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The Oxidative Bromination of Methane Over Rh/SiO_2 Catalyst

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Abstract Methyl bromide was synthesized by reacting methane with oxygen and hydrogen bromide over Rh/SiO_2 catalyst. The reaction started from the oxidation of HBr to form active bromine species ($Br^{\bullet}$ radicals and Br* surface species), which in turn reacted with CH_4 to form $CH_3^{\bullet}$ radicals and CH_3^* surface species. These $CH_3^{\bullet}$ and CH_3^* species reacted with the active bromine species to form CH_3Br and CH_2Br_2. The presence of HBr inhibited the deep oxidation and the steam reformation of CH_4 and therefore, guaranteed the high selectivity of CH_3Br. In the presence of HBr, CO was formed from the oxidation and steam reformation of CH_3Br, while CO_2 was formed from the oxidation and steam reformation of CO over Rh/SiO_2 at reaction temperature higher than 560 °C.

Keywords Methane oxidative bromination · Catalyst · Methyl bromide · Steam reformation

1 Introduction

The oxidative bromination of alkanes as an alternative approach for light alkane conversion was investigated in recent years [1–12]. In Schweizer et al's patent [13], a process was described to halogenate CH_4 to CH_3X (X is halogen), and then convert CH_3X to higher hydrocarbons or acetic acid. However, the oxidative chlorination of methane (HCl as chlorination agent) rather than the oxidative bromination of methane (OBM) was employed for the illustration in the patent. In our previous investigation, higher hydrocarbons [8], dimethyl ether [9], and acetic acid [10, 11] were synthesized through HBr mediated reactions. In all of these processes, high methane conversion and product selectivities were reached. The common reaction in these processes is the OBM reaction. In dimethyl ether or higher hydrocarbon synthesis, CH_4 was converted to the intermediate CH_3Br in the first reaction, and then CH_3Br was converted to dimethyl ether or higher hydrocarbons [8, 9]. Hence, in this case, CH_3Br is the desired product of the OBM reaction. In acetic acid synthesis, CH_4 was converted to the intermediates CH_3Br and CO in the first reaction, and then CH_3Br and CO were converted to acetic acid in the consecutive reactions. Hence, in acetic acid synthesis, CH_3Br and CO are the desired products of the OBM reaction [10, 11]. Generally, the hydrogen halides (HCl and HBr) involved reactions are understood as halogen radical reactions. However, in our previous investigation, it was found that the catalysts acted very important role in OBM reaction. Hence, the surface reactions should be the major reactions in CH_3Br and CO formation. In the previous investigations, the reaction pathways were not systematically investigated. In order to better understand the reaction and design high efficient catalysts for targeted product production, the current investigation is dedicated to the investigation of the reaction pathways for OBM reaction over the Rh/SiO_2 catalyst.

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2 Experimental

2.1 Catalyst Preparation

The catalyst Rh/SiO$_2$ (0.406 wt% Rh in SiO$_2$) was prepared according to the following process. An oxalic acid solution (solution A) was prepared by dissolving 6.30 g of oxalic acid in 100 mL of deionized water. 34.722 g of Si(OC$_2$H$_5$)$_4$ and 0.0828 g of RhCl$_3$ were added to solution A to obtain a mixture. The mixture was stirred at room temperature for 4 h to obtain a single phase solution B. Solution B was dried at 120 °C for 4 h to obtain a solid. The solid sample was heated from room temperature to 900 °C in a period of 4 h, calcined at 900 °C for 10 h, and cooled down to room temperature in ambient conditions to obtain the Rh/SiO$_2$ catalyst. The catalyst was crushed and sieved to particle size between 20 and 60 meshes.

2.2 Reactions

The OBM and other reactions described in the Sect. 3 were carried out in a quartz-tube reactor (ID 1.0 cm, length 60 cm, hot zone 30.0 cm) packed with 5.00 g of Rh/SiO$_2$ catalyst (40–60 mesh) with both ends filled with quartz sand (20–40 mesh). In the blank testing, the reactor tube was only packed with quartz sand. The flows of gas and liquid reactants and the reaction conditions will be given in the corresponding sections. The gas effluents and the liquid products were analyzed on a GC (Agilent 6890N) with thermal conductivity detectors and a GC/MS (6890N/5973N).

We measure the relative correction factors on GC (Agilent 6890N), as a result of Table 1.

The relative correction factors of N$_2$, CH$_4$, CH$_3$Br, CH$_2$Br$_2$, CO and CO$_2$ are signed as $f_0, f_1, f_2, f_3, f_4, f_5$, and the peak areas of N$_2$, CH$_4$ before reaction signed as A_0, A_1, then the peak areas of N$_2$, CH$_4$, CH$_3$Br, CH$_2$Br$_2$, CO and CO$_2$ after reaction signed as A'_0, A'_1, A'_2, A'_3, A'_4, A'_5. So we have follow calculation of conversion and selectivities.

