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Effect of Different Alumina Supported Metal Catalysts to the Naphthenic Acid Extraction Process of Petroleum Crude Oil

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Naphthenic Acids (NAs) found in crude oil are the major causes of corrosion problems in oil pipelines, distillation unit, storage, and facilities. As a result, crude oil with high NA will be marketed at lower price and considered as low quality. In this study, catalytic extraction reaction was conducted to lower the Total Acid Number (TAN) in crude oil to below than one mgKOH/g utilizing 2-methylimidazole with the aid of different types of metal supported onto Alumina. The synthesized catalysts were Ca/Al_2O_3 and Ce/Al_2O_3 from alkaline earth metal and rare earth metal group. The metals were supported onto Alumina beads by using Incipient Wetness Impregnation (IWI) methods and calcined at 700°C. Thermogravimetry Analysis-Differential Thermal Analysis (TGA-DTA) was used to determine the suitable calcination temperature for both catalysts. Petronas Penapisan Melaka crude oil was selected to be tested with the original TAN being 5.30 mgKOH/g. The parameters studied were the catalysts' loading and reaction time. The catalytic reaction was fixed at reaction temperature of 27°C. The results showed that Ca/Al_2O_3 and Ce/Al_2O_3 catalysts successfully reduced TAN value in acidic crude oil to below than 1.00 mgKOH/g. Ca/Al_2O_3 catalyst gave a better reduction with 0.08 mgKOH/g compared to Ce/Al_2O_3 catalyst which only reduced the value to 0.65 mgKOH/g. Stretching modes of (M=O) were detected before and after the reaction while CH_3 stretching, carboxylic acid (C=O), CH_2 and CH_3 bend were detected by FTIR analysis which indicated that there were impurities that had been absorbed on both catalysts after the reaction. In summary, alkaline earth metal of Ca supported with Alumina is the best catalyst in the study. The catalytic extraction technique successfully extracts NAs from the crude oil sample thus reducing the TAN value to less than 1.00 mgKOH/g.

Keywords: Crude Oil; heterogeneous catalyst; naphthenic acid

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The high naphthenic acid in crude oil is the major cause of corrosion in oil pipelines that happens at temperatures somewhere in the range of 200°C and 400°C and mainly affects the pipelines between warming heaters, air, and vacuum refining units. In refining operations, the presence of even a small number of NAs in crude oils can cause operational problems, such as foaming in different units and cation leaching in the desalination process, which in turn lead to the deactivation of the catalyst [1]. In fact, high temperature during the flow can cause the release of many molecules and accelerate the chemical reactions that have turned out to be a serious phenomenon affecting the safety of the pipeline. As a result, crude oil with high NA concentration is marketed at a lower price and considered low quality [2].

There are different techniques in the removal of naphthenic acids from highly acidic petroleum, for instance, addition of soda wash, blending, caustic addition and neutralization [3], catalytic decarboxylation [2], esterification [4], mixing of crude petroleum oils with ethanol ionic liquid (Shi et al., 2008), addition of catalyst metal oxide and catalyst for solid acid [5], solvent extraction, physical adsorption, and thermal decomposition. Some of these methods, however, are not entirely satisfactory, having certain limitations that restrict their capability in industrial units which include the adverse impacts that they have towards the environment. For instance, physical adsorption techniques are typically expensive, and applications are restricted at low temperatures to lighter distillate fractions. Catalytic hydrogenation is usually used in industry, but a large supply of hydrogen and a higher cost is required for maintenance [6]. The caustic washing method was studied as the greatest cautious and effective plan to avoid refinery corrosive streams; however, this method can cause significant emulsion problems, environmental pollution and products lost from crude oil [7].

Consequently, the purpose of this study is to identify a cost-effective method to decrease TAN of acidic crude oil to an acceptable level for refinery and produce high quality crude oil at the same time [7]. In this study, two catalysts which are Ca/Al_2O_3 and Ce/Al_2O_3 will be studied and 2-methylimidazole in polyethylene glycol will be tested as an acid removal

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agent. These catalysts with Alumina, Al_2O_3 beads as catalyst's support has high potential to be used for more than one cycle. This technique is used at lower temperatures between 27°C-35°C, which reduces corrosion in oil pipelines and distillation refineries at the same time. It will therefore produce higher crude oil quality and can be commercialized at a higher price.

EXPERIMENTAL

Material and Feedstock

Material used was supplied by QReCTM. The feedstock used was obtained from Petronas Penapisan Melaka, Malaysia with an original TAN value of 5.30 mg KOH/g. In this technique, 2-methylimidazole was used in polyethylene glycol as a naphthenic acids extractor. Titration solvent used was a mixture solution of 2-propanol, toluene, and distilled water while barium hydroxide and potassium hydroxide pellets were used as titrant. The indicator used in the titration process was phenolphthalein solution, 1% (w/v) in ethanol [7].

