

# Higher hydrocarbons from methane condensation mediated by HBr

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## Abstract

Methane condensation to higher hydrocarbons with a single-pass methane conversion of 30% and total carbon selectivity of 90% has been achieved in a system of two-stage serial reactors. Methane reacts with HBr and oxygen in the first catalyst bed at 660 °C to form CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub>, while CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub> are converted to higher hydrocarbons in the second catalyst bed at 240 °C. A reusable sorption material MgO/SiO<sub>2</sub> has been identified for the separation of HBr from H<sub>2</sub>O and olefins (performed at 200 °C), making the recovery of bromine and the purification of olefins feasible.

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**Keywords:** Methane condensation; Methane bromide; Oxidation catalyst; Higher hydrocarbon

## 1. Introduction

Traditionally, liquid fuels, such as gasoline and diesel, are obtained by the petroleum refinery processes. The Earth is rich with natural gas of which over 80% is methane. In principle, methane can be converted to higher hydrocarbon liquid fuels. However, the high stability of the C–H bonds of methane makes the conversion difficult. The current technology for the conversion of natural gas to liquid fuels is based on the Fischer–Tropsch (F–T) process [1]. Compared to other petroleum refinery processes, the F–T process is commercially less competitive because it consumes more energy.

Since the early work of Keller and Bhasin, there has been much investigation on the oxidative coupling of methane to ethylene and ethane [2]. The technology is not good enough to be commercialized because both the methane conversion and the C<sub>2</sub> selectivity are low. Periana et al. reported a process to convert methane to methanol and acetic acid [3,4]; but the problem

with this approach is that the oxidant is concentrated H<sub>2</sub>SO<sub>4</sub> and the wastes (SO<sub>2</sub> and diluted H<sub>2</sub>SO<sub>4</sub>) are difficult to recycle. Another approach for methane conversion is by means of oxychlorination of methane and the subsequent conversion of CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub> to a variety of hydrocarbons [5–10]. The technology of methane oxychlorination is not commercialized due to (i) the low methane conversion, (ii) high CO and CO<sub>2</sub> emission, (iii) low methyl chloride and methylene dichloride selectivities, and (iv) poor activity in the hydrodechlorination of methyl chloride and methylene dichloride to higher hydrocarbons. Although the oxidative bromination of methane (OBM) mediated by HBr looks “old”, the OBM reaction adopting HBr as bromination agent has only been mentioned once in a patent by Schweizer et al., and the oxidative chlorination of methane (HCl as chlorination agent) rather than the OBM reaction was employed for the illustration in the patent [11]. A literature survey on the topic confirms that the information related to the OBM reaction is very limited. Indeed, most of the related reports [12–17] are on the oxidative chlorination of methane in which CO is a major by-product (selectivity over 20%). Previously, Zhou et al. developed a bromine-mediated process to convert the alkane to value-added compounds such as dimethyl ether, alkanes, alkenes, and esters [18–23]. In these reactions, the alkane reacts with elemental bromine to form alkyl bromides, which

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interact with metal oxides to form hydrocarbons or oxygenates. In these reactions, except the reaction between element bromine and alkane, alkyl bromides react stoichiometrically with metal oxides to form hydrocarbons or oxygenates. Recently, Zhou et al. reported a Ru/SiO<sub>2</sub> catalyst [24–26] for efficient methane oxy-bromination to CH<sub>3</sub>Br and CO, which in turn were converted to dimethyl ether (CH<sub>3</sub>Br only) or (CH<sub>3</sub>Br with CO) to acetic acid. However the catalyst reported was not as efficient (in terms of methane conversion and methyl bromide selectivity) as what is reported here. The subject of this work is also to describe a two-step process for the synthesis of higher hydrocarbons from methane by a catalytic pathway.

Although Schweizer's patent described the conversion of CH<sub>3</sub>Br to higher hydrocarbons [11], there is no disclosure of the catalyst and reaction data. Hence, the OBM reaction with HBr as bromination agent is a subject worth studying. It is important to design catalysts, which are active and selective for the OBM reaction. It is therefore meaningful to (i) deepen the study into effective catalysts, (ii) make this approach practical by finding the sorption material for the separation of hydrocarbons from HBr, and (iii) identify durable materials for construction of a reactor for this kind of reaction. The purpose of this work is to develop a process for the practical conversion of methane to hydrocarbons and/or synthesis intermediates as illustrated in reactions (1) (in the ideal case without forming CO and CO<sub>2</sub>) and (2):



$$\Delta H^\circ = -332.6 \text{ kJ}$$



In order to achieve such a goal, we have designed a two-stage system (serially connected fixed-bed reactors) for reactions (1) and (2). Reaction (1) is exothermic ( $\Delta H^\circ = -332.6 \text{ kJ}$ ) and the formation of a whole range of C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> olefins in reaction (2) is exothermic as well, as shown in Table 1.

Table 1  
 $\Delta H^\circ$  of reactions in CH<sub>3</sub>Br conversion to olefins

Compounds	$\Delta H^\circ$ (kJ)
C <sub>2</sub> H <sub>4</sub>	52.4
C <sub>3</sub> H <sub>6</sub>	50.6
1-Butene	0.1
<i>Cis</i> -2-butene	-7.1
<i>Trans</i> -2-butene	-11.4
Isobutene	-16.9
Cyclobutane	27.7
1-Pentene	-21.1
<i>Cis</i> -2-pentene	-27.6
2-Methyl-2-butene	-41.7
Cyclopentane	-76.4
<i>Trans</i> -2-pentene	-31.9
2-Methyl-1-butene	-35.2
3-Methyl-1-butene	-27.5
C <sub>6</sub> H <sub>12</sub> isomers	-123.4 < $\Delta H^\circ$ < -27.5

## 2. Experimental

### 2.1. The preparation of Rh/SiO<sub>2</sub> (0.406 wt% Rh in SiO<sub>2</sub>) catalyst for methane oxidative bromination

An oxalic acid solution (solution A) was prepared by dissolving 6.30 g of oxalic acid in 100 mL of deionized water. 34.7 g of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and 0.0828 g of RhCl<sub>3</sub> were added to solution A and the mixture was stirred at room temperature for 4 h to give a single phase solution B. Solution B was dried at 120 °C for 4 h to form 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 environment to give the Rh/SiO<sub>2</sub> catalyst. The catalyst was crushed and sieved to 20–60 mesh. The specific surface area of the catalyst was 0.26 m<sup>2</sup>/g.

