Novel platinum/carbon catalysts with cluster size control for hydrogen fuel cells

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Project Overview

At present, ca. 25 g Pt per 50 kW PEM fuel cell (electrode: 0.32 mg cm^{-2}). Pt ~ \$22 g^{-1}

Aims of project:

- **Reduce Pt requirement**
- **Ideally replace Pt with cheaper, more abundant metal**

Approach:

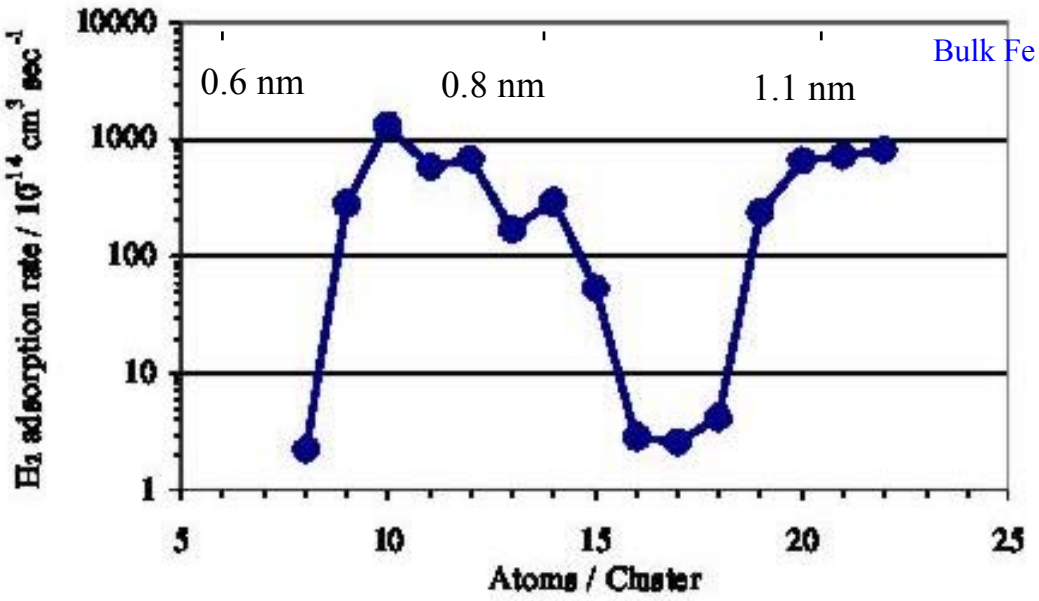
- **Cluster chemistry via Mass Spectrometry**

