Synthesis, characterization and evaluation of nanostructured materials: new challenges.

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Outline

1. Proem: a story about petroleum complexity

2. Introduction: IMP chemical products for petroleum industry.


4. TiO$_2$ nanotubes.

5. Nanostructured polymer particles.

6. Conclusive remarks.
After the generous “Feathered snake”, Quetzalcoatl, had filled the upper skies with fresh and pure waters...

Relation of the village of the Holly Spirit of Coatzacoalco, 1582
1. Proem: a story about petroleum complexity

After the generous “Feathered snake”, Quetzalcoatl, had filled the upper skies with fresh and pure waters, his mockery and daring brother, Tezcatlipoca, “Smoking mirror”, stained the sea and filled the earth with a black and thick bitumen that the natives call “chapopochtli” (“Smoking liquid”).

Relation of the village of the Holly Spirit of Coatzacoalco, 1582
Long chain paraffins are responsible of viscosity

Figure 4.1.1. SARA fractions of petroleum.
2. Introduction: IMP chemical products for petroleum industry.

**Crude oil**

- **Maltenes**
  - Saturates
  - Aromatics
  - Resins
- **Asphaltenes**

*Figura 4.1.1.* SARA fractions of petroleum.

- Number and asphaltene size
- Dispersions stability

Water/oil Emulsion → Foam

Natural surfactants of petroleum
2. Introduction: IMP chemical products for petroleum industry.

**Mexican crude oils**

*Figura 4.15. Micrographs w/o emulsions of Mexican crude oils (exportation and refining requisits \( \phi_{H_2O} = 0.5 \% \text{ v} \)).*
La causa de la menor producción es que Pemex reportó recientemente un aumento importante y atípico en la presencia de agua en la producción de crudo, por lo cual la producción efectiva de crudo se ve reducida”, señaló la dependencia en su momento.
2. Introduction: IMP chemical products for petroleum industry.

Value chain of petroleum

- Exploitation
  - Drilling fluids
  - Foams
  - Water control
  - Asphaltene precipitation...

- Conditioning
  - Foam suppressors
  - Demulsifiers
  - Flow improvers...

- Transport
  - Corrosion inhibitors
  - Coatings...

- Refining
  - Hydrocracking
  - Hydrodesulfuration
  - Demulsifiers
  - Defoamers
  - Molecular meshes...
  - Membranes...

- Petrochemicals and chemicals
  - Catalysts
  - Coatings
  - Adhesives

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2. Introduction: IMP chemical products for petroleum industry.

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Organic chemistry

- Amines
- Ionic liquids

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Petrochemicals and chemicals
- Catalysts
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Macromolecular chemistry
- Polyethers
- Block copolymers
- Polyamides
- Polystyrenes
- Acrylics
- Polyisoprenes
- Vinylics...
2. Introduction: IMP chemical products for petroleum industry.

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Supramolecular chemistry
- Macromolecular assembly
- Polymer functionalization
2. Introduction: IMP chemical products for petroleum industry.

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- **Petrochemicals and chemicals**
  - Adhesives
  - Coatings

Nanochemistry

- Nanoparticles
- Nanotubes
- Nanostructured polymer particles

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2. Introduction: IMP chemical products for petroleum industry.

Value chain of petroleum

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- Petrochemicals and chemicals

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Nanochemistry

- Nanoparticles
- Nanotubes
- Nanostructured polymer particles

1. Nanoporous silicates structures
   MCM-41 (3.5 nm), hexagonal
   MCM-48 (3.0 nm), cubic
   SBA-15 (6.5 nm), hexagonal
   SBA-16 (9.0 nm), cubic

2. IMP Nanoporous silicates structures
   IMP-1

3. Nanoporous carbon-silicates structures
   PAN MCM-41
   PAN MCM-48

4. Nanoporous silicate-carbon structures + carbon nanotubes
   NiMoC-CN-PAN-MCM41
   NiMoC-CN-PAN-MCM48
   NiMoC-CN-Zeolite Y

