Nanocatalysis and New Chemistry with Nanoporous Materials

2004. 10. 29
공업화학/화공학회 공동 나노심포지움

박 상 언
인하대 화학과

화학공학의 이론과 응용 제10권 제2호 2004년

LNGC Laboratory of Nano-Green Catalysis, Dep't of Chemistry, Inha Univ.

Contents

- Nanotechnology
- New Chemistry
- Nanocatalysis
- Nanoporous Materials
- Microwave Synthesis of Nanoporous Materials
- Fabrication via Microwave
  - Nanostacking
  - Nanofabrication via Nanoglue

Chemical Technology and Industry from 20th to 21st Century

	20 세기		21 세기
화학 기술	구조제어 (Structural Control)		기능제어 (Performance Control)
	분자제어 (Molecular Control)		양자제어 (Quantum Control)
	합성기술 (Synthesis)	→	분리기술 (Anti-Synthesis)
	환경이물질 (Foreign Substance)		환경공생물질 (Friendly Substance)
화학 산업	화학물질의 생산 (Production of Chemical Substance)		복합재료,화학 시스템 공급 (Supply of Complex Materials and Chemical Systems)

신화학의 특징

- 새로운 원료
- 성에너지화
- 생친화적
- 환경친화적
- 원료효율화
- 나노소재
- 초미세화
- 초고속화
- **Point of Use**

분자공학적
나노기술

Ryoji Noyori

Molecular Catalysis : Today and Tomorrow

Chemistry is beautiful, exciting, and beneficial for the Science of substances and materials

Logical basis of the science and nanotechnology.

Creation of high values from almost nothing.
Chemical synthesis with Practical Elegance.
Relative Efficiency vs Absolute efficiency

