Journal of Petroleum Science and Engineering 121 (2014) 134–141

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Adsorption kinetics and catalytic oxidation of asphaltene on synthesized maghemite nanoparticles

Behruz Mirzayi *, Nazila Naghdi Shayan

Chemical Engineering Department, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran

ARTICLE INFO

Article history:
Received 21 April 2014
Accepted 29 June 2014
Available online 8 July 2014

Keywords:
asphaltene
adsorption kinetic
maghemite nanoparticle
oxidation

ABSTRACT

Objective: The purpose of this article is to assess adsorption kinetics and catalytic oxidation of asphaltene onto synthesized maghemite (γ-Fe_2O_3) nanoparticles.
Methods: To synthesize the maghemite nanoparticles (MNPs), the co-precipitation of ferric and ferrous ions method was used as a facile and cheap method. Morphology, crystalline and chemical structure of the synthesized MNPs were investigated by transmission electron microscope (TEM) and X-ray diffraction (XRD) analyses. The Lagergren pseudo-first- and second-order models were applied for determination of adsorption kinetics and its mechanism. Furthermore, thermogravimetry analysis (TGA) of both pure asphaltene and asphaltene–maghemite (MNPs with adsorbed asphaltene, MNP/Asph) was carried out.
Results: The results of XRD and TEM analyses showed that the γ-Fe_2O_3 nanoparticles are crystalline and roughly spherical in shape with about 10 nm in size. It was found that the experimental kinetic data are in good agreement with the pseudo-second-order model; moreover, the Langmuir isotherm model fits well the adsorption data. Furthermore, TGA results showed that the onset temperature of asphaltene oxidation and temperature of the maximum rate of oxidation decrease by ~203 °C and ~123 °C, respectively. The same results were also obtained through analyzing heat flow curves of differential thermal analysis (DTA).
Conclusion: Maghemite nanoparticles (MNPs) were synthesized using an easy and low-cost method. Asphaltene adsorption kinetics on MNPs followed the pseudo-second-order Lagergren model. TGA and DTA analyses demonstrated the drastic catalytic effect of the MNPs.
Practice/implications: The synthesized MNPs were used for the adsorption of asphaltene. Study on asphaltene adsorption kinetics and the catalytic effect of MNP on asphaltene is a very useful attempt in the control or elimination of asphaltene deposition in the petroleum industry.
© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Crude oil is a complex mixture of heavy molecules, divided into four main categories: saturated hydrocarbons, aromatics, resins and asphaltene. Asphaltene is the most polar and heaviest molecule of crude oil, which is insoluble in normal alkanes and completely soluble in aromatic solvents such as benzene and toluene (Groenzin and Mullins, 2000). Asphaltene bears the most heteroatom and organometallic compounds (i.e. hybrid organic radicals that are attached to the metal atom) in crude oil. Asphaltene also forms poly-aromatic molecules with alkyl side chains. Measurement of asphaltenes' molecular weight is very difficult due to their tendency to aggregate; however, research studies have shown that the average molecular weight of asphaltene varies between 500 and 2000 g/mol (Sheu, 2001). Asphaltenes are surface-active substances and because of this feature, they have great tendency to stick onto various surfaces such as steel oil storage tanks, pipelines and mineral materials and cause serious problems including clogging the pipelines. Hence, this problematic feature of asphaltene makes us look for an efficient method for the removal of asphaltene from petroleum solutions. In this regard, metal surfaces such as gold and steel (Ekholm et al., 2002; Alboudwarej et al., 2005), metal oxides such as Al_2O_3, TiO_2 and Fe_3O_4 (Dudášová et al., 2008), and mineral surfaces such as clay (Bantignies et al., 1998), limestone and kaolin can be used as adsorbents of asphaltene molecule (Syunyaev et al., 2009).

