The effectiveness of K/Al$_2$O$_3$ and Ca/Al$_2$O$_3$ heterogeneous catalysts in the extraction of naphthenic acid from petroleum crude oil

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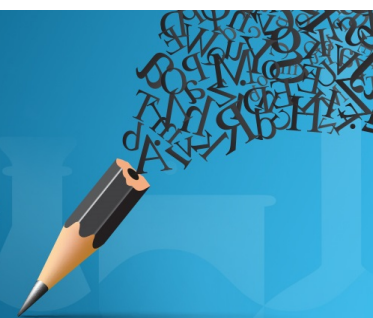# The Effectiveness of K/Al₂O₃ and Ca/Al₂O₃ Heterogeneous Catalysts in the Extraction of Naphthenic Acid from Petroleum Crude Oil

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Abstract. The rising demand for conventional crude oil has made it a major source of energy in recent years, but raw crude oil contains Naphthenic Acids (NAs), which may cause severe operational issue for the oil refineries within the petroleum industry. The value and quality of the oil treated will also be affected by the presence of this molecule. As a result, removing NAs from crude oil is more important to avoid corrosion. The purpose of this study is to create a catalytic extraction method using ethanolic 2-methylimidazole and heterogeneous K/Al₂O₃ and Ca/Al₂O₃ catalysts to remove the NAs from crude oil with high Total Acid Number (TAN) crude oil. Aqueous Incipient Wet Impregnation (IWI) method was used to make the catalysts preparation. To improve the TAN value, various parameters such as reaction temperature (27-45ᵒC), catalyst loading (5-20wt%), and catalyst calcination temperature (700-1000ᵒC) were investigated. X-ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy- Energy Dispersive X-ray (SEM-EDX), Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetry Analysis (TGA) were used to analyzed the catalysts were. When utilizing a Ca/Al₂O₃ catalyst, 89% of the TAN was removed in mg KOH/g, however when using K/Al₂O₃ catalyst, 83% of the TAN was removed by employing a catalyst loading at 20wt%, reaction temperature of 35ᵒC and reaction time of 15 minutes. As a result, the treated acidic crude oil satisfies the PETRONAS criteria of having a TAN of less than 1.0 mg KOH/g.

INTRODUCTION

Crude oil is a naturally occurring hydrocarbon mixture discovered underground. Naphthenic acids (NAs), fatty acids and phenol make up 95% of the overall concentration of acid in crude oil [1]. The NAs found in crude oil are a mixture of high concentrations comprising one or more cycloalkyl groups [2] which have an impact on process equipment and transportation facilities, lowering crude oil quality and sales price [3]. R(CH₂)nCOOH is the typical chemical formula for a NAs, where n is the carbon number and R represents one or more cyclopentane or cyclohexane ring [4]. The amount of potassium hydroxide (KOH) necessary to neutralize the acidity of one gram of oil sample in

milligrams is known as the Total Acid Number (TAN) [5,6]. Acid in the crude oil can be tested using semi-micro colour titration, according to ASTM D664 [7]. Catalytic decarboxylation [8], dilution, caustic washing, [9] and ionic liquid [10] are some of the methods for removing and reducing the NAs. However, neither of these methods is completely suitable due to the drawbacks that generate problem in the petroleum industry. Catalytic decarboxylation is a destructive process that operate at greater temperatures up to 700ºC and utilised higher energy [11]. The acidic compound remains in the dilution method. Although the caustic washing approach can effectively remove NAs, it produces a large amount of effluent and emulsion that is difficult to manage. For the ionic liquid, this process required a large amount of solvent, which was environmentally harmful and inefficient [12]. To tackle this problem, a simple catalytic extraction approach based on 2-methylimidazole in ethanol with K/Al_2O_3 and Ca/Al_2O_3 catalysts is required to remove the NAs and reduce the TAN to 1 mg KOH/g. The catalytic extraction technique has a number of advantages including the fact it only requires a small amount of chemical reagent liquid to removal of NAs, the process does not produce any emulsion, operates at a lower temperature of 35ºC and it is cost-effective way to remove acid from crude oil. The purpose in this research was to come up with environmentally friendly cost -effective strategy for decreasing the TAN.

