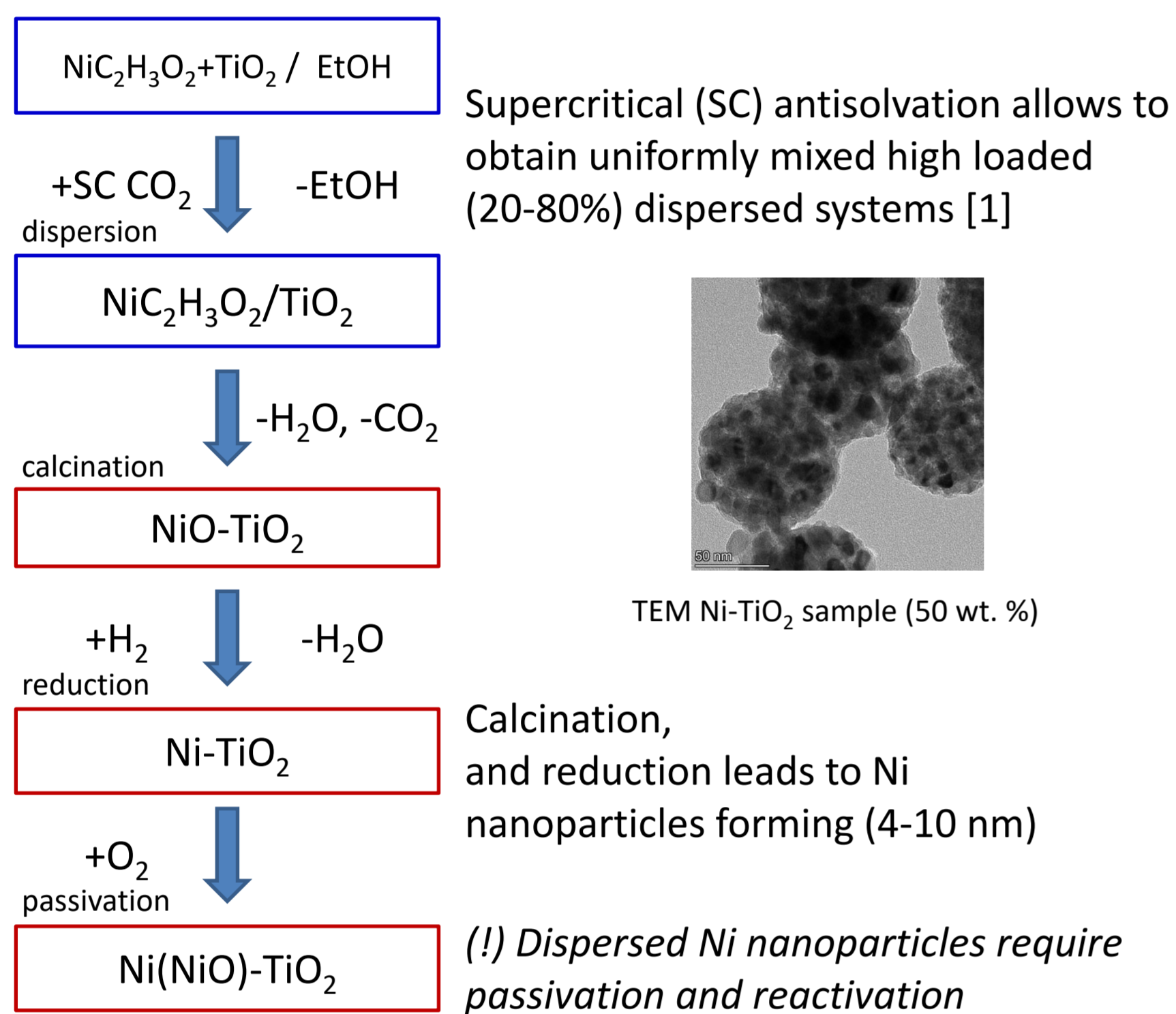


Electron spin resonance *in situ* study of Ni catalyst in catalytic transfer hydrogenation reaction conditions

