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Chrom/Nanocomposite ZrO₂-Pillared Bentonite Catalyst for Castor Oil (*Ricinus communis*) Hydrocracking

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Keywords: catalyst, Chrom/NanocompositeZrO₂-Pillared Bentonite, hydrocracking, biogasoline, castor oil

Abstract. It has been carried out preparation of Chrom/NanocompositeZrO₂-Pillared Bentonite catalyst with varying the amount of impregnating precursor at 0 to 3% (w/w). Material characterization of catalyst was carried out using X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Infrared Spectroscopy (IR), Transmission Electron Microscope (TEM), Brunauer, Emmett, Teller (BET) and acidity measurement of ammonia-adsorption method. The results of research showed that pillarization was able to increase the basal spacing, surface area, diameter of pore and total volume of pore in catalyst, however increasing of impregnated Cr metal on bentonite caused the decreasing of basal spacing and surface area of catalyst but it would also caused the increasing amount of acid site. The experimental results showed that the catalyst could convert the castor oil into a liquid phase of 78.80% (w/w) with a biogasoline content of 32,73% (w/w).

1. Introduction

Oil fuel (BBM) has been one of energy resources that takes spotlight of the world's community due to the increasing consumption of it every year. Renewable energy resources such as vegetable oil can be alternative energy solutions replacing BBM. Implementing catalytic hydrocracking process, triglyceride in vegetable oil can be converted into hydrocarbon in the form of gasoline and diesel [1].

The main component of castor oil is risinoleic acid (~90%) with little of oleic acid and palmitic acid. The existence of hydroxyl group on risinoleic acid causes castor oil having different characteristic with other vegetable oil and it is fascinating to study. Studies about vegetable oil hydrocracking become hydrocarbon that have been carried out i.e. palm oil [1,2], olive oil [2], and castor oil [2,3]. The results have shown that vegetable oil can be converted into oil fuel consist of gasoline, diesel, and kerosene.

Impregnating material of catalyst can be in form of zeolite, alumina, silica, and clay. Clay material is fascinating to study further since its chemical and physical properties that can be modified with multiple methods, furthermore the developed catalysts in hydrocracking process of oil are catalysts with big pore size such as zeolite (~8 Å) to be able in cracking fraction of heavy oil. The clay with distributed pillar creating two dimension to establish mesoporous material. One of pillaring agents that can be used are oxide metal that results in increasing thermal stability of bentonite. Oxide metal itself is catalyst, therefore the use of oxide metal has double function i.e. function as pillaring agent and catalyst as well. Several oxide metals used as pillaring agents such as, Al₂O₃ [5,6,7], ZrO₂ [8-14], TiO₂ [15,23-26], Fe₂O₃ [16] and Cr₂O₃[17,22]. Among those oxide metals zirconium is special pillaring agent with good thermal stability (700-800 °C) and ability to increase basal spacing to 19-24 Å [4].

Study in synthesis on impregnation of Cr metal on Nanocomposite ZrO₂-Pillared Bentonite for application of castor oil hydrocracking has not ever been carried out. This study will learn the effect of weight percentage of Cr towards the properties of Nanocomposite ZrO₂-Pillared Bentonite and its application towards the hydrocracking reaction of castor oil. The combination between Cr as catalyst with ZrO₂ both as pillaring agent and catalyst on bentonite as impregnating material is expected to result the catalyst with the best properties that will be able to convert castor oil into gasoline fraction in maximal result.

2. Experimental

Materials used in the research were natural bentonite (Beijing Zhongjing Pets Products Co. Ltd), castor oil (*Ricinus communis*), zirconyl chloride octahydrate (ZrOCl₂·8H₂O), Chromium nitrate nonahydrate Cr(NO₃)₃·9H₂O, fluoride acid, and silver nitrate. The laboratory equipment includes hydrocracking reactor and cooler, glassware, magnetic stirrer, analyte balance, mortar, sieve (250 mesh), and Furnace. Analytical instrument consists of FTIR, X-ray diffractometer, Atomic Absorption Spectrophotometer, Gas Sorption analyser (BET), Gas Chromatography-Mass Spectrometry, and Transmission Electron Microscopy.

