Synthesis of mesoporous oxides as catalysts or catalytic supports for various redox processes

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Scheme of the scientific work:

Reading of literature on a given problem (more the better) ⟹ getting an idea for some kind of improvement ⟹ lab work on idea realization (synthesis part)

⟱

getting evidences if you have succeeded in the lab (characterization + catalytic testing) ⟸ summarizing the obtained results by presenting them at conferences and/or writing a publication

Scheme of lab work (synthesis part):

Choosing the suitable precursors ⟹ **Choosing the type of synthesis process to use** ⟹ **Choosing the synthesis conditions (T, p, solvent, time)**

⇓

Use of various additives (templates, precipitating agents, etc.) ⟹ **Use of additional treatments (hydrothermal, evaporation, filtration, calcination, etc.)**

⇓

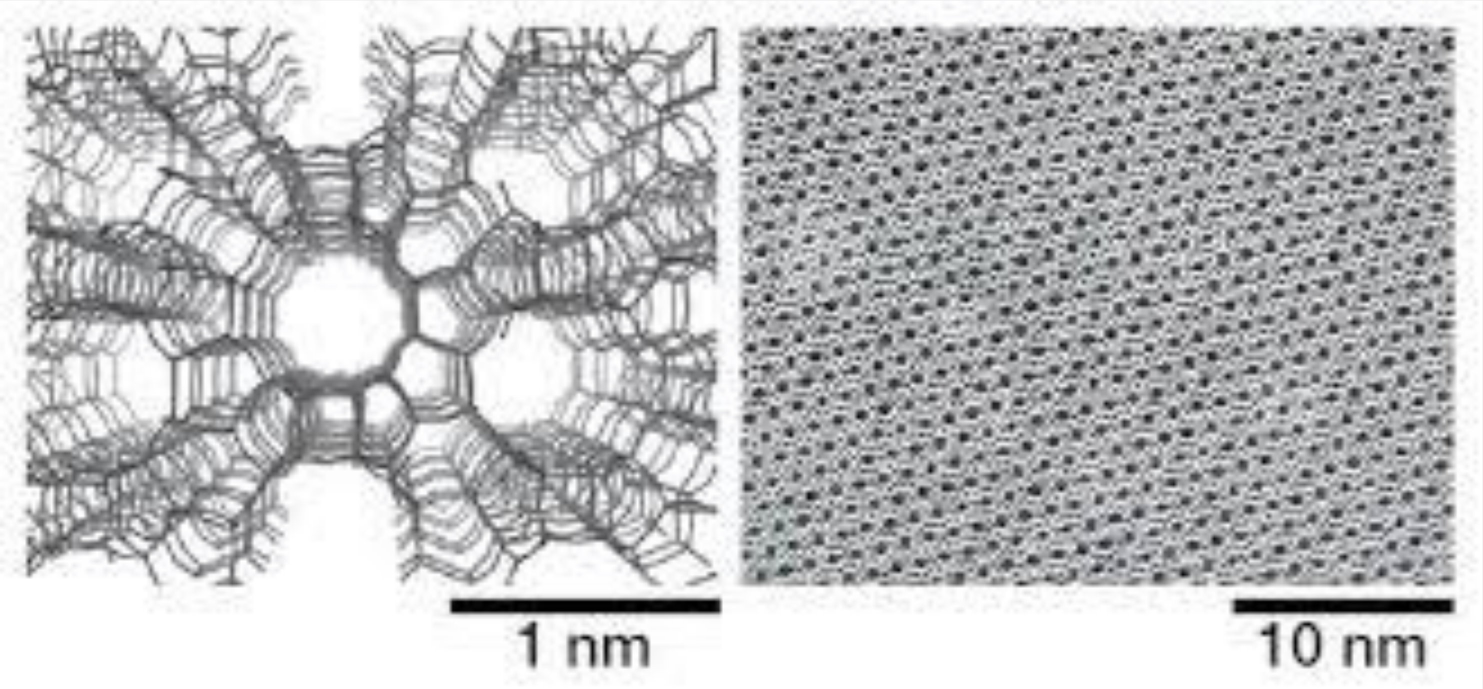
Use of post-synthetic modification in order to get the final material

Outline

- **Why mesoporous oxides?**
- **Synthesis and characterization of ordered mesoporous silicas**
- **Introduction of metal/metal oxide active phase within mesoporous silicas**
- **Metal/metal oxide active phase within ordered mesoporous silicas**
- **Some applications as catalysts for redox processes**
- **Synthesis of mesoporous metal oxides**
- **Introduction of a transition metal/metal oxide component within mesoporous metal oxides**
- **Multicomponent mesoporous metal oxide systems**
- **Characterization and application of obtained composites in various redox processes.**

Why mesoporous oxides?

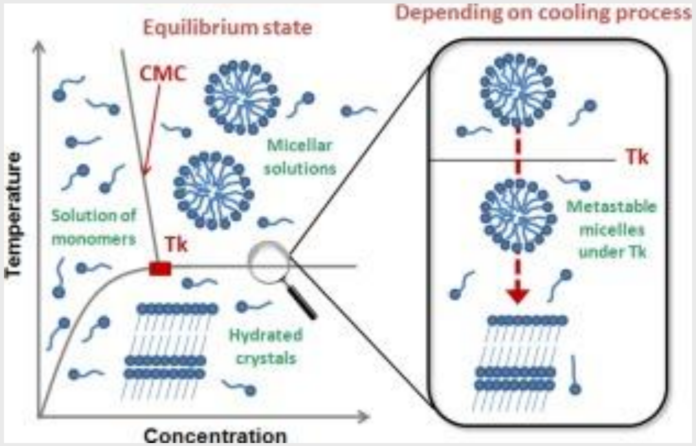
Zeolites – well ordered, microporous and crystalline aluminosilicate materials

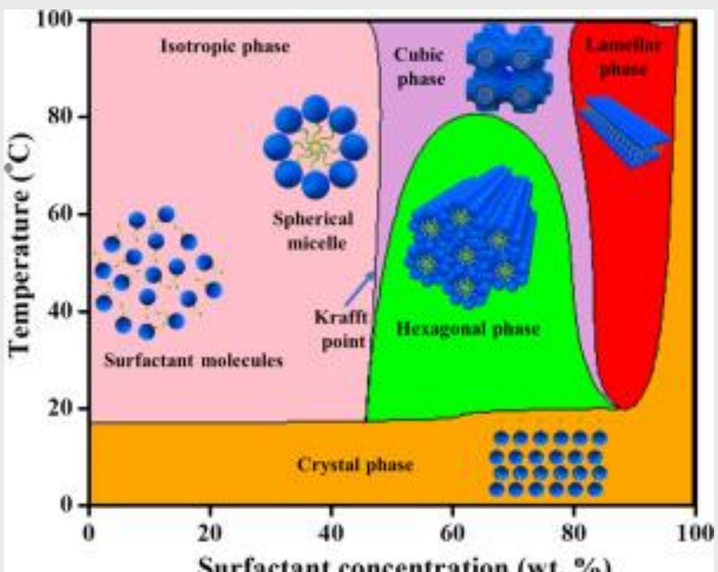


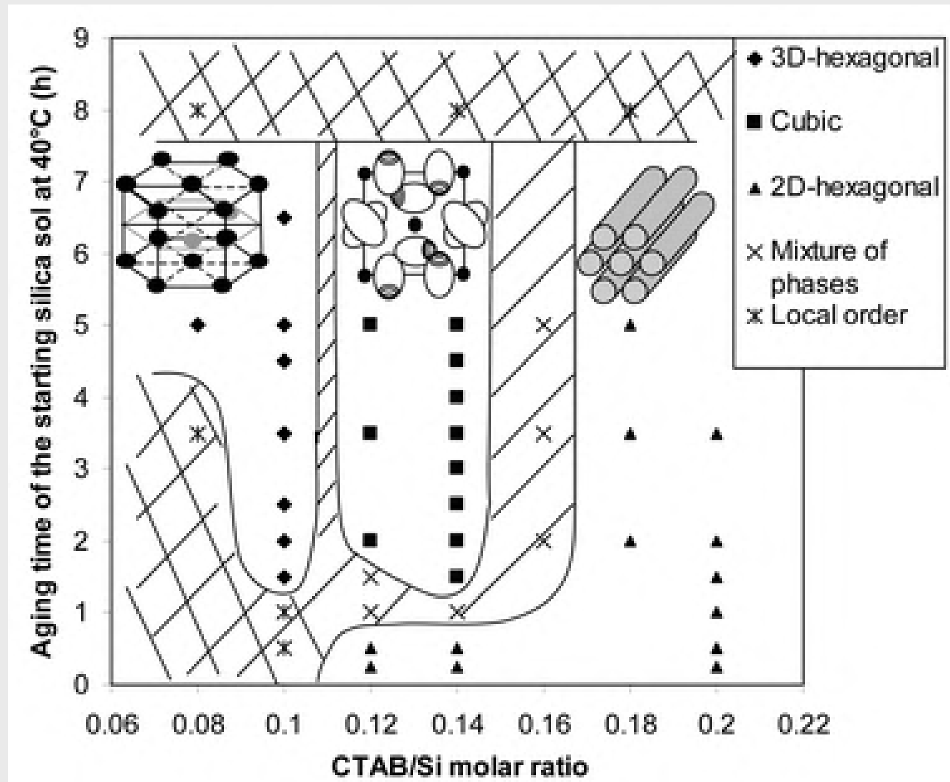
Main disadvantage: small pore sizes (<< 2 nm) and hence deteriorated transportation + facile coke formation

Synthesis of ordered mesoporous silicas

Mesoporous range: 2 – 50 nm → **Facile transportation of bulky molecules**





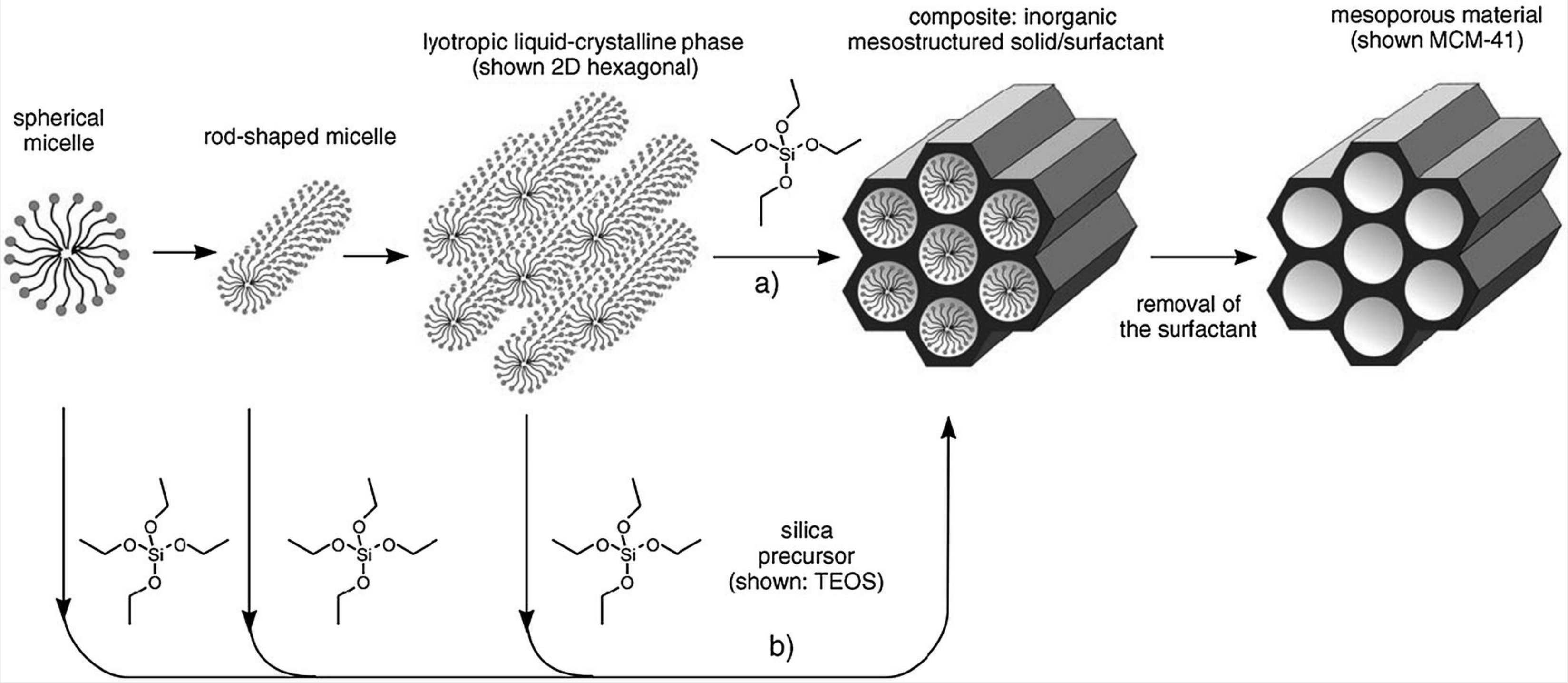


$C_nH_{2n+1}(CH_3)_3N^+$, (n = 12 – 20)

