Amphiphilic Nanohybrid Catalysts for Reactions at the Water/Oil Interface in Subsurface Reservoirs

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ABSTRACT: A novel technique is proposed for potential use in oil reservoirs. The technique consists in incorporating amphiphilic nanoparticles into the water injection. These hybrid nanoparticles can simultaneously act as emulsion stabilizers as well as carriers for catalytic species, e.g., metals. They can be active for in situ reactions, such as partial oxidation and hydrogenation, which may result in changes in rheological and interfacial properties of the oil, as well as modifying the wettability of the walls. These changes might be efficiently used to improve the oil recovery process. Specifically, partial oxidation of organic compounds lowers the water–oil interfacial tension and consequently increases the capillary number ($N_c$) of the system. Alternatively, partial hydrogenation of polynuclear aromatics can enhance the viscosity of the oil phase in the emulsion, thus improving the mobility ratio (MR). In addition, partial hydrogenation can be an effective pretreatment of the oil to favor the subsequent partial oxidation.

1. INTRODUCTION

Production from large oil fields is stopped many times when extraction becomes uneconomic, even though a significant fraction of the original oil in place (OOIP) has not yet been recovered. Development of alternative techniques to recover greater amounts of oil economically is an important challenge for engineers and researchers working in the oil industry. The incorporation of chemicals into the oil well as part of Enhanced Oil Recovery (EOR) strategies has been investigated for several decades. Recently, researchers have started to evaluate the potential impact of nanotechnology in subsurface reservoir characterization and oil recovery. In addition to the traditional phenomena, involving capillary, viscous, and gravitational forces, researchers are investigating the role of nanoscale interactions (electro-steric effects) in reservoir operations. It is believed that nanotechnology has the potential to transform the modeling and application of chemical EOR. As an example of these activities, researchers have proposed the use of nanoparticles to modify the wettability of porous media, which would alter the interaction between the rock and the fluids, increasing oil recovery (e.g., by increasing the relative permeability of the oil). In addition, the use of nanoparticles to reduce the oil–water interfacial tension (IFT) and enhance the recovery of oil has been experimentally tested. It has been claimed that, by using a combination of nanoparticles and an anionic surfactant, a decrease in IFT is obtained, which is ~70% greater than that reached using the surfactant alone. Moreover, when the same combination of particles and surfactant was used in packed columns, a 10% increase in oil recovery was obtained, compared to that obtained without particles. Other authors are investigating nanoparticles as contrast agents for the detection of the water/oil interface in the reservoir and visualization of residual oil.

Two major variables that may have a direct impact in the EOR process and can be modified by the addition of different chemicals and particles are the capillary number ($N_c$) and the mobility ratio (MR). The capillary number is defined as $N_c = \frac{v_d \mu_w}{\sigma}$, where $v_d$ is the Darcy velocity (fluid flux per unit of area), $\mu_w$ the viscosity of the mobilizing fluid (water), and $\sigma$ the interfacial tension (IFT) between the oil and the water. Typical $N_c$ values are ~$10^{-7}$ after water flooding. The injection of surfactants to reduce the oil–water IFT has been practiced for more than 35 years. Surfactant formulations based on alcohols dissolved in polyglycoside are generally very effective for enhancing oil recovery. In addition to decreasing the oil–water IFT, emulsifiers act as stabilizers of the interface, leading to a greater interfacial area and a decrease in the capillary forces that act on the oil inside the pores. Both wettability and entry pressure requirements affect the displacement of oil by water. When the rock is water-wet, spontaneous imbibition of the rock displaces oil from the pores. In addition, if during drainage the pressure gradient exceeds the required entry pressure (proportional to oil–water IFT) for the water, the displacement of oil from larger pores can be achieved at lower pressure gradients by decreasing the IFT.

The mobility ratio (MR) is a function of the relative permeability ($k_i$) of the porous media toward oil and water, respectively, and the viscosity ($\mu_i$) of the oil and the mobilizing fluid (water), respectively:

$$MR = \frac{(k_w/k_o)}{\left(\mu_w/\mu_o\right)}$$

To achieve displacement of the oil by the water, MR must be lower than unity. This condition can be obtained by increasing the viscosity of the sweeping fluid, relative to that of the oil, since a high $\mu_w/\mu_o$ value is favorable for oil displacement.

