

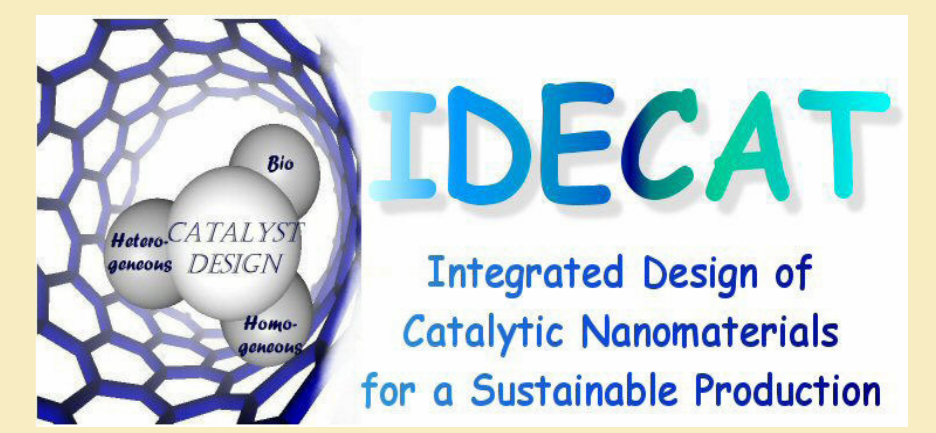
Structure-Activity Relationship Study of Pt/H-Mordenite Catalyst for *n*-Butane Isomerization



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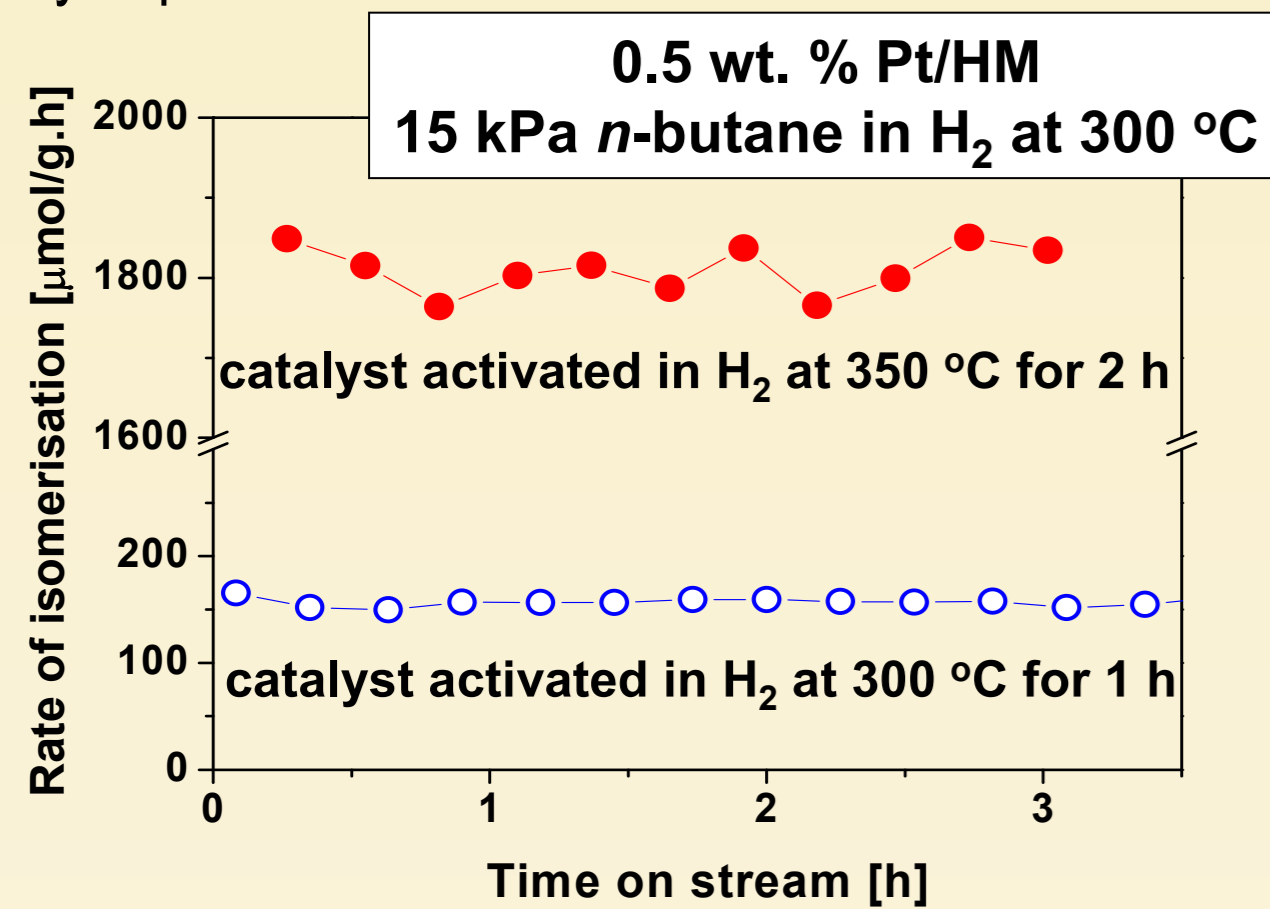
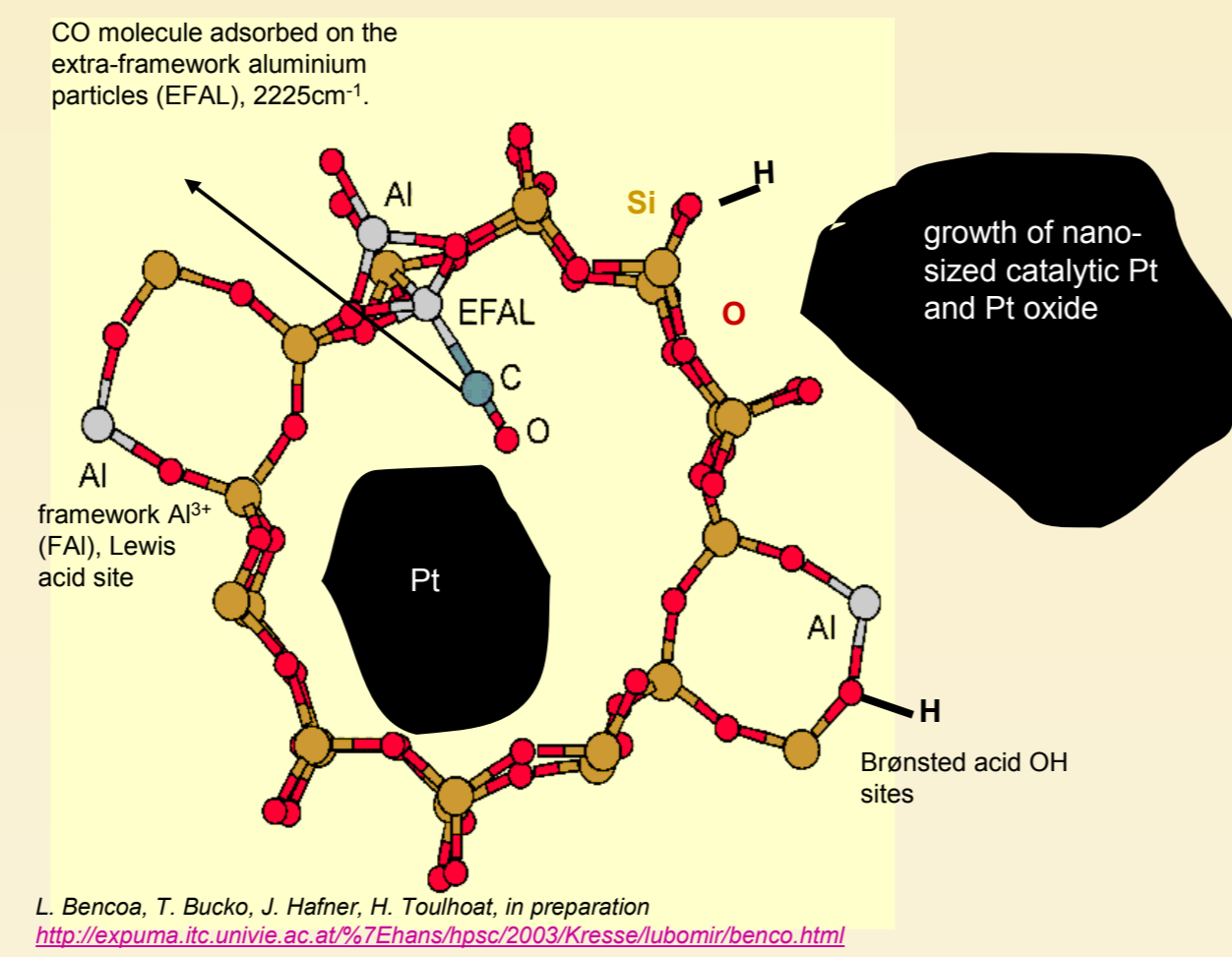
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Introduction

