Production and Storage of Hydrogen Using C1 Chemistry

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Overview

Timeline

- Start: June 2, 2005
- End: June 1, 2008
- 28 % complete

Barriers

- Produce hydrogen from coal with minimum CO_2 production.
- Hydrogen storage/carrier media.

Budget

- Total project funding
  - DOE - $6,000,000
  - CFFS - $1,500,000
- Funding received in FY05 - $2,000,000

Partners

CFFS: U of Kentucky, West Virginia U, U of Pitts., U of Utah, Auburn U

Advisory Board: Eastman, ConocoPhillips, Chevron Texaco, US Air Force, US Army

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Objectives

- Develop innovative technology for producing hydrogen from coal-derived syngas or from hydrogen rich liquids and gases produced from coal-derived syngas.
- Develop better methods of producing hydrogen-rich liquids and gases from coal.

Approach

The Consortium for Fossil Fuel Science includes professors and students from five universities – **Kentucky, West Virginia, Pitt, Auburn, and Utah.** They are conducting a collaborative research program focused on the production of hydrogen and clean hydrogen-rich liquids and gases from coal using **C1 chemistry.**

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Accomplishments

Because this is a new contract, most of the research projects being addressed have been underway for less than a year. One exception is a project at the University of Kentucky dealing with the production of hydrogen by **Non-Oxidative Catalytic Dehydrogenation**, which began in our previous DOE contract and continued into the current program. This project will be the primary focus of this presentation and its accomplishments will be discussed in detail. Accomplishments of the other, newer, research projects in the CFFS hydrogen research program will be summarized more briefly.

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Accomplishments – Catalytic Dehydrogentation

- Binary Fe-M (4.5%Fe-0.5%M/Al_2O_3, M=Ni, Mo, or Pd) catalysts have excellent activity and lifetimes for non-oxidative dehydrogenation of gaseous alkanes, yielding pure hydrogen in one step. No CO or CO_2 is produced.
- Carbon is produced primarily in the form of nanotubes. Multi-walled nanotubes (MWNT) are dominant but stacked-cone nanotubes (SCNT) are easily produced by varying the temperature and feed gas.
- A continuous process for catalytic dehydrogenation of methane using these catalysts was developed using a mixed-mode, fluid-bed/fixed bed, reactor.

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Accomplishments – Catalytic Dehydrogentation

- Mössbauer and XAFS spectroscopy indicate that the active phase is an Fe-M-C austenitic alloy bound to the alumina by an Fe-aluminate, hercynite.
- Fe-M alloy catalysts on Mg-Al oxide have been tested. Although the hydrogen production is lower, the nanotubes are easily cleaned by dissolving the support.
- Pt nanoparticles on SCNT are excellent catalysts for stripping hydrogen from high hydrogen content liquids (cyclohexane, tetralin, decalin, etc.) leaving rechargeable aromatic phases.

Accomplishments of newer CFFS projects

- A process for co-production of hydrogen and methyl formate from methanol has been developed. ***U. of Pittsburgh***
- Promising catalysts for the water-gas shift (WGS) reactions were prepared by gas phase deposition of dispersed Pd nanoparticles on ceria aerogels. ***U. of Utah***
- Low temperature aqueous reforming of ethylene glycol and other polyols yields large percentages of hydrogen with very little CO. ***U. of Pittsburgh***
- Reforming of methanol in supercritical water yields ~98% H_2 with CO and CO2 percentages <2 %. ***Auburn U.***

Accomplishments of newer CFFS projects

- Partial oxidation of propane was investigated using Pt/CeO2 catalysts. Proper adjustment of operating parameters were shown to yield a hydrogen-rich syngas. ***West Virginia U.***
- Projects focused on the production of hydrogen-rich liquid fuels via the Fischer-Tropsch (F-T) synthesis reaction are ongoing at all of the five CFFS universities and are discussed in a recent report and many publications that are available at our web site – www.cffs.uky.edu .

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Catalytic dehydrogenation

The remainder of this presentation presents a more detailed summary of CFFS research on catalytic dehydrogenation. The reactions of interest for gases are given below.

Methane: $CH_4 \rightarrow C + 2H_2$ (25 wt% H_2)

Ethane: $C_2H_6 \rightarrow CH_4 + C + H_2$

$\rightarrow 2C + 3H_2$ (20 wt% H_2)

Propane: $C_3H_8 \rightarrow CH_4 + 2C + 2H_2$

$\rightarrow 3C + 4H_2$ (18.2 wt% H_2)

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Catalysts Employed

- Binary Fe-based catalysts (0.5%M-4.5%Fe)/ γ-Al_2O_3 (M=Mo, Ni, or Pd)
- Prepared by co-precipitation and incipient wetness methods.
- Pre-reduced in hydrogen at 700 ºC for 2 hrs in situ in reactor.

