CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Monolith

The monolith, from Corning Glass, used in this study is cordierite. Table 4.1 gives physical properties of the monolith obtained from characterization data.

Table 4.1 Physical properties of the monolith

Property	Description
Monolith configuration	Cylinder (3.5 cm diameter x 4.0 cm long)
Channel configuration	Square (1 mm x 1 mm)
Cell density	64 cells/cm^2
Alumina washcoat	20 %
Washcoat thickness	about 35 microns
BET surface area	28.87 m^2/g monolith
Average pore diameter	96.28 °A

SEM picture of the square-channel monolith used in this study is shown in Figure 4.1. It is observed from Figure 4.2 that the alumina washcoat is concentrated particularly at the corners of the square channels. Figure 4.3 shows surface morphology of alumina washcoat. The alumina is generally coated on a monolith surface by dipping into a slurry of alumina and followed by drying and calciming. The process is repeated several times. As a consequence, it is suspected that the washcoat may significantly dissolve or lost from the surface when water passes through the monolith. Moreover, the
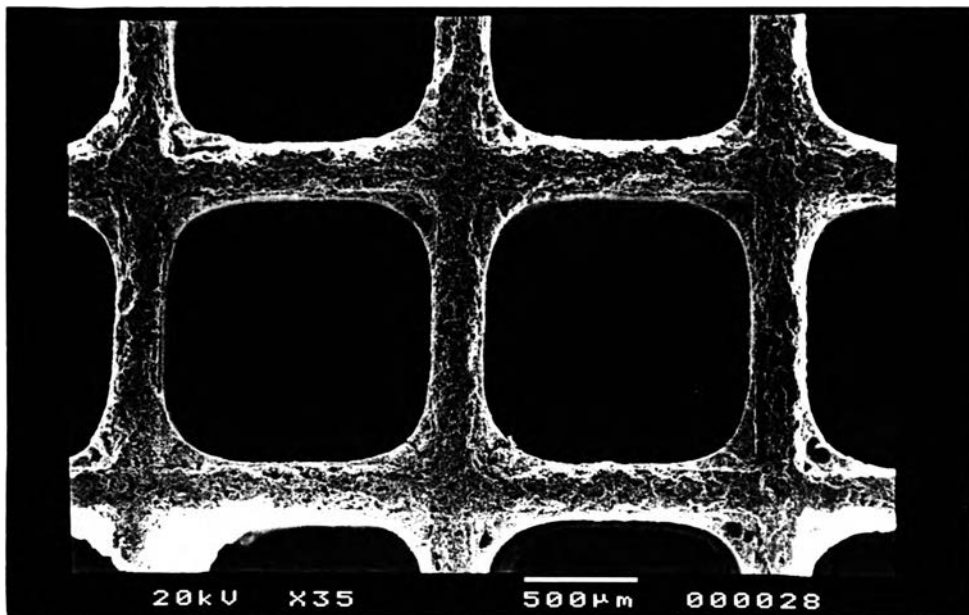
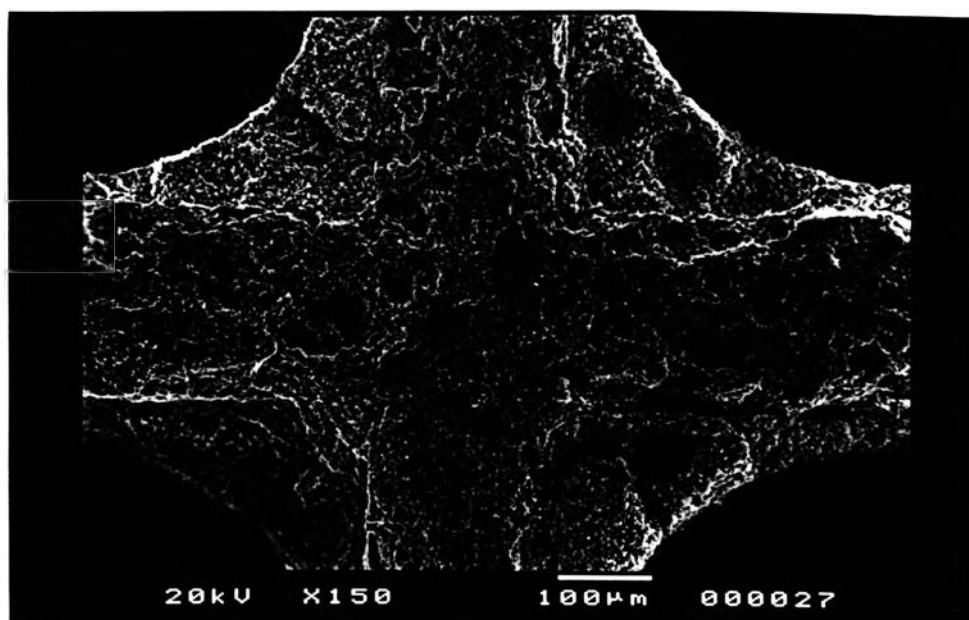Figure 4.1 The square-channel monolith.

