CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalytic Activity Testing

4.1.1 Product Distribution for the Oxidative Bromination of Methane

In order to investigate the product distribution of the oxidative bromination of methane (OBM) reaction, the reaction was tested without packing materials. The reaction conditions was as follows; 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O. HBr/H_2O at 48 wt% was used instead of HBr to avoid explosion and hot spots (Liu *et al.*, 2010). The reaction temperature was 660 °C, and the reaction was tested at atmospheric pressure. The results are shown in Figure 4.1. Four products are found in this experiment including; methyl bromide (CH_3Br), carbon monoxide (CO), ethylene (C_2H_2) and dibromomethanes (CH_2Br_2). The steady state is observed after aprroximately one hour reaction time. As expected, methyl bromide is a primary product due to its highest selectivity around 60% while carbon monoxide selectivity is about 30-40 % in the product distribution. Yang *et al.* (2008) proposed that the major part of carbon monoxide is from the steam reforming and the oxidation of methyl bromide. The selectivity to methyl bromide and carbon monoxide could be adjusted by changing reaction conditions and/or using different catalyst. Dibromomethane is considered as by-products from secondary radical reaction. Besides, ethylene is also found in small amount which might be occurred through oxidative coupling of methane. In addition, tribromomethanes ($CHBr_3$) cannot be detected in this experiment. Moreover, carbon dioxide is not observed in this reaction as observed in the work done by Yang *et al.* (2008) who also suggest that the presence of HBr partially blocks the deep oxidation of methane, steam reformation of methane and steam reformation of methyl bromide so the carbon dioxide is not formed.

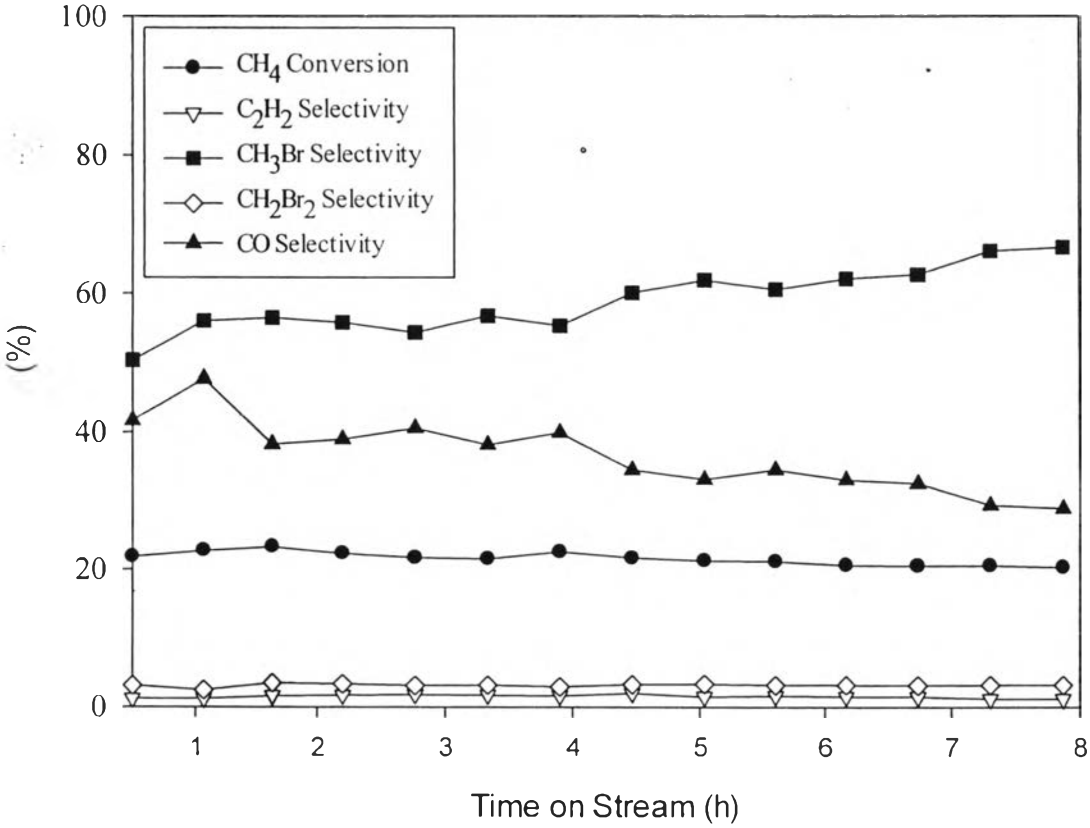

Fig. 4.1 Methane conversion and product distributions as a function of time on stream. Reaction conditions: 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 660 °C.

4.1.2 Effect of Ba/SiO_2 and W/SiO_2 Catalyst Preparation on the OBM Reaction

In order to investigate the effect of catalyst preparation on the OBM reaction, barium oxide and tungsten oxide on silica catalysts were prepared by 2 techniques—incipient wetness impregnation and sol-gel techniques as mentioned in previous chapter. Prior to the reaction, 2 g of catalyst was crushed and sieved between 40 and 60 mesh and then packed in quartz tube reactor. The reaction conditions are as follows; 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48 wt% HBr/H_2O, reaction temperature 660 °C, and at atmospheric pressure.

The product formed in the reaction are methyl bromide, carbon monoxide and negligible of dibromomethane. To compare the activity of barium and tungsten metal on OBM reaction, metal loading of barium and tungsten are varied as shown in Table 4.1.

