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Removal of Naphthenic Acids from High Acidity Korean Crude Oil Utilizing Catalytic Deacidification Method

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Abstract

Catalytic deacidification is a fascinating method to decrease the naphthenic acids (NAs) concentration of highly acidic petroleum crude because these acids caused serious corrosion in refinery equipment. Korean crude oil with a total acid number (TAN) of 8.32 mg KOH/g was used to test the performance of catalytic deacidification technology. A basic chemical with a dosing of 4% ammonia solution in polyethylene glycol (NH_3-PEG) was used as the acid removal agent with concentrations of 100, 500, and 1000 mg/L. Cerium oxide, zinc oxide and tin oxide based catalysts supported onto alumina prepared with different calcination temperatures and types of dopants were used to aid in the deacidification reaction. The potential catalyst was characterized by BET, EPR and CO_2-TPD for its physicochemical properties. The results showed 93.3% reduction for Korean crude oil using Cu/Ce (10:90)/Al_2O_3 calcined at 1000 ^oC. This catalyst has the highest BET surface area of 87.12 m^2/g with higher dispersion of Cu^{2+} species on the CeO surface detected using EPR spectra and higher total basic site measured using CO_2-TPD. These properties contributed to the excellent catalytic performance which remove the NAs in the Korean crude oil and concurrently reduced the TAN value below than one.

Keywords: Naphthenic Acids, Korean crude oil, Total acid number, NH_3-PEG, Basic catalyst

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1. Introduction

The presence of naphthenic acids (NAs) compounds contributes to the acidity of crude oils and is one of the major sources of corrosion in oil pipelines and distillation units in oil refineries [1-2]. Consequently, crude oils with high NAs concentrations are considered to be of poor quality and marketed at a lower price [3]. Total acid number (TAN) is defined as the number of milligrams of potassium (KOH) required to neutralize the acid in one gram of oil, and a commonly accepted criterion for the oil acidity, although the correlation with corrosive behavior is still controversial [4].

The removal of NAs from crude oil is regarded as one of the important processes in heavy oil upgrading. Current industrial practices either depend on dilution or caustic washing methods to reduce the TAN number of heavy crude oils [5]. However, neither of these approaches is entirely satisfactory. For instance, blending a high TAN crude oil with a low TAN one may reduce the NAs content to an acceptable level, but the acidic compounds still remain. Caustic treatment can substantially remove NAs, but the process generates significant amounts of wastewater and emulsion that are problematic to treat. In particular, once an emulsion is formed, it is very difficult to remove.

Catalytic removal of NAs has been studied for many years. It has been reported that transition metal catalyst could reduce the acidity of crude oil under the hydrogen atmosphere