Catalyst Preparation

In this study, monometallic calcium and cerium catalysts were studied. Generally, an aqueous Incipient Wet Impregnation (IWI) method was implied to both catalysts. Catalyst concentration for screening purposes for all types of calcium nitrate, $Ca(NO_3)_2$ and cerium nitrate, $Ce(NO_3)_3$ were around 30%. In this catalyst preparation, aluminum trioxides, Al_2O_3 was used as support material with a diameter of 4 to 5 mm. Each of the catalyst metal salts used was weighed differently according to its molecular weight. The formula is as given below:

$$\text{Catalyst metal salts needed} = (30/100) \times 5\text{g} \times \text{MW salt}/\text{MW (Ca or Ce)} \qquad (1)$$

Based on the formula, 6.14 g of Ca salt and 3.49 g Ce salt were weighed in a beaker and diluted with 50 ml distilled water while stirring. In another beaker, 5 g of alumina beads, Al_2O_3 was weighed and soaked with 50 mL of distilled water with mild heating. Then, the salt solution prepared was poured into the beaker containing Alumina beads while stirring. After the salt solution had turned into paste, the beaker was then heated in an oven for 24 hours at 80 to 90°C. After that, the catalyst was calcined at 700°C for 2 hours.

Catalyst Characterization

The potential catalyst was characterized by several methods to investigate its physicochemical properties. The result will be sufficiently useful to understand the relationship between their catalytic performance and their properties towards the extraction reaction [8]. In this study, the characterization methods used include Thermal Gravimetry Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).

Thermal Gravimetry Analysis (TGA)

TGA-SDTA 851 Mettler Toledo used simultaneous thermal analyzer for the TGA-DTA curves. Then, 1 bead of the catalyst sample was weighed in 900 μL alumina crucible and heated at a temperature of 25 to 1000°C in nitrogen gas flowing at 15°C/min (50 μL/min). The weight loss graph against temperature was obtained from the microbalance connected to the processing system for thermal analysis. The raw data was analyzed using TA Universal Analysis to compare the weight loss between different types of catalyst sample.

Fourier Transform Infrared Spectroscopy (FTIR)

The evidence for the presence of the functional group will be observed by using FTIR-ATR Spectroscopy. Using a Perkin Elmer SpectrumTM 400 FTIR spectrometer, the catalyst infrared spectrum was studied. A bead of the catalyst was put on germanium crystal. The wavenumber of the sample's spectrum was recorded from 4000 to 450 cm^{-1}. It is possible to determine a specific functional group type by comparing the functional group with the standard catalyst frequency pattern.

Extraction Process

The reagent was prepared using 10% (w/w) 2-methylimidazole together with 90% of polyethylene glycol. Crude oil and reagent of 2-methylimidazole in polyethylene glycol with a mass ratio of 0.6:0.4 was put into an Erlenmeyer flask filled with a magnetic stirrer. 3 beads, 5 beads and 7 beads of selected catalysts were added into the mixture. The mixture was stirred for 15 minutes at a temperature of 27°C during the reaction. The mixture then was placed in a centrifuge tube after the reaction and centrifuged for 20 minutes at a speed of 50 x 106 rpm to separate the chemical reagent from the crude oil with the acid compound. The deacidified crude oil ended up at the top layer of the solution in the centrifuge tube while chemical reagent of 2-methylimidazole with the acids compound extracted from crude oil was at the bottom layer [9]. The experiment was repeated with 5 minutes and 10 minutes of reaction times using the same steps. There were two parameters used in this process which were catalysts loading and reaction times.

Total Acid Number (TAN) Determination

A 0.2 g of deacidified crude oil was measured and placed in a titration beaker after treatment with 2-methylimidazole in polyethylene glycol. A 40 mL of titration solvent mixture with a ratio of 49.5 2-propanol: 50 Toluene: 0.5 distilled water was poured into the sample of crude oil. To determine the TAN value, the semi micro color indicator titration method was used. Phenolphthalein solution, 0.1 mL was used as an indicator. Stable red colors were observed, indicating the endpoint for the titration method. Potassium hydroxide (0.01 mol/L) solution with barium hydroxide was used as a titrant. The sample's TAN value in milligrams of potassium hydroxide per gram of sample (mg KOH / g) was calculated and expressed using this equation:

$$\text{TAN} = 56.1 \text{ x c x } (V_{KOH} - V_B)/m \qquad (2)$$

Where:

56.1 = the molecular weight of KOH in g/mole
C = the concentration in mole/L of standard volumetric KOH solution
V_{KOH} = the volume in mL, of titrant required for the determination
V_B = the volume in mL, of titrant required for blank test
m = the mass in grams, of the test portion

Reusability Testing

After one complete extraction reaction, Ca/Al_2O_3 and Ce/Al_2O_3 catalyst was washed with isopropyl alcohol to remove impurities and adsorbed NA compound on the catalyst. Then, the catalyst was dried in an oven for 1 hour at a temperature of 80°C before used in the next cycle. The same steps for catalytic extraction process were used for the second cycle.

