UNIVERSITI TEKNOLOGI MARA

CATALYTIC EXTRACTION OF NAPHTHENIC ACIDS FROM ACIDIC PETROLEUM CRUDE OIL UTILIZING AN ETHANOLIC 2-METHYLIMIDAZOLE OVER Ca/Al_2O_3 AND K/Al_2O_3 CATALYSTS

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ABSTRACT

Naphthenic acids (NAs) corrosion is a major problem to the oil refinery equipment in the petroleum industry when processed at high temperature of 220-340^oC. The acidity level in the crude oil is measured by the Total Acid Number (TAN) value. In this study, a catalytic extraction method was introduced to lower the TAN in crude oil to below than one mg KOH/g utilizing ethanolic 2-methylimidazole catalysed by Ca/Al_2O_3 and K/Al_2O_3 heterogeneous catalysts. The roles of 2-methylimidazole in ethanol was to help the reducing of TAN in crude oil by adding the catalysts and increasing the catalytic activity. Calcium nitrate ($Ca (NO_3)_2$) and potassium nitrate (KNO_3) were utilized as a catalyst precursor and were supported onto alumina oxide (Al_2O_3). The Ca/Al_2O_3 and K/Al_2O_3 were successfully prepared by the Incipient Wetness Impregnation (IWI) method and calcined at different calcination temperature of 700, 900 and 1000^oC. The parameters studied were the effect of reaction temperature, reaction time, catalysts without reagent, catalyst loading, calcination temperatures and reusability. The catalytic extraction reaction was fixed at a reaction time of 15 minutes at 35^oC. The prepared catalyst were then characterized by using X-Ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetry Analysis-Differential Thermal Analysis (TGA-DTA), and Brunauer-Emmett-Teller (BET) to obtained its physicochemical characteristic. Based on characterization of FTIR analysis, stretching mode of pure metal oxide (M=O) were detected for both fresh and used catalyst. Functional group of CH_3, carboxylic acid (C=O), CH_2, O-H and C-N were detected at the catalyst after reaction, which indicates that impurities have been adsorbed on both catalysts after reaction. Based on TGA-DTA analysis, temperature 700^oC is suitable since all impurities in the precursor had been removed. XRD results of both catalysts showed a semicrystalline phase with the presence of Al_2O_3 rhombohedral, monoclinic and hexagonal species. SEM micrograph illustrated an inhomogeneous distribution of various particle sizes, which confirmed the presence of Ca and K metals on the prepared catalyst. EDX results confirmed the presence of 6.69% by weight composition of Ca and 6.50% for K metal in the prepared catalyst. Characterization using BET analysis showed the Ca/Al_2O_3 catalyst calcined at 700^oC gave the highest surface area of 83.32 m^2/g and 120.11 m^2/g for K/Al_2O_3. The result shows that Ca/Al_2O_3 and K/Al_2O_3 catalysts had successfully reduced TAN value from acidic crude oil below one mg KOH/g. From the results, the Ca/Al_2O_3 catalyst gave a better reduction of TAN with 0.46 mg KOH/g compared to the K/Al_2O_3 catalyst which only reduced up to 0.93 mg KOH/g.In summary, the catalytic extraction reaction had successfully reduced the acid number in the crude oil sample to the lowest TAN value by operating at lower temperatures and cost-effective way to remove acid from crude oil.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

Nowadays, the global economy is highly depending on fossil fuels such as petroleum crude oil, that can be classified into two groups, sweet crude and sour crude. Sour crude oil has more than 1.5% of hydrogen sulfide and is toxic and corrosive. Meanwhile, sweet crude contains less than 0.5% of hydrogen sulfide which lead to the high quality of crude oil, while sour crude is highly acidic (Soliman, 2019; Yepez, 2005). Crude oil is a combustible substance that is found in beneath the earth's surface. In geologic formations, a mixture of hydrocarbons and other organic substances can be found. Because of the presence of these highly mixed components in the crude oil, some of the components will vaporise when heated (Leffler, 2008). Crude oil comprises of a complex hydrocarbons mixture that ranges from 50% to 97% of oil content and 6% to 10% of it is nitrogen, oxygen, and sulphur (Suganuma & Katada., 2020). Sulphur species are found in crude in concentration ranging from 0.05-10 wt.%, with the great majority of crudes falling in the 1-4 wt.% (Fahim et al., 2010).

Sulphur species including elemental sulfur through hydrogen sulfide, carbonyl sulfide, as well as inorganic and organic sulphur compounds (Ho et al., 1974). The oxygen compounds have a wide range of structures include alcohol ethers, carboxylic acids, phenolic compounds, ketones, esters, and anhydrides. Most of these species are not particularly corrosive, but the carboxylic acids, collectively known as naphthenic acids, can cause serious corrosion during the refining process (Redondo et al.,2020; Turnbull et al., 1998). Metals including copper, nickel, vanadium, and iron make up less than 1% of overall composition. The hydrocarbons present in crude oil contain mostly paraffinic, with some naphthene's and simple also complex aromatic structures (Marshall et al., 2004). According to Hughey et al. (2002), used mass spectrometry to demonstrate that the composition of crude is extremely complex, and they identified 11,127 different species in a crude sample.