

DEACTIVATION AND REGENERATION OF Ni/ZA CATALYST IN HYDROCRACKING OF POLYPROPYLENE

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ABSTRACT

The phenomena of catalyst deactivation and the effects of regeneration method on the characteristics and activity of Ni/ZA catalyst after being used in a continuous cracking reaction of polypropylene have been studied. Ni/ZA catalyst was prepared using sonochemical method with total metal intake of 4%. Characteristics and activity of fresh, spent, and regenerated catalyst were evaluated to get a better understanding about the catalyst deactivation. Characteristics which have been observed include catalyst acidity, porosity, crystallinity, and surface morphology. Catalytic activity test of Ni/ZA catalyst on polypropylene cracking reaction at temperature of 500 °C with H₂ flow rate of 20 mL/min and catalyst:feed ratio of 1:2 (w/w) showed the decrease of some catalyst characteristics such as specific surface area, total pore volume, and acidity due to coke fouling over a five-times continuous experiment. Regeneration of catalyst with oxidation-reduction method has been able to increase the activity and acidity of catalyst up to 7.47% and 38.54%, respectively, compared to those of spent catalyst, while the catalyst surface area and total pore volume decreased up to 32.83% and 26.92%, respectively.

Keywords: deactivation; Ni/ZA; polypropylene; regeneration

ABSTRAK

Fenomena deaktivasi katalis dan pengaruh metode regenerasi terhadap karakteristik dan aktivitas katalis Ni/ZA setelah digunakan dalam reaksi perengkahan polipropilena dengan reaktor sistem kontinu telah dipelajari. Katalis Ni/ZA dipreparasi menggunakan metode sonokimia dengan total logam teremban 4%. Karakteristik dan aktivitas katalis baru, bekas dan teregenerasi diuji untuk mendapatkan pemahaman yang lebih baik tentang fenomena deaktivasi katalis. Karakteristik katalis yang dipelajari meliputi keasaman, porositas kristalinitas, dan morfologi permukaan. Uji aktivitas katalis Ni/ZA dalam perengkahan polipropilena pada 500 °C dengan laju H₂ 20 mL/menit dan rasio katalis:umpan 1:2 (b/b) menunjukkan penurunan beberapa karakteristik katalis seperti luas permukaan spesifik, volume total pori, dan keasaman yang disebabkan oleh kokas setelah lima kali eksperimen. Regenerasi katalis dengan metode oksidasi-reduksi mampu meningkatkan aktivitas dan keasaman katalis masing-masing hingga 7,47% dan 38,54%, dibandingkan dengan katalis bekas, sedangkan luas permukaan spesifik dan volume total pori berkurang masing-masing hingga 32,83% dan 26,92%.

Kata Kunci: deaktivasi; Ni/ZA; polipropilena; regenerasi

INTRODUCTION

Waste plastics are the most rapidly growing solid waste and create a very serious environmental challenge due to their huge quantities and their disposal problems. Pyrolysis and catalytic cracking can be used to recycle waste plastics by converting them to hydrocarbon mixtures. These methods do not require polymer type sorting. Catalytic cracking of pyrolysed waste plastics (resulted in 90.48% liquid [1]) is preferred because it typically produces smaller hydrocarbons and yields higher value liquid and gaseous products [2]. The waste plastics such as polyethylene, polystyrene, and polypropylene are rich in carbon and hydrogen—the

building blocks of petroleum, so that the possibility of converting them into liquid fuels is a productive alternative for plastic recycling [3].

Many studies in catalytic cracking of waste plastics have been done by using metal supported catalysts such as Ni/silica–alumina catalysts [4-5], PtHZSM-5, PtHY, and PtHMCM-41 [2], Ni/h-ZSM-5, Ni/h-Beta, Ni/Al-MCM-41, and Ni/Al-SBA-15 [6-7]. Indonesian natural zeolite is an aluminosilicate material that can be used as a solid acid catalyst and catalyst support. It was reported that zeolite has a high catalytic activity, resist to agglomeration, has high porosity, and is stable under high temperature [8]. Loading Ni as an active metal on Indonesian natural zeolite can be a great

