



CO₂ Hydrogenation over Oxide-Supported PtCo Catalysts: The Role of the Oxide Support in Determining the Product Selectivity

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Abstract: By simply changing the oxide support, the selectivity of a metal–oxide catalysts can be tuned. For the CO₂ hydrogenation over PtCo bimetallic catalysts supported on different reducible oxides (CeO₂, ZrO₂, and TiO₂), replacing a TiO₂ support by CeO₂ or ZrO₂ selectively strengthens the binding of C, O-bound and O-bound species at the PtCo–oxide interface, leading to a different product selectivity. These results reveal mechanistic insights into how the catalytic performance of metal–oxide catalysts can be fine-tuned.

The performance of a catalyst depends strongly on its binding properties. According to the Sabatier principle,^[1] a good catalyst should bind the reaction intermediates strongly enough to activate the reactants and weakly enough to allow for product desorption. Various approaches have been applied to optimize the structure of a catalyst and to tune the binding properties and therefore the catalytic activity. Typically, the binding energies of various adsorbates vary linearly with changing the local structure of a catalyst or its composition to form alloys.^[2] As a result, the catalytic activity towards a reaction can be enhanced by accelerating the activity-limiting steps along the reaction pathway,^[3] however, it makes the control of product selectivity more difficult, which often requires the non-linear tuning of the binding energies of different adsorbates.

Herein, we report a possibility to move away from the linear scaling principle by taking advantage of strong metal–oxide interactions to selectively modify the binding energies of particular adsorbates. The special synergy between metals and oxides can introduce large electronic perturbations in the metals,^[4] provide heterogeneous sites,^[3d,5] or induce variations in the structure or phase of the supported metal particles,^[6] which directly affect the bonding properties and correspond-

ingly the catalyst performance. Carbon dioxide (CO₂) hydrogenation on PtCo bimetallic catalysts supported on different reducible oxides (CeO₂, ZrO₂, and TiO₂) was taken as a case study. When different oxide supports were used, the binding of the metal–oxide interface to various reaction intermediates changed; however, the response was very different depending on the species. This non-linear response enables the significant tuning of the selectivity of metal oxide catalysts whereas the overall reactivity was much less affected. A combination of ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and density functional theory (DFT) calculations for the model catalysts and transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and extended X-ray absorption fine structure (EXAFS) analysis for the corresponding powder catalysts provided insight into how the performance of metal–oxide catalysts can be fine-tuned.

The catalytic conversion of CO₂ into methane (CH₄),^[6c,7] methanol (CH₃OH),^[3d,8] and carbon monoxide (CO)^[6c,9] has gained tremendous interest in recent years. The generation of CH₄ from CO₂ is not profitable considering the large shale gas reserves and its low volumetric energy density. CH₃OH synthesis has been well studied, but the current market demand for CH₃OH would only reduce the global CO₂ emission by 0.1 % if all CH₃OH was produced from CO₂.^[10] Therefore, one of the most desirable routes for CO₂ conversion is the production of CO, the feedstock for the Fischer–Tropsch process to produce chemicals and fuels. Achieving a high selectivity to the desired CO product rather than CH₄ and CH₃OH is critical, yet challenging in practical applications.

Metal-based catalysts on oxide supports enable the conversion of CO₂. Copper-based catalysts have been found to convert CO₂ and hydrogen into CH₃OH,^[8a,11] whereas platinum-, gold-, and silver-based catalysts promote the conversion of CO₂ into CO.^[12] Herein, we demonstrate how the selectivity of PtCo catalysts can be fine-tuned by using oxide supports. Whereas a PtCo/TiO₂ catalyst effectively converts CO₂ and H₂ into CO, PtCo/CeO₂ and PtCo/ZrO₂ catalyze the selective formation of CH₄. As PtCo/CeO₂ and PtCo/ZrO₂ behave similarly (see the Supporting Information), either PtCo/CeO₂ or PtCo/ZrO₂ was used as a representative system for comparison with PtCo/TiO₂.

