Surface Spectroscopy and Catalytic Properties of Model Platinum Catalysts Exposed to Hydrocarbons

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BACKGROUND AND MOTIVATION

- Hydrocarbonaceous deposits are normally present on Pt during hydrocarbon reactions [1, 2].
- Carbon deposition is dehydrogenated during evacuation [3] and appear as "graphitic" (C 1s ~284.5 eV), "polymeric" (=C_xH_y; C 1s ~285.8 eV) and "deactivating" (C 1s ~284.1 eV) carbon. The latter may correspond to "disordered" carbon [4]. C atoms on Pt ("PtC": C 1s ~283.2 eV) can also be present.
- Activity and selectivities of "skeletal" reactions of hexane (isomerization, C_5-cyclization, aromatization, fragmentation) are influenced by the amount and chemical state of carbon.
- This depends of the temperature of treatment and the presence of H_2.

AIM:

To investigate temperature and hydrogen pressure effects

⇨on the amount and structure of surface carbon;

⇨on the catalytic activity and selectivities of Pt after these treatments.

EXPERIMENTAL

Catalyst:

Pt black: reduced from H_2PtCl_6(aq) with N_2H_4, sintered: 473 K [5].
Specific surface (BET) =2.6 m^2g^{-1}; D=0.9 %.

Experiments:

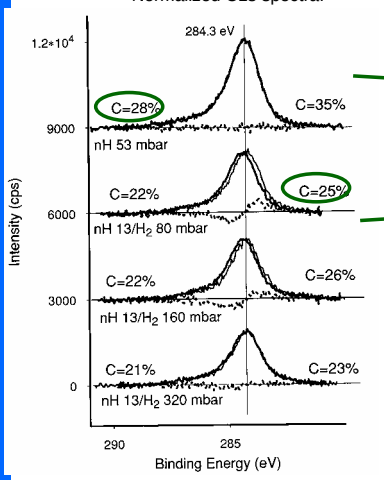
Analogous catalytic spectroscopic and catalytic studies.

- XPS and UPS measurements after *in-situ* treatments at 483 or 603 K.
- Catalytic testing in a closed-loop reactor, V=70 ml [5].
  1. Carbonizating pretreatments: different mixtures of hexane (nH) and H_2 at 483 or 603 K for 20 minutes.
  2. Test reactions (5 min): transformation of hexane, p(nH):p(H_2)=13:160 mbar, T=603 K. Products: fragments (<C_6) isomers, methylcyclopentane (MCP), hexenes and benzene.

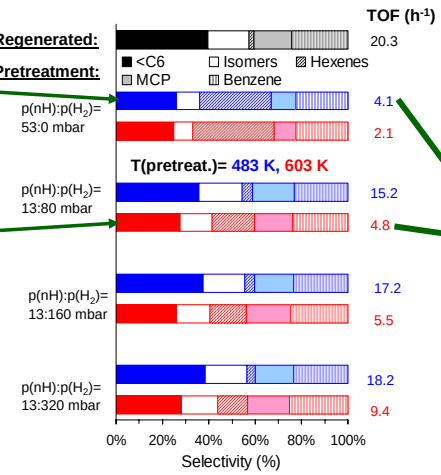
RESULTS AND DISCUSSION

Differences in XPS C 1s peaks
after two pretreating temperatures with various mixtures of nH and H_2

Normalized C1s spectra!

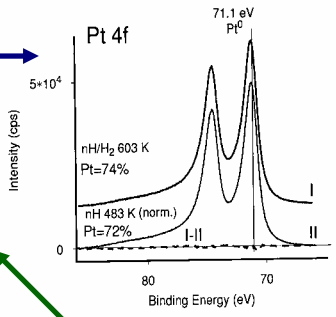


Activities and selectivities
(in test reactions):



Comparison of two selected pretreatments
with equal amounts of carbon

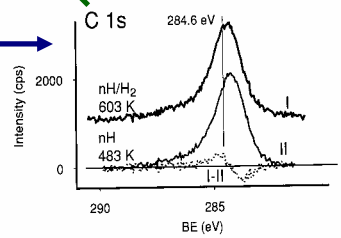
Pt 4f peaks normalized: same shape in both cases.



"Massive C":

- slightly less residual **activity;**
- stronger **selectivity** changes.

- C 1s peaks as measured:, similar amounts of C but in different state: 483 K, with no H_2 ➔ more "massive" C.



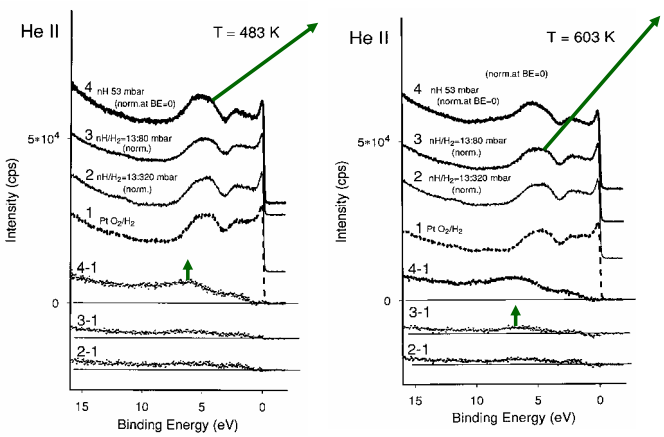
XPS: No difference after treatments with no H_2 and at the highest H_2 pressure; excess in the "PtC" region at 483 K and excess in the "massice carbon" region at 603 K at intermediate H_2 pressures.

Catalysis:

– No H_2: marked activity loss; selectivities: C_6 saturated ⇩, hexenes ⇧.
– With H_2: much less activity loss at 483 K; selectivities closer to that of regenerated Pt.
– More H_2: selectivities at 483 and 603 K gradually approach each other.

Differences in UPS

T=483 K Spectra normalized at the Fermi-edge. **T=603 K**



- **UPS: "overlayer-type" carbon deposit without H_2;**
- **Much less C accumulation with H_2.**
- **Small difference between 483 and 603 K.**

CONCLUSIONS

⇨ **Up to 20% C on regenerated Pt [5] ➔ "invisible carbon" [6].**

⇨ **More C with less H_2 and higher T.**

⇨ **XPS ⩓ T influences the state of C at intermediate p(H_2); the effect disappears with no H_2 AND at highest p(H_2). Hardly any chemical interaction between Pt and C.**

⇨ **UPS ⩓ carbon is present as a surface overlayer.**

⇨ **Residual activity is affected mainly by the amount of carbon and is much higher after treatments at 483 K.**

⇨ **More "massive" carbon decreases the selectivities of C_6 saturated products: MCP and isomers while hexene selectivity increases.**

ACKNOWLEDGEMENT

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