Controlling selectivities in CO$_2$ reduction through mechanistic understanding

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Catalytic CO$_2$ conversion to energy carriers and intermediates is of utmost importance to energy and environmental goals. However, the lack of fundamental understanding of the reaction mechanism renders designing a selective catalyst inefficient. Here we show the correlation between the kinetics of product formation and those of surface species conversion during CO$_2$ reduction over Pd/Al$_2$O$_3$ catalysts. The operando transmission FTIR/SSITKA (Fourier transform infrared spectroscopy/steady-state isotopic transient kinetic analysis) experiments demonstrates that the rate-determining step for CO formation is the conversion of adsorbed formate, whereas that for CH$_4$ formation is the hydrogenation of adsorbed carbonyl. The balance of the hydrogenation kinetics between adsorbed formates and carbonyls governs the selectivities to CH$_4$ and CO. We apply this knowledge to the catalyst design and achieve high selectivities to desired products.
Heterogeneous catalytic CO₂ reduction has been attracting great attention, because it not only mitigates the risks associated with increasing CO₂ concentration in the atmosphere but also offers a variety of pathways for producing fuels and industrial chemicals. Under atmospheric pressure, methanation and reverse water gas shift (RWGS) reactions are the two pathways for thermocatalytic CO₂ reduction on Group VIII metals. Although methanation produces synthetic natural gas, RWGS generates CO, an important component of syngas. Considerable efforts have been devoted to developing catalysts to achieve high selectivity towards either CH₄ or CO. RWGS generates CO, an important component of syngas.

Our previous work on Pd/Al₂O₃ bifunctional catalysts has proposed the selective adsorption of formates and carbonyls over Pd/Al₂O₃ catalysts, which was demonstrated by a combined transmission FTIR spectroscopy/SSITKA investigation. Using this knowledge, we show that CH₄ and CO selectivities are governed by the balance of the hydrogenation kinetics between adsorbed formates and carbonyls over Pd/Al₂O₃ catalysts, which was demonstrated by a combined operando transmission FTIR spectroscopy/SSITKA investigation. Using this knowledge, we show that tailor-made catalysts can be prepared to achieve high selectivity to either of the two desired products.

Results

Figure 1a, b show normalized mass spectrometry (MS) responses of gases in the effluent after the feed gas was switched at 0 s from ¹²CO₂/H₂/Ar to ¹³CO₂/H₂ at 533 K. The fast disappearance of Ar gas in <4 s indicates a short gas hold-up time for the system. The disappearance of ¹²CO₂ was almost as fast as Ar, indicating weak interaction between ¹²CO₂ and the catalyst and the reactor walls. In the meantime, the concentration of ¹³CO₂ signal increased accordingly, with the concentration and the conversion (2.5%) of carbon dioxide (¹²CO₂ + ¹³CO₂) constant during the switch. The decaying signals of ¹²CH₄ and ¹²CO and the rising signals of ¹³CH₄ and ¹³CO crossed at y = 0.5, indicating constant rates for methane and carbon monoxide formation regardless of isotopic substitution. These symmetrical responses indicate that the steady state of the catalyst surface was not perturbed during the switch. The concentrations of products ¹²CH₄ and ¹³CO decreased more slowly than that of ¹²CO₂ and disappeared at ~600 s. This indicates large mean residence times for C-containing surface intermediates leading to the products, and that intermediates which equilibrate with CO₂ are not involved in the rate-determining steps for CO₂ methanation and RWGS.

Figure 1c shows the corresponding operando FTIR contour plot. Before the switch, the absorption band between 2,300 and 2,400 cm⁻¹ (red range) is attributed to gaseous ¹²CO₂. The spectral range between 1,800 and 2,100 cm⁻¹ (blue and green range) is assigned to chemisorbed carbonyls (¹¹CO) on the surface of Pd metal particles. The absorption bands around 1,400 (yellow range) and 1,600 cm⁻¹ (red range) arise from adsorbed formates (H¹²COO⁻) on the surface of the Al₂O₃.
ICH decreased from 107 to 55 s with increasing temperature. 

