Acetic acid synthesis from methane by non-synthesis gas process

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Abstract

Acetic acid was synthesized from methane by non-syngas process. In the process, methane was brominated with hydrogen bromide (40 wt.% HBr/H$_2$O) and oxygen to give CH$_3$Br and CO over a Ru/SiO$_2$ catalyst. The as-generated CO and CH$_3$Br reacted with water under the catalysis of RhCl$_3$ to produce acetic acid, methanol, and methyl acetate. In the first step oxidative bromination reaction, 30.1% of methane single pass conversion with 72.4% of CH$_3$Br selectivity and 25.5% of CO selectivity was attained. In the second step, almost 100% CH$_3$Br conversion was reached.
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1. Introduction

Acetic acid is an important feedstock in chemical industry. Currently, more than 15 billion pounds of acetic acid was consumed annually in the world. Traditionally, acetic acid is synthesized by methanol carbonylation [1]. However, synthesis gas process is a highly energy consuming process. More than one-fourth of nature gas or coal must be burned to generate heat for nature gas (above 800 °C) or coal (above 1200 °C) steam reforming. Meanwhile, large amount of green house gas was formed. Methane is the major component of nature gas, and also a rich nature resource. It is highly desirable to develop energy saving methods for converting methane to oxygenates, such as methanol and acetic acid. There are considerable efforts to convert methane to acetic acid by non-synthesis gas process. Periana and co-workers successfully converted methane to acetic acid in concentrated sulphuric acid by using palladium sulphate as catalyst [2]. The oxidant was concentrated sulphuric acid. In the process, SO$_2$ was generated as by-product, which is difficult to recycle. We now report a non-synthesis gas process to synthesize acetic acid.

2. Experiment

The catalyst for methane oxidative bromination was prepared by impregnating 1.9973 g of SiO$_2$ (60–100 mesh) with 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.

In the processes, methane was converted to bromomethane, CO and H$_2$O through the reaction with oxygen and HBr (40 wt.% in water) over Ru/SiO$_2$ catalyst. The reaction is strong exothermic. Once reaction is started, heat is not needed from outside to maintain the reaction. In a typical experiment, 1 g of catalyst was loaded into a glass tube (OD 8.0 mm) reactor. The flow rate of HBr/H$_2$O (40 wt.% in water) was 4.0 ml/h. The flow rate of methane (>99.5%), oxygen (>99.5%) and the reaction temperature are listed in Table 1. After the reaction was stabilized for at least 2 h online, the reaction effluent was analyzed on a HP–GC (6890N), and also the products were double checked on a HP–GC/MS (6890N/5973N).

The acetic acid synthesis reaction was carried out in a pressurized batch reactor (a stainless steel autoclave with a poly tetrafluoroethylene container (inside volume 1.60 ml)). Water and catalyst were pre-loaded into the reactor. Before

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Table 1
Methane oxidative bromination results over Ru/SiO$_2$

T (°C)	CH$_4$ (ml/min)	O$_2$ (ml/min)	CH$_4$ conversion (%)	Selectivity (%)		
				CH$_3$Br	CH$_2$Br$_2$	CO
530	5.0	10.0	19.1	90.0	1.7	8.4
560	5.0	15.0	30.1	72.4	2.1	25.5

loading CH$_3$Br into the reactor, CH$_3$Br and the reactor (with catalyst and water) were cooled to −50 °C, and then CH$_3$Br (the amount is listed in Table 2) was loaded into the reactor at −50 °C. The reactor was sealed, purged by CO, and pressurized to 26 atm with CO (>99.0%) in every run, and then heated to the desired reaction temperature. The reactions were carried out under stirring. In every run, 12 mg of RhCl$_3$ was used as catalyst, while except the reactions (entries 10–12) in Table 2, in all of the other run, 0.1100 g of KI was used as co-catalyst. The products were quantified by GC and GC/MS.

In order to avoid bromine loss, we tried to convert CH$_2$Br$_2$ to acetic acid. In a typical experiment, 30 mg of RhCl$_3$, 20 mg of triphenylphosphine, 0.400 ml of CH$_2$Br$_2$ (99.0%) and 0.400 ml of water were loaded into a batch reactor (a stainless steel autoclave with a poly tetrafluoroethylene container, which has an inside volume of 1.60 ml), then pressurized to 20 atm by CO. The reaction had been run at 180 °C for 6 h. The products were analyzed on the HP–GC and GC/MS.