Synthesis of ordered mesoporous silicas

sol gel process:

1. Aqueous surfactant solution with surfactant concentration above Cmc



2. TEOS hydrolysis: $Si(OC_2H_5)_4 + H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$; $Si(OH)_4 \rightarrow SiO_2 + 2H_2O$

3. Preferential polymerization of silicate oligomers at the surfactant boundary surface

4. Calcination for surfactant removal

Synthesis of ordered mesoporous silicas

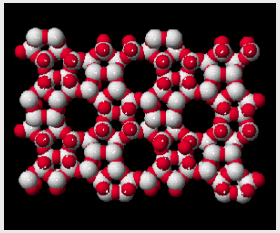
Ionic surfactant – $C_nH_{2n+1}(CH_3)_3N^+$ cation

$C_nH_{2n+1}(CH_3)_3N^+$ + source of Si (TEOS) + pH>11

Molecular template process

n=6-10
T=200°C (hydrothermal treatment)
high solubility of surfactant molecules

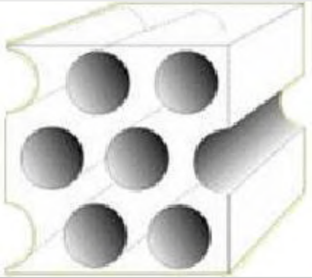
Microporous ZSM-5 zeolite



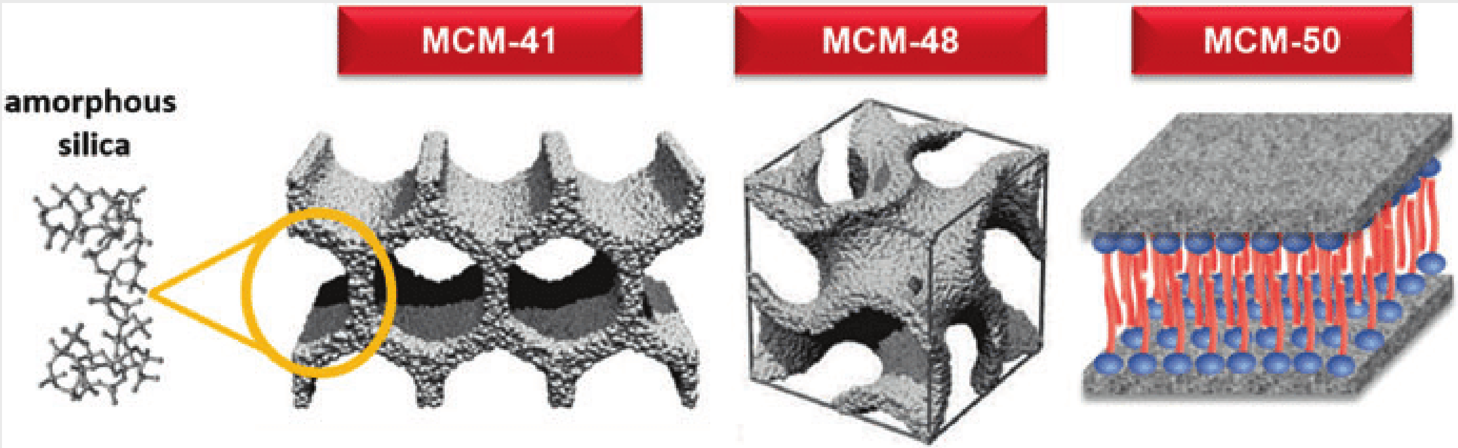
Supramolecular template process

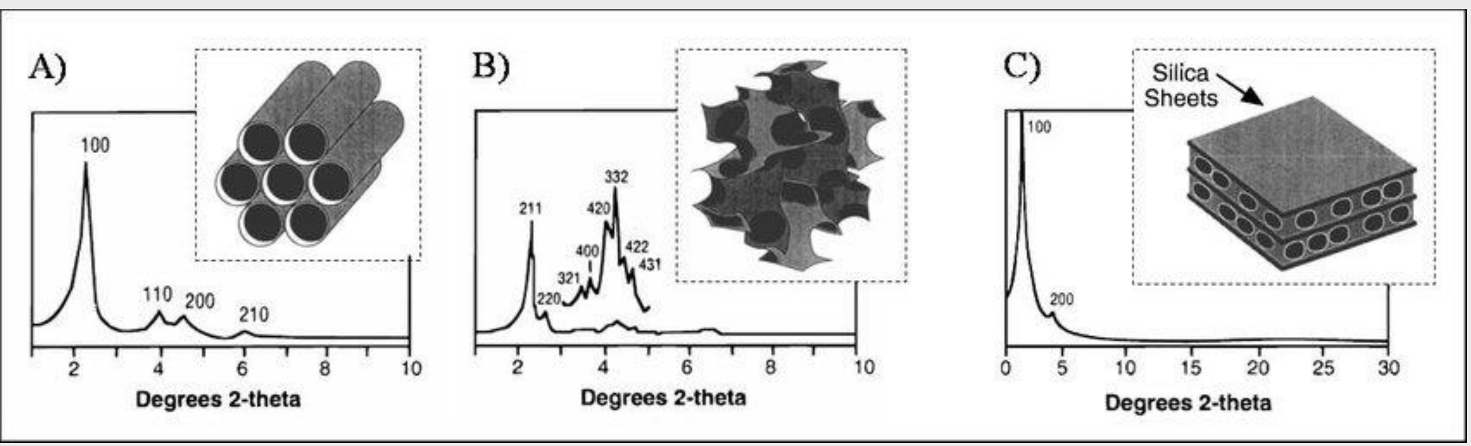
n=12-22
T=100-150°C (HT)
low solubility of surfactant molecules

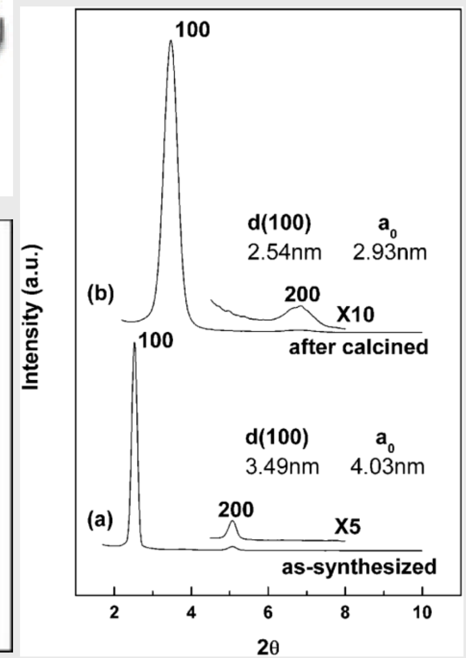
Ordered mesoporous silica (MCM-41)