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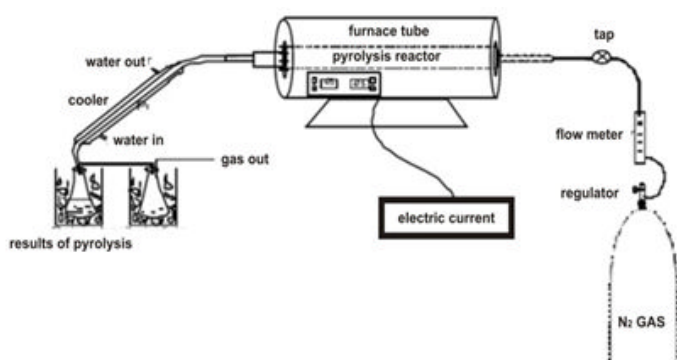


Fig 1. One-step pyrolyser reactor

choice to get a high-performance catalyst with high activity, stability, and resistance towards high temperature [9].

In this study, sonochemical method was used in catalyst preparation. Sonochemical preparation arises from acoustic cavitation, namely the formation, growth, and collapse of bubbles in a liquid [10]. This method generated the synthesized particles into regular and uniform form. For instance, irradiation of ultrasonic wave on the preparation of Ni/CeO₂-MgO-La₂O₃/Al₂O₃ catalyst affected the structure of catalyst molecules, and further increased the surface area of catalyst. This also yielded smaller and more uniform size of catalyst granules [11]. In the synthesis of nano size γ -Al₂O₃ catalyst, all of the results including crystallite size, surface area, average pore diameter, and pore volume, as well as the activity in the dehydration reaction of methanol to dimethyl ether showed that sonochemical method had a competitive potential in catalyst preparation due to its major roles in formation of particles and crystal structures [12]. Compared to incipient wetness method, the sonochemically-prepared Mo₂C/ZSM-5 catalyst was much more uniform with a 15-fold enhancement of surface Mo versus the bulk material [13]. The Pt-ZSM-5 catalyst synthesized by in-situ method with ultrasonic irradiation resulted in smaller crystals of ZSM-5 than that without ultrasonic irradiation. It indicates that the ultrasonic irradiation had a significant effect on the morphology of Beta zeolite. Moreover, the catalyst showed higher activity and selectivity to *iso*-pentane isomer [14].

In the catalytic cracking process reaction, the study of catalyst deactivation is one of the most important aspects to improve the catalytic performance. Deactivation of catalysts may be having an important commercial economic consideration with respect to catalyst life time [15]. The regeneration, therefore, is needed to overcome the high-cost production of hydrocracking reaction.

The main possible cause of catalyst deactivation has been considered to be the accumulation of

carbonaceous materials [16] and active metal leaching [17], as well as the structural changes of the catalyst components due to poisoning and sintering [1,18]. Coke will be significantly formed during the first hours of hydrogenation processes, and catalyst deactivation by this carbonaceous material appears to rapidly reach a pseudo steady-state level [17]. The deactivated catalyst can be reactivated (regenerated) based on the reason of deactivation process. Deactivation due to the blockage of active site by coke can be reactivated by oxidation [19] followed by hydrogenation to produce a zero-valence metal catalyst [28]. To gain better understanding about the deactivation phenomena of Ni/ZA catalyst, the properties and the activity of Ni/ZA catalyst before and after being used in catalytic cracking of polypropylene are presented.

EXPERIMENTAL SECTION

Materials

Natural zeolite (ZA) was purchased from PT. Prima Zeolita. The zeolite was prepared by washing using aquademin from Brataco, Pty Ltd, and filtering them using a particulate filter. To activate the zeolite 1% of HF (85%, E. Merck) solution, 6 N of HCl (37%, E. Merck) solution, and 1 M NH₄Cl %, E. Merck) solution, respectively were used. All chemicals are of analytical grade. Ni/ZA catalyst was prepared by sonochemical method using Ni(NO₃)₂·6H₂O (p.a., E. Merck) as the metal precursor. Hydrogen, oxygen, and nitrogen of 99.9% purity were provided by Samator Gas, Pty Ltd. Polypropylene was obtained from pyrolysis of polypropylene plastic using a one-step pyrolyser (Fig. 1) [20] under nitrogen atmosphere at 475 °C. The liquid produced from this process was analyzed by GC and being compared later to the hydrocracked products. This liquid product was then used as feed in the hydrocracking reaction. NH₃ 25% which was purchased from E. Merck was used in the catalyst acidity determination.

