Jurnal Natural
Vol. 20, (2) 2020
DOI 10.24815/jn.v20i2.16889
pISSN 1411-8513
eISSN 2541-4062

ORIGINAL RESEARCH

Microwave Assisted Co/SiO_2 preparation for Fischer-Tropsch synthesis

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Abstract. Cobalt catalyst has been widely used for Fischer-Tropsch (FT) Synthesis in Industry. The most common method to prepare cobalt catalyst is impregnations. Metal is deposited on porous support by contacting dry support with solution containing dissolved cobalt precursor. This step will follow by drying, calcination and reduction. The heating step used in this conventional method, however, may lead to the formation of metal silicate which is inactive site for catalysis. In this study, author explore the use of microwave to prepare catalyst compared to conventional drying method. Cobalt catalyst with SiO_2 support was prepared and characterized. Particle size, surface area, and cobalt content were investigated. Crystallite size of 3-8 nm was formed which was reported to be the optimum size for cobalt catalyst in FT Synthesis. Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM) image revealed that microwave catalyst showed better uniformity and cobalt dispersion on silica support. Thermo-Gravimetric Analysis (TGA) study also indicated that this catalyst has good stability at Low Temperature Fischer-Tropsch Synthesis. The catalysts were then applied plasma assisted FT process over a range of power plasma (20-60W) to investigate the effect on the conversion and selectivity. The results showed that microwave catalyst exhibit lower CO conversion at 42.06% compared to conventional method at 68.32%. However, microwave catalyst is more favourable for long chain hydrocarbon selectivity.

Keywords: cobalt catalyst, silica support, plasma reactor,

INTRODUCTION

There is significant attraction for conversion of syngas to liquid fuels via the renowned process called Fischer-Tropsch (FT) synthesis. FT synthesis can be defined as a process to convert synthesis gas containing hydrogen and carbon monoxide to hydrocarbon products using catalyst commonly cobalt and iron. This trend has been driven by the need to seek for alternative fuel as well as growing demand for clean fuel.

Based on temperature, FTsynthesis can be categorized into two groups: High Temperature Fischer-Tropsch (HTFT) and Low Temperature Fischer-Tropsch (LTFT). While the former operates at 300 – 350 °C and pressure of 20-40 bars, the later runs at 200 – 250 °C with pressure of 20-45 bars. LTFT has better selectivity toward long chain hydrocarbon, whereas HTFT process is used for producing light olefin products. In this paper, the author limits the study to LTFT.

Catalyst play important role on the activity of FT synthesis including increase hydrogen and carbon monoxide (CO) conversion and tuning the right selectivity toward desired product. The developments of selective FT catalysts, which can increase the selectivity to desired products that is C_{5+} for LTFT, contribute to the most challenging research in the field of the FT synthesis. An increase of CO conversion may have effect on decrease of selectivity towards C_{5+} as the relationship between the the two is complicated [1, 2]. Although catalysts derived from group VIII metals i.e. Ru, Co, Fe and Ni can be used for the FT synthesis, iron and cobalt are commercially used due to their price, of which cobalt offers better resistance to deactivation [3].

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Received: June 2020 | Revised: June 2020
Accepted: June 2020

The design of catalyst for FT synthesis should satisfy higher surface area (> 100 m^2/g), porosity, stability and optimum metal-support interaction. For cobalt case, weak metal-support interaction helps high cobalt reducibility but provides agglomeration of supported cobalt particles. In contrast, strong interaction between cobalt and metal-support could lead to the formation of cobalt silicate which is not favourite phase to catalyse FT synthesis [4]. Once the new catalyst has been made, it is important to test the performance and compare with that of conventional catalysts [3].

Co particles size on supporting material had a strong effect on the selectivity of C_{5+} hydrocarbons over CH_4 [5]. The CH_4 selectivity was higher for the catalysts with smaller Co particles and decreased with increasing Co particle size in the range of 2.6–8 nm. The C_{5+} selectivity increased with the mean size of Co nanoparticles. A further increase in Co particle size above 6-8nm had little effect of the C_{5+} selectivity. An increase pore size of the support leads to increase of Co_3O_4 Crystallite size. This due to large pore size was easy to reduce resulting from weaker interaction between cobalt oxide species with support. However the specific pore size of 6-10 nm (Co_3O_4 crystallite size 13-14 nm) offer best catalytic performance, (CO Conversion 65.7-56.5 %; C_{5+} of 87.2-85.9%; and CH_4 11-11.8%). Narrower pore size contribute to the increase of CH_4 of 36.4% and decrease of C_{5+} selectivity of 59.9% [6].

