



Oxidation of asphaltenes adsorbed onto NiO nanoparticles

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ABSTRACT

Differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) plots help identifying reaction zones and enable activation energy calculations. Recently, Nassar et al. [1,2] reported major shifts in the DTG combustion peaks and reaction zones between virgin and adsorbed asphaltenes onto commercial metal oxide nanoparticles. They attributed the accompanying reduction in activation energy to a significant catalytic role played by the nanoparticles, especially for NiO nanoparticles. It should be noted that in these experiments only monolayer adsorption from toluene model solutions was encountered. More recently, our group reported multilayer adsorption of asphaltenes from heavy oils onto in situ prepared and commercial NiO nanoparticles [3]. Contrary to the previous literature, the thermal behavior of these asphaltenes revealed a surface role entailing an enhanced exposure of adsorbed asphaltenes to the oxidant stream. In this work, we critically re-evaluated the claim of catalytic effect of nanoparticles [1,2,4,5] and provide an experimental protocol which demonstrates a surface effect.

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1. Introduction

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been widely employed for studying the thermal behavior of crude oils and their fractions [6]. These instruments enable simultaneous measurement of mass and heat variations with temperature, and, hence, provide good insight on the nature of reactions taking place. Plots of the differential thermogravimetry (DTG) and DSC were used to draw maps with most probable reactions in a given temperature interval. Tadema [7] was the first to use differential thermal analysis (DTA) to characterize the thermal behavior of crude oil. He identified a low temperature oxidation (LTO) region between 220 and 350 °C and a high temperature oxidation (HTO) region above 350 °C. Kök [8] studied the pyrolysis and oxidation of two heavy crudes using DSC and TGA. Under inert atmosphere, he identified a distillation region between 25 and 400 °C and a visbreaking region between 400 and 600 °C, whereas under oxidizing atmosphere, three reaction zones were identified and labeled as LTO, up to 390 °C, fuel deposition (FD), between 390 and 490 °C, and HTO, above 490 °C. Kök and Iscan [9] later named the second region as medium temperature oxidation (MTO). In an attempt to identify major reactants within a reaction zone, Cijajolo and Barbella [10] explored the pyrolysis and oxidation of some heavy oils and their separate fractions. Using DTG plots, under inert atmosphere, they reported volatilization of paraffinic and aromatic fractions below 400 °C, and pyrolysis

of polar and asphaltenic fractions, leading to carbon residue formation, above 550 °C. Under oxidizing atmosphere, on the other hand, simultaneous evaporation and liquid phase oxidation of the paraffinic and aromatic fractions occurred below 400 °C, pyrolysis of oxidized polar materials, asphaltenes and some aromatics dominated between 400 and 550 °C, and, finally, combustion of the carbonaceous residue proceeded at above 500 °C. For crudes with high asphaltenic fractions, understanding the thermal behavior of asphaltenes becomes an essential component of heavy oil upgrading [11] and leads to more effective modes of utilizing such crudes. Cijajolo and Barbella [10] reported that, even under oxidizing atmosphere, asphaltenes are stable and do not undergo evaporation until 520 °C, where pyrolysis and polymerization reactions take place and carbonaceous residue accompanied by low molecular weight gases form. Moschopedis et al. [12], on the other hand, attributed mass loss of Athabasca asphaltenes under inert atmosphere below 350 °C to the elimination of groups located on the periphery. Ali and Saleem [11] studied the thermal behavior of Arabian asphaltenes and reported complete conversion, with minimum carbon residue, under severe pyrolysis condition of above 520 °C.

Burger and Sahuquet [13] used DTA plots to study the catalytic effect of some metallic additives on crude oil combustion and reported zones for low temperature partial oxidation, combustion of crude oil fractions and, finally, coke combustion. Moreover, they concluded that the presence of heavy metals oxides not only increased coke deposition but also catalyzed the HTO reactions. Drici and Vossoughi [14] investigated the effect of clays, silica and alumina, with different specific surface areas, on the combustion of crude oils using DSC and DTG plots. Their results showed that reducing the crude oil/surface area ratio improved LTO peaks and

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