  H_2 *vs.* CO adsorption rates

- **Chemical synthesis of optimal clusters**

Cluster Chemistry

H_2 adsorption onto Fe clusters

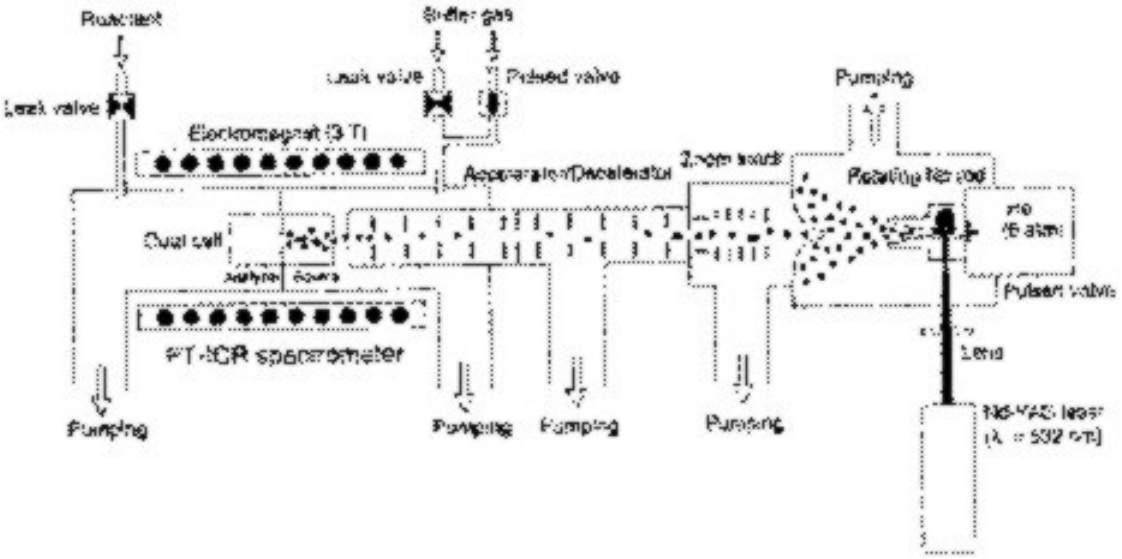


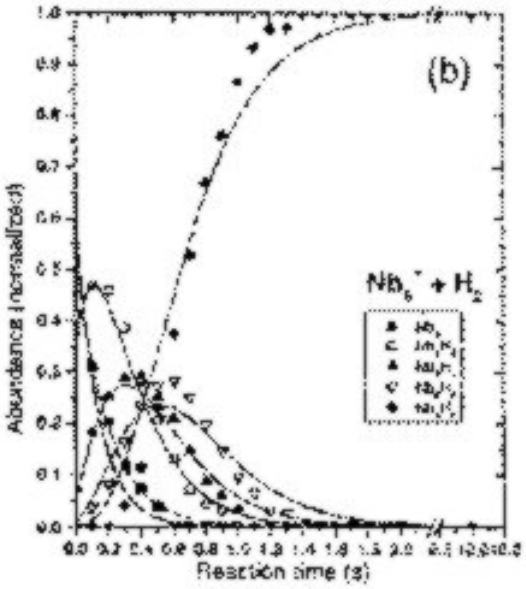
- **Large differences in H_2 adsorption rate as function of cluster size**
- **Adsorption rate of CO onto TMs varies by factor of only 2-3**

Riley and Parks, *NATO ASI Ser. B*. **158**, 727, (1987)

Cluster Chemistry

Laser Ablation FT Mass Spectrometry: adsorption of H_2 and CO by clusters of known size





Vakhtin and Sugawara, *Chem. Phys. Lett*. **299**, 553, (1999)

Catalysts and Supports

Typical catalyst

10 – 20wt.-% Pt or Pt/Ru on carbon

Issues: control of crystallite/cluster size
loss of surface area through sintering

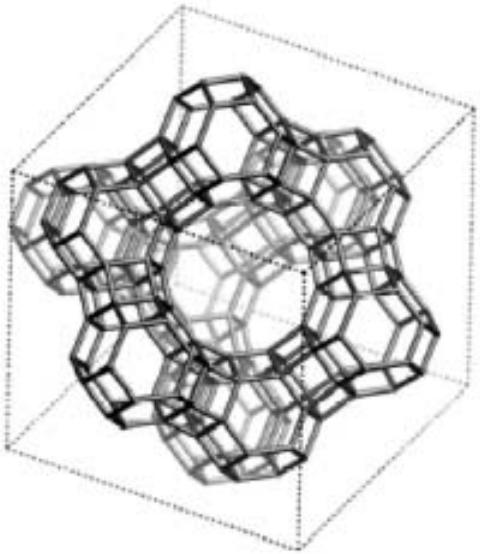
Carbon required for electron conduction

Novel model catalysts

Pt-zeolite/carbon composite

- Crystallite size control
  - ion exchange level
  - thermal treatment
- Reduced sintering
  - constraints of cavity & carbon matrix

Pt-zeolite Preparation



Zeolite X (FAU)

