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Transition metal oxide nanoparticles as surfaces for surface-assisted laser desorption/ionization mass spectrometry of asphaltenes

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Abstract

We report the first use of NiO, Fe₃O₄, TiO₂, and Co₃O₄ nanoparticles as surfaces for surface-assisted laser desorption/ionization (SALDI) mass spectrometry of asphaltenes. Higher *signal-to-noise* ratios (S/Ns) for asphaltene species were observed using NiO and Fe₃O₄ nanoparticles for SALDI as compared to LDI, where both surfaces consistently provided 2- to 3-fold improved S/Ns. The new SALDI detection method showed reliable adsorption data measuring supernatant solutions after 24 hour asphaltene adsorption on NiO, Fe₃O₄, and Co₃O₄. These results indicated that NiO has a higher adsorption affinity than Fe₃O₄ and Co₃O₄ for asphaltene molecules, corroborating reported asphaltene adsorption on metal oxide nanoparticles.

Keywords

Asphaltenes; mass spectrometry; nanoparticles; surface-assisted laser desorption/ionization; transition metal oxides

1. Introduction

Asphaltenes are compositionally complex, highly dense, and high molecular weight molecules found in organic compounds such as heavy oil, crude oil, bitumen, and vacuum residues (Speight 2004; Leyva et al., 2013). Asphaltenes contribute significantly to the problems associated with crude oil transportation, recovery, and upgrading due to their high viscosity, aromaticity, and polarity (Speight 2004; Adams 2014). The removal and recovery of asphaltene molecules from heavy oil will facilitate the production of easily refinable and transportable crude oil (Kazemzadeh et al., 2015a; Kazemzadeh et al., 2015b). In addition, enhanced detection and adequate molecular weight characterization of asphaltene molecules will aid the elucidation and understanding of its complex structure and composition (McKenna et al., 2013; Pomerantz et al., 2015).

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Transition metal oxide (TMO) nanoparticles possess distinctive properties such as large surface area-to-volume ratios, low porosity, high dispersion rates, high photo-absorption, and low heat capacities (Fernández-García and Rodríguez 2009). These unique properties of TMO nanoparticles make them viable and cost-effective surfaces (Pomerantz et al., 2015; Wu et al., 2014) for surface-assisted laser desorption/ionization (SALDI) mass spectrometry (MS) and adsorbents (Kazemzadeh et al., 2015a; Nassar et al., 2011a; Madhi et al., 2017) for asphaltene molecules. The use of TMO nanoparticles as surfaces for SALDI enhances analyte detection with minimal sample preparation as well as a significant reduction in low mass solvent peaks found in traditional MALDI experiments (Arakawa and Kawasaki 2010; Law and Larkin 2011). Due to the characteristic advantages of nanoparticles as surfaces for SALDI MS and the excellent adsorption properties of nanoparticles, the combined use of TMO nanoparticles as substrates (*i.e.*, as surfaces and adsorbents) for asphaltenes provides the opportunity to generate new and rapid methods of analysis for asphaltene samples. To date these experiments have not yet been explored.

Herein, we present the first experimental MS data utilizing NiO, Fe₃O₄, and Co₃O₄ nanoparticles as surfaces for SALDI MS of asphaltenes and showed that NiO and Fe₃O₄ nanoparticles with a large surface area increases detection of asphaltenes in comparison to the traditional LDI method. We also demonstrate the use of TiO₂ nanoparticles as a surface for SALDI MS of the supernatant asphaltene molecules obtained after adsorption of asphaltene molecules on NiO, Fe₃O₄, and Co₃O₄ nanoparticles.

2. Experimental

2.1. Materials

Commercial NiO and Co₃O₄ nanoparticles were purchased from Sigma-Aldrich, St. Louis, MO. Commercial Fe₃O₄ and TiO₂ nanoparticles were obtained from US Research Nanomaterials, Inc., Houston, TX. Standard toluene (99.9 % purity) and methanol (99.9 % purity) solvents were bought from Sigma-Aldrich, St. Louis, MO. The nanoparticles, toluene, and methanol samples were used “as is”.