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Naphtha Cracking

Ethylene

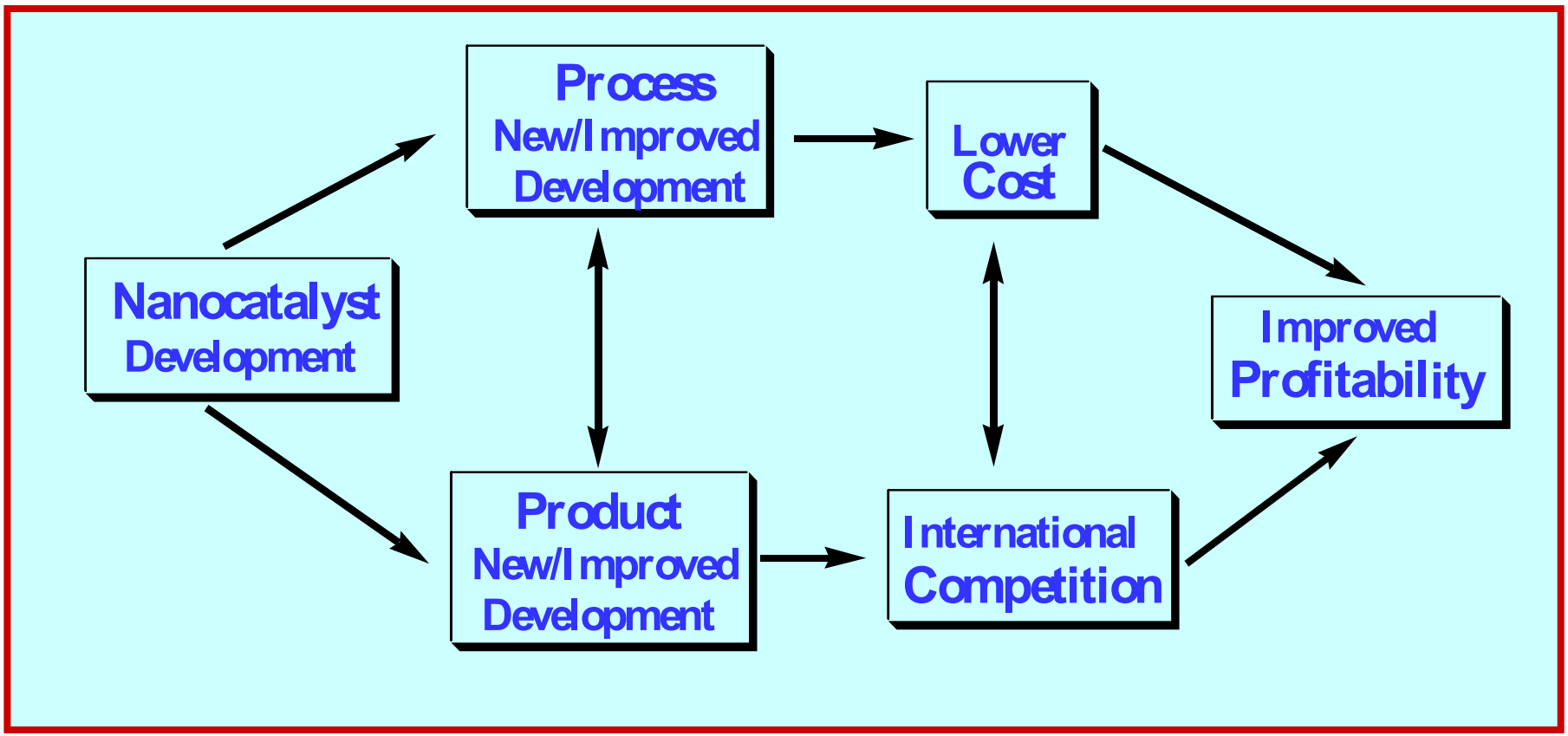
Propylene

Mixed C_4 (isobuthylene) → ✗ **MTBE**

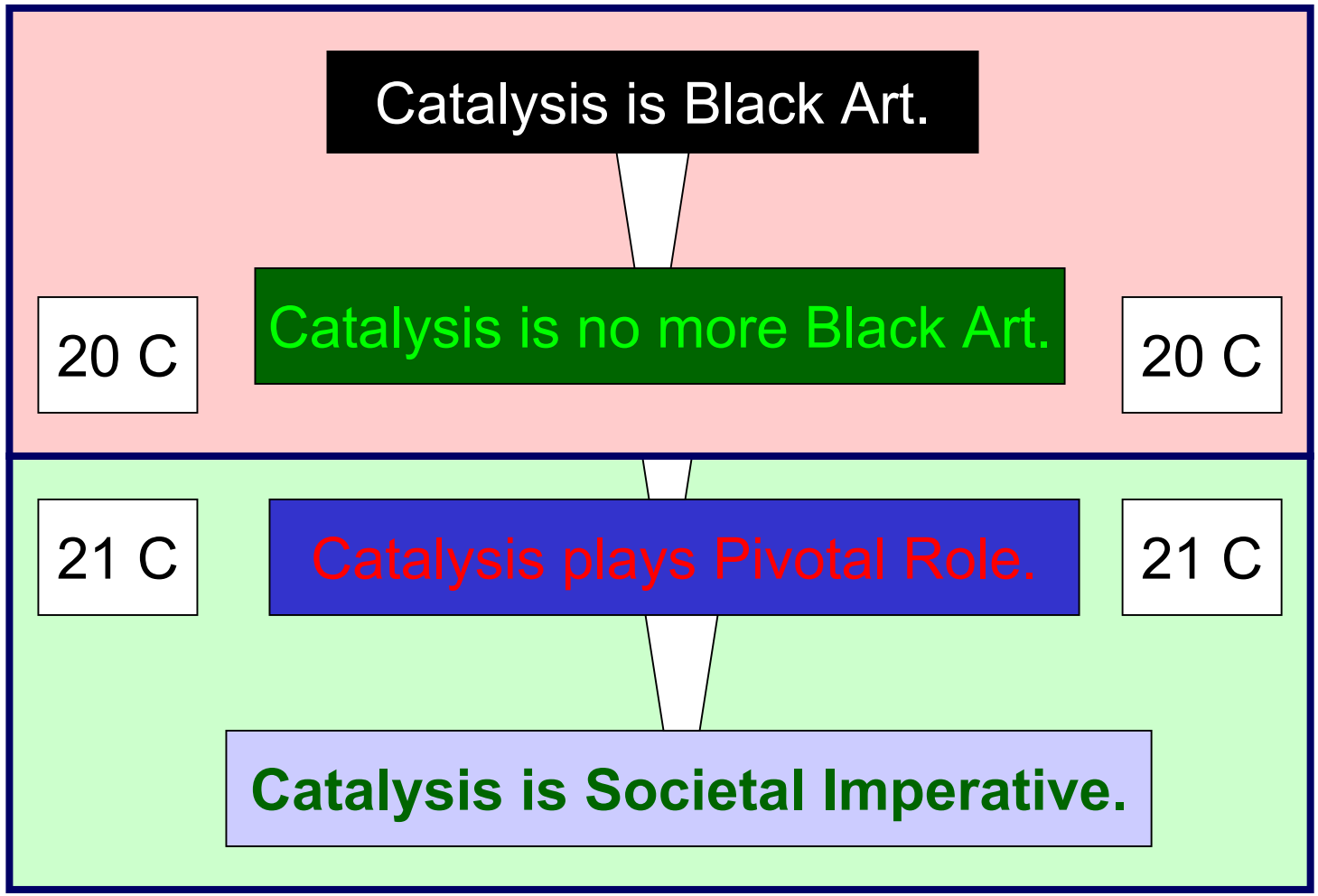
국내 생산량 **60**만톤/년

↳ 석유화학 재개편 필요

Impact of Nanocatalysts on Business Development



From Black Art to Nanocatalysis



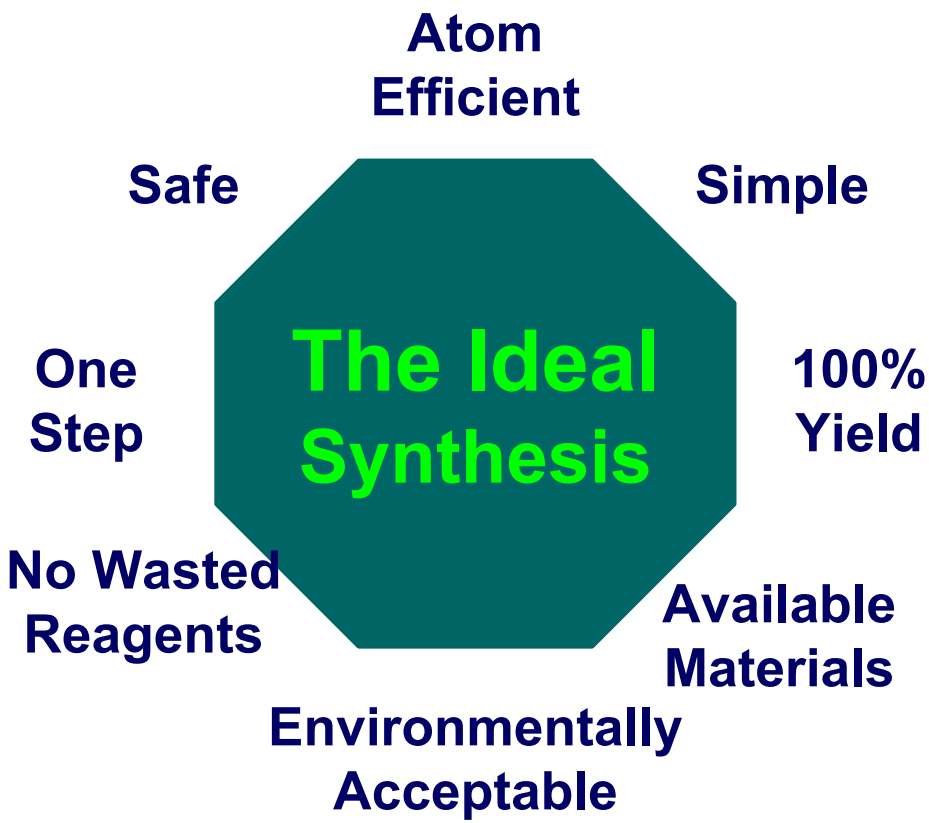
NanoCatalysis & New Chemistry

Nano for Sale

	Application	Company	Description
1	Catalysts	EXXONMOBIL	FCC
2	Data Storage	IBM	High Density Data Storage (nanoscale layering)
3	Drug Delivery	Gliead Sciences	Liposome(100nm lipid spheres)
4	Materials	Carbon Nanotechnolgy	Smalley
5	Materials Enhancement	Nanophase Technologies	Nanocrystalline particles(ceramics, sunblocks,catalysts)

"Understanding Nanotechnology," Scientific American(2000).

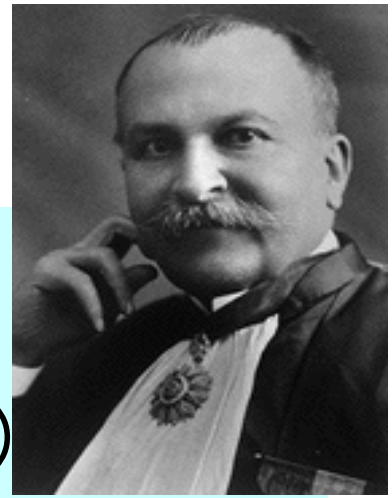
Nanocatalysis for New Chemistry



Catalysis is required to play as a Pivotal Role.
Somorjai, UC. Berckely

- One-Step Reaction
- Green Chemistry
- Environmental Catalysis
- Biomimic
- Miniaturization for
- Hi-Speed Screening

History of Nanocatalysis



- 1st Example
  - Nobel Prize in Chemistry for 1912
  - with Victor Grignard(Grignard reagent)
  - For hydrogenating organic compounds in the presence of **finely divided metals**
  - Postulation of the **unstable intermediaries**
  - for the margarine, oil hydrogenation, and synthetic methanol industries.
  - Selectivity of catalytic action and also the selectivity of catalysts to poisons, as well as introducing the **use of supports** and showing the **enhanced activity**

Catalysis in Organic Chemistry (1913).

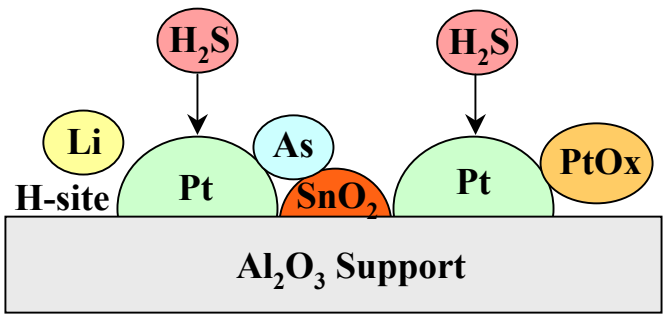
Nano Sized Catalytic Active Sites

- *Nanophase* below 100 nm
- *High Density Active Sites* : Defects (grain boundaries, interfaces, dislocations, vacancies)
- *High Diffusivity* through nano size interface
  - *Fast kinetics*
- Nano sized promoters :
  - *Higher selectivity* due to poison trapping & poisoning of side reaction sites

Scheme of microwave-induced preparation of bimetal Pt-Sn/ Al_2O_3

n-Dodecane $\xrightarrow[Pt\text{-}Sn/Al_2O_3]{\text{dehydrogenation}}$ **1-Dodecene**

Present Passivation Scheme (Commercial Catalyst)

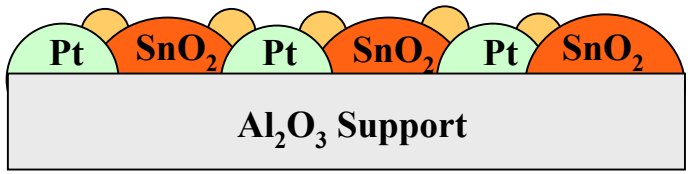


Conversion: 12% at 480°C

Olefin Selectivity: 89%

New Passivated Catalyst via Nanochemical Approach (KRICT)