Pt-doped H-mordenite (Pt/HM) is used as a solid acid catalyst for the isomerization of light alkanes [1]. Optimization of the acid site distribution and the metal site reactivity of this bi-functional material are necessary for obtaining an active and stable catalyst. Therefore the preparation and even more the activation of the catalyst are very important.

Pt/HM catalysts with differing activity are activated by various procedures and then their interaction with *n*-butane or CO is investigated by microcalorimetry [2] and FTIR spectroscopy.



Experimental

Preparation of Pt/H-mordenite series:

- HM was impregnated with (NH₄)₂PtCl₆ (1 wt% Pt)
- dried at RT
- calcined at 300 – 800 °C

Activation: inert atmosphere at 450 °C or in H₂ at 375 °C

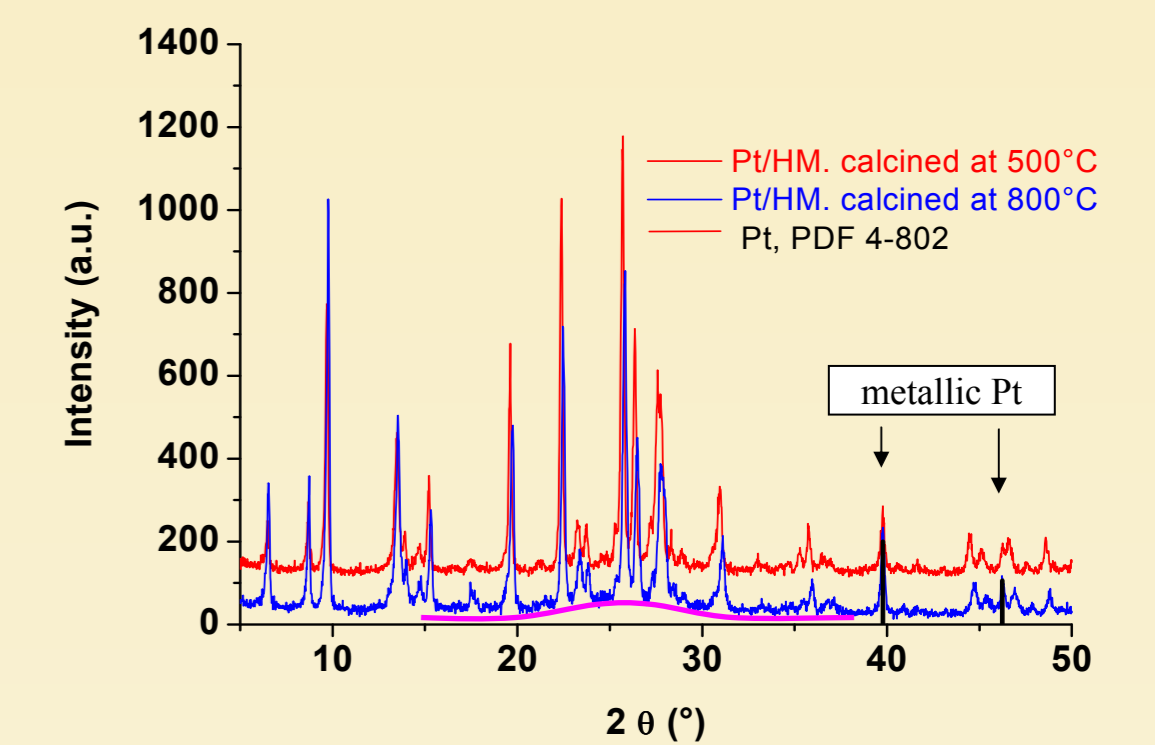
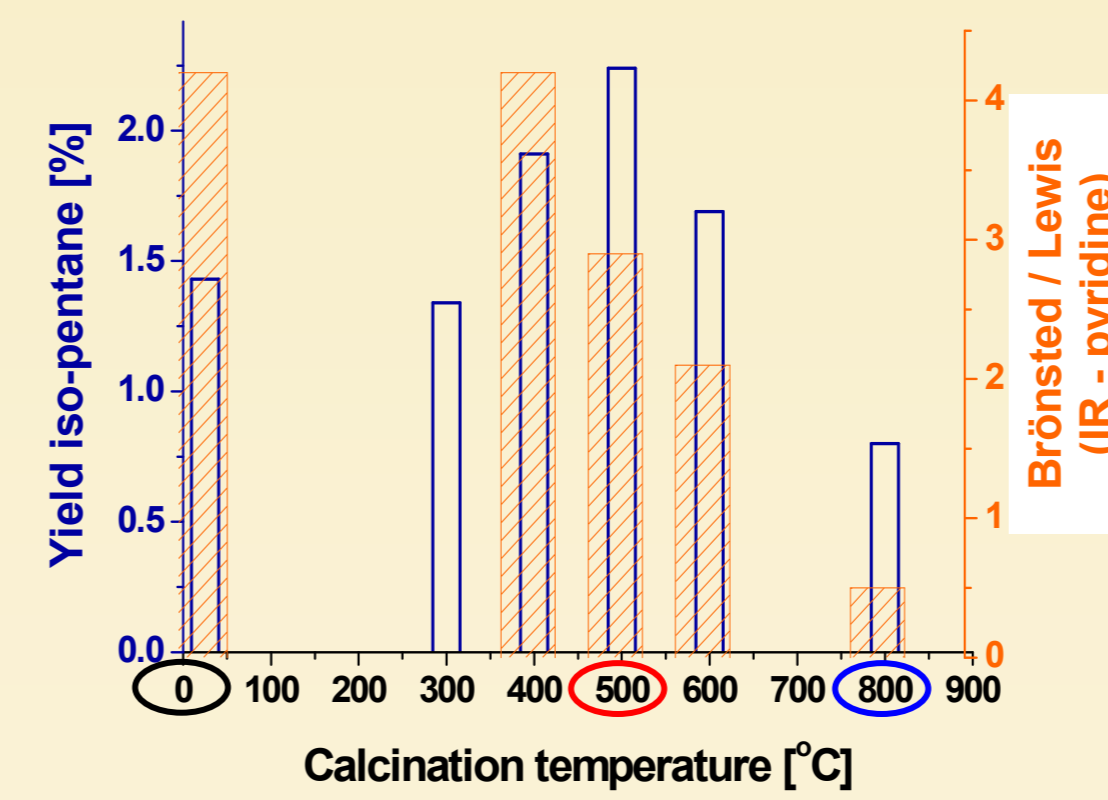
Methods:

- PE2000 FTIR spectrometer; spectra are normalized to wafer area weight
- Microcalorimeter SETARAM MS 70 with volumetric system
- UV-vis-NIR PerkinElmer Lambda 950 with Harrick DR attachment and HVC reaction chamber; on-line GC

