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Selective methane bromination over sulfated zirconia in SBA-15 catalysts

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ABSTRACT

Methane activation via bromination can be a feasible route with selective synthesis of mono-bromomethane. It is known that the condensation of brominated products into higher hydrocarbons can result in coking and deactivation in the presence of di-bromomethane. In this study, selective production of methyl bromide was investigated over sulfated ZrO_2 included SBA-15 structures. It was observed that the higher the ZrO_2 amounts the higher the conversion, while the catalyst remained >99% selective for the monobrominated methane. Over 25 mol.% ZrO_2 included SBA-15 catalyst with a BET surface area of 246 m^2/g, methane was brominated with 69% conversion at 340 °C and only CH_3Br was selectively produced.

1. Introduction

Natural gas conversion by halogenation was proposed in 1980s by Olah [1–3] and Benson [4,5]. This method involves extracting hydrogen from methane and producing methyl halide (a methanol like molecule) under relatively mild conditions, then the condensation of methyl halide to achieve the production of higher hydrocarbons or oxygenates is an alternative route for commercial methane conversion into hydrocarbons through syn-gas route (Fig. 1).

After the formation of methyl halide, methyl chloride or bromide can be condensed onto hydrocarbons over acidic catalysts. The hydrolysis of methyl halides to oxygenates (dimethylether and methanol) were reported over γ-alumina and γ-alumina-supported metal oxide/hydroxide catalysts such as V_2O_5, MnO_2, Cr_2O_3, MgO, ZrO_2, BaO, TiO_2, ZnO, and Fe_2O_3. Conversions around 25% were reported over $ZnO/Al(OH_3)/\gamma\text{-}Al_20_3$ catalysts indicating a promising route to produce methyl alcohol and dimethyl ether [1,2]. Furthermore, hydrocarbon formation from methyl chloride on ZSM-5 gives a product distribution of 43.1% aliphatics and 57.1% aromatics at 369 °C, which is similar to the product distribution if methanol was used as a raw material [6]. Methyl chloride and methyl bromide conversion into higher hydrocarbons over H-SAPO-34 catalysts also resulted in similar product distributions to a methanol feed [7]. WO_3/Al_2O_3 catalysts give rise to 42.8% selectivity for C_2–C_5 hydrocarbons at 327 °C with a methyl chloride conversion of 36% [8,9]. $AlBr_3$ is another catalyst studied for the condensation of CH_3Br. The product distribution was predominantly saturated C_1–C_3 hydrocarbons, not too attractive for the petrochemical industry [10]. However, monochlorination or monobromination of methane is the necessary condition for the application of the halogenation route to synthesize hydrocarbons from methane [11]. Cross-coupling between CH_2Br_2 and CH_3Br was seen in the higher output of aromatics and subsequent coke formation when both species are present in the reaction medium for hydrocarbon synthesis [12–16]. It was concluded that CH_2Br_2 condenses predominantly to absorbed carbon in the absence of CH_3Br [15]. Therefore, it is important to obtain high selectivity for CH_3Br in the methane bromination reaction.

Gas phase bromination of methane is not selective towards CH_3Br at high methane conversions [17]. Contrary to the gas phase halogenation of methane, catalytic methane halogenation was reported to show high selectivity [1]. Olah proposed the catalytic dehydrohalogenation of methane by extracting hydrogen from methane molecule and producing methyl halides under relatively mild conditions [3]. He studied a set of superacids catalysts, such as supported Lewis acid oxyhalide (or halide) catalysts, $FeOCl/Al_2O_3$, $TaOF_3/Al_2O_3$, $NbOF_3/Al_2O_3$, $ZrOF_2/Al_2O_3$, SbF_5–graphite, and TaF_5–Nafion-H and Nafion-H for mono chlorination and $SbOF_3/Al_2O_3$ and $TaOF_3/Al_2O_3$ for mono bromination of methane. In addition to these, $Pd/BaSO_4$ and Pt/Al_2O_3 catalyzed chlorination reactions were also studied. Their results showed that $ZrOF_2$–Al_2O_3 was the best catalyst which gives 96% selectivity for monochloromethane at 34% methane conversion. On the other hand, in bromination $SbOF_3$–Al_2O_3 was the best with 99% selectivity for mono-bromomethane at 20% methane conversion. $Pd/BaSO_4$ and Pt/Al_2O_3 catalysts were also reported to be very effective with selectivities also exceeding 90% but not reproduced elsewhere yet.

