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Sorption of Asphaltenes onto Nanoparticles of Nickel Oxide Supported on Nanoparticulated Silica Gel

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ABSTRACT: The aim of this study is to analyze the effect of temperature and NiO content on the asphaltene uptake by a hybrid nanomaterial composed of nickel oxide nanoparticles supported on a nanoparticulated matrix of silica gel. The silica gel nanoparticles were synthesized by sol–gel method. The silica-supported nanomaterial was prepared by an incipient wetness technique. At constant temperature, adsorption of asphaltenes onto the hybrid nanomaterials increased with increasing its nickel oxide content. Regardless of the asphaltene concentration, asphaltene uptake by the hybrid nanomaterials decreased with increasing temperature. Experimental data on asphaltene sorption isotherms were adequately adjusted by the Freundlich model. The calculated thermodynamic properties for the sorption of asphaltenes onto the nanoparticulated-materials confirmed the spontaneity and exothermic nature of this process.

1. INTRODUCTION

The global reserves of heavy oil, extra-heavy oil, and bitumen are very large and spread across many countries, mainly Canada, Venezuela, Russia, and the U.S.A. Colombia is increasing its production of this kind of unconventional oil resource, and so, it has the potential of becoming an important regional player.^{1–4}

Heavy and extra-heavy oils are characterized by high viscosities and high densities compared to conventional oils.⁵ They could originate as conventional oils that formed in deep formations but migrated to superficial strata where they underwent degradation by several agents, and as a consequence, the lightest hydrocarbons escaped. These unconventional oils are deficient in hydrogen and have high carbon, sulfur, heavy metals, and asphaltene contents.⁵

Asphaltenes are defined as the fraction of oil, bitumen, or vacuum residue that is insoluble in low molecular weight paraffins such as *n*-heptane or *n*-pentane, while being soluble in light aromatic hydrocarbons such as toluene, benzene, or pyridine.^{6,7} The structure of asphaltenes is formed by polyaromatic cores attached to aliphatic chains containing heteroatoms such as nitrogen, oxygen, sulfur, and metals such as vanadium, iron, and nickel.^{7,8} Asphaltenes contain polar and nonpolar groups (“amphiphilic” behavior) and tend to form colloidal aggregates. It has widely been documented that viscosity of heavy oils can dramatically increase by the asphaltene aggregation phenomenon.⁹ Asphaltene precipitation and deposition can occur at different stages during petroleum production causing formation damage and plugging of pipeline and production equipment.⁷

The adsorption of previously precipitated asphaltenes onto mineral surfaces can lead to formation damage in oil reservoirs by reducing the oil effective permeability.⁷ If the polar group of the molecular structure of asphaltenes is adsorbed onto the rock surface, rock wettability can be altered from water-wetting to oil-wetting, affecting final oil recovery. The sorption phenomenon is governed by intermolecular forces associated

to the main functional groups (carboxylic, phenolic, etc.) presented in the molecular structure of asphaltenes.⁷

Several researchers have studied the adsorption of asphaltenes onto solid surfaces focused on understanding process phenomenology.^{10–22} Pernyeszi et al.^{19,20} studied the effect of different types of materials (clays minerals and two cores taken at different well depths) on asphaltene adsorption. Authors found that isotherms showed a type I behavior according to the IUPAC criteria. Gonzalez et al.²³ reported that isotherms of asphaltene sorption onto mineral surfaces followed a Langmuir-type behavior, with a maximum adsorption capacity of 1–2 mg/m². Other works studying the adsorption of asphaltenes on adsorptive clays also concluded that isotherms exhibited a type I behavior, indicating the formation of a monolayer onto the porous matrix surfaces.^{7,24,25} On the other hand, several researchers have reported multilayer adsorption of asphaltenes.^{26–28} Acevedo et al.²⁶ obtained adsorption rate constants and adsorption isotherms on silica surfaces for toluene solutions of Furiel asphaltenes. Authors reported a slow tendency from L-type to H-type adsorption isotherms measured at different times. They argued that their results were affected by the formation of asphaltene multilayer at the silica surface and the adsorption of aggregates (dimers, trimers, etc.) as well as single asphaltene molecules. Marczewski and Szymula^{27,28} argued that adsorption measurements of asphaltenes on several minerals are not well described by a simple model such as the Langmuir model. They criticized some researchers because they concluded shortly that isotherms are of Langmuir type and their conclusions are based only on the general shape of isotherms, without deeper insight into its course. According to the authors, adsorption isotherms contain initial lines of Freundlich characters with slope coefficients or/and inflections characteristic of lateral interactions, as well as

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multiple steps that may be related to surface phase reorientation, multilayer formation, or hemimicelle formation.

