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Efficient Synthesis of Ethanol and Acetic Acid from Methane and Carbon Dioxide with a Continuous, Stepwise Reactor

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The synthesis of C_2-oxygenates such as ethanol and acetic acid accomplished by CH_4 dissociation and subsequent CO_2 insertion onto methyl radicals, named the stepwise reaction technology, has been demonstrated to be both feasible and efficient through initial experiments conducted in microreactor units. This article describes the development of this technology, highlighting the aforementioned stepwise technology using a dual-reactor system, which can ensure that two raw gases enter the reactor uninterruptedly and are not mixed after reaction. The system productivity for acetic acid and ethanol displayed efficiencies greater than 5–10 times that of previous microreactor units. The investigation of mechanism indicates that acetic acid arises from insertion of CO_2 into $M{-}CH_x$, while ethanol is formed either by hydrogenation of acetic acid or by hydration of C_2H_4, which results from homo-coupling of CH_4. The latter route is the preferred of the two. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1279–1284, 2010
Keywords: CH_4, CO_2, acetic acid, ethanol, stepwise technology

Introduction

The direct synthesis of C_2-oxygenates from CH_4 and CO_2 is thermodynamically unfavorable, but can be overcome through a stepwise reaction technology. This has been demonstrated extensively in theory and experiment.[1–3] Figure 1 illustrates this stepwise process. First, CH_4 is adsorbed on the surface of catalysts and dissociated to generate a surface carbonaceous $M{-}CH_x$ species, as has been accepted in the two-step reaction sequence for methane homologation.[4–7] Next, CO_2 is inserted into $M{-}CH_x$ bond, and finally hydrogenation of the intermediates yields acetic acid.

The stepwise reaction technology can be divided into an isothermal process and a nonisothermal process, according to the temperatures at which the two steps proceed. The thermodynamic driving force behind the isothermal process is the pressure difference of hydrogen between the two steps. The reaction procedure is described as follows[3]:

The balance of the first step:

$$CH_4 + M \rightarrow M{-}CH_x + \frac{1}{2}(4-x)H_2 \times (\text{evolved, low pressure})(x = 0 \sim 3) \quad (1)$$

The balance of the second step:

$$M{-}CH_x + CO_2 + \frac{1}{2}(4-x)H_2(\text{supplied}) \rightarrow CH_3COOH + M \quad (2)$$

The global balance:

$$CH_4 + CO_2 + \frac{1}{2}(4-x)H_2(\text{supplied}) \rightarrow CH_3COOH + \frac{1}{2}(4-x)H_2(\text{evolved}) \quad (3)$$

Consequently, the Gibbs free energy of the global balance can be calculated as

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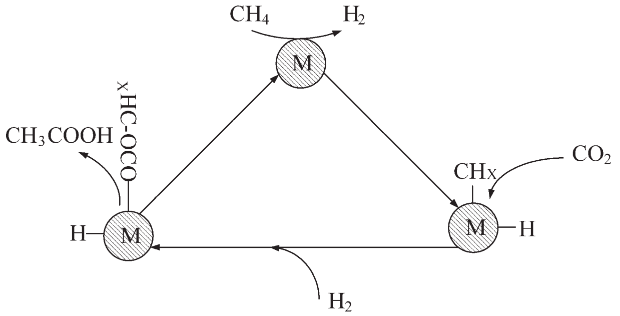

Figure 1. Schematic representation of the stepwise conversion of CH_4 and CO_2 to acetic acid.

$$\Delta G = \Delta G_1[CH_4 + CO_2 \rightarrow CH_3COOH] + \Delta G_2[\frac{1}{2}(4-x) \times H_2(\text{supplied}) \rightarrow \frac{1}{2}(4-x)H_2(\text{evolved})] \quad (4)$$

or

$$\Delta G = \Delta G_1 + \frac{1}{2}(4-x)\text{RT ln } pH_2(\text{evolved})/pH_2(\text{supplied}) \quad (5)$$

In Eq. 4, $\Delta G_1 > 0$. However, this can be counteracted by a greater negative value of ΔG_2. Thus, a Gibbs free energy for the global balance of $\Delta G < 0$ can be obtained.[3]

