RED MUD AS CATALYST FOR ETHYL-BENZENE HYDRO-DEALKYLATION

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Abstract- Red mud is an industrial waste of the bauxite processing industry. In this paper the utilization of red mud as catalyst is considered since it contains a lot of metals compounds such as Fe_2O_3, Al_2O_3, SiO_2, TiO_2, V_2O_5, MgO, MnO_2, ZnO, ZrO_2, Ni, Ga having catalytic properties. The hydrogenation / hydro-dealkylation reaction of the ethyl-benzene was studied in batch reactor at temperature of 450°C over differently treated red mud samples. The cyclohexane and toluene were the main reaction products. The hydrocarbon cracking reaction was also evidenced by the formation of methane. The conversion of ethyl-benzene was about 50% over untreated and calcined red mud. The acidic treatment of red mud followed by calcination at 400°C increased the conversion of ethyl-benzene up to 58%. The morphology and surface properties of the red mud were also studied. Pulse sorption and BET data were correlated with the catalytic activity of the red mud in the hydro-dealkylation reaction of the ethyl-benzene.

Keywords- Ethyl-Benzene, Hydro-dealkylation, Red Mud as Catalyst, Surface Properties.

I. INTRODUCTION

Red mud is a waste of the bauxite processing industry obtained during the alkaline extraction of alumina from bauxite ore [1]. The worldwide aluminum production in large scale has generated huge amounts of red mud for decades. Only in Hungary about 50 MT of unutilized red mud is deposited at different disposal sites and imposes potential threat onto the environmental elements (soil, surface and ground water, air) due to its caustic properties (pH~12) [2].

Several suggestions/trials for the comprehensive utilization of the red mud such as recovery of metal components in red mud [2] and utilization as coagulant material for wastewater treatment processes [3] or as construction material manufacturing material had been proposed. The red mud can be utilized in constructional material manufacturing such as tiles, road building material, ceramics, bricks etc. [4], [5]. Unfortunately, these technologies have not been used in wide scale. The utilization technologies are not only environmental benign, but - in a long term – are more costeffective as well in comparison with the storage and related long-term risks [1], [2]. Our investigation is focused on the utilization of the red mud as catalysts. Even after the elaboration of the appropriate technology for the utilization of the red mud it will not solve the problem related with its disposal and storage. However, it shows the alternative way for inexpensive utilization of the red mud as catalyst.

Reducing the aromatics compounds by hydrogenation is one of the ways to improve the fuel composition and diminish the discharge of the harmful compounds to environment[6]. Nobel metal-based and less expensive nickel-based catalysts are widely used for saturation of hydrocarbons containing benzene rings [6]-[9]. For example the hydrogenation of the ethyl-benzene (C_8H_{10}) on nickel/alumina results ethylcyclohexane (C_7H_{14}) as main product [8]. The red mud mainly contains a mixture of metal oxides of Fe_2O_3 33-40%, Al_2O_3 15-19%, SiO_2 10-15%, TiO_2 4-6%, V_2O_5 0.2-0.4%, MgO 0.3-1.0%, MnO_2 0.4-1.0%, ZnO 0.03%, ZrO_2 0.03%, Ni 0.04%, Ga 0.005% etc. [10], [11]. Due to this it can be considered as a potential alternative catalyst for hydrogenation as well as for cracking as well [1]. The purpose of this paper is to study the catalytic properties of red mud in the ethyl-benzene hydrogenation / hydro-dealkylation and to study the influence of the acidic treatment on the catalytic activity of the red mud.

II. EXPERIMENTAL

A. Sample preparation

The red mud sample used for the experiments was taken from the red mud dry disposal facility of Ajka. About 25 kg of sample was provided for the experiments, having pH~13. The calcined red mud sample was put into an oven and was kept at 105-110 °C for overnight, followed by calcination at 400°C for 8 h, then grounded till fine powder form. Part of the red mud samples was treated with sulfuric acid and nitric acid to reduce the pH value of the red mud from 12.2 to ~3.5. The red mud having acid treatment was calcined in air at 400°C overnight. The samples studied and their abbreviations are summarized in

Table I.

Table I. Samples information and GC analysis data for the liquid products of the ethyl-benzene hydro-dealkylation reaction with or without red mud at 450°C.

Sample abbreviation	Sample description	P_{int}/ P_{max}[a]	Reagent/ Product yield, ml	Product: liquid/ gaseous phases, %
0	without red mud	30/ 102	20/ 17.5	87.5/ 12.5
2.5	with calcined red mud	30/ 108	20/ 8.0	40/ 60
3	with HNO_3 treated and calcined red mud	30/ 115	20/ 7.0	35/ 65
4	with H_2SO_4 treated and calcined red mud	30/ 121	20/ 1.0[b]	5/ 95

a. Initial and maximum pressure during the experiment; b. Reaction was stop after reaching 450°C

B. Morphology and surface properties of red mud

The specific surface areas of the samples were determined by low-temperature nitrogen adsorption, -196°C (BET) using Micromeritics ASAP 2000 type equipment. The sample in amount of about 1.0000 g was accurately weighted and pretreated at 160°C under vacuumin order to clean and remove the adsorbed compounds from the solid surface. Pretreatment was stopped when the vacuum value of the pretreatment reached≤1.33Pa.