Characterization of ordered mesoporous silicas

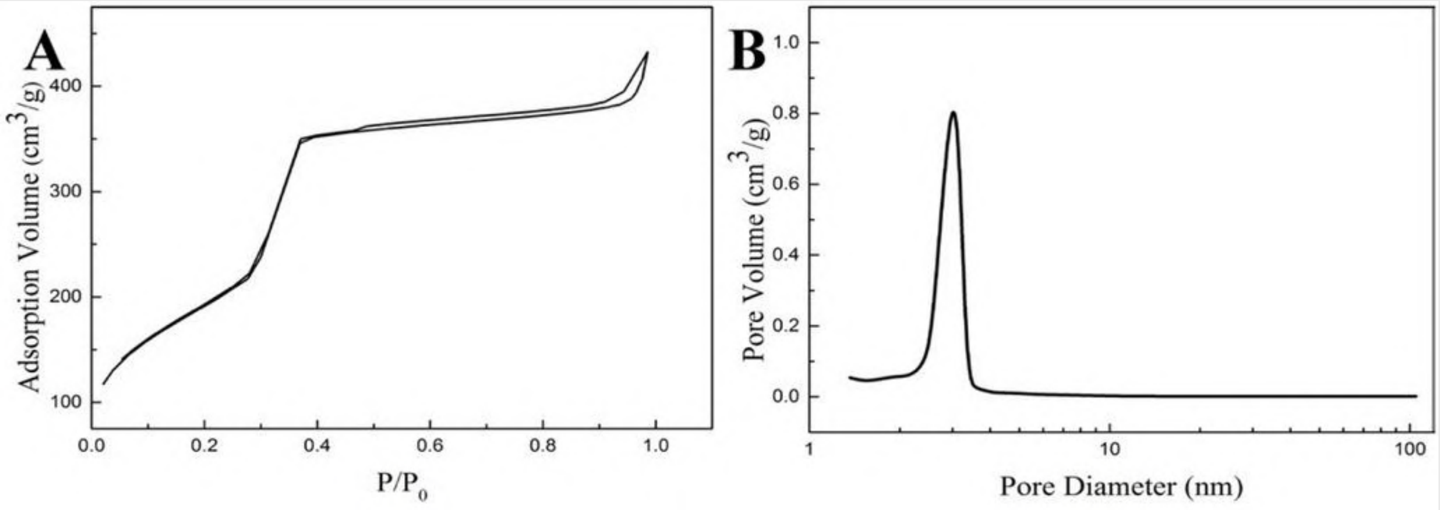


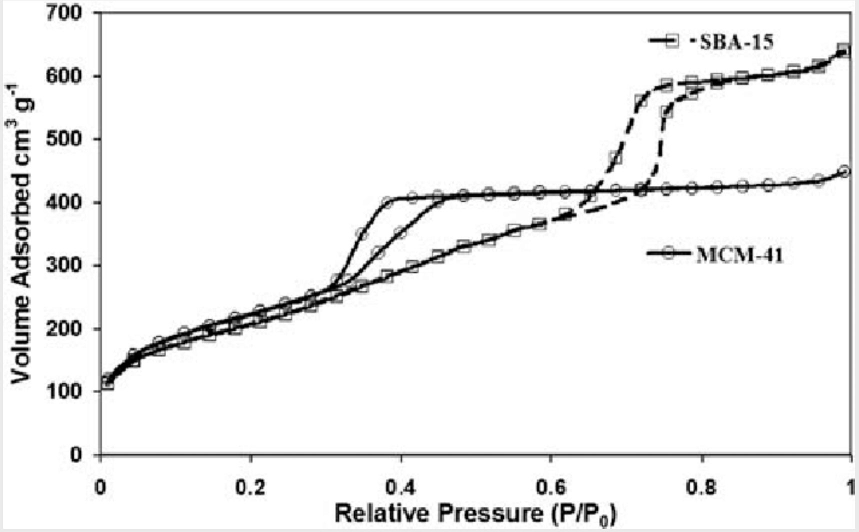




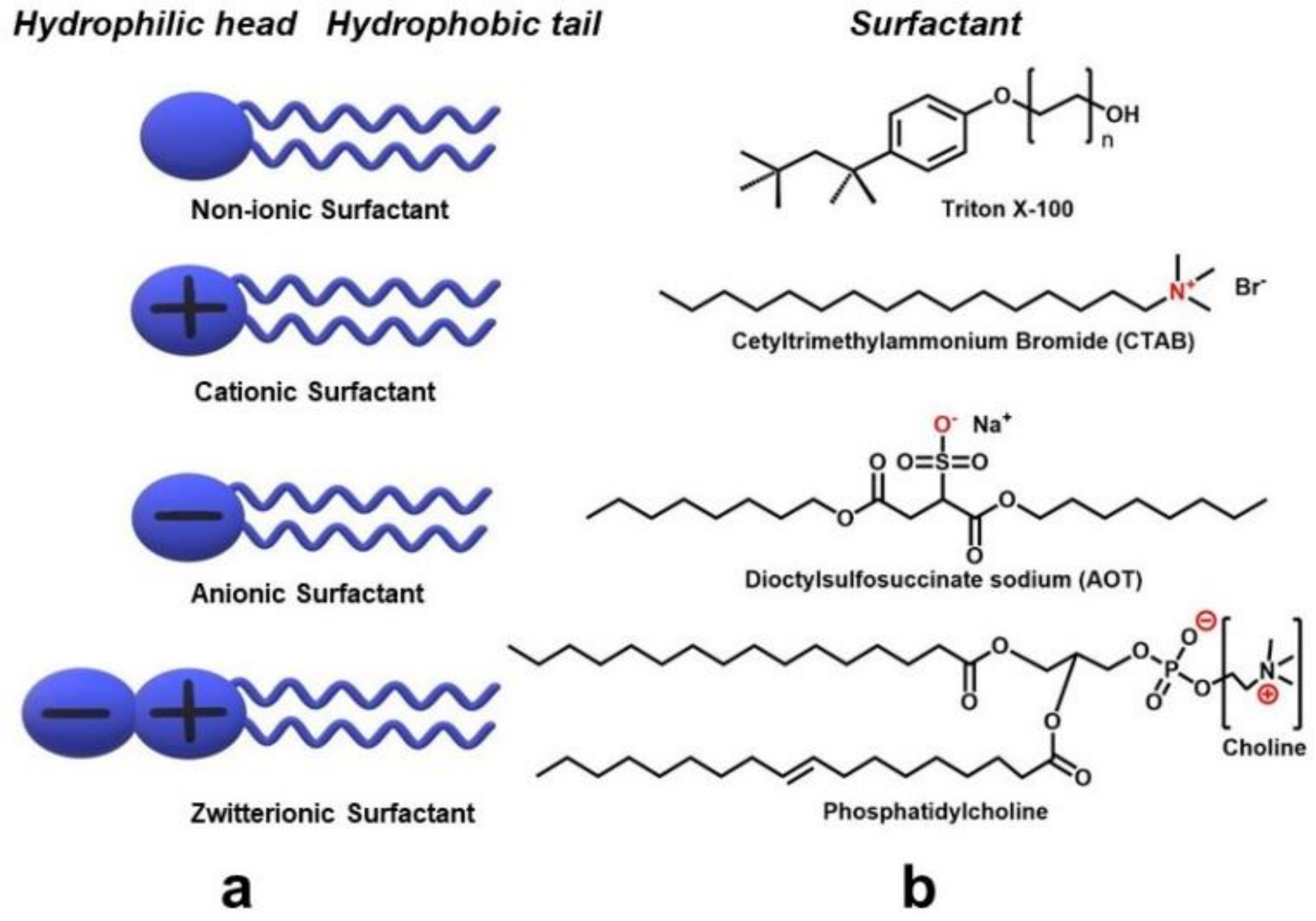
Main characteristics from application point of view: 1) type of mesoporous structure; 2) pore size and wall thickness and 3) specific surface area and total pore volume

Characterization of ordered mesoporous silicas



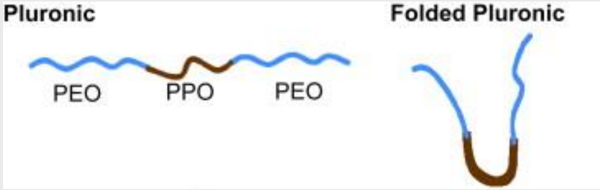


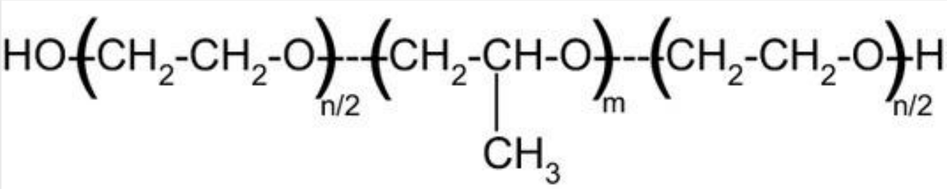
Synthesis of ordered mesoporous silicas



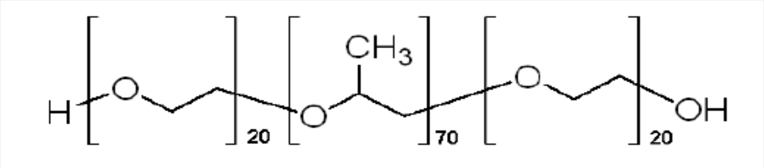
Synthesis of ordered mesoporous silicas

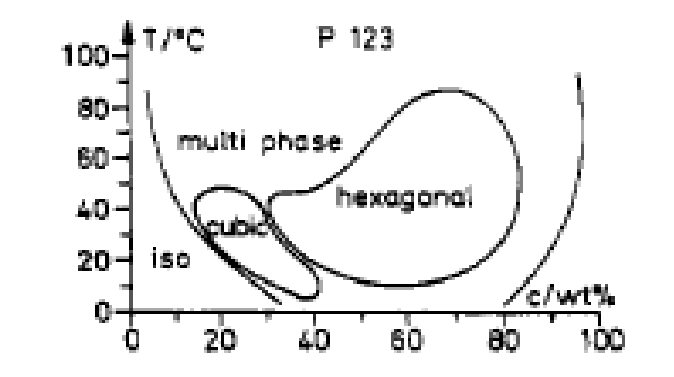
neutral block copolymer surfactant – $(PEO)_y$-$(PPO)_x$-$(PEO)_y$

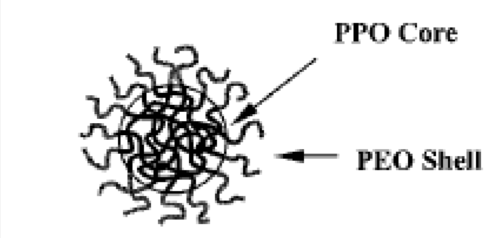




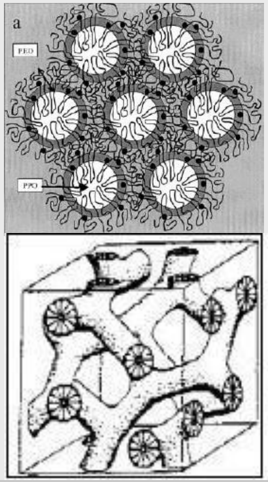
Pluronic 123 - $(PEO)_{20}$-$(PPO)_{70}$-$(PEO)_{20}$



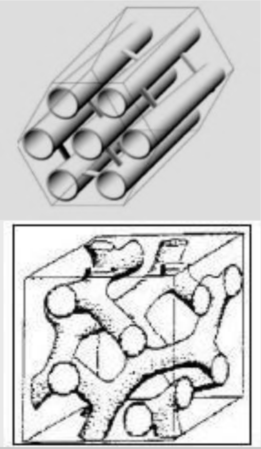




TEOS →



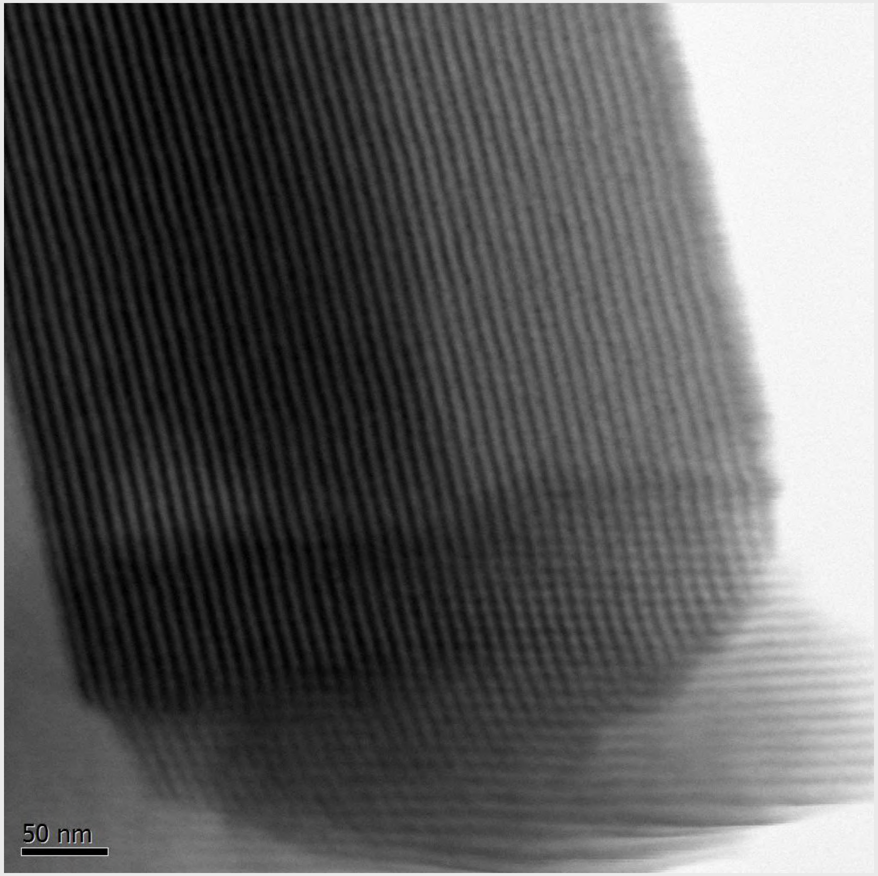
T →

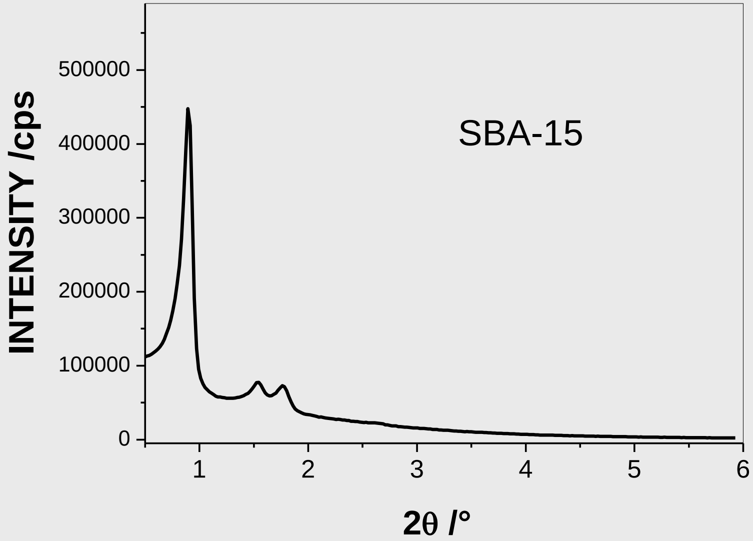


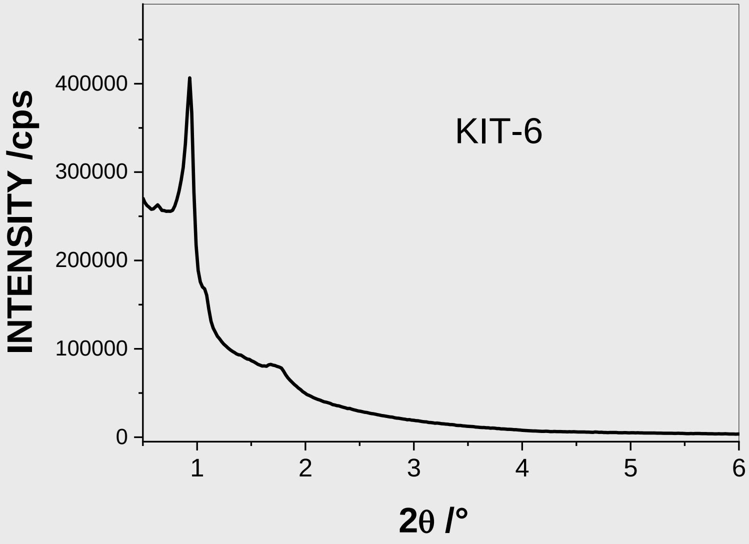
SBA-15

KIT-6

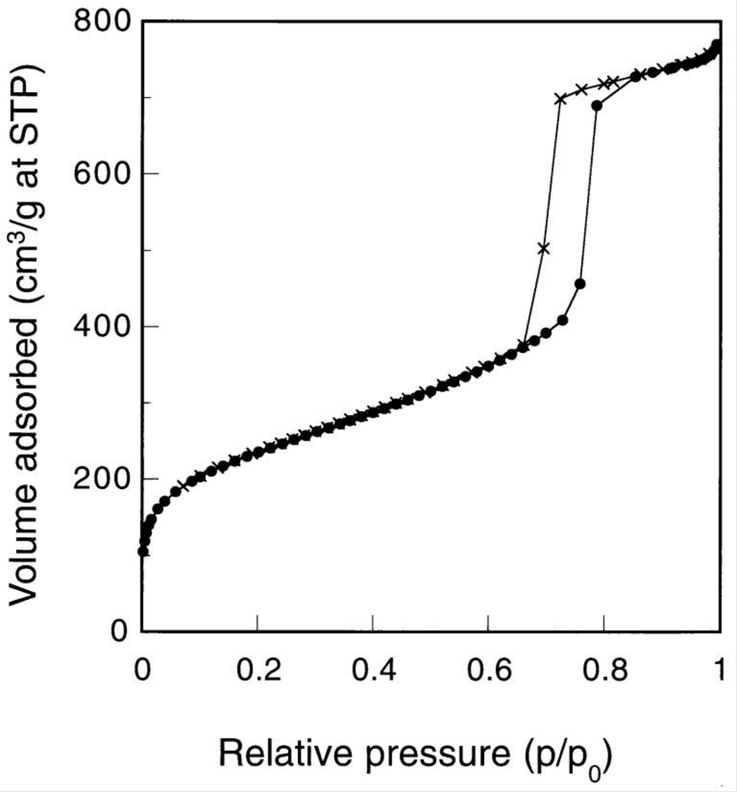
Characterization of ordered mesoporous silicas