The effectiveness of the different polymers employed is dependent on their chemical structure and their interaction with the surfactants and alkalis used for IFT reduction, as well as the wettability of the rock.
well as their impact on apparent viscosity. For example, hydrolyzed polyacrylamide and Xanthan gum are examples of polymers that have been widely studied for EOR applica-
tions. In these studies, the rheology of the aqueous solution of these polymers combined with anionic surfactants and alkali has been investigated. It was found that, by using adequate concentrations, viscosities as high as 210 cP could be reached.\(^\text{14}\)

Oil-in-water (O-in-W) emulsions can be produced by addition of surfactants, which can improve the mobility of the oil by increasing the sweep efficiency. By changing the oil/water ratio and the salinity of the water, different emulsion types (either O-in-W or W-in-O) can be obtained. The rheological and interfacial properties are affected by these changes, which may result in enhanced oil recovery and variations in pressure drop, as measured in sand pack flood studies.\(^\text{15}\) Effect of pore blocking and diversion of injection fluids caused by addition of silica nanoparticles have been investigated in multiphase flow experiments in core floods. It has been observed that even though particles may propagate through sandstone cores, an addition of polymers usually is required to mobilize residual oil effectively.\(^\text{16}\)

Silica nanoparticles have been widely studied as stabilizers of Pickering emulsions for different applications. In a series of articles, Binks et al.\(^\text{17–25}\) have described systematic studies of the formation, stability, and structure of this type of emulsion. They represent a novel alternative to conventional emulsions and may prove to be advantageous in subsurface oil reservoir applications, because of their higher thermal and mechanical stability. By functionalizing the surface of the silica particles with silanol groups, the hydrophilic–lipophilic balance (HLB) of the particles can be adjusted, so the type of resulting emulsion (O-in-W or W-in-O) can be systematically changed.\(^\text{16}\) In contrast to regular emulsions stabilized by surfactant molecules, the stability of Pickering emulsions is greatly affected by different parameters. Among the most critical ones, we can mention composition of the organic and aqueous phases, contact angle among the water–solid–oil phases, particle size, particle concentration, and particle–particle interaction at the interface.\(^\text{17–25,255}\)

According to theoretical calculations, confirmed by experimental results, stable emulsions are formed when the particle size is within the range of 0.01–1.0 \(\mu\text{m}\). Outside this range, stability is hindered by either flocculation (when particles are too large) or Brownian motion (when particles are too small).\(^\text{26–28}\)

The effectiveness of particles in stabilizing emulsion droplets is strongly dependent on the extent of particle–particle interactions. For example, water-wetted particles tend to stabilize oil-in-water emulsions, while oil-wetted particles stabilize W-in-O emulsions. When they are mixed, their stabilizing action is neutralized, leading to a rapid coalescence of the emulsion droplets. Such observation suggests that the strength of the rigid film of particles at the water/oil interface depends significantly on the particle–particle interaction, which ultimately affects the emulsion stability.\(^\text{29}\)

The composition of the oil and aqueous phases is also important in determining the type of emulsion, because the surface of the particles is sensitive to the adsorption of surface-active molecules that can change the HLB or wettability of the particle, as well as the concentration of ionic species in the aqueous phase that can modify the electrostatic interaction between particles and, in consequence, their state of aggregation.

Particle concentration is another important parameter that directly affects the volume fraction of emulsion, stability, and droplet size of Pickering emulsions.\(^\text{30–32}\) Droplet size decreases with increasing particle concentration not only due to an increased interfacial area that accommodates more particles, but also due to the modification of rheological properties.\(^\text{33}\) At low concentration of particles at the fluid/liquid interface, the viscosity coefficients dominate the rheological parameters.\(^\text{150}\) However, at high concentrations, elastic contributions become significant, due to particle–particle interaction. As a result, the fluid at the colloid-laden interface develops a viscoelastic or pseudo-plastic behavior.\(^\text{154}\)

In a recent study, we have demonstrated the stabilization of Pickering emulsions by nano-hybrid particles composed of single-walled carbon nanotubes (SWCNT) and silica.\(^\text{34}\) We showed that we could control the droplet size and the effective volume fraction of emulsion by simply adjusting the water/oil (W/O) ratio and the amount of nano-hybrids. More recently, we further investigated the application of the concept to catalysis by incorporating active species on the surface of nano-hybrids, which catalyze reactions at the oil/water interface.\(^\text{35}\) Some of the reactions used to demonstrate the concept include metal-catalyzed hydrodeoxygenation and base-catalyzed aldol condensation of molecules with different solubilities, some water-soluble and some oil-soluble.\(^\text{166}\) The concept of “phase selectivity” was put forward by conducting hydrogenation on only one of the phases, while avoiding reaction in the other phase.\(^\text{168}\)

