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Synthesis ZrO_2-Montmorillonite and Application as Catalyst in Catalytic Cracking of Heavy Fraction of Crude Oil

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Abstract

Research on synthesis and characterization of ZrO_2-Montmorillonit and its application as catalyst in heavy fraction of crude oil (HFCO) conversion has been investigated. Synthesis of catalyst was done by pillarization of ZrO_2 into silicate interlayer of montmorillonite structure. The success in synthesis is shown by XRD and BET surface area measurement in that basal spacing d001 was increase after pillarization. Activity test of material was showed that ZrO_2 dispersion affected catalytic activity in liquid production and the activity was increased asn increasing temperature in the range of 473K-673K. Composition of liquid product indicated that ZrO_2-Montmorillonit tend to produce kerosene related to metal oxide distribution in synthesis. © 2008 CREC UNDIP. All rights reserved.

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Keywords: *montmorillonite; cracking; crude oil*

Introduction

Crude oil, a restricted and non renewable energy source, is the main source of energy and fuel in indonesia. In additional, Indonesian crude oil consist of heavy fraction in a high precentage (about 60%) so an efficent conversion of crude oil into liquid fuel is so important. Catallytic reactions consist of cracking and hydrocracking became important to the refinery processing. In order to minimize energy consumed during the process, best characters of solid catalyst such as high surface area and thermal stability, high conversion and selectivity into gasoline product, are needed. Several investigation are focused on optimization in catalyst synthesis, mainly in the form of metal and metal oxide dispersed onto the stable solid support. As well as synthetic silica alumina materials, natural montmorillonite, a kind of smectite class of clay, is a potential mineral to contribute as solid support for metal oxide catalyst. The lack of thermal stability of clays could be eliminated by pillarization process. This process cosist of two important steps : intercalation of silica sheet of smectite layer with polyoxocation of metal and calcination stable metal oxide. Research process to the polyoxocation to form a stable oxide.

Research on preparation and characterization of pillared clays has grown continously with the aim

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to improve physicochemical properties and catalytic activity in several important reaction. Several metal oxides have been reported for this purpose, such as Al, Zr, Ti, Cr, and mixed metal: such as Ga-La, Cr-Al in order to gain designed character of materials. Although the Al polyoxocation is by far the most studied pillaring agent in both scientific and patent literature, in the term of cracking catalyst, zirconium oxide pillared catalyst became important related to its high thermal stablity properties and Lewis acidity that play important role in the cracking mechanism (Moreno et.al., 1999, Olezska, 2004). By far, pillarization of montmorillonite by ZrO_2 reported by several author showed the potential application in such high temperature reaction. Zirconium oxide pillared clays exhibit a significantly high d (001) value to ~20Å and high surface areas (mostly 200-300 m^2/ g) depending on several preparation variables (Bartley and Burch, 1989, Kloprogge, 1999, Gil et.al, 2000).

In this investigation, synthesis, characterization and utilization of zirconium oxide pillared montmorillonite in heavy fraction of crude oil was conducted. Physicochemical properties of pillared montmorillonite synthesized were characterized by evaluate XRD pattern of materials (by X ray Diffraction (XRD)), BET surface area analyzer, Zr content (X-ray Fluorescence) and thermal stability (DTA-TGA). Catalytic activity of material in heavy fraction of crude oil was determined by the selectivity profile to produce kerosene, gasoline and gas oil fraction in cracking reaction

Experimentals

Catalysts preparation and characterisation Techniques

Natural montmorillonite sample was taken from Boyolali, Central of Java and heavy fraction of oil derived by vacum fractional distillation to crude oil taken from Conoco Philip Co., Gresik, East Java. Preparation of zirconium pillared montmorillonite in this study is refer to previuos research (Fatimah and Wijaya, 2004) as modification to as reported by Bartley and Burch (1981), Wenyang et.al (1991) and Maes et.al. (1997). Preparation was started by preparation of Zr^{4+} Keggin ion. This polyoxocation was obtained by refluxing $ZrOCl_2.8H_2O$ precursor with ethylene glycol solution for 4 h.As produced, slow titration of a solution into montmorillonite suspension and stirred for 3 days. The following processes are neutralization (until Cl- free) and drying. Material resulted by this step was designated as ZrO_2-M pre calc. Then sample was calcined at 400°C for 3 h and designated as ZrO_2-M.

