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Regeneration of Spent Nickel Catalyst by Hydrometallurgical Method

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ABSTRACT. Nickel Catalyst is one of the common catalysts found in chemical industries. However, this catalyst has a limited lifetime, indicated by having performance or activity drop so it is potentially become dangerous waste if the handling is not proper. The spent nickel catalyst needs to be processed to recover and avoid pollution towards the environment. The Hydrometallurgy method is a proper method to process nickel catalyst waste. The purpose of this research is to investigate the characteristic of a regenerated nickel catalyst when it is treated with HCl and H_2SO_4 as the lixiviant. In this research, the spent nickel catalyst was treated with HCl and H_2SO_4 in the presence of 2% H_2O_2 reductant under room conditions and mixing rate at 200 rpm for 30 minutes of reaction. The leaching filtrate was precipitated using NaOH solution while the formed precipitate was heated at 800 °C for 3 hours. The regenerated catalyst was characterized using FTIR and SEM-EDX. The SEM images showed regenerated catalyst prepared using the HCl solution has a different morphology compared to the one using the H_2SO_4 solution. Based on FTIR analysis, both samples exhibit Ni-O and C-O groups. Based on elemental analysis, the highest nickel concentration was obtained by using HCl with a Ni content of 25.98%w/w, compared to sulfuric acid (H_2SO_4) with a Ni content of 10.94%w/w. The Ni content can be improved by the addition of a washing step after the sintering process.

1. INTRODUCTION

Nickel is a flexible metal making it to be produced as different alloys of metals. Indonesia is one of the producers out of 23 countries as the largest nickel producers in the world with consumer markets including China, America, and Japan. Nickel ore is a raw material that can be converted to metallic nickel through the production process. However, initially, nickel ore was formed from the fusion and enrichment of minerals on rocks stored in a particular region and is an unrenewable natural resource. Referring to the map of the Geological Agency in 2020, Indonesia has a resource of nickel ore of 11.887 million tons with a reserve of ore of 4.346 million tons. This makes nickel much used, as in the manufacture of catalysts [1-3].

Catalysts are substances used to speed up chemical reactions. One of the most commonly used catalysts is the nickel catalyst, as it can be used to speed up reactions in the processes of oxidation, hydrogenation, and epoxidation. For example, PT. Petro Oxo Nusantara utilized a nickel-based catalyst that is applied to alumina refractors (Ni/Al_2O_3) and is used as a 2-Ethyl Hexenal hydrogenation process to produce 2-Ethyl Hexanol. It is estimated that the price of nickel in Indonesia has a fairly high value, which is around Rp. 320 million per ton (www.tradingeconomics.com/commodity/nickel). Considering the quantity and economic value and hazard of waste catalysts NiO/Al_2O_3, a process is needed to recover nickel from the waste. In addition, the currently used catalysts will also experience activity decay resulting in hazardous waste formation. As the result, the spent nickel waste must be processed as a method to reuse and to avoid environmental pollution. Since the average life of the nickel catalyst is 3 to 5 years, the processing of spent irreversible passivated catalyst is a crucial step. In addition, the spent NiO/Al_2O_3 catalyst is also categorized as toxic and hazardous waste due to its toxic and carcinogenic nature, which will harm every living organism [4].

The process of obtaining nickel from solid waste containing nickel can be conducted via the hydrometallurgical process. The hydrometallurgical process is the process of purifying a mineral through a water medium. Leaching or extraction of solid by liquid is considered a chemical process that utilizes liquid to selectively extracts a compound. In Hydrometallurgy, leaching is a process that utilize reagents or leaching agents that dissolve in water to react with metals. This method is also a very promising method because it is able to produce nickel with high purity under mild conditions with low energy intensity. In addition, solvents can be recycled and reused to reduce production costs [5-6].

Several studies have been focusing on obtaining the high leaching efficiency of nickel from the spent nickel catalyst. For example, to achieve high selectivity and leaching efficiency, high-temperature soda-assisted roasting is applied as a pretreatment process. Leaching using organic acids is also an interesting topic, however the leaching process requires high leaching temperatures, long leaching time, and a high amount of solvent, resulting in high acid consumption per gram of recovered nickel [7-10]. This study aims to regenerate nickel oxide from a spent nickel catalyst. The lixiviant used in this research is sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) with an addition to H_2O_2 as a reducing agent. The leaching processes were performed at room temperature. Hydrometallurgical leaching is an endothermic reaction that requires high temperature in order to achieve high leaching efficiency. A small amount of hydrogen peroxide can improve the efficiency making the overall process eco-friendly, energy-saving, and cost-effective. The Nickel can be recovered by chemical precipitation, and the regenerated NiO can be obtained via the sintering process. To the best of our knowledge, such an approach has never been investigated by previous researchers.