### 2.2. The preparation of MgO/ZSM-5 and MgO/SiO<sub>2</sub>-R catalyst for CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub> condensation

The MgO/ZSM-5 catalyst was prepared by impregnating HZSM-5 (10.00 g, Si/Al = 360, 330.1 m<sup>2</sup>/g) with aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (8.97 g in 30 mL H<sub>2</sub>O). The mixture was dried at 120 °C for 4 h and calcined at 450 °C for 8 h to form the MgO/ZSM-5 catalyst. The specific surface area of the catalyst was 251 m<sup>2</sup>/g. The sample powder was pressed, crushed, and sieved to 20–60 mesh. The amount of MgO in the catalyst was 12.4 wt%.

The MgO/SiO<sub>2</sub>-R catalyst was prepared by the following method. First, SiO<sub>2</sub> was prepared. The procedure was: 60.0 mL of silicon tetraethoxide was added to 400 mL of oxalic acid solution (0.50 M) and the mixture was stirred at room temperature overnight to be converted to a gel. The gel was dried at 120 °C for 6 h and then calcined at 450 °C for 4 h to obtain SiO<sub>2</sub>. The SiO<sub>2</sub> was crushed and sieved to 20–60 mesh. The XRD measurement showed that the SiO<sub>2</sub> was amorphous. For the preparation of MgO/SiO<sub>2</sub>-R (201.1 m<sup>2</sup>/g), 8.97 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 10.0 g of SiO<sub>2</sub> (prepared as described) were mixed with 30.0 mL of deionized water. The mixture was kept at room temperature for 12 h, dried at 120 °C for 4 h, and then calcined at 450 °C for 8 h to be converted to a catalyst MgO/SiO<sub>2</sub>. The specific surface area was 201 m<sup>2</sup>/g, and the amount of MgO in the material was 12.4 wt%.

### 2.3. The preparation of MgO/SiO<sub>2</sub>-s for HBr sorption

For the preparation of SiO<sub>2</sub>, 60.0 mL of silicon tetraethoxide was added to 400 mL of oxalic acid solution (0.50 M) and the mixture was stirred at room temperature overnight to afford a gel. The gel was dried at 120 °C for 6 h, and then calcined at 450 °C for 4 h to obtain SiO<sub>2</sub>. The SiO<sub>2</sub> was crushed and sieved to 40–60 mesh. The XRD measurement showed that the SiO<sub>2</sub> was amorphous. The MgO/SiO<sub>2</sub>-s was prepared by mixing 20.0 g of the SiO<sub>2</sub> (765 m<sup>2</sup>/g as prepared), 21.3 g of Mg(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O, and 100 mL of H<sub>2</sub>O. The mixture was dried at 120 °C for 6 h and calcined at 450 °C for 4 h to give

the MgO/SiO<sub>2</sub> sample. The amount of MgO in the material was 16.7%.

#### 2.4. Olefin purification

Since over 90% of the products are olefins, a mixture of HBr and propene was used for simulating product-purification. To saturate propene with HBr, 48 wt% HBr/H<sub>2</sub>O solution (3.0 mL/h) and propene (5.0 mL/min) were introduced into a glass tube (i.d. 1.5 cm, length 35.0 cm) containing quartz sand (20–40 mesh) at 200 °C. For control analysis, the gas effluent was examined by weight analysis (HBr reacted with AgNO<sub>3</sub> (4.0 M, 5.0 mL)), and the HBr concentration in propene was found to be 5.3% (mol). Then, the HBr–propene gas mixture was passed through a HBr-sorption tube (i.d. 1.5 cm, length 35.0 cm) containing 10.0 g of MgO/SiO<sub>2</sub>-s at 200 °C. The effluent from the sorption tube was connected to a bubbler (total volume 20 mL) containing 5.0 mL of 4.0 M AgNO<sub>3</sub> solution for monitoring the presence of HBr. Once AgBr formation was detected (usually it took 10–12.5 h under the adopted experimental settings), the volume of propene was recorded as the maximum amount of propene purified by 10.0 g of MgO/SiO<sub>2</sub>-s. For the regeneration of MgO/SiO<sub>2</sub>-s and recovery of bromine, the sorption tube was purged with N<sub>2</sub> (5.0 mL/min) for 5 min and heated in O<sub>2</sub> (5.0 mL/min) at 450 °C for 6 h to regenerate MgO/SiO<sub>2</sub>-s. Usually, after the fourth cycle of the regeneration, the MgO/SiO<sub>2</sub>-s material reached its maximum sorption capability. In this case, each gram of MgO/SiO<sub>2</sub>-s could purify 0.405 L of propene and remove 0.109 g of HBr. In the fourth and fifth regeneration cycles with a propene flow of 5.0 mL/min (containing 5.3% HBr) over 10.0 g of MgO/SiO<sub>2</sub>-s, it took 12.5 h (with 3.75 L of propene purified) to observe AgBr formation. In this case, the concentration of bromide ions in the AgNO<sub>3</sub> solution unit was found to be about  $1.4 \times 10^{-13}$  M, representing  $7.0 \times 10^{-16}$  mol of Br<sup>-</sup> ions in the AgNO<sub>3</sub> solution (4.0 M, 5.0 mL). This amount of Br<sup>-</sup> ions was brought into the AgNO<sub>3</sub> solution by 3.75 L of propene. Therefore, the average HBr concentration in propene after purification was estimated to be below  $1.87 \times 10^{-16}$  mol/L. In other words, the propene obtained after the purification process is cleared of HBr.