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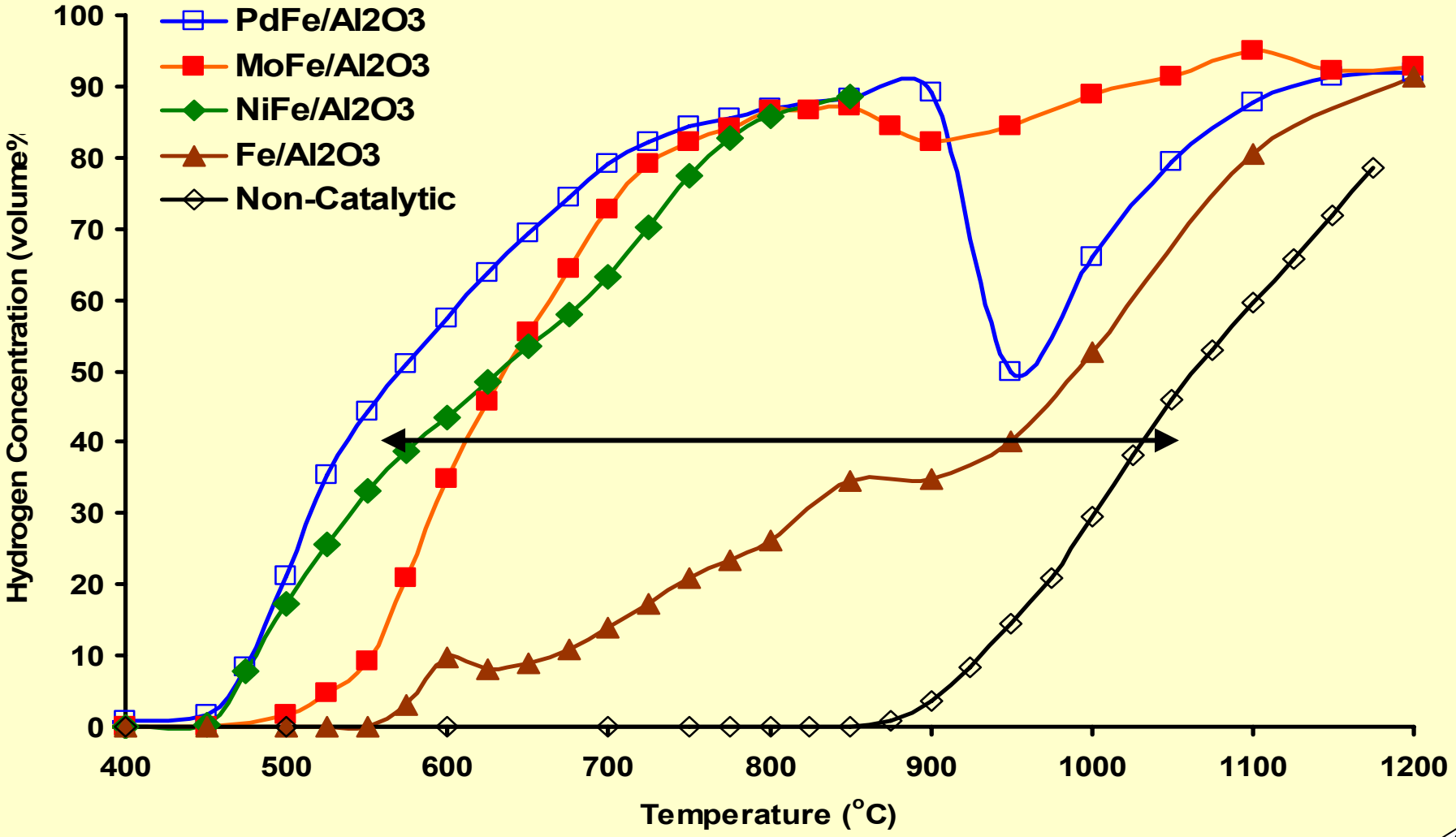
Catalytic Dehydrogenation of Methane



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Decomposition temperatures are lowered by 450-500 ˚C.
Hydrogen production is maximized at ~700-800 ˚C

