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XAFS study of catalytic nanosystems promising for environmental catalysis

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Application area:

Industrial useful substratums:

Methane

Acid conversion of a synthesis gas

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

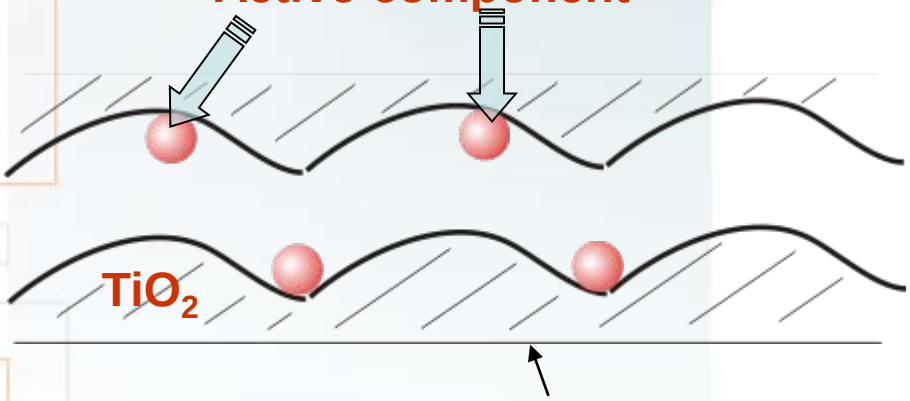
Membrane

d_{pores}= 2-1000 nm

TIPS RAS

Catalytic conversion of hydrocarbons into hydrogen containing gas

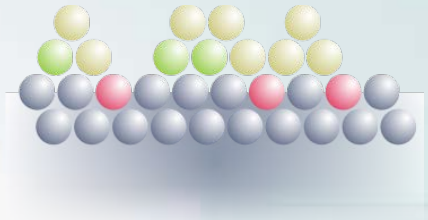
Basicle principle of formation



Tasks:

Objects to analized with complex methods:

- Original catalitics systems
- Calcined with different conditions systems



Application systems

$Pd\text{-}Co/TiO_2$

$Pd\text{-}Mn/TiO_2$

To understand principle of formation bi-metall active centres of supports and there structural features

Tasks of XAFS method:

With XAFS-spectroscopy we can:

- **Establish a symmetry of the immediate environment, charge state of atoms and local structure**

Using anouther methods such as X-ray Photoelectron Spectroscopy and XRF spectroscopy we can know:

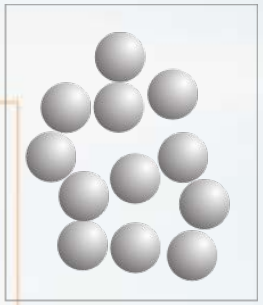
- Elements composition on a surface
- Size of particles
- Phase state

Systems with Pd-Co. Preparation:

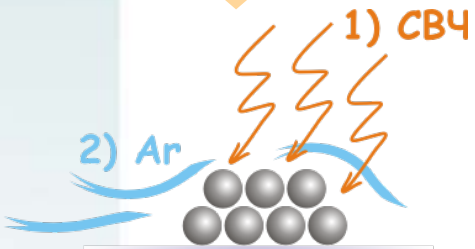
Parents compounds:
н-butoxide Ti
$PdCo(\mu\text{-}OOCMe)_4(NCMe)$

Coprecipitation in toluene with the addition of an alcohol-water mixture for hydrolysis

Next steps

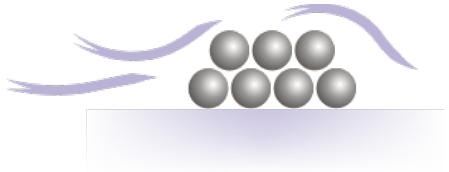


1) Drying with 25^0C (gel)