S.S. Yakushkin, I.T. Kandarakova, N.S. Nesterov, A.A. Philippov, O.N. Martyanov

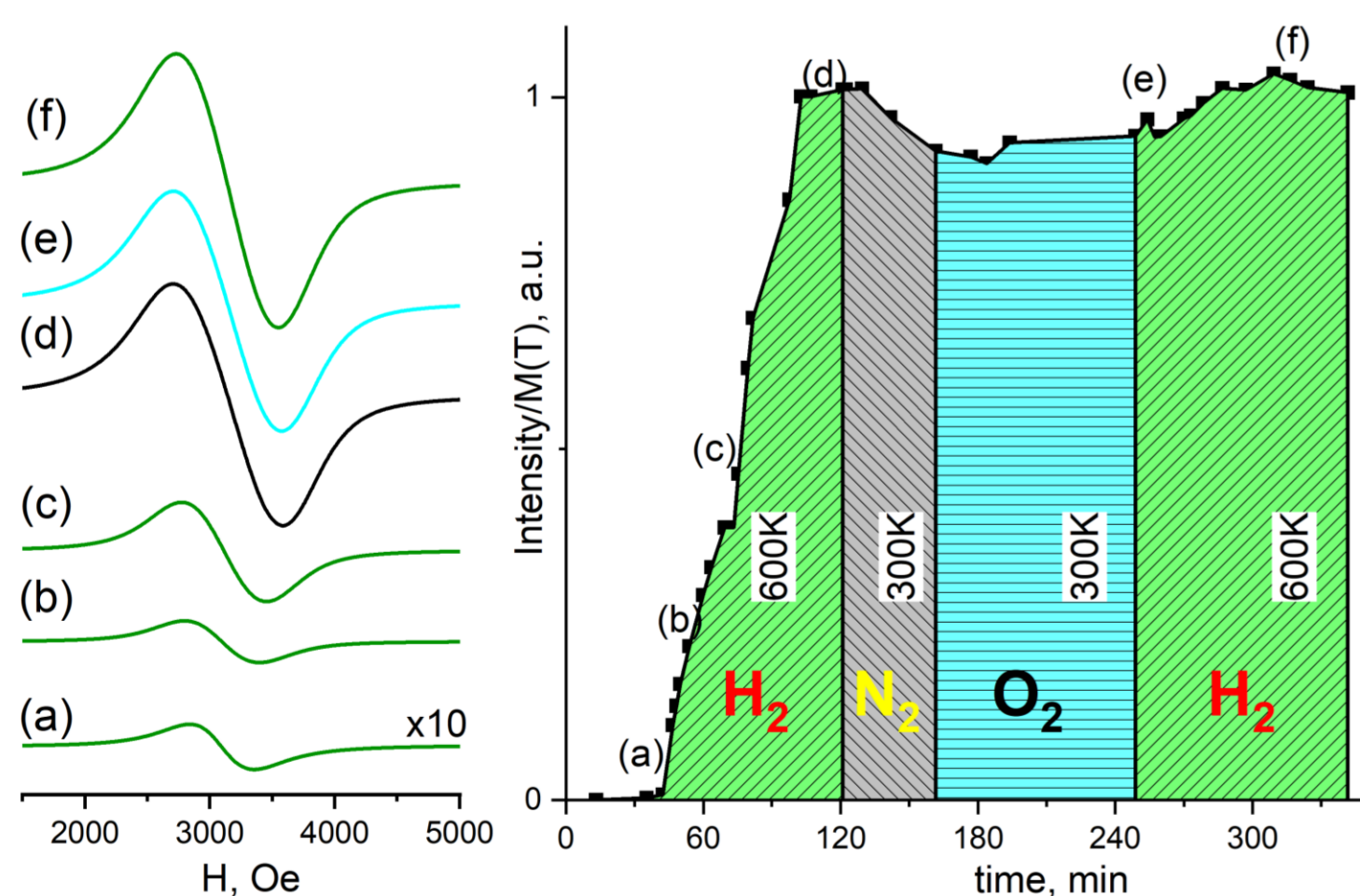
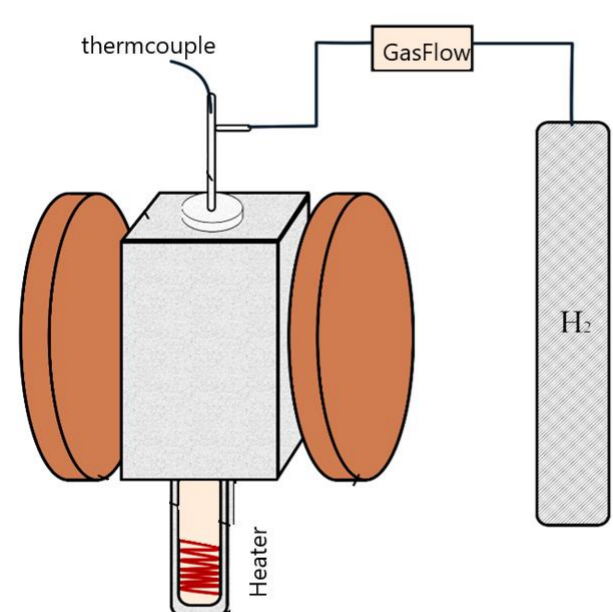
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia. stas-yk@catalysis.ru