MATERIALS AND METHODS

Material and Feedstock

The feedstock was crude oil obtained from Petronas Penapisan Melaka, Malaysia with an original TAN value of 4.38 mg KOH/g. Materials from QReCTM were used as supplied. In this method, 10% of 2-methylimidazole was mixed with 90% of ethanol as a NAs extractor. Titration solvents included 2-propanol, toluene and distilled water while titrants included of KOH and BaOH. In order to determine TAN, a phenolphthalein solution was utilised as an indicator.

Preparation and Characterization of Catalysts

Calcium nitrate $Ca(NO_3)_2$ and potassium nitrate KNO_3 were utilised as a catalysts and were supported onto alumina beads Al_2O_3. Because of its high catalytic performance, nitrate salt was chosen as the metal precursor in preparation of the catalyst in this work [13]. According to their molecular weight, both metal salts were weighed differently. In a beaker 8.84 g of $Ca(NO_3)_2$ and 3.88 g of KNO_3 were weighed and dissolved in distilled water while stirring. 5 g of alumina beads were weighed and soaked in distilled water in another beaker. The precursor was put dropwise into a beaker that containing alumina beads that had already been dipped into distilled water and stirred constantly at room temperature for 24 hours to standardise the solution. To remove water and allow a coating of metal on the surface of the supported catalyst, the prepared catalyst was dried in an oven at 80-90ºC for 24 hours. The metal precursors and impurities were subsequently removed by calcination in the furnace at 700, 900 and 1000ºC for 5 hours at heating rate of 5ºC/min. Several techniques, such as XRD and SEM-EDX, were used to analyse the potential catalyst's chemical and physical properties. The XRD method was recorded using a (XRD) Diffractometer D5000 Siemens Crystalloflex with Cu K α radiation (γ = 1.5400 Å) and (SEM-EDX) model TESCAN VEGA3 from Novatiq scientific Singapore.

Extraction Process

The reagent was made by combining 10% w/w 2-methylimidazole with 90% ethanol. In a beaker with magnetic stirrer, crude oil and ethanolic of 2-metylimidazole were mixed at a ratio of 0.4:0.6 (6 ml of reagent and 4 ml of crude). Selected heterogeneous catalysts were blended into a crude oil solution at a concentration 5,10,15 and 20 wt.% by weight. At a temperature of 27, 30 and 35, 40 and 45ºC, the mixture was agigated for 15 minutes. The mixture was placed in a centrifuge tube at the end of the reaction and centrifuged with a speed of 4000 rpm for 15 minutes to separate the chemical reagent containing acids compound from the crude oil. The top layer of solution in the centrifuge tube was a 2-methylimidazole as a chemical reagent with an acid component recovered from crude, whereas the bottom layer was mostly deacidified crude oil [14].

Total Acid Number (Tan) Determination

A deacidified crude oil sample was weighing 0.2 g and placed in a 100 mL beaker. The sample was then diluted with 40 mL of titration solvent at a ratio of 40.5 2-propanol: 50 toluene: 0.5 distilled water. The indicator utilised was phenolphthalein solution, with stable red colour as the titration method's end-point. The potassium hydroxide 0.01 mol/L and barium hydroxide solution used as a titrated. The TAN value of the sample was calculated by using the equation (1) in milligrams of potassium hydroxide per gram of sample (mg KOH/g) to express the result [15].

$$TAN = [56.1 \text{ x } c \text{ x } (V_{KOH} - V_B)] / m \qquad (1)$$

Where 56.1 is the molecular mass of KOH (g/mol), c is the concentration of the standard volumetric potassium hydroxide solution (mol/L), V_{KOH} is the volume of titrant used to reach the equilibrium point (mL), V_B is the volume of titrant required for the blank titration (mL), and m is the sample mass (g).

RESULTS AND DISCUSSION

X-Ray Diffraction Spectroscopy

Fig. 1(i) and Fig. 1(ii) show the XRD patterns for Ca/Al_2O_3 and K/Al_2O_3 catalysts after calcination at 700, 900, 1000°C and after used catalyst at 1000°C. The catalysts Ca/Al_2O_3 and K/Al_2O_3 were both amorphous with a low degree of crystallinity indicating that the particle was vibrated in place in a more random arrangement and had short-range order [16]. The intensity of the characteristic lines increase as the calcination temperature rises [17]. The phase was dominated by Al_2O_3 cubic, rhombohedral and hexagonal phases, according to the diffractogram pattern of both catalysts. The existing of broad peaks correlates to the Al_2O_3 cubic phase as the catalyst support in Fig. 1(i) for Ca/Al_2O_3 catalyst calcined at 1000°C showed a low degree of crystallinity and lack of periodicity, as demonstrated by the presence of broad peaks. The catalyst calcined at 900°C suggesting that the metal oxide active components were dispersed through alumina support. The type and phase of the species in the material can vary as the temperature rises during the synthesis of the catalyst [18]. Peaks assignment at 700°C and after usage catalyst at 1000°C also revealed Al_2O_3 cubic phase dominance. Ca/Al_2O_3 catalyst calcined at 700°C yielded 2θ values of 32.86,37.16, 45.81, 61.00 and 67.28° while catalyst used at 1000°C yielded 2θ = 19.70, 33.15, 37.37, 45.72, 67.02, 67.36°.

