In-Situ FT-IR Spectroscopy Investigation of CH$_4$ and CO$_2$ Reaction

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Abstract: An exclusive trace of CH$_4$ direct carboxylation with CO$_2$ by a stepwise technology was investigated using in-situ FT-IR spectroscopy. The results showed that CH$_4$ was dissociated to atomic hydrogen and M-CH$_x$ species on catalyst surface when it was first introduced in the system, then CO$_2$ was inserted into the intermediate to direct carboxylate. Finally, the subsequent adsorption of CH$_4$ provided active hydrogen for the species of previous surface reaction, thus leading to the formation of the product. It was also found that the first introduction of CO$_2$ on the surface of the “clean” catalyst might likely react with surface H species, which had an irreversible effect on the catalytic activity of CH$_4$.

Keywords: CH$_4$; CO$_2$; CH$_3$COOH; step-wise route; in-situ FT-IR; Cu-Co

1. Introduction

Chemical conversion of CO$_2$ into value-added fuels and chemicals is regarded as an attractive strategy to simultaneously reduce the CO$_2$ emissions and relieve the shortage of fossil-fuels both in the energy and chemical industries [1]. To date, much attention has been paid to CO$_2$ hydrogenation routes [2]. However, the high energy and H$_2$ consumptions, as well as the rigor operating conditions related to this process, are major challenges.

Instead of using H$_2$, the high H/C ratio and abundant reserves of CH$_4$ make it a viable source of both energy and hydrogen for CO$_2$ conversion. In fact, CH$_4$ is an ideal H supplier to replace H$_2$, while CO$_2$ can provide oxygen for the chemical fixation of CH$_4$. Thus, the simultaneous conversion of CO$_2$ and CH$_4$ to C$_2$$_x$ oxygenates (e.g., acetic acid) is an ideal combination of a reduction reaction and an oxygenation reaction. Moreover, due to the stoichiometric ratio of C and O atoms, the co-conversion of CO$_2$ and CH$_4$ into acetic acid (CO$_2$ + CH$_4$→CH$_3$COOH) is 100% atom economy, which can increase the atom utilization and avoid the formation of H$_2$O comparing with CO$_2$ hydrogenation. Unfortunately, the reaction is thermodynamically unfavorable under moderate conditions ($\Delta G_{298K} = 71.2$ kJ/mol). Many works are devoted to selectively break the C–H bond in CH$_4$ and simultaneously utilize the inertness of CO$_2$ to realize C-C coupling for the synthesis of high-value chemicals [3–7]. Most of these works are based on theoretical calculation and experiments which always require additional energy supply (such as plasma), few in-situ characterizations studies have been conducted. Weng et al. [8] employed in-situ time-resolved FT-IR to investigate the partial oxidation of methane to syngas at 500 $^\circ$C, which indicated that significant different mechanisms were proceeded over supported Rh and Ru catalysts. Besides, the in-situ FT-IR spectroscopy was also conducted to investigate the surface reaction of CH$_4$ with NO$_x$ species [9–12].
Our group was committed to investigating the direct conversion of CH$_4$ with CO$_2$ to acetic acid by stepwise reaction technology (Scheme 1) that bypassed the thermodynamic limitation and demonstrated the feasible and efficient through initial experiments in micro-reactor units at low temperatures over Cu-Co and Co-Pd catalyst [13–15]. However, the possible reaction intermediates in this process had not been elucidated. In addition, to the best of our knowledge, there were no detailed studies focus on direct carboxylation of CH$_4$ to investigate the reaction mechanism over Cu-Co catalyst at a lower temperature using in-situ technologies. Therefore, in this study, an exclusive trace of adsorbed CH$_4$ direct carboxylation with CO$_2$ was performed using the stepwise technology by in-situ FT-IR spectroscopy to gain a deeper understanding of the results of the interaction between CH$_4$ and CO$_2$.