Figure 4.2 The alumina washcoat concentrated particularly at
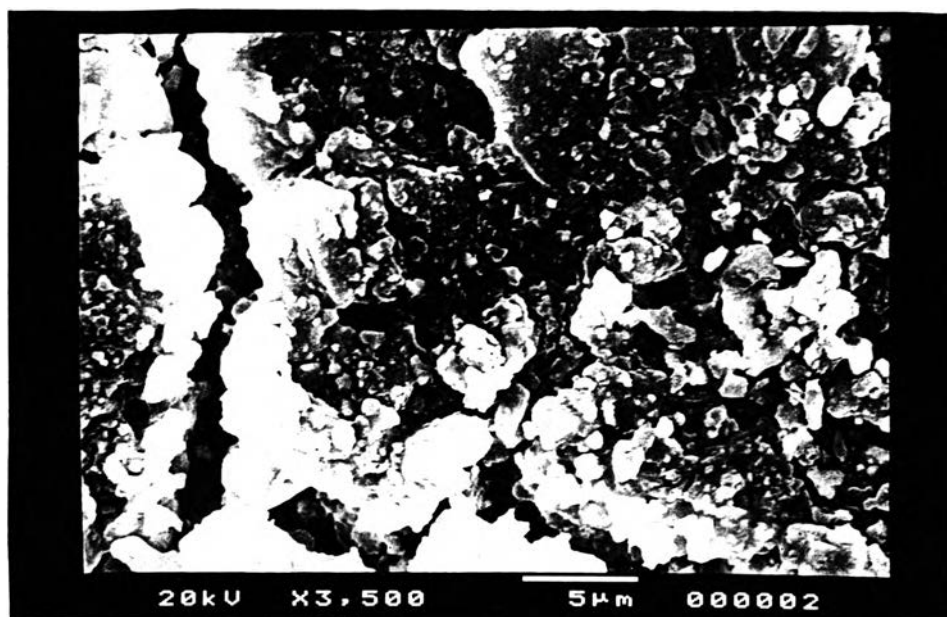the corners of the channels.

Figure 4.3 Alumina washcoat morphology on monolith surface.

alumina washcoat binding strength on the monolith might be another reason for washcoat loss from the surface.

4.2 Catalyst Characterization

Catalysts prepared in this study and reduced either by formaldehyde solution or by thermal reduction are summarized in Table 4.2. It is known that aldehydes are readily oxidized to yield carboxylic acids by very mild oxidizing agents such as Ag^+ or Cu^{2+}. However, oxidation by Ag^+ requires an alkaline medium; to prevent precipitation of the insoluble silver oxide, a complexing agent was added; ammonia (Pine, 1987). Tollen's reagent which is well known in organic chemistry is a mixture of $AgNO_3$ with aqueous ammonia, producing diamminosilver (I) ion, $Ag(NH_3)_2^+$ or so called silver-amine complex ion. As it does this, silver is reduced from the +1 oxidation state to

Table 4.2 Summary of catalysts prepared for single-pass killing study

Catalyst	Precursor solution	Silver loading (% Ag / Al_2O_3)*	Reduction technique	Reduction condition
Blank	-	-	-	-
A	$Ag(NH_3)_2^+$	22.4	Formaldehyde	Room Temp./ 30 min
B	$Ag(NH_3)_2^+$	21.5	Formaldehyde	100 °C/30 min
C	$Ag(NH_3)_2^+$	14.4	Formaldehyde	100 °C/30 min
D	$Ag(NH_3)_2^+$	2.9	Formaldehyde	100 °C/30 min
E	$AgNO_3$	35.7	Thermal	800 °C/24 hr
F	$AgNO_3$	24.0	Thermal	800 °C/12 hr
G	$AgNO_3$	9.9	Thermal	800 °C/24 hr
H	$Ag(NH_3)_2^+$	20.9	Thermal	800 °C/24 hr

* Silver loading calculated was based on 20 % Al_2O_3 washcoat on monolith.

metallic silver (Solomons, 1990). This concept was applied to prepare catalysts used in this study.

The ion-exchange is believed to occur because in such strong basic silver-amine complex solution used, the alumina should show its negatively charged surface. Hence, $Ag(NH_3)_2^+$ which is a positive ion complex can be adsorbed by the means of ion-exchange. $Ag(NH_3)_2^+$ adsorbed on the alumina washcoat surface will be then reduced to metallic silver by immersing the monolith into formaldehyde solution. Because high temperature treatment was not required, smaller silver crystallites were produced for the catalysts prepared by this technique, when compared to the catalysts prepared by thermal reduction.
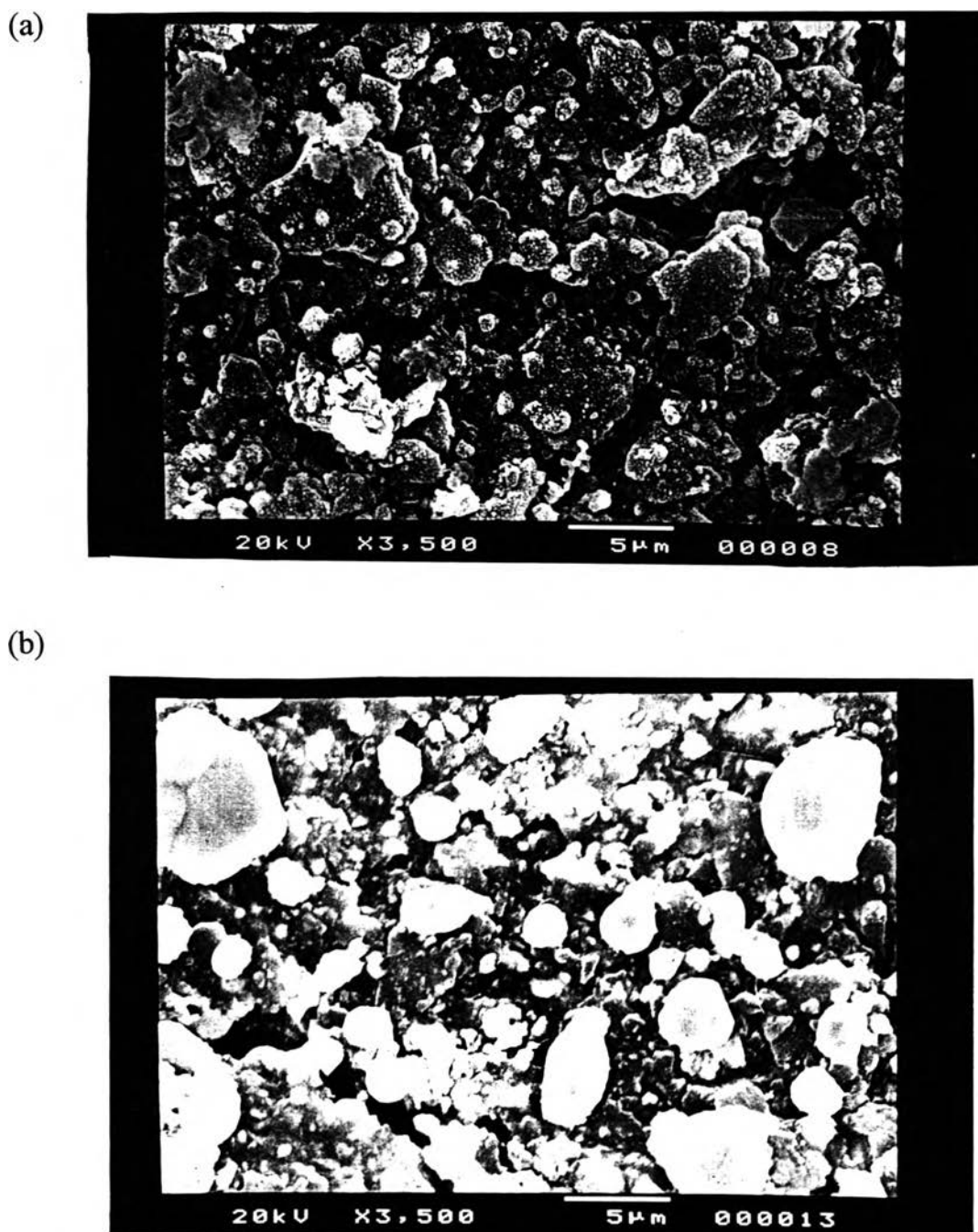
(a)

