NANOSIZED EFFECTS IN CATALYTIC PROCESSES FOR ECOLOGY AND POWER SUPPLY SYSTEM

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Reduction of the size parameters of a substance to nanometer scale causes appearance of unique properties which can be used in practice for development of novel materials and technologies

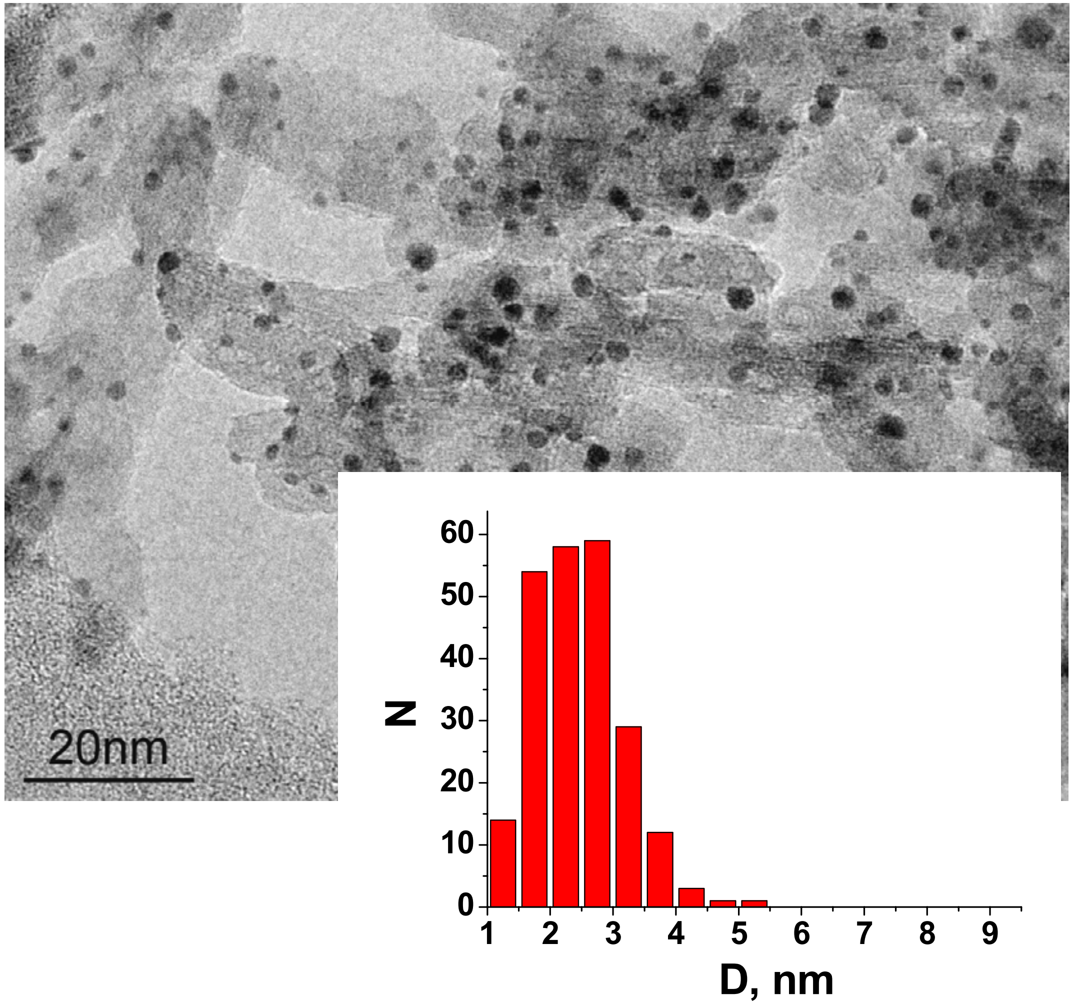
Not only physical properties, but also reactivity of a substance in nanometer scale will be changed. As consequence, we can create new chemical sensors, CATALYSTS, adsorbents etc.

OUTLINE OF THE TALK

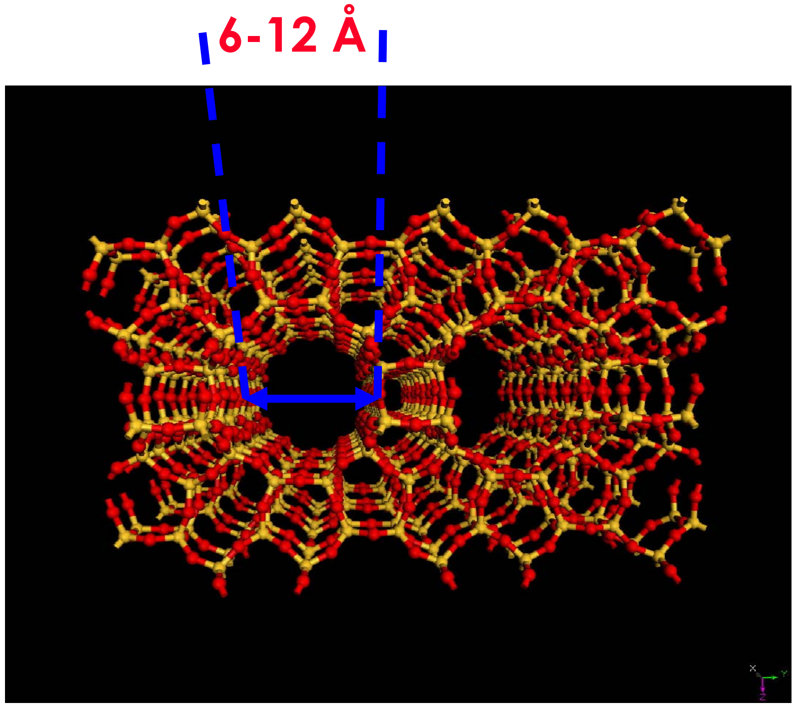
- NANOTECHNOLOGY, NANOMATERIALS and CATALYSIS (hundred years in collaboration)
- SIZE EFFECTS IN CATALYSIS BY METALS (BIC experience):
  - ✓ methane oxidation over Pt/Al_2O_3;
  - ✓ low-temperature CO oxidation over gold nanoparticles;
  - ✓ hydrodesulfurization of gasoline over bimetallic sulfide catalysts.
- SUMMARY

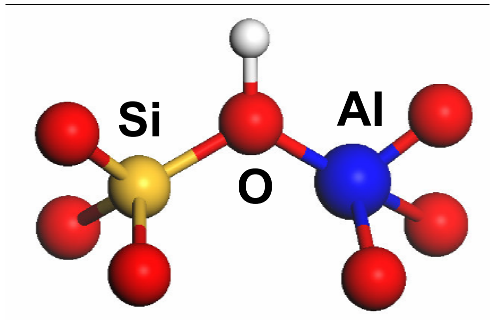
NANOTECHNOLOGY, NANOMATERIALS and CATALYSIS

