Catalytic Co-Conversion of CH₄ and CO₂ Mediated by Rhodium–Titanium Oxide Anions RhTiO₂⁻

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Abstract: Catalytic co-conversion of methane with carbon dioxide to produce syngas (2H₂ + 2CO) involves complicated elementary steps and almost all the elementary reactions are performed at the same high temperature conditions in practical thermocatalysis. Here, we demonstrate by mass spectrometric experiments that RhTiO₂⁻ promotes the co-conversion of CH₄ and CO₂ to free 2H₂ + CO and an adsorbed CO (CO_ads) at room temperature; the only elementary step that requires the input of external energy is desorption of CO_ads from the RhTiO₂CO⁻ to reform RhTiO₂⁻. This study not only identifies a promising active species for dry (CO₂) reforming of methane to syngas, but also emphasizes the importance of temperature control over elementary steps in practical catalysis, which may significantly alleviate the carbon deposition originating from the pyrolysis of methane.

The production of chemical feedstocks from catalytic co-conversion of methane and carbon dioxide, two abundant substances occurring in nature, reduces chemical industry’s dependency on traditional fossil fuels and contributes to the mitigation of the greenhouse effect.¹ Dry (CO₂) reforming of methane[²] [DRM, reaction (1)] is a potential route to produce syngas (a mixture of carbon monoxide and hydrogen) that is a crucial feedstock for alcohols, olefins, and Fischer–Tropsch products.³ However, the inherent stability of both molecules, CH₄ and CO₂, as well as the highly endothermic nature of DRM to syngas requires this thermo-catalysis to be run at high temperatures (T > 1000 K), which inevitably leads to coke deposition and catalyst deactivation.⁴ Identifying each elementary step of a catalytic cycle offers the possibility to precisely optimize the reaction process and reduce energy consumption. However, catalytic DRM to syngas involves adsorption of CH₄ and CO₂, activation of four C–H bonds to dehydrogenate methane, cleavage of C=O bonds in CO₂, H–H and C₃H₆–O₃CO coupling, and desorption of two H₂ and two CO molecules, making it experimentally challenging to follow each of the elementary steps in condensed phase studies.

Gas phase reactivity studies of isolated chemical species that compositionally resemble the local active sites of condensed phase catalysts provide a unique approach to probe the reaction intermediates and understand the molecular-level details of elementary steps involved in the catalytic reactions of practical importance.⁵ While a great number of chemical entities (e.g., polyatomic clusters) have been experimentally discovered to activate CH₄⁶–⁸ or CO₂⁶–⁸ under specific reaction conditions, the number of identified species that promote the co-conversion of CH₄ and CO₂ is very limited to date.⁹ The atomic cation Ta⁺ is able to co-convert one CH₄ and two CO₂ molecules to H₂ + CO + C₃H₆O at room temperature, but the resulting TaO₂⁺ is difficult to reduce to Ta⁺.¹⁰ Although catalytic co-conversion of CH₄ and CO₂ was later established over the bimetallic oxide anion RhVO₄⁻, only co-adsorption of CH₄ and CO₂ takes place at room temperature. An increase in the reaction temperature leads to efficient formation of methyl radicals.¹¹ Very recently, selective DRM was achieved at room temperature by using Rh₃VO₃⁺ anions in combination with photo-irradiation to produce the second H₂ and CO molecules.¹² Herein, we demonstrate that RhTiO₂⁻ co-converts CH₄ and CO₂ to 2H₂ + CO at room temperature without photo-irradiation. The only elementary step that requires input of external energy to complete the catalytic cycle is the desorption of the second CO molecule.

Figures 1 and S1 show the mass spectra for the reactions of mass-selected RhTiO₂⁻ anions (I) with CH₄ and CO₂ in a linear ion trap reactor at room temperature under thermal
The reaction times are 1.6 ms for (b,g) and 2.5 ms for (c–f). The first for 1.6 ms, all of the RhTiO$_2$ determined as (2.2\ Angew. Chem. Int. Ed.\[0.2]\)