5. Nanoporous carbon structures
   PAN SBA-15
   CM SBA-15
   CM MCM-48

   Substitution reactions

6. Nanoporous boron nitride structures
   BN nanospheres

(Dr. Eduardo Terrés, eterres@imp.mx)
1. NANOPOROUS SILICATES

**STRUCTURES**

- MCM-41 (3.5 nm), hexagonal
- MCM-48 (3.0 nm), cubic
- SBA-15 (6.5 nm), hexagonal
- SBA-16 (9.0 nm), cubic

**ON THE ROLE OF CROSS-LINKING DENSITY OF SURFACTANTS ON THE STABILITY ON SILICA-TEMPLATED STRUCTURE**


**NEW NiMo CATALYSTS SUPPORTED ON AL-CONTAINING SBA-16 FOR 4,6-DMDBT HYDRODESULFURIZATION EFFECT OF THE ALUMINATION METHOD**


2. Nanoporous silicates IMP structures

IMP-1 (C₂H₅OH)

Patente U.S. 7 005 118 B2
“Synthetic Mesoporous Material With Radially Assembled Nanotubes”
Eduardo Terrés Rojas, José Manuel Domínguez Esquivel
2. Nanoporous silicates IMP structures

IMP-2 (CH₃OH)

IMP-3 (C₃H₇OH)

IMP-2 (CH₃OH)

IMP-4 (CH₃COOH)

HIGH THROUGHPUT STUDY ON THE INDUCTION OF RADIAL DISTRIBUTION OF NANOTUBES AND SPHERICAL MORPHOLOGY IN SILICA PARTICLES BY SHORT-CHAIN POLAR CO-SOLVENTS”

3. Nanoporous silicate – carbon structures

PAN MCM-41

PAN MCM-48
4. Nanoporous silicate –carbon structures
+ carbon nanotubes

NiMoC-CN-PAN-MCM41
5. Nanoporous carbon structures

CM-MCM48

Hydrogen storage CM-MCM48

6. Nanoporous boron-nitride structures

Determination of structural properties of TiO$_2$ (anatase) Nanotubes

Definition of the problem

1. The structure is nanotubes or nanofibers

2. They present a one-dimensional crystal structure along the axis [010], Figure 1.

3. HRTEM shows a regular crystal arrangement in the transverse direction.

4. X-ray diffraction does not show characteristic peaks in crystalline structures.

Houston, we have a problem!

(Fernando Álvarez Ramírez, falvarez@imp.mx)
In the nanotube two of the network parameters can be found by HRTEM:

- Axial distance.
- Intra-spiral distance.

The nanotube is formed by a nano-sheet in spiral or tubular structure.

The sheets made of TiO$_2$ exist by themselves.
If the formation mechanism follows the sequence (1) bulk, (2) sheet and finally (3) nanotube then we only need to determine the basic unit of construction.
Axial Distance

Intra-spiral distance

0.37 nm

9.00 nm

Not defined region
Symmetries of tubular and spiral geometry

Crystal interlayer distance

Intra-spiral distance

Transverse periodic distance

Axial periodic distance
Transformation of superficial distances in the package to the tube

(Fernando Álvarez Ramírez, falvarez@imp.mx)
Evolution of the diffraction pattern
Evolution of the diffraction pattern
Evolution of the diffraction pattern

(Adsorption of nitrogen compounds)
Nanostructured latex particles may be synthesized by emulsion polymerization techniques.

First Stage Polymer  
Second Stage Polymer

(Flavio S. Vázquez Moreno, fvmoreno@imp.mx)
5. Nanostructured polymer particles.

Semicontinuous Emulsion Polymerization

Feed Tank

- Monomer
- Surfactant
- Initiator
- Water

Main Reactor

Seed

- (Monomer)
- Surfactant
- Initiator
- Water
5. Nanostructured polymer particles.

**Semicontinuous Emulsion Polymerization**

*Feed Tank*
- Monomer
- Surfactant
- Initiator
- Water

*Main Reactor*
- (Monomer)
- Surfactant
- Initiator
- Water

*Second stage*

**Pre-emulsion**

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Nanostructured polymer particles.