Magnetic nanoparticles offer promising applications in a variety of areas such as environmental, catalyst and chemical reactions, biomedical, coatings and pigments, data storage, tribology, hygiene and cosmetics, separation and purification sciences (Reiss

* Corresponding author. Tel.: +98 451 5512910; fax: +98 451 5512904.
E-mail address: mirzayib@uma.ac.ir (B. Mirzayi).

http://dx.doi.org/10.1016/j.petrol.2014.06.031
0920-4105/© 2014 Elsevier B.V. All rights reserved.

and Hutten, 2005; Alam et al., 2013; Koh et al., 2013). Magnetic nanoparticles, as a new potential agent for the removal of heavy organic compounds from crude oil, are also of interest to many researchers. Nanoparticles have been applied in enhancing oil recovery from reservoirs, and different types of metal nanoparticles have also been used to remove oil deposits (Nassar et al., 2011d; Abu Tarboush and Husein, 2012; Franco et al., 2013). Among the reasons for the use of nanoparticles for asphaltene adsorption is the unique characteristics of nanoparticles, for example, high surface to volume ratio and functionalizable surface. Until now, some commercial nanoparticles have been used to adsorb precipitated asphaltene from oil. These nanoparticles are NiO, CaO, MgO, TiO_2, Co_3O_4, Fe_3O_4 (Nassar et al., 2011d) and recently AlNi nanoparticles (Franco et al., 2013).

Asphaltene adsorption onto the nanoparticles surface depends on the type and amount of force required, creating the interaction between asphaltene and the surface. Asphaltene contains different functional groups such as carboxylic, pyrrolic, pyridininc, thiophenic and sulfide. The functional groups allow the adsorption of asphaltene on the surface of nanoparticles by sharing electrons. Different justification for asphaltene adsorption onto nanoparticles was presented. Among them are asphaltene surface charge, and/or van der Waals force and/or interaction between surface and polar asphaltene molecule (Nassar et al., 2011d; Valencia et al., 2012; Franco et al., 2013).

To date, many studies have been carried out on asphaltene adsorption kinetics onto different surfaces. In this regard, pseudo-first- and -second-order Lagergren models were proposed to explain the kinetics of asphaltene adsorption. Syunyaev et al. showed that asphaltene adsorption onto mineral surfaces follow the first-order adsorption kinetic model. The reason is that, the surface porosity of mineral adsorbent causes the time to be spent on mass transfer within the cavity (Syunyaev et al., 2009). Also Acevedo et al. showed that asphaltene adsorption onto a silica gel follows a first-order kinetic model. They found that the adsorption process is controlled by three diffusion phenomena: diffusion to the adsorbent surface, then to the interface and finally diffusion into the pores of porous surfaces (Acevedo et al., 2000). Pernyeszi et al. reported that the Langmuir isotherm fits well the adsorption of asphaltene from toluene on Illite, Bentotite and Kaolinite (Pernyeszi et al., 1998). Marczewski and Szymula showed that asphaltene adsorption on mineral surfaces is quite distant from the Langmuir isotherm, as a simple model (Mirzayi et al., 2014). Their adsorption measurements showed, because of lateral interactions, multilayer formation, or hemi micelle formation; the Freundlich model is in good agreement with experimental data. Mohammadi et al. used the modified form of the Langmuir isotherm to fit the adsorption isotherm of asphaltene onto mineral surfaces (Mohammadi et al., 2012). The results of linear and nonlinear isotherms indicated that Kaolin, Smectite and Fluorite follow the Langmuir isotherm, while Hematite mineral follows the multilayer adsorption isotherm.

Nassar used commercial alumina nanoparticles (γ-Al_2O_3) as adsorbent for the asphaltene molecule (Nassar, 2010). The results of asphaltene adsorption kinetics on alumina nanoparticles indicated that the asphaltene molecules attach onto the alumina surface in a very short time, because of the small size of nanoparticles and also adsorption of asphaltene on the external surface of the nanoparticles. The adsorption isotherms were also determined and fitted very well to the Langmuir model. In other research asphaltene adsorption from four oil samples was carried out onto Fe_3O_4 nanoparticles (Nassar et al., 2012). The results of adsorption kinetics showed that the equilibrium was reached within less than 10 min. In addition, the modeling of adsorption kinetics indicated that asphaltene adsorption onto Fe_3O_4 nanoparticles surface follows the second-order Lagergren kinetic model.