Figure 1. Mass spectra for the reactions of RhTiO$_2$ with He (a) and 0.90 Pa CH$_4$ (b), RhTiO$_2$CH$_4$, with 0.05 Pa CO$_2$ (c), RhTiO$_2$CO$_2$ with 0.03 Pa CO (d), RhTiO$_2$CH$_4$, with 0.03 Pa C$^{18}$O$_2$ (e), and RhTiO$_2$C$^{13}$CH$_4$, with 0.03 Pa CO$_2$ (f) in the single ion trap experiment in which methane and carbon dioxide are delivered into the same ion trap. Panel (g) shows the mass spectrum for the reaction of mass-selected product ion RhTiO$_2$C$^{13}$CH$_4$, with 0.02 Pa CO$_2$ in the double ion trap experiment in which methane and carbon dioxide are delivered into different ion traps. The arrows show the loss of neutral products from the ionic species or the adsorption of methane onto the ionic species. The reaction times are 1.6 ms for (b,g) and 2.5 ms for (c–f). The spectra for collision-induced dissociation (CID) of RhTiO$_2$C$^{13}$CH$_2$O$^-$ (h), RhTiO$_2$C$^{13}$CH$_2$O$^-$ (i), and RhTiO$_2$CH$_2$O$^-$ (j) generated from the reactions of RhTiO$_2^-$ with C$^{13}$CH$_4$/CH$_4$ and CO$_2$ in the same ion trap are shown in the bottom three panels in which the center-of-mass collisional energies are shown.

collision conditions. Upon the interaction with 0.90 Pa CH$_4$, at first for 1.6 ms, all of the RhTiO$_2^-$ anions were depleted and transformed to the adsorption product RhTiO$_2$CH$_4^-$. [2, Figure 1b and reaction (2a)]. Only very small amounts of RhTiO$_2$CH$_2$ ions are dehydrogenated giving rise to the formation of RhTiO$_2$CH$_2^-$(2-H$_2$) + H$_2$ [reaction (2b)]. The isotopic labeling experiment with CD$_4$ (Figure S2) confirms the formation of the adsorption product, but the desorption of D$_2$ molecules did not occur. The pseudo-first (second) order rate constant ($k_1$) for the reaction of RhTiO$_2^-$ with CH$_4$ was determined as $(2.2 \pm 0.4) \times 10^{-11}$ cm$^3$ s$^{-1}$ (Figure S2), corresponding to a reaction efficiency of $(2.2 \pm 0.4)\%$.\[0.2]\] The kinetic isotopic effect ($k_{\text{CH}_4}/k_{\text{CD}_4}$) was estimated to be $1.3 \pm 0.2$.

RhTiO$_2^-$ + CH$_4$ $\rightarrow$ RhTiO$_2$CH$_4^-$  \hspace{1cm} (2a)

$\rightarrow$ RhTiO$_2$CH$_2^-$(2-H$_2$) + H$_2$  \hspace{1cm} (2b)

After all of the RhTiO$_2^-$ anions were converted to RhTiO$_2$CH$_4^-$, CO$_2$ molecules were pulsed into the ion trap and several new product signals appeared. Figure 1c reveals that in addition to the co-adsorption complex RhTiO$_2$CH$_2$O$^-$ (3), a strong peak assigned to RhTiO$_2$CH$_2$O$^-$ (P1) was observed, corresponding to the loss of the first H$_2$ molecule [reaction (3a)]. A CO molecule can desorb from P1 to form an appreciable amount of RhTiO$_2$CH$_2$O$^-$(P2 = P1–CO, reaction (3b)). The detection of RhTiO$_2$CO$^-$ (P3 = P2–H$_2$) with relatively weak intensity implies that desorption of the second H$_2$ molecule from P2 [reaction (3c)] is possible, but less efficient. Summarizing, RhTiO$_2^-$ promotes the co-conversion of CH$_4$ and CO$_2$ to two free H$_2$ molecules, one free CO molecule (2H$_2$ + CO, syngas) at room temperature. Note that a product peak assigned to RhTiO$_2$CO$_2^-$ generated from the CH$_4$/CO$_2$ exchange was also observed [reaction (3d)]. Isotopic labeling experiments with CD$_4$ (Figure 1d) confirm the reaction channels (3a)–(3d).