Ni-TiO₂ catalysts



in situ FMR reduction by H₂

Processes of the Ni nanoparticles formation can be studied by ferromagnetic resonance (FMR) *in situ*



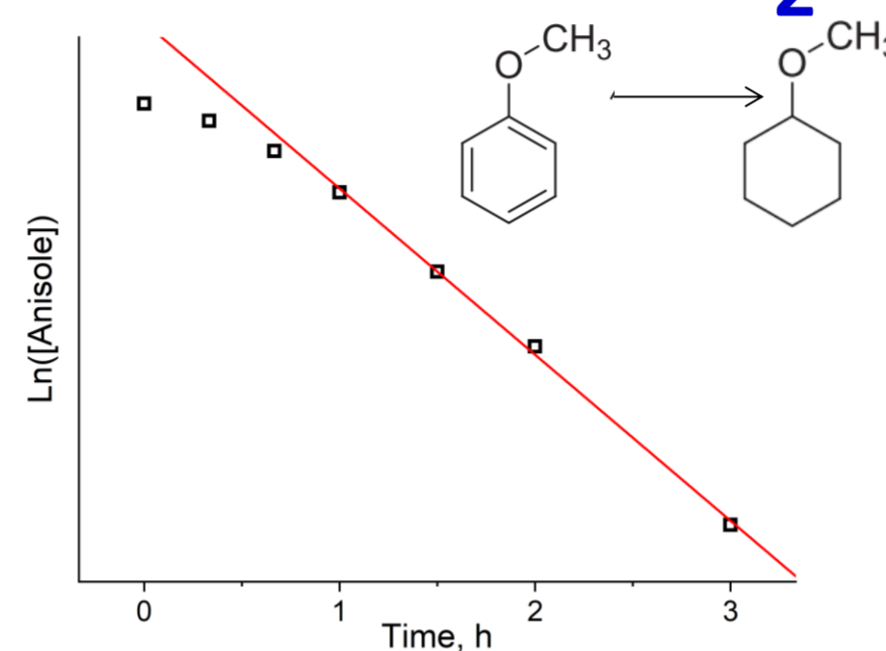
In situ FMR reducing/passivation/reactivation of Ni-TiO₂ catalyst

Reduction of Ni-TiO₂ sample occurs at 600 K ((a)-(b)-(c))

Passivation in ~1% O₂ flow at 300 K leads to formation of NiO layer on the nanoparticles surface ((d)-(e))

Repeated reduction leads to the oxide layer removal ((e)-(f))