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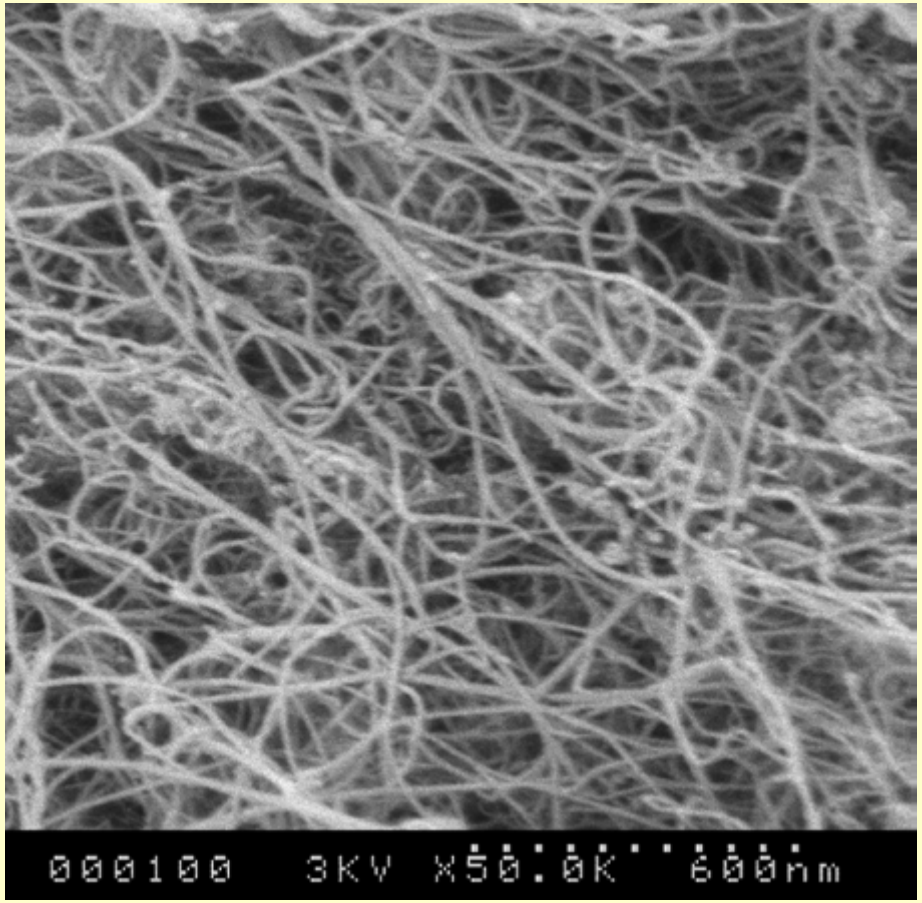
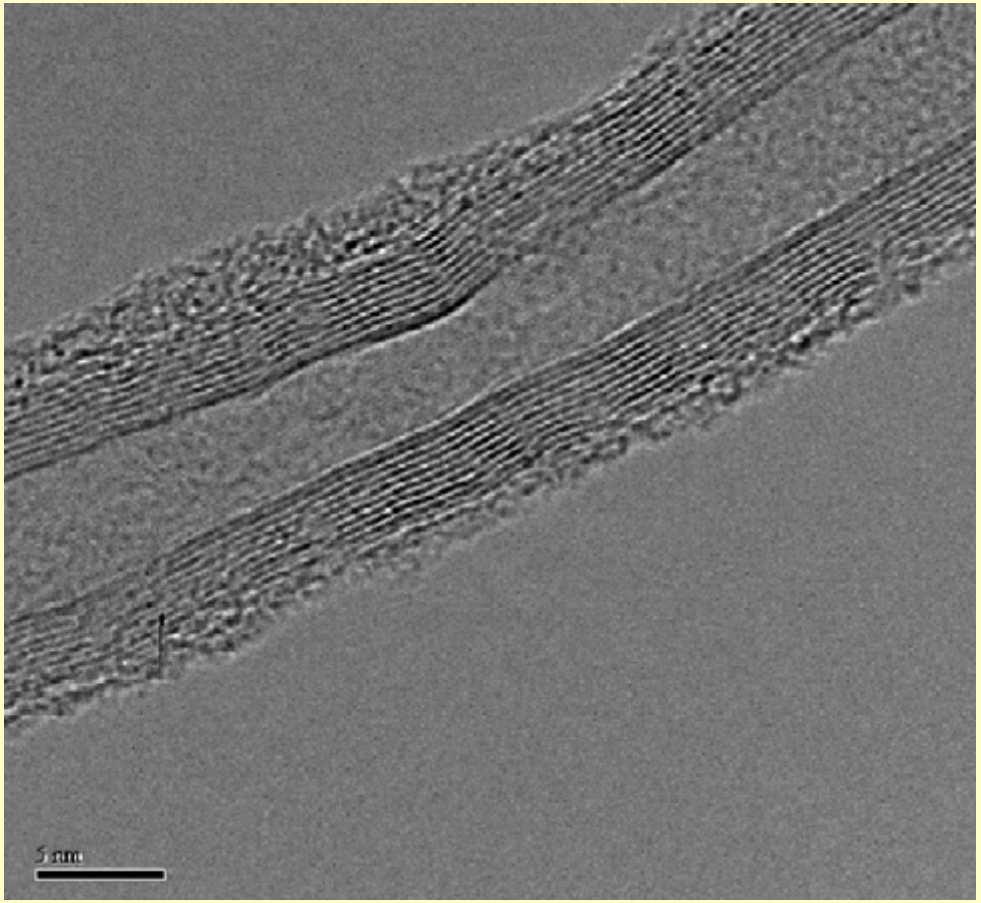


500 nm



5 nm

SEM and HRTEM of carbon nanotubes (MWNT) produced by decomposing undiluted methane at 700 °C over 0.5%Mo-4.5%Fe/ γ-Al_2O_3 pre-reduced at 700 °C

