The Role of Nanotechnology in the Petroleum and Petrochemicals Industries

[The Role of Nanotechnology in Meeting Future Energy Demands]

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Outline

1. We need no introduction?!!
2. Petroleum and Petrochemicals Industries [the big picture]
3. How is nanotechnology (NT) ‘Special’?
4. NT in Petroleum and Petrochemicals
5. CENT as an example
6. Conclusions
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Erosion and Corrosion Nanocoatings for Oil & Gas Industry, David Reisner, INFRAMAT, USA

Fabrication of In2O3 Nanostructures And Their Hydrogen Gas Sensing Properties, Ahsanulhaq Qureshi, KING FAHAD UNIVERSITY OF PETROLEUM AND MINERALS, Saudi Arabia

Carbon Nanotubes and Manganese Dioxide as A Fixed Bed Composite For Lead (II) Removal From Water, Tawfik Awadh, KING FAHAD UNIVERSITY OF PETROLEUM AND MINERALS, Saudi Arabia

Synthesis of Mesoporous Chromium Silicates Molecular Sieves in Strong Acidic Media by Assembly of Preformed CrS1 Precursors with Triblock Copolymer, L. Chérif, Algeria

The effect of nanostructuring and composition modification on the oxidation behavior of stainless steel coatings, A. Al-Mathami, SAUDI ARAMCO, Saudi Arabia

Influence of ZnO Nanoparticle Addition on the Performance of PVC Films, I. Elashmawia, NATIONAL RESEARCH CENTRE, Egypt

From yesterday’s two sessions on nanotechnology.. it looks like we know it all 😊
What does “Nano” have to do with huge (large-scale) industries?

Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.

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Petroleum and Petrochemicals Industries
[the big picture]

**Feedstock:**
- Find it
- Improve it

**Process:**
- Selectivity
- Yield

**Equipment:** don’t wear/ corrode

**Product quality:** purity, strength, specs …

**Safety:** corrosive materials, inflammable materials, poisonous gases.

**Side-effects:** emissions (SOx, NOx, water pollutants…etc.)
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How is nanotechnology 'special'?

Optical qualities

Bulk Gold = Yellow

Nanogold = Red

Quantum effects

R

atomic

bulk scaling

x
How is nanotechnology 'special'?

Extremely important for catalysis, sensors, purification and the like.

Specific surface
How is nanotechnology 'special'?

Nanomaterials are really.. really “tiny”..

Video

We can ‘see’ through sandstone and carbonate plugs!!

The whole micrograph is only 1/5 of a hair-width!!
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Nanotechnology cartoons
I ‘had’ problems with:
Robots in blood arteries

Then, S. Aramco (2008) shocked me!
Robots 7000 ft below ground in complete darkness, wandering ‘inside’ rocks
DHAHRAN, November 19, 2008 -- The EXPEC Advanced Research Center (EXPEC ARC) won the prestigious New Horizons Idea Award at the 2008 World Oil Awards. The award was granted for the research and innovation of Resbots (reservoir robots).

Resbots are nanorobots, less than 1/100th the size of the human hair, that can move through the reservoir. They will be deployed as a microscopic army with injected water into the reservoir. During their journey, they will analyze reservoir pressure, temperature and fluid type, and store that information in onboard memory. They will then be picked up from the produced crude at the producing wells to download that information and tell us everything about the reservoir they have encountered during their journey, thus effectively mapping the reservoir.

2 years later:
Novel Hybrid Reservoir Nano-Agents for Enhanced Oil Recovery
Proposal submitted by Z. Yamani et. al. for S. Aramco EXPEC ARC funding!!

Goal: smart tracing, sensing, and sniffing devices for on-line implementation in oil fields
NT in Petroleum-EOR

EOR: primary, secondary, tertiary recovery

Improve on current single well chemical tracers (SWCT)

Measure residual oil saturation

Map the oil reservoir

There are a LOT of difficulties and uncertainties; yet, **IF** this technology improves EOR by even a single percent, that is a LOT of **Oil**!!
NT in Petroleum-EOR

Challenging problem:
- “right” size,
- dispersibility,
- functionalization,
- harsh environment,
- choice of markers/ sensitive detection (chemical, optical, electrical, magnetic)
NT in Petroleum-EOR

Then what..??