A series of Rh, Pd, Co, Co—Pd, Co—Cu single- and bi-metal catalysts have been used for the synthesis of acetic acid from CH_4 and CO_2 by the stepwise technology, of which Pd-Co bi-metal catalysts was found the best.[1,3,8] DFT (density functional theory) calculation[9] also shows that the reactions involved in the stepwise technology could effectively carried out on Co—Pd bi-metal catalysts under atmospheric pressure and isothermal conditions. The reaction pathway is: CH_4 is firstly adsorbed on Co to form CH_xCo ($x = 0, 1$), and then CH_x overflowed from Co to Pd leading to CH_yPd ($y = 1$–3), finally CO_2 inserts into CH_yPd, followed by hydrogenation to form acetic acid. These processes are all advantageous in thermodynamics under atmospheric pressure and isothermal conditions. Two optimum temperature ranges obtained from DFT calculation are in agreement with the experimental results.

It has been discovered that addition of excess H_2 to the CH_4 activation step can promote the formation of activated M—CH_x, and, subsequently, the overall formation of acetic acid.[10,11] In successive works, we also determined that water vapor can improve the yield and selectivity of acetic acid formation, as it prevents produced acetic acid decomposition.[12] As such, the best feed-in mode is: $CH_4 + H_2 + H_2O$ in the first step and $CO_2 + H_2 + H_2O$ in the second step.

Previously, the reactor system used for the stepwise technology has used a single reactor, and two raw gases $CH_4 + H_2 + H_2O$ and $CO_2 + H_2 + H_2O$ were injected into reactor alternatively. This set-up is shown in Figure 2A. The intermittent introduction of two raw gases induces a reduction in the conversion efficiency per unit time. Further, the composition of outlet gases includes both the first and second step off-gases, complicating the abstraction process. Based on these shortcomings, we have developed a new reactor design in this work. As shown in Figure 2B, this is a dual-reactor system, with a 2-position 4-port electromagnetic valve in the front and rear of the dual-reactor system, and the implementation of a time relay or PLC to control the transposition of two electromagnetic valves. Under the developed reaction conditions, CH_4, H_2, and H_2O enter reactor A to carry through the first reaction step (CH_4 activation and dissociation), forming M—CH_x. At the same time, CO_2, H_2, and H_2O enter reactor B to carry through the second reaction step to produce acetic acid. The off-gas of CH_4 activation and dissociation is vented from the outlet of tail gas of the first reaction step, and the off-gas of CO_2 reaction is vented from the outlet of tail gas of the second reaction step. As soon as a reaction time expires, the time relay sends a signal to the two 2-position 4-port electromagnetic valves to exchange the valve position. As such, CH_4, H_2, and H_2O enter reactor B and, CO_2, H_2, and H_2O enter reactor A to carry out reaction, while off-gases still are vented from the same outlets as those before exchange, that is, the off-gas of

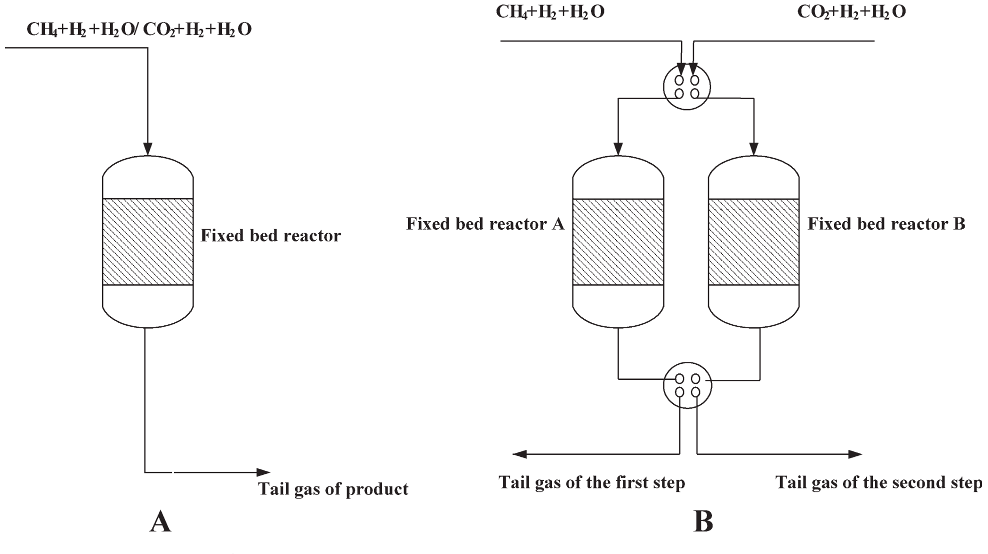

Figure 2. Single versus stepwise reaction processes and set-ups.

