The Effect of Binder Concentration on the Ability of Gelcasting Porous Ceramics as TiO2 Support Catalysts

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Abstract. This study aims to determine the effect of binder concentration on the ability of porous ceramics as TiO2 support catalyst. The porous ceramic synthesis used was the gelcasting method using natural clay as matrix, cassava starch as binder and CMC as dispersant. The concentration of cassava starch binder used were 2%, 4%, 6%, 8%, 10%. The methods used in catalyst supporting are adsorption method and sol gel coating method. Analysis of TiO2 catalyst content in porous ceramics using XRF instrument. The results obtained showed that the concentration of cassava starch affects the ability of porous ceramics as TiO2 catalyst support. The largest percentage of TiO2 catalyst with adsorption method was achieved at a binder concentration of 8% with a catalyst percentage of 38.9% while with sol gel coating method was achieved at a binder concentration of 4% with a catalyst percentage of 20.11%.

Keywords: Binder, Cassava Starch, Porous Ceramic, Gelcasting, Support Catalysts

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INTRODUCTION

Ceramic are an industrial product that is very important and was growing rapidly lately. This is due to the rapid development of science and technology which has influenced and changed various aspects of life. As is the existence of science and technology about ceramics, a ceramic product can be produced for various needs of the mechanical, electronic, filter and even aerospace technology industries.

One type of ceramic that was being developed is porous ceramic. The synthesis of porous ceramics has been widely carried out, including using the dry-pressing method (Harefa,2009), extrusion (Mongkolkachit, 2010), and slip casting (Ramlan, 2009;Tambunan, 2008; Sukania, 2007). These method has several constraints, for example it requires large pressure, must use a porous mold, and the manufacturing method is quite complicated Yang, 2018. One method that can overcome its limitation is the gelcasting method.

The gelcasting method is a colloidal ceramic synthesis method that involves in situ polymerization in a ceramic body. The basic principle of the method is the polymer dispersed into the silica alumina geopolymer. In the gelcasting process, the ceramic powder is dispersed in a solution containing monomer and crosslinker. To obtain high porosity ceramics, monomer and crosslinker ratio variations were studied due to pore formation in the ceramic body based on the loss of the polymer system in the ceramic body when sintering.

Similar research has been carried out by Dhara, 2002 and Liu, 2001 to make porous ceramics based on alumina and kaolin, AMAM monomer and MBAM initiated by APS with tetramethyl ethylene diammine (TEMED) catalyst with an APS: TEMED ratio of 2:1. The resulting pore diameter was about 1.50 µm on average. The ratio of monomer and crosslinker as binder affects the porosity of the ceramic, the higher the ratio of monomer and cross binder, the porosity increased. The monomer and crosslinker ratio also affects the pore character Putri, 2018 and the hardness of ceramic Putri, 2016.

Previous research has carried out the synthesis of porous ceramics using the gelcasting method with polyacrylamide polymer as a binder. The monomer used is acrylamide (AM) with a crosslinker of methylene bisacrylamide (MBAM) Putri, 2013Putri, 2018. However, this polymer is toxic, so an alternative is needed in producing environmentally friendly porous gelcasting ceramics. using several natural materials as a binder including starch Alag, 2018, sago starch Jamaludin, 2014, Jamaludin, 2015, rice flour Wan, 2014. In this study, polymers from natural materials will be used, namely cassava starch (starch) as a binder. which will play the role of the pore template.

Porous ceramics have been successfully made and used as filters in the pouring of liquid metals, are used as absorbents for organic and inorganic waste, also can be used as catalyst carriers for the photodegradation of dyes Putri, 2018. One type of catalyst that is most widely used in the photodegradation process is TiO_2, because it has a fairly high photocatalytic activity.

Several methods used in the process of application porous materials as a support catalysts are impregnation, ion exchange or adsorption, co-precipitation, and coating or deposition methods. The impregnation method is a method commonly used to carry catalysts on metals but the method is less efficient because the method is quite complicated. Another method that is easier and most often used is the adsorption by Barmeh, 2019; adsorption of the Al_2O_3 catalyst onto the ceramic body was carried out by Ismagilov, 1997; adsorption of the catalyst onto the Ag-ceramic bodies was carried out by Julbe, 2001.