Pt/Al_2O_3



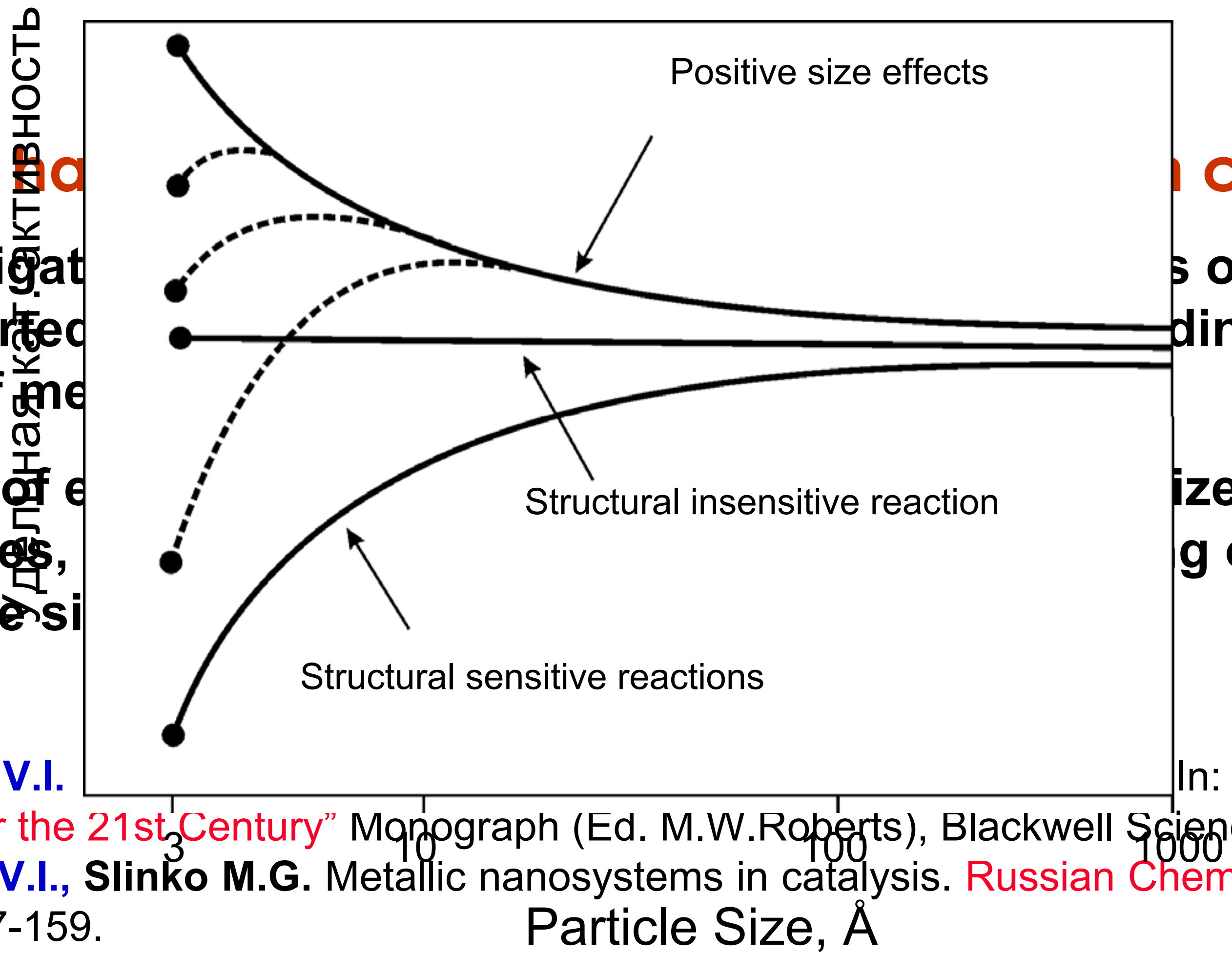
Zeolites





NANOTECHNOLOGY, NANOMATERIALS and CATALYSIS

Nanosized effects in catalysis by metals are known for a long time since the Boudart's discovery of structural sensitive and structural insensitive reactions



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1) Investigat … s of the supportec … ding on the mean size of me …

2) Study of e … ized metallic particles, … g of the mean particle si …

1. **Bukhtiyarov V.I.** … In: Interfacial Science, "Chemistry for the 21st Century" Monograph (Ed. M.W.Roberts), Blackwell Science, 1997, 109-128.
2. **Bukhtiyarov V.I., Slinko M.G.** Metallic nanosystems in catalysis. Russian Chemical Reviews, 2001, v. 70, n.2, 147-159.

OUTLINE OF THE TALK

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- **SIZE EFFECTS IN CATALYSIS BY METALS (BIC experience):**
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  - ✓ **low-temperature CO oxidation over gold nanoparticles;**
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- **SUMMARY**

Methane Oxidation over Pt/Al_2O_3

Natural gas has a great perspectives for different applications (energy production, fuel for cars, etc)

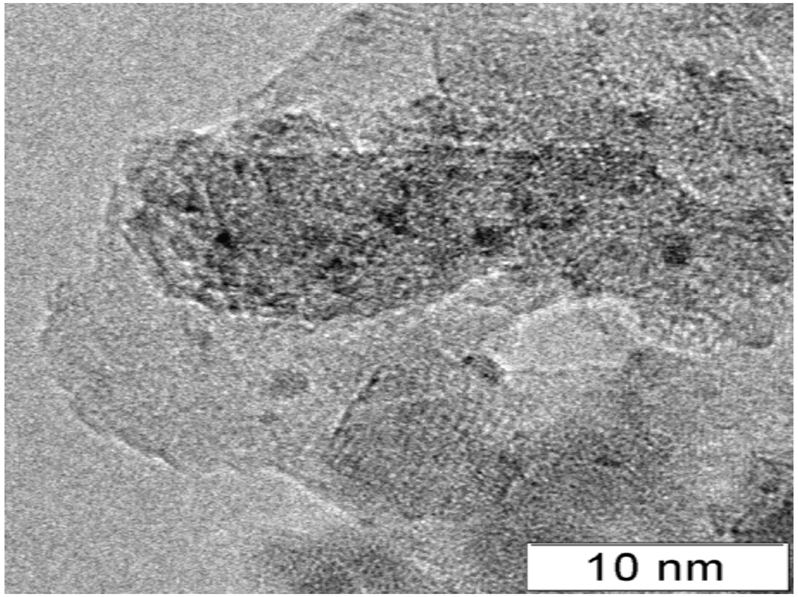
But we have to provide complete oxidation of methane at relatively low temperatures:

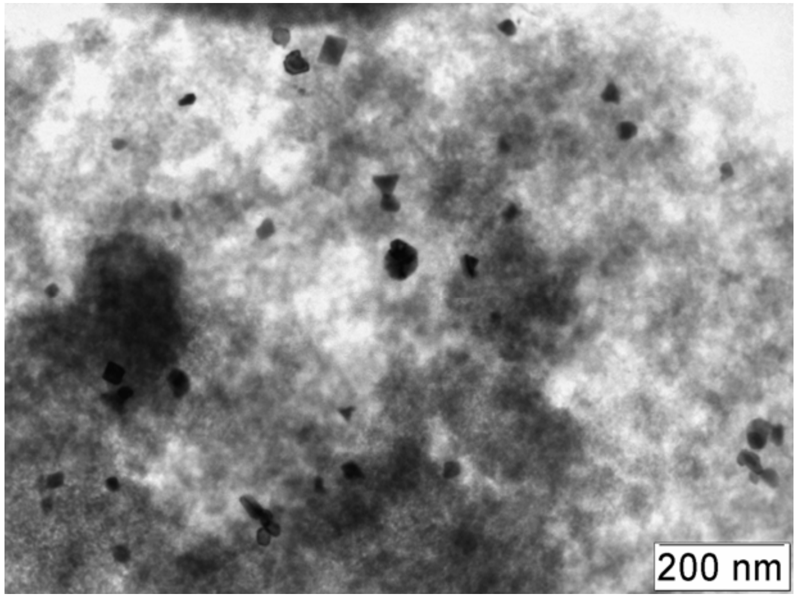
$$CH_4 + O_2 \longrightarrow CO_2 + H_2O + Q$$

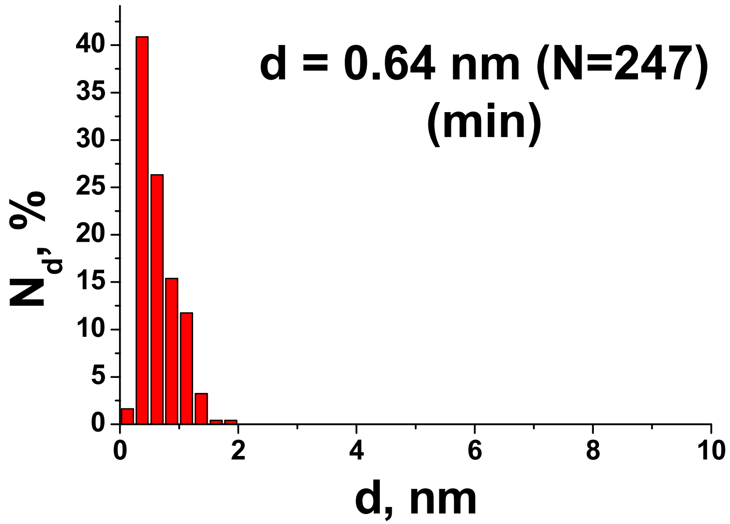
Pt/Al_2O_3 catalysts can be used for this purposes, but optimization of platinum loading should be provided

