

CHAPTER IV

RESULTS AND DISCUSSION

Liu *et al.* (2010) successfully converted methane to methyl bromide with high yield and selectivity. Accordingly, our work followed the reaction conditions as the previous work in order to find the suitable solid materials for oxidative bromination reaction.

4.1 Catalytic Activity Testing

4.1.1 Product Distribution for the OBM Reaction (Blank Tube)

In order to study the pathway of gas phase reaction, the oxidative bromination of methane was run without packing materials or blank tube. The reaction conditions were listed as follows; 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 660 °C. The results were shown in Figure 4.1. Four products were found in this experiment including; methyl bromide (CH₃Br), carbon monoxide (CO), ethylene (C₂H₂) and dibromomethanes (CH₂Br₂). All products provided the constant selectivity after an hour of time on stream. It was found that methyl bromide was a primary product due to the highest selectivity around 70% while carbon monoxide selectivity was almost 30% in the product distribution. Yang *et al.* (2008) proposed that the major part of carbon monoxide was formed from the steam reforming and the oxidation of methyl bromide. The selectivities to methyl bromide and carbon monoxide could be adjusted by changing reaction conditions and/or using different catalyst (It will be discussed later). Dibromomethanes was considered as by-products from secondary radical reaction. However, tribromomethanes (CHBr₃) could not detect in our experiment. Besides, ethylene was also found in small amount which might be occurred through oxidative coupling of methane reaction.

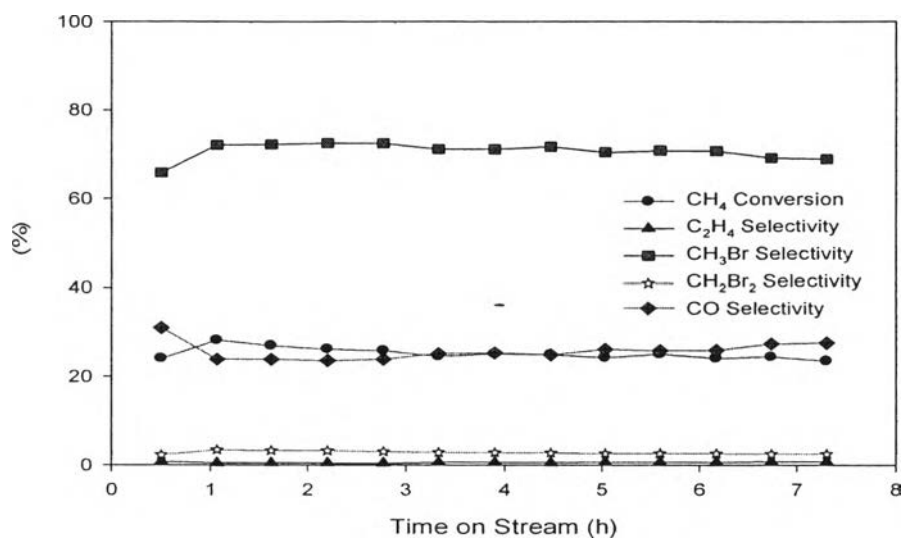


Fig. 4.1 Methane conversion and product distributions as a function of time on stream. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 660 °C.

4.1.2 Screening of Different Material Supports for the OBM Reaction

In order to investigate the suitable material support, various types of material—including SiO₂, Al₂O₃, HZSM-5, and activated carbon—were brought to study. The results in Figure 4.2 indicated that under the same reaction conditions, the methane conversion was around 15-20% over Al₂O₃, HZSM-5, and activated carbon. The maximum of methane conversion could be obtained from SiO₂ which is relatively similar to blank tube (20-28%). Unlike the methane conversion results, each material support gave the remarkable difference of methyl bromide selectivity. Among all material supports, SiO₂ gave the highest selectivity around 50% of methyl bromide while it rarely found in other material supports. Lin *et al.* (2010) explained that SiO₂ was chosen as supports because the inert carries with low surface area would give relatively high selectivity to methyl bromide. However, methyl bromide selectivity for the case of no catalyst (blank tube) was 20% higher than for SiO₂. This is consistent with the previous work reported by (Liu *et al.*, 2010). They explained that free radical reaction in gas phase was suppressed with the reduction of dead volume by packing inert particles.

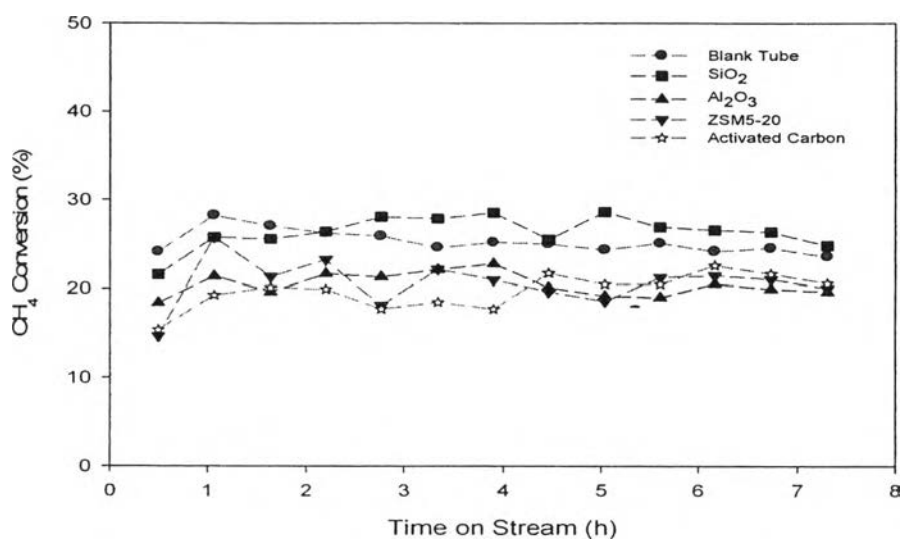


Fig. 4.2 Methane conversion as a function of time on stream at various material supports. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 660 °C.

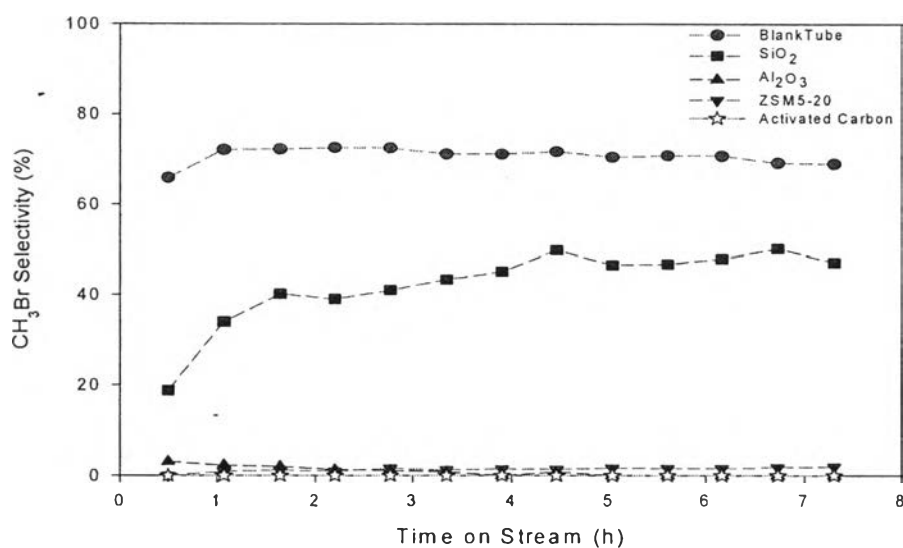


Fig. 4.3 Methyl bromide selectivity as a function of time on stream at various material supports. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 660 °C.