(b)

Figure 4.4 SEM pictures of catalysts C and G at x 3,500.

(a) Catalyst C (14.4% Ag) reduced by formaldehyde solution.

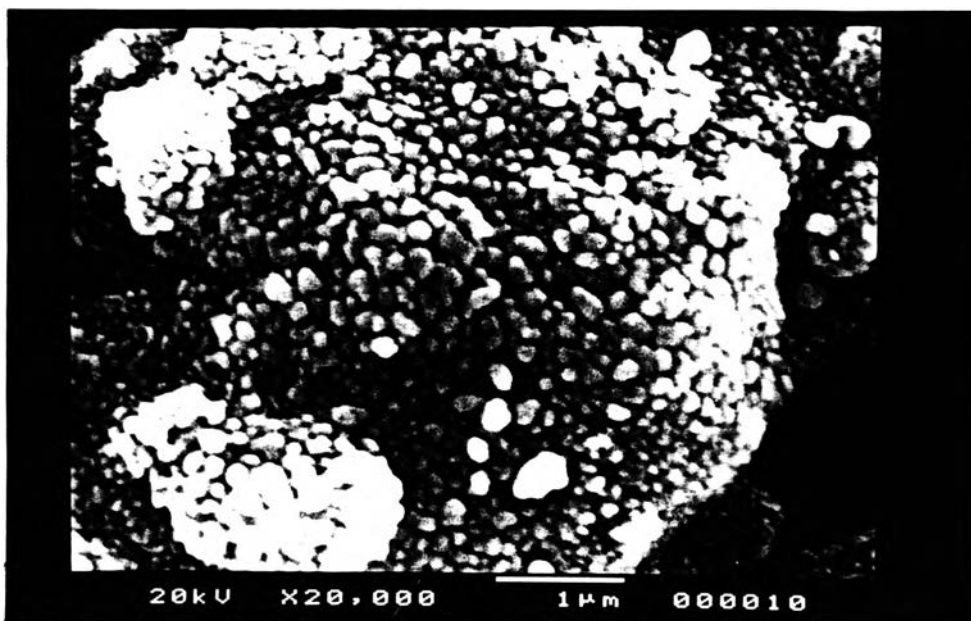(b) Catalyst G (9.9 % Ag) reduced by thermal reduction.

Figure 4.5 SEM picture of catalyst C (14.4 % Ag) at x 20,000.

It is observed in Figure 4.4b that catalyst G (9.9% Ag) prepared by thermal reduction shows much larger silver crystallites obtained, comparing to catalyst C (14.4 % Ag) produced by reduction in formaldehyde solution (Figure 4.4a).

The closer SEM picture of catalyst C is shown in Figure 4.5. The overlap of silver particles is observed on the washcoat surface.