It has been argued that nanotechnology can have a great potential for the *in situ* upgrading of heavy oils. The idea is that highly adsorptive nanomaterials have the ability to quickly capture asphaltenes from crude oils by its high affinity, improving oil mobility and avoiding asphaltene aggregation and deposition onto the rock surface. With such proposal, the Alberta Ingenuity Centre for In-Situ Energy at the University of Calgary has developed several studies investigating the characteristics of nanoparticles of various metal oxides as adsorbents for asphaltenes extracted from oil sands.^{7,29–32} Researchers from the Alberta Ingenuity Centre for In-Situ Energy at the University of Calgary performed experiments evaluating the adsorption of asphaltenes on nanoparticles of Fe_3O_4 , Al_2O_3 , Co_3O_4 , TiO_2 , MgO , CaO , and NiO , and obtained isotherms following a Langmuir type behavior. The authors reported a fast equilibrium time, < 2 h, due to the extent of dispersion of nanoparticles and external adsorption phenomena. They also reported that a relationship between adsorption affinity and catalytic activity is also found to exist.^{31,32} Dudášová et al.³³ analyzed the effect of asphaltene source (asphaltenes extracted from different crudes: Gulf of Mexico, West Africa, North Sea, and Brazil) on their adsorption from aqueous solution onto inorganic hydrophilic and hydrophobic nanoparticles (TiO_2 and SiO_2). Data were fitted to Langmuir type adsorption isotherms and showed a higher dependence on the type of nanoparticle than that of the asphaltenes source. Hydrophobic silica was the material with the lowest adsorption capacity.

To the best of our knowledge, studies related to the equilibrium thermodynamic properties of sorption of asphaltenes on hybrid nanomaterials such as nanoparticles of metal oxides supported on a nanoparticulated matrix, at different temperatures, have not been reported in literature. The aim of this study is to analyze the effect of temperature and content of NiO on surface nanosilica on the asphaltene uptake by a hybrid material composed of nickel oxide nanoparticles supported on a nanoparticulated matrix of silica gel. The silica gel was synthesized by sol–gel method. The silica-supported nanomaterial was prepared by an incipient wetness technique, widely used to prepare heterogeneous catalysts.^{34,35} Asphaltenes were isolated from a Colombian heavy crude oil.

2. EXPERIMENTAL SECTION

2.1. Materials. Asphaltenes were isolated from “The HOCHA” crude oil, which is a heavy oil (19.2° API) produced from a reservoir located in the south of Colombia. Ethanol was purchased from Fisher Scientific Co, and *n*-heptane (99%) was purchased from Merck and Sigma Aldrich.

2.2.1. Methods. *Asphaltenes Isolation Protocol.* Asphaltene samples were isolated by following a standardized procedure. An excess of *n*-heptane was added to the crude oil in a volume ratio of 40/1. The mixture was sonicated for 2 h at 25 °C and further stirred at 300 rpm for 20 h. The precipitated fraction was filtered using a 8 μm Whatman filter paper and washed with *n*-heptane at a ratio of 4/1 (g/mL). Asphaltene samples were centrifuged at 5000 rpm for 15 min and left to rest for 24 h. The cake was washed with *n*-heptane several times until the color of the asphaltenes became shiny black. Then, the sample was dried in a vacuum oven at 25 °C for 12 h. Finally, the obtained asphaltene was homogenized in a mortar.⁷ Precipitated asphaltenes were redissolved in toluene for preparing a stock solution at 3000 mg/L. Solutions with different

concentrations, 150, 250, 400, 750, 1000, and 1500 mg/L, were prepared from the stock solution by dilution.