RESULTS AND DISCUSSION

Characterization

Thermal Gravimetry Analysis-Differential Thermal Analysis (TGA-DTA)

Fig. 1 shows the TGA thermogram of Ca/Al_2O_3 which displays the three significant losses. For Ca catalyst with Alumina support, weight loss at the first stage was 3.53% from temperature of 34 to 300°C, the second stage with weight loss of 5.13% at 300 to 450°C while the third stage was from 450 to 700°C with weight loss of 18.08%. From temperature 34 to 300°C, crystal water and surface water from supported catalyst were removed. At 300 to 450°C, complete removal of water and formation of metal oxide, CaO, occurred while at 450 to 700°C, surface hydroxyl molecule and nitrate compound were break down from the samples [8].

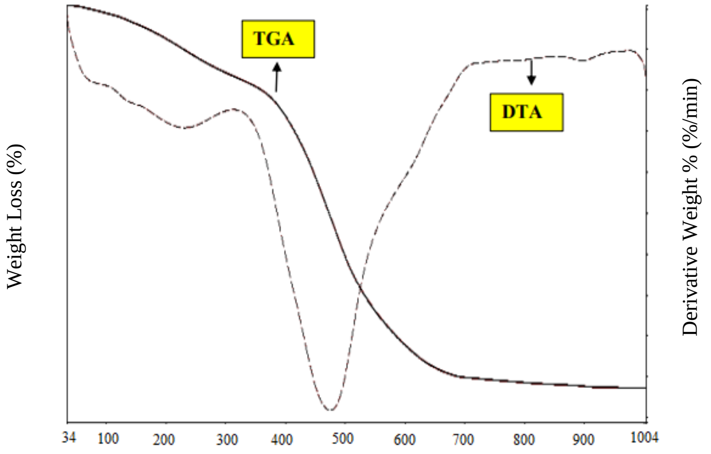

Figure 1. Thermogram of Ca/Al_2O_3 catalyst after aging in an oven at 80-90°C for 24 hours.

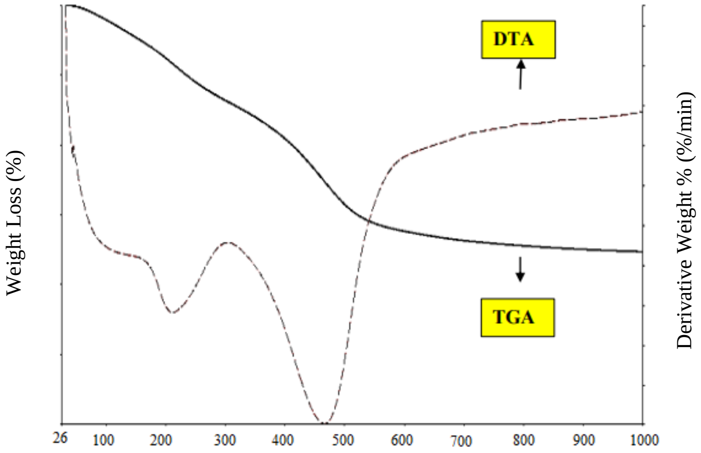

Figure 2 Thermogram of Ce/Al_2O_3 catalyst after aging in an oven at 80-90°C for 24 hours.

Fig. 2 displays the TGA thermogram of Ce/Al_2O_3 which shows the weight loss of the sample. Ce catalyst demonstrated three significant weight losses which are 2.86% weight loss at the first stage from the temperature of 25 to 200°C, 6.08% weight loss at the second stage at 200 to 290°C while for the third stage, from 290 to 580°C, weight loss is 15.99%. From temperature 25 to 200°C, crystal water and surface water molecule were removed from the sample. At 200 to 290°C, formation of pure metal oxide and complete removal of water from the sample happened while at 290 to 580°C, surface hydroxyl molecule and nitrate compound were decomposed from the catalyst analyzed [8].

