Research Article

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Single Layer and Multilayers of Ru/Al_2O_3 Using Washcoating Method on Stainless Steel Substrate for Fischer Tropsch Synthesis in Microchannel Reactor

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Abstract
Major challenge of using metal based microchannel reactor is catalyst active phase deposition onto the metal surface. Washcoating method is one of the effective procedure for depositing supported catalyst onto the substrate surface. In order to control quality of the catalytic washcoated layer, stability of catalyst slurry, amount of catalyst solution and number of coatings were focused. The catalyst slurry used in this work contained 20wt% of 10%Ru/Al_2O_3, 5wt% of polyvinyl alcohol, 1% of acetic acid and water. The suitable pH of catalyst solution was in a range of 2–4. For the single layer coating, the good adherance of catalytic layer was observed. The highest %weight loss was 0.07% at pH value of 8. From the effect of catalyst slurry volume, 0.1 and 0.2 mL gave relatively low catlyst loading difference of before and after adhesion test. The average thickness of 0.2 mL single layer washcoating was 121.73 µm. Multilayer washcoating, the results clearly showed that the obtained washcoated layer can be used to apply onto the metallic substrate not only single layer but also multilayer. The double layer washcoating gave the highest catalyst loading per unit area for every volume of catalyst slurry. The 0.2 mL gave relatively good adherence and uniform washcoating layer in multilayer coating process. For single layer washcoat on microchannel structure, the obtained thickness was 5 µm.

Keywords: Washcoat, Fischer-tropsch synthesis, Microchannel reactor

1 Introduction

Gas To Liquid (GTL) technology has been identified as promising process for Natural Gas (NG) monetization [1], [2]. The NG is first converted into syngas which mainly consists of carbon monoxide (CO) and hydrogen (H_2) by reforming process. Then synthetic liquid fuel is catalytically synthesized by Fischer-Tropsch synthesis (FT) [1], [3]. FT synthetic fuels are considered to be high quality transportation fuels owing to their high cetane number, as well as low sulfur content and aromatic compounds [4], [5]. The FT reaction is an exothermic polymerization reaction, a large amount of heat of reaction are released during FT process. The removal of heat from the system in order to maintain required operating conditions plays an important role in overall reactor performance. Recently, a concept of microchannel reactor has been widely studied.

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Microchannel reactors could provide predominant advantages over conventional reactor, especially remarkable improvement of mass and heat transfer, on-site production and safety in case of preventing runaway situation [3], [6]. Therefore, a concept of metal based microchannel reactor could provide superior advantages especially for heat transfer improvement [4], [5]. One of the challenges in using microchannel reactors for heterogeneous reaction is to introduce catalytic layer onto a substrate, such as metal surface of the microreactor [5]. A variety of methods for introducing catalytic layer onto the substrate surface have been introduced for example Chemical Vapor Deposition method [7], *In situ* grown coating [8]. However, these methods resulted in cracking and subsequently peeling of the catalyst layer. Especially for in situ growing method, relatively long period of time for growing catalyst support onto the substrate prior to introducing active metal catalyst is required [9]. Moreover, these methods are relatively expensive and low tuning ability in term of layer thickness and catalyst loading. One of the most popular and versatile method to deposit catalyst slurry onto metal substrates is washcoating method [10], [11]. For the washcoating method, pre-synthesized catalyst is typically combined with additives, such as binder and surfactant to make catalyst slurry [8], [12]–[14]. In this method, the lower coating time is required because the use of pre-synthesized or commercial catalyst. Moreover, the major advantage of washcoated catalyst layer is mesoporosity of the layer would be obtained resulting in lower diffusional resistance [8], [9], [15]. The first requirement to achieve successful washcoating process is stable catalyst slurry [15]. The stability depends on several factors, such as the presence of additives, solid particle distribution in the slurry, pH value, and surface charges etc. [8], [13], [15]. Hence, the pH value of medium and surface charge of solid particle should be focused in catalyst slurry preparation process. However, physicochemical properties of the washcoated layer is not only affected by catalyst slurry preparation procedure but also washcoating techniques [12], [13]. The washcoated layer also requires homogeneity, certain catalyst loading and good adhesion property [12]. The two of main parameters during coating process that would affect quality of final coated layer are amount of catalyst solution and number of coating layers. Thus, in this work, investigation of coating parameters is studied in order to develop the simple and reproducible catalyst deposition procedure. The studied parameters are effect of pH value, surface charges of solid particles in catalytic slurry, amount of catalyst slurry, number of coatings, adhesion property and surface morphology.