2. MATERIALS AND METHOD

2.1 Materials

The spent nickel catalyst is obtained from PT. Petro Oxo Nusantara. Based on XRF analysis, the catalyst consists of 85%w/w NiO, 2%w/w of Mo_3O_4, 5%w/w of Al_2O_3, and 8%w/w of SiO_2. 1 M HCl and 1 M H_2SO_4 were prepared by the dilution of concentrated acids (Merck, Germany). 2 M NaOH used as a precipitating agent was prepared by diluting 40 g of NaOH flakes (Asahi, Indonesia) into 1 L of solution.

2.2 Equipment

The equipment used in the study is a beaker glass, flasks, a glass funnel, a magnetic stirrer, plastic wrap, an electric oven, an electric furnace, filter paper, a porcelain cup, mortar and pestle, and a sieving screen with 100 mesh size.

2.3 Research Variable

In this study, there are two variables used, namely:

1. The first lixiviant is H_2SO_4 (1M, 30 °C, 200 rpm)
2. The second lixiviant is HCl (1M, 30 °C, 200 rpm)

5 gr of catalyst were reacted with 100 mL lixiviant for 30 minutes in every experiment.

2.4 Methods

2.4.1. The Leaching Process

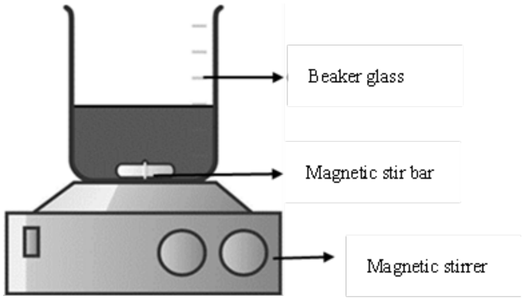

Figure 1. Spent Nickel Catalyst Waste Leaching Process

Prior to leaching, the spent nickel catalyst powders were ground and sieved to obtain fine particles. Powder with fine particles tends to have high leaching efficiency due to its large surface area and improved diffusivity. In

Figure 1, the leaching process is carried out using a beaker glass; at this stage, the lixiviant was inserted into the glass beaker that was already placed on the hot plate magnetic stirrer, 2% v/v H_2O_2 was added followed by continuous mixing at a rate of 200 rpm maintaining a temperature of 30°C. The spent nickel catalyst powder (sieved using a 100-mesh screen) was added to the lixiviant. After 30 minutes, the solution color becomes dark green. The solution was separated from the residue by gravity filtration using filter paper. The dark green filtrate was reacted with 2 M NaOH solution until the solution forms a light green precipitate. The precipitates were separated using gravity filtration without washing and placed in a porcelain cup and dried in an electric oven until a dry solid was achieved. The precipitates were ground using mortar and pestle and sieved using 100-mesh screen to obtain fine precursor powders.

2.4.2. The Sintering Process

At this stage, the precursor powders were inserted into the muffle furnace and sintered at 800 °C for three hours (ramping rate 10 °C/min). After the furnace was cooled down, the regenerated nickel oxides catalysts were obtained. The regenerated catalysts were ground and sieved using 100-mesh screen prior characterization step and labeled as NiO-HC and NiO-HS according to the lixiviant, i.e., HCl and H_2SO_4, respectively.

2.4.3. Characterization of the regenerated Nickel Oxide

To investigate the morphological feature and elemental composition, the samples were analyzed using Scanning Electron Microscope (SEM) – Energy Dispersive X-Ray Spectroscopy (EDX) (JCM7000, JEOL, Japan). The samples were sputtered with gold and placed on carbon tape. The functional groups of the samples were examined using Fourier Transformed Infra-red spectroscopy (FTIR) by Shimadzu (Japan) with a wavenumber range of 4000-400 cm^{-1}. The leaching efficiency was calculated by comparing the absorption of the filtrate to the leaching solution of nickel catalyst reacted with aqua regia solution. The experiment was conducted for three times to assure the repeatability and consistency of the study. The absorbance data are measured using Atomic Absorption Spectroscopy (AAS) by Shimadzu (Japan).

$$\%E = \frac{A_{sample}}{A_{aquaregia}} \times 100\% \qquad (1)$$

Since the absorbance is directly proportional to the concentration, therefor equation 1 can be modified into equation 2

$$\%E = \frac{CNi_{sample}}{CNi_{aquaregia}} \times 100\% \qquad (2)$$

Where CNi is the concentration of Ni (mg/L), and %E is the leaching efficiency.

