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Extended Abstract

Surface Modification of Aluminium Oxide (Al_2O_3) Nanoparticles (NPs) on Detection of Crude Oil Production †

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Abstract: Surface modification is one of several techniques on improving the characteristic of certain elements. The surface of material can be modified by coating it with certain coating material. In this study Aluminium Oxide (Al_2O_3) nanoparticles (NPs) is used and its coating material are Oleic Acid and Silica Dioxide. The main objectives of this study are to observe the properties of Al_2O_3 NPs after being coated with OA and SiO_2 at paraffin oil and brine water interface and to investigate the changes of NPs structure and chemical properties using three analysis which are Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and X-Ray Powder Diffraction (XRD). Al_2O_3 NPs was coated with OA and then followed by SiO_2 coating. After that, the modified NPs was analyzed by these analysis (SEM, FTIR and XRD). The modified Al_2O_3 NPs then were injected into mixture of paraffin oil and brine water. Al_2O_3 NPs coated with OA inhibit hydrophobic tails which prevent the molecules of NPs to mix with water. While for NPs coated with SiO_2, its aggregate well at the interface and most of it sticking to test tube wall. However, some of the NPs dissolve in water. SEM analysis images of before and after coating show different in thickness indicate the successfulness in coating. OA and SiO_2 can be seen attach to Al_2O_3 NPs quasi-spherical surface. While FTIR and XRD peaks show that there are changes in chemical properties and existence of contaminant at Al_2O_3 NPs crystallite structure. These analysis and observation of NPs confirming the successful of coating. Thus, can help in detection of crude oil production and improve the performance of Al_2O_3 NPs.

Keywords: surface modification; nanoparticles; Aluminium Oxide (Al_2O_3); coating methods

1. Introduction

In these past decades, there have been an extensively developed in using metal oxide NPs. There are so many applications of these NPs nowadays such as, catalysts, sensors, semiconductors, medical science [1], capacitors and also batteries [2]. Among all the metal oxide NPs existed, Aluminum oxide are one of the common NPs that had been known for several centuries [3]. The NPs are modified by using coating method. There are many coating materials exist but for Aluminum oxide the most common is oleic acid. Silica dioxide coating not a very common material thus the properties and behavior will be observed in this study.

Recently, Surface modification of NPs is one of the techniques to increase oil recovery [4]. Currently, water-flooding is a most preferred technique in enhancing oil recovery because of the higher sustained oil production rates that are obtained compared with the case if no water being injected [5]. However, increasing injection of water may lead to a breakthrough which will resulted in decreasing of oil production rates [6]. So, in this study surface modification of NPs are conducted using Silica Dioxide and Oleic Acid as a coating material. Aluminum oxide is selected among other because of its conductivity and it is also a common oxide make it easy to obtain.

Thus, in this study the objectives are, to observe the properties of Aluminum Oxide (Al_2O_3) NPs when coated with Silica Dioxide and Oleic Acid and to investigate the changes of chemical properties and structure of modified NPs using three analysis which are Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and X-Ray Powder Diffraction (XRD). Al_2O_3 NPs was coated with two different coating material which are Oleic Acid and Silica Dioxide then injected into test tube containing mixture of paraffin oil and brine water. The behavior of these NPs was observed. After that, these NPs was taken to analysis for further confirmation of its structure and chemical properties.

2. Materials and Methods

Aluminium Oxide (Al_2O_3) NPs powder (average particle size, 5 μm) was obtained at Chemical Store of Faculty of Chemical and Natural Resources Engineering at Universiti Malaysia Pahang. Brine water and paraffin oil also were obtained at Chemical Store.

2.1. Oleic Acid Coating

According to Ruoyu H. et.al. [7] To prepare for Oleic Acid coating, a desired amount of Oleic Acid was mixed with o-xylene in flask to form the solution. Al_2O_3 powder was added to react for 1 h at 50 °C under stirring. Then the particles were collected by centrifugal separation. The collected particles were washed three times with toluene. The particles then were dried inside oven at 50 °C.

