

## Synthesis and Characterization Catalyst $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Using XRD Analysis

Selpiana Selpiana<sup>1,\*</sup>, David Bahrin<sup>1</sup>, RR Yunita Bayu Ningsih<sup>2</sup>, Aditia H Akbar<sup>1</sup>, Ayu Permatasari<sup>1</sup>

<sup>1</sup>Chemical Engineering, Faculty of Engineering, Universitas Sriwijaya, Jl. Raya Indralaya-Prabumulih Km. 32 Indralaya 30662, Indonesia

<sup>2</sup>Mining Engineering, Faculty of Engineering, Universitas Sriwijaya, Jl. Raya Indralaya-Prabumulih Km. 32 Indralaya 30662, Indonesia

\*Corresponding Author: [selpiana@ft.unsri.ac.id](mailto:selpiana@ft.unsri.ac.id)

### Abstract

Catalysts have an essential role in chemical processes because they can control reactions and produce the desired product. In general, catalysts function to speed up chemical reactions that can take place by lowering the activation energy. By decreasing the activation energy, the minimum energy required for the collision is reduced so that the reaction can occur faster. Selection of the suitable material to be used as a catalyst is an effort that must be made to achieve a successful process and obtain cost efficiency. The choice of material as metal and support was the aim of this research. Aluminum (Al) was the material chosen as metal and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the support. The method used in the synthesis of this catalyst was dry impregnation. It is hoped that more metal will stick to the support. In this study, catalyst synthesis was carried out with two variations of treatment. The first treatment was using Al as metal and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the support. The second treatment did not use metal only  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the support. The resulting material was characterized by XRD analysis. The analysis found that in the diffraction pattern of Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the peaks appeared at  $2\theta = 37^\circ$ ;  $46^\circ$  and  $67^\circ$ . The impregnation process went well. Aluminum was evenly distributed (sticks) to the pore surface of the support and entered the pores.

*Keywords: Catalyst, metal-support, Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, dry impregnation, XRD*

### Abstrak

Katalis memiliki peranan penting dalam proses kimia karena dapat mengendalikan reaksi dan menghasilkan produk yang diinginkan. Pada umumnya katalis berfungsi untuk mempercepat reaksi kimia yang dapat berlangsung dengan menurunkan energi aktivasi. Melalui penurunan energi aktivasi tersebut maka energi minimum yang dibutuhkan untuk terjadinya tumbukkan berkurang, sehingga reaksi dapat terjadi lebih cepat. Pemilihan material yang tepat yang akan digunakan sebagai katalis merupakan upaya yang harus dilakukan agar dicapai keberhasilan proses dan diperoleh efisiensi biaya. Pemilihan material sebagai metal dan pengemban merupakan tujuan penelitian ini. Aluminium (Al) merupakan material yang dipilih sebagai metal dan  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sebagai pengemban. Metode yang digunakan dalam sintesis katalis ini adalah impregnasi kering, diharapkan lebih banyak metal yang menempel pada pengemban. Pada penelitian ini dilakukan sintesis katalis dengan dua variasi perlakuan, perlakuan pertama yaitu dengan menggunakan Al sebagai metal dan  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sebagai pengemban, perlakuan kedua tidak menggunakan metal hanya  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sebagai pengemban. Material hasil impregnasi dikarakterisasi dengan analisa XRD. Dari hasil analisa diperoleh bahwa pola difraktogram Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, puncak-puncak muncul pada  $2\theta = 37^\circ$ ,  $46^\circ$  dan  $67^\circ$ . Proses impregnasi berjalan dengan baik. Al tidak hanya terdistribusi merata saja (menempel) di permukaan pori penyangga dan tapi masuk ke dalam pori-porinya.

*Kata kunci: Katalis, metal-pengemban, Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Impregnasi kering, XRD*

### Article Info

Received 28 November 2021

Received in revised 24 January 2022

Accepted 25 January 2022

Available online 20

February 2022

## INTRODUCTION

A catalyst is a substance that can direct or control the rate of a chemical reaction, even though the substance itself does not react permanently [1]. Catalysts can affect the rate of a reaction by lowering the activation energy. Activation energy is an inhibitor that prevents less energetic molecules from reacting [2]. The decrease in activation energy causes the energy needed for collisions to decrease so that the reaction can occur more quickly [3]. The change in the direction of the reaction aims to produce the desired product with high selectivity [4]. In addition to speeding up the reaction rate, catalysts can initiate the occurrence of a certain product, direct the reaction towards a certain product, and minimize or eliminate unwanted side reactions [5].