1.3 nm cavity

0.74 nm window

Si/Al 1.2 – 2.0

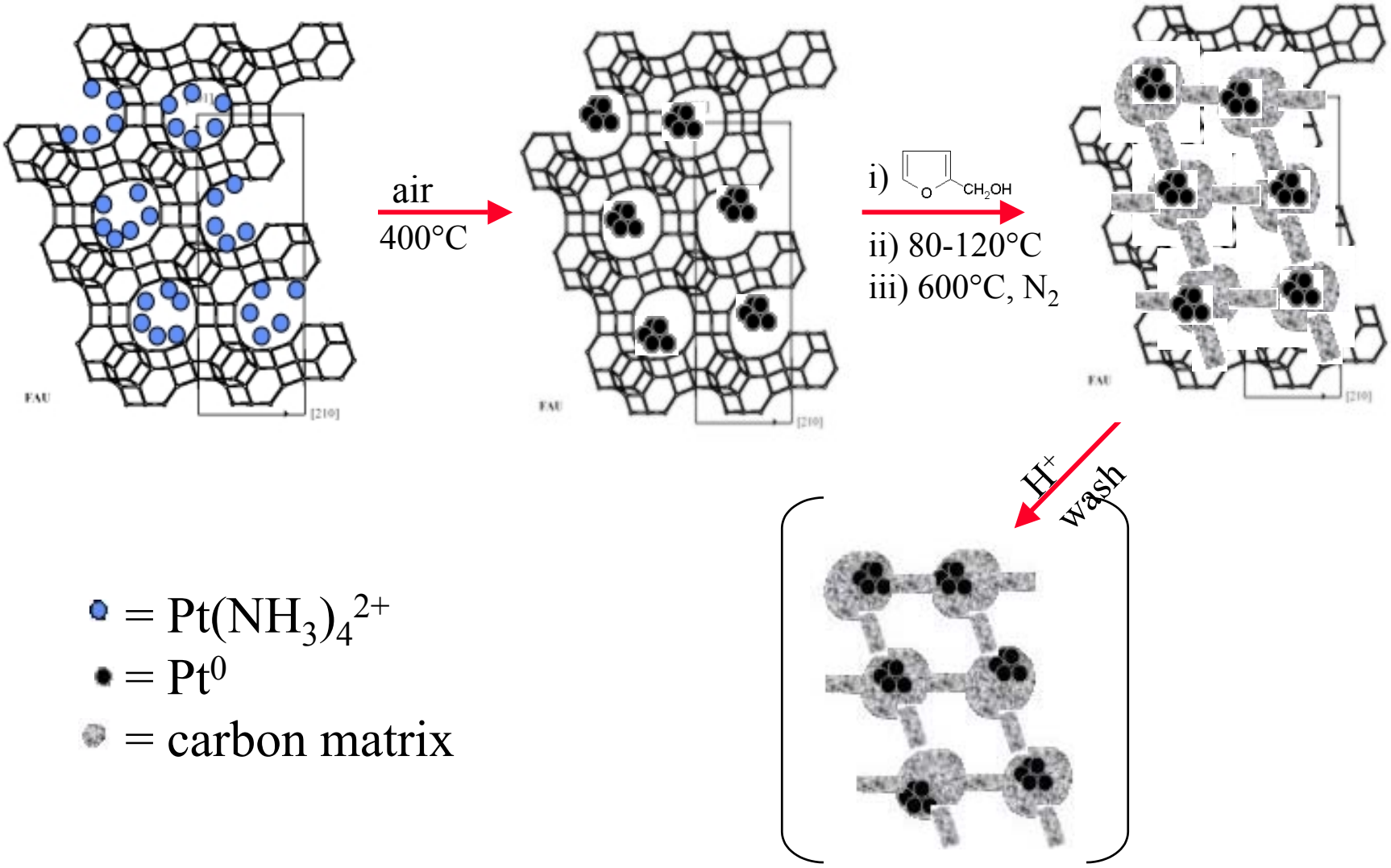
High ion exchange capacity

NaX powder (Aldrich 13X); Si/Al = 1.8; 630 m^2g^{-1}

Ion exchange 1-3x with 0.025M $Pt(NH_3)_4(NO_3)_2$ @ 80°C

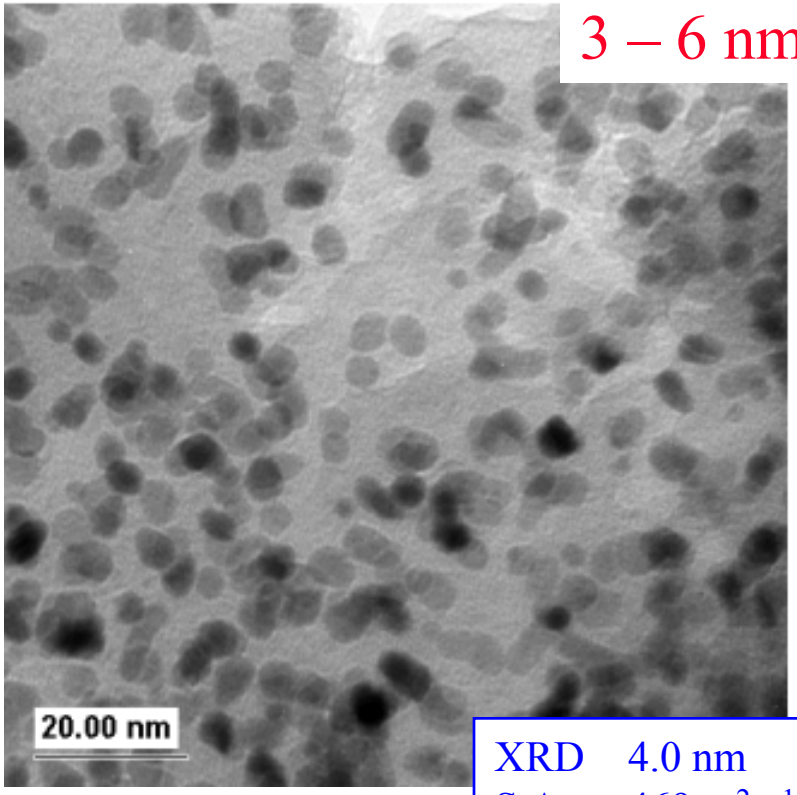
→ 10 – 20wt.-% Pt (25 – 50% capacity)