Sample characterization

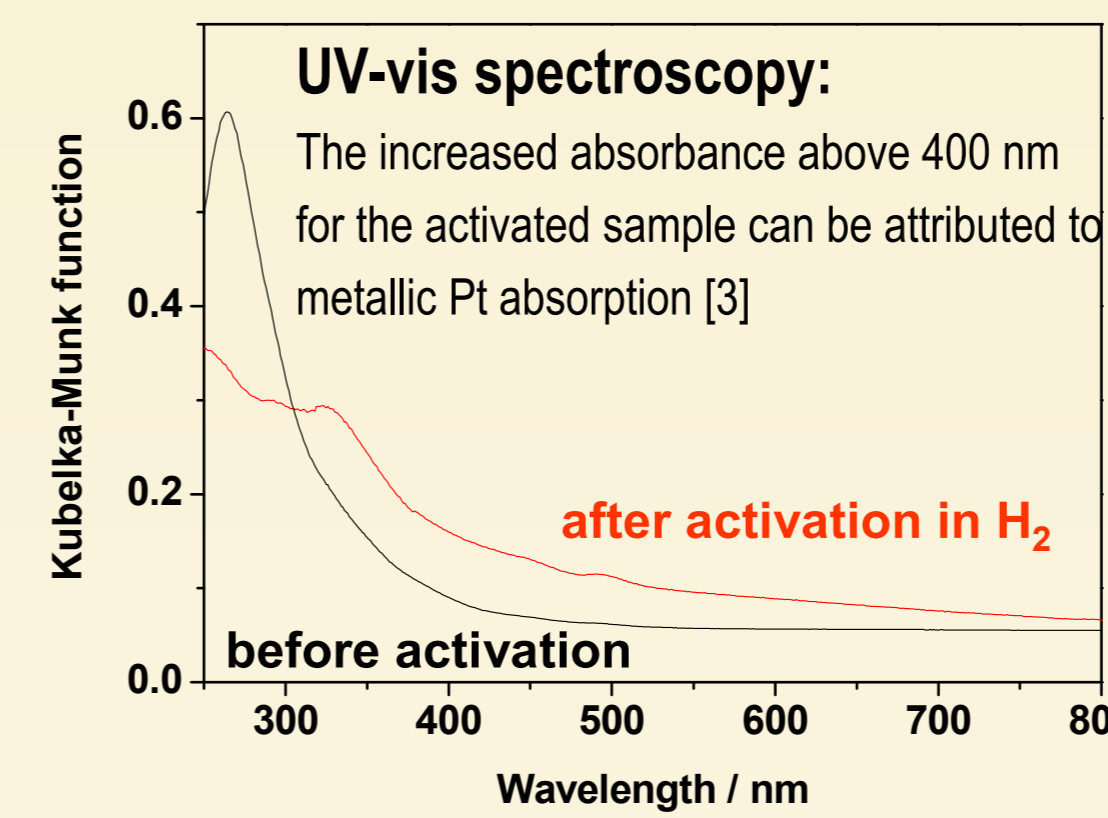
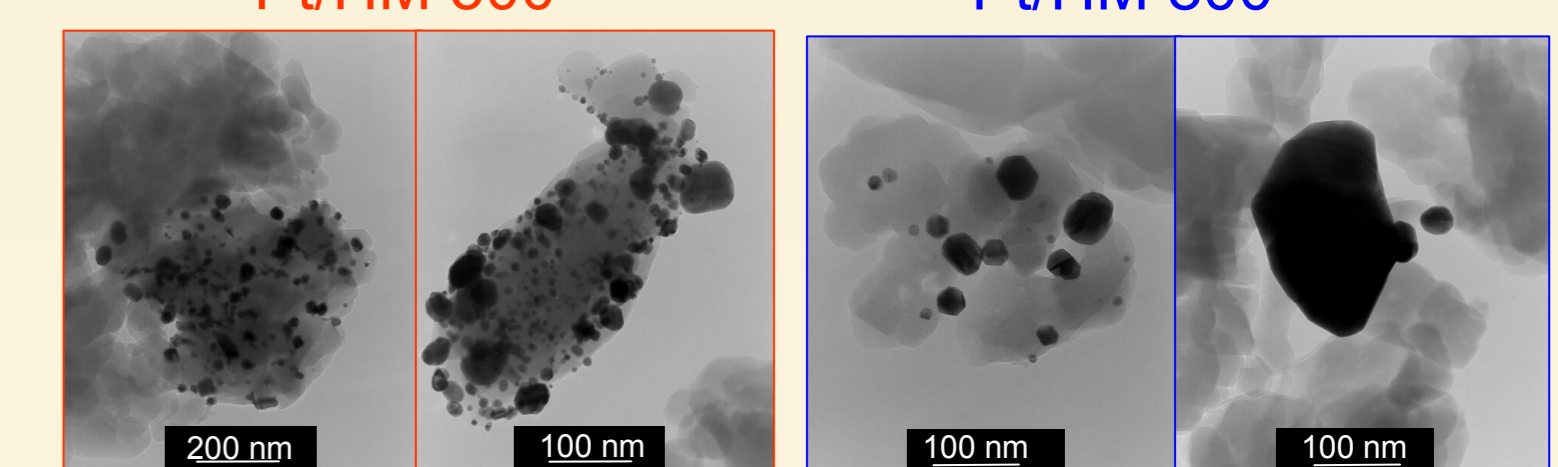
Selected samples – the catalyst with the **highest** (calcined at 500 °C, Pt/HM 500), and with the **lowest** (calcined at 800 °C, Pt/HM 800) activity for alkane isomerization and the bare HM.

XRD: crystalline phases: Mordenite and Pt



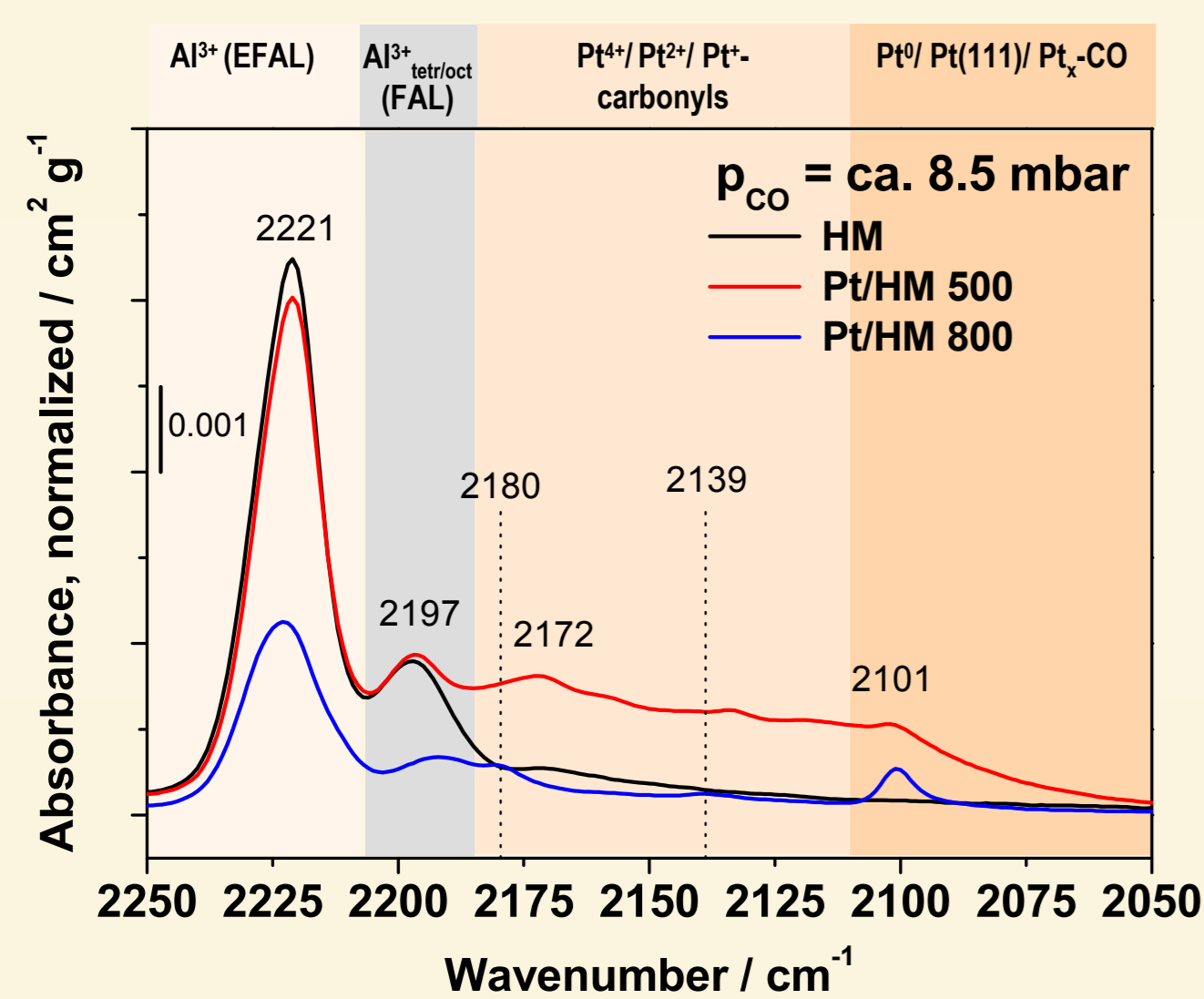
- metallic Pt (hexagonal shape of the Pt particles)
- inhomogeneous distribution of Pt particles
- Pt/HM 500 contains smaller Pt particles
- After H₂ reduction the Pt particles range from 1–3 nm for both calcined samples

