Soot Oxidation in Diesel Exhaust on Silver Catalyst Supported by Alumina, Titanium and Zirconium

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Abstract. Diesel Particulate Filter (DPF) is used to limit the emission of particulate matter (PM). The operation of DPF has two consecutive functions which are filtration of PM and regeneration. Performance of DPF is reduced by clogging of the filter. This problem is improved by soot oxidation in the regeneration process. The soot is completely oxidized by oxygen when temperature is higher than 600 °C. However, the exhaust gas temperature in normal operating of the diesel engine is lower than the temperature of soot complete oxidation. The problem of low temperature in soot oxidation is improved by oxidation catalyst because the oxidation catalyst is used to reduce light of temperature in soot oxidation. The study's purpose is to compare the oxidation activity of silver catalyst supported on alumina (Al_2O_3), Titanium oxide (TiO_2), and Zirconium oxide (ZrO_2). The compression of soot oxidation on silver catalyst loaded on several support which showed silver base on alumina was the best of soot oxidation compared with titanium oxide and zirconium oxide. The behaviour of soot oxidation in silver base on titanium oxide and zirconium oxide were similar activity.

Keyword. Soot oxidation, Silver catalyst, TiO_2, ZrO_2

1 Introduction

Air pollution from the emissions of diesel vehicles, such as particulate matter (PM) and nitrogen oxides (NOx), has been caused harm to human health [1]. There are many technologies to reduce the pollution such as using the biodiesel as fuel in diesel engine, and installation of exhaust gas after-treatment system. The diesel engine used biodiesel as fuel that it showed low emission such as hydrocarbon, carbon monoxide, smoke[2].Currently, diesel particulate filter (DPF) is the device used to control effectively PM emissions[1, 3-4]. The operating of DPF consists of two sequential processes, which are trapping of soot and regeneration. First, the trapping of soot is the process of soot to deposit in porous walls of DPF [3]. Next, the regeneration of DPF is required to reduce the problem of DPF blockages. In normal, soot is oxidized by oxygen at a temperature higher than 600 °C [5–7], which is over the exhaust gas temperature in diesel engine.

The oxidation of soot was promoted using an oxidation catalyst, which assisted to burn soot at lower then temperatures of exhaust gas in diesel engine. Noble-metal (such as Ag, Au, Pd, Ru, and Pt etc.) were used as the active metal in oxidation catalyst [8-9]. Silver was interested as the oxidation catalyst because it prompted active oxygen species [10–12] and showed high stability [3]. Moreover, silver is cheaper than other noble metals (e.g., Pt) [13]. The oxygen species or active oxygen may be classified in to peroxide (O^-) and superoxide (O^{2-}). The active oxygen transfer to soot which was considered to be an important for soot oxidation activity [4, 14] .

Soot oxidation activity was promoted by not only the active metal but also the support materials, such as, Al_2O_3 TiO_2, ZrO_2, and CeO_2. Alumina was widely used as the support material of oxidation catalysts, such as, Pt/Al_2O_3 [15] and Ag/Al_2O_3 [3, 12]. Silver catalyst 16 wt% coated on alumina showed best soot oxidation [3]. The Ag/ZrO_2 showed a promising candidate for oxidizing soot with O_2 when the mole fraction of adding Ag to ZrO_2 was 30 % in citric acid-assisted sol-gel (SG) methods [11]. Moreover, it showed very active catalysts in a fresh or aged state [12]. The titanium oxide, which used with silver catalyst, showed high oxidation efficiency of soot in the tight contact between catalyst and soot [16]. From, several works of literature caused interest in the oxide materials to use with silver metal such as Al_2O_3, TiO_2, and ZrO_2.