Instrumentation

Ni/zeolite catalyst prepared was analyzed for the Ni content using Atomic Absorption Spectrophotometer Perkin Elmer Aanalyst-100, the porosity properties using a Surface area analyzer NOVA 1200e Quantachrome, and the crystallinity using X-Ray Diffractometer (XRD) Shimadzu-6000. All of the reaction performed in this research used a continuous flow-fixed bed reactor. Products obtained at the end of reactions were analyzed by using a Gas Chromatograph GC Agilent Technologies 6820 equipped with an HP5 semipolar column (30 m length,

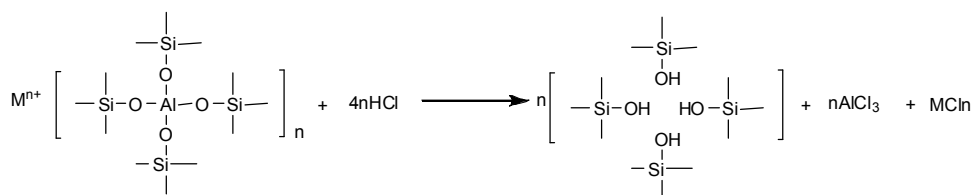


Fig 2. Dealumination reaction [29]

Table 1. Some characteristics of Ni/ZA catalyst prepared with different method

Sample	Characteristics		
	Ni loaded (%)	Total Acidity (mmol/g)	Specific Surface Area (m ² /g)
ZA ^[9]	NA	0.9	35.1
H-ZA	NA	1.9	51.2
Ni/ZA	93.06	2.1	95.7
Ni/ZA ^[25]	95.3	4.0	118.6
Ni/ZA ^[9]	99.4	1.1	90.6

0.32 mm diameter), and FID detector. The product with the highest fraction was analyzed using Gas Chromatograph QP-2010SE SHIMADZU equipped with MS detector, a Rastek RXi-5MS column (30 m length, 0.25 mm internal diameter), and He as the carrier gas.

Procedure

Preparation of Ni/ZA catalyst

The natural zeolite from Prima Zeolita underwent an acid treatment to obtain the activated natural zeolite (H-ZA). The details can be found elsewhere [9]. To prepare Ni/ZA catalyst, 40 g of H-ZA sample and 7.9226 g of Ni(NO₃)₂·6H₂O were weighed and then dissolved in 30 mL of aquademin. The mixture was then sonicated for 1 h at a frequency of 40 KHz. The mixture was then put in oven at temperature of 120 °C for 12 h to remove the solvent. This sample was called as Ni/ZA sample. Finally, the Ni/ZA sample was calcined using nitrogen at 500 °C for 5 h, oxidized at 400 °C for 2 h, and reduced at 400 °C for 2 h to obtain Ni/ZA catalyst.

Characterization of Ni/ZA catalyst

Ni/ZA catalyst was characterized by using atomic absorption spectrophotometer Perkin Elmer Analyst-100 for determining Ni content. The total acidity of catalyst was determined using a gravimetric method with ammonia as an adsorbate. Catalyst porosity was determined using a NOVA 1200e Gas Sorption Analyzer. The specific surface area of catalyst was calculated using Brunauer, Emmet, and Teller (BET) method, whereas the total pore volume and average pore radius were calculated using Barrett, Joyner, Halenda (BJH) method. The crystallinity of the catalyst was analysed using Shimadzu X-Ray diffractometer with Cu K_α radiation at λ of 0.154 nm. The diffraction pattern

was recorded at 2θ between 3° and 80°. The catalyst morphology was observed by field-emission scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX) JEOL JSM-6360LA. The SEM images were taken at an accelerating voltage of 6 kV. Prior to the observation, samples were sputtered using Pt on a sputtering instrument.

Activity of Ni/ZA catalyst on the catalytic cracking of polypropylene

The liquid polypropylene (500 g) was introduced into the reactor. The activity test of Ni/ZA catalyst was carried out in reaction of polypropylene cracking with ratio of catalyst-feed of 0.5 (in weight) for a five-times experiment at temperature of 500 °C and hydrogen flow rate of 20 mL/min for 60 min. The product was analyzed using GC and GC-MS. Samples of catalyst (fresh and spent catalysts) were then characterized for the acidity by gravimetric method, Ni content by AAS, catalyst crystallinity by XRD, porosity by gas sorption analyzer NOVA 1200e Quanta chrome, and catalyst morphology by SEM-EDX.