CH$_4$ conversion (N$_2$ as the internal standard):

$$X_{CH_4}\% = \left(1 - \frac{A_0 \times A'_1}{A_1 \times A'_0}\right) \times 100\%$$

Table 1 The relative correction factors

Substances	N$_2$	CH$_4$	CH$_3$Br	CH$_2$Br$_2$	CO	CO$_2$
Signs	f_0	f_1	f_2	f_3	f_4	f_5
The relative correction factors	3.06	1.89	1.00	2.49	2.42	1.48

TCD, carrier: H$_2$

CH$_3$Br selectivity:

$$Y_{CH_3Br}\% = \frac{f_2 \times A'_2}{f_2 \times A'_2 + f_3 \times A'_3 + f_4 \times A'_4 + f_5 \times A'_5} \times 100\%$$

CH$_2$Br$_2$ selectivity:

$$Y_{CH_2Br_2}\% = \frac{f_3 \times A'_3}{f_2 \times A'_2 + f_3 \times A'_3 + f_4 \times A'_4 + f_5 \times A'_5} \times 100\%$$

CO selectivity:

$$Y_{CO}\% = \frac{f_4 \times A'_4}{f_2 \times A'_2 + f_3 \times A'_3 + f_4 \times A'_4 + f_5 \times A'_5} \times 100\%$$

CO$_2$ selectivity:

$$Y_{CO_2}\% = \frac{f_5 \times A'_5}{f_2 \times A'_2 + f_3 \times A'_3 + f_4 \times A'_4 + f_5 \times A'_5} \times 100\%$$

3 Results and Discussion

3.1 The Characterization of Catalyst

The XPS analysis shows that, in fresh catalyst, the rhodium was in Rh^{3+} state and in the used catalyst, the rhodium was in element state. Hence, we write the catalyst as Rh/SiO$_2$ in the following sections. The XRD characterization showed that both the fresh and used catalyst contained cristobalite phase [8].

3.2 The OBM Reaction Over Rh/SiO$_2$

The direct reaction between methane and bromine shows that CH$_4$ reacted with Br$_2$ to form CH$_3$Br at room temperature (mixed at room temperature and kept for 24 h, CH$_3$Br was detected by GC/MS). This reaction is the well-known bromine radical reaction. When HBr/H$_2$O (40 wt%, 6.0 mL/h) reacted with O$_2$ (5.0 mL/min) over Rh/SiO$_2$ (5.00 g), there was significant amount of Br$_2$ formed at temperature higher than 270 °C. These investigations indicate that it is possible to produce CH$_3$Br by the reaction of CH$_4$ with O$_2$ and HBr over the Rh/SiO$_2$ catalyst. In a reaction, when CH$_4$ (20.0 mL/min), O$_2$ (5.0 mL/min), N$_2$ (5.0 mL/min), and HBr/H$_2$O (6.0 mL/h, 40% liquid) were fed into the Rh/SiO$_2$ catalyst bed, the methane conversion and product selectivities are shown in Fig. 1. The reaction occurred at temperature higher than 460 °C over Rh/SiO$_2$ catalyst. At 480 °C, CH$_4$ conversion reached 0.31% and only CH$_3$Br was detected as product. CO was formed at temperature higher than 480 °C. The formation of CO$_2$ was observed at temperature above 620 °C. There was no hydrogen formation in the reaction. Below 660 °C, the main products were CH$_3$Br and CH$_2$Br$_2$. The total selectivity of CO and CO$_2$ was below 10.0%. The results indicate that CH_3Br is the primary product (since CH_3Br is the only product at relatively lower reaction temperature). CH_2Br_2 and CO might be formed in the consecutive reactions of CH_3Br. CO_2 might be formed from the oxidation of CO.

3.3 The Oxidation of Methane Over Rh/SiO_2

In the absence of HBr, when CH_4 (20.0 mL/min), O_2 (5.0 mL/min), N_2 (5.0 mL/min), and H_2O (6.0 mL/h, liquid) were fed into the catalyst bed, there was no reaction observed below 480 °C. Methane conversion reached 0.22% at 500 °C. Only H_2 and CO were formed as products between 480 and 520 °C. Above 520 °C, except H_2 and CO, CO_2 was also formed as the product (Fig. 2). The phenomenon indicates that CO_2 came from the oxidation of CO. Comparing the results of Fig. 1 with that of Fig. 2, the presence of HBr partially blocked the deep oxidation of methane (with low CO and CO_2 selectivities).

3.4 The Steam Reformation of Methane Over Rh/SiO_2

The results of CH_4 steam reformation over catalyst Rh/SiO_2 were shown in Fig. 3. CO and H_2 were obtained as the products between 500 and 680 °C. The steam reformation of methane occurred at temperature higher than 540 °C, which was higher than that in methane oxidation (520 °C Fig. 2). Hence, when without HBr and in the presence of O_2, CO might be formed from the oxidation and the steam reformation of CH_4 over catalyst at temperature higher than 540 °C. Since the conversion of CH_4 steam reformation is low (Fig. 3, only 3.3% of CH_4 conversion was obtained at 680 °C), the major part of CO (in Fig. 2) might be formed from the oxidation of CH_4.

