



BNL-113828-2017-JA

**Adsorbate-mediated strong metal-support
interactions in oxide-supported Rh catalysts**

**John C. Matsubu, Shuyi Zhang, Leo DeRita, Nebojsa S. Marinkovic,
Jingguang G. Chen, George W. Graham, Xiaoqing Pan, Phillip Christopher**

Submitted to Nature Chemistry

February 2017

Chemistry Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Adsorbate-Mediated Strong Metal–Support Interactions in Oxide-Supported Rh Catalysts

John C. Matsubu¹, Shuyi Zhang^{2,3}, Leo DeRita¹, Nebojsa S. Marinkovic⁴, Jingguang G. Chen^{4,5}, George W. Graham^{2,3}, Xiaoqing Pan^{2,6}, Phillip Christopher^{1,7,8*}

¹Department of Chemical & Environmental Engineering, University of California, Riverside, Riverside, California 92521, United States

²Department of Chemical Engineering and Materials Science, University of California – Irvine, Irvine, California 92697, United States

³Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States

⁴Department of Chemical Engineering, Columbia University, New York, New York 10027, United States

⁵Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, United States

⁶Department of Physics and Astronomy, University of California—Irvine, Irvine, California 92697, United States

⁷Program in Materials Science, University of California, Riverside, Riverside, CA 92521, USA

⁸UCR Center for Catalysis, University of California, Riverside, Riverside, CA 92521, USA

*Corresponding Author E-mail: christopher@enr.ucr.edu

Table of contents summary:

Developing approaches to tune reactivity and selectivity of supported metal heterogeneous catalysts is critical for designing environmentally friendly chemical conversion processes. A reversible, structural catalyst transformation was identified, which involves an adsorbate-mediated oxide support encapsulation of Rh nanoparticles, that enabled dynamic tuning of CO₂ reduction selectivity.

Abstract:

Optimization of supported metal catalysts predominantly focuses on engineering the metal site, where physical insights based on extensive theoretical and experimental contributions have enabled rational design of active sites. While it is well known that supports can influence the catalytic properties of metals, insights into how metal support interactions can be exploited to optimize metal active-site properties are lacking. We utilize in-situ spectroscopy and microscopy to identify and characterize a support effect in oxide-supported heterogeneous Rh catalysts. This effect is characterized by strongly bound adsorbates (HCO_x) on reducible oxide supports (TiO₂ and Nb₂O₅) inducing oxygen-vacancy formation in the support and causing HCO_x functionalized encapsulation of Rh nanoparticles by the support. The encapsulation layer is permeable to reactants, stable under reaction conditions, and strongly influences the catalytic properties of Rh, enabling rational and dynamic tuning of CO₂ reduction selectivity.

Main Text:

The identification of optimal active sites on supported metal catalysts often focuses on engineering composition or geometry of the metal site for maximizing reaction rate or controlling reaction selectivity.¹⁻⁵ Much less is known about how metal support interactions can be exploited to control the reactivity of heterogeneous metal oxide supported metal catalysts, although support characteristics can influence catalytic reactivity or selectivity as considerably as characteristics of the metal.^{6,7} Demonstrated mechanisms of support effects on metal reactivity include small cluster stabilization,⁸ charge transfer,⁹⁻¹² support participation in catalysis,^{7,13,14} and oxide encapsulation of metal nanoparticles.¹⁵⁻¹⁹

Encapsulation of metal nanoparticles by reducible oxide support overlayers is the only mechanism by which supports can affect catalysis at a majority of active sites on metal particles with diameters larger than 1-2 nm,¹² and was designated by Tauster¹⁵ as strong metal support interactions (SMSI). The SMSI encapsulation state forms due to high temperature H₂ treatment of reducible oxide-supported Pt-group metals, causing a reduction of the oxide support to sub-stoichiometric oxygen concentrations and inducing oxide migration on top of metal nanoparticles. It has been hypothesized that bonding between cationic support metal atoms and the metal catalyst surface makes migration of the support onto the metal thermodynamically favorable.²⁰

Excitement surrounding the discovery of SMSI overlayers was stoked by the suggestion that the SMSI state could be used to tune metal catalyst reactivity via partial decoration of metals by oxide overlayers.¹⁶ However, the SMSI encapsulation state rarely finds an intermediate configuration where partial metal coverage by the oxide allows interaction with a majority of exposed metal sites. Instead, the oxide overlayer either covers all metal sites, rendering catalysts inactive, or retreats off the metal due to re-oxidation of the reduced support by H₂O or O₂,^{21,22} creating a situation where only a small fraction of metal sites are influenced by the partially reduced support, specifically at the metal-support interface.²³⁻²⁶ The poisoning or receded SMSI overlayer structures that exist under catalytic reaction conditions have curtailed the use of SMSI overlayers to increase reactivity or control selectivity on supported metal catalysts.

Here we demonstrate an SMSI encapsulation state that forms due to treatment of TiO₂ and Nb₂O₅ supported Rh nanoparticles in CO₂-H₂ (CO₂-rich) environments at temperatures of 150-300 °C. *In-situ* spectroscopy and microscopy show that high coverage of adsorbates (HCO_x) on the support induces oxygen vacancy formation, driving migration of the HCO_x-functionalized support onto the metal. This adsorbate-mediated SMSI (A-SMSI) encapsulation state is stabilized against re-oxidation by H₂O and modifies the reactivity of all remaining exposed Rh sites, appearing to be comprehensive in covering Rh but amorphous and permeable to reactants. Formation of the A-SMSI state induces a selectivity switch in the CO₂ reduction reaction from CH₄ production on bare Rh particles to CO production in the A-SMSI state, effectively rendering Rh less active for C-H bond formation. Our results show that the A-SMSI state represents a powerful support effect, enabling rational manipulation of metal catalyst reactivity.

Results

Effect of *in-situ* pretreatments on CO₂ reduction catalysis

In a recent analysis of TiO₂ supported Rh (Rh/TiO₂) catalysts for the reduction of CO₂ by H₂, we observed a dynamic decrease in the rate of CH₄ production and increase in the rate of CO

production when operating at CO₂:H₂ ratios greater than 1.⁵ Based on an assignment of CO production occurring at isolated Rh atoms and CH₄ production occurring at Rh nanoparticle surfaces, the reactivity change was attributed to Rh nanoparticle disintegration into isolated Rh atoms. However, the disproportionate magnitude of change in CO and CH₄ production rates (Supplementary Fig. 1) cannot be rationalized by the disintegration mechanism, suggesting that a more complex physical catalyst transformation was responsible for the changing selectivity.