Fig. 1(ii) shows a high signal to noise ratio for a K/Al_2O_3 catalyst calcined at 700°C and low signal to noise ratio for catalysts calcined at 900 and 1000°C. Because of the lower particle size, these catalysts have a higher surface area due to their extremely amorphous characteristic. Only the Al_2O_3 cubic phase dominated at 900°C and 1000°C after using catalyst. Calcined at 900°C, the K/Al_2O_3 catalyst yielded a value of 2θ =32.60, 37.35, 41.30, 45.86 and 67.11°. Also, after the catalyst was used at 1000°C gave the same phase as 900°C was Al_2O_3 cubic phase at 2θ = 32.09, 46.01, 58.50, 66.88 and 68.30°. At the greatest calcination temperature of 1000°C, Al_2O_3 dominated the catalyst again, but this time with various lattices of hexagonal phases produced at 2θ =15.73, 32.26, 45.73, 58.30° and a strong diffraction peak at 66.86°. The result reveal that the cubic phase of the Al_2O_3 species functions as an active site and speeds up the K/Al_2O_3 catalyst's catalytic reaction process. Because Ca/Al_2O_3 and K/Al_2O_3 catalysts have a smaller rate of deactivation, there was no significant difference between fresh and used catalysts. The amorphous shape of Fig. 1(i) and (ii) catalyst makes the CaO and K_2O phase invisible. The loss of CaO and K_2O peaks in the XRD pattern was most likely owing to the small size of CaO and K_2O particles which were too small to be detected by XRD, as well as low Ca and K loading in the catalyst, as demonstrated in EDX data [3].
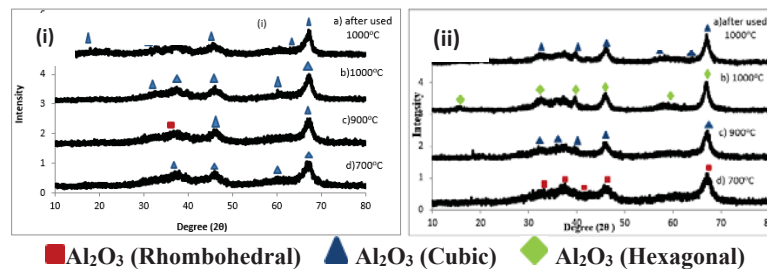

FIGURE 1. The XRD diffractogram of (i) Ca/Al_2O_3 and (ii) K/Al_2O_3 with catalyst calcined temperature of 700, 900,1000 and after used catalyst at 1000°C

Scanning Electron Microscopy

Fig. 2 shows a SEM micrograph of Ca/Al_2O_3 whereas Fig. 3 displays a SEM image for K/Al_2O_3 catalyst that was calcined at 700, 900 1000°C and after used catalyst at 1000°C with a magnification of 5000x. Both catalysts have a rough surface morphology and an inhomogeneous spherical form, as well as a mix of small and large particle sizes. The reduced particle size plays have a significant impact on the catalytic activity [19]. As a result, the smaller particle disintegrated quickly in the oil, but the larger particle has persisted. The micrographs clearly showed that the particle sizes of Ca/Al_2O_3 catalyst calcined at 1000°C Fig. 2(c) are larger particle than those of Ca/Al_2O_3 catalyst calcined at 700 and 900°C. The catalyst calcined at 700 and 900°C was not effectively disseminated, resulting in a mixture of small particle sizes with irregular shape, as seen in Fig. 2(a) and (b). Smaller particle sizes catalysts have a larger surface area, allowing reactions occur at the catalyst's surface [20]. The catalyst surface was densely packed as shown in Fig. 2(d), reducing the surface area of the catalyst. The catalyst's surface area will be reduced as a result of its densely packed surface, lowering its catalytic activity.
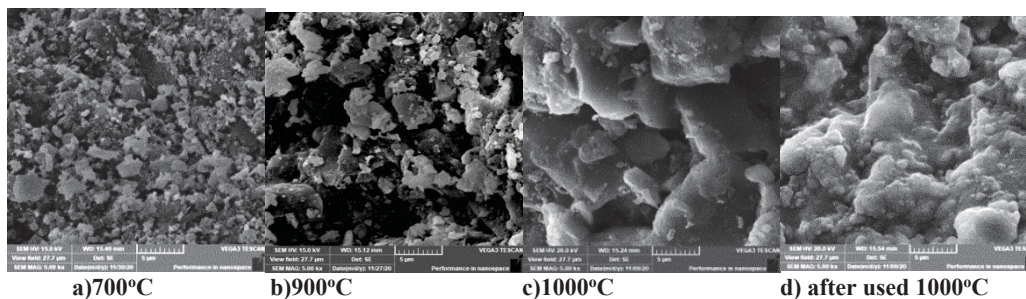

