

“Green catalysts” for hydrogen production

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Training Event 2

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important basic chemical
in the chemical industry

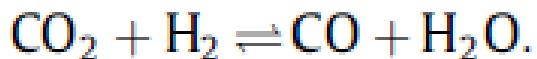
Methanol

appropriate alternative of
the fossil liquid fuels



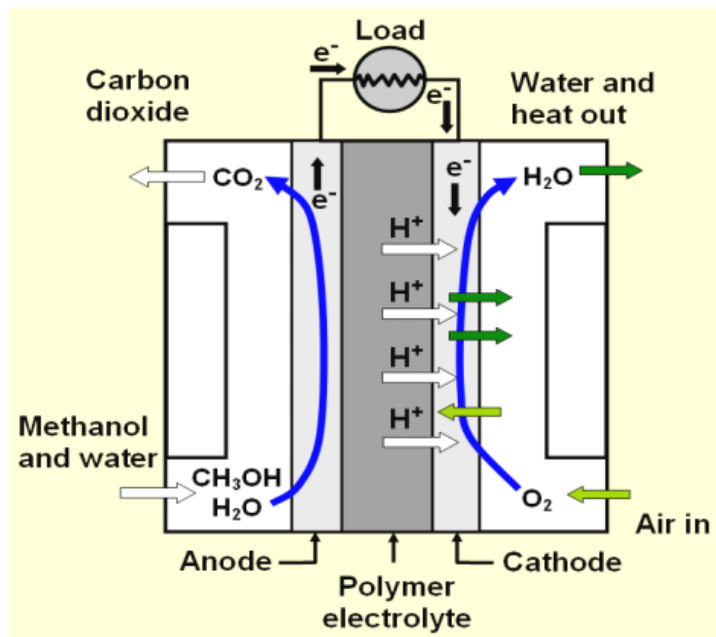
- It could be produced by well-known technologies from natural gas, coal and different renewable sources, such as black liquor from paper industry, animal waste, biomass, etc.

Cu/ZnO/Al₂O₃





- Pure methanol or mixtures with gasoline could be used directly in the vehicles as a fuel without significant technical changes



- The direct methanol fuel cells (DMFC), which use methanol as the feedstock, are promising substitute to batteries that can be applied in laptops, cell phones, and even military equipment.





Methanol as a hydrogen carrier

Steam reforming



Partial oxidation



Oxidative steam reforming



Decomposition





Cheep and efficient catalysts for methanol decomposition

Noble-metal-based catalysts

Pd/ZrO₂
PdZn alloys
Pt, Au

Non-noble-metal-based catalysts

Cu/ZnO
Transition metals or
metal oxides supported
on Al₂O₃, TiO₂, ZrO₂,
Fe₂O₃, CeO₂

**Complex role
of catalyst support**

- Stabilization of active phase in high dispersion
- Synergistic effects
- Formation of complex active sites
- Facile electron transfer between active phase and support



Activated carbon as environmentally friendly and economically effective catalyst support