#### 2.5. Recovery of HBr from H<sub>2</sub>O

After the methane oxidation reaction in the first reactor, there was a decrease in HBr concentration due to the consumption of bromine and the newly generated water. In each passing of CH<sub>3</sub>Br, about 25% bromine (mol) was removed from the original 48 wt% HBr/H<sub>2</sub>O solution, and the rate of water generation was about 0.29 mL/h under the adopted reaction conditions (20.0 mL/min of CH<sub>4</sub>, 5.0 mL/min of O<sub>2</sub>, 5.0 mL/min of N<sub>2</sub>, 6.5 mL/h of 48 wt%, calculated according to 30% CH<sub>4</sub> conversion and 100% CH<sub>3</sub>Br selectivity). The HBr/H<sub>2</sub>O solution from the first reactor was used for washing products generated in the second reactor, and ca. 96.2% of HBr was recovered from the hydrocarbon stream. Therefore, it was possible to recover all the bromine from the 0.6 mL/h HBr/H<sub>2</sub>O solution (in each

passing we fed 6.5 mL/min of HBr/H<sub>2</sub>O (48.0 wt%) solution. In order to keep total Br and water constant in circulation, one needed to remove water at a rate of about 0.6 mL/min) and fed the bromine back to the system, and it was possible to maintain the bromine balance in the cycling-system. In the process of recovering bromine, we pumped a HBr/H<sub>2</sub>O solution (48 wt%) at a rate of 0.6 mL/h, and passed N<sub>2</sub> (carrier gas, 5.0 mL/min) into the HBr sorption tube (ID 1.5 cm, length 35.0 cm) containing 10.0 g of MgO/SiO<sub>2</sub>-s at 200 °C. The outlet was connected directly to a bubbler (total volume 20 mL) containing 5.0 mL of 4.0 M AgNO<sub>3</sub> aqueous solution for monitoring the presence of HBr. We found that MgO/SiO<sub>2</sub>-s can remove all the HBr in water (i.e. no sign of AgBr formation in the AgNO<sub>3</sub> unit). The MgO/SiO<sub>2</sub> material was regenerated in oxygen (5.0 mL/min) at 450 °C with the simultaneous recovery of Br, which was fed back to the reactor for the OBM reaction.

#### 2.6. Catalyst evaluation

The OBM reaction was carried out in the first reactor (a quartz-tube reactor, i.d. 1.0 cm, length 60 cm, hot zone 30.0 cm) packed with 5.0 g of Rh/SiO<sub>2</sub> catalyst (40–60 mesh) with both ends filled with quartz sand (20–40 mesh). The blank reaction was carried out in the same reactor tube only filled with quartz sand (20–40 mesh) at 660 °C with reactant flows: 20.0 mL/min of CH<sub>4</sub>, 5.0 mL/min of O<sub>2</sub>, 5.0 mL/min of N<sub>2</sub>, and 6.5 mL/h of HBr/H<sub>2</sub>O (48 wt%). The condensation of CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub> was carried out in the second reactor (i.d. 1.5 cm, length 35.0 cm) containing 8.0 g of MgO/ZSM-5 catalyst with both ends filled with quartz sand (20–40 mesh). Typically, the reactions were carried out with CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub> (internal standard for accurate calculation), and HBr/H<sub>2</sub>O being fed into the first reactor, and then the gas effluent was fed directly into the second reactor. The space velocities of reactants in both reactors (the OBM reaction reactor and the CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub> condensation reactor) will be given in the following corresponding sections. The gas effluent and the liquid products were analyzed on a GC with a thermal conductivity detector (Agilent 6890N) and a GC/MS (6890N/5973N).

#### 2.7. XRD, BET measurement, and FTIR investigation

The XRD examination of samples was performed over a Philips PW3040/60 X-ray diffraction spectrometer with Cu K $\alpha$  irradiation. The BET measurement of the samples was performed on a Beckman Coulter SA 3100 adsorption instrument with N<sub>2</sub> as adsorbent. The samples were out-gassed at 250 °C. The FTIR investigations were performed on a Nexus 670 FT-IR equipment (Thermo Nicolet) with a high vacuum reaction cell (HVC) from Harrick Science. A KBr beamsplitter and two CaF<sub>2</sub> windows were employed. Each spectrum was collected with 32 scans at 4 cm<sup>-1</sup> resolution. A spectrum was recorded as background after the reactor cell was evacuated (at 200 °C) to  $2.5 \times 10^{-4}$  Pa. Then the catalyst was exposed to CH<sub>3</sub>Br (1 atm) at 200 °C for 10 min. After purging the cell with high purity N<sub>2</sub> for 30 min, a spectrum was acquired.

Table 2  
Methane oxidative bromination over Rh/SiO<sub>2</sub> at 660 °C

CH <sub>4</sub> (mL/min)	O <sub>2</sub> (mL/min)	N <sub>2</sub> (mL/min)	HBr/H <sub>2</sub> O (mL/h)	X <sub>1</sub> (%)	Selectivity (%)			
					CH <sub>3</sub> Br	CH <sub>2</sub> Br <sub>2</sub>	CO	CO <sub>2</sub>
15.0	5.0	5.0	6.5	36	79	8	10	3
20.0	5.0	5.0	6.5	30	83	7	7	2

Note: X<sub>1</sub> denotes methane conversion.