a)700°C **b)900°C** **c)1000°C** **d) after used 1000°C**

FIGURE 2. SEM micrographs of Ca/Al_2O_3 at different calcination temperatures a) 700°C, b) 900°C, c) 1000°C and d) after used catalyst at 1000°C with 5000x magnification

a)700°C **b)900°C** **c)1000°C** **d) after used 1000°C**

FIGURE 3. SEM micrographs of K/Al_2O_3 at different calcination temperatures a) 700°C, b) 900°C, c) 1000°C and d) after used catalyst at 1000°C with 5000x magnification

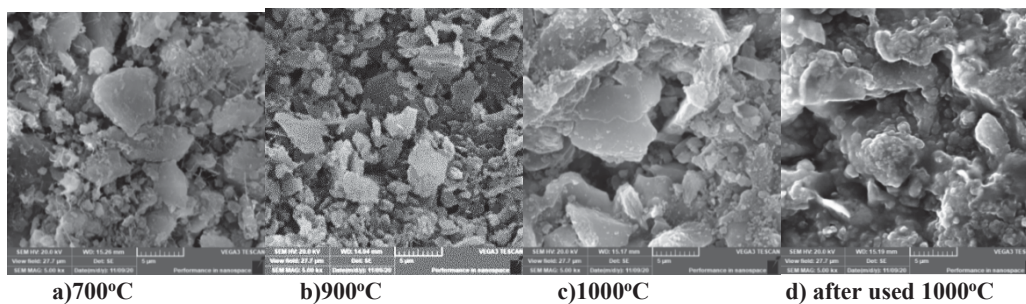The rough surface morphology of the catalyst was inhomogeneously distributed and highly amorphous, indicating that the active components of metal oxide are highly disseminated in the alumina support, as shown in Fig. 3(a) and(b). The catalyst dispersion will be higher if the particle size of the catalyst lower. The catalyst exhibited an aggregation of smaller particles at both calcination temperatures, increasing the surface area of the catalyst [19]. The catalyst surface was not well scattered and densely packed, as shown in Fig. 3(c) and (d), indicating a mixture of tiny and larger particle sizes. The result showed that the particle size of K/Al_2O_3 catalyst calcined at 1000°C was greater than that of K/Al_2O_3 catalyst calcined at 700 and 900°C.

Energy Dispersive X-Ray Analysis

The elemental composition and distribution of the Ca/Al_2O_3 and K/Al_2O_3 catalysts at 700, 900, 1000°C, as well as the after used catalyst at 1000°C are shown in Table 1 (i) and (ii). The elemental constituents are visible in the SEM using EDX mapping. The percentage of the element present in the sample can be determined using EDX analysis to determined how much catalyst is coated on the support. EDX analysis of Ca/Al_2O_3 catalyst revealed that the weight composition of Ca in the catalyst calcined at 1000°C is 6.69% while has the weight composition at 700°C is 3.99wt.%