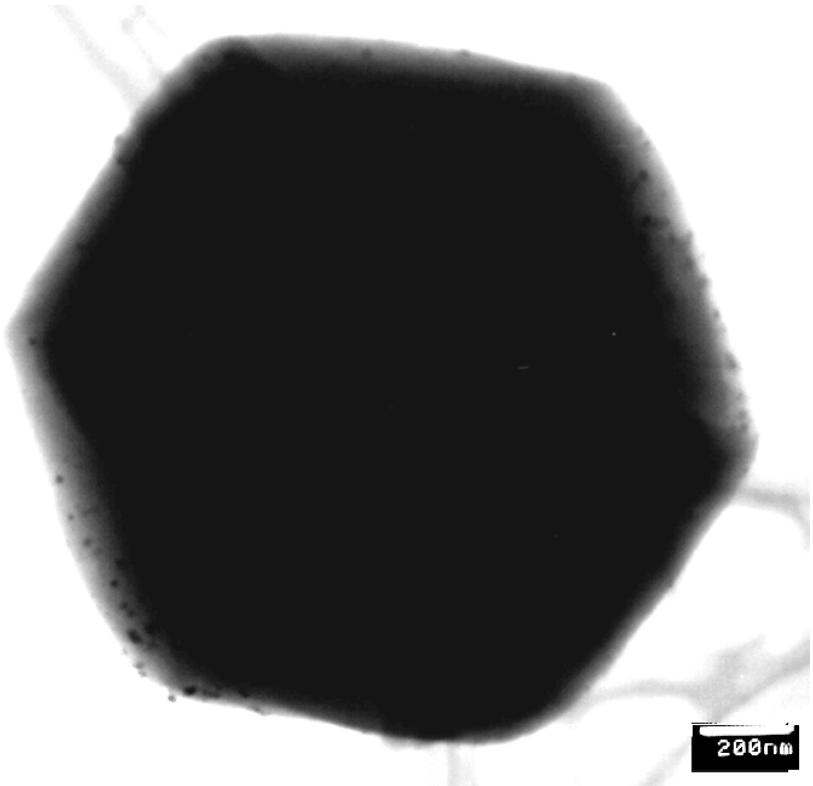
No H_2S

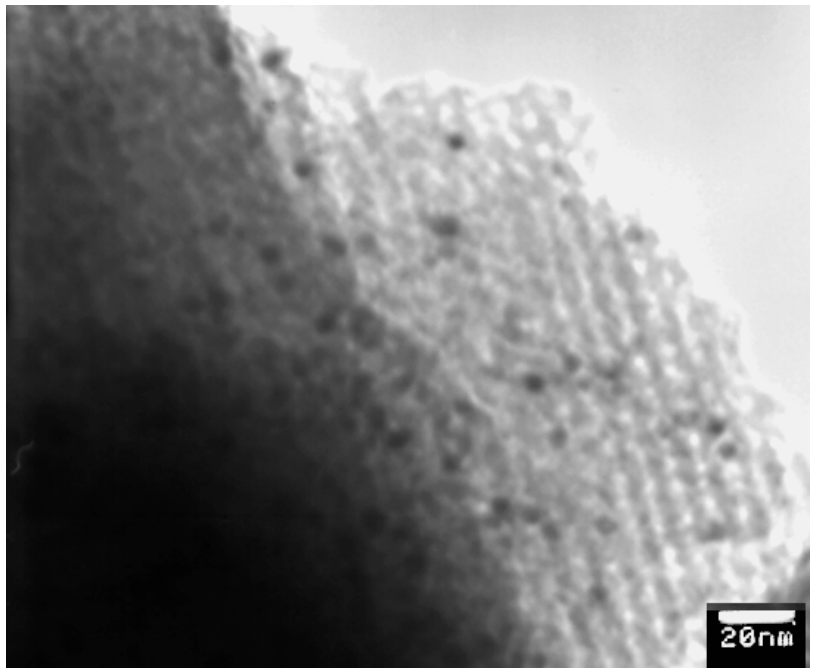


Conversion: 14% at 480°C

Olefin Selectivity: 93%

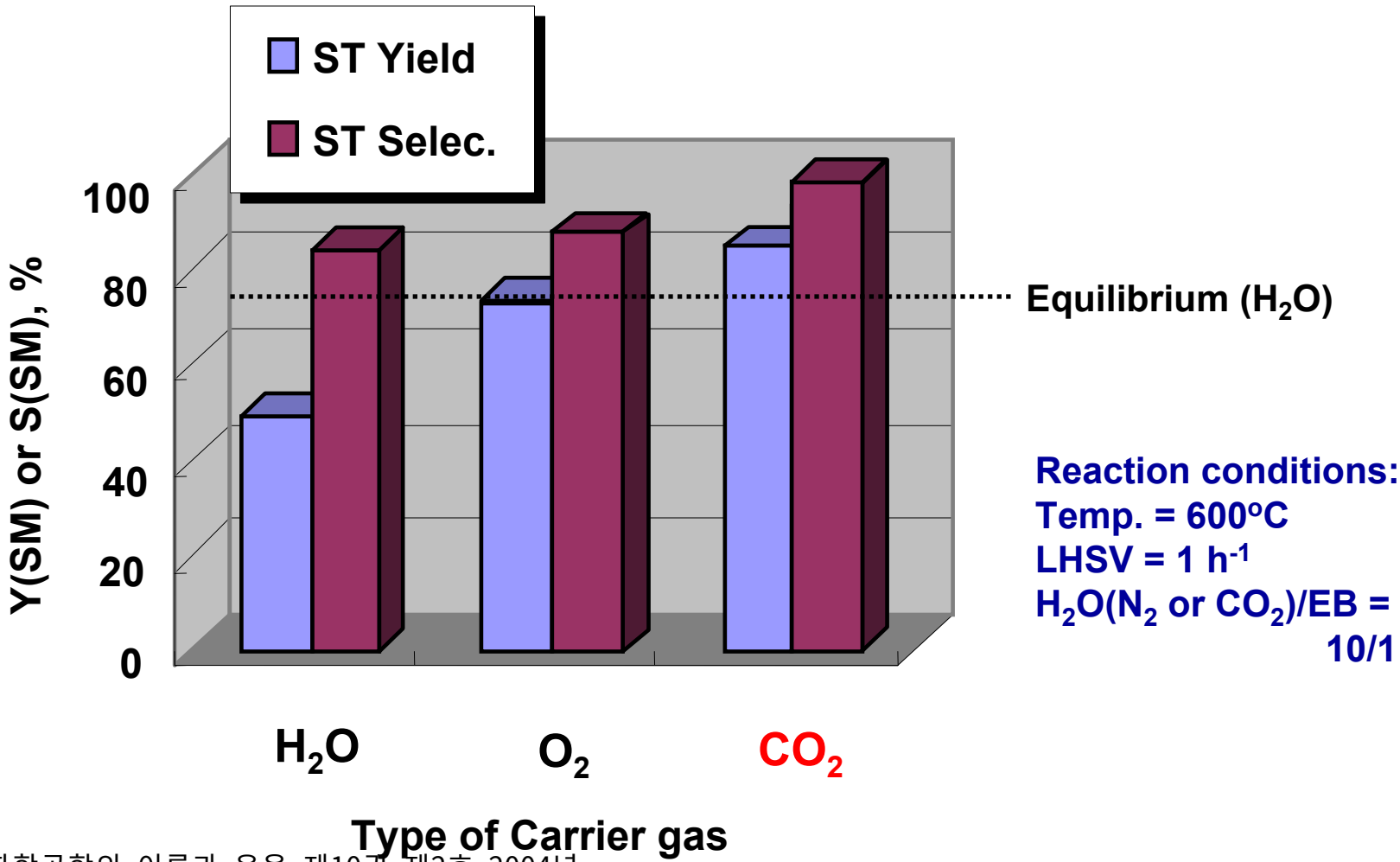
Microwave-induced preparation of bimetal incorporated Pt-Sn/ SBA-16





TEM image of 2%Pt- 2% Sn-SBA-16 Catalysts with microwave preparation

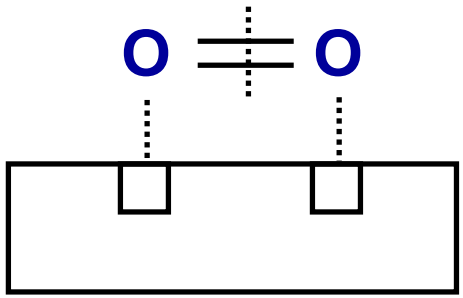
Effect of Carrier Gases onto Ethylbenzene Dehydrogenation



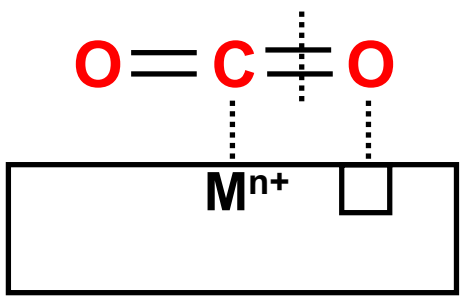
Reaction conditions:
Temp. = 600°C
LHSV = 1 h^{-1}
H_2O(N_2 or CO_2)/EB = 10/1

Dissociative Chemisorption of Oxidants on Catalyst Surface

$$O_2 \xrightarrow{e} O_2^- \xrightarrow{e} 2O^- \xrightarrow{2e} 2O^{2-}$$



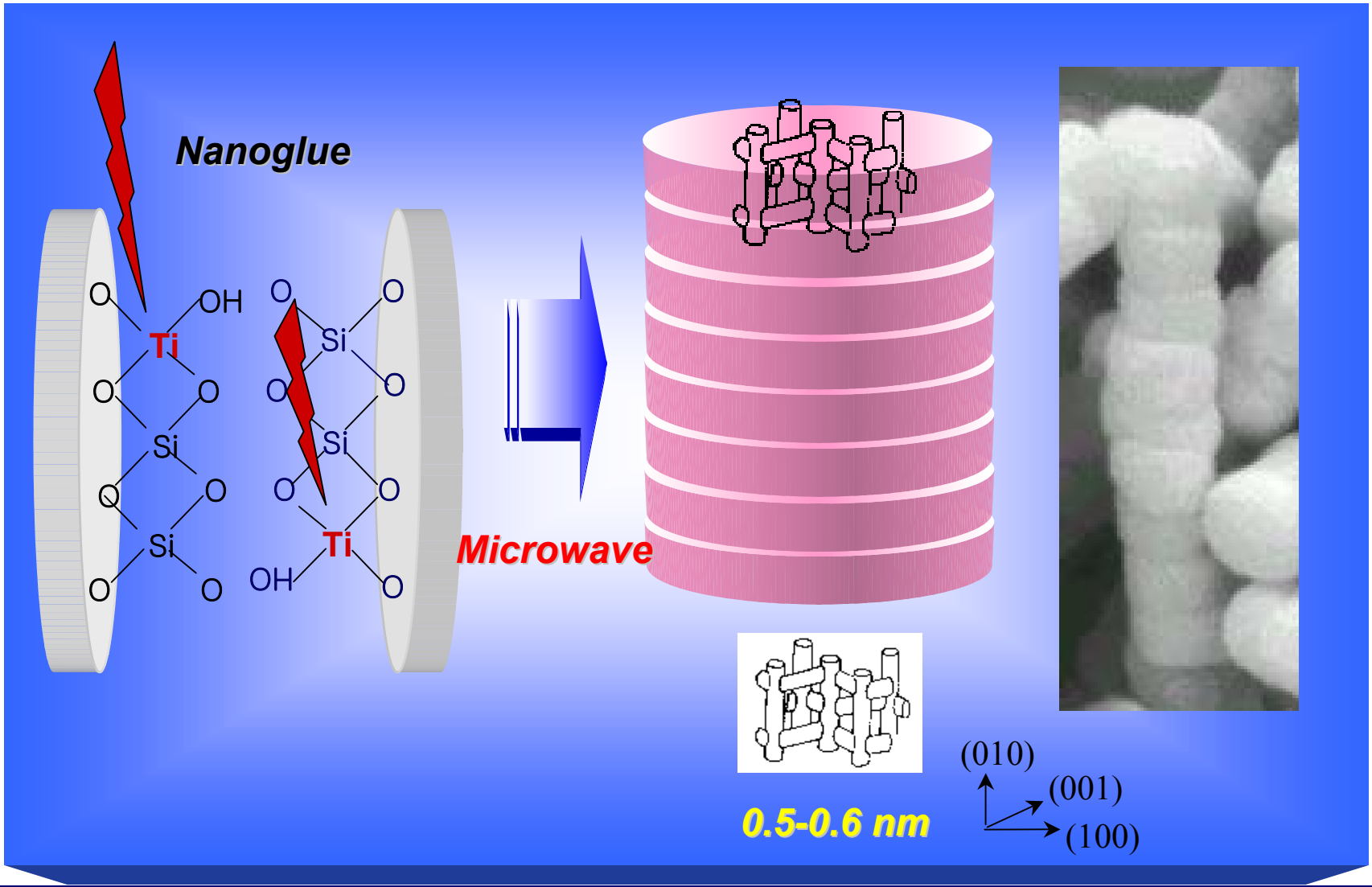
At least two reduced vanadium ions in the vicinity are necessary for dissociative chemisorption of an oxygen molecule.