2.2. Sample preparation

The dried asphaltenes (extracted with *n*-heptane and fractionated according to IP 143/90) utilized in this work were donated by the National High Magnetic Field Laboratory at Florida State University and have been previously characterized (McKenna, et al., 2013). Briefly, the asphaltenes were extracted from Arabian crude oil with the addition of *n*-heptane at a 1:40 (g/mL) ratio. The *n*-heptane-asphaltene mixture was boiled under reflux for 60 ±5 min and placed in the dark for 24 hours. Subsequently, the mixture was filtered and the supernatant was decanted to obtain precipitated asphaltenes. The precipitated asphaltenes were further refluxed (at a rate of 2–4 drops/min) and washed with *n*-heptane to remove any remaining unwanted chemicals. The resulting asphaltenes were homogenized, ground using a pestle and mortar and dried under dry nitrogen. A stock solution of asphaltenes (500 mg/L) was prepared by dissolving a calculated amount of asphaltenes in toluene. Known asphaltene concentrations of 1, 10, 20, 40, 60, 80, and 100 mg/L were prepared for asphaltene calibration curve (obtained using a UV-2600 UV-Visible spectrophotometer

(Shimadzu Corp., Kyoto, Japan) at $\lambda = 375$ nm). All glassware containing asphaltenes were wrapped in aluminum foil and kept in the dark to prevent exposure to light.

The supernatant asphaltenes utilized for the SALDI MS experiments were prepared based on a previously reported batch adsorption method (Nassar et al., 2011a). Briefly, 100 mg of each type of nanoparticle (*i.e.*, NiO, Fe₃O₄, and Co₃O₄) were separately added to 10 mL asphaltene solutions with an initial concentration of 148 (± 2) mg/L in tightly sealed 15 mL glass vials. The samples were subsequently agitated at 200 rpm for 24 hours (at 24 ± 2 °C) using a classic series C24 incubator shaker (New Brunswick Scientific Co., a subsidiary of Eppendorf Inc., Enfield, CT) for attainment of total equilibrium. The solution mixture was then centrifuged for 15 min at 3600 rpm using a Marathon 8K benchtop centrifuge (Fisher Scientific, now Thermo Fisher Scientific, Waltham, MA). Mixtures were decanted to separate the nanoparticles containing adsorbed asphaltenes from the supernatant asphaltenes. SALDI surfaces were prepared using slurry mixtures of NiO, Fe₃O₄, TiO₂, and Co₃O₄ nanoparticles in methanol. A 1- μ L aliquot of each nanoparticle slurry was deposited on the SALDI plate and vacuum dried. Subsequently, 1 μ L aliquots of asphaltenes (or supernatant asphaltenes) were deposited on the vacuum-dried TMO nanoparticle SALDI surfaces.

2.3. Nanoparticles' surface characterization

The precise particle size was obtained using a focused ion beam scanning electron microscope, Versa 3D (FIB-SEM), FEI company, Hillsboro, OR operating under high vacuum at 30 kV and equipped with Everhart-Thornley detector. These were essential as the purchased nanoparticles provided a range of potential sizes. The TMO nanoparticle surface areas were determined using an Autosorb iQ gas sorption analyzer (Quantachrome Instruments, Boynton Beach, FL). Nitrogen adsorption isotherms were obtained at an outgas duration, outgas temperature, and bath temperature of 16 h, 140 °C, and -196 °C, respectively under vacuum ($\sim 6.58 \times 10^{-5}$ Torr).

2.4. Surface-assisted laser desorption ionization mass spectrometry (SALDI MS)

All SALDI/LDI mass spectra were acquired using a home-built and calibrated TOF mass spectrometer in the linear mode, equipped with a 50-Hz pulsed nitrogen laser (model VSL-337ND, Laser Science Inc., Franklin, MA) operating at a λ of 337 nm. The acceleration and detection voltages were 17 kV and -1.7 kV, respectively. All acquired mass spectra were an average of 100 single laser shots. Calibration of the mass spectrometer was performed using ions from peptide calibration standards consisting of Bradykinin fragment 1–7, Angiotensin II, P₁₄R, ACTH fragment 18–19, and Insulin Oxidized B. The operating vacuum chamber pressure ($\sim 8.0 \times 10^{-7}$ to $\sim 1.0 \times 10^{-6}$ Torr) was measured using an Agilent Varian XGS-600 ion gauge controller (Agilent Technologies, Santa Clara, CA) and a T-075-P type ionization gauge tube (Duniway Stockroom Corp., Fremont, CA). The MS data were recorded and acquired using a Tektronix DPO3054 digital oscilloscope (Tektronix, Inc., Beaverton, OR) and a home-written LabVIEW 2014 program (National Instruments Corp., Austin, TX) running on a Windows 7 (Microsoft Corp., Redmond, WA) Dell desktop computer, respectively. All mass spectra were processed using Igor Pro 6 technical graphing and data analysis software (WaveMetrics, Inc. Portland, OR). Multiple LDI and SALDI mass spectra were acquired for reproducibility purposes.

