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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_2O) and oxygen to give CH_3Br and CO over a Ru/SiO_2 catalyst. The as-generated CO and CH_3Br 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_3Br selectivity and 25.5% of CO selectivity was attained. In the second step, almost 100% CH_3Br conversion was reached.

Keywords: Methane; Bromomethane; Acetic acid; Oxidative bromination; Catalyst

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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_2O 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_2O (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 on-line, 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_3Br	CH_2Br_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_3Br into the reactor, CH_3Br and the reactor (with catalyst and water) were cooled to −50 °C, and then CH_3Br (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_2Br_2 to acetic acid. In a typical experiment, 30 mg of $RhCl_3$, 20 mg of triphenylphosphine, 0.400 ml of CH_2Br_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_3I (It might be formed in situ), we run the acetic acid synthesis reaction by using CH_3I as a reactant instead of CH_3Br at similar reaction conditions to those of CH_3Br. 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_3Br, CH_2Br_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_3Br 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_3Br hydrolysis, CH_3Br and/or CH_3OH carbonylation, and the esterification of acetic acid occurred. The data indicated that CH_3Br 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_3Br 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_2O (g)	CH_3Br (g)	X (%)	Selectivity (%)		
							$CH_3CO_2CH_3$	CH_3OH	CH_3CO_2H
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_3Br conversion.