RhTiO$_2$CH$_4^-$ + CO$_2$ $\rightarrow$ RhTiO$_2$CH$_2$O$^-$(2H$_2$) + H$_2$  \hspace{1cm} (3a)

$\rightarrow$ RhTiO$_2$CH$_2$O$^-$(2H$_2$) + H$_2$ + CO  \hspace{1cm} (3b)

$\rightarrow$ RhTiO$_2$CO$^-$(2H$_2$) + 2H$_2$ + CO  \hspace{1cm} (3c)

$\rightarrow$ RhTiO$_2$CO$_2^-$ + CH$_4$  \hspace{1cm} (3d)

RhTiO$_2$CO$_2^-$ + CH$_4$ $\rightarrow$ RhTiO$_2$CH$_2$O$^-$ + 2H$_2$  \hspace{1cm} (4)

To clarify the O- and C-atom source for CO production, additional isotopic labeling experiments with C$^{13}$O$_2$ and C$^{18}$H$_4$ were conducted. Identification of the product ions RhTiO$_2$C$^{13}$H$_4$C$^{18}$O$_2$ and RhTiO$_2$C$^{13}$CH$_4$C$^{18}$O$_2$ upon the interaction of RhTiO$_2$CH$_4^-$ with C$^{13}$O$_2$ (Figure 1e) shows that the O atom in CO originates from either CO$_2$ or RhTiO$_2^-$, Next to the product ion RhTiO$_2$C$^{13}$H$_4$C$^{18}$O$_2^-$, two new signals of RhTiO$_2$C$^{13}$H$_2$C$^{18}$O$_2^-$ and RhTiO$_2$C$^{13}$C$^{18}$H$_2$O$_2^-$ were observed in the reaction of RhTiO$_2$C$^{13}$H$_2$O$_2^-$(P1, Figure 1f), indicating that both CH$_4$ and CO$_2$ can provide a carbon atom for CO generation. Moreover, the weak peaks corresponding to RhTiO$_2$C$^{13}$H$_2$C$^{18}$O$^-$, RhTiO$_2$C$^{13}$CO$^-$, and RhTiO$_2$C$^{13}$CO$^-$ in Figure 1c,f confirm desorption of the second H$_2$ molecule.

In order to confirm the proposed sequential desorption mechanism, we spatially separated the addition of the reactants using two ion trap reactors (instead one). Product ions RhTiO$_2$C$^{13}$H$_2$ were produced in the first reactor, mass-selected and then interacted with a gas pulse of CO$_2$ in the second ion trap reactor (Figure 1g). These experiments unambiguously confirm the reactions (3a)–(3d). However, the RhTiO$_2$C$^{13}$H$_2$CO$^-$ product was absent, implying that the co-adsorption complexes (3, 3 I, 3 II, and 3 III) observed in Figure 1c–f originated from the methane adsorption onto RhTiO$_2$CO$_2^-$/RhTiO$_2$C$^{13}$O$_2^-$(reaction (4)). The CID experiments of mass-selected intermediate complexes RhTiO$_2$C$^{13}$H$_2$O$_2^-$(3III, Figure 1f), RhTiO$_2$C$^{13}$H$_2$CO$_2^-$ (P1, Figure 1f), and RhTiO$_2$C$^{13}$H$_2$O$_2^-$ (P2, Figure 1c) with Xe were also conducted. The loss of CO and CO$_2$ molecules from P1 and the loss of H$_2$ from P2 correspond to reaction channels
(3b) and (3c), respectively. The desorption of $^{13}$CH$_4$ molecule from 3$^{13T}$ supports reaction (4).

These experimental results demonstrate that CH$_4$ and CO$_2$ are co-converted to $2H_2 + CO$ at room temperature in the presence of RhTiO$_2$ and form RhTiO$_2$CO as the product ion. The CID experiments of mass-selected RhTiO$_2$CO$^-$ with Xe were carried out. When the center-of-mass collisional energy was increased to above 3 eV, the loss of the second CO and regeneration of RhTiO$_2$ were observed [Figure S3 and reaction (5)]. Thus, a catalytic cycle involving DRM to syngas [reaction (1)] over RhTiO$_2$ was experimentally achieved. Note, no co-conversion was observed when the reaction gases were applied to the ion trap in reverse order, first CO$_2$ followed by CH$_4$ (Figures S4 and S5).

$$\text{RhTiO}_2\text{CO}^{-} \rightarrow \text{RhTiO}_2 + \text{CO} \quad (5)$$

The structure of the RhTiO$_2$$^-$ anion was characterized by photoelectron spectroscopy (PES) combined with density functional theory (DFT) calculations (Figure S6).[10] The lowest-lying isomer of RhTiO$_2$$^-$ is a singlet that has a three-membered ring of Rh-Ti-O with a terminal oxygen (O) atom connected to Ti. Due to the absence of a reactor coupled with our PES apparatus and the relatively low ion intensities of reaction products, the structures of RhTiO$_2$CH$_2^{-}$, RhTiO$_2$CH$_2$CO$_2^{-}$, RhTiO$_2$CH$_2$O$^-$, and RhTiO$_2$CO$^-$ were not experimentally characterized. The possible structures of these ionic species were computationally determined.