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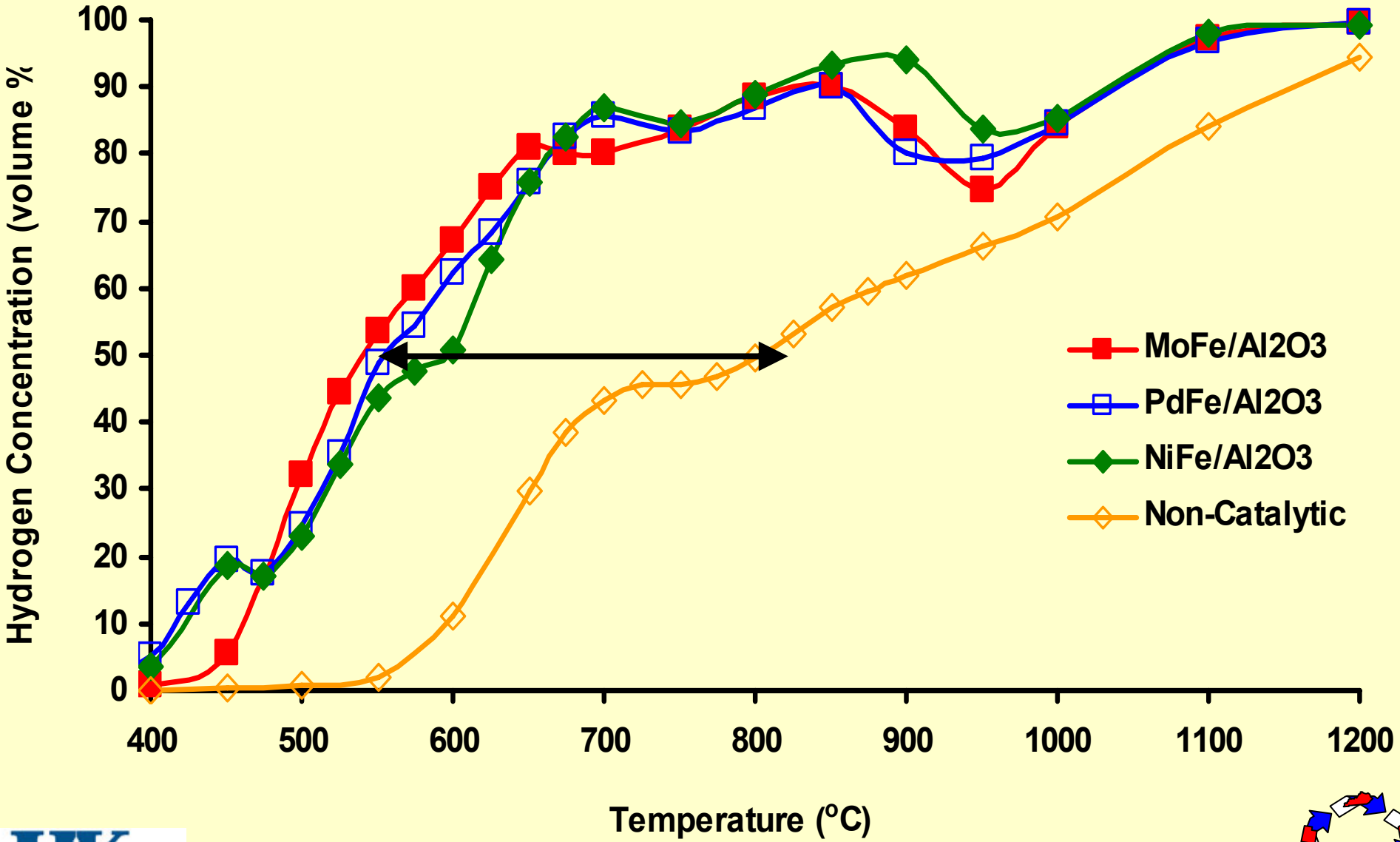
Catalytic decomposition of Ethane



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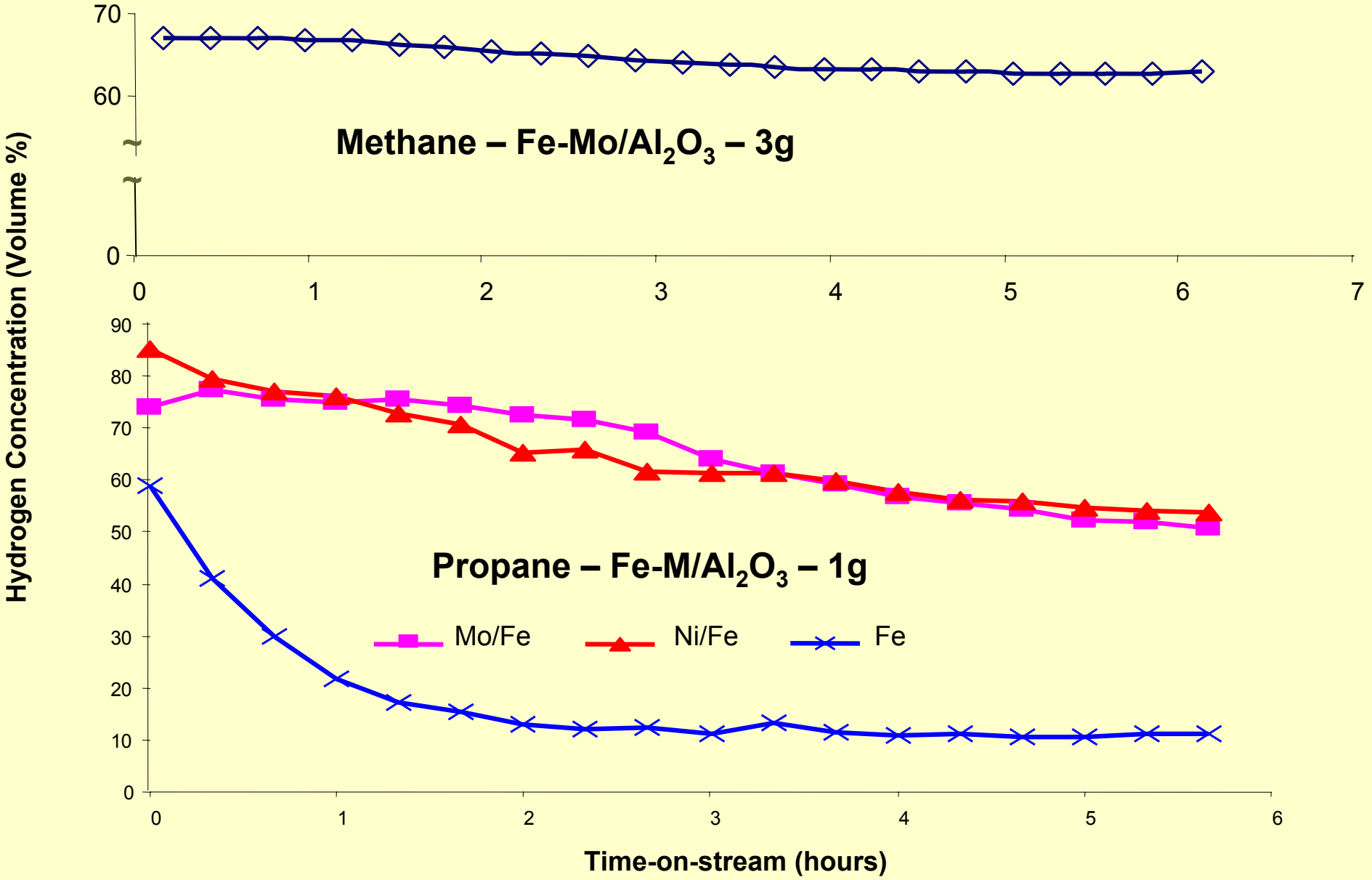

The catalysts exhibit reasonably good lifetimes, with deactivation rates of ~1-5% per hour in a plug-flow reactor.

