Graphical Abstract

CO₂ Hydrogenation on Pt, Pt/SiO₂ and Pt/TiO₂: Importance of Synergy between Pt and Oxide Support

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Abstract

In the current study we combined density functional theory (DFT), kinetic Monte Carlo (KMC) simulations and experimental measurements to gain insight into the mechanisms of CO₂ conversion by hydrogen on the Pt nanoparticle (NP). The results show that in spite of the presence of active, low-coordinated sites, Pt NP alone is not able to catalyze the reaction due to the weak CO₂ binding on the catalyst. Once CO₂ is stabilized, the hydrogenation of CO₂ to CO via the reverse-water-gas shift (RWGS) reaction is promoted; in contrast, the enhancement for further *CO hydrogenation to CH₄ is less significant and no CH₃OH is observed. The selectivity to CO is mainly determined by CO binding energy and the energetics of *CO hydrogenation to *HCO, while that for CH₄ and CH₃OH is determined by the competition between hydrogenation and C-O bond scission reactions of the *H₂COH species. Using SiO₂ and TiO₂ as the support, Pt NP is able to promote the overall CO₂ conversion, while the impact on the selectivity is rather small. The theoretically predicted trend in activity and selectivity is in good agreement with the experimental results. The enhanced activity of Pt/oxide over Pt is originated from the sites at the Pt-oxide interface, where the synergy between Pt and oxide plays an important role.

1. Introduction

Chemical recycling of carbon dioxide (CO_2) has attracted considerable attentions recently. In particular, the activation of CO_2 in combination with hydrogen (H_2) to produce valuable chemicals such as carbon monoxide (CO), methane (CH_4) and methanol (CH_3OH) has been widely investigated in the past few decades.[1-13] These reactions are not only environmentally important due to its potential in reducing CO_2 emissions, but also have great industrial significance. As the product, e.g. CH_3OH , can serve as a liquid fuel as well as a raw material for the synthesis of other organic compounds.[14, 15] Previous studies have shown that Cu is very selective to convert CO_2 to CH_3OH by H_2 , and the activity and selectivity can be further promoted by forming alloys or using oxides as supports.[1, 16-23] In comparison, Pt-based catalysts behave differently and are reported to be highly selective to CO [2], which undergoes the reverse-water-gas shift (RWGS) reaction via either carboxyl ($^*\text{HOCO}$) or formate ($^*\text{HCOO}$) intermediates.[1, 24-26] The production of CH_4 is also observed during this process; however, the corresponding selectivity is much lower than that of CO . [2] It is desirable to promote and control the selectivity of a catalyst to convert CO_2 to CO , CH_3OH or CH_4 . To accomplish this task, it is important to understand the underlying mechanisms and identify the key elementary steps that determine the selectivity of CO_2 hydrogenation; yet it remains elusive due to the complexity of the reaction network.

Pt is used as a catalyst in many industrially important chemical reactions. It has displayed its potential applications as a catalyst for reforming reactions such as reforming of ethanol ($\text{C}_2\text{H}_5\text{OH}$) [27, 28] and n-Hexane[29], the water-gas-shift (WGS) reaction at low temperature[30-32], the direct oxidation of CH_4 to syngas[33-37], and CO oxidation. [38-41] CO_2 activation by H_2 undergoes the RWGS reaction on Pt(111) and leads to the production of

CO via the $^*\text{HOCO}$ intermediate [42-44], while the produced CO can be further hydrogenated to CH_4 via C-O bond cleavage.[43] However, in practice Pt catalysts are in the form of nanoparticles (NPs) supported primarily on oxides, which can behave differently from Pt(111).[2, 31, 42, 45, 46] Compared to Pt(111), the enhanced activity of Pt NPs supported on oxides towards the WGS reaction and ethanol ($\text{C}_2\text{H}_5\text{OH}$) steam reforming reactions has been attributed to the presence of active, low-coordinated sites of small Pt particles and the large electronic perturbations in contact with the oxide support, which are both associated with the strong metal-support interaction (SMSI).[45, 47] Yet the corresponding mechanistic studies on the Pt NPs with and without oxide supports are rather limited.

In this study we carried out DFT calculations to investigate the reaction network for the hydrogenation of CO_2 to CO, CH_4 and CH_3OH on a small (~ 1 nm) Pt NP. Furthermore, the energetics obtained from DFT calculations were used to perform Kinetic Monte Carlo (KMC) simulations to estimate the overall activity and selectivity at typical experimental conditions. Our results show that the presence of active, low-coordinated sites in the Pt NP alone is not sufficient to catalyze CO_2 hydrogenation due to the poor ability for CO_2 adsorption and therefore activation. Once CO_2 is stabilized, Pt is found to be highly selective to CO rather than to CH_4 and the formation of CH_3OH is prohibited. Depositing the Pt NP on oxide supports such as SiO_2 and TiO_2 is able to stabilize CO_2 at the Pt-oxide interface and therefore facilitate the hydrogenation of CO_2 to CO and CH_4 ; yet the impact on the selectivity is rather small. The theoretically predicted trend in activity and selectivity is well supported by the corresponding experimental results. Furthermore, the current study also identifies key parameters to control the activity and selectivity of Pt-based catalysts toward CO_2 hydrogenation, which provide a solid basis for catalyst screening at a theoretical level.

2. Methodology

2.1 Computational methods

Self-consistent density functional theory (DFT) [48, 49] calculations were performed using the Vienna *Ab-initio* Simulation Package (VASP) code.[50, 51] A plane wave cut-off energy of 400 eV was used for total energy calculations. The Brillouin zone was sampled at the Γ -point. All the computations were conducted in the spin unrestricted manner using PAW potentials.[52, 53] Electronic exchange and correlation effects were described within the generalized gradient approximation (GGA) using PW91 functionals.[54] The Fermi level was broadened using a Fermi-Dirac smearing of $\sigma = 0.2$ eV. Ionic positions were optimized until the Hellman-Feynman force on each ion was smaller than 0.02 eV/Å. The Pt nanoparticle was simulated by a semispherical Pt₄₆ cluster, which was constructed from Pt bulk and was relaxed in 15 Å of vacuum in each x, y and z directions. Such model was shown being able to well describe the catalytic performance for metal nanoparticles observed experimentally.[55, 56] The climbing image nudged elastic band (CI-NEB) method[57] as implemented in VASP was used to locate the transition state. The activation energy (E_a) of a chemical reaction is defined as the energy difference between the initial and transition states while the reaction energy (ΔE) is defined as the energy difference between the initial and final states. The kinetic Monte-Carlo (KMC) simulations were performed with a Kinetix module implemented in Material Studio 5.5.[58]