The most favorable pathways for the reactions of RhTiO$_2^-$ with CH$_4$ and RhTiO$_2$CH$_4$ with CO$_2$ are shown in Figures 2, S7–S11. Methane binds to the Rh atom of RhTiO$_2$ under activation of the first C–H bond by oxidative addition (I$_1$–I$_2$) and formation of the stable intermediate I$_2$. This is followed by the cleavage of the Rh–O bond in I$_2$, H-atom transfer from the Rh atom to the O$_2$ atom (I$_2$–I$_3$), activation of the second C–H bond by the Rh atom and formation of I$_4$, which contains a Rh–H bond, an OH group, and a three-membered Rh-CH$_2$-Ti ring. Dehydrogenation of I$_4$ to RhTiO$_2$CH$_2$ is not feasible due to high activation energy barriers (1.24–1.28 eV of I$_4$–TS13/TS15 in Figure S7) and the hot I$_4$ is stabilized by collisions with the buffer gas (He), in agreement with the experimental observation that the RhTiO$_2$CH$_2$ mass peak dominates the mass spectrum (Figure 1b).

The reaction of RhTiO$_2$CH$_2^-$ (I$_4$) with CO$_2$ commences with the adsorption of CO$_2$ and its activation involving the formation of a Rh–C bond in the encounter complex I$_5$. Next, one of the C–O bonds is cleaved (I$_5$–I$_6$ and I$_6$–I$_7$, Figure S8); during this process, the H atom originally bound to Rh transfers to one of the O atoms (I$_2$–I$_3$ and I$_6$–I$_7$ in Figures 2 and S8), resulting in formation of the lowest energy structure, intermediate I$_7$ (Figure S11), which consists of a four-membered O-Rh-CH$_2$-Ti ring, two (Ti)-OH groups, and a (Rh)–CO moiety. One of the hydroxy H atoms then transfers back to Rh and H$_2$C–O coupling occurs (I$_7$–I$_{24}$–I$_{25}$ in Figure S8). Subsequently, the Rh–O bond is ruptured, followed by the successive activation of the third and the fourth C–H bond by the Rh atom (I$_{25}$–I$_{18}$–I$_{19}$) and formation of I$_9$ containing a Rh–C–O–Ti moiety. After a series of structural rearrangements involving the CO moiety and H-atom transfers (I$_9$–I$_{10}$, I$_{10}$, which contains two (Rh)–CO moieties, two bridging and one terminal H atoms, is formed. After several more conversion steps, during which one of the CO moieties in I$_{10}$ moves towards the Ti atom, molecular hydrogen is formed and evaporated to produce RhTiO$_2$CH$_2$CO$_2^-$ (P1, $\Delta H_d = -3.28$ eV).

