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Ni–W/nano zeolite Y catalysts for n-heptane hydrocracking

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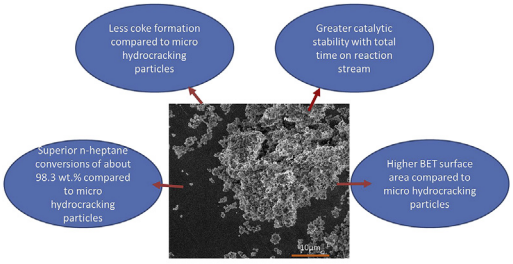
HIGHLIGHTS

- Hydrocracking particles made from high Si/Al ratio nano zeolite Y-NiO-WO_3.
- Nano hydrocracking particles showed superior n-heptane conversion of 98.3 wt. %.
- Nano hydrocracking particles gave higher surface area than micro counter part.

GRAPHICAL ABSTRACT



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ABSTRACT

Zeolite nanoparticles have attracted much interest in various catalytic applications due to their reportedly superior performance when compared with the microparticle counterpart. In this study, we report hydrocracking catalysts made from nano zeolite Y- NiO-WO_3. The nano hydrocracking particles were compared for their performance with the micro hydrocracking particles. Both were prepared through the impregnation of nickel and tungsten salts, and tested under similar catalytic conditions at 350 °C and 400 °C, using n-heptane as the feed molecule. The nanoparticles registered superior total conversions of 98.3 wt. % and 95.7 wt. % at 350 °C and 400 °C respectively while the micro counterpart gave overall conversions of 78.3 wt. % and 34.6 wt. % at 350 °C and 400 °C respectively at the end of total time on stream of 180 min. The higher conversions for the nano zeolite Y hydrocracking particles suggest more accessibility of the active sites for the reaction to occur. This work may provide a further insight on utilizing zeolite nanoparticles for different catalytic applications, especially in conjunction with metallic elements.

1. Introduction

Zeolites are widely utilized as catalysts in the petroleum refining industry [1]. Their crystalline hydrated networks of alumina and silica possess ordered porosity at the molecular level, providing them with a high surface area and making them viable candidates for cracking high molecular weight hydrocarbons into more useful, lighter products [2–4]. Commercially, zeolites are widely available in the micro particle form. However, the micropore dimensions poses diffusional limitations [5] and restricted mass transfer of the reactant and product molecules within the catalyst. The latter affects product selectivity and catalyst lifetime due to clogged pores owing to coke formation [6]. To address these limitations, there is a growing interest in synthesizing zeolites in the nano particle form. The nano particle form has proven to be more promising in terms of higher total conversion as well as improved selectivity, due to

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higher accessibility of active sites and hence greater probability for the reaction to occur on those active sites, [7,8]. For example, Konno et al. [9] studied different H-ZSM-5 particle sizes for n-hexane cracking. The final conversions decreased rapidly for the micro particle while the nano form showed greater conversion stability. Likewise, Tago et al. [10] compared the activity of H-ZSM-5 using nano sized and micron sized particles where the nano zeolite showed superior performance for olefin production from acetone. Many other similar studies have been reported [8,11–13] where the higher accessible surface area of the nano particles have shown improved catalytic performances compared with the micro particles.

Never the less, there are limited studies in the literature on utilizing zeolite nanoparticles for hydrocracking application [14,15], the limitation being the availability of high Si/Al zeolite nano particles. Nano zeolites are usually synthesized hydrothermally [8,16]. However, it is challenging to hydrothermally synthesize nano zeolites especially if one has to utilize a high Si/Al ratio, which is commonly used as a hydrocracking catalyst. One approach is to ball mill the micro sized particles [1,17]. However, ball milling causes destruction in the crystal structure and hence loss of crystallinity. To address this limitation, recently, Zhuman et al. [18] reported a size reduction in zeolite Y micro particles through ball milling with a damping material using carbon nanostructures (CNS). The incorporation of CNS during ball milling of micro zeolite-Y produced nano zeolite-Y particles of high crystallinity which proved to be promising for hexa-decane cracking [18].

In this study, we use high Si/Al ratio zeolite-Y nano particles to fabricate hydrocracking catalysts by incorporating the hydrogenation components, nickel and tungsten oxides. The hydrogenation elements are necessary for a bifunctional mechanism whereby both acidic and metallic sites play the role [19,20] for long chain hydrocarbon cracking to obtain high value n-paraffins and iso-paraffins [21]. The present study provides greater insight on utilizing high Si/Al ratio nano zeolites for catalytic application and the superior selectivity for a product when compared to the micro zeolite counterpart due to less diffusional limitations.