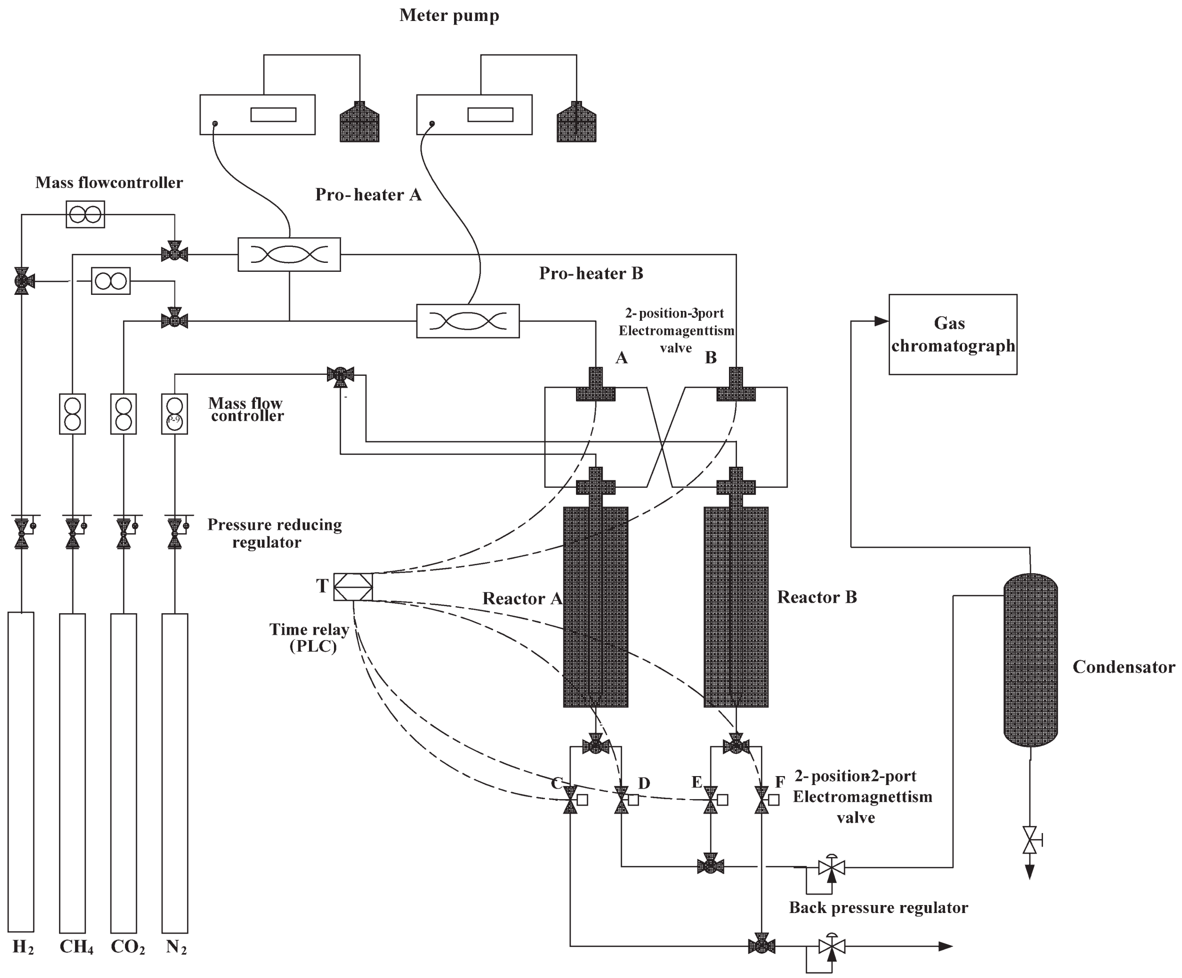

Figure 3. New reactor system flow chart for the stepwise route.