P1 still possesses sufficient internal energy to enable desorption of the first CO molecule (P2, $\Delta H_d = -1.71$ eV) as well as the subsequent desorption of the second H$_2$ molecule (P3, $\Delta H_d = -0.59$ eV; in the case that the RhTiO$_2$CH$_2$ is not fully thermalized before reacting with CO$_2$, the formation of P3 is possible). Note, the reaction course from P1 to P2 involves an important intermediate I$_{11}$ that contains two equivalent CO moieties, [C$_{CH_2}$O$_{cluster}$] and [C$_{CO}$–O$_{CO}$], bound to the Rh atom. Either C$_{CH_2}$O$_{cluster}$ or (CO)$_2$CO can be desorbed to produce theionic product RhTiO$_2$CH$_2$O$^-$ (P2), consistent with the observed reaction channels in the isotopic labeling experiment (Figure 1). The reaction path for preferential evaporation of the second H$_2$ molecule from P1 (P1 $\rightarrow$ RhTiO$_2$C$_2$O$^-$ + H$_2$, $\Delta H_d = -2.32$ eV) was also considered. Although it is thermodynamically more favorable than P1 $\rightarrow$ RhTiO$_2$CH$_2$O$^-$ + CO, a high energy barrier (1.18 eV of P1 $\rightarrow$ TS49, in Figure S12) is encountered before H$_2$ desorption. The rate ($4.3 \times 10^3 \text{s}^{-1}$) of traversing TS49 from P1 was estimated to be two orders of magnitude lower than that for CO evaporation (I$_{11}$–P2, $1.4 \times 10^5 \text{s}^{-1}$) so that CO is preferentially desorbed from P1. The RhTiO$_2$CO$_2^-$ + H$_2$
channel was not observed. After dehydrogenation of RhTiO$_2$CH$_2$O$_2$– (P2–P3), the RhTiO$_2$CO$_2$– ion with CO bound to Rh is formed. Desorption of the second CO to regenerate RhTiO$_2$ and close the catalytic cycle of DRM to syngas is overall endothermic by 2.74 eV (Figure S13). This requires supplying additional external energy as shown by the CID experiments. The direct elimination of HCHO and CH$_2$OH from the reaction of RhTiO$_2$CH$_2$O$_2$– with CO$_2$ was also considered. These reaction pathways (Figures S14 and S15) are kinetically less favorable than the H$_2$ loss channel [reaction (3a)] and ultimately also entropically unfavorable. Therefore, we conclude that the probability for formation of HCHO or CH$_2$OH is negligible.

Methane conversion has been extensively explored in gas phase studies, which revealed that only a few transition metal-containing oxide ions react with a single CH$_4$ molecule to generate syngas at room temperature. These are the monometallic species ReO$_4$–[9] and RuO$_2$–[10] as well as the bimetallic systems RhAl$_2$O$_4$[11] and RhAl$_2$O$_4$.[12] However, only a single free H$_2$ molecule was produced from one CH$_4$ molecule, because the oxide ions commonly bind the remaining two H atoms in form of two hydroxy groups that are reluctant to liberate H atoms. While the situation is similar in RhTiO$_2$–/CH$_4$, i.e., the adsorption complex I contains an OH group (Figure 2), which makes H$_2$ release unfavorable (2–H$_2$ in Figure 1b). By sharp contrast, the introduction of CO$_2$ into the reaction system enables the conversion of the four H atoms in CH$_4$ to two free H$_2$ molecules at room temperature, greatly enhancing the conversion efficiency of CH$_4$ to H$_2$. This work also confirms that by selecting a suitable oxide support (e.g., TiO$_2$ cluster), the single Rh atom is sufficiently active to enable the co-conversion of methane with carbon dioxide to syngas, in sharp contrast to the VO$_2$ cluster support, for which the Rh$_2$ dimer is indispensable for syngas production.[14]

In condensed phase thermocatalysis of DRM to syngas, methane activation is generally viewed as the rate-determining step and almost all the elementary reactions are performed at the same high temperatures that easily caused pyrolysis of methane (CH$_4$–C+2H$_2$), leading to carbon deposition and catalyst deactivation.[2] Considerable efforts have been devoted to reduction of carbon deposition by engineering the composition and morphology of catalysts.[4,11] Our gas phase study on the thermocatalytic DRM to syngas on RhTiO$_2$– provides first experimental evidence that both the conversion of CH$_4$ to 2H$_2$gas + CO$_2$/CO$_{ads}$ and reduction of CO$_2$ to CO$_{ads}$/CO$_{gas}$ can be achievable at room temperature, the only elementary step that requires high temperatures is CO$_{ads}$ desorption (rate-determining step). The insights into the elementary steps of this study should motivate the engineering of high temperature in practical catalysis. This may significantly alleviate the carbon deposition originating from the pyrolysis of methane.

In conclusion, the co-conversion of CH$_4$ and CO$_2$ to syngas mediated by RhTiO$_2$ has been achieved in the gas phase. The experimental identification of multiple ionic reaction intermediates confirms that, in principle, the reaction of CH$_4$ + CO$_2$––H$_2$gas + CO$_2$/CO$_{ads}$ can occur at room temperature. This is also supported by quantum chemical calculations. Only the final step of CO$_{ads}$ desorption requires the input of external energy (e.g., high temperature) to complete the full catalytic cycle. The working conditions for each elementary step of syngas production identified herein underline that the temperature control is very important for optimization of the reaction process and reduction of carbon deposition and energy consumption in practical catalysis.

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Conflict of interest
The authors declare no conflict of interest.

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