chemical
inertness

high
temperature
stability

preparation from low
cost and waste
sources

tunable
texture

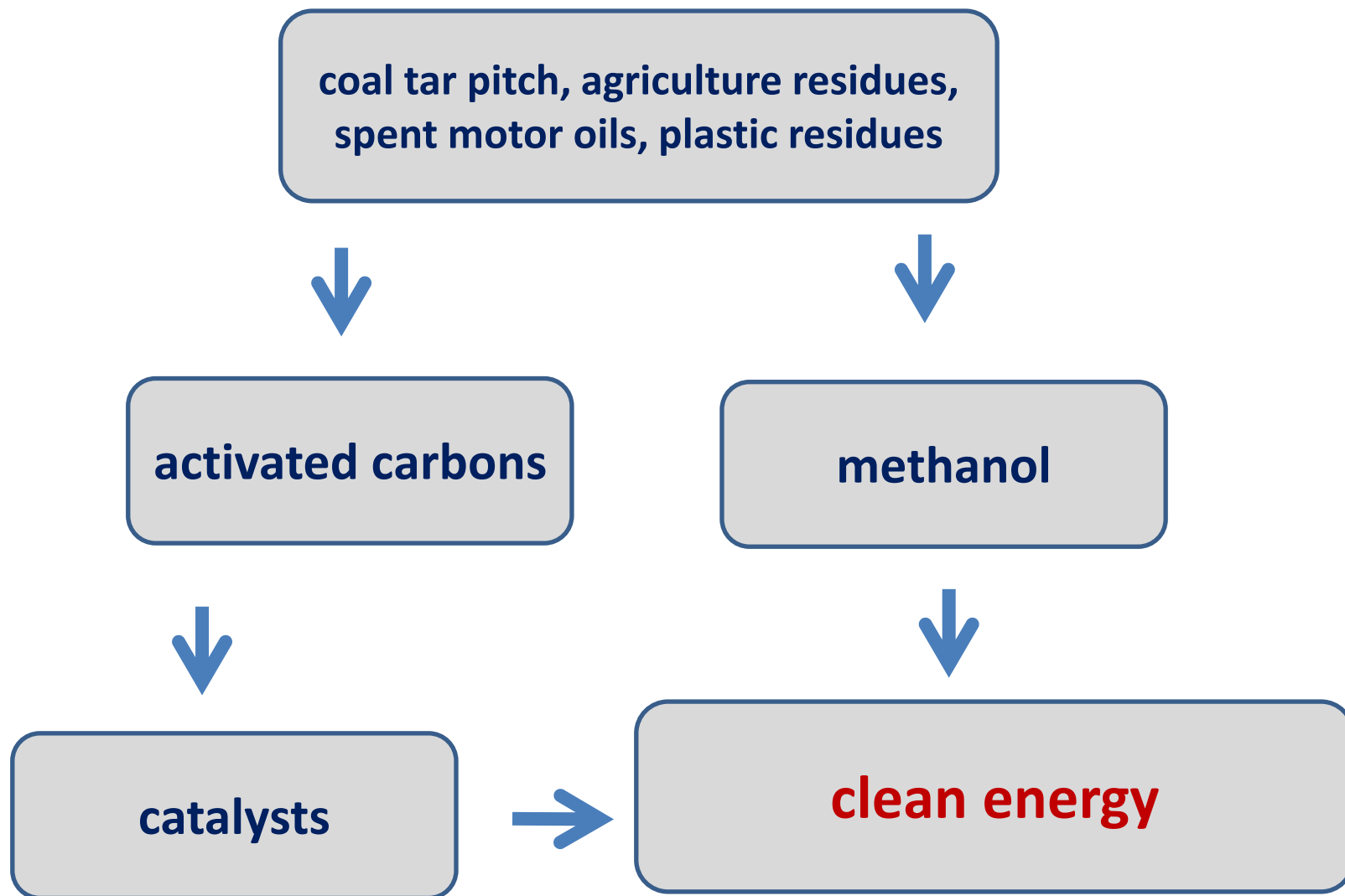
surface
functionality

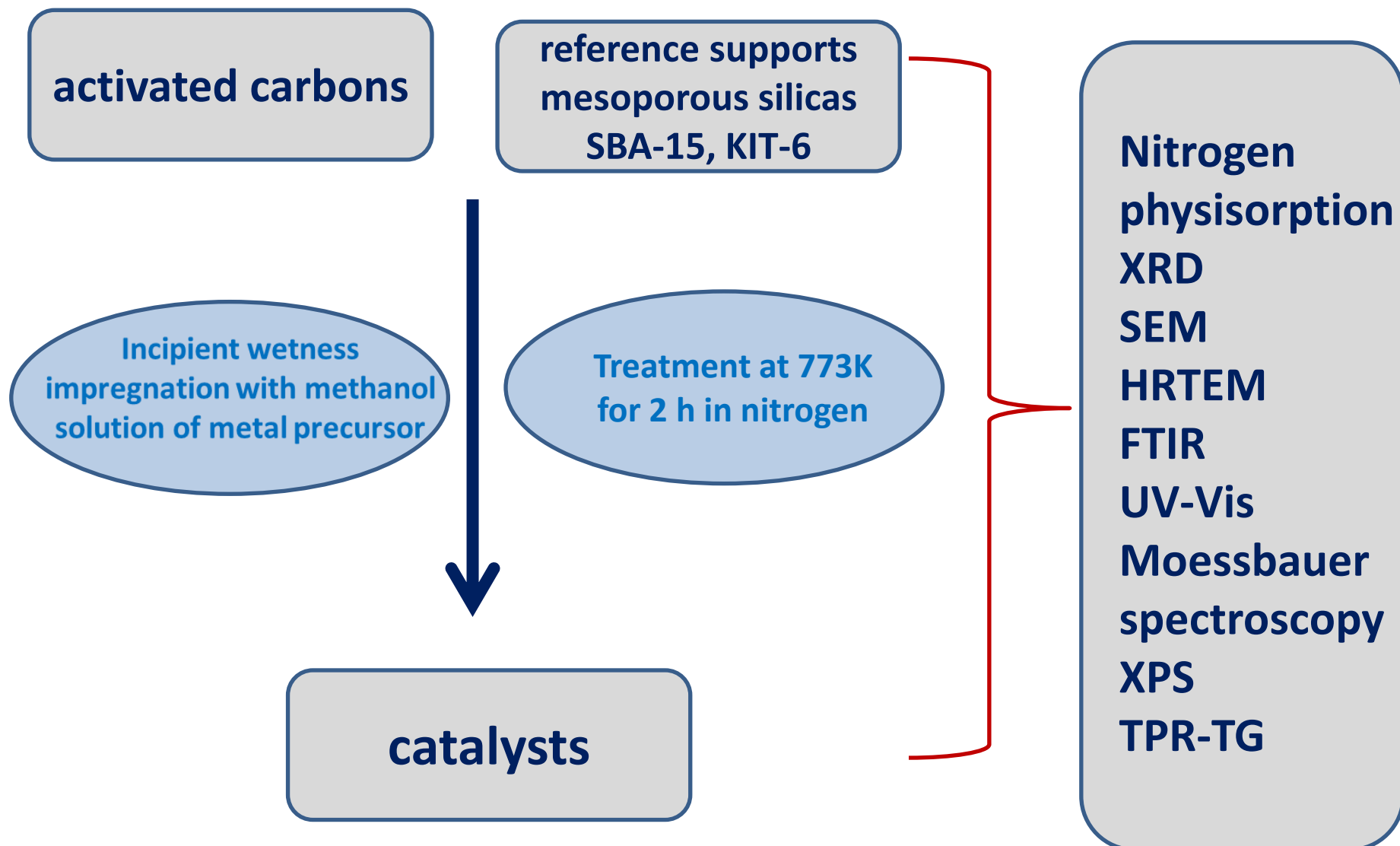
reductive
properties



Activated carbon as environmentally friendly and economically effective catalyst support

Catalysts	Reactions
Iron oxide/activated carbon	removal of organic compounds from aqueous solution
Iron oxide/activated carbon	H₂S elimination
Iron oxide/activated carbon	hydroxylation of benzene to phenol with H₂O₂
Iron and cobalt oxide/activated carbon	NO_x reduction
Barium promoted cobalt and cobalt–iron alloys/activated carbon	hydrogenation of organic compounds
Pt and Ru/activated carbon	methanol decomposition to syngas
MoO₃ /activated carbon (Mo₂C)	production of hydrogen from ethanol, methanol and dimethyl ether



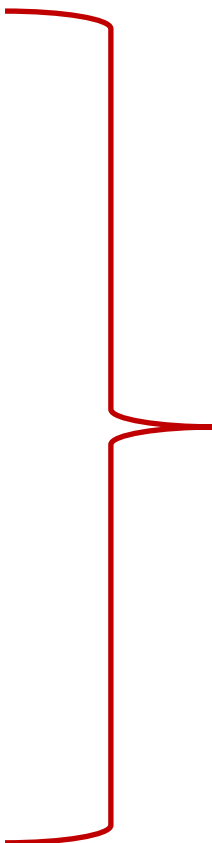




**Methanol
(1.57 kPa in Ar
50 ml/mn)**

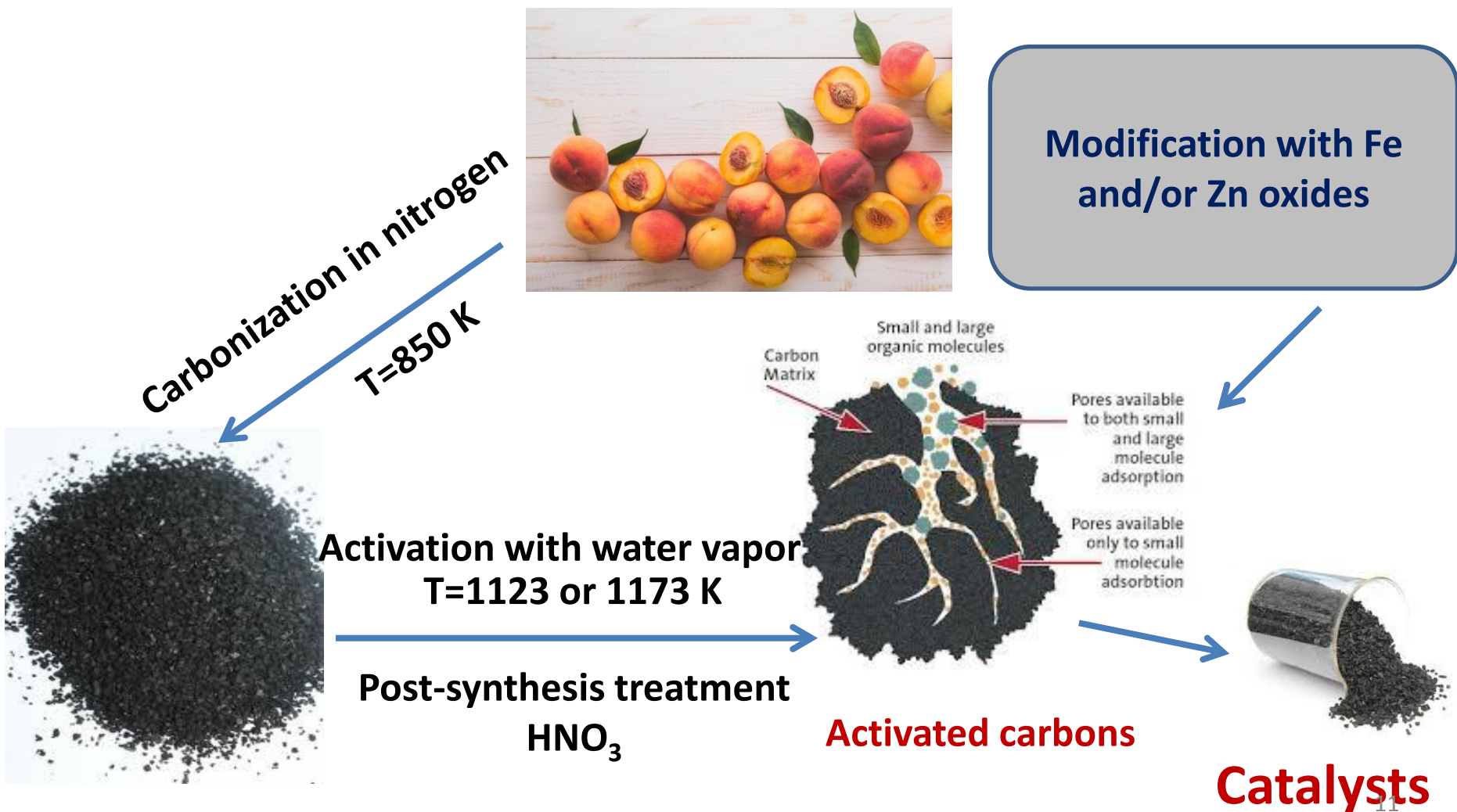
**Flow type fixed bed
reactor
(50 mg catalyst)**

GC with TCD and FID

- 
- **Conversion at different temperatures**
 - **By-products and selectivity to CO and H₂**
 - **Stability under time on stream**
 - **Nature of the catalytic active sites**
 - **Mechanism of the catalytic process**
 - **Optimization of the catalysts**



• Impact of carbon support texture and surface functionality on the formation of the catalytic active phase





Activated carbons characterization

Sample	S_{BET} m^2	S_{mi} m^2	V_{t} cm^3	V_{mi} cm^3	$V_{\text{mi}}/$ V_{mes}
AC(1123)	1258	1116	0.61	0.45	2.8
AC(1123,NA)	787	680	0.47	0.36	3.3
AC(1173)	1257	1082	0.63	0.44	2.3
AC(1173,NA)	1228	1041	0.64	0.42	2.0
KIT-6	872	278	1.23	0.14	0.1

- mixed micro-mesoporous texture
- the relative part of the micropores decreases with the increase of the activation temperature
- the post-synthetic treatment of AC(1123) with HNO_3 results in a decrease of the BET surface area and total pore volume combined with an increase in the $V_{\text{mic}}/V_{\text{mes}}$ ratio
- the changes in the texture characteristics are negligible after the AC(1173) treatment with HNO_3



Activated carbons characterization

Sample	Carboxyl, mol.kg ⁻¹	Lactone, mol.kg ⁻¹	Hydroxyl, mol.kg ⁻¹	Carbonyl, mol.kg ⁻¹
AC(1123)	-	-	0.29	1.07
AC(1123, NA)	0.28	0.37	0.46	1.15
AC(1173)	-	-	0.65	0.90
AC(1173, NA)	0.19	0.25	0.66	1.15

- Increase in the number of surface acidic groups after the post-synthesis treatment with HNO₃