CH_4 reaction still is vented from the outlet of tail gas of the first reaction step, and the off-gas of CO_2 reaction is vented from the outlet of tail gas of the second reaction step.

Experimental

Reaction apparatus

Based on analysis, we built a new set of reaction apparatus, and it has been shown in Figure 3. Because the reaction is conducted at very specific temperatures, the selection of the electromagnetic valve is limited. As such, we selected two 2-position 3-port electromagnetic valves and four 2-position 2-port electromagnetic valves (two constant-opening, two constant-closing) to replace the 2-position 4-port electromagnetic valves in Figure 2. In Figure 3, for example, a flux of $CH_4 + H_2 + H_2O$ enters reactor A via 2-position 3-port electromagnetic valve A to adsorb on a catalyst, and then effuses via 2-position 2-port electromagnetic valve C. At this time, a flux of $CO_2 + H_2 + H_2O$ enters reactor B via 2-position 3-port electromagnetic valve B and then effuses via 2-position 2-port electromagnetic valve E. As soon as a reaction time expires, the time reply sends a signal to the electromagnetic valves A, B, C, D, E, and F, making the flux of $CH_4 + H_2 + H_2O$ enter reactor B and the flux of $CO_2 + H_2 + H_2O$ enters reactor A to react with adspecies from last step, and then effuses via 2-position 2-port electromagnetic valve D and F, respectively. In the repeated way, the

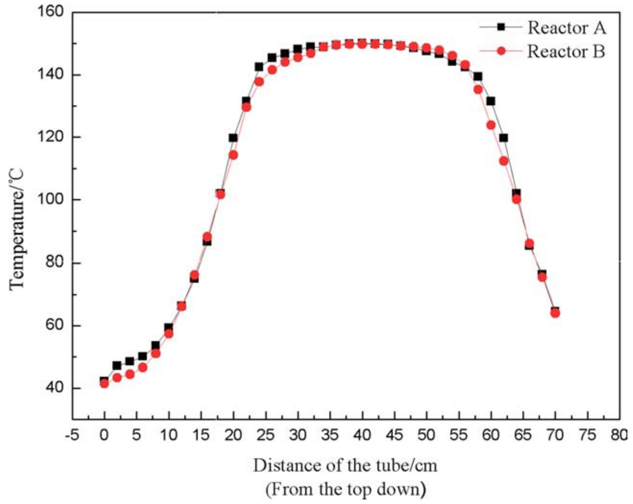

Figure 4. The temperature distribution curve of reactor A and B.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

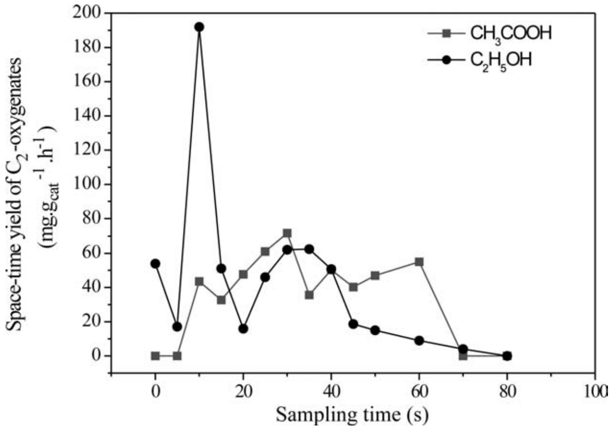

Figure 5. Formation rate of oxygenic compounds over CoPd/TiO_2 at varying sampling times.

Operation conditions: reaction temperature = 423 K, pressure = normal, CH_4 flux = 50 ml min^{-1}, H_2 of CH_4's = 10 ml min^{-1}, H_2O of CH_4's = 0.1 ml min^{-1}, CO_2 = 50 ml min^{-1}, H_2 of CO_2's = 10 ml min^{-1} and H_2O of CO_2's = 0.1 ml min^{-1}, the residence time is 1.2 s based on the flux of CH_4 or CO_2.

stepwise reaction can be carried out continuously. This improved the robustness of the overall set-up.