In order to explore the role of CH$_3$I (It might be formed in situ), we run the acetic acid synthesis reaction by using CH$_3$I as a reactant instead of CH$_3$Br at similar reaction conditions to those of CH$_3$Br. The results are listed in Table 3.

3. Results and discussion

In the reaction, up to 30% methane conversion was reached in a single pass (Table 1). CH$_3$Br, CH$_2$Br$_2$, and CO were detected as major carbon containing products. CO$_2$ and CHBr$_3$ were not detected as by-products within the detection limit of the thermal conductivity detector (TCD). However, our mass spectrometer analysis showed small amount of CO$_2$ and trace amount of CHBr$_3$ in the effluent. Our study also indicated that in the oxidative bromination of methane, bromomethane and CO were produced simultaneously, and the selectivities to bromomethane and carbon monoxide can be adjusted by changing reaction conditions or/and using different catalysts (we shall report elsewhere). We can choose to produce more carbon monoxide in order to offer reactants for acetic acid synthesis. Currently, we can generate CO with more than 25% selectivity at a methane conversion of 30%. For this work, we are currently focusing on finding catalysts which can co-generate CO and CH$_3$Br with a mol ratio close to 1:1.

From the results listed in Table 2, we can find that the major reaction products are acetic acid, methanol, and methyl acetate. In the reaction system, CH$_3$Br hydrolysis, CH$_3$Br and/or CH$_3$OH carbonylation, and the esterification of acetic acid occurred. The data indicated that CH$_3$Br conversion increases with the increase in reaction temperature. Lower reaction temperature favours the formation of methanol (entries 1 and 2). Increase the water to bromomethane ratio favours the CH$_3$Br conversion, while the products distribution varies differently. The acetic acid selectivity increases when the water to bromomethane ratio increases from 5/6 to 1/1, and then with the further increase in the water to bromomethane ratio from 1/1 to 5/2, acetic acid selectivity decreases, while the methanol selectivity variation shows a reverse trend of that of acetic acid (entries 2 and 4–6, Table 2). Longer reaction time favours the formation of acetic acid (entries 6–9, Table 2). The acetic acid selectivity increased with the increase in reaction time, while the methanol selectivity variation shows

Table 2
Results of acetic acid synthesis from bromomethane and CO on RhCl$_3$ catalyst

Entry	KI (g)	t (h)	T (°C)	H$_2$O (g)	CH$_3$Br (g)	X (%)	Selectivity (%)		
							CH$_3$CO$_2$CH$_3$	CH$_3$OH	CH$_3$CO$_2$H
1	0.1100	4.0	160	0.500	0.300	43.3	13.4	45.5	41.0
2	0.1100	4.0	175	0.500	0.300	51.2	15.9	33.3	50.8
3	0.1100	4.0	180	0.500	0.300	71.4	25.5	32.6	41.9
4	0.1100	4.0	175	0.500	0.600	19.6	13.8	61.4	24.7
5	0.1100	4.0	175	0.500	0.500	34.1	16.5	26.9	56.6
6	0.1100	4.0	175	0.500	0.200	70.9	17.5	37.3	45.1
7	0.1100	2.0	175	0.500	0.200	64.5	19.2	47.9	32.9
8	0.1100	10.0	175	0.500	0.200	89.1	11.3	16.0	72.7
9	0.1100	20.0	175	0.500	0.200	99.0	0.32	0.65	99.0
10	0	4.0	175	0.500	0.200	30.5	9.7	73.0	17.3
11	0	4.0	175	0.500	0.300	18.8	7.1	74.2	18.7
12	0	4.0	175	0.500	0.600	6.7	3.0	74.2	22.8

t: reaction time, T: reaction temperature, X: CH$_3$Br conversion.