In the activation of methane with a halogen atom, other than the gas phase reactions, heterogeneous systems require acid

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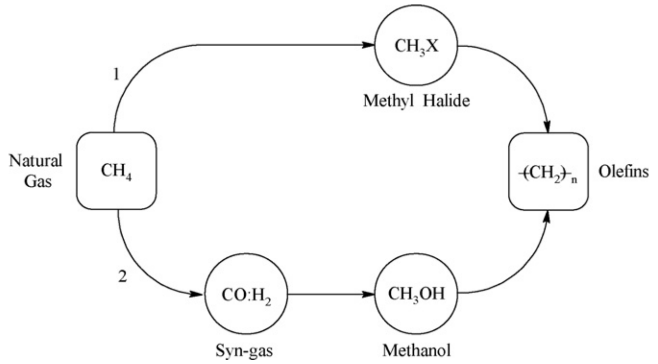

Fig. 1. Alternative methane conversion into higher hydrocarbons through halogenation: 1. Halogenation route, 2. Commercial methanol to olefins (MTO) route.

centers to polarize the halogen molecule in order to scissor the carbon hydrogen bond by electrophilic insertion reaction (Eq. (1)) [2].

$$CH_4 \xrightarrow{Br^+} \left[H_3C \begin{matrix} H \\ \\ Br \end{matrix} \right]^+ \xrightarrow{Catalyst-Br^-} CH_3Br + HBr \qquad (1)$$

Sulfated zirconia (SZ) is a good candidate for bromination of methane, because it shows high catalytic activity in the isomerization of small hydrocarbon molecules at low temperatures, which requires strong acid sites. On the other hand, the relatively small surface area and the low pore volume of the SZ limit its applications. Therefore, the combination of the advantages of a mesoporous molecular sieve and sulfated zirconia should greatly expand the catalytic activity. Such a material will have the advantages of high acidity, high surface area, uniform pores with adjustable pore diameters. A good distribution of active centers in the mesoporous structure can separate the adsorbed reactants from each other on the catalyst surface. This can inhibit further contact of the adsorbed species, which eventually results in the inhibition of further halogenation. In other words, by the separation of active centers it can be possible to obtain high selectivity towards mono brominated methane molecule.

In this study, it was demonstrated that sulfated zirconia included SBA-15 catalyst possessing high amount of Brønsted acid centers [18] converts methane to CH_3Br with very high selectivities (99%) at 340 °C with 69% methane conversion. With this catalyst, the bromination temperatures were reduced from 500 °C in gas phase to 340 °C in heterogeneous phase for similar conversions.

2. Experimental

2.1. Catalyst preparation

Pure, ZrO_2 included, and $SO_4{}^{2-}/ZrO_2$ modified SBA-15 type catalysts were prepared according to literatures [19,20] and the details were reported elsewhere [18]. In order to prepare pure SBA-15 molecular sieve, 9 ml of tetraethyl orthosilicate (TEOS) was added to 150 ml of 1.5 M HCl solution containing 4 g of triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO_{20}-$PO_{70}EO_{20}$, Aldrich). The mixture was stirred for 24 h at 313 K and was allowed to react at 373 K overnight in Teflon bottles. The solid material obtained after filtering was finally calcined in airflow at 773 K for 5 h. In the preparation of the ZrO_2 included SBA-15, zirconia was introduced in solution simultaneously with TEOS in the form of $ZrOCl_2 \cdot 8H_2O$ at four different loadings: 5, 15, 25, and 30 mol.% ZrO_2 with respect to the content of SiO_2. Finally, the sulfated catalysts were prepared by sulfating in a 0.25 M H_2SO_4 solution.