### 2.8. Corrosion testing of metals and alloy

In the corrosion testing, a metal piece of Ni, Zr, Ti, or the alloy FeCrAl was placed in the center of the catalyst bed (5.0 g of Rh/SiO<sub>2</sub>) in a quartz-tube reactor (i.d. 1.0 cm, length 60 cm, hot zone 30.0 cm). The corrosion testing was carried out in the process of catalytic reaction at 660 °C in an atmosphere composed of methane (20.0 mL/min), oxygen (5.0 mL/min), and HBr (48 wt%) in water (6.5 mL/h). After 54 h of in situ reaction, the metal piece was analyzed by EDS (X-ray energy-dispersive spectrometer, INCA-300 by Oxford Instrument) and microscopy.

## 3. Results and discussion

### 3.1. Catalytic performance

We discovered an active catalyst Rh/SiO<sub>2</sub>, which is more active than Ru/SiO<sub>2</sub> that we discovered before [24]. When feeding 15.0 mL/min of CH<sub>4</sub>, 5.0 mL/min of O<sub>2</sub>, 5.0 mL/min of N<sub>2</sub> (internal standard), and 6.5 mL/h of 48 wt% HBr/H<sub>2</sub>O (48 wt% HBr/H<sub>2</sub>O was used instead of HBr to avoid explosions and hot spots) into the catalyst bed (5.0 g catalyst, 6.2 mL, gas hourly space velocity 1459 h<sup>-1</sup>) at 660 °C, a methane single-pass conversion of 36% and an overall selectivity for methyl bromide and methylene dibromide of 87% was obtained (Table 2). The products formed in the reaction include methyl bromide, methylene dibromide, CO, CO<sub>2</sub>, H<sub>2</sub> (trace), and a small amount of C<sub>2</sub>–C<sub>5</sub> hydrocarbons (selectivity <0.03%). If the feed was changed to 20.0 mL/min of CH<sub>4</sub>, 5.0 mL/min of O<sub>2</sub>, 5.0 mL/min of N<sub>2</sub>, and 6.5 mL/h of HBr/H<sub>2</sub>O (48 wt%) (5.0 g catalyst, 6.2 mL, gas hourly space velocity 1508 h<sup>-1</sup>), a methane single-pass conversion of 30% and a total selectivity for bromomethanes of 90% were obtained. In the blank reaction, a methane single-pass conversion of 10.1% with 99.9% bromomethanes (97.2% of CH<sub>3</sub>Br and 2.7% of CH<sub>2</sub>Br<sub>2</sub>) selectivity was obtained. The catalyst was found stable in online reaction of 2 weeks. We found no changes in methane conversion and bromomethanes selectivity. The XRD measurement showed that there was no change in catalyst structure after reaction (only poorly crystallized cristobalite phase observed, Fig. 1).

In reaction (2), we found that MgO/ZSM-5 is an excellent catalyst: all of the CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub> from the first-stage reactor (at CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, and 48 wt% HBr/H<sub>2</sub>O feedings of 15.0, 5.0, 5.0, and 6.5 mL/h, respectively, at 660 °C) was converted to higher hydrocarbons at 240–260 °C (Table 3). The major products were C<sub>3</sub>–C<sub>13</sub> hydrocarbons (more than 90% were olefins).

The catalyst MgO/ZSM-5 was found stable within a period of 2 weeks.

### 3.2. Bromine removal and recovery

The obtained hydrocarbons were washed thoroughly with a solution of 40 wt% HBr/H<sub>2</sub>O (the diluted HBr/H<sub>2</sub>O obtained after the OBM reaction can be utilized here) and treated for HBr-sorption over MgO/SiO<sub>2</sub>-s at 200 °C as described in the

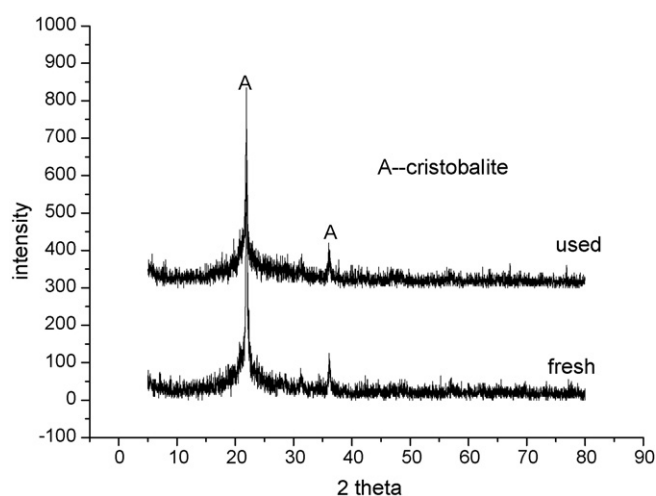


Fig. 1. XRD of fresh and used Rh/SiO<sub>2</sub>.

Table 3  
Product selectivity (%) over MgO/HZSM-5 at 240 °C

Alkenes and alkanes	S <sub>1</sub> (%)
C <sub>2</sub>	3.3
C <sub>3</sub>	5.7
C <sub>4</sub>	49.1
C <sub>5</sub>	26.7
C <sub>6</sub>	4.1
C <sub>7</sub>	6.3
C <sub>8</sub>	0.9
C <sub>9</sub>	0.5
Aromatics	S <sub>2</sub> (%)
C <sub>8</sub>	0.9
C <sub>9</sub>	0.4
C <sub>10</sub>	0.7
C <sub>11</sub>	0.7
C <sub>12</sub>	0.2
C <sub>13</sub>	0.5

Note: S<sub>1</sub> denotes selectivities of alkenes and alkanes; S<sub>2</sub> denotes selectivities of aromatics.