To understand the controllability and mechanism of the observed dynamic change in CO₂ reduction selectivity, a series of oxide-supported Rh catalysts with varying oxide composition and Rh weight loading were synthesized, see Supplementary Information. To explore the effect of various pretreatments on CO₂ reduction selectivity, Rh/TiO₂ catalysts were reduced at 450 °C in H₂, evaluated for reactivity at 1%CO₂:1%H₂:98%He and 200 °C (reaction conditions were chosen for catalyst stability, see Supplementary Fig. 2,3, and used throughout the report except when stated otherwise), exposed to various environments (see Supplementary Table 1), and evaluated again for reactivity at 1%CO₂:1%H₂:98%He and 200 °C. Only treatments in CO₂:H₂ environments with CO₂:H₂ feed ratio greater than 1 induced a rapid (on the time scale of 4 hours) selectivity switch from CH₄ production on the reduced catalysts to CO production on the treated Rh/TiO₂ catalysts.

After identifying optimal treatment conditions (20%CO₂:2%H₂:78% He at 250 °C for 4 hours, hereafter 20CO₂:2H₂ treatment) for inducing a selectivity switch from CH₄ to CO production, the reversibility was tested by exposing the 20CO₂:2H₂ treated catalyst to H₂ environments. H₂ treatment at temperatures greater than 350 °C for 4 hours restored the original CH₄ selectivity of the reduced catalyst, see Supplementary Fig. 4. A complete cycle is shown in Fig. 1(A) for 6% Rh/TiO₂, where CH₄ selectivity decreased from 98% after reduction (450 °C for 4 hours) to 11% following 20CO₂:2H₂ treatment and returned to 98% CH₄ selectivity after re-reduction (450 °C for 4 hours). The switch in CO₂ reduction selectivity was induced by a 40-fold decrease in CH₄ formation rate from ~28 to 0.7 mmol CH₄/h/g_{Rh}, and a 10-fold increase in CO formation rate from 0.5 to 5 mmol CO/h/g_{Rh} and was completely reversible for multiple cycles of reduction and 20CO₂:2H₂ treatments, Supplementary Fig. 5. Typical H₂ conversions measured at 1%CO₂:1%H₂:98%He and 200 °C were below 8%. To ensure the change in selectivity following 20CO₂:2H₂ treatment was not due simply to lower reactant conversion, selectivity was compared at identical conversions (4%), Supplementary Fig. 6 at 300 °C and Supplementary Fig. 7 at 200 °C, where large differences were still observed. Stability of the CO producing state was tested at varying H₂ treatment temperatures, reaction temperatures and reactant partial pressures, which showed robust behavior despite being in conditions where significant H₂O concentration is produced, Supplementary Figs 4,6-8.

The influence of 20CO₂:2H₂ treatment on CO₂ reduction selectivity was tested for various Rh weight loadings on TiO₂, see Fig. 1(B) and Supplementary Figs 9-14. Consistently, 20CO₂:2H₂ treatment decreased CH₄ production and increased CO production, which was reversible upon re-reduction. Low CH₄ selectivity on lower Rh weight loading catalysts following reduction was due to high concentrations of isolated Rh atom active sites. The largest selectivity changes were observed for higher Rh weight loadings that predominantly consist of Rh nanoparticle active sites, suggesting that 20CO₂:2H₂ treatment modified the reactivity of Rh nanoparticles. The negligible change in CO production on 0.2% Rh/TiO₂, Supplementary Fig. 9, where nearly all catalytic sites are isolated Rh atoms, indicates that the 20CO₂:2H₂ treatment has little effect on the reactivity of isolated Rh atoms. The production rate of ethane and propane (C₂+ products)

was also suppressed by the 20CO₂:2H₂ treatment, as shown for 2% Rh/TiO₂ in Fig. 1(C), which is consistent with prior work, where catalysts exhibiting high CH₄ selectivity typically produce more C₂+ products.²⁷ The results in Fig. 1 demonstrate that the reactivity of Rh/TiO₂ for the CO₂ reduction reaction is dynamically tunable via 20CO₂:2H₂ and H₂ treatments, where Rh nanoparticle reactivity following 20CO₂:2H₂ treatment is consistent with the catalytic behavior of more noble (Pt, Pd, Cu) metal catalysts.^{28–30}

Rh structure stability during treatments

Considering that isolated Rh atoms are selective for CO production and Rh nanoparticles are selective for CH₄ production, it could be hypothesized that 20CO₂:2H₂ treatment disintegrates Rh nanoparticles to form isolated Rh atoms on the TiO₂ surface.^{31,32} *In-situ* X-ray absorption spectroscopy (XAS) following the Rh K-edge on a 2% Rh/TiO₂ catalyst during 20CO₂:2H₂ treatment showed no measurable difference between the reduced and 20CO₂:2H₂ treated catalyst, with a constant Rh-Rh coordination number, Supplementary Fig. 15,16. XAS results were consistent with *ex-situ* scanning transmission electron microscopy (STEM) images of 2% Rh/TiO₂ catalysts following reduction and 20CO₂:2H₂ treatment that showed no evidence of Rh structural changes, Supplementary Fig. 17. Based on the lack of structural changes in Rh observed by XAS and STEM and disproportionate changes in the rate of CH₄ and CO production (Fig. 1(A) and Supplementary Fig. 1), the switch in reactivity induced by 20CO₂:2H₂ treatment is attributed to modified Rh-TiO₂ interactions.