2.2. Reaction tests

The schematic representation of the reaction setup is given in Fig. 2. Methane (CH_4, 99.98% pure) was fed to the reactor at the desired amounts by use of a mass flow controller (MKS Instruments).

A modified Stefan tube was used to deliver bromine to the reactor. Liquid bromine was stored in a quartz container, with a narrow neck (1 mm ID). The tip of the bottle was bent 90° and mounted concentrically to a quartz tube. The tip was oriented counter currently to ensure good blending and relatively lower Br_2 concentrations. Nitrogen was used as the carrier gas, and its flow was controlled by a mass flow controller. The flow of the carrier gas (N_2) through the quartz tube allowed the carrier to drag the bromine vapor coming out of the bottle through the neck. Later they are mixed with methane, and are fed to the reactor with a rough estimate of the ratio of Br_2:CH_4 = 10:1. Typically 0.6–0.9 ml of liquid Br_2 (liquid) was placed in the container, which lasted 5 h, giving rise to an average $F_{Br_2} = 7.76 \times 10^{-3}$ mol/h.

During the runs, 0.2 g of catalyst was placed in a quartz reactor, 0.4 cm ID, supported by quartz wool at both ends. The reactor was placed in a home made tubular furnace. The system was run for 3 h to achieve steady state which was continuously monitored by the gas chromatograph in terms of gas composition.

Homogeneous gas phase kinetics were monitored at two different space times using two reactors with ID = 0.1 and 1.0 cm. The reactor with 1.0 cm ID was filled with glass beads OD = 0.3 cm to provide good mixing.

A condenser operating at the freezing point of water (~0 °C) was mounted at the exit of the reactor to collect the unconverted bromine vapor. The liquid products, i.e. CH_3Br, was collected in the second condenser operated at −78 °C achieved by acetone dry ice mixture. The analysis of the exit gases were performed by a GC (Varian 3900) equipped with a flame ionization detector (FID) and a capillary column (Varian FactorFour^{TM}, 15 m × 0.25 mm ID, d.f. = 0.25 μm) and the methane conversion was calculated from the difference between the reactor inlet and outlet methane concentrations.

The product selectivity was determined by the analysis of the brominated product by liquid ^{1}H NMR measurements. After all runs the liquid was analyzed by the liquid ^{1}H NMR. About 1 ml of

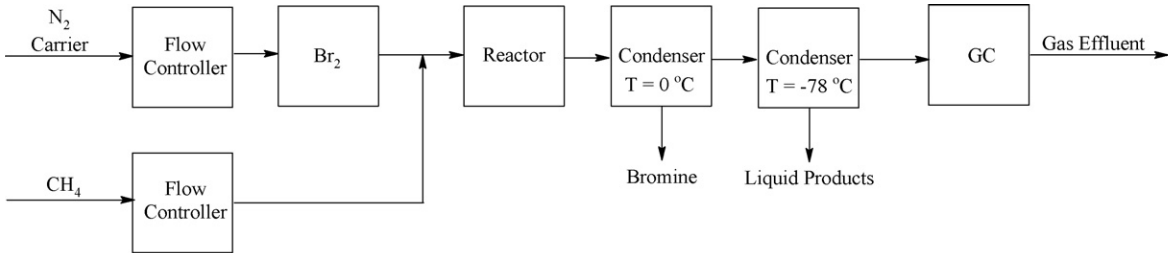

Fig. 2. Schematic representation of the reaction setup.

the product was dissolved in ca. 5 ml of $CDCl_3$ and the liquid ^1H NMR experiments were performed in a 400 MHz Bruker AVANCE spectrometer. The ppm scale was with respect to liquid TMS.

3. Results and discussion

The experiments of the reaction of CH_4 and Br_2 were performed within the temperature interval of 300–400 °C. The results of the homogeneous gas phase bromination with the quartz reactor (ID = 0.1 cm) revealed that detectable amounts of product were only formed at temperatures as high as 380 °C. The reactions were performed at CH_4 and N_2 flow rates of 0.0034 and 0.16 ml/s, respectively, which corresponds to a residence time of 0.86 s. The methane conversion is within the limits of the fluctuations of the observable methane amounts by GC. Therefore for these experimental conditions, conversion could not be calculated since methane conversion is as low as the detection limits.