Table 3
Results of acetic acid synthesis on $RhCl_3$ catalyst from CH_3I

Entry	t (h)	T (°C)	H_2O (g)	CH_3I (g)	X (%)	Selectivity CH_3CO_2H (%)
1	0.5	175	0.500	0.300	96.2	>99.5
2	1	175	0.500	0.300	97.1	>99.5

t: reaction time, T: reaction temperature, X: CH_3I conversion.

the reverse trend. These results implied that methanol might be or at least be part of the primary product in acetic acid synthesis. The results also indicated that if the reaction time is long enough, almost all of CH_3Br could be converted to acetic acid. Our study showed that using KI as co-catalyst can accelerate the acetic acid synthesis reaction. By Comparing entries 2 and 11, entries 4 and 12, and entries 6 and 10 in Table 2, we can find that without using KI as a promoter, the conversions of CH_3Br are much lower than those when KI was used. Also, from the data of entries 10–12, when KI was not used, we can find that the major product is methanol, which has selectivity over 73%. These results indicated that the product distribution depends on whether KI is used or not as co-catalyst. When KI is used as co-catalyst, acetic acid is the major product, while without using KI, methanol is the major product (selectivity over 73%). Hence, it is clear that KI can accelerate the acetic acid synthesis reaction. The possible reason might be that there might be an intermediate CH_3I formed in the reaction, and then the carbonylation reaction of CH_3I is much faster than that of CH_3Br.

In order to explore the possible reaction pathway, we carried out reactions by using CH_3I instead of CH_3Br. The results are listed in Table 3. From the data in Table 3, it can be found that the carbonylation reaction of CH_3I is much faster than that of CH_3Br (compare the results in Table 2 with those in Table 3). The patent literature from industry research also proved that KI can accelerate the alcohol carbonylation reaction [3,4]. In the process, CH_3I was assumed to be the key intermediate, and also KI and CH_3I have been proved to have the same effect on alcohol carbonylation reaction [5].

In Table 1, we found that CH_2Br_2 was also formed as a by-product in the methane oxidative bromonation reaction. It is highly desirable to make use of CH_2Br_2 in order to avoid bromine loss. Our results showed that when the reaction was run at 180 °C for 6 h, a CH_2Br_2 conversion of 29.5% was reached with acetic acid as major product (more than 90% selectivity); the rest was methyl acetate and α-bromoacetic acid. The results indicated that CH_2Br_2 can be converted to acetic acid or important synthesis intermediate, such as α-
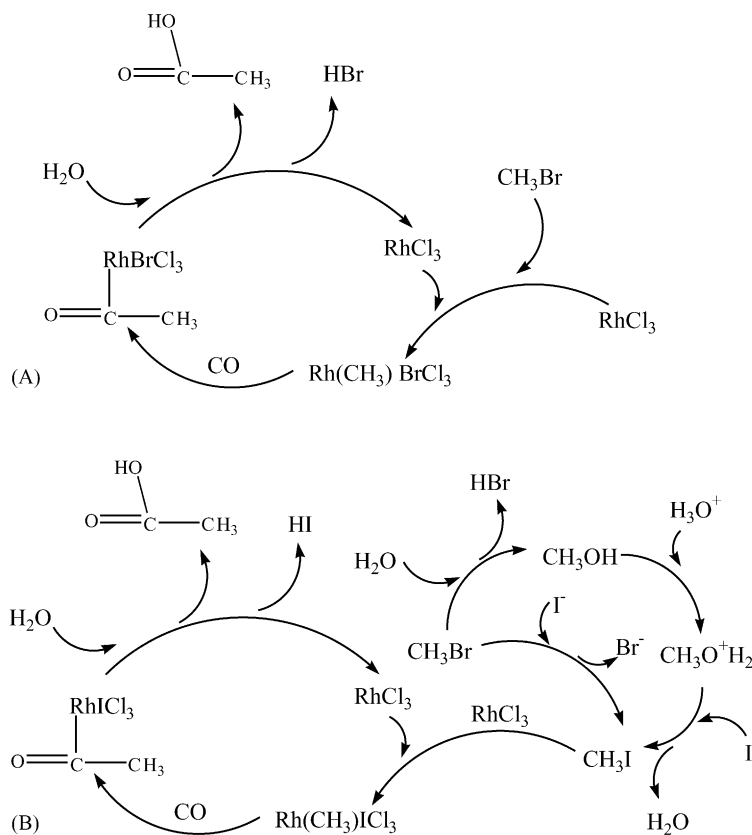
Scheme 1.

bromoacetic acid, which may find applications in fine chemical synthesis.

Based on the above results, the acetic acid synthesis reaction might experienced the following pathways: (i) the direct carbonylation of CH_3Br to form CH_3COBr and then hydrolysis to acetic acid (Scheme 1A), (ii) when KI was used as co-catalyst, CH_3Br reacted with KI to form CH_3I, then following the traditional pathway to form acetic acid [1], (iii) CH_3Br might be hydrolyzed to methanol in the first step, then methanol reacted with HI (in situ generated) to generate CH_3I, and then followed the traditional way to acetic acid.