Based on TGA analysis of both catalysts, we can conclude that calcination at 700°C is a more suitable temperature for Ca/Al_2O_3 catalyst while above 500°C is the suitable calcination temperature for Ce/Al_2O_3 catalyst to remove all impurities and metal precursors such as nitrate ions from the catalyst before the reaction.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was conducted to determine the type of functional group that exists on potential catalysts, Ca and Ce catalysts, before and after reaction, by comparing to standard frequency pattern. Ca catalyst was the best catalyst and the most efficient in reducing TAN of crude oil to less than 1.0 mg KOH/g compared to Ce catalyst at calcination 700°C. Fig. 3 and Fig. 4 show the FTIR spectrum of Ca/Al_2O_3 and Ce/Al_2O_3 catalysts calcined at calcination temperature of 700°C, before and after catalytic extraction process to compare both peaks before and after reaction for each catalyst. By comparing those peaks, the presence of any functional group and any impurities that exist on the catalysts' surface after the reaction can be identified and studied.

Before reaction, it showed only one stretching frequency on the catalyst at wavenumber of 570.09 to 513.74 cm^{-1} and 556.43 to 549.63 cm^{-1} of Ca/Al_2O_3 and Ce/Al_2O_3 catalysts referring to the stretching modes of metal=oxygen (M=O) which showed the complete formation of metal oxide after being prepared using the IWI method. After reaction, peak at wavenumber of 2918.17 to 2850.05 cm^{-1} and 2952.90 to 2851.36 cm^{-1} were observed for Ca/Al_2O_3 and Ce/Al_2O_3 catalysts respectively that indicated the CH_3 stretching might be coming from the NAs or the crude oil itself. The IR signals was also found at 1724.15 cm^{-1} and 1724.43 cm^{-1} on both Ca/Al_2O_3 and Ce/Al_2O_3 catalysts corresponding to the vibrations of carboxylic acid functional group (C=O) which indicated the presence of NA species that was attached on the catalyst's surface. This is because, NAs have the general formula RCOOH, where R represents the naphthene mostly consisting of cyclopentane and cyclohexane derivatives; the carboxylic acid group is usually attached through a CH_2 group or chain, containing up to five or more CH_2 groups, rather than directly to the ring [6].

Based on IR spectra, CH_2 and CH_3 bend were observed at 1462 to 1102.1 cm^{-1} of Ca/Al_2O_3 and at 1462.46 to 1160.35 cm^{-1} of Ce/Al_2O_3 due to the usage of 2-methylimidazole in PEG as chemical reagent while stretching modes of M=O resulted from the complete formation of pure metal oxide catalyst when the calcination was above 650°C. High calcination gave a complete formation of pure metal oxide and completely removed the existence of impurities present in catalyst samples.

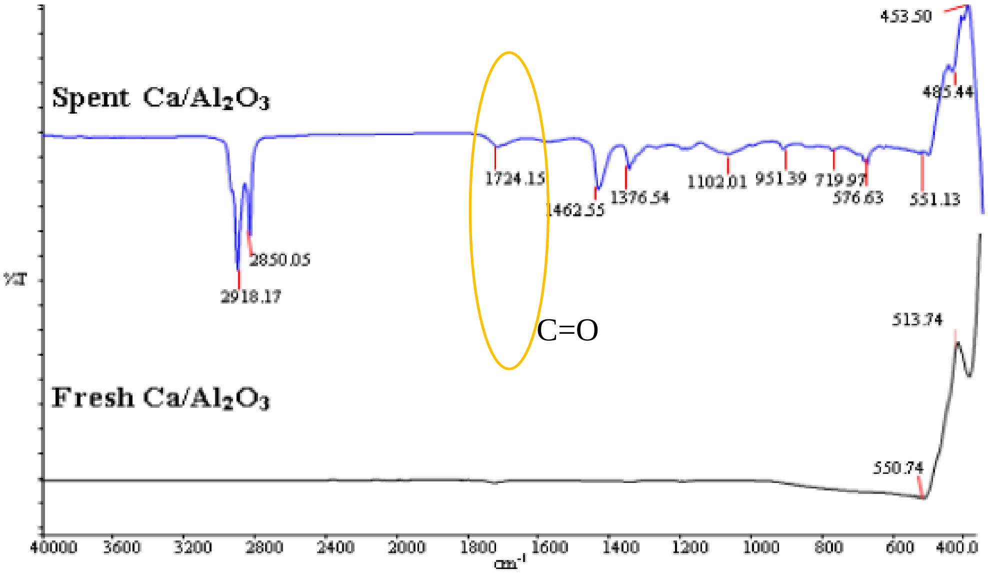

Figure 3. FTIR spectra of Ca/Al_2O_3 catalyst calcined at 700°C.