Based on the phase, the catalyst is divided into two, namely homogeneous and heterogeneous catalysts. Homogeneous catalysts are catalysts in the same phase as the reaction mixture phase [6], while heterogeneous catalysts are in different phases with reactants and products [7]. Cracking catalysts in the form of heterogeneous (solid) catalysts with metal-bearing systems are widely used in the cracking process of long-chain hydrocarbon fractions, such as plastics (long-chain polymers) or crude oil into short-chain hydrocarbon fractions. Heterogeneous catalysts that are only metal or single metal which have low heat stability, so they can undergo a sintering effect that can deactivate the catalyst or decrease its surface area. Accordingly, single metal or metal catalysts need to be spread over the support material. Which has a large surface area, pores, is stable to heat and chemicals, and mechanical strength. The goal is to avoid the sintering effect (melting of the catalyst) [8].

The holding system can increase the catalyst's ability, providing several advantages, including forming a homogeneous and uniform dispersion system throughout the pores. This homogeneous system results in an increased active surface area. The life of the catalyst and the resistance to deactivation of the catalyst also increased due to the more stable condition of the particles. Another advantage is that it can prevent the accumulation of the active metal components during the catalytic reaction. The metal is evenly distributed on the carrier, and the sintering process cannot occur easily.

Metal is usually in the metal carrier system expressed on the carrier material in small amounts. Most of the metal or metal atoms are present on the surface of the carrier. Heterogeneous catalysts have two types of active sites, namely acid sites and metal sites. Acid sites are found in carrier materials such as

alumina or zeolite, which serve as metal sites' distribution sites. In contrast, metal sites are derived from impermeable metal to produce an active surface. Heterogeneous catalysts are generally composed of several components, including the active component (active side), support, and promoter [9].

The active component is a catalyst component that is responsible for chemical reactions. The selection of active components is the first step in making heterogeneous catalysts. This component serves to speed up and direct the reaction. In solid catalyst catalysis, the reaction occurs on the catalyst's surface. Hence, the support required for a catalyst is that it has a large surface area and pores evenly dispersed on the surface. The promoter is the third compound that can be added in a heterogeneous catalyst and usually in small amounts. The addition of a promoter aims to improve the performance of the catalyst [10].

This research aimed at synthesizing a catalyst that was used in cracking plastic waste by considering the selected metal-bearing system. In this study, Aluminum (Al) is metal. Al is a metallic material consisting of atoms formed in a three-dimensional arrangement in a crystalline phase [11]. Aluminum can attract electrons compared to other metals, so it is very suitable as an active component in catalysts and even corrosion resistance. Alumina has good thermal conductivity, high stability (strength, stiffness, and hardness), and has a large pore structure [12]. The catalyst preparation method chosen is dry impregnation because metal transfer into the carrier occurs rapidly. The transfer of active components into the carrier pores occurs by convection. The dry impregnation process is more effective than the wet impregnation method [13].

## MATERIALS AND METHODS

### Materials

This research is an experimental activity. Catalyst preparation was carried out at the Process Engineering Laboratory, Chemical Industrial Products, Faculty of Engineering, Sriwijaya University. In contrast, material characterization was carried out using XRD analysis (Bruker D8 Advanced) in Research Center Nanoscience and Nanotechnology (RCNN), ITB.

The materials used are  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Merck, 99%), AlCl<sub>3</sub> (Merck, 99.999%), and *distilled water* (Brataco Chemical). As a fixed variable, namely the amount and type of raw material, while for the independent variable, metal (Al) and no metal were used to synthesize the material.

## Methods

### Synthesis $\gamma$ - $\text{Al}_2\text{O}_3$

$\gamma$ - $\text{Al}_2\text{O}_3$  was calcined at a temperature of 600 °C for 2 hours using a muffle furnace.