3) Microwave, then Ar

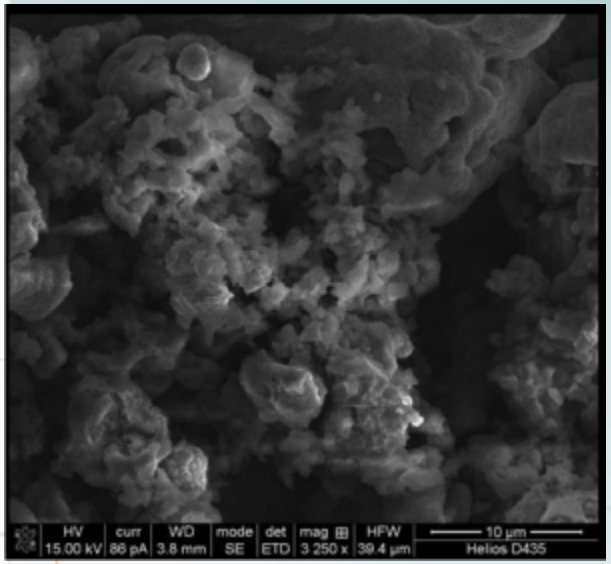
2 hours, 550^0C

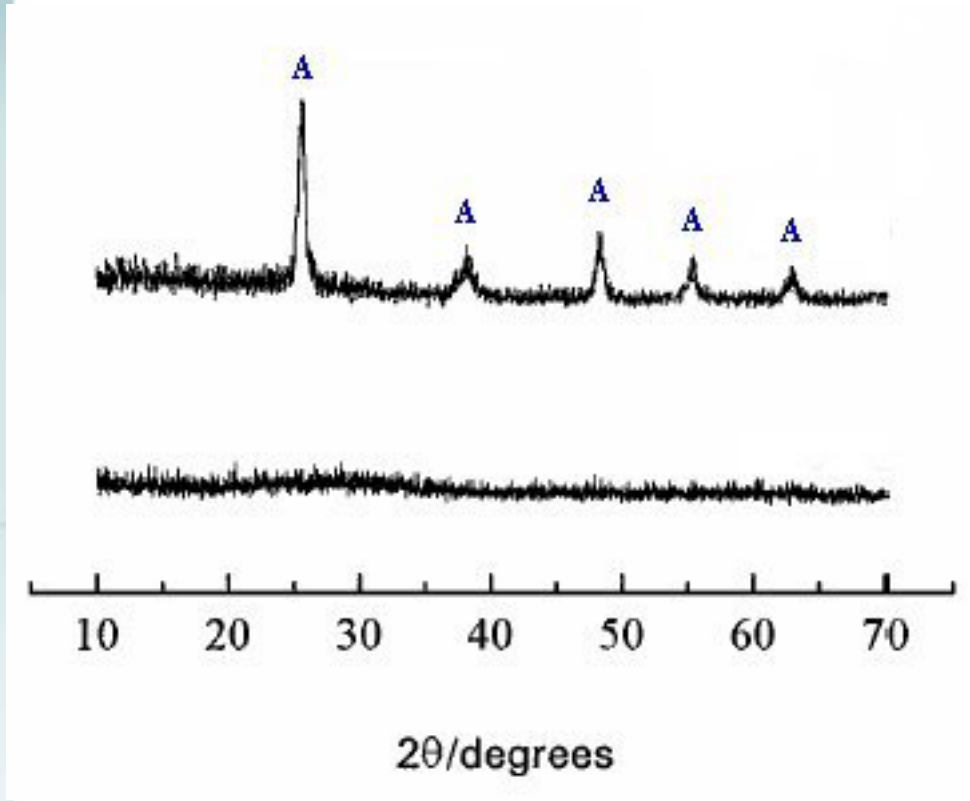


2) With Ar

5 hours, 550^0C

Study:





XRF spectroscopy

Only for TiO_2

Systems with Pd-Co: Pd-k edge

XANES (Pd-K) and FT of Pd for 1%Pd-2%Co/TiO_2 and comparison sample:

a) 1%Pd-2%Co - previous (gel, drying 25C);

