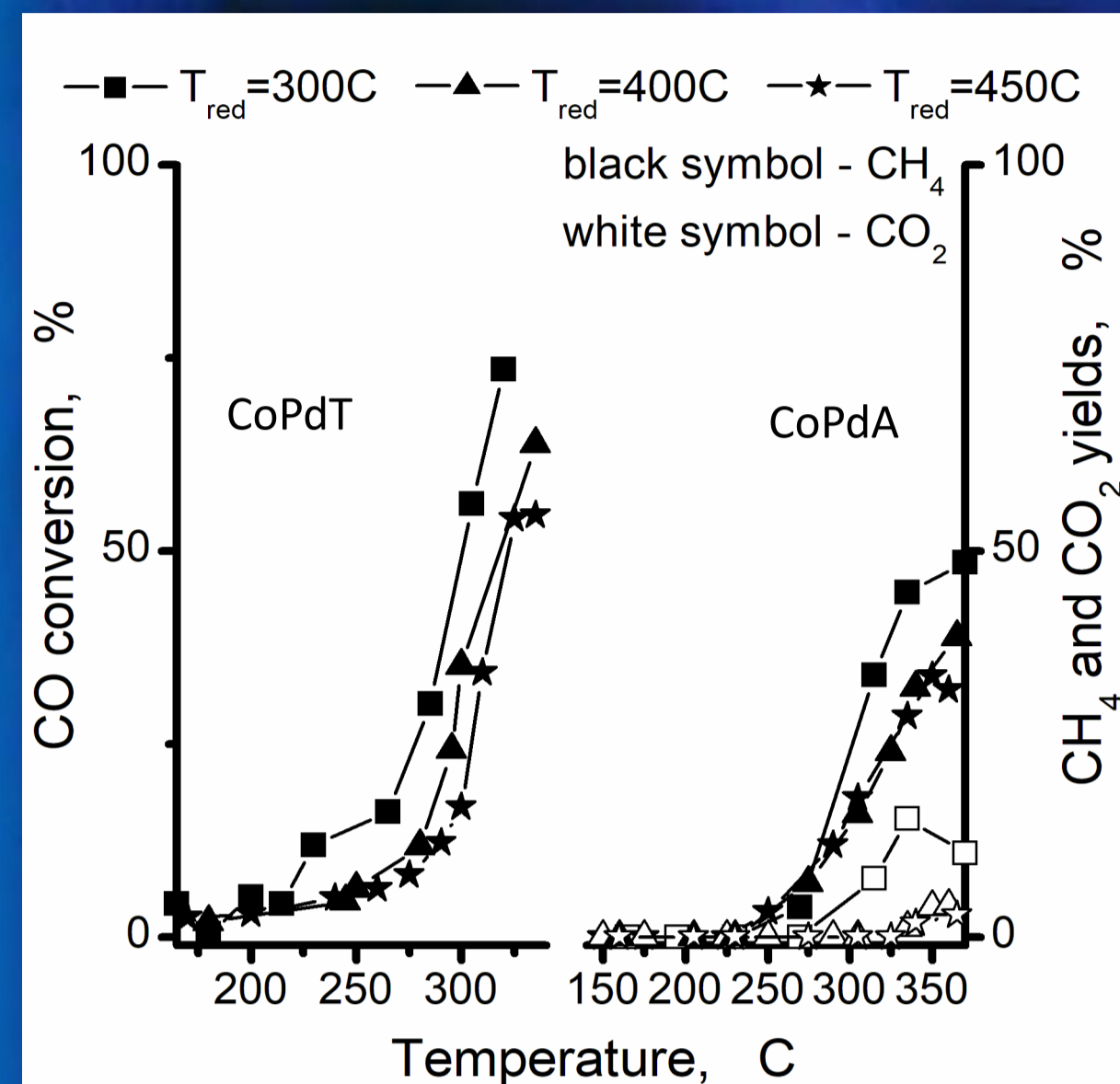


Comparative investigation of (10%Co+0.5%Pd)/TiO₂ (Al₂O₃) catalysts in CO hydrogenation at low and high pressure

M. Shopska¹, A. Caballero², S. Todorova¹, K. Aleksieva¹, K. Tenchev¹, H. Kolev¹, M. Fabian³, G. Kadinov¹

¹Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria, *E-mail: shopska@ic.bas.bg*; ²Inorganic Chemistry Department, Materials Science Institute (CSIC-US), Seville, Spain; ³Institute of Geotechnics, Slovak Academy of Sciences, Kosice, Slovakia

OBJECT and AIM: properties of the (10%Co+0.5%Pd)/TiO₂(Al₂O₃) system surface and selectivity in CO hydrogenation at low and high pressure; information about the reasons and ways of product distribution change. **PRETREATMENT:** reduction in H₂. **METHODS:** chemisorption of H₂ and CO, EPR, XPS, TPD, in situ DRIFTS, catalytic measurements, PCCS.