As CO₂ does not adsorb strongly onto single-crystal surfaces under ultrahigh vacuum conditions, PtCo/TiO₂(110) and PtCo/CeO₂(110) model surfaces were analyzed by AP-XPS to identify possible reaction intermediates for CO₂ reduction by H₂. The surface-species C 1s peaks at 292.8 eV

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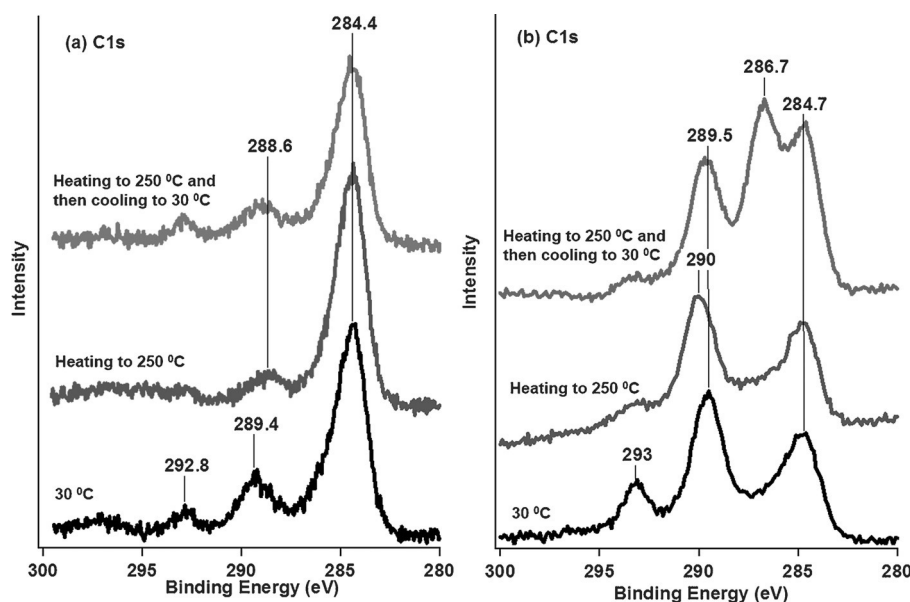


Figure 1. C 1s AP-XPS of a) PtCo/TiO₂ and b) PtCo/CeO₂ after exposure to CO₂ (100 mTorr) and H₂ (600 mTorr).

for PtCo/TiO₂(110) (Figure 1a) and 293.0 eV for PtCo/CeO₂(110) (Figure 1b) denote gas-phase CO₂. The features at 289.4 eV in Figure 1a and 289.5 eV in Figure 1b are attributed to the formation of carbonate (*CO₃) or formate (*HCOO)/carboxyl (*HOCO) species on both surfaces. These surface intermediates have previously been identified by AP-XPS on a CeO_x/Cu(111) surface after exposure to CO₂ under ambient pressure.^[3d,13] The peaks at approximately 284.4 eV in Figure 1a and 284.7 eV in Figure 1b indicate the presence of carbon on both surfaces. Upon heating to 250 °C and cooling down to room temperature, a peak at approximately 286.7 eV was observed for PtCo/CeO₂(110) but not for PtCo/TiO₂(110). This peak corresponds to the formation of methoxy (*CH₃O) species, suggesting that CO₂ hydrogenation may follow different reaction pathways on the PtCo/TiO₂(110) and PtCo/CeO₂(110) surfaces (see below).

The TEM results in Table 1 and in the Supporting Information, Figure S1 show that the size distributions for the three catalysts are fairly similar. Furthermore, the formation of Pt–Co bonds was confirmed for all catalysts by EXAFS (Tables 1 and S2 and Figure S2). CO₂ hydrogenation was evaluated in a flow reactor at 300 °C, with the activity

being presented in terms of both the conversion and the turnover frequency (TOF) by normalizing against the CO uptake for each catalyst. The CO₂ conversion over the three catalysts was very similar, indicating that the selectivity can significantly vary while the conversion hardly changes (Table 1). The ratio of CO/CH₄ formed over the PtCo/TiO₂ catalyst was 85, which is far higher than those for PtCo/CeO₂ (12) and PtCo/ZrO₂ (8.5), revealing that PtCo/TiO₂ selectively produces CO, whereas the other two supports favor the formation of CH₄.

