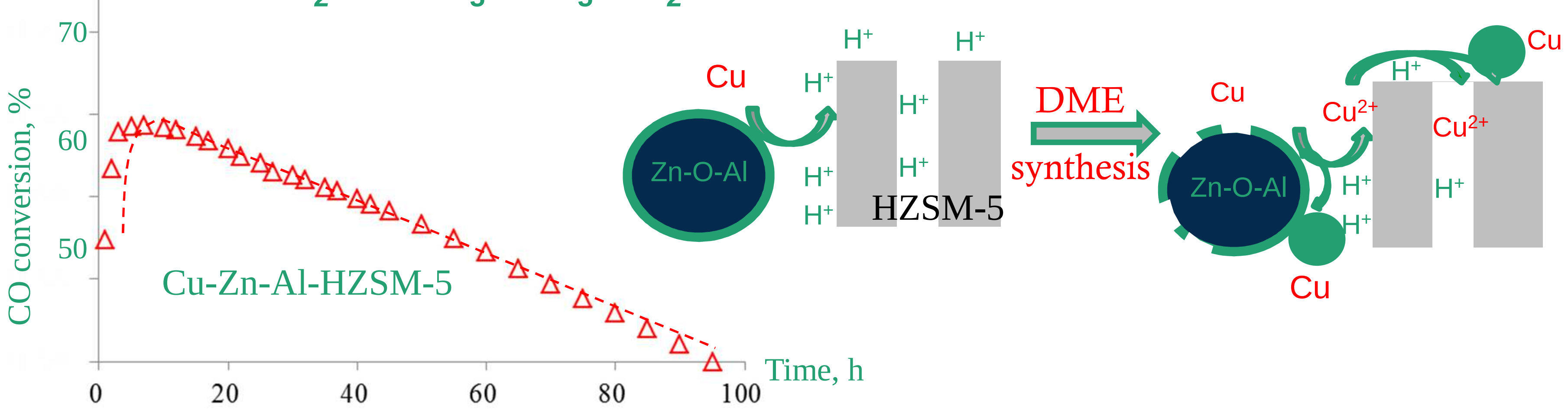


X-ray patterns recorded between five XANES scans with position sensitive detector
Reduction in H_2 at 290 C, DME Reaction (H_2=4 ml/min,CO=2ml/min), P=20 bar, T=260 ° C
copper particles size calculated using Scherrer equation at $2\theta=43.0$

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}$$

Deactivation mechanism of CZA-HZSM-5

$$2CO + 4H_2 \longrightarrow CH_3OCH_3 + H_2O$$

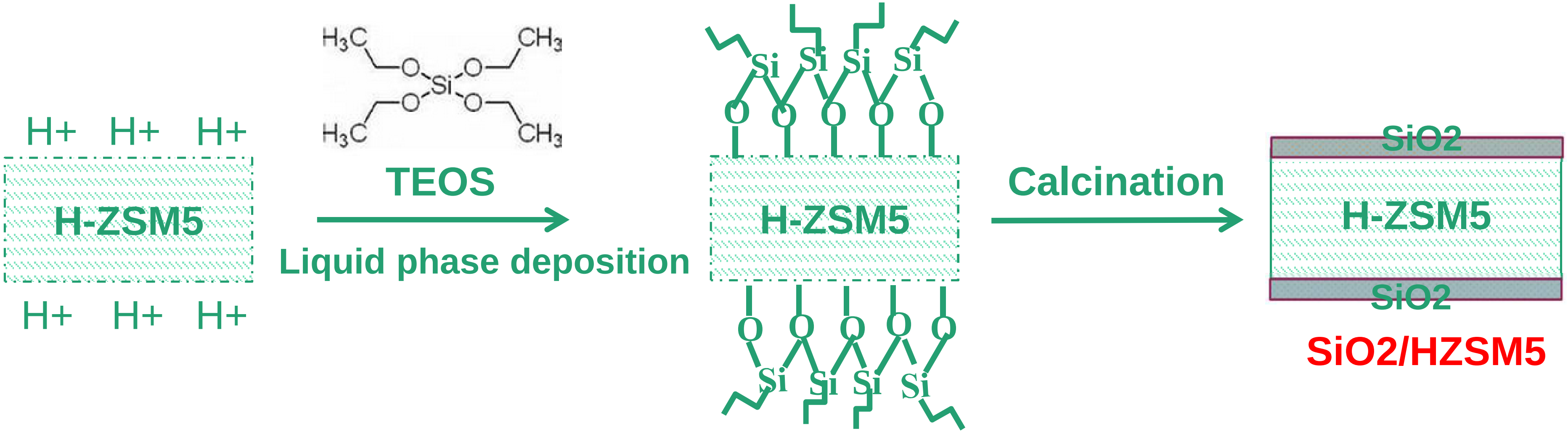


The reason of deactivation over the hybrid catalyst CZA-HZSM5 is mainly Cu sintering and ion exchange of Cu^{2+} with the protons of Zeolite HZSM-5