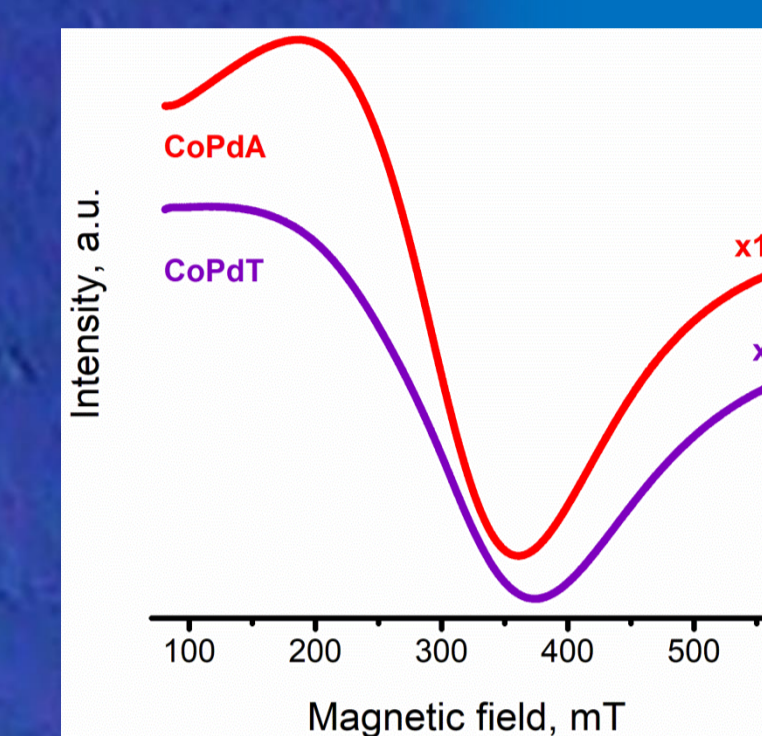
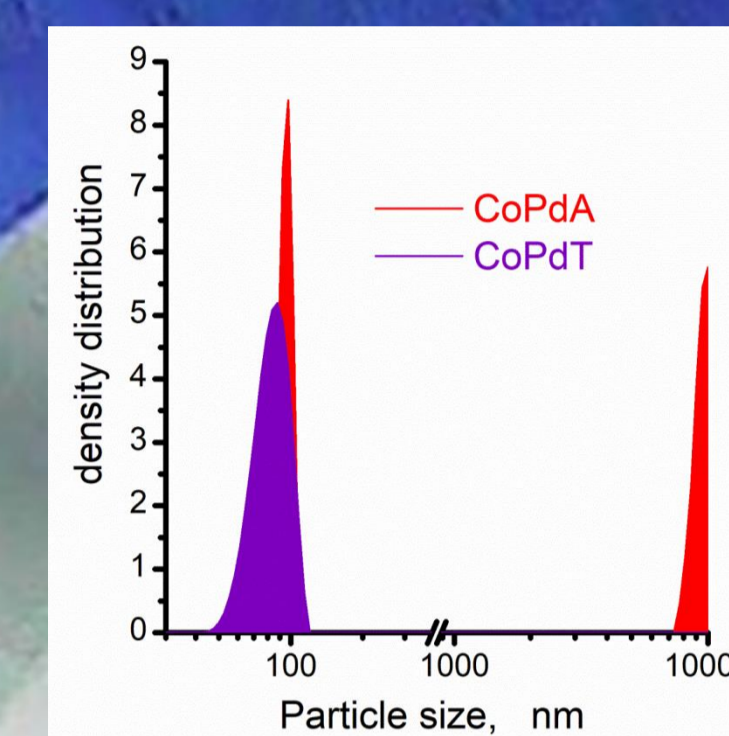