The acidity of the samples was studied using the pulse chemisorption of ammonia (NH_3) acid probe molecule at 30°C using Micromeritics Pulse ChemiSorp 2705 type device. The amount of the investigated sample was precisely weighted before experiments. For each run a sample about 1.0000 g of was used. The sample was place in U shape sample holder and was flushed with helium overnight. The helium gas flow rate was set to 20 ml/min. Ammonia injection of 1 ml was repeated several times till no more NH_3 was chemisorbed. The number of NH_3 injections depended on the property of sample.

C. Catalytic test

The ethyl-benzene hydro-dealkylation reactions were carried out in a steel 100 ml Parr reactor at elevated temperatures. Continuous stirring of the reaction mixture was provided in the reactor and reaction temperature was controlled by Parr 4848 Reactor Controller unit. Temperature setting accuracy was +/-2°C. The initial hydrogen pressure at room temperature was 30 bar. Starting mixture for all runs contained ethyl-benzene 20 ml (C_8H_{10}) and red mud in amount of 5g. At the end of reaction time (4 h) the reactor was cooled to room temperature.

D. Analysis of the reaction products

After cooling down the reactor to room temperature the reaction products were analyzed. The analysis of the gas and liquid samples were carried out by GC off-line analysis. Gas was collected in Tedlar bag (SKC-232, 3 L, USA). The hydrocarbon compositionof the gasand liquid samples was investigated by GC (Agilent, GC 7890A type) having non-polar J&W HP-5 type capillary column (30 m x 0.320 mm, 0.25 μm film thickness) and flame ionization detector, FID. Temperature of FID was set to 300°C. Gas sampling in amount of 0.025 ml was injected to GC. Liquid sample (2 μl) was diluted in CS_2 (1.5 ml), after homogenization it was injected onto GC in amount of 1μl having split ratio of 10:1. The temperature and the total flow of inlet unit was adjusted to 250°C and 24.02 ml/min respectively. Temperature program of the GC oven was set as follows: initial temperature was set to 39°C for 5 min; then with heating rate of 25°C/min temperature was raised to 90°C, followed by last step of heating with rate of 15°C/min to 170°C for 13 min. Total time of individual CG run was 25.37 min. The carrier was He gas having high purity and its flow rate in the column was set to 1.91 ml/min. Two parallel GC analyses were performed for each sample.

III. RESULTS AND DISCUSSIONS

A. Morphology and surface properties

The untreated red mud calcined at 400°C had a surface area of 15.4 m^2/g. The surface area of red mud increased after the acid treatment. After nitric acid treatment followed by calcination at 400°C the sample exhibited a little bit higher surface area (48.7 m^2/g) than after sulfuric acid treatment (43.2 m^2/g). During the acid treatment the red mud some of the elements, such as Na, Ca, Mg, K, Fe, Mn are dissolved and washed out from the bulk sample. It results in an increase in the total pore volume hence increased the BET value.

Also the acid treatment significantly increased the number of acid sites: NH_3 sorption increased from 14.2 on the surface of the untreated red mud to 119.6 and 144.0 μmol/g on sulfuric and nitric treated red mud respectively. The surface properties of the untreated and pretreated red mud was discussed in detailin a separate paper [12].

B. Catalytic test

The hydro-dealkylation reaction of the ethyl-benzene is shown in Fig. 1.

The sample pretreatments are summarized in Table I. The reaction time except sample No. 4.was 4 h. In case of sample No. 4.the reaction was stopped after reaching 450°C. For this sample sudden pressure increase to 121 bar was observed due to conversion of

ethyl-benzene to gaseous phase products (Table I). In case of this sample (No.4.) the reaction was carried out at 250, 350 and 400 °C as well.

The observed conversion figures were low and didn't exceed the 4 % at 400°C, therefore only the result of the reaction run at 450°C is shown.

For all runs the starting pressure of reaction was 30 barand it increased to 102-121 bar at 450°C (Table I). The highest increase in pressure was observed for the reaction

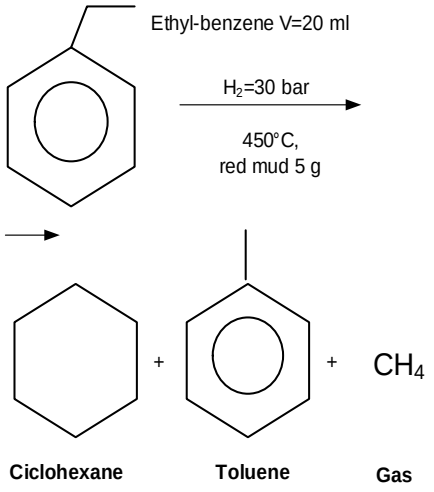


Figure.1. The hydro-dealkylation reaction of the ethyl-benzene.

where the red mud was treated with acid and as a result of this high amount of gaseous products formation was observed up to 65-95%.