![Scheme 1](image)

**Scheme 1.** Stepwise reaction technology for direct synthesis of CH$_3$COOH from CO$_2$ and CH$_4$.

2. Results

2.1. Blank Experiment

Figure 1a showed the FT-IR spectra of pure SiO$_2$ (diluent in this experiment) exposed in CH$_4$ for the first time after pretreatment in N$_2$ for 1 h. The SiO$_2$ also underwent the same reduction and purging process under N$_2$ atmosphere as that of the catalyst sample. One could see that the intensity of the two main absorption bands at 3015 cm$^{-1}$ and 1302 cm$^{-1}$ gradually increased with the introduction of CH$_4$, which was assigned to the adsorption of gas CH$_4$ and weak adsorption CH$_4$, respectively [16,17]. Amplification of 1400 cm$^{-1}$–2200 cm$^{-1}$ (see Figure 1e) showed that there were two broad hydroxyl absorption peaks at 1687 cm$^{-1}$ and 1524 cm$^{-1}$, which gradually became clear and stable with the increase of contact time.

![Figure 1a](image)

Figure 1b was the FT-IR spectra under N$_2$ purging after the first cycle of CH$_4$ adsorption. It could be seen that the peaks of CH$_4$ absorption at 3015 cm$^{-1}$ and 1302 cm$^{-1}$ gradually decreased and disappeared, while these OH absorption peaks at 1687 cm$^{-1}$, 1524 cm$^{-1}$ and 3200 cm$^{-1}$–3800 cm$^{-1}$ slightly increased with the purge of N$_2$. After N$_2$ purging, the C–H absorption could hardly be observed at 2950 cm$^{-1}$ and 2864 cm$^{-1}$, indicating that CH$_4$ could not be activated on the “clean” SiO$_2$.

![Figure 1b](image)

After N$_2$ purging, the pure SiO$_2$ was exposed in CO$_2$ for the first time and the corresponding IR spectra was presented in Figure 1c. It could be seen that few changes of the adsorbed species on the surface were observed except at 1687 cm$^{-1}$ and 1524 cm$^{-1}$, indicating that no significant surface reaction had been taken place. In the following series of repetitive cycles, the intensity of peak at 1690 cm$^{-1}$ and 1530 cm$^{-1}$ further increased, and two weak peaks at 2950 cm$^{-1}$ and 2864 cm$^{-1}$ were found, which might be the result of the interaction between CO$_2$ and CH$_4$ (Figure 1d).

![Figure 1c](image)

In conclusion, the above experiments demonstrated that the CH$_4$ activation and the co-conversion with CO$_2$ on pure SiO$_2$ were extremely weak under the reaction conditions.
Figure 1. FT-IR spectra of SiO\textsubscript{2} exposed in different atmospheres. (a) Exposed in CH\textsubscript{4} for the first time; (b) Exposed in N\textsubscript{2} after the first time of CH\textsubscript{4} adsorption; (c) Exposed in CO\textsubscript{2} for the first time; (d) IR spectra after alternate feeds of CH\textsubscript{4} and CO\textsubscript{2} three times; (e) Amplification of 1400 cm\textsuperscript{−1}–2200 cm\textsuperscript{−1} when SiO\textsubscript{2} exposed in CH\textsubscript{4} for the first time.