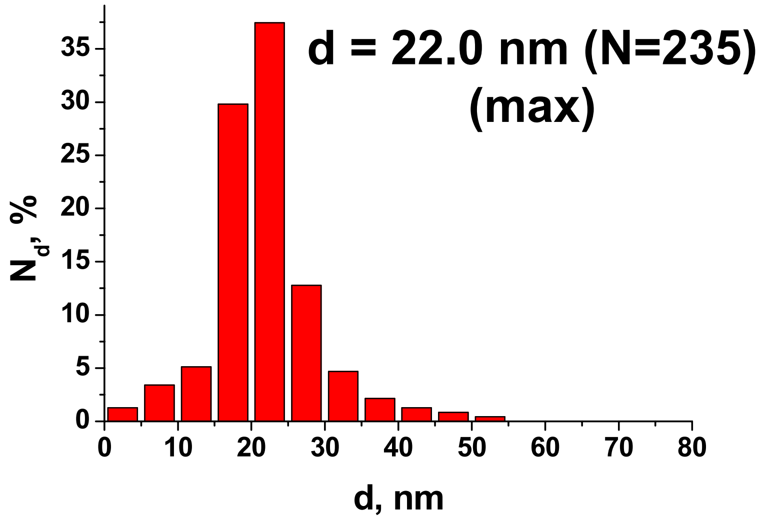
Methane Oxidation over Pt/Al_2O_3

Governing the sizes of platinum nanoparticles





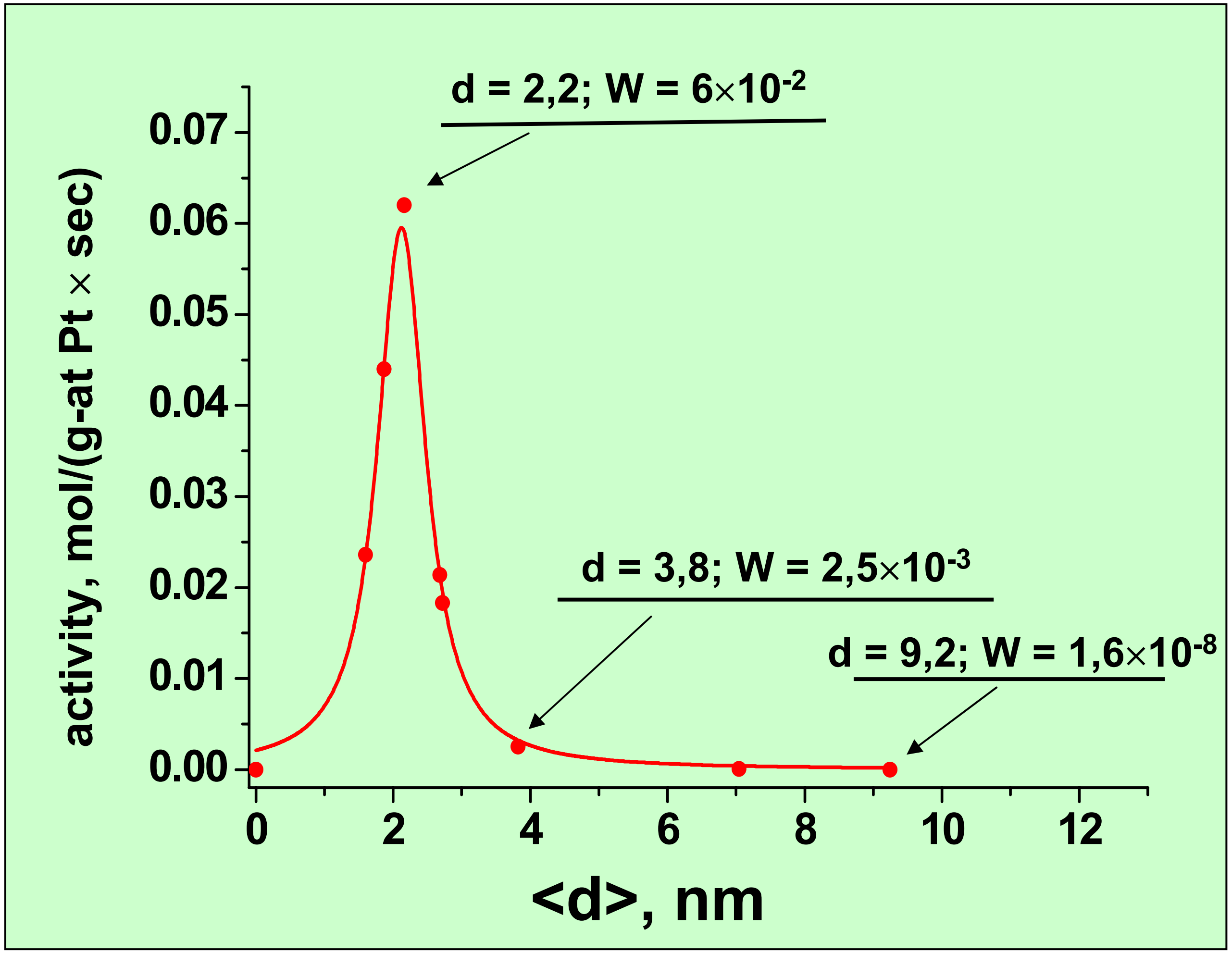




Methane Oxidation over Pt/Al_2O_3

Nanosized effects in methane oxidation over Pt/Al_2O_3

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O + Q$$



Low temperature CO oxidation: the main applications

- ✓ **Indoor air quality control**
- ✓ **Automobile exhaust gas treatment**
  (especially, during the period of engine "cold start")
- ✓ **CO removal from hydrogen for PEFC**
- ✓ **Catalytic regeneration of CO_2 in sealed CO_2 lasers**

LOW-TEMPERATURE CO OXIDATION OVER GOLD NANOPARTICLES

GOALS:

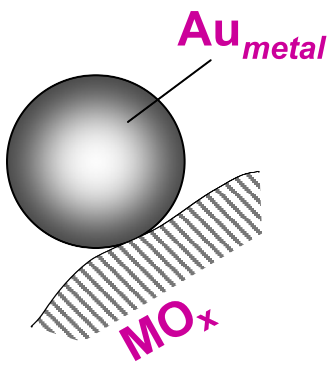
- *Preparation of nanosized gold particles на γ- и θ- Al_2O_3*
- *Study of activity of Au/Al_2O_3 catalysts in CO oxidation*
- *Improvement of the stability of gold nanoparticles on alumina*

Catalyst preparation techniques:

- ✓ **Impregnation (IMP); precursor – $HAuCl_4$**
- ✓ **Deposition-precipitation (DP); $HAuCl_4$:**

$$[AuCl_4]^- \xrightarrow[+\ MO_x]{+\ NaOH} Au(OH)_3 \cdot [AuCl_{4-n}(OH)_n]^- / MO_x \xrightarrow[O_2]{\Delta}$$

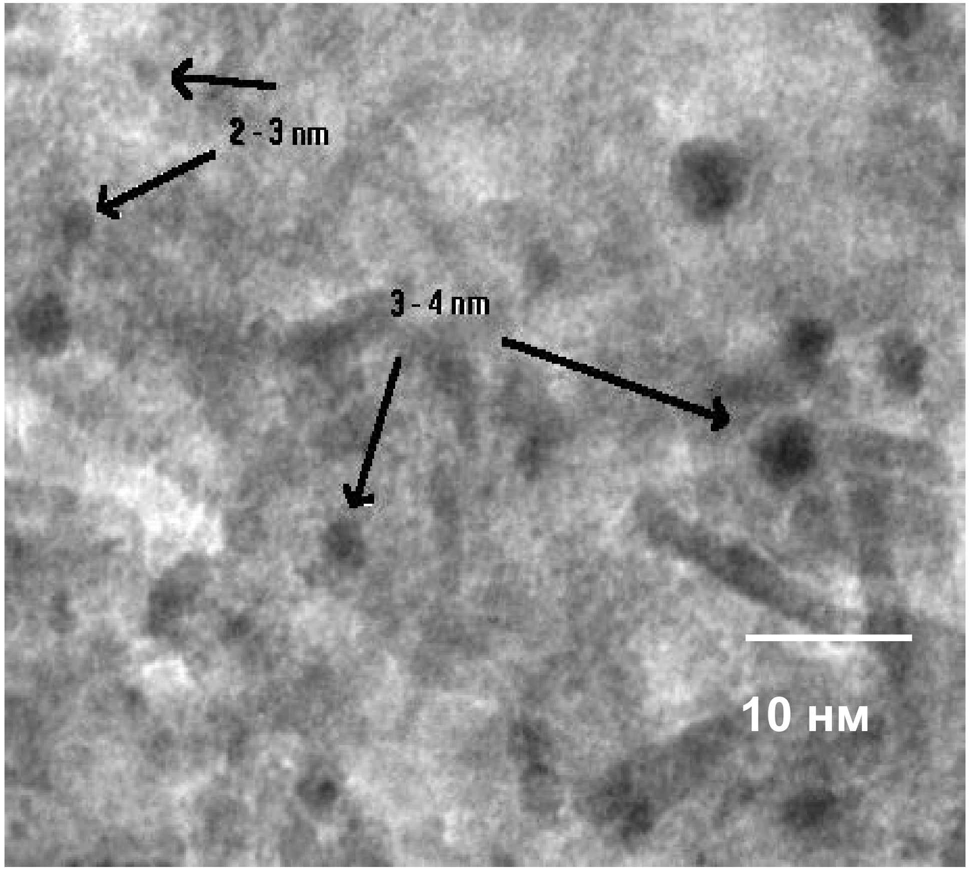
MO_x = TiO_2, Fe_2O_3, Al_2O_3 etc.



- ✓ **Chemical liquid phase grafting (CLPG); $Me_2Au(acac)$**
- ✓ **Chemical vapor infiltration (CVI); $Me_2Au(acac)$**

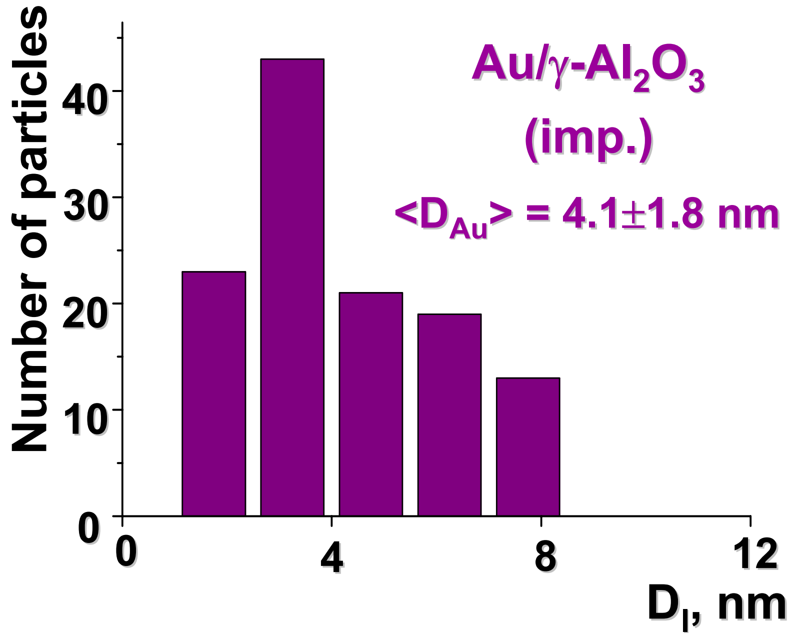
LOW-TEMPERATURE CO OXIDATION OVER GOLD NANOPARTICLES

TEM images and size distribution of gold particles in Au/Al_2O_3 catalyst prepared by impregnation technique