TEM of the calcined samples before activation:



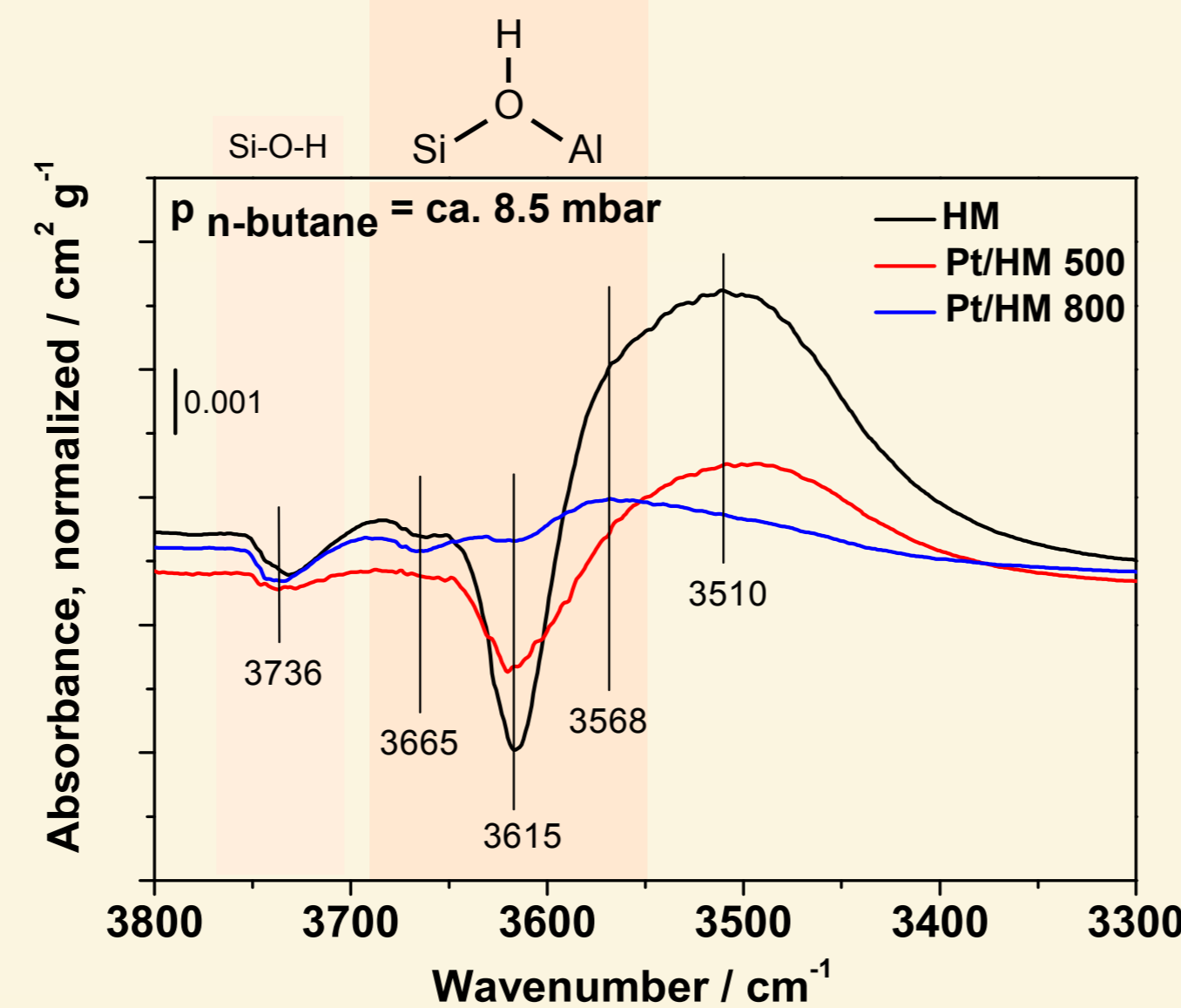
IR: CO adsorption at RT

activation in inert atmosphere at 450 °C of Pt/HM500, Pt/HM800, HM



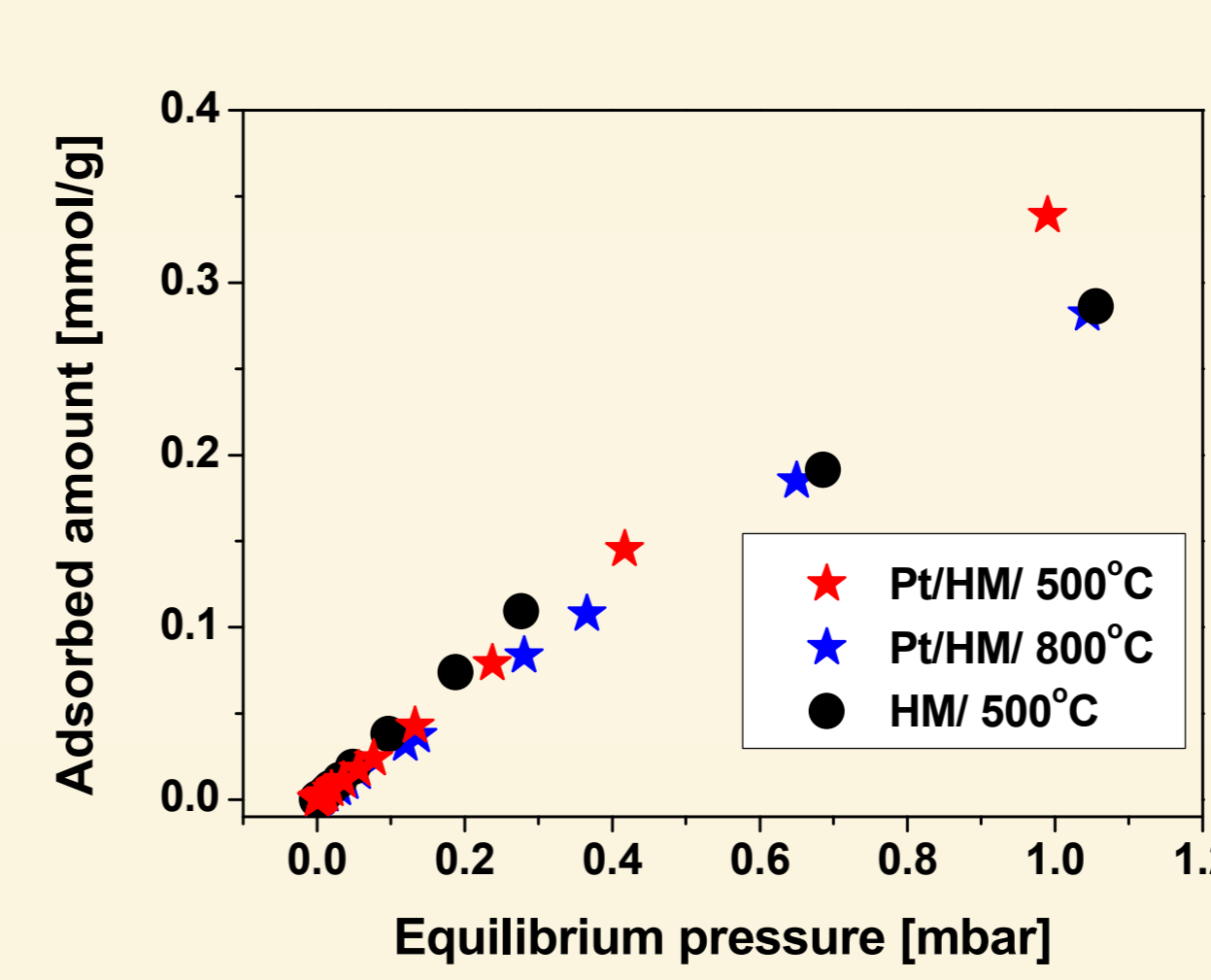
- various platinum forms: metallic and oxidized Pt
- strong Lewis acid sites (LAS)
- Pt/HM 500 contains oxidized Pt species