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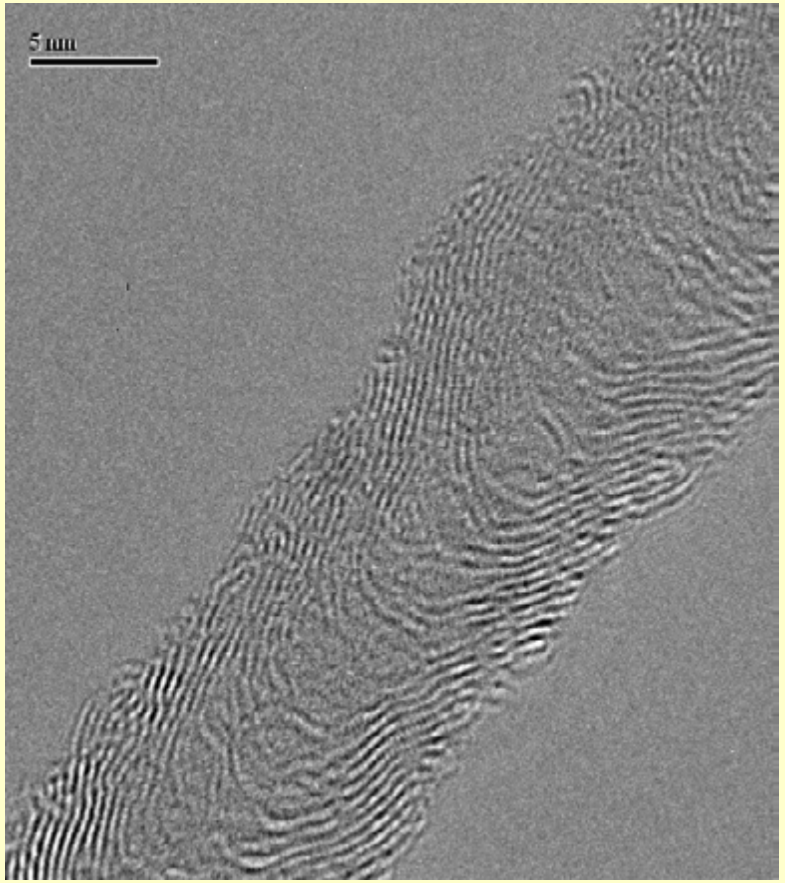
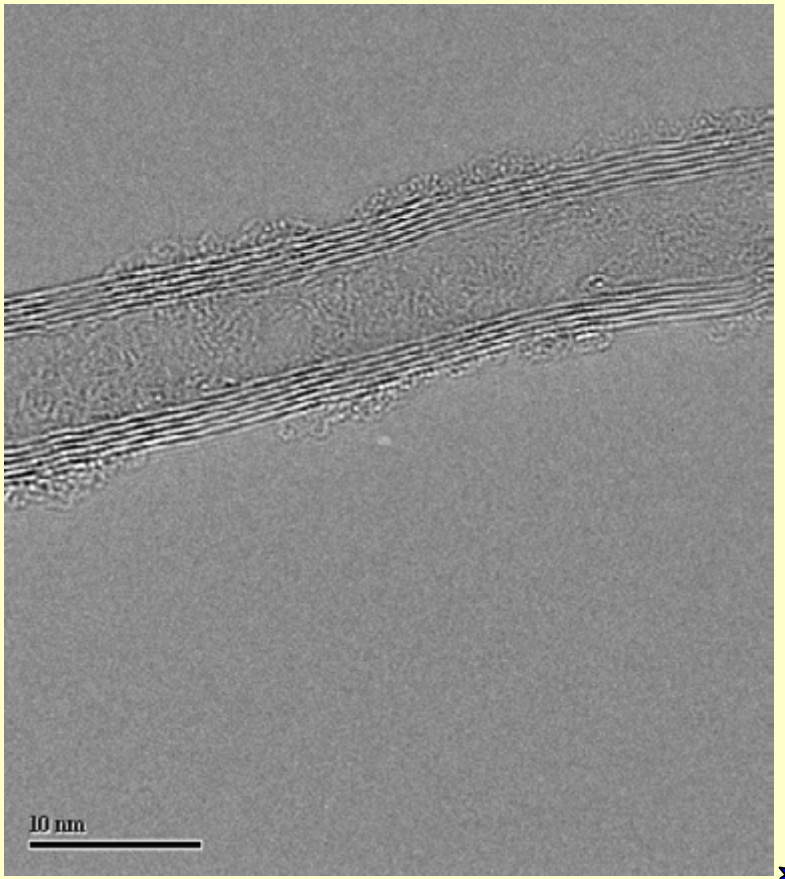
Stacked-cone nanotubes (SCNT) are produced from propane and ethane below 500 ºC and multi-walled nanotubes (MWNT) above 600 ºC.