In this contribution, we have investigated the application of nano-hybrid particles that preferentially locate at the water/oil interface and catalyze different reactions (oxidation and hydrodehydrogenation), which may have an impact on EOR. In addition to the SWCNT/silica originally synthesized, different types of nano-hybrids were compared. Multivalved carbon nanotubes (MWCNTs) grown on alumina, onion-like carbon (OC) on silica, and Janus amphiphilic particles were found to be very effective in acting as emulsion stabilizers and catalyst support.\(^\text{178}\) Janus particles are dissymmetrically functionalized silica nano-hybrids that present a structure containing a hydrophobic and a hydrophilic side.\(^\text{38}\) We have recently investigated in detail the mobility of aqueous dispersions of these nanohybrids in porous media.\(^\text{39}\) Mobility studies on glass beads and crushed Berea sand columns demonstrated that the synthesized nano-hybrids successfully flow through porous media, particularly with the aid of small amounts of polymer (e.g., 500 ppm polyacrylamide, PAM). When the column was presaturated with oil, about half of the particles passed through the column while the other half remained trapped by the oil/water interface due to their amphiphilic properties. The effect of pH, salt, polymer, and surfactant concentration was also studied and it was concluded that neither salinity nor pH have a significant effect on the stability or mobility of the dispersions. In contrast, the addition of surfactants improved the stability of the dispersions, but decreased the surface activity of the particles and the stability of the emulsions. Therefore, we can envision that this type of nano-hybrids could propagate in the water flow through the porous media and reach the oil phase. At that point, they can preferentially adsorb at the oil/water interface, where, if properly loaded with an appropriate active species, they could catalyze a desired reaction.\(^\text{200}\)

2. EXPERIMENTAL SECTION

2.1. Materials. Nano-hybrids of various characteristics were synthesized and used as supports for catalytically active species. Among the various nano-hybrids investigated, SWCNTs were grown...
Table 1. Schematic Description of the Different Nanohybrids Used as Emulsion Stabilizer and Support of Metal Clusters

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Schematic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>SWCNT/silica</td>
<td><img src="image1.png" alt="Schematic SWCNT/silica" /></td>
</tr>
<tr>
<td>(b)</td>
<td>MWCNT/alumina</td>
<td><img src="image2.png" alt="Schematic MWCNT/alumina" /></td>
</tr>
<tr>
<td>(c)</td>
<td>Functionalized MWCNT/alumina</td>
<td><img src="image3.png" alt="Schematic Functionalized MWCNT/alumina" /></td>
</tr>
<tr>
<td>(d)</td>
<td>Onion carbon/silica</td>
<td><img src="image4.png" alt="Schematic Onion carbon/silica" /></td>
</tr>
<tr>
<td>(e)</td>
<td>Partially-hydrophobized silica</td>
<td><img src="image5.png" alt="Schematic Partially-hydrophobized silica" /></td>
</tr>
</tbody>
</table>
observed, there are clear differences in the emulsions; under the conditions studied, the emulsions stabilized with SWCNT/SiO$_2$ and onion carbon/SiO$_2$ present bigger droplets (average size of 35 and 15 μm, respectively) than those stabilized with MWCNT/Al$_2$O$_3$, functionalized MWCNT/Al$_2$O$_3$, and Janus silica particles (8, 2, and 4 μm, respectively). The emulsion fraction also varies, being lower for SWCNT/SiO$_2$ and onion carbon/SiO$_2$ (10% and 30%, respectively) and reaching values of 50%, 85%, and 90% for MWCNT/Al$_2$O$_3$, functionalized MWCNT/Al$_2$O$_3$, and Janus silica particles, respectively. Thus, among all the nanohybrids investigated, functionalized MWCNT/Al$_2$O$_3$ are the most effective nanohybrids for stabilizing emulsions, with high emulsion fractions and the smallest droplet sizes. The type of emulsion formed also is dependent on which nanohybrid is used, i.e., W-in-O for the SWCNT/SiO$_2$ and MWCNT/Al$_2$O$_3$ emulsions, and O-in-W for the other three nanohybrids. This dependence of the type of emulsion with the nanohybrid used is directly related to the hydrophilic/lipophilic balance in the nanohybrids. It is well-known that more hydrophilic particles are preferentially wetted by water, which makes the interface bend concavely toward the oil, producing O-in-W emulsions, and vice versa.

Therefore, onion carbon/SiO$_2$ and Janus silica particles are more hydrophilic, while SWCNT/SiO$_2$ and MWCNT/Al$_2$O$_3$ are more hydrophobic, because of their lower density of oxidized defects. The nitric acid treatment to the MWCNT/Al$_2$O$_3$ creates hydrophilic defects on the surface of the carbon nanotubes, which makes the functionalized nanohybrids more hydrophilic and stabilizes O-in-W emulsions under the conditions studied.