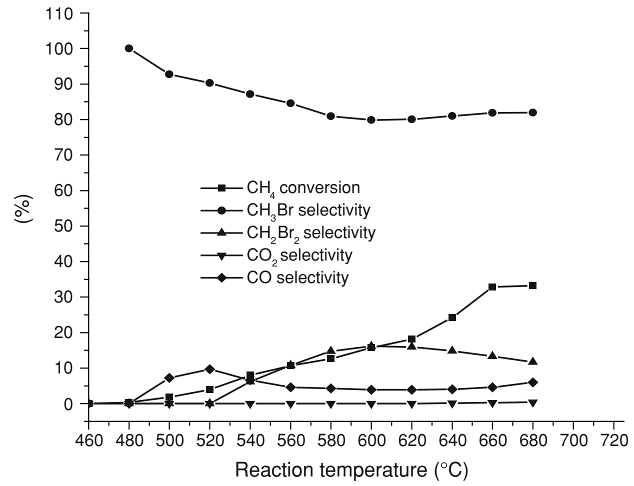


Fig. 1 OBM reaction over Rh/SiO_2 catalyst (5.00 g) at reactant flows: CH_4 20.0 mL/min, O_2 5.0 mL/min, N_2 5.0 mL/min, and liquid HBr/H_2O (40 wt%) 6.0 mL/h

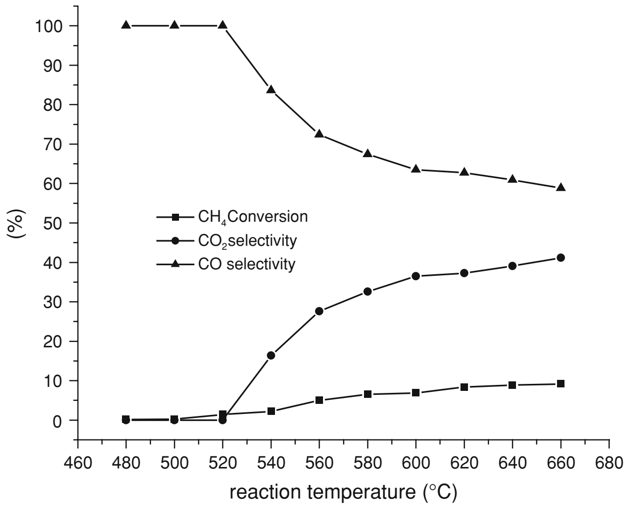


Fig. 2 Methane oxidation over Rh/SiO_2 catalyst (5.00 g) at reactant flows: H_2O 6.0 mL/h, CH_4 20.0 mL/min, O_2 5.0 mL/min, and N_2 5.0 mL/min (used as internal standard)

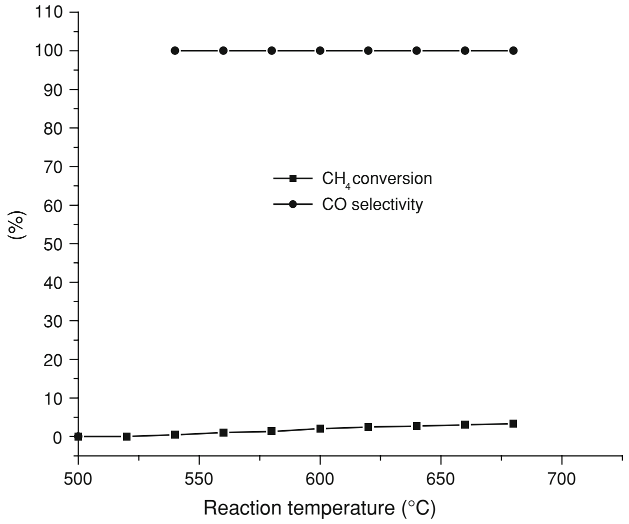
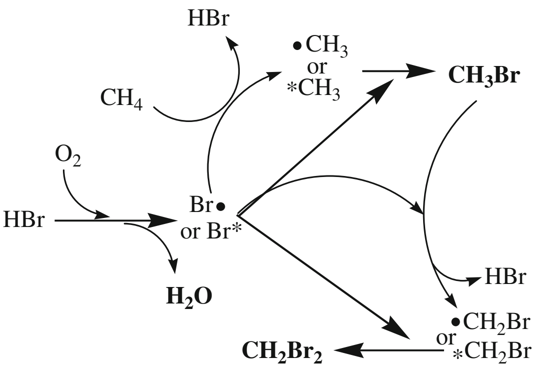


Fig. 3 The steam reformation of CH_4 over Rh/SiO_2 catalyst (5.00 g) at reactant flows: CH_4 20.0 mL/min, N_2 5.0 mL/min, and H_2O 6.0 mL/min (liquid)