The thermogravimetric (TG) methods was used to determine kinetics parameter such as activation energy (Ea) and frequency factor (f(α)) etc. Normally, the activation energy is important kinetic parameter to explain the reaction process and identify the reaction mechanism [17]. The reaction rate of a heterogeneous reaction The Arrhenius equation, which depends on temperature, was used to describe the rate of soot oxidation [18]. The rate of reaction in the case of constant heating rate can be explained by the following equation [19] :

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$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(\frac{-Ea}{RT})f(\alpha) \qquad (1)$$

when A and Ea are the frequency factor and activation energy, $f(\alpha)$ is the differential conversion function, β is heating rate and R is the universal gas constant. The mass faction of the soot oxidation decomposition (α) can be calculated by the following equation:

$$\alpha = \frac{m-m_0}{m-m_f} \qquad (2)$$

when m is the instantaneous mass of soot, m_0 is the initial mass, and m_f is the final mass. In this work used the Kissinger–Akahira–Sunose to determine activation energy to the following equation[20] :

$$\ln(\frac{\beta}{T^{1.92}}) = Const - 1.0008(\frac{Ea}{RT}) \qquad (3)$$

The activation energy can be obtained by slope from plot of $\ln(\beta/T^{1.92})$ against $1/T$ for different heating rates at a constant α [20]. From equation (3) can be calculated the activation energy by equation as the following:

$$Ea = \frac{(\text{slope at } \alpha) \times R}{-1.0008} \qquad (4)$$

The aim of the following study was to compare the soot oxidation activity of silver catalyst loaded on three metal-oxide supports (e.g., Al_2O_3, TiO_2, and ZrO_2) and find the activation energy from soot oxidation. The activity of soot oxidation was used by thermogravimetric (TG) methods in the three heating rates which were 5, 7.5, and 10 °C/min. The activation energy was calculated by KAS method.

2 Experimental

2.1. Catalyst and soot preparation

The silver catalyst used on different supporters was prepared via incipient wetness impregnation that silver nitrate to obtain 16 wt% was dissolved in an appropriate quantity of distilled water [3]. Then, the precursor solution was added dropwise to the powdered supports: γ-alumina, titanium oxide, and zirconium oxide. Then, the solvent was removed by drying at 110 °C for 8 h in an oven. Then, the dry sample will be calcined in static air at 600 °C with a heating rate of 10 °C/min for 2 h.

Soot was directly taken from the exhaust gas of a traditional diesel engine. The engine was operated at a speed of 1000–2000 rpm and load of 25–75% of the maximum load. A stain less steel mesh was rolled at one round and placed inside the exhaust pipe (50 mm ID) then, the trapped soot was collected and dried in a furnace at 110 °C for 8 h [3]. SOF was removed in furnace at 250 °C for 2 h.

2.2 Catalyst activity tests

Catalytic oxidation activity of soot was examined using the TGA method (PerkinElmer® Pyris 1). Soot (10 mg) was physically mixed with the catalyst at the designed weight ratio for 5 min in a stainless steel mortar to obtain the tight contact mode or was shaken for 5 min in a glass tube for the loose contact conditions. Then, the mixture (≈10 mg) was sampled and placed in a ceramic crucible and heated from room temperature to 110 °C with a heating rate of 10 °C/min under N_2 and, then, the purge gas was switched to O_2 until temperature 700 with heating rates of 5 °C/min, 7.5 °C/min, and 10 °C/min and the contact of soot on the catalyst is tight contact. Purified oxygen (99.999% purity) with a constant flow rate of 50 cm³/min was used as the oxidiser. The sample weight was recorded continuously with the change in the temperature. The catalytic activity was assessed by using the following: T_{20}, defined as the onset temperature at which 20% of soot was removed; T_{50}, defined as the temperature at which of soot 50% was completely consumed; T_{90}, defined as the temperature at which 90% of soot oxidation.

3 Result and Discussion

3.1 Diesel soot oxidation

The thermogram profile and its first derivative (DTG) for soot oxidation under the tight contact mode are presented in Fig. 1-3. The x-axis shows the temperature, the y-axis shows the percentage of soot oxidation in figure (a), and the y-axis shows the first derivative of soot oxidation in figure (b). An oxidation reaction was the only interaction of soot (solid carbon) because the SOF was removed in the soot preparation stage. The DTG showed the maximum reaction rate in the oxidation process [3]. In case of pure soot in all the heating rates showed the peak of DTG at 610 °C. It explained the best of oxidation reaction of pure soot at this temperature which confirmed the soot is oxidized by oxygen at a temperature higher than 600 °C[5–7].