Another method is coating Musa, 2017; TiO_2 catalyst coating to tubular ceramic bodies Wang, 2008, TiO_2 catalyst coating was also carried out Li, 2007Yang, 2018Barmeh, 2019Shakeri, 2018. There are several coating methods, namely the dip coating performed by Wang, 2008, sol gel coating using precursor $Ti(SO_4)_2$ and polyvinylpyrrolidone (PVP) conducted by Kishimoto, 2003. The catalyst carrier method that will be used in this research is the adsorption and coating method to investigation which method is the most effective to use as a TiO_2 catalyst support.

RESEARCH METHOD

Synthesis of Porous Ceramics using Gelcasting Method

5 g clay and 0.1 g CMC dispersant are added to 1.5 mL distilled water. The suspension is mixed and added with cassava starch with a variation concentration of 2%, 4%, 6%, 8%, 10% by weight of the clay. The suspension was molded, aerated to dry and heated to 70 °C for 2 hours. The ceramic body is then sintered at a temperature of 600 °C at rate of 60 °C/hour and up to 1100 °C at rate of 300 °C/hour.

Porous Ceramics as a TiO_2 Catalyst Support

a. Adsorption Methods

A total of 2.4 g of PVA was dissolved in 150 mL hot distilled water (70 °C), stirred until the PVA was completely dissolved. Add 40 mL of $TiCl_4$, 120 mL of ethanol, and 6 mL of acetic acid. The solution was stirred for 3 hours using a magnetic stirrer with a temperature of 105 °C. Furthermore, porous ceramics were added to the solution and immersed for 17 hours. Then the ceramics that have been induced are dried at 60 °C and calcined at 600 °C for 3 hours.

b. Sol-Gel Coating Method

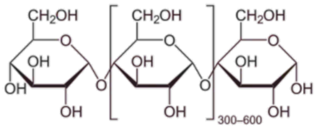
A total of 25 mL of ammonium hydroxide (NH_4OH) and 25 mL of ammonium sulfate ($(NH_4)_2SO_4$). The mixture was put into $TiCl_4$ solution, then stirred for 6 hours at 85 °C using a magnetic stirrer. The porous ceramic is then immersed in the mixture for 5 minutes while still stirring it, then the ceramic is removed from the mixture. For drying, it is carried out at 60 °C, and calcined at 600 °C for 3 hours.

Analysis of TiO_2 Content Carried Out in Gelcasting Porous Ceramic

Gelcasting porous ceramics were analyzed for their metal oxide content using Thermo Fisher Scientific's XRF with x-ray path: air, Eff. stationary: 13.0 mm and Eff. Area: 132.7 mm^2. The same treatment was done for porous ceramics that have been used as support catalyst to determine TiO_2 content successfully carried in the ceramic body.

RESULTS AND DISCUSSION

Cassava starch is used as a binder because it is a natural polymer which, when heated, releases small molecules which act as pore templates. Cassava starch will release CO_2 and water molecules from the ceramic body when sintered, according to the equation (1).



$$+ O_2 \xrightarrow{\Delta} nCO_2 \; +. \; nH_2O$$

cassava starch (1)

Porous ceramics were analyzed for metal oxide content to compare the TiO_2 content before and after it was applied as a catalyst support. The XRF spectrum of gelcasting porous ceramics with various binder concentrations was shown in Fig. 1.