The deactivated (spent) catalyst was then regenerated by being oxidized at temperature of 400 °C with oxygen gas flow rate of 10 mL/min for 4 h. Subsequently, the catalyst was reduced at temperature of 400 °C with hydrogen flow rate of 10 mL/min for 2 h [21]. The regenerated catalyst (Ni/ZA_{reg}) was then characterized and used in the catalytic cracking of polypropylene under the same condition as for fresh catalyst. The product was then analyzed by using GC.

RESULT AND DISCUSSION

Catalyst Preparation and Characterization

Acid treatment is one of the methods of zeolite activation. Activation by HF 1% was aimed to dissolve the polluting oxides such as free silica (SiO₂) and alumina (Al₂O₃) around zeolite [22] resulting in gaseous SiF₄ by releasing water [23]. It makes the pores of zeolite are more open. The acid treatment of zeolite with 6 M of HCl solution was to optimize the aluminum content in zeolite resulting in a more stability of zeolite at high temperature. In addition, the dealumination reaction (Fig. 2) also caused the change of Al position,

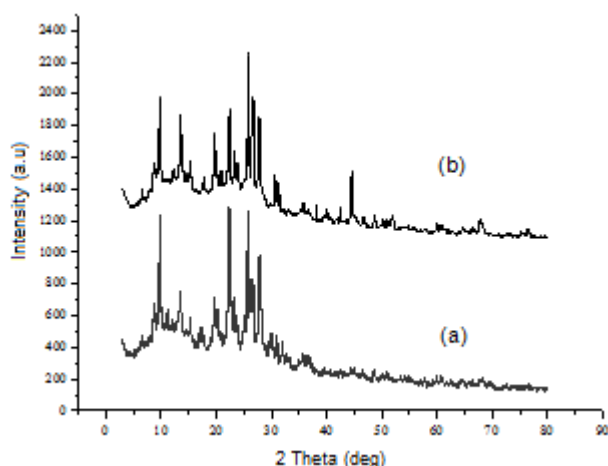


Fig 3. Diffraction pattern of (a) H-ZA and (b) Ni/ZA

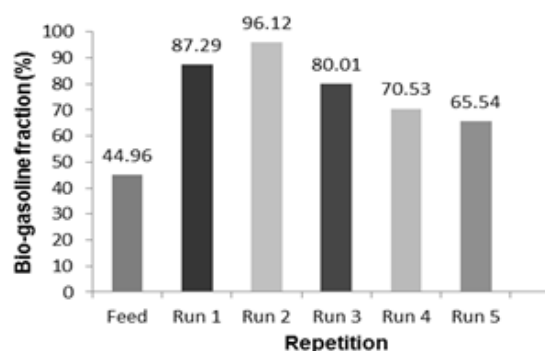


Fig 4. Conversion of polypropylene into gasoline fraction in the hydrocracking process using Ni/ZA catalyst

from inside the framework to outside the framework which could easily form AlCl_3 . The Si/Al ratio of zeolite would increase after acid treatment [24] leading to the increase in zeolite acidity and selectivity. The treatment with 1 N NH_4Cl solution was to replace the balancing cations in zeolite, such as Na^+ and Ca^{2+} , with NH_4^+ . This would promote the formation of Brønsted acid sites by the existence of proton H^+ after releasing NH_3 [22]. The loading of active metal Ni was carried out by sonochemical method. The characteristic of the catalysts will be the following.

Table 1 shows the result of catalyst characterization with sonochemical method compared to wetness impregnation method. Wetness impregnation method gave better metal intake in the zeolite surface. It was expected that it would increase the number of acid sites, especially Lewis acid sites. However, by wetness impregnation method, the total acidity of Ni/ZA catalyst as well as the surface area of the catalyst were significantly lower compared to those by sonochemical method. In addition, sonochemical method could provide a better metal dispersion [11] and generate smaller and more uniform size of catalyst due to the use of ultrasonic irradiation in the preparation [11]. These characteristics

might have a considerable effect on the catalyst activity [11].