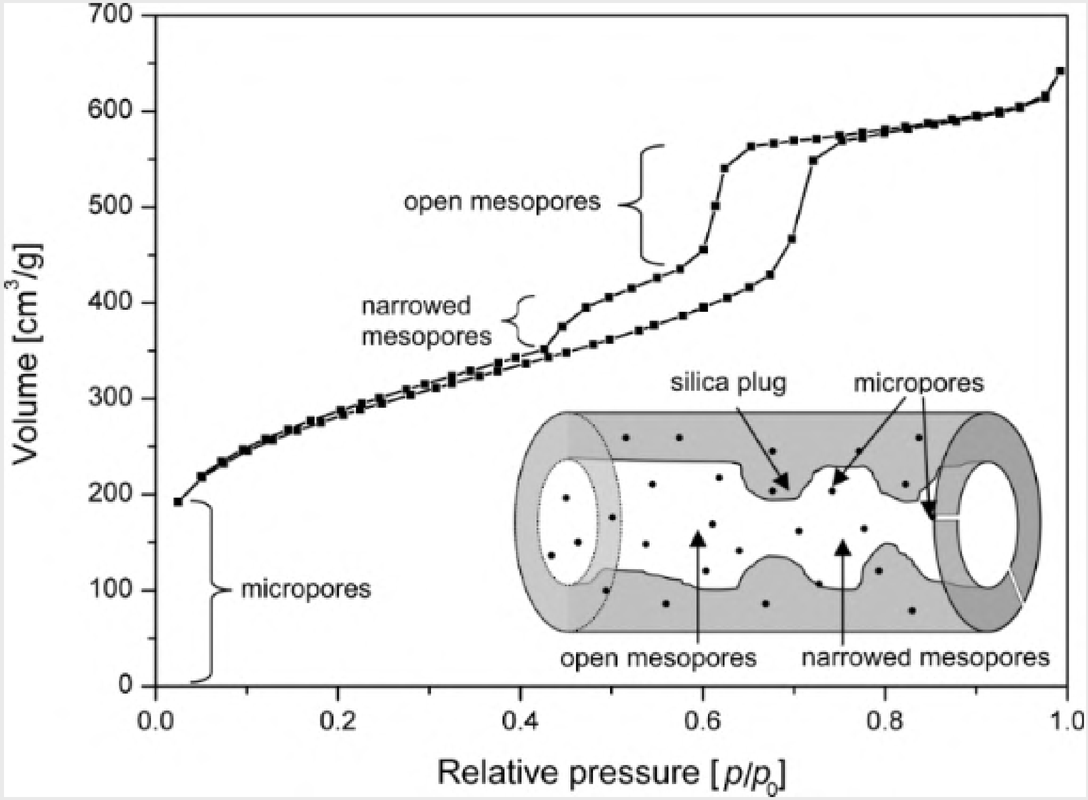






Characterization of ordered mesoporous silicas

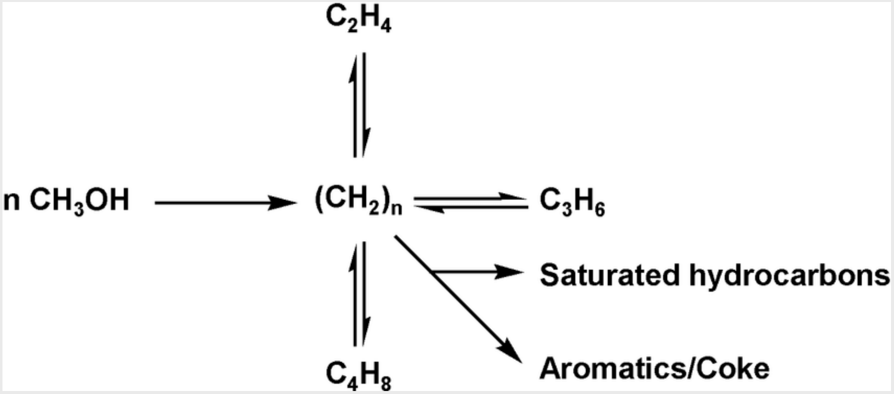




MTO process

(strong acidic sites are needed)

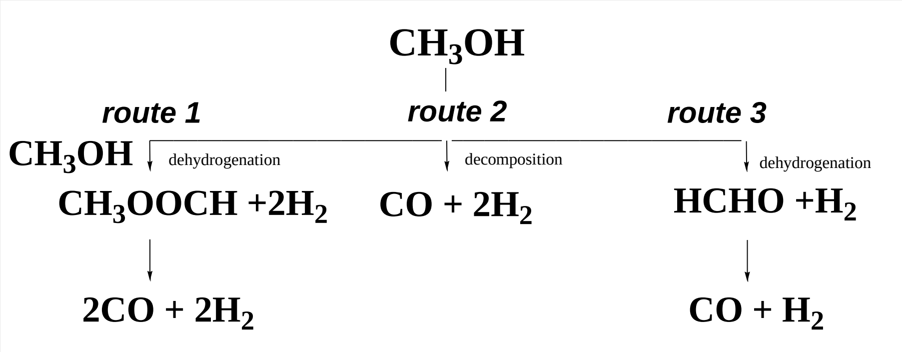
Catalysts – zeolites, aluminophosphates



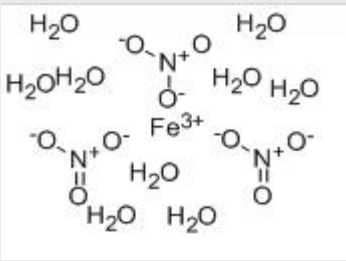
Methanol decomposition

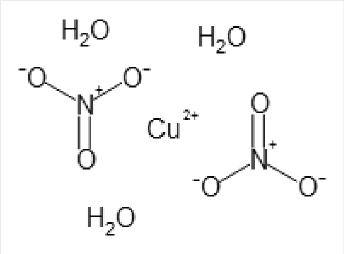
(redox sites are needed)

Catalysts – nanosized metals/metal oxides supported on ordered mesoporous silicas



1) Incipient wetness impregnation with metal nitrates

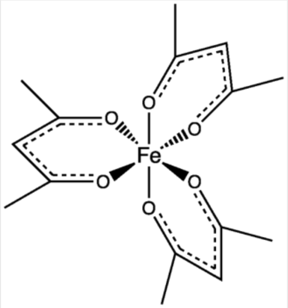


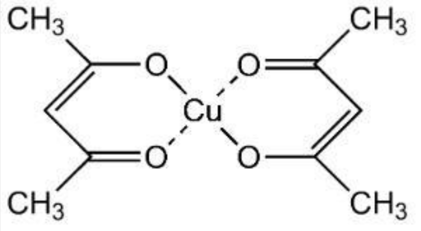


Advantages:
- easy and fast procedure
- possibility to load the desired amount at one step

Disadvantages:
- lack of good control on the dispersion of the loaded metal phase

2) Impregnation with metal acetylacetonates





Advantages:
- fine dispersion of the loaded metal phase

Disadvantages:
- more complicated procedure
- difficult control on the loaded amount

Metal/metal oxide active phase within ordered mesoporous silicas

What are the requirements for a supported metal/metal oxide phase within high surface area mesoporous silca in order to possess high and stable catalytic activity for a given redox catalytic reaction?

The supported metal/metal oxide phase should possess the following characteristcs:

- **Improved activity – favored by its presence in nanosize form thus possessing large active surface available for the reactants (high surface to core ratio)**

- **Improved redox behavior at low temperatures – favored by its improved dispersion and lack of very strong interaction with the support that would deteriorate it.**

- **High exposure to reactants – favored by its homogeneous distribution within an open support mesoporous structure that offers good transportation of reactants and products.**

- **High stability under reaction conditions – favored by its presence within the porous network where its mobility is limited or is in interaction with another component (e.g. another metal) serving as an anchoring site.**

Parameters that influence the dispersion and activity of the loaded active metal oxide species within mesoporous silica:

1) Support characteristics:
- Type of mesoporous silica structure used as support
- Pore diameter
- Total pore volume

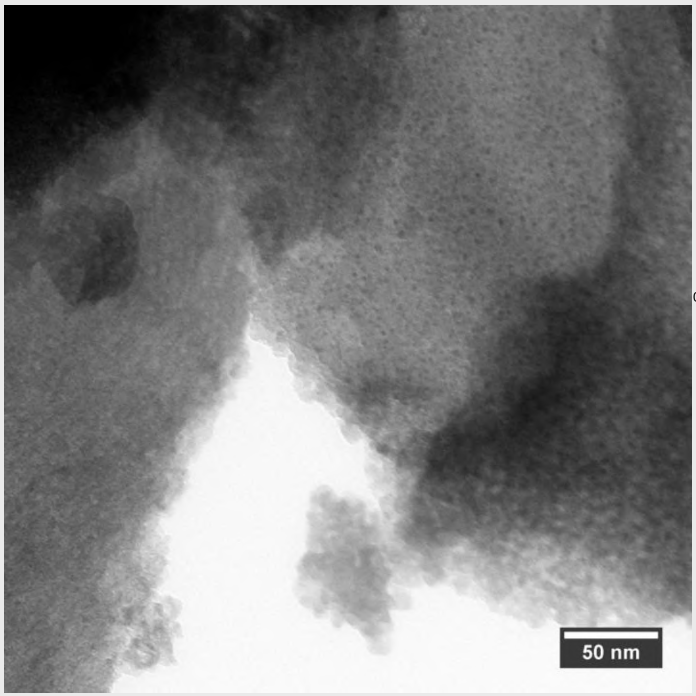
2) Supported metal/metal oxide characteristics:
- Type of metal
- Type of the metal precursor
- Content of the loaded metal/metal oxide
- State of supported metal/metal oxide phase

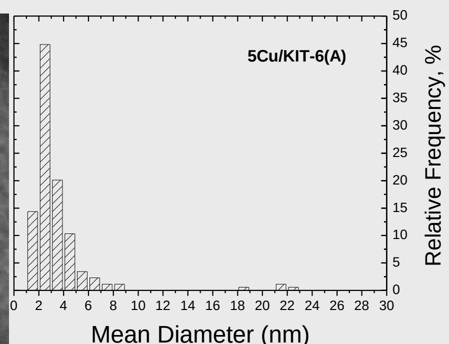
3) Procedure of metal/metal oxide loading:
- Modification approach
- Final calcination temperature

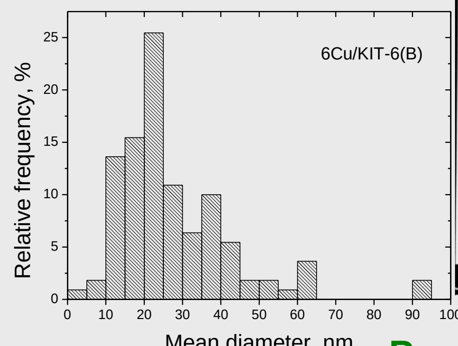
4) The type of studied catalytic reaction

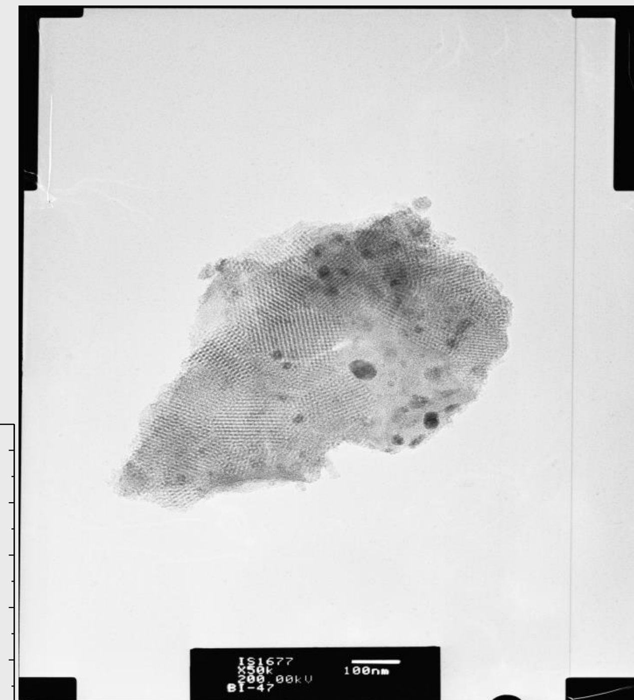
Metal/metal oxide active phase within ordered mesoporous silicas