Changes in adsorbates on Rh and TiO₂

In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to examine the effect of 20CO₂:2H₂ treatment on the species adsorbed to Rh and TiO₂ under reaction conditions. Fig. 2(A) shows *in-situ* DRIFT spectra acquired from 2% Rh/TiO₂ under reaction conditions (1%CO₂:1%H₂:98%He and 200 °C) following reduction, 20CO₂:2H₂ treatment, and re-reduction; essentially identical to Fig. 1(A). Under reaction conditions, the DRIFT spectrum of the reduced catalyst shows CO linearly bound to Rh at top (2046 cm⁻¹) and bridge (1880 cm⁻¹) sites and low adsorbate coverage on TiO₂, aside from H₂O (1620 cm⁻¹), in agreement with previous reports.^{33,34} Following 20CO₂:2H₂ treatment, the switch in CO₂ reduction selectivity was correlated with a ~50 cm⁻¹ red-shift in the frequency of linear and bridge bound CO stretching modes, and a 2-fold decrease in the integrated area of the linearly bound CO stretch. The red-shift in frequency and decreased intensity of the linear CO stretch could be explained by a decrease in CO coverage on Rh,³⁵ or physical blocking of Rh sites coupled with the polarization of CO bonds, induced by charge transfer to Rh,³⁶ a local electric-field-induced Stark effect,³⁷ or coordination of CO across a metal-support interface.²³ 20CO₂:2H₂ treatment also introduced high coverage of formate (HCO₂, 2973, 2923, 2853, 1531, and 1351 cm⁻¹) and a bicarbonate-like species (HCO₃, 1444 cm⁻¹) on the TiO₂ surface,³⁸ which were only observed under reaction conditions following the 20CO₂:2H₂ treatment. Re-reduction of the catalyst regenerated spectral characteristics of the freshly reduced catalyst, consistent with regenerated reactivity shown in Fig. 1(A).

To identify whether the ~50 cm⁻¹ red-shift and decreased intensity of the linear CO stretching mode were simply caused by a decrease in CO coverage on Rh, CO₂ was removed from the reactant stream leaving H₂ to react with adsorbates. Following removal of CO₂ from the reactant stream, CO stretches red-shifted ~35-40 cm⁻¹ as CO coverage decreased on both the reduced and 20CO₂:2H₂ treated catalysts, (spectra 1-4 on Supplementary Fig. 18 and spectra 2-5 on Fig.

2(B)). This is shown quantitatively in Fig. 2(C), where the reduced and 20CO₂:2H₂ treated catalysts exhibit a similar decrease in CO stretching frequency in H₂ flow. The coverage dependent red-shift in CO stretching frequency of 35-40 cm⁻¹ (spectra 1-4 on Supplementary Fig. 18 and spectra 2-5 on Fig. 2(B)) is consistent with the effect of reduced dipole coupling on nanoparticle catalyst surfaces,³⁵ indicating that the 20CO₂:2H₂-treatment-induced 50 cm⁻¹ red-shift (Fig. 2(A)) in CO stretching frequency was not caused by a change in local CO coverage.

The origin of the 50 cm⁻¹ shift in CO stretching frequency was further probed by executing a temperature programmed desorption (TPD) in He following the coverage dependent experiment, (spectra 6-8 in Fig. 2(B)). HCO_x species desorbed from TiO₂ above ~300 °C with a simultaneous blue-shift in frequency of the remaining linearly bound CO by ~35 cm⁻¹ to ~1996 cm⁻¹, almost identical to the frequency observed at low coverage on the reduced catalyst, Fig. 2(C). Catalyst performance was tested after HCO_x species were desorbed from the 20CO₂:H₂ treated sample and the reactivity was restored to the behavior of the original reduced catalyst state, Supplementary Fig. 19. Correlation between removal of HCO_x species from TiO₂ and blue-shift in CO stretching frequency, combined with the return of the reduced catalyst reactivity, demonstrates that modified reactivity induced by 20CO₂:2H₂ treatment is mediated by interactions between HCO_x and the TiO₂ support.

The decreased intensity of CO stretching modes on Rh under reaction conditions following 20CO₂:2H₂ treatment and resulting influence of HCO_x functionalized TiO₂ on all remaining Rh-CO bonds, both in terms of reactivity and spectroscopically, are consistent with SMSI overlayer effects.^{19,23} However, the traditional SMSI encapsulation state for Rh on TiO₂ forms at higher temperature (500 °C) and more reducing conditions (pure or diluted H₂) than the 20CO₂:2H₂ treatment and recedes off Rh in the moist atmosphere of CO₂ reduction, resulting in little influence on reactivity.²¹ Furthermore, the SMSI overlayer on Rh/TiO₂ only blocks available Rh sites for CO adsorption, but does not modify the stretching frequency of CO adsorbed at uncovered Rh sites, in contrast to the observations in Fig. 2 (A).³⁹

HCO_x-induced TiO₂ reduction

Interestingly, analysis of formic acid decomposition on TiO₂ has shown that at high formic acid coverage and temperatures greater than ~100 °C, oxygen vacancies at the TiO₂ surface form via H₂O desorption, leaving a HCO₂ covered, disordered, and reduced TiO_{2-x} surface.⁴⁰⁻⁴² Formic-acid-induced oxygen vacancy formation in TiO₂ occurs under conditions that resemble conditions we observed following 20CO₂:2H₂ treatment, where TiO₂ is covered by HCO_x. The temperature range (~150-300 °C) where 20CO₂:2H₂ treatment induced a switch in CO₂ reduction selectivity agrees with that of formic acid induced TiO₂ reduction, where TiO₂ reduction is limited at low temperature (~100 °C) by H₂O desorption kinetics and at high temperature (~300 °C) by formate desorption, Fig. 3(A). Furthermore, Fig. 3(B) shows that similar to the 20CO₂:2H₂ treatment, formic acid treatment of 2% Rh/TiO₂ decreased the rate of CH₄ production by 14-fold and increased the rate of CO production by 5-fold compared to the reduced catalyst, which was reversible upon re-reduction.

Similarity between the influence of 20CO₂:2H₂ and formic acid treatments on the reactivity of Rh/TiO₂ catalysts suggests the existence of an adsorbate-mediated SMSI (A-SMSI) state where high coverage of HCO_x induces the formation of oxygen vacancies at the TiO₂ surface, thereby causing migration of the support onto Rh. However, it could be imagined that charge donation from HCO_x functionalized, reduced TiO₂ into Rh, without migration onto Rh, is causing the

modified reactivity. To differentiate these effects, a 6% Rh/TiO₂ catalyst was sintered, increasing the Rh particle sizes from 1-3 nm to 10-50 nm in diameter, Supplementary Fig. 20. The sintered catalyst was evaluated for reactivity after reduction and 20CO₂:2H₂ treatment, where CH₄ selectivity decreased from 97% following reduction, to 4% following 20CO₂:2H₂ treatment, Supplementary Fig. 20. The almost identical influence of 20CO₂:2H₂ treatment on the sintered and un-sintered 6% Rh/TiO₂, with large differences in Rh particle sizes, strongly supports the mechanism of HCO_x-mediated migration of TiO_x onto Rh, because the charge transfer mechanism without overlayer formation would have been suppressed by the increased particle size in the sintered catalyst.¹² Thus, interaction between HCO_x-functionalized TiO₂ and the Rh active sites must be locally occurring at a metal overlayer interface as a result of coordination between the overlayer and Rh surface.

