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Direct catalytic formation of acetic acid from CO_2 and methane

Esther M. Wilcox, George W. Roberts, James J. Spivey*

Department of Chemical Engineering, North Carolina State University, P.O. Box 7905, Raleigh, NC 27695, USA

Abstract

The direct synthesis of acetic acid from methane and carbon dioxide was investigated. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments showed the formation of an adsorbed acetate on both a 5% Pd/carbon and a 5% Pt/alumina catalyst when the catalyst was exposed to a mixture of methane and carbon dioxide at a temperature of about 400 °C. Temperature programmed reaction (TPR) experiments showed the formation of gas phase acetic acid from carbon dioxide and methane at about 400 °C over a 5% Pt/alumina catalyst.

Keywords: Direct catalytic formation; Acetic acid; Methane

1. Introduction

The emissions of greenhouse gases, including carbon dioxide, are a worldwide environmental concern. One approach to reducing CO_2 emissions is to use it as a feedstock in chemical synthesis. Technology currently exists to convert CO_2 to synthesis gas (H_2 and CO), which can then be used to produce simple organic compounds, including methanol. However, the syngas production step is typically the most costly part of the overall process, in part because it is highly endothermic. The direct synthesis of chemicals from carbon dioxide would eliminate the need for the intermediate step of syngas production.

One potential target chemical is acetic acid, which is produced at an annual rate of more than six million tonnes worldwide [1]. Currently, acetic acid is produced industrially by the BP/Monsanto process, which uses a rhodium or iridium catalyst for the carbonylation of methanol.

In principle, acetic acid can be produced by the direct reaction of methane and carbon dioxide:

$$\begin{aligned} &CH_{4(g)} + CO_{2(g)} \leftrightarrow CH_3COOH_{(g)},\\ &\Delta H^{\circ}_{298\,K} = +8.62\,\text{kJ/mol},\\ &\Delta G^{\circ}_{298\,K} = +16.98\,\text{kJ/mol} \end{aligned} \quad (1)$$

The large, positive value of the Gibbs free energy change shows that reaction (1) is very thermodynamically unfavorable. Gibbs free energy minimization calculations using AspenPlus™, as seen in Fig. 1, show that the fractional conversion of methane increases with increasing pressure and temperature [2]. Fig. 1 shows that the fractional conversion of methane at conditions that are the most favorable thermodynamically, 1000 K, 100 atm and an inlet composition of 95% CO_2 and 5% CH_4, is only 1.6×10^{-6}.

A few groups have previously investigated the synthesis of acetic acid from methane and carbon dioxide. Taniguchi et al. [3] studied the reaction of methane with carbon dioxide using an aqueous vanadium catalyst, in a solution containing trifluoroacetic acid (TFA) and peroxydisulfate ($K_2S_2O_8$). The VO(acetylacetonate)$_2$ catalyst produced a yield

* Corresponding author. Present address: Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA.
E-mail address: jjspivey@lsu.edu (J.J. Spivey).

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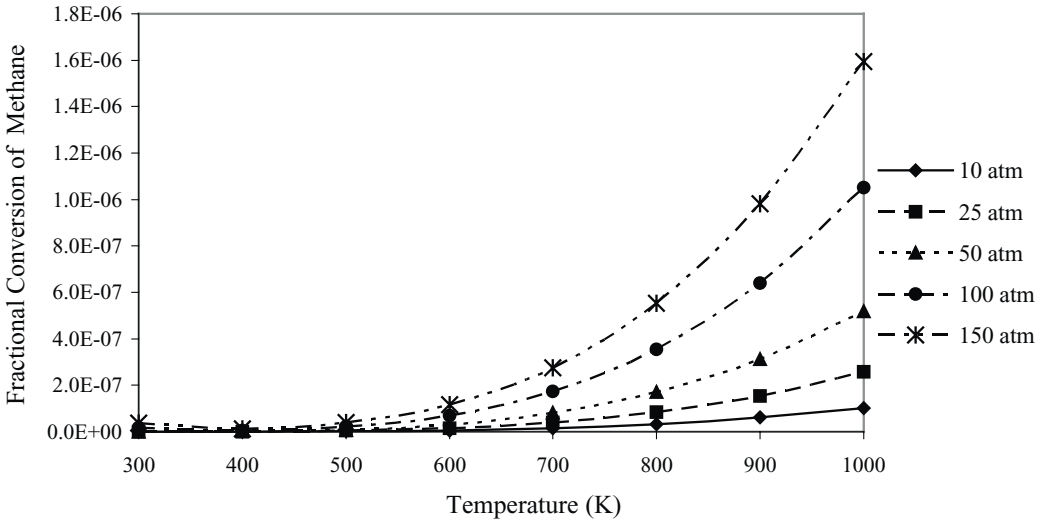