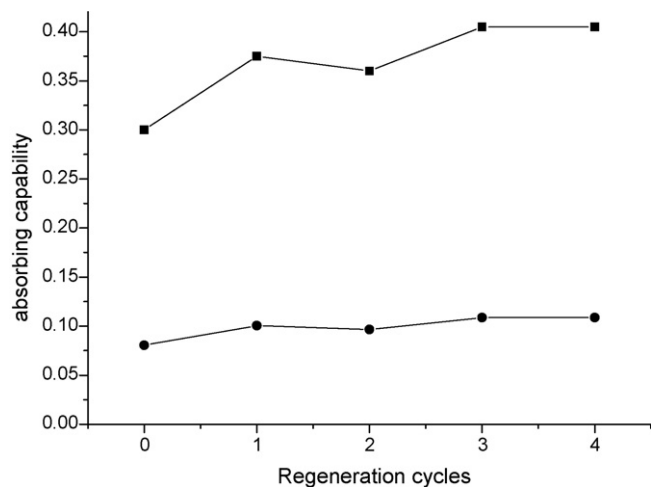


Fig. 2. Propene purification from HBr-propene mixture (containing 5.3% HBr, propene flow 5.0 mL/min). The “zero” on the X-axis refers to a fresh material. (■) L (cleaned C<sub>3</sub>H<sub>6</sub>)/g (MgO/SiO<sub>2</sub>), (●) g (HBr absorbed)/g (MgO/SiO<sub>2</sub>).

experimental section. In this work, we used a HBr-propene mixture to simulate our product stream since that it is easier to perform the analysis in that way in comparison to the case of using a product stream. The sorption material MgO/SiO<sub>2</sub>-s ended up as MgBr<sub>2</sub>/SiO<sub>2</sub> and could be regenerated by means of oxidation in oxygen at 450 °C. In the oxidation of MgBr<sub>2</sub>/SiO<sub>2</sub>, bromine could be recovered and sent back to the bromination reactor. After the HBr-sorption process, the amount of HBr in the hydrocarbon products was reduced to below  $1.87 \times 10^{-16}$  mol/L. The waste solution of HBr/H<sub>2</sub>O after the OBM reaction could be treated in a similar manner for bromine recovery and water purification (see Section 2). Fig. 2 shows that the MgO/SiO<sub>2</sub>-s material stabilized after the third run.

Clearly, the Br-involved process has advantages over the oxychlorination process in CH<sub>4</sub> condensation. First of all, relatively speaking, due to the sizes (covalent radius of Br and Cl: 1.14 and 0.99 Å, respectively) and electron affinities of Br and Cl, it is easier to have a bromine atom eliminated from CH<sub>2</sub>Br<sub>2</sub> than to have a chlorine atom eliminated from CH<sub>2</sub>Cl<sub>2</sub>. In other words, CH<sub>3</sub>Br selectivity (i.e. lower CH<sub>2</sub>Br<sub>2</sub> selectivity) is higher than CH<sub>3</sub>Cl selectivity (i.e. higher CH<sub>2</sub>Cl<sub>2</sub> selectivity), and this is advantageous for the OBM reaction to form more CH<sub>3</sub>Br, (which keeps more hydrogen in products compared to the case of forming more CH<sub>2</sub>Br<sub>2</sub>). Secondly, since the C–Br bond is weaker than the C–Cl bond, CH<sub>3</sub>Br is better than CH<sub>3</sub>Cl in the generation of higher hydrocarbons. The third advantage is that the products (mostly olefins) can be purified and Br recovered readily via the MgO/SiO<sub>2</sub>-s sorption and oxidation processes. In the case of oxychlorination, it is impossible to regenerate MgO/SiO<sub>2</sub>-s from MgCl<sub>2</sub>/SiO<sub>2</sub>-s under similar conditions.

### 3.3. Material for system construction

In this kind of reaction, corrosion could be problematic. A durable material that is resistant to corrosion in our specific reaction conditions must be found for construction of the system. We tested Ni, Zr, Ti, and FeCrAl at conditions described in Section

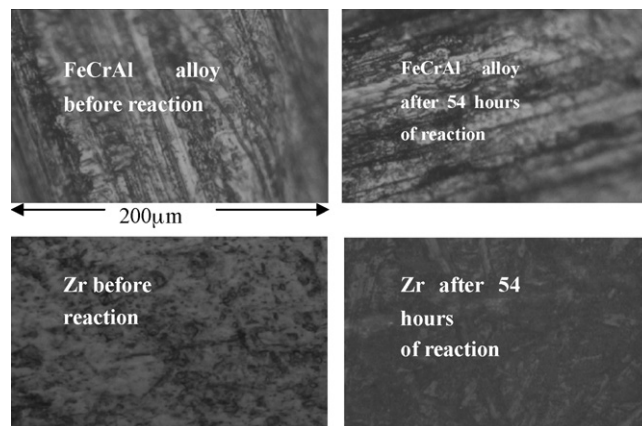


Fig. 3. Picture of FeCrAl alloy and Zr metal before and after testing in reaction stream of 20.0 mL/min of methane, 5.0 mL/min of oxygen, and 6.5 mL/h of HBr (48 wt%) in water at 660 °C (Magnification = 400×).

2.8. After 54 h of in situ testing, we found that Ti and Ni became embrittled, whereas Zr and FeCrAl were durable. The FeCrAl alloy is still lustrous after testing (see the picture in Fig. 3), while the Zr sample was somewhat darkened. In X-ray energy-dispersive analysis, the tested Zr and FeCrAl samples showed no signal of bromine but enhanced presence of oxygen and carbon. The surface compositions of FeCrAl alloy before and after reaction are listed in Table 4. Since Zr is more expensive than FeCrAl, we consider that the latter is a more suitable material for the construction of the OBM reactor.