The β -cristobalite cubic structure of SiO₂ was chosen to model the Pt NP supported on silica. The calculated lattice parameter for the β -cristobalite cubic structure of SiO₂ is 7.46 Å, which is in close agreement with previously calculated value of 7.45 Å.[59] The SiO₂(111)

surface was modeled using a three layer 5×3 unit cell. The rutile $\text{TiO}_2(110)$ support was modeled as a periodically repeating three O-Ti-O layer with 5×2 unit cell on each layer. The lattice parameters determined here for bulk rutile TiO_2 are $a = 4.69 \text{ \AA}$ and $c = 3.04 \text{ \AA}$, in close agreement with previously determined values using similar methods.[60] The Pt_{25} NP was then deposited on the $\text{SiO}_2(111)$ and $\text{TiO}_2(110)$ surfaces. The atomic positions of the bottom layer were kept fixed while the top two layers were allowed to relax with the Pt NP. A vacuum layer of $\sim 15 \text{ \AA}$ thick was added in the simulation cells of $\text{Pt}_{25}/\text{SiO}_2$ and $\text{Pt}_{25}/\text{TiO}_2$ along the direction perpendicular to the surface. The binding energy of an adsorbed species on a NP is calculated as:

$$\text{BE} = E(\text{adsorbed species} + \text{NP}) - E(\text{NP}) - E(\text{adsorbed species in gas phase}),$$

where $E(\text{adsorbed species} + \text{NP})$, $E(\text{NP})$, $E(\text{adsorbed species})$ are the total energies of the NP with adsorbed species, clean nanoparticle and adsorbed species in the gas phase, respectively.

2.2 Experimental methods

The Pt/SiO_2 and Pt/TiO_2 catalysts were synthesized by incipient wetness impregnation over commercial supports with an aqueous solution of the metal precursor $((\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2$ from Alfa Aesar). Both supports used in this work, i.e., TiO_2 with a BET surface area larger than $150 \text{ m}^2/\text{g}$ and SiO_2 with a BET surface area of $160 \text{ m}^2/\text{g}$, were purchased from *Alfa Aesar*. The metal loading of the catalysts in this work was 1.67 wt%. After impregnation, the samples were fully dried at 373 K in air and then calcined at 563 K for 2 hours (with a 33 K/min ramp to 563 K).

The number of surface Pt sites on each supported catalyst was measured via pulse CO chemisorption with an Altamira AMI-300 ip instrument. The sample ($\sim 200 \text{ mg}$) was firstly pretreated in He at 393 K for 30 min, and then reduced at 723 K for 45 min using a mixture of 10% H_2 in Ar (30 ml/min). After degassing in He and cooling down to 313 K, pulses of 10% CO

in He (0.59 ml loop) were injected. The amount of CO flowing out of the reactor was monitored by a thermal conductivity detector (TCD). The CO uptake values are 11.3 and 8.3 $\mu\text{mol}\cdot\text{g}^{-1}$ for Pt/TiO₂ and Pt/SiO₂, respectively.

High-angle annular dark-field imaging (HAADF) was performed using the JEM-2100F transmission electron microscope (TEM). TEM samples were prepared by finely grinding reduced catalyst samples and suspending the catalyst in methanol. Droplets of the methanol suspension were placed onto a lacey carbon grid. The grid was allowed to fully dry before loading the sample into the TEM.

Flow reactor studies of powder catalysts for CO₂ hydrogenation were carried out in a quartz tube reactor with an inner diameter of 4 mm under atmospheric pressure and in the temperature range from 553 to 623 K. In each experiment, a certain amount of catalyst (20–80 mesh) was loaded into the flow reactor and reduced under a 1:1 hydrogen and helium mixture (50 sccm total flow) at 723 K for 1 hour prior to reaction. The flow rates of CO₂ and hydrogen were set at 20 sccm and 40 sccm, respectively. For each experiment, the temperature was ramped to 573 K and held for over 15 hours until the reaction reached steady-state, then the temperature was changed and stayed at each temperature for 40 minutes. The concentrations of gaseous species at the reactor outlet were detected by an online gas chromatography (Agilent 7890B) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

3. Results and Discussion

3.1 Pt NPs: Reaction network based on DFT calculations

According to the previous mechanistic studies, the reaction network for the CO₂ reduction or hydrogenation can occur via several possible routes to produce CO, CH₃OH and

CH₄ as depicted in Figure 1.[4, 17, 18, 61-63] The formate pathways are initiated with the formation of the *HCOO species, which undergoes a series of hydrogenation and dissociation reactions to form CH₄ and CH₃OH. Along the RWGS + CO-Hydro pathways, the initial hydrogenation of CO₂ forms the *HOCO species, which decomposes and produce *CO and *OH. *CO then either desorbs or undergoes further hydrogenation to produce CH₃OH or CH₄.

Figure 1. Reaction network for the conversion of CO₂ to CO, CH₄ and CH₃OH, where “*X” represents X species adsorbed on a surface site.

To determine the reaction network for CO₂ hydrogenation on Pt NP, the possible reaction routes for various products including CO₂ to CO, CH₃OH and CH₄ were taken into

consideration in our DFT calculations. As you will see below, such mechanistic study on the overall reaction network allows us to pinpoint the details of reaction kinetics. More importantly it enables the identification of the key factors that control the rate of each route and therefore the activity and selectivity of the catalyst. This is of significant importance to further catalyst development.

Table 1: Binding energies (BE in eV) of chemical species involved in the hydrogenation of CO₂ on the Pt NP.