Fig. 1. Equilibrium fractional conversion of methane at various temperature and pressures from the reaction of $CO_2 + CH_4 \rightarrow CH_3COOH$ with an inlet composition of 95% CO_2 and 5% CH_4 calculated by the RGIBBS reactor model in AspenPlus™.

of 15.7% based on CH_4. Both the catalyst and the $K_2S_2O_8$ oxidant were required for the reaction to occur. However, the yield was independent of the CO_2 pressure and the reaction occurred with no CO_2 present. This suggests that the acetic acid was formed by a reaction other than reaction (1). For example, the thermodynamics of reaction (2) are favorable [4].

$$CH_4 + CF_3COOH \leftrightarrow CH_3COOH_{(g)} + CF_3H \quad (2)$$

The relatively high yield of acetic acid is inconsistent with the thermodynamics of the direct reaction of CH_4 and CO_2.

A South African patent by Freund and Wambach [5] claims a process for the direct synthesis of acetic acid from CO_2 and CH_4 using a solid catalyst, described as containing "one or more metals of groups VIA, VIIA, VIIIA" on a support of an aluminum oxide, aluminum hydroxide, or silicon dioxide. The reaction conditions are between 100–600 °C and 0.1–20 MPa. The patent claims that under these conditions a selectivity of 70–95% and an unspecified "sufficient conversion for commercial scale" can be achieved. No actual data or experimental examples are given in the patent.

Other groups have been taking approaches to overcome the thermodynamic limitations. Huang et al. [6] report the formation of acetic acid using a cyclic method over a Co-Cu catalyst. They first expose the catalyst to methane, which they claim forms a CH_x species on the surface. The gas flow is then changed to CO_2. This process is repeated several times. In addition to acetic acid, a wide variety of other species were formed. Huang et al. did not report a yield, but did report a selectivity of 21% for acetic acid.

Li et al. [7] used a dielectric barrier to react CH_4 and CO_2. While they were successful in forming acetic acid, they also formed several different hydrocarbons and oxygenates. No yield was reported, but they did report a selectivity of up to 6% for acetic acid.

The interest in reaction (1) shown in the literature suggests that this reaction could be industrially important. In addition, successful catalytic activation of the relatively unreactive methane molecule using CO_2 could enable other carboxylation reactions as well. Further work is needed to increase the yield, selectivity, and reaction rate to provide the basis for an industrially useable system, preferably based on a heterogeneous catalyst.

2. DRIFTS experiments

2.1. Experimental

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to show the formation of

the acetate species from a mixture of CO_2/CH_4. Two commercial catalysts were examined: 5% Pd/carbon from Calgon Carbon prepared by impregnation and 5% Pt/alumina from Johnson-Matthey prepared by incipient wetness. The palladium catalyst has a BET surface area of 430 m^2/g and a dispersion of 4.21% (measured by CO pulse chemisorption). The platinum catalyst has a BET surface area of 178 m^2/g and a dispersion of 27.9% (measured by CO pulse chemisorption).

Background experiments were conducted in order to determine the IR spectra for acetic acid on each catalyst. To do this, each catalyst was pretreated in flowing helium at 500 °C and 1 atm for 1 h, and then cooled to 100 °C where a background spectrum was taken. Helium was then bubbled through glacial acetic acid and introduced into the cell. This flow was maintained during the entire experiment. The temperature was increased in 50 °C increments up to 400 °C. Each temperature was maintained for 30 min, with spectra being taken every 10 min. Spectra of adsorbed acetic acid were different for each catalyst, as can be seen by comparing these spectra in Figs. 2 and 3.

The reaction of an equimolar mixture of CO_2 and CH_4 on the catalysts was then examined. A fresh sample of the catalyst was pretreated in flowing helium at 500 °C and 1 atm for 1 h, and then cooled to 100 °C and a background spectrum was taken. The catalyst was exposed to a 1 atm. flow of an equimolar mixture of CO_2 and CH_4. The temperature was increased in 50 °C increments up to 400 °C. Each temperature was maintained for 30 min, with spectra being taken every 10 min.

