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Synthesis of Active Matrix from Kaolin for Cracking Catalyst

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Abstract. The demand for fuel oil grows in tandem with population and economic development. The process of obtaining fuel from heavy-fraction feed is known as fluid catalytic cracking (FCC). Zeolite, active matrix, filler, and binder are the components of FCC catalysts. To pre-crack large feed, the active matrix is used. Matrix can be synthesized using kaolin. The purpose of this research is to obtain the best active-matrix variation with the optimum physical characteristic and acidity. The variations used were Si/Al = 6-14. The physical characteristics of the active matrix were characterized by nitrogen physisorption and the acidity by NH_3-TPD. The findings revealed that the cracking conversion and product composition are depends on physical characteristic and the acidity of matrix. The best matrix variation is SA14 with Si/Al = 14 producing matrix with surface area of 88.43 m^2/g, average pore diameter of 176.56 Å, pore volume of 0.39 cm^3/g, acidity of 0.130 mmol NH_3/g, and light cycle oil (LCO) acquisition of 18.78%-wt.

Keywords: *active matrix; FCC; kaolin; silica-alumina.*

1 Introduction

Energy demand continues to increase in line with increasing economic growth, population, energy prices, and policies set by the government. Final energy consumption by type during 2010-2015 was still dominated by fuel reaching 25% [1]. Fuel final energy will dominate national energy demand from 2015 to 2050. One solution that can suppress the need for fuel is the fluid catalytic cracking (FCC) process with aims to break down long carbon chains into shorter carbon chains. The FCC method necessitates using a catalyst composed of zeolite, active matrix, filler, and binder. The primary catalyst used to convert petroleum into fuel is zeolite. The active matrix is a component that acts as the pre-cracking component for long-chain hydrocarbon molecules, allowing them to spread into the smaller zeolite pores.

The physical properties of an active matrix have a significant impact on its efficacy. According to Chen, et al. [2], an excellent active matrix has physical properties such as a specific surface area of 350 - 600 m^2/g, a specific pore volume of 0.9-1.4 mL/g, and a pore diameter size varying from 3 - 10 nm. The active matrix's surface serves as a point of interaction between the hydrocarbon feed molecules and the active matrix's acid sites. The bigger the pore diameter, the lower the diffusional resistance. The lower the diffusional resistance, the more molecules that can enter and be transformed by the pores. Vacuum gas oil (VGO) has a diameter of 1.0-2.5 nm [3]. The strength and quantity of acid sites to perform cracking on the active matrix's surface also influence its performance. If the acid site is too powerful, over-cracking will occur, resulting in many undesirable by-products such as dry gas and coke.

Active matrix can be synthesized using various sources of silica and alumina such as aluminum sulphate and sodium silicate, but the development of active matrix from kaolin as a natural source has not been widely developed. Kaolin is an inexpensive, naturally occurring, abundant material and was employed as the sole source of silica and alumina with general composition of $Al_2O_3.2SiO_2.2\text{-}4H_2O$ [4]. In this study, active matrix synthesis from kaolin was performed using hydrothermal method. The goal of this study is to create a matrix with a specific surface area of 350-600 m^2/g, a pore volume of 0.9-1.4 mL/g, an average pore width of more than 50 Angstroms, and coke content less than 5%-mass.

2 Experiment

2.1 Matrix Synthesis from Kaolin by Hydrothermal Method

Kaolin used has undergone calcination procedure to obtain metakaolin. In demineralized water, a specified amount of NaOH was dissolved. The proper quantity of metakaolin was slowly added, and the mixture was stabilized for 10 minutes. A certain quantity of fumed silica was gradually added and stabilized for 10 minutes. Then, H_3PO_4 solution was added and stabilized for another 10 minutes. The mixture was then placed in teflon lined autoclave in furnace with temperature of 110°C for 24 hours. The slurry was then rinsed several times with demineralized water. The mass was dried and then calcined.

2.2 Matrix Characterization

The physical characteristics of the matrix, such as surface area, pore size, pore volume, and acidity, are all measured. Nitrogen Physisorption Micromeritics Tristar II Plus was used to measure the material's surface area, pore size, and pore volume. An NH_3-TPD (NH_3-temperature programmed desorption) Microtrac MRB Belcat II Particle Characterization was used for the acidity measurement. Next-generation Advanced Cartesian Geometry ED X-ray fluorescence was used to identify material compositions.

2.3 Activity Test

The active matrix's efficacy was evaluated using the TEXOL Fixed Bed Micro Reactor Unit series 3210-200-10-12 micro activity test (MAT) according to ASTM D 3907-3 and ASTM 5154-03. This technique is used to calculate the conversion and yield of VGO cracking products at temperature of 516°C with a feed-to-catalyst ratio of 2.94.

2.4 Product Analysis

Products are classified into three types: liquid, vapor, and solid. The liquid product will be classified into gasoline with C_5-C_{12}, light cycle oil (LCO) with C_{13}-C_{20}, and Heavy Cycle Oil (HCO) with $>C_{20}$. A gas chromatography Agilent Technologies 7890B with an FID detector was used to test liquid products. The gravimetric method determined the quantity of coke formed as a solid product during the VGO cracking reaction. The mass difference of the active matrix before and after heating in the furnace was used in this technique.