Table 4.1 Abbreviation of barium oxide or tungsten oxide on silica catalysts

Abbreviation	Mole of metal	%wt metal/SiO_2
$1Ba/SiO_2$	0.00293	0.40
$1W/SiO_2$	0.00293	0.54
$2Ba/SiO_2$	0.00486	0.67
$2W/SiO_2$	0.00486	0.89
$3Ba/SiO_2$	0.00971	1.33
$3W/SiO_2$	0.00971	1.79

As shown in Figure 4.2 and 4.3, the conversion and selectivity indicate that, when the reaction was carried out in the reactor packing with either pure sol-gel silica support or pure commercial silica support, both of methane conversion and methyl bromide selectivity were decreased to almost the same extent comparing with no catalyst system. These results indicate that the free radical reaction in gaseous phase was suppressed with the reduction of dead volume by packing particles (Liu *et al.*, 2010).

When the reaction was carried out with catalyst, the Ba/SiO_2 or W/SiO_2 sol-gel and impregnated catalysts can enhance the methane conversion when compared with pure silica support or no catalyst system. The methane conversion is around 24-30% over impregnated and sol-gel catalysts after 8 hour time on stream which shown in Figure 4.2. The maximum methane conversion is about 30% observed in $1Ba/SiO_2$-S, following by 28.5 % of $1Ba/SiO_2$-I. For tungsten based catalyst, $1W/SiO_2$-S has methane conversion around 28 % which is higher than $1W/SiO_2$-I (around 24%).

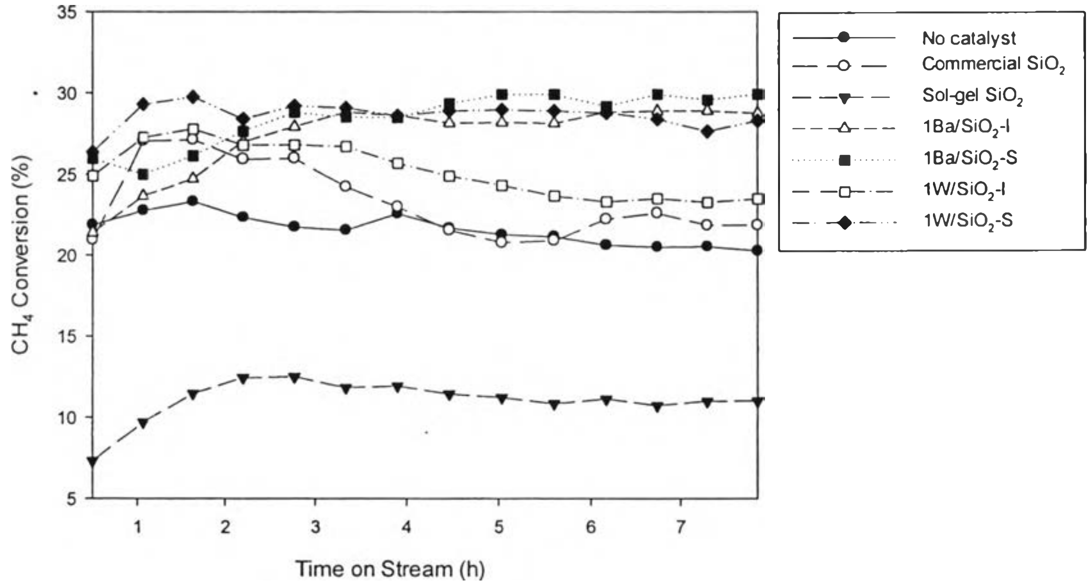

Figure 4.2 Methane conversions as a function of time on stream with various catalysts. Reaction conditions: 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48wt% HBr/H_2O, reaction temperature 660°C.

The methyl bromide selectivity is shown in Figure 4.3. Compared to other catalysts, the OBM reaction in empty tube (no catalyst) shows the highest methyl bromide selectivity which is around 65%. This is also observed in the work done by Liu *et al.*, 2010, who explained that free radical reaction in gas phase was suppressed with the reduction of void volume by catalyst particles. Moreover, commercial and sol-gel silica give the methyl bromide selectivity around 40 % whereas 1Ba/SiO_2-S provides the highest methyl bromide selectivity about 50 %, following by 1W/SiO_2-S, 1W/SiO_2-I and 1Ba/SiO_2-I with 43%, 40% and 30 %.