Species	site	BE
H	edge-bridge	-2.96
OH	edge-bridge	-3.15
H ₂ O	top-corner	-0.54
CO	top-corner	-2.29
CO ₂	top-corner	-0.29
HCOO	top-top	-3.16
HOCO	top-edge	-2.90
HCO	top-corner	-2.89
H ₂ CO	top-top	-1.09
H ₃ CO	edge-bridge	-2.50
CH ₃ OH	top-corner	-0.64
COH	edge-bridge	-4.84
HCOH	top-edge	-3.74
H ₂ COH	top-top	-2.40
CH ₂	edge-bridge	-4.84
CH ₃	top-corner	-2.49
CH ₄	top	-0.07
HCOOH	top-edge	-0.89
H ₂ COO	bridge-bridge	-3.96
H ₂ COOH	top-top	-2.39

DFT calculations were performed on a Pt NP of ~1 nm diameter shown in Figure 2a. The binding geometries of various reaction intermediates (Figure 1) are shown in Figure 2 and the corresponding BEs are listed in Table 1. One can see that all chemical species favorably bind at the low-coordinated sites (i. e. corners and edges) of the Pt NP, rather than those on the terrace. On the basis of the DFT calculated energetics the productions of CO, CH₃OH and CH₄

along different pathways are described in the following sections. Note that we did not include H_2 dissociation in current DFT study. Previous experimental and theoretical studies showed H_2 dissociation on Pt crystals occurred at much lower temperatures than that for CO_2 hydrogenation. Accordingly, the dissociation of H_2 on the Pt NP should not be problematic under CO_2 hydrogenation conditions.[64, 65] Thus, we assume that the high pressure of H_2 is able to provide enough $*H$ for the hydrogenation reaction.

Figure 2. DFT optimized geometries for (a) Pt_{46} nanoparticle, and the adsorbed species: (b) $*H$, (c) $*OH$, (d) $*CO_2$, (e) $*CO$, (f) $*HOCO$, (g) $*HCO$, (h) $*H_2CO$, (i) $*H_3CO$, (j) $*COH$, (k) $*HCOH$, (l) $*H_2COH$, (m) $*HCOO$, (n) $*H_2COO$, (o) $*HCOOH$, (p) $*H_2COOH$, (q) $*CH_2$, (r) $*CH_3$, (s) $*CH_4$ top view, (t) $*CH_4$ side view, (u) $*H_2O$, and (v) $*CH_3OH$ on the Pt nanoparticle. Pt: light grey, C: dark grey, O: red, and H: blue.

3.1.1 CO and CH_3OH synthesis via the RWGS + CO-Hydro pathways

The potential energy diagrams for CH_3OH synthesis via the RWGS + CO-Hydro pathways are shown in Figure 3. The initial hydrogenation of $*CO_2$ to $*HOCO$ is exothermic ($\Delta E = -0.09$

eV) and the corresponding E_a is 1.01 eV. $^*\text{HOCO}$ dissociation to $^*\text{CO}$ and $^*\text{OH}$ is exothermic ($\Delta E = -0.46$ eV) with an E_a of 0.75 eV.

The produced $^*\text{CO}$ can either desorb, which is highly endothermic ($\Delta E = 2.29$ eV), or convert to CH_3OH as shown in Figure 1. The initial hydrogenation of $^*\text{CO}$ forms either $^*\text{COH}$ or $^*\text{HCO}$. The formations of both $^*\text{HCO}$ and $^*\text{COH}$ are thermodynamically uphill with 0.96 eV and 1.11 eV in ΔE , respectively; yet E_a (1.29 eV) for the reaction $^*\text{CO} + ^*\text{H} \rightarrow ^*\text{HCO}$ is much lower than that (2.03 eV) for $^*\text{CO} + ^*\text{H} \rightarrow ^*\text{COH}$. Thus CO conversion to CH_3OH is likely to occur via the $^*\text{HCO}$ intermediate. The subsequent hydrogenation of $^*\text{HCO}$ may form $^*\text{HCOH}$ or $^*\text{H}_2\text{CO}$. The DFT results show that the reaction $^*\text{HCO} + ^*\text{H} \rightarrow ^*\text{H}_2\text{CO} + ^*$ is both thermodynamically ($\Delta E = 0.54$ eV) and kinetically ($E_a = 0.95$ eV) less favorable than the reaction $^*\text{HCO} + ^*\text{H} \rightarrow ^*\text{HCOH}$. Accordingly, the hydrogenation of $^*\text{HCO}$ produces the $^*\text{HCOH}$ intermediate, which is then hydrogenated to form $^*\text{H}_2\text{COH}$ with an E_a of 0.88 eV, and eventually $^*\text{CH}_3\text{OH}$ ($\Delta E = 0.31$ eV, $E_a = 1.13$ eV).

The CO production via the RWGS reaction can be hindered the high endothermicity (2.29 eV) for $^*\text{CO}$ desorption, though as shown in KMC simulations in Section 3.2 the elevated temperature is able to promote $^*\text{CO}$ desorption during the reaction due to the significant entropy contributions. For the synthesis of CH_3OH via the RWGS + CO-Hydro pathways, the $^*\text{HCO}$ formation from the hydrogenation of $^*\text{CO}$ has the highest energy barrier (1.29 eV) followed by that (1.13 eV) of $\text{H}_2\text{COH} + ^*\text{H} \rightarrow ^*\text{CH}_3\text{OH} + ^*$ in a decreasing sequence. In addition, the $^*\text{CO}_2$ hydrogenation to $^*\text{HOCO}$ should also be paid attention, with the E_a around 1 eV. Therefore, qualitatively the overall activity and selectivity of CO and CH_3OH synthesis via the RWGS + CO-Hydro pathways can be controlled by all these difficult steps; however quantitatively it is

difficult to determine which is the rate-limiting step merely based on the DFT calculations. A kinetic modeling, as will be seen below, is necessary to determine such complex kinetics.

Figure 3. Potential energy diagrams for the CH_3OH synthesis via the RWGS + CO-Hydro pathways. The energetics for each reaction intermediate is included together with the transition site (TS) for each elementary step. The lines in different colors label the different paths.

3.1.2 CH_3OH synthesis via the formate pathways

The $^*\text{HCOO}$ species has been suggested as an intermediate for Pt-based catalysts in the RWGS reaction.[66] However, it has not been proven that $^*\text{HCOO}$ is the active surface intermediate for CO oxidation by hydroxyl.[67] In fact, in our case $^*\text{HCOO}$ formation from $^*\text{CO}_2$ and $^*\text{H}$ involve bond breaking (C-Pt and H-Pt) and bond-making (O-Pt and C-H) steps, which are more than that for $^*\text{HOCO}$ formation (H-Pt bond-breaking and O-H bond-making). It can significantly raise activation barriers. Indeed, the $^*\text{CO}_2$ hydrogenation to $^*\text{HCOO}$ is slightly