In order to prevent the formation of cobalt silicate, calcination temperature and surface area of the catalyst should be taken into account. Low temperature calcination is favourable to prevent the precursor of cobalt silicate. High temperatures calcination result in larger, readily reducible crystallites which lead to low dispersion of cobalt metal on the surface [4]. Surface area supports higher than 560 m^2/g cause strong interaction between the silica surface and the cobalt cations resulting in formation of more cobalt complexes and cobalt silicate. The cobalt silicate will hinder the number of active metallic sites [7].

The potential application of microwave for preparing highly active active catalyst in FT synthesis has been explored recently . Using Co/SBA catalyst, Rodrigues et al [12] found that catalyst prepared by microwave offer better selectivity of C_{5+} (78.5%) than those prepared by conventional heating (71.9%). The increase of CO conversion for microwave prepared catalyst was also detected in this research. The others advantage of microwave irradiation are uniform distribution of the Co Particles at surface. This has been observed by Reubroycharoen et al [13] in their study using Co/SiO_2 catalyst. Microwave catalyst showed better distribution of the Co particles on support surface than those of conventional heating catalyst which was partly anglomerated on the surface. This had leading to better CO conversion of 81% compared to conventional method (69%).

Microwave assisted catalyst preparation for FT synthesis has not fully been studied. In this study, cobalt and iron on colloidal silica supporting material prepared via microwave irradiation is characterised its properties (surface areas, pore size, particle sizes and distribution of metals on the supporting surface). This method replaces long conventional drying process and is expected to offer better metal dispersion on the support. The effects of these catalysts on the selectivity of liquid hydrocarbons are then studied in FT synthesis using a fixed bed reactor. The products from the FT synthesis will be analysed on-line using a two-oven gas- chromatography.

METHODOLOGY

Catalyst Preparation

Cobalt silica catalyst were prepared by adding cobalt (II) nitrate hexahydrate (Sigma Aldrich with. purity ≥98%) into Bindzil CC301 colloidal silica containing 30% silica and 7 nm particle size) from Azkonobel at various molar ratios of cobalt (II) nitrate hexahydrate to silica gel 1:5 [14]. The precursor solution was then stirred vigorously at 933 rpm using a magnetic stirrer for 2 hours. Approximately 10 ml precursor solution was placed in a 200 ml round bottom glass and irradiated in a 1000 W commercial microwave (Panasonic NN-CT579SBPQ) for 3 minutes at 1000 W to form catalyst oxide. Cobalt nitrate was decomposed and formed black solid cobalt oxide. This catalyst were then heated in a furnace in the presence of air at 550 °C for 2 hours and followed by a reduction to activate cobalt metal phase in a hydrogen flow of 50mL/min at 550 °C for 24 hr [14]. This catalyst will be referred to as CoM.

A conventional catalyst preparation was also used to compare the result. Microwave irradiation was replaced by drying the precursor solution in the oven at 100 °C for 16 hr. Calcination and reduction of the catalyst followed the same procedure as microwave assisted catalyst. This catalyst will be referred to as CoD.

Catalyst Characterization

A Coulter SA 3100 (Beckman-Coulter), was used to analyse surface area of catalyst. Approximately 0.1 g sample were placed in a Brunauer–Emmett–Teller (BET) analysis tube. The tube containing sample was then outgassed for 120 min at a temperature of 120 °C based on literature [15]. Once the outgassing was completed, the tube was connected to an analytical port and immersed in liquid nitrogen. Surface area was obtained by the nitrogen sorption techniques as adsorbate.

The BET surface area, m^2/g, was then calculated from the equation,

$$S_{BET} = \frac{V_M x\, N_A x\, A_M}{M_V} \quad \ldots\ldots\ldots\ldots (1)$$

Where N_A is avogadros number, A_M is the cross sectional area occupied by each adsorbate and M_V is the gram molecular volume (22.4 L). A_M is assumed to be 0.162 nm^2 for nitrogen BET.