Alternate catalyst pretreatments were also examined using carbon dioxide or methane. After the helium pretreatment, as described above, the catalyst was exposed to either flowing carbon dioxide or methane at 100 °C and 1 atm for 1 h. After the additional pretreatment, an equimolar mixture of CO_2 and CH_4 was flowed over the catalyst as described above.

2.2. Results and discussion

Preliminary data showed the formation of an acetate from CO_2 and CH_4 [2]. However, those results were limited to the 5% Pd/carbon catalyst.

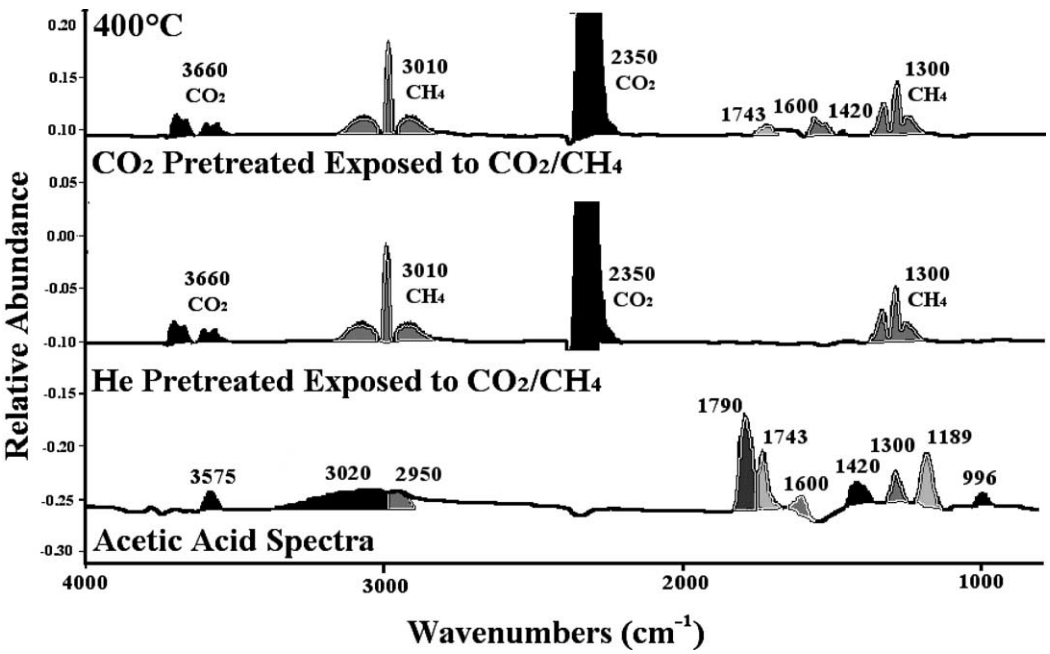

Fig. 2. Five percent Pd/carbon catalyst DRIFTS spectra at 400 °C. The spectrum for the methane pretreatment was essentially identical to that of the helium pretreatment.