To assure the purity of the sample, X-Ray Diffraction (XRD) techniques was used. NiO powder was analyzed using X-Ray Diffractometer by Bruker with diffraction angle (2θ) at 30-85° and CuKα radiation (λ=1.504 Å).

3. RESULTS AND DISCUSSIONS

3.1 Leaching Behaviour of NiO from Spent Nickel Catalyst

The leaching filtrates were analyzed using AAS to determine the absorbance or the concentration of Ni in the solution. Based on the calculation, the leaching efficiency of the spent catalyst treated using HCl and H_2SO_4 is 44.9% and 37.1%, respectively. The detailed experiment result can be seen in Table 1.

Table 1. Leaching behaviour of Spent Nickel Catalyst by HCl and H_2SO_4 solutions

Lixiviant	Leaching efficiency (%E)	Average
HCl	45.22%	44.9%
	44.91%	
	44.51%	
H_2SO_4	37.86%	37.1%
	37.18%	
	36.23%	

The efficiency is greater when HCl is used as the leaching agent. This shows that even though HCl is a monovalence acid, it has high reactivity toward nickel oxide compared to the bivalence H_2SO_4. The relatively low leaching efficiency (far less than 100%) might be caused by the endothermic leaching reaction and short leaching time (30 minutes). To achieve the desired leaching efficiency, the lixiviant must have a higher concentration, the leaching time should be longer, or the temperature should be elevated. However, to maintain the eco-friendliness and safety level of the process, recycling of leaching residue and the acid solution should be preferred or recommended for future research [5-10].

3.2 Catalyst Characterization by FTIR (Fourier – Transform Infrared Spectroscopy) and SEM – EDX (Scanning Electron Microscope – Energy Dispersive X-Ray)

The FTIR spectra of spent nickel catalyst, NiO-HC and NiO-HS are displayed in Figure 2. The FTIR analysis was conducted to compare the functional group of NiO or nickel catalysts treated using HCl and H_2SO_4 solvents. The analysis of NiO catalysts in waste nickel catalysts was performed within the wave number range of 4000/cm to 400/cm. In the FTIR analysis, the appearance of peaks on the FTIR spectra of nickel catalyst treated with HCl or NiO-HC (blue) at wave numbers 402.78/cm and 862.97/cm indicated the presence of the Ni-O group. The peak at wave number 1434.39/cm corresponds to the C-O group, which may have resulted from direct contact of the precursor sample with CO_2 in the air during the mixing process. This cause the conversion of $Ni(OH)_2$ precursor to $NiCO_3$-ish sample which is more thermally stable compare to $Ni(OH)_2$ [11]. The FTIR spectra of nickel catalyst treated with H_2SO4 or NiO-HS (red) shows two peaks observed at 396.4/cm and 1102.85/cm, corresponding to the Ni-O group and sulfate group, respectively. The presence of sulfate is the result of a side product during the precipitation process (Na_2SO_4). The spent nickel catalyst waste FTIR spectra (black) still exhibits numerous unidentified impurities which are predicted as carbonaceous impurities which poison the catalyst. In other words, based on the FTIR analysis results, the Ni-O group was detected within the wave number range of 400-1000/cm, proving that the formation of NiO is successful in every sample. The slight shift observed in NiO peaks can be caused by the presence of NaCl and Na_2SO_4 groups in the respective sample as the side product of the precipitation. [11-14].

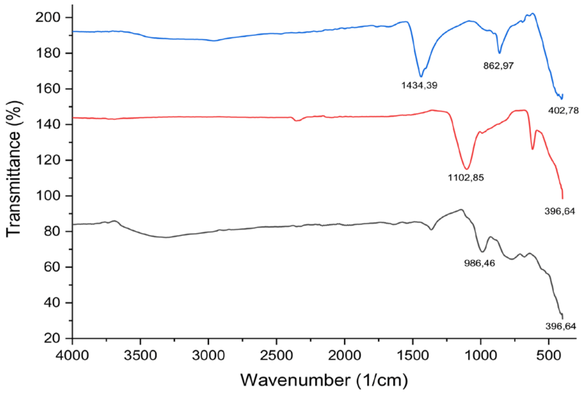

Figure 2. FTIR Spectra of NiO-HC(Blue), NiO-HS (Red), and Spent Nickel catalyst (Black)

