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CHARACTERIZATION AND DEACIDIFICATION OF ACIDIC PETROLEUM CRUDE OIL UTILIZING METAL OXIDE CATALYST SUPPORTED ON ALUMINA AND AMMONIATED-POLYETHYLENE GLYCOL SOLUTION

(Pencirian dan Penyahasidan Minyak Mentah Petroleum Menggunakan Mangkin Logam Oksida Disokong Dengan Alumina dan Larutan Ammonia-Polietilena Glikol)

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Abstract

The presence of naphthenic acid (NA) in petroleum crude oil may cause serious corrosion problem for refinery processing equipment. In this work, an alternative method to remove NA is investigated based on the catalytic deacidification reaction to achieve the target of lowering the total acid number (TAN) as required by PETRONAS to be less than 1. Ammoniated polyethylene glycol (NH_3-PEG) was formulated as a deacidifying agent with various concentrations ranging from 100 – 1000 mg/L for crude oil. Cerium oxide based catalyst supported on alumina was synthesized via wet impregnation method and characterized using X-ray diffraction spectroscopy (XRD), Brunauer–Emmett–Teller (BET) and thermogravimetry analysis-differential thermal analysis (TGA-DTA). Parameters such as amount of basic chemical dosing, type of metal oxides, catalyst calcination temperature and reusability of catalyst on the removal of NA was studied. The results showed the TAN value for crude oil was reduced by 70.6% to a TAN of 0.74 mg KOH/g by using 1000 mg/L of NH_3-PEG dosing aids by Ce/Al_2O_3 catalyst calcined at 1000 ^oC.

Keywords: total acid number, naphthenic acid, metal oxide catalyst, ammoniated-polyethylene glycol, alumina

Abstrak

Kehadiran asid naftenik (NA) dalam minyak mentah boleh menyebabkan masalah hakisan yang serius kepada peralatan pemprosesan penapisan. Di dalam kajian ini, satu kaedah alternatif untuk menyingkir NA telah disiasat berdasarkan tindak balas penyahasidan pemangkin untuk mencapai sasaran jumlah nombor asid (TAN) kurang daripada 1 seperti yang dikehendaki PETRONAS. Larutan ammonia-polietenaglikol (NH_3-PEG) telah diformulakan sebagai ejen penyahasidan dengan pelbagai kepekatan antara 100 – 1000 mg/L. Mangkin serium oksida disokong dengan alumina telah disintesis meggunakan kaedah pengisi tepuan basah dan dicirikan menggunakan spektroskopi pembelauan sinar-X (XRD), Brunauer–Emmett–Teller (BET) dan analisis termogravimetri – analisis pengkamiran terma (TGA-DTA). Parameter seperti jumlah dos kimia bes, jenis logam oksida, suhu pengkalsinan mangkin dan kebolehgunaan mangkin terhadap penyingkiran NA telah dikaji. Hasil kajian menunjukkan nilai TAN bagi minyak mentah telah dikurangkan sebanyak 70.6% kepada TAN 0.74 mg KOH/g dengan menggunakan 1000 mg/L dos NH_3-PEG dibantu oleh mangkin Ce/Al_2O_3 dikalsinkan pada 1000 ^oC.

Kata kunci: nombor jumlah asid, asidnaftenik, mangkin, ammonia-polietilenaglikol, alumina

Introduction

The initial concern about naphthenic acid corrosion dates back to the previous century, and it keeps drawing the attention of refineries until today [1]. Naphthenic acid (NA) is a complex mixture of cyclic or acyclic aliphatic organic compounds characterized by a carboxyl reactive group [2] and constitutes about 50 wt.% of the total acidic compounds in crude oil [3].Total acid number (TAN) refers to the amount of NA found in the crude oil and was measured using ASTM D664 method. TAN represents milligram of KOH per gram liquid needed to neutralize 1 g of acid present in the sample. If the acidic species in the petroleum cannot be removed during the refinement, it will influence the quality of the final product, causing problems, equipment failures, and environmental pollution. Several efforts are focused on the development ofthe current approaches to refine acidic crudes by blending with non-acidic crudes so that the TAN of the blend is no higher than about 0.5 mg KOH/g [4]. The drawback of this approach is that it limits the amount of acidic crude that can be processed. The acidic crudes can be treated with inorganic bases such as potassium and sodium hydroxide to neutralize the acids [5]. This approach, however, forms an emulsion which is very difficult to break and undesirablyleaves potassium or sodium in the treated crude. Catalytic removal of NA has been studied for many years. It has been reported that transition metal catalyst could reduce the acidity of crude oil under hydrogen atmosphere but, this process consumes large amounts of hydrogen [6] and it has not been commercialized yet. In order to solve this problem, the catalytic deacidification process was investigated in this work by using different metal oxides as catalyst supported on alumina to assist in the deacidification process together with the NH_3-PEG as basic chemical agent.