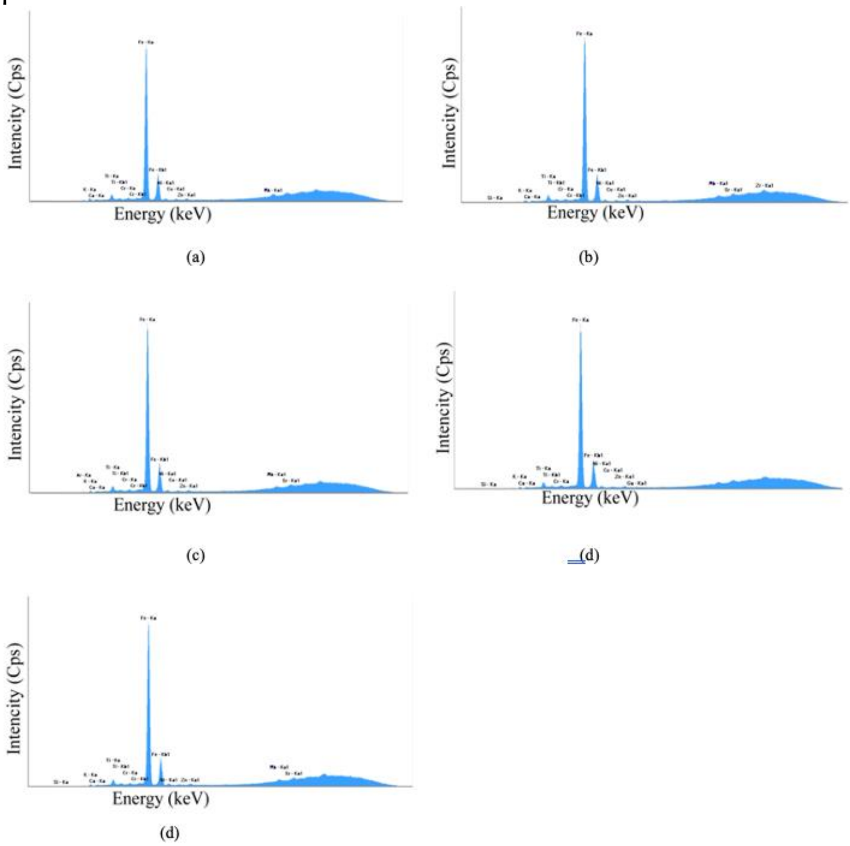


Fig. 1. XRF spectrum of gelcasted porous ceramic

Based on the XRF spectrum in Fig. 1., it can be concluded that there is metal oxide TiO_2 with a very small intensity. The results of the spectrum interpretation are in Fig. 1. shown in Table 1.

Table 1. Percentage of TiO2 on gelcasted porous ceramic

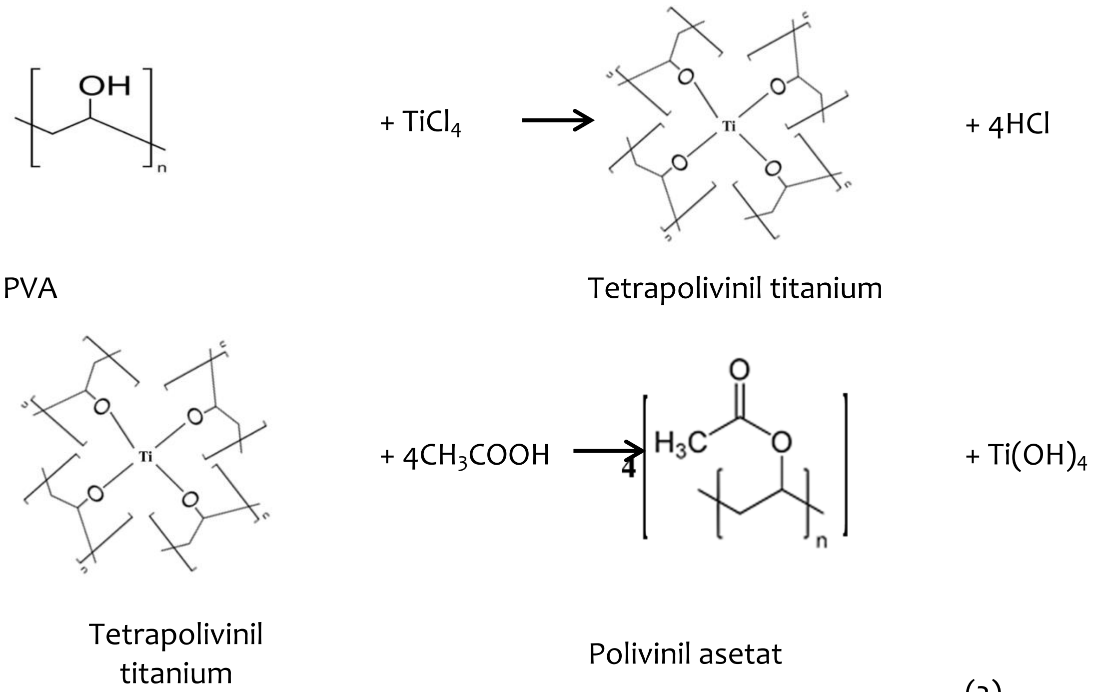
Concentration of cassava starch (%)	Percentage of TiO_2 (%)
2	1.77
4	2.01

