Catalysis Letters Vol. 100, Nos. 1–2, March 2005 (© 2005)
DOI: 10.1007/s10562-004-3085-x

Dimethyl ether synthesis from methane by non syngas process

Han Fei Xu*, Kuan Xin Wang, Wen Sheng Li, and Xiao Ping Zhou

Department of Chemical Engineering, Hunan University, P. R. China 410082

Received 11 August 2004; accepted 04 November 2004

Dimethyl ether is a potential clean fuel and intermediate for other chemical synthesis, such as gasoline, ethylene, and acetic acid. To synthesize dimethyl ether from the traditional syngas process is an energy consuming process. More than one fourth of natural gas must be burned to generate heat for the steam reformation of natural gas. Here, we show a non-syngas process to synthesize dimethyl ether. This process consists of the conversion of methane to bromomethane by reacting methane with hydrogen bromide and oxygen and the hydrolysis of bromomethane to dimethyl ether. Through this process, methane can be high efficiently converted to dimethyl ether.

KEY WORDS: oxidative bromination; catalysis; methane; dimethyl ether.

1. Introduction

Methane is the major component of natural gas, and also an abundant natural resource. Currently, methane is used as fuel or feedstock for methanol or ammonia synthesis. However, all of these processes must through steam reformation to synthesize syngas or hydrogen. However, syngas process is a highly energy consuming process. More than one fourth of natural gas must be burned to generate heat for natural gas (above 800 °C) steam reformation. Meanwhile, large amount of green house gas was formed. It is highly desired to develop energy saving process to convert methane to oxygenates, such as methanol, dimethyl ether (DME), or acetic acid. Because of the high stability of methane, it was proved to be difficult to directly convert methane to oxygenates. There are efforts to convert methane to methanol and acetic acid by non synthesis gas process. Periana *et al.* developed a two-step process to convert methane to methanol by using platinum bidiazine complexes as catalysts to convert methane to dimethyl sulfate in concentrated sulfuric acid [1], and then hydrolyzing dimethyl sulfate to methanol. More than 70% one-pass dimethyl sulfate yield was obtained based on methane. The drawbacks are on one hand, the oxidant was concentrated sulfuric acid, and SO_2 was formed as by-product, which is difficult to recycle, on the other hand, the product dimethyl sulfate needs to be hydrolyzed to methanol, while the reaction mixture has to be diluted by water, which makes the sulfuric acid recycle difficult. Periana and co-workers also successfully converted methane to acetic acid in concentrated sulfuric acid by using palladium sulfate as catalyst [2]. The oxidant was, still concentrated sulfuric acid and also SO_2 was generated as by-product, which is difficult to recycle. Olah *et al.* studied the methane chlorination and bromination, by reacting methane with chlorine or bromine to synthesize chloromethane or bromomethane, followed by the hydrolysis of chloromethane or bromomethane to synthesize methanol and dimethyl ether [3]. In Olah's report, elemental chlorine or bromine was used as reactant. HCl or HBr was formed as by-product. Extra reaction was needed to regenerate chlorine or bromine. And also in Olah group's work, they focused the work on methane chlorination and chloromethane hydrolysis reaction [3]. However, because chlorine atom is much smaller than bromine, it will be easy to form methane dichloride, methane trichloride, and methane tetrachloride as by-products. The selectivity to CH_3Cl was low. Because of the space limit around carbon and the big atomic size of Br, one carbon atom cannot hold too many bromine atoms around it. Hence, high CH_3Br selectivity can be obtained. On the other hand, bromine is a better leaving group than chlorine. The hydrolysis reaction of bromomethane will be much more faster than the hydrolysis reaction of chloromethane. Zhou *et al.* [5] developed a process to convert methane to dimethyl ether, which involved bromine as a media. In the process, methane was reacted with bromine to form bromomethane and a by-product HBr, then bromomethane was reacted with metal oxides to generate dimethyl ether and metal bromide, while HBr was also reacted with metal oxides to recover bromine. Finally, the metal bromide was reacted with oxygen to regenerate metal oxides and bromine. However, the reaction between the metal oxide and bromomethane is a stoichiometric reaction. There is solid transferring problem. The desired case will be to make the whole process a catalytic process. Hence, we are working on the direction to develop methods to convert methane to useful

---

*To whom correspondence should be addressed.

E-mail: hgx2002@hnu.cn

1011-372X/05/0300–0053/0

oxygenates, such as DME by making use of bromine as a reaction media. DME is a potential clean fuel for diesel engines. It has a potential annual world market of about 550 billion pounds. DME can also be converted to gasoline, ethylene, or acetic acid. Currently, it was synthesized from methanol or directly synthesized from syngas [6,7]. Here, we report a non-syngas process to synthesize DME.