4.1.3 Effect of Reaction Conditions for the OBM Reaction

4.1.3.1 *Effect of Reaction Temperature*

The synthesis gases (CO & H₂) were the by-products of OBM reaction. Carbon monoxide was found to be a higher portion compared to hydrogen. Some researches (Wang *et al.*, 2005, Wang *et al.*, 2006, Lin *et al.*, 2009) preferred high and equal yields of CH₃Br and CO, which could be converted to acetic acid via catalytic reaction. Conversely, our study aimed to produce only methyl bromide, thus synthesis gases were the unfavourable products required to eliminate. Adjusting reaction temperature would be possible to control the product distributions.

Considering Figure 4.4, methane conversion obviously increased when raising the reaction temperature from 400°C to 660°C. This means methane preferably converted to carbon monoxide at higher reaction temperature. However, Liu *et al.* (2010) claimed that if the reaction temperature was higher than 660°C, too much oxygen was consumed leading to lower methane conversion. Therefore, the methane conversion was not changed clearly when applying the reaction temperature between 660°C and 700 °C as shown in this figure.

Although the previous experiment indicated that the highest methyl bromide selectivity was achieved in case of blank tube, there was still the synthesis gas, accompanying in the reaction. In order to get rid of/minimize the synthesis gas, effect of reaction temperature was examined by varying from 400 °C to 700 °C. It was found that oxidative bromination with highly selectivity to methyl bromide (100%) can be achieved at reaction temperature of 400°C, whereas at higher reaction temperature partial oxidation of methane to synthesis gas was instead dominant. The reason might be higher reaction temperature promoted the partial oxidation reaction, which more thermodynamically favorable.

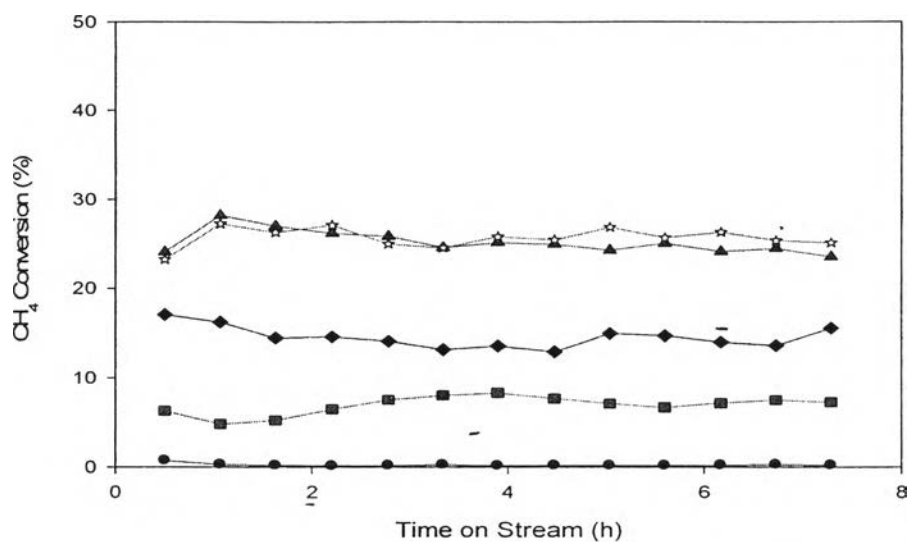


Fig. 4.4 Methane conversion as a function of time on stream at different reaction temperature. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O.

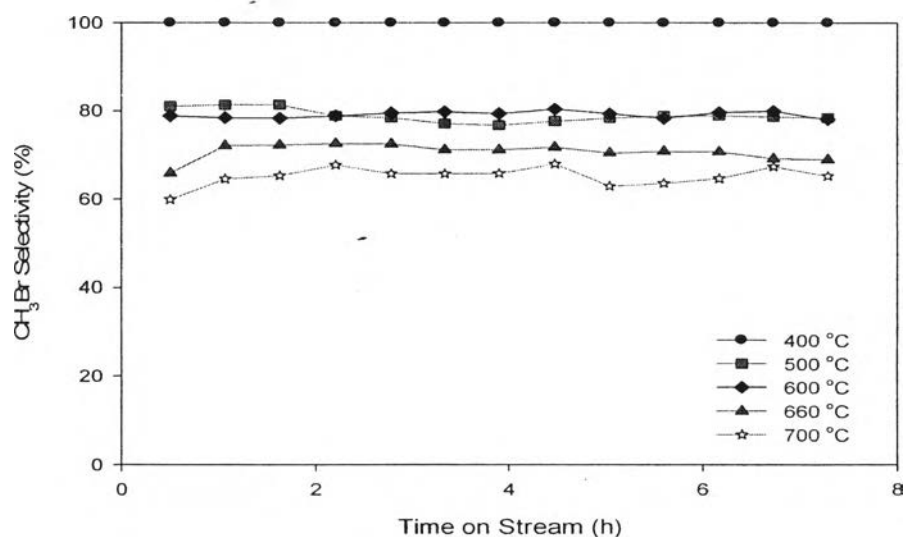


Fig. 4.5 Methyl bromide selectivity as a function of time on stream at different reaction temperature. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O.

4.1.3.2 Effect of Oxygen Content

Effect of oxygen content was investigated by varying a fraction between oxygen and nitrogen in a total of 10 ml/min. %O₂ were investigated in the range of 0%, 35%, 50%, and 60%. The results in Figure 4.6 and Figure 4.7 shows that without oxygen feed, no reaction occurred or methane conversion value was zero as shown in Figure 4.6. Xu *et al.* (2005) describe the role of oxygen in the reaction pathway that oxygen firstly reacted with HBr to form bromine radical, which further reacted with methane to form methyl bromide.

Moreover, increasing O₂ content from 35% to 50%, methane conversion enhanced, but too much O₂ in gas feed caused higher carbon monoxide selectivity. This coincide with the previous work reported by Lin *et al.* (2009). They found that, lowering CH₄:O₂ ratio or increasing oxygen content facilitates bromine radical formation and methyl bromide oxidation as following equation;



From the experimental results, it can be predicated that the reaction needs oxygen to form bromine radical, leading to produce methyl bromide. Nevertheless, too much oxygen content in the feed encouraged methyl bromide oxidation which generated carbon monoxide as the main product, making methyl bromide selectivity lower. Thereby, 50% O₂ in gas feed was the suitable value providing the highest methyl bromide selectivity and methane conversion.