Some previous studies demonstrated that asphaltene can be converted to lighter products by thermal and/or catalytic processing in the presence of adsorbents (Benito et al., 1997). Recently it has been shown that among all the adsorbents of asphaltene, nanoparticles are good candidates for catalytic cracking or oxidation of asphaltene. In this area several studies have been reported which demonstrated the catalytic effect of various kinds of commercial nanoparticles on heavy oil fractions. These nanoparticles include nano-size nickel (Greff and Babadagli, 2013) NiO, CaO, MgO, TiO_2, Co_3O_4 (Nassar et al., 2011d), Fe_3O_4, AlNi (Franco et al., 2013), γ-Al_2O_3 (Nassar et al., 2011c), NiO, Co_3O_4 and Fe_3O_4 (Nassar et al., 2011b, 2012) and combined NiO nanoparticles and mesoporous–macroporous Kaolin (Hassan et al., 2013).

Nassar et al. investigated the catalytic effect of different commercial metal oxide nanoparticles on the thermo-oxidative decomposition of asphaltene at non-isothermal and isothermal conditions (Nassar et al., 2011a, 2013). The results showed that the presence of nanoparticles decreases the activation energy of asphaltene oxidation and enhances the reaction rate. Moreover, the nanoparticles can decrease the temperature of cracking reaction and the amount of activation energy. Asphaltene oxidation onto NiO, Co_3O_4 and Fe_3O_4 nanoparticles has already been investigated by Nassar et al. (2011b). All the nanoparticles showed high catalytic activity for asphaltene oxidation in the following order $NiO > Co_3O_4 > Fe_3O_4$. The other important findings of the mentioned study were the suppression of oxidation temperature of asphaltene by 140, 136 and 100 °C with respect to non-catalytic oxidation in the presence of NiO, Co_3O_4, and Fe_3O_4 nanoparticles, respectively (Nassar et al., 2011b). The adsorption kinetics and isotherms thermally cracked asphaltene from Athabasca vacuum residue on to Fe_3O_4 nanoparticles were studied by Nassar et al. (2012). According to the obtained results, the presence of Fe_3O_4 nanoparticles with asphaltenes caused a significant decrease in the oxidation temperature. The effect of nanoparticles towards catalytic oxidation of asphaltene also demonstrated that Fe_3O_4 nanoparticles can serve as an excellent adsorbent/catalyst for heavy oil recovery and upgrading.

The present research studies asphaltene adsorption and oxidation on synthesized maghemite nanoparticles (γ-Fe_2O_3). Maghemite, as one of the ferrimagnetic iron oxides, is very similar to magnetite (Fe_2O_3) but the only difference between them is the existence of iron cations Fe^{3+} and vacancies in maghemite. Maghemite nanoparticles (MNPs) as a novel adsorbent are expected to offer an attractive and inexpensive option for the removal of pollutions (Mirzayi et al., 2014). By considering a simple route for the synthesis of maghemite, high surface area, and magnetic property which can be easily oriented using external magnetic fields, the maghemite nanoparticles were used in this study to investigate (1) the asphaltene adsorption kinetics/isotherm and (2) oxidation onto these nanoparticles. For this purpose, the MNPs were synthesized using an easy and low-cost method. Then the nanoparticles were used for the adsorption of asphaltene from a neat solution. Using the resulting experimental data, the kinetics and isotherm behavior of asphaltene adsorption onto maghemite nanoparticles were studied. Finally, the catalytic effect of MNPs on asphaltene oxidation was investigated using thermogravimetry analysis.

2. Materials and methods

2.1. Materials

A sample of crude oil from Iranian oil fields was prepared. Toluene, normal heptane, $FeCl_2 \cdot 4H_2O$ and $FeCl_3$ salts, HCl (37%)

Download English Version:

https://daneshyari.com/en/article/1755064

Download Persian Version:

https://daneshyari.com/article/1755064

Daneshyari.com