In summary, comparing the behavior of the different nanohybrids (emulsion fraction and droplet size), it can be concluded that the resulting interfacial area follows the sequence: functionalized MWCNT/Al$_2$O$_3$ > Janus silica particles > MWCNT/Al$_2$O$_3$ > onion carbon/SiO$_2$ > SWCNT/SiO$_2$.

Once the effectiveness of the nanohybrids for stabilizing emulsions was demonstrated, metal particles were deposited on their surface and used as catalysts for the partial oxidation of tetralin and the hydrogenation of polynuclear aromatics in emulsion systems. Figure 2 shows a schematic illustration of the hydrogenation of polynuclear aromatics at the water/oil interface in the nanohybrid-stabilized emulsions. In the case of carbon nanotube-based-nanohybrids, we have shown in a previous study that the carbon nanotubes are oriented toward the organic phase, while the metal oxide nanoparticles remain closer to the aqueous phase.

The type of nanohybrids used also affects the dispersion of the metal particles. Figure 3 shows TEM images of the different nanohybrid-supported Pd catalysts in this work. Although the catalyst preparation conditions were identical in all cases (incipient wetness impregnation of the aqueous solution of the metal precursor), the size of the metal cluster varied with the type of nanohybrids used as support. That is, the average sizes of the Pd cluster were 4.9, 4.6, 3, 2.5, and 2.1 nm, for SWCNT/Al$_2$O$_3$, onion carbon/SiO$_2$, MWCNT/Al$_2$O$_3$, Janus silica particles, and functionalized MWCNT/Al$_2$O$_3$, respectively.

The trend is clear: the higher the density of anchoring sites on the support, the higher the metal dispersion.

Having in mind a potential application in subsurface reservoirs, we studied the catalytic activity of several nano-hybrids (see Table 2) for oxidation and hydrogenation reactions of interest in subsurface conversion. Figure 4 illustrates the concept of simultaneous injection of the aqueous dispersion of the nanoparticles and the gaseous reactant to react in situ for subsurface applications. As an example of a possible in situ reaction, the partial oxidation of hydrocarbons appears as a desirable conversion to increase the polarity of the oil molecules located at the interface. This conversion might significantly reduce the oil/water IFT, enhancing the capillary number. At the same time, if the oxidized molecules migrate to the water phase due to their enhanced water affinity, the viscosity of the mobilizing fluid will increase and, consequently, the sweeping efficiency of this fluid would improve.

3.2.1. Partial Oxidation of Oil Constituents. **Catalyst** Activity. Tetralin oxidation was carried out at 80 °C and 200 psi under a constant 200 sccm flow rate of air. The water/oil volume ratio in the liquid phase was 0.5, and the total volume was 30 mL. The total nanohybrid catalyst mass was 60 mg with a metal loading of 10 wt %. Different nanohybrid supports and different metals were used for this reaction. Table 2 summarizes the conditions studied.
Figure 2. Schematic representation of the hydrogenation of phenanthrene at the water/oil interface in the nanohybrid-stabilized emulsions. The reactants and intermediate products are only soluble in the organic phase, while the hydrophobic part of the nanohybrids (CNT) contains most of the catalytically active species (Pd clusters).

Figure 3. High-resolution TEM images of the catalysts prepared with 5 wt % Pd supported on different nanohybrids (see Table 1): (a) SWCNT/SiO$_2$, (b) MWCNT/Al$_2$O$_3$, (c) functionalized MWCNT/Al$_2$O$_3$, (d) onion carbon/SiO$_2$, and (e) Janus silica nanoparticles.
the characteristics of the catalysts tested in the partial oxidation reactions.

The activity of different metal catalysts loaded on the SWCNT/SiO$_2$ nanohybrids was tested under the same reaction conditions. A sample of bare nanohybrids without any metal was used as a blank for comparison. The tetralin conversion, product yields, and selectivities obtained over the various samples after a reaction period of 24 h are summarized in Table 3. The main products of the reaction are 1-tetralone and 1-tetralol, as previously reported,$^{46-51}$ with traces of naphthalene and dihydronaphthalene.

The results clearly show that Pd and Cu lead to much higher conversions than the other metals. Regarding the selectivity toward the two possible products, Cu clearly displays the highest selectivity toward the ketone (84.5%). For this specific application, tetralone is the desired product, since it is more stable than the alcohol, which undergoes dehydration, losing its polarity.

With the two most active metals (Pd and Cu), different metal loadings (6 and 10 wt %) were compared. The results are presented in Table 4. For the Pd catalysts, an increase in conversion with the metal loading is observed. In contrast, the Cu catalysts showed the opposite behavior, since it is probable that high metal loading in Cu catalysts leads to metal agglomeration and, consequently, lower activity. Thus, runs at varying...