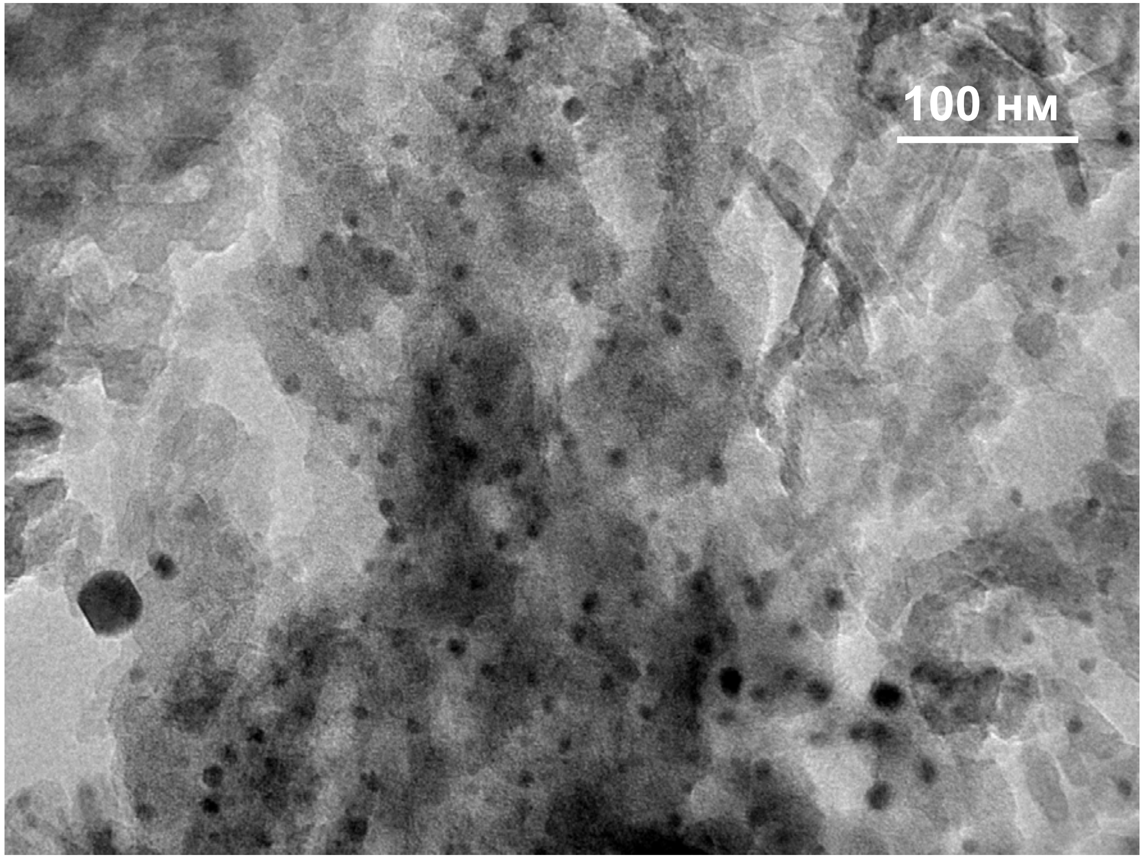
Key steps of catalyst preparation:

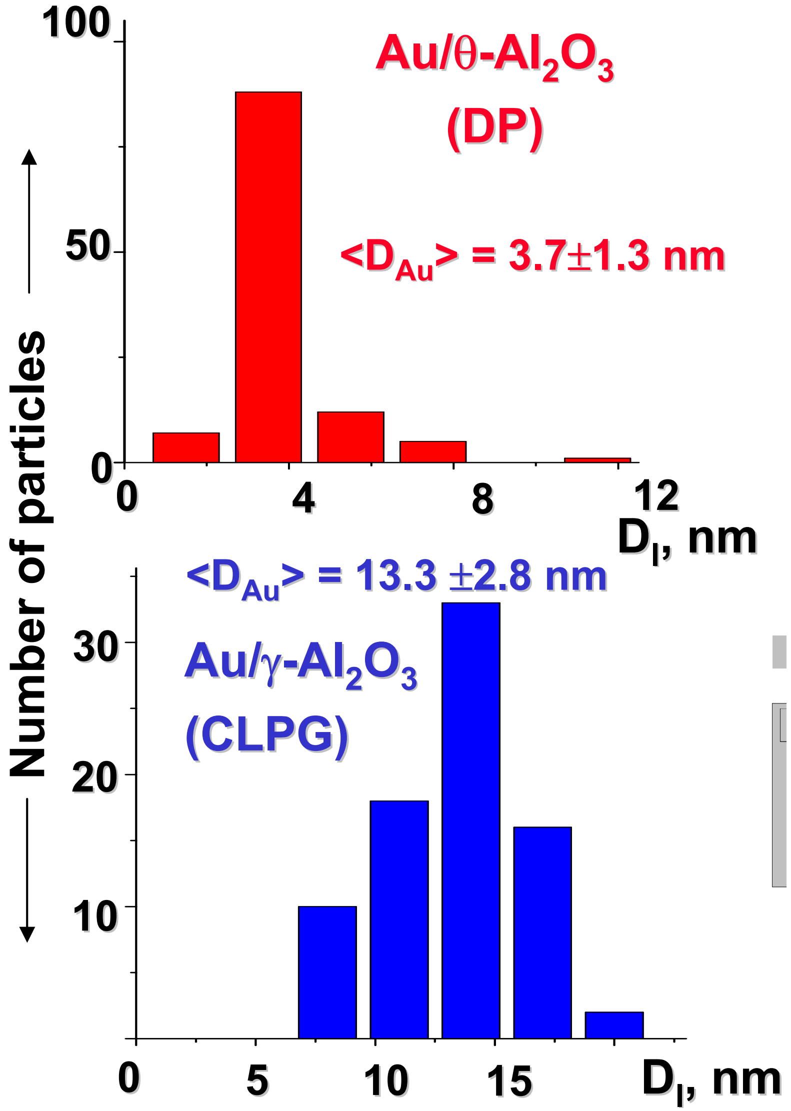
- ✓ Incipient wetness impregnation of γ-Al_2O_3 with $HAuCl_4$ solution
- ✓ Reduction by H_2 at 400°C



LOW-TEMPERATURE CO OXIDATION OVER GOLD NANOPARTICLES

The mean sizes of Au particles in Au/Al_2O_3 catalysts prepared with DP and CLPG: XRD and TEM data





Activity in CO oxidation (313 K) of Au/Al_2O_3 catalysts prepared with various methods

<table>
<tr><th colspan="2">Preparation method</th><th>$<D_{au}>$, nm</th><th>Rate, mol $CO_2 \times$ $(g\ Au)^{-1} \cdot s^{-1}$</th><th>TON, $s^{-1} \times 10^4$</th></tr>
<tr><td colspan="2">DP</td><td>3.7</td><td>240</td><td>21</td></tr>
<tr><td colspan="2">CLPG</td><td>13.3</td><td><1</td><td>–</td></tr>
<tr><td rowspan="2">CVD</td><td>(T_d=600°C)</td><td>3.8</td><td>95</td><td>6.7</td></tr>
<tr><td>(T_d=20°C)</td><td>25-35</td><td><1</td><td>–</td></tr>
<tr><td rowspan="2">Impregnation</td><td>H_2 reduction</td><td rowspan="2">4.1</td><td><1</td><td>–</td></tr>
<tr><td>after treatment with $((CH_3)_4N)OH$</td><td>14</td><td>1.3</td></tr>
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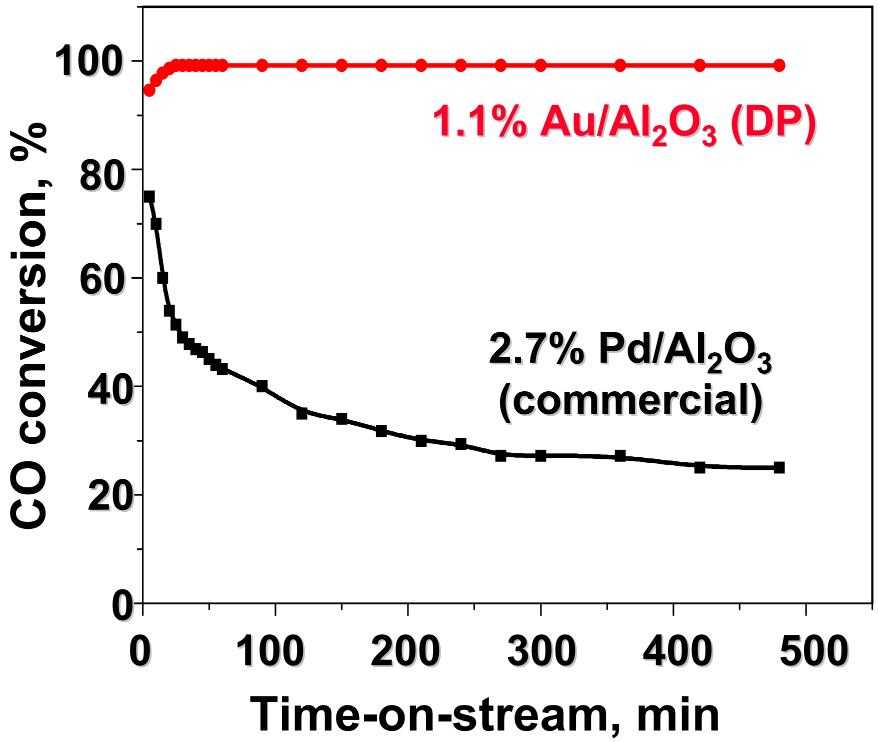
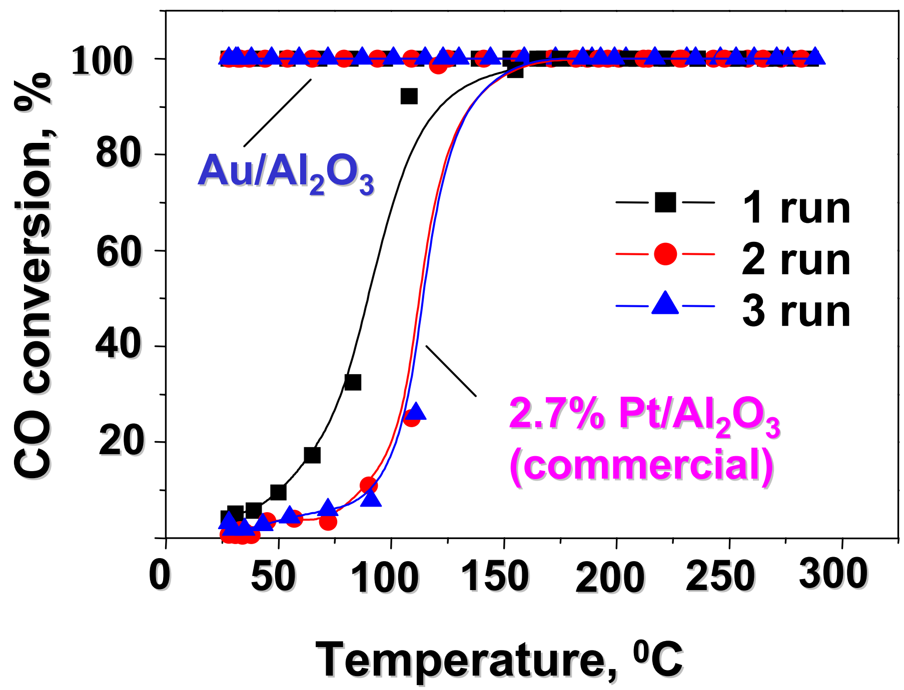
LOW-TEMPERATURE CO OXIDATION OVER GOLD NANOPARTICLES