□ : Oxygen vacancy

Single Site Mechanism

Nanofabrication of Nanoporous Materials: Self-Assembly by Microwave



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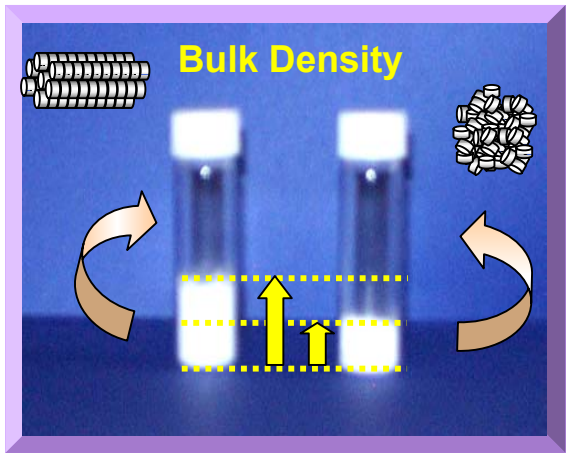
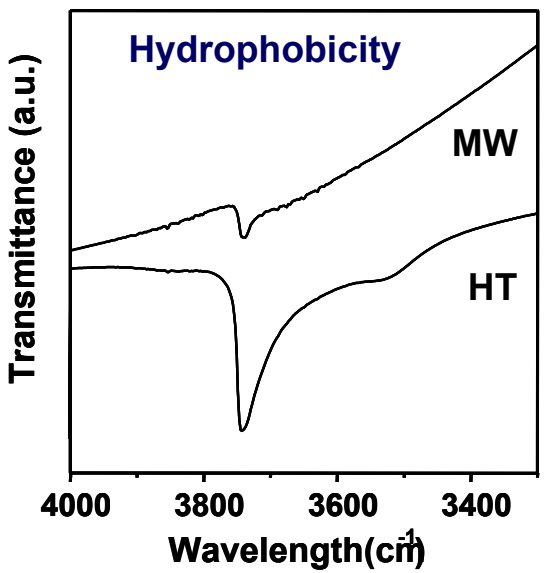
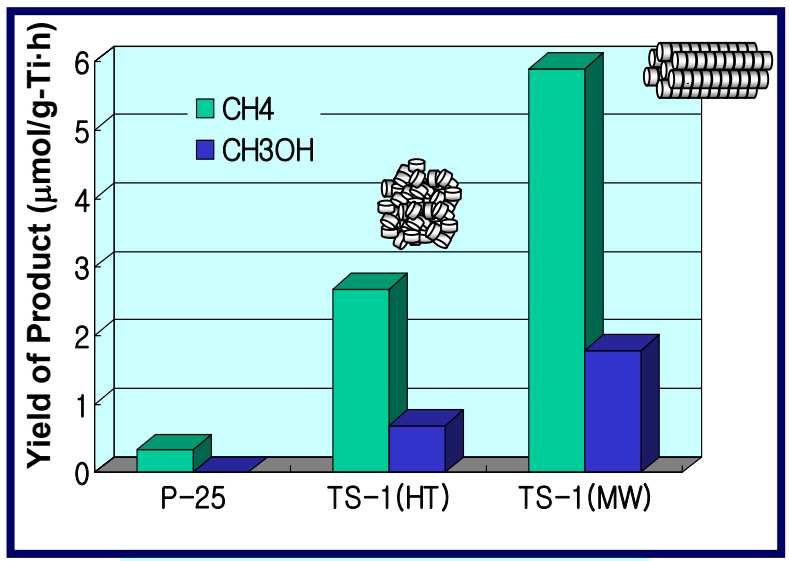
Best Presentation Award @ 224th ACS ,Boston, 2002.

Characteristic Properties of Fibrous Ti-MFI crystals



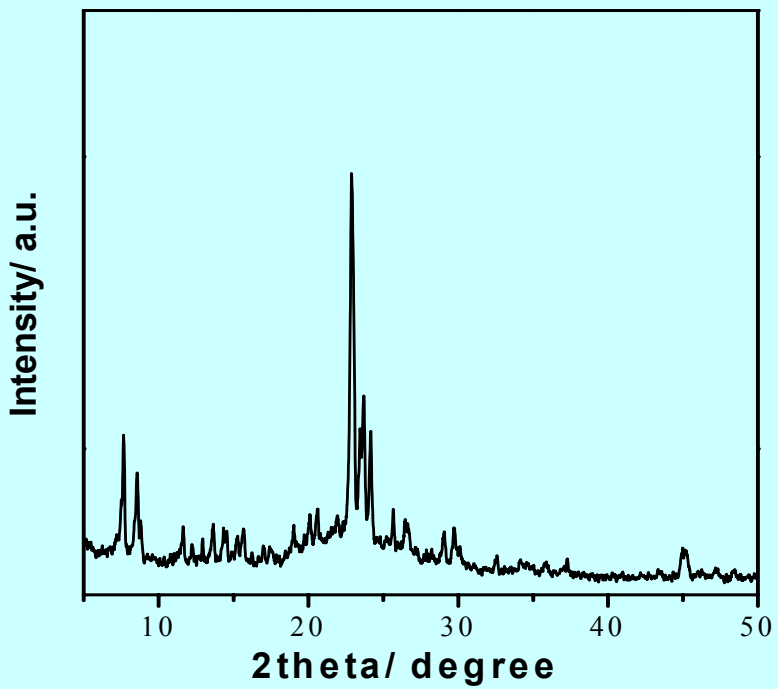
- Bulk Density
- Shape Selective adsorption of hydrocarbons
  : para-Xylene and ortho-Xylene
- Hydrophobicity : Surface Hydroxyl group
- Photocatalytic properties
- Epoxidation of styrene