Materials and Methods

Materials

All the materials were purchased from QRëC™ and used without further treatment. 2-propanol and toluene were used as extraction solvents. Ammonia solution 28% mixed with polyethylene glycol (MW 300, 400 and 600) were used as deacidifying agents. Phenolphthalein indicator solution, 1% in ethanol was used as an indicator in the deacidification process. Potassium hydroxide pellets and barium hydroxide were used as titrants. The feedstock used in this study was crude oil obtained from Petronas Penapisan Melaka, Malaysia labelled as crude B with a TAN of 2.52 mg KOH/g.

Preparation of 0.4 % NH_3-PEG

Ammonia solution (40 mL) was added dropwise into a sample bottle containing 9.96 mL polyethylene glycol. The mixture of NH_3-PEG was vigorously stirred using a magnetic bar for an hour. The reaction of NH_3 with PEG to form NH_3-PEG was hastened by soaking the bottle in an ice bath. The solution, which was then ready for blending with the crude oil, was set aside in a dark bottle to avoid sunlight penetration.

Catalyst preparation

The catalyst was synthesized by wet impregnation method according to the report by Toemen et al. [7].The required amount of cerium nitrate in a beaker was dissolved with a small amount of distilled water. The solution was then mixed via continuous stirring using a magnetic bar for 30 minutes at ambient temperature to homogenize the mixture. Alumina beads with diameters of between 4 to 5 mm were used as support material. The support was dipped into the catalyst solutions for 24 hours and then transferred onto an evaporating dish lined with glass wool. Subsequently, it was aged in an oven at 80 – 90 ^oC for 24 hours to eliminate moisture and allow coating of the metal on the surface of the supported catalysts.

This was followed by calcination in the furnace at 400, 700, 900 and 1000 ^oC for 5 hours using a ramp rate of 10 ^oC/min to eliminate all metal precursors, excess water and impurities. The developed catalysts were analyzed by BET, FESEM-EDX and XRD to characterize the physicochemical properties of the catalyst.

Catalysts characterization

Potential catalyst was characterized by several techniques to study its physicochemical properties. The information obtained is highly useful in order to understand the relationship between the properties and its catalytic performance towards the deacidification activity. In this research, the characterization techniques used were X-ray diffraction spectroscopy (XRD), Brunauer–Emmett–Teller (BET) and thermogravimetry analysis-differential thermal analysis (TGA-DTA).

Total acid number (TAN) determination

An amount 0.2 g crude B was measured and placed in a titration beaker. As much as 40 mL of the titration solvent, which is a mixture of toluene: 2-propanol: distilled water (50:49.5:0.5) was poured into the crude oil sample in the titration beaker. After that, 100 ppm of 4% NH_3–PEG solution together with the prepared catalyst was added into 0.1 – 0.15 g crude oil sample. The solution was heated to 35 – 40 ^oC to stimulate the catalyst in the mixture. The petroleum crude oil sample was then titrated with potassium hydroxide solution (0.01 mol/L). Total acid number value for crude B (TAN = 2.52 mg KOH/g) was determined by semi-micro color indicator titration method. The indicator used was phenolphthalein solution (0.1 mL), the end-point for the titration method was indicated when the stable red color was observed. The titration method was performed on crude B before and after the catalytic deacidification technology. In order to express the results, TAN value of the sample was calculated in milligrams of potassium hydroxide per gram of sample (mg KOH/g) by using the equation below (Equation 1):

$$\text{TAN} = \frac{56.1 \times c \times (V_{KOH} - V_B)}{m} \quad (1)$$

where c is the concentration of the standard volumetric potassium hydroxide solution (in mol/L), V_{KOH} is the volume of titrant required for the determination (in mL), V_B is the volume of titrant required for the blank test, (in mL), and m is the mass of the test portion (in gram).