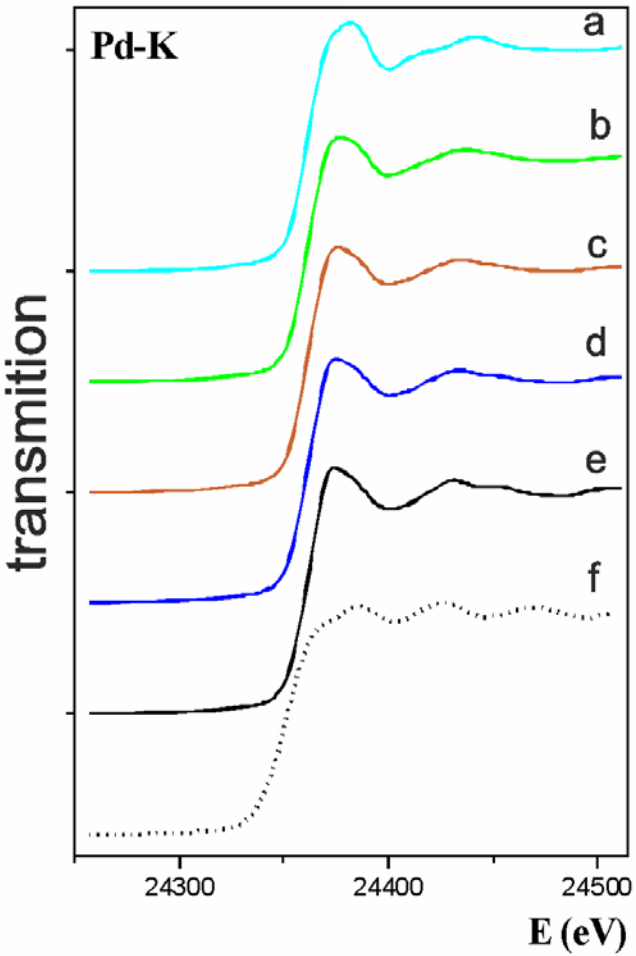
b) 1%Pd-2%Co/TiO_2 (550C, microwave, calcination);

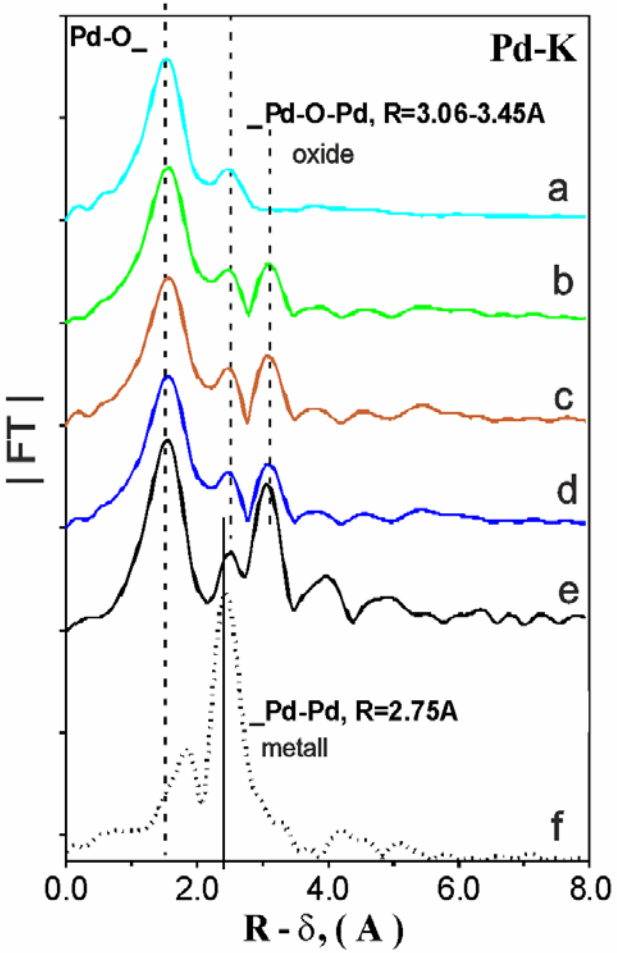
c) 1%Pd-2%Co/TiO_2 (550C, air);

