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Comparative Catalytic and Photocatalytic Reduction of NO_3^- by the In Situ Generated Solar H_2 over Pt-Cu/TiO_2 Catalysts

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Introduction

-**Nitrate** - one of the most common problems regarding possible contaminants of groundwater;
-**Promising technology**- Catalytic hydrogenation of nitrate have been proposed for the first time by Vorlop et al.[1];
-**Studies**-Reaction mechanism based on catalytic reduction over bimetallic catalysts using a noble metal (Pd, Pt) and a transition metal (Cu, Sn, In) in the presence of hydrogen as the reductant[2];
-**The photochemically produced hydrogen** could play an important role for the effective reduction of NO_3^-;
-**Assumption**-In structure sensitive reactions, N-N bond formation rates is related to preferential orientation of Pt nanocrystal facets[3].

Objectives

-**To develop** materials in order to study the nitrate removal from aqueous phase;
-**To tackle nitrate removal** from aqueous phase by two approaches: (i) nitrate catalytic reduction by external H_2 (dark reaction) and (ii) nitrate photocatalytic reduction by in situ generated H_2 under UV-light irradiation;
-**To study the effect of well-defined Pt Np's** loading on the catalytic reactivity;
-**To make deeper insight** into NO_3^- catalytic reduction and photocatalytic reduction mechanisms;
-**To study the ability of obtaining and using** the in situ generated H_2 as reducing agent.

Materials and Methods

MATERIALS
- **Support**:TiO_2 P-25
- **Metals precursors**: $H_2PtCl_6 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$
- **Thermosensitive polymer**[4,5] : triblock copolymer structure - consist in a poly(ethylene glycol) (PEG) middle block (PEG, Mn≈4000 Da) and poly(NIPAM-co-TBAM) statistical copolymers as side chains (3 mol% TBAM in the initial monomer mixture)
- **Prepared catalysts**

	Denomination
2wt% (Pt-Cu)/TiO2	Pt-Cu I
0.5wt% Pt/2wt% (Pt-Cu)/TiO2	Pt-Cu D
1.5wt% Pt/TiO2	Pt I
0.5wt% Cu/TiO2	Cu I

- **Thermosensitive polymer**[5,6]-used to control the structure and growth of the Pt nanocrystals

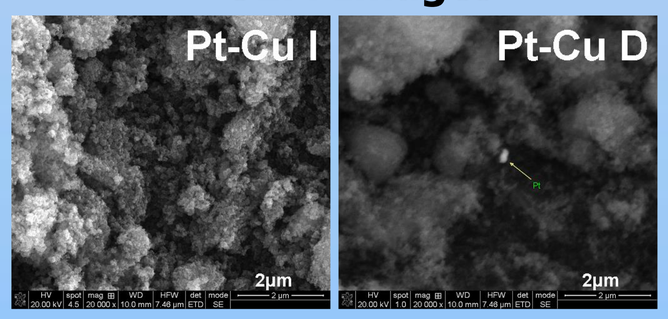
Characterization
- Scanning Electron Microscopy (SEM);
- Transmission Electron Microscopy (TEM);
- CO Pulse Chemisorption;
- UV-Vis analysis.

Catalytic tests
- Catalytic hydrogenation of aqueous nitrate solution in dark conditions by external H_2 supply;
- Photocatalytic aqueous nitrate solution;
- Water splitting under ultraviolet (UV) light irradiation.

Results

SEM Images

Pt-Cu I (Wetness impregnation)

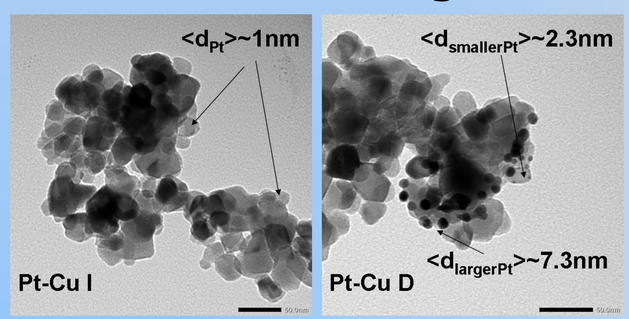


Fine Pt particles (<1nm) on TiO_2

EDS mapping and spectra confirmed the presence of Pt and Cu on the TiO_2 surface

Pt-Cu D (Pt Np's deposition)

TEM Images



Round-shaped Pt Np's of about 7-10 nm are obtained with the thermosensitive polymer

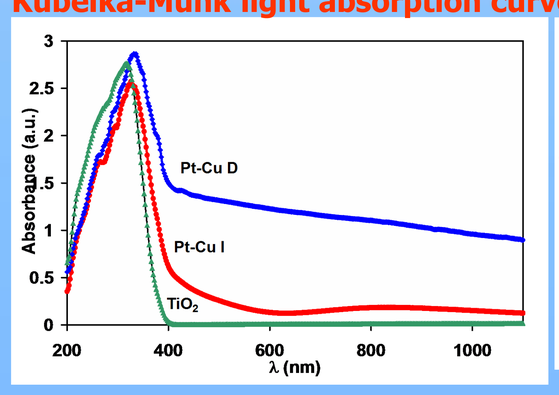
CO Pulse Chemisorption Data

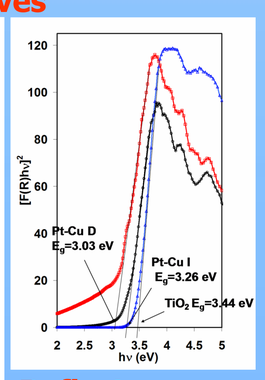
Catalyst	Met. Surf. Area (m^2/g)	Pt Crystallite Size (nm)	Pt Dispersion (%)
Pt-Cu I	1.63	0.86	43.96
Pt-Cu D	0.92	2.03	18.61

Decreasing the particle sizes results in improved dispersion and an increase in the number of active sites on the surface of the catalyst.