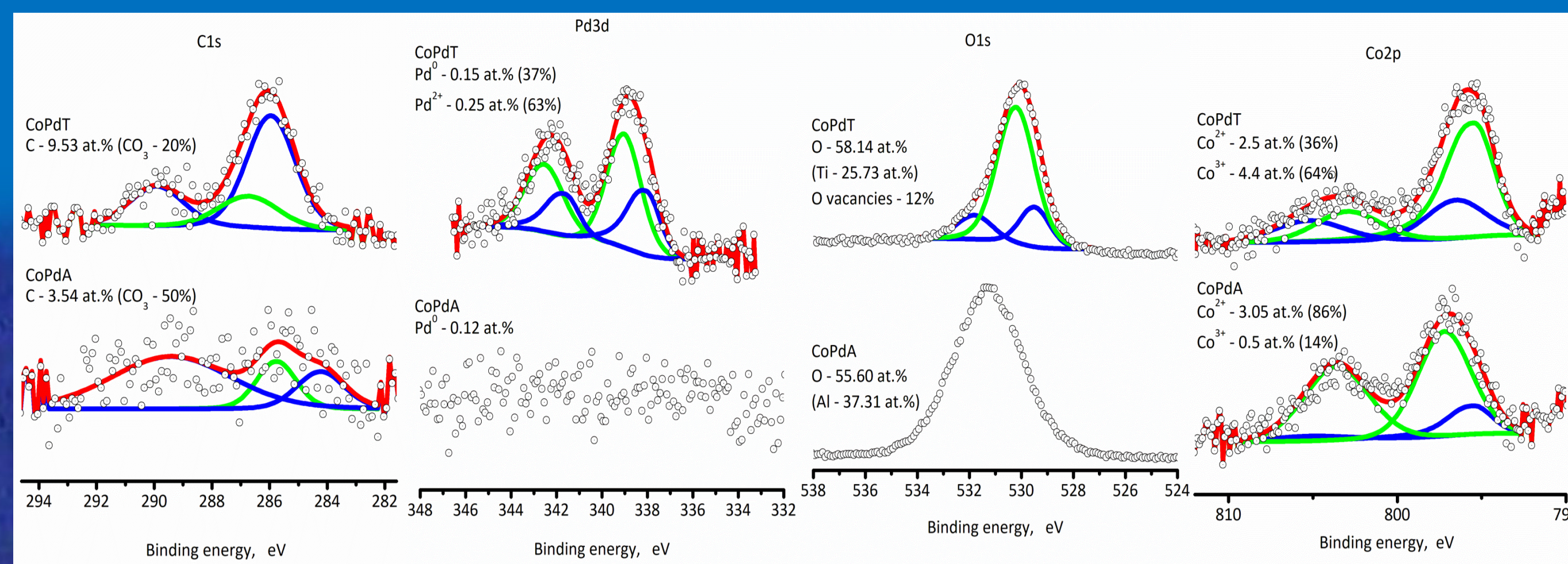