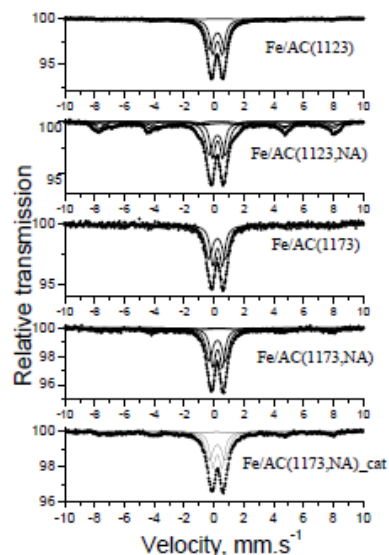
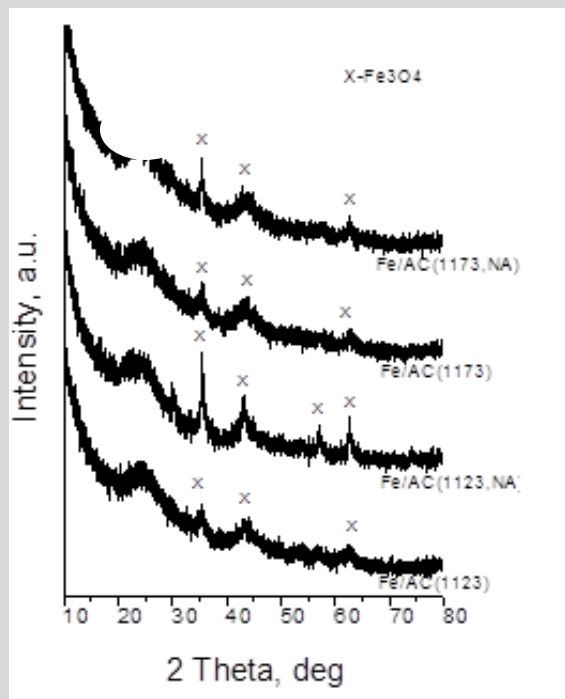
Iron modified activated carbons

Sample	S_{BET} , m^2	S_{mi} , m^2	V_{t} , cm^3	V_{mi} , cm^3	$V_{\text{mi}}/$ V_{mes}
Fe/AC(1123)	772	680	0.44	0.34	4.4
Fe/AC(1123,NA)	736	640	0.42	0.32	3.2
Fe/AC(1173)	861	719	0.54	0.38	2.4
Fe/AC(1173,NA)	932	792	0.50	0.35	2.3
Fe/KIT-6	729	187	1.06	0.09	0.1

- pore blocking as a result of metal particles deposition
- predominant location of metal oxide species into the mesopores
- restriction of the deposition of the metal species into the micropores by surface carboxyl and lactone groups



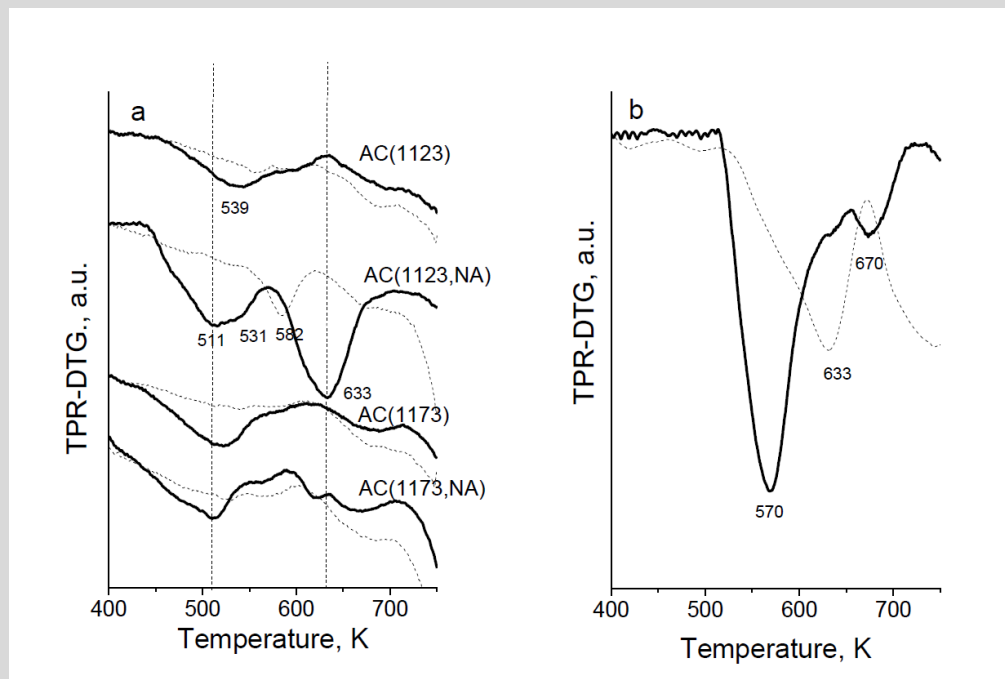
Iron modified activated carbons



- Presence of ultra dispersed Fe³⁺ containing particles (up to 3-4 nm) and larger Fe₃O₄ nanoparticles
- The average crystallite size increases with the increase of the activation temperature and post-synthetic treatment of AC with nitric acid



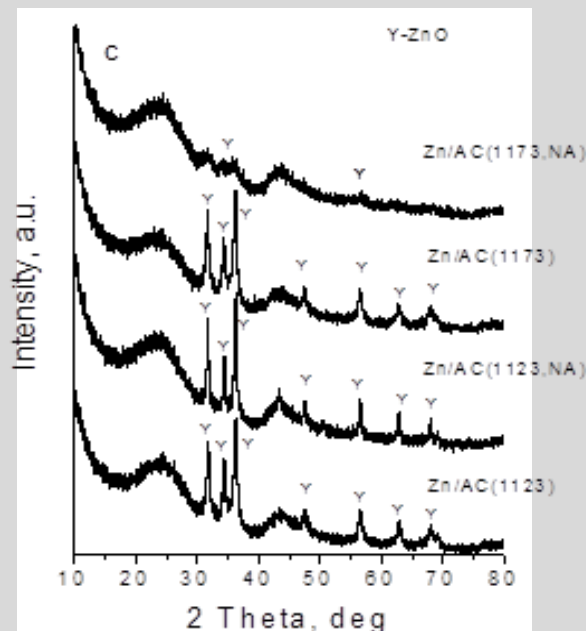
Iron modified activated carbons



- TPR profiles for the AC and silica supported samples confirms the assumption for the reduction activity of AC support
- The higher reduction temperature for the AC supports with lower amount of surface functional groups evidences stronger interaction of the iron particles with the carbon basal planes than with the surface functional groups



Zinc modified activated carbons

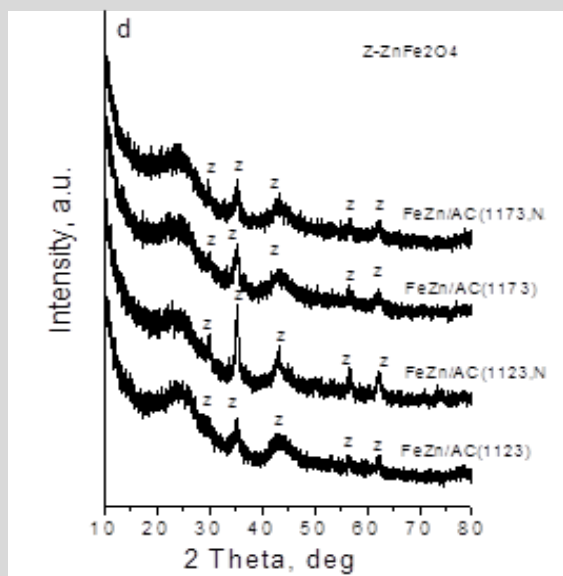


Sample	S_{BET} , m^2	S_{mi} , m^2	V_{t} , cm^3	V_{mi} , cm^3	$V_{\text{mi}}/$ V_{mes}
Zn/AC(1123)	982	853	0.51	0.37	2.6
Zn/AC(1123,NA)	769	672	0.42	0.32	3.2
Zn/AC(1173)	1063	908	0.55	0.37	2.1
Zn/AC(1173,NA)	1017	880	0.52	0.36	2.3
Zn/KIT6	349	36	0.59	0.05	0.1

- **XRD:** ZnO nanoparticles with average crystallite size of about 20 nm
- **N_2 physisorption:** almost random distribution of ZnO species into the micro/mesopores and on the external surface of AC