**Table 2. Catalysts Tested on Tetralin Partial Oxidation**

<table>
<thead>
<tr>
<th>metal</th>
<th>metal loading (wt %)</th>
<th>(a) Support: SWNT on Silica</th>
<th>(b) Support: MWNT on Alumina</th>
<th>(d) Support: Onion Carbon/Silica</th>
<th>(e) Support: Janus Silica Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>6, 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>6, 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3. Results for the Catalyst Screening for Tetralin Oxidation at 80 °C and 200 psi**

<table>
<thead>
<tr>
<th>metal</th>
<th>tetralin conversion (%)</th>
<th>Products Yield, Y (%)</th>
<th>Selectivity, S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.0</td>
<td>tetralone</td>
<td>tetralol</td>
</tr>
<tr>
<td>Pd 6.0</td>
<td>64</td>
<td>36</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu 4.8</td>
<td>84</td>
<td>16</td>
<td>0.74</td>
</tr>
<tr>
<td>Fe 1.3</td>
<td>0.85</td>
<td>42</td>
<td>0.69</td>
</tr>
<tr>
<td>Cr 1.0</td>
<td>0.69</td>
<td>33</td>
<td>0.35</td>
</tr>
<tr>
<td>blank 0.49</td>
<td>0.35</td>
<td>29</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*Conditions: reaction time, 24 h; O/W ratio, 0.5; total volume, 30 mL; catalyst weight, 60 mg; metal loading, 10 wt %; and air flow, 200 sccm. Support (a) (nanohybrid SWNT/silica) was used.*

**Table 4. Comparison of Metal Loadings for the Cu, Pd on Catalysts on Support (a) (Nanohybrid SWNT/Silica) for Tetralin Oxidation at 80 °C and 200 psi**

<table>
<thead>
<tr>
<th>metal</th>
<th>metal loading (%)</th>
<th>Selectivity, S (%)</th>
<th>Products Yield, Y (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>tetralin conversion (%)</td>
<td>tetralone</td>
<td>tetralol</td>
</tr>
<tr>
<td>Pd 6 3.0</td>
<td>68</td>
<td>32</td>
<td>2.0</td>
</tr>
<tr>
<td>10 6.0</td>
<td>64</td>
<td>36</td>
<td>4.0</td>
</tr>
<tr>
<td>Cu 6 8.2</td>
<td>89</td>
<td>11</td>
<td>7.3</td>
</tr>
</tbody>
</table>

*Conditions: reaction time, 24 h; O/W ratio, 0.5; total volume, 30 mL; catalyst weight, 60 mg; and air flow, 200 sccm. Support (a) (nanohybrid SWNT/silica) was used.*
reaction times were evaluated on the two most active materials, i.e., 10 wt % Pd and 6 wt % Cu supported on the SWCNT/SiO₂ nanohybrids.

Figure 5 shows that both metal catalysts exhibit similar activity evolution with reaction time. That is, the conversion is initially negligible, with zero derivative at zero time, but the slope begins to increase with time, indicating an induction of activity. The induction period lasts for several hours, i.e., ∼18 h for the Cu catalyst and ∼24 h for the Pd catalyst. Similarly long induction periods have been previously observed in other partial oxidation reactions.\\(^1\),\\(^2\) It is generally accepted that these induction periods are related to the rather slow generation of hydroperoxides. They are intermediates in this type of reactions, which typically involve a series of complex free radical steps. In the specific case of the oxidation of tetralin, it has been shown that a crucial intermediate is tetralin 1-hydroperoxide,\\(^2\) which readily decomposes to yield 1-tetralone and 1-tetralol, the two main products experimentally observed.\(^5\),\\(^6\) As a result of this decomposition, the free radicals formed further attack tetralin, accelerating the overall reaction, which proceeds autocatalytically.\\(^7\)