2.2.2. Nanomaterials Synthesis. Silica nanoparticles were synthesized by the sol–gel method following an acid route. The gel was prepared from TEOS (tetraethoxysilane), ethanol, water, and HNO_3 . Synthesis was carried out following the procedure described by Nogami and Moriya³⁶ and Brinker.³⁷ The molar ratio of $\text{TEOS}/\text{H}_2\text{O}$ was 1/4. Catalyst was added at 5 wt %. Reactants were continuously stirred for 24 h at room temperature, further centrifuged at 4000 rpm for 5 min, and left to stand overnight. Nanoparticles were washed with ethanol. Obtaining the size of particles at nanoscale required controlling the acidity, basicity, and/or the TEOS/water molar ratio.

In the incipient wetness technique, synthesized nanosilica was impregnated with aqueous solutions of nickel nitrate $\text{Ni}(\text{NO}_3)_2$ at different concentrations (5 and 15 wt %) for 3 h, further dried at 120 °C for 6 h and calcined at 450 °C for 6 h.³⁵ The obtained hybrid nanomaterials are called, in this study, supported hygroscopic salts (SHS) and are denoted by the initial letter of the support followed by the symbol of the cation of resultant metal oxide after calcination and the weight percentage of the aqueous solutions of nickel nitrate $\text{Ni}(\text{NO}_3)_2$ used for the impregnation. Thus, SNi15 denotes a SHS synthesized by using nanosilica gel as support and contains 15 wt % $\text{Ni}(\text{NO}_3)_2$, which would produce after calcination a nanosilica having NiO nanoparticles on its surface.

2.2.3. Samples Characterization. Samples of nanomaterials were characterized by N_2 adsorption at -196 °C and X-ray diffraction (XRD). Nitrogen adsorption isotherms were obtained with an Autosorb-1 from Quantacrome after outgassing samples overnight at 140 °C under high vacuum (10^{-6} mbar). BET surface area (S_{BET}) values were calculated using the model of Brunauer, Emmet, and Teller (BET).^{38,39} X-ray diffraction patterns were recorded with a Philips PW1710 diffractometer using $\text{Cu K}\alpha$ radiation. The mean crystallite size of the particles (d_p) was obtained by applying the Scherrer equation to the main diffraction peak.³⁵

2.2.4. Adsorption Experiments. A calibration curve of UV absorbance versus asphaltene concentration at 400 nm was constructed from the prepared solutions with known concentrations. Toluene was used as solvent agent for dilution, as well as a blank.⁷

A constant mass of nanoparticles of the SHS and of pure silica (100 mg) were added to asphaltene solutions of constant volume (10 mL). Each solution was stirred at 200 rpm for 24 h at 25, 40, 55, and 70 °C in order to reach the sorption equilibrium. The time evolution of the measured asphaltene concentration indicated that a time of 2 h was enough to reach the sorption thermodynamic equilibrium. When asphaltene solutions with high concentrations (greater than 250 mg/L) were tested, an additional dilution with toluene was necessary in order to obtain the desired absorbance value within the calibration curve.

3. ISOTHERM MODELS

3.1. Langmuir Model. The Langmuir model has been widely used to correlate experimental data of sorption equilibrium.³⁸ This model assumes that the process occurs on a homogeneous surface by monolayer adsorption. It was originally derived from kinetic data of adsorption and desorption, taking into account that equilibrium is obtained when the rates of adsorption and desorption are equal. The Langmuir equation can be expressed as follows:

$$N_{\text{ads}} = N_{\text{ads,max}} \left(\frac{K_L C_E}{1 + K_L C_E} \right) \quad (1)$$

where N_{ads} is the amount of asphaltenes adsorbed onto the nanoparticles (mg/g), C_E is the equilibrium concentration of asphaltenes in the solution phase (mg/L), K_L is the Langmuir equilibrium adsorption constant related to the affinity of binding sites (L/mg), and $N_{\text{ads,max}}$ is defined as the monolayer

saturation capacity, representing the maximum amount of asphaltenes per unit mass of adsorbent (mg/g).

3.2. Freundlich Model. Freundlich proposed an empirical expression representing the isothermal variation of adsorption of a quantity of mass adsorbed by unit mass of solid adsorbent with equilibrium concentration.³⁸

$$N_{\text{ads}} = K_F C_E^{1/n} \quad (2)$$

where K_F is the Freundlich constant related to the adsorption capacity ((mg/g)(L/mg)^{1/n}) and $1/n$ is the adsorption intensity factor (unitless).