- **The use of metal acetylacetonate as a precursor in comparison with metal nitrate one leads to the deposition of more finely dispersed metal oxide phase distributed more homogeneously within the ordered mesoprous silica support**







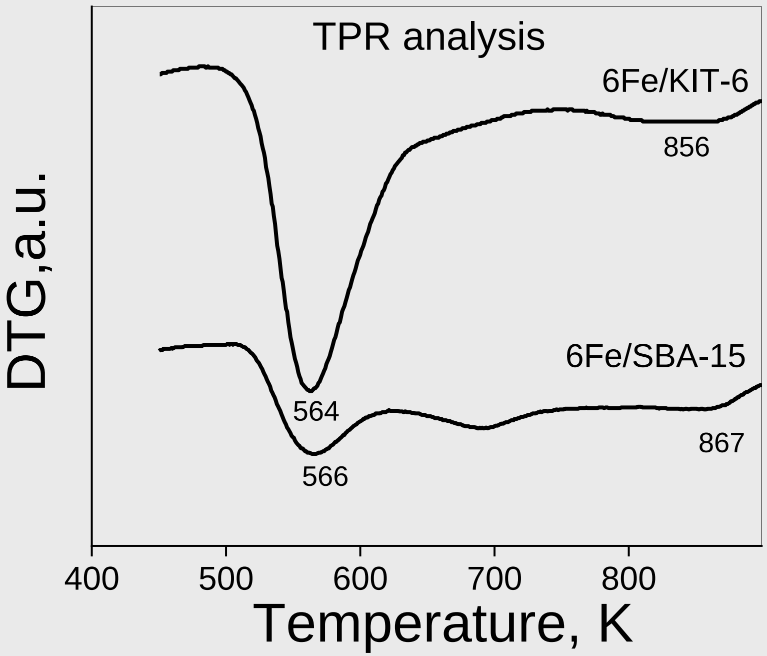


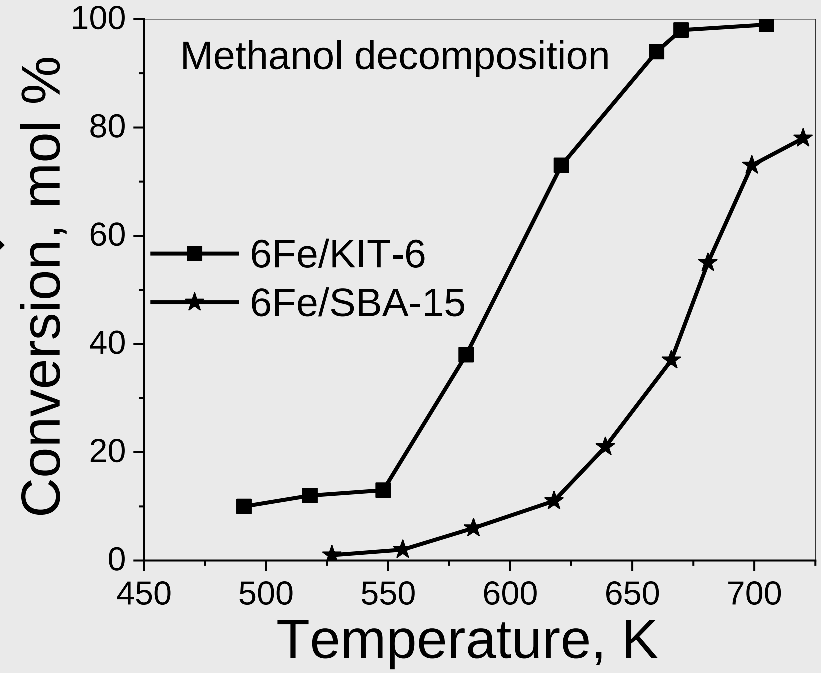
Finely dispersed copper oxide within KIT-6 silica by using copper acetyl acetonate as copper precursor

Presence of large copper oxide particles on the outer surface of KIT-6 silica after impregnation with copper nitrate

Metal/metal oxide active phase within ordered mesoporous silicas

There is close relation between the reducing ability of the loaded metal oxides and their methanol conversion ability.

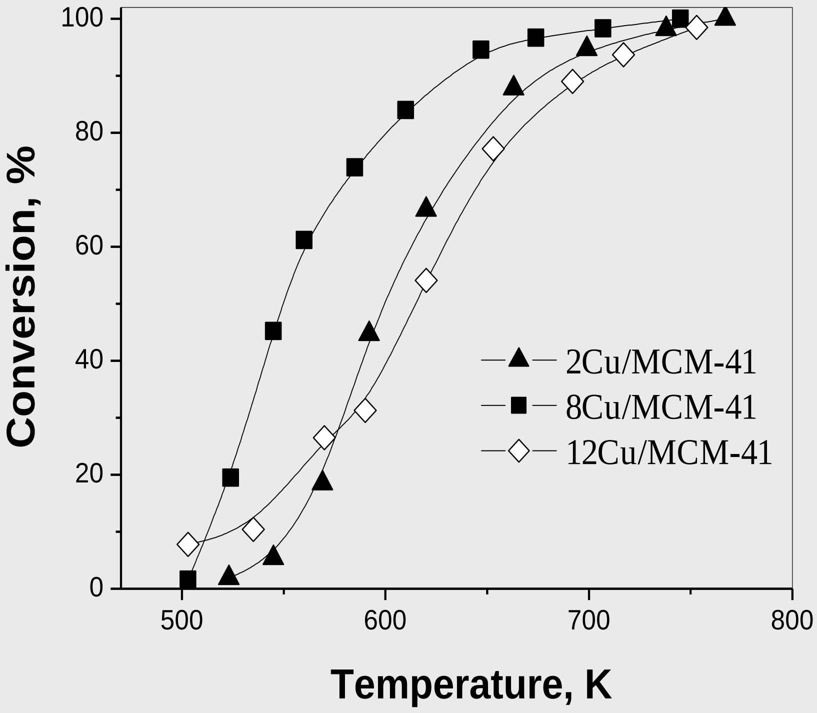




- **small oligonuclear $(FeO)_n$ species – very active at low temperatures (500-650 K)**
- **bulky clusters of Fe_2O_3 – active at ~700K**
- **isolated Fe^{3+} ions in strong interaction with the support – inactive in the studied temperature interval**

Metal/metal oxide active phase within ordered mesoporous silicas

Influence of the content of the supported metal on the catalytic properties in methanol decomposition reaction



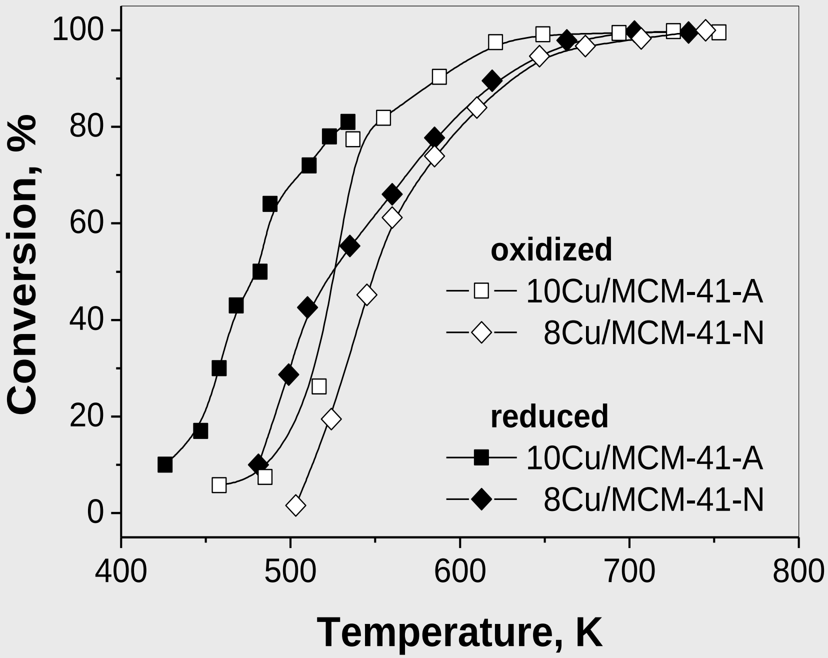
- **Predominant presence of finely dispersed metal oxides within the MCM-41 pore structure that are very active – this is the case of 8Cu/MCM-41**

- **Predominant presence of larger (bulk) metal oxide particles on the outer MCM-41 surface – exposed but with low activity due to their low overall reactive surface (low shell/core ratio) – this is the case of 12Cu/MCM-41**

- **Presence of high amount of isolated metal ions that are in strong interaction with the support silanols – not active but can stabilize finely dispersed metal oxide species in their vicinity – this is the case of 2Cu/MCM-41**

Metal/metal oxide active phase within ordered mesoporous silicas

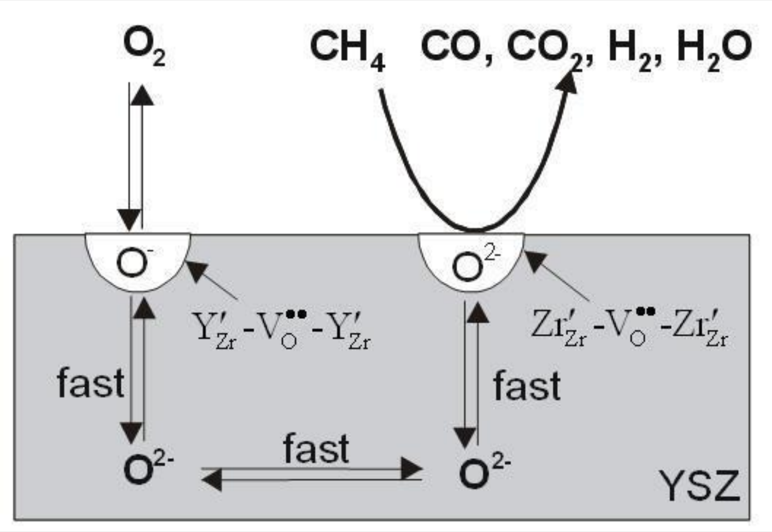
Influence of the supported active phase



- **The metallic copper is more active than copper oxide in the reaction**
- **Above 550 – 600 K the pre-reduced and oxidized catalysts show close catalytic activity due to unification of the active phase under reaction conditions**
- **The catalysts obtained by using copper acetylacetonate as copper precursor show higher activity than their analogues obtained by copper nitrate due to higher active phase dispersion**

Volatile organic compounds (VOCs) – a major challenge!

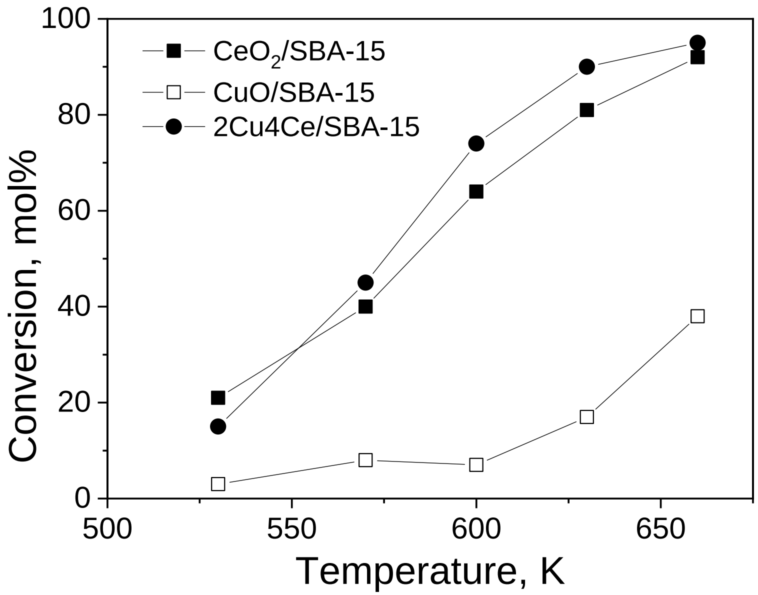
Mars-van Krevelen mechanism of VOCs oxidation