### 3.4. Reaction mechanism

#### 3.4.1. Deduction based on reactivity

We explored the pathways for the formation of bromomethanes. When CH<sub>4</sub> (15.0 mL/min), O<sub>2</sub> (5.0 mL/min), N<sub>2</sub> (5.0 mL/min), and H<sub>2</sub>O (6.5 mL/h) were fed over the Rh/SiO<sub>2</sub> catalyst at 660 °C, oxygen consumption was 100%, methane conversion was 75%, and H<sub>2</sub>, CO, and CO<sub>2</sub> were the major products (methane partial oxidation). The selectivities (only carbon containing compounds were counted) of CO and CO<sub>2</sub> were 44% and 56%, respectively. When H<sub>2</sub>O (6.5 mL/h) and CH<sub>4</sub> (15.0 mL/min) were fed into the catalyst bed at 660 °C, methane was reformed to H<sub>2</sub>, CO, and CO<sub>2</sub> at a methane conversion of 25% (methane steam reformation). The CO and CO<sub>2</sub> selectivity were 85% and 14%, respectively. We observed that in the absence of methane, HBr/H<sub>2</sub>O (6.5 mL/h, 48 wt%) reacted with O<sub>2</sub> to form Br<sub>2</sub>, and Br<sub>2</sub> reacted with CH<sub>4</sub> to form CH<sub>3</sub>Br over the Rh/SiO<sub>2</sub> catalyst above 200 °C. Since H<sub>2</sub> was detected only in trace amount in the OBM reaction, the methane partial oxidation and methane steam reformation should not be the major routes for CO and CO<sub>2</sub> formation. CO and CO<sub>2</sub> might be formed

Table 4  
The surface atomic mol compositions before and after reaction

	Fe	Cr	Al	O	C
Before reaction (mol%)	49	14	4	9	25
After reaction (mol%)	34	12	6	17	31



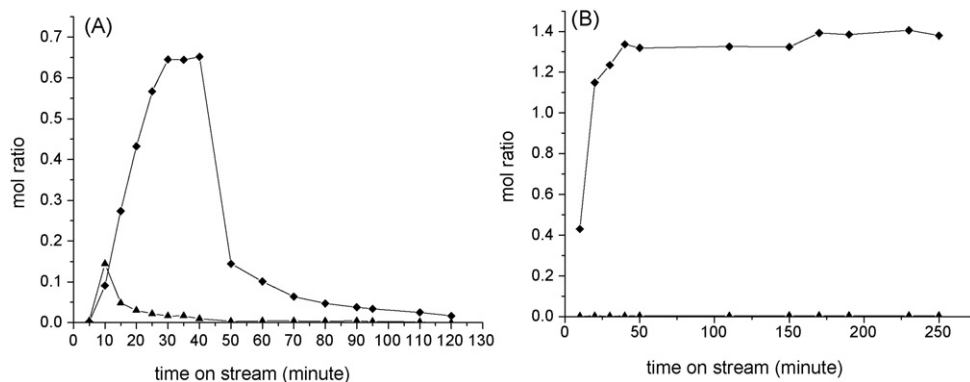
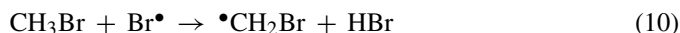


Fig. 4.  $\text{CH}_3\text{Br}$  conversion ( $\text{CH}_3\text{Br}$  7.0 mL/min and  $\text{N}_2$  5.0 mL/min) over 8.0 g fresh catalyst at 240 °C, (A) over MgO/HZSM-5 and (B) over MgO-HZSM-5 mechanically mixed from MgO and HZSM-5; (◆)  $\text{CH}_3\text{Br}/\text{N}_2$ , (▲)  $\text{CH}_3\text{OCH}_3/\text{N}_2$  mol ratio in the effluent.

from the deep oxidation of bromomethanes. The results indicate that reactions (3)–(11) should be the major routes for  $\text{CH}_3\text{Br}$  and  $\text{CH}_2\text{Br}_2$  formation over the Rh/SiO<sub>2</sub> catalyst. We deduce that the presence of HBr inhibits the steam reforming and deep oxidation of methane:



When  $\text{CH}_3\text{Br}$  (7.0 mL/min), 48.0 wt% HBr/H<sub>2</sub>O (6.5 mL/h), and  $\text{N}_2$  (5.0 mL/min, as reference gas) were passed over Rh/SiO<sub>2</sub>, the conversion of methyl bromide was 52%. The composition of effluent was 30% of  $\text{CH}_3\text{Br}$ , 2% of  $\text{CO}_2$ , 0.2% of  $\text{CH}_2\text{Br}_2$ , 14% of  $\text{CH}_4$ , 0.1% of  $\text{CO}$ , 46% of  $\text{N}_2$ , and 7% of  $\text{H}_2$ . Carbon was also a major product. Therefore, the dominating reactions should be  $\text{CH}_3\text{Br}$  reformation (reaction (12)) and  $\text{CH}_3\text{Br}$  decomposition (reaction (13)). What is worth noting is that there is only a negligible amount of  $\text{CO}$  and  $\text{CO}_2$  formed in these reactions. Therefore, the major reactions could be reactions (12) and (13):



When  $\text{CH}_3\text{Br}$  (7.0 mL/min),  $\text{O}_2$  (5.0 mL/min),  $\text{N}_2$  (5.0 mL/min), and 48.0 wt% HBr/H<sub>2</sub>O (6.5 mL/h) were fed into the Rh/SiO<sub>2</sub> catalyst bed,  $\text{CH}_3\text{Br}$  conversion was 76%. The products were  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_2\text{Br}_2$  with selectivity of 26%, 56%, 13%, and 5%, respectively. There was no formation of hydrogen and carbon. It can be deduced that  $\text{CO}$  and  $\text{CO}_2$  were formed from the oxidation of  $\text{CH}_3\text{Br}$ .