Several nanohybrid supports were tested using Pd as the active metal with a loading of 10 wt %. The results on the different nanohybrids are compared in Table 5. It can be observed that the silica Janus particles and the MWCNT/ alumina hybrids showed a 5-fold increase in activity, compared to the first generation of nanohybrids based on SWCNT on silica. This activity enhancement is mainly attributed to the better capability of these particles of forming emulsions with smaller droplet sizes, resulting in a higher interfacial area than that obtained with the SWCNT on silica (see Figure 1). In addition, when comparing MWCNT to SWCNT and OC, the former has a better capability of anchoring Pd particles, because of the higher number of defects on their surface, which, as illustrated in Figure 3, provides active sites for metal deposition. The series of reactions over time using the MWCNT on alumina catalyst were carried out, and the results are shown in Figure 6. As stated before, the values of tetralin conversion and products yield are higher than those observed in Figure 5 for the SWCNT/silica catalysts. However, the activity induction period was still evident, since the conversion grew nonlinearly (e.g., 10% after the first 18 h of reaction, but 30% after 24 h). Investigating ways to shorten the activation period, we found that, when the catalyst was prereduced in H₂, the induction pattern changed drastically. For instance, a series of reactions was conducted at different reaction times, comparing the behavior of MWCNT/alumina-supported metal catalysts, with and without a pretreatment under a 200 sccm flow of H₂ at 80 °C and 200 psi for 3 h. The comparison is summarized in Figure 7 and clearly shows that prereducing the catalyst in H₂ significantly shortens the induction period. It is evident that the prereduction activates the catalyst to a state that would take longer.

**Table 5. Result of the Reaction Using 10 wt % Pd Catalysts on Different Supports for Tetralin Oxidation at 80 °C and 200 psi**

<table>
<thead>
<tr>
<th>nanohybrid support</th>
<th>tetralin conversion (%)</th>
<th>Selectivity, S (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) SWNT on silica</td>
<td>6.0</td>
<td>64</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>(b) MWCNT on alumina</td>
<td>27.9</td>
<td>65</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>(d) onion carbon on silica</td>
<td>6.7</td>
<td>63</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>(e) silica Janus particles</td>
<td>30.2</td>
<td>59</td>
<td>41</td>
<td></td>
</tr>
</tbody>
</table>

*Conditions: reaction time, 24 h; O/W ratio, 0.5; total volume, 30 mL; catalyst weight, 60 mg; and air flow, 200 sccm.*

dx.doi.org/10.1021/ef300119p | Energy Fuels XXXX, XXX, XXX–XXX
much longer to be obtained under reaction conditions. For example, after 12 h of reaction, the conversion of tetralin on the pretreated catalyst is more than 4 times greater than on the untreated catalyst. However, after 24 h, the difference in conversion is much smaller. We believe that this difference in length of the induction period is due to the generation of the active sites by the prereduction step. It appears that the fully oxidized Pd species that result from the initial catalyst calcination under air are not active for partial oxidation, but rather partially reduced Pd species are needed for activity. The pretreatment seems to accelerate the formation of these species, which may provide sites for oxygen and/or tetralin adsorption. Under reaction without prereduction, these species may still form, but it seems to take much longer.

3.2.2. Changes in Interfacial Tension After Reaction. The interfacial tension of several mixtures of tetralin/tetralone and water was measured to verify that it decreases when oxidized polar groups (tetralone) are generated from the nonpolar phase (tetralin), which occurs under oxidation reaction. The measurements were compared to a model\textsuperscript{53} that predicts an exponential decay with the concentration of polar species added to a nonpolar phase. As shown in Figure 8, the fitting is very good (obtaining a mean absolute error (MAE) of 0.83 dyne/cm and an average percentage error of 5.4%) and demonstrates that indeed, the addition of small amounts of tetralone generates a considerable decrease in interfacial tension. This decrease is caused by the enrichment of the polar compound at the oil/water interface, because of a higher affinity of the polar compound to water, compared to the nonpolar bulk phase.

![Figure 8. Interfacial tension between mixtures of tetralin/tetralone and water determined experimentally (symbols) and using the exponential model proposed by Kim and Burgess.\textsuperscript{53} The mean absolute error is 0.8 dyne/cm (or 5.4%).](image)

Although the reduction in IFT shown in Figure 8 does not reach the typical reductions that one would expect for EOR techniques, it serves as an initial proof of concept for this application. If the oxidation reaction were carried out to convert molecules with lower polarity than that of tetralin, such as a long-chain olefin, the impact on the IFT reduction would be increased. Moreover, a potentially important advantage of the underground oxidation reactions in oil-wet reservoirs could be the modification of the wettability of the porous medium. If the catalytic nanoparticles migrate into the porous rock, they may catalyze the oxidation of the asphaltene-type deposits on the walls of the rock, thus changing their surface chemistry. One could anticipate that oxidized asphaltenes may convert the rock wall from oil-wet to water-wet, which could have a huge impact in oil mobility.

Tetralin has been selected as a model compound representing the complex mixtures typically found in crude oil to simplify the experimental procedures required to analyze the results of the oxidation reactions. However, we have tested the activity of these catalysts in the presence of other aromatics, olefins, paraffins, and naphthenics, with no significant changes in the measured tetralin oxidation activity. Thus, it can be expected that the results reported here can be well-extrapolated to reactions with compositions similar to that of crude oil.