Catalyst preparation

Catalysts were prepared by first impregnating TiO_2 with an aqueous solution of palladium chloride, followed by air-drying at 343 K for 2 h, and calcined at 773 K for 4 h. The resultant was again impregnated with an aqueous solution of cobalt nitrate, and the drying and calcining procedure was then repeated. Overall, the palladium and cobalt loadings were 3 and 6% by weight, respectively.

Reaction procedure

The reaction was carried out in the tube reactor of 8 mm inside diameter and 700 mm height as shown in Figure 3 and catalyst loading of 1.5 g was charged to each reaction tube. The temperature was controlled by the temperature programmer and measured by thermocouples in the side of the catalyst bed. Under the temperature of 150°C, the temperature distribution curve of reactor A and B were showed in Figure 4. It can be seen that the temperature of reactor A and B between 300 and 500 mm is constant and similar with the actual temperature. The catalysts were located in the section from 350 to 450 mm and took up about the height of 20 mm. This catalyst was first exposed to a flow of nitrogen at 80 ml min^{-1} for 10 min to remove the air. Next, hydrogen was introduced into the reactors at a flow of 50 ml min^{-1}, as the temperature was raised from 298 to 673 K. The temperature was maintained for 2.5 h. The reactors were then cooled to the desired temperature under a nitrogen flow, to begin reaction. The pressure inside the reactors was controlled by back pressure regulator. All products were analyzed by on-line gas chromatography.

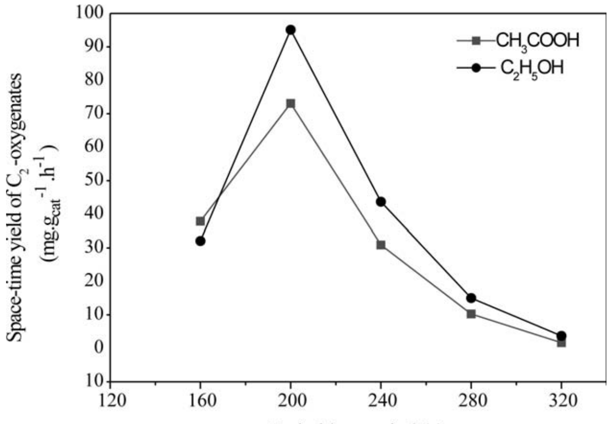

Figure 6. Formation rate of oxygenic compounds over CoPd/TiO_2 at different switching periods.

Operation conditions: reaction temperature = 423 K, pressure = normal, CH_4 flux = 50 ml min^{-1}, H_2 of CH_4's = 10 ml min^{-1}, H_2O of CH_4's = 0.1 ml min^{-1}; CO_2 = 50 ml min^{-1}, H_2 of CO_2's = 10 ml min^{-1} and H_2O of CO_2's = 0.1 ml min^{-1}.

Table 1. Influence of Feed Rates on the Space-Time Yield of Acetic Acid and Ethanol

Entry	Feed Rate of CH_4 (ml min^{-1})	Feed Rate of CO_2 (ml min^{-1})	Yield of C_2H_5OH (mg g_{cat}^{-1} h^{-1})	Yield of CH_3COOH (mg g_{cat}^{-1} h^{-1})
1	10	10	25.2	28.2
2	20	20	21.1	26.4
3	30	30	20.8	19.5
4	40	40	50.3	64.6
5	50	50	109.6	65.1
6	60	60	64.7	54.5
7	70	70	65.4	50.3
8	80	80	65.3	39.2
9	20	10	15.2	12.9
10	20	30	13.8	11.2
11	20	40	46.6	14.3

Operation condition: reaction temperature = 423 K, pressure = normal, the feed ratio of H_2 to CH_4 or CO_2 = 0.2, feed rate of H_2O= 0.1 ml min^{-1}, switching period = 200 s.