Iron and Zinc binary modifications of activated carbons

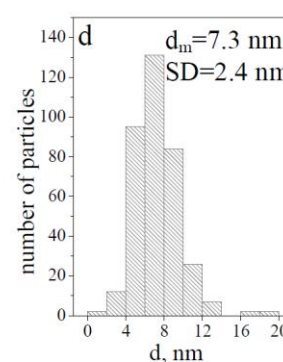
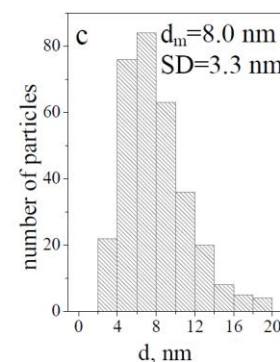
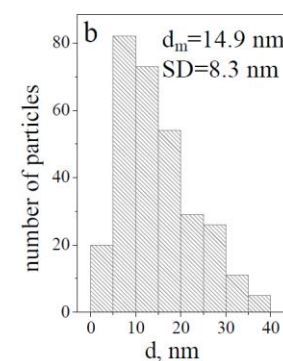
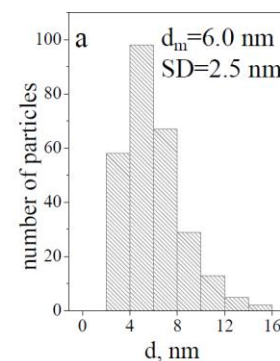
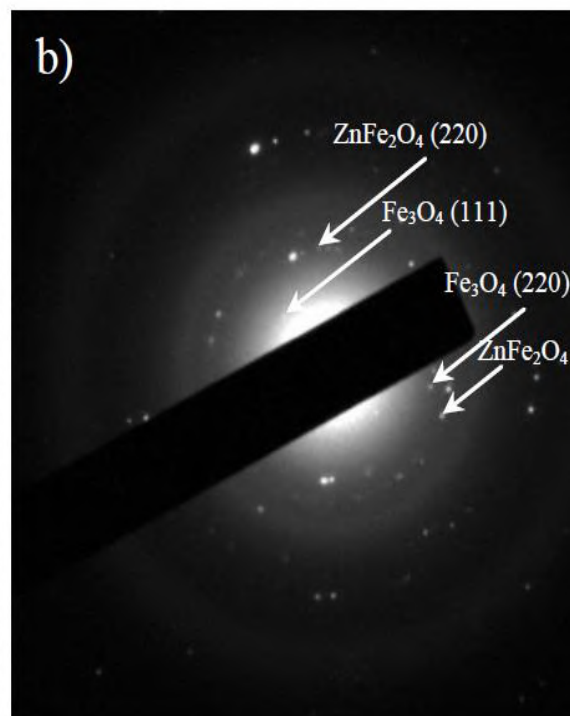
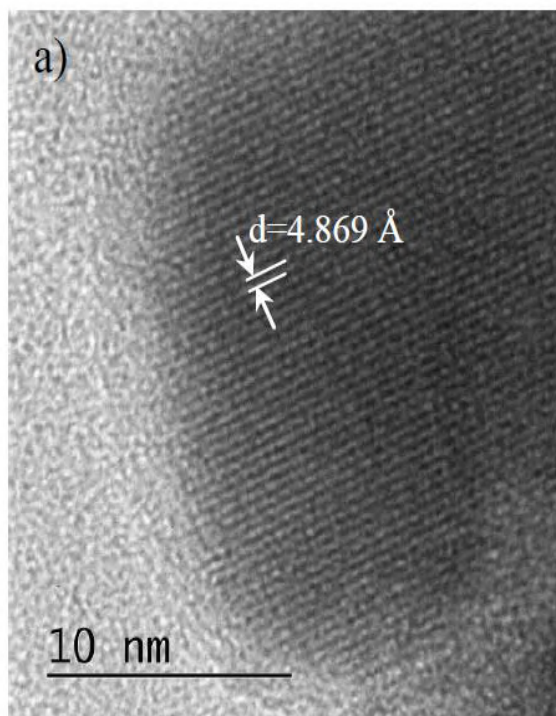


Sample	S_{BET} , m^2	S_{mi} , m^2	V_{t} , cm^3	V_{mi} , cm^3	$V_{\text{mi}}/$ V_{mes}
FeZn/AC(1123)	965	866	0.46	0.35	3.2
FeZn/AC(1123,NA)	787	704	0.40	0.32	4.0
FeZn/AC(1173)	998	831	0.57	0.37	1.8
FeZn/AC(1173,NA)	1032	889	0.52	0.36	2.3
FeZnKIT6	561	108	0.80	0.05	0.1

- **XRD:** ZnFe_2O_4 nanoparticles with average crystallite size of about 8 nm
- **N_2 physisorption:** predominant location of ferrite species in the mesopores of AC(1123) and after the AC treatment with HNO_3 , and in the micropores for AC(1173)



Iron and Zinc binary modifications of activated carbons

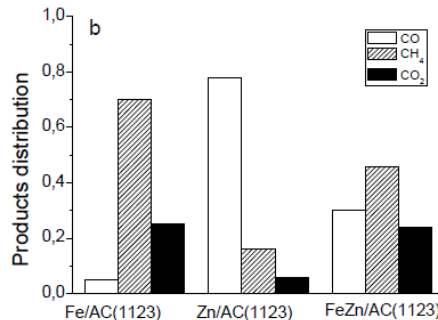
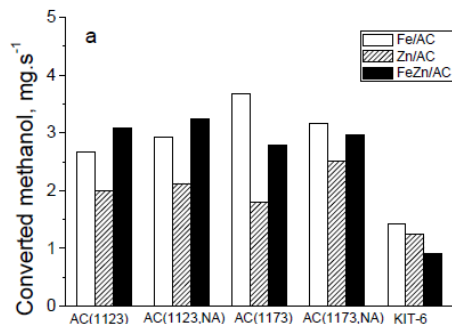


- **Moessbauer spectroscopy:** $Zn_xFe_{3-x}O_4$ with relatively high Zn content ($x \geq 0.8$)
- **HRTEM and Selected Area Electron Diffraction (SAED):** presence of $ZnFe_2O_4$, ZnO and Fe_3O_4 phases and variation in particles size distribution by the regulation of surface functionality and porous characteristics of AC support



Catalytic tests

Iron modifications: The increase of the relative part of mesopores at higher activation temperature during the carbon preparation promotes the formation of more finely dispersed, accessible for the reactants and active in methanol decomposition magnetite particles.



Zinc modifications:

The dispersion and the accessibility of the zinc oxide species are facilitated by the formation of additional amount of surface acidic groups during the carbon pre-treatment with nitric acid.

Binary iron-zinc modifications: The combination of lower temperature of carbon activation and nitric acid pre-treatment promotes the formation of highly active ferrite nanoparticles due to the limited deposition of metal oxide species into the support micropores.



Effect of AC precursor



OSAC

Co



PSAC

Co

Coal tar pitch +
furfural (1:1)
 HNO_3

SACN

Co

Coal tar pitch +
furfural (1:1)
 H_2SO_4

SACS

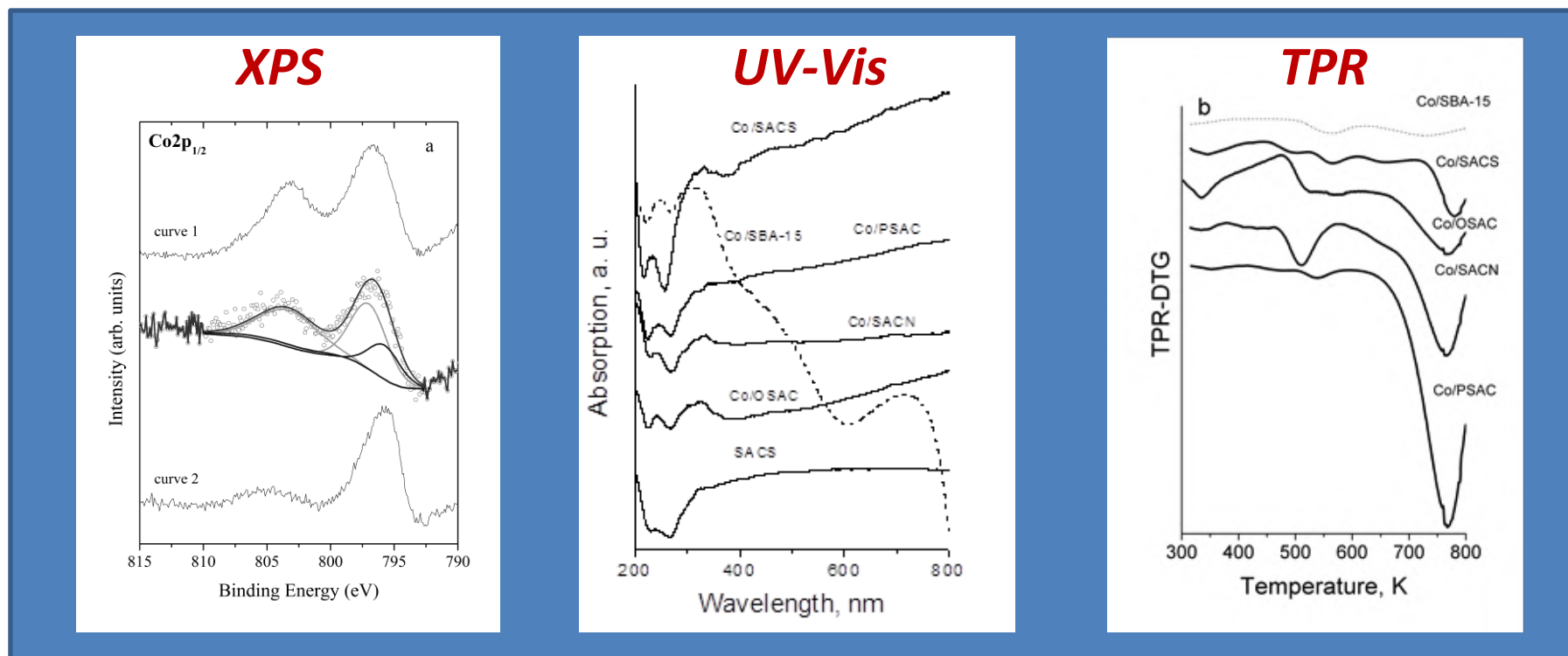
Co

Sample	S_{BET}	V_{pores}	$V_{\text{mic}}/V_{\text{mes}}$
OSAC	950	0.44	13.39
PSAC	830	0.39	6.39
SACS	680	0.24	7.17
SACN	820	0.40	2.89