Physical and chemical nature of the encapsulation state

To directly visualize the 20CO₂:2H₂-induced TiO₂ structural transformation, *in-situ* STEM analyses were performed in a closed gas cell at atmospheric pressure, as described before,^{43,44} executed during reduction and 20CO₂:2H₂ treatment of the sintered 6% Rh/TiO₂ catalyst. Following treatment at 550 °C in H₂, conditions known to form the traditional SMSI state, a crystalline bilayer of TiO_x quickly formed as a conformal coating on large crystalline Rh particles, where Ti is exclusively in the Ti³⁺ oxidation state, Fig. 4(A).^{26,45-47} In contrast, following 20CO₂:2H₂ treatment for 3 hours at 250 °C an amorphous overlayer on Rh was observed to form, Fig. 4(B), Supplementary Fig. 21-23. *In-situ* electron energy loss spectroscopy (EELS) measurements with a 1.0-1.5 Å spot size focused at various locations on the overlayer directly proved that Ti was present in the amorphous overlayer formed from 20CO₂:2H₂ treatment, Supplementary Fig. 24. Ti in the amorphous overlayer was found to exist in a combination of Ti³⁺ (~30%) and Ti⁴⁺ (~70%) oxidation states, quantified using the feature of Ti⁴⁺ with doublets at the L₂ and L₃ edges (see Supplementary information). The *in-situ* STEM and EELS analyses of 20CO₂:2H₂ treated Rh/TiO₂ catalysts conclusively demonstrate the existence of an A-SMSI overlayer on Rh. Differences in Ti oxidation state for the traditional SMSI and A-SMSI overlayers are hypothesized to be due the presence of HCO_x in the A-SMSI overlayer and related to the unique reactivity and stability of the A-SMSI overlayer in humid CO₂ reduction conditions.

Relating A-SMSI to SMSI behavior

Since the traditional SMSI and A-SMSI states both initiate via support reduction, it was hypothesized that supports known to form SMSI overlayers would also form A-SMSI overlayers. Fig. 5(A,B) show CH₄ and CO production rates, respectively, following reduction and 20CO₂:2H₂ treatment of 2%Rh on TiO₂, Nb₂O₅, CeO₂ and Al₂O₃, see Supplementary Figs 25-27. No significant change in CH₄ or CO production rates was observed on Al₂O₃ and CeO₂ supported Rh, as Al₂O₃, an irreducible support, does not exhibit SMSI behavior and CeO₂ only exhibits SMSI behavior under extremely harsh conditions.^{21,22} Rh/Nb₂O₅ responded to 20CO₂:2H₂ treatment similarly to Rh/TiO₂, exhibiting suppressed CH₄ production and increased CO production, which agrees with the known similar SMSI behavior of Nb₂O₅ and TiO₂. *In-Situ* DRIFTS analyses agreed with changes in reactivity, where only for Nb₂O₅ were the CO stretching frequencies on Rh significantly red-shifted due to 20CO₂:2H₂ treatment, see Supplementary Fig. 28-30. In contrast to TiO₂, Nb₂O₅ SMSI overlayers on Rh formed due to high temperature H₂ treatment are stable in CO₂ reduction reaction environments, rendering metal nanoparticles inactive.²⁰ The stable SMSI overlayer on Nb₂O₅ enables direct comparison of

the effects of SMSI and A-SMSI on CO₂ reduction reactivity. Fig. 5(C) shows a comparison of the impact of SMSI and A-SMSI formation on the reactivity of 2%Rh/Nb₂O₅. SMSI formation suppressed CH₄ production by ~40-fold on Rh nanoparticles, but left CO production on isolated Rh atoms unchanged. Formation of the A-SMSI state decreased CH₄ formation by ~6-fold, however, the CO production increased by ~2.5-fold, attributed to the HCO_x functionalized NbO_x overlayer effect on the reactivity of Rh nanoparticles.

Discussion

It is worth summarizing the evidence for participation of HCO_x adsorbates on the support in the formation and stabilization of the A-SMSI overlayer and in modification of Rh reactivity. Correlation between modified Rh reactivity and appearance of HCO_x on the support measured by *in-situ* DRIFTS, similarity between effects of 20CO₂:2H₂ and formic acid treatment on Rh/TiO₂ reactivity, and *in-situ* STEM/EELS results corroborate the role of HCO_x in mediating A-SMSI overlayer formation. Based on the TPD results in Fig. 2(B, C), and the identification of Ti⁴⁺ in the A-SMSI overlayer by *in-situ* EELS, we hypothesize that HCO_x species coordinate with Ti in the overlayer, thereby stabilizing the overlayer under reaction conditions by decreasing the driving force for re-oxidation by H₂O. Finally, while there is no direct evidence that HCO_x species contribute to modification of Rh reactivity, it is clear based on the particle size independent influence of the overlayer on Rh reactivity that the A-SMSI effect on Rh reactivity is a local effect at the Rh surface A-SMSI overlayer interface.