Bentonite Preparation: Bentonite was immersed in aqueduct for 24 hours. The obtained sediment was dried using oven (100°C) then immersed in HF solution 1% for 10 minutes, the result was neutralized and dried with oven (100°C) then crushed and sifted using sieve at 250 mesh. The sample is then called HF Bentonite.

Oligo-cation Zirconium Solution Preparation and ZrO₂ Pillarization: Pillaring solution of oligo-cation zirconium was synthesized using hydrolysis method. 240 mL ZrOCl₂·8H₂O, 0.1 M solution was refluxed for 2 hours then added HF bentonite slowly with ratio of Zr/bentonite at 3 mmol/g and stirred for 24 hours at room temperature. The Zr-intercalated bentonite was neutralized. Sample was dried with oven (70°C) then crushed and sieved (250 mesh). Sample was calcinated at temperature of 400°C for 2 hours. Sample is called as ZrO₂-Pillared Bentonite or ZrO₂-Bentonite.

Cr on ZrO₂-Bentonite (Cr/Nanocomposite ZrO₂-Pillared Bentonite) Impregnation: Metal impregnation of Cr on ZrO₂-Bentonite using wet impregnation method. Cr(NO₃)₃·9H₂O was added with ZrO₂-Bentonite suspension with ration variation of 1, 2 and 3% (w/w). Sample was refluxed for 5 hours, then dried with oven (80°C). Calcination at temperature of 500°C for 5 hours, then reduced by H₂ gas at temperature of 400°C for 2 hours respectively with flow rate at 20 mL/minute. Catalyst that was obtained is named as Cr/ZrO₂-B-1, Cr/ZrO₂-B-2, and Cr/ZrO₂-B-3 catalysts respectively were Cr/Nanocomposite ZrO₂-Pillared Bentonites with Cr-weigh variation of 1, 2 and 3%.

Activity and selectivity examination of Cr/Nanocomposite ZrO₂-Pillared Bentonite catalyst: Hydrocracking reaction of castor oil with ratio of catalyst towards oil was 1:5% (w/w) using up flow fixed-bed system reactor at temperature of 500 °C followed by H₂ gas flow at 20 mL/minute. The liquid product was analyzed with GC-MS.

3. Results and Discussion

Synthesis of Cr/Nanocomposite ZrO₂-Pillared Bentonite. Analysis of cation-exchange capacity (CEC) on interlayer of bentonite shows that the bentonite that has been purified with HF will experience a decrease in CEC after pillarization process i.e. 86.4 into 39.2 meq/100g. At the pillarization process of bentonite, ZrO₂-Bentonite was synthesized with intercalation process of pillarization agent zirconyl chloride octahydrate with hydrolysis method and resulted zirconium polycation [Zr₄(OH)₈(H₂O)₁₆]⁸⁺ that entered into interlayer of Na-bentonite to replace balancing cation such as Na⁺ and Ca²⁺. Polycation would expand interlayer area of bentonite and after calcination process it would transform into zirconium oxide that becomes stable pillar.

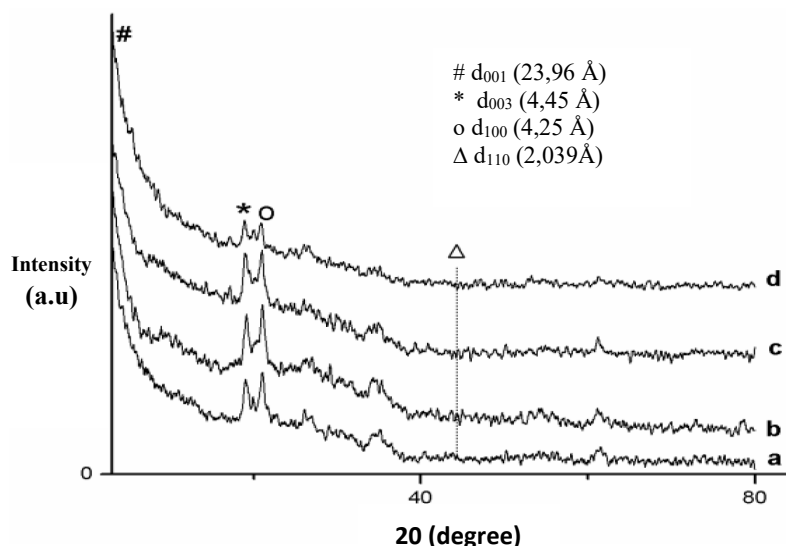


Fig. 1. Diffractogram of (a) ZrO₂-Bentonite (b) Cr/ZrO₂-B-1 (c) Cr/ZrO₂-B-2 and (d) Cr/ZrO₂-B-3