endothermic by 0.05 eV with an E_a of 1.37 eV, which is higher than that the hydrogenation to $^*\text{HOCO}$ (Figure 4). Therefore, CO production via $^*\text{HCOO}$ is not able to compete with that via $^*\text{HOCO}$, in consistent with the previous study on Pt(111) using DFT. [30] $^*\text{HCOO}$ then undergoes hydrogenation to form either $^*\text{HCOOH}$ or $^*\text{H}_2\text{COO}$, where $^*\text{HCOO} + ^*\text{H} \rightarrow ^*\text{HCOOH} + ^*$ is more favorable ($\Delta E = 0.24$ eV; $E_a = 0.78$ eV) than the reaction $^*\text{HCOO} + ^*\text{H} \rightarrow ^*\text{H}_2\text{COO} + ^*$ ($\Delta E = 1.58$ eV; $E_a = 2.10$ eV). The further hydrogenation produce $^*\text{H}_2\text{COOH}$ intermediates ($\Delta E = 0.87$ eV; $E_a = 1.80$ eV), which then dissociates into $^*\text{H}_2\text{CO}$ and $^*\text{OH}$. This reaction is slightly endothermic ($\Delta E = 0.07$ eV) and corresponds to an E_a of 0.68 eV. Once $^*\text{H}_2\text{CO}$ is formed, the hydrogenation leads to $^*\text{CH}_3\text{OH}$ production, which follows the similar route as that in the RWGS + CO-Hydro pathways. Again, qualitatively the conversion of CO_2 to CH_3OH via the formate pathways can be limited by $^*\text{HCOO}$ formation and/or the hydrogenation of $^*\text{HCOOH}$ to $^*\text{H}_2\text{COOH}$, which are highly activated processes.

Figure 4. Potential energy diagrams for the CH_3OH synthesis via the formate pathways. The energetics for each reaction intermediate is included together with the transition site (TS) for each elementary step. The lines in different colors label the different paths.

The direct dissociation of $^*\text{CO}_2$ to $^*\text{CO} + ^*\text{O}$ is also considered as a possible route to the product CO. The reaction is exothermic with ΔE of -0.34 eV; yet the corresponding E_a is 1.23 eV, which is higher than the hydrogenation to $^*\text{HOCO}$ ($E_a = 0.75$ eV). Thus, CO_2 activation on the Pt NP prefers the hydrogenation reaction to form $^*\text{HOCO}$, rather than C-O bond cleavage. Indeed, the $^*\text{HOCO}$ intermediate has also been predicted to be formed on Pt-based catalysts for CO_2 hydrogenation according to the previous theoretical studies.[43, 44] In addition, for the sequential reactions along the RWGS + CO-Hydro pathways the highest E_a is 1.29 eV for $^*\text{CO}$ hydrogenation, much lower than that along the formate pathways via $^*\text{HCOO}$ (1.80 eV for the $^*\text{HCOOH}$ hydrogenation). Such big difference in the highest E_a suggests that CO_2 hydrogenation is likely to prefer the RWGS + CO-hydro pathways rather than the formate pathways on the Pt NP.

3.1.3 CH_4 synthesis via the RWGS + CO-Hydro pathways

The synthesis of CH_4 is only considered via the RWGS + CO-Hydro pathways, which is now predicted as the favorable pathways for CO_2 hydrogenation on the Pt NP. As shown in Figure 5, the energetically most favorable pathway for the formation of $^*\text{CH}_4$ from $^*\text{CO}$ involves a series of intermediates including $^*\text{HCO}$, $^*\text{HCOH}$, $^*\text{H}_2\text{COH}$, $^*\text{CH}_2$, and $^*\text{CH}_3$. That is, the pathways for the conversion of CO_2 to CH_3OH and CH_4 on the Pt NP share identical steps until the $^*\text{H}_2\text{COH}$ intermediate is formed. To produce CH_4 , $^*\text{H}_2\text{COH}$ is the precursor for C-O bond breaking, which dissociates into $^*\text{CH}_2$ and $^*\text{OH}$ with an E_a of 0.80 eV and ΔE of 0.22 eV. $^*\text{CH}_2$ then undergoes two endothermic hydrogenation reactions to form $^*\text{CH}_4$: $^*\text{CH}_2 + ^*\text{H} \rightarrow ^*\text{CH}_3 + ^*$ ($\Delta E = 0.15$ eV; $E_a = 0.50$ eV) and $^*\text{CH}_3 + ^*\text{H} \rightarrow ^*\text{CH}_4 + ^*$ ($\Delta E = 0.36$ eV, $E_a = 0.66$ eV).

Interestingly, E_a for $^*\text{H}_2\text{COH}$ hydrogenation to $^*\text{CH}_3\text{OH}$ is 0.33 eV higher than that for C-O bond scission to form $^*\text{CH}_2$ and $^*\text{OH}$, which ensures a higher selectivity to CH_4 rather than CH_3OH on the Pt NP as demonstrated below in the KMC simulations.

Figure 5. Potential energy diagrams for the CH_4 synthesis via the RWGS + CO-Hydro pathways. The energetics for each reaction intermediate is included together with the transition site (TS) for each elementary step. The lines in different colors label the different paths.

3.2 Pt NPs: activity and selectivity based on KMC simulations

The DFT calculations have addressed the energetics for CO_2 hydrogenation on the Pt NP. This section explores how the energetics would affect the kinetics of the reaction regarding the following questions: Which are the dominant pathways for CO_2 conversion? What is the overall rates for CO_2 conversion and the production of CO , CH_4 and CH_3OH under the reaction conditions? What are the key kinetic parameters or descriptors that describe and control the activity and selectivity? To answer these questions, a KMC simulation followed by a sensitivity analysis was conducted. Various possible elementary steps were included in the KMC

simulations (Table 2), where both the formate and the RWGS + CO-Hydro pathways were taken into consideration. A prefactor of $1.0 \times 10^{13} \text{ s}^{-1}$ was used for all surface reactions. For the reactions involving gases, the contribution from the entropy was taken from the NIST database [68] and was included in the KMC simulations. The KMC simulations were carried out at the reaction conditions of $T = 573 \text{ K}$ and $P_{\text{H}_2}/P_{\text{CO}_2} = 2:1$ for 60 s. The catalytic activity of the Pt NP for CO, CH₄ and CH₃OH production in the KMC simulations was measured by the rate of CO, CH₄ and CH₃OH desorption, respectively.

Table 2: Activation energy (E_a) and reaction energy (ΔE) (in eV) of elementary reactions in the hydrogenation of CO₂ to CO, CH₃OH and CH₄ on the Pt NP.