3. Results and discussion

3.1. Nanoparticles' physical properties

The morphology of the TMO nanoparticles are spherical as determined using SEM (Figure 1). The surface area was calculated from the multi-point Brunauer-Emmet-Teller (Brunauer et al., 1938) plot. Shown in Figure 1, the average particle size of the nanoparticles increase in the order of $\text{NiO} < \text{Fe}_3\text{O}_4 < \text{TiO}_2 < \text{Co}_3\text{O}_4$. The surface area of the nanoparticles increase in the order of $\text{Co}_3\text{O}_4 < \text{TiO}_2 < \text{Fe}_3\text{O}_4 < \text{NiO}$ with values of $2.37 < 18.52 < 39.54 < 149.83 \text{ m}^2/\text{g}$, respectively. These experiments provided data essential to determining the adsorption efficiencies of asphaltenes on TMO nanoparticles (shown below) allowing for their subsequent mass analysis.

3.2. TMO Nanoparticles as surfaces for SALDI MS of asphaltenes

Figure 2 shows representative LDI and SALDI TOF mass spectra of asphaltenes for the m/z range of 300 to 750 Da. In Figure 2(a), the asphaltene samples were directly deposited (*i.e.*, no TMO nanoparticle was used as a SALDI surface) on the SALDI plate (stainless steel) and allowed to vacuum dry. A comparison of the LDI TOF mass spectrum in Figure 2(a) to the SALDI TOF mass spectra in Figures 2(b–d) reveals similar asphaltene mass distribution patterns. The observed asphaltene mass distribution pattern is comparable to the commonly obtained mass spectra patterns of asphaltenes at the low m/z range (*i.e.*, $m/z < 800 \text{ Da}$) (Wu et al., 2014; Pereira et al., 2014).

The asphaltene signal intensities obtained using NiO and Fe_3O_4 nanoparticles as SALDI surfaces (Figures 2 (b–c)) are higher than the asphaltene LDI signal intensities (Figure 2(a)). The increased signal intensities for asphaltenes using the NiO and Fe_3O_4 nanoparticles as SALDI surfaces demonstrates the advantages of using TMO nanoparticles as surfaces for MS signal improvements. The enhanced signal intensities is due to the large surface area, high photo-absorption, and low heat capacity properties of these nanoparticles. However, in Figure 2(d), the MS signal intensities for asphaltene species using Co_3O_4 nanoparticles as SALDI surfaces are lower than those obtained with LDI and its counterpart TMO nanoparticles. A plausible reason for the observed low MS signal intensities could be due to the extremely small surface area of the Co_3O_4 nanoparticles. Higher surface area of SALDI surfaces promotes efficient laser energy absorption and heat transfer to analytes for optimum desorption (Law and Larkin 2011).

A comparison of the total ion intensities observed at m/z range of 300 to 750 showed that SALDI mass spectra obtained using NiO and Fe_3O_4 nanoparticles have asphaltene species with total ion intensities of $\sim 309,456$ and $\sim 542,173$, respectively, as compared to LDI and SALDI mass spectra obtained using Co_3O_4 nanoparticles with total ion intensities of $\sim 224,920$ and $\sim 127,325$, respectively. Furthermore, a look at the *signal-to-noise* ratios (S/Ns) of selected m/z values in the mass spectra shown in Figure 2 corroborates the total ion intensity findings. For example, in Table 1, a 2- to 3-fold S/N improvement was observed (for the studied m/z range) using NiO and Fe_3O_4 nanoparticles as SALDI surfaces over LDI for asphaltene MS analyses. It is worthwhile to mention that upon comparison to the literature, most of the ionic species observed in these SALDI mass spectra of asphaltenes are

aggregates and fragment ions due to the simultaneous incidence of desorption and ionization processes during SALDI (Pomerantz et al., 2015; Wu et al., 2013). The MS result in Figure 2 suggests that TMO nanoparticles (especially those with large surface areas) efficiently desorb and favor enhanced ionization of asphaltene molecules during SALDI.