2.2. Silica Dioxide Coating

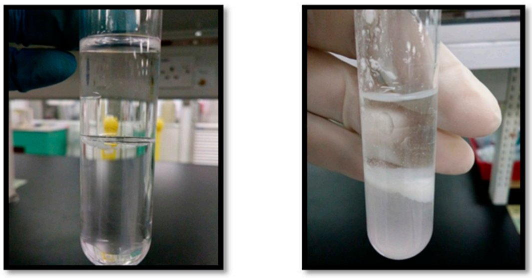
Aluminium oxide was mixed with high-purity water in a flask with vigorous agitation to form 20–30% (*w*/*w*) slurry. The slurry was stirred vigorously for 45 min. Then the slurry agitated to achieve excellent dispersion of Aluminium oxide NPs. Under the strong agitation, sodium silicate solution was added into the flask to set the pH value of slurry 9.5. The slurry was heated and maintained at 85–90 °C. Then, the sodium silicate solution was dropped again to make the ratio of Silica to Aluminium Oxide to be 2–3% (*w*/*w*). Afterwards, the pH value was set to 8.5 using dilute sulphuric acid to make the silicic acid deposit on the surface of Aluminium oxide NPs. The slurry was maintained around 85–90 °C for 2 h with vigorous agitation. The composite NPs was collected by filtration and rinsed three times with deionized water. The NPs was dried at 100 °C for 12 h [7].

3. Result and Discussion

3.1. Observation Analysis

The surface modified nanoparticles were observed at the paraffin oil and brine water interface. 10 mL of brine water is added into the test tube and another 10 mL of paraffin oil is added. The surface modified NPs, then injected into test tube and observed.

Figure 1 shows the behavior of coated Al_2O_3 NPs when injected into oil and water mixture. There is oily layer observed at oil and water interface (circle). Al_2O_3 NPs (a) coated OA shows that hydrophobic tails prevent the coated Al_2O_3 from mixing with the pure water confirming the successfulness of the surface coating. While Al_2O_3 NPs (b) coated with Silica Dioxide show some of the NPs stay at oil and brine water interface while some dissolved in water. NPs aggregate at the interface and stick to test tube.



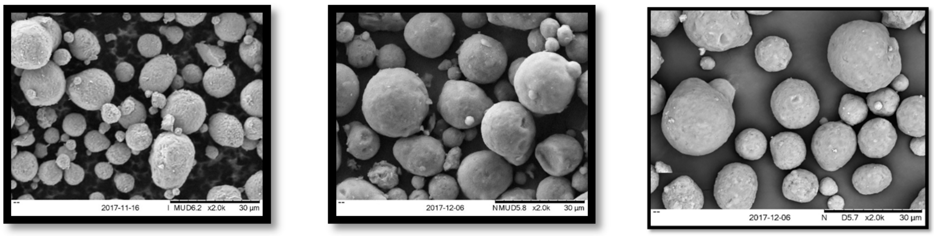
(**a**) (**b**)

Figure 1. Behavior of modified Al_2O_3 (**a**) coated with OA (**b**) coated with SiO_2.

3.2. SEM, FTIR and XRD Analysis

3.2.1. SEM Images

Figure 2 clearly shows that this Al_2O_3 surface have rough surface and quasi-spherical shape and their average diameter is about 10 nm [8]. There is crystal shape exist in this NPs. Hence, coating is possible for this kind of structure. After coating, the Al_2O_3 NPs become thicker and its average diameter change to 30 μm. At the surface of NPs, the coating material successfully attached. For SiO_2, molecules of NPs disperse well as shown in SEM image.