SCNT



MWNT

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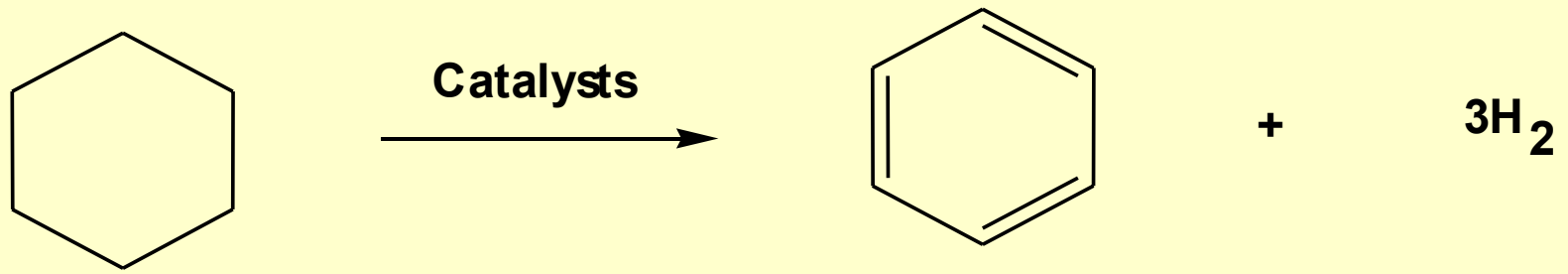
Fuel cell vehicles (FCV) require a high-hydrogen content liquid fuel as a hydrogen carrier

Examples: cyclohexane (7.1 wt.%)
methyl cyclohexane (6.5 wt.%)
decalin (7.2 wt. %)



Cyclohexane
1 mole

Benzene
1 mole/25%

Hydrogen
3 moles/75%

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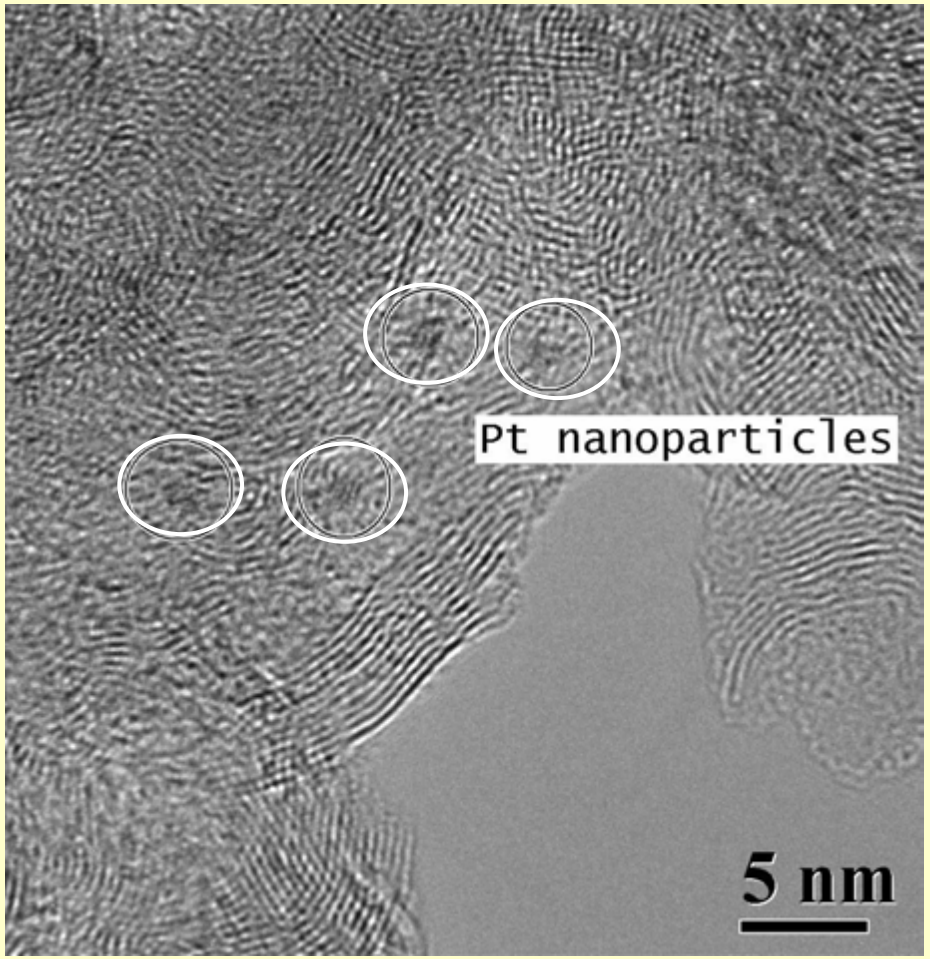
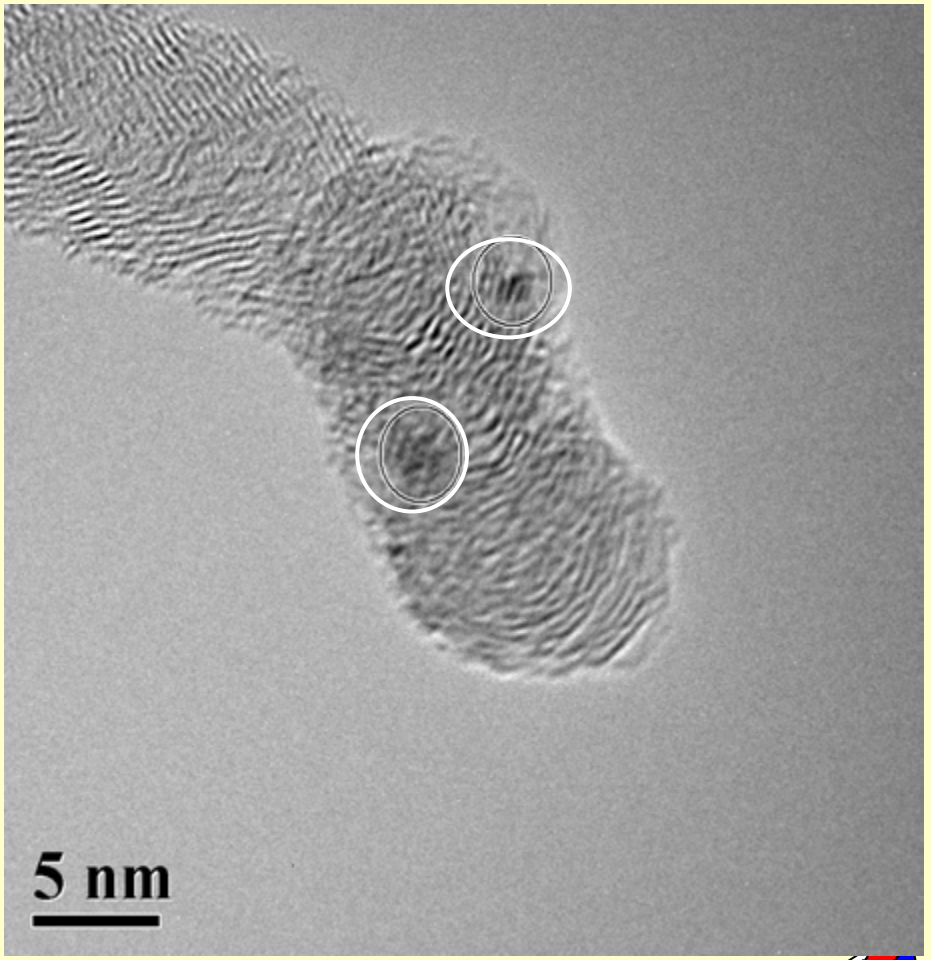
HRTEM of used catalysts 1%Pt/SCNT after dehydrogenation of cyclohexane at 315 °C. Note that the size of the Pt nanoparticles is only ~2-3 nm.