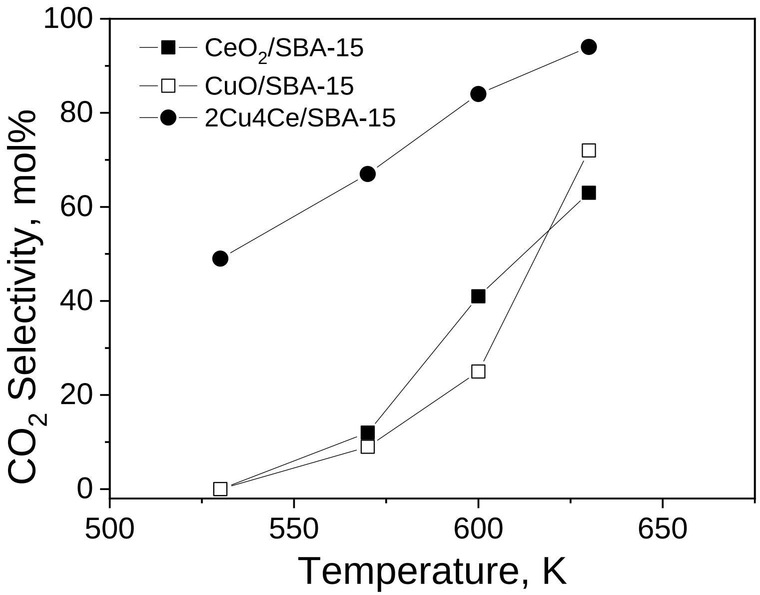


⇒ facile change of oxidation state

For VOC oxidation active sites with improved redox behavior are needed

Application





- **Both pure ceria and copper oxide modifications possess large metal oxide particles situated, however the ceria modification is much more active due to the presence of defects in the ceria lattice which favor the reaction.**
- **The highest activity is registered for the bi-component modification due to presence of only very highly dispersed and X-ray amorphous metal oxide particles within this sample.**
- **The addition of copper oxide to ceria favors the selectivity of the reaction to total oxidation as the found interaction between copper and ceria decreases the high intrinsic acidity of ceria and even further improves its redox properties.**

Synthesis of mesoporous metal oxides

evaporation induced self-assembly (EISA) approach – ordered mesoporous SnO_2 films and powders

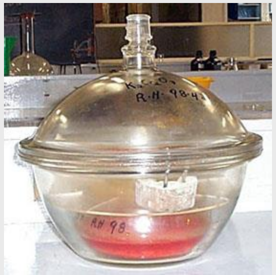
Spin-coating

→

Drying

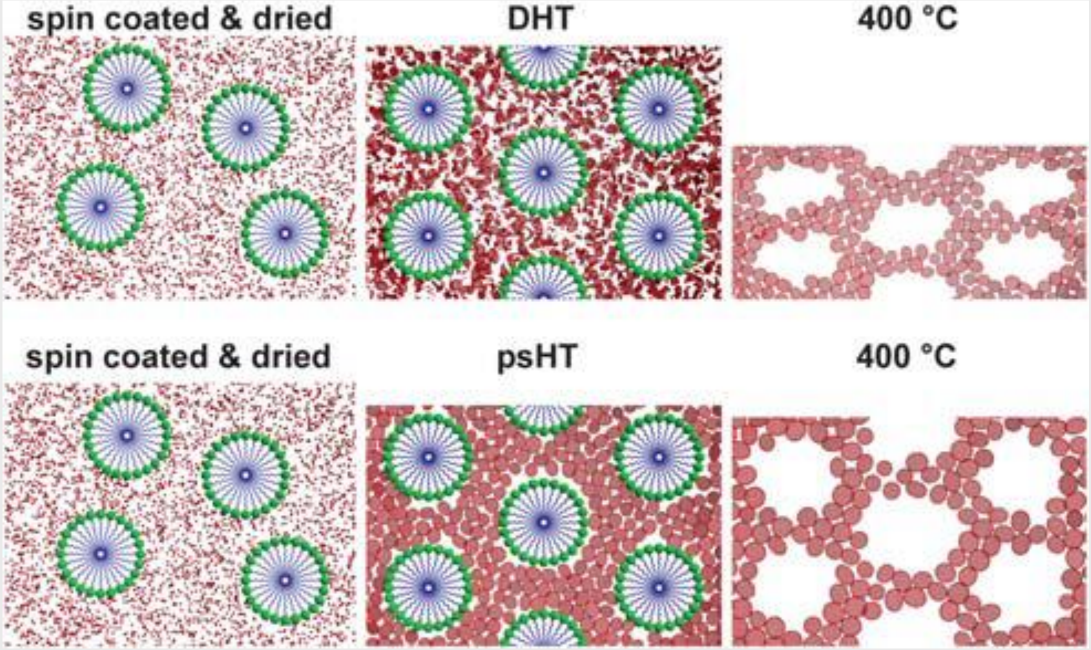
→

70/100°C and 70% humidity



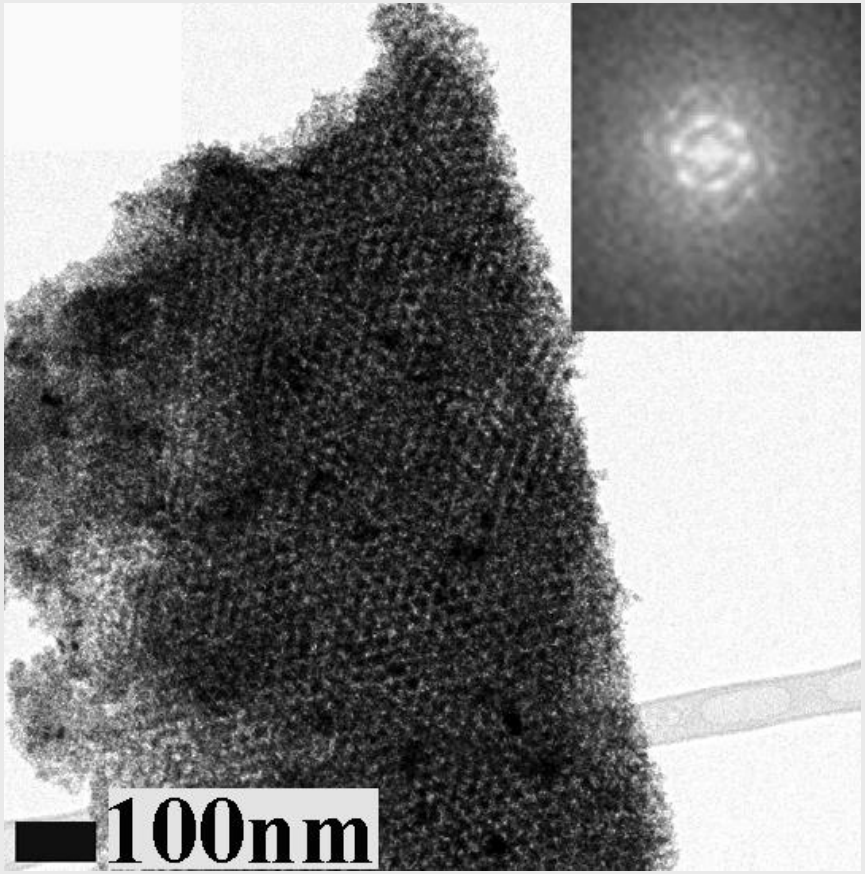
→

calcination

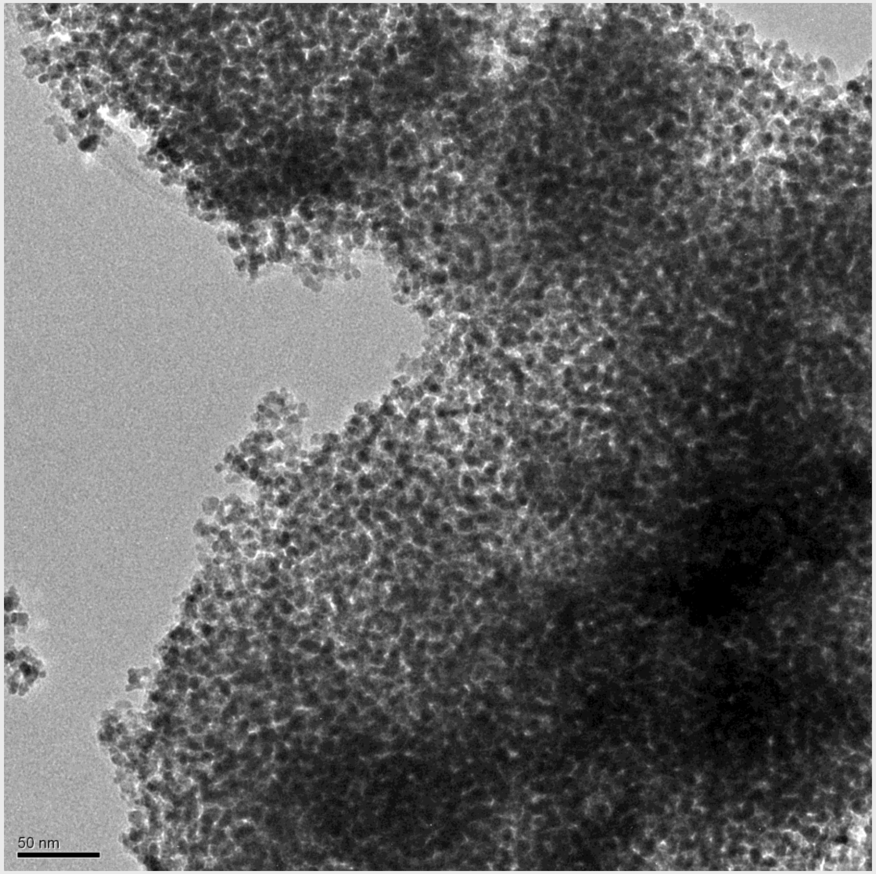


Synthesis of mesoporous metal oxides

evaporation induced self-assembly (EISA) approach – mesoporous SnO_2 films and powders



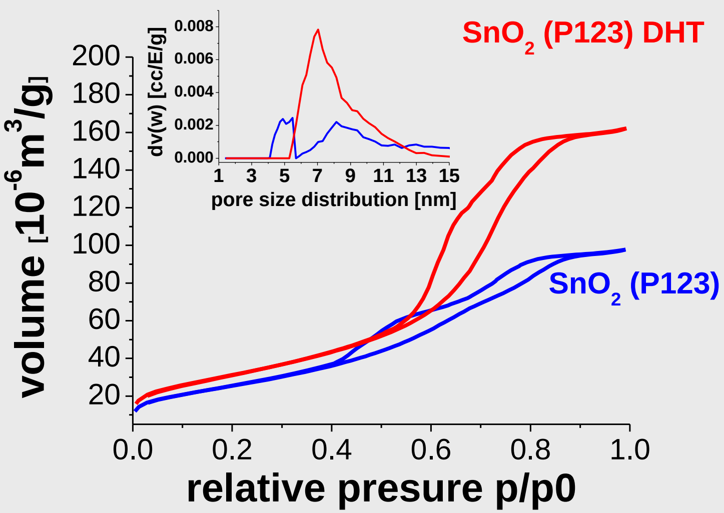
SnO_2 films with ordered mesoporous structure

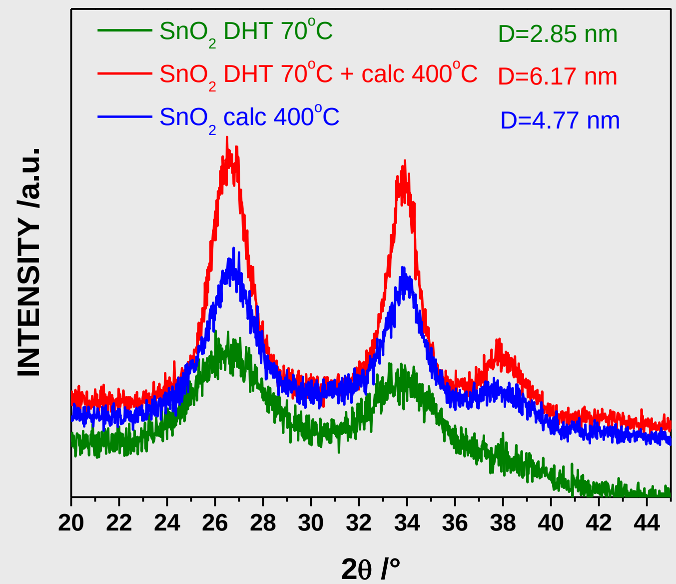


SnO_2 powders with worm-like mesoporous structure

Synthesis of mesoporous metal oxides

evaporation induced self-assembly (EISA) approach – nanosized mesoporous SnO_2 powder