Bring resbot to life??
(active vs. passive)

Propulsion; Navigation; Communication; Ammunition;

(for now!!)
The resbots are not ‘really’ robots.. but rather (just) ‘agents’
Corrosion: inhibitors, coatings..

Proppants

Artificial lifting (break emulsion, remove nasty gases)

Water shut-off

Visco-elastic surfactants

MRF: Magnetic rheological fluids
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NT in Petroleum-clean gas

molecular sieving (size exclusion)

CO₂

CH₄

Crystalline aluminosilicates
Si-O-Al structures

ERI

DDR

LTA zeolite

Hierarchical Nano-manufacturing

Zeolite seed crystals

- ZSM-5
- Type A
- Type Y etc.

Control of seed crystal size and morphology

- Plate-like
- Cubic

Oriented mono-layer coating

Secondary growth

Oriented zeolite membrane

NT in Petroleum-clean gas

NT in Petroleum-clean gas

Challenges (1) Defects

Cracks and grain boundaries

1. Rapid Thermal Treatment

2. CVD to fill intercrystallines with amorphous silica (Nakao lab, Univ Tokyo)

Tsapatsis group, Science, 2009
NT in Petroleum-clean gas

Challenges (2) Scale up

• NaA zeolite crystals had been synthesized hydrothermally.

• On the surface of a porous tubular support (12 mm OD, 80 cm L and 1 μm average pore size).

• The plant is equipped with 16 modules, each of which consists of 125 pieces of NaA zeolite membrane tubes.

Mitsui, Japan (2001)
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Hasn’t catalysis ‘always’ been nano? Or is it just a fad and a fancy name

Rational design.. zeolites.. an (nano) art.. not just science..

BASF.. in 1940s’.. try out 2500 of catalysts to specifically address one reaction. [trial and error].

Now, we study what are the active sites.. and design the materials such as to provide that specific activity.

The effect of “nano”-particle.. gold is noble, but nano-gold is not ← it is active!!

Fischer Tropsch [gas to liquid]..controlling the size of the particle enhanced the activity.

2-D and 1-D materials do exist.
Density-functional theory (DFT)

Electron density is a very convenient variable
  Physically observable
  Has intuitive interpretation
  Depends only on three spatial coordinates

DFT Simulations:

• Energetics and stability of catalytic surfaces
  • Particle nucleation, agglomeration, and sintering
  • Surface reconstruction
  • Surface alloys vs. bulk alloys
  • Surface segregation

• Gas-solid interactions
  • Adsorption strength
  • Reaction kinetics
  • Molecular transport
  • Mechanistic aspects
Nanostructure materials catalysts have attracted great attention due to:

- Enhanced catalytic activity and durability in catalytic processes, such as HDS of fuels, hydrogen generation, fuels to chemicals conversion, etc.

- Better control of their chemical and physical properties, such as surface functionalities, pore size, surface area, etc.

- Variety of methods to engineer the materials, namely solvo/hydro thermal, microwave, temperature programmed reaction, atomic layer deposition, ion beam deposition, etc.

- Possibility of being prepared and used with and without support

NT in Petroleum - catalytically selective products and clean environment

Z. Peng and H Yang, Nano Today (2009) 4, 143–164
NT in Petroleum - catalytically selective products and clean environment

These nanosheets (2nm thick) can be potentially applied in petroleum crackings and other zeolite-catalyzed processes in refining and petrochemicals.

Scaling down on zeolite layer

Only 2 nm thick

Choi et al, Nature 461, 2009
NT in Petroleum- catalytically selective products and clean environment

Nitrogen doped TiO2 nanotube array films with Pt (NT/Pt) and Cu (NT/Pt) cocatalyst annealed at 460 and 600°C under sunlight illumination (a) hydrocarbon generation and (b) CO and H₂ generation rates

Depiction of cocatalyst loaded flow-through nanotube array membrane for high rate photocatalytic conversion of CO₂ and water vapor into hydrocarbon fuels

Nano lett. 9 2009 731

Nanostructured materials for CO₂ storage electrochemical conversion of CO₂
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CNTs can absorb up to 180 times of its weight for wide range of oils and solvents in water.