TGA was performed on the catalysts after microwave treatment using TGA on a Perkin Elmer STA 6000 Model. Samples were heated from 30 °C to 500 °C using a heating ramp of 5° C/min with air flow rate of 30 ml/min. The sample loading was typically 4 – 9 mg.

A PANalytical X'Pert Pro MPD, powered by a Philips PW3040/60 X-ray generator and fitted with an X'Celerator detector was used to determine particle size and phase identification. Approximately 4.5 cm^3 of powder samples were exposed to Cu-K_α X-ray radiation at a wavelength (λ) of 1.5418 Å. X-rays were generated from a 40 kV and 40 mA Cu anode supplied. The diffraction data were collected over a range of 0 – 110°2θ with a step size of 0.0334°2θ using the scanning X'Celerator detector.

The crystalize size is calculated using Scherrer equation [17] :

$$\tau = \frac{K\lambda}{\beta\ Cos\theta}. \quad \ldots\ldots\ldots\ldots (2)$$

τ is the mean size of the crystalline domains; K is a dimensionless shape factor, in this case is 0.9 (assumes spherical crystallites); λ is the X-ray wavelength which is 1.541874; β is the line broadening at half the maximum intensity after subtracting the instrumental line broadening, in radians. 2θ; θ is the Bragg angle

Scanning electronic microscopy (SEM) was carried out on catalyst using a Hitachi S2400 instrument with a magnification range of X30 to X5000 using its secondary electron (SEI) or backscattered electron (BSE) modes. It is also fitted with a cathodoluminescence (CL) detector.

Fischer-Tropsch (FT) synthesis

The experiments were carried out in a quartz tube reactor of 30 cm length, and 2.4 cm inner diameter and 1.5 mm thickness. 2 g of catalyst was sieved to 2 mm size and placed in the center of the tube glass. Plasma power at 60 W was applied. Synthesis gases including H_2 and CO from gas cylinders (BOC) were continuously fed into the reactor with molar ratios of H_2 to CO from 3:1. The flow rates of gases were controlled electronically via mass flow controllers (Bronkhorst UK) and calibrated by digital flow control from. The gas maintain at reactant Gas Hourly Space Velocity (GHSV) of 750 to 2250 cm^3/h.g catalyst. The products were analysed on-line using a Varian 450-GC.

The conversions of H_2 were defined as:

$$= \frac{Moles\ of\ H_{2(in)} - Moles\ of\ H_{2(out)}}{Moles\ of\ H_{2(in)}} \times 100 \quad \ldots\ldots\ldots (3)$$

The conversions of CO were defined as:

$$= \frac{Moles\ of\ CO_{(in)} - Moles\ of\ CO_{(out)}}{Moles\ of\ CO_{(in)}} \times 100 \quad \ldots\ldots\ldots (4)$$

The selectivity of hydrocarbon the product was calculated based on carbon atom and defined as,

$$= \frac{Moles\ of\ CO_{(out)}}{Moles\ of\ CO\ Converted} \times 100 \quad \ldots\ldots\ldots (5)$$

RESULTS AND DISCUSSION

Decomposition of the Catalyst

TGA curves of the catalysts in the Figure 1 shows the decomposition profiles for cobalt catalyst. The endothermic weight loss of 3.25 – 5.19% can be seen at 50 – 82 °C. This can be explained by the removing of water content from the catalyst. The decomposition of nitrate groups (NO_3) started at 150 °C. The graph also informs that these catalysts are stable to use in the typical FT Synthesis of 200 – 350 °C

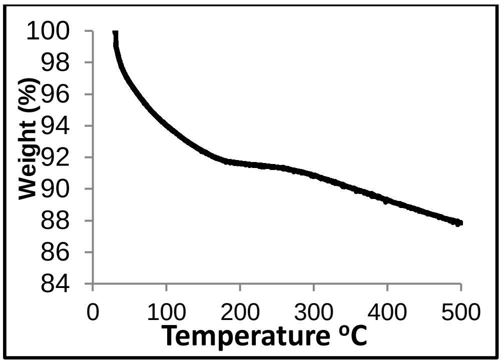


Figure 1. TGA Curves of Cobalt Silica-supported catalyst. Temperature ramp 2 °C/min.