A batch reactor equipped with an FTIR spectrometer was used to monitor surface intermediates and the gas-phase composition during the reaction. The FTIR spectra recorded after the reaction of CO₂ and H₂ on PtCo/CeO₂ and PtCo/TiO₂ powder catalysts (Figure S3)

are consistent with the findings from the AP-XPS study on the model surfaces (Figure 1). The bands at 1373 cm⁻¹ and 1610 cm⁻¹ were assigned to the symmetric and antisymmetric OCO vibrations (Table S3), respectively, of formate-like species, suggesting the presence of both HCOO* and HOCO* surface intermediates on both catalysts. Furthermore, for PtCo/CeO₂, vibrational features (bands at 1420 cm⁻¹ and 2869 cm⁻¹) indicative of the δ(CH₃) and ν_s(CH₃) modes (Table S3) in *CH₃O^[14] were also observed, suggesting the presence of the *CH₃O intermediate.

Various gas-phase reaction products were also identified by their characteristic vibrational modes. The vibrational modes ν(C=O) at 2358 cm⁻¹, ν(C≡O) at 2170 cm⁻¹, and ν(C–H) at 3016 cm⁻¹ were used to monitor the presence of CO₂, CO, and CH₄, respectively. On PtCo/TiO₂, aside from a sharp band corresponding to CO₂, CO was also detected (Figure 2a). On PtCo/CeO₂, vibrational peaks indicative of the formation of CH₄ were observed in addition to the characteristic CO band.

The involvement of these surface reaction intermediates was also confirmed by reacting CH₃OH or formic acid (HCOOH) in the batch reactor under the same conditions as for CO₂ hydrogenation to monitor and compare the reaction products. As shown in Figure 2b, the reaction products are almost identical for PtCo/CeO₂ and PtCo/TiO₂. CO and CO₂ were produced from both CH₃OH and HCOOH, indicating that *HCOO is a likely reaction intermediate on both PtCo/CeO₂ and PtCo/TiO₂. CH₄ was only produced from CH₃OH, suggesting that the surface *CH₃O intermediate is a likely precursor for the formation of CH₄. However, the conversion of CH₃OH into CH₄ occurred on both surfaces. Accordingly, the role that the TiO₂ support plays in preventing the formation of *CH₃O and therefore CH₄ on PtCo/TiO₂ must be related to the steps before *CH₃O formation.

Table 1: Particle size, coordination number (CN), CO chemisorption, steady-state CO₂ conversion, turnover frequency (TOF), and CO/CH₄ ratio for the PtCo/TiO₂, PtCo/CeO₂, and PtCo/ZrO₂ catalysts.

Catalyst	PtCo/TiO ₂	PtCo/CeO ₂	PtCo/ZrO ₂
particle size [nm]	2.3 ± 0.5	2.7 ± 1.0	2.3 ± 0.7
CN (Pt–Pt)	4.2 ± 0.6	5.1 ± 1.3	4.3 ± 2.1
CN (Pt–Co)	1.7 ± 0.5	2.7 ± 0.6	2.3 ± 1.6
CO chemisorption [μmol g ⁻¹]	18.7	36.4	39.4
CO ₂ conversion [%]	8.2	9.1	7.8
TOF [min ⁻¹]	35.3	20.1	16.0
CO/CH ₄ ratio	85	12	8.5

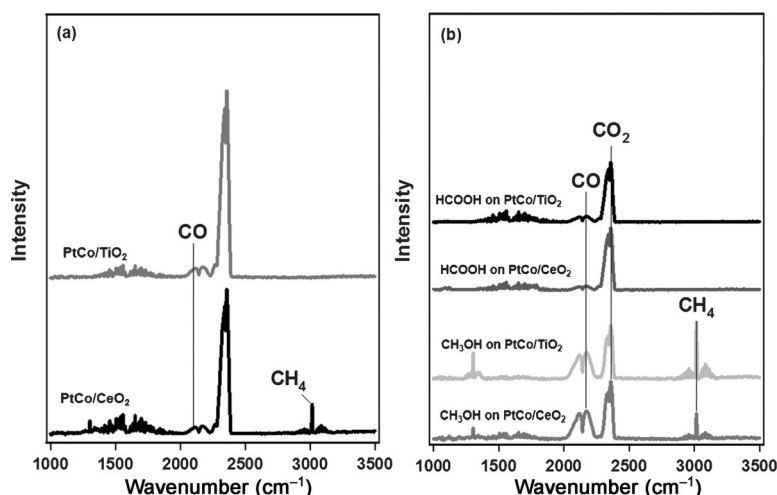


Figure 2. FTIR spectra recorded during a) CO₂ reduction in the presence of H₂ and b) the reactions of formic acid and methanol over PtCo/CeO₂ and PtCo/TiO₂ catalysts.