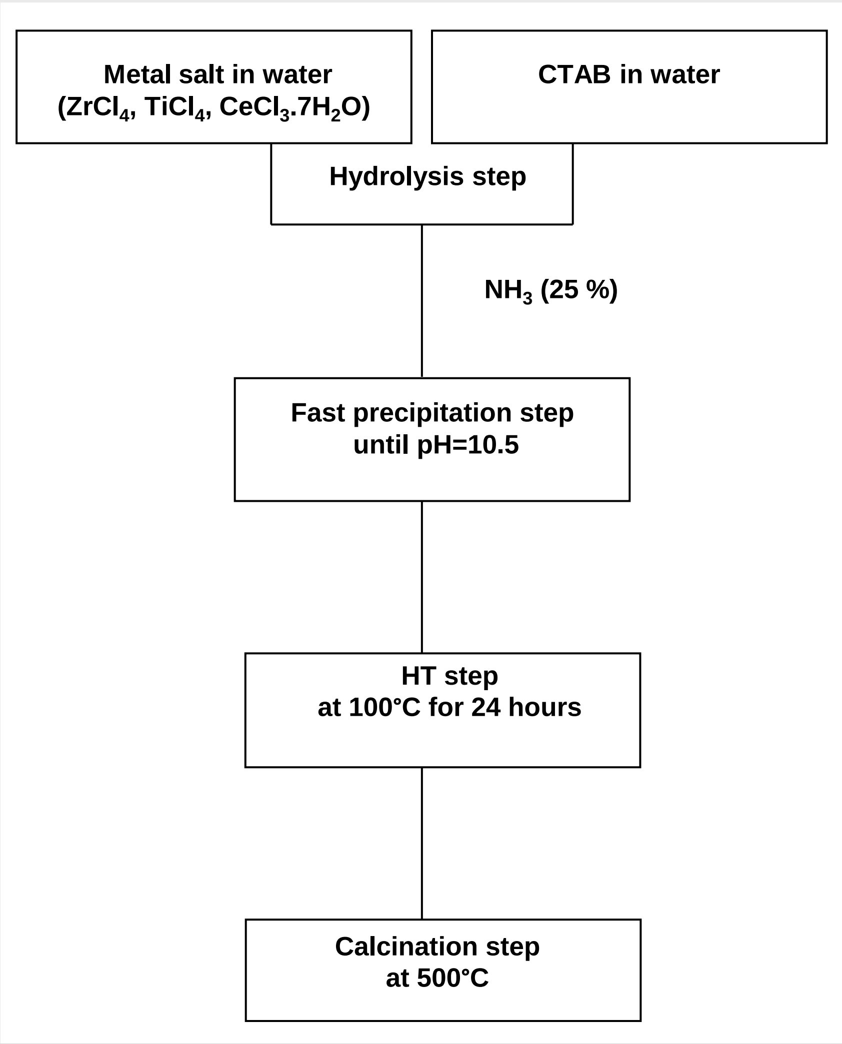


Sample	Template	Specific treatment	BET, m^2/g	V_{tot}* cc/g	D**, nm
SnO_2	(P123)	-	85	0.09	4.77
SnO_2	(P123)	DHT (1 day)	120	0.31	6.17

*total pore volume; ** main pore size evaluated from NLDFT pore size distribution - half width at half maximum

Synthesis of mesoporous metal oxides

Preparation approach

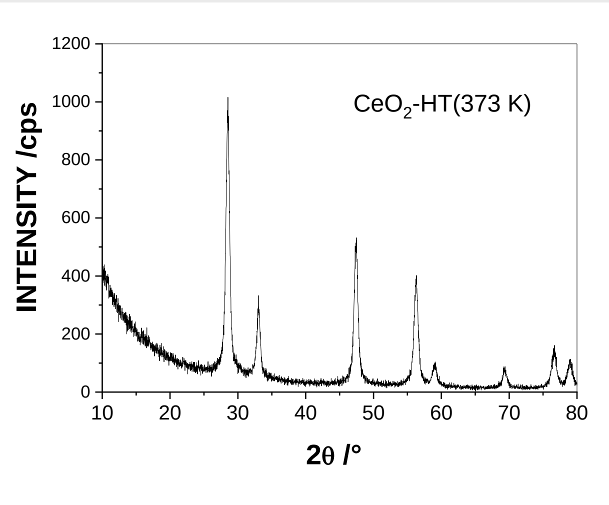


Important characteristics of transition metals + Ce:

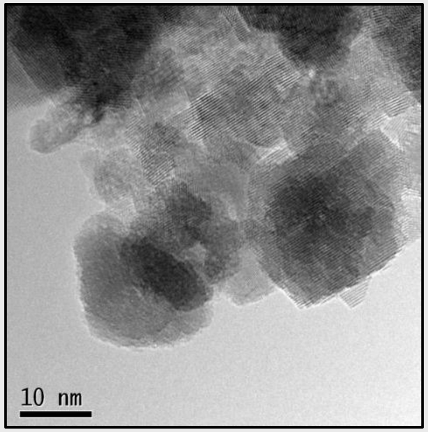
- have high reactivity toward hydrolysis and condensation
- possess different oxidation states and coordination
- their oxides tend to crystallize when heated

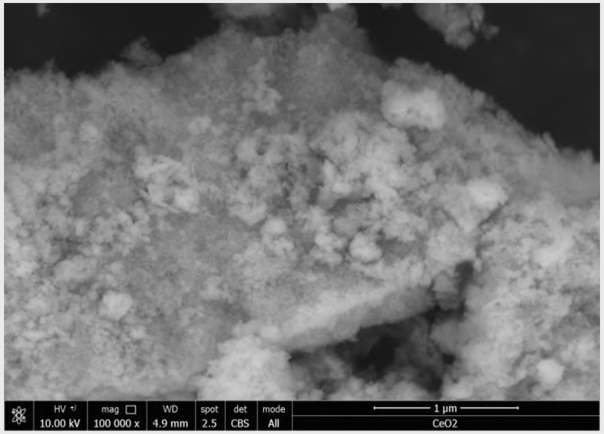
Very important step – hydrothermal treatment of the solution after the precipitation step:
Metal hydroxides are transformed into crystalline oxides – registered by XRD technique

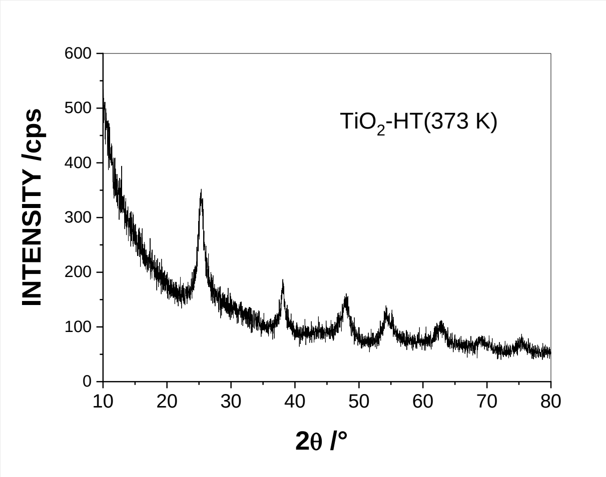
Characterization of mesoporous metal oxides



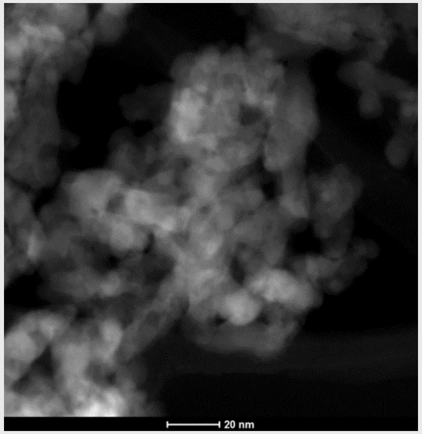
T=500°C

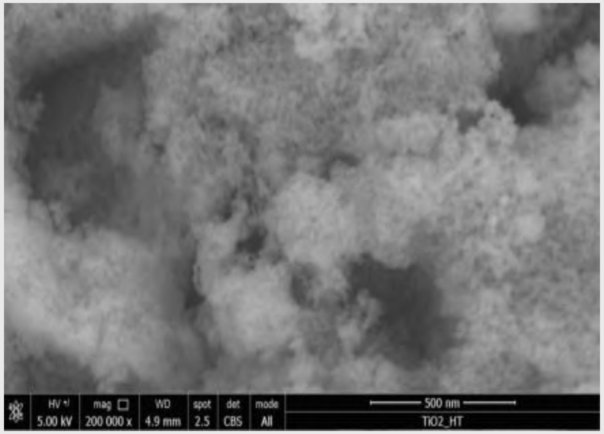






T=500°C

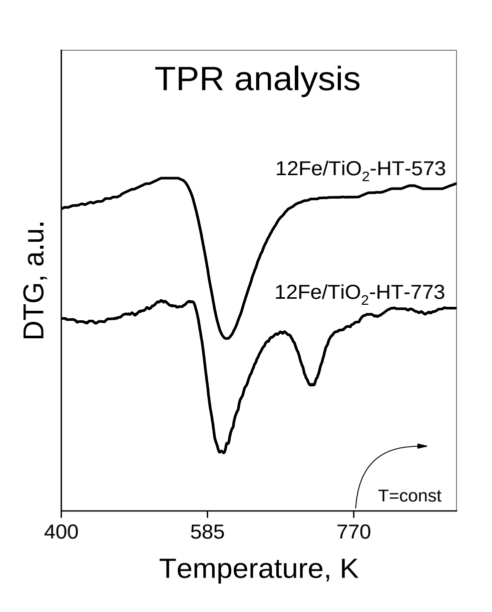


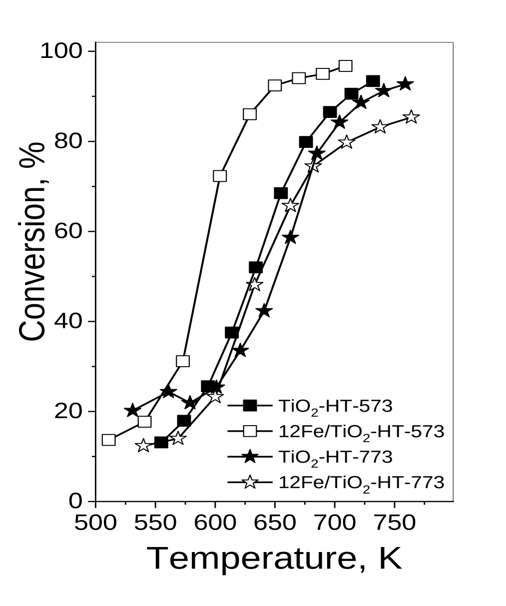


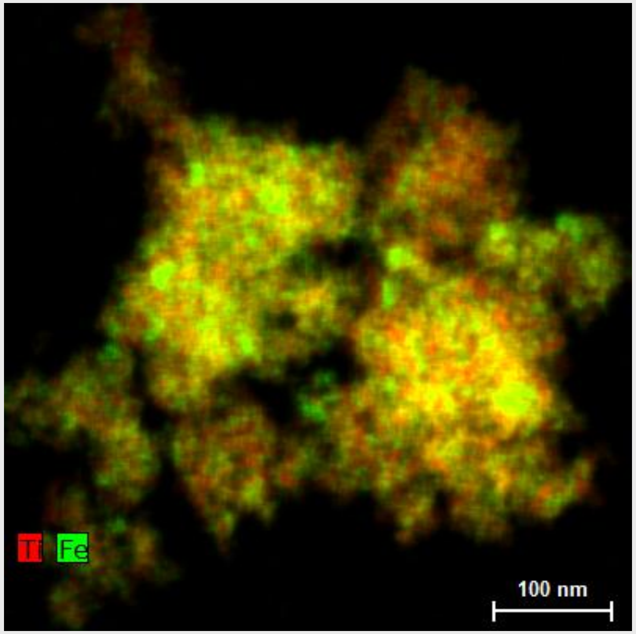
Modification, characterization and application

Preparation approach: comparison of support calcination temperature – 573 K vs 773 K

Sample	Fe, wt. %	S_{BET} m^2/g	V_{tot} cm^3/g	Crystalline phase	D, nm
TiO_2-HT-573	-	288	0.31	TiO_2 (anatase)	8.6
Fe/TiO_2-HT-573	12	97	0.22	TiO_2 (anatase) α-Fe_2O_3 (hematite)	9.1 7.6
TiO_2-HT-573	-	90	0.24	TiO_2 (anatase)	16.6
Fe/TiO_2-HT-773	12	69	0.18	TiO_2 (anatase) α-Fe_2O_3 (hematite)	14.2 25.2

