Applications of Nanotechnology in Petroleum / Energy Sector

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Science & technology / Nanotechnology
Science and Technology

The time gap

There is a time lapse between first scientific publication and commercialisation

• Tungsten filament light bulbs (10 years)
• Transistors (10 years)
• Liquid Crystal Displays (12+ years)
• Semiconductor lasers (12+ years)
• Enzyme-based glucose biosensor (10 years)

Why this time lapse? What goes on during this period?
What goes on in the “Time Gap”

• Market assessment to establish a business case
• Establish cost–benefit equation
• If a business case can be made: process and production issues are addressed
• “scale up” may pose problems, and the real costs will emerge
• Market may change for better or worse!

Development takes longer than we think
Progress in Nanotechnology

• Nanotechnology presently is in the inter-phase of *Basic & Applied domains*
• Basic knowledge strength is fast leading to market products
• However, there is a need to distinguish between *real & hype*
• Equal emphasis on nanoscience & nanotechnology
Nano-Science vs Nano-Technology

• New awareness of Chemistry, Physics and Biology especially at the molecular level
• Optimism of what is possible
• Concerns for the impact of scientific research
• Improvements to existing products in terms of performance or value
• New functionality materials
• Improve our control and understanding of processes in industry
Patents in *Nanotechnology*

- Over 5000 nanotechnology related patents issued in USA as of late March, 2006 (Mainly on Nanoparticles, Nanotubes, Fullerene etc).
- Number of patents in USA growing by over 30% every year since 2000. (National Nanotechnology Initiative (NNI) started by Clinton).
- 925 Nanotechnology related patents filed in USA in May, 2006 alone
- Nanotechnology firms & researchers are racing to secure patent protection for early stage commercial applications & trying to create license fee generating positions.
Nano technology in Petroleum / Energy
Nanotechnology in Petroleum

• Petroleum industry has been a beneficiary of nanoscience/nanotechnology; but mostly unknowingly
• Most common refining catalysts e.g. Zeolites involves nanoscience
• Industry has sufficient knowledge of bulk properties
• Advent of nanotechnology has brought in “Know Why” element
Application Profile of Nanotechnology in Petroleum/ Energy Sector

• Under Development
  Dye sensitized solar cells using TiO$_2$, H2 storage using metal hydrides, CNTs, Improved fuel cell components, Hydrodesulphurization catalysts

• Being Introduced
  Nanocrytalline Ni & metal hydride for batteries, Ceria in diesel

• Well Established
  Automotive catalysis, Refining catalysts of zeolite type
Nano catalyst in Refining & Petrochemicals
Large and Complex Industry

Gallons Per Day (World Wide)

Crude Production
- 3.2 Billion
  - Today's Infrastructure
    - Massive
    - Global
    - Highly Efficient
    - 100 Years in Making

Refining & Chemicals
- 1.8 Billion
  - Diesel
    - 950 Million
  - Chemicals
    - 850 Million
  - Fuel
    - 300 Million

Gasoline

- 300 Million
Trends in Refining Catalysis

- **Product Regulation Focus**
- **Energy Efficiency Focus**

**Short-term**

**Medium-term**

**“Refinery of the Future” or “Energy Plants”**
- Distributed Power Production
- Flexible Feedstock
- Flexible Product Production

**Longer-term**

**Tailored Structure and Structure Property Control at Nanoscale Important for Next Generation Catalysts**

**Trends:**
- Improved selectivity
- Energy efficiency
- Better utilization of hydrocarbons
- Utilization of unconventional feedstocks
- Combined reaction and separation
- Intermaterial substitution
Heterogeneous Catalysis

- Heterogeneous catalysts used in the petroleum refining and chemical industries are examples of widely applied nanoparticles.
- Traditionally, industry has relied successfully on empirical methods for synthesizing these materials but has not applied understanding of nanoparticles to make further improvements.
Shape Selective Catalysis Key to Managing Molecular Size & Shape

- MCM-41 Commercial Catalytic Nanotechnology Example
- Exciting New EM Materials Now Entering Pipeline
MCM-41: What Is It?