UV-Vis Spectra

Kubelka-Munk light absorption curves

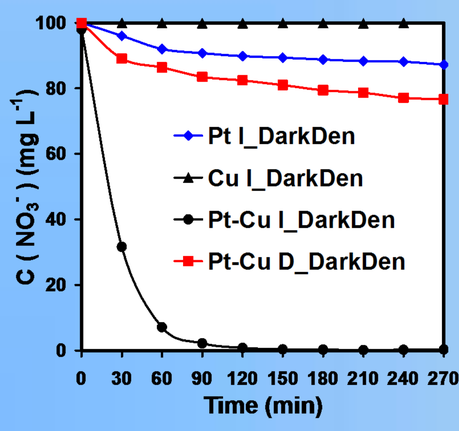




E_g (TiO_2) > E_g (Pt-Cu I) > E_g (Pt-Cu D)

Reflectance [F(R)] spectra

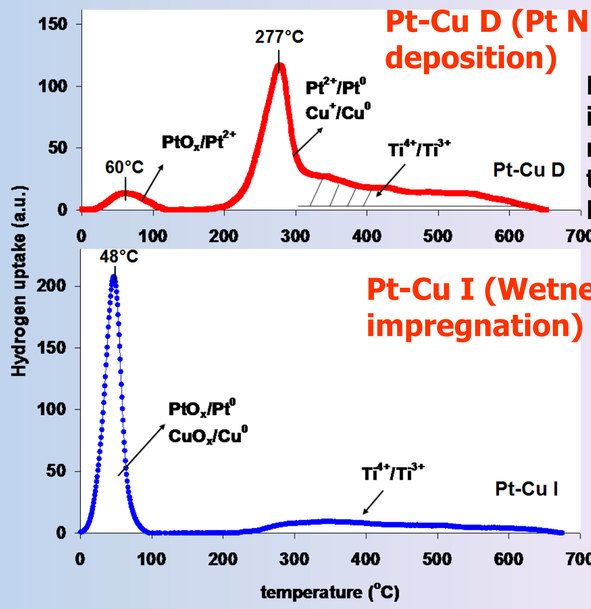
DarkDenitration



Catalytic hydrogenation of aqueous nitrate solution by external H_2 supply

Pt-Cu I has a better ability in nitrate removal

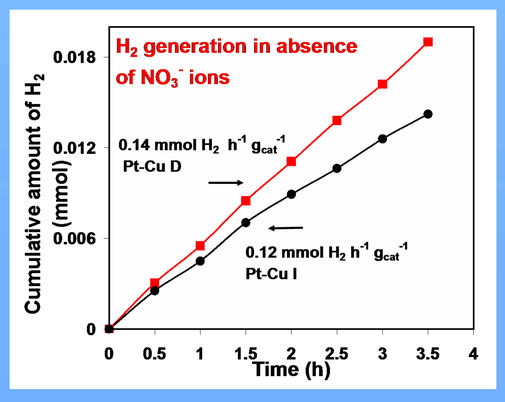
TPR Profiles



Larger Pt Np's-increase in the reduction temperature of Pt species

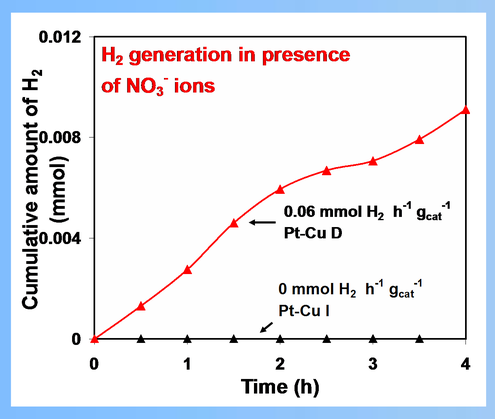
Pt and Cu each make the other more reducible

Hydrogen Generation under UV-light



Photocatalytic test for water splitting

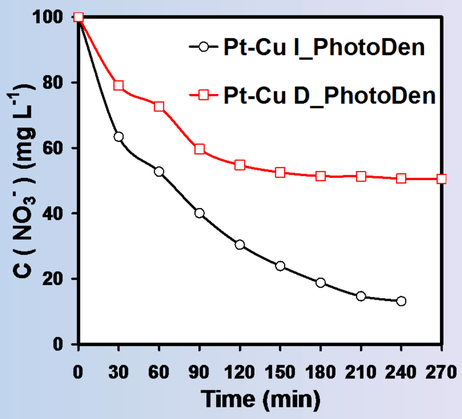
The H_2 production was more favored with Pt Np's deposition and was sensitive to surface morphologies of Pt Np's



Photocatalytic denitration test

The absence of H_2 when Pt-Cu I is used as catalyst is due to H_2 consumption by reaction with NO_3^-

PhotoDenitration



Photocatalytic nitrate reduction by the in situ-generated H_2 under UV-light irradiation

There was no H_2 formation with Pt-Cu I: either H_2 is not generated or H_2 is produced but consumed in the reduction of nitrate.

Conclusions

- The Pt-Cu I catalyst activity for the nitrate reduction can be directly related to the interactions between Pt and Cu, as well as to the high dispersion of fine Pt particles (<1nm) on TiO_2
- The photogenerated H_2 can be used in reduction reactions by a catalyst capable of activating hydrogen (external supply or generated in situ)
- The H_2 production under UV-light was more favored with Pt Np's deposition
- Our future investigation aimed to optimize the photocatalytic system having as future possible applications for hydrogen production using sunlight and water as the hydrogen source for catalytic hydrogenation reactions

Acknowledgements

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