Reactions	E_a	ΔE
*CO ₂ → CO ₂ (g) + *	0.29	0.29
*CO → CO(g) + *	2.29	2.29
*CO ₂ + *H → *HOCO + *	1.01	-0.09
*HOCO + * → *CO + *OH	0.75	-0.46
*OH + *H → *H ₂ O + *	0.53	-0.08
*CO + *H → *HCO + *	1.30	0.96
*HCO + *H → *H ₂ CO + *	0.95	0.54
*H ₂ CO + *H → *CH ₃ O + *	0.80	0.48
*CH ₃ O + *H → *CH ₃ OH + *	1.19	-0.06
*CO + *H → *COH + *	2.03	1.11
*COH + *H → *HCOH + *	0.91	0.32
*HCO + *H → *HCOH + *	0.44	0.20
*HCOH + *H → *H ₂ COH + *	0.88	0.18
*H ₂ CO + *H → *H ₂ COH + *	1.08	-0.01
*H ₂ COH + *H → *CH ₃ OH + *	1.13	0.31
*CO ₂ + *H → *HCOO + *	1.37	0.05
*HCOO + *H → *HCOOH + *	0.78	0.24
*HCOO + *H → *H ₂ COO + *	2.10	1.58
*H ₂ COO + *H → *H ₂ COOH + *	1.04	-0.51
*HCOOH + *H → *H ₂ COOH + *	1.80	0.87
*H ₂ COOH + * → *H ₂ CO + *OH	0.68	0.07
*H ₂ COH + * → *CH ₂ + *OH	0.80	0.22
*CH ₃ O + *H → *CH ₃ + *OH	0.91	-0.35
*CH ₂ + *H → *CH ₃ + *	0.50	0.15
*CH ₃ + *H → *CH ₄ + *	0.66	0.36
*H ₂ O → H ₂ O(g) + *	0.54	0.54
*CH ₃ OH → CH ₃ OH(g) + *	0.64	0.64

$*CH_4 \rightarrow CH_4(g) + *$	0.07	0.07
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The KMC simulations determine the activity and selectivity of the Pt NP under the reaction conditions. As shown in Figure 6a, the productions of CO, CH₄ or CH₃OH are not observed during the conversion of CO₂ and H₂, indicating that the activity of the Pt NP is rather low. In term of selectivity, CO is the main product with only a small amount of the produced *CO is hydrogenated to CH₄, where no CH₃OH production is observed. In addition, the KMC simulations also help identify the preferred reaction pathways. CO is mainly produced via the RWGS reaction, as *H₂COOH and *H₂COO formations are not observed during the KMC simulations. The generation of either species is essential for the conversion of CO₂ to CH₄ via the formate pathways (Figure 1). The formation of CH₄ from *CO mainly occurs via the route *HCO → *HCOH → *H₂COH → *CH₂ → *CH₃ → *CH₄ as predicted in the DFT results. Yet, very small amount of CH₄ formation is detected via the route: *HCO → *H₂CO → *H₃CO → *CH₃ → *CH₄.

Figure 6. Sensitivity of CO and CH₄ production to the variation in (a) BE(CO₂), (b) CO

desorption energy and (c) activation energy of $*H + *CO \rightarrow *HCO + *$. (d) Sensitivity of CH_4 production to variation in activation energy of $*H_2COH + * \rightarrow *CH_2 + *OH$, and (e) Sensitivity of CH_4 and CH_3OH production to variation of activation energy of $*H_2COH + *H \rightarrow *CH_3OH + *$.

Finally, the combination of KMC simulations and the sensitivity analysis allows us to reveal the origin of the observed activity and selectivity. In the sensitivity analysis, each parameter in the KMC model is shifted by a small amount from its original value and the other parameters are kept constant.[69] Such analysis also enables the identification of the key steps that control the activity and selectivity. According to the sensitivity analysis, the low activity of the Pt NP is associated with the weakly adsorbed CO_2 , which desorbs before its hydrogenation to form either $*HOCO$ in the RWGS + CO-Hydro pathways or $*HCOO$ in the formate pathways. As a result the Pt NP itself does not catalyze CO_2 conversion to CO, CH_4 or CH_3OH . Increasing the stability of CO_2 is necessary to facilitate the overall conversion (Figure 6a). In addition, the CO and CH_4 yields increase with $BE(CO_2)$ (Figure 6a); yet this is not the case for CH_3OH , and no CH_3OH yield is observed on the Pt NP even with the increased CO_2 binding. Therefore CO_2 binding is predicted to be one of the key steps, which controls the activity toward conversion of CO_2 .

Once the CO_2 binding is strengthened to facilitate the overall conversion, the CO binding becomes important (Figure 6b). In fact, it has also been identified as the key descriptor for CO_2 hydrogenation on Cu-based system.[23] The CH_4 yield increases steadily with increasing stability of $*CO$. On the contrary, $*CO$ desorbs when it is weakly bound and in such case CO is the only product resulting from the hydrogenation of CO_2 even if $*CO_2$ is stable enough. These results indicate that increasing the CO binding on the Pt NP can be effective in tuning the selectivity from CO to CH_4 . That is CO binding is another key step, which controls selectivity.

In addition, two more selectivity-controlling steps are also identified. One is $^*\text{CO}$ hydrogenation to $^*\text{HCO}$, where the variation in the corresponding E_a is able to tune the selectivity toward CH_4 (Figure 6c); the other is competition between $^*\text{H}_2\text{COH}$ dissociation to $^*\text{CH}_2 + ^*\text{OH}$ and hydrogenation to CH_3OH . The selective CH_4 formation on the Pt NP can be improved by facilitating the dissociation (Figure 6d). In term of CH_3OH , the production is only observed in KMC simulations when E_a of the $^*\text{H}_2\text{COH}$ hydrogenation is lowered to at least comparable to that of the dissociation reaction (Figure 6e). Under such condition $^*\text{H}_2\text{COH}$ hydrogenation competes with its dissociation, leading to the production of both CH_4 and CH_3OH .

Overall, the KMC simulations and sensitivity analysis show that the Pt NP alone is not a good catalyst for the conversion of CO_2 by H_2 . The overall conversion is hindered by the weak interaction between Pt and CO_2 , which favors the CO_2 desorption rather than hydrogenation under reaction conditions. By stabilizing CO_2 is stabilized on the surface, CO is the main product for CO_2 hydrogenation on the Pt NP via the RWGS pathway. Only a small amount of produced $^*\text{CO}$ is further hydrogenated to CH_4 via the CO-Hydro pathways and the $^*\text{H}_2\text{COH}$ intermediate; yet no CH_3OH yield is observed in any case. The selectivity to CH_4 can be tuned by increasing the binding of CO , facilitating $^*\text{CO}$ hydrogenation to $^*\text{HCO}$ and lowering the barrier of C-O bond cleavage of $^*\text{H}_2\text{COH}$; in contrast, the selectivity to CH_3OH can be only promoted by decreasing the activation energy of H_2COH hydrogenation to be at least comparable to that of C-O bond cleavage of $^*\text{H}_2\text{COH}$. Accordingly, promoters can be added to the Pt NP to tune these important parameters and therefore the activity and selectivity of the Pt NP toward CO_2 hydrogenation.