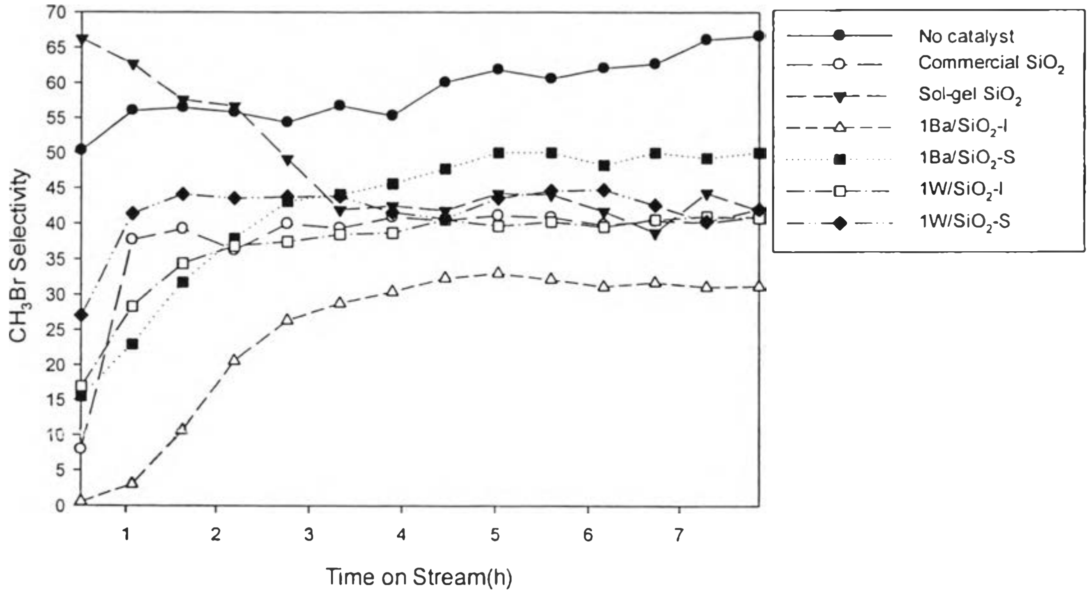

Figure 4.3 Methyl bromide selectivity as a function of time on stream with various catalysts. Reaction conditions: 20 ml/min of CH_4, 5 ml/min of O_2, 5 ml/min of N_2, 6.5 ml/h of 48wt% HBr/H_2O, reaction temperature 660°C.

From the methane conversion and methyl bromide selectivity, the results indicate that the sol-gel catalyst exhibits higher CH_4 conversion and CH_3Br selectivity than impregnated catalyst, possibly caused by the metal dispersion. The size of metal oxide on catalyst is subsequently determined by X-ray diffraction technique which is shown in the next section.

However, barium oxide or tungsten oxide on silica catalysts are further tested for yield of methyl bromide. For the total methyl bromide yield as shown in Figure 4.4, the highest methyl bromide yield was found in $1Ba/SiO_2$-S. Besides, $1Ba/SiO_2$-S is the only catalyst that shows higher CH_3Br yield than no catalyst system. Lin *et al.* (2009) studied various non-noble metal oxide supported silica catalyst for OBM reaction and found that that the redox ability of different metals had a strong impact on the product distribution. For the catalyst with metals lacking of facile redox ability, such as WO_3/SiO_2, both CH_3Br and CO were main products. Otherwise, deep oxidation proceed. Lin *et al.* (2009) also propose that WO_3 behave as a bromine absorber promoting the oxidation of CH_3Br on its surface. Therefore, 1Ba/SiO_2-I, 1W/SiO_2-S and 1/SiO_2-I are not suitable to used as a catalyst for the methyl bromide production due to a lower methyl bromide yield when compared with no catalyst system.

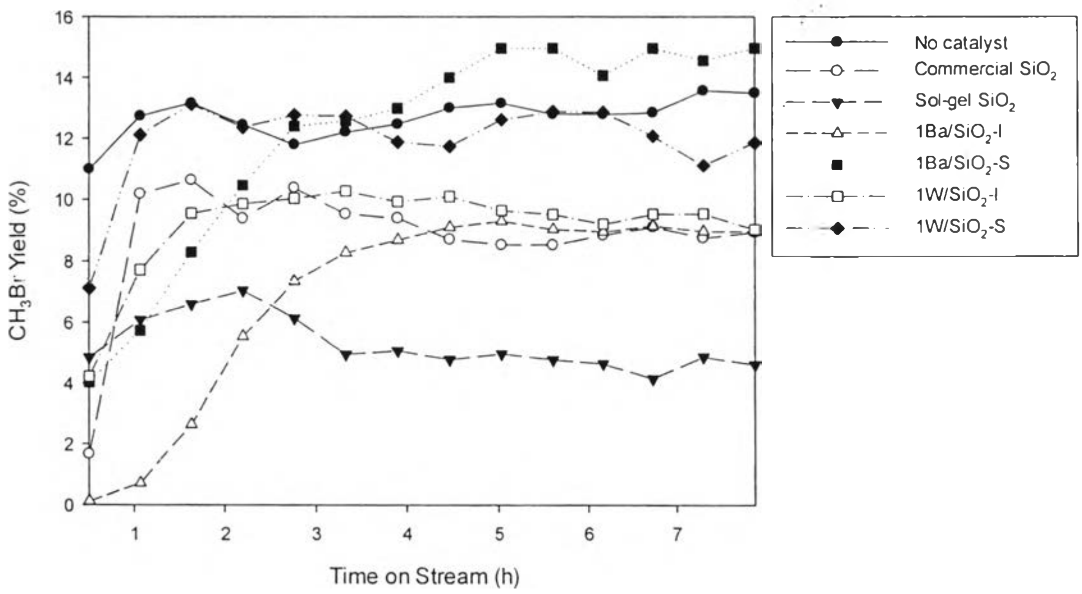

Figure 4.4 Methyl bromide yield of various catalysts at the same reaction condition.

4.1.3 Effect of Metal Loading on Impregnated Catalyst on the OBM Reaction

In order to investigate the effect of metal loading on the impregnated catalyst for the OBM reaction, the reaction is carried out by using 2 g of catalyst under the same reaction conditions. As illustrated in Figure 4.5 and 4.6, when tungsten loading is increased from 1W/SiO_2-I to 3W/SiO_2-I, methane conversion is relatively constant at 24 %, however, methyl bromide selectivity dramatically increased, from 35% to 55%.

For the barium metal, when barium loading increases from 1Ba/SiO_2-I to 2Ba/SiO_2-I, methane conversion moderately increases from 28 % to 31 %, Furthermore, methyl bromide selectivity significantly increased from 30% to 45%. If barium loading is further increased to 3Ba/SiO_2-I, methane conversion decreases by 2 %, from 31% in 2Ba/SiO_2-I to 29% 3Ba/SiO_2, and methyl bromide yield rapidly drops from 45 % to 35 %. The methane conversion does not show obvious change with the increasing of barium loading from $1Ba/SiO_2$-I to $3Ba/SiO_2$-I, but if barium loading is higher than $2Ba/SiO_2$-I, the methyl bromide selectivity decreases because of deep oxidation of methane generating more carbon monoxide (Liu *et al.*, 2010).