d) 1%Pd-2%Co/TiO_2 (550C, Ar);

e) PdO – comparison oxide;

f) Pd – foil.





Systems with Pd-Co: Co-k edge

XANES (Pd-K) and FT of Co for 1%Pd-2%Co/TiO_2 and comparison sample:

a) 1%Pd-2%Co - previous (gel, drying 25C);

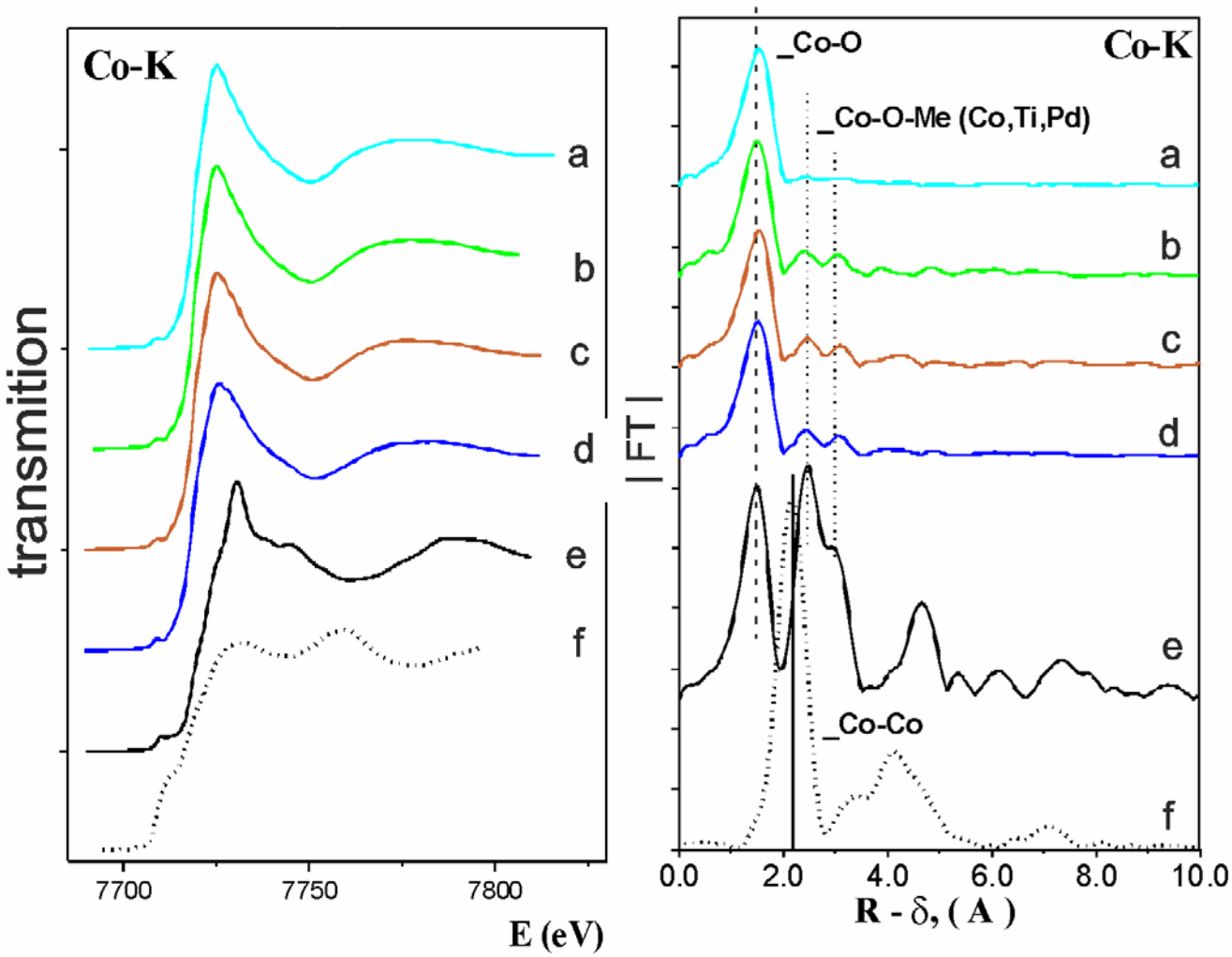
b) 1%Pd-2%Co/TiO_2 (550C, microwave, calcination);