In Section 3.3, we will study the effect of supporting the Pt NP on SiO₂ and TiO₂, which are typically employed in practical applications. In our modeling, we assume that Pt/SiO₂ and Pt/TiO₂ follow the same reaction mechanism as Pt, where only the BE values of the key intermediates involved in the activity- and selectivity-controlling steps for CO₂ hydrogenation on Pt are calculated and used for estimating the trend in catalytic properties. This assumption appears to be reasonable. As you will see below, the binding motifs for these intermediates at Pt-SiO₂ and Pt-TiO₂ interface are similar. Although the BE value provided by each system is different for the same adsorbate, the difference is less than 0.3 eV. More importantly, based on such assumption, the trend in activity and selectivity on going from Pt/SiO₂ to Pt/TiO₂ derived using only the calculated BE values is well supported by our experiment in a fixed bed flow reactor.

3.3 Pt NP supported on SiO₂ and TiO₂

3.3.1 DFT calculations

Due to the high computational cost for modeling the supported Pt₄₆ NP, a Pt₂₅ NP deposited on the SiO₂(111) surface was considered as a simplified model to describe Pt/SiO₂. To model the interface between Pt₄₆ and oxide supports, the Pt₂₅ NP supported on SiO₂ (Figure 7a) adopts similar edges and corners, though smaller in size compared to the Pt₄₆ NP in Figure 2a. To estimate the effect due to the difference in size, we calculate the BEs of key intermediates, which are involved in the activity- and selectivity-controlling steps for Pt₄₆ (CO₂, CO and HCO), on an unsupported Pt₂₅ NP. The corresponding values (BE = -0.34 eV for CO₂, BE = -2.28 eV for CO, BE = -2.88 eV for HCO) are very similar to those calculated on similar sites on a Pt₄₆ NP (Table 1). Accordingly, we believe that the Pt₂₅/SiO₂ is a reasonable simplified model to

resemble the $\text{Pt}_{46}/\text{SiO}_2$. Thus, we assume here that the results from the sensitivity analysis on the Pt NP alone can be used to qualitatively describe the catalytic behavior of Pt/SiO_2 . Although the Pt/SiO_2 samples were fully dried at 373 K in air and then calcined at 563 K for 2 hours, SiO_2 is still hydroxylated according to our Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurement (Figure S1) and the previous studies.[70] Accordingly, we saturated the dangling O bonds on the model SiO_2 surface model with hydrogen to form *OH groups (Figure 7a). Such surface motif has previously been used to model silica in studies of silica-supported Pt catalysts.[71]

The BE of CO_2 is calculated on Pt/SiO_2 , which is the key parameter to control the overall CO_2 conversion as demonstrated for Pt NP. The DFT optimized geometry in Figure 7b shows that the most favorable binding site for CO_2 is the corner sites of the Pt NP at the Pt- SiO_2 interface. The corresponding BE is stronger than that of Pt by 0.21 eV for Pt_{46} and 0.16 eV for Pt_{25} , indicating that CO_2 adsorption is enhanced by using SiO_2 support. Such enhancement is mainly due to the hydrogen bond between the O atoms of CO_2 and the hydroxyl group of hydroxylated $\text{SiO}_2(111)$ surface (Figure 7b). As demonstrated in Section 3.2, the Pt NP alone shows no activity for CO_2 conversion due to the very weak CO_2 binding. Now CO_2 binding is enhanced by using SiO_2 as a support, and consequently the overall CO_2 conversion is likely improved on Pt/SiO_2 .

Figure 7. DFT optimized geometries. (a) Pt₂₅/hydroxylated SiO₂(111), and (b) *CO₂, (c) *CO, (d) *HCO, (e) *H₂COH, (f) *CH₃OH, (g) *CH₂, and (h) *OH adsorbed on Pt/SiO₂(111). Dashed lines show hydrogen bonds. Si: green, Pt: light grey, C: dark grey, O: red, and H: blue.

The BEs of the chemical species involved in the key steps identified for the Pt NP alone ($*CO \rightarrow CO + *$, $*CO + *H \rightarrow *HCO + *$, $*H_2COH + * \rightarrow *CH_2 + *OH$ and $*H_2COH + *H \rightarrow *CH_3OH + *$) (Table 3) and the corresponding reaction energies (Table 4) on Pt/SiO₂ were also calculated to estimate the effect of the SiO₂ support on the selectivity. One can see in Figure 7 that, similar to CO₂, the preferential sites for the other intermediates are also the interfacial Pt corner sites. Again, the increased BE due to the interaction with the *OH species on the support via hydrogen bonds is also observed for *OH, *H₂COH, and in particular *CH₃OH, while a decrease in stability is obtained for *CO, *H and *CH₂. As listed in Table 3, CO binds more weakly by 0.38 eV on Pt/SiO₂ than Pt, which facilitates not only the *CO desorption, but also the hydrogenation to *HCO with the ΔE lowered by 0.17 eV compared to Pt (Table 4). According to the results from sensitivity analysis, the destabilized *CO can result in the tuning of selectivity toward CO production (Figure 6b); on the contrary, the facilitated *CO hydrogenation is likely to promote the CH₄ yield (Figure 6c). On the basis of the difference in energetics between the two

steps (0.38 eV vs. 0.17 eV), it is likely that the effect introduced by the destabilized *CO on *CO hydrogenation cannot compete with that on *CO desorption. Therefore, CO should remain as the major product on Pt/SiO₂ as that on Pt, but the selectivity to CO can be slightly increased. The calculated ΔE values of the key steps, $*H_2COH \rightarrow *CH_2 + *OH$ and $*H_2COH + *H \rightarrow *CH_3OH$ on Pt/SiO₂, are decreased by 0.30 and 0.33 eV, respectively, compared to Pt. Accordingly, as in the case of Pt, the dissociation reaction $*H_2COH \rightarrow *CH_2 + *OH$ is more favorable over the competing hydrogenation reaction $*H_2COH + *H \rightarrow *CH_3OH$ on Pt/SiO₂, and no CH₃OH yield is expected. Thus the selectivity of CO₂ hydrogenation on Pt/SiO₂ is predicted to be similar to that on Pt with a slightly increased CO selectivity.