SEM and TEM Study

The morphology of those 2 types of catalyst was shown in the Figure 2 below.

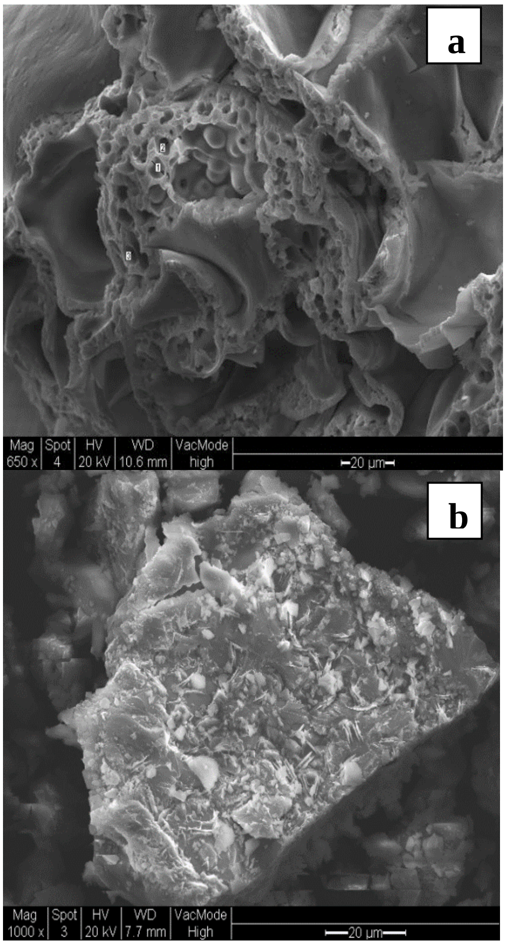


Figure 2. SEM image of Cobalt Silica Catalyst with molar ratio 1:5 prepared by: (a) microwave at 1000W and 3 minutes, (b) conventional drying at 120 °C and 16 hr.

The microwave catalyst provides better porosity to that of the drying catalyst. The Co particles are partly agglomerated on the surface and lack of uniformity in the conventional treatment. Reubroycharoen et al [13] stated that moisture removed from outside during heating process caused outward flow from the inside to the outside of the support and eventually created accumulation of metal oxide in the outer region of the support. These agglomerated particles decrease the cobalt dispersion and increased the pore size of the support.

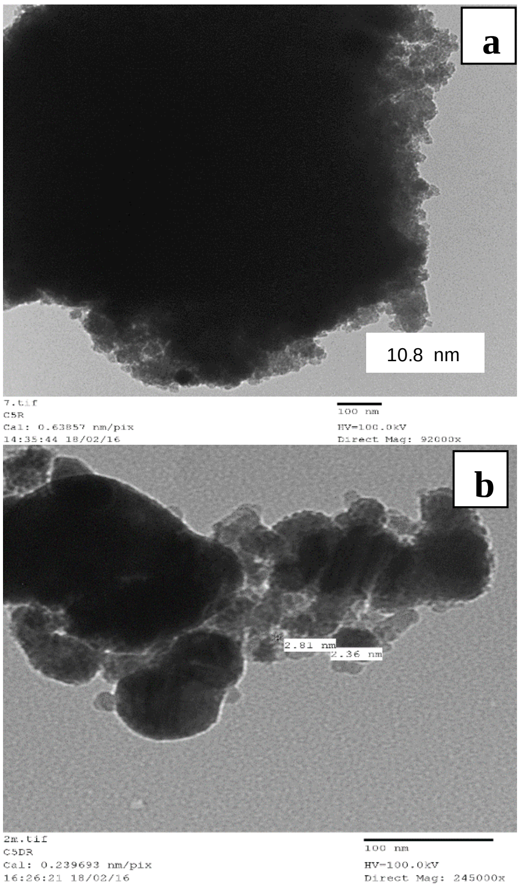
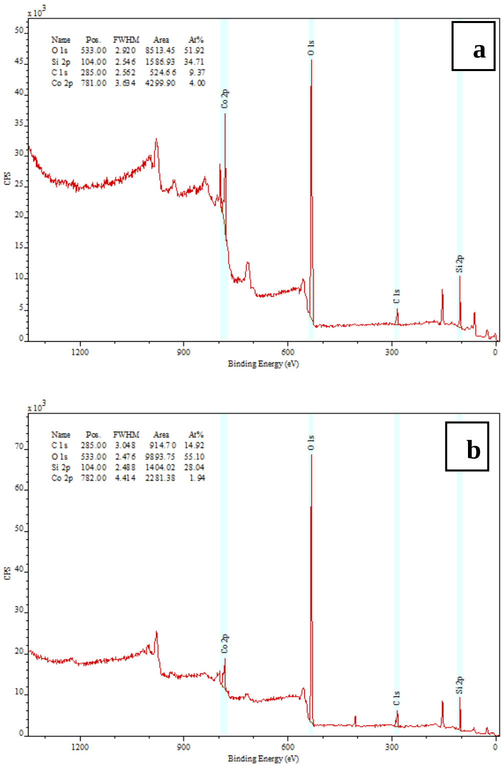