Increase of T_{red} > 300 °C - decrease in CO conversion and yields of CH₄ and CO₂. **Increase of T_{reac}** - increase of CO conversion and CH₄ and CO₂ amounts and decrease of CH₄/CO₂ selectivity ratio. CH₄/CO₂=2-19 with T_{reac}=285-335 °C for TiO₂ supported samples. CH₄/CO₂=3-24 in the interval T_{reac}=315-365 °C for Al₂O₃ supported samples.

WGS - favoured by temperature to a significant extent.

Samples with TiO₂ - more active (best activity after T_{red}=300 °C).

Samples with Al₂O₃ - poor activity; higher selectivity to CH₄ (after T_{red}=400 °C).

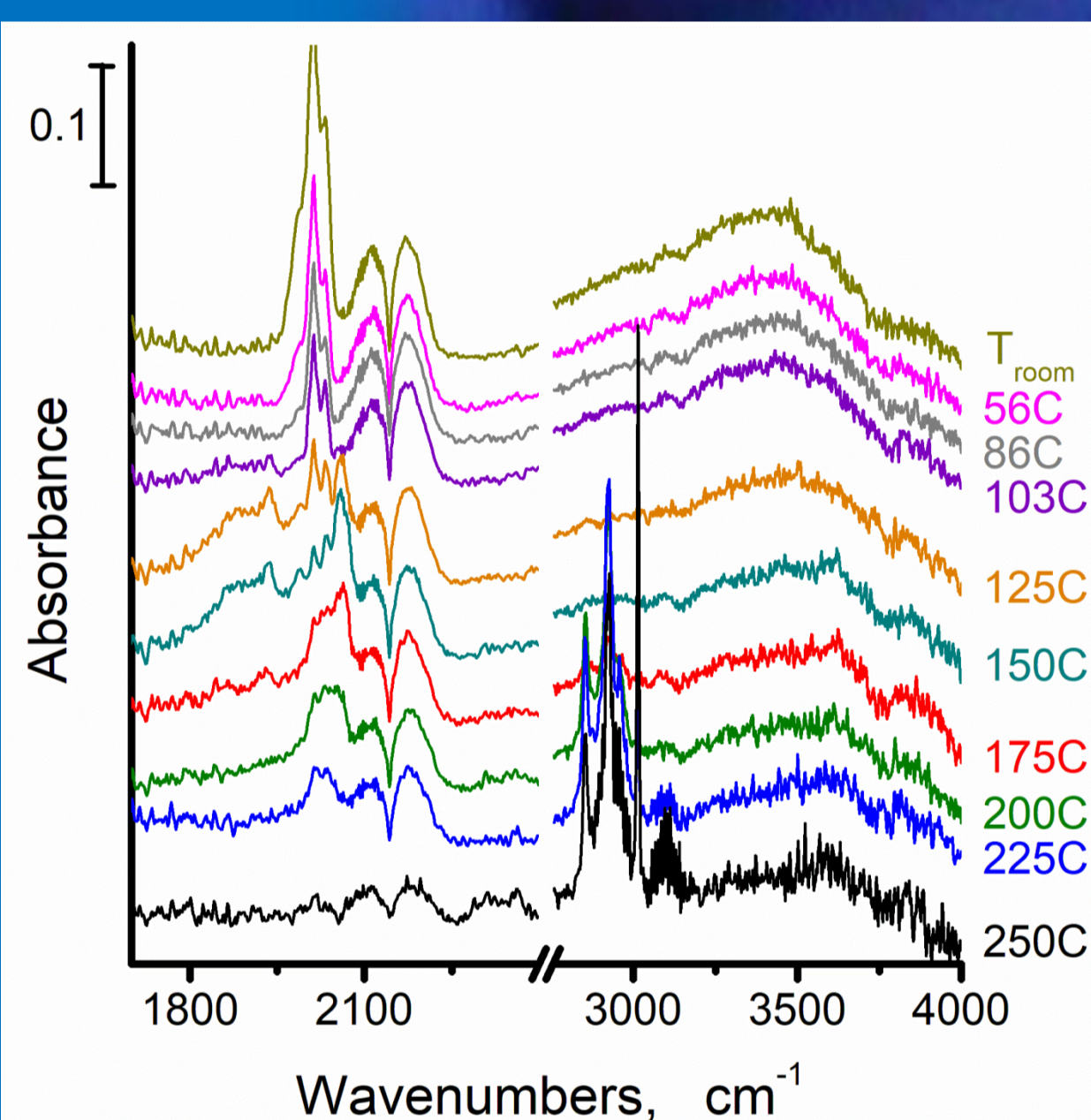


All CoPdT catalyst particles are of 40-120-nm size. CoPdA catalyst has bimodal distribution: 90-102 nm (58%) and 7500-10000 nm (42%). **Agglomerated state.**