Comparison between Au и Pd catalysts for CO oxidation in ambient conditions



Flow reactor
T = 293 K; 0.05%CO, 2% of H_2O, air for balance

Comparison between Au и Pt catalysts for abatement of exhaust gases from car engine

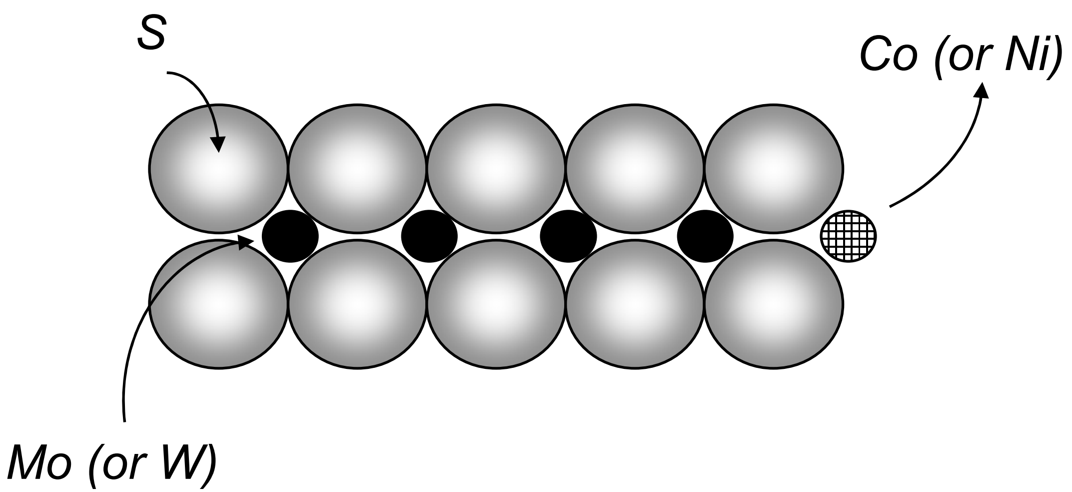


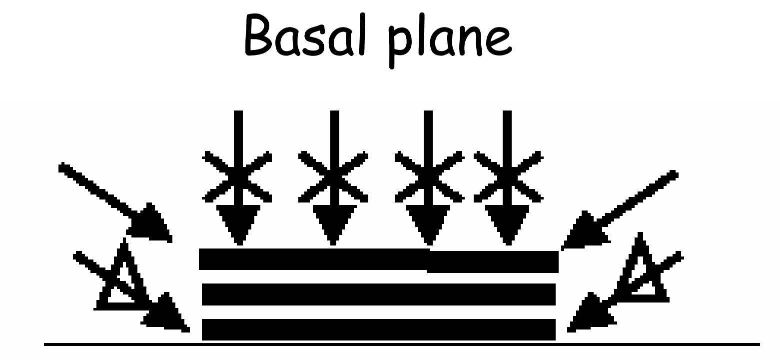
Flow reactor;
0.1%CO + 14%O_2 + 10% of H_2O (N_2 for balance);
Heating rate of 10 K/min; SV = 50 l/h

Diesel oil should contain less than < 50 ppm of sulfur-containing compounds

Active Catalysts for Hydrodesulfurization:

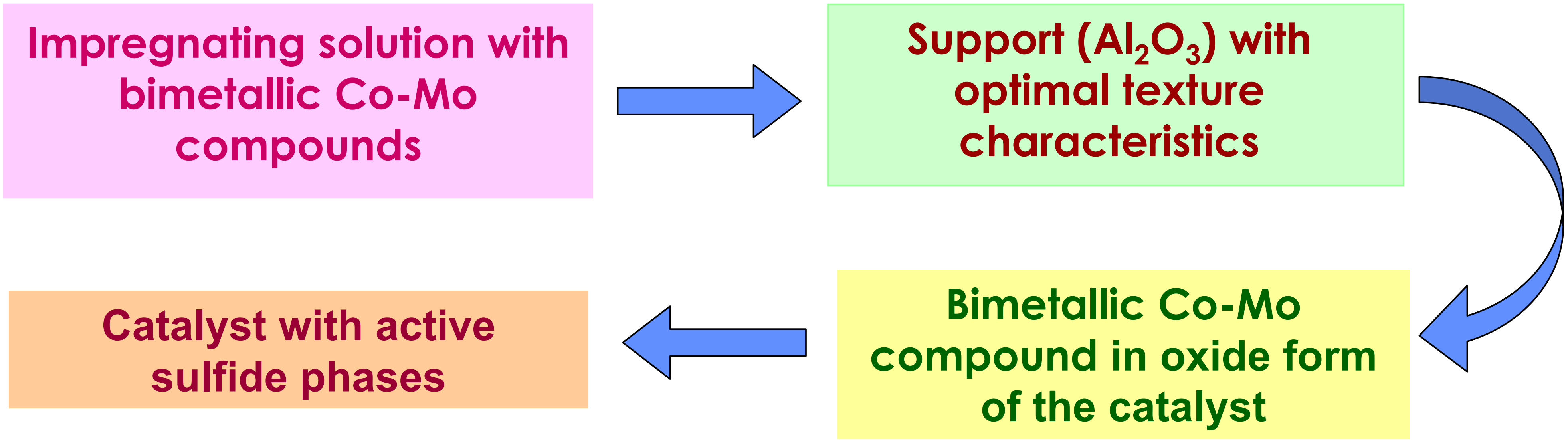
- ✓ High dispersion of Mo sulfide phase over the support surface;
- ✓ Formation of the mixed CoMoS phase with layered structure;
- ✓ Absence of oxygen atoms directly bonded with Mo atoms.





HYDRODESULFURIZATION OVER Co-Mo SULFIDE CATALYSTS

The steps of the guided formation (molecular design) of the nanocomposite, completely sulfided bimetallic active phase (BIC apprach)



HYDRODESULFURIZATION OVER Co-Mo SULFIDE CATALYSTS

Formation of bimetallic Co-Mo compounds in impregnating solution was fixed:

with NMR: intensity of Mo^{95} signal is reduced when Co^{2+} compounds is introduced in solution

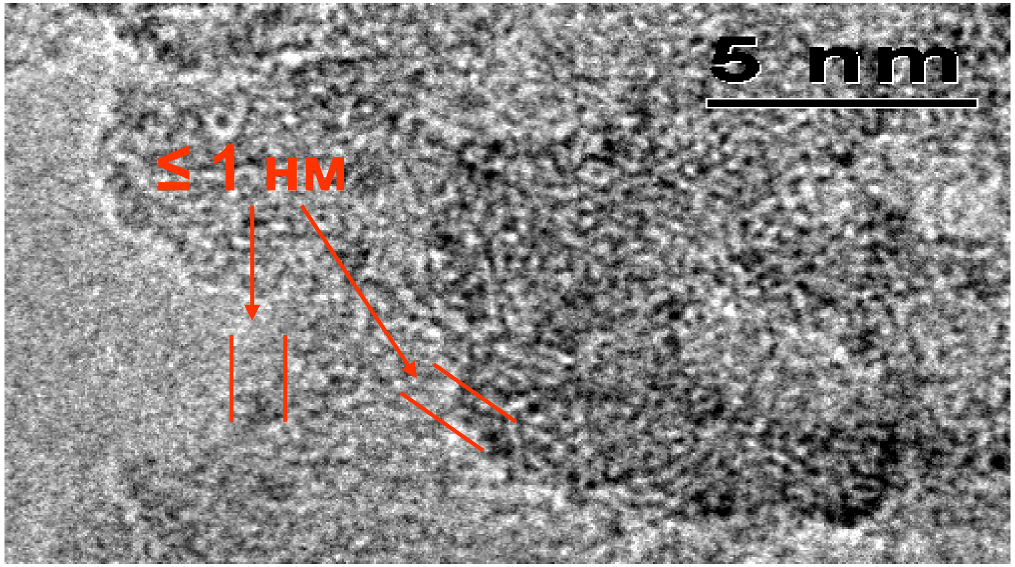
with EXAFS: appearance of Co-Mo distance in the spectra