Overall, the experimental results with CeO₂ and TiO₂ supported PtCo powder catalysts indicate that different reaction intermediates lead to the different CO/CH₄ selectivities in the flow reactor. The CO/CH₄ selectivity is much greater over PtCo/TiO₂ than over PtCo/CeO₂ (Table 1). On PtCo/TiO₂, *HCOO is formed as an intermediate, which may eventually produce CO. On PtCo/CeO₂, aside from the route that proceeds via *HCOO, a pathway via a *CH₃O intermediate is operating in parallel, which likely leads to the formation of CH₄. Yet, at this stage, it is still unclear how the oxide supports tune the selectivity, and a better understanding of the detailed reaction network and the active sites is required, which is extremely difficult to obtain using only experimental techniques. Therefore, DFT calculations were carried out to determine the mechanism of CO₂ hydrogenation at the metal–oxide interfaces.

Pt-terminated surface structures have been predicted by DFT as the thermodynamically most stable structures and detected in surface experiments over model Co/Pt(111) surfaces^[15] and Co/Pt thin films^[16] for clean surfaces and in the presence of hydrogen. Figure S4 shows the DRIFTS measurements of CO adsorption over supported PtCo/ZrO₂. The relatively intense vibrational peaks of linearly adsorbed CO on the bimetallic PtCo/ZrO₂ catalyst are much more similar to those of Pt/ZrO₂ than those of Co/ZrO₂, which is consistent with a Pt-terminated bimetallic surface. The PtCo–oxide interface was modeled by depositing a small oxide cluster on the PtCo(111) support, where a Pt_{1ML}/Co_{1ML}/Pt(111) near-surface model was used, and the hydroxylation of oxides in hydrogen-rich environments was also considered (Figure 3). Such an inverse model has previously been shown to be a reasonable system for describing the catalytic properties of metal–oxide catalysts under CO₂ hydrogenation conditions.^[3d,8a,17] Owing to the deficiencies of standard DFT calculations in describing CeO_x, as discussed in more detail in the Supporting Information,^[18] PtCo/TiO₂ and PtCo/ZrO₂ were used as representative catalysts for the selective

formation of CO and CH₄, respectively, in our theoretical study.

The reaction network for CO₂ hydrogenation typically includes a pathway based on a reverse water–gas shift (RWGS) followed by CO hydrogenation (Figure S5) and the formate pathway.^[19] Our results show that the binding geometries of the reaction intermediates are similar on both PtCo/TiO₂ and PtCo/ZrO₂ (Figures S6 and S7). In general, C-bound species prefer Pt sites with an η¹-C_{Pt} bonding mode, whereas O-bound species prefer to bind to reduced M^{δ+} cations in the metal oxides with η¹-O_M^{δ+} configuration. For species bound through both C and O (C,O-bound species; for example, *CO₂, *HOCO, *CO, *CHO, *CHOH, *CH₂O, and *CH₂OH), the metal–oxide interfacial sites are favored with η²-C_{Pt}O_M^{δ+} configuration. Thus the metal–oxide interface is likely to play an important role in activating chemically inert CO₂ and facilitating its subsequent conversion.^[3d,8a]

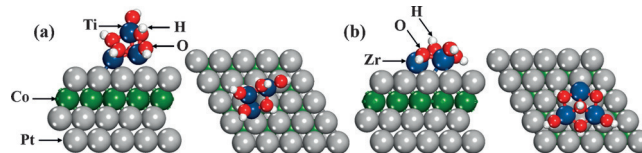


Figure 3. Side and top views of the DFT-optimized structures for model hydroxylated Ti₃O₆/PtCo(111) (a) and Zr₃O₆/PtCo(111) (b) surfaces.