In the first case, as shown in Table 2, entries 10–12, acetic acid was still formed when KI was not used. This result indicated that CH_3Br can be directly carbonylated to acetic acid. Under the same reaction conditions ($175\,^\circ C$, 4.0 h, 26 atm, CH_3OH 0.300 ml, reactor volume 1.60 ml, catalyst $RhCl_3$ 12 mg), using methanol to instead of CH_3Br, only 5.9% methanol conversion with 9.7% acetic acid selectivity (the rest is methyl acetate) was reached. These results showed that in the CH_3Br reaction, higher acetic acid yield (comparing with the results in Table 2 entries 10–12) was obtained than that in the methanol reaction. Hence, there might occur direct carbonylation of CH_3Br.

To verify the second pathway, CH_3Br was reacted with KI on $RhCl_3$ catalyst in the batch reactor that we used for acetic acid synthesis. At $150\,^\circ C$ and 4 h reaction, large amount of

CH_3I was detected mass spectrometrically. In the acetic acid synthesis reaction, when we used KI as co-catalyst, there was always very small amount of CH_3I detected in the products on mass spectrometer. Based on these results, it is conceivable that the secondary pathway opened to the acetic acid formation (Scheme 1B).

From the data of entries 2, 4, 6, 10–12 in Table 2, it is very clear, the carbonylation reaction is slow without KI, while the CH_3Br hydrolysis reaction is fast; methanol is the major product. The data of entries 6–9 showed that when reaction time was short, methanol was the major product. It is possible that methanol reacted with HI (in situ generated) to form CH_3I, which gives acetic acid. This is supported from our study (using methanol instead of CH_3Br without KI as co-catalyst, only 5.9% methanol conversion with 9.7% acetic acid selectivity was obtained on $RhCl_3$ catalyst at $175\,^\circ C$ and for 4 h). Hence, KI took part in the reaction and accelerated the acetic acid synthesis reaction. With the reaction going on for longer time (such as 20 h), almost all of the methanol formed from CH_3Br hydrolysis can be converted to acetic acid. Clearly, the third reaction pathway opened to the acetic acid formation (Scheme 1B). Based on the above discussion, the possible acetic acid reaction pathways can be summarized in Scheme 1.

We can now compare our process (Scheme 2B) with the current commercial process (Scheme 2A) for acetic acid syn-
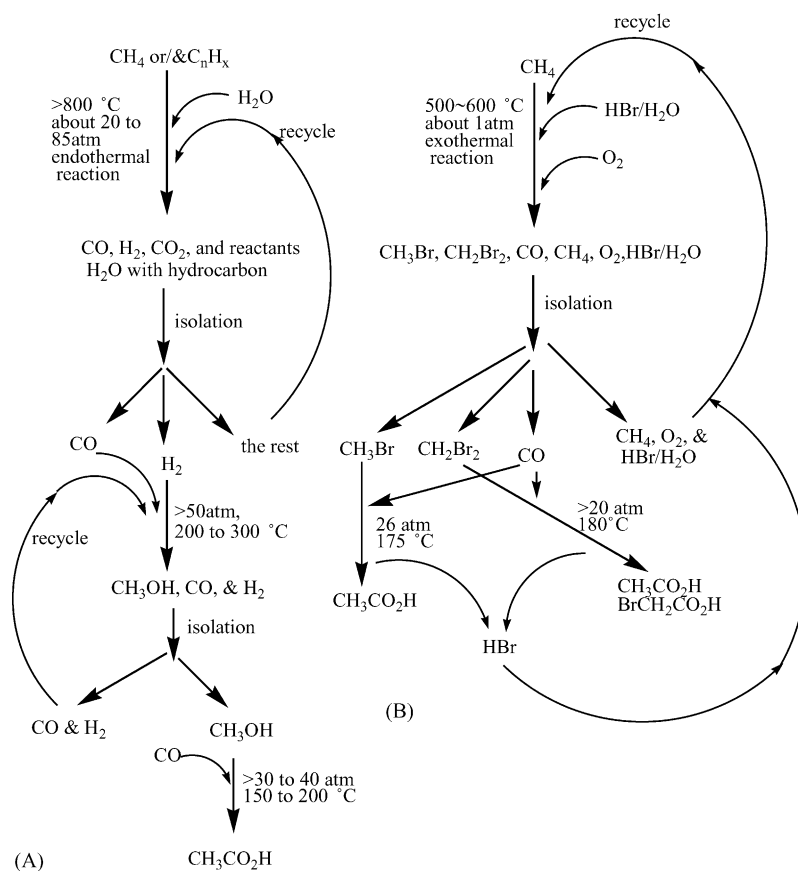
Scheme 2.