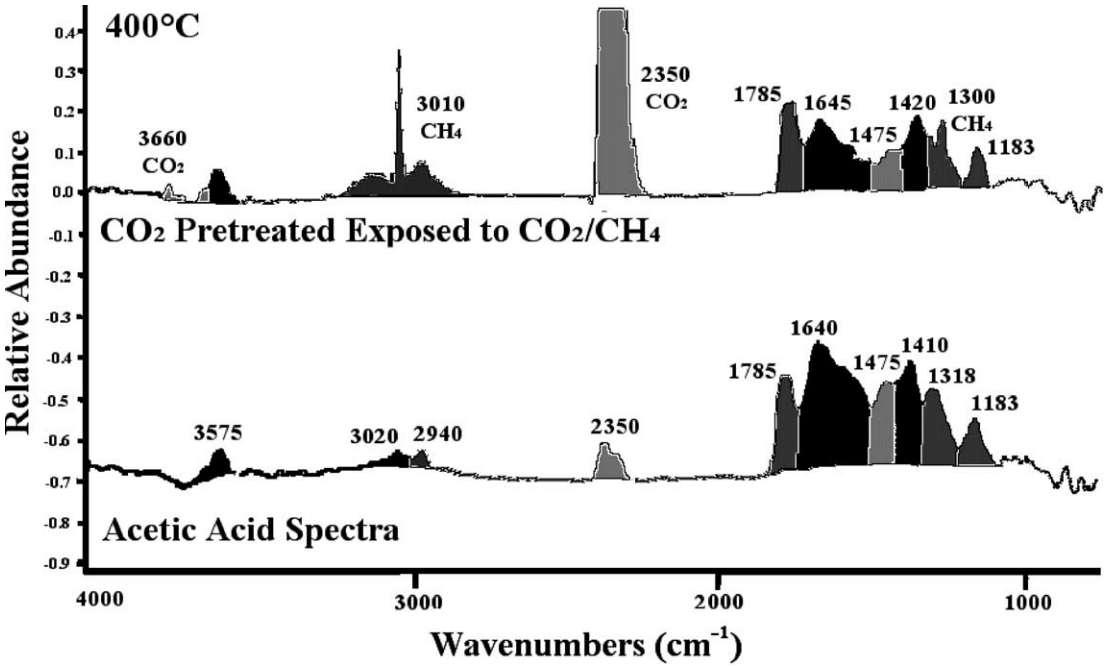

Fig. 3. Five percent Pt/alumina catalyst DRIFTS spectra at 400 °C. The spectrum for the methane pretreatment was essentially identical to that of the helium pretreatment.

2.2.1. 5% Pd/carbon catalyst

The IR spectra, with the background subtracted, for the Pd/carbon catalyst at 400 °C can be seen in Fig. 2. The acetic acid spectra shows peaks corresponding to the monomer (gas phase), dimer (liquid phase) and adsorbed acetic acid.

For the helium-only pretreatment, only four distinct peaks were observed. The peaks at 3010 and 1300 cm^{-1} correspond to the C–H stretch in methane [6]. The peaks at 3660 and 2350 cm^{-1} correspond to the O=C=O stretch in carbon dioxide [6]. No other peaks are observed, indicating that no reaction occurred during this experiment. An identical spectra was observed for the methane pretreatment.

However, when the catalyst was pretreated with carbon dioxide, distinct acetate peaks were observed. In addition to the CO_2 peaks at 3660 and 2350 cm^{-1}, and the CH_4 peaks can be seen at 3010 and 1300 cm^{-1}, four acetate peaks can be seen. The peak at 1790 cm^{-1} corresponds to the C=O stretch in a dimer of acetic acid [8], and the peak at 1743 cm^{-1} corresponds to the C=O stretch in a monomer of acetic acid [8]. The 1420 cm^{-1} peak can be attributed to the O–H deformation in a dimer of acetic acid [9]. Finally, the 1600 cm^{-1} peak corresponds to the O–C=O stretch in a monodenate absorbed acetate [9]. The acetate peaks were only observed at temperatures above 350 °C.

These experiments have shown the formation of an acetate group from a equimolar mixture of CO_2 and CH_4 on a 5% Pd/C catalyst. The pretreatment of this catalyst with CO_2 plays a vital role in the formation of the acetate. The acetate peaks were only seen when the catalyst was pretreated in CO_2, and not when the catalyst was pretreated in helium or methane. When only the carbon support was used, no acetate formation was observed with either pretreatment.

2.2.2. 5% Pt/alumina catalyst

The IR spectra, with the background subtracted, for the Pt/alumina catalyst at 400 °C can be seen in Fig. 3. The acetic acid spectra shows peaks corresponding to the monomer (gas phase), dimer (liquid phase) and adsorbed acetic acid.

Unlike the 5% Pd/carbon catalyst, the pretreatments had little effect on the 5% Pt/alumina catalyst. The IR spectra for the helium pretreatment experiment shows

CO_2 peaks at 3660 and 2350 cm^{-1}, and CH_4 peaks at 3010 and 1300 cm^{-1}. In addition, there are several other peaks, which are associated with an acetate. The peak at 1790 cm^{-1} corresponds to the C=O stretch in a dimer of acetic acid. The 1475 cm^{-1} peak can be attributed to the O–C=O stretch deformation in a dimer of acetic acid, and the 1193 cm^{-1} peak to the C–O stretch. Although shifted from the acetic acid background spectra, the 1675 cm^{-1} peak corresponds to the O–C=O stretch in a monodenate absorbed acetate. Acetate peaks were first observed at 200 °C and increased with temperature. When only the alumina support was used, no acetate formation was observed with either pretreatment.