CO and CH₄ production on PtCo/TiO₂ preferentially proceeds through RWGS and CO hydrogenation (Figure 4a). The adsorption of CO₂ leads to the formation of a carboxylate (CO₂^{δ-}) that is strongly bound at the PtCo–TiO₂ interface as a bent O–C–O motif in an η²-C_{Pt}O_{Ti}^{δ+} configuration (Figure S5b). Such a binding motif favors the hydrogenation to *HOCO (Figure S5c) with a reaction energy (Δ*E*) of −0.56 eV and a small activation energy (*E*_a) of 0.23 eV, as the transition only involves one O–H bond formation with a small distortion in the geometry of *CO₂. In contrast, *CO₂ hydrogenation to *HCOO is kinetically and thermodynamically less favorable (Δ*E* = −0.25 eV, *E*_a = 0.51 eV). The produced *HOCO then dissociates into *CO and *OH (Δ*E* = −0.26 eV, *E*_a = 0.93 eV), and *OH is hydrogenated to form *H₂O (*E*_a = 0.43 eV) while *CO either desorbs or undergoes further hydrogenation reactions. The hydrogenation of *CO to *CHO is exothermic by only −0.05 eV. The corresponding *E*_a (1.40 eV) is comparable to the BE of CO (−1.51 eV; see Table S4). However, under the reaction conditions, the entropy contribution significantly lowers the barrier for *CO desorption by 1.28 eV at 300 °C, and the desorption barrier is much lower than that for the hydrogenation to *CHO. Thus, corroborating our experimental finding (Table 1), the DFT results show that CO(g) is the main product of CO₂ hydrogenation over PtCo/TiO₂.

The minor side products result from the *CHO intermediate, which can be hydrogenated to either *CH₂O or