and the weight composition of Ca in the catalyst calcined at 900°C is 5.33wt.%. EDX examination of K/Al_2O_3 revealed that the maximum K loading (wt.%) was found at 900°C with 6.50 wt.%, followed by 5.63 wt.% at 700°C and 2.46 wt.%. at 1000°C. For the metal oxide catalyst in this investigation, the weight percentage for Al was the highest at s 51.36 wt.%. for 1000°C calcination temperature. After calcined at 1000°C, the percentage of K loading reduced to 2.46 wt.% possibly because the K metal had been diffused into the bulk matrix of the catalyst [21]. The wt.% for K metal decreased as the calcination temperature was raised, owing to the additional oxygen produced by high-temperature burning [3]. The amount of support material in the catalyst is greater than the amount of metal because the support material controls, homogenise and stabilises the metal oxide phase. The presence of Ca, K, O, N, S, C and Al in the potential catalyst was then confirmed using the EDX. The result of the elemental analysis revealed that elements are inhomogeneously distributed on the surface of the supported catalyst's surface. It can be seen that the composition of Ca and K elements decreasing after utilizing the catalyst at 1000°C. It was owing to the agglomeration of Al, which will obstruct the Ca and K species, hence lowering the element's composition. The Ca and K loadings in the catalyst after reaction reduced dramatically to 0.48 wt.% for Ca and 0.36 wt.% for K, owing to of Ca and K particle migration into the porous area of the alumina support during the reaction [21,22].

TABLE 1. Elemental composition from EDX analysis for (i) Ca/Al_2O_3 and (ii) K/Al_2O_3 catalyst calcined at 700, 900, 1000°C and after used catalyst at 1000°C

Calcination Temperature (°C)	Element	Weight Composition (%)	Calcination Temperature (°C)	Element	Weight Composition (%)
700	Al	49.97	700	Al	49.34
(i) Ca	3.99	(ii)	K	5.63
	O	46.04		O	45.03
900	Al	46.07	900	Al	48.79
	Ca	5.33		K	6.50
	O	48.61		O	44.72
1000	Al	47.97	1000	Al	51.36
	Ca	6.69		K	2.46
	O	45.34		O	46.18
1000(after used catalyst)	Al	5.97	1000(after used catalyst)	Al	5.91
	Ca	0.48		K	0.36
	O	69.44		O	69.55
	C	23.86		C	23.47
	S	0.24		S	0.24
	N	0.01		N	0.47

Effect of Reaction Temperature

Fig. 4 shows how TAN removal decreases as reaction temperature rises, at 45°C, the acid removal rate was equal to 40%. The original TAN from 4.38 mg KOH/g was lowered to 2.62 mg KOH/g. the rate of acid elimination may be affected by differences in reaction temperature. Despite this, just a small amount of TAN value was lowered. Despite the lower TAN value, the PETRONAS criteria were not met, as the TAN value should be less than one [15]. Because it clouds lower the value of TAN to 3.17 mg KOH/g, the optimal reaction temperature 35°C was chosen for further study based on economic concerns. The reaction temperature was chosen because it is a cost-effective and environmentally friendly approach, which is now required by the majority of petroleum sector. Although high temperature trigger the decomposition of hydrocarbon in oil, temperature above than 35°C were not investigated in this study since they could affect the catalyst's reusability.
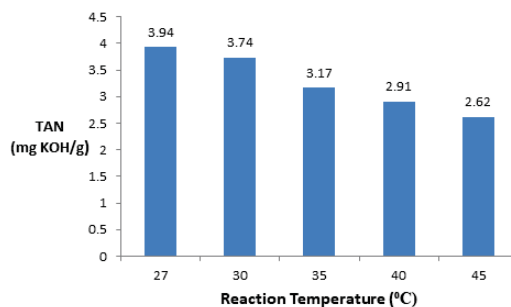

FIGURE 4. Effect of different reaction temperature towards TAN value with reaction temperature 27-45°C and constant reaction time at 15 minutes