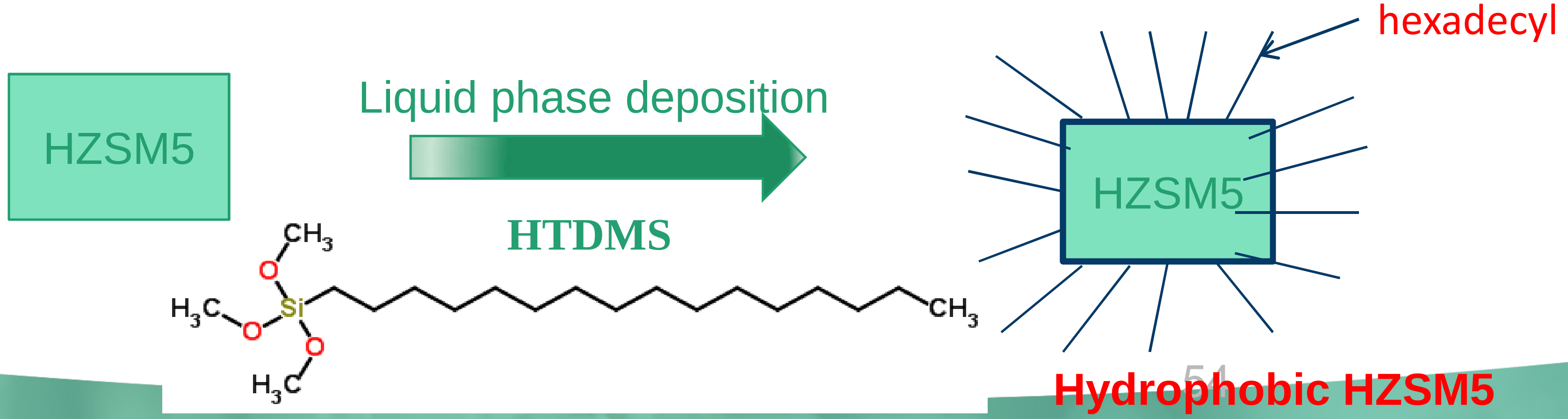
How to solve the problem of Cu sintering and ion exchange ?

Modified HZSM5 by silane reagents

- **Silylated HZSM-5 by tetraethoxysilane (TEOS) modification**



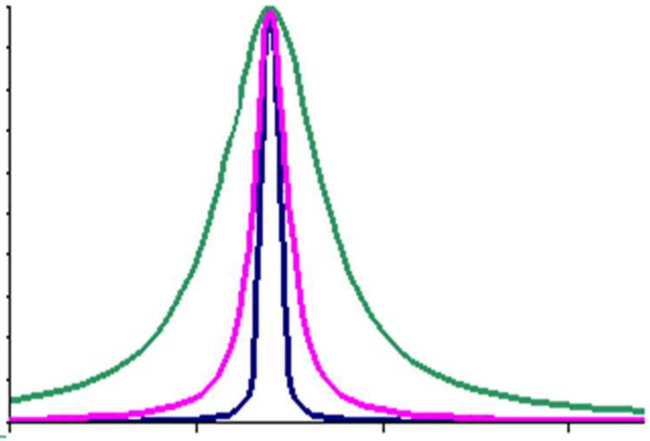
- **Silylated HZSM-5 by Hexadecyltrimethoxysilane (HTDMS) without calcination**

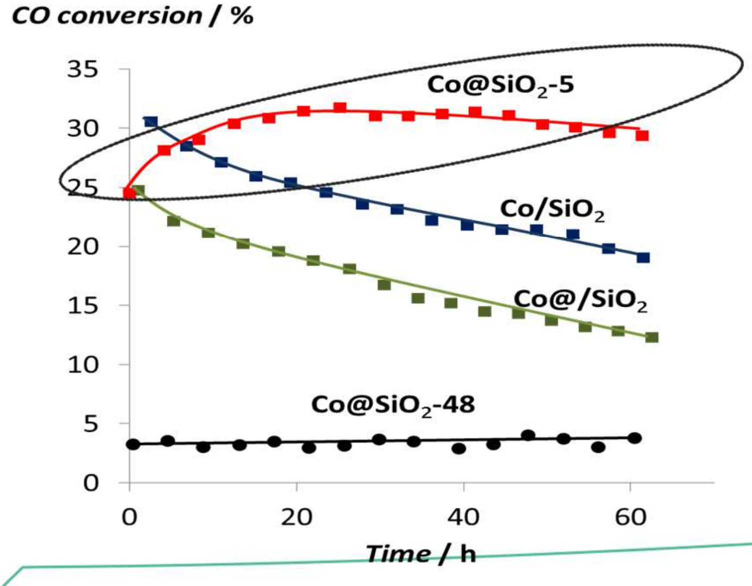


Most important parameters affecting the selectivity and selectivity have been identified

Highly selective catalysts

Very stable catalysts





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Thank you for your attention!