4. ESTIMATING OF THE THERMODYNAMIC PROPERTIES

Key thermodynamic properties were calculated to characterize the adsorption phenomenon and process spontaneity. They were estimated from the classical expression for the Gibbs free energy change ($\Delta G_{\text{ads}}^\circ$):⁷

$$\Delta G_{\text{ads}}^\circ = -RT \ln K \quad (3)$$

where R is the universal constant for ideal gases, T is the absolute temperature, and K is the distribution coefficient, which can be expressed as the ratio between the amount of asphaltenes adsorbed onto the nanoparticles per liter of solution at equilibrium (C_a) and the equilibrium concentration of asphaltenes in the solution phase (C_E). The changes of sorption enthalpy ($\Delta H_{\text{ads}}^\circ$) and entropy ($\Delta S_{\text{ads}}^\circ$) were calculated from the plot of $\Delta G_{\text{ads}}^\circ$ versus temperature.³⁸

$$\Delta G_{\text{ads}}^\circ = \Delta H_{\text{ads}}^\circ - T \Delta S_{\text{ads}}^\circ \quad (4)$$

A plot of $\ln K$ versus $1/T$ should be a straight line. $\Delta H_{\text{ads}}^\circ$ and $\Delta S_{\text{ads}}^\circ$ can be computed from the slope and intercept of the plot, respectively.⁷ $\Delta G_{\text{ads}}^\circ$ was computed using eq 3.

5. RESULTS AND DISCUSSION

Surface characteristics of the samples are presented in Table 1. The sample of pure silica (S) has an external surface area of 40

Table 1. Surface Characteristics of S and SHS Samples

material	S_{BET} (m ² /g)	$d_{\text{p-S}}$ (nm)	$d_{\text{p-NiO}}$ (nm)
S	40	90	
SNi5	36	90	15
SNi15	23.5	90	15

m²/g. As expected, the surface area of the samples decreased with increasing the NiO content. It indicated that deposition of the metal oxide blocked some of the pores of the silica support. The XRD-measured mean crystallite size of silica nanoparticles ($d_{\text{p-S}}$) was 90 nm. Regarding the NiO nanoparticles, the value of this parameter ($d_{\text{p-NiO}}$) was similar (15 nm) for the two SHS samples tested.

Figure 1 depicts the asphaltene sorption isotherms of the S and SHS samples at 25 °C. SHS samples adsorbed more asphaltenes than the S sample within the whole range of asphaltene concentration tested, and that difference was more noticeable at higher concentrations. In fact, at 25 °C and an asphaltene concentration around 550 mg/L, the SNi15 sample adsorbed 135.65 mg/g of asphaltene, whereas the S sample adsorbed 54.95 mg/g. Sorption isotherms of all samples showed an increase in the sorbed amount of asphaltenes as

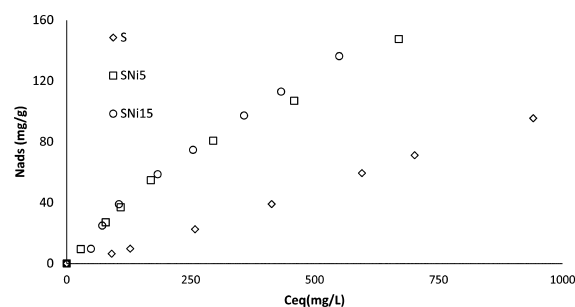


Figure 1. Asphaltene sorption isotherms at 25 °C as a function of NiO content.

asphaltene concentration increased. These results are in agreement with those reported by Dudášová et al., who evaluated the adsorption phenomenon of asphaltenes onto nanoparticles of hydrophilic and hydrophobic silica gel.³³

From Figure 1, it can also be inferred that the three samples of nanomaterials evaluated in this study showed a high affinity concerning asphaltene sorption. This can be attributed to the intermolecular forces between the most polar components of asphaltenes (mainly functional groups and heteroatoms) and the NiO supported on the silica surface, as well as to the high dispersion of the NiO on the surface of the hybrid nanomaterials. In the concentration range at which samples could be compared (0–750 mg/L), the asphaltene uptake was slightly higher on the SNi15 than on the SNi5. This is because the NiO on the surface blocks some of the porosity of the silica gel, producing a 56% lower S_{BET} value for SNi15 than for SNi5. Although the NiO can absorb asphaltene, it cannot compensate for this loss of asphaltene uptake. In other words, asphaltene adsorption on the surface of the SNi15 is slightly higher than the asphaltene uptake by SNi5, likely due to the low dispersion of the NiO.