6	2.20
8	2.16
10	1.77

Porous ceramics are then used as catalyst support for TiO_2. The methods used to develop TiO_2 catalysts are the adsorption method and the sol-gel coating method:

Adsorption Methods

The adsorption method or ion exchange is the process of exchanging Ti^{4+} ions from dissolving PVA which is then added to $TiCl_4$ as a Ti^{4+} source which will form $Ti(OH)_4$ with the addition of acetic acid as a source of OH and ethanol as a solvent, the reaction shown in equation (2):



(2)

The adsorption method aims to insert $Ti(OH)_4$ into the ceramic pores by immersing the ceramic in the mixture for 17 hours to maximize the process of inserting $Ti(OH)_4$ into the ceramic pores. Furthermore, the calcination process at a temperature of 600 °C aims to oxidize $Ti(OH)_4$ to TiO_2, besides the second sintering process aims to remove residues such as water and polyvinyl acetate. The results of this method showed that there were differences in the levels of TiO_2 that were successfully carried into ceramics with different starch concentrations. The results of the analysis using XRF are shown in Fig. 2.

Based on the spectrum in Fig. 2, it shows an increase in the intensity of TiO_2 metal oxide before and after adsorption. The interpretation of the percentage of TiO_2 catalyst successfully developed is shown in Table 2.

Based on Table 2, the concentration of cassava starch 2% to 4% decreased the percentage of TiO_2 and increased to 8% cassava starch concentration and decreased again at 10% concentration. This is thought to be related to the process and character of the pores formed in the ceramic body. The optimum binder concentration in porous ceramics as catalyst support for TiO_2 by the adsorption method occurs at a concentration of 8% cassava starch with percentage of TiO_2 about 38.9%.

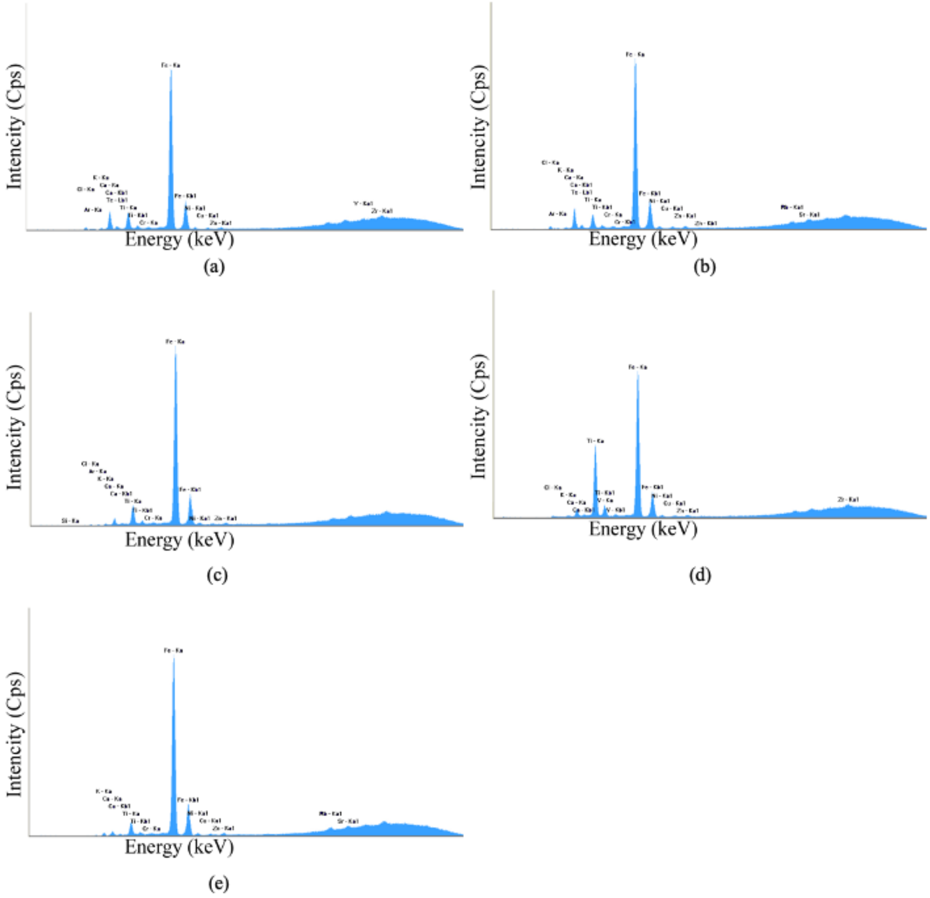


Fig. 2. XRF spectrum of gelcasted porous ceramic as a support catalyst by adsorption method