Physicochemical characterisation of the samples included surface area analyzer- (nitrogen adsorption at 77 K) using NOVA1000 , X-ray diffraction (XRD-Shimadzu X6000), and Zr content determination by X-ray Fluorescence. Identification. X-ray powder diffraction patterns were obtained by using a Shimadzu X6000 diffractometer, at 40 kV and 30 mA, and employing Ni filtered Cu Ka radiation.

Activity Test

Catalytic performance of Zirconium oxide pillared montmorillonite was evaluated in cracking of heavy fraction of crude oil (HFCO). Reaction was carried out in a fixed bed stainless steel reactor with inner diamm. of 1.5 cm and 25 cm in length.

The pelletized catalyst (0,2 g, 200 mesh) was placed in catalyst holder within the reactor and mass ratio of catalyst to feed is 0.2. An ultra high purity of N_2 gas was used as feed vapor carrier. Result of reaction was analyzed by gas chromatography –mass spectrometry(GC-MS Shimadzu QP-5000).

Results and Discussion

Physicochemical characters of raw montmorillonite used in this research are presented in Table 1.

Table 1. Characterization Data of raw Montmorillonite

No.	Properties	Results
1	Cation Exchange Capacity (CEC)	62,3 mmol/100g
2	Specific surface area	59,782 m^2/g
3	Basal spacing d_{001}	14,47 Å
4	SiO_2 content (gravimetry)	26,14 % (b/b)
5	Al_2O_3 (spectrophotometry)	5,68 %(b/b)
6	Surface acidity (pyridine adsorption method))	0,389 mmol/g

In order to identify basal spacing d_{001} increase, XRD measurement was performed to raw montmorillonite, Zr-intercalated montmorillonite before calcination/pre calcined (ZrO_2-M pre calc) and ZrO_2-montmorillonite(ZrO_2-M). XRD patern of these materials is presented in Fig.1 .

The patterns shows specifics reflection correspond to the montmorillonite mineral identitiy; d_{001} reflection at around 5-6° and other reflection at around 20°. The third reflection at around 23o