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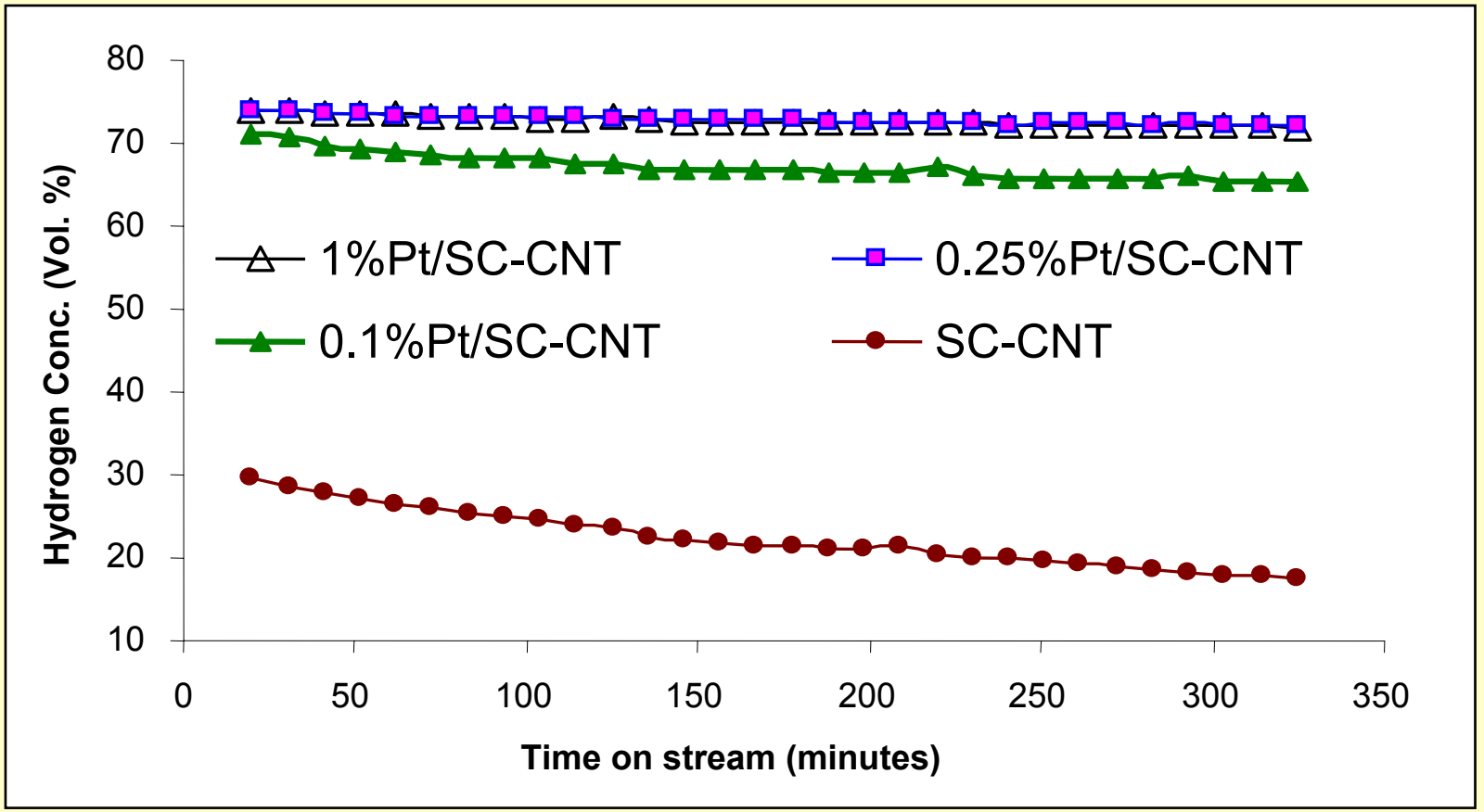
Hydrogen production from cyclohexane at 315 ºC by Pt/SCNT catalysts. 75 vol.% hydrogen represents conversion of cyclohexane to benzene and hydrogen. Similar results were obtained for methylcyclohexane.