We hypothesize mechanisms by which A-SMSI overlayer formation could induce the observed switch in CO₂ reduction selectivity. The downshift in CO stretching frequency could suggest the CO bond is significantly polarized, which would decrease the CO-Rh bond strength, allowing CO to desorb before being hydrogenated.²⁸⁻³⁰ Another plausible mechanism is that local modification of the Rh electronic structure, due to coordination with the A-SMSI overlayer, decreases surface coverage of atomic hydrogen, minimizing the driving force for CO hydrogenation.³⁰ Finally, the transformation in local active site environment could also change the CO₂ reduction mechanism, allowing the overlayer to play a direct role as an active site.⁷

The formation mechanisms and characteristics of the A-SMSI overlayers proposed here, and traditional SMSI overlayer described by Tauster, are schematically depicted in Fig. 6. In both overlayers, migration of the support onto the catalytically active metal is induced by oxygen vacancy formation in the support. For SMSI overlayer formation, H₂ treatment at ~500 °C induces oxygen vacancy formation in the support, driving the formation of an impermeable, crystalline and fully reduced metal-oxide overlayer on flat facets of metal particles. Formation of the A-SMSI overlayer is mediated by high coverage of HCO_x on the support at 150-300 °C, which causes oxygen-vacancy formation, and drives formation of a porous and partially reduced metal-oxide overlayer on the catalytically active metal. For SMSI overlayers formed with TiO₂, the overlayer is rapidly oxidized in the humid environment of the CO₂ + H₂ reaction, causing recession of the support off the metal and negating influence on the catalytic reactivity of the underlying metal. SMSI overlayers formed with Nb₂O₅ are stable under humid reaction conditions and thus suppress the reactivity of catalytic nanoparticles. However, the A-SMSI overlayers derived from TiO₂ and Nb₂O₅ are stable under humid reaction conditions, enabling the overlayer to strongly influence reactivity of the catalytically active metal.

In summary, it has been demonstrated that HCO_x adsorbates on TiO₂ and Nb₂O₅ supported Rh catalysts can induce oxygen vacancy formation in the support and drive the formation of an A-

SMSI overlayer on Rh. The A-SMSI overlayer is porous, enabling access for reactants to interact with the Rh surface, and stable under humid reaction conditions. The existence of the A-SMSI overlayer locally modifies the reactivity of the underlying Rh nanoparticle surface, opening new avenues for tuning and controlling the reactivity of supported metal catalysts.

Methods

Catalyst Synthesis

All catalysts were synthesized via an aqueous wetness impregnation approach. The necessary mass of $(\text{Rh}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O})$ (Sigma-Aldrich-#83750) for each weight loading was dissolved in an evaporation dish with distilled water. Supports were mixed with the aqueous Rh solution, dried at 95 °C for 4 h, ground with a mortar and pestle, and calcined in a tube furnace at 450 °C in air for 4 hours. To induce Rh particle size growth, a 6% Rh/TiO₂ sample was heated in N₂ at 800 °C for 3 hours. All treatments to the catalysts were performed *in-situ* prior to kinetic and characterization analyses.

Catalyst Testing

CO₂ reduction reaction rates and selectivity were measured using 15–20 mg of catalyst at 200 °C in a 1/4" OD borosilicate packed bed reactor operating at atmospheric pressure and running under differential reactor conditions (conversion of limiting reagent <8%) with the effluent quantified by online gas chromatography (GC, SRI MG #3). CO₂ was separated from other gases using a Haysep D column, while H₂, N₂, CH₄, and CO were separated using a molecular sieve (MS13X) packed column. The separated gases were then quantified using a flame ionization detector (FID) and a thermal conductivity detector (TCD). The total reactant flow rate in all studies was 100 standard cubic cm per minute (sccm). Specifics regarding reactant concentrations and pretreatment conditions can be found in the Supplementary Information.

DRIFTS Characterization

DRIFTS measurements were executed to identify how the various treatments explored in this study impact the species adsorbed on the catalyst surface. Generally, catalysts were loaded into a Harrick Praying Mantis high temperature reaction chamber (ZnSe windows) mounted inside of a Thermo Scientific Praying Mantis diffuse reflectance adapter, set inside of a Thermo Scientific Nicolet iS10 FT-IR spectrometer with a MCT-A detector. Measurements were taken with 128 scans, 4 cm⁻¹ resolution, and a 30-40 standard liters per minute N₂ purge of the spectrometer and Praying Mantis adapter box. Typically, 10 mg of the catalyst sample was packed on top of 100 mg of α -alumina. The reactor effluent was routed to the GC to monitor reactivity of the catalyst and ensure consistent behavior with experiments performed in the glass reactors.

STEM and EELS Characterization

All STEM analysis was executed on a JEOL 3100R5 with double Cs corrector operated at 300kV. The 2%Rh/TiO₂ samples were suspended in methanol via sonication and drop casted onto lacy carbon-on-copper grids for *ex-situ* analysis and a special SiN heater chip for *in-situ* observation, which utilized a Protochips Atmosphere system. The purity of gases used in the *in-situ* experiment was 99.9995%. All reported temperatures were based on the Protochips calibration.

EELS was performed to identify the existence of Ti in the amorphous A-SMSI overlayer and characterize the valence state. EELS data was collected in-situ when the sample was sandwiched between two SiN membranes, with a total thickness of 80nm, using the Gatan #965 Quantum Imaging Filter (GIF). The spot size was 1.0-1.5Å in diameter and typical acquisition time was 10 seconds. The Ti valence was quantified by using Multiple Linear Least Square (MLLS) Fitting with Digital Micrograph.

XAS Characterization

XAS experiments were performed at Beamline 2-2 at the Stanford Synchrotron Radiation Light source (SSRL). A double-crystal Si (220) monochromator was used to scan X-ray energy from -100 to 200 eV and -200 eV to 1300 eV relative to the Rh K-edge (23,220 eV) for XANES and EXAFS spectra, respectively. About 20 mg of 2% Rh/TiO₂ catalyst was placed in 2.4 mm OD quartz tubes and into a resistance heating-capable Claussen cell⁴⁸ with gas flowing through the powder. Rh foil was placed between the transmission and reference X-ray detectors and measured simultaneously with the nanoparticle samples for X-ray energy calibration and data alignment. Data processing and analysis were performed using the IFEFFIT package.⁴⁹ The amplitude and phase photoelectron scattering functions for the first nearest neighbor (1NN) photoelectron path were calculated using the FEFF6 program⁵⁰ and used to fit the EXAFS equation in R-space.