### Synthesis $\text{Al}/\gamma$ - $\text{Al}_2\text{O}_3$

$\text{AlCl}_3$  as much 445 g was dissolved in 181 mL of distilled water, while stirring with the addition of distilled water until homogeneous. The solution was added with 360 g of  $\gamma$ - $\text{Al}_2\text{O}_3$ , the addition was carried out little by a little while stirring, then dried at an initial drying temperature of 32 °C for 6 hours and continued with final drying for 15 hours at 110 °C. The drying product was then calcined for 2 hours at 600 °C in a muffle furnace. The material produced from the catalyst synthesis was characterized by using XRD analysis.

## RESULTS AND DISCUSSION

### Catalyst Synthesis

In this study, the synthesis process of  $\text{Al}/\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was carried out in three stages, namely impregnation, drying, and calcinations. Impregnation is a metal dispersion step (metal) from a precursor solution into the support pores. Based on research conducted by Shah et al. [14], 20% of metal dispersed into the catalyst support is the best ratio because it has high activity and selectivity. The success of the metal dispersion process into the support is influenced by the method chosen during impregnation. The metal dispersion process in this study was carried out using the dry impregnation method. Since, in this method, the precursor solution transferred into the support by capillary action. Metal diffusion transported into the support pores during the drying process, so the possibility of metal losses dispersed into the support is very slight [15].

Dry stage impregnation began with the process of dissolving the precursor salt with a suitable solvent. This study used  $\text{AlCl}_3$  as the precursor salt and water as the solvent agent. The reason for choosing  $\text{AlCl}_3$  as the precursor salt is easily soluble in water with a solubility value of 45.1 g/100 mL  $\text{H}_2\text{O}$  at a temperature of 30°C [16].

Solvent addition in the dry impregnation process was carried out to a minimum [13]. In this study, the addition of water was based on the stoichiometric ratio of  $\text{AlCl}_3$  to water. The following is a reaction between  $\text{AlCl}_3$  and water ( $\text{H}_2\text{O}$ ):



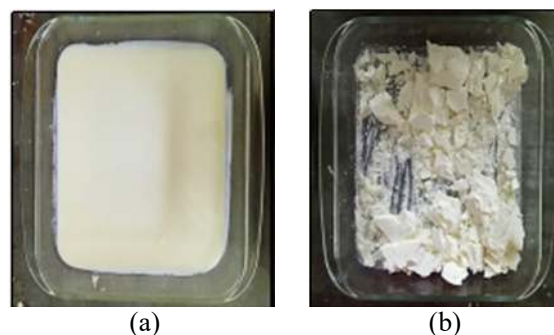
Distilled water was added gradually until all the  $\text{AlCl}_3$  salt was dissolved until homogeneous. The resulting  $\text{AlCl}_3$  solution then was mixed with 80% wt

$\text{Al}_2\text{O}_3$  of the required catalyst mass [14]. Mixing  $\text{Al}_2\text{O}_3$  as support was done gradually while stirring; the goal was to mix evenly. Figure 1 shows the results of the process of mixing  $\text{AlCl}_3$  solution with  $\gamma$ - $\text{Al}_2\text{O}_3$ .



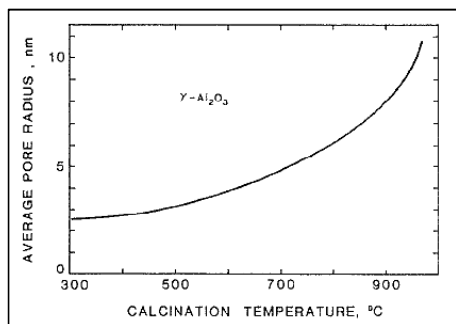
**Figure 1.** Results of Dissolution of  $\text{AlCl}_3$  with  $\text{Al}_2\text{O}_3$

The drying stage in the dry impregnation method was divided into two, namely initial drying and final drying. Initial drying was carried out at a temperature of 32 °C with a drying time of 6 hours. This drying aims to process the diffusion of  $\text{AlCl}_3$  solution into  $\text{Al}_2\text{O}_3$  by capillary action [13].



**Figure 2.** (a) After Initial Drying, (b) After Final Drying.

Calcination was the last step in the synthesis of  $\text{Al}/\gamma$ - $\text{Al}_2\text{O}_3$  catalyst. The calcination step must be carried out directly after the final drying process because the samples resulting from the final drying have hygroscopic properties. Sample calcination was carried out using a muffle furnace with a temperature setting of 600 °C for 2 hours. The choice of temperature 600 °C aimed to remove impurities, strengthen the interaction and mobility of the metal with the support, and increase the pore size of the support so that the pore surface area of the support will be larger. Figure 3 showed a graph of the relationship between the calcination temperature and the pore radius.