Nano metal oxide as air purification catalyst

Germicidal UV Lamp
Super Oxide Ions
Hydro-peroxides
Hydroxide Ions
Ozonide Ions

Nanotechnology can improve the quality of our live
Advanced Ceramics & Their Applications

• **Structural**: Wear parts, bioceramics, cutting tools, engine components, armour.
• **Electrical**: Capacitors, insulators, integrated circuit packages, piezoelectrics, magnets and superconductors
• **Coatings**: Engine components, cutting tools, pipes, rotors, propellers, turbine blades and industrial wear parts
• **Chemical and environmental**: Filters, membranes, catalysts, and catalyst support

NT in Petroleum-tough materials
NT in Petroleum - 3S detection of $\text{H}_2$, $\text{H}_2\text{S}$, $\text{NO}_x$, …

Future Sensors

Miniaturization scaling down..

Sub 100 nm Patterning
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Nanomaterials for the Petrochemicals Industry
Nanomaterials

Carbon, Inorganic and Hybrid

- Nanosize materials have different properties than microsize materials.
- Very high surface to volume ratio.
- High strength to weight ratio.
- Exceptional mechanical, thermal, and electrical properties.

www.nanocor.com
Polymer Nanocomposites

Polymer nanocomposite is defined as combination of polymer matrix and a material which has at least one dimension in nanometer scale.

Looking for a jump in qualities at low levels of incorporation (less than 1%).

- Improved Mechanical Properties
- Improved Barrier Properties
- Flame Retardant Properties
- Improved Electrical and Thermal Conductivities
- Lower Thermal Expansion
- Low Specific Gravity Compared to Traditional Composites

Degree of property enhancement is a function of particle dispersion and Matrix-Particle interaction.
Substantial improvement in the Mechanical and in the Barrier properties of nanocomposites of injection- molded and extruded polypropylene at small (6 %) nanofiller fraction.

### Polypropylene- Layered Silicate (Clay) Nanocomposite

#### Mechanical Properties of Injection Molded HPP Nanocomposites

<table>
<thead>
<tr>
<th>Process</th>
<th>PP Type</th>
<th>Addition Level (%)</th>
<th>Tensile Mod. (Mpa)</th>
<th>Flexural Mod. (Mpa)</th>
<th>HDT (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection</td>
<td>Homopolymer</td>
<td>-</td>
<td>1412</td>
<td>1148</td>
<td>87</td>
</tr>
<tr>
<td>Molding</td>
<td>(Low melt flow)</td>
<td>6%</td>
<td>2804 (+98%)</td>
<td>2043 (+78%)</td>
<td>116 (+33%)</td>
</tr>
<tr>
<td>Injection</td>
<td>Homopolymer</td>
<td>-</td>
<td>1327</td>
<td>1196</td>
<td>86</td>
</tr>
<tr>
<td>Molding</td>
<td>(medium melt flow)</td>
<td>6%</td>
<td>2180 (+64%)</td>
<td>1777 (+49%)</td>
<td>109 (+26%)</td>
</tr>
</tbody>
</table>

#### Barrier Properties of Polyolefin Nanocomposite Films

<table>
<thead>
<tr>
<th>Film Process</th>
<th>PP Type</th>
<th>Addition Level (%)</th>
<th>OTR (cc-mil/m² day)</th>
<th>CO₂ (cc-mil/m² day)</th>
<th>H₂O (g-mil/m² day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast</td>
<td>Random</td>
<td>-</td>
<td>3.35 E-03</td>
<td>1.38 E-04</td>
<td>0.22</td>
</tr>
<tr>
<td>Cast</td>
<td>Copolymer</td>
<td>6%</td>
<td>2.54 E-03 (+24%)</td>
<td>0.72 E-03 (+7%)</td>
<td>0.19 (-14%)</td>
</tr>
<tr>
<td>Cast</td>
<td>TPE</td>
<td>-</td>
<td>1.82 E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6%</td>
<td>1.27 E-03 (+30%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Properties of Extruded Nanocomposites of Maleated Polyethylene, and of slightly Oxidized Polyethylene containing Exfoliated Layered Silicate

Greater than an order of magnitude improvement in modulus for both modified polyethylenes
Proper functionalization of nanomaterials is critical for increased matrix compatibility and optimum dispersion.