We observe no 12CO2 and Ar did not change with temperature, further indicating that HCOO* and CO* are reactive intermediates rather than spectators and, the rate-determining steps for CH4 and CO formation are related to CO* and HCOO*. It is noteworthy that no other species (e.g., bicarbonate) were observed under steady-state reaction conditions and no carbon deposition was identified in our previous study on Pd/Al2O3 during CO2 reduction. Therefore, CO* and HCOO* are the two most abundant surface species and will be the focus of the following discussion.

To gain insight into the interaction between *CO and Pd on the 5% Pd/Al2O3, room temperature 12CO adsorption followed by temperature-programmed 12CO desorption were studied by FTIR (Supplementary Fig. 1). At room temperature 12CO on Pd showed IR features at 2,098, 2,052, 1,960 and 1,928 cm⁻¹. When the temperature was raised to 533 K, 12CO with features at 2,098 and 1,960 cm⁻¹ desorbed, whereas 12CO with bands at 2,052 and 1,928 cm⁻¹ did not desorb but was hydrogenated to CH4 once H2 was introduced. This reveals the existence of two types of adsorption sites on the Pd particles that bind CO weakly (12COs) and strongly (12COw). The stability of *CO at high temperatures is due to the dissociated *H, which adsorbs near to *CO on the Pd surface and transfers electron density to Pd to strengthen the Pd-CO bond. The FTIR spectrum of 12CO is very similar to that of 12CO obtained in CO2 reduction at 533 K, indicating that all 12CO observed under reaction conditions were 12CO. However, 12COs could not be observed during CO2 reduction at ≥ 533 K due to its rapid desorption. As we observe no 12COs under steady-state reaction conditions, the 12CO product generated after the switch was mainly from the conversion of the other abundant species, 12CO2.

Normalized MS responses of 12CH4 and 12CO with increasing temperature are shown in Supplementary Fig. 2, whereas those for 13CH4 and 13CO are not displayed. The faster decay in both 12CH4 and 12CO signals at higher temperatures indicates the higher reactivities of intermediates. In contrast, the decay curves of 12CO2 and Ar did not change with temperature, further indicating that any elementary step that directly involves CO2 is not the rate-limiting step for the formation of CH4 and CO. The real mean surface residence times τ₀ of intermediates leading to 12CH4 and 12CO (denoted as ICH and ICO) together with the τ₀-derived activation energies E for 12CH4 and 12CO formation (Supplementary Fig. 4) are summarized in Table 1. The τ₀,ICH at 533 K was 134 s and gradually decreases with increasing temperature, reaching 41 s at 573 K. Similarly, the τ₀,ICO decreased from 107 to 55 s with increasing temperature from 533 to 573 K. The activation energies are 75 and 53 kJ mol⁻¹ for the formation of CH4 and CO, respectively, in line with the values we obtained previously in a plug-flow reactor. Series of corresponding *CO FTIR spectra of CO and HCOO* collected at 533–573 K are shown in Supplementary Figs. 5, 6, respectively. The shift of IR bands representing 12CO and H12COO* to those representing 13CO and H13COO* became faster with increasing temperature, but still remained much slower than the shift of the IR band of 12CO to that of 13CO. The decay trends of 12CO and H12COO* FTIR intensity with increasing temperature were very similar to the decay trends of MS signals of 12CH4 and 12CO products (Supplementary Fig. 2), further indicating that HCOO* and CO* are related to the rate-determining steps for CH4 and CO formation. In addition, the disappearances of 12CO2 and H12COO* follow an apparent first-order kinetics. The activation energies based on the Arrhenius plots of the two first-order rate constants (Supplementary Figs. 5, 6) are listed in Table 1. The activation energy for the conversion of 12CO2 was 73 kJ mol⁻¹, an identical value to that determined for 12CH4 formation from the MS data. This result suggests that the rate-determining step along the CH4 formation path is the conversion of *CO. The activation energy of H12COO* conversion was 52 kJ mol⁻¹, very similar to the 53 kJ mol⁻¹ determined for the 12CO formation by MS, indicating that the conversion of HCOO* is the rate-determining step for CO formation.