**Figure 3.** Correlation between Calcination Temperature and Pore Radius [17]

Figure 3 showed that in the calcination temperature range of 300-900 °C,  $\text{Al}_2\text{O}_3$  changed to the  $\gamma\text{-Al}_2\text{O}_3$  phase. The higher the calcination temperature, the higher the average pore radius was. The dispersion of the active metal in the pore support evenly distributed along with the increase in the average pore radius so that the surface area of the active metal increases. The choice of calcination temperature of 600 °C in this study was due to the melting point of aluminum of 660.32 °C [18]. Therefore, when the calcination temperature increased to 900 °C, aluminum as an active metal would experience a sintering effect that could deactivate the catalyst or decrease its surface area. The calcination time of 2 hours aimed to remove impurities that are remaining after the final drying process because the presence of other remaining compounds could reduce the activity and selectivity of the catalyst [19].

The calcined catalyst was carried out in stages of size reduction to have a uniform size. Figure 4 shows the results of the catalyst sample after calcination process of final drying.



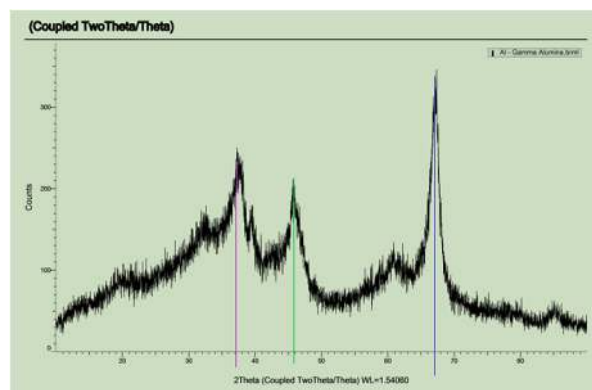
**Figure 4.**  $\text{Al}/\gamma\text{-Al}_2\text{O}_3$  Catalyst after Calcination Temperature 600 °C

#### Catalyst Characterization

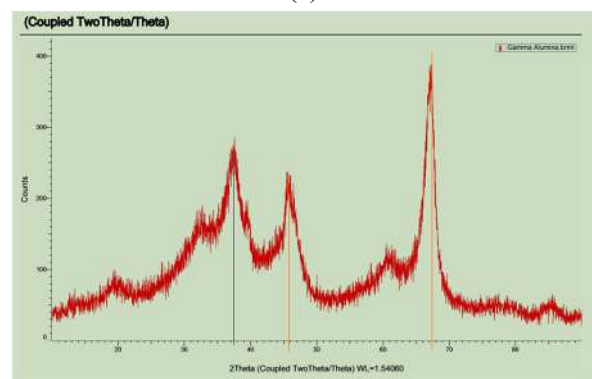
X-ray diffraction (XRD) is an effective method for determining the crystal structure of materials. This analysis is carried out to detect crystalline materials

with crystal domains greater than 3-5 nm. In addition, this method can also be used to characterize the bulk crystal structure and chemical phase of the analyzed material. Materials can be classified as crystalline and amorphous materials. The crystalline material can be single crystal or polycrystalline. Crystalline materials are composed of atoms in a regular three-dimensional pattern. Amorphous materials are materials with atomic conditions that are not arranged regularly [17]. An X-ray is a form of electromagnetic radiation having a wavelength range of 0.01-0.7 nm, proportional to the distance between the lattice planes in the crystal. These scattered waves produce a diffraction pattern. Diffraction from different atomic planes provides information about the arrangement of atoms in the crystal. The result of the diffractogram pattern is used for quantitative and qualitative analysis [20].

The quantitative analysis can be done by calculating the comparison of the relative peak intensity of the material with the reference as seen in Figure 5.