Impregnation of Cr on ZrO₂-Bentonite will decrease basal spacing from peak with d₀₀₁ characteristic and expand 2θ. The characteristic of peak of Cr metal (JCPDS card No 06-06394) lays on d₁₁₀ (Figure 2). The pillarization process can increase basal spacing of bentonite that shows the success of pillarization process; however the exceeding impregnation process of Cr metal can decrease its basal spacing back (Table 2). This can happen because during the impregnation process, the previously established pillars will fall along with the increasing amount of Cr.

IR Spectra of natural bentonite has specific peaks at wavenumber of 3631 and 3446 cm⁻¹ [18]. Those peaks appeared at 3626,17 cm⁻¹ in which the absorption band of stretching vibration of Al-OH layer of octahedral structure and 3448,72 cm⁻¹ that shows stretching vibration of Si-OH (Figure 3). After pillarization process and metal impregnation at wavenumber of 3626,17 cm⁻¹ shifting to 3749,62 cm⁻¹ that showed the bond building between ZrO₂ with tetrahedral layer of Si-OH. The wavenumber can also indicate the presence of Si-OH bond that lied at the undetected end of the original bentonite.

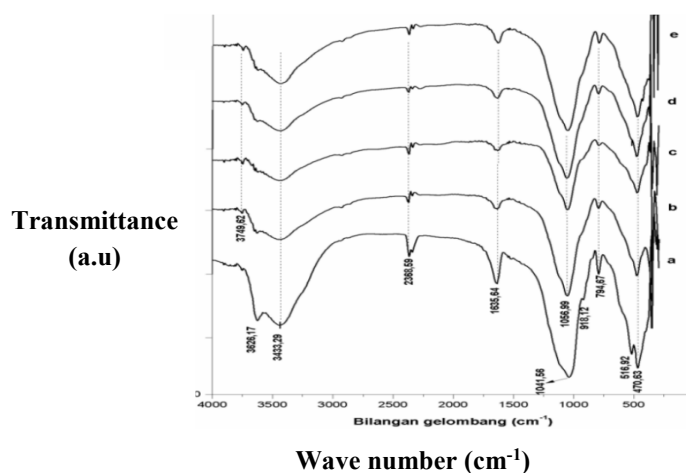


Fig. 2. FTIR spectra of (a) HF Bentonite catalyst (b) ZrO₂-Bentonite (c) Cr/ZrO₂-B-1 (d) Cr/ZrO₂-B-2 and (e) Cr/ZrO₂-B-3

Band absorption of wavenumber at 1635.64 cm⁻¹ shows bending-vibration OH of water molecule. This increasing intensity indicates that the water-saving capacity and acidity of pillared bentonite have increased due to photon production through dissociation of water molecule. The presence indication of asymmetrical stretching vibration Si-O-Si was shown by the magnitude of band absorption at wavenumber area of 1041,56 cm⁻¹, in which after pillarization and metal

impregnation process, it shifted to wavenumber of $1056,99\text{ cm}^{-1}$. This happened because after the pillarization process there was formed a bond between O atoms of Si-O-Si with zirconium of the pillar.

The number of acid site in this research was the total acidity that included Lewis and Brønsted acid. The presence of oxide metal of ZrO_2 and Cr metal on the surface of catalyst will increase the number of active sites at the surface of catalyst (Table 2). Zirconium at the interlayer of bentonite will increase the acidity of solid [9, 21]. Silanol group (Si-OH) is resulted of the bond disconnection of at tetrahedral layer, through treatment using acid and contact with water.