3.3. Asphaltene calibration plot & MS analysis of adsorbed asphaltenes on TMO nanoparticles

Figure 3 represents the calibration curve of asphaltenes (within a 1 to 100 mg/L range) and SALDI TOF mass spectra of supernatant asphaltenes after asphaltene adsorption on TMO nanoparticles. The calibration plot showed a linear response ($R^2 = 0.998$) for asphaltene UV-Visible absorbance measurements. The equation of the calibration line ($Y = 1.43 (\pm 0.02) \times 10^{-2} X - 0.59 (\pm 0.20) \times 10^{-1}$) in Figure 3(a) was used to estimate the supernatant asphaltene concentration obtained after the 24 hour adsorption on TMO nanoparticles. Note that the concentrations of asphaltenes adsorbed on the TMO nanoparticles were less than 120 mg/L to ensure that the absorbance was linear with concentration (absorbance did not exceed 2.0).

TiO₂ nanomaterials are proven sensitive surfaces for SALDI analysis of complex molecules (Radisavljević et al., 2012), hence we utilized TiO₂ nanoparticles as the SALDI surface for the MS results presented in Figure 3. These data show the representative mass spectra for m/z range 450 to 650 Da for the asphaltene molecular species from the supernatant asphaltenes obtained after the 24 hour adsorption experiments using NiO, Fe₃O₄, and Co₃O₄ nanoparticles as adsorbents. Henceforth, NiO-SA, Fe₃O₄-SA, and Co₃O₄-SA will denote supernatant asphaltenes obtained after the 24 hour adsorption of asphaltenes on NiO, Fe₃O₄, and Co₃O₄ nanoparticles, respectively. In Figures 3(b–d), for comparison purposes, the equilibrium concentration (C_e) values for the asphaltene samples analyzed are between ~4 to 5 mg/L. The C_e values were calculated using the equation of line obtained from the asphaltene calibration curve in Figure 3(a).

It should be noted that there is a reduction in the total detected ionic species in the SALDI mass spectra of asphaltenes seen in Figure 3 (as compared to Figure 2) due to the low concentrations (resulting from the adsorption of asphaltenes on the TMO nanoparticles) of the supernatant asphaltene samples. This is to be expected and provides additional credibility to the asphaltene adsorption of TMO nanoparticles. Figure 3(b) shows that ionic species below m/z of 525 Da were absent (*i.e.*, ionic species with $S/N > 3$) in the mass spectrum obtained from NiO-SA sample. However, for Fe₃O₄-SA and Co₃O₄-SA, ionic species ($S/N > 3$) were present in the m/z range below 525 Da (see Figures 3(c & d)). At an m/z range above 525 Da, ionic species were observed in the mass spectra of the NiO-SA, Fe₃O₄-SA, and Co₃O₄-SA samples. The absence of ionic species at m/z below 525 Da for the NiO-SA sample could be related to the selective and high adsorption affinity of NiO nanoparticles for asphaltene molecules. It is possible that most of the asphaltene species that contributed to the absence of ionic species at m/z below 525 Da for NiO-SA sample are asphaltene molecules with functional groups that interact efficiently with NiO nanoparticles. For example, Zimmer et al. (2013 and 2015) published work on the selective extraction of model compounds present in asphaltene molecules using various metal oxide nanoparticles. In the studies, they showed that NiO nanoparticles had a high extraction selectivity towards

pyridine or molecules with pyridyl functional groups (Zimmer et al., 2013 and 2015). It is known that the asphaltenes used in this work consist of nitrogen containing groups (McKenna et al., 2013). Hence, the possible presence of highly abundant pyridyl molecules (which selectively interact with NiO nanoparticles) in the asphaltene samples analyzed in this report could be responsible for the observed high adsorption affinity seen with NiO.