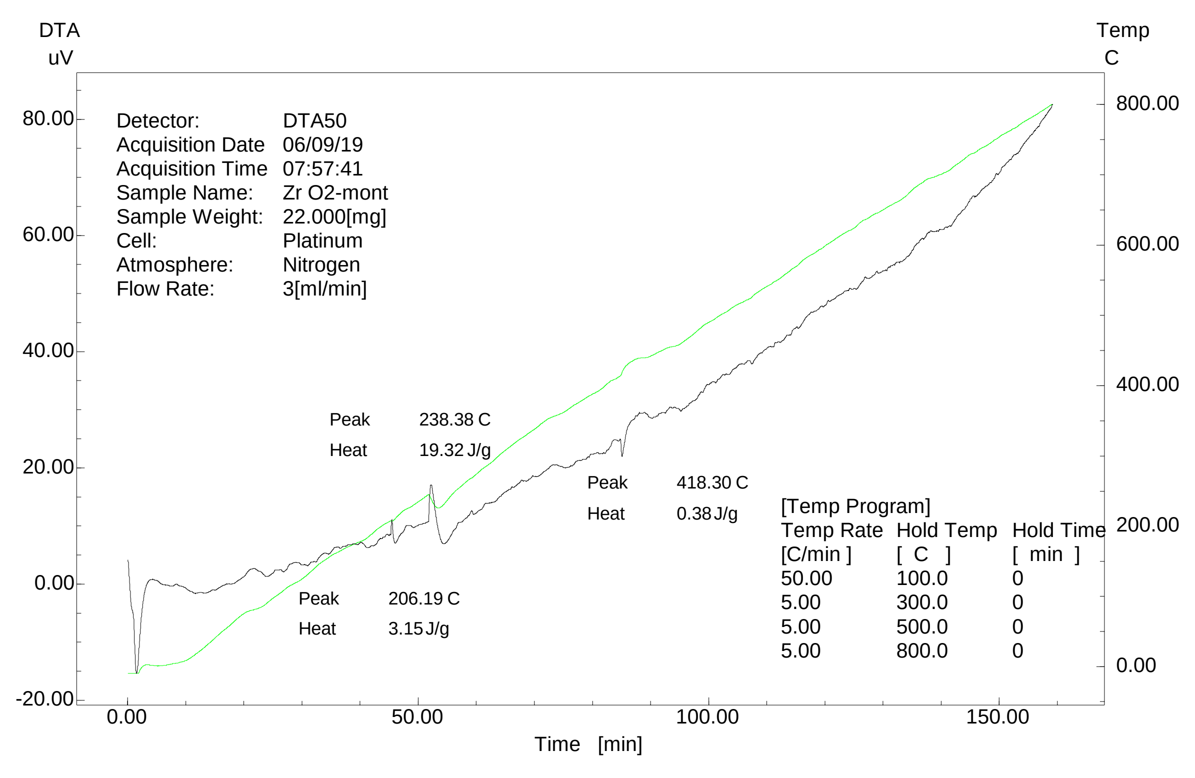

Figure 2. DTA profile of ZrO_2-M

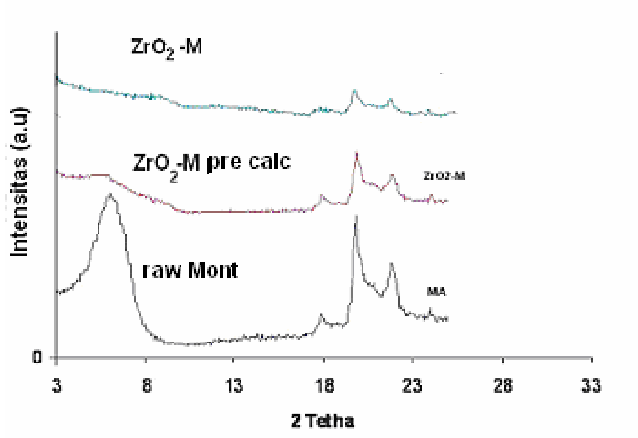

Figure 1. XRD patterm of raw montmorillonite,Zr-intercalated montmorillonite before calcination (ZrO_2-M pre calc) and ZrO_2-montmorillonite (ZrO_2-M).

correspond to the silica sheet in the structure. High intensity of d_{001} reflection indicate that there is high crystallinity and content of montmorillonite mineral in the sample, and furthermore, d_{001} value is equal to 14,47 Å. As silica sheet thikness is equal to 9.6Å, theoritic silicate interlayer space in raw montmorillonite is equal to 4.87Å. There is a shift of d_{001} reflection into lower angle correlate to the increase of $d_{00}1$ as effect of intercalation and pillarization process. Although depicting reflection of d_{001} at 5,87° (15,18Å), intensity of relection of ZrO_2-M is lower than do raw montmorillonite sample. The intensity is also lower compared to precalcinated sample(ZrO_2-M precalc) as indication that there is a thermal and chemical reaction effect to the montmorillonite structure, in other hand this change correlated to the increasing of d_{001} reflection; 15,05Å in ZrO_2-M pre calc and 15,18Å in ZrO_2-M. Refer to several publication in synthesis of metal oxide pillared clays, this data is an evidence that there is a thermal transformation involving dehydration reaction to the intercalating species during calcination(Hutson et.al, 1998, Canizares et.al, 1999, Gil et.al, 2000).