Effect of Ca/Al$_2$O$_3$ and K/Al$_2$O$_3$ Catalyst Loading

As shown in Fig. 5, four different catalysts loadings of 5, 10, 15 and 20 wt% were utilised in the reaction, with a reaction time of 15 minutes and reaction temperature of 35°C. With the addition of heterogeneous catalyst with greater calcination temperature, the TAN of crude oil was further reduced. This means that adding the catalyst during the reaction, helps to further reduce the NAs in crude oil since the reaction occurs at the catalyst's surface, where the NAs structure binds to the catalyst's surface, lowering the TAN value [23]. The goal of using a heterogeneous catalyst in the crude oil sample is to get the best TAN value possible, which should be less than 1 mg KOH/g, according to the PETRONAS guidelines. Because NAs is a pollutant, a catalyst with basic characteristic is required in this investigation. Because the catalyst is easy to remove and reuse after the reaction process, Al$_2$O$_3$ beads were utilised as support in this study. At calcination temperature of 700, 900 and 1000°C, the effect of several types of metal catalysts on the TAN reduction is shown in Fig. 5. The TAN value produced by using 20 wt% catalyst loading was 0.57 mg KOH/g based on the result of the Ca/Al$_2$O$_3$ catalyst calcined at 700°C. The calcination temperature was increased to 900°C and 20wt.% was used to further reduce the TAN value. The TAN was efficient in lowering the acid number in crude oil from 0.57 to 0.51 mg KOH/g. When the calcination temperature was increased to 1000°C, the Ca/Al$_2$O$_3$ catalyst successfully reduced the TAN value from 4.38 to 0.46 mg KOH/g with a reduction of 89.5%.
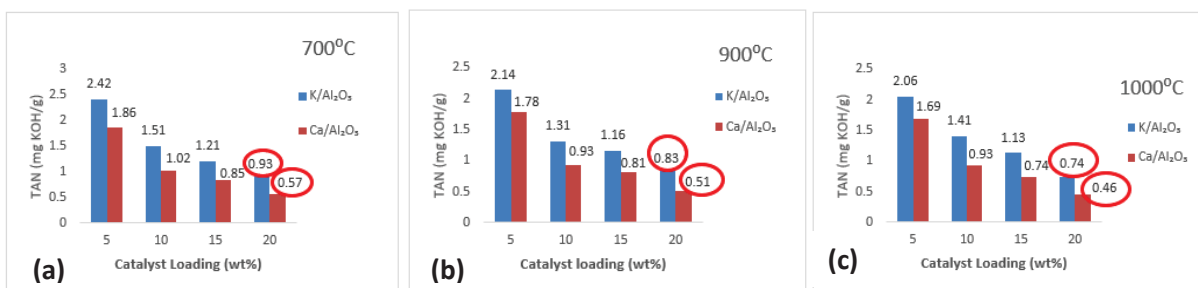

FIGURE 5: Effect of different Ca/Al$_2$O$_3$ and K/Al$_2$O$_3$ catalyst loading of 5, 10, 15 and 20 wt.% towards the TAN value of crude oil with different calcination temperature of (a) 700°C (b) 900°C and (c) 1000°C (reaction temperature: 27-35°C, reaction time: 15 minute, mass ratio of crude oil and reagent 0.4 : 0.6)

The usage of K/Al$_2$O$_3$ catalyst calcined at 1000°C calcination temperature had successfully reduced the acid number of the crude oil with the amount of catalyst loading of 20 wt% at 35°C, resulting in 0.76 mg KOH/g with an 83.11% reduction. At 700°C, the TAN was reduced to 0.93 mg KOH/g, whereas at 900°C, the TAN was reduced by 81%, from 0.93 to 0.83 mg KOH/g. The trend of TAN value was drop to below one with an increase in the calcination temperature from 700 to 1000°C and reaction temperature at 35°C. As a result, the Ca/Al$_2$O$_3$ catalyst calcined at 1000°C was chosen as the best catalyst in this investigation with a catalyst loading of 20 wt% since it was able to lower the TAN value below 0.5 mg KOH/g. The result obtained agreed with the EDX characterization result, indicating that the Ca/Al$_2$O$_3$ monometallic oxide catalyst compared to the K/Al$_2$O$_3$ catalyst. EDX analysis of the elemental composition revealed that the weight percentage of Ca was the greatest for 1000°C catalyst mixture at 6.69% weight composition. Ding *et al*,.2009 [20] did a study on the elimination of NAs using catalytic decarboxylation using alkaline earth metal catalysts and found that the CaO catalyst performed better than the other catalyst such as MgO and ZnO. The Ca catalyst appeared to be more effective and necessary in removing NAs from crude oil, as it efficiently lowered the initial TAN value to 0.46 mg KOH/g.