c) 1%Pd-2%Co/TiO_2 (550C, air);

d) 1%Pd-2%Co/TiO_2 (550C, Ar);

e) Co_3O_4 – comparison oxide;

f) Co – foil.



System with Pd-Co:

model	Pd-O	Pd-Pd	Pd-Me
#1 Me=Pd	2.0 Å 3.6-3.8	3.04 Å 0.9-1.0	3.34-3.4 Å 4.8-5.1
#2 Me=Co	2.0 Å 3.6-3.8	3.04 Å 0.9-1.0	3.4-3.6 Å 4.8-5.1

The main parts of Pd stay in oxide phase. It's a result from comparing distances and coordination numbers with crystallographic data

model	Co-O	Co-Co	Co-O-Me	Co-O-Me
sample	1.96 Å 3.9-4.1	2.85 Å 0.2	3.32 Å 0.6	3.76 Å 0.3

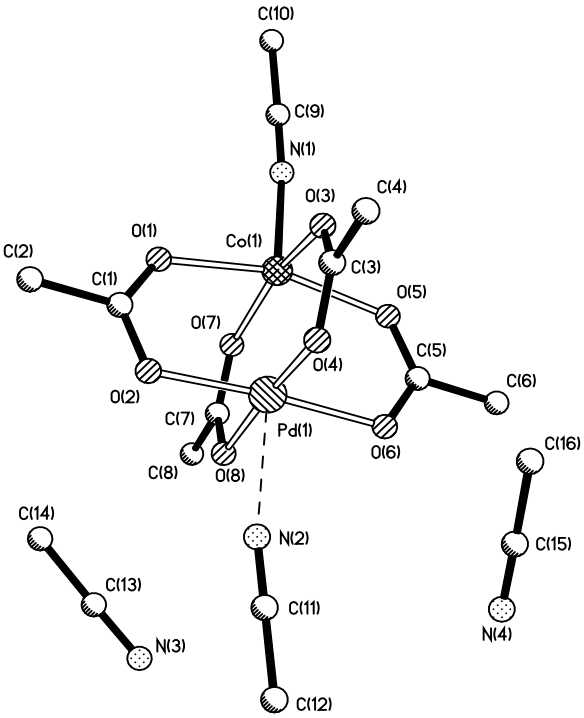
Presumably we saw formation of non-stoichiometric compounds with structural properties similar mixed oxides Co-Ti и Pd-Co