3 Result and Discussion

3.1 Chemical and Physical Analysis of Metakaolin

Table 1 shows the results of the oxide composition of metakaolin using X-ray fluorescence, the physical characterization by nitrogen physisorption and acidity characterization by NH_3-TPD of metakaolin used as raw material. The oxide analysis identified SiO_2 and Al_2O_3 as the predominant oxides with SiO_2/Al_2O_3 %-mass ratio of 1.43. Therefore, additional silica is needed to obtain desired silica-alumina ratio. Relatively high Fe presence in metakaolin produced a slight decrease of crystallization rate [5]. Due to the inert nature of kaolin, the kaolin must be calcined to form active SiO_2 and Al_2O_3 [6]. The best activation temperature to produce metakaolin from kaolin is between 700-850°C. This temperature leads to a loss of chemical water, breakdown in the crystalline structure and consequently a phase transformation to amorphous with high reaction ability [7].

Table 1 Metakaolin oxide composition and characteristic

Chemical Composition	%-mass	Characteristic	Value
SiO_2	55.90	SSA (m^2/g)	16.8
Al_2O_3	39.00	Avg. Pore Diameter (Å)	156
Fe_2O_3	1.12	Tot. Pore Vol (mL/g)	0.07
TiO_2	0.40	Total Acidity (mmol NH_3/g)	0.017
K_2O	0.63		

3.2 Physical Characteristics and Acidity of Matrix Synthesized by Hydrothermal Method

Based on the Si/Al composition five different varieties of matrices were synthesized. The physical characteristics and acidity of each prepared matrix are displayed in Table 2 as total surface area, average pore diameter, total pore volume, and acidity.

Table 2 Physical characteristics and acidity of matrix synthesized by hydrothermal method

Sample Code	Si/Al	P (%-wt)	Physical Characteristic			Total Acidity (mmol NH_3/g)
			SSA (m^2/g)	Avg. Pore Diameter (Å)	Tot. Pore Vol (mL/g)	
Metakaolin	1.43	-	16.8	156	0.07	0.017
SA6	6	1	44.26	117.94	0.13	0.166
SA8	8	1	58.95	123.75	0.18	0.146
SA10	10	1	85.32	144.54	0.31	0.160
SA12	12	1	76.13	151.62	0.29	0.132
SA14	14	1	88.43	176.56	0.39	0.130

From Table 2, we can see that the surface area of the active matrix produced is in the range of 44.26-88.43 m^2/g, which is less than the target expected of 350 - 600 m^2/g, the average pore diameter in the range of 117.94-176.56 Å which is more than the target of 50 Å, and total pore volume in the range of 0.13-0.39 mL/g which is less than target of 0.9-1.4 mL/g. Overall, the matrix produced in this study has yet to meet the target, so further development whether in the synthesis method or in the synthesis condition, such as temperature or time, must be done.

SA14 matrix composed of Si/Al = 14 has the highest surface area, average pore diameter, and total pore volume but has the lowest total acidity. The second highest physical characteristic was obtained by SA10, composed of Si/Al = 10, which has a marginally smaller value of the physical characteristic. However, SA10 has higher total acidity, increasing the potential for cracking activity [8].

3.3 Cracking Activity

Table 3 provides a summary of the data analysis of cracking results. Matrices produced in this research have not reached a high conversion value, which is in the range of 27.61-36.97%-wt because the relatively low acidity causes less number of acid sites in the active matrix to split the feed into smaller hydrocarbon [9] and surface area of the matrix causes less diffusion of macromolecules within catalyst particles, leading to a low cracking activity for heavy oil [10]. SA14, composed of Si/Al=14, has the highest light cycle oil (LCO) yield. This matrix is equivalent to the SA12 matrix, which has an LCO yield that is marginally smaller and it has a slightly lower gas product. By considering the cracking activity such as conversion and product composition which depends on the physical characteristic and acidity of matrix, it can be determined that SA14 produces the most optimum matrix.

Table 3 also reveals that the coke concentration for each active matrix evaluated for activity ranges between 1.15-2.11 %-wt. Coke content of less than 5%-wt is considered relatively low coke content, hence all the matrices have reached the objective. This low coke content is possible because of the low activity of the matrix, as the coke content was related proportionally to the catalyst activity [11].

Table 3 Active matrix cracking products

Sample Code	VGO Conversion (%-wt)	Liquid Product			Gas Product (%-wt)	Coke (%-wt)
		Gasoline (%-wt)	LCO (%-wt)	HCO (%-wt)		
SA-6	36.97	1.58	16.54	63.03	17.70	1.15
SA-8	27.93	2.29	18.06	72.07	5.74	1.83
SA-10	30.74	1.91	17.43	69.26	10.00	1.41
SA-12	27.61	1.58	18.15	72.39	6.65	1.22
SA-14	30.75	2.18	18.78	69.25	7.67	2.11

4 Conclusion

From data shown, we can conclude that the cracking conversion and product composition are depends on physical characteristic and the acidity of matrix. The optimum matrix variation is SA14 with Si/Al = 14 producing matrix with surface area of 88.43 m^2/g, average pore diameter of 176.56 Å, pore volume of 0.39 cm^3/g, acidity of 0.130 mmol NH_3/g, and light cycle oil (LCO) acquisition of 18.78%-wt. Matrix produced in this study has not met the target, so it needs further development in synthesis method or synthesis condition.

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