2.2. Cu-Co Catalyst Sample Experiment

Figure 2 displayed the FT-IR spectra of Cu-Co catalyst for the first cycle of CH\textsubscript{4} adsorption, N\textsubscript{2} purge, and CO\textsubscript{2} adsorption. As seen, compared with pure SiO\textsubscript{2}, obvious C-H absorption peaks could be observed in the region of 2800 cm\textsuperscript{−1}–3000 cm\textsuperscript{−1} after the adsorption of CH\textsubscript{4} (see Figure 2a). Besides, the peaks of 1690 cm\textsuperscript{−1} and 1530 cm\textsuperscript{−1} appeared faster and stronger (Figure 2b). Moreover, with the introduction of CH\textsubscript{4}, negative peaks appeared in the region of 3200 cm\textsuperscript{−1}–3800 cm\textsuperscript{−1} which belonged to hydroxyl, and the peaks intensity decreased slightly when CO\textsubscript{2} was introduced (Figure 2c). These results suggested that CH\textsubscript{4} had been activated on Cu-Co catalyst surface, which would be discussed later.
After N₂ purging, the pure SiO₂ was exposed in CO₂ for the first time and the corresponding IR spectra was presented in Figure 1c. It could be seen that few changes of the adsorbed species on the surface were observed except at 1687 cm⁻¹ and 1524 cm⁻¹, indicating that no significant surface reaction had been taken place. In the following series of repetitive cycles, the intensity of peak at 1690 cm⁻¹ and 1530 cm⁻¹ further increased, and two weak peaks at 2950 cm⁻¹ and 2864 cm⁻¹ were found, which might be the result of the interaction between CO₂ and CH₄ (Figure 1d).

In conclusion, the above experiments demonstrated that the CH₄ activation and the co-conversion with CO₂ on pure SiO₂ were extremely weak under the reaction conditions.

### 2.2. Cu-Co Catalyst Sample Experiment

Figure 2 displayed the FT-IR spectra of Cu-Co catalyst for the first cycle of CH₄ adsorption, N₂ purge, and CO₂ adsorption. As seen, compared with pure SiO₂, obvious C-H absorption peaks could be observed in the region of 2800 cm⁻¹–3000 cm⁻¹ after the adsorption of CH₄ (see Figure 2a). Besides, the peaks of 1690 cm⁻¹ and 1530 cm⁻¹ appeared faster and stronger (Figure 2b). Moreover, with the introduction of CH₄, negative peaks appeared in the region of 3200 cm⁻¹–3800 cm⁻¹ which belonged to hydroxyl, and the peaks intensity decreased slightly when CO₂ was introduced (Figure 2c). These results suggested that CH₄ had been activated on Cu-Co catalyst surface, which would be discussed later.

Figure 2. FT-IR spectra of Cu-Co catalyst exposed in different atmospheres for the first cycle (a) CH₄; (b) N₂; (c) CO₂.

Figure 3 showed the FT-IR spectra of CH₄/CO₂ repeated feeds. The peaks intensity of 3200 cm⁻¹–3800 cm⁻¹, 2700 cm⁻¹–3000 cm⁻¹, and 1400 cm⁻¹–1700 cm⁻¹ continued to increase with CH₄/CO₂ repeated feeding into the reaction, indicating that the activation and surface reaction of CH₄ and CO₂ were further proceeding. Meanwhile, the results demonstrated that the generated species accumulated on the catalyst surface.
3. Discussion

3.1. Activation of CH$_4$ on “Clean” Catalyst Surface

Generally, the characteristic absorption of C–H bond occurred in three regions: 3000 cm$^{-1}$–2700 cm$^{-1}$, 1475 cm$^{-1}$–1300 cm$^{-1}$ and 1000 cm$^{-1}$–650 cm$^{-1}$ [18]. Among them, 1000 cm$^{-1}$–650 cm$^{-1}$ fell in the fingerprint area, and there were many influence factors that were
complex and difficult to give an unequivocal identification. For 1475 cm\(^{-1}\)–1300 cm\(^{-1}\), since the SiO\(_2\)
had a strong absorption and coverage, the variation was difficult to observe. Therefore, this study mainly focused on the C–H bond absorption in the region of 3000 cm\(^{-1}\)–2700 cm\(^{-1}\).

In the first cycle, CH\(_4\) was introduced after the catalyst was reduced and swept by N\(_2\) for 1 h. Thus, it was considered that the interaction between CH\(_4\) and the catalyst was carried out on a “clean” surface, reflecting the activation of CH\(_4\) by the catalyst itself. Compared with pure SiO\(_2\), Figure 2b clearly showed that the bonds in the region of 2800 cm\(^{-1}\)–3000 cm\(^{-1}\) increased significantly on the Cu-Co catalyst, indicating that CH\(_4\) had been activated by the catalyst.