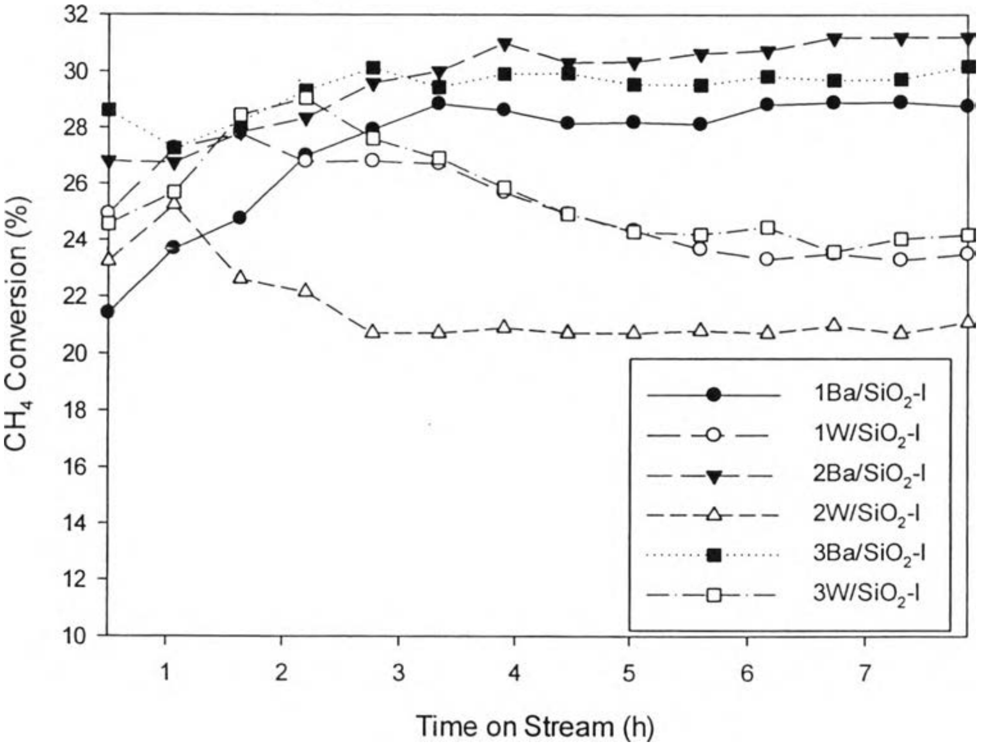

Figure 4.5 Methane conversion of different metal loading on impregnated catalysts at the same reaction condition.

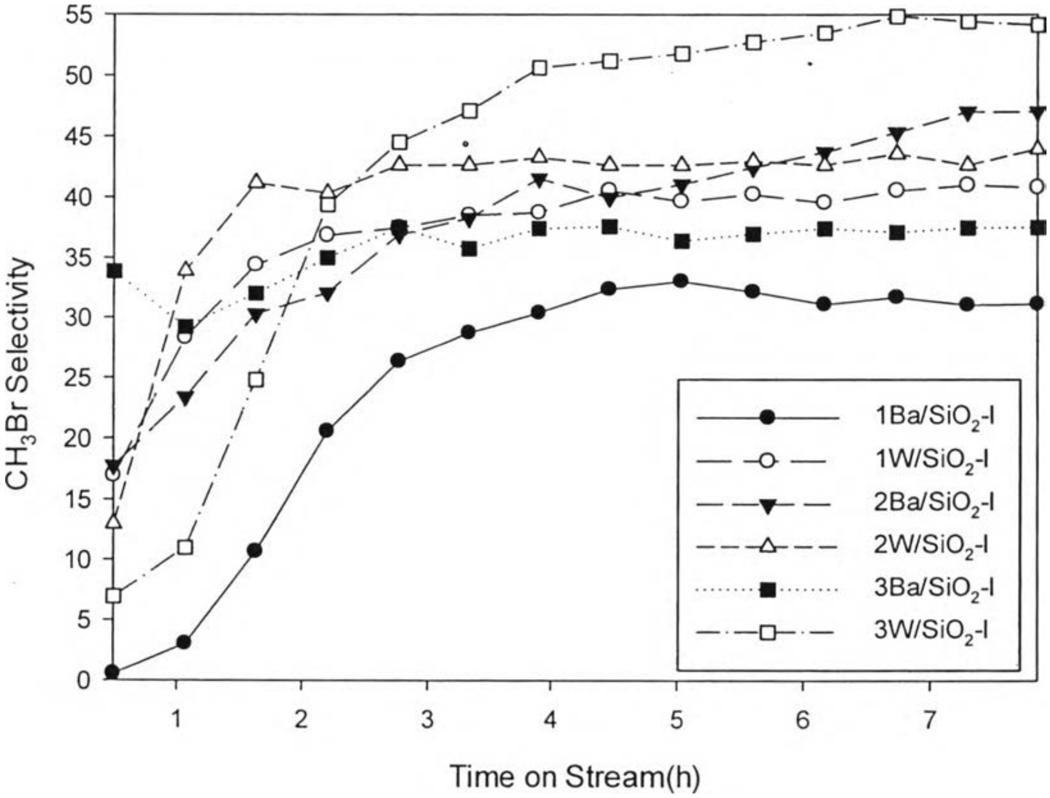

Figure 4.6 Methyl bromide selectivity of different metal loading on impregnated catalysts at the same reaction condition.