Sample	Acidic groups, meq/g			
	Carboxylic	Lactonic	Hydroxyl	Carbonyl
OSAC	0.02	0.09	0.55	1.07
PSAC	-	-	0.49	0.98
SACS	-	-	-	-
SACN	0.01	0.06	0.41	0.88



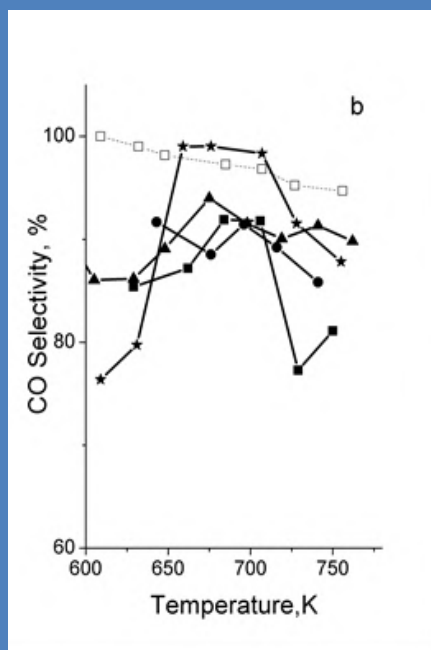
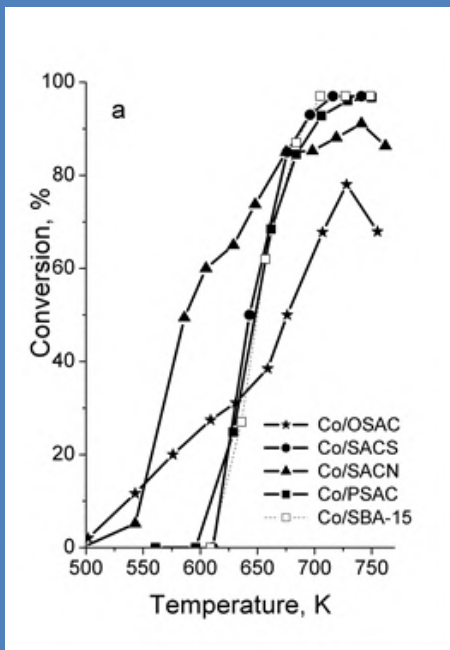
Cobalt modifications of AC



Co-existence of metallic cobalt and CoO_x species in different state and proportion depending on the nature of the activated carbon support



Cobalt modifications of AC



- The surface functionalities of activated carbons do not have dominant effect on the formation of cobalt phase and its catalytic activity. The crucial role of texture characteristics of carbon supports is demonstrated.

- The location of cobalt phase into the mesopores reveals formation of more uniform and accessible to reactants cobalt species and provides higher catalytic activity for Co/SACN.

- The presence of cobalt oxide phase, randomly distributed into micro- and mesopores of SACS and PSAC facilitate the catalytic activity and stability, but at relatively higher temperatures.

- The predominant location of cobalt species into the micropores of OSAC hinders their participation in the catalytic process.



Effect of AC precursor



ACPS

Fe

ACOS

Fe

ACAS

Fe

ACGS

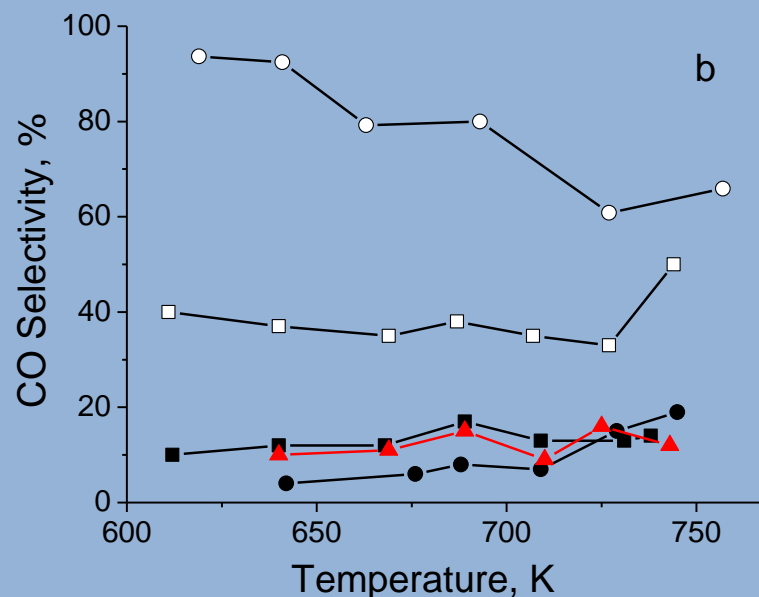
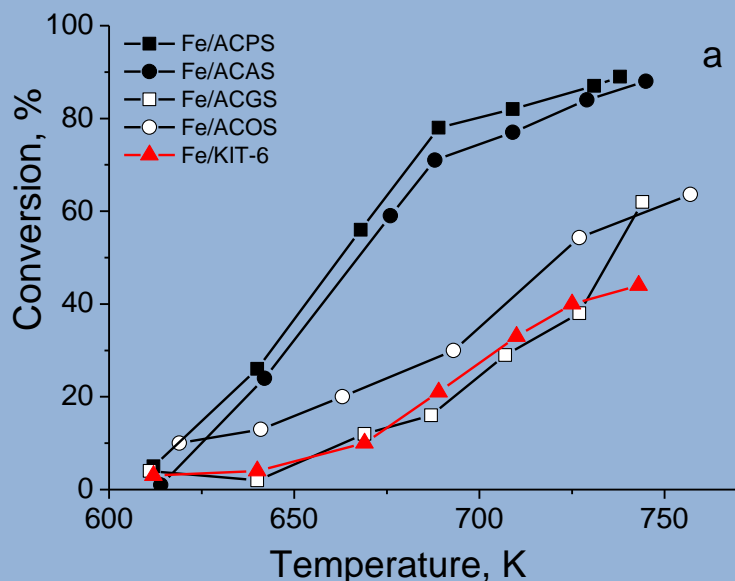
Fe

Sample	S_{BET} , m^2/g	V_t , cm^3/g	$V_{\text{mi}}/V_{\text{mes}}$
ACPS	1258	0.61	2.76
ACAS	921	0.46	4.29
ACGS	603	0.29	4.95
ACOS	950	0.44	13.39
KIT-6	872	1.23	0.13

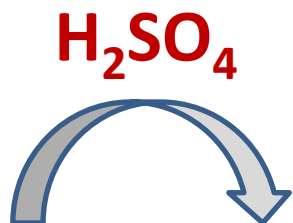
Sample	Hydroxyl mmol/g	Carbonyl mmol/g	Basic groups mmol/g
ACPS	0.29	0.94	1.04
ACAS	2.05	3.27	1.34
ACGS	1.59	2.98	1.24
ACOS	0.55	1.07	1.19



Iron modifications of AC



- The mesoporosity facilitates the formation of a stable under the reaction medium highly dispersed magnetite phase, which ensures high catalytic activity but relatively low selectivity to CO.
- The microporosity facilitates deposition of less accessible particles into the micropores and larger magnetite particles on the external surface which easily transforms under the reaction medium to metallic Fe and/or Fe_3C . This provides relatively low catalytic activity and higher selectivity to CO.



furfural



Spent motor oil



coal tar pitch

carbonization
873 K



activation
1173 K

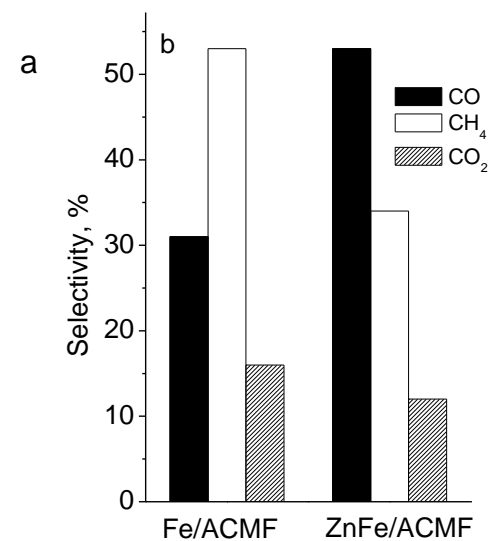
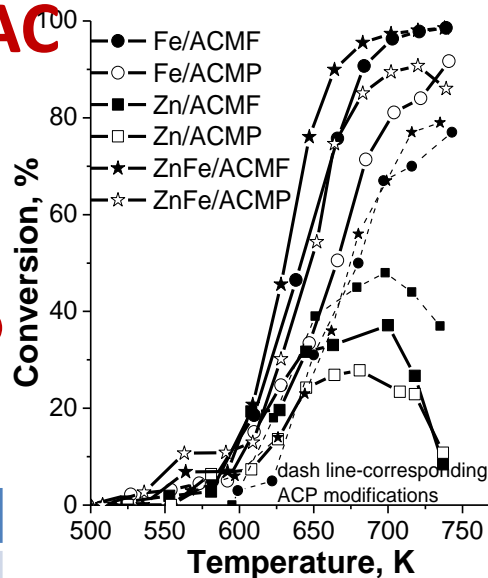
ACMF