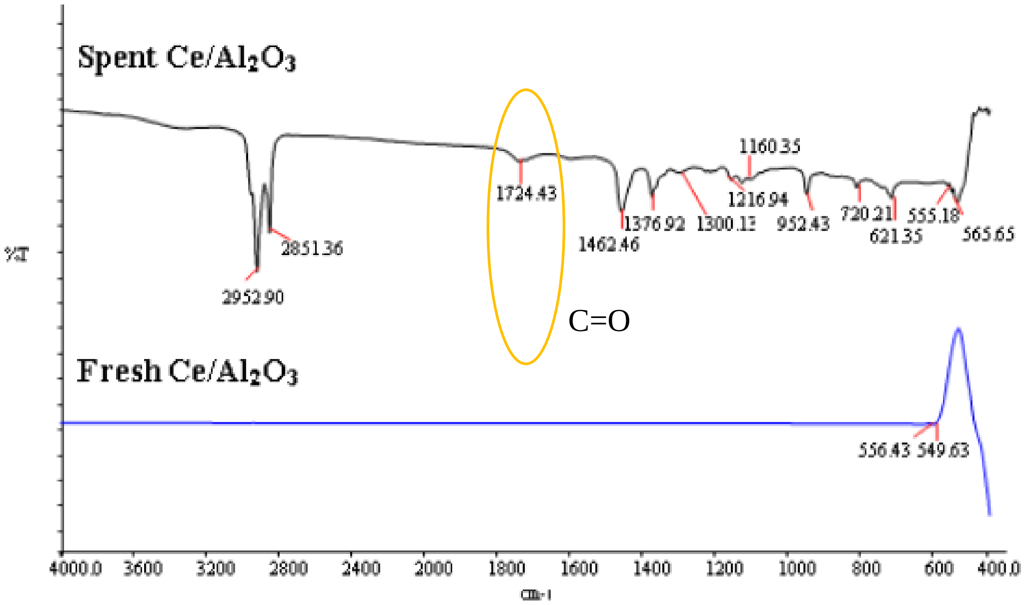

Figure 4. FTIR spectra of Ce/Al_2O_3 catalyst calcined at 700°C.

Total Acid Number (TAN) for Untreated Crude Oil

TAN for measured crude oil was used as a benchmark and reference in order to study the efficiency of chemical reagent and catalyst used in lowering and reducing NAs in the crude oil by comparing it with the treated crude oil. Crude oil obtained from Petronas Penapisan Melaka (PPM) was tested directly from the sample container by using semi-micro color titration method. The original TAN for the PPM crude oil was 5.30 mg KOHg/g.

Deacidification without Catalyst

To measure the effectiveness and efficiency of the reagent and catalyst, the TAN value of the untreated crude oil was used as a benchmark to be compared to the TAN value of the treated crude oil. The crude oil with reagent and without catalyst was investigated to measure the efficiency of reagent to reduce the TAN value which was 2.90 mg KOH/g. The higher TAN value suggests higher levels of naphthenic acid in crude oil [10]. Fig. 5 shows the comparison for the original TAN and the TAN with reagent and without catalyst.

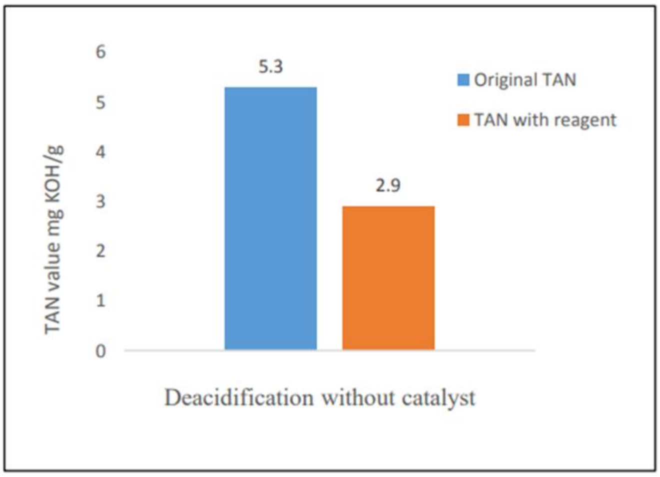

Figure 5 Original TAN and TAN with reagent and without catalyst at reaction temperature 27°C in 15 min.

Effect of Reaction Time

The amount of catalyst added in catalytic reaction was standardized to 3 beads, 5 beads and 7 beads at three different reaction times. From the plotted graph in Figure 6, it could be observed that the most effective number of NAs in crude oil was 7 beads for both of Ca/Al_2O_3 and Ce/Al_2O_3 catalysts. The ideal response time for 7 beads of Ca/Al_2O_3 and Ce/Al_2O_3 catalysts was 10 minutes because 0.08 mg of KOH/g and 0.65 mg of KOH/g had the best results. With a reaction time of 5 minutes for all catalysts loading, the TAN value was higher because both catalysts had limited time for the reaction to remove NAs in the crude oils.