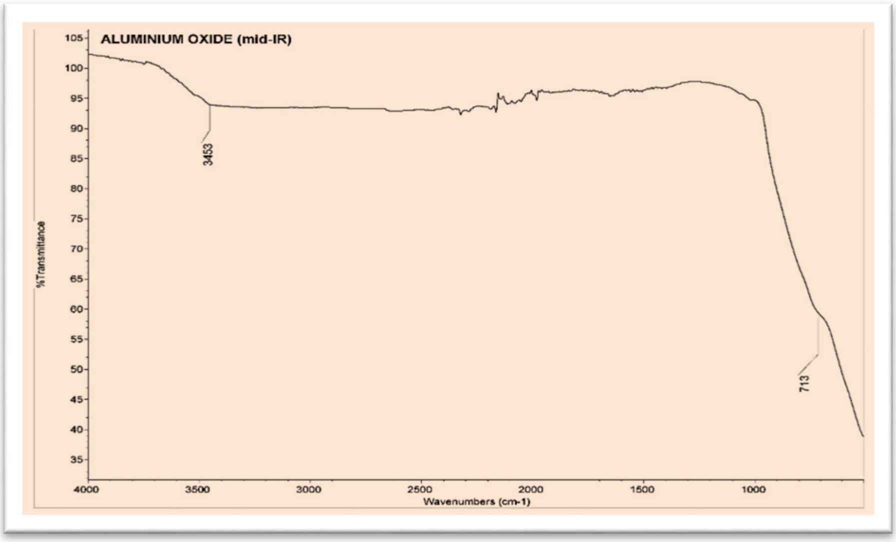


(**a**) (**b**) (**c**)

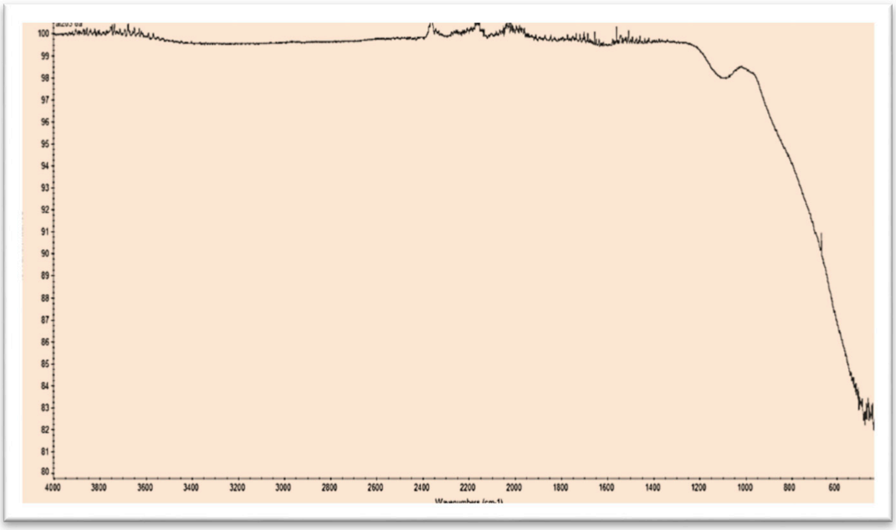
Figure 2. SEM images of Al_2O_3 NPs (**a**) before coating (**b**) after coating (OA) (**c**) after coating (SiO_2) at 2000× magnification.