In order to compare between barium oxide or tungsten oxide on silica impregnated catalysts, effect of metal loading on the methyl bromide yield is investigated. For the impregnated catalysts as shown in Figure 4.7, when tungsten loading is increased, methyl bromide yield is relatively constant, from 1W/SiO$_2$-I to 2W/SiO$_2$-I. However, if tungsten loading is increased from 2W/SiO$_2$-I to 3W/SiO$_2$-I, methyl bromide yield slightly increases from 8% to 12 %. In the case of barium, as barium loading increase, methyl bromide yield slightly increases from 8% in 1Ba/SiO$_2$-I to 15 % in 2Ba/SiO$_2$-I but decreases to 10% in 3Ba/SiO$_2$-I. Therefore, the optimum of methyl bromide yield in impregnated catalyst is 2Ba/SiO$_2$-I providing the highest methyl bromide yield around 14%.

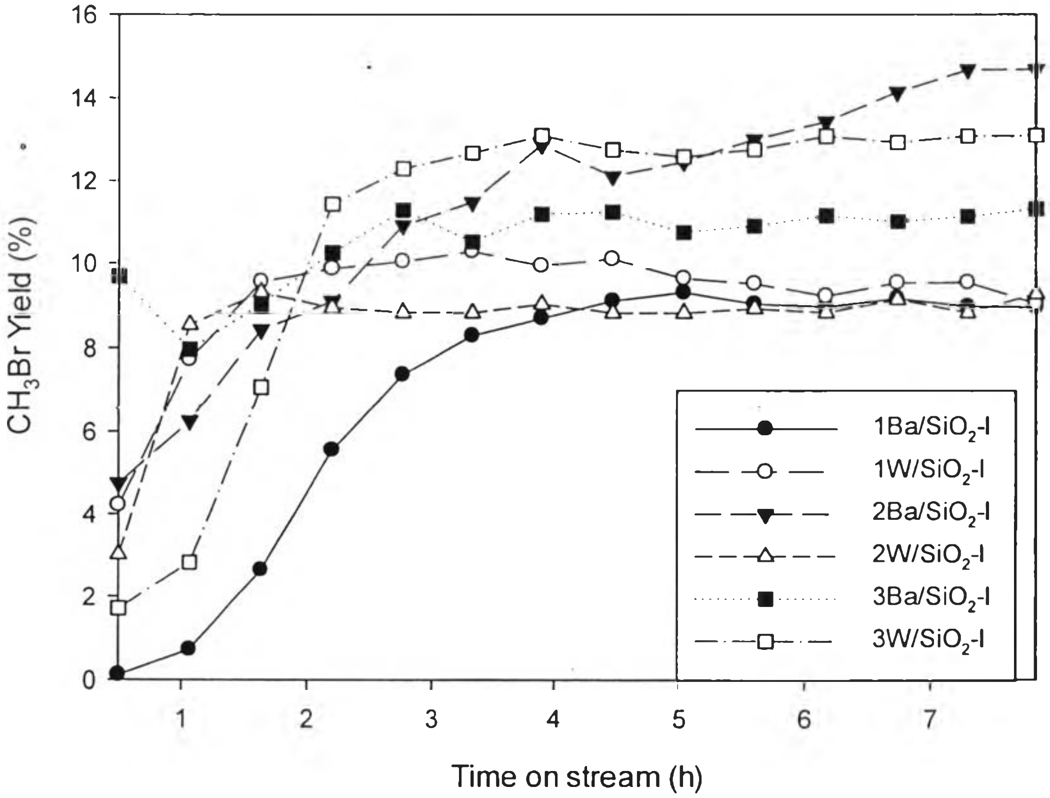

Figure 4.7 Methyl bromide yield of different metal loading on impregnated catalysts at the same reaction condition.

4.1.4 Effect of Metal Loading on Sol-gel Catalysts on the OBM Reaction

In order to investigate the effect of metal loading on sol-gel catalyst for the OBM reaction, the reaction is carried out by using 2 g of catalyst under the same reaction conditions. As illustrated in Figure 4.8 and 4.9, when tungsten loading is increased from 1W/SiO$_2$-S to 2W/SiO$_2$-S, methane conversion increases from 28 % to 31 %, however, methyl bromide selectivity is no obvious change at 42 %. After more adding high metal loading to 3W/SiO$_2$-S, methane conversion and methyl bromide selectivity decreases to 28% and 33%, respectively. This situation could be explained that high tungsten loading results in more tungsten atom expose on the surface of the catalyst, leading to deeper partial oxidation of methane which consumed too much oxygen to product more carbon monoxide (Liu *et al.*, 2010).

For the barium metal, when barium loading increases from $1Ba/SiO_2$-I to $3Ba/SiO_2$-I, methane conversion moderately decreases from 30 % to 27 %, Furthermore, methyl bromide selectivity significantly decreases, from 60% to 35%. The change of methane conversion and methyl bromide selectivity caused by the specific surface area of catalysts has been changed during the metal loading step. Specific surface area is subsequently determined by BET surface area analysis which is shown in the next section.