| Table 1 Real mean surface residence times for ICH (τ₀,ICH) and ICO (τ₀,ICO), and activation energies for CH4 (ECH4) and CO (ECHCO) formation and adsorbed *COs (E*COs) and HCOO* (E*HCOO*) conversions in CO2 reduction at 533–573 K |
|-----------------|------------------|-----------------|-----------------|-----------------|-----------------|
| Temp. (K)       | τ₀,ICH (s)       | τ₀,ICO (s)      | ECH4 (kJ mol⁻¹) | ECO (kJ mol⁻¹)  | E*COs (kJ mol⁻¹) | E*HCOO* (kJ mol⁻¹) |
| 533             | 134             | 107             | 75              | 53              | 73              | 52               |
| 543             | 92              | 85              | 75              | 53              | 73              | 52               |
| 563             | 49              | 57              | 53              | 73              | 52              |                  |
| 573             | 41              | 55              | 53              | 73              | 52              |                  |

Uncertainties in activation energies are ±2 kJ mol⁻¹.
formed product 2 (smaller r_f)_{CH4}^{27}. Therefore, the temperature effect on these parameters, r_f_{CH4}, r_f_{CO}, N_{ICCH}, N_{ICO}, further demonstrates that HCOO* is the intermediate shared by the processes of both CO_2 methanation and RWGS.

**Discussion**

Based on above results and SSITKA theory\textsuperscript{16,17}, a scheme relating HCOO*, +CO, and +CO_2 species in CO_2 reduction is proposed in Fig. 3. The reduction of formate produces +CO that first occupies strong adsorption sites on the Pd particles. Once the strong adsorption sites of Pd particles are saturated (the pool of +CO is completely filled), the excess +CO can only occupy the weak adsorption sites of Pd particles to form +CO_w. The +CO will be further hydrogenated to CH_4 while the +CO_w will desorb. The scheme shows that the rate of CO formation (r_{CO}) is determined and equal to the rate of HCOO* conversion (r_{HCOO*}) subtracted by the rate of CH_4 formation (r_{CH4}):

$$r_{CO} = r_{HCOO*} - r_{CH4}$$  \hspace{1cm} (1)

The rate of CH_4 formation is equal to the rate of +CO_2 conversion (r_{CO_2}, the rate-determining step for CH_4 formation), which is proportional to the concentration of +CO_2. The completely filled pool of +CO in the 533–573 K temperature range suggests that r_{CO_2} has reached its maximum, r_{CO_2,max}, at each given temperature between 533–573 K. Therefore, it is the balance between the rate of HCOO* reduction to +CO (r_{HCOO*}) and the maximum rate of +CO_2 conversion (r_{CO_2,max}) that determines whether CO is observed in the gas phase or not. If r_{HCOO*} > r_{CO_2,max}, both CH_4 and CO will be observed (e.g., the case in Fig. 3). If, however, r_{HCOO*} \leq r_{CO_2,max}, which means that all the +CO produced from HCOO* are not sufficient to saturate all strong adsorption sites on the Pd metal for CH_4 formation (i.e., the pool of +CO_2 in Fig. 3 is not full or just full), then all +CO will be +CO_w and will be further hydrogenated to CH_4. In this case, CO_2 reduction will only be methanation and the rate of CH_4 formation r_{CH4} (r_{CO}) will not reach its maximum r_{CO_2,max}.

As the conversions of both HCOO* and +CO require the presence of *H (absorbed hydrogen) involved\textsuperscript{24}, r_{CH4} (r_{CO_2}) is determined by the concentrations of +CO_2 ([+CO_2]) and *H ([*H]), as well as the rate constant of +CO conversion (k_1):

$$r_{CH4} = r_{CO_2,max} = k_1[[+CO_2][^*H]]$$  \hspace{1cm} (2)

and r_{HCOO*} is determined by the concentration of HCOO* ([HCOO*]) and *H ([*H]), and rate constant of HCOO* reduction (k_2):

$$r_{HCOO*} = k_2[HCOO*][^*H]$$ \hspace{1cm} (3)

$$r_{CO} = r_{HCOO*} - r_{CH4} = r_{HCOO*} - r_{CO_2,max} = k_2[HCOO*][^*H] + k_1[[+CO_2][^*H]]$$ \hspace{1cm} (4)