Figures 2, 3, and 4 show the experimental isotherms of asphaltene sorption for the S, SNi5, and SNi15 samples at 25,

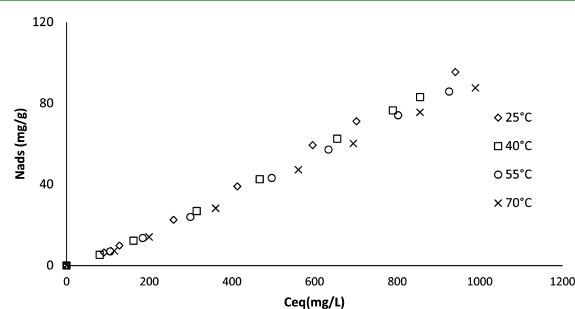


Figure 2. Asphaltene sorption on the S sample at different temperatures.

40, 55, and 70 °C. The range of asphaltene concentration was between 150 and 1500 mg/L. Asphaltene uptake of the SNi15 sample was higher than the maximum uptake reported by Dudášová et al.³³ under similar experimental conditions. This increased uptake can be explained by the high hydrophilicity of the nanoparticles and the high dispersion of NiO achieved using the impregnation method described in section 2.2.2.

At a constant asphaltene concentration, asphaltene uptake decreased as temperature increased (see Figures 2, 3, and 4). This result suggests that the adsorption of asphaltenes onto the nanoparticles surface is an exothermic process. Furthermore,

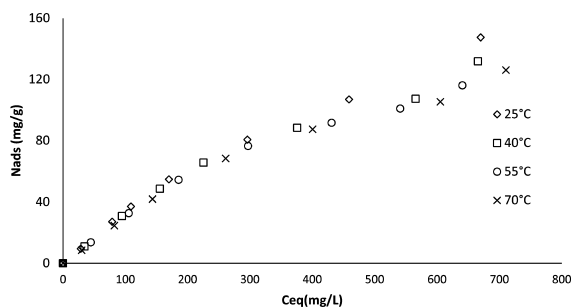


Figure 3. Asphaltene sorption isotherms on SNI5 sample at different temperatures.

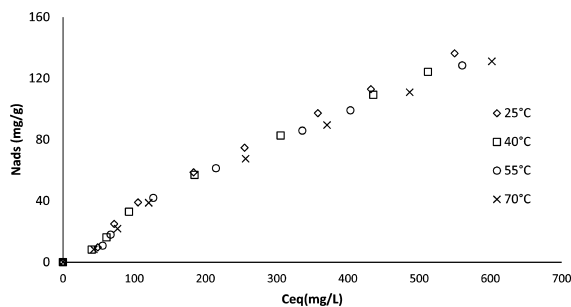


Figure 4. Asphaltene sorption isotherms on SNI15 sample at different temperatures.

the size of asphaltene aggregate is strongly affected by temperature. As temperature increases, the aggregate size decreases, and so, the asphaltene uptake decreases.⁷

In spite of its limitations for the specific case under study, the Langmuir model was used for analyzing the effect of temperature on sorption isotherms. The model parameters calculated for the isotherms of asphaltene adsorption on SHS samples are presented in Table 2. For each SHS, the $N_{\text{ads,max}}$ calculated by linear regressions slightly decreased as temperature increased. This is in agreement with the assumptions of the Langmuir model, which considers that sorption active sites are fixed but they may diminish the affinity of binding sites due to the effect of temperature.^{7,40}

As shown in Table 2, the Langmuir model had correlation coefficients from 0.85 to 0.92. There were noticeable differences between experimental data and the values obtained with this model, mainly in the high concentration region. It was because this model assumes a homogeneous surface, which is not true for the synthesized hybrid nanomaterial. Additionally, in the sorption experiments, even at the highest concentrations tested, the isotherms did not show a plateau (maximum

adsorbed uptake). As expected, the Freundlich model allowed obtaining a better fit of the experimental results ($R^2 > 0.94$, see Table 2), suggesting that asphaltenes were adsorbed onto a heterogeneous surface by multilayer adsorption.