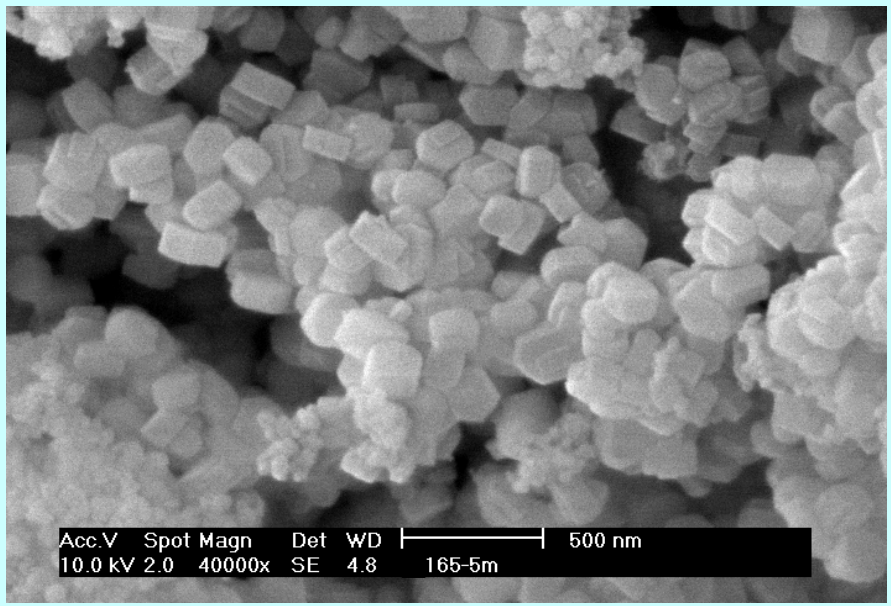




$CO_2 + H_2O \rightarrow CH_4$, CH_3OH

Continuous Microwave Synthesis of Silicalite-1

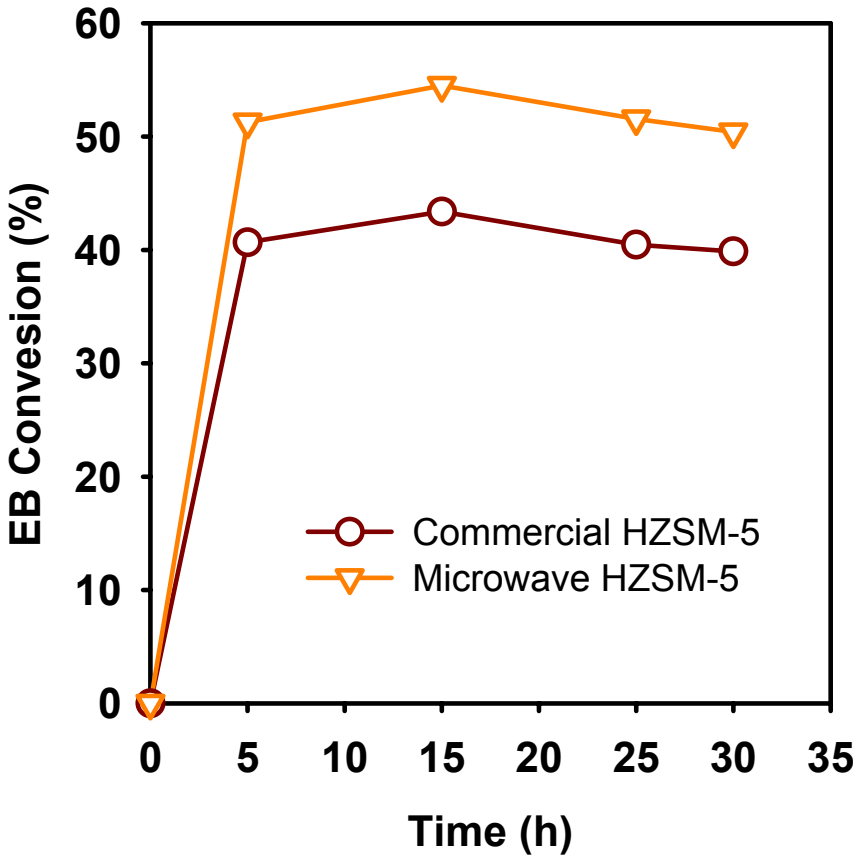


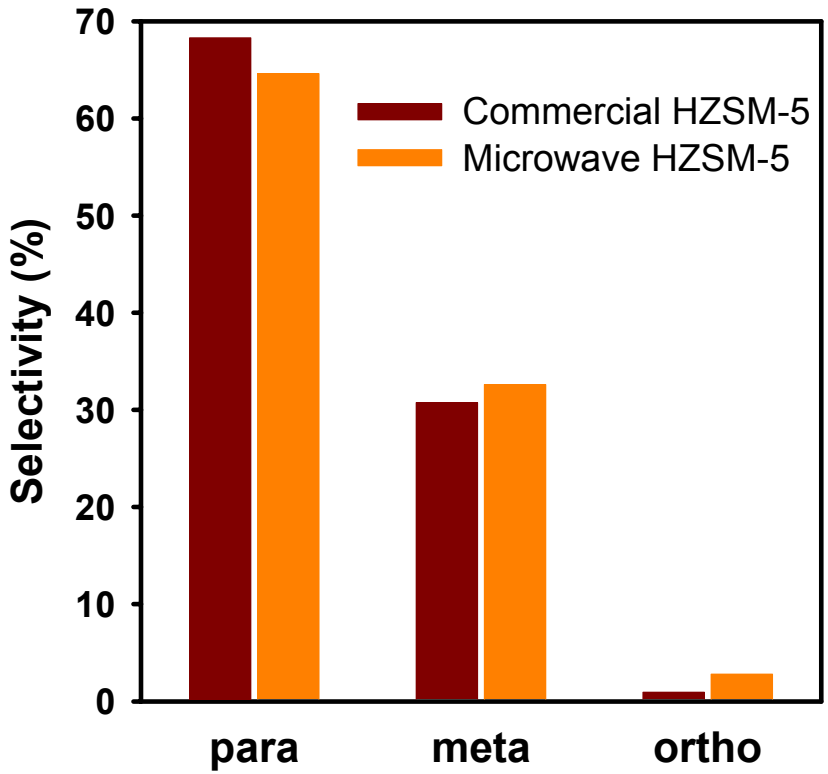


165 °C for 5 min

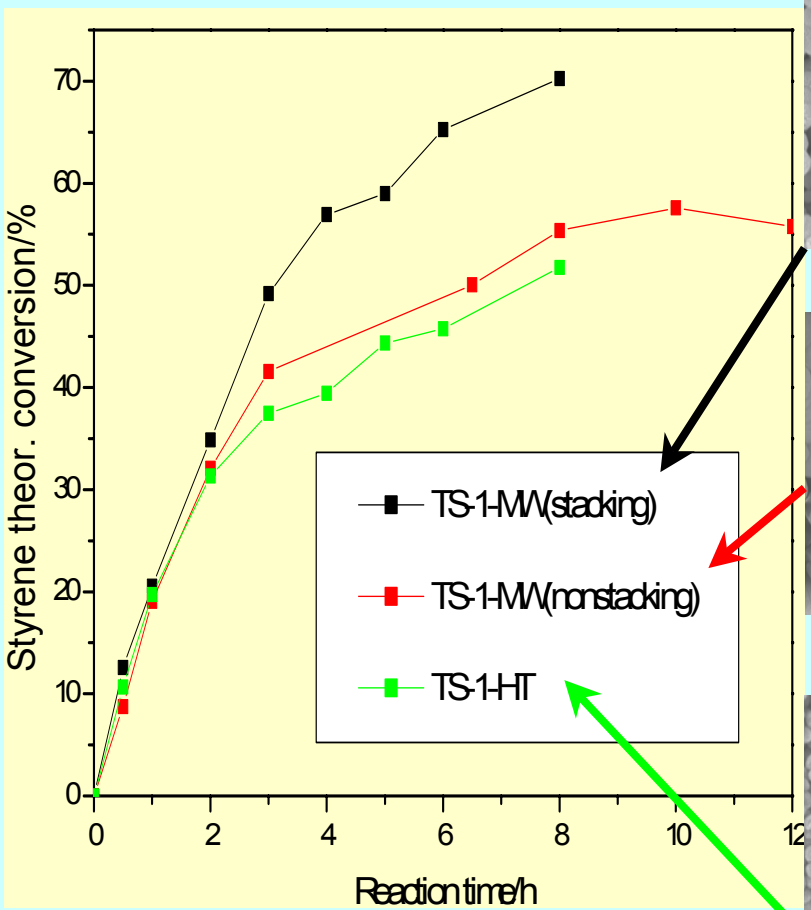
S.-E. Park, et al., Kor. Pat. Appl. 00-62545호