model	Co-Co	Co-Me	Co-Ti
$CoTiO_3$	2.99	3.39	3.74
$PdCoO_2$	2.83	3.38	-

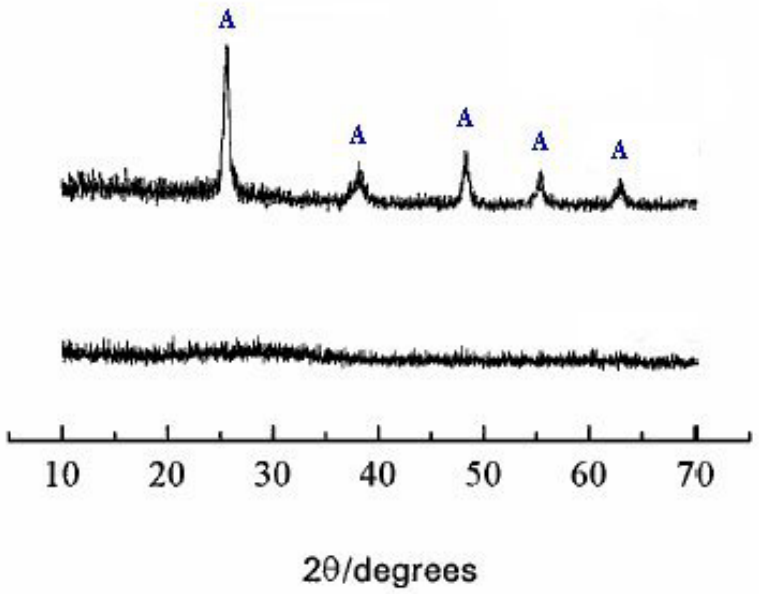
System with Pd-Mn. Preparation:

Sol-Gel method

- Precursor
- Gel formation
- Drying (Ar) and calcinization (500 ^{0}C)