Table 2. Percentage of TiO2 on gelcasted porous ceramic as a support catalyst by adsorption method

Concentration of cassava starch (%)	Percentage of TiO_2 (%)
2	9,10
4	6,77
6	9,96
8	38,9
10	5,20

Sol-Gel Coating Method

The sol-gel coating method is a method that aims to grow a thin layer on the surface of a porous material evenly. The sol-gel coating method begins by mixing ammonium hydroxide (NH_4OH) and ammonium sulfate ($(NH_4)_2SO_4$) first as a source of OH- ions which are then added to $TiCl_4$ solution which will then form a $Ti(OH)_4$

solution which will fill the pores. and coat the ceramic surface. The reaction that occurs shown in equation (3).

$$NH_4OH \xrightarrow{(NH4)2SO4.} NH_4^+OH^-$$

$$4(NH_4^+ OH^-) + TiCl_4 \longrightarrow Ti(OH)_{4.} + 4NH_4Cl \qquad (3)$$

The mixture was stirred using a magnetic stirrer for 6 hours at 85 °C which aims to accelerate the formation process of $Ti(OH)_4$. The stirring process also affects the size of the $Ti(OH)_4$ particles formed. Furthermore, the ceramics were immersed in the solution while still stirring for 5 minutes then calcined at a temperature of 600°C for 3 hours. The results of the analysis TiO_2 content that were successfully carried into the ceramic by the sol-gel coating method are shown in Fig. 3.

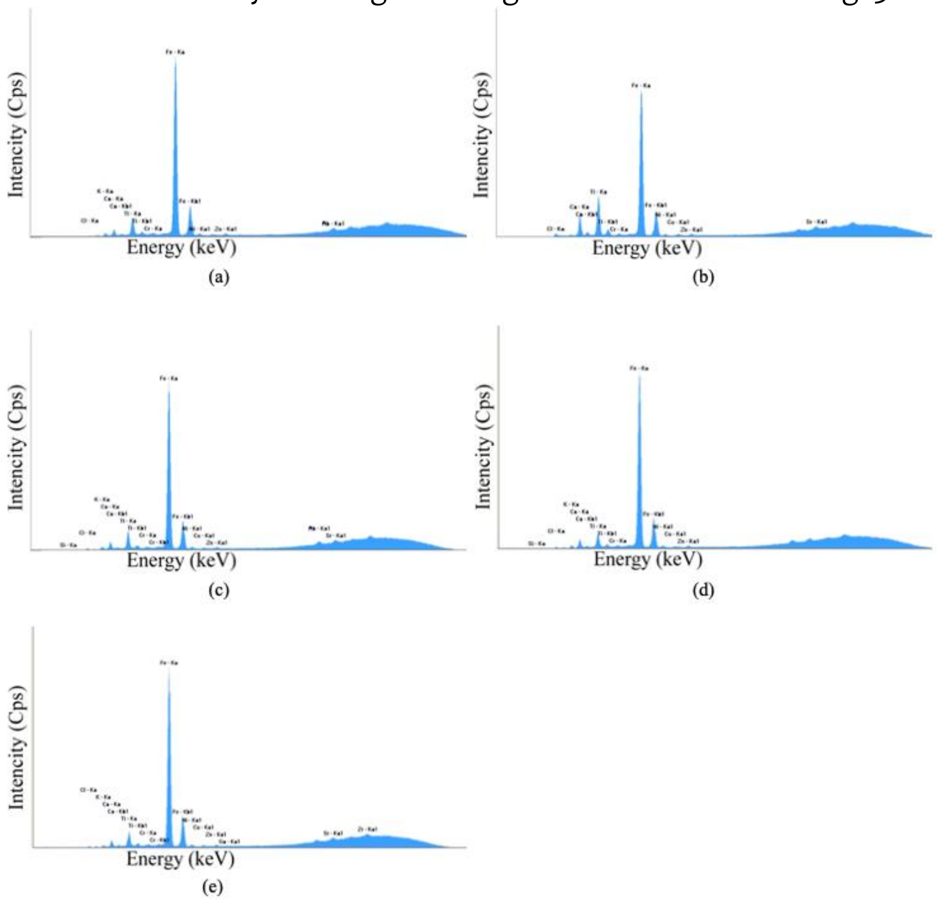


Fig. 3. XRF spectrum of gelcasted porous ceramic as a support catalyst by coating sol-gel method

Based on Fig. 3 shows an increase in the intensity of TiO_2 metal oxide before and after coating. The interpretation of the percentage of TiO_2 catalyst successfully developed is shown in Table 3.