The calculated thermodynamic parameters for the sorption of asphaltenes on the SNI5 and SNI15 samples are given in Table 3. A negative value of $\Delta G_{\text{ads}}^\circ$ indicates the status of

Table 3. Calculated Values of $\Delta G_{\text{ads}}^\circ$, $\Delta H_{\text{ads}}^\circ$ and $\Delta S_{\text{ads}}^\circ$ for Asphaltene Adsorption on the SHS Samples at Different Temperatures

material	temp. (°C)	$-\Delta G_{\text{ads}}^\circ$ (KJ/mol)	$-\Delta H_{\text{ads}}^\circ$ (KJ/mol)	$\Delta S_{\text{ads}}^\circ$ (J/molK)	R^2
SNI5	25	24.63	2.66	81.40	0.99
	40	25.47			
	55	27.32			
	70	28.71			
SNI15	25	24.36	2.65	80.35	0.99
	40	25.67			
	55	26.98			
	70	28.24			

feasibility and spontaneity of thermodynamic processes; that is, it characterizes the natural tendency of a system to undergo spontaneous changes.^{38,39} In addition, these negative values of $\Delta G_{\text{ads}}^\circ$ indicated a stronger exothermic sorption process. The negative values obtained for the enthalpy change confirmed the exothermic nature of the sorption process. The values obtained for $\Delta H_{\text{ads}}^\circ$ were in agreement with those reported by Nassar.⁷

The positive values obtained for the entropy change indicated an increased randomness at the solid–liquid interface during the sorption process. This result agreed with the finding that asphaltene adsorption was a rapid process that decreased with temperature.

5. CONCLUSIONS

A hybrid nanomaterial composed of nickel oxide nanoparticles (15 nm) supported on a nanoparticulated-matrix of silica gel (90 nm) was synthesized, and its ability for adsorbing asphaltenes isolated from a heavy crude oil was evaluated at different temperatures. From this experimental and modeling approach the following conclusions can be drawn: (1) At constant temperature, adsorption of asphaltenes onto the hybrid nanomaterials increased with increasing its nickel oxide content. The high affinity for asphaltenes can be explained by their high hydrophilicity and the high dispersion of NiO achieved in their synthesis. (2) Regardless of the asphaltene

Table 2. Estimated Adsorption Parameters using the Langmuir and Freundlich Models for SHS Samples at Different Temperatures

material	temp. (°C)	Langmuir model			Freundlich model		
		$N_{\text{ads,max}}$ (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(L/mg) ^{1/n}	1/n	R^2
SNI5	25	322.58	0.00112	0.85	0.60	0.86	0.98
	40	321.73	0.00107	0.85	0.67	0.82	0.98
	55	319.69	0.00102	0.85	0.70	0.81	0.98
	70	319.45	0.00097	0.85	0.56	0.85	0.98
SNI15	25	384.62	0.00098	0.92	0.27	1.02	0.94
	40	383.53	0.00094	0.92	0.25	1.02	0.97
	55	383.42	0.00089	0.92	0.24	1.01	0.97
	70	383.61	0.00085	0.92	0.26	0.99	0.97