In comparison to the catalysts prepared by thermal reduction, catalyst prepared by silver-amine complex solution produced smaller silver particles eventhough it contained higher silver content on the surface. This can be illustrated by comparing the two catalysts shown in Figure 4.6. The change in surface morphology of catalyst obtained by thermal reduction is also observed in Figure 4.6a. The surface become more smooth because the high temperature, 800 °C, collapses the pores. Silver crystallites grow due to sintering effect. Moreover, the mobilization of silver promotes the growth of particles.
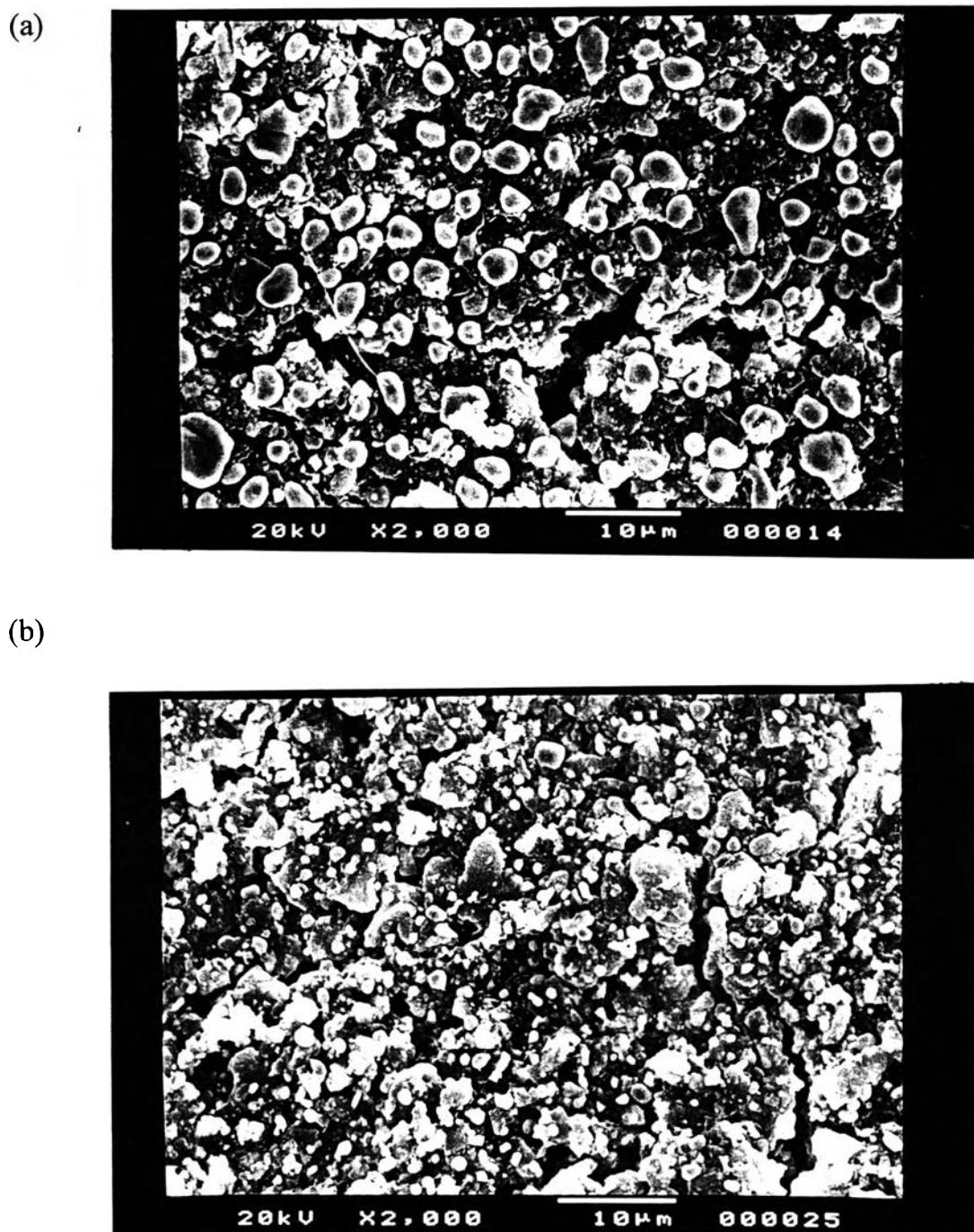
Figure 4.6   (a) Catalyst G (9.9% Ag) prepared via silver nitrate solution and reduced at 800 °C for 24 hours.

(b) Catalyst H (20.9 % Ag) prepared via silver-amine complex solution and reduced at 800 °C for 24 hours.

4.3   Single-pass Killing Study

Table 4.3 summarizes the experimental results of the single-pass killing study of catalysts, including blank monolith. It can be observed from Table 4.3 that blank monolith itself does not adsorb bacteria onto its surface in detectable amount. However, either multiplication or death might occur during the experiment, but as the results indicated neither one.

Catalyst A and catalyst B were prepared by ion-exchange technique and were reduced in formaldehyde solution at room temperature and at 100 °C in water bath, respectively. The plot of killing efficiencies of both catalysts is shown in Figure 4.7. The plot of silver content in output samples of both catalysts is exhibited by Figure 4.8. It can be concluded for the two catalysts, which have nearly the same loading, that the catalyst reduced in formaldehyde solution at boiling temperature is more active in bacterial destruction and is better bounded on the surface, producing lower silver content found in output sample. To see the effect of silver loading on killing efficiency of catalysts reduced in formaldehyde solution at 100 °C, Figure 4.9 shows the comparison among catalyst B (21.5 % Ag), catalyst C (14.4 % Ag), and catalyst D (2.9 % Ag). Figure 4.10 exhibits silver contents in output samples of these three catalysts. The sharp drop of killing efficiency is observed from Figure 4.9 when the silver loading is decreased. It is found that the more silver loading on the surface was, the more silver lost into water (Figure 4.10). One possible explanation is that at the slow rate required to achieve highest E.coli killing, the erosion was too rapid, particularly for the catalyst with higher silver loading. Moreover, multiplication of E.coli was investigated in catalyst D (2.9 % Ag) with 0.10 ppm silver content found in the output sample. This confirms that the E.coli killing results from oxidation reaction pathway. It is not the effect of silver ions dissolved.

Table 4.3 Experimental results of single-pass killing study

Catalyst	Contact Time (sec)[1]	% $E.coli$ killed[2]	Silver Content (ppm)[3]
Blank	2.9	-3.3[4]	-
	3.8	4.5	-
	5.7	0.0	-
A	2.9	53.3	0.90
	3.8	56.8	1.45
	5.7	91.8	3.22
B	2.9	63.2	0.42
	3.8	65.5	0.60
	5.7	93.9	2.65
C	2.9	5.5	0.16
	3.8	34.2	0.40
	5.7	60.0	1.16
D	2.9	-5.3[4]	0.10
	3.8	29.4	0.21
	5.7	56.3	0.88
E	2.9	88.0	2.77
	3.8	94.0	3.81
	5.7	99.6	4.75
F	2.9	83.0	4.08
	3.8	94.5	5.26
	5.7	100.0	7.14
G	2.9	74.2	1.98
	3.8	91.1	2.39
	5.7	98.5	2.82
H	2.9	82.2	1.99
	3.8	90.9	3.42
	5.7	97.6	3.63

[1] Contact time was calculated by monolith void volume divided by flow rate used. The average void volume of monolith is 19 ml.

[2] % $E.coli$ killed was calculated by following :

(Initial count - Final count)(100)/Initial count

[3] Silver content found in outlet sample was determined by AAS.