Ni-TiO₂ catalyst in the reaction

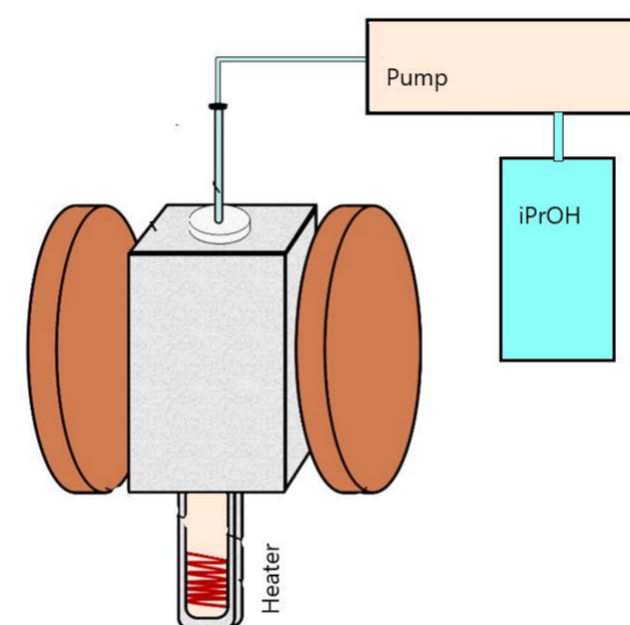


Ni-TiO₂ catalyst shows activity in the catalytic transfer hydrogenation reaction in supercritical i-PrOH media

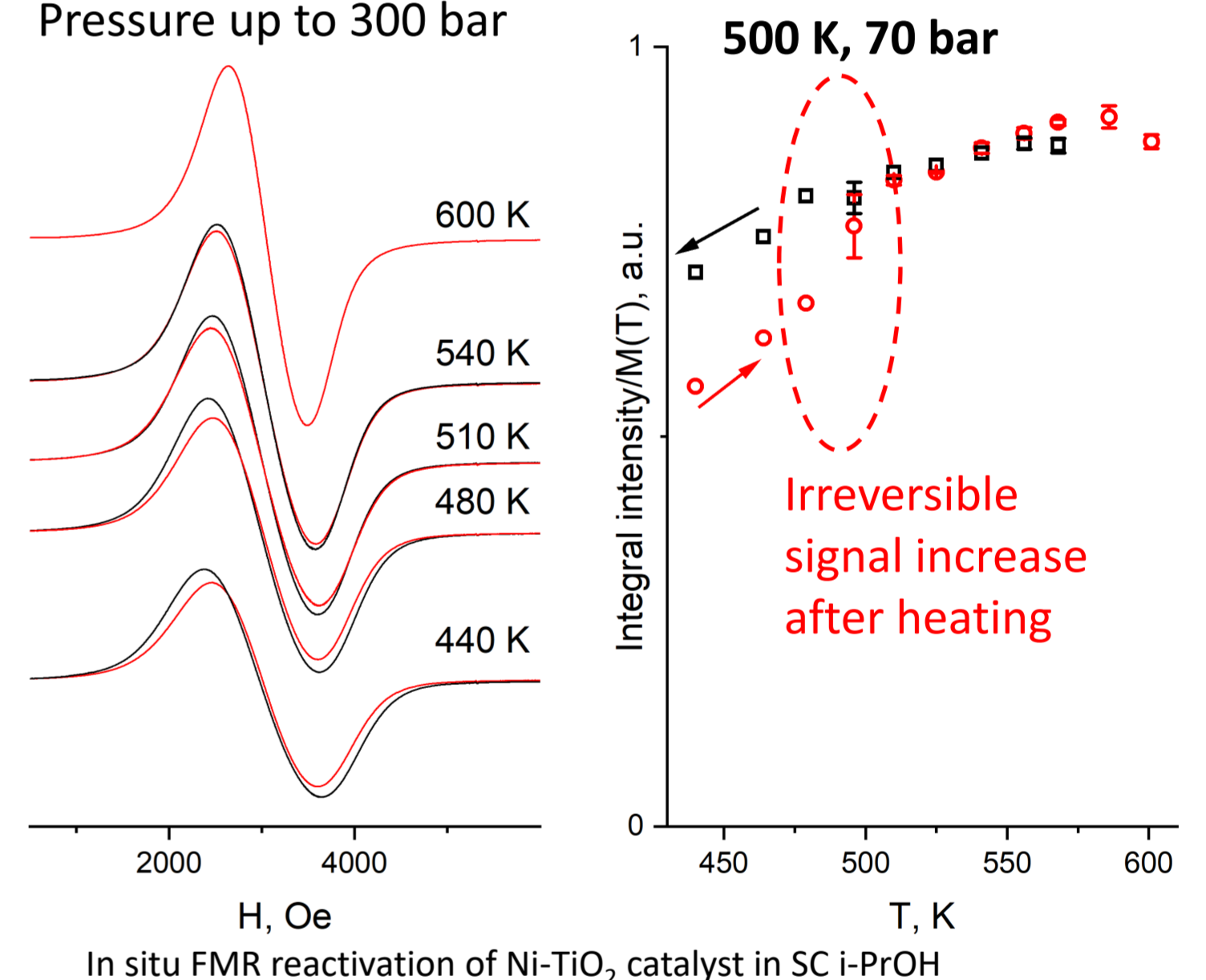
It was shown, the catalytic activity increases with time as if the reduction of the catalyst happens [2]