2 Experimental

2.1 *Catalyst slurry preparation and washcoating method*

In this work, the metal support plates were made from stainless steel (SS316). It were first cleaned with deionized water. Then, the plates were pretreated using thermal treatment method at 900°C to improve the adhesion between the washcoated layer and metallic substrate by forming a surface oxide layer [8], [14]. The catalyst solution was prepared according to Truter *et al*. [8]. A 20wt% of 10%Ru/Al_2O_3 powder prepared by wet impregnation technique, 5% of polyvinyl alcohol (PVA, Mw 31,000–50,000, Sigma-Aldrich), 1% of conc. acetic acid (Analytical Standard, Sigma-Aldrich) and 74% of deionized water were combined and stirred at 65°C and 160 rpm for 3 h and thereafter kept stirring at room temperature for 3 days. The obtained solution was pour onto metal substrate plate, which was then put in a vacuum oven (282A, Fischer Scientific) at 120°C for 24 h. For multilayer coating, excess catalyst from the first layer was removed by sonication treatment. The sonication treatment method as described in section 2.2. Then the following layers was applied onto the previous one to form multilayers. The zeta potential of the solution was mesured using zeta potential analyzer (MALVERN Zetasizer Nano ZS90) in order to determine surface charges of solid particles in the slurry. The pH of prepared slurry was adjusted by diluted acetic acid. The washcoating layer morphology was observed using optic microscopy (NIKON SMZ800)

2.2 *Catalyst slurry preparation and washcoating method*

In order to analyze adhesion property of washcoated layer, solvent treatment by ultrasonic technique was used in this work. The coated plates were immerged in 10 mL petroleum ether and sonicated in ultrasonic cleaner (ELMA-P30H Ultrasonic cleaner, frequency

37 kHz) for 30 min at room temperature. The adherance of washcoated layer was evaluated based on weight loss following Equation (1) [8].

$$\%Weight\ loss = \left(\frac{W_{before} - W_{after}}{W_{before}} \right) \times 100\% \quad (1)$$

Where W_{before} and W_{after} were weight of catalyst coated on the substrate plate before and after solvent treatment, respectively.

3 Results and Discussion

The washcoating process was done following three major steps. The first step was to prepare stable catalyst slurry to be deposited. The second step was surface treatment of the substrates. The third step, metallic substrates was washcoated by pouring the certain amount of catalyst slurry onto the substrate.

3.1 *Catalyst slurry properties*

The key parameter that controls inter-particles interactions is the zeta potential of solid particles in catalyst slurry. The zeta potential indicates electrostatic equilibrium on the interface. This variable could be used to indicate a suitable pH range reflexing stability of the catalyst slurry. The relation of zeta potential as a function of pH are shown in Figure 1.

It can be seen that the slurry with pH value of 2–4 gave the highest value of zeta potential in the range of 9.32–10.36 mV. This is beacuse, in this pH range, the charges in catalyst slurry could maximize electro static force between metal surface and catalyst particles. When pH value of the slurry is too high or too low, it means that electro static field pushes the particles in opposite direction to metal surface. Therefore, pH value of 2–4 were considered as the most suitable pH range maximizing replusion between particles [14]. Moreover, the results were in a good agreement with L.C. Almeida *et al*. suggesting that suitable pH for washcoating of Ru/Al_2O_3 were in a range of 3–4 [12].

3.2 *Single layer washcoating*

In order to study adherance behavior, ultasonic technique was used by measuring weight loss caused by ultrasound exposition. The results obtained from single layer

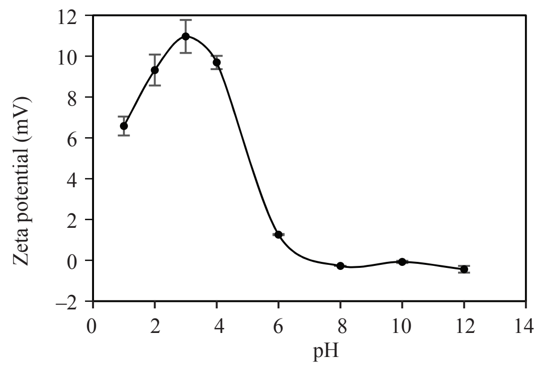

Figure 1: Zeta potential of Ru/Al_2O_3 as a function of pH.