With the introduction of CH\(_4\), a large negative peak appeared in the OH absorption region at 3200 cm\(^{-1}\)–3800 cm\(^{-1}\) (Figure 2a,b). The intensity of the peak increased with the increase of contact time, while it decreased slightly after the introduction of CO\(_2\). The appearance of negative peaks indicated that OH groups were continuously consumed during the process of CH\(_4\) adsorption and activation. According to the literature [16], it was pointed out that the adsorbed methyl groups on metal sites could react with OH groups and then spilled onto the carrier. In this process, the following reactions were most likely to occur. Take Cu/SiO\(_2\) as an example:

$$\text{Si-OH} + \text{Cu-CH}_3 \rightarrow \text{SiOCH}_3 + \text{1/2H}_2 + \text{Cu}.$$  

Therefore, it was suggested that the decrease of surface OH in this study was due to the interaction between surface C–H species and adjacent OH groups, which caused the transition of CH\(_4\) activation site to inactive site. Obviously, the spillover of these CH\(_x\) species on the surface favored to empty the metal active sites and thus activated more amount of CH\(_4\).

3.2. Reaction of Adsorbed CH\(_4\) and CO\(_2\)

After the first introduction of CH\(_4\), pure N\(_2\) was purged to remove the free and weakly adsorbed CH\(_4\) for 20 min, CO\(_2\) was then introduced to investigate the reaction between CO\(_2\) and surface species. Rasko and Solymosi [19,20] studied the reaction of CH\(_3\) species (formed by the decomposition of diazomethane) with CO\(_2\) on different carriers and metal surfaces. The results showed that the adsorbed CH\(_3\) species could react with CO\(_2\) to produce CO and H\(_2\)O under very mild conditions even at room temperature. The reason was that the introduction of CO\(_2\) led to the decrease or even disappearance of the CH\(_3\) species peak at 2800 cm\(^{-1}\)–3000 cm\(^{-1}\), and the generation of CO also could be detected. However, in our study, the introduction of CO\(_2\) did not lead to the consumption of adsorbed CH\(_x\) species. On the contrary, these CH\(_x\) species increased. The results indicated that, on the one hand, there was no reaction occurred between surface CH\(_2\) species and CO\(_2\) to form CO and H\(_2\) under the used catalyst and experimental conditions. On the other hand, it also suggested that CO\(_2\) might react with surface H species deriving from CH\(_4\) activation, which led to the rise of surface hydroxyl species. The two aspects were consistent with our previous experimental results [13].

3.3. Activation of CH\(_4\) on “Polluted” Catalyst Surface

The adsorption and activation of CH\(_4\) on the “polluted” catalyst surface could be divided into two situations: One was that the surface of the reduced “clean” catalyst was first filled with CO\(_2\), and then CH\(_4\) was introduced after N\(_2\) purge for 20 min. Another was that CH\(_4\) was re-introduced after a cycle of reaction, at which time the catalyst surface was adsorbed by CO\(_2\). Figure 4a was the FT-IR spectra when CO\(_2\) was first introduced. It was shown that no CH\(_x\) species were formed on the surface of “clean” catalysts when CO\(_2\) was first introduced, suggesting that there was no adsorbed hydrogen on the catalyst surface after reduction and N\(_2\) purging process for 1 h, thus no hydrogenation reaction occurred. When CH\(_4\) was introduced, surface CH\(_x\) species were generated (Figure 4b). Compared with the first introduction of CH\(_4\), the intensity and peak type of CH\(_x\) species changed greatly, while the peak position had negligible changes. Although no strict quantitative determination had been made in this experiment, the ratio of catalyst and diluent in each sample was almost the same. Thus, it
was concluded that the decrease in the peak area of CH$_x$ species was caused by the first adsorption of CO$_2$. Considering that the position of CH adsorption peak moved from 2939 cm$^{-1}$ to 2963 cm$^{-1}$, it was considered that the first introduction of CO$_2$ led to the oxidation of catalyst active components.