Comparing the results of Fig. 1 with that of Fig. 2, the presence of HBr switched the deep oxidation of methane to the direction of CH_3Br formation reaction. The possible reason could be that the adsorption of HBr over the catalyst poisoned the deep oxidation of methane. The above investigations show that the reaction pathway might be that HBr reacts with O_2 to form active bromine species, such as the bromine radicals ($Br^\bullet$) and the adsorbed species (Br^*) over the surface of the catalyst, then the active bromine species react with CH_4 to form HBr and methyl species ($CH_3^\bullet$ radicals and the adsorbed surface species CH_3^*), and then the methyl species react with active bromine species to form CH_3Br and CH_2Br_2 as shown in Scheme 1. In order to identify if the gas phase or the surface reactions are the major reactions in OBM reaction, farther investigations were conducted in the following sections.



Scheme 1 Reaction pathways for CH_3Br and CH_2Br_2 formation

3.5 The Gas Phase OBM Reaction Over Quartz Sand

In order to obtain the information of the gas phase reaction, the OBM reaction was run at temperatures between 340 and 660 °C with a feeding of CH_4 (20.0 mL/min), O_2 (5.0 mL/min), N_2 (5.0 mL/min, used as internal standard), and HBr/H_2O (40.0 wt%, 6.0 mL/min) over quartz sands (40–60 mesh). The results are shown in Fig. 4. The reaction over quartz sands shows that the methane conversion was much lower (below 10.0%) than that obtained over Rh/SiO$_2$. The reaction started from 500 °C, which was higher than that over Rh/SiO$_2$ (the reaction started from 480 °C). The major product was CO below 530 °C. When switching the reaction stream to CH_4 (20.0 mL/min), O_2 (5.0 mL/min), N_2 (5.0 mL/min), and H_2O (6.0 mL/h), there was no reaction observed between 400 and 680 °C over quartz sand. Hence, the gas phase reaction with HBr feeding was also initiated from the bromine radical reaction. The investigations show that the surface reactions are the major reactions in the formation of CH_3Br and CH_2Br_2.

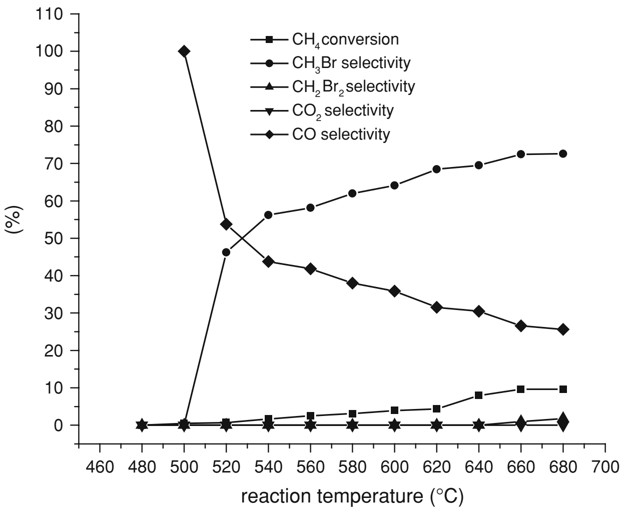


Fig. 4 Methane oxidative bromination over quartz sand at reactant flows: CH_4 20.0 mL/min, O_2 5.0 mL/min, N_2 5.0 mL/min, and HBr/H_2O (40 wt%, liquid) 6.0 mL/h

3.6 Methane Steam Reformation in the Presence of HBr Over Rh/SiO$_2$

In the OBM reaction shown in Fig. 1, CO was formed as the major by-product (CH_3Br and CH_2Br_2 are the desired products). In order to clarify what kinds of reactions lead to the formation of CO, we carried out reactions between CH_4 (20.0 mL/min) and HBr/H_2O (40 wt%, 6.0 mL/h liquid) keeping N_2 (5.0 mL/min) as the internal standard. There was no reaction observed over Rh/SiO$_2$ at temperature lower than 680 °C. Comparing with the results of Fig. 3 (without HBr, in which H_2 and CO were formed as products), the above results show that the presence of HBr blocked the methane steam reformation reaction. This could also be understood as that the adsorption of HBr on Rh/SiO$_2$ blocked the adsorption of methane over the Rh/SiO$_2$ catalyst.

The above investigations show that, in the presence of HBr, CO was formed from the HBr initiated oxidation of methane, but not formed from the steam reformation of methane. The results of Fig. 1 show that CH_3Br was formed as the only product below 500 °C. Hence, there is reason to speculate that the HBr initiated oxidation reaction forms CH_3Br as the primary product in OBM reaction. The consecutive steam reformation and oxidation of CH_3Br might be the approaches to form CO in the OBM reaction.