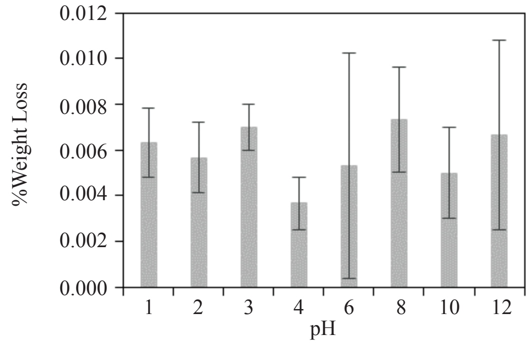

Figure 2: Effect of pH value of Ru/Al_2O_3 catalyst solution on adhesion of SS316 surface.

washcoat can be seen in Figure 2, where the slurry with pH4 exhibited the lowest weight loss after solvent treatment. These results were in a good agreement with the previous section. Surface morphology of washcoated layer should be considered as an important aspect because catalytic surface is the location that chemical reaction take place. Therefore, homogeniety and consistency of the surface would be very important for catalytic activity. The different coating technique lead to different finished surface property [8], [9].

Figure 3 showed morphology of washcoated surface obtained from different pH value. It can be seen that the washcoated layer obtained from pH value higher than pH6 showed less homogeniety and uniformity. This may be due to at high pH range, the charges of solid paritcles in the solution were neutral form leading to lower stability of colliodal solution [12]–[14]. Another important parameter, which plays an important role in washcoating process is volume

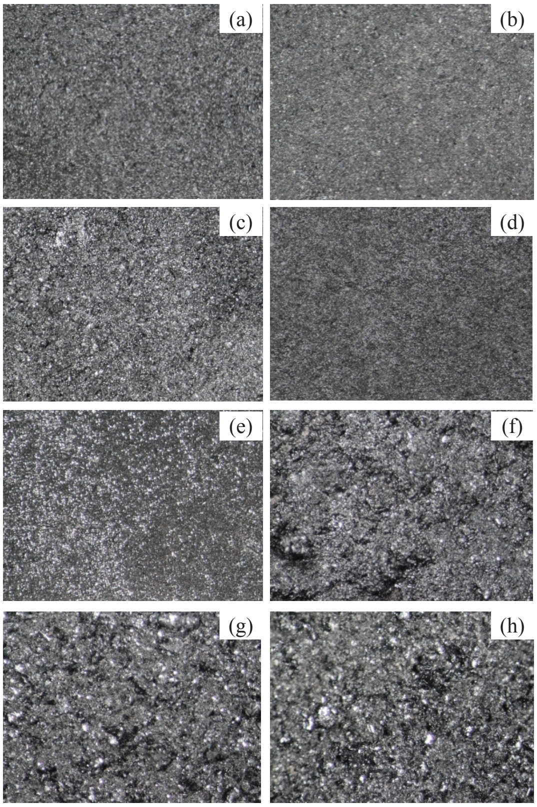

Figure 3: Surface morphology image (X30) of catalytic washcoated layer at different pH value (a) pH1 (b) pH2 (c) pH3 (d) pH4 (e) pH6 (f) pH8 (g) pH10 (h) pH12.

of used catalyst slurry. As mentioned above, the advantages of wash coating method are versatility and simplicity. However, the lack of information about systematic design procedure and reproducability were noticable. Thus the certain amount of catalyst slurry which was deposited onto the metallic substrate was focused in this part after the most suitable pH value was obtained. The volume of washcoat slurry was varied in range of 0.1–0.5 mL for a substrate area of 6.45 cm^2 (2.54 cm × 2.54 cm).

The effect of specific loading obtained from varying volume of catalyst solution are shown in Figure 4. It can be clearly seen that the higher volume of solution was applied the higher catalyst loading was obtained before adhesion test. With 0.3–0.5 mL of catalyst solution, the results showed vast difference of weight per unit area after adhesion test indicating that adhesion property decreased when quantity of used solution increased. In the contary, the specific loading before and after adhesion test of 0.1 and 0.2 mL were relatively close. The crossectional image of washcoated layer on the metallic substrate are shown in Figure 5. The average thickness of 0.2 mL single washcoated layer was 121.73 μm.

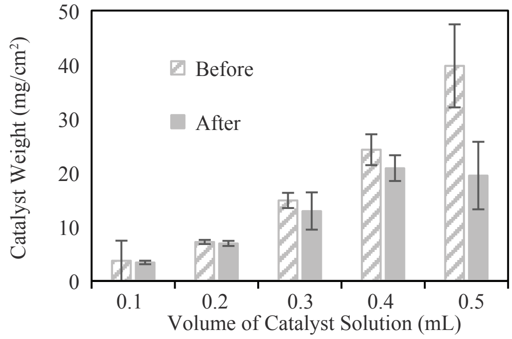

Figure 4: The effect of volume of catalyst solution on specific loading before and after adhesion test.