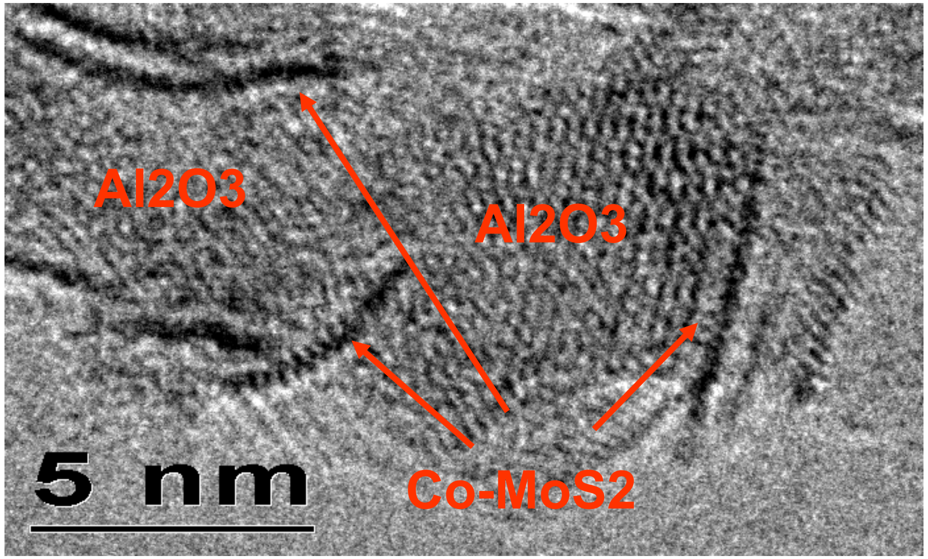
Formation of bimetallic Co-Mo compounds in the catalyst was fixed:

with EXAFS: Mo-Mo, Co-Mo distances were the same in solution and in the catalysts

with IR: 9 main signals were the same in solution and in oxide form of the catalyst

Bimetallic Co-Mo sulfide phases: Transmission electron microscopy (TEM)





А **Б**

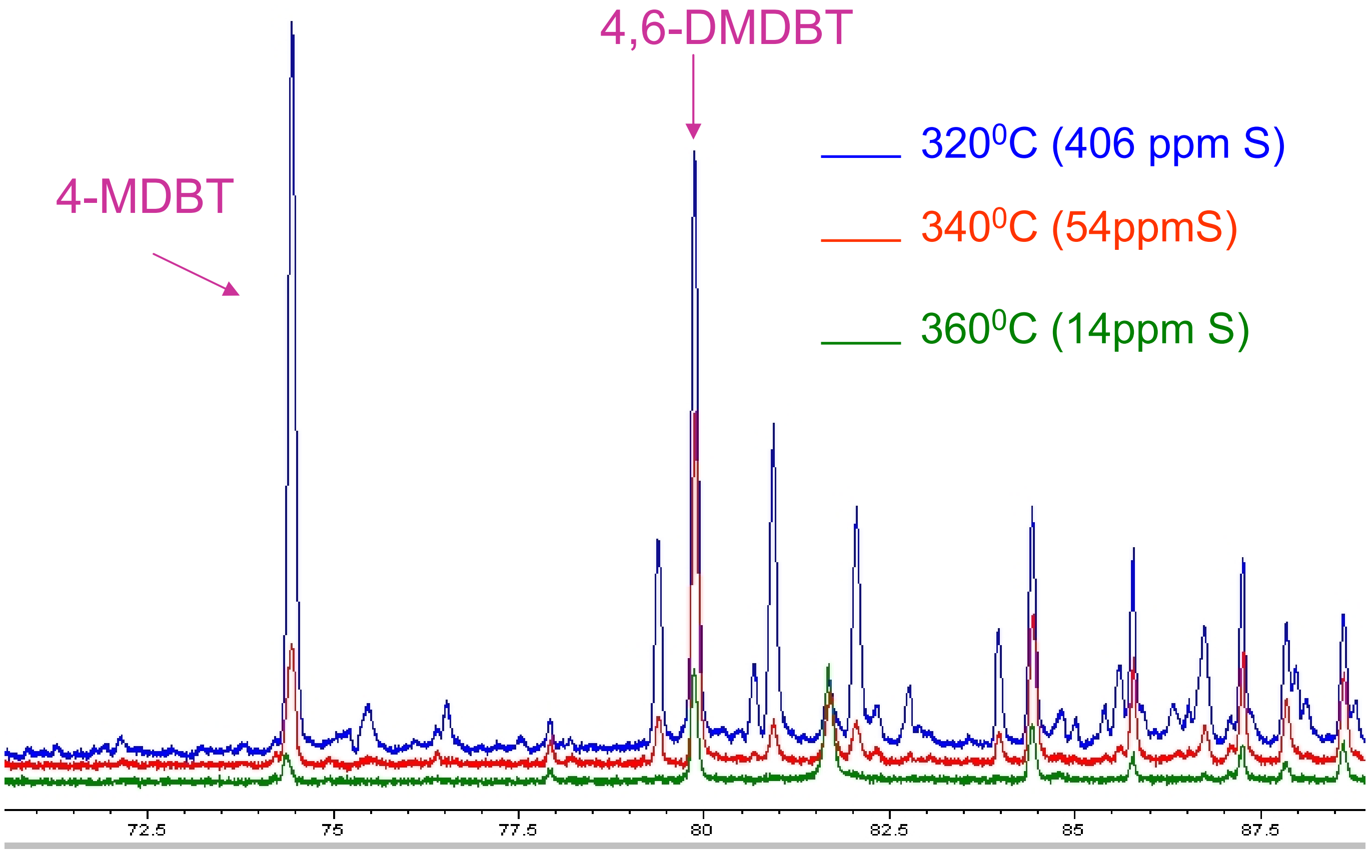
HRTEM images of $Co\text{-}Mo/Al_2O_3$ catalysts

А - *before reaction*. «single» Co-Mo –clusters (size less than 1 nm) on alumina surface.

Б - *after reaction*. Flat clusters of $Co\text{-}MoS_2$ on alumina surface. Atomic structure can be seen

HYDRODESULFURIZATION OVER Co-Mo SULFIDE CATALYSTS

The contents of the specific sulfur compounds in the product depending on the reaction temperature (P-3,5MPa, H_2/oil-300, LHSW – 2hour^{-1})



The catalyst remove the sterically hindered alkyl-dibenzothiophenes

HYDRODESULFURIZATION OVER Co-Mo SULFIDE CATALYSTS

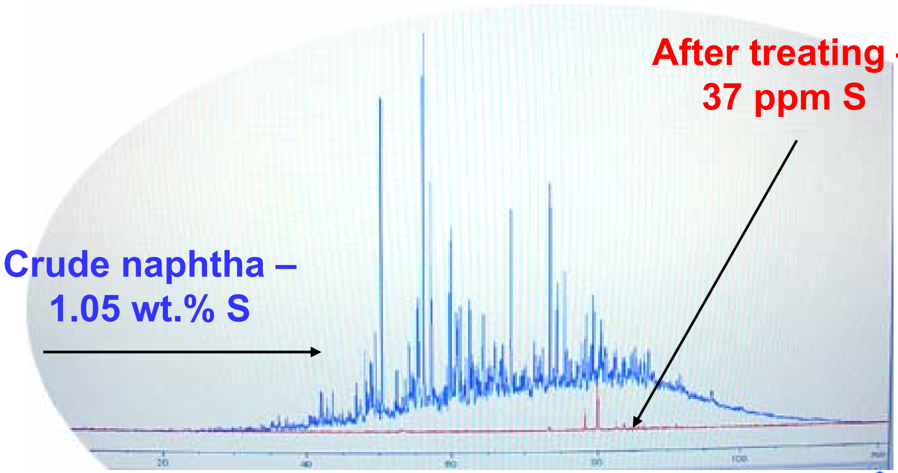
In the framework of National Innovative Project

«Development and manufacturing application of novel catalysts and catalytic technologies for production of motor fuels» (2003–2006),

BIC SB RAS has developed the catalysts for deep hydrodesulfurization of the diesel naphtha allowing production of the fuel with very low sulfur content (< 50 ppm)

- **Technology of the catalyst production will be applied in JSC «Industrial Catalysts», Ryazan.**
- **Pilot set of the catalysts (25 т) will be produced in first half of 2007**

Application of the catalysts on hydrodesulfurization plants allows production Euro-3 diesel fuel