Performance of a nanocomposite is based on three characteristic:

- Properties of polymer and nanofiller.
- Interfacial interaction between the nanofiller and the polymer matrix.
- Orientation of the nanofillers.

In Search of a Quantum Leap in performance improvement at less than 1% nanoparticle
Extraordinary synergistic effect on the mechanical properties of polymers resulting from incorporating binary combinations of nanocarbons

- Nanotubes and nanodiamond
- Nanotubes and graphene

Material Hardness (MPa) Modulus (GPa)
PVA 38 0.66
PVA – 0.2 ND 43.7 0.87
PVA – 0.6 SWNT 290 7.8
PVA – 0.4 SWNT + 0.2 ND 367 9.30
PVA – 0.4 ND + 0.6 SWNT 550 13

At 1 % or less of Nano Carbon Mixture

ND = Nanodiamond

(Elastic Modulus (E) and Hardness (H) for PVA Composites with Binary Nanoparticles)

(CNR. Rao, Proceedings of the National Academy of Sciences, PANS, 106, 32,13187, 2009)
Wear Rate Reduction in Polymers by the Incorporation of Nanomaterials

Fluoropolymers (TEFLON)

**Characteristics**

- Low Friction
- High Temperature
- Chemically Inert
- Hydrophobic
- High Wear Rate
  - Lower wear rate by incorporation of filler particles - at the expense of other properties
  - **Nanofillers** – more effective at small percentages - can have high number density and surface area

Comparison of wear rate of various PTFE nanocomposites

It takes 10% of unfunctionalized nanoparticle to lower the wear by 2 orders of magnitude
Teflon Nanocomposites (PTFE) with Functionalized Nanoparticles

- Alpha Alumina ($\alpha$-$\text{Al}_2\text{O}_3$)  
  Surface functionalized with fluorinated Groups

- Show an Unprecedented four order of magnitude drop in wear rate of PTFE at a 1% volume of $\alpha$-$\text{Al}_2\text{O}_3$  
  (W.G. Sawyer, et. al., Wear, 267, 653, 2009)

Wear rate for nanocomposites with treated and pristine $\alpha$-$\text{Al}_2\text{O}_3$

AFM of a) PTFE, b) 0.5 vol. % $\Delta$-$\text{Al}_2\text{O}_3$-PTFE, c) 0.5 vol. % 40nm treated $\alpha$-phase $\text{Al}_2\text{O}_3$-PTFE, and d) 0.5 vol. % 40nm untreated $\alpha$-phase $\text{Al}_2\text{O}_3$-PTFE.
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What is CENT?

Center of Excellence in NanoTechnology

www.kfupm.edu.sa/cent
CENT: Vision and Mission

Vision:
CENT shall be an internationally recognized leading research center that develops innovative research and cutting edge knowledge in the field of Nanoscience and Nanotechnology.

Mission:
CENT will be the platform through which KFUPM shall develop a Nanotechnology Program that enables its scientists and faculty members to carry out world-class Nanoscience and Nanotechnology based research in areas of strategic importance for the Kingdom, and support the same through teaching at KFUPM.
1. To build up a world class human resources research capacity including highly qualified scientists and staff and trained graduate students in the field of nanomaterials synthesis and their characterization & applications.

2. To develop a research infrastructure including state of the art facilities that enables the Center to achieve its goals.

3. To develop innovative nanotechnology-based solutions in strategic areas for the Kingdom related mainly to petroleum and petrochemicals industries.

4. To establish Industrial Partnerships with relevant companies and entrepreneurship as a step toward commercialization, in coordination with DTV.