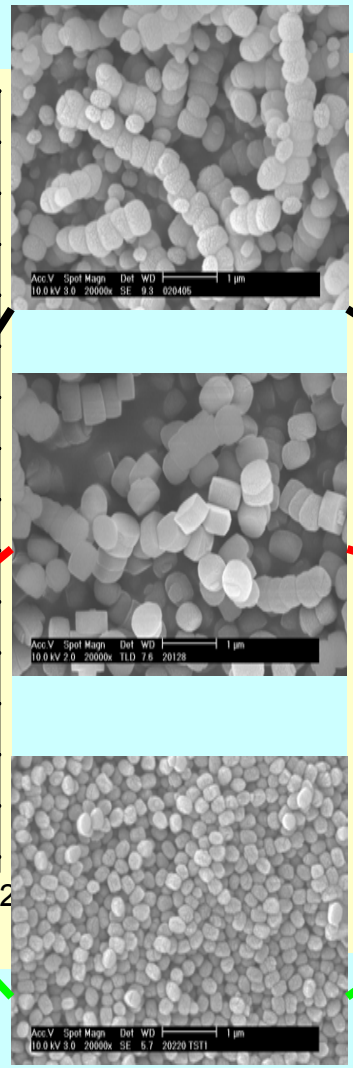
Para-diethylbenzene

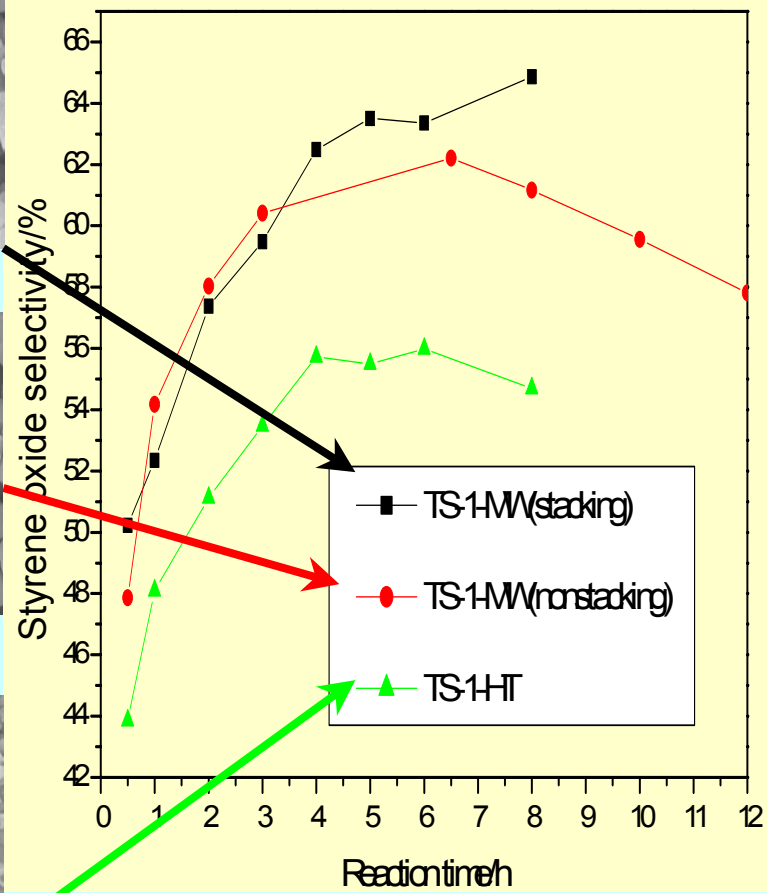




나노 조립에 의한 촉매 활성 및 선택성







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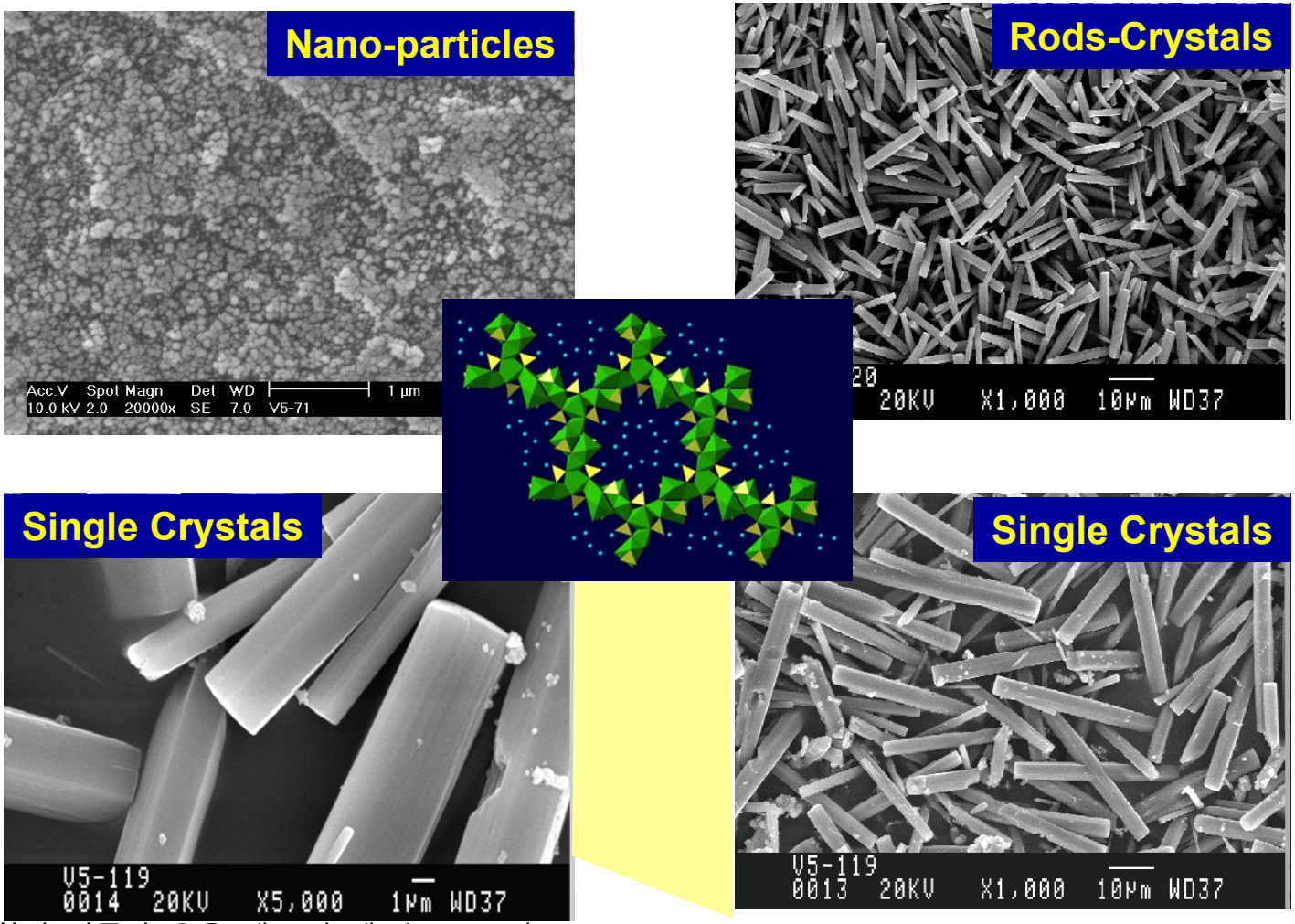
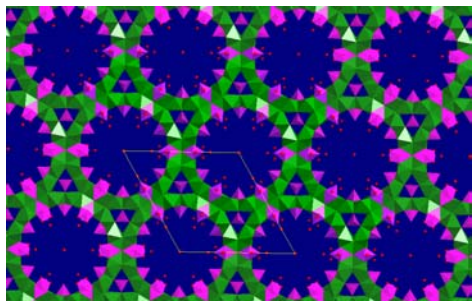
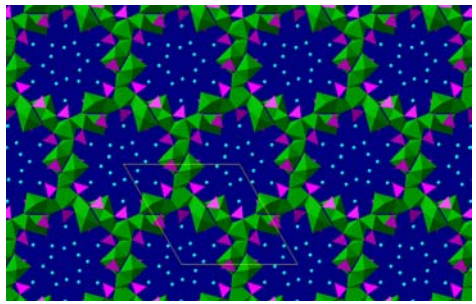
S.-E. Park et al., unpublished data.