(a)



(b)

**Figure 5.** XRD diffractogram pattern, (a)  $\gamma\text{-Al}_2\text{O}_3$  and (b)  $\text{Al}/\gamma\text{-Al}_2\text{O}_3$

Based on research conducted by Okamoto [21], that type (gamma) alumina has a specific diffractogram

pattern, producing peaks at  $2\theta = 37^\circ$ ;  $46^\circ$  and  $67^\circ$ . Based on Figure 5 (a), the diffractogram pattern  $\text{Al}_2\text{O}_3$  showed a shift in the peaks, namely  $2\theta = 37.46^\circ$ ;  $46^\circ$  and  $67.35^\circ$ . Peak shift was from  $37^\circ$  to  $37.46^\circ$  and  $67^\circ$  to  $67.35^\circ$ . From the resulting XRD pattern, there were no new peaks; only peak shifts occurred. This was presumably because the calcination and drying processes had not run perfectly.

In figure 5 (b), the  $\text{Al}/\gamma\text{-Al}_2\text{O}_3$ , yield impregnation of aluminum (Al) metal was on an alumina carrier. From the resulting pattern, it could be seen that the peaks appeared at  $2\theta = 37^\circ$ ;  $46^\circ$  and  $67^\circ$ . Based on this data, it means that there is no peak shift or the formation of new compounds. The peaks produced in Figure 5 (b) correspond to the pattern of the  $\gamma\text{-Al}_2\text{O}_3$  diffractogram of research results [21], which mean that the impregnation process is running well. Al was evenly distributed (sticking) on the surface of the support pores and entered the pores.

Based on the XRD test, the percentage value of crystallinity  $\text{Al}/\gamma\text{-Al}_2\text{O}_3$  was 37.1 and the amorphous percentage value was 62.9. Crystallinity percent is a value that expresses the ratio between the crystal area and the total crystal and amorphous area, while the amorphous percent is a value that defines the amount of content in a solid that does not have a crystal structure and is irregular. While the percentage of crystallinity  $\text{Al}_2\text{O}_3$  was 31 and the percentage of amorphous was 69.

## CONCLUSION

The dry impregnation method can synthesize the catalyst with metal Al and carrier  $\text{Al}_2\text{O}_3$ . From the XRD analysis results, the impregnation process of Al metal and alumina carrier was running well. Al is evenly distributed (sticks) to the pore surface of the support and enters the pores.

## ACKNOWLEDGMENT

The authors would like to thank LPPM Universitas Sriwijaya for funding this research.

## REFERENCES

- [1] C. Squire, M. Andrews, and M. Tamboukou, *Catalyst Handbook*, 2nd ed. New York: CRC Press, 2013.
- [2] Q. Song, H. Zhao, J. Jia, L. Yang, W. Lv, J. Bao, X. Shu, Q. Gu, P. Zhang, "Pyrolysis of municipal solid waste with iron-based additives: A study on the kinetic, product distribution and catalytic mechanisms," *J. Clean. Prod.*, vol. 258, p. 120682, 2020, doi: 10.1016/j.jclepro.2020.120682.
- [3] C. N. Arenas, M. V. Navarro, and J. D. Martínez, "Pyrolysis kinetics of biomass wastes using isoconversional methods and the distributed activation energy model," *Bioresour. Technol.*, vol. 288, p. 121485, 2019, doi: 10.1016/j.biortech.2019.121485.
- [4] A. Dey, S. K. Sinha, T. K. Achar, and D. Maiti, "Accessing Remote meta- and para-C(sp<sup>2</sup>)-H Bonds with Covalently Attached Directing Groups," *Angew. Chemie - Int. Ed.*, vol. 58, no. 32, pp. 10820–10843, 2019, doi: 10.1002/anie.201812116.
- [5] S. Sun, H. Li, and Z. J. Xu, "Impact of Surface Area in Evaluation of Catalyst Activity," *Joule*, vol. 2, no. 6, pp. 1024–1027, 2018, doi: 10.1016/j.joule.2018.05.003.
- [6] J. N. Harvey, F. Himo, F. Maseras, and L. Perrin, "Scope and Challenge of Computational Methods for Studying Mechanism and Reactivity in Homogeneous Catalysis," *ACS Catal.*, vol. 9, no. 8, pp. 6803–6813, 2019, doi: 10.1021/acscatal.9b01537.
- [7] J. M. Thomas and W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*. VCH, 1997.
- [8] M. Ozawa, T. Okouchi, and M. Haneda, "Three way catalytic activity of thermally degenerated Pt/ $\text{Al}_2\text{O}_3$  and Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> modified  $\text{Al}_2\text{O}_3$  model catalysts," *Catal. Today*, vol. 242, pp. 329–337, 2015, doi: 10.1016/j.cattod.2014.06.013.
- [9] S. Lee, A. Patra, P. Christopher, D. G. Vlachos, and S. Caratzoulas, "Theoretical Study of Ethylene Hydroformylation on Atomically Dispersed Rh/ $\text{Al}_2\text{O}_3$  Catalysts: Reaction Mechanism and Influence of the ReOxPromoter," *ACS Catal.*, vol. 11, no. 15, pp. 9506–9518, 2021, doi: 10.1021/acscatal.1c00705.
- [10] X. Cui, W. Li, P. Ryabchuk, K. Junge, and M. Beller, "Bridging homogeneous and heterogeneous catalysis by heterogeneous single-metal-site catalysts," *Nat. Catal.*, vol. 1, no. 6, pp. 385–397, 2018, doi: 10.1038/s41929-018-0090-9.
- [11] T. T. Quoc, D. Nguyen Trong, and Ş. Țălu, "Study on the Influence of Factors on the Structure and Mechanical Properties of Amorphous Aluminium by Molecular Dynamics Method," *Adv. Mater. Sci. Eng.*, vol. 2021, 2021, doi: 10.1155/2021/5564644.
- [12] R. Zotov, E. Meshcheryakov, A. Livanova, T. Minakova, O. Magaev, L. Isupova, I. Kurzina,