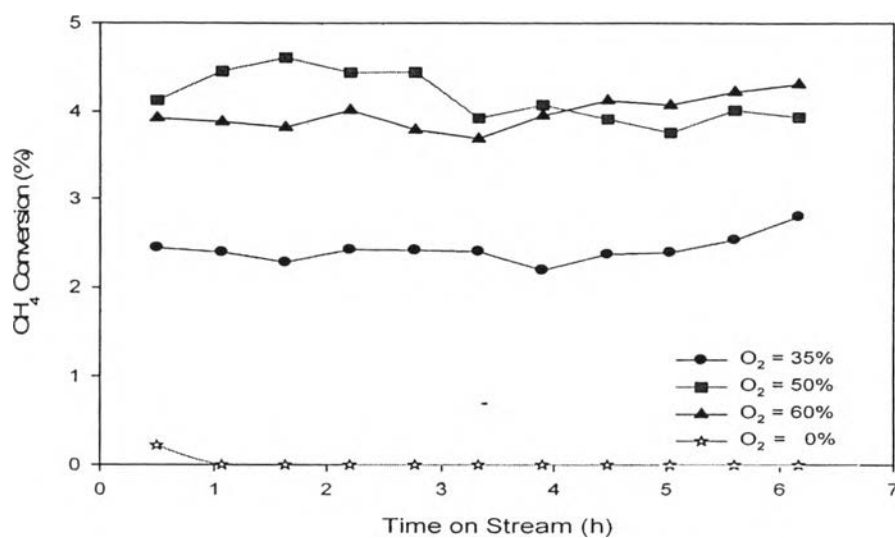


Fig. 4.6 Methane conversion as a function of time on stream at different O_2 . Reaction Conditions: 20 ml/min of CH_4 , 6.5 ml/h of 48 wt% $\text{HBr}/\text{H}_2\text{O}$, reaction temperature 400 °C, 0.5 wt% Rh/SiO_2 (calcined at 450 °C 6 h).

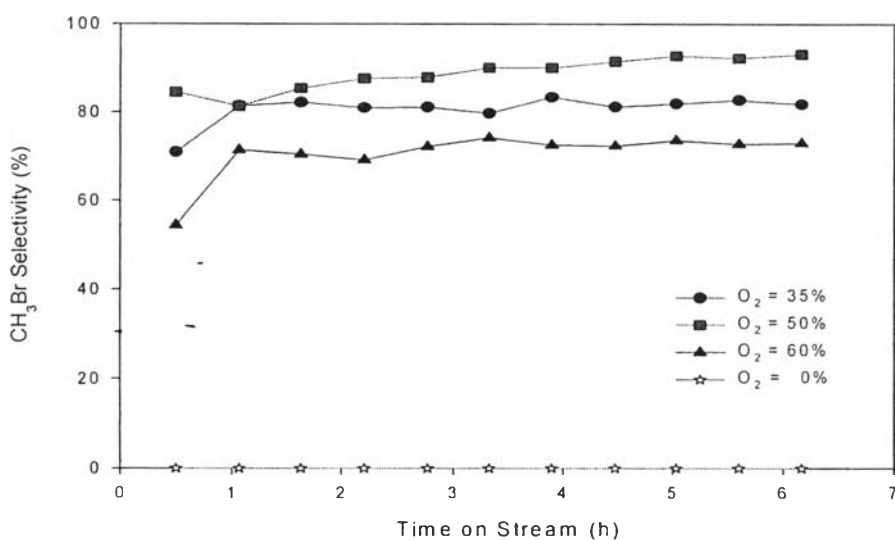


Fig. 4.7 Methyl bromide selectivity as a function of time on stream at different O_2 . Reaction Conditions: 20 ml/min of CH_4 , 6.5 ml/h of 48 wt% $\text{HBr}/\text{H}_2\text{O}$, reaction temperature 400 °C, 0.5 wt% Rh/SiO_2 (calcined at 450 °C 6 h).

4.1.4 Effect of Rh/SiO₂ Catalyst for the OBM Reaction

To improve the methane conversion while keeping the high selectivity of methyl bromide, Two grams of 0.3 wt% Rh/SiO₂ was used to studied as catalyst. The reaction temperature was chosen as 400 °C since the previous experiment shows that this condition could minimize synthesis gases. The flow gases of CH₄, O₂, N₂, and liquid 48 wt% HBr/H₂O were 20 ml/min, 5 ml/min, 5 ml/min, and 6.5 ml/h, respectively. According to Figure 4.8 and Figure 4.9, when adding only SiO₂ as the support, methane conversion increased from 0.2 to 1.5% compared to the blank tube. In addition, Rh plays an important role in activation of methane because the methane conversion reached the maximum value around 2% while methyl bromide selectivity was still 100% over 0.3 wt% Rh/SiO₂ catalyst.

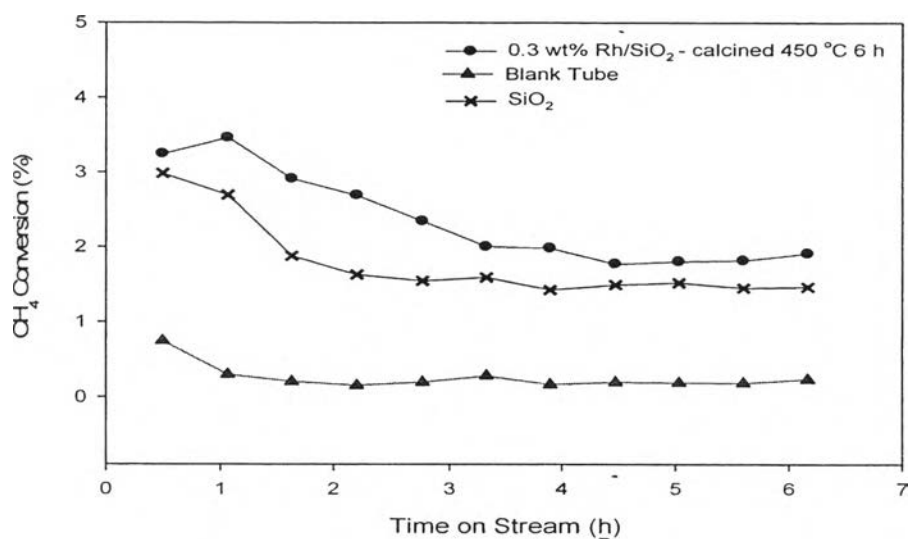


Fig. 4.8 Methane conversion as a function of time on stream at various materials. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C.

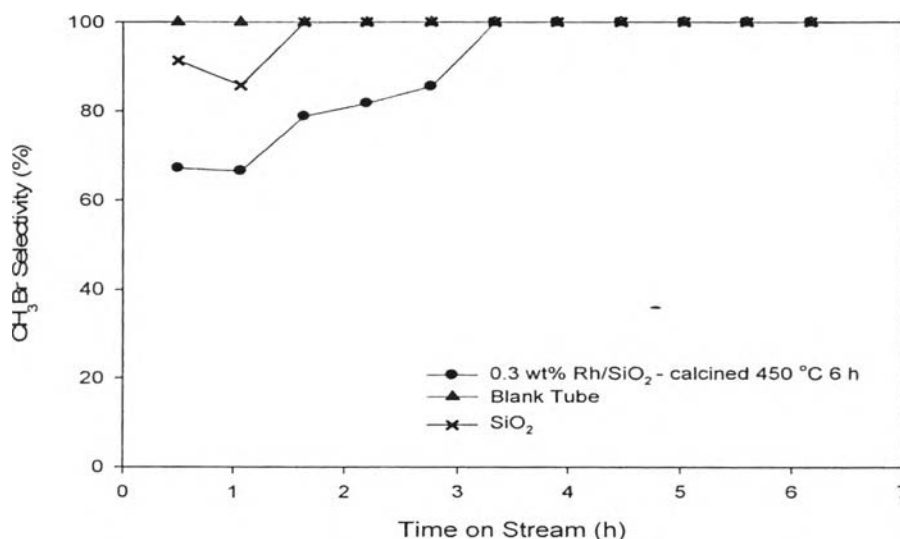


Fig. 4.9 Methyl bromide selectivity as a function of time on stream at various materials. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C.