It is known that +CO_2 and HCOO* do not share and compete for active sites, as they are located on Pd metal and Al_2O_3 support, respectively\textsuperscript{22}. Therefore, [+CO_2] and [HCOO*] can be independently changed to tune the rate of CO formation, r_{CO}, as well as the reaction product distribution. In the case of a completely filled pool of +CO (e.g., the case in Fig. 3), if aiming at a higher CH_4 selectivity, [+CO_2] should be increased or [HCOO*] should be decreased. One method, e.g., is to add more metal sites onto the Al_2O_3 support. The increased metal loading will not only result in an increased number of metal sites for forming +CO but also lead to a decreased number of support sites that can accommodate HCOO*. It means that the capacity of +CO pool (Fig. 3) is enlarged, meanwhile that of HCOO* is decreased. This, consequently, may lead to a situation where the result of Eq. (4) decreases even to 0, showing less or complete absence of CO in the gas phase. This hypothesis was tested on Pd/Al_2O_3 catalysts with different Pd loadings but similar Pd particle size distributions (Fig. 4), which minimized the potential effects of metal particle size on k_1 and k_2 influencing r_{CO_2,max} and r_{HCOO*}. If the scheme and hypothesis are correct, Pd/Al_2O_3 catalysts with higher Pd loadings should exhibit higher CH_4 selectivity than those with lower Pd loadings. Furthermore,
this is exactly what the reactivity data of Fig. 4 shows: CH4 selectivity increased from 45 to 90% as the Pd loading was increased from 2.5 to 10% (Fig. 4). Previous studies on Ru/Al2O3 and Ni/SiO2 catalysts have also shown that CH2 selectivity in CO2 reduction reaction increased with the metal loading12, 28, 29, consistent with the findings reported in this work.

In the case of an incompletely filled pool of *CO2 when CH4 selectivity is always 100%, if one aims at a higher CH4 formation rate, [*CO2] needs to be increased. For instance, Karelovic et al.20 reported that the rate of CO2 methanation over Rh/Al2O3 was greatly increased by adding Pd/Al2O3, which has no activity towards CO2 methanation at 473 K. They attributed the synergistic effect to the supply of dissociated H* from Rh/Al2O3 to Pd/Al2O3. It is noteworthy that although CO2 methanation cannot proceed on Pd/Al2O3 at 473 K, this temperature is high enough for RWGS reaction to occur producing CO22, 31. We propose that CO or *CO produced by/on Pd/Al2O3 could diffuse onto the Rh domains, increasing the concentration of *CO2 on Rh. The total amount of *CO2 produced by both Pd/Al2O3 and Rh/Al2O3 is not enough to saturate all the active Rh sites for CH4 formation (to fill up the *CO2 pool of Rh, Fig. 3). Therefore, the CH2 selectivity remained ~100% but the methanation rate was higher on the Pd/Al2O3-Rh/Al2O3 mixture than on Rh/Al2O3 alone. The role of the Pd/Al2O3 component was to provide extra CO (*CO) to the empty sites of Rh. The synergistic effect at lower catalyst temperature (423 K) was found to be negligible. Our study showed that RWGS cannot occur over Pd/Al2O3 at 423 K31, so the added Pd/Al2O3 cannot supply additional CO to Rh/Al2O3 catalyst for the further *CO hydrogenation to CH4 on Rh/Al2O3. Therefore, the above analysis of their results show that for an incompletely filled pool of *CO2 with 100% CH4 selectivity (fHCOO ≤ fHCOO,max) on a catalyst, adding a component (promoter) which can produce CO (*CO) is a strategy for increasing the rate of CO2 methanation.

In conclusion, CO2 methanation and RWGS are not two parallel reactions during the CO2 reduction over Pd/Al2O3 catalysts. Instead, they share the initial steps and intermediates from bicarbonates to formates until after formate decomposition. The rate of formate decomposition to CO2 is larger than the rate of "CO hydrogenation to CH4 and the excess CO* desorbs. The rate-determining step for CO2 reduction and for RWGS is the conversion of HCOO*, whereas that for CH4 formation is the hydrogenation of CO. The balance of the hydrogenation kinetics between HCOO* and "CO governs the selectivities to CH4 and CO. Given that "CO and HCOO* are mainly on metal (Pd) and support (Al2O3), respectively, the balance could be tuned to achieve the desired CH4 and CO selectivities by optimizing the loading of the metal and the surface area of the support. This work has important implications for other bifunctional systems where the balance between different catalytic functions determines the rates and product distribution.