The peak intensity of CH$_x$ species with the introduction of CH$_4$ in different cycles was presented in Figure 5. It could be seen that the peak intensity of CH$_x$ species increased linearly in the first cycle, whereas the peak intensity first decreased and then increased for other cycles. This was mainly due to that the first cycles occurred on the “clean” surface of the catalyst, while the adsorption and activation of CH$_4$ were carried out on a “non-clean” surface for others. Obviously, on the “polluted” catalyst surface, the subsequent passing of CH$_4$ provided hydrogen for the hydrogen-deficient species generated in the previous cycle. Meanwhile, one also could see that the degree of reduction increased with the accumulation of CH$_x$ species on the surface, which indicated that the desorption of these CH$_x$ species occurred on the catalyst surface. These results explained the formation of CH$_3$COOH, HCOOH and other oxygenated products without the condition of H$_2$ supplementation using the stepwise technology. Obviously, it could be inferred that the direct conversion of CH$_4$ and CO$_2$ to CH$_3$COOH by two-step reaction without hydrogen replenishment was due to that the subsequent adsorption of CH$_4$ provided thermodynamic power for the previous step, thus leading to the formation of products, which was also consistent with our previous experimental results [13]. The relevant reaction process could be described as follows:

$$\text{CH}_4 + \text{M} \rightarrow \text{CH}_3\text{M} \rightarrow \text{CH}_4\text{CO}_2\text{M} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_x\text{M}$$
4. Experimental

4.1. Catalyst Preparation

Cu-Co catalyst was synthesized by a co-precipitation method. The Cu:Co atomic ratio in the starting solution was kept at 1:1. Typically, two aqueous solutions, a solution of Cu(II), Co(II) nitrates (analytical reagent, Tianjin, China) and a mixed solution of Na₂CO₃ (analytical reagent, Tianjin, China) precipitant, were added dropwise to 250 mL of deionized water under vigorous stirring. The pH value was maintained at 6–8. The precipitate was aged at 343 K for 1 h under stirring, and filtered, washed, dried at 393 K for 16 h, and then calcined at 623 K for 6 h. The as-synthesized catalyst was crushed and sieved to particles in the range of 40–60 meshes before use.

4.2. Test of In-Situ FT-IR

The in-situ FT-IR experiments were performed on a Perkin Elmer Spectrum 2000 FT-IR spectrometer (PerkinElmer, USA). The above catalyst was mixed with high purity SiO₂ to make thin sheets and placed in in-situ IR cells for the test. Before the experiment, the catalyst was reduced in 10% H₂/N₂ at a flow rate of 20 mL/min under atmospheric pressure. The reduction temperature was programmed to increase from room temperature to 473 K with a heating rate of 5 K/min and maintained at 473 K for 2 h. After reduction, the reaction system was purged with N₂ at 473 K for 1 h. Then CH₄ and CO₂ were alternately switched to react, during which N₂ was purged with 20 min or not. At the same time, the spectral data were recorded using TimeBase software (PerkinElmer company, MA, USA) at the frequency of one graph per minute.
5. Conclusions

In conclusion, a possible reaction mechanism for the direct conversion of CH$_4$ and CO$_2$ to CH$_3$COOH by a step-wise technology had been proposed based on the in-situ FT-IR spectroscopy. Results showed that CH$_4$ was dissociated to atomic hydrogen and M-CH$_x$ species on catalyst surface when it was first introduced in the system, then CO$_2$ was inserted into the intermediate to direct carboxylate. Finally, the subsequent CH$_4$ adsorption provided active hydrogen for the species of previous surface reaction, thus leading to the formation of the product. The activated CH$_4$ also could be transferred to unreduced oxides through interaction with adjacent hydroxyl groups, which favored to empty the metal active sites and thus greatly enhanced the catalytic activity of CH$_4$. However, the first introduction of CO$_2$ on the surface of the “clean” catalyst might likely react with surface H species, which had an irreversible effect on the catalytic activity of CH$_4$.

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