4.1.5 Effect of Rh Loading on SiO₂ for the OBM Reaction

Under the same reaction conditions of Figure 4.10 and 4.11, when Rh loading increased from 0.3 wt% to 0.5 wt%, methane conversion increased, nonetheless, methyl bromide selectivity slightly decreased. This situation could be explained that higher Rh loading results in more Rh atom exposed on the surface of the catalyst, leading to partial oxidation reaction easily occurred. Methane thus converted to carbon monoxide, and methane conversion increased while methyl bromide selectivity decreased. However, it cannot be decided yet which one is better between higher or lower metal loading, yield of methyl bromide will be the key factor identifying the suitable type of Rh/SiO₂ catalyst.

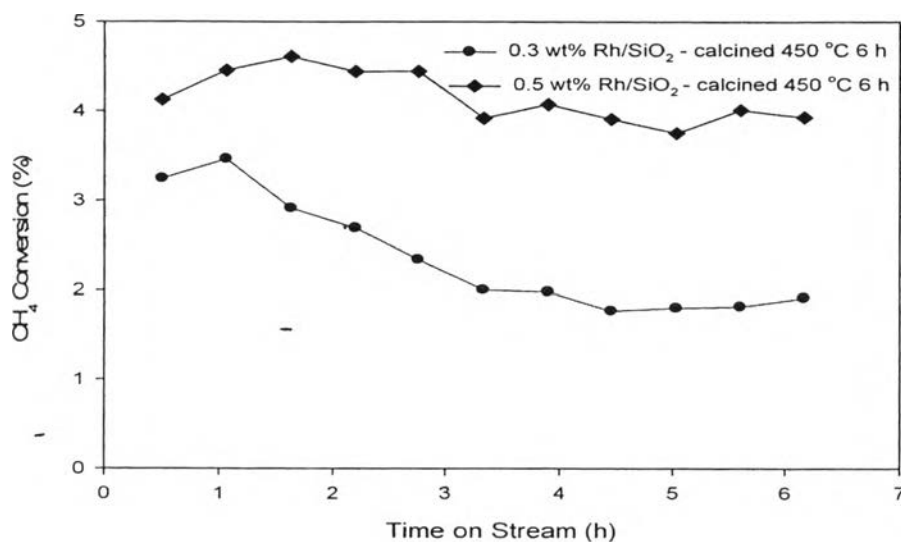


Fig. 4.10 Methane conversion as a function of time on stream at different Rh loading on SiO₂. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C.

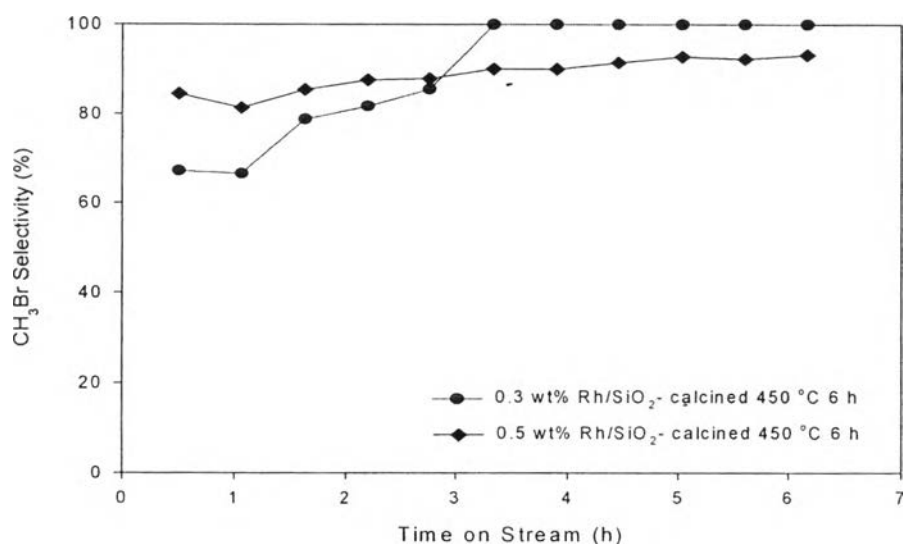


Fig. 4.11 Methyl bromide selectivity as a function of time on stream at different Rh loading on SiO₂. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C.

4.1.6 Effect of Calcination Conditions of Rh/SiO₂

The variation of methane conversion and product distribution were also affected by the different calcination conditions of the catalyst as reported by Liu *et al.* (2010). Thereby, our experiment had been studied the effects of calcination conditions by varying temperature and time. In the catalyst preparation step, Rh/SiO₂ catalyst was calcined at 450 °C for 6 h and another set was calcined at 900 °C for 10 h. Moreover, 0.3 and 0.5 wt% Rh loading was performed at reaction temperature of 400 °C confirming the trend of results. The flow gases of CH₄, O₂, N₂, and liquid 48 wt% HBr/H₂O were 20 ml/min, 5 ml/min, 5 ml/min, and 6.5 ml/h, respectively.

From the results given in Figure 4.12 and Figure 4.13, it was observed that methane conversion decreased with the increasing in catalyst calcination temperature and calcination time for both types of Rh loading. The change of methane conversion might be caused by the form of catalysts has been changed during the calcination step. Temperature program reduction technique was used to confirm this assumption which was shown in the characterization part.

Even though the higher temperature and longer time of calcination was not satisfied for methane conversion, selectivity result indicated that 0.5 %wt Rh/SiO₂ catalyst treated under higher temperature provided the higher methyl bromide selectivity as shown in Figure 4.15.

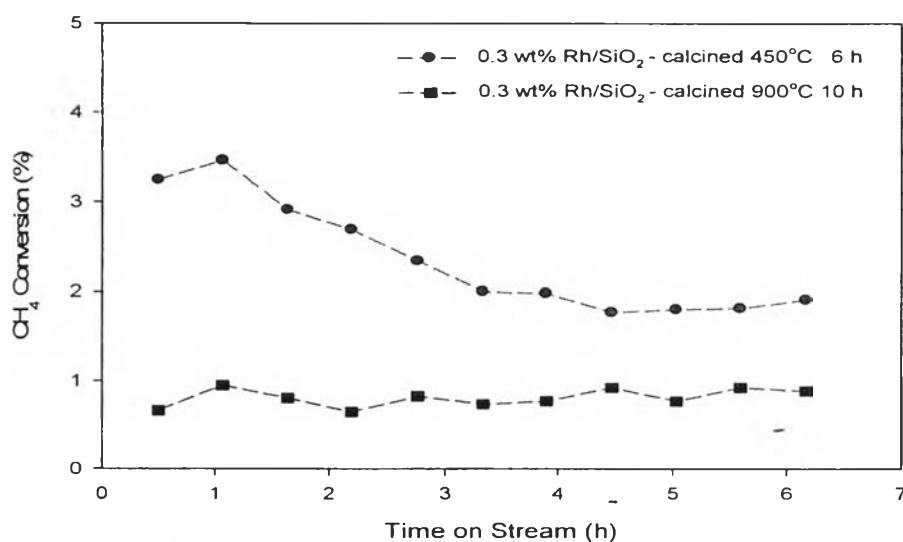


Fig. 4.12 Methane conversion as a function of time on stream at different calcination conditions. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C, 0.3 wt% Rh/SiO₂.