In the case of soot used in conjunction with silver supported by alumina. The oxidation of soot was well promoted by Ag/Al_2O_3 as observed from the experimental results from all heating rates. The heating rate was 5 °C/min. The peak of DTG showed the maximum oxidation rate temperature was reduced from 610 °C, in the case of non-catalyst soot, to 353 °C (shows in Fig.1) In case of the heating rate was 7.5 °C/min and 10 °C/min. The result showed similarly the oxidation of soot with case of 5 °C/min. In the case of the heating rate was 7.5 °C/min and 10 °C/min. The result showed similarly the oxidation of soot with a case of 5 °C/min from the peak of DTG at 359 °C and 405 °C in cases 7.5 °C/min and 10°C/min, respectively (shows in Fig. 2-3).
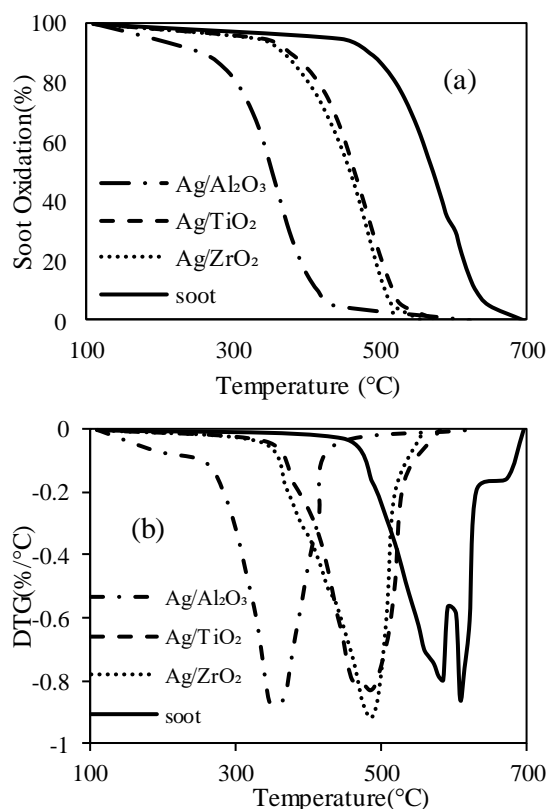
Fig. 1. (a) Thermogravimetric and (b) first derivative profiles of soot oxidation; soot/catalyst weight ratio of 1/5 and heating rate of 5°C/min.
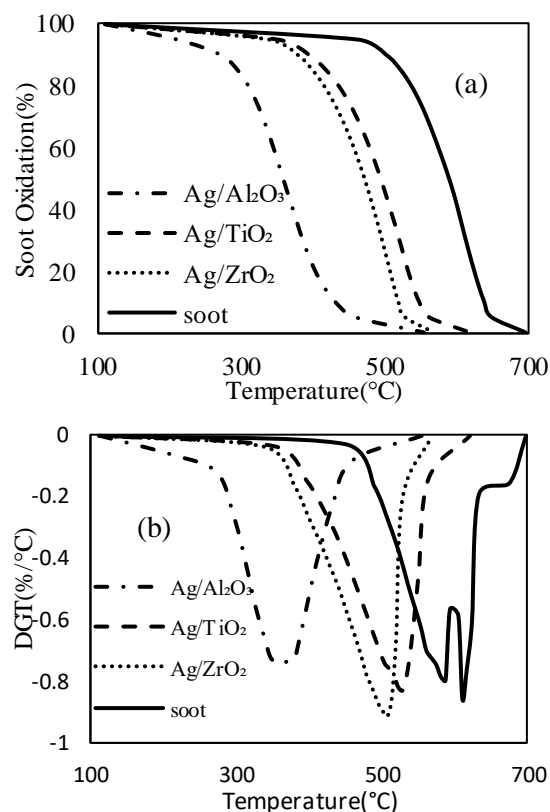

Fig. 2. (a) Thermogravimetric and (b) first derivative profiles of soot oxidation; soot/catalyst weight ratio of 1/5 and heating rate of 7.5°C/min.