Results and Discussion

Catalytic deacidification of Crude B: Effect of different molecular weight of PEGs

The deacidification activities for crude B increased significantly when using PEG with molecular weights of 300, 400, 600 and 1500 as shown in Figure 1. This observation is proven by the decrease in TAN values ofcrude B along these PEGs. Lower TAN values of 1.68mg KOH/g were obtained for crude B by using both MW PEG of 600 and 1500. These results showed that the deacidification activities for crude B were decreased by using these PEGs. However, in this work, PEG with MW 600 was chosen as the solvent for deacidification agent due to higher percentage of NA removal for crude B and its cheaper cost compared to other PEGs.

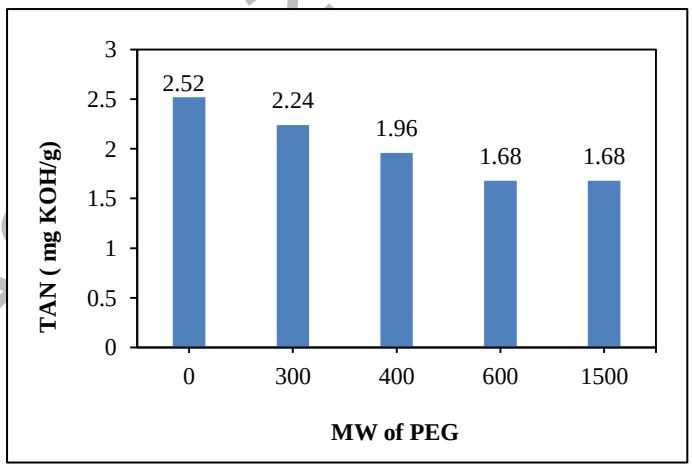

Figure 1. Effect of the different molecular weights of PEG on TAN values of crude B. [Initial TAN value for crude B (2.52 mg KOH/g)]

Effect of different basic chemical dosing

The deacidification performances of different dosing amount of NH_3-PEG in the range of 100-2500 mg/L were compared in order to select a suitable dosing amount for removal of naphthenic acid in the crude oil sample and the result is presented in the Figure 2.

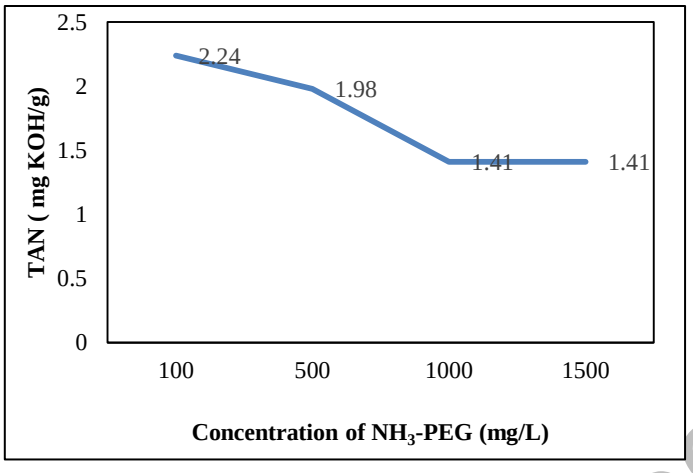

Figure 2. Effect of different dosing amount of NH_3-PEG on the TAN value.

It could be seen from Figure 2, the TAN number of crude B decreased with increasing dosing amounts of NH_3-PEG. When the dosing rose to 1000 mg/L the TAN number was decreased to 1.41 mg KOH/g and after that the curve become flat. The amount of dosing employed in the study should be appropriate enough to react with the NA in the crude oil B, because huge amounts of NH_3-PEG may form a stable emulsion, which would probably stabilize the NA in crude B and reduce the deacidification reaction. Even though high concentration of NH_3-PEG was added, there is no change of the TAN value. This explained that using 1000 mg/L is sufficient to deacidify the acid in crude B because if the concentration was increased more than 1000 mg/L it will cause operational difficulties and waste.