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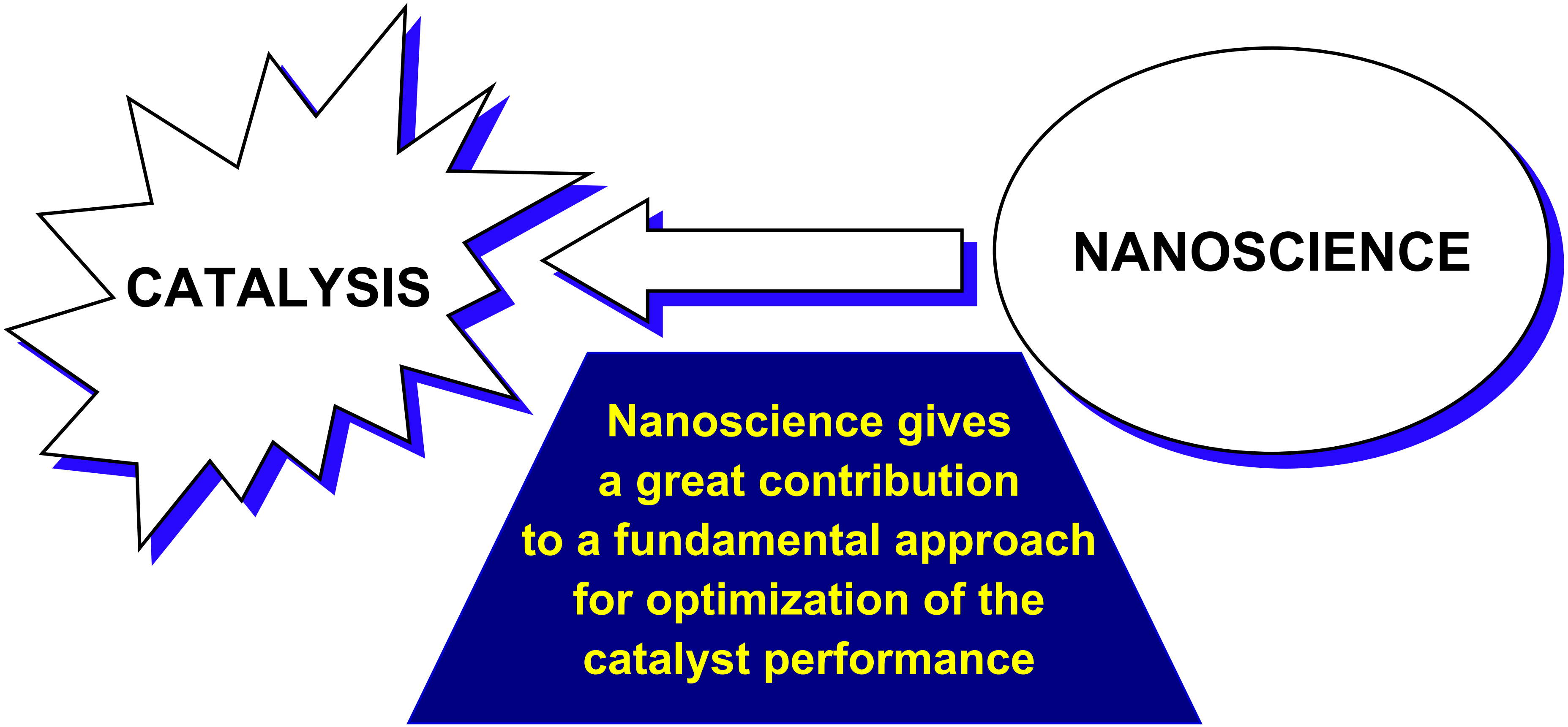
  - ✓ **hydrodesulfurization of gasoline over bimetallic sulfide catalysts.**
- **SUMMARY and ROADMAP for the FUTURE**

SUMMARY and ROADMAP for the FUTURE

Industrial catalysis has involved nanoparticles since beginning of the 20-th century

Addition of the “nano” prefix to many technical terms is not simple replacement of the unit of Ångstroms



SUMMARY and ROADMAP for the FUTURE

Definition of catalytic «nanoscience» as a separate scientific topic is connected with:

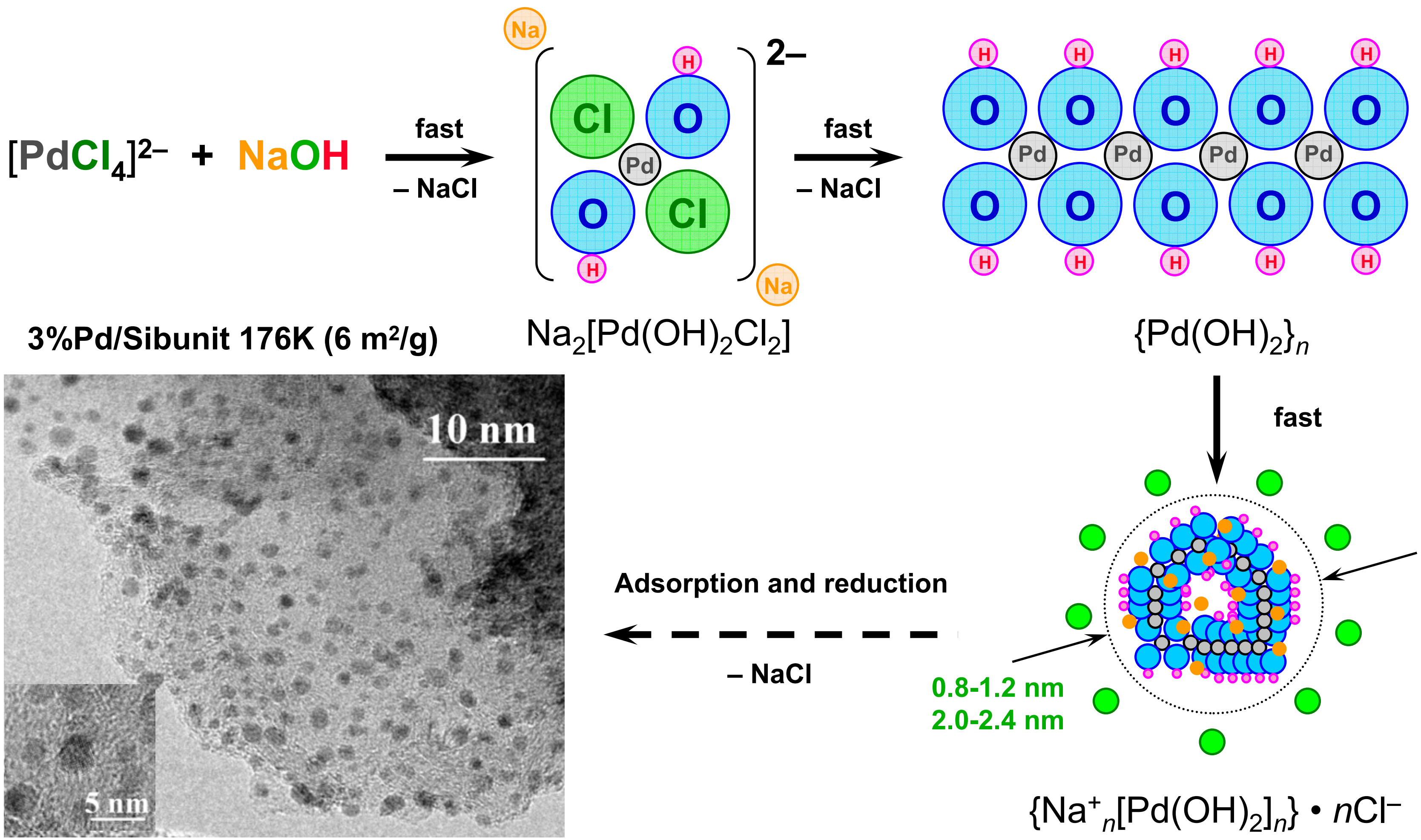
1) Development of the preparation procedure of stable nanosized metallic particles with homogeneous and variable size particle distribution (epitaxial growing, formation of polynuclear complexes or colloids in precursor solution, application of mesophase materials as supports of a catalyst);

2) Development of the methods for physical-chemical characterization of the nanosized metallic particles and determination of their size distribution (HR TEM, STM/AFM, EXAFS, XANES, XPS, UV-Vis);

3) Understanding the reasons of unique properties of the nanostructures and search of their practical applications.