3. TPR experiments

3.1. Experimental

In order to study the formation of gas phase acetic acid, temperature programmed reaction experiments were conducted using an Altamira™ AMI 1 system. In addition to a thermal conductivity detector, this system has an online mass spectrometer. Thermodynamics show that the gas phase concentration of acetic acid should be very low, but within the detection limits of the TPR system. A flow diagram of the system is shown in Fig. 4.

Since the DRIFTS experiments indicated that the 5% Pt/alumina catalyst performs better than the 5% Pd/carbon, only the 5% Pt/alumina catalyst was used in the TPR experiments.

For each experiment, approximately 0.1 g of catalyst was pretreated in flowing He at 500 °C and 1 atm for 1 h. The system was then cooled to 50 °C, and the catalyst was exposed to flowing carbon dioxide at 1 atm for 1 h. The catalyst was then exposed to the flowing reaction gas, either pure methane or an equimolar mixture of CO_2 and CH_4. The temperature was ramped up to 400 °C, held there for an hour and then the system was allowed to cool to room temperature. Mass spec data were taken throughout the entire experiment.The mass spec of pure acetic acid is shown in Fig. 5 [10]. The peaks at 12, 13, 14, 15 and 16 amu are peaks that methane also exhibits. The peaks at 28, 44, 45 and 46 amu are also exhibited by carbon dioxide. Since both carbon dioxide and methane are present in the system, none of the above peaks can be used to determine whether acetic acid is present. Furthermore, since the thermodynamics indicate that the amount of acetic acid produced by this reaction will be very small, only the most dominant peaks, those at 43 and 60, were monitored.

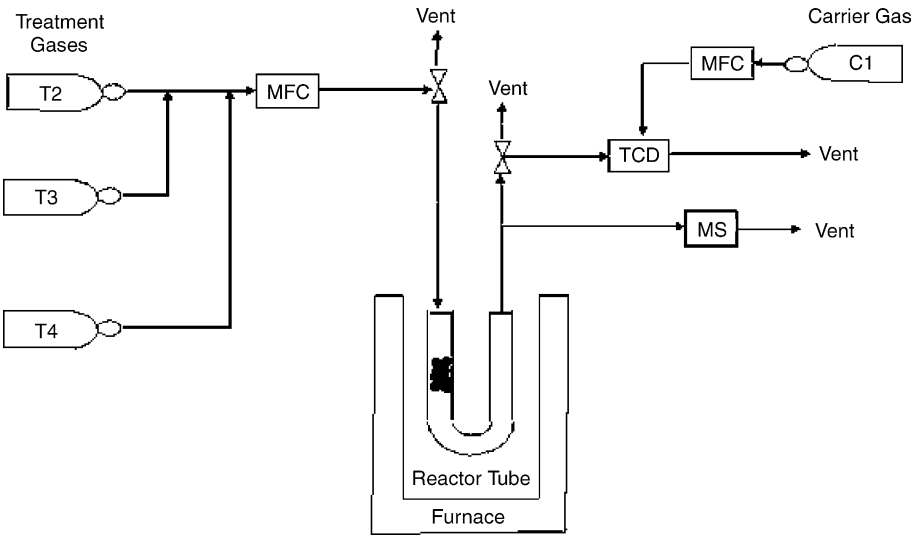

Fig. 4. Flow diagram of Altamira™ AMI 1 TPR system.