Many Options for Tailoring Microstructure and Reactivity

- Vary Pore Size 1.5nm to >10nm
- Clad the Surface
- Vary Chemical Composition
- Anchor Metals and Catalysts

Surfactant Micelle → Micelle Rod → Silicate → Hexagonal Array → Calcination → MCM-41
Hybricats: Vision for the Future

Tailored Multifunction Zeolite--Metal Oxide Hybrids

Today's Capabilities

High Activity Metal Oxide Nano-structures

Combine Best Features

Shape Selective Zeolites

Tomorrow's Catalysts

• Higher Activity/Selectivity
• Poison Tolerant/Longer Life
• Improved Regenerability
• Combined Reaction/Separation
Nanostructured catalysts in Petroleum Refining

HYDROTREATING CATALYSTS (CoMo/Al₂O₃, NiMo/Al₂O₃)
• Dispersion of nanostructured MoS₂ slabs with promoter atoms generates high active catalyst systems

• IOC R&D has initiated research for the development of HDS catalysts (R. P. Verma et al, US Patent 6,855,653, 2005)

NANOSTRUCTURED ALUMINA
• Nano crystallite alumina found to have superior characteristics as supports in hydrotreating, reforming catalysts
  • High surface area and tailor made pore structure
  • Mixed phases generation to tailor metal-support interactions
Nano Fuel Additives
Fuel Additives

- *Fuel additives are substances added to the fuel to improve some of the desired properties.*
- Additives can reduce the total mass of particulate matter (PM), with variable effects on CO, NOx and HCs emission.
- Additives can range from less than 10 parts per million (ppm) to greater than 100 ppm in the fuel.
- A fuel economy improvement of up to 7% achieved.
A diesel oxidation catalyst (DOC) converts pollutants i.e. CO & gaseous hydrocarbons into harmless gases by means of oxidation.

Reduce the mass of the liquid-phase HCs (unburnt fuel / oil) by 90% under certain operating conditions. The liquid HCs, or soluble organic fraction (SOF), contribute up to 30 percent of the total particulate mass.
Reported Nano Fuel Additives

• Ce, Cu, Pt, Mn & Fe based Additives

• Details of *Ce based nano fuel additive*
Ce based nano fuel additive

Cerium oxide nanoparticles are added to fuel to improve performance by promoting:

- Soot burn within the combustion cycle
- Oxidising carbon deposit buildup within the engine resulting in more efficient performance and improved fuel economy.
It undergoes a transformation from the CeO$_2$ (+4) state to the Ce$_2$O$_3$ (+3) valence state via a relatively low energy reaction.

The carbon combustion activation temperature is reduced from approximately 700ºC (for micron sized) to 300ºC (for nanosized) material as the surface area of the nanomaterial is increased by a factor of 20.

CeO$_2$ may be used as an oxygen storage material in catalysis.

$$2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 0.5\text{O}_2$$
**MECHANISM**

**Hydrocarbon Combustion**

\[(2x+y)\text{CeO}_2 + C_x H_y = [(2x+y)/2]\text{Ce}_2\text{O}_3 + x/2 \text{CO}_2 + y/2 \text{H}_2\text{O}\]

**Soot Burning**

\[4\text{CeO}_2 + C_{\text{soot}} = 2\text{Ce}_2\text{O}_3 + \text{CO}_2\]

**No\textsubscript{x} Reduction**

\[\text{Ce}_2\text{O}_3 + \text{NO} = 2\text{CeO}_2 + 1/2\text{N}_2\]
5ppm Envirox 1D in diesel  diesel without additives

Cerium dioxide nanoparticle coated 5 – 25 nm
Commercial Fuel Combustion Nanocatalysts

- Catalysts from Oxonica are using particles only of 10 nanometres across, which creates a greater surface area for catalysing the reactions.
- Envirox successfully tried their catalysts in buses in Hong Kong.
- Scottish are testing of Envirox catalysts in 1000 of their diesel-fuelled vehicles.
- Test results are not yet known.
Nano technology in Lubricants
Nanotechnology in Lubricants

- Reduces Friction, wear & temperature significantly at higher loads
- Diminishes galling, seizing 7 fretting of metal surfaces
- Nanosized MoS$_2$ & graphite
- World’s First Commercial Solid Lubricant based on Spherical Inorganic Nano-Particles NanoLub™ by ApNano Materials Inc. (discovered at the Weizmann Institute of Science, Israel.)