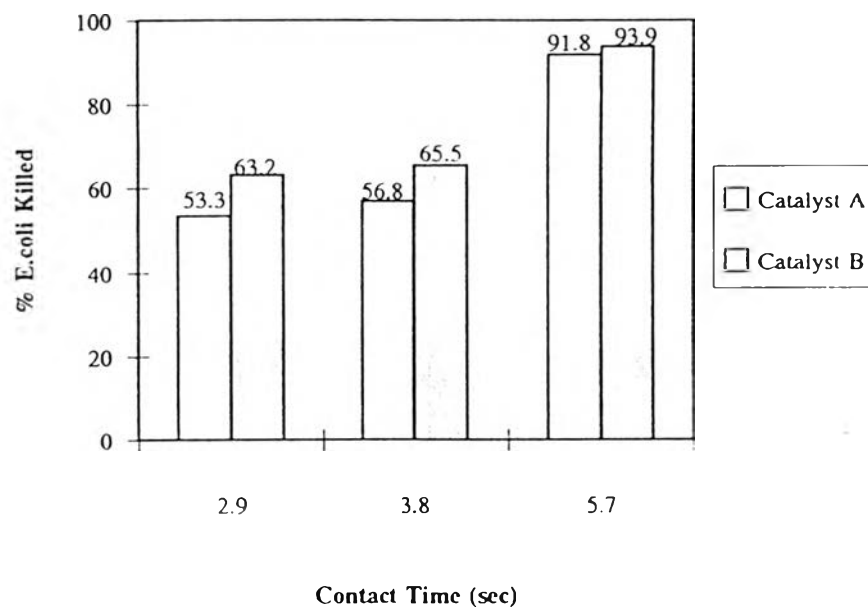[4] The minus sign shows that the multiplication of $E.coli$ occurred.

Figure 4.7 Effect of formaldehyde solution temperatures on killing efficiencies of catalyst A and catalyst B.
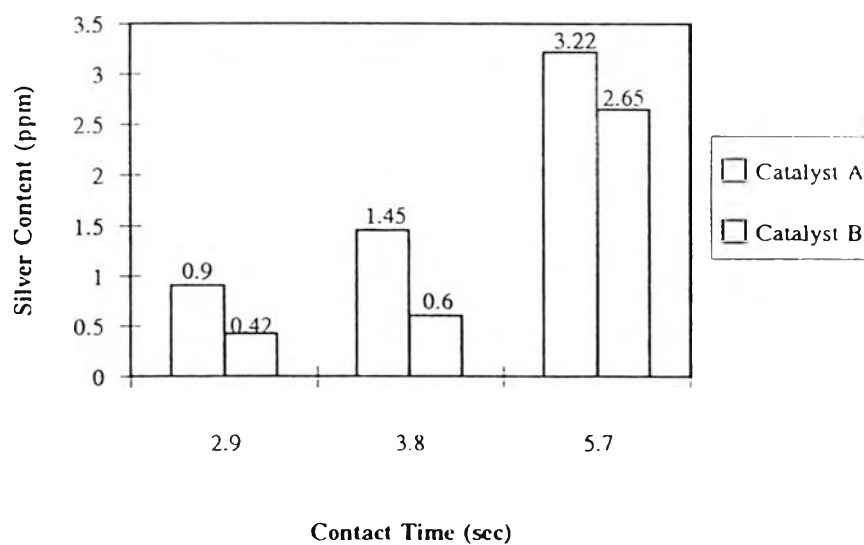

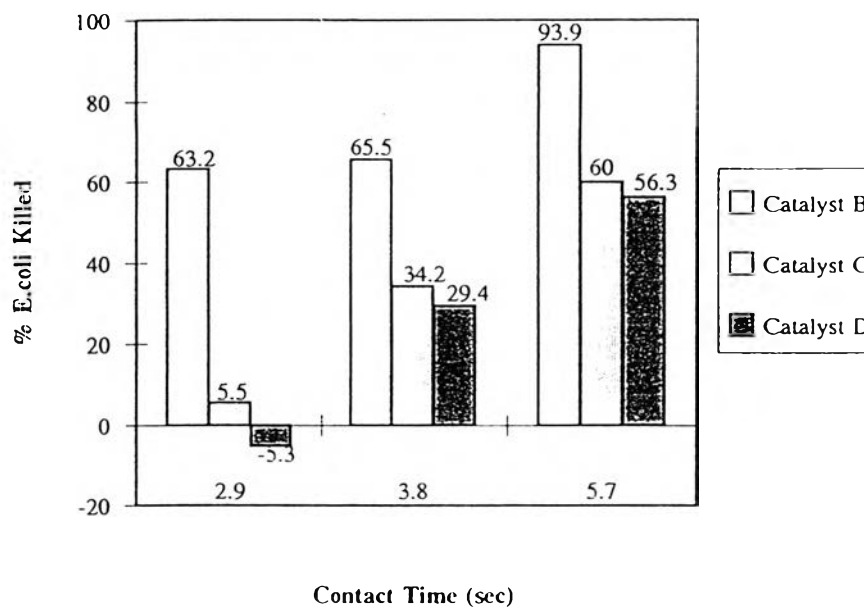Figure 4.8 Silver content found in output samples of catalyst A and catalyst B.

Figure 4.9 Effect of silver loadings on killing efficiencies of catalyst B,
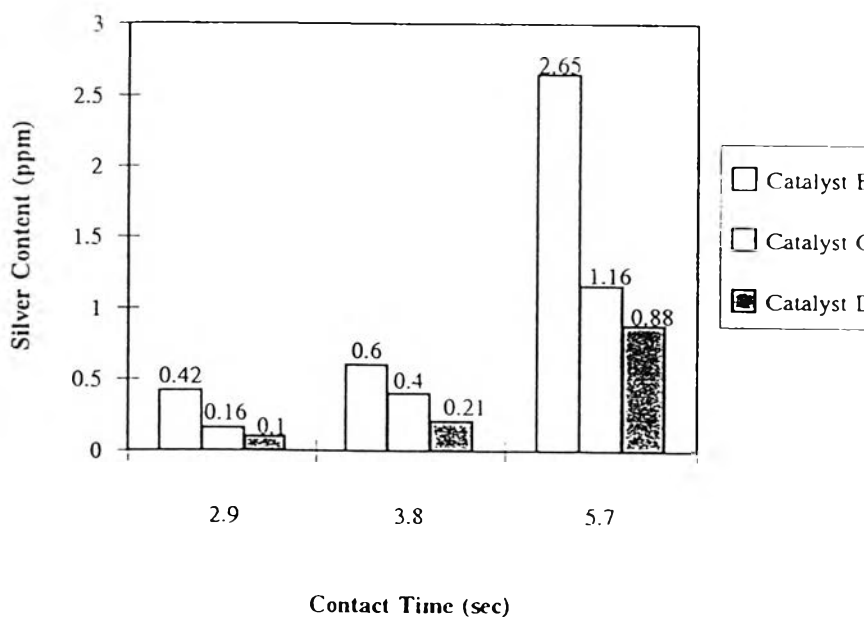catalyst C, and catalyst D reduced in formaldehyde solution.