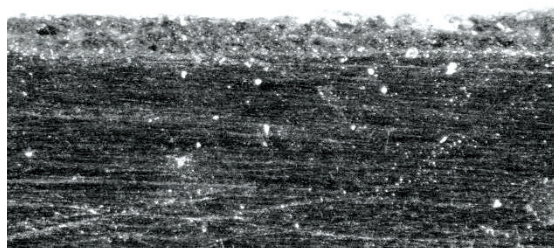

Figure 5: Crossection microscope picture (X30) of 0.2 mL single layer washcoating.

3.3 *Multilayer washcoat*

In order to increase catalyst loading, multilayer washcoating procedure has to be developed. Thus, effect of number of coating on adhesion quality was presented in this section. Figure 6 shows the effect of catalyst solution volume and number of coatings and it clearly showed that the obtained washcoat slurry can be used to apply onto the metallic substrate not only a single layer but also multilayer. As mentioned before, the excess solid was removed by sonication techique. Hence, the achieved catalyst loading could be used to describe washcoating property of each individual coating. Apparently, the lowest specific loading was achieved by single layer coating for both 0.2 and 0.3 mL.

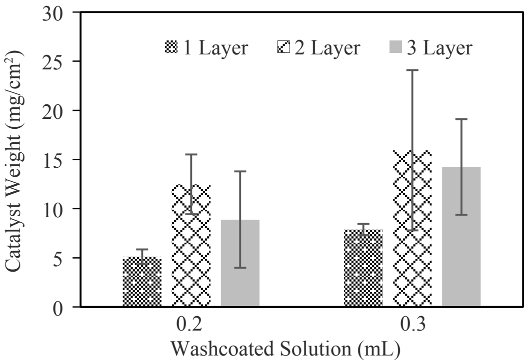

Figure 6: Catalyst weight comparison obtained from single layer and multilayer washcoating at pH4.

The highest catalyst loading was gained by double layers coating. These results are in a good agreement with A. Scheuer *et al*. [16] and Truter *et al*. [8] as theirs reports suggested that double layer washcoat are commonly used in automotive application and gave relatively high adherance quality. This is due to catalyst washcoat would adhere better on the surface of catalyst layer compared to rough metallic surface [8], [16]. From the overall perspective, 0.3 mL solution gave slightly higher catalyst loading per unit area compare to 0.2 mL. However, air bubbles formed between layers could not be removed during multilayer washcoat for 0.3 mL solution. Surface morphology of multilayer coating (three layers) are shown in Figure 7.

Figure 7(a) shows the coating with 0.2 mL slurry and it showed relatively good consistency of the obatined catalytic layer and air bubbles on the surface could not be observed. On the other hand, the catalytic layer obtained from 0.3 mL solution exhibited inconsistency and air bubbles on the surface can be seen in Figure 7(b). The presence of air bubbles could make a cratered surface resulting in incompatibility between layers [8].

3.4 *Washcoat on microchannel*

Preliminary study of washcoating technique could not be completely successful without testing the procedure on microchannel structure substrate. Therefore, parallel microchannel structure was coated by using the most stable catalyst slurry from the previous section, which was pH value of 4 with 0.2 mL solution. Parallel-straight microchannel structure reactor usually has

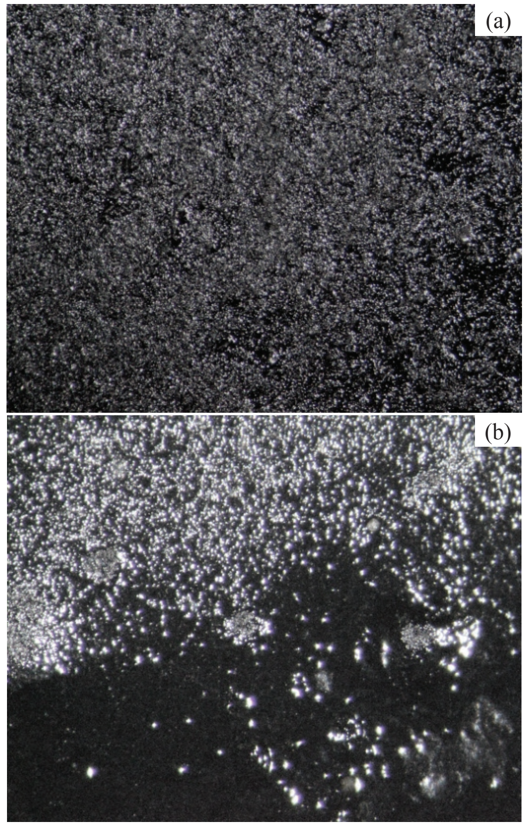

Figure 7: Surface morphology image (X10) of multilayer catalytic washcoat with different catalyst volume (a) 0.2 mL (b) 0.3 mL