After the completion of reaction the gas and liquid products and the red mud residue were separated at room temperature and analyzed.The thermal conversion (reaction without red mud) of the ethyl-benzene was observed at 450°C and it was about 7% (Table II).

The main products of the hydro-dealkylation step were toluene and cyclohexane in the liquid reaction phase (Table II, Fig. 2.).In addition to toluene and cyclohexane formation hydrocarbons having carbon number C≤16 was observed. Since these compounds were formed in small amount in less than 1%, their formation is not discussed separately but it was taken into consideration in calculation of the product yield. Therefore the total conversion of ethyl-benzene was higher than the formation of toluene and cyclohexane altogether (Table II). Metal components are required in the hydrogenation step such as iron, nickel, vanadium [13] and those metals are present in red mud. In the presence of calcined red mud the conversion of ethyl-benzene into toluene and cyclohexane was 45.2%. It increases up to 51.4% after the

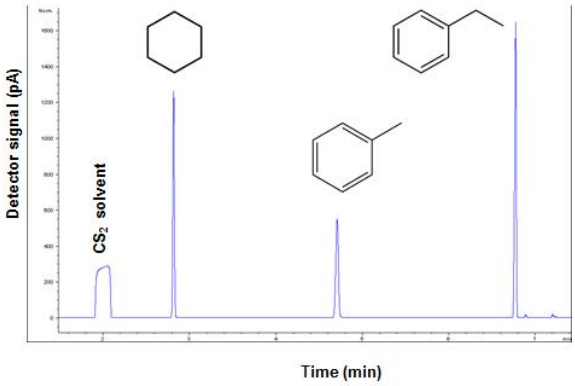


Figure.2. GC pattern of the liquid samples after the hydro-dealkylation of ethyl-benzene at 450°C with red mud treated with nitric acid

Table II. GC analysis data for the liquid products of the ethyl-benzene hydro-dealkylation reaction with or without red mud at 450°C

Sample	Toluene, yield, %	Cyclohexaneyield, %	Ethyl-benzene total conversion, %
0	0.7	6.7	7.5 (7.4)[a]
2.5	18.2	27.0	50.1 (45.2)
3	22.2	29.2	57.7 (51.4)
4	15.5	23.4	45.1 (38.9)

a. yield of toluene, % + yield of cyclohexane, %

treatment of the red mud with nitric acid. During all runs the formation of less harmful cyclohexane compound was higher than that of toluene (Table II).

The cracking reaction also took place resulting in the formation of less valuable gaseous products, mainly methane. A GC analysis of the gas sample is shown in Fig. 3. The hydrocracking step of the dealkylation reaction takes place on the actives site of the catalysts having acid properties. The mechanism of the hydrocarbon cracking reaction was discussed in details asin [13]. The amount of gaseous products increased with increase of the ethyl-benzene conversion: the lowest figure, 12.5%, was obtained on calcinedsample No.0. and the highest value, 95%, was obtained on sample No.4. (Table I.). This well correlates with BET and acidity measurement results of the red mud samples studied. The highest formation of methane product were formed during reaction with red mud having the high surface area (43 m^2/g) and the highest number of acid sites (144.0 μmol/g) detected by ammonia adsorption.

CONCLUSIONS

The hydro-delakylation reaction of the ethyl-benzene in the presence of red mud used as catalyst starts above 400°C.

In the presence of calcined red mud the conversion of ethyl-benzene (50%) to toluene (C_7H_8), cyclohexane

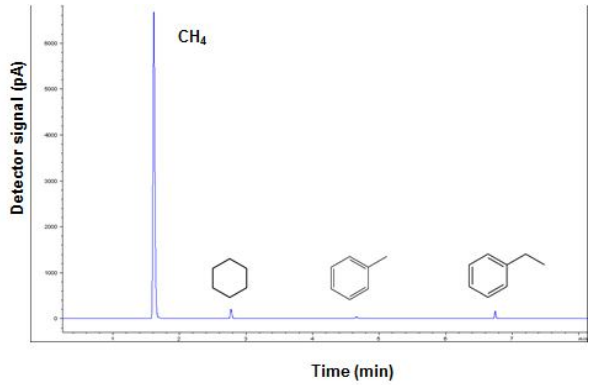


Figure.3. GC pattern of gas sample obtained in the ethyl-benzene hydro-dealkylation reaction at 450°C with red mud treated with sulfuric acid

(c-C_6H_{12}) and methane (CH_4) was significantly higher incomparisons with the thermal hydro-dealkylation/hydro-cracking reaction of the ethyl-benzene at 450°C inwhich case the conversion value was about 7%.

During the hydro-dealkylation of ethyl-benzene mainly toluene and cyclohexane are formed and their highest yields were 22% and 29% respectively in the presence of nitric treated red mud. Gas product also formed since the red mud contains active metal compounds which are able to catalyze the hydrocracking reaction as well. The results showed that in case of sulfuric acid treated red mud its hydrocracking activity is higher than after treatment with nitric acid. Further investigations should be carried out in order to study the change in the conversion of the hydrogenation of aromatics compounds (e.g. with using different pretreatments for the red mud before carrying out the catalytic tests).

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