At 15 minutes reaction time for Ca/Al_2O_3 and Ce/Al_2O_3, the TAN value slightly increased from 0.08 to 0.16 and 0.65 to 0.75 mg KOH/g respectively for 7 beads of both catalysts. Therefore, it is suitable to use 10 minutes as the optimal reaction time because when the reaction time was increased to 15 minutes, the TAN value slightly increased. This finding is supported by the study of Shi et al. (2008) where it was observed that the acid-removal rate also increased when the reaction time increased, but the acid- removal rate increased quite slowly and remained constant for 10 minutes [11]. Similar trends were also observed and reported by Tsai et al. (2011), at first, the reaction rate was faster and the conversion rapidly increased, and then, with the reaction gradually approaching equilibrium, the conversion increased more gently before reaching a stable state. To conclude, although 5 beads at 10 minutes for Ca/Al_2O_3 catalyst can reduce NAs in crude oil to below 1 mg KOH/g, however, for Ce/Al_2O_3 catalyst, the TAN value still exceeded 1 mg KOH/g which produced highly acidic crude oil. For usage of 3 beads for both catalysts, it cannot be used at all because TAN value is still very high which makes it unsuitable for refinery pipelines and it will still lead to corrosion problem.

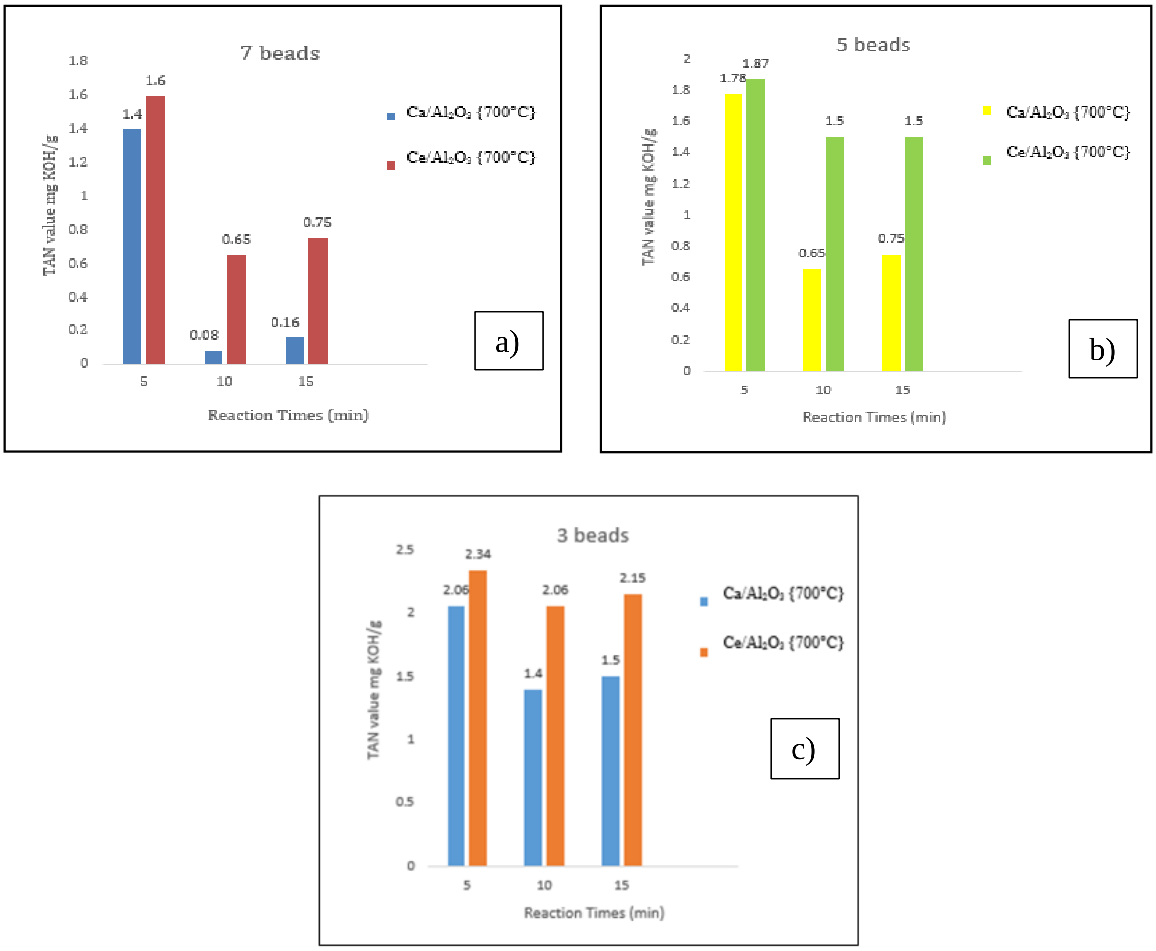

Figure 6 Effect of reaction time on the reduction of TAN crude oil with catalysts calcined at 700°C (a) 7 beads (b) 5 beads (c) 3 beads.