© Useful in Lubrication Applications ranging from Machines & Toolings to Automotives and to Jets and Satellites.

© Semi-Industrial Facility to produce 150kg/day planned.
Nano Technology – Boundary Lubrication

• Boundary lubricating additives form reaction layers, which are of the order of few Nano meters thick, to protect moving surfaces from wear and tear in engine components.

• To understand their mechanism of action, advanced equipments have been used to study their behaviour down to Nano scale.

• The equipments used are AFM, Grazing Angle FTIR, SFA, Nano Tribometer and Nano Indenter, etc.
Advantage of Nanotechnology in Lubricant Development

• Surface properties instead of bulk properties are investigated
• Helps in designing additives for specific application
• Helps in generation of “know-why” in addition to “Know-how”
• Reduces number of costly evaluation tests
Nanotribology

- Atomic scale understanding of fundamental processes of surface in motion is called **Nanotribology**.
- Advent of probes to examine interacting surfaces at microscopic level *(AFM-uses small tips to probe the surface)*
- *(Size of atom 0.3 nm ; 1 nm= $10^{-9}$ m)*
Nanomaterials in E&P
Nanotechnology in E&P Sector

• **Smart Fluids**
  Nanosized superfine powders suspended in conventional drilling fluids leads to improvement in drilling process

• **Better Equipment**
  Nano SiC coated drilling bits for hardness

• **New sensors** for improving exploration in deep waters
Nanomaterials in Hydrogen Storage
Nanotechnology in Hydrogen Storage

• Of the known methods for hydrogen storage (cryogenic liquid, compressed gas, and metal hydrides), metal hydrides offer the best compromise weighing both safety and cost.

• The metal hydride systems of current industrial interest have been classified as $AB_5$ (e.g., LaNi$_5$), $AB$ (e.g., FeTi), $A_2B$ (e.g., Mg$_2$Ni), and $AB_2$ (e.g., ZrV$_2$).
Nanotechnology in Hydrogen Storage

- The hydrogen storage capacity, the number of times the storage can be done reversibly, and the kinetics of hydrogen adsorption/desorption are intimately linked to the alloy microstructure.

- Powder/ particles having nanostructured features have definite advantages on above.

Contd..
Carbon Nanotubes
Carbon Nanotubes (CNTs)
Exclusive Properties of CNTs

- Extraordinary mechanical & electromechanical properties
- Chemical & electrochemical: Facilitate molecular adsorption, doping & charge transfer
- Thermal & thermoelectric: Inherited from graphite, nanotubes display the highest thermal conductivity
Applications of CNTs

- Chemical & biological separation, purification & catalysis
- Energy storage (hydrogen storage, fuel cells & lithium battery)
- Composites for coating, filling & structural materials
- CNTs can adsorb 10 wt% H\textsubscript{2} at room temperature; while activated carbon can store 5.3 wt% H\textsubscript{2} at 77 K.
CNT’s : Challenge Ahead

• CNTs are still very expensive to produce, and the development of more affordable synthesis techniques is vital to the future of carbon nanotechnology.

• If cheaper means of synthesis cannot be discovered, it would make it financially impossible to apply this technology to commercial-scale applications.
ROAD AHEAD……...

• The hard part isn’t discovery; its Development & Commercialization.

• Partnerships, high throughput methods & modeling for decreasing Cycle Times to Commercialize Breakthrough R&D.

• Collaboration between nanotechnology developers with Application developers is essential.
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