Figure 4.10 Silver content found in output samples of catalysts B,
catalyst C, and catalyst D reduced in formaldehyde
solution.

4.4   Effect of Dissolve Silver Ions on Bacterial Destruction

In order to verify the effect of dissolved silver ions on the killing efficiency, a study of toxicity test was performed. Figure 4.11 shows effects of both dissolved silver concentration and contact time on the killing efficiency. At a fixed concentration, samples were removed to test by membrane filtration method after exposure periods. Three drops of EDTA were dropped into the samples immediately after collection. The disinfection kinetics is normally observed to follow Chick's law as follows :

$$dN/dt = -kN$$

Where N = number of organisms at time t

   t = time

   k = constant, $time^{-1}$

If N_0 is the number of organisms at time equals to 0, the integration of the above equation is

$$N/N_0 = e^{-kt} .$$

Particular attention will be paid to the disinfection kinetics at silver content of 0.10 ppm. The exponential fitted equation from the experimental data is

$$N/ 100 = e^{-0.0278t}$$

with $r^2 = 0.9922$. Comparing to catalyst D (Figure 4.9 and 4.10) which the silver content was found to be 0.10 ppm at 2.9 second contact time, if the silver ion really dissolved in the system water, 0.8 % of *E.coli* should be killed, not multiplication. It can be concluded that the presence of silver in the water was mainly in tiny particles of metallic silver rather than in dissolved form of silver.
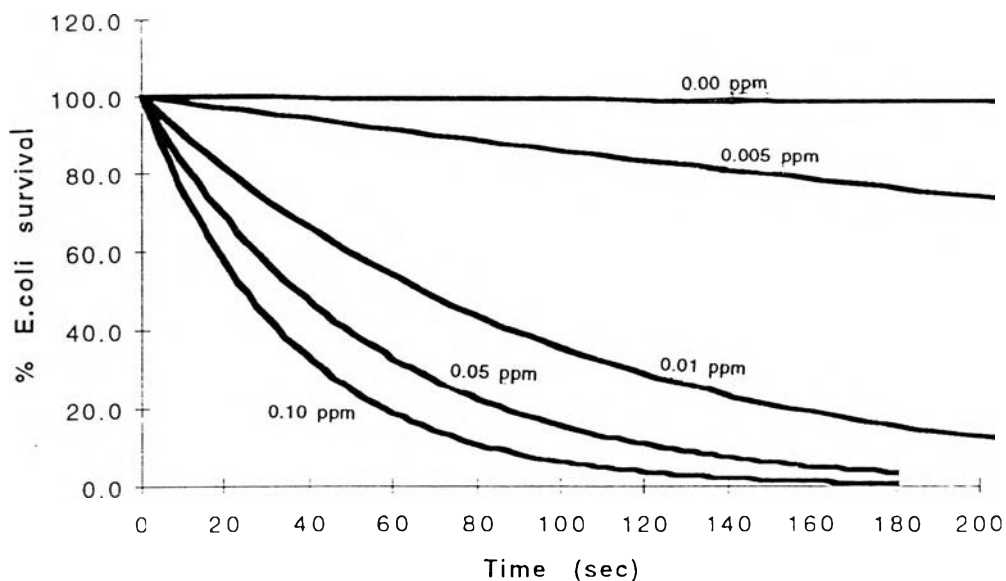
Figure 4.11 Effect of silver ion on *E.coli* killing.

Catalyst reduced by thermal reduction, eventhough it produced much larger silver crystallite sizes comparing to catalyst reduced in formaldehyde solution, was more active (Figure 4.12). This can be explained by the unique and unusual property of silver particle sizes of silver catalyst. In addition, only a slight decrease in killing efficiency, when the contact time was decreased, was observed for catalyst reduced by thermal reduction. In contrast, for the catalysts reduced by formaldehyde solution, a significant decrease in killing efficiency was obtained when the contact time was decreased. Figure 4.12 illustrates this observation.