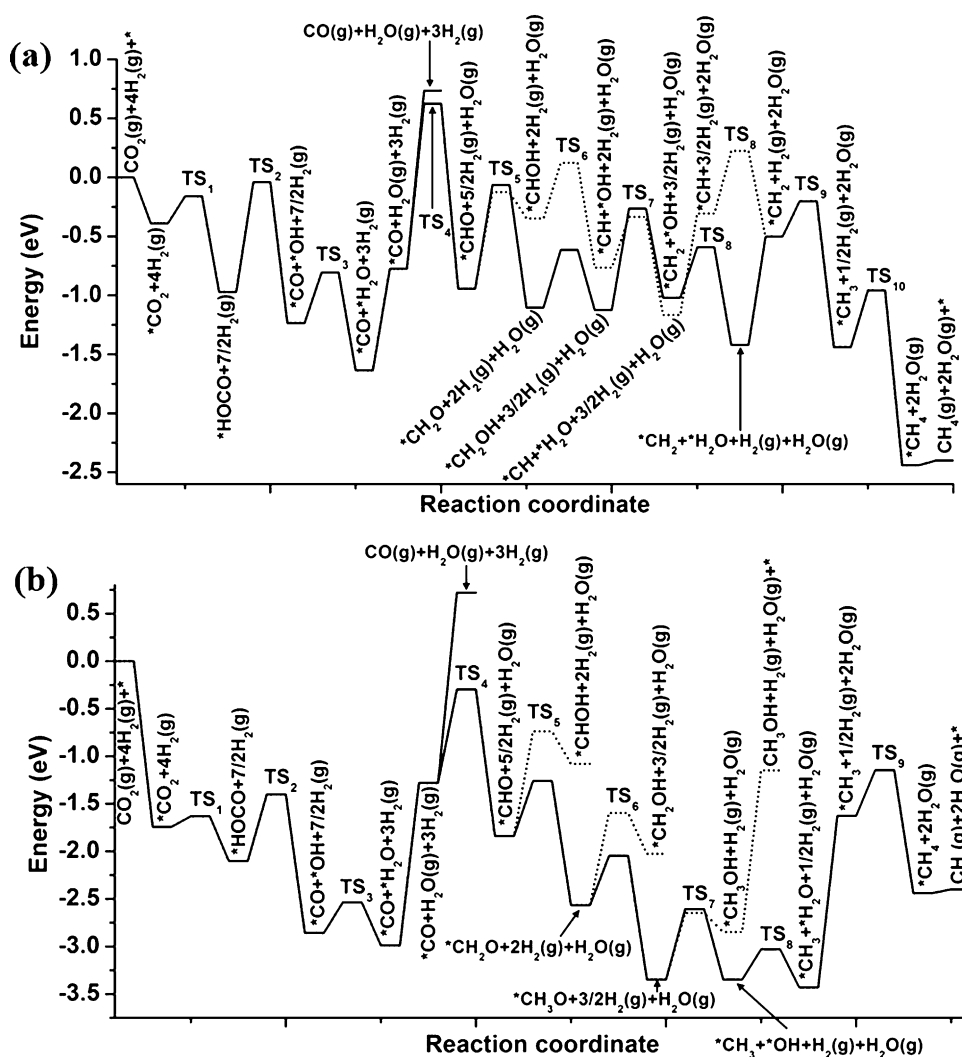


Figure 4. Potential energy diagrams for the synthesis of CO and CH₄ through the RWGS and CO hydrogenation pathway on model hydroxylated Ti₃O₆/PtCo(111) (a) and Zr₃O₆/PtCo(111) (b) surfaces.

*CHOH. Figure 4a shows that the two steps are competitive with a difference in E_a of only 0.06 eV (0.82 eV vs. 0.88 eV). *CHOH is the precursor for C–O bond cleavage to form *CH and *OH ($\Delta E = -0.42$ eV, $E_a = 0.47$ eV). *CH then undergoes three exothermic hydrogenation reactions to form CH₄, where the highest barrier is calculated for $\text{H} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{*}$ ($E_a = 0.48$ eV). The produced *CH₂O is further hydrogenated to form *CH₂OH ($E_a = 0.49$ eV), which dissociates into *CH₂ and *OH ($\Delta E = 0.10$ eV and $E_a = 0.86$ eV), eventually leading to *CH₄ production. The formation of *CH₃O ($E_a = 0.60$ eV) is less favorable. The DFT results agree well with the experiments on the PtCo/TiO₂ model and powder catalysts, where the *CH₃O intermediate and therefore CH₃OH(g) are not observed during CO₂ hydrogenation. Therefore, the minor side product for CO₂ hydrogenation over PtCo/TiO₂ is CH₄(g), which is consistent with the experimental results (Table 1).

For comparison, on PtCo/ZrO₂, the binding of C,O-bound and O-bound species at the interface is selectively strengthened as O–Zr^{δ+} bonds are formed (Table S4 and Figure S7), whereas for the C-bound species, the BEs of the Pt–C

interactions are the same as for TiO₂/PtCo(111). According to the calculated partial density of states (PDOS, Figure S8), the promoted O–Zr^δ interaction is associated with an increased density of states near the Fermi level compared to Ti^{δ+}. Thus, although the CO₂ hydrogenation follows the same pathway in both cases, differences in the reaction and activation energies are clearly observed (Figure 4b). On PtCo/ZrO₂, *CO₂ hydrogenation to *HOCO ($\Delta E = -0.39$ eV, $E_a = 0.11$ eV), *HOCO dissociation to *CO and *OH ($\Delta E = -0.75$ eV, $E_a = 0.70$ eV), as well as *CO hydrogenation to *CHO ($\Delta E = -0.48$ eV, $E_a = 0.98$ eV) are energetically more favorable; in contrast, *CO desorption is more difficult owing to the stronger CO BE (−2.00 eV). In this case, even when including entropy contributions, the energy required for *CO hydrogenation is comparable with that necessary for *CO desorption. Therefore, CO is only formed as a minor product over PtCo/ZrO₂ whereas the major products should result from *CO hydrogenation, such as CH₄ and/or CH₃OH.