concentration, asphaltene uptake by the hybrid nanomaterials decreased with increasing temperature, which indicated that the adsorption of asphaltenes onto the nanoparticulated material was an exothermic process. (3) Experimental data on asphaltene sorption isotherms were adequately adjusted by the Freundlich model, suggesting that asphaltenes were adsorbed onto a heterogeneous surface by multilayer adsorption. (4) The calculated thermodynamic properties for the sorption of asphaltenes onto the nanoparticulated materials confirmed the spontaneity and exothermic nature of this process.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Energy Information Administration. World Consumption of Primary Energy by Energy Type and Selected Country Groups, 1980–2006. www.eia.doe.gov/pub/international/iealf/table18.xls; accessed Sept 23, 2010.
- (2) Babadagli, T. Development of mature oil fields—A review. *J. Pet. Sci. Eng.* **2007**, *57*, 221–246.
- (3) Ruiz R.; Rojas, J. *THAI Toe-to-Heel Air Injection—Numerical Simulation of THAI Heavy Oil Recovery Process*; White Paper. Schlumberger: 2007. Available online: www.slb.com/services/software/reseng/~media/Files/software/white_papers/whitepaper_numstimulation.ashx.
- (4) Navarrete, N. Major new oil developments: Technological and operational, challenges and solutions. Colombia potential. *WPC Regional Meeting—IV Oil and Gas Investment Conference*, 2010.
- (5) http://www.npc.org/Study_Topic_Papers/22-TTG-Heavy-Oil.pdf. Accessed Dec 26, 2011.
- (6) Bouhadda, Y.; Bormann, D.; Sheu, E.; Bendedouch, D.; Krallafa, A.; Daaou, M. Characterization of Algerian Hassi-Messaoud asphaltene structure using Raman spectrometry and X-ray diffraction. *Fuel* **2007**, *86*, 1855–1864.
- (7) Nassar, N. N. Asphaltene adsorption onto alumina nanoparticles: kinetics and thermodynamic studies. *Energy Fuels* **2010**, *24*, 4116–4122.
- (8) Groenzin, H.; Mullins, O. Molecular size and structure of asphaltenes from various sources. *Energy Fuels* **2000**, *14*, 677–684.
- (9) Mousavi-Dehghani, S.; Riazi, M.; Vafaie-Sefti, M.; Mansoori, G. An analysis of methods for determination of onsets of asphaltene phase separations. *J. Pet. Sci. Eng.* **2004**, *42*, 145–156.
- (10) Xing, C.; Hilt, R.; Shaw, J. Sorption of Athabasca vacuum residue constituents on synthetic mineral and process equipment surfaces from mixtures with pentane. *Energy Fuels* **2010**, *24*, 2500–2513.
- (11) Turgman-Cohen, S.; Fischer, D.; Kilpatrick, P. Asphaltene adsorption onto self-assembled monolayers of alkyltrichlorosilanes of varying chain length. *ACS Appl. Mater. Interfaces* **2009**, *6*, 1347–1357.
- (12) Turgman-Cohen, S.; Fischer, D.; Kilpatrick, P.; Genzer, J. Asphaltene adsorption onto self-assembled monolayers of mixed aromatic and aliphatic trichlorosilanes. *Langmuir* **2009**, *25*, 6260–6269.
- (13) Ese, M.; Galet, L.; Clausse, D.; Sjöblom, J. Properties of Langmuir surface and interfacial films built up by asphaltenes and resins: Influence of chemical demulsifiers. *J. Colloid Interface Sci.* **1999**, *20*, 293–301.
- (14) Rudra, A.; Karan, K.; Horton, J. A combined QCM and XPS investigation of asphaltene adsorption on metal surfaces. *J. Colloid Interface Sci.* **2009**, *332*, 22–3.
- (15) Abdallah, W.; Taylor, S. Surface characterization of adsorbed asphaltene on a stainless steel surface. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *258*, 213–217.
- (16) Xie, K.; Karan, K. Kinetics and thermodynamics of asphaltene adsorption on metal surfaces: A preliminary study. *Energy Fuels* **2005**, *19*, 1252–1260.
- (17) Mendoza, J.; Castellanos, I.; Ortiz, A.; Buenrostro, E.; Durán, C.; López, S. Study of monolayer to multilayer adsorption of asphaltenes on reservoir rock minerals. *Colloids Surf., A* **2009**, *340*, 149–154.
- (18) Kumar, K.; Dao, E.; Mohanty, K. J. AFM study of mineral wettability with reservoir oils. *Colloid Interface Sci.* **2005**, *289*, 206–217.