Figure 4.13 shows that eventhough catalyst reduced by thermal reduction gives higher killing efficiency, silver content found is also higher in comparison to the catalysts reduced by formaldehyde solution. Some possibilities on this will be discussed later.
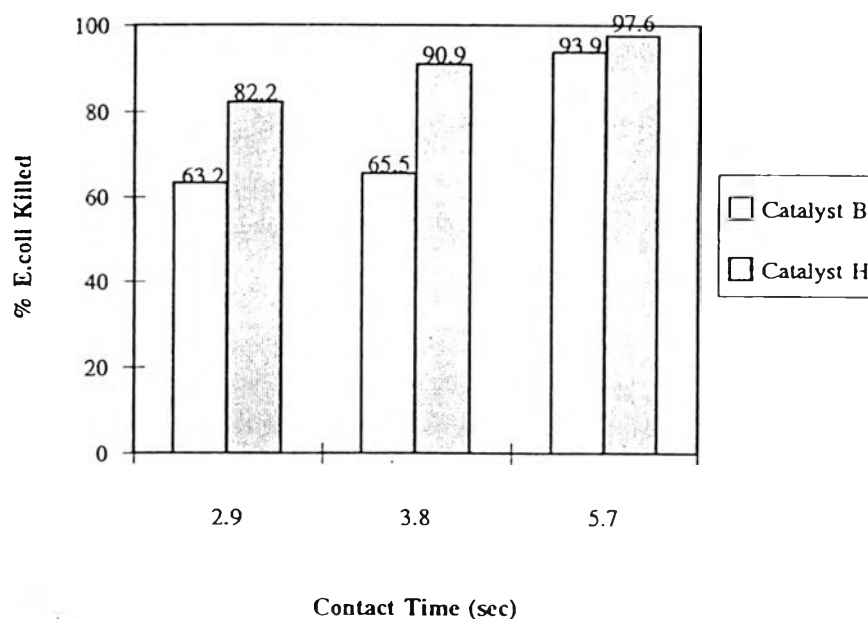
Figure 4.12 Effect of reduction technique of catalyst B (21.5 % Ag) reduced in formaldehyde solution and catalyst H (20.9 % Ag) reduced by thermal reduction. (Both catalysts prepared via silver-amine complex solution.)
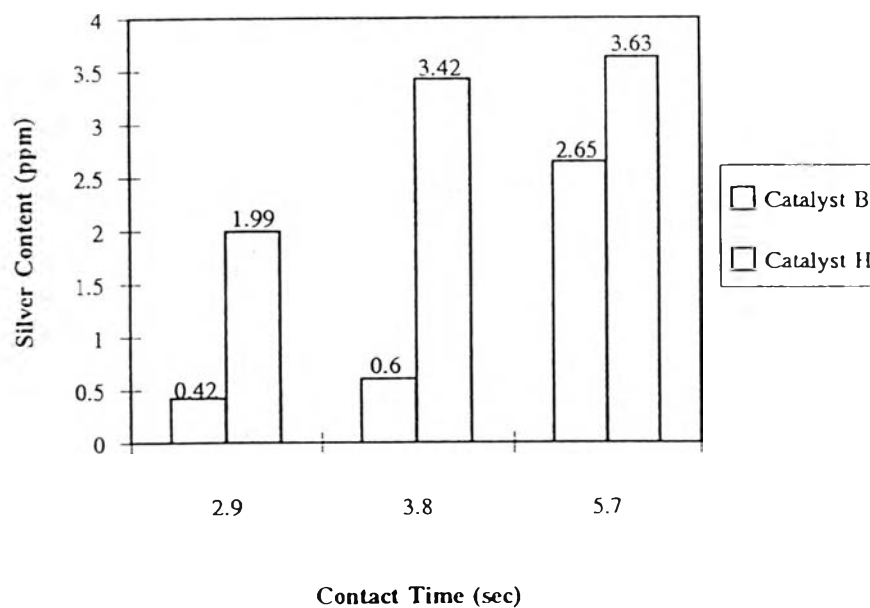

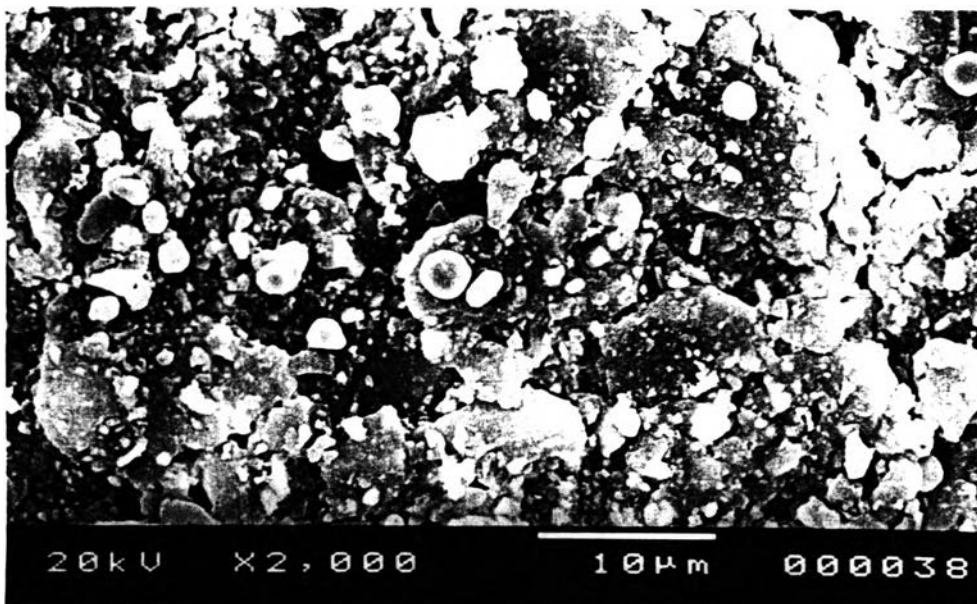Figure 4.13 Silver content found of catalyst B and catalyst H.

Figure 4.14 Surface morphology of used catalyst (catalyst H).

The change of catalyst surface after used in experiment is shown in Figure 4.14 for catalyst H (20.9 % Ag). It was observed metallic silver was detached from surface.

Catalyst E (35.7 % Ag) reduced at 800 °C for 24 hours, catalyst F (24.0 % Ag) reduced at 800 °C for 12 hours, and catalyst G (9.9 % Ag) reduced at 800 °C for 24 hours were compared for their killing efficiencies as plotted in Figure 4.15. It can be concluded that the killing efficiency increased with an increase in the silver loading when the contact time was short. As increasing in the contact time, there was no significant effect of the silver loading on the killing efficiency.