3.7 The Steam Reformation of CH$_3$ Br Over Rh/SiO$_2$

In the steam reformation of CH_3Br, CH_3Br (7.0 mL/min), H_2O (6.0 mL/h, liquid), and N_2 (5.0 mL/min) were fed into Rh/SiO$_2$ catalyst bed. Products CO, CO_2, CH_4, H_2, and HBr were formed (Fig. 5). The reaction occurred at temperature higher than 500 °C. From 500 to 580 °C, products HBr, H_2, CH_4, and CO were formed. Above 580 °C, except CO, CH_4, H_2, and HBr, CO_2 was also detected. There was trace CH_2Br_2 detected by GC/MS at temperature higher than 600 °C. The CO selectivity decreased with the increase of the reaction temperature from 500 to 660 °C, and then increased with the increase of the reaction temperature from 660 to 680 °C. The selectivity of CH_4 increased when the reaction temperature increased from 500 to 580 °C and reached a maximum value of 50% at 580 °C. At reaction temperature higher than 580 °C, the selectivity of CH_4 decreased. The selectivity of CO_2 increased with the increase of the reaction temperature

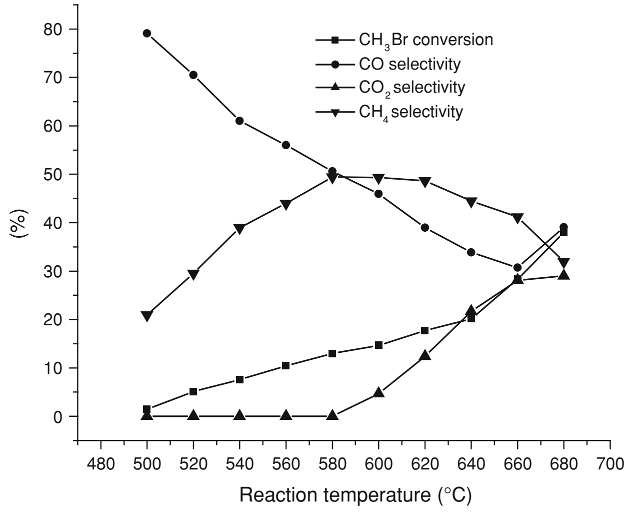


Fig. 5 The steam reformation of CH_3Br over Rh/SiO_2 (5.00 g). The reactant flows are 7.0 mL/min of CH_3Br, 6.0 mL/h of H_2O (liquid), and 5.0 mL/min of N_2

from 580 to 680 °C. In the absence of extra HBr feeding, reactions (1) to (3) could be predicted in the steam reformation of CH_3Br:

$$CH_3Br + H_2O \rightarrow CO + 2H_2 + HBr \tag{1}$$

$$CH_3Br + H_2 \rightarrow CH_4 + HBr \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

3.8 The Steam Reformation of CH_3Br in the Presence of HBr Over Rh/SiO_2

In a feeding of CH_3Br (7.0 mL/min), HBr/H_2O (6.0 mL/h, 40 wt% liquid), and N_2 (5.0 mL/min), the steam reformation of CH_3Br occurred at relatively higher temperature (Fig. 6). The products H_2, CH_4, CO, and HBr were formed between the reaction temperatures 540 and 560 °C. At elevated reaction temperatures between 560 and 580 °C, except H_2, CH_4, CO, and HBr, CH_2Br_2 was also formed. Above 580 °C, except H_2, CH_4, CO, CH_2Br_2, and HBr, CO_2 was also produced as one of the products. Comparing the results of Fig. 6 with that of Fig. 5, in the presence of HBr, the reaction started at relatively higher temperature (540 °C). It could be found that, in the presence of HBr, the CH_3Br reformation conversion increased more rapidly with the increase of the reaction temperature than that of without feeding HBr (Fig. 5). The results of Figs. 5 and 6 indicate that the presence of HBr partially blocked the steam reformation of CH_3Br at reaction temperature below 560 °C and enhanced the steam reformation of CH_3Br at higher reaction temperature (higher than 560 °C). In both with and without HBr feeding cases, CO_2 was formed at reaction temperature higher than 580 °C.

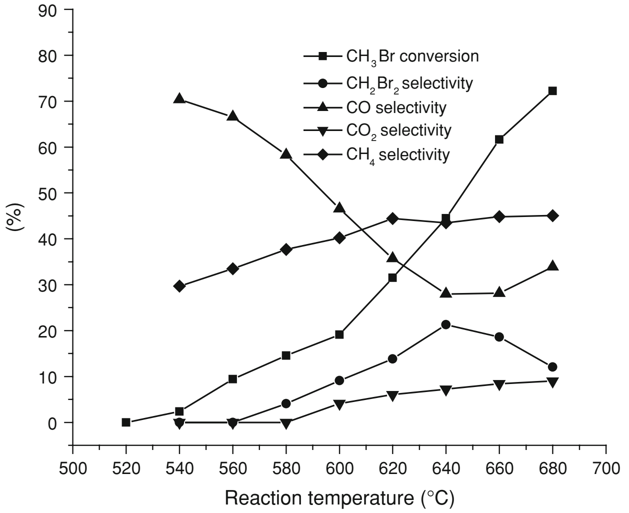


Fig. 6 The steam reformation of CH_3Br over Rh/SiO_2 (5.00 g). The reactant flows are 7.0 mL/min of CH_3Br, 6.0 mL/h of HBr/H_2O (40 wt% liquid), and 5.0 mL/min of N_2