The cases of Ag/TiO_2 and Ag/ZrO_2 showed a similar promotion in soot oxidation due to similar soot oxidation temperatures. Ag/ZrO_2 showed the peak of DTG at temperatures values were 485 °C, 508 °C, and 541 °C for heating rates of 5, 7.5, and 10, respectively (shows in Fig.1-3). Ag/TiO_2 showed the peak of DTG at temperature values were 485 °C, 528°C, and 528 °C for heating rates of 5 °C/min, 7.5°C/min, and 10°C/min, respectively (shows in Fig. 1-3). However, the comparison of Ag/TiO_2 and Ag/ZrO_2 showed that Ag/ZrO_2 had a better-promoting effect on oxidation because the temperature at peak of DTG in the case of Ag/ZrO_2 represented a lower temperature than the case Ag/TiO_2.

Fig.4-6 show T_{20}, T_{50} and T_{90} from the experiment had three heating rates which were 5 °C/min, 7.5 °C/min, and 10°C/min. According to Fig.4-6 explained the temperature of percenter of soot decomposition since it was oxidized by oxygen. The T_{20} explained the 20% of soot oxidation. T_{20} may be indicated as a light of temperature which was the start of soot oxidation. In case of Ag/Al_2O_3 presented excellent to reduce the light of temperature for soot oxidation from 523 °C in case of pure soot was reduced to 305 °C with heating rate 5 °C/min. The results at heating rate 7.5 °C/min and 10 °C/min showed to similar in case of 5 °C/min, they were T_{20}=310 °C and T_{20} = 342 °C with heating rates of 7.5 °C, and 10°C, respectively. In case of Ag/TiO_2 presented T_{20} were 417 °C, 438 °C, and 452 °C with heating rates of

5°C/min, 7.5°C/min, and 10 °C/min, respectively. The result from Ag/ZrO_2 showed T_{20} were 404 °C, 416 °C, and 437 °C with heating rates of 5 °C/min, 7.5°C/min, and 10 °C/min, respectively. The result in several cases in the experiment presented shows light of temperature for soot oxidation as follows: Ag/Al_2O_3< Ag/ZrO_2< Ag/TiO_2< pure soot. It showed the effect of metal oxides supporter to promote soot oxidation because light of temperature for soot oxidation was reduced from pure soot oxidation. In the case of soot oxidation from Ag/TiO_2 and Ag/ZrO_2. The T_{20} were similar values, it explained the light of soot oxidation which show similar activity in all the heating rates.