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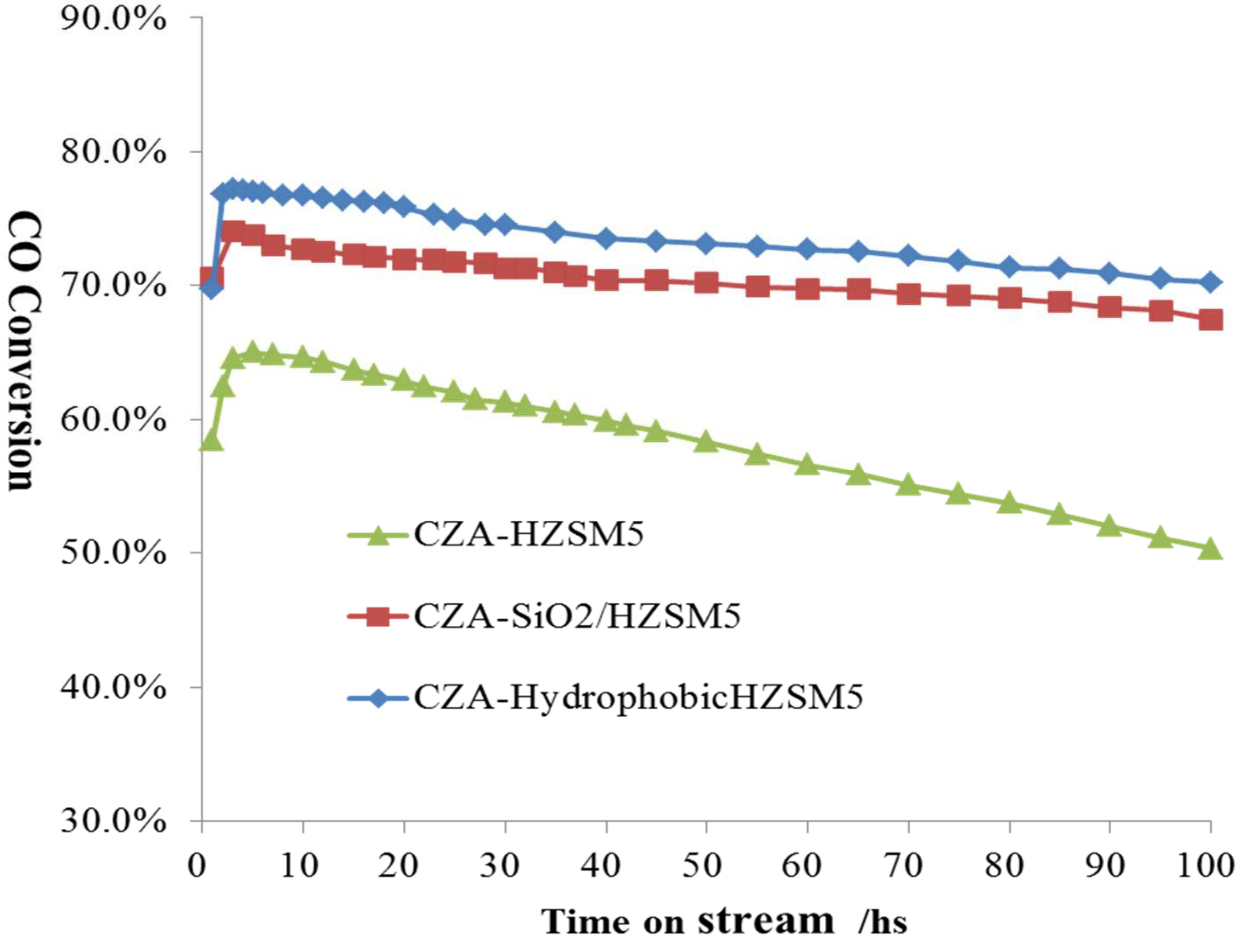
Deactivation of CZA-X hybrid catalysts



Conditions: Cu-based catalyst / solid acid catalyst(weight ratio) =5/3;

T= 260 C, P=20 bar, H_2 /CO=2, SV=3600 ml/(h·g_{cat})