Table 3. Percentage of TiO2 on gelcasted porous ceramic as a support catalyst by coating sol-gel method

Concentration of cassava starch (%)	Percentage of TiO_2 (%)
2	7.82
4	20.11
6	8.03
8	6.03
10	6.39

Based on Table 3, the concentration of cassava starch 2% to 4%, there was an increase in the percentage of TiO_2 and decreased to 10% cassava starch concentration. This is presumably because the greater concentration of cassava starch used, it will produce a type of blind pores so that the catalyst cannot enter the ceramic surface. The optimum binder concentration in porous ceramics as catalyst support for TiO_2 by the adsorption method occurs at a concentration of 4% cassava starch with percentage of TiO_2 about 20.11%.

The percentage of TiO_2 catalyst that was successfully impregnated into the porous ceramic body was still lower compared to the research results of Barmeh, 2019 which succeeded impregnate about 48.10% using coating method. It was also done by Li, 2007 which succeeded in impregnating as much as 80% TiO_2 catalyst in the ceramic body using the coating method. Thus, it is necessary to carry out further studies related to the characterization of gelcasting porous ceramics using cassava starch as a binder.

CONCLUSIONS

The results obtained showed that the concentration of cassava starch affects the ability of porous ceramics as TiO_2 catalyst support. The largest percentage of TiO_2 catalyst with adsorption method was achieved at a binder concentration of 8% with a catalyst percentage of 38.9% while with sol gel coating method was achieved at a binder concentration of 4% with a catalyst percentage of 20.11%.

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REFERENCES

Alag H. K. and R. S. Zamel. (2018). "Studying the Properties of Porous Alumina Using Starch as a Binder," J. Al-Nahrain Univ. Sci., vol. 21, no. 3, pp. 112–118, 2018, doi: 10.22401/jnus.21.3.13.

Barmeh A., M. R. Nilforoushan, and S. Otroj. (2019) "Photocatalytic and self-cleaning properties of glazed ceramic tiles coated with TiO2 and Al-doped TiO2 thin films," J. Aust. Ceram. Soc., vol. 55, no. 4, pp. 1091–1097, 2019, doi: 10.1007/s41779-019-00322-w.

Dhara S., R. K. Kamboj, M. Pradhan, and P. Bhargava. (2002). Shape forming of ceramics via gelcasting of aqueous particulate slurries. Bull. Mater. Sci., vol. 25, no. 6, pp. 565–568, 2002, doi: 10.1007/BF02710552.

Harefa F. B. (2009). Pemanfaatan Limbah Padat Pulp Grits Dan Dregs Dengan Penambahan Kaolin Sebagai Bahan Pembuatan Keramik Konstruksi.

Ismagilov Z. R. (1997) "Porous alumina as a support for catalysts and membranes. Preparation and study," React. Kinet. Catal. Lett., vol. 60, no. 2, pp. 225–231, 1997, doi: 10.1007/BF02475683.

Jamaludin A. R., S. R. Kasim, A. K. Ismail, M. Z. Abdullah, and Z. A. Ahmad. (2015) "The effect of sago as binder in the fabrication of alumina foam through the polymeric sponge replication technique," J. Eur. Ceram. Soc., vol. 35, no. 6, pp. 1905–1914, 2015, doi: 10.1016/j.jeurceramsoc.2014.12.005.

Jamaludin A. R., S. R. Kasim, M. Z. Abdullah, and Z. A. Ahmad. (2014) "Sago starch as binder and pore-forming agent for the fabrication of porcelain foam," Ceram. Int., vol. 40, no. 3, pp. 4777–4784, 2014, doi: 10.1016/j.ceramint.2013.09.023.

Julbe A., D. Farrusseng, and C. Guizard. (2001) "Porous ceramic membranes for catalytic reactors - Overview and new ideas," J. Memb. Sci., vol. 181, no. 1, pp. 3–20, 2001, doi: 10.1016/S0376-7388(00)00375-6.