Effect of different metal oxides and calcination temperatures of catalyst

In the preparation of the catalyst, the types of metal oxide catalyst and calcination temperatures are determinant of catalyst activity. The catalytic deacidification was carried out under reaction temperature ranging between 35 to 40^{o}C with addition of 100-1000 mg/L of NH_3-PEG dosing in the presence of Ce/Al_2O_3, Zn/Al_2O_3 and Sn/Al_2O_3 catalysts calcined at different temperatures of 400, 700 and 1000^{o}C for 5 h. Figure 3 portrays the effect of different metal oxide catalysts prepared at different calcination temperatures towards the catalytic deacidification process.

A noticeable difference was recorded for the catalytic deacidification process fulfilling the expected target of TAN to be less than one. An increase in the calcination temperature for all catalysts from 400 to 1000 ^{o}C caused a decrease of the TAN value for crude B. For these studies, the Ce/Al_2O_3 catalyst calcined at 1000 °C gave the lowest value of TAN of 0.74 mg KOH/g followed by Sn/Al_2O_3 catalyst calcined at 1000 ^{o}C (TAN = 1.68 mg KOH/g) and Zn/Al_2O_3 catalyst calcined at 1000 ^{o}C with a TAN of 1.41 mg KOH/g. As for the Ce/Al_2O_3 catalyst, the calcination temperature below than 1000 ^{o}C cannot reduce the TAN value below than one due to incomplete metal oxide formation and the amorphous properties of this catalyst which produced less amount of basic surface active sites available for the catalytic deacidification reaction. However, an increase in the calcination temperature up to 1000 ^{o}C for this catalyst managed to reduce the TAN below than one due to its polycrystallinity properties as shown in XRD data which generated a larger amount of total basic surface active sites led to a successful catalytic deacidification reaction. Furthermore, excellent redox properties of CeO due to the very fast reduction of Ce^{4+}/Ce^{3+} as reported by Ayastuy et al. [8] results in the formation of oxygen vacancies at the surface, making the NA removal more efficient. Thus, Ce calcined at 1000 ^{o}C was chosen as the catalyst to be further optimized in this study.

Reusability testing over Ce/Al_2O_3 catalyst

The potential Ce/Al_2O_3 catalyst calcined at 1000 ^{o}C was tested several times under optimum reaction conditions in order to study the reusability of this catalyst. It was tested by using the same catalyst until the catalyst was deactivated. After one catalytic reaction was completed, the catalyst was rinsed with 2-propanol to remove any adsorbed naphthenic acid compounds. The catalyst was then dried in an oven at 80 ^{o}C and re-used for the second reaction. The process was repeated for the next consecutive run. Figure 4 shows the plot of reusability testing over

Ce/Al_2O_3catalyst. It can be seen that the TAN value was maintained (0.74 mg KOH/g) until the fifth cycle. However, the catalyst started to deactivate (spent catalyst) at the sixth testing as a slight decrease inthe activity is seen as indicated by the increasing TAN value to 0.84 mg KOH/g.