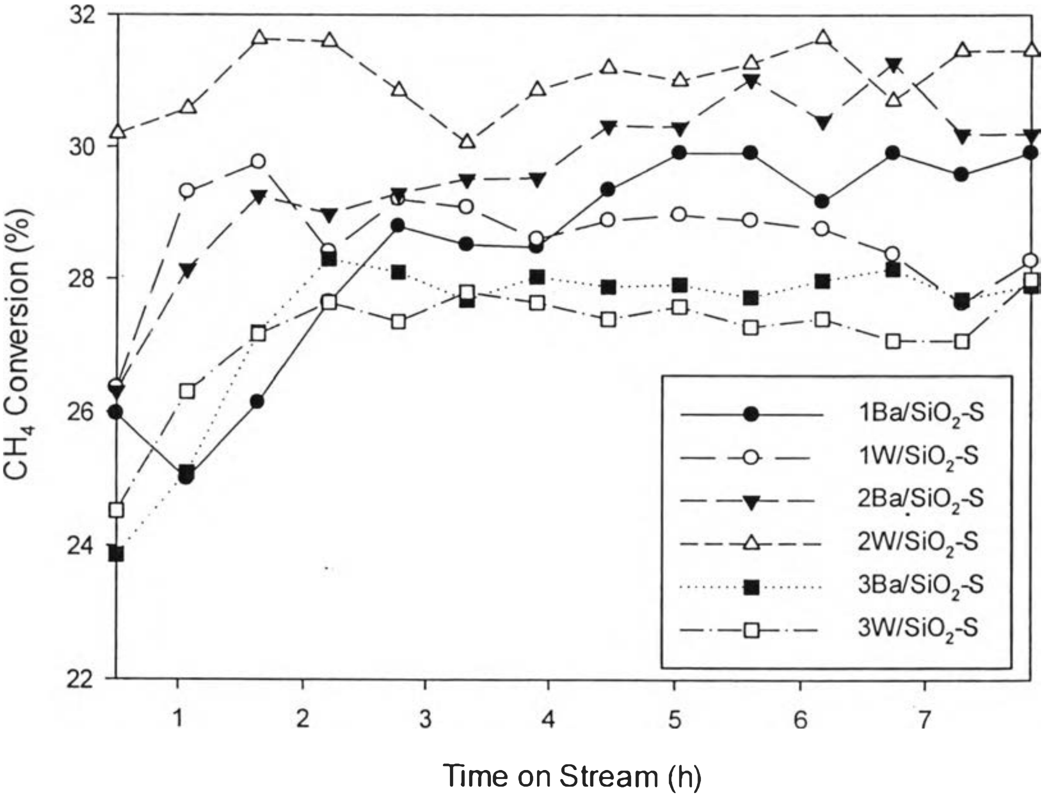

Figure 4.8 Methane conversion of different metal loading on sol-gel catalysts at the same reaction condition.

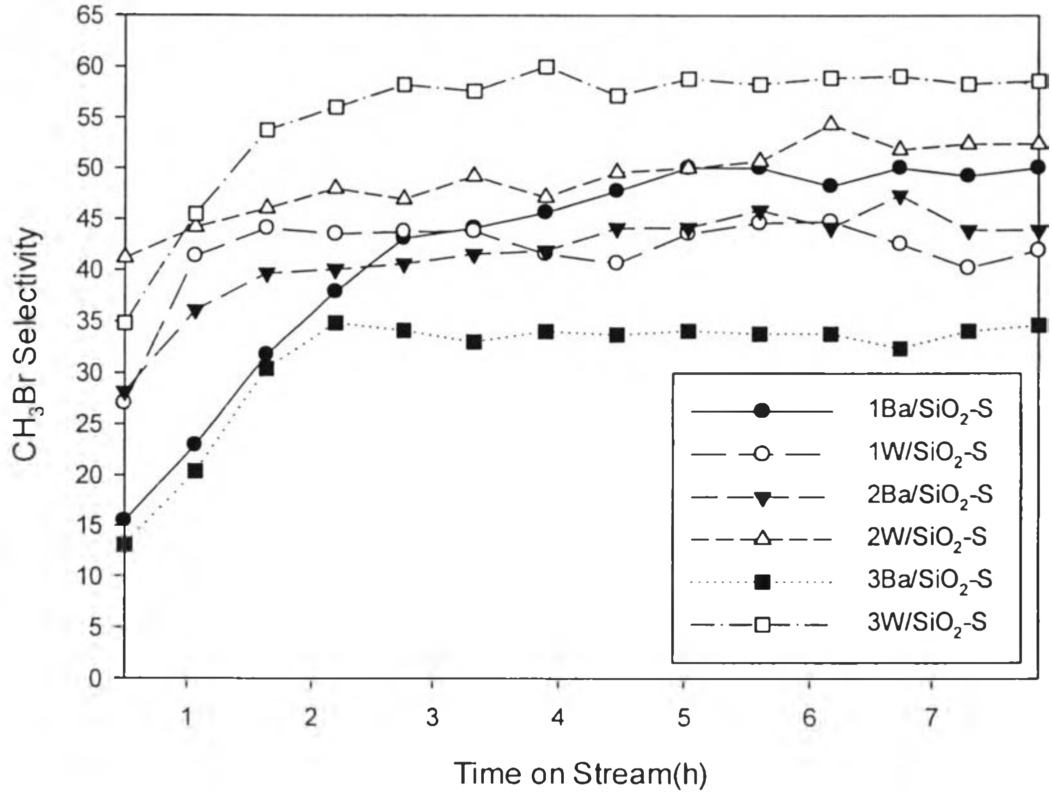

Figure 4.9 Methyl bromide selectivity of different metal loading on sol-gel catalysts at the same reaction condition.

Effect of metal loading on the methyl bromide yield is investigated. For the sol-gel catalysts as shown in Figure 4.10, the methyl bromide yield moderately increases when tungsten loading is increased. Methyl bromide yield increased from 14% in 1W/SiO_2-S to 16% in 2W/SiO_2-S and this yield does not change when tungsten loading increases to 3W/SiO_2-S. However, there is a large reduction of methyl bromide yield when barium loading is increased. Methyl bromide yield drops rapidly from 15% in 1Ba/SiO_2-S to 8 % in 3Ba/SiO_2-S. All of these, the optimum of methyl bromide yield in sol-gel catalyst is observed in 2W/SiO_2-S due to the highest methyl bromide yield around 16%.