The soot oxidation performance was explained by T_{50} and T_{90}. They were temperature at soot decomposition at 50%(T_{50}) and 90%(T_{90}) from initial mass. The results of T_{50} in case of Ag/Al_2O_3 was shown in Fig.4-6. The T_{50} were 353 °C with a heating rate of 5 °C/min. In the case of heating rates were 7 °C/min and 10°C/min that they showed T_{50} = 359 °C and T_{90}= 398 °C, respectively. The T_{90} were 353 °C with a heating rate of 5 °C/min, 359 °C with 7 °C/min and 398 °C with 10 °C/min. The results of a silver catalyst supported by alumina showed a good assister to promote soot oxidation. As it reduced the T_{50} and T_{90} by half from the case of pure soot. The T_{50} and T_{90} in the case of a silver catalyst supported by titanium oxide is shown in Fig.4 - Fig.6.
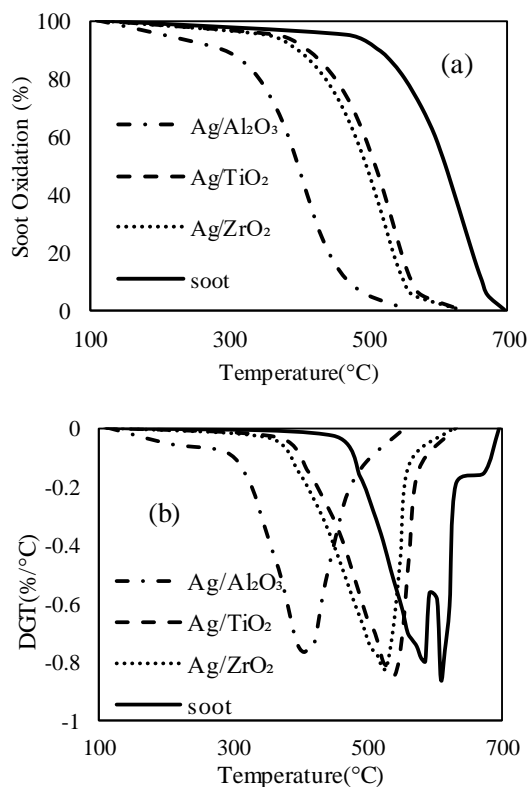
Fig. 3. (a) Thermogravimetric and (b) first derivative profiles of soot oxidation; soot/catalyst weight ratio of 1/5 and heating rate of 10°C/min.

Fig. 4. T_{20}, T_{50}, and T_{90} of soot oxidation (heating rate 5°C/min)
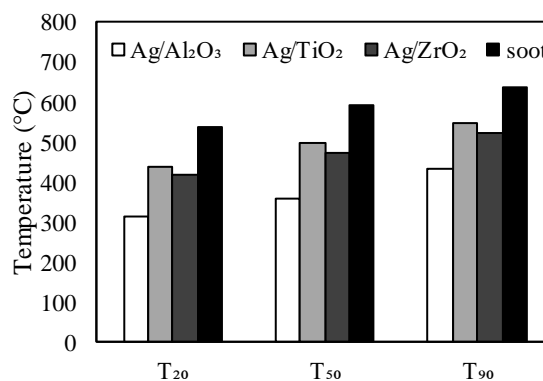
Fig. 5. T_{20}, T_{50}, and T_{90} of soot oxidation (heating rate 7.5°C/min)
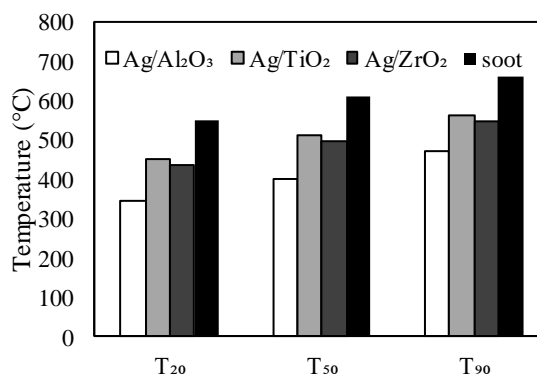
Fig. 6. T_{20}, T_{50}, and T_{90} of soot oxidation (heating rate 10°C/min)

In these cases, the T_{50} were 466 °C, 495 °C, and 509 °C with heating rates of 5 °C/min, 7.5°C/min, and 10 °C/min, respectively. T_{90} were 519 °C, 549 °C, and 562 °C with heating rates of 5 °C/min, 7.5°C/min, and 10 °C/min, respectively. In case of silver catalyst supported by zirconium oxide presented T50 = 461 °C with heating rate 5 °C/min, T_{50} = 473 °C with heating rate 7.5 °C/min, and T_{50} = 495 °C with heating rate 10 °C/min. The T90 from Ag/ZrO$_2$ were 519 °C, 549 °C, and 562 °C with heating rates of 5 °C/min, 7.5°C/min, and 10 °C/min, respectively. The results of T50 and T90 from Ag/TiO$_2$ and Ag/ZrO$_2$ showed a similar performance to promote soot oxidation. Because T50 and T_{90} in the case of Ag/ZrO$_2$ and Ag/TiO$_2$ were slightly different temperatures. It confirmed the similar activity in soot oxidation. The comparison of soot oxidation performance in several case showed as follows: Ag/Al$_2$O$_3$< Ag /ZrO$_2$< Ag /TiO$_2$< pure soot. From the results of silver catalyst supported by alumina showed high performance for soot oxidation from the result. Because of it presented to low T50 and T_{90} which compared with Ag/TiO$_2$, Ag/ZrO$_2$, and pure soot in all heating rates.