thesis. In the current commercial process, methane or light alkanes are converted to CO and H_2 by steam reforming at a temperature over $800\,^{\circ}C$ and pressure from 20 to 85 atm (the feedstock water and nature gas are compressed into the reformer). This is an endothermic reaction. Heat must be supplied to maintain the reaction temperature, which is usually practiced by burning hydrocarbon (about 1/4). After the reaction, the product mixture of H_2, CO, CO_2 and alkanes was separated to obtain CO and H_2, and the rest of the other materials are recycled back to the syngas generator or burned to generate heat. The following step is needed for synthesizing methanol over a CuZnAlO catalyst. The methanol synthesis reaction needs high pressure (50 atm or some process over 75 atm), and because this process has a very low single pass conversion, there is huge amount of CO and H_2 to be recycled in the reactor system [6]. Methanol thus obtained reacts with CO over $RhCl_3$ or some other catalysts and promoter, such as KI, CH_3I, or other organic iodide to produce acetic acid. This reaction is carried out at 30–40 atm [7,8].

In our case, the fist step is the oxidative halogenation of methane with HBr/H_2O and oxygen, and in the same reaction, CO was co-generated. The reaction is an exothermic reaction. The heat generated in the reaction can be used to maintain the reaction temperature. This process does not generate green house gases. However, the use of oxygen needs air separation and the handling of corrosive materials needs special construction materials, which have some trade-off here. The following acetic acid synthesis is carried out at relatively low reaction pressure 26 atm, which saves some energy compared to the patent process [3,4]. It can be found that, producing acetic acid through our process is more straightforward. However, it is hard to make accurate evaluations of our process vis the existed process at this stage. To bring this technology to practice, there is still a lot of work to be done.

In the current acetic acid synthesis process, KI or CH_3I are used as promoter of catalyst $RhCl_3$ [3,4]. The major contaminants are iodides. In our case, from GC/MS analysis, we did not detect bromides. The contaminant is small amount of CH_3I. Since CH_3Br is gas at room temperature and is not soluble in acetic acid water solution, it is very easy to separate it from acetic acid.

4. Conclusion

In this work, we proved that without using synthesis gas, acetic acid can be synthesized from methane by a two-step process. In the process, HBr was recycled. Compared to the traditional process, the priorities of the current process for acetic acid synthesis are as follows: (i) there is almost no CO_2 generated, and (ii) since the oxidative bromonation of methane is an exothermic reaction, the processes are energy saving processes. The drawback of the processes is that HBr is corrosive. However, if the methane oxidative bromonation reaction is kept in gas phase, Ni alloy is durable to HBr. We had tested a NiCr alloy in the oxidative bromonation reactor. The experiment showed that the NiCr alloy is durable to HBr corrosion in the gas phase. In the acetic acid synthesis reactor, since the reaction temperature (below $180\,^{\circ}C$) is not high, current technologies have resolved the corrosion problem. In order to synthesize acetic acid by the current process without supplying CO from outside, more work is needed to find efficient catalyst to give high CO selectivity in the first step reaction.

References

[1] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, Carbonylation Direct Synthesis of Carbonyl Compounds, Plenum Press, New York and London, 1991.
[2] R.A. Periana, O. Mironov, D. Taube, G. Bhalla, C.J. Jones, Science 301 (2003) 814.
[3] F.E. Paulik, A. Hershman, W.R. Knox, J.F. Roth, US Patent 03769329 3/12/1970.
[4] F.E. Paulik, A. Hershman, W.R. Knox, J.F. Roth, US Patent 03813428 5/28/1974.
[5] C.E. Hickey, P.M. Maitlis, J. Chem. Soc., Chem. Commun. (1984) 1609.
[6] J.A. Moulijn, P.W.N.M. van Leeuwen, R.A. van Santen, Stud. Sci. Catal. 79 (1993).
[7] J.F. Roth, J.H. Craddock, A. Hershman, F.E. Paulik, Chemtech 1 (1971) 600.
[8] H.D. Grove, Hydrocarbon Proc. 76 (1972).