2. Experimental

The catalyst was prepared by impregnating 1.9973 g of SiO_2 (60–100 mesh) in 6.750 mL of $RuCl_3$ solution (0.00040 g/mL). The sample was kept in air at room temperature for 30 min, then dried at 383 K for 4 h, and finally calcined at 723 K overnight to obtain the catalyst (0.1 wt% Ru/SiO_2).

In the process, methane was converted to bromomethane by reacting with oxygen and HBr (40 wt% in water) over 0.10 wt% Ru/SiO_2 catalyst. The reaction is a strong exothermic reaction (see reaction (1)). Heat is not needed from outside to maintain the reaction.

$$2CH_4 + 2HBr + O_2 \longrightarrow 2CH_3Br + 2H_2O \quad (1)$$
$$\Delta H^\circ = -332.6\,kJ$$

In a typical experiment, 1.0000 g of catalyst was loaded into a glass tube (OD 8.0 mm) reactor. The flow of HBr/H_2O (40 wt% in water) was 4.0 mL/h. The flow of methane, oxygen and the reaction temperature were listed in table 1. After reaction was stabilized for at least 2 h, the reaction effluent was analyzed on a HP-GC (6890N) and HP-GC/MS (6890N/5973N).

Dimethyl ether synthesis reactions were carried out in stainless steel autoclaves at auto-generated pressure. The autoclave has a poly tetrafluorine ethylene container inside (volume 1.60 mL). In every run, 18 mg of $RuCl_3$ catalyst and water (The amount is listed in table 2.) were loaded into the reactor at room temperature, and then cooled to −50 °C to load liquid CH_3Br (pre cooled to −50 °C). The reactors were sealed at low temperature and placed in an oven to carry out the reactions. The temperature of the oven was set to the desired reaction temperature as listed in table 2. After reaction, the reactors were taken out and cooled to room temperature primarily, and then cooled to −50 °C in a refrigerator. Tetrahydrofuran (THF) was used as solvent, which was also pre-cooled to −50 °C before using. Each time, 1.0 mL of cooled THF was used to dilute the reaction mixture. Since DME has high solubility in the water-THF solvents (The solution is acidic, which also makes DME more soluble.) at 0–5 °C. All of the operations were conducted within temperature 0–5 °C. GC/MS (HP6890N/5973N) was used to identify products, while GC (HP6890N) with a thermal conductivity detector was used for product quantification.

3. Results and discussion

Table 1 shows the results of methane oxidative bromination. Up to 31.8% methane conversion with 78.8% CH_3Br selectivity was reached in a single pass. CH_3Br, CH_2Br_2, and CO were detected as major carbon containing products. No CO_2 and $CHBr_3$ were detected within the detection limit of the GC thermal conductivity

Table 1

Methane oxidative bromination results over Ru/SiO_2 catalyst

T (°C)	CH_4 (mL/min)	O_2 (mL/min)	CH_4 conversion (%)	Selectivity (%)		
				CH_3Br	CH_2Br_2	CO
530	5.0	15.0	27.6	80.0	1.9	18.2
530	5.0	20.0	24.4	89.4	1.7	8.8
560	5.0	20.0	31.8	78.8	2.3	18.9

Table 2

Methanol and DME synthesis over $RuCl_3$ catalyst

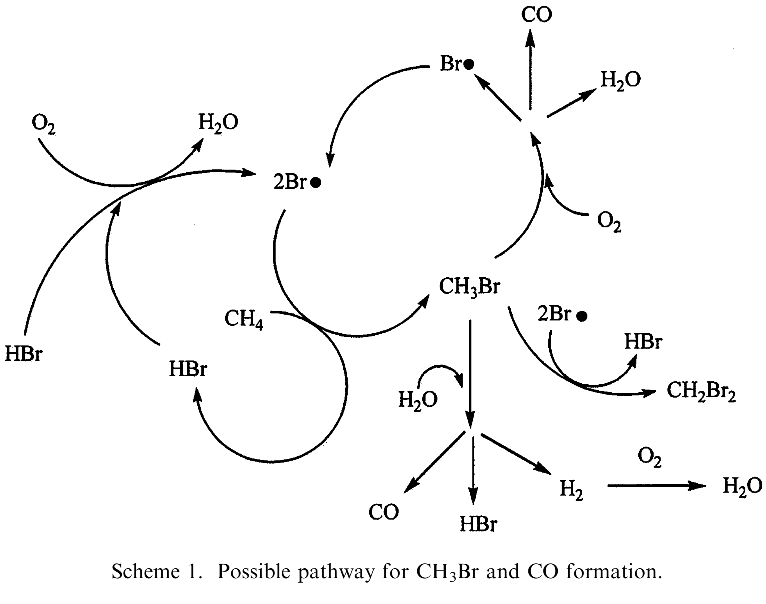
Serial No.	*T* (°C)	*t* (hour)	H_2O (g)	CH_3Br (g)	Conversion (%)	Selectivity (%)	
						DME	CH_3OH
1	150	6.0	0.700	0.500	66.1	22.2	77.8
2	170	6.0	0.700	0.500	83.2	55.0	45.0
3	180	6.0	0.700	0.500	97.0	58.7	41.3
4	180	6.0	0.400	0.500	60.5	43.7	56.2
5	180	6.0	0.600	0.500	87.0	62.7	37.3
6	180	4.0	0.700	0.500	71.8	48.7	51.3
7	180	10.0	0.700	0.500	98.3	68.9	31.0

Note: *T* refers to the reaction temperature. *t* refers to the reaction time.