Figure 3. TEM image of a) of CoMR, Cobalt Silica Catalyst (molar ratio 1:5) after Microwave and Reduction b) CoDR, Cobalt Silica Catalyst (molar ratio 1:5) after drying and Reduction

In order to have better understanding on the effect of reduction, both microwave catalyst and dried catalyst was exposed to TEM analysis. It can be seen from Figure 3 that both catalysts agglomerated after reduction at 550°C in hydrogen flow of 50 ml/min. It is interesting to note that the microwave catalyst maintains the particle size at around 10 nm which is suggested ideal for FT Synthesis compared to narrow particle size of dried catalyst at 2-3 nm. This result in agreement with the X-ray Photoelectron Spectroscopy (XPS) analysis of the two catalyst in Figure 5.

XPS Study

The analysis found that cobalt content on the catalyst surface of microwave catalyst was twice the amount of dried catalyst at 4%. This shows that microwave treatment offer much better cobalt loading on the surface of support compared to the conventional drying treatment.



Name	Pos.	FWHM	Area	At%
O 1s	533.00	2.920	8513.45	51.92
Si 2p	104.00	2.546	1586.93	34.71
C 1s	285.00	2.562	524.66	9.37
Co 2p	781.00	3.634	4299.90	4.00

Name	Pos.	FWHM	Area	At%
C 1s	285.00	3.048	914.70	14.92
O 1s	533.00	2.476	9893.75	55.10
Si 2p	104.00	2.488	1404.02	28.04
Co 2p	782.00	4.414	2281.38	1.94

Figure 4. XPS analysis of Elemental Composition of C5D, Cobalt Silica Catalyst with molar ratio 1:5 prepared by: (a) microwave, (b) conventional drying

BET Study

BET surface area analysis were performed on both catalyst of microwave and drying treatment. After reduction, the analysis were repeated to understand the effect of the process. The result can be seen in the Table 1.

Based on Table 1 above microwave and drying catalyst have quite similar surface area at 227.7 m^2/g and 234.17 m^2/g, respectively. It is interesting to note that after reduction took place, drying catalyst provide much higher surface area at 345 m^2/g compared to microwave catalyst which decrease at 197.17 m^2/g. The pore volume of drying catalyst is higher than that of microwave catalyst which may give the reason why drying catalyst poses higher surface area that microwave one.

Table 1. Physical properties of cobalt silica catalyst with microwave and Drying treatment

Catalyst	Surface Area (m^2/g)	Average Pore Diameter (nm)	Pore Volume (cm^3/g)
CoM	227.7	3.97	0.170
CoMR	197.17	3.8	0.214
CoD	234.17	3.8	0.212
CoDR	345	3.82	0.270

M= microwave, D = Drying, R = reduction

X-Ray Diffraction (XRD) Study

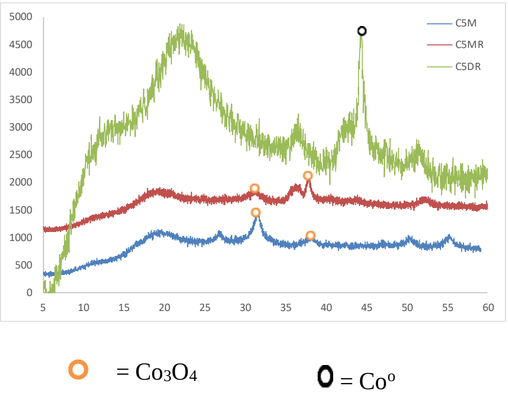


Figure 5. XRD result for Cobalt Silica Catalyst after microwave (C5M), microwave catalyst after reduction (C5MR) and drying catalyst after reduction (C5DR)