Results and Discussion

Selection of sampling times

The stepwise route is a nonstable state process, and off-gas composition varies at varying times, due to the alternate feeding of two raw gases. Thus, the change in off-gas composition with time was investigated. Figure 5 shows the space-time yield of acetic acid and ethanol at different

Table 2. Table 2 Formation rate of Oxygenic Compounds Over CoPd/TiO_2 at Different H_2 Feed Rate of CH_4's Flow

Entry	H_2 of CH_4's (ml min^{-1})	H_2 of CO_2's (ml min^{-1})	Yield of C_2H_5OH (mg g_{cat}^{-1} h^{-1})	Yield of CH_3COOH (mg g_{cat}^{-1} h^{-1})
1	0	10	55.2	47.5
2	5	10	89.8	60.2
3	6.6	10	78.3	54.8
4	10	10	46.8	40.2
5	15	10	47.2	59.5

Operation condition: reaction temperature = 423 K, pressure = normal, CH_4 feed rate = 50 ml min^{-1}, CO_2 feed rate = 50 ml min^{-1}, each flux of H_2O = 0.2 ml min^{-1}, switching period = 200 s.

Table 3. Formation Rate of Oxygenic Compounds Over CoPd/TiO_2 at Different H_2 Feed Rate of CO_2's Flow

Entry	H_2 of CH_4's (ml min^{-1})	H_2 of CO_2's (ml min^{-1})	Yield of C_2H_5OH (mg g_{cat}^{-1} h^{-1})	Yield of CH_3COOH (mg g_{cat}^{-1} h^{-1})
1	5	0	2.6	4.2
2	5	5	113.5	40.5
3	5	10	89.8	60.2
4	5	15	33.8	4.8

Operation condition: reaction temperature = 423 K, pressure = normal, CH_4 feed rate = 50 ml min^{-1}, CO_2 feed rate = 50 ml min^{-1}, each flux of H_2O = 0.2 ml min^{-1}, switching period = 200 s.

sampling times. From Figure 5, it is evident that the release time of acetic acid and ethanol ranges from 0 to 80 s, and that the amount is steady and moderate during the time period between 20 and 45 s. As such, we selected 30 s as the standard sampling time for all experiments.

Switching period

The selection of an appropriate switching period for the stepwise technology is a key link. It must guarantee that CH_4 is absorbed and activated on the catalyst adequately to form M—CH_x, while CO_2 is inserted into M—CH_x and successively hydrogenated. Figure 6 shows the formation rate of oxygenic compounds over CoPd/TiO_2 at different switching periods. It can be seen that the space-time yield of oxygenic compounds increases with the switching period increasing. When the switching period is equal to 200 s, space-time yield of oxygenic compounds is the maximum. The space-time yield of oxygenic compounds decreases with the switching period increasing subsequently. As a result, we select 200 s as the switching period for all experiments.

Effect of CH_4 *and* CO_2 *feed rates*

The influence of the CH_4 and CO_2 feed rates on space-time yields was investigated, and varying combinations of CH_4 and CO_2 feed rates are analyzed in Table 1. Evidently, the influence of both feed rates on the space-time yield of acetic acid is the same as that of ethanol. The space-time yield of ethanol and acetic acid both are higher at CH_4/CO_2 feed ratio of 1:1 when both CH_4 and CO_2 fluxes are 50 ml min^{-1}.

Influence of H_2 *feed rate*

The influence of the H_2 feed rate is shown in Tables 2 and 3. In both Tables, the H_2O feed rate of $CH_4 + H_2 + H_2O$ or $CO_2 + H_2 + H_2O$ is fixed. We determined that, when fixing the H_2 feed rate of $CO_2 + H_2 + H_2O$, the H_2 feed rate of $CH_4 + H_2 + H_2O$ does not significantly influence the yield of acetic acid, but significantly on that of ethanol. Overall, the optimal H_2 feed rate is 5 ml min^{-1}; when fixing the H_2 feed rate of $CH_4 + H_2 + H_2O$, the influence of the H_2 feed rate of $CO_2 + H_2 + H_2O$ is similar, and the optimal results were also obtained at a H_2 feed rate of 5 ml min^{-1}. Thus, when the H_2 feed rate of $CH_4 + H_2 + H_2O$ is 5 ml min^{-1} and the H_2 feed rate of $CO_2 + H_2 + H_2O$ is also 5 ml min^{-1}, the productivity of acetic acid and ethanol is maximized.