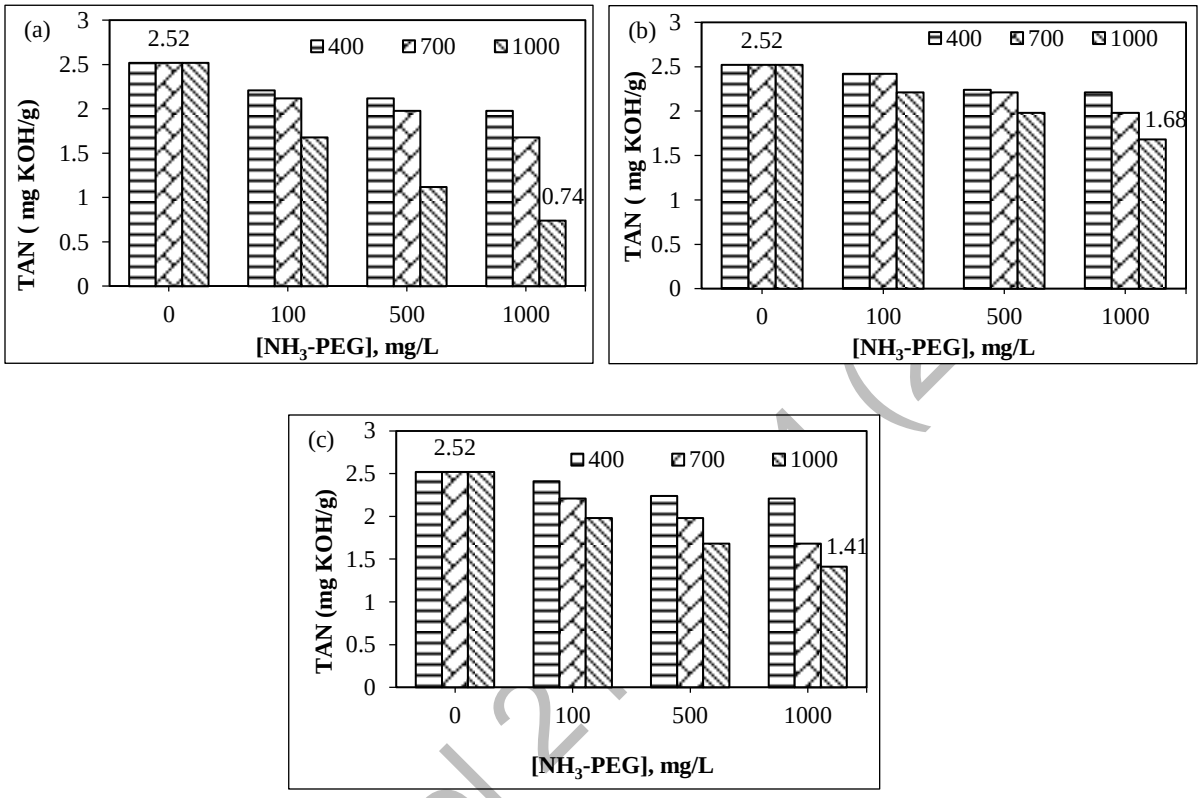

Figure 3. Effect of a) Ce,) Zn and c) Sn catalysts supported on alumina calcined at 400, 700 and 1000 ^oC on the reduction of TAN value

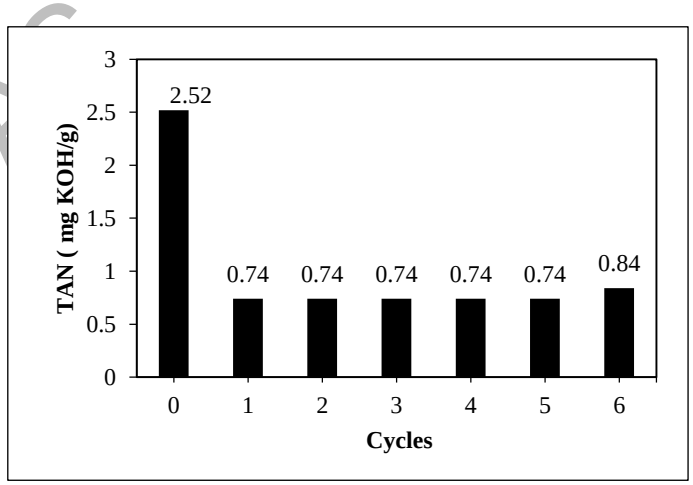

Figure 4. TAN value for six cycles of catalytic deacidification. Reaction conditions: Catalyst = Ce/Al_2O_3, calcination temperature of catalyst: 1000 ^oC.

Characterization of the potential catalyst: TGA-DTA

After aging the catalysts which had been prepared by wetness impregnation method in an oven for 24 hours at 80 – 90 ◦C, the catalyst was analyzed by using TGA-DTA. Figure 5 shows the TGA thermogram of Ce/Al_2O_3 catalyst which illustrate four significant weight lost curves which occurred at 80, 130, 250 and 480 ◦C.

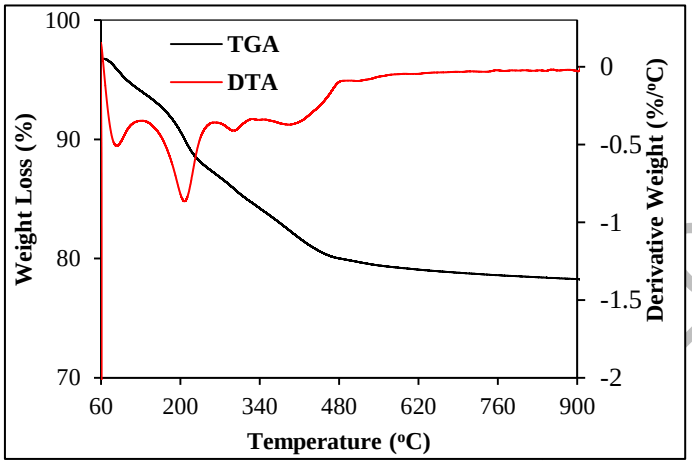

Figure 5. TGA-DTA thermogram of Ce/Al_2O_3 catalyst after aging in an oven for 24 hours at 80 – 90 ^oC.