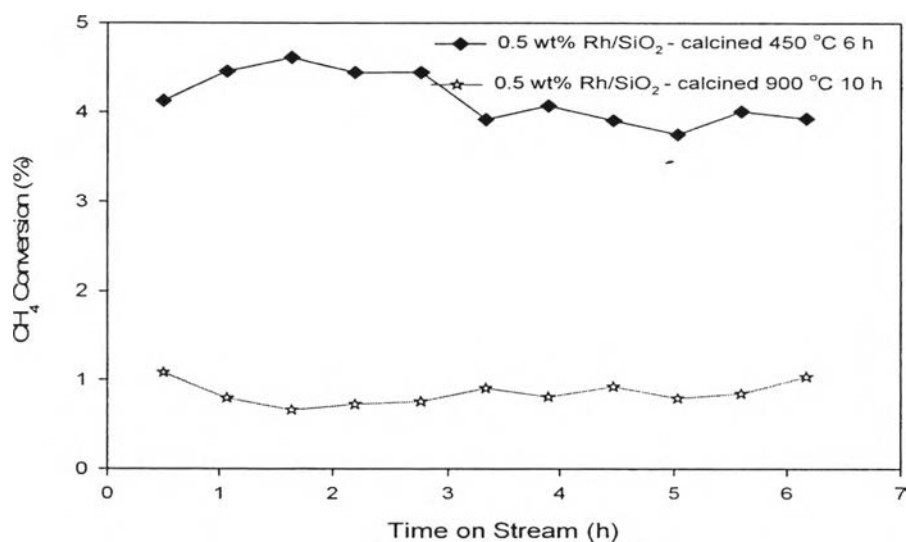


Fig. 4.13 Methane conversion as a function of time on stream at different calcination conditions. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C, 0.5 wt% Rh/SiO₂.

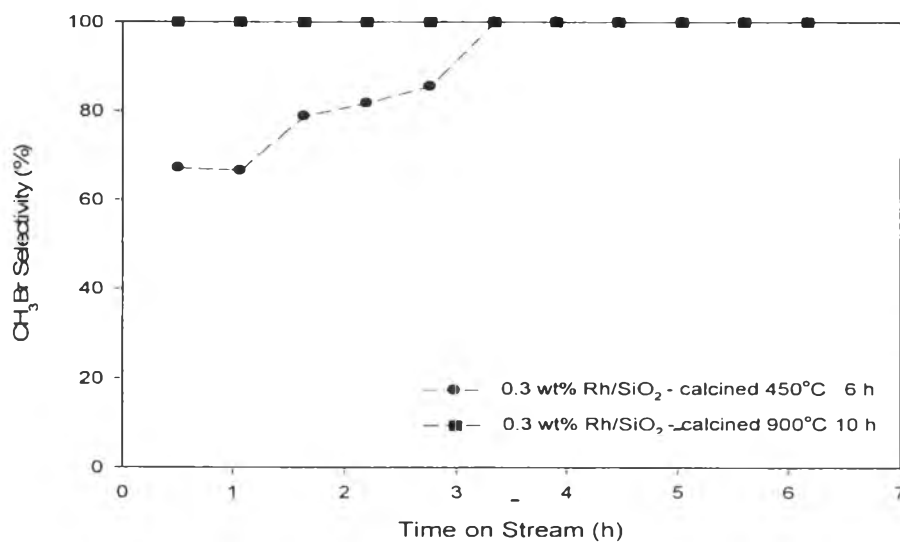


Fig. 4.14 Methyl bromide selectivity as a function of time on stream at different calcination conditions. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C, 0.3 wt% Rh/SiO₂.

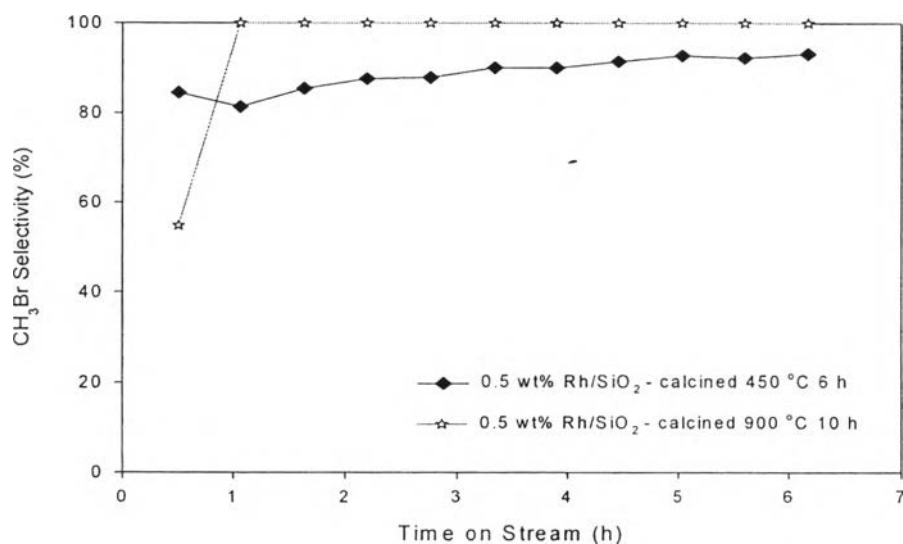


Fig. 4.15 Methyl bromide selectivity as a function of time on stream at different calcination conditions. Reaction Conditions: 20 ml/min of CH₄, 5 ml/min of O₂, 5 ml/min of N₂, 6.5 ml/h of 48 wt% HBr/H₂O, reaction temperature 400 °C, 0.5 wt% Rh/SiO₂.

Figure 4.8-Figure 4.15 shows the experimental results of OBM reaction studied at reaction temperature of 400 °C. Apparently, various parameters—material types, %Rh loading, and calcinations conditions—affected to the methane conversion and methyl bromide selectivity and all data were summarized in Table 4.1 which determine a maximum methyl bromide yield.

As shown in Table 4.1, although 0.5 wt% Rh/SiO₂ calcined at 450 °C for 6 h could not give 100% of methyl bromide selectivity, methane conversion was obviously higher than other types of catalyst. Considering in term of yield, this catalyst consequently provided the maximum yield of methyl bromide up to 3.6%. This means highest yield of methyl could be gained if the reaction was done at relatively low temperature around 400 °C and the catalyst should be calcined at milder conditions with proper %Rh loading.