In the steam reformation of CH_3Br, a big difference between HBr/H_2O and H_2O feeding cases is that, in the presence of HBr, CH_2Br_2 was formed as a major by-product from 560 to 680 °C and the selectivity of CH_2Br_2 was higher than that of CO_2. The formation of CH_2Br_2 indicates that there were CH_2Br^* and Br^* species over the surface of the catalyst at temperature higher than 560 °C. Hence, except the reactions (1), (2), and (3) shown previously, in the presence of HBr, the surface reactions (4)–(7) could also be predicted.

$$CH_3Br + * \rightarrow CH_2Br^* + H^* \tag{4}$$

$$HBr + * \rightarrow H^* + Br^* \tag{5}$$

$$CH_2Br^* + Br^* \rightarrow CH_2Br_2 \tag{6}$$

$$H^* + H^* \rightarrow H_2 \tag{7}$$

3.9 The Oxidation of CH_3Br in the Presence of HBr Over Rh/SiO_2

When CH_3Br (7.0 mL), O_2 (5.0 mL), HBr/H_2O (40 wt%, 6.0 mL/h liquid), and N_2 (5.0 mL) were fed into the Rh/SiO_2 catalyst bed, the reaction started at 460 °C (Fig. 7). CH_2Br_2, CO, CO_2, CH_4, and HBr were formed as the products. There was only trace amount of H_2 detected. In this case, CH_2Br_2 was the major product below 620 °C, while CO and CO_2 became the major products at higher reaction temperature (higher than 620 °C). The CH_3Br conversion in the oxidation reaction was much higher than that in the steam reformation reactions shown in Figs. 5 and 6. The selectivity of CH_2Br_2 increased from 58.7% to 82.6% with the increase of the reaction temperature from 460 to 540 °C and reached the maximum of 82.6% at 540 °C. Above 540 °C, the CH_2Br_2 selectivity decreased.

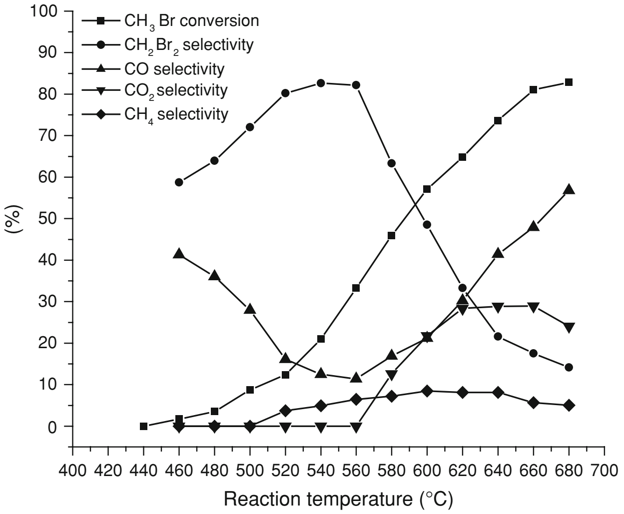


Fig. 7 The oxidation of CH$_3$Br over Rh/SiO$_2$ (5.00 g). The reactant flows are 7.0 mL/min of CH$_3$Br, 5.0 mL/min of O$_2$, 6.0 mL/h of HBr/H$_2$O (40 wt% liquid), and 5.0 mL/min of N$_2$

The CO selectivity decreased (from 41.3% to 11.4%) with the increase of reaction temperature from 460 to 560 °C, and then increased from 11.4% to 56.8% with the increase of reaction temperature from 560 to 680 °C. The results show that CO could come from the steam reformation and the oxidation of CH$_3$Br. In the presence of O$_2$, the methane selectivity was much lower than that in the cases of without O$_2$ (Figs. 5 and 6). In the presence of O$_2$, CO$_2$ was formed at relatively lower temperature. In Fig. 7, CO$_2$ was detected at temperature higher than 560 °C, but in the cases of without O$_2$, CO$_2$ was detected at temperature higher than 580 °C as shown in Figs. 5 and 6.