The total weight loss for this sample is 16.69%. Freewater molecule and nitrate compound was removed from the supported catalyst starting from a temperature of 80 ^oC until 340 ^oC. Meanwhile at 480 ^oC onward; nitrate compounds and surface hydroxyl molecule were decomposed from the samples [9]. From this investigation, the calcination temperature of 400 ^oC is insufficient to remove all the nitrate compounds that originate from the metal precursor. This observation is in agreement with the results shown in "effect of different metal oxides and calcination temperatures of catalyst" in which using Ce/Al_2O_3 catalyst calcined at 400 ^oC, the TAN value of crude B cannot be reduced to lower than one as the catalyst calcined at this temperature resulted in incomplete formation of metal oxide.

BET analysis

One of the most characteristic properties of the surface of a solid is its ability to adsorb gases and vapors. The potential catalyst of fresh and spent Ce/Al2O3 were characterized by nitrogen adsorption analysis. Table 1 summarizes their BET surface area and BJH desorption average pore diameter.

Table 1. BET surface area and BJH desorption average pore diameter of the fresh and spent forms of Ce/Al_2O_3 catalyst

Condition	SBET (m^2g^{-1})	Pore Diameter (A)
Fresh	70	19
Used	62	25

Isotherm shape depends on the solid porous texture. Figure 6 shows the NA isotherm of fresh and used Ce/Al_2O3 catalyst. NA/desorption isotherm of Ce/Al_2O_3 catalyst prepared exhibit the characteristic of mesoporous structure with Type IV with incorporation of some mesopores with the presence of hysteresis loop type H3. Results showed that the surface area of used catalyst (70 m^2/g) was slightly decreased than fresh Ce/Al_2O_3 catalyst (62 m^2/g) probably due to some surface areas which were covered with contamination from crude oil during catalytic

deacidification reaction. However, this occurrence does not affect the catalytic activity after using for one time as proved by catalytic deacidification in reusability testing.

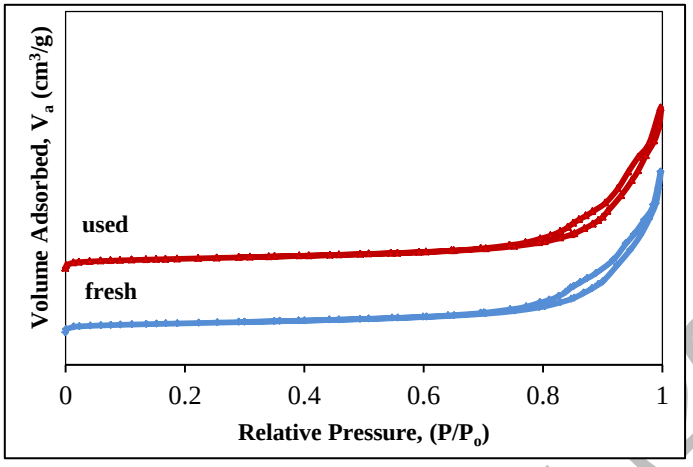

Figure 6. Nitrogen adsorption-desorption isotherms for fresh and used Ce/Al_2O_3 catalyst

Figure 7 shows the pore size distribution curves of the fresh and used Ce/Al_2O_3 catalystcalcined at temperature of 1000°C. The pore size distributions calculated from the desorption branch by the Barret–Joyner–Halenda (BJH) method were very similar for both samples, presenting a very wide pore distribution covering the range of 19–40 nm.