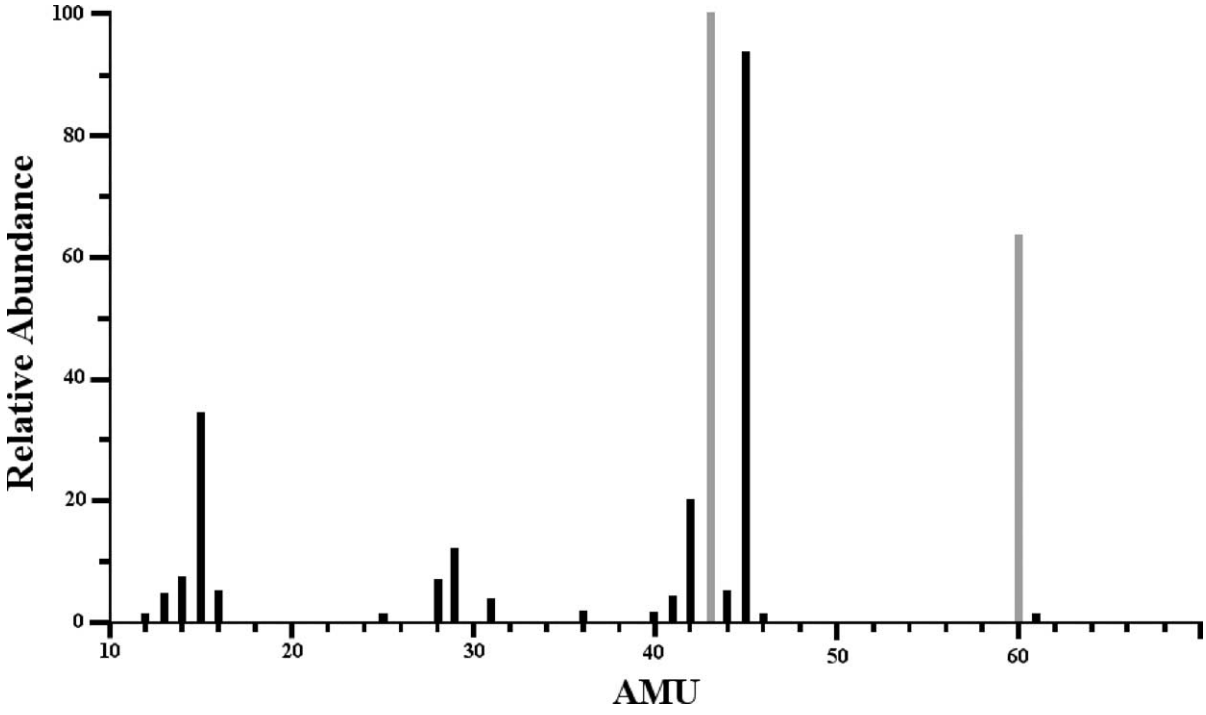

Fig. 5. Background acetic acid mass spectrum [10].

3.2. Results and discussion

Fig. 6 shows the mass spectrum data taken during the experiment in which methane was passed through the CO_2-pretreated catalyst. This graph starts at the time at which the catalyst was exposed to pure methane. As can be seen in this figure, both the mass 43 and mass 60 peaks begin to

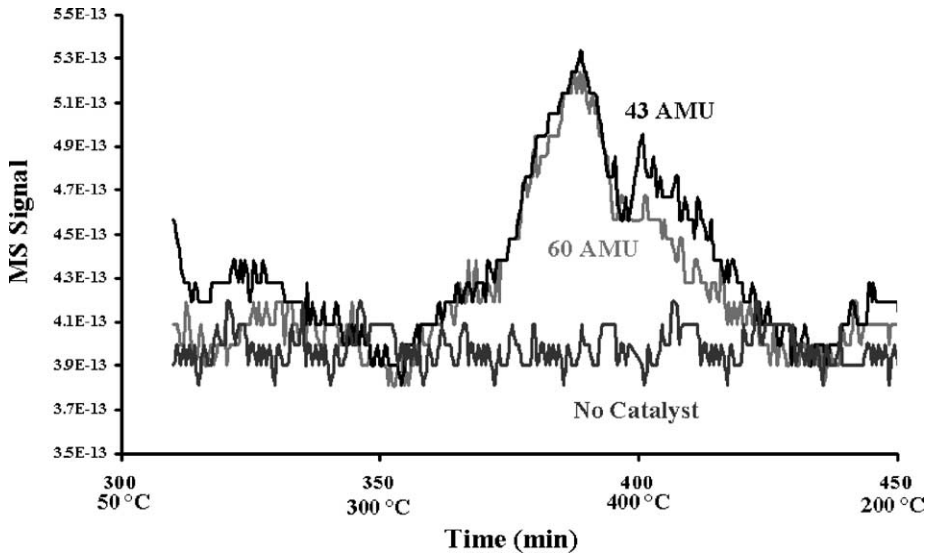

Fig. 6. CH_4 experiment MS data.