2. Expereimental

2.1. Catalyst preparation

Nickel (II) acetate tetra hydrate (NiAc), ammonium metatungstate hydrate (AMT) were purchased from Sigma-Aldrich (St. Louis, MO). Zeolite-Y (CBV 720, SiO: $Al_2O_3 = 30$) was purchased from Zeolyst International. Two hydrocracking catalysts were prepared: i) zeolite micro-Y particles, and ii) zeolite nano-Y particles produced through ball milling as reported in Ref. [18]. Both catalysts were prepared as follows: nickel and tungsten salt solutions were introduced onto zeolite through the wet impregnation method [22,23]. The ratio of the salts were kept in such a way that the end catalyst had Ni: W atomic ratio of 1:3 [24,25]. The catalyst was dried overnight at 120 °C overnight after which it was calcined at 550 °C at a heating rate of 1 °C/min for 2 h under ambient conditions. Calcination decomposes the salt for pure zeolite-NiO–WO_3 particles. The furnace was allowed to cool to room temperature before taking out the sample. For convenience, we will be referring to the hydrocracking catalyst made from micro zeolite Y particles as HDC MP while that made from ball milled nano zeolite Y particles as HDC NP.

2.2. Catalyst characterization

HDC MP and HDC NP were characterized for their morphology through high resolution scanning electron microscopy (HRSEM) operating at 5 kV. The samples were coated with gold using a precision etching coating system (Gatan Model 682, Germany) with a coating thickness of about 5–7 nm. X-ray diffraction analysis (XRD) was used to study the structural integrity of the hydrocracking catalysts through an X-ray diffractometer (PANalytical, Emperean). The machine was operated at 45 kV and 40 mA with Ni-filtered CuKα ($\lambda = 1.5056$ Å) radiations in 5–90° half angle range. Nitrogen adsorption experiment was conducted through Brunauer, Emmett and Teller (BET), NOVA®-*e* Series Model 25 Quantachrome Instruments. The sample was degassed at 300 °C for 4 h prior to the analysis. The surface area of the calcined catalysts was calculated through multipoint BET method. Data in the relative pressure range of 0.05–0.30 was used for this purpose.

2.3. Catalytic test

n-heptane (Aldrich, >99 mol. %) feed was used a model compound. The hydrocracking tests were carried out in a continuous fixed-bed flow reactor with an inner diameter of 9 mm. The catalysts were used as prepared. 500 mg of fresh catalyst was loaded into the reactor, where it was first reduced by flowing through hydrogen stream for 3 h at 550 °C. Hydrogen pressure of 5 bars was used. Subsequently, the temperature was allowed to decrease to the testing temperatures; 350 °C and 400 °C. n-heptane was introduced and the products, both gaseous and liquid were collected at 1 h intervals for a total on stream time of 3 h. Weight hourly space velocity (WHSV) equal to 4 h^{-1} and a hydrogen to hydrocarbon molar ratio of 3:1 was used.

Liquid products were analyzed by an off line gas chromatography mass spectrum (GC MS), GC 7890B-MS5977A equipped with a 5 column Nonpolar column. Nitrogen was used as a carrier gas. Gaseous products were analyzed offline using a 7890A GC system, 8-column RGA with a FID detector for hydrocarbon analysis. The spent catalyst was treated to remove the absorbed hydrocarbons through toluene extraction after which thermo-gravimetric analysis (TGA) was performed in order to get the %coke formed. PerkinElmer TGA 4000 was used for this purpose where spent catalyst samples (20–30 mg) were placed in a sample pan and heated from room temperature to 1000 °C at a rate of 10 °C/min with an oxygen flow of 20 ml/min. The weight percentages from the liquid, gaseous and coke analysis were taken into account for the mass balances and the remaining amount was accounted as hydrocarbon losses which are apparent during the testing phases.

Total conversion was calculated by the unconverted n-heptane obtained in the liquid product.

$$\%\ \text{total conversion} = \frac{\mathrm{Xi} - \mathrm{Xf}}{Xi}\ X\ 100$$

where Xi is the initial heptane/feed mass, X_f is the final heptane mass.

% Selectivity was calculated as follows:

$$\%\ \text{Selectivity} = \frac{\mathrm{Xp}}{Xi - Xf}\ X\ 100$$

where, X_p is mass of individual product. All the percentages mentioned in the results are wt. % until and unless otherwise stated.

Kinetic constants for the reaction were determined assuming a pseudo-first order kinetic equation and using the following relation as proposed by Vazquez et al. [26]:

$$-\ln(1 - \mathrm{C}) = \frac{\mathrm{k.P}}{1 + Rm}.\ \frac{\mathrm{W}}{Fo}$$