The as-prepared NiO samples were characterized using SEM-EDX. The SEM images of NiO-HS and NiO-HC are depicted in Figure 3. The NiO HC particles exhibit quasi-spherical/cubical particles; on the other hand, NiO-HS particles exhibit a flake-like shape. ImageJ software was used to calculate the particle size of the sample [15,16]. Based on statistical calculation, the average particle size of NiO-HC is 84 nm with a maximum primary particle size of 134 nm and a minimum particle size of 50 nm. Meanwhile, the NiO-HS average particle size is 107 nm with a maximum primary particle size of 214 nm and a minimum particle size of 42 nm.

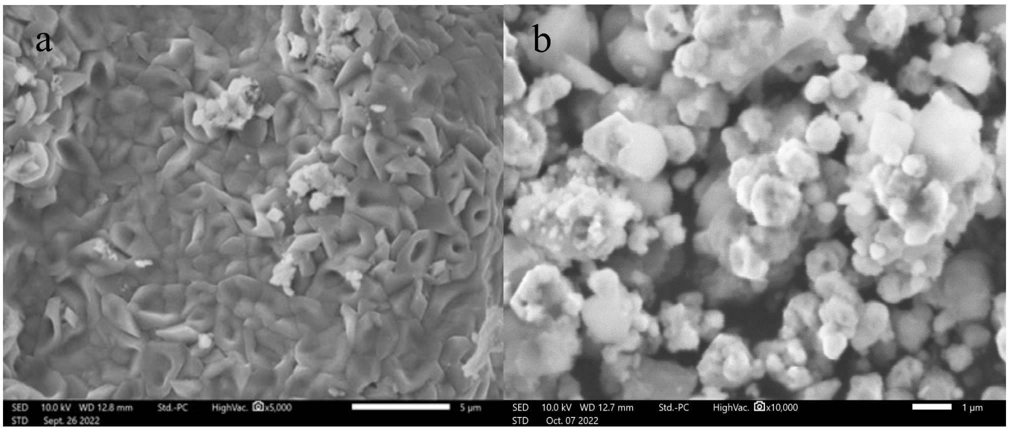

Figure 3. SEM Images of (a) NiO-HS sample and (b) NiO-HC sample

The EDX test results are shown in Figure 4. The EDX test in this study aims to demonstrate the presence of the nickel content in the regenerated NiO samples. The EDX test was conducted after the morphology analysis using the same equipment.

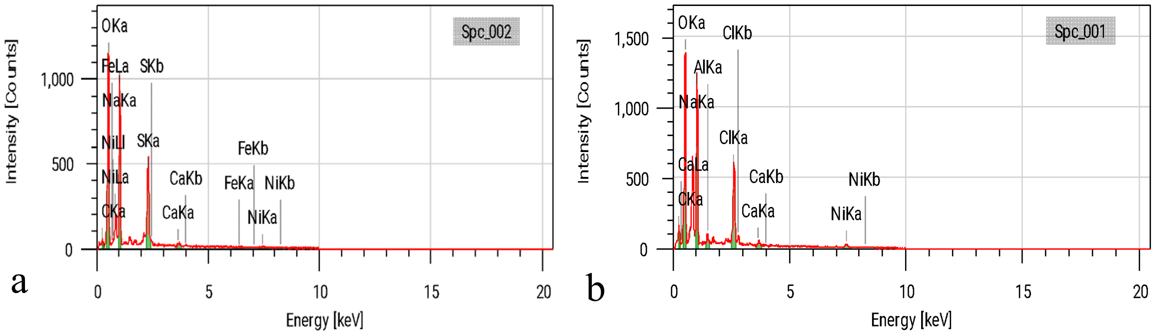

Figure 4. EDX spectra of (a) NiO-HS and (b) NiO-HC

Axis Y indicates the amount of the intensity of each element which is proportional to the concentration of the element in the sample, and Axis X marks the level of energy of every element, which is distinctive for every element. Each element has a specific energy level, where 2 points in the spectrum will be detected, for nickel metals are at energy levels in the range of 200-400 and 7-8 keV. The detailed quantitative analysis of the element is listed in Table 1.