in situ FMR, reactivation in SC i-PrOH

FMR *in situ* experiment on magnetic nanoparticles in the supercritical media

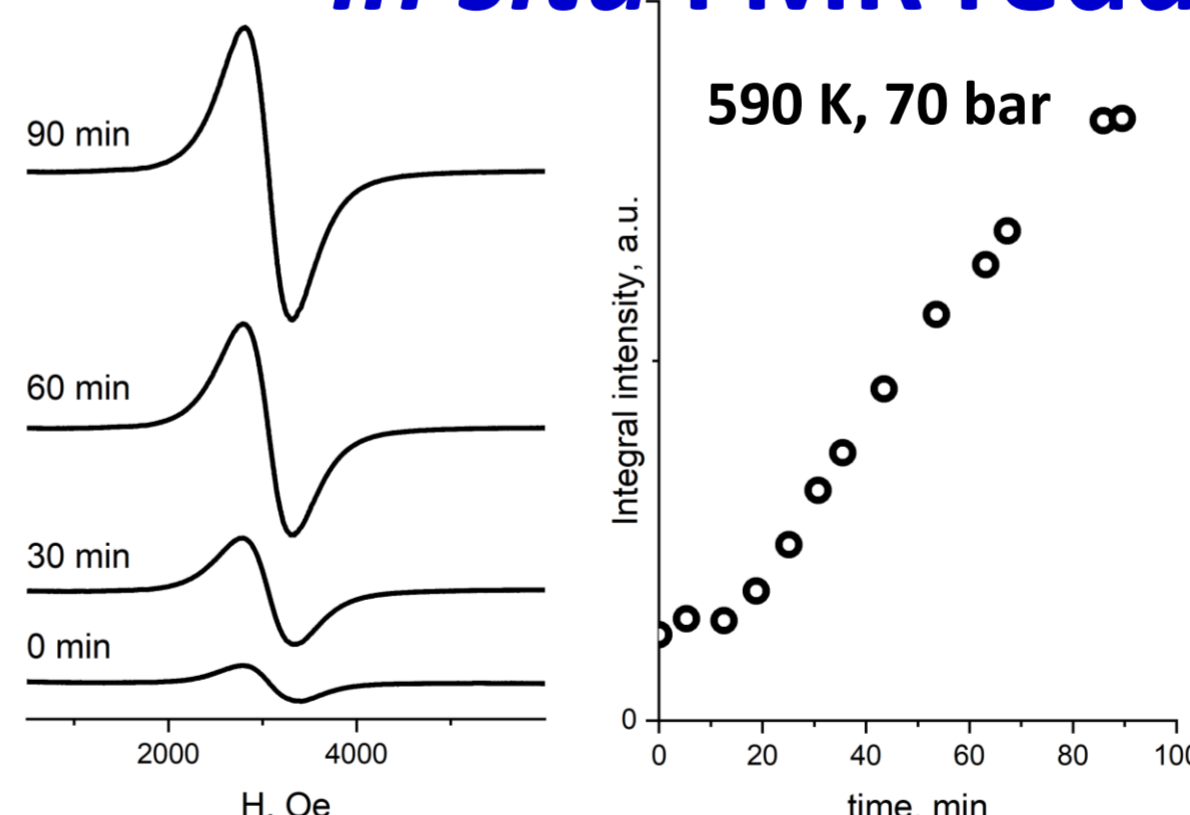


Sapphire capillary
Temperature up to 1000 K
Pressure up to 300 bar



Ni-TiO₂ catalyst was studied in i-PrOH media right after passivation. It has been shown the reduction of NiO layer on the nanoparticles surface occurs in supercritical i-PrOH

in situ FMR reduction by SC i-PrOH

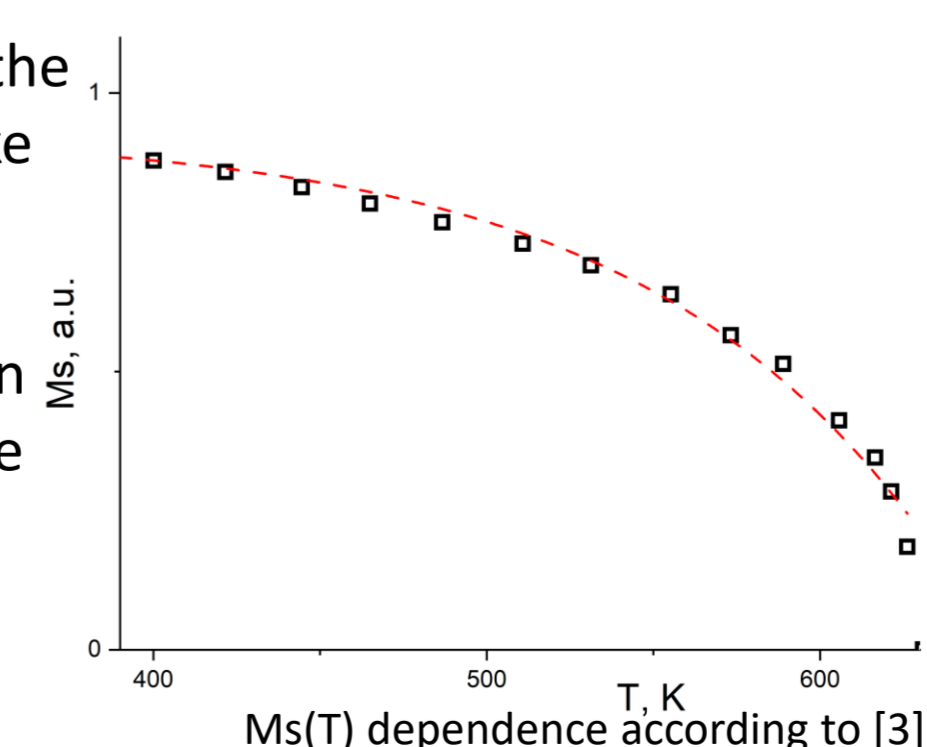


In situ FMR reduction of NiO-TiO₂ sample in SC i-PrOH

Supercritical i-PrOH is capable of reducing NiO-TiO₂ sample without using gaseous H₂

Reduction temperature is 590 K, but the reduction speed for the SC i-PrOH is lower than for gaseous H₂

FMR signal depends from the magnetization of Ni. To take this into account the experimental data were normalized by Ni saturation magnetization temperature dependence



[1] N.S. Nesterov, V.P. Paharukova, V.A. Yakovlev, O.N. Martyanov, *J. Supercrit. Fluids* **2016**, *112*, 119.

[2] A.A. Philippov, N.S. Nesterov, V.P. Pakharukova, O.N. Martyanov, *Appl. Catal. A Gen.* **2022**, *643*, 118792.

[3] P. Weiss, R. Forrer, *Ann. de phys.* **5**, 153, **1926**.