3.3.1. Hydrogenation of Polynuclear Aromatics. Catalyst Activity. For the study of hydrogenation reactions,\textsuperscript{497} MWCNT on alumina nanohybrids were pretreated with nitric acid (16 M) at 100 °C for 6 h to create anchoring sites at the MWCNT walls. With this particular pretreatment, the Pd nanoparticles become preferentially coordinatized at the oxidized MWCNT sites,\textsuperscript{54} since the density of defects on the MWCNT increases upon oxidation with nitric acid. This enhancement in the metal—support interaction improves the metal dispersion over the hydrophobic carbon nanotubes, which is responsible for the conversion of the hydrocarbons present in the organic phase. In addition, this oxidation treatment of the MWCNT/alanina also enhances the repulsive forces between MWCNT, because of the higher density of charge that is caused by the carboxylic acid groups. This repulsion results in a better dispersion of the nanoparticles in the liquid phase, increasing the emulsification efficiency of the nanohybrid.

The hydrogenation reactions were run for 24 h at 200 °C and 900 psi under a constant 110 scm flow of H\textsubscript{2}. The water/oil volume ratio in the mixture was kept equal to 1 and the total mass of catalytic nanohybrid of MWCNT(ox)/alumina was 30 mg. The active metal employed was Pd (5 wt %).

Figure 9 shows the different products obtained in the hydrogenation of phenanthrene over the 5 wt % Pd on MWCNT(ox)/alumina after a 24 h reaction period under 900 psi of H\textsubscript{2} and 200 °C, including the individual yields obtained at a total conversion of 89.39%. The main product was 9,10-dihydrophenanthrene (67.2% yield), followed by 1,2,3,4,5,6,7,8-octahydrophenanthrene (15.6% yield), 1,2,3,4,4a-octahydrophenanthrene (8.7% yield), and 1,2,3,4- tetrahydrophenanthrene (1.2% yield).

One of the possible effects of hydrogenation on rheological properties could be associated with the increased flexibility of the polyaromatic molecules when the aromaticity is broken. This interesting effect could explain the change of the state of matter observed when the phenanthrene (which is a solid at room temperature) is selectively hydrogenated toward the 9,10-dihydrophenanthrene (a liquid at room temperature). Hence, based on this observation, we decided to study the effect of the extent of hydrogenation of the polyaromatic molecules on the dynamic viscosity (\(\mu\)).

For this analysis, we employed the known approach of combining experimental data with Quantitative Structure—Property Relationship (QSPR) software.\textsuperscript{55,56} This method allowed us to predict the dynamic viscosity of molecules that are not commercially available. The QSPR software used for this purpose was MDL QSAR provided by MDL Information Systems, Inc. In this approach, experimental measurements of a given property, such as viscosity, become related to the molecular structure using linear models in terms of molecular descriptors (MD), which are readily calculated from the structure of the molecule.
The first step in this method is the construction of a database of the property of interest for molecules with similar structure to those of the unknown (e.g., aromatics, naphthenics, etc.). For building this database, we used viscosity data from the work of Ivanciuc et al. for 27 polyaromatics and polynaphthenics. A model was generated with this set of molecules and tested by the cross-validation method, which confirmed that the training set was statistically reliable and, as demonstrated in Figure 10, it was described very well by the regression equation shown below. The square correlation coefficient ($r^2$), standard deviation (SD), and mean absolute error (MAE) of the resulting model (eq 1) were 0.9817, 0.3594 cP, and 0.26 cP, respectively.

$$
\mu_{(cp)} = -20.23H_{\text{max pos}} - 11.05Q_v + 2.07x_2 - 8.61x_{p9} \\
+ 6.48xp_{9} + 0.66SsCH_3 + 32.34 \tag{1}
$$

where $H_{\text{max pos}}$ is the largest E-state in a hydrogen atom in the molecule, $Q_v$ the molecular and group polarity index, $x_2$ the connectivity simple second-order chi index, $x_{p9}$ the connectivity simple ninth-order path chi index, $xp_9$ the connectivity valence sixth-order path chi index, and $SsCH_3$ the count of all the $-CH_3$ groups in the molecules.