$Pd(\mu\text{-}OOCMe)_4Co(OH_2)$



XRF spectroscopy
Only for TiO_2

System with Pd-Mn: Pd-k edge

XANES (Pd-K) and FT of Co for Pd-Mn/TiO_2 and comparison sample

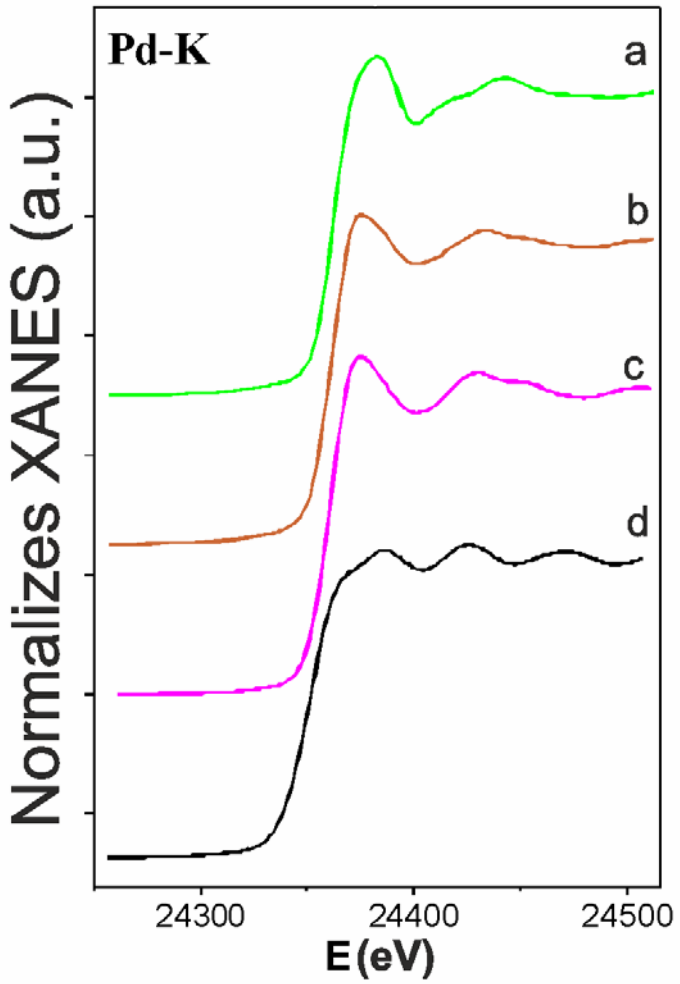
a) Pd-Mn/TiO_2 - gel

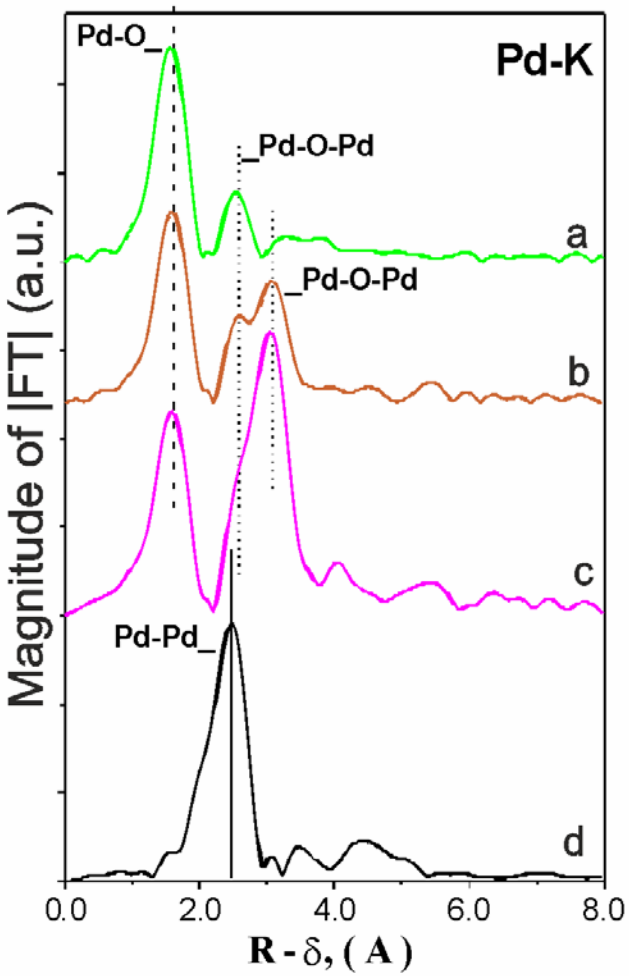
b) Pd-Mn/TiO_2 – oxide, T=500C

c) PdO comparison sample

d) Pd – foil

№	#1 – Pd-Mn/TiO_2 (gel)		#2 – Pd-Mn/TiO_2 (metall)		PdO		Pd^0 metall	
	R, Å	N	R, Å	N	R, Å	N	R, Å	N
Pd-O	1.98	4.1	2.00	3.8	2.01	4.0	---	---
Pd-Pd	2.99	2.0	3.03	2.5	3.02	4.1	2.76	12
Pd-Pd	3.50-3.55	~1.0	3.45	3.4	3.43	8.0	---	---





System with Pd-Mn: Mn-k edge

XANES (Pd-K) and FT of Co for Pd-Mn/TiO_2 and comparison samp

а) Pd-Mn/TiO_2 - gel
б) Pd-Mn/TiO_2 – oxide, T=500C
в) Mn0 (.*0.5)
г) MnO (.*0.5)
д) Mn_3O_4 (*0.5)
е) Mn_2O_3 (*0.5)
ж) MnO_2 (*0.5)