3.2 Activation energy

The results of the analysis for the determination of Ea used KAS method, it is necessary to find the slope of the plot of $\ln(\beta/T^{1.92})$ against $1/T$ for different heating rates at a constant α=0.1 to α=0.9 which showed soot decomposition.

The case of soot oxidation on the catalyst base on alumina supporter was presented in Fig. 7. it showed α for determine slope of the plot of $\ln(\beta/T1.92)$ against $1/T$. From result of calculation in this condition made to activation energy were between 33-49 kJ/mol. Fig.8 and Fig.9 show the plot of $\ln(\beta/T^{1.92})$ against $1/T$ and in case of silver catalyst base on titanium oxide can be calculate the activation energy were between 64-79 kJ/mol and case of silver catalyst base on zirconium oxide can be calculate the activation energy were between 71-81 kJ/mol. In case pure soot, the plot of $\ln(\beta/T^{1.92})$ against $1/T$ is shown in Fig.10, can be fined the activation energy were between 103-128 kJ/mol. Fig.11 presents the comparison of the activation energy from soot

oxidation in four condition. From results of activation energy were one to explain the performance of soot oxidation. The several cases of silver catalyst base on different metal oxides support showed different activation energy too. This result showed highest of activation energy in pure soot. However. soot loaded on silver catalyst supported by oxide metal. It showed to reduce the activation energy. In the best case of soot oxidation was a silver catalyst supported by alumina because the result of maximum rate oxidation reaction, T_{20}, T_{50}, T_{90}, and activation energy which the most reduced form pure soot oxidation. It attributed alumina well to promote soot oxidation activity. In case of silver catalyst base on titanium oxide and zirconium oxide showed similar of the result to reduce the activation energy, T20, T50, and T90 from the oxidation of pure soot.
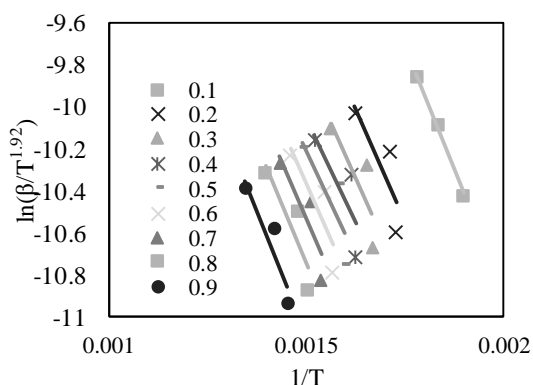

Fig. 7. The plot of $\ln(\beta/T^{1.92})$ against $1/T$ for different heating rates at a constant $\alpha=0.1$ to $\alpha=0.9$ in Ag/Al₂O₃.
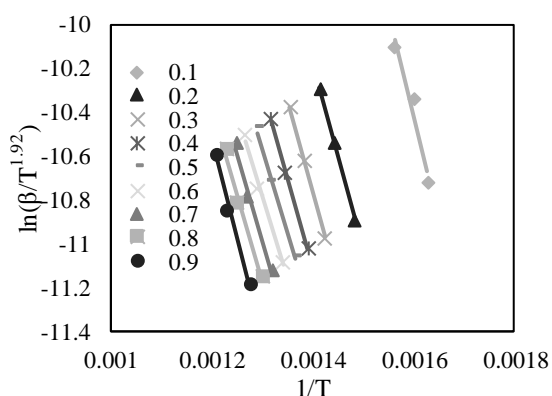

Fig. 8. The plot of $\ln(\beta/T^{1.92})$ against $1/T$ for different heating rates at a constant $\alpha=0.1$ to $\alpha=0.9$ in Ag/TiO₂.