The SALDI MS data presented in Figure 3 also corroborate the adsorption affinity (K_L) results reported in the literature for the adsorption of asphaltenes on metal oxide nanoparticles (Nassar et al., 2011a and 2011b). For example, Nassar et al. (2011a and 2011b) reported a K_L trend for the adsorption of asphaltenes as $\text{NiO} > \text{Co}_3\text{O}_4 > \text{Fe}_3\text{O}_4$. The larger K_L for NiO indicates a stronger interaction with asphaltene molecules and is in part related to NiO's large surface area. In this report, NiO nanoparticles have a larger surface area than Fe_3O_4 and Co_3O_4 nanoparticles. Factors such as the nature and types of functional groups on asphaltenes (depending on the source of the asphaltene sample and extraction methods) and experimental conditions (*e.g.*, temperature, pH, and concentration) affect the extent of asphaltene interaction with various nanoparticles (Adams 2014). Hence, for efficient asphaltene removal and recovery, a combination of TMO nanoparticles could be employed to target various asphaltene species.

4. Conclusion

We employed NiO, Fe_3O_4 , TiO_2 , and Co_3O_4 nanoparticles as surfaces for SALDI MS of asphaltenes, where all corresponding surface areas were accurately determined for the specific nanoparticles used. MS results suggest that TMO nanoparticles (with large surface areas) are excellent surfaces for SALDI MS analysis of complex mixtures such as asphaltenes. In addition, spectrophotometric and SALDI TOF MS techniques show that NiO nanoparticles have a higher adsorption affinity than Fe_3O_4 and Co_3O_4 nanoparticles for asphaltene molecules. These proof of concept SALDI MS experiments focused on low mass detection to show the utility of these experiments without the low mass interferences inherent in other MS methods. These SALDI MS experiments will be extended to explore the detection capabilities of monomers and dimers using TMO nanoparticles as well as the determination of fragments generated by the use of the N_2 laser.

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a) NiO Nanoparticles (24.87-38.34 nm) **b) Fe₃O₄ Nanoparticles (25.49-49.51 nm)** **c) TiO₂ Nanoparticles (39.60-62.36 nm)** **d) Co₃O₄ Nanoparticles (58.11-93.50 nm)**

Figure 1.
SEM images of (a) NiO, (b) Fe₃O₄, (c) TiO₂, and (d) Co₃O₄ nanoparticles.

Figure 2. Representative (a) LDI and SALDI TOF mass spectra of asphaltene (500 mg/L) deposited on (b) NiO, (c) Fe₃O₄, and (d) Co₃O₄ nanoparticles' surfaces.

Figure 3.

(a) Plot of average absorbance values as a function of asphaltene concentration (1 – 100 mg/L). Error bars are reported at the 95 % CL for $n = 3$ experimental trials. Representative SALDI TOF mass spectra of supernatant asphaltenes (layered on TiO₂ nanoparticles) obtained after 24 h adsorption of asphaltenes on (b) NiO, (c) Fe₃O₄, and (d) Co₃O₄ nanoparticles. The equilibrium asphaltene concentration (C_e) of the asphaltenes are placed on top of each mass spectrum.

Table 1

Signal-to-noise ratio (S/N) comparison for asphaltene ionic species obtained using LDI and SALDI.

<i>m/z</i>	Signal-to-Noise Ratios (S/Ns)			
	LDI	NiO	Fe ₃ O ₄	Co ₃ O ₄
375.50	5.41	15.78	11.62	5.45
397.25	11.14	33.23	22.88	13.14
419.05	17.09	35.56	24.75	10.48
439.25	14.85	24.70	31.25	15.63
461.00	15.46	33.15	30.40	16.69
479.55	17.48	39.81	33.85	14.94
482.55	19.83	46.98	36.64	18.17
488.80	13.85	35.86	23.68	9.83
501.44	14.86	39.11	76.12	12.06
504.30	25.77	54.60	51.80	22.45
519.80	15.06	38.96	31.01	17.80
526.00	16.38	49.79	32.93	12.22
541.30	37.81	93.50	50.22	33.91
547.55	19.54	50.18	25.16	10.22
572.30	10.52	23.10	17.40	8.65