Pd-Mn/TiO_2 - gel

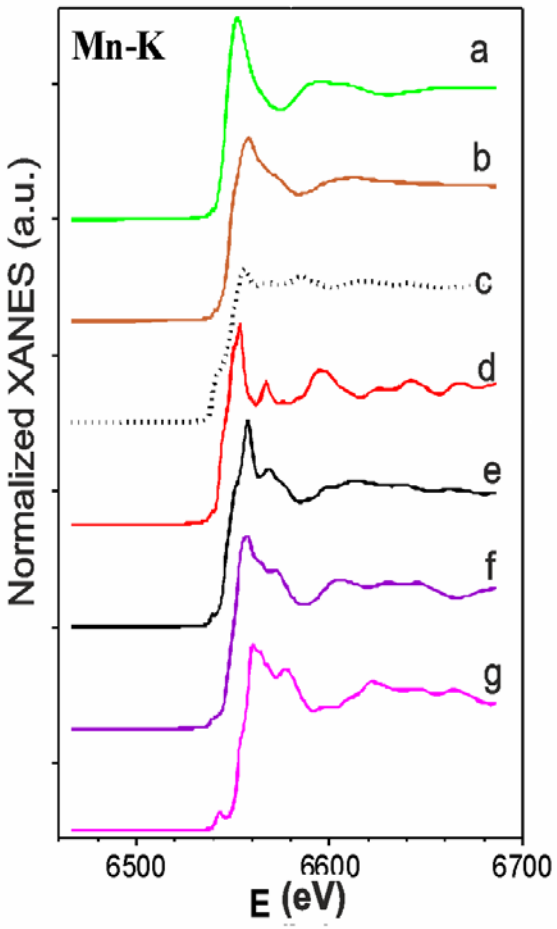
R_{Mn-O} =~2.11Å, N=~4.9.

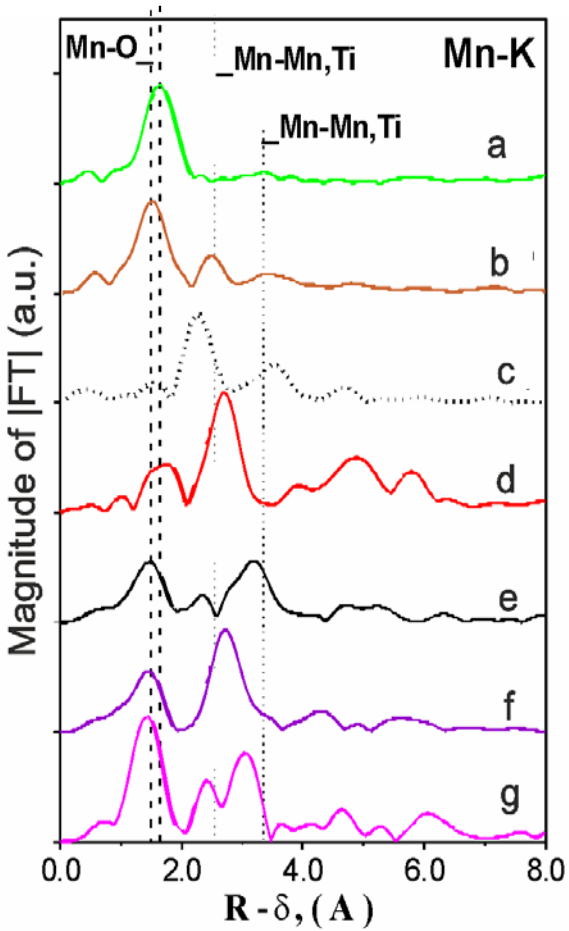
Pd-Mn/TiO_2 T=500C

R_{Mn-O} =~2.03 Å, N=~4.5;
R_{Mn-Me} (Mn, Ti) =~2.96-3.02Å, N=~2;
$R_{Mn-Me\ (Mn,\ Ti)}$ =~3.7-3.8Å, N=~1

Anatize

R_{Ti-O} =~1.94-1.98Å, N=6;
R_{Ti-Ti}=~3.0-3.04Å, N=4;
R_{Ti-Ti}=~3.74-3.78Å, N=4





Results:

For Pd-Co:

- We supposed that systems has strong interraction between Pd and Co in a precipitation stage. In this situation Co take place in strucrure of supporte to locate atoms of Pd. They formatited a mixed oxide that are not non-stoichiometric

For Pd-Mn:

-As a result we supposed that for gel state for Pd-Mn systems formed to a defect nanophase PdO, that consists of basic Pd-Mn comples and PdO

- We saw deffects of **MnO_x nanophase with stabilization of ions with local deffects**

Thanks for your attantion