Table 4. Dependent of the Space-Time Yield of Products on Different Feed Way

Feed Way	Formation Rate (mg g_{cat}^{-1} h^{-1}) C_2H_5OH	Formation Rate (mg g_{cat}^{-1} h^{-1}) CH_3COOH
$CH_4 + CO_2/H_2$	11.2	8.2
$CO_2/H_2O + H_2$	12.4	4.2
$CO_2 + H_2O/H_2$	24.1	10.1
$CH_4 + H_2O/H_2$	55.9	7.8
$CH_4/H_2O + H_2$	51.2	6.4
$CH_4 + H_2 + H_2O/CO_2 + H_2 + H_2O$	88.3	53.1

Table 5. Influence of H_2O Feed Rate on Reaction Progress

Entry	H_2O of CH_4's (ml min^{-1})	H_2O of CO_2's (ml min^{-1})	Yield of C_2H_5OH (mg g_{cat}^{-1} h^{-1})	Yield of CH_3COOH (mg g_{cat}^{-1} h^{-1})
1	0.0	0.0	6.2	4.1
2	0.1	0.1	31.1	11.0
3	0.2	0.2	56.5	29.4
4	0.4	0.4	47.4	11.9
5	0.0	0.1	7.9	6.2
6	0.0	0.2	5.1	4.1
7	0.0	0.4	12.8	7.9
8	0.1	0.2	24.8	8.9
9	0.1	0.4	20.7	11.2
10	0.2	0.1	64.1	43.2
11	0.2	0.4	45.2	25.8
12	0.4	0.1	13.7	5.1
13	0.4	0.2	8.8	5.1

Operation conditions: reaction temperature = 423 K , pressure = normal, CH_4 feed rate = 50 ml min^{-1}, CO_2 feed rate = 50 ml min^{-1}, H_2 of CH_4's = 5 ml min^{-1}, H_2 of CO_2's = 20 ml min^{-1}, switching period = 200 s.

The fact that the feed rate of H_2 at $CH_4 + H_2 + H_2O$ is the same as that at $CO_2 + H_2 + H_2O$ suggests that the respective formation processes for acetic acid and ethanol proceed through different mechanisms. Table 4 summarized the data of the dependence of the space-time yield of products on feed way. Table 4 proposes that acetic acid arises from the reaction of CO_2 with CH_4, while ethanol is more produced by itself of CH_4.

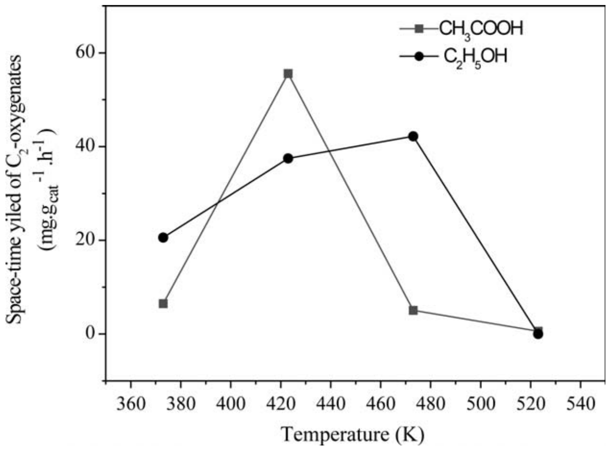

Figure 7. Formation rate of oxygenic compounds over CoPd/TiO_2 at different temperature.

Operation conditions: pressure = normal, CH_4 feed rate = 50 ml min^{-1}, CO_2 feed rate = 50 ml min^{-1}, H_2 of CH_4's = 5 ml min^{-1}, H_2 of CO_2's = 20 ml min^{-1}, each flux of H_2O = 0.2 ml min^{-1}, switching period = 200 s.

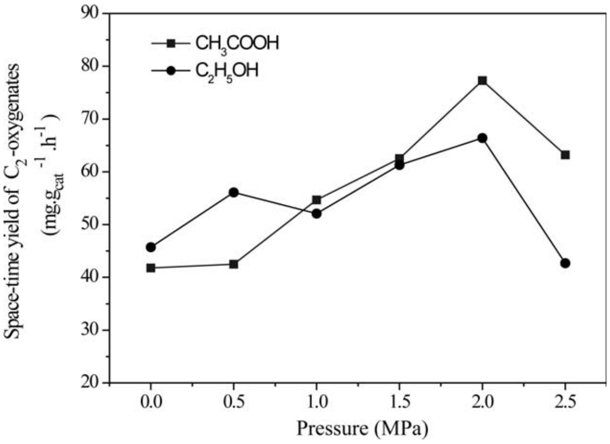

Figure 8. Formation rate of oxygenic compounds over $CoPd/TiO_2$ at varying pressures.