This model was used to predict the dynamic viscosity of the 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene, 1,2,3,4,4a-octahydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthen, and tetradecanohydrophenanthrene, and the results are shown in Table 6. Initially, the reduction of the side or central ring of the phenanthrene is enough to change the state of matter of the bulk phenanthrene from solid to liquid. This could be attributed to the change in the shape of the molecule, that, in the case of the phenanthrene, is completely flat, allowing the arrangement of the molecules in a crystal structure, while in the case of the 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene, the arrangement is less planar, with viscosities of 3.457 and 3.549 cP, respectively. Then, further hydrogenation of the phenanthrene yields to the 1,2,3,4,4a-octahydrophenanthrene (6.123 cP) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (4.285 cP), with higher viscosities than those obtained during the first hydrogenation. This reverse effect in the dynamic viscosity could be ascribed to the increase of the dispersion forces between molecules and the larger molecular volume obtained upon hydrogenation. Finally, the complete hydrogenation of the phenanthrene to tetradecanohydrophenanthrene increases the viscosity up to 19.82 cP.

### 3.3.3. Other Benefits of the Partial Hydrogenation

In addition to the impact on the oil viscosity, partial hydrogenation is an effective pretreatment previous to the partial oxidation of the aromatic compounds. That is, partially hydrogenated aromatic compounds (e.g., tetralin) are more

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Table 6. Change in the QSPR Molecular Descriptors and the Viscosity of Phenanthrene upon Hydrogenation Reaction of Phenanthrene

<table>
<thead>
<tr>
<th>compound</th>
<th>$H_{\text{max pos}}$</th>
<th>$Q_v$</th>
<th>$x_2$</th>
<th>$x_{p9}$</th>
<th>$xp_9$</th>
<th>$SsCH_3$</th>
<th>property viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,10-dihydrophenanthrene</td>
<td>1.2284</td>
<td>1.3272</td>
<td>5.9941</td>
<td>0.8958</td>
<td>0.9319</td>
<td>0.0000</td>
<td>3.54</td>
</tr>
<tr>
<td>1,2,3,4-tetrahydrophenanthrene</td>
<td>1.2114</td>
<td>1.437</td>
<td>5.9941</td>
<td>0.8958</td>
<td>1.0521</td>
<td>0.0000</td>
<td>3.45</td>
</tr>
<tr>
<td>1,2,3,4,5,6,7,8-octahydrophenanthrene</td>
<td>1.1424</td>
<td>1.7018</td>
<td>5.9941</td>
<td>0.8958</td>
<td>1.4162</td>
<td>0.0000</td>
<td>4.28</td>
</tr>
<tr>
<td>1,2,3,4,4a,9,10,10a-octahydrophenanthrene</td>
<td>1.1424</td>
<td>1.6528</td>
<td>5.9941</td>
<td>0.8958</td>
<td>1.6164</td>
<td>0.0000</td>
<td>6.12</td>
</tr>
<tr>
<td>tetrahydrophenanthrene</td>
<td>0.5191</td>
<td>2.1147</td>
<td>5.9941</td>
<td>0.8958</td>
<td>2.5776</td>
<td>0.0000</td>
<td>19.85</td>
</tr>
</tbody>
</table>
reactive toward partial oxidation than their saturated (e.g., decalin) and completely aromatic (e.g., naphthalene) counterparts. For example, while tetralin is readily oxidized under mild conditions (as shown in this work), decalin and naphthalene cannot even start to be oxidized. The main reason for this difference in activity is the presence of the α carbon in the 1-position in tetralin. This C atom has two H atoms weakly bound, because of the resonance stabilization of the aromatic ring. Consistent with this, we observe that tetralin is only oxidized at the C1 position, and no products of partial oxidation at a different C atom are observed.

Furthermore, selective hydrogenation to target products could also be used to convert components in the oil phase of the emulsions to increase the viscosity of the sweeping fluid. As a result, this decrease in mobility ratio will result in enhancement of the oil recovery.

4. CONCLUSIONS

From the results presented in this paper the following conclusions can be drawn:

1. In addition to be able to stabilize emulsions, the catalysts resulting from the deposition of metals on nanohybrid supports are active for both oxidation and hydrogenation of organic compounds at the oil/water interface.

2. The oxidation of aromatic compounds and hydrocarbons at the interface reduces the oil–water IFT, since the species with higher dipole moment (oxygenates) dominate the interface. The reduction of the IFT improves the capillary number, which should enhance the oil recovery.

3. The complete hydrogenation of the polyaromatic molecules increases the viscosity of the resulting products. The selective hydrogenation could be an appropriate strategy to increase the mobility of the sweeping fluid (emulsion), improving the mobility ratio.

4. As a result, the combination of oxidation and hydrogenation reactions would enhance the oil recovery by simultaneously increasing the capillary number (decreasing the interfacial tension) and enhancing the mobility ratio (increasing the viscosity of the sweeping phase), with the same effect as the currently used injections of surfactant and polymer water solutions.

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Notes

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