Material was designed as cracking catalyst application, therefore thermal stability character is so important to identify. DTA profile of ZrO_2-M is presented in Fig.2. Three significant peak of DTA are shown at the temperature of 206.19 °C, 238.38°C and 418.30°C. First peak at 206.19 °C predicted as indication of crystal water dehydration followed by heat release (exoterm) of 3.15 J/g, the second peak probably indicate the phase transformation of $Zr(OH)_x$ into ZrO_2 as dehydroxylation reaction and the third probably caused by ZrO_2

decomposition. BET surface area analysis data of the materials is presented in Table 2.

The surface area of the pre calcined and calcined zirconium oxide pillared montmorillonite seems to be not related to the crystallinity of materials. It may caused by pore distribution of materials in that there is a modal pore produced as indication the metal oxide agregation in surface or called as house-of cards formation as reported in previuos publication. It can be detected from higher pore radius in ZrO_2-M than do in raw montmorillonite.

Table 2. BET surface area analysis data of raw montmorillonite, ZrO_2-M pre calc and ZrO_2-M

Parameter	Raw Mont	ZrO_2-M pre calc	ZrO_2-M
Specific surface area (m^2/g)	74,70	69,86	79,05
Pore Volume (cm^3/g)	50,88	58,95	62,50
Pore radius (Å)	13,62	16,88	15,81

Catalytic Activity

Catalytic activity of materials in HFCO cracking first evaluated by precetage of product distribution. Product distribution as fucntion of reaction temperature by using thermal condition, raw montmorillonite and ZrO_2-M as catalyst is presented in Figure 3.

Effect of catalyst is shown by liquid production in catalytic cracking using both of raw montmorillonite and ZrO_2-M catalyst. Its indicate that there is a cationic mechanism during reaction as alternate step to the radical mechanism in thermal reaaction. This assumption is also proven by high percentage of gas production in all temperature by thermal condition. Percentage of Liquid yield was increase as the use of raw montmorillonite and ZrO_2-M catalyst respectively as indication that there was a positif effect of ZrO_2 distribution in materials. Active site in surface tend to produce liquid product and decrease gas product as the change of mechanism involved. Temperature was also affected the liquid production. It could be concluded that ZrO_2-M catalyst was play an important role in the cationic mechanism and activated by temperature.

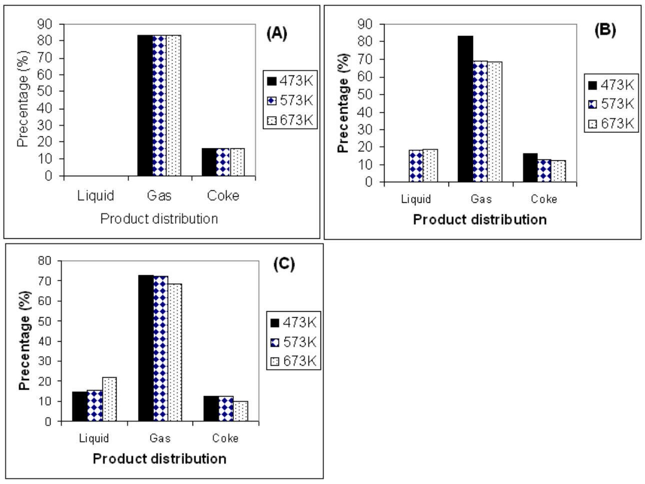

Figure 3. Product distribution of HFCO cracking at varied temperature (a) thermal condition (b) using raw montmorillonite as catalyst (c) using ZrO_2-M as catalyst

Furthermore, from GC-MS analysis of the liquid products, selectivity of catalyst were evaluated. Selectivity to the special product are devided into kerosene, gasoline and gas oil product. Data in the histogram is presented in Figure 4.

Activity of the catalyst is required to determine the ability of the catalysts to convert a reactant into a desired product in a certain reaction. More intensive analysis to the liquid product resulted selectivity data that defined as persentage weight of specific fraction in the liquid.

Composition of liquid were obtained from peak area distribution in GC-MS analysis and expressed as peak area of selected fraction devided to total peak area of liquid product. According to Fessenden and Fessenden(1986), liquid petroleum distillates were grouped into gasoline (C_5-C_{10}), kerosene (C_{11}-C_{12}), gas oil (C_{13}-C_{17}), and heavy gas oil (C_{18}-C_{25}).