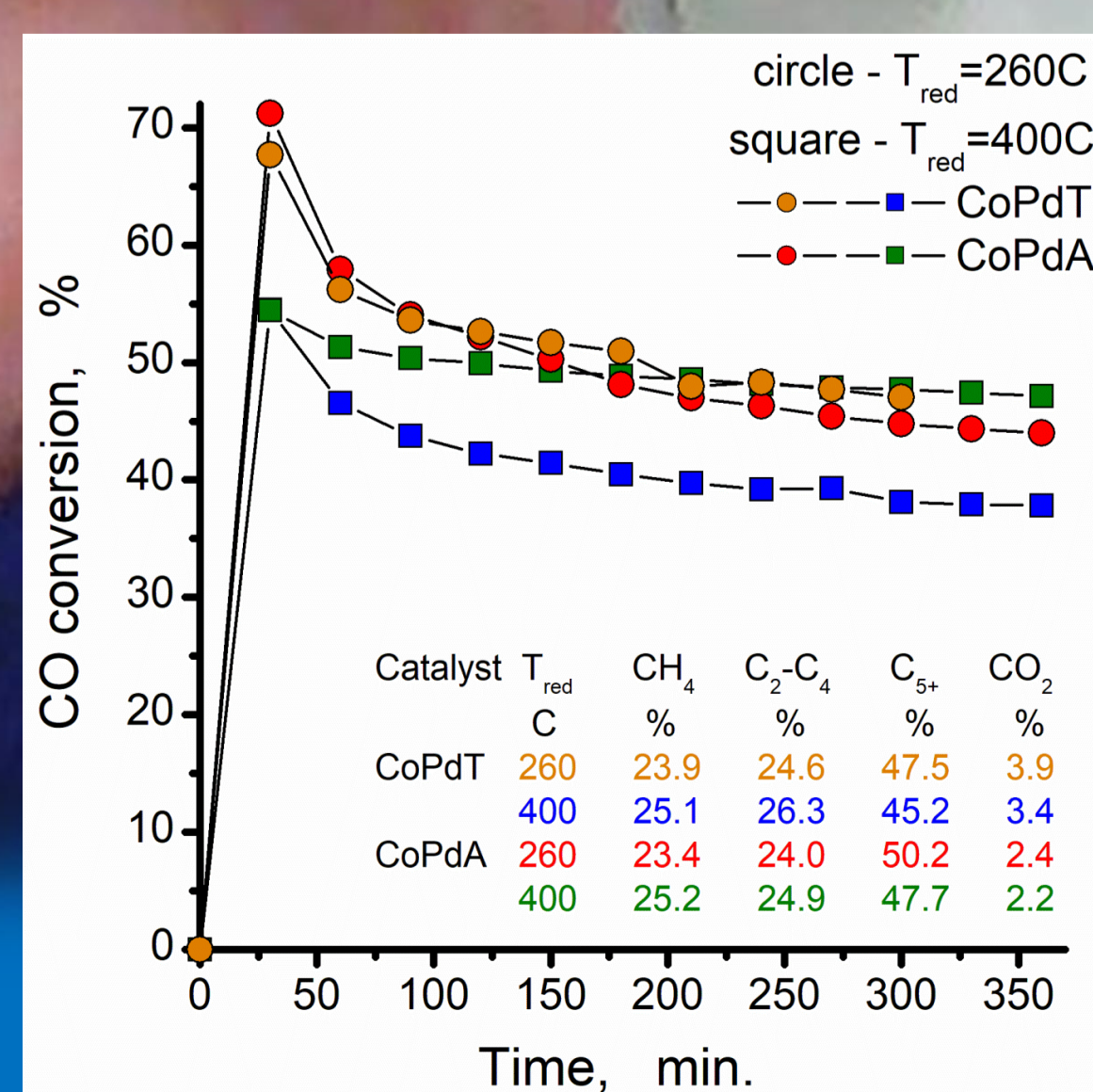
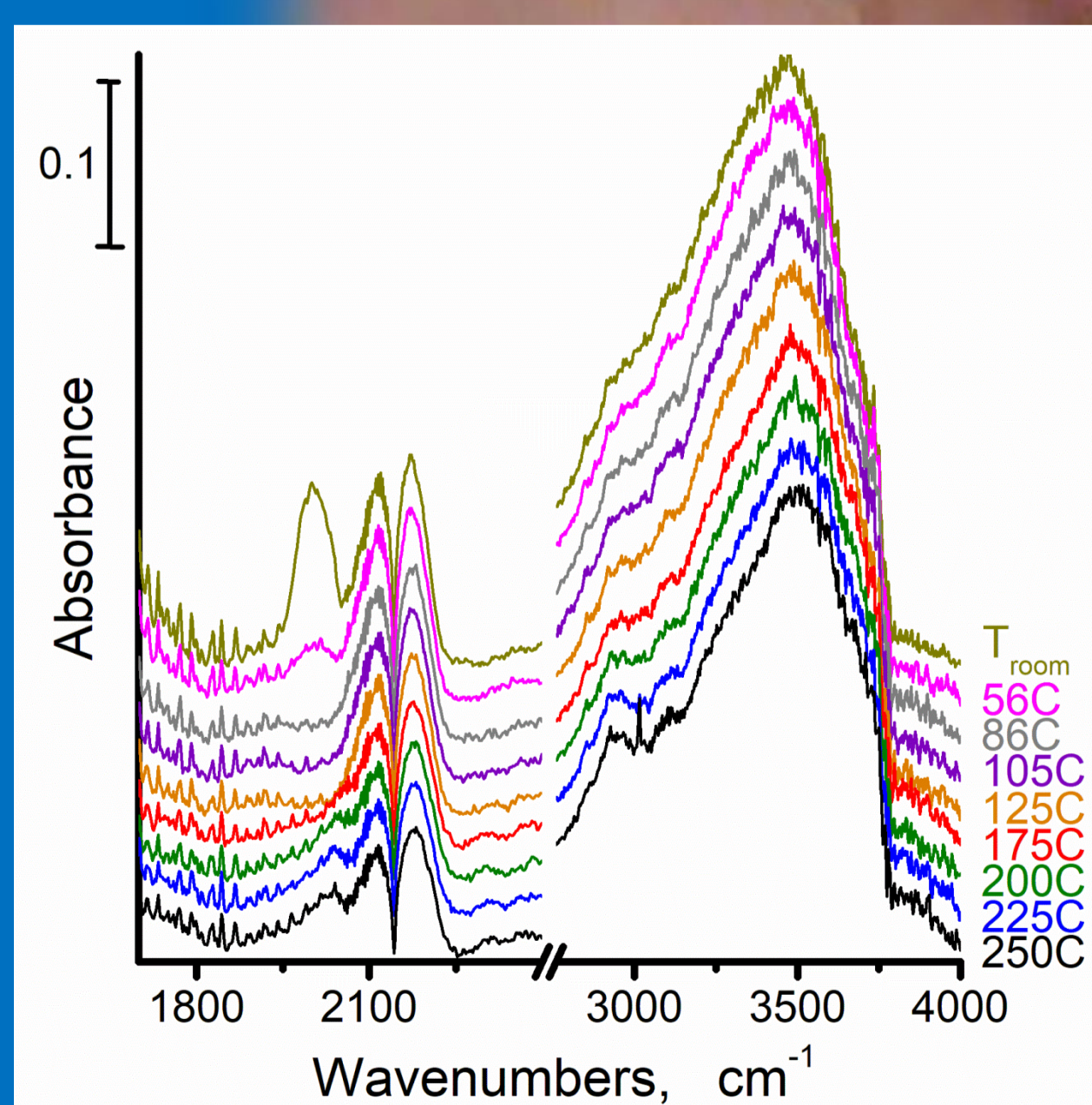
Co²⁺ ions; CoPdT > CoPdA; CoPdA has large amount of cobalt in diamagnetic state as Co, CoPd alloy particles and/or Co³⁺.