rectangular channel shape and size of the channel and the shape of the channel can be changed according to design of reactor and manufacturing techniques. The parallel straight channel with rectangular shape of 0.5 mm × 0.6 mm height and width was used in this work. The overall size of microchannel plate was 10 mm × 10 mm width and length. The aim of washcoating on micro channel is to be a guidance for real application in reaction engineering perspective. The crossectional image of uncoated and coated microchannel structure are shown in Figures 8 and 9.

It can be clearly seen that the obtained washcoat layer on microchannel substrate shows small non–uniformity compared to washcoated layer on flat surface, especially in the corner of the channel. However, the obtained shape of microchannels were still in the nearly rectangular shape. For this reason, we could hypothesize that the transport behavior of fluids in the

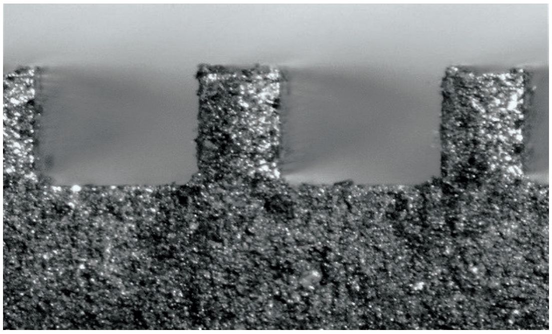

Figure 8: Crossection microscope picture (X20) of uncoated microchannel substrate.

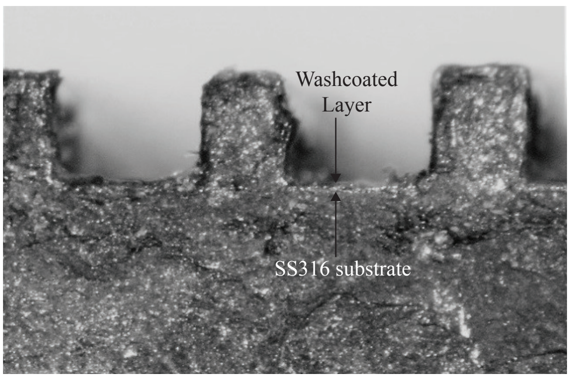

Figure 9: Crossection microscope picture (X20) of 0.2 mL single layer washcoating on microchannel.

microchannel would not be affected by the change of channel shape. Moreover, this part could be useful as a guideline for mathematical or numerical model of fluids transport phenomena in microchannel reactor. According to surface area of microchannel structure which was higher than that of flat surface, the obtained thickness of the coated layer was changed. The average thickness was 5 µm approximately.

4 Conclusions

The aim of this work is to develop a simple and reproducible Ru/Al_2O_3 catalyst deposition procedure for FT reaction in microchannel reactor, the washcoating method, to introduce catalyst slurry onto metallic substrate (SS316). The effect of pH value, surface charges of solid particles in catalytic slurry, amount of catalyst slurry, number of coatings, adhesion property and surface morphology were focused. The washcoating process was done with three major steps: catalyst slurry preparation, metal surface treatment and catalyst slurry deposition onto the metal substrate. In order to prepare stable catalyst solution, the effect of slurry pH value on zeta potential were tested. The pH value of two to four gave the highest zeta potential. Thus, it could be noted that, suitable pH was in a range of two to four. The results from single layer adhesion test were in good agreement with zeta potential test suggesting that pH 1 to 4 gave relatively low weight loss. The highest %weight loss was 0.007% resulting from pH value of eight. From the effect of catalyst slurry volume, 0.1 and 0.2 mL gave relatively low difference of specific loading of before and after adhesion test. The average thickness of 0.2 mL single layer washcoating was 121.73 µm. For washcoating on microchannel structure, the average thickness of washcoated layer was 5 µm. Moreover, the results showed that shape of the microchannel was not changed after washcoat with thin layer of the obtained catalyst slurry. The multilayer coating was performed in order to increase the specific catalyst loading. In this work, the double layer washcoating gave the highest catalyst loading per unit area for every volume of catalyst slurry. The 0.2 mL gave relatively good adherence and uniform washcoating layer for multilayer coating process.

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