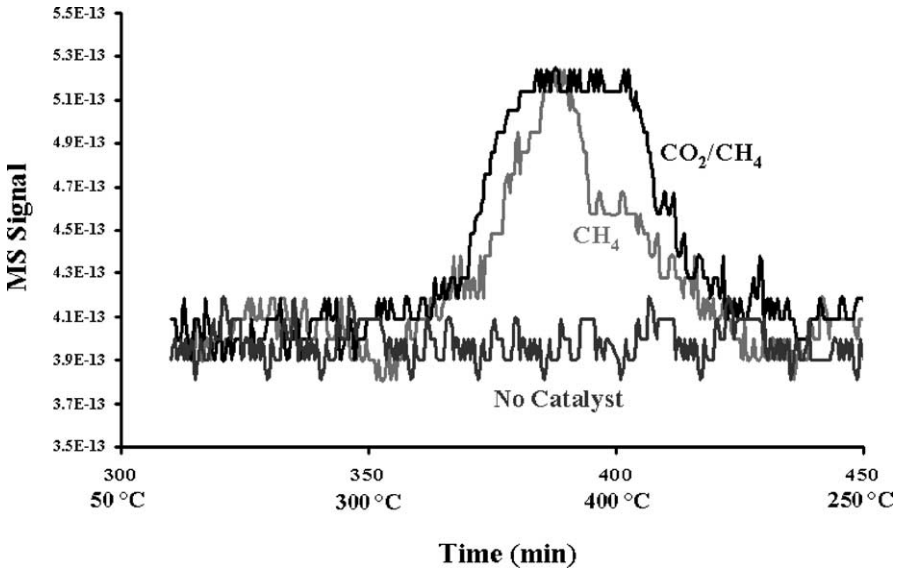

Fig. 7. Comparison of mass 60 amu.

increase when the temperature reaches about 375 °C. The peak signal increases to a maximum, and then sharply decreases, even though the temperature remains between 375 and 400 °C. The peak shape can be attributed to the adsorbed carbon dioxide reacting with methane. As the methane flow continues, the adsorbed CO_2 is gradually consumed. Since there is no additional carbon dioxide in the system during the methane treatment, the used CO_2 is not being replaced. Fig. 6 also shows that no reaction takes place at identical conditions in the absence of a catalyst.

Fig. 7 compares the mass spectrum data taken during the CO_2 + methane experiment to that of the previous experiment (Fig. 6). From Fig. 7, it can be seen that the 60 amu peak for the CO_2/CH_4 experiment begins to increase when the temperature reaches about 375 °C. Once the peak reaches a maximum, it remains there until the system starts to cool down from 400 °C, at which point a decrease back down to the noise level is observed.

The difference between the peak widths in these two experiments can be explained by the presence of carbon dioxide in the gas that was flowing through the catalyst. In the pure methane experiment, there was no carbon dioxide to replace that which was consumed in the reaction. In the second experiment, there was additional carbon dioxide in the feed which could replace the reacted CO_2.

A full mass spectrum taken at 400 °C shows peaks that corresponded to methane and carbon dioxide. We also observed a small, yet distinct peak at 60 amu. No other peaks were observed. This indicates that only acetic acid is formed. We have no evidence of any other reaction products, such as methylformate. When only the alumina support was used, no acetic acid peaks were observed. We have estimated an acetic acid yield of 1.5×10^{-6}.

4. Conclusions

This work investigated the possibility of forming acetic acid from CO_2 and CH_4 over solid catalysts. Using DRIFTS, we have shown that an acetate group can be formed on the surface of a 5% Pd/carbon or a 5% Pt/alumina catalyst exposed to an equimolar mixture of CO_2 and CH_4. The formation of acetate on the 5% Pd/carbon catalyst was dependant on a CO_2 pretreatment. Additionally, the acetate peaks were larger on the 5% Pt/alumina spectra, indicating that this catalyst is more active.

TPD experiments showed the formation of gas phase acetic acid from the reaction of carbon dioxide with methane using the 5% Pt/alumina catalyst. Additionally, the full mass spectrum showed only peaks corresponding to CO_2, CH_4 and acetic acid, indicating that no by-products were formed.

When both DRIFTS and TPD experiments were run with no catalysts, or the catalyst supports only, no acetic acid was formed.

While our yield is very low, we have made improvements over previous work in regards to the selectivity. In order to provide a useful industrial process, more work must be done to overcome the thermodynamics. Some possibilities include a cyclic process [6], or coupling the direct synthesis reaction with a second more favorable reaction.

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