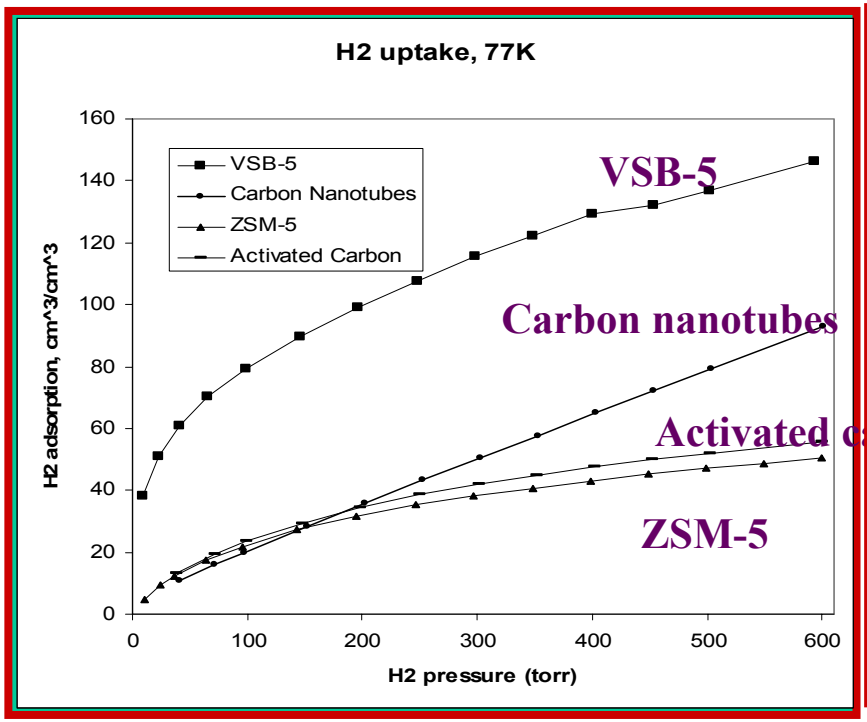
Morphology control of VSB-5

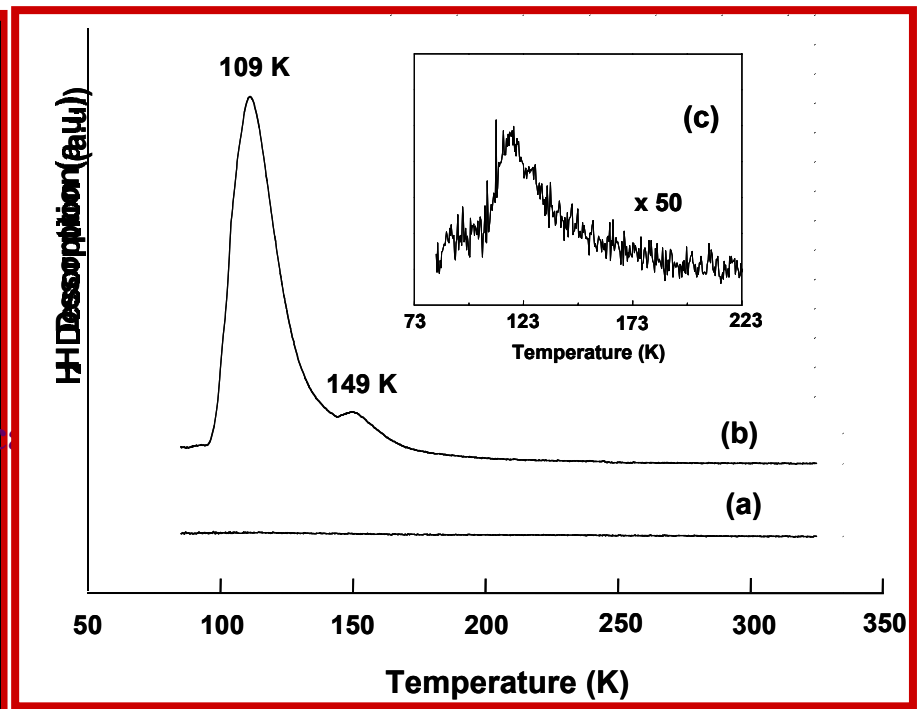
Nanoporous Nickel(II) Phosphates



Hydrogen Storage via Adsorption

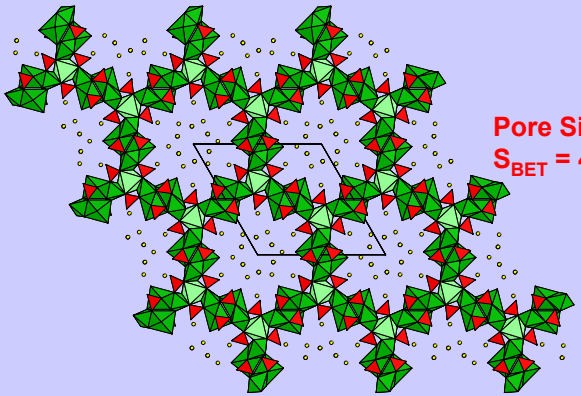





J.-S. Chang, S.-E. Park, et al., J. Am. Chem. Soc., 125, 1309, 2003.

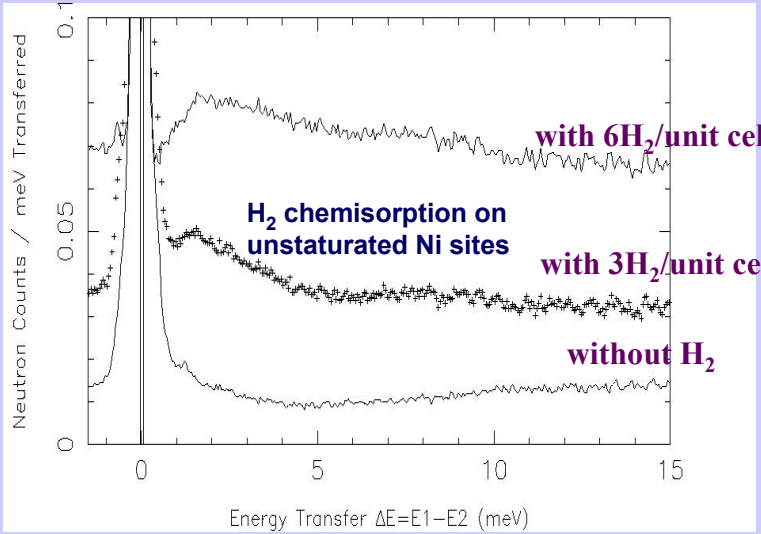
New Adsorbent for H_2 Sorption

A New Nanoporous Nickel Phosphate

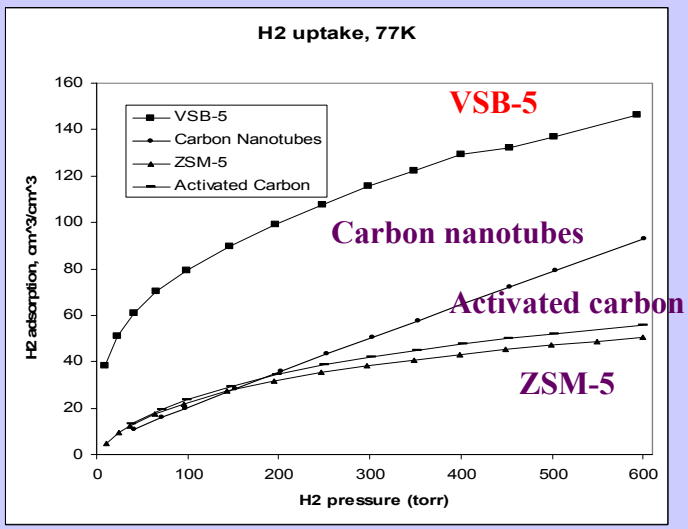


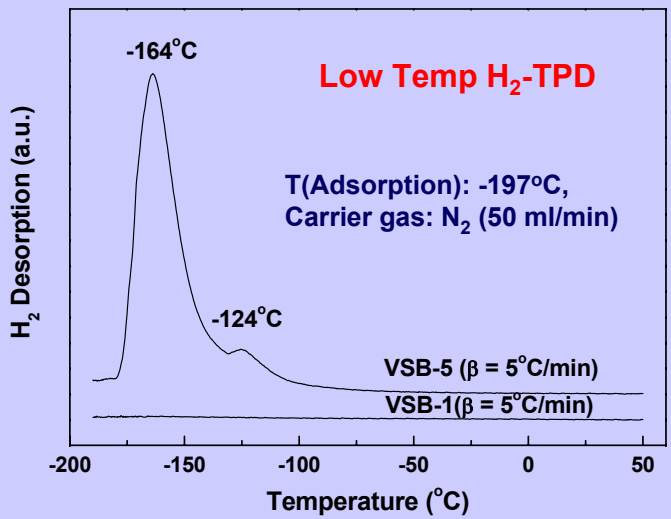
Pore Size: 11.3 Å
S_{BET} = 495 m^2/g

Rotational Tunneling Spectra



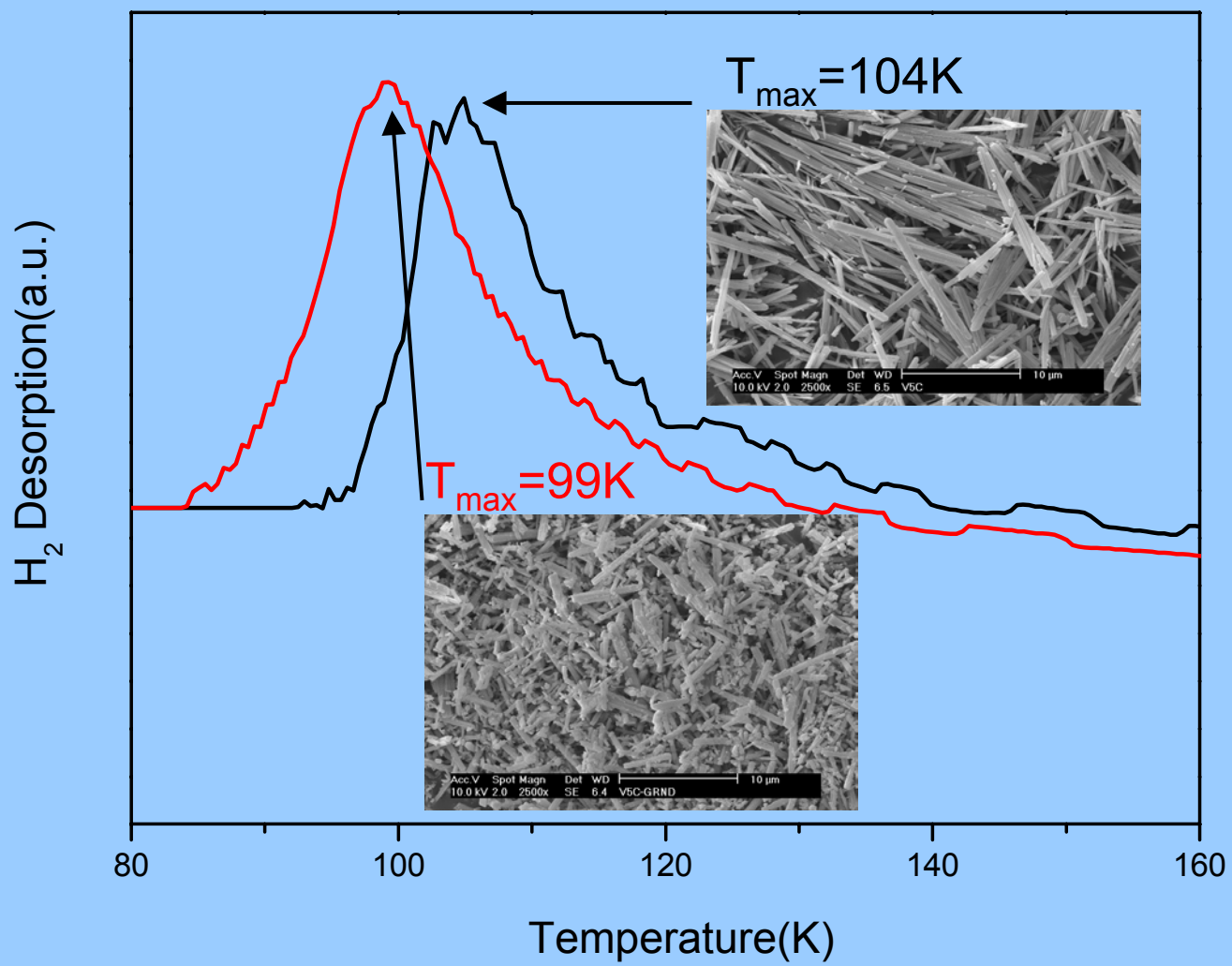
H_2 Adsorption Isotherm at 77K





S.-E. Park and A.K. Cheetham, *Angew. Chemie Int. Ed.*, 40, 2831 (2001);
J. Am. Chem. Soc., 125(5), 1309 (2003).