Operation conditions: reaction temperature = 423 K, CH_4 feed rate = 50 ml min^{-1}, CO_2 feed rate = 50 ml min^{-1}, H_2 of CH_4's = 5 ml min^{-1}, H_2 of CO_2' s = 20 ml min^{-1}, flux of H_2O = 0.2 ml min^{-1}, switching period = 200 s.

Influence of H_2O *feed rate*

H_2O is a critical component of the stepwise system. In the formation of acetic acid, it ensures product stability, preventing decomposition. In the formation of ethanol, there are two synthesis routes that are operative: either hydrogenation of acetic acid forms ethanol, in which H_2O does not participate; or CH_4 activation to $M{-}CH_x$ takes place followed by coupling and dehydrogenation to $CH_2{=}CH_2$ and hydrating to ethanol. The latter route is the preferred of the two. The influence of H_2O feed rate is shown in Table 5 and; we also highlight varying combinations of H_2O feed rate of $CH_4 + H_2 + H_2O$ and $CO_2 + H_2 + H_2O$.

Table 5 suggests that the influence of H_2O feed rate on the yields of acetic acid and ethanol is similar, and as such, when the yield of ethanol reaches a maximum, the yield of acetic acid does also. The optimal H_2O feed rate was determined to be a combination of 0.2 ml min^{-1} for $CH_4 + H_2 + H_2O$ and 0.1 ml min^{-1} for $CO_2 + H_2 + H_2O$. Additionally, the productivity is very low at any H_2O feed rate of $CO_2 + H_2 + H_2O$ when H_2O feed rate of $CH_4 + H_2 + H_2O$ is zero, which indicates that H_2O favors the activation of CH_4.

Influence of reaction temperature and pressure

The optimum temperature was confirmed by a series trial of temperatures ranging from 373 to 523 K. As shown in Figure 7, the maximum space-yield of ethanol was measured at 473 K, while that of acetic acid was measured at 423 K. The total production at 423 K is the best.

Increased pressure is advantageous to the reaction with regard to the global reaction Eq. 3, but, as for the stepwise technology, two steps are both limiting steps. The second step is accelerated by an increase in pressure, while the effect is dual for the first step, as evident from reaction Eq 1. The effect of pressure is positive when $x > 2$ and negative when $x < 2$; there is no effect when $x = 2$. Prior precedent[4–7] has shown that the coupling of CH_4 via a two-step reaction sequence is decelerated by increased pressure. Figure 8 shows the dependence of reaction progress on pressure. Overall, increased pressure (up to 2.0 MPa) results in more productive synthesis of acetic acid and ethanol. Between 2.0 and 2.5 MPa, the overall productivity is decreased, highlighting the dual effects of pressure.

Conclusions

The work presented herein describes a continuous stepwise reactor design, which adopts a dual-reactor system bearing electromagnetic valves in the front and rear of the dual-reactor system. Our experimental results have tested and subsequently validated this design. We successfully achieved an efficient production of both acetic acid and ethanol by using the new reactor system, with overall optimal yields obtained at a highest temperature of 423 K, pressure of 2.0 MPa, a switch time of 200 s, catalyst mass of 1.5 g per reactor, space-velocities of CH_4 at 50 ml min^{-1}, CO_2 at 50 ml min^{-1}, H_2 of CH_4's at 5 ml min^{-1}, H_2 of CO_2's at 5 ml min^{-1}, H_2O of CH_4's at 0.2 ml min^{-1}, and H_2O of CO_2's at 0.1 ml min^{-1}. When compared with previous processes, the new reactor system improved overall efficiency of production of acetic acid and ethanol by over 5–10 times. This work also indicates that acetic acid arises from the reaction of CO_2 with CH_4, while ethanol is more produced by itself of CH_4.

Acknowledgments

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