In the investigation of  $\text{CH}_3\text{Br}$  condensation to higher hydrocarbons in a reactant atmosphere of  $\text{CH}_3\text{Br}$  (7.0 mL/min) and  $\text{N}_2$  (internal standard, 5.0 mL/min) below 260 °C, MgO (109.5 m<sup>2</sup>/g, as purchased), MgO/SiO<sub>2</sub>-R, SiO<sub>2</sub> (prepared as in MgO/SiO<sub>2</sub>-R preparation), and HZSM-5 (Si/Al = 360, as purchased) were found to be catalytically inactive. As for a freshly prepared MgO/ZSM-5 catalyst, despite not being significantly active in the beginning, a  $\text{CH}_3\text{Br}$  conversion higher than 76% was obtained after 50 min of on-line reaction (Fig. 4A) and dimethyl ether was the major product in the first 50 min. After bromination of the fresh catalyst in HBr/H<sub>2</sub>O vapour (6.0 mL/min of 40 wt% HBr/H<sub>2</sub>O, 240 °C, 2 h), MgO/ZSM-5 became active and more than 90% of  $\text{CH}_3\text{Br}$  was converted to higher hydrocarbons even in the primary 30 min. The MgO-ZSM-5 (MgO loading 12.4 wt%) sample prepared by mechanically mixing powders of MgO (109.5 m<sup>2</sup>/g) and HZSM-5 was found inactive (Fig. 4B).

### 3.4.2. Deduction based on FTIR investigation

Fig. 5 shows that after  $\text{CH}_3\text{Br}$  adsorption over pre-brominated MgO/ZSM-5 and fresh MgO/ZSM-5, bands at 1193, 1267, 1275, 1284, 1405, 1468, 1620, 1611, and 1602 cm<sup>-1</sup> were observed. The bands at 1620, 1611, and 1602 cm<sup>-1</sup> are assigned to C=C stretching vibrations of olefins. The band at 1405 cm<sup>-1</sup> is

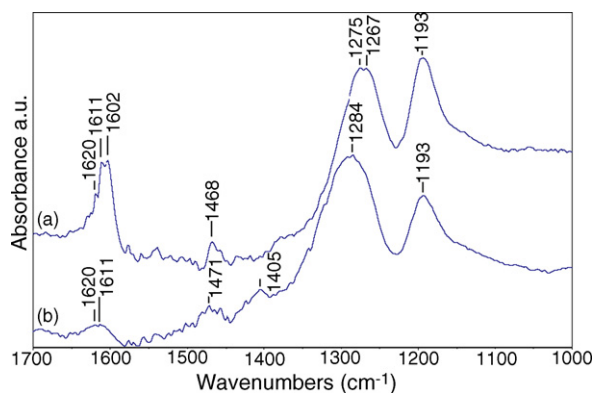


Fig. 5. FTIR spectra collected after the reactor was evacuated at 200 °C to  $2.5 \times 10^{-4}$  Pa and (a) a brominated (6.0 mL/min of 40 wt% HBr/H<sub>2</sub>O solution at 240 °C, 2 h) MgO/HZSM-5 and (b) a fresh MgO/HZSM-5 catalyst exposed to  $\text{CH}_3\text{Br}$  (1 atm) at 200 °C for 10 min, and then purged with  $\text{N}_2$  for 30 min.

assigned to the *cis* CH asymmetric rocking vibration, the bands at 1275 and 1284  $\text{cm}^{-1}$  to the *trans* CH asymmetric rocking vibration, the band at 1267  $\text{cm}^{-1}$  to the *cis* CH symmetric rocking vibration, and the band at 1193  $\text{cm}^{-1}$  to the O–CH<sub>3</sub> rocking vibration [27]. The band at 1468  $\text{cm}^{-1}$  is attributed to asymmetric C–O bond stretching vibration of the carbonate ion  $\text{CO}_3^{2-}$  [28]. These results indicate that the olefin formation rate over pre-brominated MgO/ZSM-5 is higher than that over the fresh MgO/ZSM-5.

All of the above results suggest that the catalyst functions in the form of MgBr<sub>2</sub>/ZSM-5. There must be a certain kind of synergism between HZSM-5 and MgBr<sub>2</sub> to make MgBr<sub>2</sub>/ZSM-5 active for the CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub> condensation. We believe that the reaction mechanism is similar to the “carbon pool” mechanism for methanol condensation to higher olefins suggested by Dahl and Kolboe [29] and proven later by Song et al. [30]. In the OBM reaction, one always detects about 0.03% (molar) of C<sub>2</sub>–C<sub>5</sub> hydrocarbons in the effluent. These hydrocarbons could be converted to aromatic compounds in the pores of HZSM-5 through hydrogen transfer steps and the aromatic compounds could then act as “carbon pool”. It is known that MgBr<sub>2</sub> is a typical Lewis acid that can catalyze the alkylation of aromatics in the presence of CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub>. With the side-chains of aromatics being eliminated on the acid sites in the pores of HZSM-5 [29,30], the generation of olefins is an expected outcome. The olefins undergo further reactions such as polymerization (catalyzed by HZSM-5), hydrogen exchange, cyclization, and isomerization through carbon cations to form a whole series of hydrocarbons [31]. The “carbon pool” mechanism also explains why MgO, MgO/SiO<sub>2</sub>, SiO<sub>2</sub>, MgO-ZSM-5 (mechanically mixed MgO and HZSM-5), and HZSM-5 are not active. The reason is that none of these catalysts can facilitate all the three reactions that occur over MgBr<sub>2</sub>/ZSM-5, viz. (i) aromatization of C<sub>2</sub>–C<sub>5</sub> hydrocarbons, (ii) alkylation of aromatic compounds, and (iii) elimination of side-chains of aromatics.