CONCLUSIONS

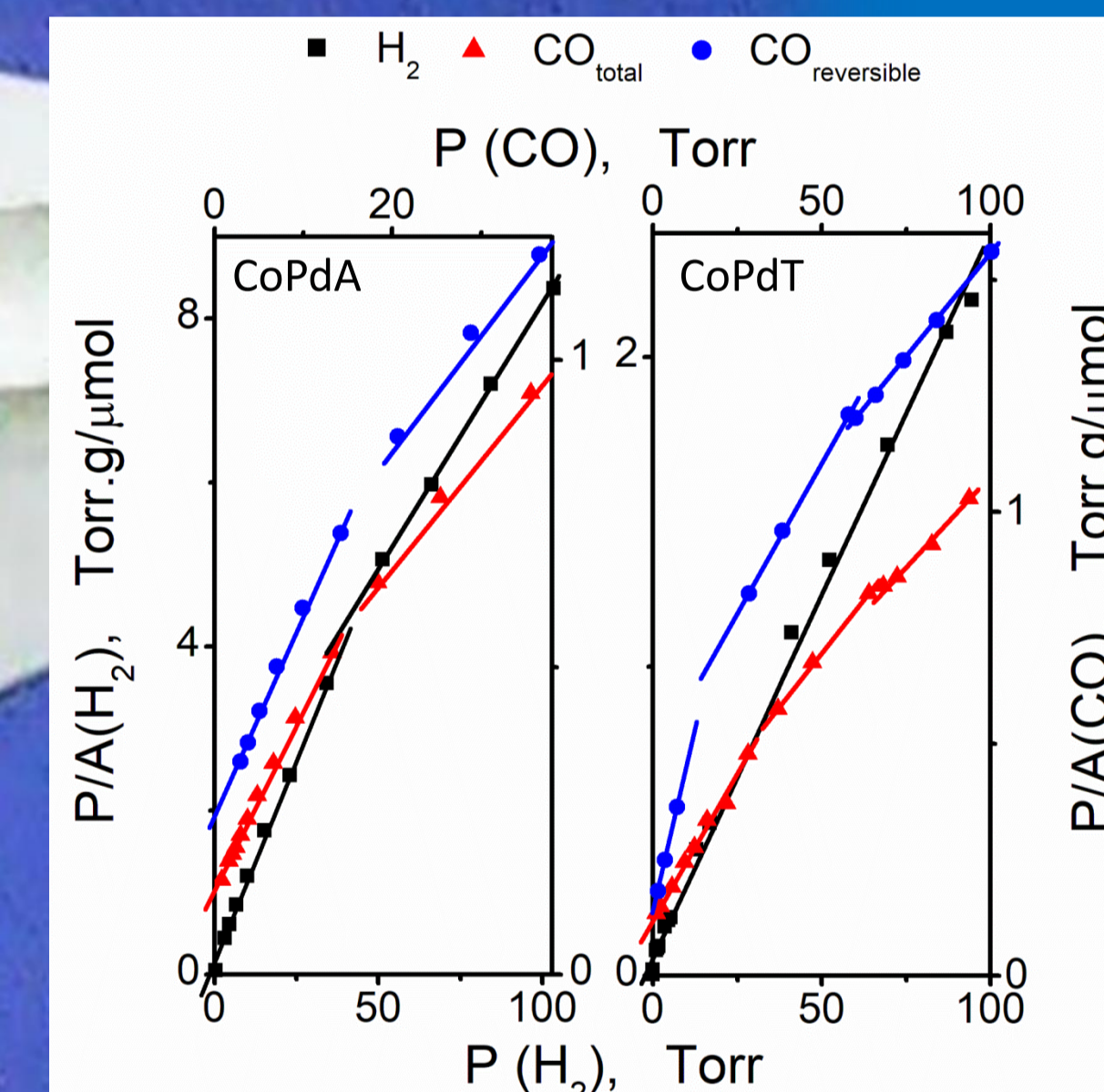
Al₂O₃-supported Co-Pd catalysts pretreated in H₂ were more selective toward CH₄ and produced a lower CO₂ amount during CO hydrogenation at 1 atm compared to catalysts with TiO₂. This tendency was preserved at 10 atm due to SMSI (CoPdT), which was not reduced by contact with H₂O and air determining sites for carbonate species formation and CO₂ production. CoPdT produced less C₅₊ because of stable adsorption of C_xH_y intermediates.



Bands characteristic of CH_x groups: increase in intensity at T_{reac} ≥ 175 °C for CoPdA and 150 °C for CoPdT. This mainly concerned the band of CH₂ groups at 2926 cm⁻¹. I_{CH₂}/I_{CH₃} = 1.2-2 for CoPdT in the interval 175-250 °C - steady adsorption of CH_x intermediates. CH₄ became perceptible in spectra at 200 °C (CoPdT) and 225 °C (CoPdA). The intensity increased with T_{reac} much more significantly with CoPdT within 225-250 °C (a 3.7-fold increase of the 3015 cm⁻¹ band). **Registered particularity showed that both systems have potential to produce higher hydrocarbons than CH₄ even at 1 atm.**