- Pt/HM 800 is characterized by polycrystalline Pt

IR: n-butane adsorption at RT

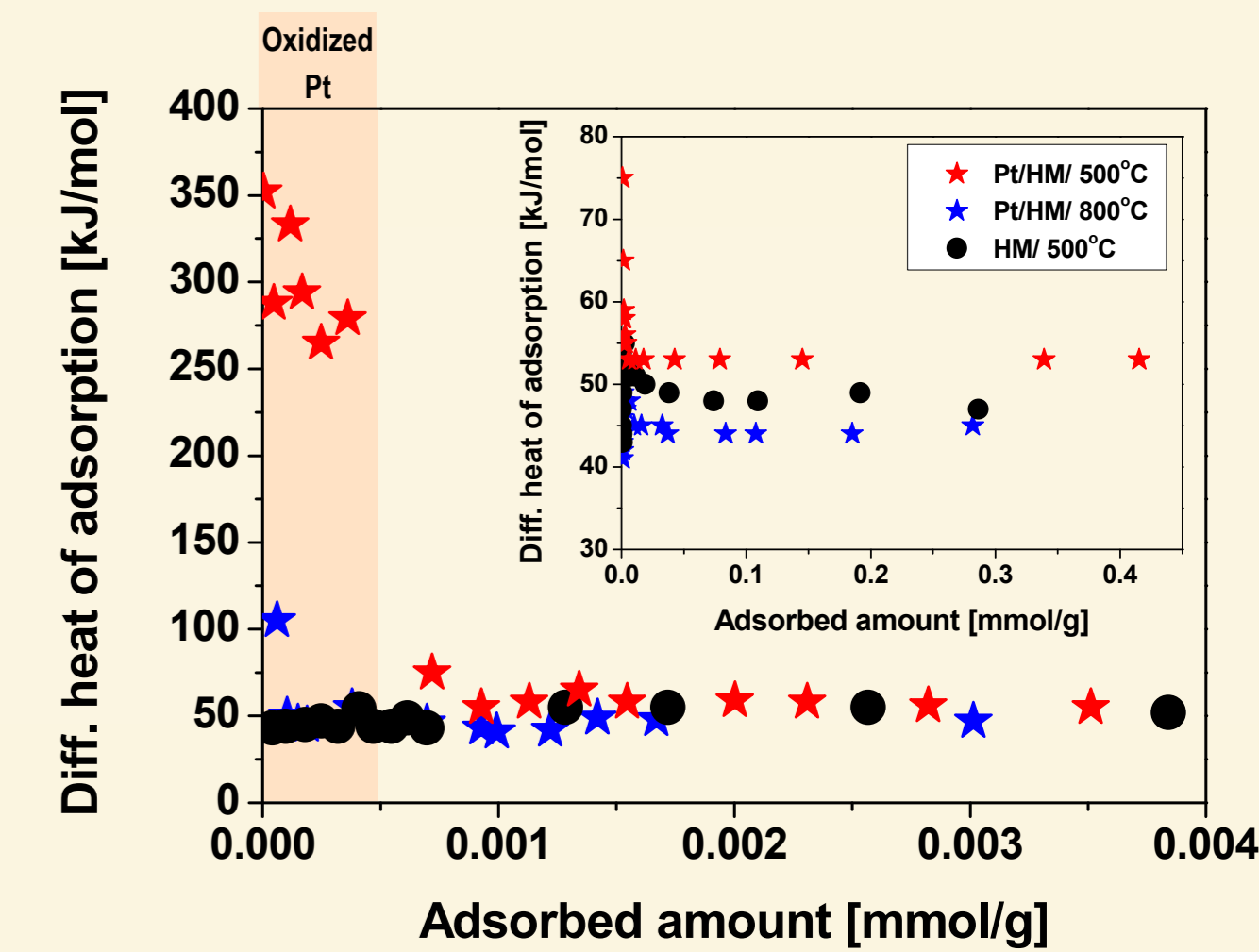


- Pt/HM 500 and HM show significant shift of OH bands of ~111 cm⁻¹ and more OH groups than Pt/HM 800
- Pt/HM 800 shows a small change in the OH region
- *n*-butane interacts with acidic OH groups of the zeolite