Table 1. Results of determination on basal spacing of d_{001} peak, specific surface area, average porous diameter, total porous volume and acidity of catalyst

Catalyst	2θ (°)	(Å)	Δd_{001} ($d_{001-9,6}$) (Å)	Surface area (m^2/g)	Average pore diameter (Å)	Total pore volume (cc/g)	Number of acid site (mmol/g)
HF Bentonite	5,676	15,56	5,96	96,64	38,31	0,22	4,46
ZrO_2 - Bentonite	3,158	27,95	18,35	164,04	38,37	0,28	7,22
Cr/ ZrO_2 -B-1	3,155	27,98	18,38	105,80	38,15	0,16	7,25
Cr/ ZrO_2 -B-2	3,535	24,97	15,37	101,07	38,49	0,17	7,78
Cr/ ZrO_2 -B-3	3,685	23,96	14,36	102,00	38,21	0,17	8,21

*calculated based on ratio % (w/w) of produced liquid fraction

Contributing towards the Brønsted acidity in clay. The Lewis acid sites appeared because the isomorphous substitution on tetrahedral or octahedral layer of clay such as Si^{4+} by Al^{3+} and Al^{3+} by Mg^{2+} or contribution of Zr and Cr metal on bentonite. The number of acid site is affected by the properties of pillar and condition in synthesis such as reflux's temperature and mole amount of pillaring agent [19, 20].

Based on Table 2 it is learned that the specific surface area of bentonite was increasing after pillarization using ZrO_2 , that indicates the success of pillarization process using ZrO_2 on interlayer of bentonite. Impregnation process of active metal on pillared bentonite decreasing specific surface area of catalyst that occurred with assumption that Cr metal entered, blocking the pores or interlayer and surface on interlayer of bentonite. This was proved by the occurrence of decreasing volume of total pore of catalyst, while the average porous diameter was not experiencing significant modification.

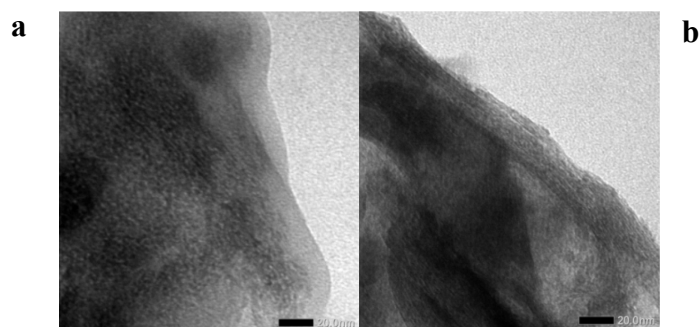


Fig.3. Morphology of (a) ZrO_2 -Bentonite and (b) Cr/ ZrO_2 -B-3catalyst

The interlayer arrangement and also the thickness of silicate layer on ZrO₂-Bentonite and Cr/ZrO₂-B-3 that shown by parallel dark lines that show layered structure of clay (Figure 3). The homogeneity of interlayer in silicate of Cr/ZrO₂-B-3 appeared more identical and the impregnation of Cr metal on ZrO₂-Bentonite did not ruin the pillars of ZrO₂.

Activity and Selectivity Examination of Cr/Nanocomposite ZrO₂-Pillared Bentonite

Bentonite Catalyst. The impregnated Cr metal onto ZrO₂-bentonite was analysed using X-ray fluorescence respectfully resulted Cr content at 0,26, 0,46 and 0,63% that respectively were Cr-impregnation at 1, 2 and 3%. Activity of catalyst was described by the catalyst performance in converting castor oil into liquid product, gas product and coke. While selectivity of catalyst was described by the catalyst performance to yield gasoline fraction. Product distribution of hydrocracking in castor oil shown on Table 2.

Table 2. Conversion result and distribution of liquid product in hydrocracking of castor oil

Catalyst	Yield (% w/w)			Product (%)	
	Liquid	Coke	Gas	Gasoline	Total gasoline
HF Bentonite	66,23	0,32	33,46	-	-
ZrO ₂ -Bentonite	65,59	0,32	34,09	22,31	28,31
Cr/ZrO ₂ -B-1	71,73	1,06	27,21	24,50	31,09
Cr/ZrO ₂ -B-2	78,80	0,94	20,25	25,79	32,73
Cr/ZrO ₂ -B-3	77,10	0,49	22,41	25,62	32,51

Liquid product that was obtained from Cr/Nanocomposite ZrO₂-Pillared Bentonite catalyst was more than the other catalyst. It was caused by the Cr metal that has role as active site therefore it was more optimum to catalyse the hydrocracking reaction. Cr metal actively took role in bond formation and disconnection since it has low energy-half filled orbital. The valence electrons of d orbital were mingled with electrons of s and p orbital that provided low energy-electronic state in great amount and it is an ideal state to push catalytic reaction. Therefore, it is concluded that Cr/Nanocomposite ZrO₂-Pillared Bentonite catalyst has the most catalytic activity in converting castor oil in hydrocracking reaction.