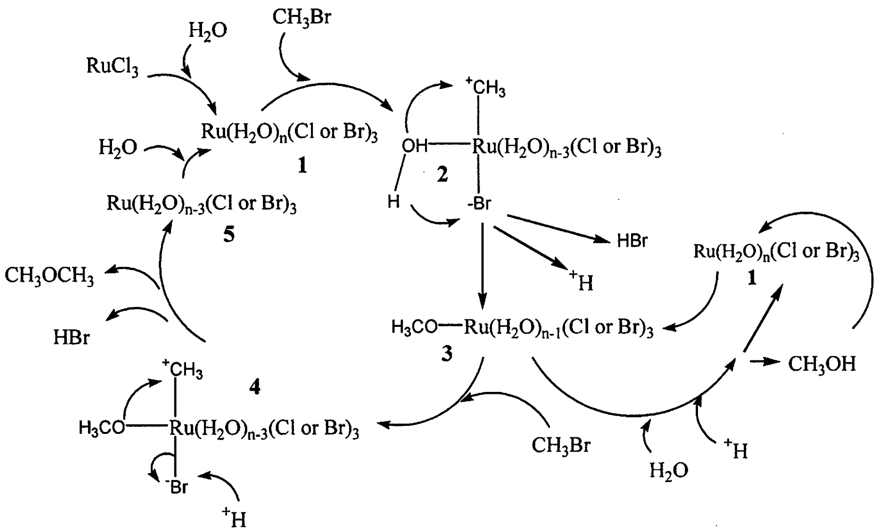
detector (TCD). However, our mass spectroscopy analysis showed trace amount of CO_2 and $CHBr_3$ (CH_2Br_2 and $CHBr_3$ can be pump back to methane oxidative bromination reactor to make use of bromine) in the effluent. Comparing with the results reported by Olah group [3], we reached higher methane single passing conversion. However, our CH_3Br selectivity was lower than that reported by Olah group. In our case, the reactants (oxygen, HBr, and methane) and catalyst were different from that reported by Olah group (Bromine reacted with methane). In our case, the co-production of CO reduced the bromomethane selectivity. However, CO can be used to react with CH_3Br and water to synthesize acetic acid. Our research highlights on this reaction. The using of large amount of water (HBr/H_2O) can avoid hotspots in catalyst bed, and keep HBr in water phase in the whole process making separation easy. The reaction heat could be used to generate steam to run the compressor for DME synthesis. In this reaction, we had run the Ru/SiO_2 catalyst for more than 2 months and did not find activity decrease. The Ru/SiO_2 catalyst is much stable than $SbOF_3/Al_2O_3$ and $TaOF_3/Al_2O_3$ catalysts reported Qlah *et al.* [3]. The results indicate that without using HBr/H_2O in the reaction, methane almost did not react with oxygen at 560 °C over Ru/SiO_2 catalyst, and also, when without methane, HBr reacted with oxygen to form Br_2.

The data in table 2 indicates that the bromomethane hydrolysis reaction could be carried out at pretty low temperature. Methanol and DME were detected as products. Higher reaction temperature and higher H_2O to CH_3Br ratio favor the hydrolysis reaction. Longer reaction time favors the formation of DME (entrances 6, 3, and 7). The results indicate that methanol might be the primary product, while DME was formed from coordinated methoxyl group or methanol (At least one carbon was from methanol or methoxyl group as shown in scheme 2), since methanol selectivity was high at the beginning of the reaction. This result also implies that longer reaction time favors the DME formation, which is important in practice, since DME is much easier to be separated from the reaction mixture than methanol. In Olah's work [3], bromomethane was hydrolyzed at atmospheric pressure (gas phase) in a fixed bed reactor, and the bromomethane conversion was only 23% at 375 °C. In our work, a homogeneous catalyst $RuCl_3$ was used in a batch model reaction, which was, a two-phase (gas–liquid) system. At a reaction temperature between 150 and 180 °C, bromomethane conversion from 66% to 98% was obtained. The drawback of the batch process is that the space-time yield is lower than that in a plug flow fixed, bed reactor. However, our process provides an alternative way for DME synthesis from methane without through the syngas process. Also, if methanol is recycled back to the reactor, it can be further converted to DME. In this case, DME can be synthesized as the only product.