Microcalorimetry: n-butane adsorption at 40 °C

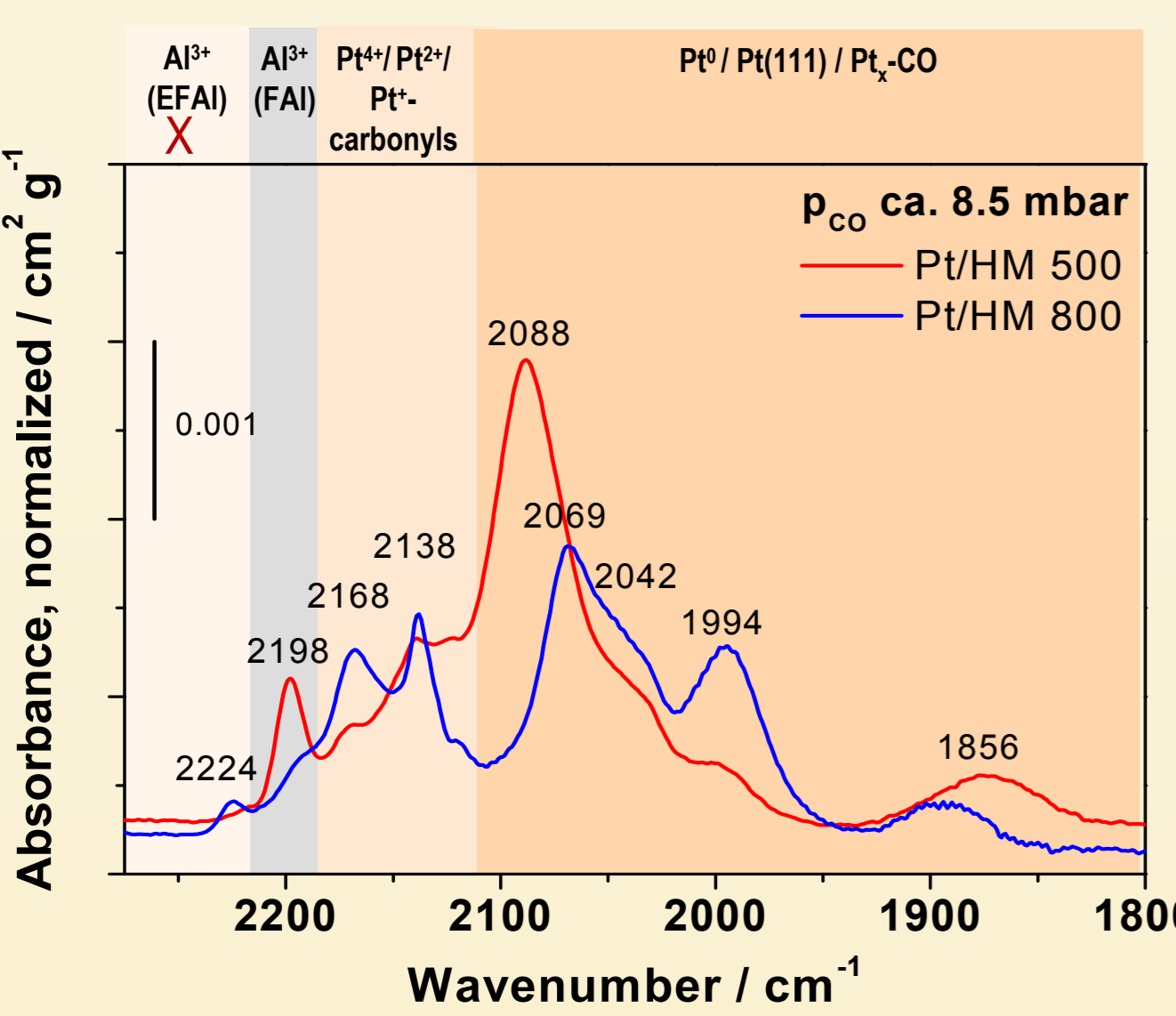


- Pt/HM 500 has more adsorption sites for *n*-butane (~70 μmol/g) than Pt/HM 800 and HM at 1 mbar; in good correlation with the IR results.

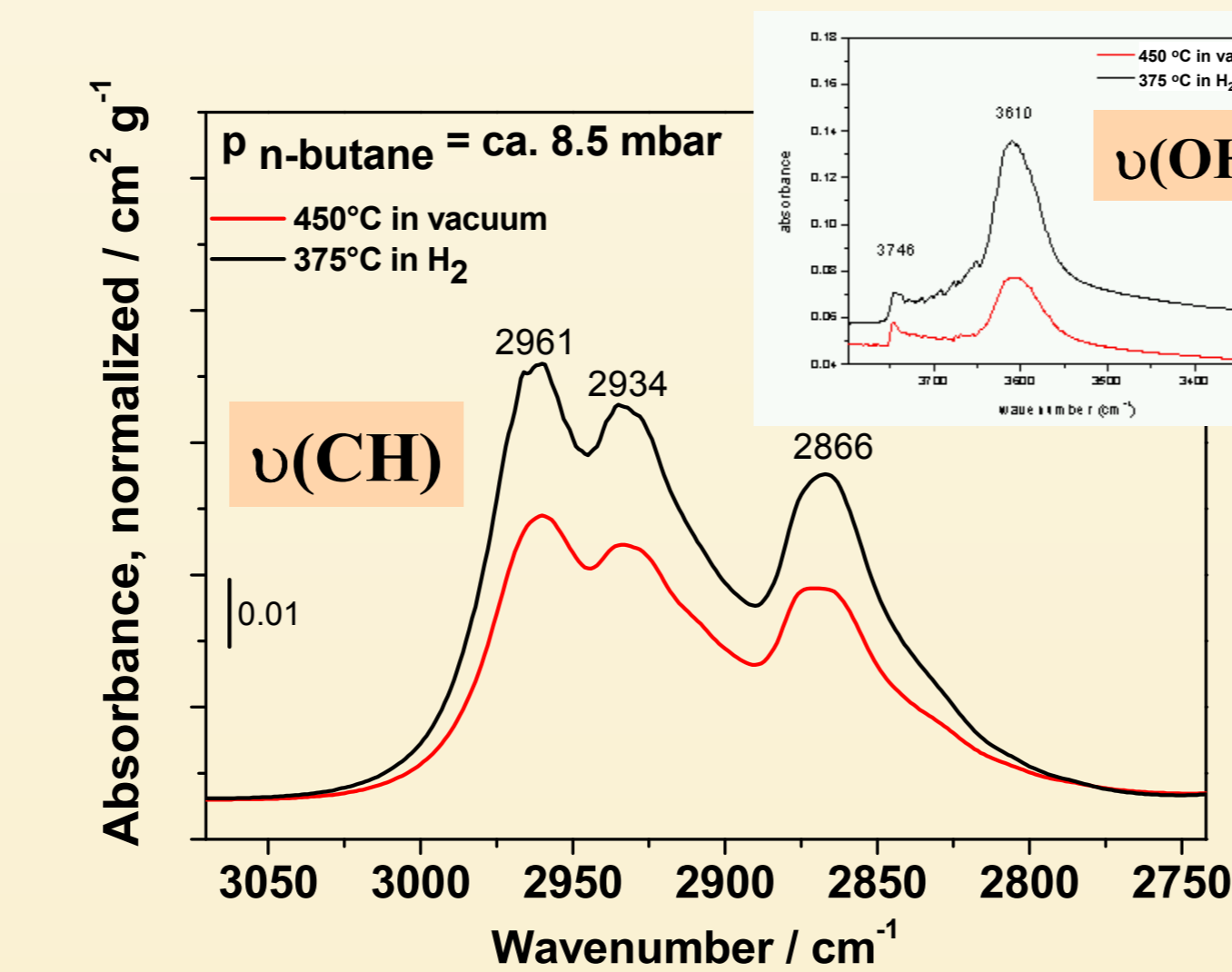


- Pt containing catalysts exhibit high initial heats of adsorption (low coverage); interaction of *n*-butane with oxidized Pt (IR).
- Majority of sites equivalent (high coverage); slightly higher average for Pt/HM 500 than for Pt/HM 800 due to LAS (IR)