Hydrocracking using Cr/ZrO₂-B-2 catalyst showing the highest activity of catalyst in converting castor oil. It can be happened due to the overactive catalyst along with the great amount of Cr in cracking castor oil consequently the gas phase or light phase will be built a lot and experience perfectly uncondensed saturation, indicated by the higher gas phase. The liquid product of activity examination of catalyst towards hydrocracking of castor oil with variation in catalyst analysed using GC-MS. Gasoline fraction is hydrocarbon compounds that are calculated based on the area of peaks in chromatogram of sample compounds used in hydrocracking of castor oil that are in accordance with the list of data resulted by GC-MS analysis of pure gasoline of Shimadzu Application Data Sheet No. 21. Selectivity of catalyst towards the gasoline fraction shown by Cr/ZrO₂-B-2 catalyst. The more the gasoline is produced, the better the catalyst is to carry out the catalysis reaction therefore it has good selectivity of catalyst.

Zirconia (ZrO₂) pillar after being dehydrated will have Lewis acid site, in which it contributes as active site in catalysis reaction using ZrO₂-bentonite catalyst. Impregnation of Cr metal into ZrO₂-bentonite has huge effect towards the acid site, in which the more the impregnated Cr metal, the more the number of acid site on catalyst, this situation is very determining in activity and selectivity of hydrocracking of castor oil. Cr metal is group of transition metal that has half-filled electron configuration as a result the Cr metal performs well if used in multiple catalytic reaction particularly in hydrocracking reaction. d orbital on Cr metal is more effective to weaken σ bond on H₂ therefore it has greater catalysis capability if compared with the one without metal, this fact is shown by the greater activity and selectivity of Cr/Nanocomposite ZrO₂-Pillared Bentonite catalyst that ZrO₂-bentonite catalyst. The acidity of catalyst affects the product distribution and its selectivity. The greater selectivity towards the gasoline fraction using Cr/ZrO₂-B-2 bentonite

compared with Cr/ZrO₂-B-3 catalyst. This is possible happen since even though the impregnation of 3% Cr metal into catalyst enables to increasing the number of acid sites, however it is not followed with the increasing strength of its acid sites or even the strength of its acid sites are lower compared with Cr/ZrO₂-B-2 catalyst, therefore the catalyst with greater strength of acid sites is effective in catalytic hydrocracking process of triglyceride into gasoline fraction. Furthermore Cr/ZrO₂-B-2 has the largest pore diameter will ease the larger molecule to enter into pores of catalyst then the hydrocracking process occurs and produces smaller molecule such as gasoline fraction. Hydrocracking reaction of castor oil using catalyst to result main product (hydrocarbon) and also uncontrollable side products (aldehyde, ketone and carboxylic acid). This situation occurred based on physical and chemical interaction that involved one or more chemical reaction. Castor oil is consisted of fatty acid compounds as different ester that has role hydrocracking reaction therefore enabling to result a number of unwanted products that still contain oxygen.

The compound that appeared in product of hydrocracking of castor oil that are still the compound mixture among aliphatic, cyclic hydrocarbons, hydrocarbons of aldehyde, ketone, and carbocyclic acid. The compound with the largest GC area shown by peak 12 that is compounds of heptane. While the product composition of aliphatic hydrocarbon based on chromatogram that consists of C₆-C₁₁ hydrocarbon dominated by the compounds such as heptane with its isomer, 1-nonene and 1-heksene.

Conclusion

ZrO₂-pillared and Cr metal-impregnated bentonite is sufficiently effective in hydrocracking process of castor oil into gasoline fraction. Cr/Nanocomposite ZrO₂-Pillared Bentonite catalyst has larger area that natural bentonite. The produced compound of hydrocracking of castor oil resembles gasoline fraction i.e. C₆-C₁₁ hydrocarbon.

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