References

1. Christopher, P. & Linic, S. Engineering Selectivity in Heterogeneous Catalysis: Ag Nanowires as Selective Ethylene Epoxidation Catalysts. *J. Am. Chem. Soc.* **130**, 11264–11265 (2008).
2. Studt, F. *et al.* Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat. Chem.* **6**, 320–324 (2014).
3. Calle-Vallejo, F. *et al.* Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors. *Science* **350**, 185–189 (2015).
4. Holewinski, A., Idrobo, J.-C. & Linic, S. High-performance Ag–Co alloy catalysts for electrochemical oxygen reduction. *Nat. Chem.* **6**, 828–834 (2014).
5. Matsubu, J. C., Yang, V. N. & Christopher, P. Isolated Metal Active Site Concentration and Stability Control Catalytic CO₂ Reduction Selectivity. *J. Am. Chem. Soc.* **137**, 3076–3084 (2015).
6. Behrens, M. *et al.* The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts. *Science* **336**, 893–897 (2012).
7. Graciani, J. *et al.* Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO₂. *Science* **345**, 546–550 (2014).
8. Farmer, J. A. & Campbell, C. T. Ceria Maintains Smaller Metal Catalyst Particles by Strong Metal-Support Bonding. *Science* **329**, 933–936 (2010).
9. Ioannides, T. & Verykios, X. E. Charge Transfer in Metal Catalysts Supported on Doped TiO₂: A Theoretical Approach Based on Metal–Semiconductor Contact Theory. *J. Catal.* **161**, 560–569 (1996).
10. Bruix, A. *et al.* A New Type of Strong Metal-Support Interaction and the Production of H₂ through the Transformation of Water on Pt/CeO₂(111) and Pt/CeO_x/TiO₂(110) Catalysts.

- J. Am. Chem. Soc.* **134**, 8968–8974 (2012).
11. Campbell, C. T. Catalyst–support interactions: Electronic perturbations. *Nat. Chem.* **4**, 597–598 (2012).
 12. Lykhach, Y. *et al.* Counting electrons on supported nanoparticles. *Nat. Mater.* **15**, 284–288 (2015).
 13. Saavedra, J., Doan, H. A., Pursell, C. J., Grabow, L. C. & Chandler, B. D. The critical role of water at the gold-titania interface in catalytic CO oxidation. *Science* **345**, 1599–1602 (2014).
 14. Green, I. X., Tang, W., Neurock, M. & Yates Jr., J. T. Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO₂ Catalyst. *Science* **333**, 736–739 (2011).
 15. Tauster, S. J., Fung, S. C. & Garten, R. L. Strong Metal-Support Interactions. Group 8 Noble Metals Supported on TiO₂. *J. Am. Chem. Soc.* **100**, 170–175 (1978).
 16. Tauster, S. J. Strong Metal-Support Interactions. *Acc. Chem. Res.* **20**, 389–394 (1987).
 17. Dulub, O., Hebenstreit, W. & Diebold, U. Imaging Cluster Surfaces with Atomic Resolution: The Strong Metal-Support Interaction State of Pt Supported on TiO₂(110). *Phys. Rev. Lett.* **84**, 3646–3649 (2000).
 18. Datye, A. K., Kalakkad, D. S., Yao, M. H. & Smith, D. J. Comparison of Metal-Support Interactions in Pt/TiO₂ and Pt/CeO₂. *J. Catal.* **155**, 148–153 (1995).
 19. Haller, G. L. & Resasco, D. E. Metal–Support Interaction: Group VIII Metals and Reducible Oxides. *Adv. Catal.* **36**, 173–235 (1989).
 20. Sakellson, S., McMillan, M. & Haller, G. L. EXAFS evidence for direct metal-metal bonding in reduced Rh/TiO₂. *J. Phys. Chem.* **90**, 1733–1736 (1986).
 21. Deleitenburg, C. & Trovarelli, A. Metal-Support Interactions in Rh/CeO₂, Rh/TiO₂, and Rh/Nb₂O₅ Catalysts as Inferred from CO₂ Methanation Activity. *J. Catal.* **156**, 171–174 (1995).
 22. Uchijima, T. SMSI effect in some reducible oxides including niobia. *Catal. Today* **28**, 105–117 (1996).
 23. Boffa, A., Lin, C., Bell, A. T. & Somorjai, G. A. Promotion of CO and CO₂ Hydrogenation over Rh by Metal Oxides: The Influence of Oxide Lewis Acidity and Reducibility. *J. Catal.* **149**, 149–158 (1994).
 24. Vannice, M. A. & Sen, B. Metal-Support Effects on the Intramolecular Selectivity Crotonaldehyde Hydrogenation over Platinum. *J. Catal.* **115**, 65–78 (1989).
 25. Shi, X. Y. *et al.* Real-space observation of strong metal-support interaction: State-of-the-art and what’s the next. *J. Microsc.* **262**, 203–215 (2015).
 26. Bernal, S. *et al.* Some contributions of electron microscopy to the characterisation of the strong metal-support interaction effect. *Catal. Today* **77**, 385–406 (2003).
 27. Porosoff, M. D., Yan, B. & Chen, J. G. Catalytic reduction of CO₂ by H₂ for synthesis of CO, methanol and hydrocarbons: challenges and opportunities. *J. Mater. Chem.* (2016). doi:10.1039/x0xx00000x
 28. Porosoff, M. D. & Chen, J. G. Trends in the catalytic reduction of CO₂ by hydrogen over supported monometallic and bimetallic catalysts. *J. Catal.* **301**, 30–37 (2013).
 29. Panagiotopoulou, P., Kondarides, D. I. & Verykios, X. E. Selective methanation of CO over supported noble metal catalysts: Effects of the nature of the metallic phase on