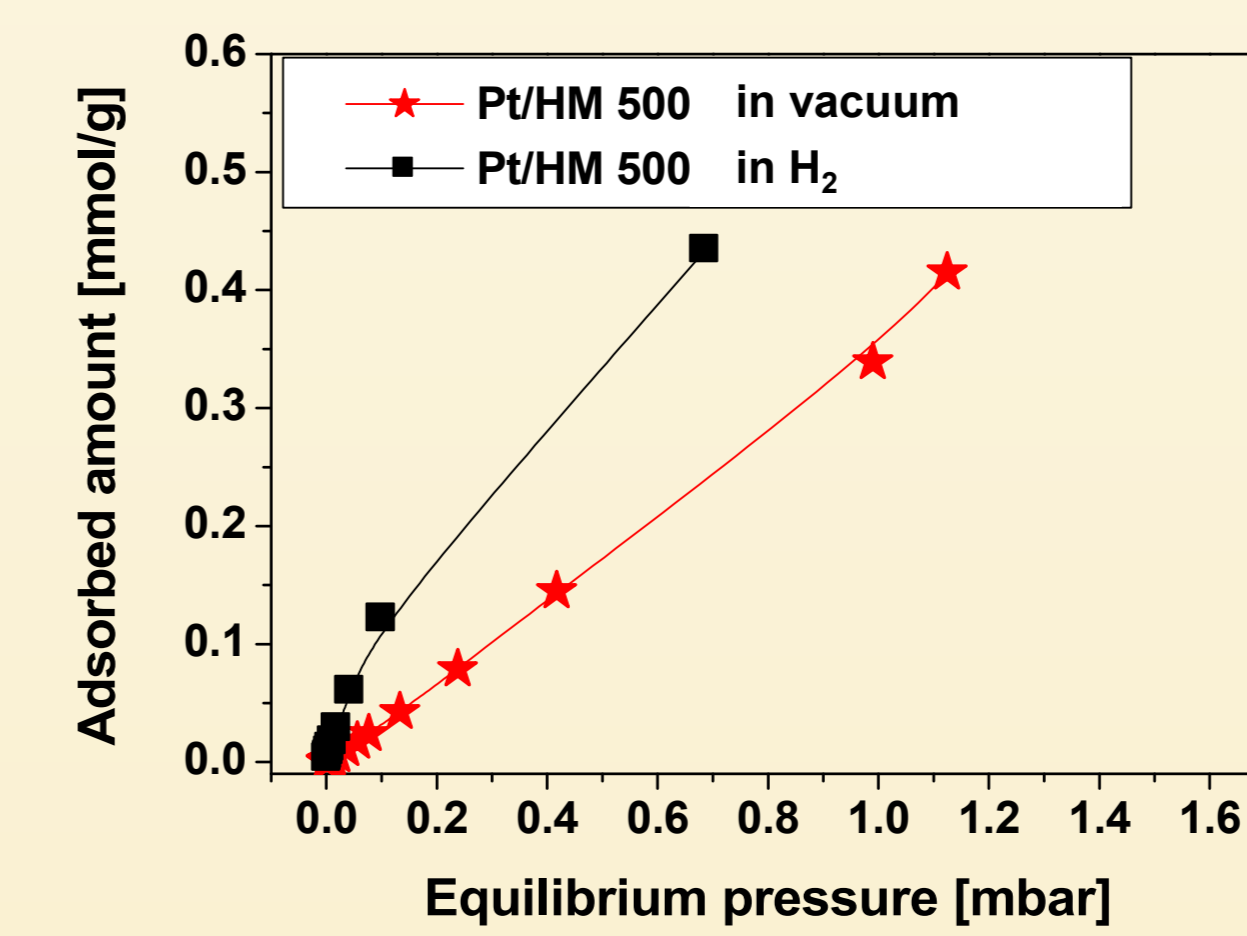
activation in H₂ at 375 °C of Pt/HM 500 (comparison with inert atmosphere)



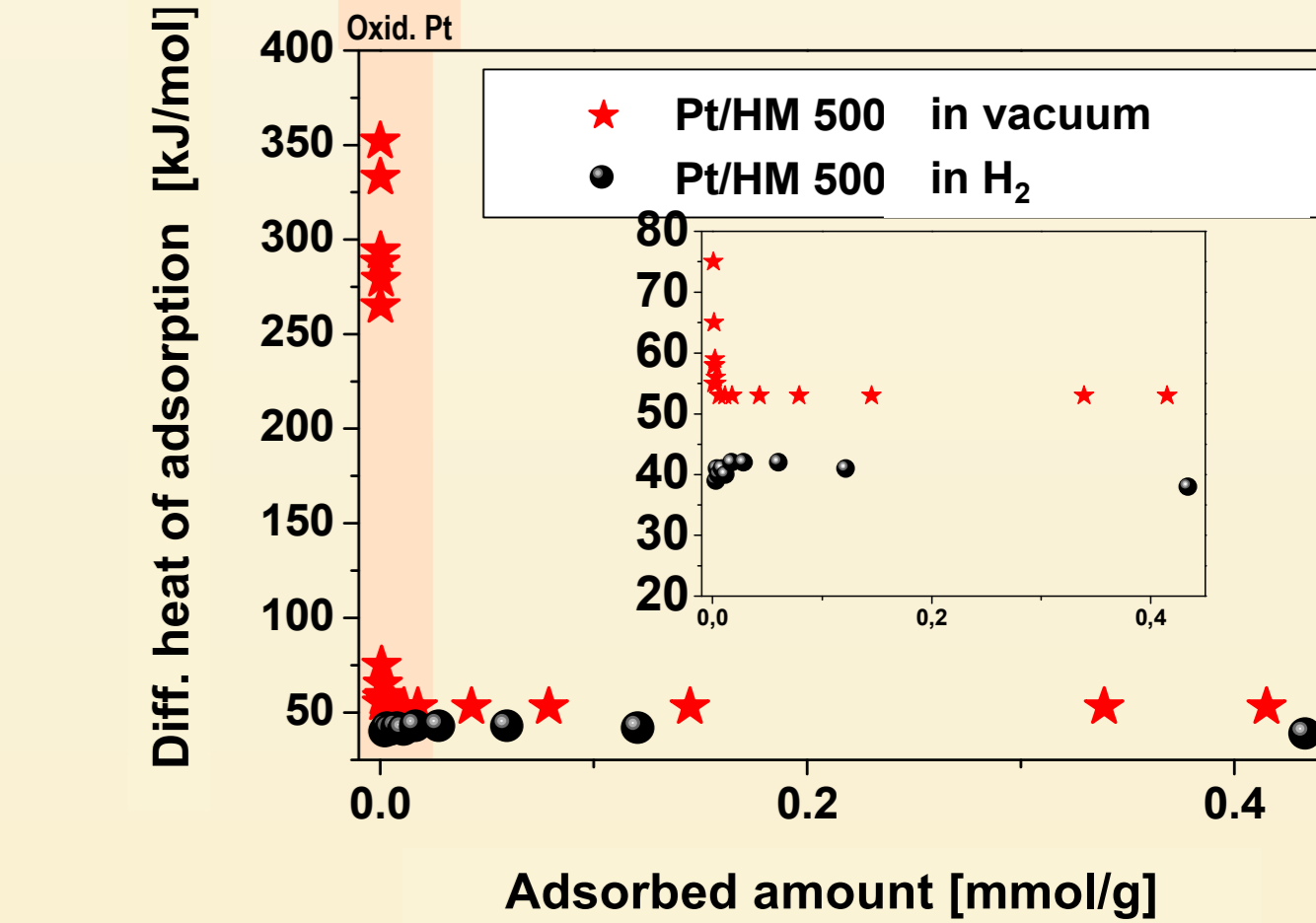
- Loss of strong Lewis acid sites
- active Pt/HM 500 contains a significant fraction of metallic Pt
- Pt/HM 800 is characterized by more oxidized Pt species than Pt/HM 500