3.2.2. FTIR Analysis

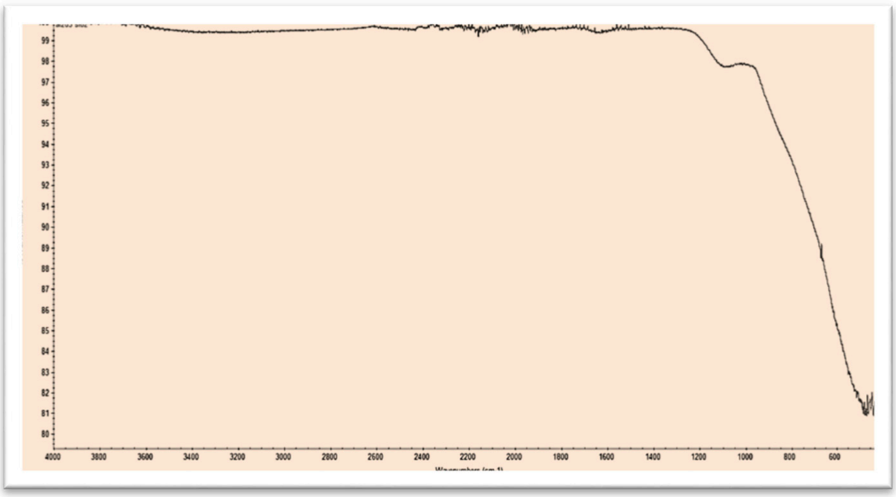
This Figure 3 shows the FTIR analysis. For bare Al_2O_3 NPs, there are only small peaks that can be observed. At 713 cm^{-1}, after decreasing of line, only slight peak can be seen there. For Oleic Acid, obvious stretching vibrations are observed at ~1100 cm^{-1}. According to John Coates, at frequency ~1100 cm^{-1} C-O bond of secondary alcohol can be expected to exist [9]. Comparing to bare Al_2O_3, no stretching around ~1500 cm^{-1} to ~1000 cm^{-1} indicating that there are changes in chemical properties of Al_2O_3 NPs. For Al_2O_3 NPs after it is coated with SiO_2, stretching vibrations can be seen at ~1100 cm^{-1} also which have no different with OA coating. Around ~2400 cm^{-1} to ~1800 cm^{-1}, unsymmetrical vibration fluctuated for OA coating which indicated the noise. The surrounding noise may affect the wavelength vibration when conducting FTIR.



(**a**)



(**b**)