It was observed in our study that when HBr was absent, methane did not react with oxygen at temperature below 560 °C and when methane was absent, HBr reacted with oxygen to form bromine over Ru/SiO_2 catalyst. Based on these results, we suggested the reaction pathway as shown in scheme 1. The first step might be that HBr reacted with oxygen to form bromine radicals and water, and then bromine radicals reacted with methane to form CH_3Br and HBr. If bromomethane reacted with bromine radicals again, CH_2Br_2 could be formed as by product. Of course, CH_3Br can be further oxidized to CO, H_2O, and bromine radicals. However, according to this pathway, we still cannot explain why CO_2 was not detected as a major product. More detail work in this area is in progressing. At our reaction conditions, the methane steam reformation did not occur. Hence, the possibility of methane steam



Scheme 1. Possible pathway for CH_3Br and CO formation.



Scheme 2. Possible pathway for DME, and methanol formation.

reformation to form CO can be ruled out. However, the steam reformation of CH_3Br to form CO, HBr, and H_2 is possible. Although we did not detect hydrogen as a product in the reaction, the steam reformation of CH_3Br is still possible. Since that at our reaction conditions, excess amount of oxygen was used and the oxygen could burn off the hydrogen formed in the steam reformation reaction.

For bromomethane hydrolysis reaction, a pathway shown in scheme 2 is suggested. When $RuCl_3$ was dissolved into water, it might combine with water to form complex **1**, and then CH_3Br substituted two water molecules around Ru and coordinated to Ru ion and intermediate compound **2** was formed. Intermediate compound **3** could be formed through the intramolecular reformation and decomposition of intermediate compound **2**.

Intermediate compound **3** could be hydrolyzed to methanol and complex **1** or intermediate compound **3** could react with one more CH_3Br to form intermediate compound **4**. Also, methanol formed in the reaction could combine with compound **1** to form intermediate compound **3**. This explains that longer reaction time favors the DME formation (table 2).

Intermediate compound **4** could decompose to DME and reacted with water to regenerate the catalyst.

Scheme 1 and scheme 2 are only the possible reaction pathways for methane oxidative bromination and bromomethane hydrolysis reaction to prepare DME. To achieve a fully understanding of the reaction pathways, detail research work is necessary.

4. Conclusion

In this work, we proved that without using syngas, DME can be synthesized from methane by a two-step process. In the process, HBr/H_2O was recycled, Comparing to the traditional process, the priorities of the current process for DME synthesis are in the following aspects: (I) there is almost no CO_2 generated, (II) the oxidative bromonation of methane is an exothermic reaction, which is an energy self-giving process, (III) extra heat can be used to power the next step DME synthesis, (IV) DME (boiling point −24.8 °C) is easy to be isolated from HBr/H_2O solution, while in traditional process, DME must be separated from hydrogen, CO, and CO_2, (V) the process is flexible, except DME, it can also be used to synthesize methanol or acetic acid (Since CO was co-produced, the process could be used to co-produce acetic acid by reacting CH_3Br, CO, and H_2O.). The drawback of the process is that HBr is corrosive. However, if the methane oxidative bromination reaction was carried out in gas phase, Ni alloy is durable to HBr. We had tested NiCr alloy in the oxidative bromonation reactor. The experiment showed that NiCr alloy was durable to HBr corrosion in gas phase. In the DME synthesis reactor, since the reaction temperature (below 180 °C) is not high, current technologies have resolved the corrosion problem.

Acknowledgments

This work was supported by academic development fund of Hunan University and National Key Analysis Laboratory at Hunan University.

References

[1] R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, Science 280 (1998) 560.
[2] R.A. Periana, O. Mironov, D. Taube, G. Bhalla and C.J. Jones, Science 301 (2003) 814.
[3] G.A. Olah, B. Gupta, M. Farina, J.D. Felberg, W.M. Ip, A. Husain, R. Karpeles, K. Lammertsma, A.K. Melhotra N.J. Trivedi, J. Am. Chem. Soc. 107 (1985) 7097.
[4] M. Girodani, Ann. Chim. Appl. 25 (1935) 163.

[5] X.P. Zhou, A. Yilmaz, G.A. Yilmaz, I.M. Lorkovic, L.E. Laverman, M. Wiss, J.H. Sherman, E.W. McFarland, G.D. Stucky and P.C. Ford, Chem. Commun. 18 (2003) 2294.

[6] M.W. Twigg(ed.), *Catalyst Handbook* (Wolfe, London, 1989).

[7] M. Mizuguchi, T. Ogawa, M. Ono and K. Tomura, JP 10182527 A2 (1998).