Methods
Catalyst synthesis and SSITKA experiments. The Pd/Al2O3 catalysts were prepared on a γ-Al2O3 powder (Sasol, Puralox SBA-200) by the incipient wetness method using Pd(NH3)2(NO3)2 as the precursor. After impregnation, the samples were dried at 373 K for 24 h and then calcined at 773 K for 2 h in air (flow rate = 60 mL min−1) and followed by reduction at 773 K for 1 h in 10% H2/He (flow rate = 60 mL min−1) to obtain the Pd/Al2O3 catalysts31. Forty-one milligrams of 5 wt% Pd/Al2O3 was pressed onto a tungsten mesh and loaded into a home-made upadone transmission IR cell32. The cell has a very small internal dead volume (∼0.2 cm3 after the catalyst loading), resulting in a short gas hold-up time. This renders the system suitable for obtaining accurate kinetic information about intermediates and products during the SSITKA experiments. Before experiments, the catalyst was pretreated by calcination at 673 K for 1 h under air with a flow rate of 10 mL min−1, followed by reduction at 673 K for 1 h under 20% H2 in He with a flow rate of 10 mL min−1. The reactant gas mixture was composed of 4 mL min−1 H2, 1 mL min−1 12CO, 1.0 mL min−1 Ar and He as the diluent with a total gas flow of 10 mL min−1 at atmospheric pressure. Ar gas was used as an inert tracer to correct for gas hold-up of the system and for gas re-adsorption. After the reaction reached steady state at the reaction temperature of 533 K, the reactant was switched from H2/13CO2/Ar to H2/12CO2. During the switch, the gaseous effluent from the cell and the species on the catalyst surface were monitored by MS and FTIR, respectively. The switch was performed in the temperature range of 533–573 K, where the CO2 conversion was <8%. In order to obtain the real mean surface residence times (τd) of intermediates leading to CH4 and CO, space velocity experiments were conducted by varying the total flow rate from 10 to 25 mL min−1 at constant partial pressures of CO2 and H2 to exclude gas hold-up and re-adsorption effects.

Data analysis. The SSITKA theory has earlier been described extensively16, 33. The integration of the normalized step-decay or step-input response always yields the overall mean surface-residence time, τ, of all adsorbed surface intermediates, which lead to CH4 and CO products (τ = ∫ f(t)dt). The error <5% caused by gas phase hold-up (∼3 s) could be ignored due to the fast decay of standard Ar gas and CO2 gas. The rate constant is simply the reciprocal of average surface residence time for the active surface intermediates (k = 1/τ)9, 11. The number of adsorbed species (NCO) and (CO) can be obtained from integration of decay rates (τ) of CH4 and CO products (N = ∫ τ(t)dt). In addition, N is usually closely related to the number of active sites on the catalysts for product formation. In this study of CO2 reduction over 41 mg of 5% Pd/Al2O3, the NCO completely originates from H212COO*, which was demonstrated to be located on the Al2O3 support. As not all H212COO* was converted to 12CO, the amount of sites for formates on Al2O3 is estimated to be at least 1.86 μmol, i.e., NCO31 obtained at 533 K. For CH4 formation via 12CO and a portion of H212COO*, the upper limit of the amount of active Pd sites for CO2 (forming CH4) is 1.95 μmol, i.e., NCO31 at 533 K. This value accounts for 90% of the surface Pd atoms. The total amount of intermediates (NICO + NCO31) on the surface of the catalyst slightly decreased from 3.81 μmol at 533 K to 3.38 μmol at 573 K, which was caused by the decreased amount of H212COO* on the surface shown in Supplementary Fig. 7.

Data availability. The data that support the findings of this study are available from the corresponding author on request.

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Author contributions

X.W. designed and built up the SSITKA/Operando-FTIR/MS/GC system and performed all the experiments, analyzed the data and wrote the paper. H.S. revised the paper. I.S. managed the project and revised the paper.

Additional information

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