Catalyst Preparation



20wt.-% PtX, heated to 400°C in air

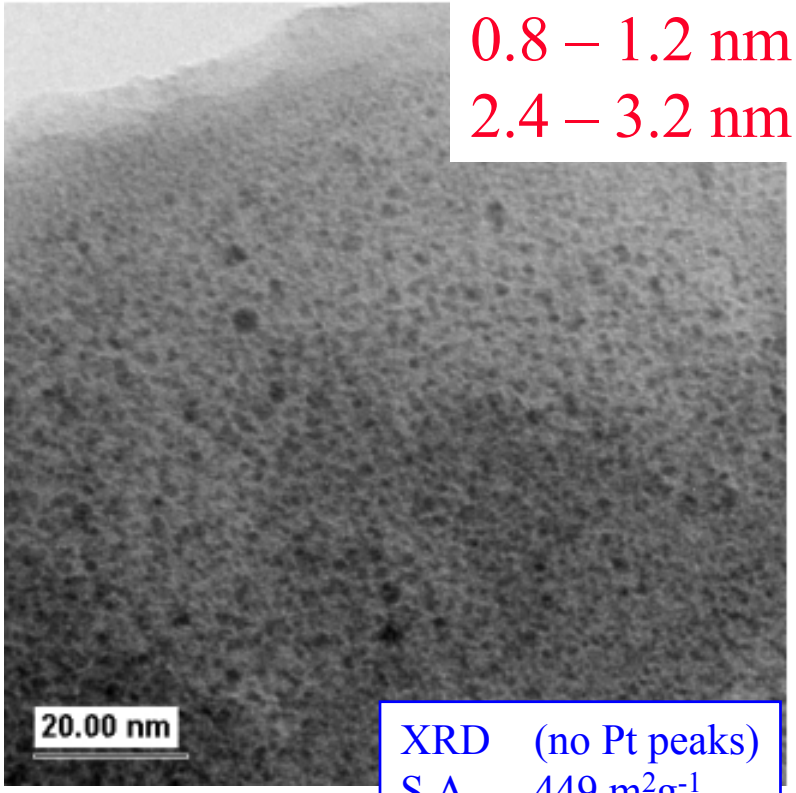
5 °C min^{-1}



3 – 6 nm

XRD 4.0 nm
S.A. 469 m^{2}g^{-1}

< 1 °C min^{-1}

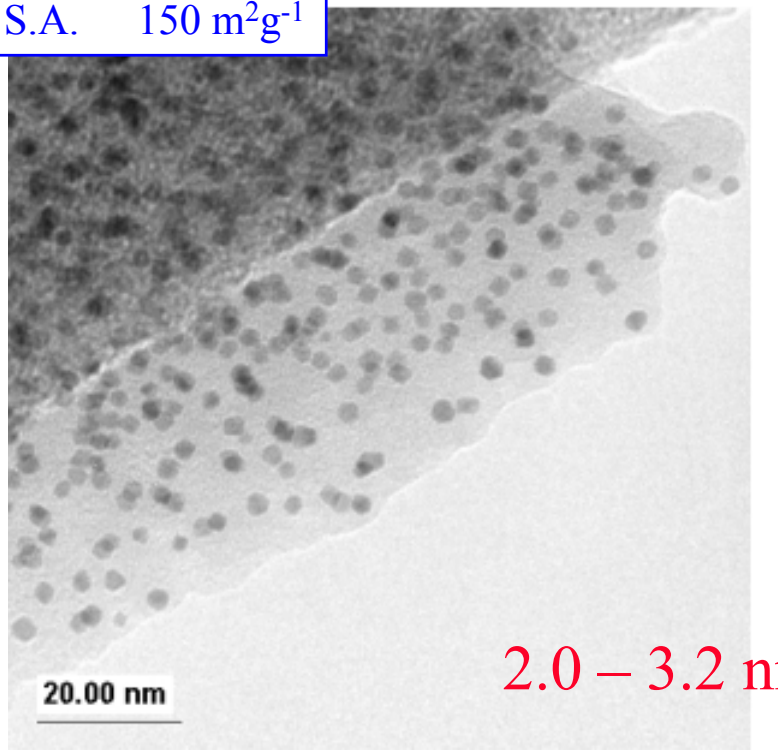


0.8 – 1.2 nm
2.4 – 3.2 nm

XRD (no Pt peaks)
S.A. 449 m^{2}g^{-1}

20wt.-% PtX/Carbon composites

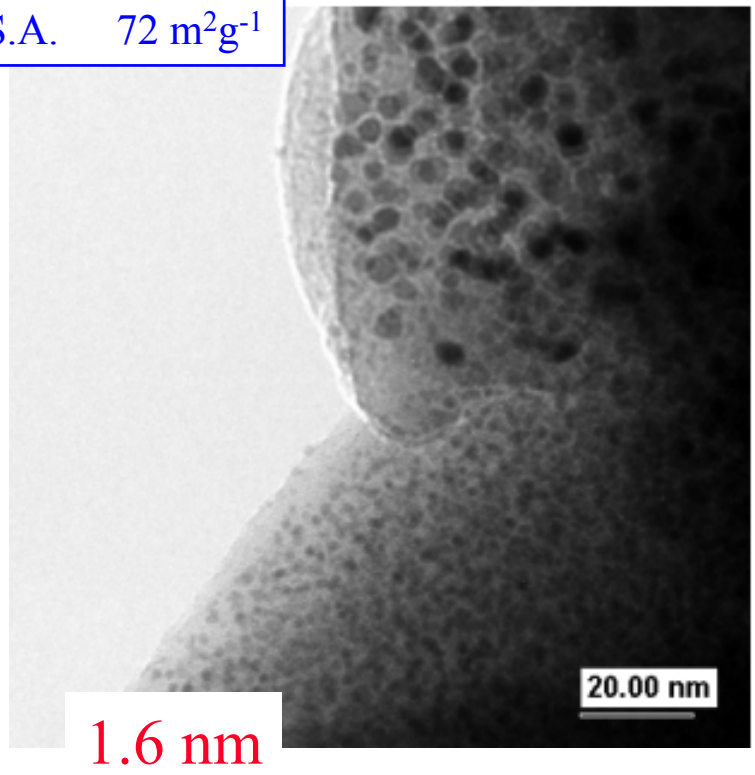
XRD	3.4 nm
C	3 wt.-%
S.A.	150 m^2g^{-1}



i) FFA/120°C; ii) N_2/600°C

XRD	4.2 nm
C	3 wt.-%
S.A.	72 m^2g^{-1}

2.4 – 4.0 nm



i) 400°C; ii) FFA/120°C; iii) N_2/600°C

Summary

Pt-exchanged zeolites/carbon

- Model system for cluster control
  - ion exchange level
  - carbon loading
  - heat treatment

- Narrow cluster size dispersions obtained at sizes across range 0.8 to 3.2 nm (*ca*. 12 to 300 atoms)

- Pt is electrochemically active in zeolite/carbon composite

- Zeolite may be removed by acid treatment