The crystallinity of catalyst was investigated using XRD. Fig. 3 presents the diffraction patterns of H-ZA and Ni/ZA. It can be observed that both patterns have nearly the same pattern. However, a shifting of d value was observed due to the metal loading in the zeolite pores that might cause an increase in the distance among zeolite lattices [9,26].

Activity of Ni/ZA Catalyst in the Hydrocracking of Polypropylene

The conversion of polypropylene in the hydrocracking process is defined by the gasoline fraction produced. It was simply calculated from the percentage of area of light fraction with retention time below 4 min in the total ion chromatogram. Fig. 4 presents the conversion of polypropylene into gasoline fraction over five-times hydrocracking process using sonochemically-prepared Ni/ZA catalyst.

Under the same condition, sonochemically-prepared Ni/ZA catalyst used in this study was able to increase the gasoline fraction by 94.1% (from 44.96% in the original polypropylene to 87.29% in the hydrocracked one), while Prasetyaningsih [30] reported that Ni/ZA catalyst prepared with wetness impregnation method could only increase 11.55% of gasoline fraction. Furthermore, in the second run of hydrocracking reaction without changing the catalyst, the increase in the gasoline fraction was more than double (from 44.96% to 96.12%). It might be caused by the left products on the catalyst bed after the first run which could not be desorbed yet in the first run. The use of catalyst for the second run would enable the release of those products to be removed from the catalyst bed.

The sample from the second run had the highest fraction of gasoline. This sample then underwent a GC-MS analysis to study the component of the hydrocracking product (Table 2). The identification of the compounds in the hydrocracked product was based on the library software available in the GC-MS instrument. The total gasoline fraction detected by GC-MS was lower (59.4%) compared to the conversion of the corresponding run (96.12%). It might be due to the evaporation of some compounds during analysis as well as storage.

As expected, the gasoline fraction in the third, fourth, and fifth run decreased by 77.96%, 56.87%, and 45.77%, respectively. It seemed that the catalyst start to be deactivated. The main reason of catalyst deactivation in the hydrocracking of hydrocarbon materials like polypropylene is due to coke fouling. The coke could be formed because the hydrocracking

Table 2. Component of gasoline fraction produced from the hydrocracking of polypropylene using Ni/ZA catalyst at 500 °C

Retention time (min)	Compound	Percentage (%)
2.692	2,3-dimethyl hexane	3.54
2.767	2,3-dimethyl-3-hexene	1.96
2.842	4,4,5-trimethyl-2-hexene	5.33
2.900	1,3,5-trimethyl cyclohexane	8.96
2.975	1,1,3-trimethyl cyclohexane	8.53
3.025	NA	4.91
3.133	NA	0.89
3.200	2,2-dimethylcyclopentyl cyclohexane	1.15
3.308	3,5-dimethyl octane	1.16
3.425	1,2,4-trimethyl benzene	2.88
3.558	4-methyl decane	12.78
3.750	1,3,5-trimethyl benzene	4.50
3.808	4,6,8-trimethyl-1-nonene	2.81

Table 3. Catalyst characteristics

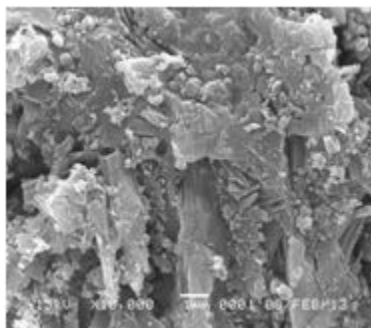
Sample	Characteristics			
	TA (mmol/g)	SSA (m ² /g)	TPV (cm ³ /g x 10 ⁻³)	APR (Å)
Ni/ZA	2.1	95.7	174.8	16.7
Ni/ZA _{spent}	1.9	72.2	169.4	46.9
Ni/ZA _{Regenerated}	2.6	48.5	123.8	51.0

TA = Total acidity

SSA = Specific surface area

TPV = Total pore volume

APR = Average pore radius

**Fig 5.** SEM image of Ni/ZA catalyst after being used over five times of runs

reaction system was running out hydrogen leading to re-polymerization reaction between activated species in the reaction system. As the result, the coke deposit would be produced as the product of re-polymerization reaction.