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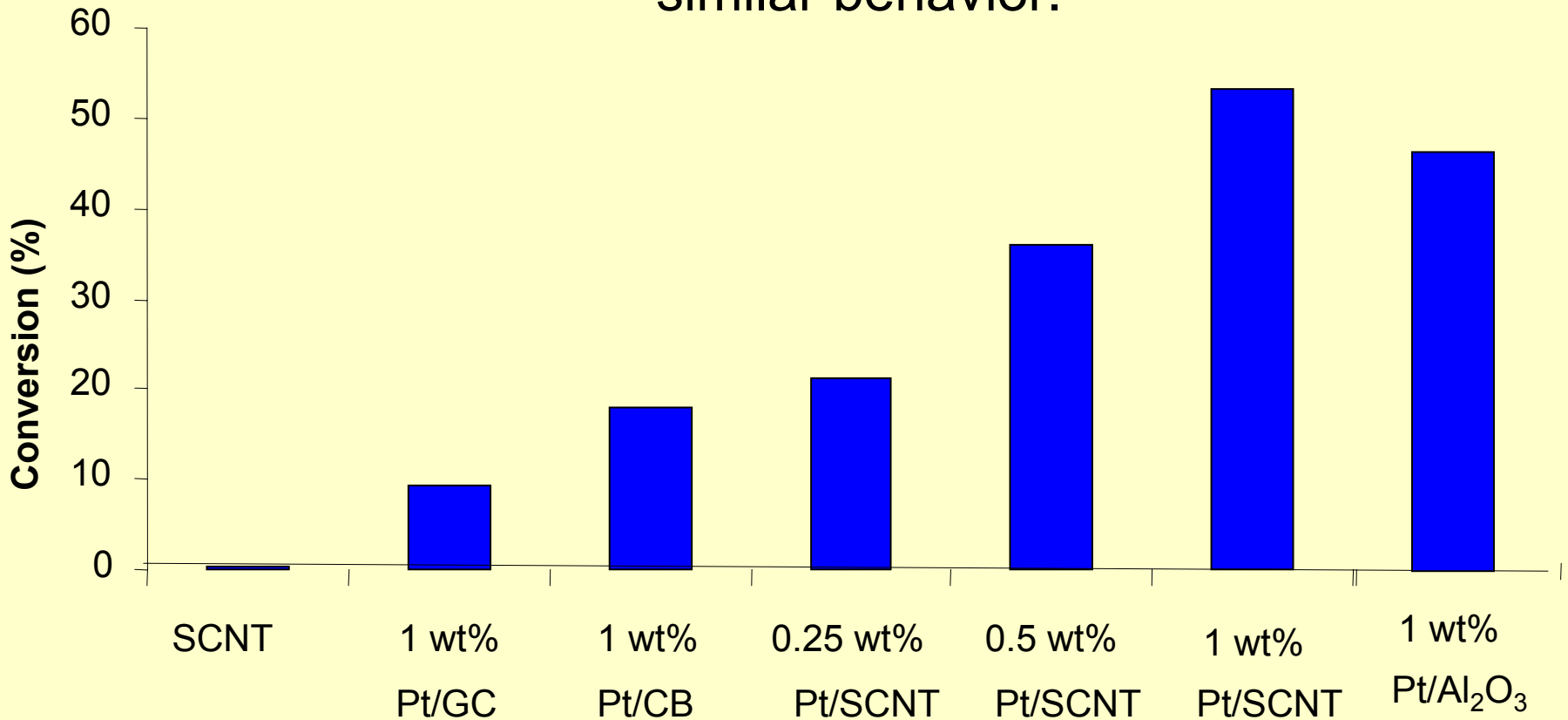
Comparison of Pt/SCNT to Pt on other supports (Al_2O_3, granular carbon/GC, and carbon black/CB) for tetralin dehydrogenation at 240 ºC. Decalin shows similar behavior.



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Summary

- Catalytic dehydrogenation is an alternative one-step method of producing pure hydrogen from hydrocarbon gases and liquids that produces no CO or CO_2. All carbon is produced as a potentially valuable by-product, carbon nanotubes.
- Although production of carbon nanotubes is preferable to producing carbon dioxide, large scale uses for nanotubes could make the process much more appealing.
- Partial catalytic dehydrogenation of liquid hydrocarbons may be a viable method of producing hydrogen on-board in vehicles, particularly if high hydrogen content liquids can be synthesized that can be dehydrogenated at <~100 ˚C.

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Future Work

- Develop new supports for Fe-M dehydrogenation catalysts that are easily dissolved and have good activity and lifetimes.
- Develop synthesis processes for monodisperse metallic nanoparticles (~5 nm) for dehydrogenation applications, both as supported and as unsupported catalysts (late 2006).
- Develop a continuous dehydrogenation reactor that utilizes unsupported nanoparticle catalysts and includes a spooling process for nanotube collection (2007).
- Develop liquids for vehicular applications that can be catalytically dehydrogenated/hydrogenated at ~100 ˚C (2007).
- Explore large scale uses for nanotubes; one possibility is as environmental sorbents.

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