CONCLUSION

In this study, catalytic extraction was shown to be an effective method for removing an acidic component from a crude oil sample by satisfying the PETRONAS requirement for the TAN value, which must be less than 1 mg KOH/g to avoid corrosion concerns. In this study, we proposed an environmentally acceptable and cost-effective approach for reducing TAN in acidic crude oil in this work. The heterogeneous catalyst of Ca/Al$_2$O$_3$ was successfully reduced original TAN from 4.38 to 0.46 mg KOH/g with TAN reduction which was 89.5% while for K/Al$_2$O$_3$ catalyst was successfully reduced TAN to 0.76 mg KOH/g with 83.11% reduction using the optimum parameter of 1000°C calcination temperature, reaction temperature at 35°C and catalyst loading of 20wt% utilizing 2-metylimidazole in ethanol. When both heterogeneous catalysts were evaluated, it was found that the Ca/Al$_2$O$_3$ catalyst was more successful in decreasing TAN than the K/Al$_2$O$_3$ catalyst.

ACKNOWLEDGEMENT

REFERENCES

1. H.Zhen and H.L.Yu. Energy Sources *38*(20), 3042-3047 (2016).
2. P.C. Mandal, M.A. Abdalla and M.D.Moniruzzaman,. International Journal of Applied Engineering Research, *10*(89), 69-74 (2015).
3. N.A.M.Shohaimi, W.A.W.A.Bakar and J.Jaafar. Journal of Industrial and Engineering Chemistry, **20**(4), 2086-2094 (2014).
4. H.P.Dias, G.R.Gonçalves, J.C. Freitas, A.O. Gomes, E.V Castro, B.G Vaz and W.Romão. Fuel, **158**, 113-121 (2015).
5. W.A.N.G.Hao , LI, D. M. Yan, W. U and D.I.N.G Yu. Journal of Fuel Chemistry and Technology, **48**(1), 44-51 (2020).
6. S.N.Shah, M.Pranesh, J.J.Raj, M.A.Mutalib, K.C.Lethesh, O.B.Ghanem,and Z.Ullah. Separation and Purification Technology, *196*, 96-105 (2018).
7. Annual Book of ASTM Standards, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, 261-267 (1999).
8. X.Fu, Z. Dai, S.Tian, J.Long, S. Hou, and X.Wang. Energy & fuels, *22*(3), 1923-1929 (2008).
9. B.S.Rana, D.W.Cho, K.Cho, and J.N.Kim. Fuel, *231*, 271-280 (2018).
10. L.Shi,G.Wang, and B.Shen. Petroleum science and technology, *28*(13), 1373-1380 (2010).
11. H.Y. Oh, J.H. Park, Y.W.Rhee, and J.N.Kim. Journal of Industrial and Engineering Chemistry, *17*(4), 788-793 (2011).
12. L.J. Shi, B.X. Shen, and G.Q.Wang. Energy & Fuels, *22*(6), 4177-4181 (2008).
13. W.A.W.A.Bakar R.Ali, A.A.A Kadir, and W.N.A.W.Mokhtar. Fuel processing technology, **101**, 78-84. (2012).
14. Y.Sun, and L.Shi. Fuel, *99*, 83-87(2012).
15. N.M.Shukri, W.A.W.A.Bakar, J.Jaafar, and Z.A. Majid. Journal of industrial and Engineering Chemistry, **28**, 110-116 (2015).
16. N. H.Aziz, N.A.M.Shohaimi and N.S.C. Harun. Trans Tech Publications Ltd. **Vol. 1025**, pp. 284-289. (2021).
17. K.Cho, B.S.Rana, D.W.Cho, H.T.Beum, C.H.Kim and J.N.Kim. Applied Catalysis A*: General*, **606**, 117835 (2020).
18. D.C.Cárdenas-Espinosa and J.C.Vargas. In Studies in Surface Science and Catalysis 175, pp. 385-388 (2010).
19. X.L.Yang, W.Q.Zhang, C.G.Xia, X.M.Xiong, X.Y.Mu and H.Hu. Catalysis Communications. **11**(10), 867–870 (2010).
20. L.Ding, P.Rahimi, R.Hawkins, S.Bhatt, and Y.Shi. Applied Catalysis A*: General*, **371**(1-2), 121-130 (2009).
21. W.A.W.A.Bakar, R.Ali and N.S.Mohammad. Arabian Journal of Chemistry, **8**(5), 632-643 (2015).
22. M.Safariamin, L.H.Tidahy, E.Abi-Aad, S.Siffert and A.Aboukaïs. Comptes Rendus Chimie, **12**(6-7),748-753 (2009).
23. K.Cho,B.S.Rana,D.W.Cho, H.T.Beum, C.H.Kim and J.N.Kim. Applied Catalysis A: *General*, **606**, 117835 (2020).