Table 3: Binding energies (BE in eV) of chemical species involved in the hydrogenation of CO₂ on the Pt/SiO₂, Pt/TiO₂ and Pt NP.

Species	Pt/SiO ₂	Pt/TiO ₂	Pt
CO ₂	-0.50	-0.61	-0.29
H	-2.84	-2.58	-2.96
OH	-3.20	3.10	-3.15
CO	-1.91	-1.62	-2.29
HCO	-2.64	-2.77	-2.89
H ₂ COH	-2.55	-2.56	-2.40
CH ₃ OH	-1.03	-0.92	-0.64
CH ₂	-4.65	-4.78	-4.84

Table 4: Reaction energy (ΔE) (in eV) of key elementary steps in the hydrogenation of CO₂ on the Pt/SiO₂, Pt/TiO₂ and Pt NP.

Reactions	Pt/SiO ₂	Pt/TiO ₂	Pt
*CO + *H $\rightarrow$ *HCO + *	0.79	0.30	0.96
*H ₂ COH + * $\rightarrow$ *CH ₂ + *OH	-0.08	-0.12	0.22
*H ₂ COH + *H $\rightarrow$ *CH ₃ OH + *	-0.02	-0.16	0.31

Similar calculations were carried out for Pt₂₅/TiO₂(110) as shown in Figure 8a. Different from SiO₂(111), TiO₂ is a reducible oxide. For example, Pd/TiO₂ has been employed as a

hydrogen sensor and reducing oxide powder in a H_2 atmosphere[72], which leads to the surface reduction and the formation of oxygen vacancies.[73, 74] The previous studies have reported the formation of hydrocarbonate via CO_2 and OH on Ru/TiO₂:[75] however the CO_2 hydrogenation conditions applied in the present study is at relatively high temperature ranging from 553 to 623 K, which hinders the hydroxylation a measurements and promotes the oxygen vacancy formation. To confirm that, the DRIFTS measurements were performed to compare the concentrations of the hydroxyl group on TiO₂ and SiO₂, as illustrated in Figure S1. While the SiO₂ surface is characterized by an intense and relatively sharp $\nu(O-H)$ mode at 3746 cm^{-1} , the same spectral region of TiO₂ is characterized by relatively weak and broad features. Based on the DRIFTS results, hydroxyl groups were not included in the DFT calculations over TiO₂(110), while TiO₂(110) surfaces with and without oxygen vacancies were both taken into considerations. Again the CO_2 binding is calculated to estimate the overall activity. The results show that CO_2 binds on neither stoichiometric TiO₂(110) nor the Pt-TiO₂ interface as strongly as that of Pt NP; in contrast, CO_2 binding is strengthened by 0.32 eV compared to Pt when an oxygen vacancy is generated at Pt-TiO₂ interface (Table 3). As shown in Figure 8b, CO_2 interacts with Pt at the Pt-TiO₂ interface. The molecule is bent in a way that one of the O atoms in CO_2 tries to fill the oxygen vacancy. The C-O bond cleavage results in filling of the vacancy; yet it can be regenerated by hydrogen for adsorbing additional CO_2 under the reaction conditions. On the basis of calculated $BE(CO_2)$, a higher CO_2 conversion on Pt/TiO₂ than Pt/SiO₂ and Pt is expected. Again the active sites at the metal-oxide interface play an important role in stabilizing CO_2 and therefore enhancing its subsequent hydrogenation.

Besides CO_2 , we also calculated the bindings of other key intermediates identified for CO_2 hydrogenation on Pt. Different from CO_2 , the BEs of all other intermediates on Pt/TiO₂ are

calculated without O vacancies, which are likely to be filled by O atoms generated from CO₂ dissociation. CO binding is also studied for estimating the selectivity. As shown in Table 3, *CO desorption is easier on Pt/TiO₂ than Pt, due to the weaker binding by 0.67 eV (Table 3), where the C atom prefers the interfacial Pt sites (Figure 8c); however, ΔE for the reaction $*CO + *H \rightarrow *HCO + *$ decreases significantly (by 0.66 eV) (Table 4). According to the sensitivity analysis for Pt, the decreased CO binding is likely to favor the selective CO production, while the facilitated *CO hydrogenation may hinder the formation of CO and promote CH₄ selectivity. Considering the comparable energetics for both processes, it is expected that the selectivity to CO and CH₄ may remain nearly the same as Pt. Such similarity is also obtained due to the similar decrease in ΔE of the selectivity-controlling steps $*H_2COH \rightarrow *CH_2 + *OH$ (0.34 eV) and $*H_2COH + *H \rightarrow *CH_3OH$ (0.47 eV) on Pt/TiO₂ with respect to Pt (Table 4). Thus, Pt/TiO₂ is predicted to be similar to Pt regarding the selectivity to CO and CH₄. Note that we did not calculate the activation barriers for the key steps on both supported systems. The previous DFT calculations of CO₂ hydrogenation on metal/oxide systems show that the trend in the calculated reaction energy is able to well represent that in activation barrier, [76-78] which is our primary interest in the current paper. Indeed, as you will see in section 3.3.2, the trends in activity and selectivity from Pt/SiO₂ to Pt/TiO₂, which is predicted only based on the reaction energies calculated for the key steps, are well supported by our experiments in a fixed bed flow reactor.

Figure 8. DFT optimized geometries. (a) Pt₂₅/TiO₂(110) with oxygen vacancy, and side (top) and top (bottom) views of (b) *CO₂, (c) *CO, (d) *HCO, (f) *H₂COH, (e) *CH₃OH, (f) *CH₂, (g) *H₂COH and (h) *OH adsorbed on Pt/TiO₂(110). Black circle in (a) depicts the position of oxygen vacancy on TiO₂(110). Ti: Light blue, Pt: light grey, C: dark grey, O: red, and H: blue.