4 Conclusion

The oxidation activity of silver catalyst supported on alumina (Al₂O₃), titanium oxide (TiO₂), and zirconium oxide (ZrO₂) were tested by the thermogravimetric analysis (TG) to compare soot oxidation performance. The result silver catalyst support by alumina, titanium, and zirconium. It was success to promoted the soot oxidation because the temperature of soot oxidation reaction, maximum of oxidation rate and activation
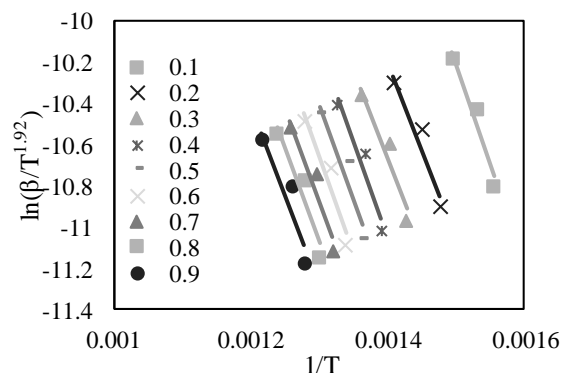

Fig. 9. The plot of $\ln(\beta/T^{1.92})$ against $1/T$ for different heating rates at a constant $\alpha=0.1$ to $\alpha=0.9$ in Ag/ZrO₂.
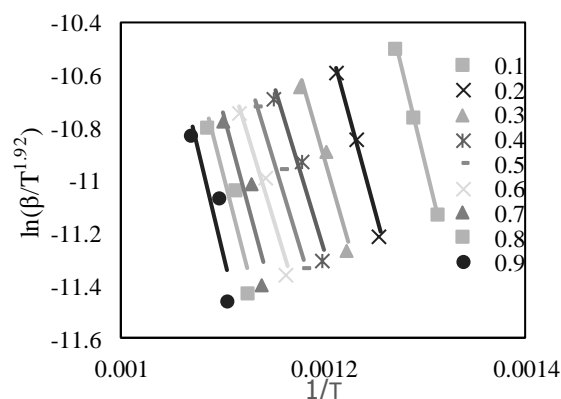

Fig. 10. The plot of $\ln(\beta/T^{1.92})$ against $1/T$ for different heating rates at a constant $\alpha=0.1$ to $\alpha=0.9$ in pure soot.
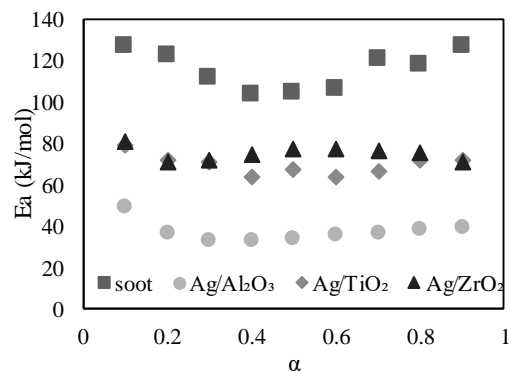

Fig. 11. the comparison of the activation energy from soot oxidation

energy were decrease from temperature in normal soot oxidation. However, the different support in metal oxide group showed the different soot oxidation activity because the activation energy was different which make to different soot oxidation. Ag/Al₂O₃ presented Ea = 33-49 kJ/mol, it showed good assister for soot oxidation. Ag/TiO2 presented Ea = 64-79 kJ/mol and Ag/ZrO₂ presented Ea = 71-81 kJ/mol that the rank of activation energy were similar values, it showed similar of the soot oxidation performance. In future work, the researchers will study the structural characterizations in several catalysts supported by the oxide metal such as specific surface area, crystal structure, and electric state of surface area, etc because some the characteristics of surface properties may assist to promote soot.

Acknowledgement

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