- (19) Pernyeszi, T.; Dékány, I. Sorption and elution of asphaltenes from porous silica surfaces. *Colloids Surf., A* **2001**, *194*, 25–39.
- (20) Pernyeszi, T.; Patzkó, A.; Berkesi, O.; Dékány, I. Asphaltene adsorption on clays and crude oil reservoir rocks. *Colloids Surf., A* **1998**, *137*, 373–384.
- (21) Alkafef, S. F.; Algharib, M. K.; Alajmi, A. F. Hydrodynamic thickness of petroleum oil adsorbed layers in the pores of reservoir rocks. *J. Colloid Interface Sci.* **2006**, *298*, 13–19.
- (22) Saraji, S.; Goual, L.; Piri, M. Adsorption of asphaltenes in porous media under flow conditions. *Energy Fuels* **2010**, *24*, 6009–6017.
- (23) Gonzalez, G.; Moreira, M. B. C. The wettability of mineral surfaces containing adsorbed asphaltene. *Colloids Surf.* **1991**, *58*, 293–302.
- (24) Marlow, B. J.; Sresty, G. C.; Hughes, R. D.; Mahajan, O. P. Colloidal stabilization of clays by asphaltenes in hydrocarbon media. *Colloids Surf.* **1987**, *24*, 283–297.
- (25) López-Linares, F.; Carbognani, L.; González, M.; Sosa-Stull, C.; Figueras, M.; Pereira-Almao, P. Quinolin-65 and Violanthrone-79 as model molecules for the kinetics of the adsorption of C7 athabasca asphaltene on macroporous solid surfaces. *Energy Fuels* **2006**, *20*, 2748–2750.
- (26) Acevedo, S.; Ranaudo, M. A.; García, C.; Castillo, J.; Fernández, A.; Caetano, M.; Goncalves, S. Importance of asphaltene aggregation in solution in determining the adsorption of this sample on mineral surfaces. *Colloids Surf., A* **2000**, *166*, 145–152.
- (27) Marczewski, A. W.; Szymula, M. Adsorption of asphaltenes from toluene on mineral surface. *Colloids Surf., A* **2002**, *208*, 259–266.
- (28) Szymula, M.; Marczewski, A. W. Adsorption of asphaltenes from toluene on typical soils of Lublin region. *Appl. Surf. Sci.* **2002**, *192*, 301–311.
- (29) Nassar, N. N.; Hassan, A.; Pereira-Almao, P. Effect of surface acidity and basicity of aluminas on asphaltene adsorption and oxidation. *J. Colloid Interface Sci.* **2011**, *360*, 233–238.
- (30) Nassar, N. N.; Hassan, A.; Pereira-Almao, P. Metal oxide nanoparticles for asphaltene adsorption and oxidation. *Energy Fuels* **2011**, *25*, 1017–1023.
- (31) Nassar, N. N.; Hassan, A.; Pereira-Almao, P. Comparative oxidation of adsorbed asphaltenes onto transition metal oxide nanoparticles. *Colloids Surf., A* **2011**, *384*, 145–149.
- (32) Nassar, N. N.; Hassan, A.; Pereira-Almao, P. Application of nanotechnology for heavy oil upgrading: Catalytic steam gasification/cracking of asphaltenes. *Energy Fuels* **2011**, *25*, 1566–1570.
- (33) Dudášová, D.; Simon, S.; Hemmingsen, P.; Sjöblom, J. Study of asphaltenes adsorption onto different minerals and clays. Part I. Experimental adsorption with UV depletion detection. *Colloids Surf., A* **2008**, *317*, 1–9.
- (34) Thomas, J. M.; Thomas, W. J. *Principles and Practice of Heterogeneous Catalysis*; VCH: Weinheim, Germany, 1997.
- (35) Cortés, F. B.; Chejne, F.; Carrasco-Marín, F.; Pérez-Cadenas, A.; Moreno-Castilla, C. Water sorption on silica- and zeolite-supported

hygroscopic salts for cooling system applications. *Energy Convers. Manage.* **2012**, *53*, 219–223.

(36) Nogami, M.; Moriya, Y. J. Glass formation through hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ with NH_4OH and HCl Solution. *J. Non-Cryst. Solids* **1980**, *37*, 191–201.

(37) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Assink, R. A.; Kay, B. D.; Ashley, C. S. Sol–gel transition in simple silicates II. *J. Non-Cryst. Solids* **1984**, *63*, 45–59.

(38) Rouquerol, F.; Rouquerol, J.; Sing, K. S. W. *Adsorption by Powders and Porous Solids*; Academic Press: London, 1999.

(39) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multi-molecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–19.

(40) Cortés, F. B.; Chejne, F.; Carrasco-Marin, F.; Moreno-Castilla, C.; Perez-Cadenas, A. F. Water adsorption on zeolite 13X: Comparison of the two methods based on mass spectrometry and thermogravimetry. *Adsorption* **2010**, *16*, 141–6.