ACMP

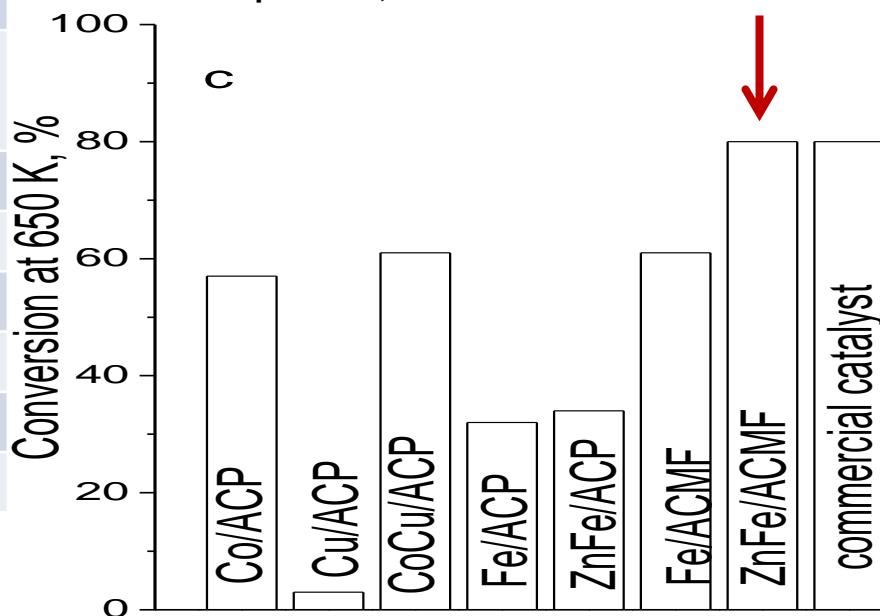


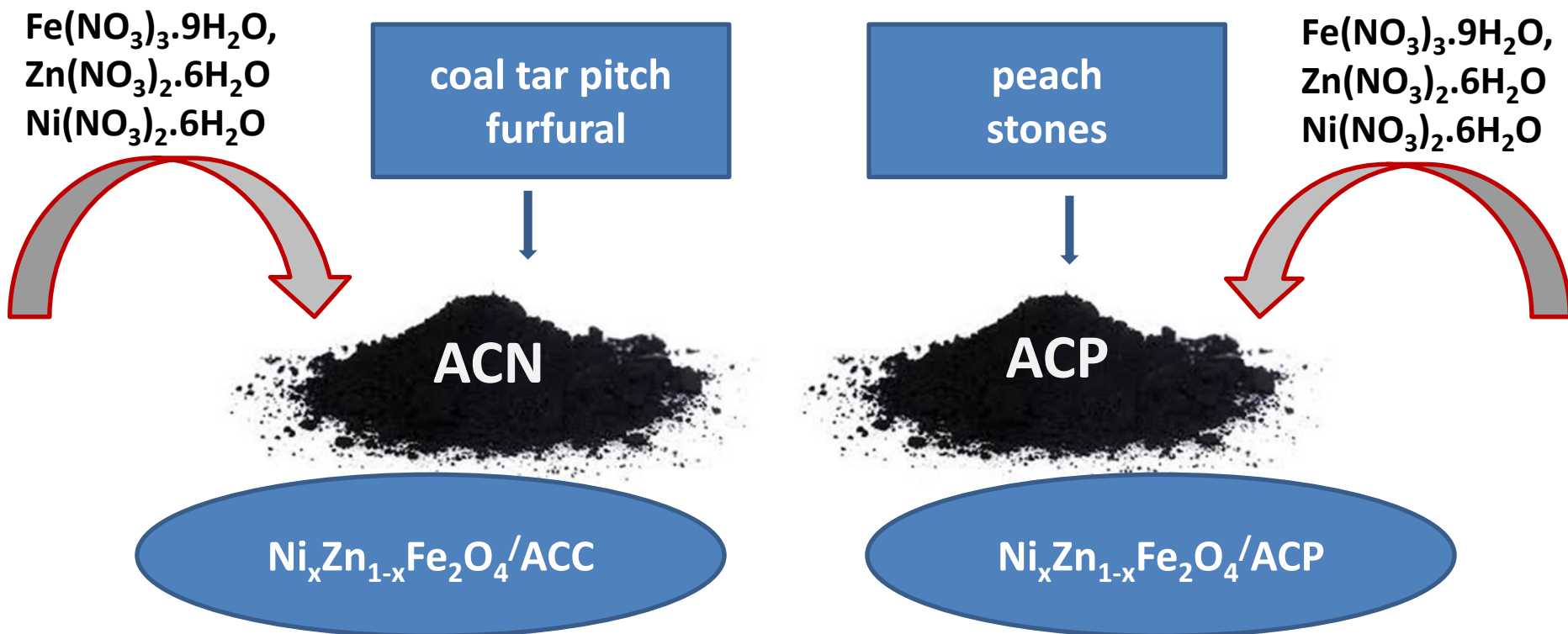
Fe and Zn modifications of ACP

Sample	S_{BET} , m^2/g	V_{tr} , cm^3/g	V_{mi} , cm^3/g	V_{mes}/V_{mic}
ACMF	1212	0.84	0.39	1.15
ACMP	959	0.69	0.25	1.76



Characteristics	Sample	
	ACMF	ACMP
Acidic unctional groups, meq/g		
Carboxyl	0.15	0.05
Lactonic	0.80	-
Hydroxyl	0.18	0.05
Carbonyl	0.98	1.00
Basic groups, meq/g	0.47	1.36
pH	7.9	8.5





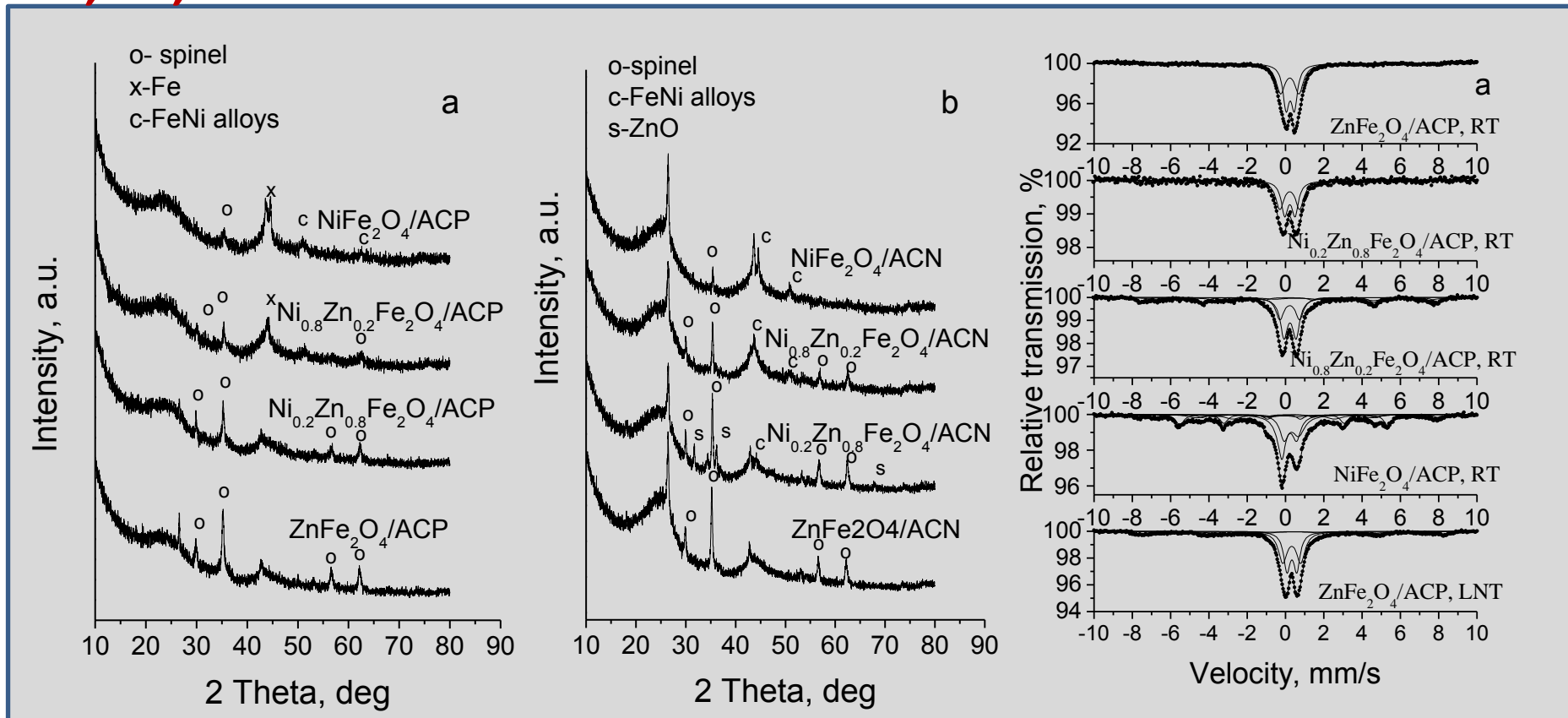
Sample	Carboxyl	Lactone	Hydroxyl	Carbonyl	Basic groups
ACP	0.05	0.24	0.29	1.07	1.04
ACN	0.01	0.12	0.21	1.36	0.98