- catalytic performance. *Appl. Catal. A Gen.* **344**, 45–54 (2008).
30. Avanesian, T., Gusmão, G. S. & Christopher, P. Mechanism of CO₂ reduction by H₂ on Ru(0001) and general selectivity descriptors for late-transition metal catalysts. *J. Catal.* (2016). doi:10.1016/j.jcat.2016.03.016
 31. Solymosi, F., Bánsági, T. & Novák, É. Effect of NO on the CO-Induced Disruption of Rhodium Crystallites. *J. Catal.* **112**, 183–193 (1988).
 32. Serna, P. & Gates, B. C. Zeolite-supported rhodium complexes and clusters: switching catalytic selectivity by controlling structures of essentially molecular species. *J. Am. Chem. Soc.* **133**, 4714–7 (2011).
 33. Karelavic, A. & Ruiz, P. Mechanistic study of low temperature CO₂ methanation over Rh/TiO₂ catalysts. *J. Catal.* **301**, 141–153 (2013).
 34. Henderson, M. A. & Worely, S. D. An Infrared Study of the Hydrogenation of Carbon Dioxide on Supported Rhodium Catalysts. *J. Phys. Chem.* **89**, 1417–1423 (1985).
 35. Lundwall, M. J., McClure, S. M. & Goodman, D. W. Probing Terrace and Step Sites on Pt Nanoparticles Using CO and Ethylene. *J. Phys. Chem. C* **114**, 7904–7912 (2010).
 36. Brabec, L. & Nováková, J. Ship-in-bottle synthesis of anionic Rh carbonyls in faujasites. *J. Mol. Catal. A Chem.* **166**, 283–292 (2001).
 37. Deshlahra, P., Conway, J., Wolf, E. E. & Schneider, W. F. Influence of Dipole–Dipole Interactions on Coverage-Dependent Adsorption: CO and NO on Pt (111). *Langmuir* **28**, 8408–8417 (2012).
 38. Bando, K. K., Sayama, K., Kusama, H., Okabe, K. & Arakawa, H. In-situ FT-IR study on CO₂ hydrogenation over Cu catalysts supported on SiO₂, Al₂O₃, and TiO₂. *Appl. Catal. A Gen.* **165**, 391–409 (1997).
 39. Haller, G. L. *et al.* Geometric and Electronic Effects of SMSI in Group VIII-TiO₂ Systems. *Proc. 8th Intern. Congr. Catal.* **5**, 135–144 (1984).
 40. Henderson, M. A. Complexity in the Decomposition of Formic Acid on the TiO₂(110) Surface. *J. Phys. Chem. B* **101**, 221–229 (1997).
 41. Diebold, U. The surface science of titanium dioxide. *Surf. Sci. Rep.* **48**, 53–229 (2003).
 42. Morikawa, Y. *et al.* First-Principles Theoretical Study and Scanning Tunneling Microscopic Observation of Dehydration Process of Formic Acid on a TiO₂(110) Surface. *J. Phys. Chem. B* **108**, 14446–14451 (2004).
 43. Zhang, S. *et al.* Dynamic structural evolution of supported palladium–ceria core–shell catalysts revealed by in situ electron microscopy. *Nat. Commun.* **6**, 7778 (2015).
 44. Zhang, S. *et al.* Revealing particle growth mechanisms by combining high-surface-area catalysts made with monodisperse particles and electron microscopy conducted at atmospheric pressure. *Journal of Catalysis* **337**, 240–247 (2016).
 45. Bowker, M. *et al.* Model catalyst studies of the strong metal-support interaction: Surface structure identified by STM on Pd nanoparticles on TiO₂(110). *J. Catal.* **234**, 172–181 (2005).
 46. Liu, J. J. Advanced Electron Microscopy of Metal-Support Interactions in Supported Metal Catalysts. *ChemCatChem* **3**, 934–948 (2011).
 47. Logan, A. D., Braunschweig, E. J., Datye, A. K. & Smith, D. J. Direct observation of the surfaces of small metal crystallites: rhodium supported on TiO₂. *Langmuir* **4**, 827–830 (1988).

48. Chupas, P. J. *et al.* A versatile sample-environment cell for non-ambient X-ray scattering experiments. *J. Appl. Crystallogr.* **41**, 822–824 (2008).
49. Newville, M. IFEFFIT: Interactive XAFS analysis and FEFF fitting. *J. Synchrotron Radiat.* **8**, 322–324 (2001).
50. Zabinsky, S. I., Rehr, J. J., Ankudinov, A., Albers, R. C. & Eller, M. J. Multiple-scattering calculations of x-ray-absorption spectra. *Phys. Rev. B* **52**, 2995–3009 (1995).
51. R.E. Benfield. Mean coordination numbers and the non-metal-metal transition in clusters. *J. Chem. Soc. Faraday Trans.* **88**, 1107-1110 (1992)
52. K. Sasaki, N. Marinkovic, in C.S.S.R. Kumar (Ed.), *X-ray and neutron techniques for nanomaterial characterization*, (Springer, Berlin, 2016)

Acknowledgments:

P.C. acknowledges funding from University of California, Riverside and the National Science Foundation, grant # CHE-1301019. G.W.G and X.P. acknowledge the National Science Foundation, grants # CBET-1159240 and DMR-0723032. XAS measurements were performed on Beamline 2-2, which was supported in part by the Synchrotron Catalysis Consortium, US Department of Energy Grant No. DE-SC0012335. Alexander V. Dudchenko is acknowledged for his efforts in Arduino automation of the packed bed reactor experimental apparatus.

Author Contributions:

J.C.M and P.C. developed the project, analyzed the data and wrote the paper. J.C.M. performed all catalyst synthesis, catalyst testing and FTIR analysis. L.D. assisted with FTIR data collection. S.Z. performed STEM experiments. G.W.G and X.P. assisted with STEM data analysis. N.M. and J.G.C. performed and analyzed XAS experiments. P.C. oversaw the project.

Figure Captions

Figure 1. Controlling CO₂ reduction selectivity on Rh via catalyst pretreatment. (a) Rate of CO and CH₄ production and selectivity to CH₄ over 6% Rh/TiO₂ measured at 200 °C with a feed composition of 1% CO₂, 1% H₂, 98% He, following pure H₂ at 450 °C for 4 hours (reduction) and 20% CO₂, 2% H₂ and 78% He at 250 °C for 4 hours (20CO₂:2H₂) treatments. Between treatments, CH₄ selectivity was reversibly controlled from 98% to 11%. (b) Effect of 20CO₂:2H₂ treatment on CH₄ selectivity as a function of Rh weight loading (%). (c) Effect of 20CO₂:2H₂ treatment on Ethane + Propane (C₂₊) production rate over 2% Rh/TiO₂ catalyst as a function of feed composition with equimolar CO₂ and H₂ feed and a balance of He. 20CO₂:2H₂ treatment consistently decreased CH₄ and C₂₊ selectivity. Experimental errors for rate and selectivity measurements were consistently less than ± 6%. In plots where reactivity data following different treatments are separated along the x-axis, CO and CH₄ formation rate and CH₄ selectivity are in orange, green and purple, respectively. When reactivity or selectivity following different treatments is plotted on the same x-axis, reduced catalyst data is in red, and 20CO₂:2H₂ treated catalyst data is in blue.