Effect of Catalyst Loadings

In the catalytic deacidification process, one of the parameters used was catalyst loading. Catalyst loading refers to the amount of the catalyst added in chemical reagent and crude oil during extraction reaction to enhance the catalytic activity. Three different catalyst loadings used in the reaction were 3 beads, 5 beads and 7 beads at optimal reaction time which is 10 minutes. Ca/Al_2O_3 and Ce/Al_2O_3 monometallic catalyst calcined at 700°C were used as constant variable. From the result, it shows that the most effective in lowering acid number of the crude oil was 7 beads of catalyst loading for both catalysts.

Liu et al. (2019) stated that a high dosage of catalyst increases the number of active sites that come into contact with oil, thus increasing the possibilities of contact, thereby reducing the yield of NAs [12]. This means that the more catalysts added during the reaction, the greater number of NAs can enter the pores of the catalyst. Therefore, increasing the catalytic activity of Ca/Al_2O_3 and Ce/Al_2O_3 catalyst will decrease the amount of TAN in crude oil to less than 1.0 mg $KOHg^{-1}$. It can be concluded that by using a catalyst, it helps to reduce NA from crude oil by reacting on the catalyst's surface, where the NA structure binds on the catalyst surface, thus increasing the TAN quality [8].

Fig. 7 proposed the plotted graph for the effects of catalyst loading of monometallic catalyst, Ca/Al_2O_3 and Ce/Al_2O_3 on the reduction of TAN for crude oil at constant calcination temperature. For Ca/Al_2O_3 catalyst, the TAN value obtained was 1.40 mg KOH/g by using 3 beads loadings while 7 bead catalyst loading showed TAN value of 0.08 mg KOH/g which is almost nearly TAN= 0. The TAN of 0.65 mg KOH/g was obtained for 5 beads catalyst loadings and 5 beads loadings was chosen as the optimal parameter because it can reduce the original TAN of 5.30 to 0.65 mg KOH/g. Although catalyst loading of 7 beads can decrease TAN value to almost 0, but to reduce the cost of the reaction, lower catalyst loading is much preferable as it also reduces the TAN to less than 1 mg KOH/g as needed by the industry [7]. Also, as cited by Wang et al. (2014), more catalyst quantities can provide more reaction area, but more catalyst quantities can consume more energy and cost [12]. Therefore, optimum catalyst loading is preferable based on economic and industrial factors.

Meanwhile for Ce/Al_2O_3 catalyst, the TAN value was only reduced to 2.06 mg KOH/g by using 3 beads catalyst loading which was only slightly lesser than without using any catalyst that was 2.9 mg KOH/g. The results were 1.50 and 0.65 mg KOH/g for 5 beads catalyst loading and 7 beads catalyst loading respectively. Thus, the higher the catalyst loading used, the lower the TAN value, as observed from the plotted data. The contrast between these two Ca/Al_2O_3 and Ce/Al_2O_3 catalysts shows that Ca/Al_2O_3, catalyst has been more active in eliminating NAs from crude oils as it can reduce the original TAN value to nearly 100% using 7 beads catalyst loading, while for Ce/Al_2O_3 catalyst can only reduce the original TAN value to 0.65 mg KOH/g. This is likely due to Calcium Catalyst's high basicity relative to Cerium Catalyst [7]. From the result shown in Figure 7, it can be observed that most effective amount of catalyst loading added in order to reduce the number of NAs in crude oil was 7 beads for both Ca/Al_2O_3 and Ce/Al_2O_3 catalysts calcined at 700°C as TAN value of the crude oil was 0.08 and 0.65 mg KOH/g for each catalyst respectively.