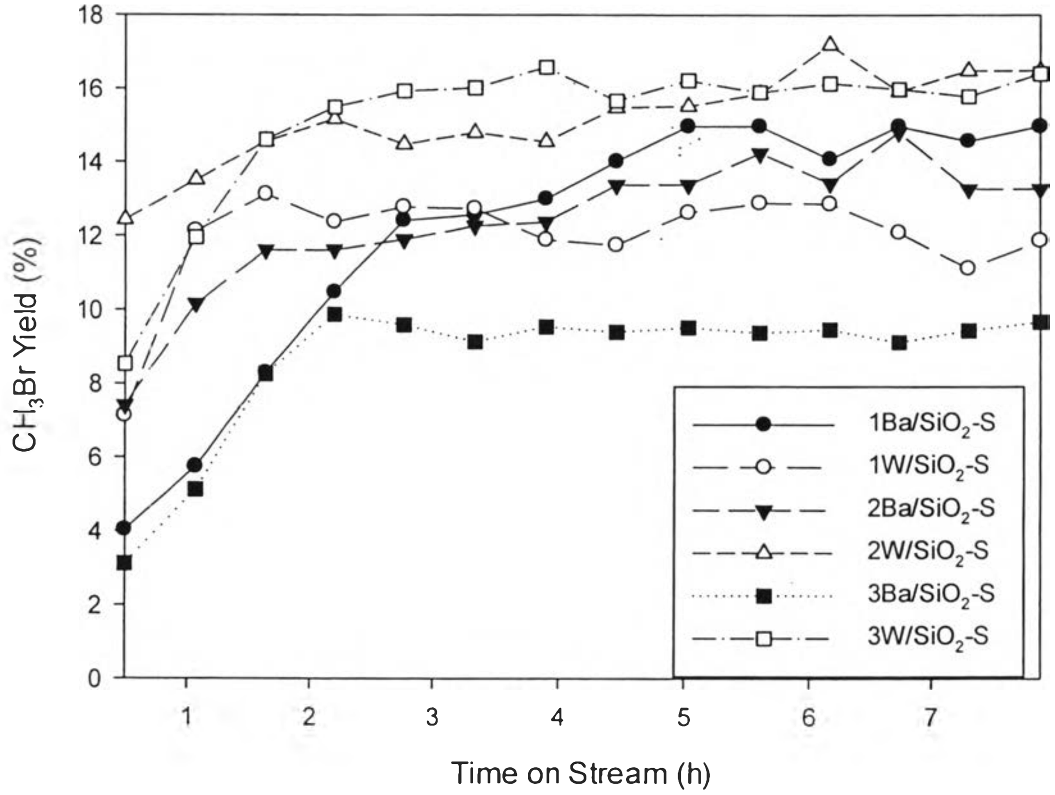

Figure 4.10 Methyl bromide yield of different metal loading on sol-gel catalysts at the same reaction condition.

4.2 Catalytic Characterization

4.2.1 X-ray Diffraction (XRD)

The crystalline structures of the catalysts were determined by X-ray diffraction as shown in Figure 4.11. For the Ba/SiO_2-S and W/SiO_2-S catalysts, only one broad peak between 2θ =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). Moreover, there was no obvious peak related to any crystalline phase. This suggests that metal oxide on catalyst is very well dispersed and/or crystal sizes smaller than the detection limit of the instrument.

However, the barium oxide and tungsten oxide crystalline were detected in the impregnated catalyst, The peaks of BaO (1,1,0) and (2,0,0) can be detected at 2θ = 28 and 42, respectively. Whereas, the WO_3 (0,0,1) can be mainly detected at 2θ = 22. The results indicate that metal oxide crystalline size of impregnation catalysts is bigger than sol-gel catalysts. These results support to the Figure 4.2 and 4.3 that the sol-gel catalysts exhibited a better catalytic performance than impregnated catalysts due to very well metal oxide dispersed and smaller size of metal oxide.