Figure 2. IR analysis of selectivity switch. (a) *In-situ* DRIFT spectra collected from 2% Rh/TiO₂ at reaction conditions (180 °C, 1% CO₂, 1% H₂, 98% He), for reduced (red), 20CO₂:2H₂-treated (blue) and re-reduced (black) catalyst. Upon 20CO₂:2H₂ treatment, the CO stretching frequency of linear and bridge Rh-carbonyl groups decreased by 50 cm⁻¹, their intensity dropped 2-fold, and TiO₂-bound HCO_x species appeared. Re-reduction reversed all effects of the 20CO₂:H₂ treatment. (b) DRIFT spectra of 2% Rh/TiO₂ under reaction conditions after reduction (spectrum 1), after 20CO₂:2H₂ treatment (spectrum 2), CO₂ flow removed (only 1% H₂) for 5, 15, 60 minutes (spectra 3-5). Spectra 6-8 were collected during TPD in He at 213, 312, and 370 °C, respectively, immediately following collection of spectrum 5. Vertical dotted line represents CO stretch frequency on reduced 2% Rh catalyst under reaction conditions. Corresponding increases in carbonyl stretching frequency with HCO_x desorption suggest they are related. (c) Peak positions of the linear CO stretching frequency during experiments in Fig. 2(B) and Supplementary Fig. 18. The reduced (red) and 20CO₂:2H₂-treated (blue) catalysts exhibited a similar decrease in CO stretching frequency in H₂ flow, suggesting the shift in (a) carbonyl frequency was not due to a decrease in CO coverage.

Figure 3 Identifying the mechanism of A-SMSI formation. (a) CH₄ selectivity on 2% Rh/TiO₂ as a function of 20CO₂:2H₂ treatment temperature shown in blue measured at 200 °C with a feed composition of 1% CO₂, 1% H₂, 98% He (100 sccm total). The catalyst was re-reduced after each sequential 20CO₂:2H₂ treatment, and the reactivity under identical reaction conditions is shown in red. The experiment involved an identical protocol as in Supplementary Fig 5, but with increasing temperature during the 20CO₂:2H₂ treatment for each cycle. Lines are to guide the eye. (b) Rate of CH₄ and CO production and CH₄ selectivity after reduction, formic acid treatment, and re-reduction on a 2%Rh/TiO₂ catalyst measured under reaction conditions at (200 °C, 1% CO₂, 1% H₂, 98% He, 100 sccm total). Formic acid treatment was 25 sccm He bubbled through formic acid at room temperature for 4 hours with a catalyst bed temperature of 200 °C. Agreement in temperature where 20CO₂:2H₂ treatment affected CH₄ selectivity and formic acid induced oxygen vacancy formation⁴⁰⁻⁴² in (a), along with the influence of formic acid on reactivity in (b), suggests an adsorbate-mediated SMSI. Experimental errors for rate and selectivity measurements were consistently less than ± 6%.

Figure 4. Visualizing SMSI and A-SMSI States. *In-situ* STEM images of sintered 6%Rh/TiO₂ following treatment in, (a) 5%H₂ and 95% N₂ at 550 °C for 10 minutes inducing the formation of a TiO_x SMSI crystalline bilayer, containing exclusively Ti³⁺, on surface of Rh nanoparticles (NP), and (b) 20CO₂:2H₂ at 250 °C for 3 hours causing the formation of an amorphous A-SMSI overlayer, containing a mixture of Ti³⁺ and Ti⁴⁺, on the surface of Rh NPs. Images were collected at atmospheric pressure. Samples were pre-sintered at 800 °C in N₂ to increase the Rh particle size from 1-3 nm to 10-50 nm and improve contrast in the micrographs.

Figure 5. Relating SMSI and A-SMSI behavior. (a) CH₄ and (b) CO production rate on 2% Rh on various supports following reduction and 20CO₂:2H₂ treatment under standard reaction conditions (200 °C, 1% CO₂, 1% H₂, 98% He). The supports were chosen for known differences in SMSI behavior, where Al₂O₃ and CeO₂ do not exhibit SMSI behavior at reasonable conditions, while TiO₂ and Nb₂O₅ exhibit SMSI behavior. The lack of change in reactivity for Al₂O₃ and CeO₂ supported Rh 20CO₂:2H₂ treatment and the large changes in CO and CH₄

production for the TiO_2 and Nb_2O_5 supported samples suggests that A-SMSI overlayer formation is related to reducibility of the support and characteristics of oxygen vacancy formation. (c) Rate of CH_4 and CO production on 2% $\text{Rh}/\text{Nb}_2\text{O}_5$ after 300 °C reduction, 400 °C reduction and 300 °C reduction followed by $20\text{CO}_2:2\text{H}_2$ treatment. This figure shows the reactivity differences between SMSI and A-SMSI states for $\text{Rh}/\text{Nb}_2\text{O}_5$, as the Nb_2O_5 SMSI state blocks Rh NP's from driving CH_4 formation while leaving isolated Rh atoms able to produce CO , and the Nb_2O_5 A-SMSI state alters Rh NP reactivity toward producing CO . Experimental errors for rate and selectivity measurements were consistently less than $\pm 6\%$.

Figure 6. SMSI and A-SMSI overlayer structure and behavior. (a) Schematic showing bare Rh particle on TiO_2 or Nb_2O_5 with exposed Rh sites that favor CH_4 production. (b) $20\text{CO}_2:2\text{H}_2$ treated catalyst that forms a permeable A-SMSI overlayer composed of TiO_x species and HCO_x . (c) The stable A-SMSI overlayer under CO_2 reduction conditions modifies Rh catalytic behavior. (d) $\text{Rh}/(\text{TiO}_2$ or $\text{Nb}_2\text{O}_5)$ following treatment with high temperature (500 °C) H_2 , forming an impermeable SMSI overlayer. Crystalline bilayer structure observed for TiO_2 has yet to be confirmed for Nb_2O_5 SMSI state. (e) Reactivity results suggest there is a stable NbO_x SMSI overlayer that is impermeable in CO_2 reduction conditions, completely suppressing the reactivity of Rh nanoparticle surfaces. (f) TiO_x SMSI overlayer recedes off Rh when exposed to CO_2 reduction conditions due to H_2O induced re-oxidation of TiO_x to TiO_2 . The catalytic behavior of (f) is nearly identical to (a).