- “Influence of the composition, structure, and physical and chemical properties of aluminium-oxide-based sorbents on water adsorption ability,” *Materials (Basel)*, vol. 11, no. 1, 2018, doi: 10.3390/ma11010132.
- [13] J. Regalbuto, *Strong Electrostatic Adsorption of Metals onto Catalyst Supports*. in *Catalyst Preparation: Science and Engineering*, 297, 2006.
- [14] J. Shah, M. R. Jan, and Adnan, “Catalytic activity of metal impregnated catalysts for degradation of waste polystyrene,” *J. Ind. Eng. Chem.*, vol. 20, no. 5, pp. 3604–3611, 2014, doi: 10.1016/j.jiec.2013.12.055.
- [15] M. A. Islam, D. W. Morton, B. B. Johnson, B. K. Pramanik, B. Mainali, and M. J. Angove, “Metal ion and contaminant sorption onto aluminium oxide-based materials: A review and future research,” *J. Environ. Chem. Eng.*, vol. 6, no. 6, pp. 6853–6869, 2018, doi: 10.1016/j.jece.2018.10.045.
- [16] M. L. Williams, “Handbook of Chemistry and Physics,” *Occup. Environ. Med.*, vol. 53, no. 7, pp. 504–504, 1996, doi: 10.1136/oem.53.7.504.
- [17] C. Perego and P. Villa, “Catalyst preparation methods,” *Catal. Today*, vol. 34, no. 3–4, pp. 281–305, 1997, doi: 10.1016/S0920-5861(96)00055-7.
- [18] C. Chatillon, N. Eustathopoulos, D. Chatain, and V. Laurent, “Wettability of monocrystalline alumina by aluminium between its melting point and 1273 K,” *Acta Metall.*, vol. 36, no. 7, pp. 1797–1803, 1988.
- [19] C. W. Tang, C. C. Kuo, M. C. Kuo, C. Bin Wang, and S. H. Chien, “Influence of pretreatment conditions on low-temperature carbon monoxide oxidation over CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> catalysts,” *Appl. Catal. A Gen.*, vol. 309, no. 1, pp. 37–43, 2006, doi: 10.1016/j.apcata.2006.04.020.
- [20] C. F. Holder and R. E. Schaak, “Tutorial on Powder X-ray Diffraction for Characterizing Nanoscale Materials,” *ACS Nano*, vol. 13, no. 7, pp. 7359–7365, 2019, doi: 10.1021/acsnano.9b05157.
- [21] Y. Okamoto *et al.*, “A study on the preparation of supported metal oxide catalysts using JRC-reference catalysts. I. Preparation of a molybdena - Alumina catalyst. Part 1. Surface area of alumina,” *Appl. Catal. A Gen.*, vol. 170, no. 2, pp. 315–328, 1998, doi: 10.1016/S0920-860X(98)00064-7.