The higher selectivity of CH$_2$Br$_2$ in the oxidation of CH$_3$Br indicates that the primary product is CH$_2$Br$_2$, which could be formed both in the gas phase and over the surface of catalyst. In the gas phase, HBr might react with O$_2$ to form bromine radicals, and then the bromine radicals reacted with CH$_3$Br to form CH$_2$Br$^\bullet$ radicals, which could react with Br$^\bullet$ radicals to obtain CH$_2$Br$_2$. Over the surface of the catalyst, the results in Fig. 6 show that there were CH$_2$Br* surface species, which could react with the Br* surface species or react with gas phase Br$^\bullet$ radicals to form CH$_2$Br$_2$. The presence of O$_2$ removed part of the adsorbed H* species over the surface of the catalyst and reduced the recombination possibility of H* and Br* species. Hence, the presence of O$_2$ also enhanced the combination of Br* with CH$_2$Br* species, which led to the increase of CH$_2$Br$_2$ selectivity. This viewpoint was also confirmed by the formation of CH$_4$ in the cases of with O$_2$ (Fig. 7) and without O$_2$ (Figs. 5 and 6). In the cases of without O$_2$, much higher CH$_4$ selectivity was reached, but in the presence of O$_2$, the selectivity of CH$_4$ was much lower (comparing the CH$_4$ selectivity in Fig. 7 with that in Figs. 5 and 6). The reason is that the hydrogenation of CH$_3$Br needs H* species. Removing H* by O$_2$ reduced the CH$_4$ formation rate.

In the steam reformation of CH$_3$Br, CH$_4$ was always formed as an hydrogenation product of CH$_3$Br. Hence, CO and CH$_4$ were always formed together as shown in Figs. 5 and 6. However, in the oxidation of CH$_3$Br (Fig. 7), CO was produced without forming CH$_4$ between 460 and 500 °C. Hence, below 500 °C, CO was produced from the oxidation of CH$_3$Br. From the comparision of CH$_3$Br conversions in the steam reformation (Fig. 6) and the oxidation (Fig. 7), most part of CO should be produced from the oxidation reaction below 560 °C, while above 560 °C, CO was produced from the oxidation and steam reformation of CH$_3$Br (Fig. 7).

Based on the investigations, the following reactions (8)–(25) could be predicted:

The possible surface reactions (8)–(18):

$$\mathrm{CH_3Br} \rightarrow \mathrm{CH_3^*} + \mathrm{CH_2^*} + \mathrm{CH^*} + \mathrm{C^*} + \mathrm{H^*} + \mathrm{Br^*} \tag{8}$$

$$\mathrm{CH_3^*} + \mathrm{CH_2^*} + \mathrm{CH^*} + \mathrm{C^*} + \mathrm{H_2O} \rightarrow \mathrm{CO} + \mathrm{CO_2} + \mathrm{H^*} \tag{9}$$

$$\mathrm{H^*} + \mathrm{CH_3^*} \rightarrow \mathrm{CH_4} \tag{10}$$

$$\mathrm{H^*} + \mathrm{Br^*} \rightarrow \mathrm{HBr} \tag{11}$$

$$\mathrm{CH_3Br} + * \rightarrow \mathrm{CH_2Br^*} + \mathrm{H^*} \tag{12}$$

$$\mathrm{HBr} + * \rightarrow \mathrm{H^*} + \mathrm{Br^*} \tag{13}$$

$$\mathrm{CH_2Br^*} + \mathrm{Br^*} \rightarrow \mathrm{CH_2Br_2} \tag{14}$$

$$\mathrm{H^*} + \mathrm{O_2} \rightarrow \mathrm{HO_2^*} \tag{15}$$

$$\mathrm{H^*} + \mathrm{HO_2^*} \rightarrow 2\mathrm{HO^*} \tag{16}$$

$$\mathrm{H^*} + \mathrm{HO^*} \rightarrow \mathrm{H_2O^*} \tag{17}$$

$$\mathrm{CH_3^*} + \mathrm{CH_2^*} + \mathrm{CH^*} + \mathrm{C^*} + \mathrm{O_2} \rightarrow \mathrm{CO} + \mathrm{CO_2} + \mathrm{H_2O} \tag{18}$$

The possible gas phase reactions (19)–(25):

$$\mathrm{HBr} + \mathrm{O_2} \rightarrow \mathrm{Br^\bullet} + \mathrm{HO_2^\bullet} \tag{19}$$

$$\mathrm{CH_3Br} + \mathrm{HO_2^\bullet} \rightarrow {}^\bullet\mathrm{CH_2Br} + \mathrm{H_2O_2} \tag{20}$$

$$\mathrm{H_2O_2} \rightarrow 2\mathrm{HO^\bullet} \tag{21}$$

$$\mathrm{CH_3Br} + \mathrm{HO^\bullet} \rightarrow {}^\bullet\mathrm{CH_2Br} + \mathrm{H_2O} \tag{22}$$

$$\mathrm{CH_3Br} + \mathrm{HO^\bullet} \rightarrow {}^\bullet\mathrm{CH_2Br} + \mathrm{H_2O} \tag{23}$$

$$\mathrm{CH_3Br} + \mathrm{Br^\bullet} \rightarrow \mathrm{CH_2Br} + \mathrm{HBr} \tag{24}$$

$$\mathrm{CH_2Br^\bullet} + \mathrm{Br^\bullet} \rightarrow \mathrm{CH_2Br_2} \tag{25}$$

As shown in Fig. 4, in the reaction of CH$_4$ (20.0 mL/min), O$_2$ (5.0 mL/min), N$_2$ (5.0 mL/min), and HBr/H$_2$O (40 wt%, 6.0 mL/h) over quartz sand, there was no CO$_2$ formation. In the OBM reaction (Fig. 1), CO$_2$ was formed at temperature higher than 620 °C and the selectivity was lower than 0.4% (at 680 °C), which indicates that CO$_2$ might come from the oxidation of CO and the reaction could occur both on the surface of the catalyst and in the gas phase.