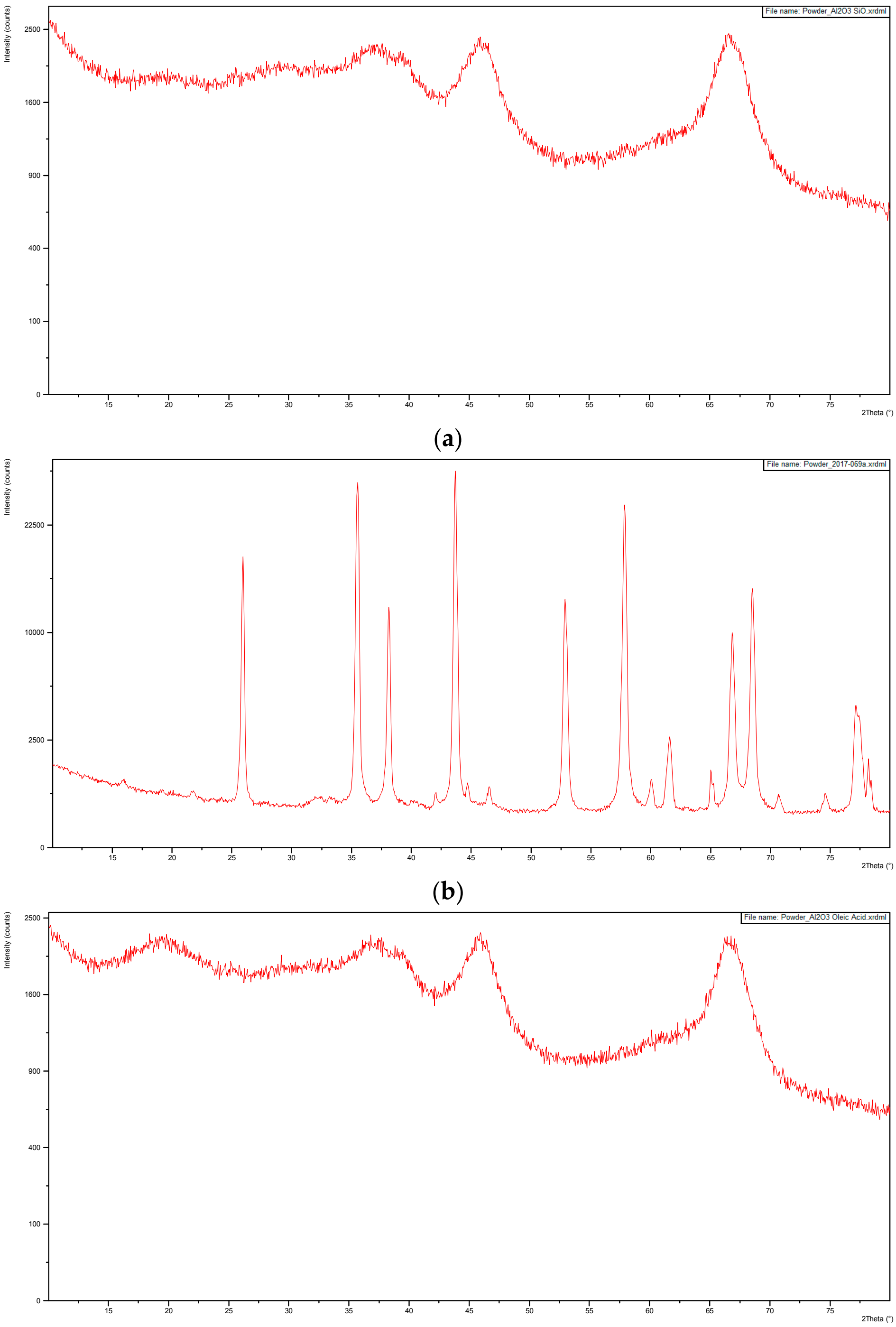


(**c**)

Figure 3. FTIR spectra for (**a**) bare Aluminium oxide (Al_2O_3) NPs [10] (**b**) coated OA Al_2O_3 NPs (**c**) coated SiO2 Al_2O_3 NPs.

3.2.3. XRD Analysis

Figure 4 shows XRD patterns of Al_2O_3 (a) bare (b) coated with OA (c) coated with SiO_2. The peaks for bare Al_2O_3 indicate that this NPs is in crystalline shape. The peaks show the detection of coating substance at crystalline nanomaterials. XRD patterns for NPs coated with OA and SiO_2 does not show important changes. Both coating have broad peak compared to bare Al_2O_3 NPs. This broad peak indicates that there are changes in crystalline structure of NPs. According to Scott, peak broadening may indicate that crystallite size of nanomaterials become smaller and defect in the crystal structure is detected [11,12]. It is obviously can confirm that OA and SiO_2 manage to attach at NPs surface.



(**a**) (**b**) (**c**)

Figure 4. XRD patterns for Al_2O_3 NPs (**a**) bare (**b**) coated with OA (**c**) coated with SiO_2.

4. Conclusions

Overall, it can be concluded that following method proposed by Ruoyu Hong et. al.,[7] coating of NPs can be considered successful. The behavior of different coating material of Al_2O_3 NPs at the paraffin oil and brine water interface differ from each other. Coated OA inhibit hydrophobic tail while coated with SiO_2, improve the dispersion of the NPs. Improvement of this NPs can help in increasing recovery of oil because of its hydrophobicity. SEM, FTIR and XRD analysis confirming the successfulness in coating NPs. For future works, coating material of NPs could be changed. For example, coating with biocompatible polymers can help in medical purposes. For Magnetic Resonance Imaging (MRI), the contrast agent can reduce longitudinal relaxation time. This contrast agent is nanoparticles coated with biocompatible polymer [8].

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Conflicts of Interest: The authors declare no conflict of interest. Authors identify and declare any personal circumstances or interest that may be perceived as inappropriately influencing the representation or interpretation of reported research results.

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