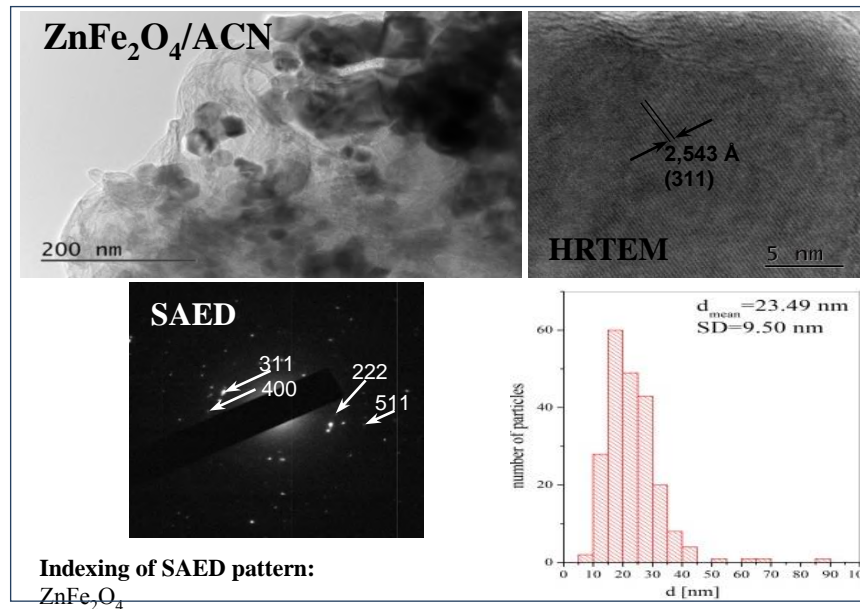
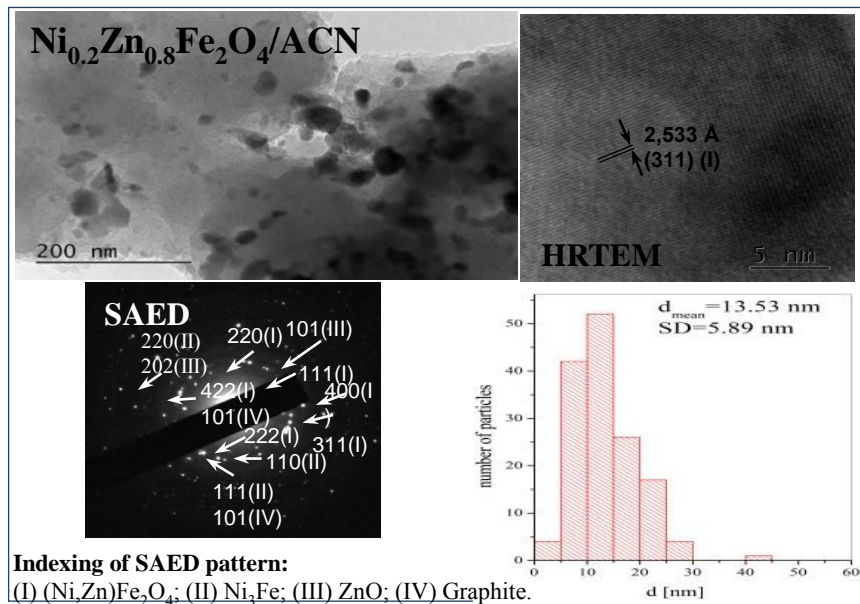
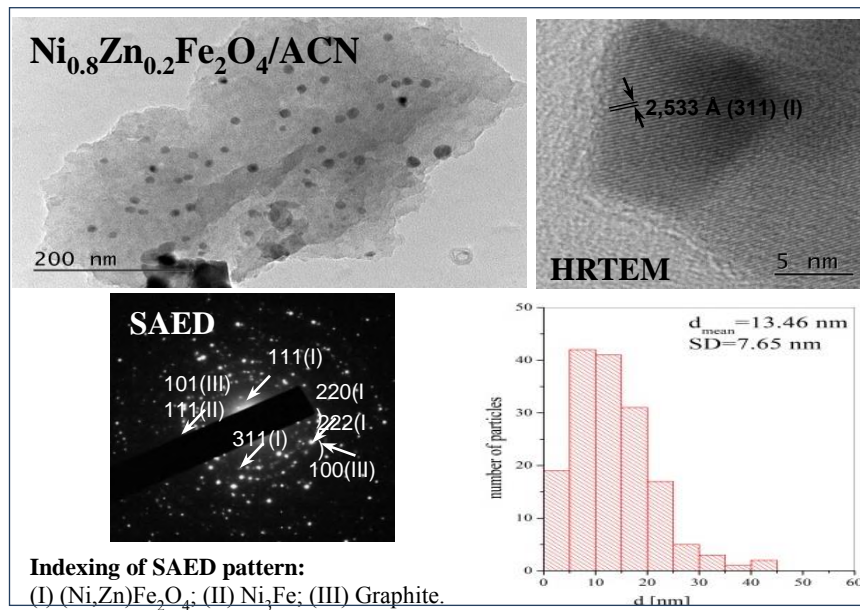
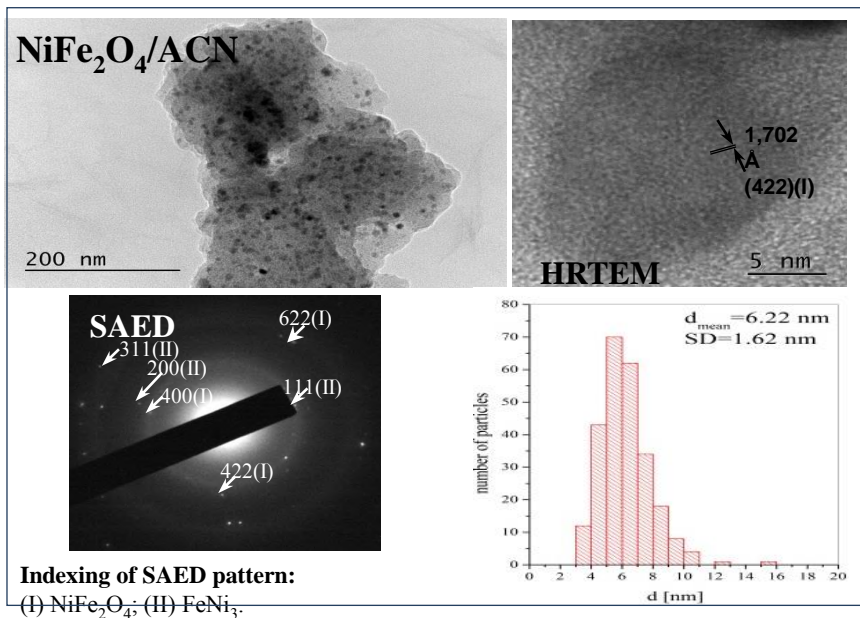
Sample	S_{BET} m^2g^{-1}	V_t cm^3g^{-1}	V_{mi} cm^3g^{-1}	D_{av} nm	Δ_{BET} %	ΔV_t %	$V_{\text{mic}}/$ V_{mes}
ACP	846	0.53	0.37	1.9			2.3
$\text{NiFe}_2\text{O}_4/\text{ACP}$	697	0.40	0.30	1.8	18	24	3.0
$\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4/\text{ACP}$	700	0.42	0.32	1.8	17	21	3.2
$\text{Ni}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4/\text{ACP}$	680	0.41	0.32	1.8	19	23	3.6
$\text{ZnFe}_2\text{O}_4/\text{ACP}$	661	0.39	0.31	1.8	22	26	3.9
ACN	659	0.40	0.32	2.4			4.0
$\text{NiFe}_2\text{O}_4/\text{ACN}$	455	0.25	0.21	1.8	31	37	5.2
$\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4/\text{ACN}$	436	0.22	0.17	1.9	34	45	3.4
$\text{Ni}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4/\text{ACN}$	452	0.26	0.22	1.8	31	35	5.5
$\text{ZnFe}_2\text{O}_4/\text{ACN}$	395	0.22	0.18	1.8	40	45	4.5