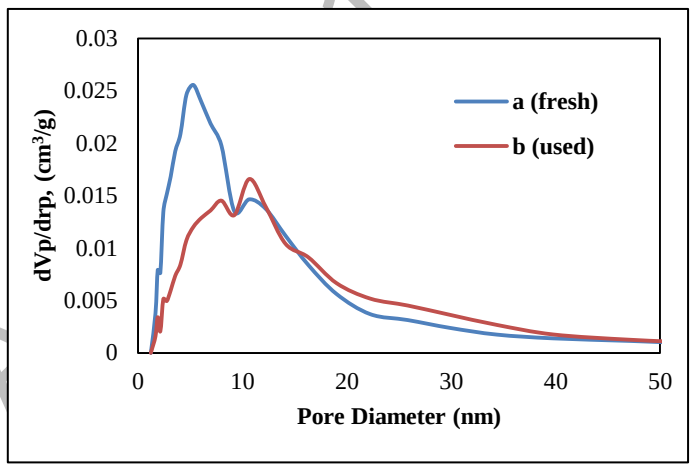

Figure 7. Pore size distribution of a) fresh and b) used Ce/Al_2O_3 catalyst calcined at 1000 °C for 5 hours

XRD analysis

In order to confirm the reusability of the Ce/Al_2O_3 catalyst, the diffractograms of fresh and used Ce/Al_2O_3 catalysts, both calcined at 1000 °C for 5 hours are compared in Figure 8 to investigate any transformation that occurred on the surface of this catalyst before and after being used (after 1st catalytic testing) in the catalytic deacidification process of crude B. Both diffractograms displayed the polycrystallinity phase dominated by the CeO_2 (fcc) species and some of the alumina orthorhombic (o) phase. The CeO_2 species for both fresh and used catalysts showed 2θ valuesat 28.6, 47.5, 56.5, 32.9, 76.6 and 78.9°. Meanwhile the alumina orthorhombic phase occurred at 2θ of 67.3 and 36.5°. This data shows that no change in the diffractograms of both fresh and used catalysts occurs which indirectly prove that

the Ce/Al_2O_3catalyst possesses a higher thermal stability, smaller rate of deactivation and higher reusability.This is shown via the reusability testing, whereby the catalyst can be used up to the fifth cycle with an excellent catalytic deacidification activity.

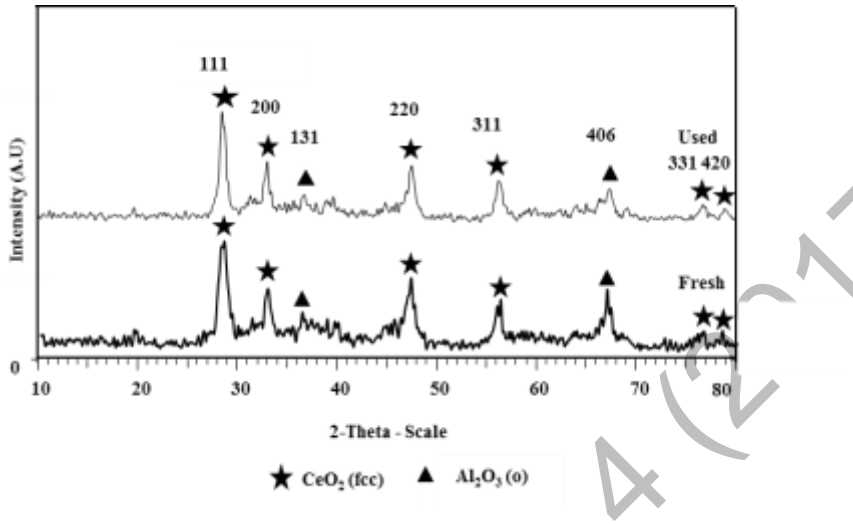

Figure 8. XRD diffractograms of fresh and used Ce/Al_2O_3 catalysts calcined at 1000 ^oC for 5 hours

Conclusion

The technology applied was successful in meeting the PETRONAS benchmark of a TAN less than 1 mg KOH/g for crude oil B. The result from the catalytic deacidification process revealed that Ce/Al_2O_3 catalyst prepared at a calcination temperature of 1000 ^oC has the potential to enhance the reduction of TAN in crude oil. Physical characterization by BET analysis showed that this catalyst has the largest surface area. This revelation is significant as a greater surface area offers more surface-active sites for catalytic deacidification to take place. Furthermore, XRD diffractograms portrayed unchanged composition after this catalyst isused in the catalytic deacidification reaction which indirectly proved that this catalyst possesses a higher thermal stability, smaller rate of deactivation and higher reusability.

Acknowledgement

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