SUMMARY and ROADMAP for the FUTURE

Adsorption of heteronuclear hydrocomplexes



SUMMARY and ROADMAP for the FUTURE

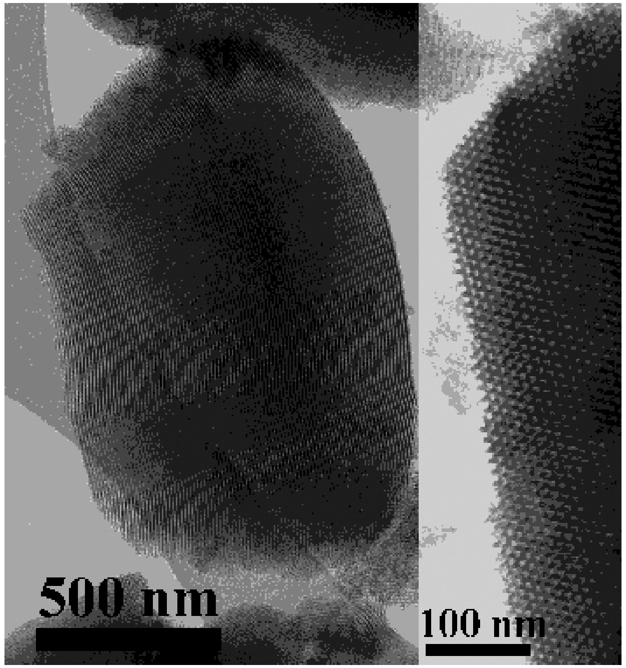
IPHE-GENIE (International Partnership for a Hydrogen Economy for GENeration of New Ionomer membranEs) interrelations

No.	Participant name	Short name	Country
1	Energy research Centre of the Netherlands	ECN	NL
3	FuMA-Tech GmbH	FUMATECH	D
4	CNRS Montpellier	CNRS	F
5	Dongyue Shenzhou New Materials Company	DSNM	PRC
6	Shanghai Jiao Tong University	SJTU	PRC
7	Boreskov Institute of Catalysis	BIC	RU

SUMMARY and ROADMAP for the FUTURE

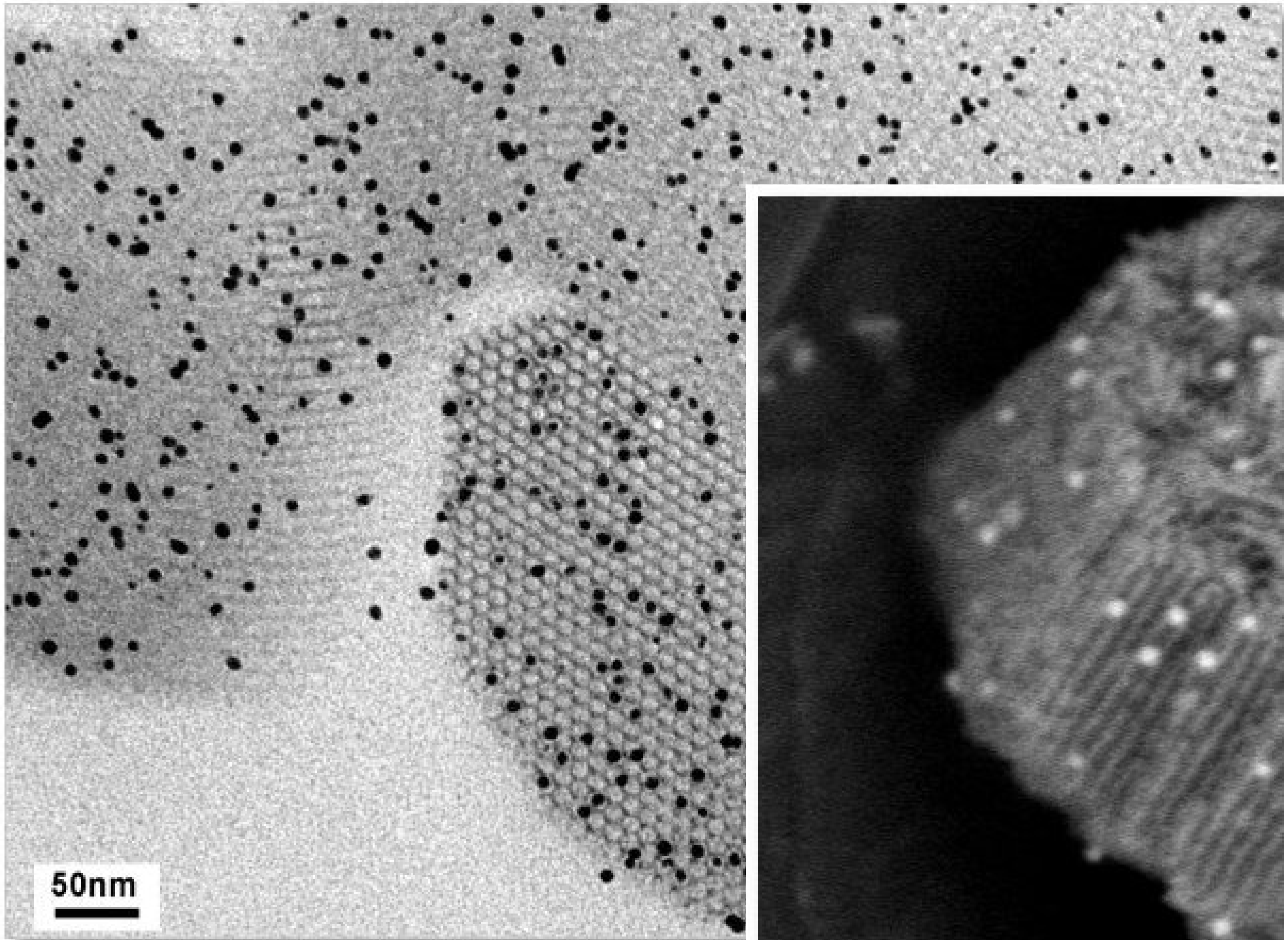
Application of mesophase mesoporous materials (MMM) as supports for the metallic supported catalysts

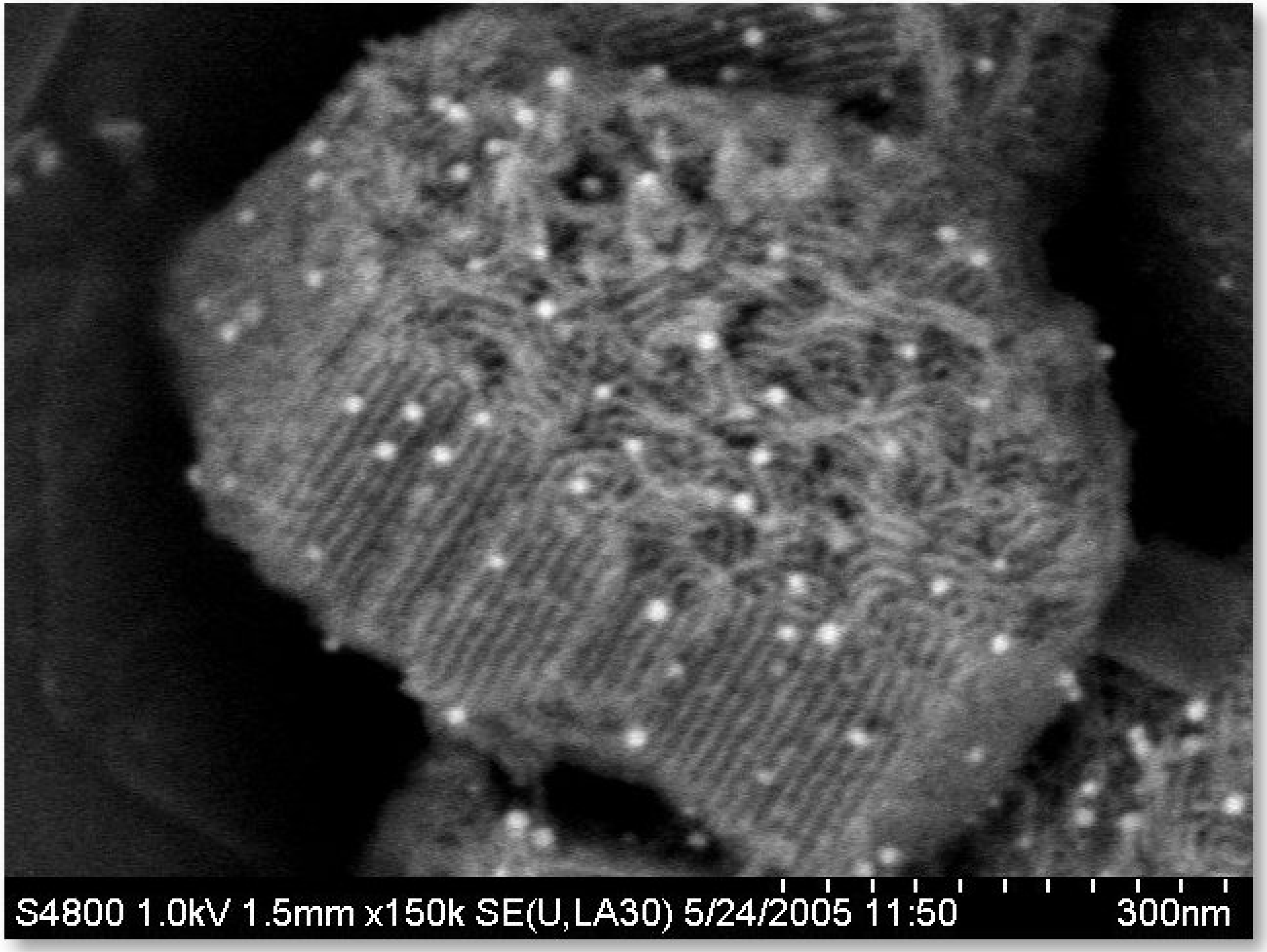
- ✓ Possibility to regulate (govern) by pore distribution for preparation of mesophase and nanoturbular materials (silicon dioxides, carbon)
- ✓ Limitation of the sizes of nanosized metallic particles by diameter of the support pores



We prepared the collaborative projects "Carbon-based challenging nanostructured materials for catalytic applications" between Fritz-Haber-Institute (Germany), Institute of Chemical Physics (China) and Boreskov Institute of Catalysis (Novosibirsk)

SUMMARY and ROADMAP for the FUTURE





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