3.10 The Oxidation of CH_3Br in the Presence of HBr Over Quartz

When feeding CH_3Br (7.0 mL/min), O_2 (5.0 mL/min), N_2 (5.0 mL/min), and HBr/H_2O (40%, 6.0 mL/h) to a quartz bed, the results of Fig. 8 show that CH_4 and CO_2 were not formed over quartz sand between 450 and 680 °C. The gas phase oxidation of CH_3Br only formed CH_2Br_2 below 600 °C. CH_2Br_2 and CO were formed at relatively higher reaction temperature between 600 and 680 °C. Over Rh/SiO_2, CH_4 was formed as one of the products in the oxidation of CH_3Br (Fig. 7). However, there was no CH_4 formation in the oxidation of CH_3Br over quartz sand (Fig. 8). The results indicate that Rh/SiO_2 is necessary for the hydrogenation reaction of CH_3Br to form CH_4, which also confirmed that CH_4 was formed on the surface of Rh/SiO_2. The investigations of CH_3Br oxidation over Rh/SiO_2 and quartz indicate that all of the CO_2 was formed from the oxidation and steam reformation of CO over the surface of Rh/SiO_2 catalyst. Hence, below 600 °C, we have the gas phase reactions (26) to (31) over quartz sand.

$$HBr + O_2 \rightarrow HO_2^{\bullet} + Br^{\bullet} \tag{26}$$

$$HBr + HO_2^{\bullet} \rightarrow H_2O_2 + Br^{\bullet} \tag{27}$$

$$H_2O_2 \rightarrow 2HO^{\bullet} \tag{28}$$

$$HBr + 2HO^{\bullet} \rightarrow H_2O + Br^{\bullet} \tag{29}$$

$$CH_2Br + Br^{\bullet} \rightarrow HBr + CH_2Br^{\bullet} \tag{30}$$

$$CH_2Br^{\bullet} + Br^{\bullet} \rightarrow CH_2Br_2 \tag{31}$$

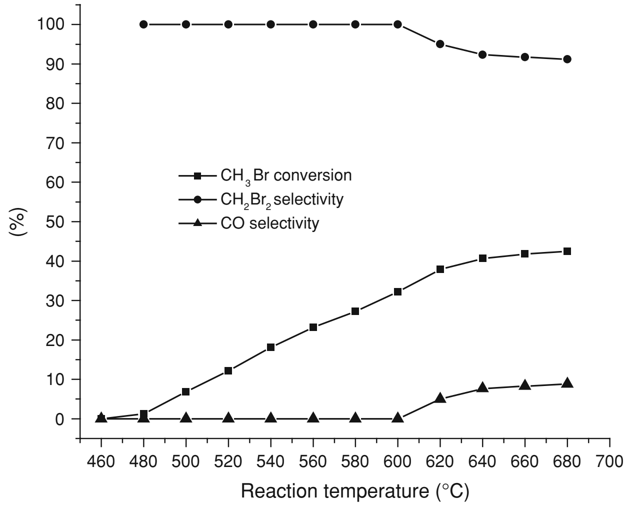


Fig. 8 CH_3Br oxidation over quartz sand at reactant flows: CH_3Br 7.0 mL/min, O_2 5.0 mL/min, N_2 5.0 mL/min, and HBr/H_2O(40 wt%) 6.0 mL/h

4 Conclusion

In conclusion, the OBM reaction occurred both in the gas phase and over the surface of the catalyst Rh/SiO_2, but the surface reactions contributed the major part in the formation of CH_3Br and CH_2Br_2. The possible pathway is that HBr reacted with oxygen to form bromine radicals and adsorbed bromine species. The bromine radicals and adsorbed bromine species might react with methane to form CH_3Br. CH_3Br could react with $Br^{\bullet}$ radicals to form CH_2Br_2 in the gas phase. CH_3Br could also adsorb onto the Rh/SiO_2 surface to form CH_2Br^* species, which could react with $Br^{\bullet}$ radicals and/or Br^* species to form CH_2Br_2. The major part of CO was formed from the steam reformation and the oxidation of CH_3Br. The gas phase oxidation of CH_3Br only produced CH_2Br_2 and CO. CO_2 was formed in the oxidation of CO over the surface of the catalyst at temperature higher than 560 °C. The presence of HBr inhibited the deep oxidation and the steam reformation of methane.

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