Hydrogen TPD from VSB-5 with different aspect ratios



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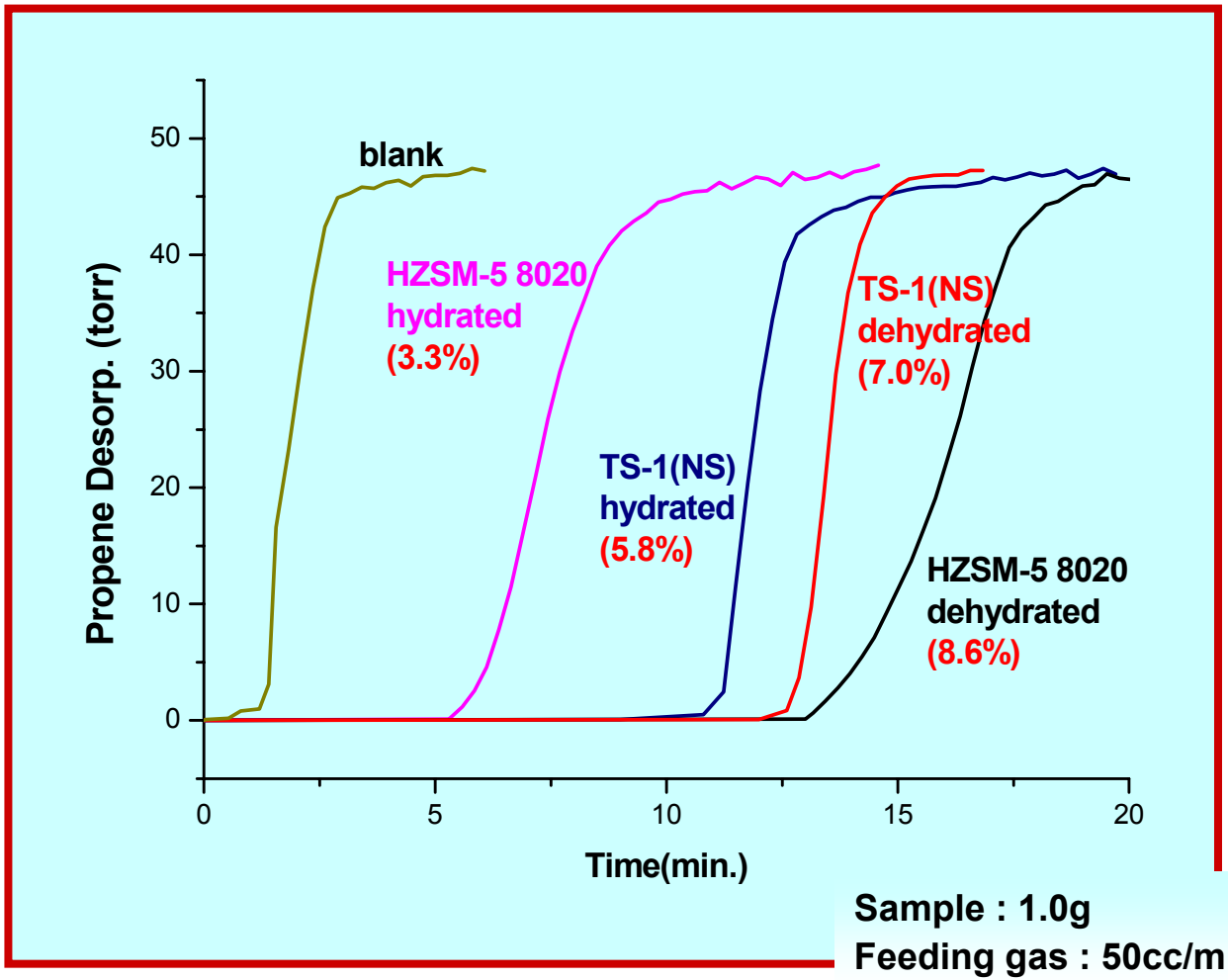
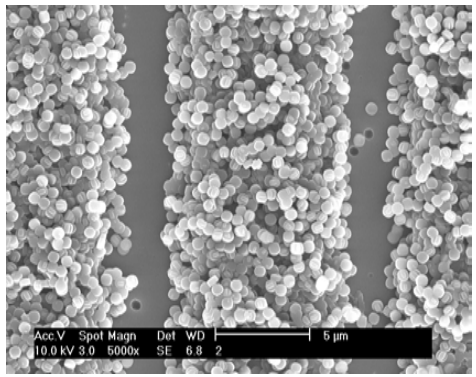
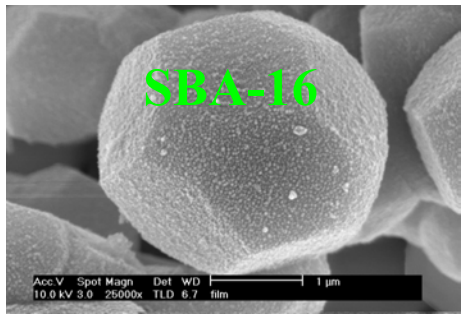
Propylene Adsorption over TS-1(NS) and HZSM-5

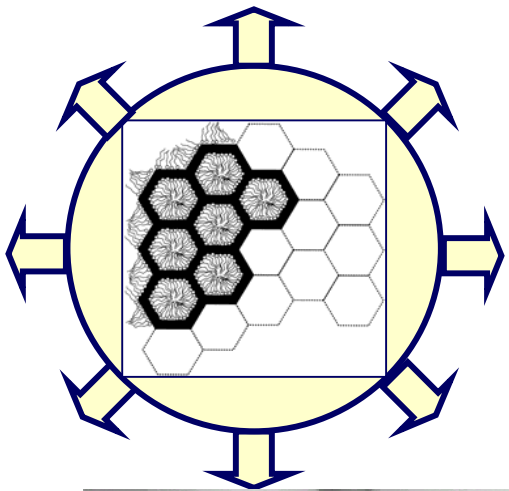


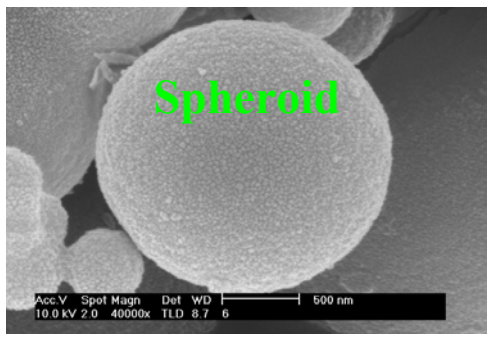
Sample : 1.0g
Feeding gas : 50cc/min.
(Propylene(47torr) in N_2 balance)
Adsorption Temp : 30°C
*** % : % of adsorbed propylene**

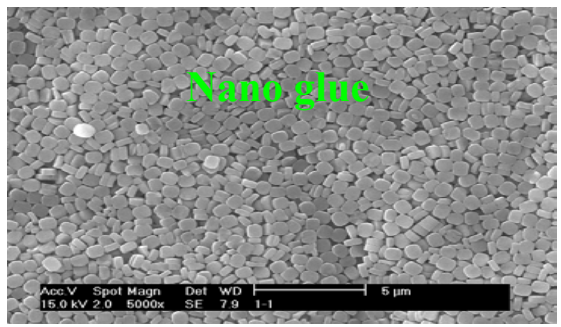
Self-Assembly of Nanoporous Materials via Microwave

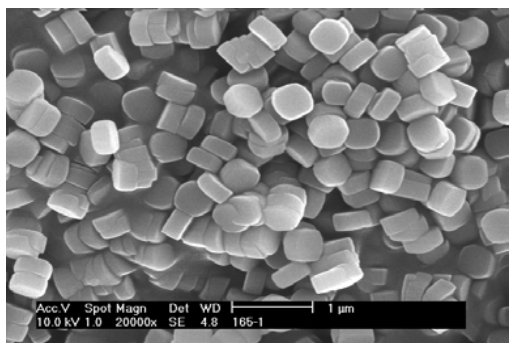


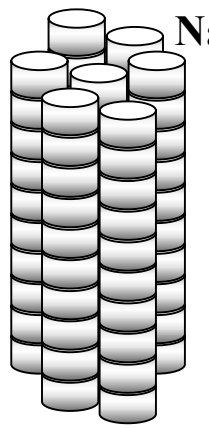












Nanostacking

CONCLUSION

- ♣ **Nanocatalysis** is expected to give many opportunities of novel application by fabricating nanoporous materials with microwave.
- ♣ **Self-assembly** processes are accompanied in the synthesis of nanoporous materials and fabrication of crystallite, and facilitated by the **microwave**.
- ♣ Microwave synthesis reduced the **synthesis time** with **smaller** and **uniform** crystallites.
- ♣ Nanofabrication of uniform nanocrystallites could be possible by using **nanoglues** which are capable of **selective absorption of microwave energy**.
- ♣ **Nanogluing by microwave** allows to fabricate micropatterned zeolite coatings for the application into **microreactor** & monolayer coatings for **membrane**.