It can be seen from Figure 4 that selectivity of ZrO_2-M is not significantly different with selectivity of raw montmorillonite, but from both of heavy fraction selectivity data, it concluded that at relative low temperature (473K), there is a high conversion of heay fraction into kerosene fraction. Gasoline was higher distributed in liquid product by using raw montmorillonite than do ZrO_2-M catalyst in all varied temperature and was increased in elevated temperature. In the same catalyzed liquid production, kerosene distribution was not affected by temperature. In contrast, by using ZrO_2-M catalyst, kerosene production was increased by increasing temperature. This data indicated that ZrO_2-M catalyst tend to produce kerosene fraction in a high selectivity. This data was in agreement with as reported by Wenyang et.al (1991) in that lower gasoline distribution was produced in higher content of Zr in Zr-Al-pillared montmolrillonite. Pore size distribution is main factor controlling this mechanism.

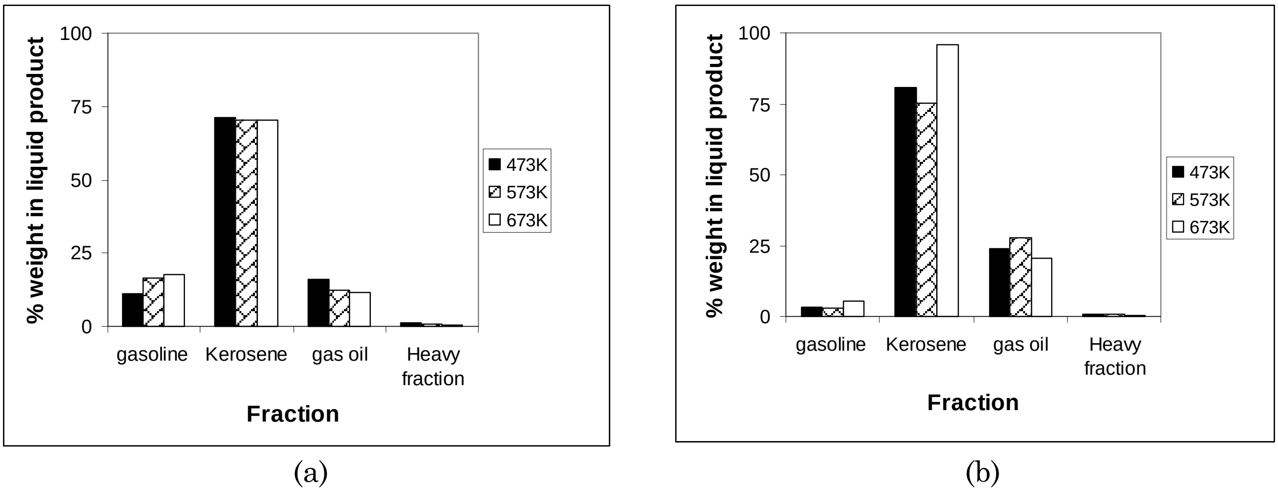

Figure 4. Composition of Liquid produce by using (a) montmorillonite catalyst (b) ZrO_2-montmorillonite

When the pillaring agent was added in excess, the amount of pillaring agent in the clay layers became denser, the pores became smaller, and the cracking activity decreased. The dense aggregate produce in a house of cards formation in this synthesis and reported before was important consideration to optimize physicochemical character of ZrO_2-montmorillonite in further research.

Conclusions

Pillarization of montmorillonite with zirconium oxide was produce active catalyst in HFCO cracking. Higher basal spacing d001 of montmorillonite resulted in synthesis was not linear with specific surface area indicate that there is a metal oxide aggregation as house of cards represented. Due to this character, although there is a positive effect of ZrO2 dispersion in montmorillonite structure to the liquid production, selectivity of catalyst to produce kerosene fraction was higher than to produce gasoline fraction.

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