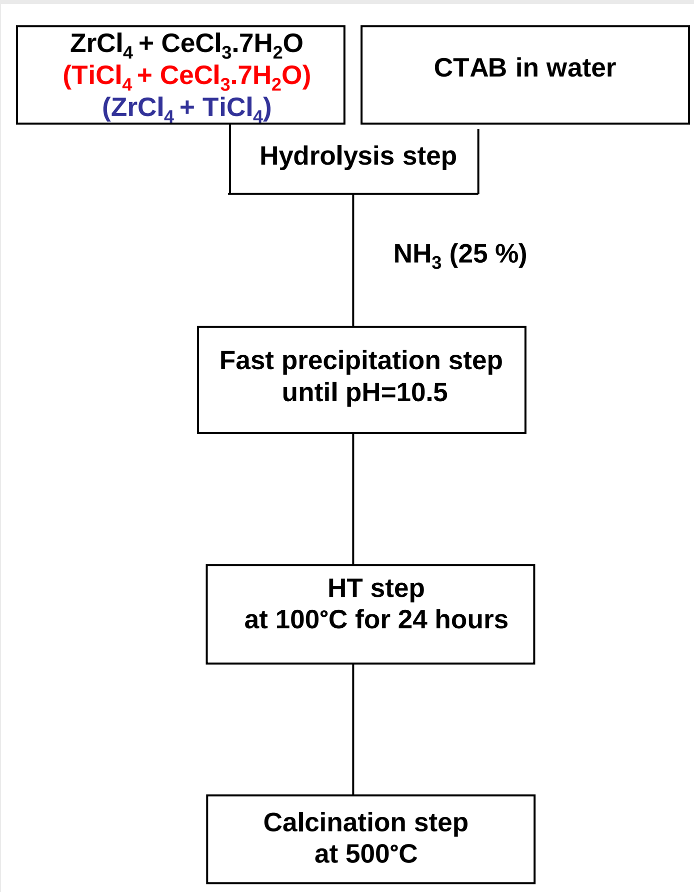


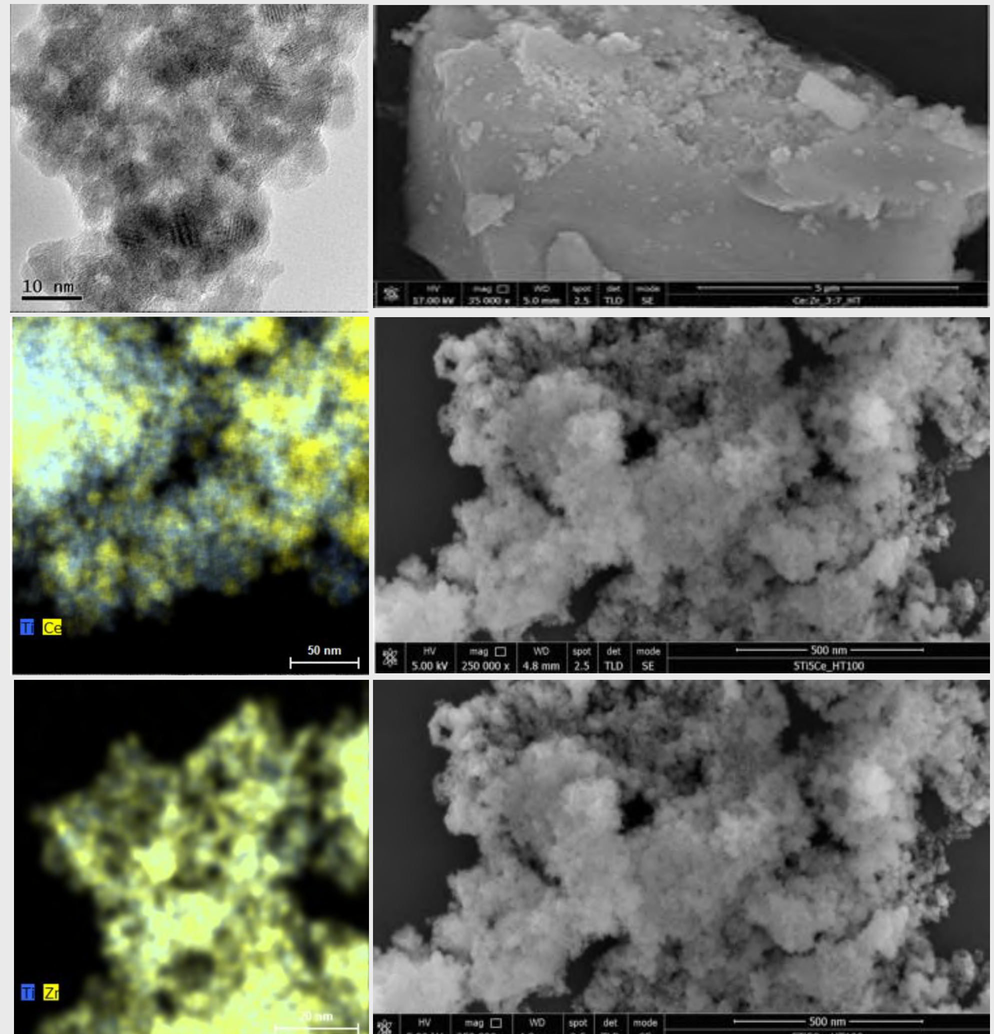




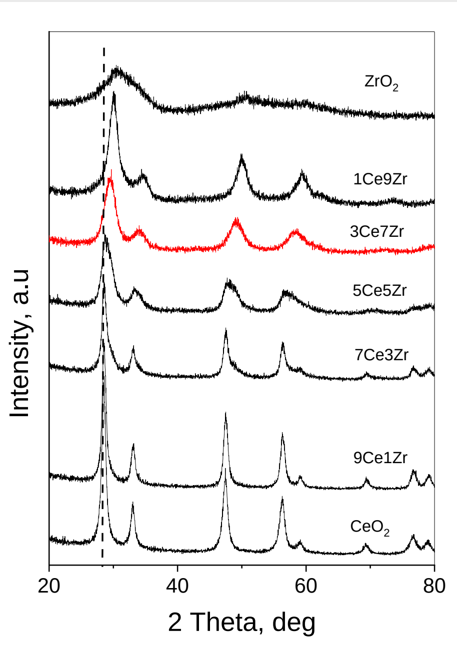
Synthesis of bicomponent mesoporous metal oxides

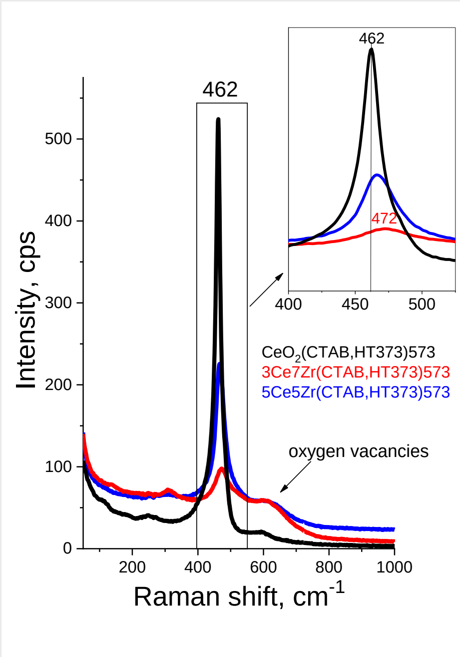
Template-assisted precipitation followed by hydrothermal treatment and calcination

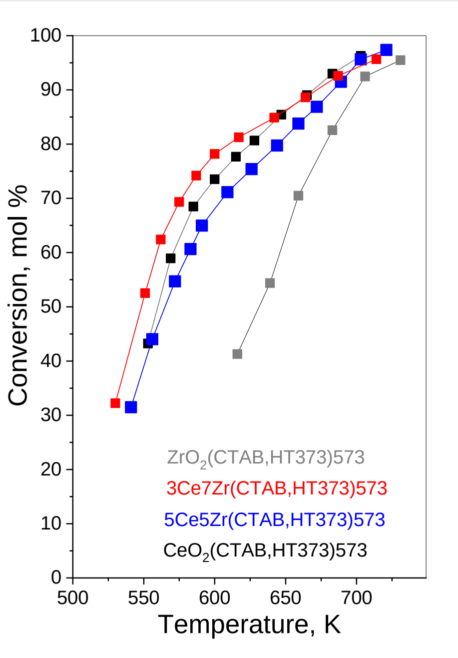




Characterization and application

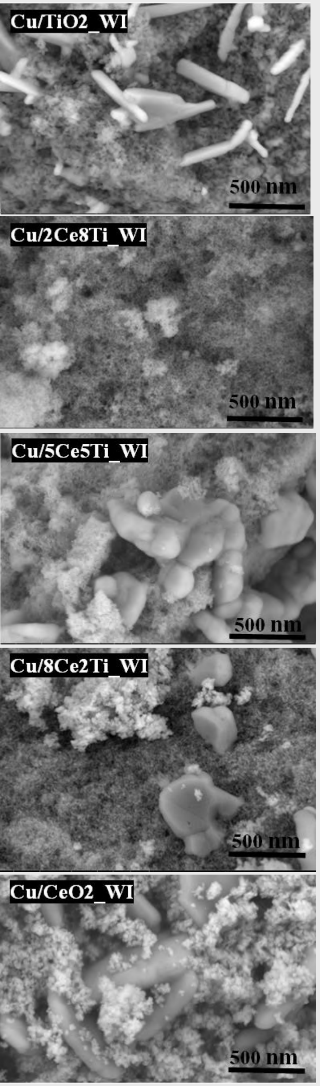




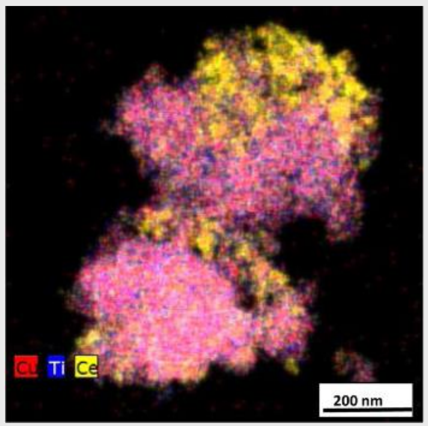


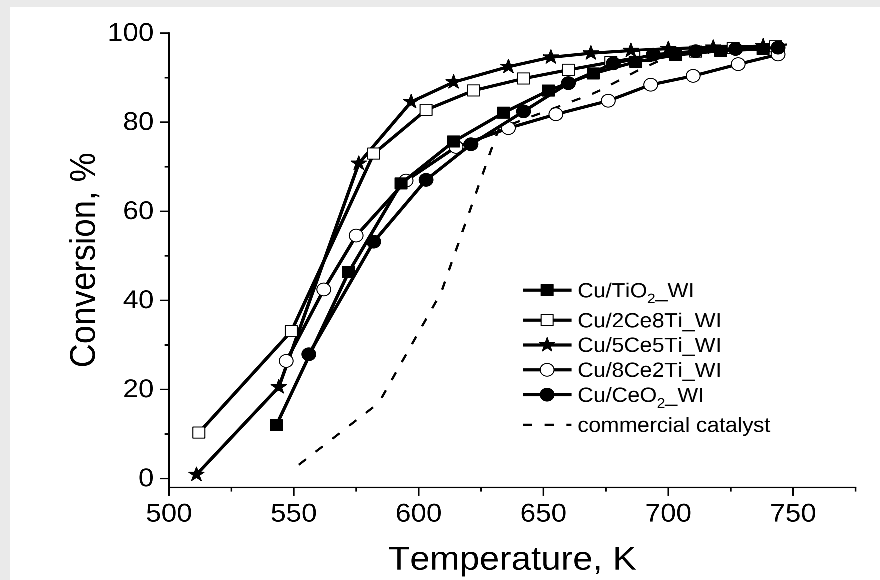
Sample	S_{BET}, m^2/g	V_{tot}, cm^3/g	Space group	Crystallite size, nm
ZrO_2(CTAB, HT373)573	296	0.42	$P4_2/nmcZ$ (tetragonal ZrO_2)	1.2
1Ce9Zr(CTAB, HT373)573	196	0.16	$P4_2/nmcZ$	5.1
3Ce7Zr(CTAB, HT373)573	167	0.14	Fm3m (cubic CeO_2)	3.5
5Ce5Zr(CTAB, HT373)573	150	0.14	Fm3m (44.0 %) $P4_2/nmcZ$ (56.0 %)	8.1 5.4
7Ce3Zr(CTAB, HT373)573	118	0.14	Fm3m (58.4 %) $P4_2/nmcZ$ (41.6 %)	12.8 5.0
9Ce1Zr(CTAB, HT373)573	93	0.20	Fm3m (95.0 %) $P4_2/nmcZ$ (5.0 %)	13.6 4.3
CeO_2(CTAB, HT373)573	58	0.27	Fm3m	11.7

Multicomponent metal oxide systems



Support composition	Supports		WI modifications	
	BET $m^2 g^{-1}$	Vt mlg^{-1}	BET $m^2 g^{-1}$	Vt mlg^{-1}
TiO_2	85	0.29	40	0.24
2Ce8Ti	166	0.62	102	0.49
5Ce5Ti	99	0.45	69	0.39
Ce2Ti	55	0.30	38	0.28
CeO_2	46	0.26	24	0.20





The catalytic properties of the multicomponent system are determined by the activity of the formed CuO crystallites and the facile electron transfer within the "conjugated" Ti-Ce-Cu redox centres in the interface layer.

THANK YOU FOR YOUR KIND ATTENTION !