To gain better representation of coke fouling suspected to be the main reason in catalyst deactivation, the spent catalyst after a five-times run was analyzed using SEM-EDX. Fig. 5 shows the SEM image of the spent catalyst. The disordered appearance of the materials on the catalyst surface was suspected as coke. To have better identification, some metals which could be found on the catalyst surface were determined semi-quantitatively using EDX. The elements determined

semi-quantitatively were Si (28.7 wt.%), Al (4.0 wt.%), O (37.8 wt.%), K (1.3 wt.%), Ni (4.6 wt.%), and C (23.6 wt.%). By assuming that fresh Ni/ZA catalyst did not contain any carbon, it is clear that the coke formation (23.6%) during hydrocracking of polypropylene did happened leading to deactivation of the catalyst.

Regeneration of Ni/ZA Catalyst

Deactivation of catalysts is a critical issue in catalyzed processes. It is related to the high cost production as well as the public demand for the corresponding process. Regeneration of heterogeneous catalysts is one of the promising steps to remove or eliminate the cause of catalyst deactivation, besides metal recovery and catalyst disposal. In this study, the heterogeneous Ni/ZA catalyst was regenerated by using consecutive oxidation and reduction method. The characteristics of fresh, spent, and regenerated Ni/ZA catalyst are presented in Table 3. It can be seen that the oxidation and reduction method could increase the acidity of catalyst. The removal of coke deposit as well as the oxidation of compounds strongly adsorbed on the catalyst surface might take place, resulting in the exposed acid sites of the catalyst [27].

However, the increase of the catalyst acidity after regeneration process was not followed by the increase

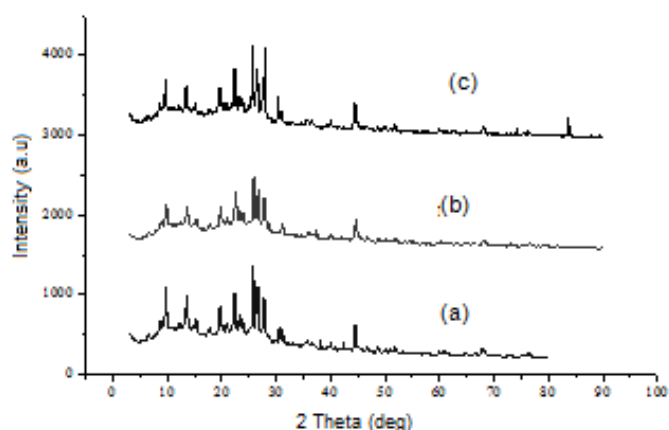


Fig 6. Diffraction patterns of (a) fresh, (b) spent, and (c) regenerated Ni/ZnO catalysts

in specific surface area and total pore volume of the catalyst. It might be caused by the blockage of the catalyst pores even after the regeneration process. In addition, the formation of new phase due to interaction of metal-support leading to agglomeration during the regeneration process might occur. The formation of this phase could be seen in Fig. 6 showing the observed new peak at 2 Theta of 83.6°. The d shifting and the decrease in intensity of diffraction pattern did happen to spent Ni/ZnO catalyst. It is probably caused by thermal treatment within a long period during the hydrocracking process and the formation of coke on catalyst surface. After being regenerated, the intensity of the diffraction pattern of the regenerated catalyst significantly increased.

After being regenerated, the catalyst was reused in the hydrocracking of polypropylene under the same condition. It is observed that the gasoline fraction increased by 7.47% compared to that of spent catalyst (from 65.54% to 70.44%). It was possible due to the increase in the number of acid sites which have important roles in hydrocracking reaction. The increase of the number of acid sites might be due to the oxidation of organic compounds attached on to the acid sites as well as the reduction of dispersed active metal into its zero-valence state leading to the increase in the number of Lewis acid sites.

CONCLUSION

The sonochemically-prepared Ni/ZnO showed better characteristics compared to the Ni/ZnO catalyst prepared by conventional method. In addition it showed better activity in the hydrocracking of polypropylene under the same condition. After being used over a five-time experiment, the decrease in catalyst activity was observed due to the decrease in the number of acid sites as well as specific surface area of the catalyst. Coke

fouling was found to be 23.6% increase. The regeneration process was successful to increase the activity and acidity of catalyst but the specific surface area and total pore volume decreased which might be agglomeration of metal-support during regeneration process.

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