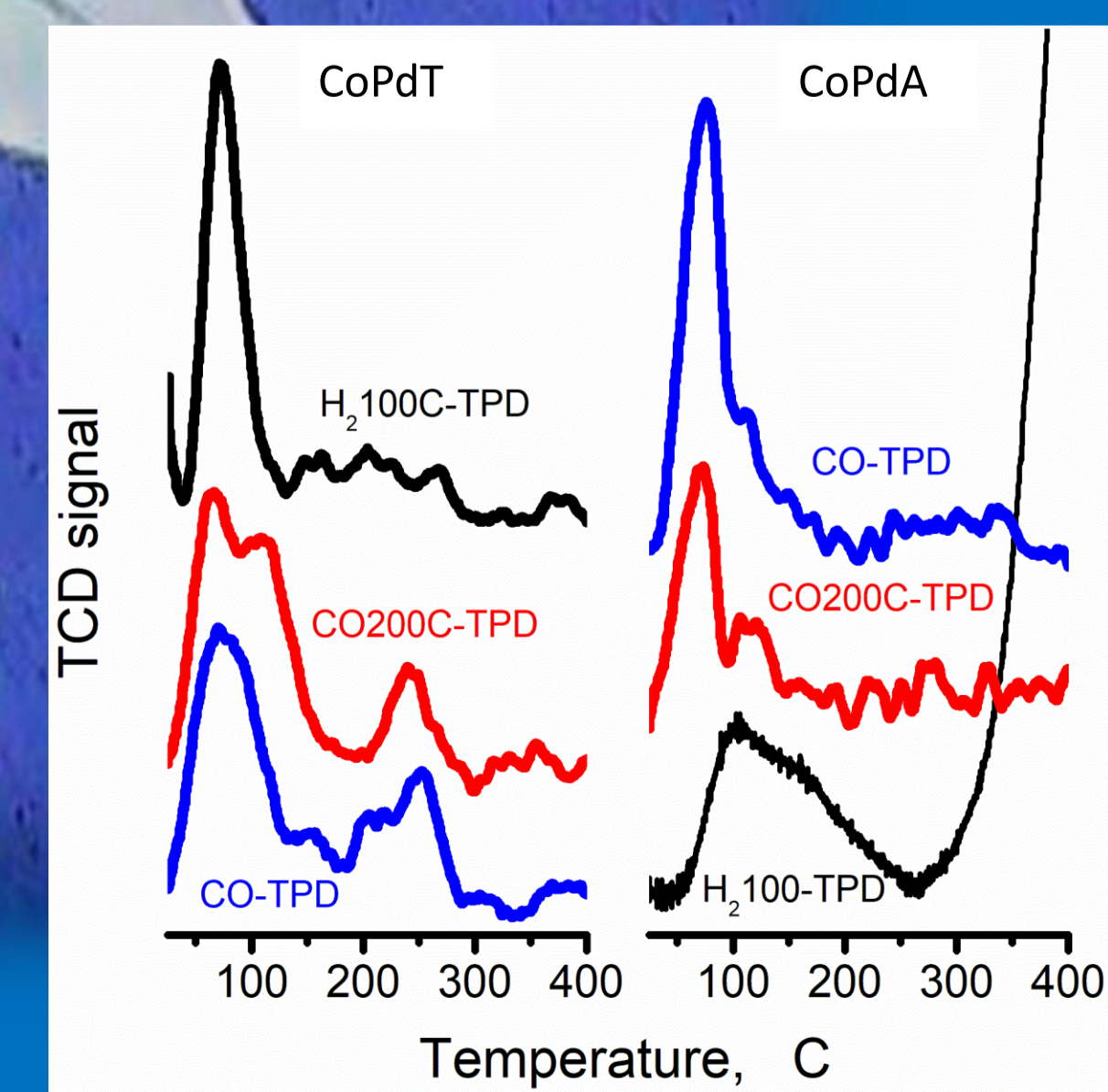


CO conversion and selectivity depended on T_{red}; CH₄ is the main product; CH₄/CO₂ - CoPdA > CoPdT; CO conversion decreased carbon deposition on the surface, difficult diffusion due to C₅₊ hydrocarbon synthesis, consumption of reagent in oxide phase reduction, particle agglomeration. Reduction at 400 C - **CoPdT preserved higher CO₂ production - SMSI provides active sites.** CoPdA - stable CO conversion. The modified properties and larger particle size favour CO dissociation over Co. Higher total pressure and increased P_{H₂} enriched formation of shorter C_xH_y fragments and decreased their combination.



H₂ and CO adsorption: higher diversity of adsorbed H₂ and CO species on CoPdT. **H₂ desorption:** opposite situation; high temperature H₂ (T > 360 °C, CoPdA) - less reactive and a low mobile form; **CO desorption:** T_{des} ≤ 200 °C - linear and bridge species - an increase at the expense of high temperature species with CoPdT, with CoPdA only alternate their quotas; linear CO species prevail over bridge ones depending on T_{ads} and support; bridge species increase with T_{ads}.

T_{des} ≥ 200 °C - carbonate(-like) species - a significant amount with CoPdT; common temperature intervals - favour interaction/decomposition facilitating formation of hydrocarbons and CO₂; high temperature region - CoPdA catalyst shows negligible desorption



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