The experiments on the quartz reactor (ID = 1.0 cm) filled with glass beads (ID = 0.3 cm), were conducted at CH_4 and N_2 flow rates of 0.0034 and 0.16 ml/s, respectively, which corresponds to a residence time of 60.6 s, almost 70 times greater than the first case. The maximum methane conversion calculated under these conditions was 8.3% (Fig. 3).

Finally, the reactor (0.4 cm ID) was filled with 0.0801 g of SBA-15 with a pore volume of 1.198 cm^3/g and ~0.2 g of Zr-SBA-15 and SZr-SBA-15 catalysts. The corresponding residence time is at ca. 0.6 s. The CH_4 and N_2 flow rates were kept at similar levels with the reactions run without any catalysts, 0.0036 and 0.16 ml/s. The increase in the reaction temperature resulted in an increase in the conversion of methane; however it was as low as 4% for the reactor with pure SBA-15 at 380 °C. Over the zirconia included catalysts the conversions were similar with SBA-15 (2.8%, over Zr(15)SBA-15 at 380 °C).

For the reaction over the sulfated catalyst—SZr(15)SBA-15, methane conversions were quite high as compared to homogeneous or SBA-15 reactions at 340 °C. The highest conversion observed was as high as 29% at 380 °C. The highest activity (69% at 340 °C) were observed over SZr(25)SBA-15.

Methane bromination reaction may yield brominated products, such as, CH_3Br, and CH_2Br_2. The brominated products were analyzed by liquid NMR and only CH_3Br formation was observed. The ^1H NMR spectra of the products were given in Fig. 4. There was only a single intense line observed at 2.45 ppm. According to literature [21] CH_3Br and CH_2Br_2 can be distinguished by the lines at 2.68 and 4.95 ppm w.r.t. TMS, respectively. Thus, the single line observed at 2.45 ppm was attributed to CH_3Br.

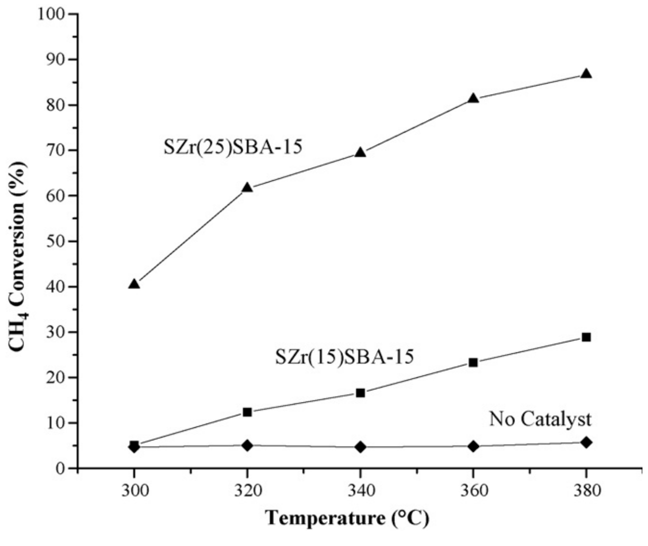

Fig. 3. Methane conversions as a function of temperature over different catalysts and homogeneous reaction results.

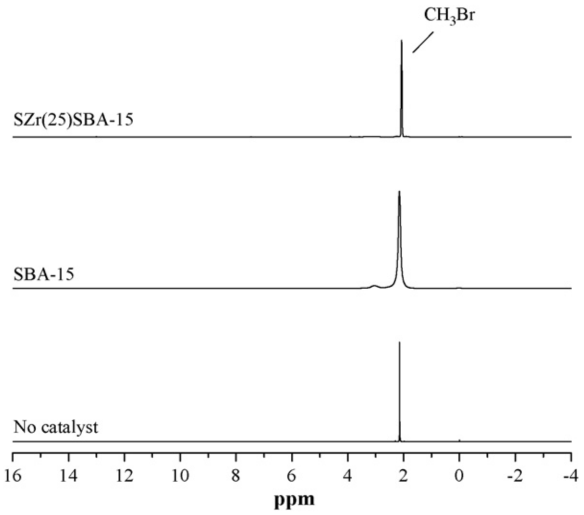

Fig. 4. Liquid ^1H NMR of the products dissolved in $CDCl_3$ and taken at Bruker AVANCE-400 after the methane bromination reaction with no catalyst, SBA-15 and sulfated SBA-15 with 25 mol.% ZrO_2.