Table 4.1 Methyl bromide yield of the OBM reaction

	CH ₄ Conversion (%)	CH ₃ Br Selectivity (%)	CH ₃ Br Yield (%)
Blank Tube	0.193	100	0.193
SiO ₂	1.471	100	1.471
0.3 wt% Rh/SiO ₂ (calcined at 450 °C 6 h)	1.857	100	1.857
0.3 wt% Rh/SiO ₂ (calcined at 900 °C 10 h)	0.857	100	0.857
0.5 wt% Rh/SiO ₂ (calcined at 450 °C 6 h)	3.937	91.982	3.621
0.5 wt% Rh/SiO ₂ (calcined at 900 °C 10 h)	0.879	100	0.879

4.2 Catalyst Characterization

4.2.1 Surface Area Analysis (BET)

Table 4.2 shows the BET surface area of each support materials. The specific surface area of activated carbon is the highest value, while others have insignificant different specific surface area. However, Figure 4.3 shows the best performance of SiO₂ in term of methyl bromide selectivity. Therefore, it was proved that methane conversion was independent from the specific surface area but the unique property of each material support was superior factor. Lin *et al.* (2010) suggested that suitable material supports for OBM reaction should have low specific surface area as well as inert properties.

Table 4.2 Specific surface area of different material supports

Material Supports	Surface area (m ² /g)
SiO ₂	337
Al ₂ O ₃	316
ZSM-5	352
Activated Carbon	613

Different calcination conditions also affected to the specific surface area of the catalyst as shown in Table 4.3. When the catalyst was calcined at higher temperature, the corresponding surface area of catalyst decreased from 338 m²/g to 254 m²/g. Liu *et al.* (2010) offered that if the desired products were methyl bromide and carbon monoxide, the catalyst with a relatively high specific surface area was preferred and it should be calcined at low temperature. The reason might be more Rh atom, exposed on the catalyst surface, catalyze the deep oxidation of reaction.

Table 4.3 Specific surface area of 0.5 wt% Rh/SiO₂ catalysts—different calcinations

Catalysts	Specific Surface area (m ² /g)
0.5 wt% Rh/SiO ₂ (calcined at 450 °C 6 h)	338
0.5 wt% Rh/SiO ₂ (calcined at 900 °C 10 h)	254

4.2.2 X-ray Diffraction (XRD)

The XRD patterns of the studied catalysts are shown in Figure 4.16. For silicon dioxide support, only one broad peak between $2\theta = 15$ and 30° was observed, indicating a typical amorphous structure of silica support. The results also agree with Reyes *et al.* (2000) and Moya *et al.* (2011). Besides, there was no discernible peaks related to any crystalline phase of rhodium can be observed. This might be related to the low loading and the high dispersion of Rh on SiO_2 in the supported oxide material, which was confirmed by SEM analysis.

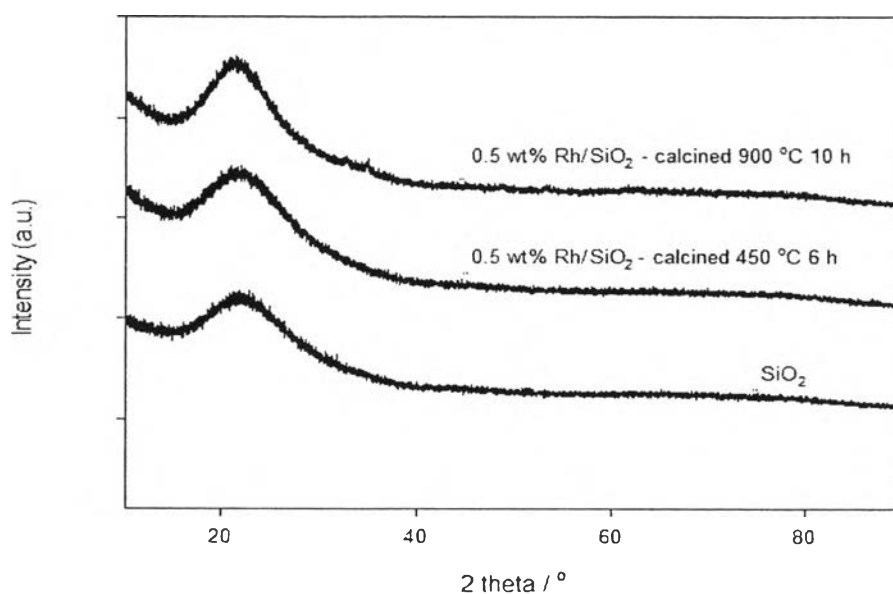


Fig. 4.16 X-ray diffraction patterns of SiO_2 and 0.5 wt% Rh/ SiO_2 catalysts—different calcination conditions.

4.2.3 Temperature Program Reduction (TPR)

Figure 4.17 shows TPR profiles obtained after the catalyst was calcined at different calcination temperature and time. Since rhodium has oxidation state +I, +II, and +III, and stable oxide Rh_2O_3 , Rh_2O_3 species on surface is relatively easy to be reduced. Hence, TPR profile of Rh/SiO_2 catalysts, which consists of only one peak, should attributed to the reduction of Rh_2O_3 to metallic Rh (Borer *et al.*, 1993). The hydrogen consumption corresponds to a full reduction of rhodium oxide to Rh^0 , i.e., $(\text{Rh}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Rh} + 3\text{H}_2\text{O})$.

Moreover, the catalyst calcined at 450 °C for 6 h, the reduction peak was observed at 35 °C, whereas the catalyst calcined at 900 °C for 10 h, the peak shift to higher reduction temperatures. It was likely that higher calcination temperature and longer holding time results in stronger interaction between Rh and SiO_2 support, thereby making Rh more difficult to be reduced. This condition also leads to less Rh atom exposed on the surface.

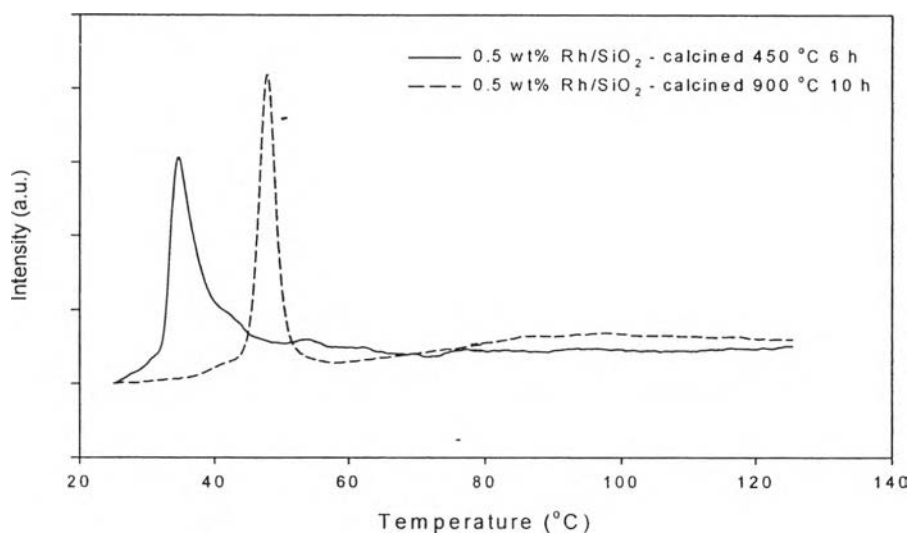


Fig. 4.17 TPR profiles of 0.5 wt% Rh/SiO_2 catalysts—different calcination conditions.