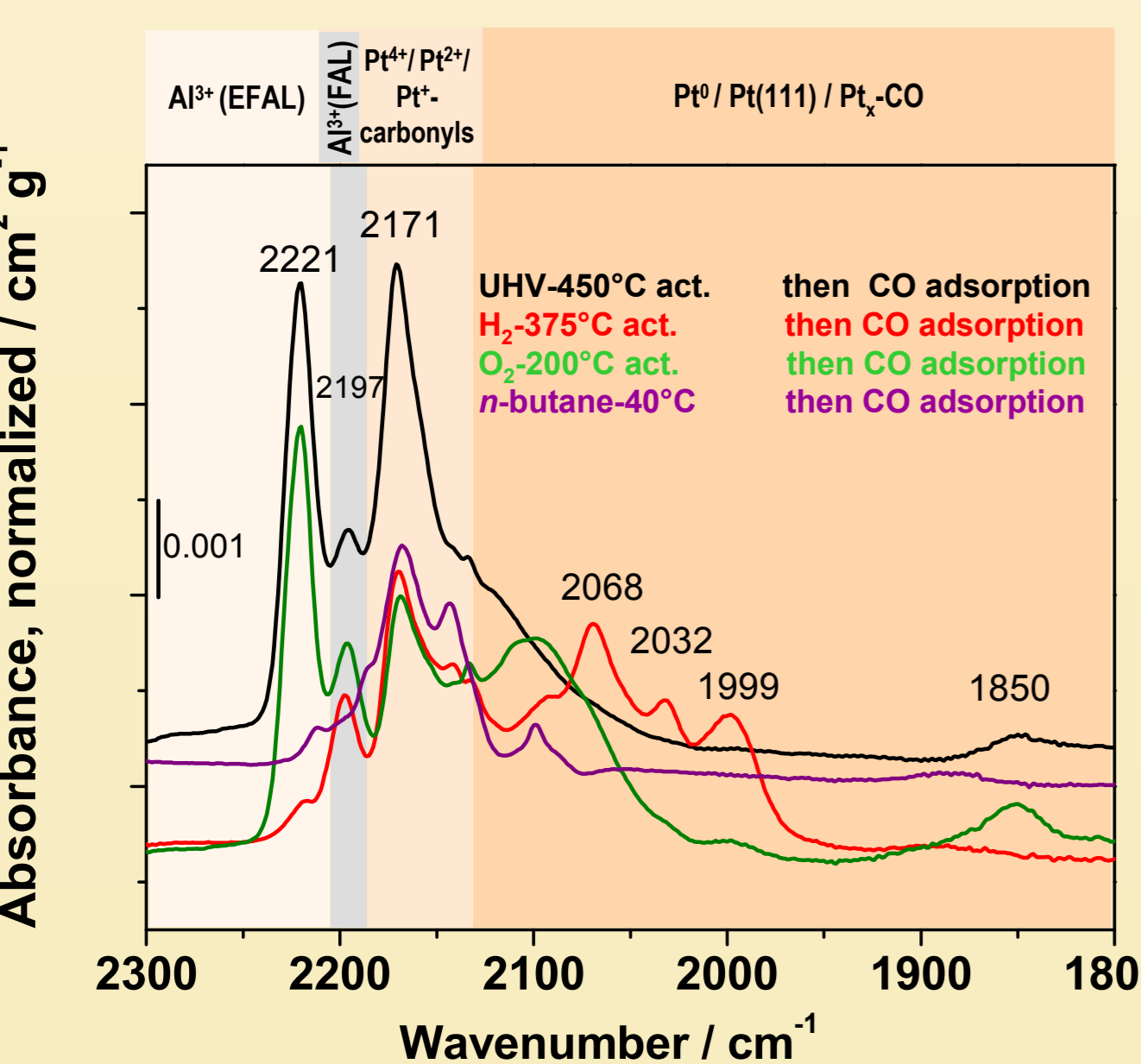
- H₂ reduction leads to:
 - more adsorption sites for *n*-butane
 - more Brønsted OH species
 - acidity of Brønsted OH groups not changed (diff. spectra not shown)
- activation temperature and atmosphere determine number of sites



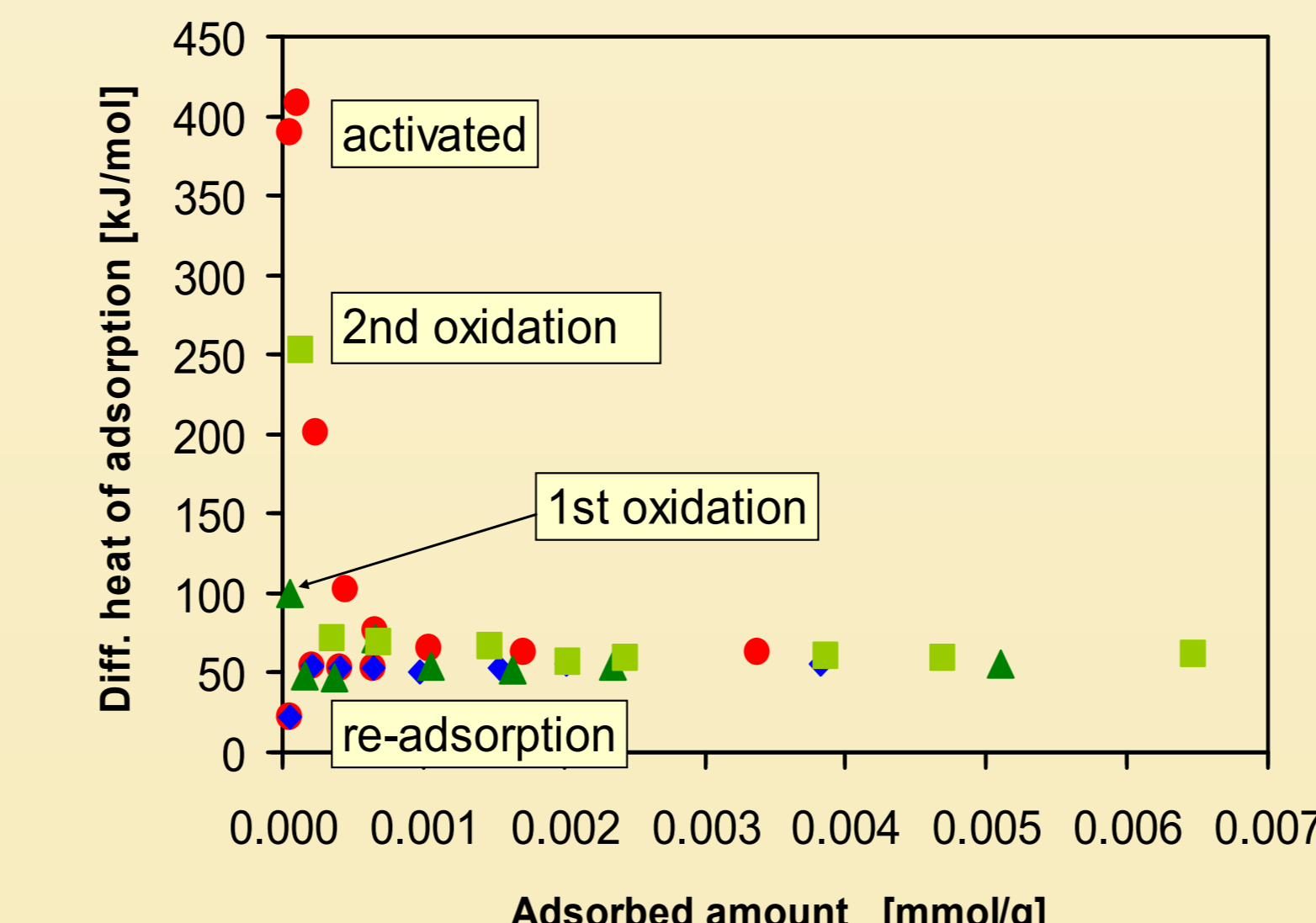
- H₂ reduction of active Pt/HM 500 generates more adsorption sites (Brønsted acidic OH groups and metallic Pt (IR)) for *n*-butane than activation in inert atmosphere (450 and 200 μmol/g at 0.7 mbar, respectively).
- very weak interaction of the active surface with the reactant *n*-butane, ~ 40 kJ/mol
- H₂ reduction of less active Pt/HM 800 (not shown): 330 μmol/g at 0.7 mbar, ~ 40 kJ/mol



activation in inert, reducing and oxidizing atmosphere of Pt/HM 500



- H₂ reduction of the oxidized Pt is accompanied by disappearance of strong Lewis acid sites
- O₂ treatment results in oxidized Pt → high initial heats at low *n*-butane coverage; regenerates strong Lewis acid sites
- during *n*-butane adsorption, similar to H₂ treatment, strong Lewis acid sites disappear and oxidized Pt is reduced
- loss of the sites producing the high initial heats



Conclusions

The active states of Pt/HM are characterized by:

- Brønsted acidic OH groups
- a small amount of strong Lewis acid sites
- well dispersed metallic platinum particles (1-3 nm)
- weak interaction of the surface acid sites with alkanes.

Alkanes reduce Pt oxide (as found by re-oxidation studies) → Dynamics of surface sites on Pt/HM catalysts during alkane isomerization reaction.