Tabel 1. Nickel Catalyst EDX Characteristics Result

Element	Content (% wt.)	
	NiO-HS	NiO-HC
C	3.85±0.36	5.66±0.34
O	40.49±1.21	28.87±0.81
Na	24.34±0.93	19.70±0.68
S	18.21±0.88	-
Ca	2.05±0.45	1.79±0.32
Fe	0.13±0.48	-
Ni	10.94±4.87	25.98±5.44
Cl	-	16.89±0.72
Al	-	1.11±0.17

The results of EDX analysis in Table 1 showed % the NiO-HS has a nickel content of 10.94 ± 4.87 %wt and the NiO-HC has a nickel content of 25.98 ± 5.44 %wt. In NiO-HS sample, Na and S are larger than the Ni. This is in agreement with the FTIR analysis where the side product exists in the final sample. This is also applied to the NiO-HC sample where the Na and Cl is present in significant amount. Thus, it can be concluded that double replacement reaction occur during the reaction process can be expressed in the following reaction [17,18] (3-6):

Leaching reaction:

$$NiO_{(s)} + 2HCl_{(aq)} \rightarrow NiCl_{2(aq)} + H_2O_{(l)} \tag{3}$$

$$NiO_{(s)} + H_2SO_{4(aq)} \rightarrow NiSO_{4(aq)} + H_2O_{(l)} \tag{4}$$

$$NiCl_{2(aq)} + 2NaOH_{(aq)} \rightarrow Ni(OH)_{2(s)} + 2NaCl_{(aq)} \tag{5}$$

$$NiSO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Ni(OH)_{2(s)} + Na_2SO_{4(aq)} \tag{6}$$

Since the NaCl and Na_2SO_4 is highly soluble, the removal of such impurities can be performed by simple washing step. The X-ray diffraction spectra of NiO-HC after washing treatment can be seen in figure 5. The sample exhibited the cubical phase of NiO with no observable impurities. This shows that simple washing can remove the side-products. The peaks detected in the pattern proved that during the sintering process, highly crystalline product is achieved. Moreover, the presence of side-products in the precursor may help with the formation of high-crystalline NiO or any oxides material based on recent studies [19,20]. Based on overall analysis, NiO is successfully prepared from the spent nickel catalyst. However, to achieve better quality, the sample should be washed. In addition, the NiO characteristic should be further investigated based on its structure, surface area, and reactivity in the next research.

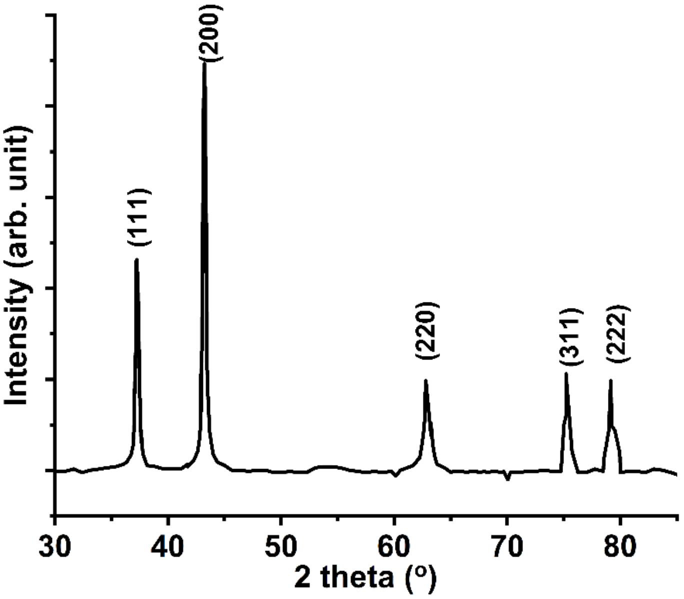

Figure 5. XRD Pattern of NiO-HC after washing

4. CONCLUSION

Based on research and analysis, the following conclusions can be drawn:

1. The extraction of the nickel from spent catalyst via hydrometallurgical leaching was successfully carried out at room temperature by adding H_2O_2 to increase the percentage of the nickel recovery.
2. Based on the FTIR data, each sample have Ni-O bond with several impurities from the side products. Based on the SEM analysis, the sample's morphology is affected by the leaching agents.
3. The highest nickel content was obtained by HCl treatment, which was 25.98%wt. Meanwhile using sulfuric acid (H_2SO_4) treatment achieve a 10.94% Ni composition in the product. The composition can be improved by adding a washing step post sintering process which is confirmed by XRD analysis.

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