4.2.4 H₂ Chemisorption

The results from H₂ chemisorption technique was shown in Table 4.4. The data informed that the H/Rh value of Rh/SiO₂ catalyst calcined at 900 °C 10 h was twice as low as the same catalyst calcined at 450 °C 6 h. It could be implied that high calcined temperature, the support might be collapsed and/or the metal was likely to be agglomerated, and consequently less Rh atom exposed on the surface. Then, H₂ molecule was more difficult to adsorb on the metal surface, making the metal dispersion was lower. The results of H₂ chemisorption technique thus supported the result from temperature program reduction again.

Table 4.4 Metal dispersion of 0.5 wt% Rh/SiO₂ catalysts—different calcination conditions

Catalysts	H/Rh
0.5 wt% Rh/SiO ₂ (calcined at 450 °C 6 h)	0.0713
0.5 wt% Rh/SiO ₂ (calcined at 900 °C 10 h)	0.0380

4.2.5 Scanning Electron Microscopy and Energy Dispersion X-ray

Spectroscopy (SEM-EDX)

4.2.5.1 *Silicon dioxide (SiO₂)*

Figure 4.18 shows SEM images of SiO₂ particles in the magnification 250x, confirming the formation of amorphous structure. The EDX spectrum of amorphous silicon dioxide was observed in Figure 4.19. This spectrum shows only the presence of silicon and oxygen in relation to the stoichiometric ratio Si:O = 1:2.

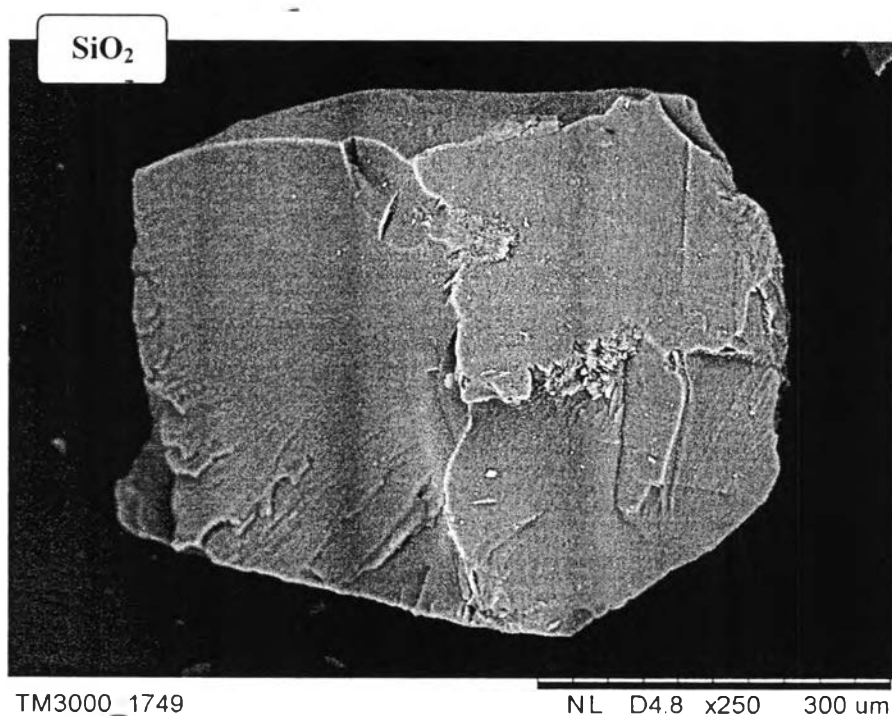


Fig. 4.18 SEM image of SiO₂ in the magnification 250x.

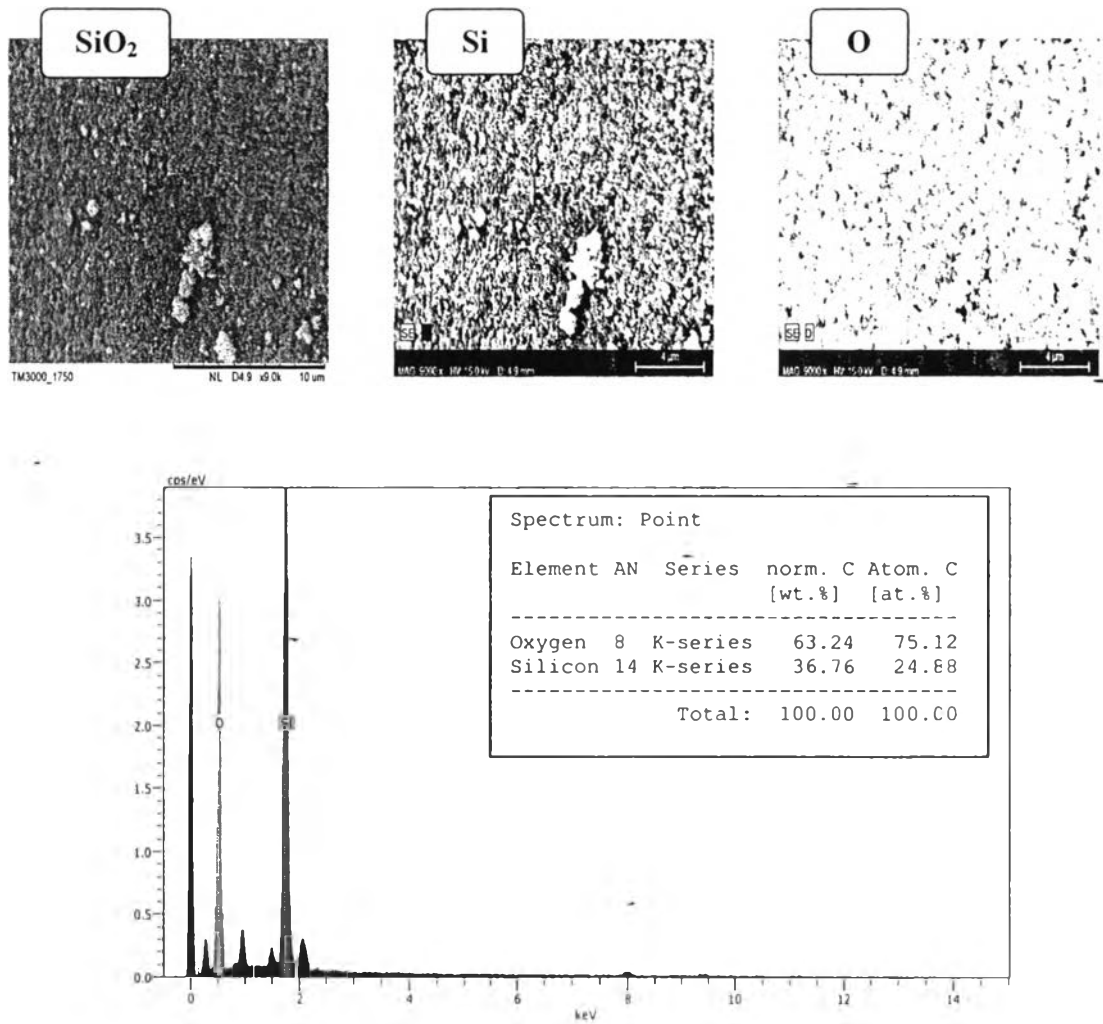


Fig. 4.19 EDX image of SiO₂ in the magnification 9000x.