Furthermore, *CHO on the PtCo/ZrO₂ interface is preferentially hydrogenated to *CH₂O ($\Delta E = -0.74$ eV, $E_a = 0.58$ eV) rather than *CHOH ($\Delta E = 0.76$ eV, $E_a = 1.10$ eV; Figure 4b). The sequential hydrogenation of *CH₂O results in *CH₃O formation ($\Delta E = -0.72$ eV, $E_a = 0.52$ eV) in contrast to the endothermic formation of *CH₂OH ($\Delta E = 0.54$ eV, $E_a = 0.97$ eV). This is in good agreement with the experimental detection of the *CH₃O intermediate on the PtCo/ZrO₂ model surface (Figure 1) and powder catalyst (Figure S3). Hydrogenation of *CH₃O to give *CH₃OH ($\Delta E = 0.50$ eV, $E_a = 0.70$ eV) or *CH₃ and *OH ($\Delta E = 0.01$ eV, $E_a = 0.74$ eV) is likely to be competitive; however, owing to the favorable binding at the PtCo–ZrO₂ interface, desorption of *CH₃OH is uphill in energy by 1.72 eV. Furthermore, the formed *CH₃OH is not stable and prefers dissociation to *CH₃O ($E_a = 0.20$ eV) over desorption ($E_a = 1.72$ eV). In contrast, *CH₃ hydrogenation to *CH₄ is much easier ($\Delta E = -0.95$, $E_a = 0.48$ eV). Therefore, as observed experimentally (Table 1), the DFT calculations predict that CH₄ is the major product resulting from the hydrogenation of *CO on PtCo/ZrO₂. Finally, the most

difficult step, and likely the activity-controlling step, along the reaction pathway (Figure 4) varies from $^*\text{HOCO}$ dissociation on PtCo/TiO_2 to $^*\text{CO}$ hydrogenation to $^*\text{HCO}$ on PtCo/ZrO_2 ; however, the corresponding barriers are similar (0.93 eV vs. 0.98 eV). Accordingly, only a small decrease in TOF is expected, which agrees well with our measurements (Table 1).

In summary, our experimental and theoretical investigations have shown that by changing the oxide support from TiO_2 to CeO_2 or ZrO_2 , the selectivity of bimetallic PtCo catalysts in CO_2 hydrogenation can be tuned while the overall activity is hardly affected. CeO_2 or ZrO_2 supported PtCo catalysts display high selectivity towards CH_4 , whereas CO is preferentially formed with a TiO_2 support. According to an AP-XPS analysis of model surfaces and the FTIR spectra of the powder catalysts, the difference in selectivity is likely associated with different dominant reaction pathways. $^*\text{HCOO}/^*\text{HOCO}$ are observed as reaction intermediates on PtCo/TiO_2 whereas both $^*\text{HCOO}/^*\text{HOCO}$ and $^*\text{CH}_3\text{O}$ are observed on PtCo/CeO_2 and PtCo/ZrO_2 . The DFT study well describes the experimental observations and indicates that the metal–oxide interface promotes the heterogeneity of the active sites. Unlike the binding of C-bound species, the binding of C,O-bound and O-bound species is tuned selectively at the interface. Changing the support from TiO_2 to ZrO_2 does not affect the dominant RWGS and CO hydrogenation pathway; however, CO formation is hindered, and CH_4 is preferentially formed over ZrO_2 . The synergy between the metal and oxide at the metal–oxide interface thus plays an important role in tuning the selectivity of CO_2 hydrogenation reactions over oxide-supported PtCo bimetallic catalysts.

Experimental Section

The catalysts were prepared by the incipient wetness impregnation method with an aqueous solution of the respective metal precursors ($(\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Alfa Aesar). The metal loadings (wt%) of the PtCo bimetallic catalysts were 1.7% Pt and 1.5% Co. After impregnation, the samples were dried at 60 °C overnight and calcined in air at 290 °C for 2 h. The PtCo bimetallic catalyst was selected because it led to higher CO_2 conversion than the corresponding monometallic catalysts.^[3c]

The DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) code.^[20] Electron–ion interactions were treated by the projector-augmented wave (PAW) method. The exchange and correlation energies were described using the generalized gradient approximation with the Perdew–Wang (PW91) functional. A cutoff energy of 400 eV and a $3 \times 3 \times 1$ Monkhorst–Pack k point grid were used. For further details of the theoretical models and the synthesis/characterization methods, see the Supporting Information.

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