Overall, using either SiO₂ or defected TiO₂ with oxygen vacancy as support, Pt NP is able to bind CO₂ more strongly than Pt alone. Accordingly, the overall CO₂ conversion should be enhanced. In addition, the stabilization of CO₂ on Pt/TiO₂ with oxygen vacancy is more significant than that on Pt/SiO₂ and therefore a higher activity for Pt/TiO₂ is expected. In terms of selectivity, for all the systems studied, CO remains as the major product and the CH₃OH yield is strongly inhibited. Pt/TiO₂ is predicted to be slightly more selective to CH₄ than Pt/SiO₂ due to its capability in facilitating *CO hydrogenation. According to the DFT calculations, the different behaviors of Pt/oxide from Pt are originated from the sites at the Pt-oxide interface, where the synergy between Pt and oxide plays an important role.

Figure 9. HAADF TEM micrographs and particle size distributions for the catalysts: (a) Pt/TiO₂ and (b) Pt/SiO₂.

3.3.2 Experimental results

To verify the trends predicted by our theoretical study, CO₂ hydrogenation over SiO₂ and TiO₂ supported Pt powder catalysts was studied in a fixed bed flow reactor. The particle size distributions are shown in Figure 9 using HAADF TEM, which are calculated by measuring horizontal particle diameters in several different images for each catalyst. As shown in Figure 9, the average Pt sizes are about 1 nm and 2 nm for Pt/TiO₂ and Pt/SiO₂, respectively, which are in the similar range of particle size studied in DFT calculations. Table 5 shows the steady-state conversion and the corresponding turnover frequency (TOF) of these two catalysts at different temperatures. The weight hourly space velocity (WHSV) is 119.7 and 24.7 h⁻¹ for Pt/TiO₂ and Pt/SiO₂, respectively. The TOF values show that Pt/TiO₂ is clearly more active than Pt/SiO₂ for

CO₂ hydrogenation, in good agreement with the predictions based on DFT and kinetic modeling. Furthermore, as shown in Table 6, by comparing the results at either the same temperature or at a similar CO₂ conversion, the ratio of CO/CH₄ over Pt/SiO₂ catalyst is higher than that over Pt/TiO₂, indicating a higher CO selectivity for Pt/SiO₂ as predicted by DFT. Finally, no CH₃OH yield is observed for both systems.

Table 5: Summary of conversion and turn over frequency (TOF) of Pt/TiO₂ and Pt/SiO₂

Temperature (K)	CO ₂ conversion (%)		H ₂ conversion (%)		TOF (times/site/min)	
Reactor	Pt/TiO ₂	Pt/SiO ₂	Pt/TiO ₂	Pt/SiO ₂	Pt/TiO ₂	Pt/SiO ₂
553	2.99	2.03	1.50	0.93	109.7	21.00
563	3.69	2.60	1.85	1.19	135.7	26.96
573	4.51	3.35	2.26	1.54	165.6	34.71
583	5.42	4.31	2.75	1.97	199.1	44.68
593	6.49	5.30	3.27	2.41	238.7	54.98
603	7.63	6.39	3.85	2.91	280.4	66.23
613	8.90	7.64	4.48	3.48	327.1	79.23
623	10.23	8.99	5.20	4.10	376.1	93.16

Table 6: Summary of selectivity of Pt/TiO₂ and Pt/SiO₂

Temperature (K)	CO selectivity (%, carbon basis)		CH ₄ selectivity (%, carbon basis)		CO:CH ₄ ratio (-)	
Reactor	Pt/TiO ₂	Pt/SiO ₂	Pt/TiO ₂	Pt/SiO ₂	Pt/TiO ₂	Pt/SiO ₂
553	99.22	100.0	0.78	0.0	127.8	+∞
563	99.16	100.0	0.84	0.0	118.2	+∞
573	99.08	100.0	0.92	0.0	108.0	+∞
583	98.99	99.9956	1.01	0.0044	98.4	22601.4
593	98.87	99.9955	1.13	0.0045	87.8	22434.5
603	98.73	99.9947	1.27	0.0053	78.0	18824.1
613	98.57	99.9930	1.43	0.0070	69.0	14290.0
623	98.39	99.9905	1.61	0.0095	61.2	10569.3

The theoretically predicted trend on both activity and selectivity for CO₂ hydrogenation on Pt/SiO₂ and Pt/TiO₂ is well reproduced experimentally. More importantly, it also implies that the key parameters identified in kinetic modeling to control the activity and selectivity can be

effective to estimate the possible effects of using modifiers, such as oxide supports, on the catalytic behavior of Pt for CO₂ hydrogenation. On such basis, it would be possible to perform theoretical screening of modifiers to tune the activity and selectivity of Pt catalysts in future studies.

4. Conclusions

The catalytic conversion of CO₂ by H₂ on the Pt NP was studied by combining DFT calculations, KMC simulations and experimental measurements. DFT calculations show that corners and edges of the Pt NP are active for the adsorption of chemical species involved in the hydrogenation of CO₂. The reaction prefers to undergo the RWGS + CO-Hydro pathways, rather than the formate pathways. CO is produced from the RWGS reaction, which can either desorb or further react with hydrogen to produce CH₄ or CH₃OH. It is predicted that in spite of the presence of active, low-coordinated sites, Pt NP alone is not able to catalyze the reaction. The overall activity is hindered by the weak bonding with CO₂. The selectivity strongly depends on four parameters: BE(CO), and energetics for $*CO + *H \rightarrow *HCO + *$, $*H_2COH + * \rightarrow *CH_2 + *OH$ and $*H_2COH + *H \rightarrow *CH_3OH + *$. Weakening the binding of CO on the Pt NP leads to higher selectivity to CO, while the increased binding of CO and therefore the facilitated $*CO$ hydrogenation to $*HCO$ hinders CO yield and increase that for CH₄ or CH₃OH. The ratio for CH₄/CH₃OH is primarily determined by the competition between the C-O bond dissociation and the hydrogenation reactions of $*H_2COH$.

Using both SiO₂ and defected TiO₂ with oxygen vacancy as support, Pt NP is able to enhance the overall CO₂ conversion via increased CO₂ binding. The enhancement is more significant for Pt/TiO₂ than Pt/SiO₂ and therefore higher activity is expected for Pt/TiO₂. In

terms of selectivity, CO remains the major product and the formation of CH₃OH is strongly inhibited for both systems, while Pt/TiO₂ is predicted to be slightly more selective to CH₄ than Pt/SiO₂ due to its selective capability in facilitating *CO hydrogenation. Such trend in activity and selectivity is well supported by the corresponding experimental results. The combined theoretical and experimental results indicate that the enhanced activity of Pt/oxide over Pt is originated from the sites at the Pt-oxide interface, where the synergy between Pt and oxide plays an important role.

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