Kishimoto T. and H. Kozuka. (2003) "Sol-gel preparation of TiO2 ceramic coating films from aqueous solutions of titanium sulfate (IV) containing polyvinylpyrrolidone," J. Mater. Res., vol. 18, no. 2, pp. 466–474, 2003, doi: 10.1557/JMR.2003.0059.

Li H. Y. et al.. (2007) "Photo-Catalytic Properties of Ceramic Coating of TiO2," Key Eng. Mater., vol. 336–338, pp. 1901–1903, 2007, doi: 10.4028/www.scientific.net/kem.336-338.1901.

Liu Y. F., X. Q. Liu, G. Li, and G. Y. Meng. (2001). Low cost porous mullite-corundum ceramics by gelcasting," J. Mater. Sci., vol. 36, no. 15, pp. 3687–3692, 2001, doi: 10.1023/A:1017961414108.

Mongkolkachit C., Wanakitti S., and Aungkavattana P. (2010). Investigation of Extruded Porous Alumina for High Temperature Construction. Mater. Technol., vol. 20, no. 3, pp. 123–125.

Musa M. A., J. M. Juoi, Z. Mohd Rosli, and N. D. Johar. (2017) "Characterization of TiO2 coating deposited on ceramic substrate," Solid State Phenom., vol. 264 SSP, no. September, pp. 38–41, 2017, doi: 10.4028/www.scientific.net/SSP.264.38.

Putri S. E. (2013) "Pengaruh Perbandingan monomer AM dan Crosslinker MBAM pada Pembuatan Keramik Berpori Secara Gelcasting Dengan Bahan Dasar Lumpur Lapindo The Influence of Ratio AM Monomer and MBAM Crosslinker on Synthesis of Porous Ceramic by Gelcasting Method Using Lapin," pp. 38–45,

Putri E., D. E. Pratiwi, R. Triandi, D. Mardiana, and S. Side. (2018). "Performance Test of Gelcasted Porous Ceramic as Adsorbent of Azo Dyes," J. Phys. Conf. Ser., vol. 1028, no. 1, 2018, doi: 10.1088/1742-6596/1028/1/012039.

Putri S. E. and D. E. Pratiwi. (2016). The Effect of Mole Ratio of Acrylamide (AM) Monomer and Methylene-bis-acrylamide (MBAM) Crosslinker Toward the Hardmess of Gelcasting Porous Ceramics," Proceeding Int. Conf. Math. Sci. Technol. Educ. their Appl., vol. 1, no. 1, pp. 412–415, 2016.

Ramlan R. (2009). Pemanfaatan Karet Busa (Spons) Sebagai Model Cetakan pada Pembuatan Keramik Berpori. J. Penelit. Sains, vol. 12, no. 2, pp. 1–4.

Shakeri A., D. Yip, M. Badv, S. M. Imani, M. Sanjari, and T. F. Didar. (2018) "Self-cleaning ceramic tiles produced via stable coating of TiO2 Nanoparticles," Materials (Basel)., vol. 11, no. 6, 2018, doi: 10.3390/ma11061003.

Sukania I. W. (2007). Seminar Nasional Mesin dan Industri (SNMI3) 2007. pp. 67–72.

Tambunan T. D. (2008). Pembuatan Keramik Berpori Sebagai Filter Gas Buang Dengan Aditif Karbon Aktif. Univ. Sumatera Utara, 2008.

Wan W., C. e. Huang, J. Yang, and T. Qiu. (2014) "Study on Gelcasting of Fused Silica Glass Using Glutinous Rice Flour as Binder," Int. J. Appl. Glas. Sci., vol. 5, no. 4, pp. 401–409, 2014, doi: 10.1111/ijag.12060.

Wang W. Y., A. Irawan, and Y. Ku. (2008) "Photocatalytic degradation of Acid Red 4 using a titanium dioxide membrane supported on a porous ceramic tube," Water Res., vol. 42, no. 19, pp. 4725–4732, 2008, doi: 10.1016/j.watres.2008.08.021.

Yang Z., N. Chen, and X. Qin. (2018). Fabrication of porous Al2O3 ceramics with submicron-sized pores using awater-based gelcasting method," Materials (Basel)., vol. 11, no. 9. doi: 10.3390/MA11091784.