5. To contribute to the development of teaching graduate programs and training students in the field of nanotechnology.

6. To promote public awareness regarding the benefits and the risks of nanotechnology.
CENT Areas of Focus

focusing on the petroleum and petrochemicals industries

1. Nano-engineered Catalytic Materials
2. Nano-structured Materials for Sensing Applications
3. CNT Applications
Equipments

- Focused Ion Beam Stations
- Advanced Optical Microscope
- Tensile testing machine for metals and polymers
- Gas Chromatograph
- Gas Chromatograph Mass Spectrometer
- Ultra Performance LC
- Micro CT Scanner
- Autoclave
Spectrofluorometer with combined steady state and lifetime capabilities

Glove Box

Raman System

Pulsed Laser Deposition System

Surface area analyzer

Furnace

Semiconductor device analyzer

Tunable pulsed dye laser
CENT Capabilities and Research Areas of Interest

- Development of highly active and **nanostructured catalysts** for ultra-clean fuel. This includes the removal of sulfur and nitrogen containing compounds. In addition, removal of heavy metal complexes from natural gas is also under the scope of CENT research activities.

- CENT team has the expertise to conduct research and development activities in the area of **nano-composites**, such as PP/CNT, PE/CNT, PTFE/CNT, etc., for many applications, including electronic packaging, coating, and electrochemical devices.

- CENT team has also the expertise and “know how” to convert the **oil residues** into manageable and valuable products.

- Develop sensors with quick responses and cost effective. With expertise of CENT team, it is possible to invent new **nanostructured materials** for sensing volatile organics and inorganics with ultra-low concentrations.

- Research and development of catalyst based on core-shell and nanostructure materials for **clean energy processes**, such as photocatalysis, hydrogen generation, carbon carbon, and fuel cells.
CENT sponsored NSTIP Projects
[May 2010]

Development of advanced and functional nano-structured mesoporous zeolites for hydrodesulphurization and other catalytic applications in petroleum and petrochemicals

Zeolite Nanosheets as a Materials Platform for Improved Refining Catalysts

Carbon Nanofibers Grown on 3-D Solid Structures for Applications in Energy-Related Catalysis

Development and characterization of high surface area metal carbides modified mesoporous carbons and ceramics for clean fuel and catalysis applications

Development of nano-structured metal phosphides for ultra-clean fuel and fuel cell applications

Development of Nitrogen-Modified CNTs as Pt-Free Catalysts for Fuel Cells

Electrochemical engineering of nano-structured materials for clean energy and energy conversion applications

Synthesis of Metal-Organic Framework Nanostructures for uptake of CO₂ and Hydrogen Storage

Design of Smart Fluids for Acid Delivery in Well Stimulation Treatment
CENT sponsored NSTIP Projects
[May 2010]

**Electrospinning of Semiconductor Metal-oxide and Polymer Nanofibres for Ultra-sensitive Amperometric Sensor**

**Synthesis of Mesoporous and Microporous Metal-oxides Nanostructured Materials for Hydrocarbons and NO\textsubscript{x} Sensors**

**Comparative Study of Conversion of Carbon dioxide into high-value hydrocarbons using nano- structured materials by solar and laser irradiation**

**Development of highly efficient visible-light-driven nanostructured materials for photocatalytic applications**

**Photocatalytic Splitting of Water over mixed metal oxyhalides-based Catalyst using Laser Radiation**

Activity of laser enhanced nano-structured oxides of tungsten, nickel, zinc, iron and titanium against Candida and Aspergillus

**Lanthanide-doped oxide nanoparticles for Multi-modality Molecular Imaging Agents**
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<th>Developing CENT labs on campus</th>
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Conclusions

• Nanotechnology is an interesting subject. 😊

• Nanotechnology is not ‘all’ fake dreams!! 😊😊

• There many challenges ahead of us.

• Nanotechnology has a LOT to do with the petroleum and petrochemicals industries

• CENT: nanotechnology platform at KFUPM-Dhahran-KSA.

• In coordination with other sisters centers and industries, we are developing human competency, building capacity, transferring experience, and advancing technology in the fields of:

  1. Catalysis,
  2. Gas sensing, and
  3. Environment [including photocatalysis and CNT work]
Acknowledgements:

The CENT research teams, both employees and affiliates

Thank you for your attention