4.2.5.2 Rh/SiO_2 – calcined 450 °C 6 h

For 0.5 wt% Rh/SiO_2 catalyst calcined at 450°C for 6 h, Figure 4.20 revealed that the bulk particles of the Rh/SiO_2 had non-uniform structure and rhodium were presented in ensembles and well dispersed on the SiO_2 support. Small spots could be seen on the EDX image (Figure 4.21) with high dispersion. This coincided with the results of XRD.

For the SEM-EDX of the catalyst calcined at 900°C for 10 h were not shown here since there was no clearly in the morphology when the catalyst has been calcined at different conditions.

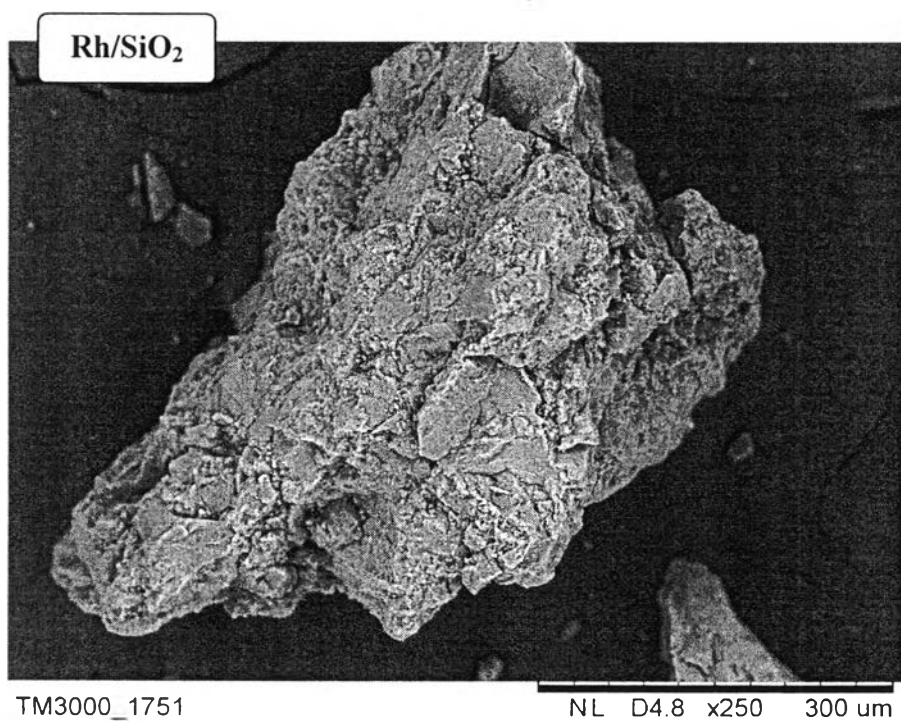


Fig. 4.20 SEM image of Rh/SiO_2 in the magnification 250x.

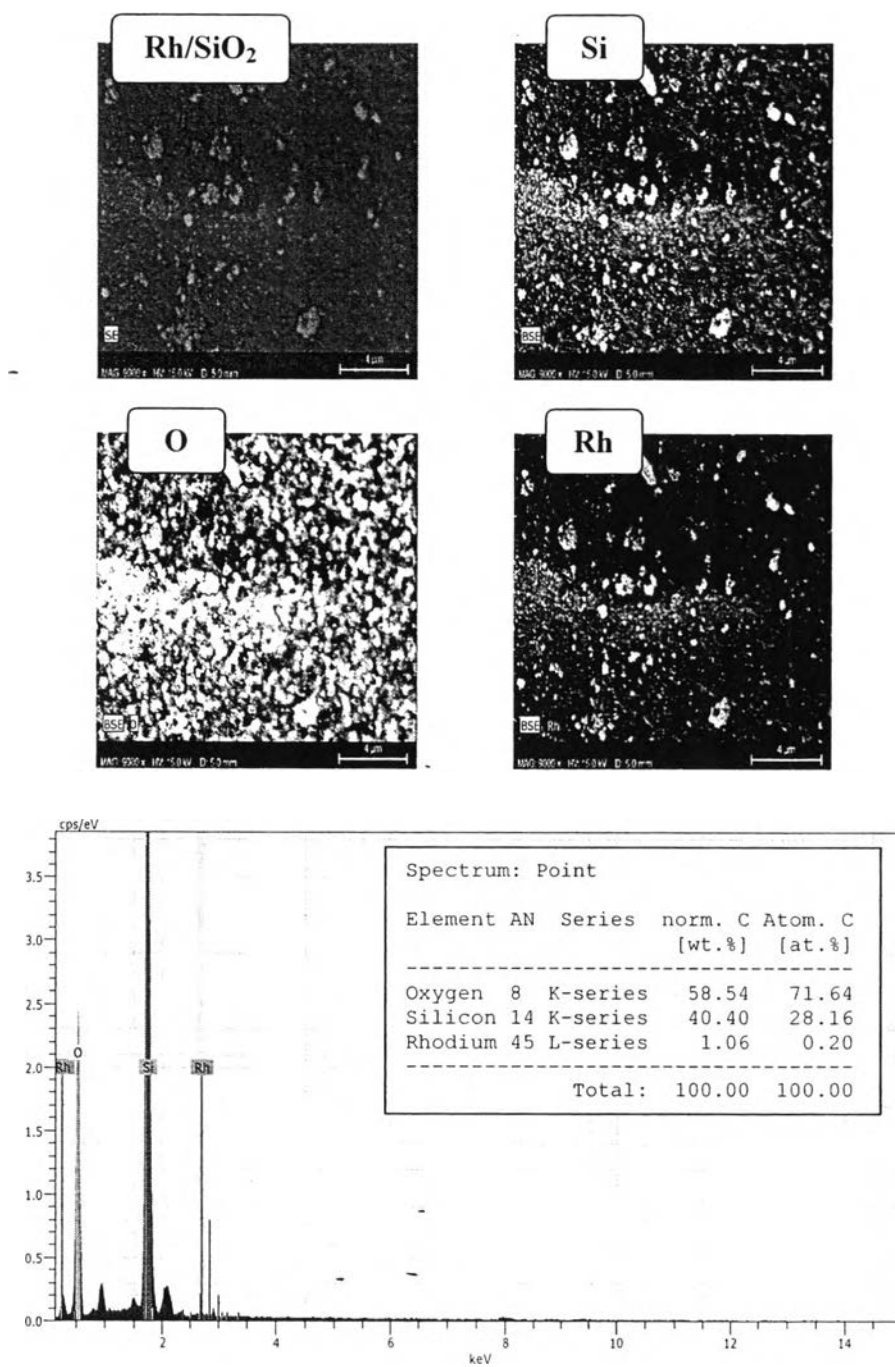


Fig. 4.21 EDX image of Rh/SiO₂ in the magnification 9000x.