Fe, Ni, Zn modifications of AC

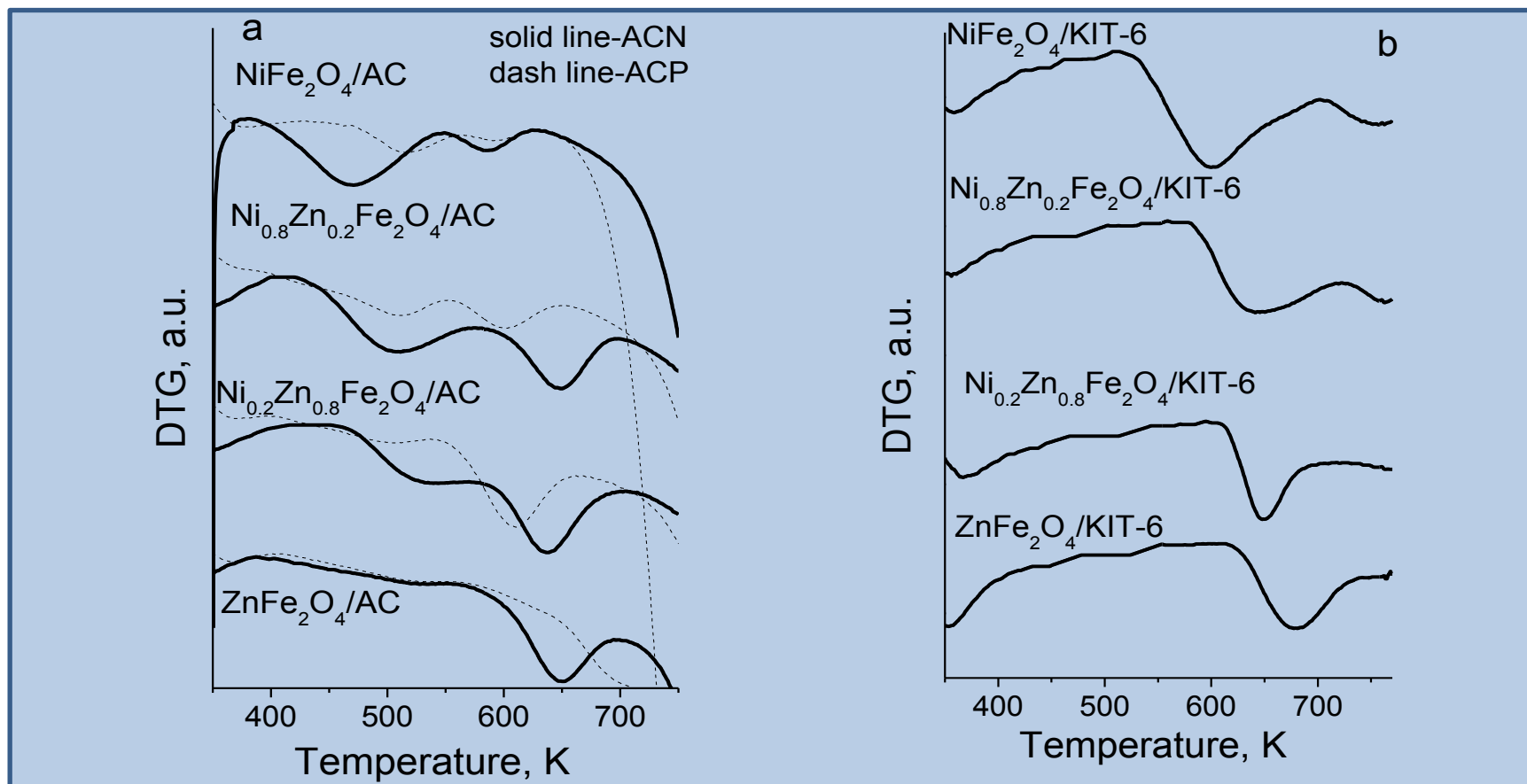


- XRD analyses demonstrate formation of mixed oxides as well as Fe, NiFe alloys and ZnO contaminants
- The average crystallite size of 10-19 nm for ACP and 30-50 nm for ACN
- The Mössbauer parameters correspond to magnetite substituted by Ni²⁺ and Zn²⁺ ions

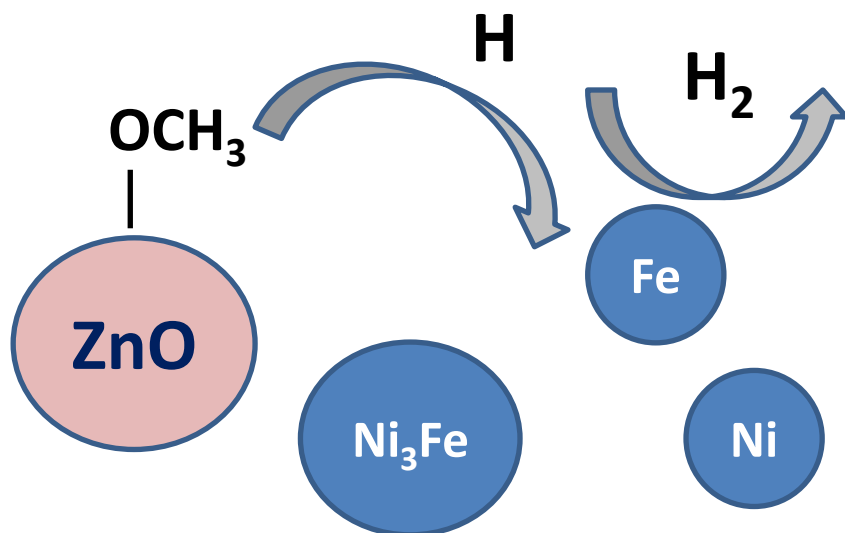
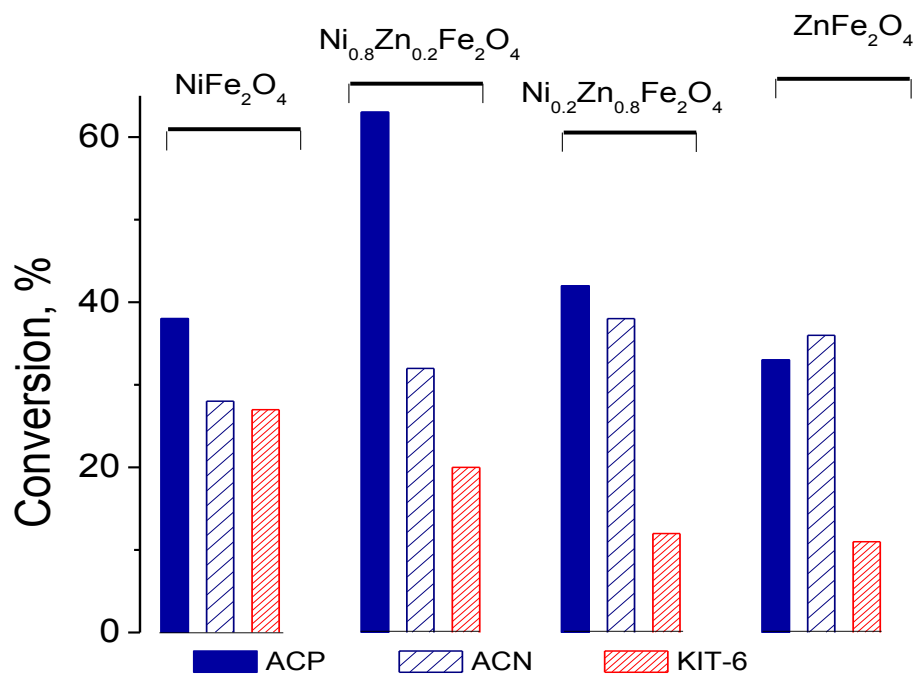




Fe, Ni, Zn modifications of AC



- the reductive transformations in the spinels are facilitated by the carbon matrix
- the observed weight loss overcomes about 1.5 to 3 times the expected theoretical one indicating gasification of the AC supports



Higher catalytic activity for the AC based catalysts as compared to the silica analogues

The lower catalytic activity for most of the ACN modifications could be attributed to lower dispersion of the active phase in them

The simultaneous formation of metals (alloys) and ZnO in the binary NiZn ferrite modifications promotes the catalytic activity in a synergistic mode

Conclusions

Activated carbons obtained from different wastes or low cost materials could be suitable support for the preparation of effective catalysts for methanol decomposition with a potential for hydrogen production. The optimization of the catalytic behaviour is closely related to the knowledge on the relation between the waste precursor, textural and surface characteristics of activated carbons as well as to the phase transformations which occur under the reaction medium.

Conclusions

The state of the supported metal oxide species could be simply regulated by the procedure of activated carbon preparation and post-synthetic treatment, but this effect strongly depends on the nature of the loaded metal oxide.

Conclusions



The activated carbon support possesses reductive properties and strongly affects the formation of metal active phase. The dominant effect of texture over the surface functionality of the activated carbon support on the deposition of active phase is assumed. Complex effect of the surface functional groups, which acts both as an anchoring centres for the metal oxide precursor and “blocking” the carbon micro- and mesopores on the formation of the loaded metal oxide phase is established.



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Assoc. Prof. Dr. Boyko Tsyntsarski
Assoc.Prof. Dr. Nikolay Velinov
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Assoc.Prof. Dr. Daniela Paneva
Ass. Prof. Dr. Gloria Issa
Ass. Prof. Dr. Radostina Ivanova
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A scenic landscape featuring a calm, blue lake in the foreground, surrounded by lush green vegetation and rocky slopes. In the background, a large, rugged mountain peak is visible, partially shrouded in mist or low clouds. The sky is a clear, vibrant blue with scattered white clouds. The overall scene is bright and picturesque, typical of a mountainous region in Bulgaria.

**Thank you for your attention
and welcome to Bulgaria!**