As can be seen from Figure 4.16, the silver loss increased when the contact time increased and the silver loss decreased with an increase in the calcination time. From the experimental results, it indicates that a better catalyst can be achieved by preparing at higher temperature and longer calcination time.
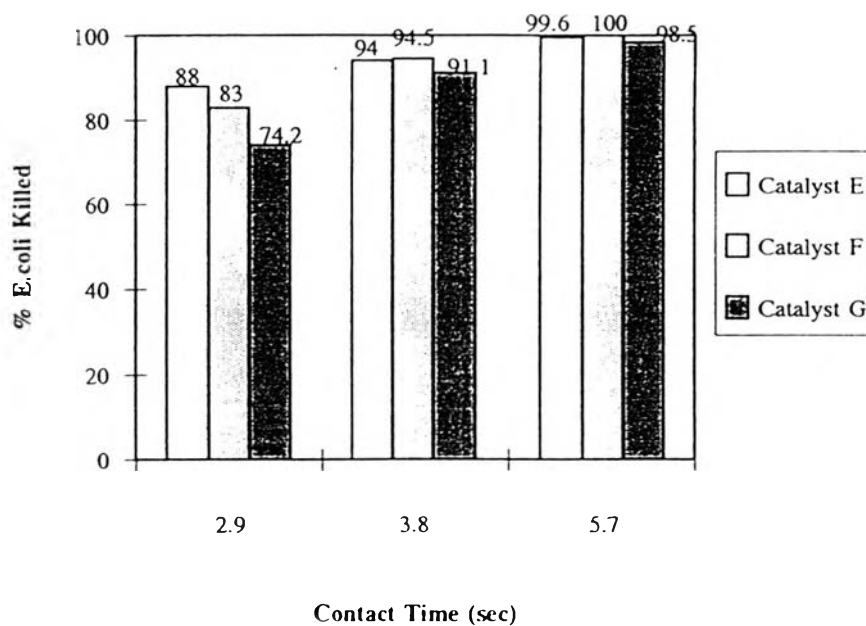
Figure 4.15 Effect of thermal reduction conditions of catalyst E, catalyst F,
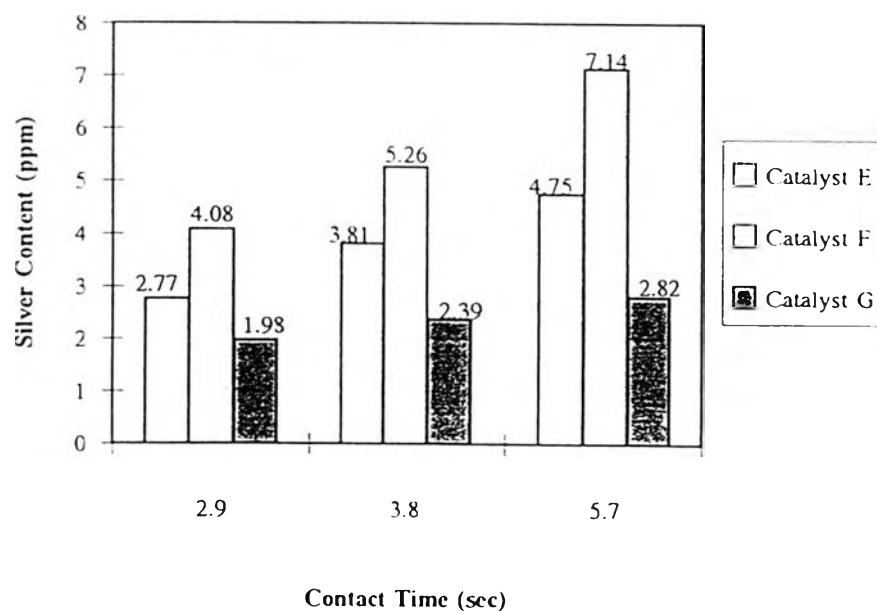

Figure 4.16 Silver contents in treated waters when using catalysts reduced at different thermal reduction conditions.

4.5   Silver Loss from Monolith Surface

Focusing on the silver contents found in the output samples of catalyst E (35.7 % Ag), catalyst F (24.0 % Ag), and catalyst G (9.9 % Ag), catalyst F produced much higher silver content than the others eventhough nearly the same number of E.coli was killed. This may be concluded that the killing of bacteria did not come from silver ion but oxidation pathway. In another word, if bacteria were really killed because of the effect of silver ion, catalyst F should much more effective than the others. Too much silver loading on the surface did not increase the catalyst efficiency very much but higher silver content was found.

The reasons why silver was lost from monolith surface will be discussed here. Many studies confirmed that one of the most important factors of silver catalyst is the support used. It is widely known that alpha-alumina is an unique support material for the commercial silver catalysts employed in ethylene oxide production. Other conventional and non-conventional support materials offer reduced or zero selectivities towards the partial oxidation route. All the silver catalysts that have long been studied are for gas phase oxidation reaction but there is no literature about the silver catalysts used for aqueous phase oxidation reaction. The adhesion of silver metal on the surface might not be strong enough to offer the resistance to the liquid flow. The preparation of catalyst is an art rather than a science, this can cause the variations in the performance of the catalysts (Lee at al., 1989).

Lee, Verykios, and Pitchai (1989) found that the variation of average silver crystallite size of supported catalysts was better controlled by varying the metal loading of the catalysts. Other techniques, such as sintering, were not used because it has been shown that sintering of silver catalysts results in

significant alterations of the morphology of the metal particles which influences their catalytic performance. They also found that selectivities of catalysts increased initially with increasing crystallite size but attained a constant value for catalysts with an average particle size of 500 Angstorms or more. This can support the results of this study that the catalysts thermally reduced at 800 °C for 24 hours with about 3.6 times higher silver loading showed slightly higher or nearly the same killing efficiency when compared catalyst E (35 % Ag) to catalyst G (9.9 % Ag) (see Table 3.3). From economic point of view, high silver loading is worth nothing in performance but results in a higher cost.

Another reason for silver loss from surface is the poisoning of catalyst surface by some impurities suspended in the water. This might occur because ions such as Na^+, K^+, Mg^{2+}, OH^-, PO_4^{3-}, and Cl^- present in the buffered water used for the killing study. However, only small amounts of silver might dissolve due to either water acidity or basicity.

Effect of support pretreatment and promoter is another factor to produce better silver catalyst as widely studied by many authors (Harriott, 1969 and Bulushev et al., 1995). This can affect surface properties such as electron density, surface acidity, active species stability, and interaction strength between metallic silver and support.