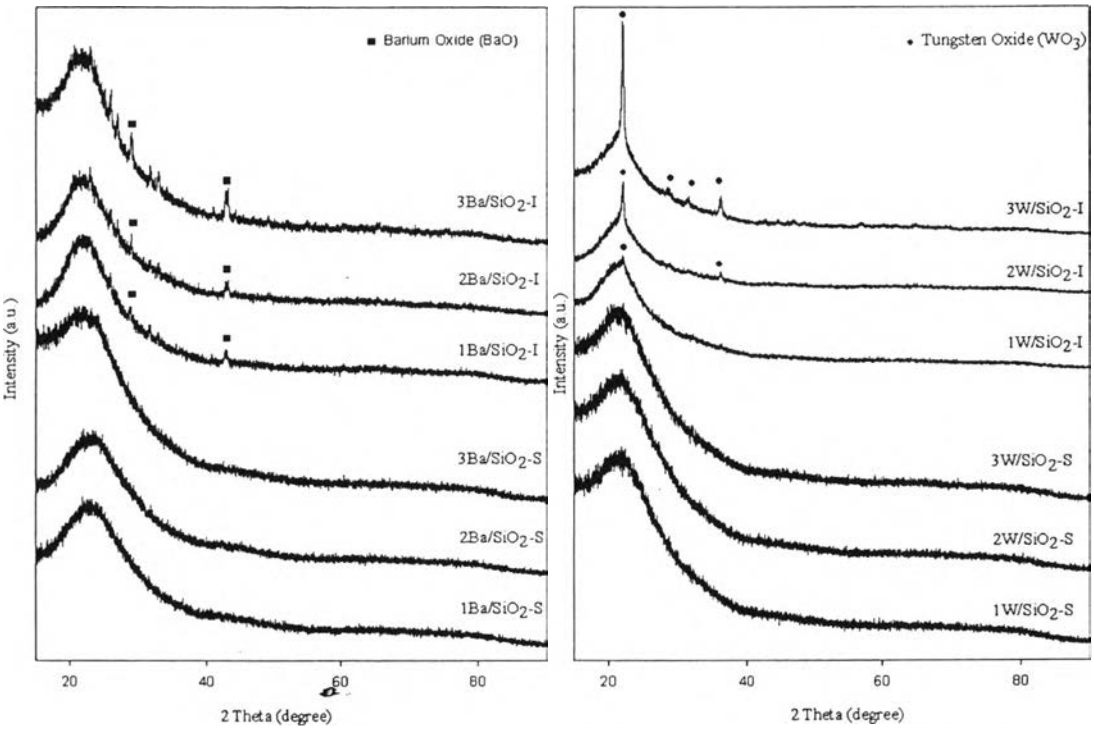

Figure 4.11 XRD spectra of the sol-gel and impregnated catalysts.

The crystalline size of BaO and WO_3 impregnated catalysts calculated by Scherrer's equation are summarized in Table 4.2. It can be clearly seen that the crystalline size of WO_3 (0,0,1) is increased by increasing tungsten loading, jumping from 2.02 nm in 1W/SiO_2-I to 23.55 nm in 3W/SiO2-I, possibly because when increased metal loading, the metal aggregation was occurred.

Moreover, for Barium crystalline, BaO (2,0,0) crystal size also have a similar trend with WO_3, rising from 11.88 nm in 1Ba/SiO2-I to 15.59 nm in 3Ba/SiO_2-I. Nevertheless, BaO (1,1,0) crystal size remain constant at 49 nm when increasing barium loading from 1Ba/SiO_2-I to 3Ba/SiO_2-I.

Table 4.2 Crystalline size of metal oxide impregnated catalysts by Scherrer's equation

Catalyst	2 theta (degree)	Phase name	Crystalline size(nm)
$1Ba/SiO_2$-I	28.66	Barium Oxide(1,1,0)	49.11
	42.56	Barium Oxide(2,0,0)	11.85
$2Ba/SiO_2$-I	28.83	Barium Oxide(1,1,0)	48.41
	42.80	Barium Oxide(2,0,0)	15.81
$3Ba/SiO_2$-I	28.83	Barium Oxide(1,1,0)	49.79
	42.70	Barium Oxide(2,0,0)	15.59
$1W/SiO_2$-I	22.17	Tungsten Oxide(0,0,1)	2.02
$2W/SiO_2$-I	21.72	Tungsten Oxide(0,0,1)	2.88
$3W/SiO_2$-I	21.93	Tungsten Oxide(0,0,1)	23.55

4.2.2 Surface Area Analysis (BET)

The characteristics of the silica support and prepared catalysts including BET surface area, pore volume and average pores size are summarized Table 4.1. The results show that the specific surface area of the sol-gel catalyst is higher than the impregnated catalysts. However pore volume and average pores size of impregnated catalysts is larger than sol-gel catalyst.

Moreover the specific surface area and pore volume of sol-gel and commercial silica support were decreased after loading barium or tungsten, possibly due to the pore blocking of doped metal. In addition, the W/SiO_2 catalyst exhibited very low surface area when compared with the Ba/SiO_2 because the W/SiO_2 catalysts were calcined at higher temperature to obtain tungsten oxide.

For tungsten sol-gel and impregnated catalysts, when tungsten loading is increased, the specific surface area slightly decrease from 606 m^2/g in $1W/SiO_2$-S to 363 m^2/g in $3W/SiO_2$-S and 149 m^2/g in $1W/SiO_2$-I to 50 m^2/g in $36W/SiO_2$-I. However, In case of barium sol-gel and impregnated catalysts, when increasing barium loading in barium sol-gel and impregnated catalysts, the specific surface area and pore volume were changed insignificantly.

However, Figure 4.8 and 4.9 shows the decreasing in methane conversion and methyl bromide selectivity. Therefore, it was proved that methane conversion and methyl bromide selectivity were dependent on the specific surface area of the catalyst but the different catalyst preparations were superior factor. In the case of high metal loading of Ba/SiO_2-S provide relatively higher specific surface area (814 m^2/g of 3Ba/SiO_2) than low metal loading (736 m^2/g of 1Ba/SiO_2) as shown in Table 4.1. Moreover, the high CH_3Br selectivity of OBM reaction was obtained from a low specific surface area of catalyst (Liu *et al.*, 2010). For more consideration in this reason, when the catalyst had high surface area, the methyl bromide product could be easily convert to carbon monoxide by partial oxidation of methyl bromide reaction.

Table 4.3 Specific surface area, pore volume and average pores size s of the support and prepared catalysts

Catalyst	Surface area (m^2/g)	Pore volume (ml/g)	Average pores size (nm)
Sol-gel SiO_2	857	0.65	3.0
Commercial SiO_2	171	1.89	44.1
1 Ba/SiO_2-S	736	0.61	3.3
2 Ba/SiO_2-S	720	0.62	3.4
3 Ba/SiO_2-S	814	0.60	2.9
1 Ba/SiO_2-I	149	0.81	22.1
2 Ba/SiO_2-I	133	0.98	29.4
3 Ba/SiO_2-I	140	1.05	29.8
1 W/SiO_2-S	606	0.44	2.9
2 W/SiO_2-S	602	0.48	3.2
3 W/SiO_2-S	363	0.29	3.2
1 W/SiO_2-I	50	0.82	65.2
2 W/SiO_2-I	29	0.76	63.2
3 W/SiO_2-I	36	0.54	60

Xx/SiO_2-S = catalyst prepared by sol-gel method
Xx/SiO_2-I = catalyst prepared by incipient wetness impregnation technique