Figure 5 above shows the change of cobalt phase during catalyst treatment including microwave, reduction and after FT Synthesis. There was only Co_3O_4 peaks detected at 31.59° and 37.98° after microwave irradiation (C5M). Cobalt metallic phase was not formed during this treatment. This finding is in agreement with the work carried out by Reubroycharoen et al. [13] which used 700 W commercial microwave to prepare Co/SiO_2 catalyst at irradiation time from 4 to 45 min [13]. Reubroycharoen et al [13] found that only Co_3O_4 were present across all the irradiation time. Microwave irradiation only was not able to decompose cobalt nitrate to cobalt metallic phase. Further catalyst reduction was required to allow the decomposition of cobalt oxide to cobalt metallic phase which can be seen on XRD spectra of C5MR. Cobalt metal is detected at 53.15° for microwaved catalyst after reduction. There is no cobalt oxide present in C5DR catalyst however cobalt silicate was clearly notice at 36.81°. Cobalt metal is detected at 44.39° for drying catalyst after reduction

Catalyst Performance

The catalytyc evaluation of both catalyst were listed in Table 2. Cobalt catalyst prepared by conventional method, provide better conversion compared to that of microwave assisted catalyst.. However, microwave catalyst shows higher selectivity towards long chain hydrocarbon selectivity.

Table 2. Conversion and selectivity of cobalt catalyst microwave assisted and conventional method on Plasma Catalytic Fischer-Tropsch Synthesis at plasma power of 60 W

Catalyst	Conversion (%)		Selectivity (%)			
	H_2	CO	CO_2	CH_4	C_2-C_4	C_{5+}
CoM	31.1	42.1	12.4	16.6	7.8	63.2
CoD	37.4	68.3	20.5	16.9	11.7	50.9

The very important factor the influence plasma is specific input energy (SIE) which defined as equation,

$$SIE = [Power / Flow\ rate)] / 1000 \quad \text{..........}(6)$$

Where SIE unit is kJ/L, Power unit is Watt and flow rate unit is L/s.

In order to achieve a higher specific input energy (SIE), the plasma power was varied between 20 – 60 W while flow rate was fixed at 10 ml/min. Figure 6 showed the effect of SIE on CO conversion and C_{5+} selectivity for Cobalt microwave-assisted catalysts. The conversion of CO increase from 22.17 – 42.06% with the increase of SIE in the range of 90 – 360 kJ/L. Previous study has showed that increasing plasma power at a constant excitation frequency effectively enhances the electric field, electron density and gas temperature in the discharge[17]. It can be noted that rising of SIE decreases the selectivity of C_{5+} hydrocarbon from ~78 to ~63%. The methanation reaction taken into effect at high energy input for this catalyst

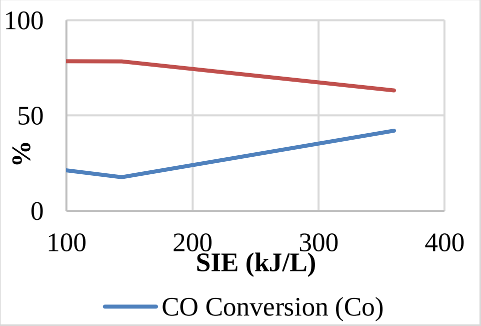


Figure 6. Effect of Specific Input Energy (SIE) on Conversion and C_{5+} Selectivity

CONCLUSION

Cobalt silica-supported catalyst was prepared by microwave irradiation and compared to conventional drying method. The result showed that conventional catalyst offers better conversion but microwave irradiation is promising method as it could maintain high selectivity towards C_{5+} and provide stability over low temperature Fischer Tropsch Synthesis. Plasma Reactor employed for FT Synthesis was also managed to deliver fair conversion at low plasma power of 20-60 W. Further investigation is required to understand the dispersion and reducibility of the metal on the surface.

ACKNOWLEDGEMENTS

The author thanks Directorate General of Higher Education Ministry of Education and Culture of Indonesia and Universitas Syiah Kuala for providing financial support.

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