#### 4. Conclusions

In the process described in this article, reactions are run at atmospheric pressure and the reactions in the two reactors are exothermic. Compared to the Fischer–Tropsch (F–T) syngas process for the production of higher hydrocarbons and the Mobil syngas-methanol process for the production of olefins and aromatics [32–34], the described methane condensation process for higher hydrocarbons is energy-saving and releases less amount of CO<sub>2</sub>. By adopting technologies from petroleum industries, the hydrocarbons can be easily converted to other important synthesis intermediates. Since the durable material such as FeCrAl alloy is available, the process is a potential alternative way for methane conversion to higher hydrocarbons, especially olefins.

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#### References

- [1] F. Fischer, H. Tropsch, *Brennst. Chem.* 4 (1923) 276.
- [2] G.E. Keller, M.M. Bhasin, *J. Catal.* 73 (1982) 9.
- [3] R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* 280 (1998) 560.
- [4] R.A. Periana, O. Mironov, D. Taube, G. Bhalla, C.J. Jones, *Science* 301 (2003) 814.
- [5] R.P. Noceti, C.E. Taylor, US Patent 4769504, (1988). The United States of America as represented by the United States.
- [6] G.A. Olah, H. Doggweiler, J.D. Felberg, S. Frohlich, M.J. Grdina, R. Karpeles, T. Keumi, S. Inaba, W.M. Ip, K. Lammertsma, G. Salem, D.C. Tabor, *J. Am. Chem. Soc.* 106 (1984) 2143.
- [7] C.M. White, L.J. Douglas, J.P. Hackett, R.R. Anderson, *Energy Fuels* 6 (1992) 76.
- [8] Y. Sun, S.M. Campbell, J.H. Lunsford, G.E. Lewis, D. Palke, L.M. Tau, *J. Catal.* 143 (1993) 32.
- [9] D.K. Murray, T. Howard, P.W. Goguen, T.R. Krawietz, J.F. Haw, *J. Am. Chem. Soc.* 116 (1994) 6354.
- [10] J.R. Anderson, *Appl. Catal.* 47 (1989) 177.
- [11] A.E. Schweizer, M.E. Jones, D.A. Hickman, US Patent 6452058, (2002). Dow Global Technologies Inc.
- [12] P. Lersch, F. Bandermann, *Appl. Catal.* 75 (1991) 133.
- [13] W.C. Conner Jr., W.J.M. Pieters, A.J. Signorelli, *Appl. Catal.* 11 (1984) 59.
- [14] E.M. Fortini, C.L. Garcia, D.E. Resasco, *J. Catal.* 99 (1986) 12.
- [15] W.J.M. Pieters, W.C. Conner Jr., E.J. Carlson, *Appl. Catal.* 11 (1984) 35.
- [16] W.C. Conner Jr., W.J.M. Pieters, A.J. Signorelli, *Appl. Catal.* 11 (1984) 49.
- [17] M.A. McDonald, M.F. Zaroachak, W.J. Graham, *Chem. Eng. Sci.* 49 (1994) 4627.
- [18] X.P. Zhou, A. Yilmaz, G.A. Yilmaz, I.M. Lorkovic, L.E. Laverman, M.J. Weiss, J.H. Sherman, E.W. McFarland, G.D. Stucky, P.C. Ford, *Chem. Commun.* (2003) 2294.
- [19] X.P. Zhou, I.M. Lorkovic, G.D. Stucky, P.C. Ford, J.H. Sherman, P. Grosso, US Patent 6,462,243, (2002). GRT, Inc.
- [20] X.P. Zhou, I.M. Lorkovic, G.D. Stucky, P.C. Ford, J.H. Sherman, P. Grosso, US Patent 6,472,572, (2002). GRT, Inc.
- [21] X.P. Zhou, I.M. Lorkovic, J.H. Sherman, US Patent 6,486,368, (2002). GRT, Inc.
- [22] I.M. Lorkovic, M. Noy, M. Weiss, J. Sherman, E. McFarland, G.D. Stucky, P.C. Ford, *Chem. Commun.* (2004) 566.
- [23] A. Yilmaz, X.P. Zhou, I.M. Lorkovic, G.A. Yilmaz, L. Laverman, M. Weiss, S. Sun, D. Schaefer, J.H. Sherman, E.W. McFarland, P.C. Ford, G.D. Stucky, *Microporous Mesoporous Mat.* 79 (2005) 205.
- [24] H.F. Xu, K.X. Wang, W.S. Li, X.P. Zhou, *Catal. Lett.* 100 (2005) 53.
- [25] K.X. Wang, H.F. Xu, W.S. Li, X.P. Zhou, *J. Mol. Catal. A: Chem.* 225 (2005) 65.
- [26] K.X. Wang, H.F. Xu, W.S. Li, C.T. Au, X.P. Zhou, *Appl. Catal. A: Gen.* 304 (2006) 168.
- [27] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, 1991, pp. 70–73.
- [28] V.Y. Borokov, *J. Phys. Chem. B* 108 (2004) 4811.
- [29] I.M. Dahl, S. Kolboe, *J. Catal.* 149 (1994) 458.
- [30] W. Song, D.M. Marcus, H. Fu, J.O. Ehresmann, J.F. Haw, *J. Am. Chem. Soc.* 124 (2002) 3844.
- [31] B.C. Gates, *Catalytic Chemistry*, Wiley, 1992, pp. 254.
- [32] C.D. Chang, A.J. Silvestri, *J. Catal.* 47 (1977) 249.
- [33] C.D. Chang, W.H. Lang, A.J. Silvestri, US Patent 3,998,898, (1976). Mobil Oil Corp.
- [34] S.A. Butter, A.T. Jurewicz, W.W. Kaeding, US Patent 3,894,107, (1975). Mobil Oil Corp.