The high product selectivity (>99%) was attained over SZr(25)SBA-15, SBA-15 and homogeneous reaction conditions. The conversions of methane to CH_3Br over the sulfated catalysts were higher than the reaction in the homogeneous gas phase, over SBA-15 and Zr-SBA-15. The highest conversion (69% at 340 °C) over SZr(25)SBA-15 was observed with high CH_3Br selectivity (>99%). While the homogeneous reaction can give rise to a distribution of mono and dibrominated methane products [17], in the presence of an acidic catalyst, high selectivities towards monobrominated compounds were observed, in good agreement with the product selectivity that was observed over strong superacid catalysts reported by Olah [1].

The results of the reaction tests at 340 °C were summarized and compared with literature in Table 1. It was seen that the methane conversions were quite high over the sulfated zirconia catalyst (69%) and the selectivity of the CH_3Br is 99%. The use of catalyst improves the conversion from 8 to 69%. The reaction temperature 340 °C is reasonable as compared to the methanol to olefins route (~350 °C). As far as the implementation of the process to a large scale production facility are concerned, higher temperatures (500 °C) are not desired – the case in homogeneous gas phase reactions – due to the operating costs as well as the selectivity problems. The improvement in the methane conversion from 8 to 69% provided by the use of SZr-SBA-15 at lower temperatures (340 °C) should reduce the operation costs in case of a large scale production.

The catalytic reactions were run at the reaction conditions for about 1 h and coking was not observed. However, longer stability tests were not performed on the catalysts. Given the fact that methylbromide starts to decompose ca. 400 °C, at lower temperatures, coking and stability problems are expected to be less severe.

The halogenated products ($CH_{4-n}X_n$) and hydrogen bromide (chloride) are not environmentally benign materials. The desired product of methane bromination reaction is methyl bromide and unfortunately it is an ozone depleting material. The production and distribution of CH_3Br was abandoned by Montreal Protocol. Therefore the halogenated products should be handled carefully. The HBr (HCl) could be neutralized by bubbling the exit gas through a NaOH solution. After the hydrocarbon synthesis in the overall reaction scheme, the unconverted product (i.e., CH_3Br)

Table 1
The reaction conditions, methane conversion and methyl bromide selectivity.

Catalyst	Br_2:CH_4	GHSV (mL/g h)	T (°C)	CH_4 conversion (%)	CH_3Br select. (%)
In this study					
SZr(25)SBA-15	10:1	3000	340	69	99
SZr(15)SBA-15	10:1	3000	340	14	99
No catalyst	10:1	60 s	340	8	99
Olah et al. [2]					
$SbOF_3/Al_2O_3$	1:5	100	200	20	99
$TaOF_3/Al_2O_3$	1:15	50	250	14	99
Pt/Al_2O_3	1:2	300	200	8	99
Lorkovic et al. [13]					
No catalyst	1:10	0.3 s	500	70	62

must be recycled. This could be done by a Hofmann elimination type reaction (Eq. (2)). This remains to be difficult to achieve, but required for the overall synthesis route to be applicable [11].

$$2C_2H_5O^-Na^+ + 2CH_3Br \rightarrow 2C_2H_5OH + C_2H_4 + 2NaBr \quad (2)$$

4. Conclusions

Selective production of mono-bromomethane (CH_3Br) was achieved at relatively high methane conversions (69%) with a proven proton donor strong acidic catalyst with relatively highest acidity (sulfated 25 mol.% ZrO_2/SBA-15). It is a very promising result for the cost effective replacement of syn-gas methane conversion route.

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