5. Nanostructured polymer particles.

**Mushroom**

PBuA/PS: 40/60 wt %

$D_p = 300 \text{ nm}$

Staining agent:

Osmium tetroxide

5. Nanostructured polymer particles.

Salami

PIs/PS

Toughening agent

Microtomed particle

Staining agent:

Phosphotungstic acid

500 nm
5. Nanostructured polymer particles.

PS/PMeA: 70/30 \( D_{pz} = 202 \text{ nm} \)

5. Nanostructured polymer particles.

Mickey Mouse

PS/PMeA: 70/30  \( D_{pz} = 202 \text{ nm} \)

5. Nanostructured polymer particles.

Hollow particles

P (BuA-co-MMA) /PMMA: 60/40 wt %

$D_{pz} = 420 \text{ nm}$

TEM
PBuA/PS : 50/50 wt %

\[ D_{pz} = 450 \text{ nm} \]

Toughening agents
Atomic force micrograph

Scanning electron microscopy

Heavy crude oil viscosity

Effect of the influence of molecular and nanostructured polymers on the viscosity of a heavy crude oil as a function of temperature.
5. Nanostructured polymer particles.

EPA, Clean Air Act

Supresion of volatil organic compounds

5. Nanostructured polymer particles.

Water borne coatings

- Polar functionalities (improved adhesion to metal supports)
- Crosslinked core (hard)
- Low permeability to water and salts
- Improved toughening

Core grafted to shell
Shell (soft)
5. Nanostructured polymer particles.

Atomic force microscopy

\[ \nu = \frac{1}{8} \]

Computational simulation

\[ \nu = \frac{1}{48} \]
5. Nanostructured polymer particles.

Maximal protection

Monte Carlo Simulation

Parameter of hydrophobicity 0.3

$R_{por} \left( \Omega \text{cm}^2 \right)$

$D_{pz} \text{(nm)}$

$\rho(z)$

$t = 2 \text{ h}$
$t = 1.5 \text{ h}$
$t = 0.5 \text{ h}$
$t = 1 \text{ h}$
$t = 0$

Best particle size
5. Nanostructured polymer particles.

- Carbon steel
- Core/shell particles functionalized with AA

![Graph showing the relationship between Log \( R_{por} \) (\( \Omega \text{ cm}^2 \)) and [AA] (% w) for 12 h and 24 h]
Composite coatings doped with TiO$_2$ nanotubes

5. Nanostructured polymer particles.

Drying rate of composite coatings

**Nanostructured particles**

**Nanostructured particles doped with TiO$_2$ nanotubes**

Water loss (wt %) vs. Time (min)

TPR-01
TPR-02
TPR-03
TPR-04
TPR-05
TPR-06
TPR-07

Water loss (wt %) vs. Time (min)

TPRN-01
TPRN-02
TPRN-03

T = 25 °C
5. Nanostructured polymer particles.

Adhesion on glass and 1018 Steel substrates

Coatings of nanostructured particles doped with TiO$_2$ nanotubes

Metal adhesion

Glass adhesion

Coatings of nanostructured particles
5. Nanostructured polymer particles.

Blistering evaluation

Coatings of nanostructured particles doped with TiO$_2$ nanotubes

Coatings of nanostructured particles

TPRN-1

No swelling

Día 8

TPRN-1
Magnetic nanostructured polymer particles

Magnetic demulsifying using magnetite (Fe₃O₄@A) nanoparticles coated with an acrylic Shell, dispersed in hexane and submitted to a external magnetic field.

J. Liang; N. J; S. Song; W. Hou, Magnetic demulsification of diluted crude oil-in-water nanoemulsions using oleic acid-coated magnetite nanoparticles, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 466, 197-202, 2015
Conclusive remark

IMP researchers develop integral and real solutions for energy and chemical industries.
Epilogue

Red Tezcatlipoca

Black Tezcatlipoca
Epilogue
Epilogue

Iglesia de San Bartolomé

Atepehuacan
Epilogue
Venus (Morning star)

Quetzalcoatl

Science

Venus (Evening star)
Red Tezcatlipoca

Creative energy
Thank you so much!!