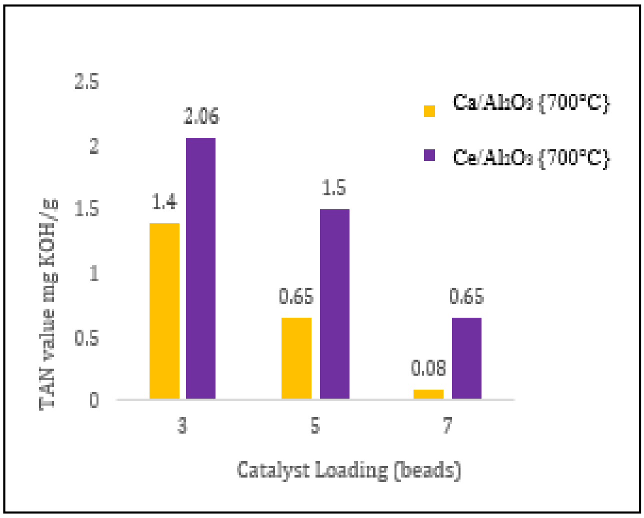

Figure 7. Effect of catalyst loading on the reduction of TAN for crude oil with catalysts calcined at 700°C in 10 min.

Reusability Testing

The monometallic catalyst of Ca/Al_2O_3 and Ce/Al_2O_3 was chosen as the best catalyst at reaction time of 10 minutes. In order to study the reusability of both catalysts, Ca/Al_2O_3 and Ce/Al_2O_3 catalysts undergo a few series of catalytic extraction process under optimum conditions. In this reaction, the amount of catalyst for Ca/Al_2O_3 and Ce/Al_2O_3 added was 5 beads and 7 beads respectively since it was the optimum amounts of catalysts loading added to reduce the TAN value to below than 1.00 mg KOH/g. The study was performed on crude oil to investigate the ability and the performance of Ca/Al_2O_3 and Ce/Al_2O_3 catalysts in reducing the amount of acid in crude oil after three cycles using the same catalyst.

The result for the reusability testing for Ca/Al_2O_3 and Ce/Al_2O_3 catalyst was illustrated in Figure 8. Figure 8 shows that Ca/Al_2O_3 and Ce/Al_2O_3 catalysts could be reused up to two cycles since at three consecutive runs, TAN value of the crude oil for Ca/Al_2O_3 catalyst was increased from 0.65 to 1.4 mg KOH/g while for Ce/Al_2O_3 catalyst was increased from 0.75 in second cycle to 1.96 mg KOH/g. The increasing value of TAN for the crude oil at the third cycle was due to the deactivation of the catalyst sample and formation of impurities from the accumulation of particles resulting from the reaction of chemical reagent with crude oil [8].

As for the comparison between the two monometallic catalysts, the Ca/Al_2O_3 and Ce/Al_2O_3 catalysts showed comparable performance in the reusability test, which was close to earlier findings for the single cycle, although it is evident that the Ca/Al_2O_3 efficiency is slightly higher in the third cycle compared to Ce/Al_2O_3. In conclusion, the reusability of a catalyst can reduces the cost of production, which is very beneficial for industrial oil production [14].

CONCLUSION

The objective of this study was successfully attained. In this research study, it has been proven that the total acid number (TAN) of Petronas Penapisan Melaka crude oil was successfully reduced to less than 1.0 mg KOH/g at optimum condition with the aid of monometallic catalyst of Ca/Al_2O_3 and Ce/Al_2O_3 utilizing 2-methylimidazole in polyethylene glycol as chemical reagent. The highest reduction of TAN was obtained by using 7 beads of Ca/Al_2O_3 catalyst with 10 minutes reaction time at 27°C and catalyst calcination temperature of 700°C where the TAN was reduced from 5.3 mgKOH/g to 0.08 mgKOH/g.

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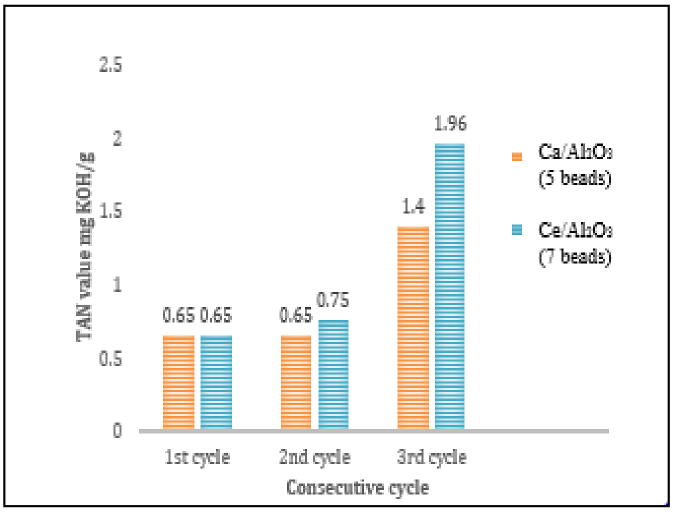

Figure 8. TAN values for the crude oil of Ca/Al_2O_3 and Ce/Al_2O_3 catalyst calcined at 700°C using 5 beads and 7 beads respectively at 10 minutes after three consecutive cycles.

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