Steering CO₂ hydrogenation toward C–C coupling to hydrocarbons using porous organic polymer/metal interfaces

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The conversion of CO₂ into fuels and chemicals is an attractive option for mitigating CO₂ emissions. Controlling the selectivity of this process is beneficial to produce desirable liquid fuels, but C–C coupling is a limiting step in the reaction that requires high pressures. Here, we propose a strategy to favor C–C coupling on a supported Ru/TiO₂ catalyst by encapsulating it within the polymer layers of an imine-based porous organic polymer that controls its selectivity. Such polymer confinement modifies the CO₂ hydrogenation behavior of the Ru surface, significantly enhancing the C₂₄ production turnover frequency by 10-fold. We demonstrate that the polymer layers affect the adsorption of reactants and intermediates while being stable under the demanding reaction conditions. Our findings highlight the promising opportunity of using polymer/metal interfaces for the rational engineering of active sites and as a general tool for controlling selective transformations in supported catalyst systems.

CO₂ hydrogenation | C–C coupling | polymer/metal interface

With the pressing environmental challenges imposed by CO₂ emissions, efforts must be devoted to mitigating them (1). Hydrogenation of captured CO₂ into valuable chemicals offers this opportunity while also reducing our dependence on fossil fuels (2). The catalytic transformation of CO₂ into C₁ products (carbon monoxide, methane, methanol, and formic acid) has been extensively studied with remarkable progress (3), but these molecules suffer from lower specific energy density compared to higher-molecular-weight hydrocarbons (C₂₊). Engineering of active sites plays a crucial role in increasing the C/H ratio on the catalyst surface and thus enhancing the coupling probability. While progress in the synergistic stepwise conversion of CO₂ to hydrocarbons has led to C₂₊ products (4, 5), less has been achieved in affecting the reactivity of pristine metal surfaces toward improving direct C–C coupling selectivity.

It is well accepted that local interactions, such as metal-support or metal–ligand interactions, determine the binding strength of reaction intermediates that affect product distribution (6). Indeed, as predicted by scaling relationships, the binding strength of appropriate intermediates is directly related to reaction rates, and they can be used to tune reaction selectivity (7). As an example, the reactivity of TiO₂-supported Rh catalysts can be switched from methanation to reverse water gas shift (RWGS) when an adsorbate-mediated strong metal–support interaction overlay is formed under reaction conditions (8). This layer weakens CO binding and drastically alters the reaction selectivity, thus demonstrating how overlayers can tune surface reactivity in a potentially predictable way.

Modifying active sites with organic ligands offers a promising approach to tune the binding of reactants and intermediates thanks to the wide range of chemical functional groups that can be introduced using organic components (9–12). For CO₂ hydrogenation in particular, Medlin and coworkers showed how the selectivity toward RWGS can be significantly enhanced on Pt/TiO₂ and Pd/TiO₂ catalysts through TiO₂ surface modification with molecular ligands. The inclusion of amino groups notably promoted CO₂ activation and increased rates (13).

Owing to their tunable pore structure and richness in chemical functionality, porous organic polymers provide many opportunities for catalyst surface modification, with strong potential in hierarchical pore construction (14), linkage composition (15), morphology engineering (16), and tuning of catalytic properties (17). Most importantly, polymers with amine or imine functionality have been proven able to adsorb and activate CO₂ (18, 19). We therefore hypothesize that these materials could modify the surface reactivity of metals embedded within the polymer pore structure in activating CO₂. We thus report the uniform encapsulation of a Ru/TiO₂ supported catalyst within a tunable layer of an imine-based porous organic polymer (IPOP) with controllable morphology and chemical functionality. Such polymer confinement modifies the CO₂ hydrogenation behavior of the Ru surface, significantly enhancing the C₂₄ production turnover frequency (TOF), whereas the starting Ru/TiO₂ makes mostly methane. Kinetic measurements demonstrate an 80-fold and 10-fold increase in the CO and C₂₄ production TOF, respectively, with the IPOP coating. We further demonstrate that the polymer effect on selectivity is general and occurs on several Ru/metal oxide supported catalysts.
and with a similar magnitude of selectivity control. Such polymer-induced reactivity control provides promising opportunities for the rational engineering of active sites not only for CO₂ conversion but as a general tool for other selective transformations using supported catalysts.

**Results and Discussion**

**Synthesis and Characterization of IPOP/Ru/TiO₂ Hybrid Catalyst.** The design of organic/inorganic hybrids involved multiple sequential steps such that the individual components could be easily tuned (Scheme 1). To synthesize the IPOP/Ru/TiO₂ hybrid catalysts, a Ru/TiO₂ sample was first prepared by deposition of colloidal Ru nanoparticles on a commercial titania support (20). The Ru/TiO₂ was then used as a template for solution-phase polymer growth based on imine condensation reaction between 1,3,5-Tris(4-aminophenyl)benzene and terephthalaldehyde (or paraphthalaldehyde, p-PA) to form p-IPOP (Scheme 1).

Transmission electron microscopy (TEM) was used to characterize the morphology of as-synthesized catalysts and examine the degree of encapsulation. Fig. 1A and SI Appendix, Fig. S1 show ∼3 nm Ru nanoparticles supported on TiO₂ crystallites in the Ru/TiO₂ sample. After IPOP growth, a low-contrast material uniformly surrounds the Ru/TiO₂ particles in the IPOP/Ru/TiO₂ sample (Fig. 1B). High-resolution imaging demonstrates that the layer is not crystalline and that it homogeneously coats the whole surface, with an average thickness of ∼15 nm (Fig. 1C).

Energy-dispersive X-ray scattering (EDS) analysis of the p-IPOP/Ru/TiO₂ sample was performed on high-angle annular dark-field scanning TEM (HAADF-STEM) images to map the spatial distribution of the elements (Fig. 1D), which show brighter areas corresponding to the Ru/TiO₂ catalyst particles enveloped in a low-contrast overlayer. By comparing the STEM image and the corresponding EDS maps (Fig. 1E–G), it is found that nitrogen from IPOP is present across the image, while Ti and Ru are evident only in the interior of the grains. Thus, we conclude that Ru/TiO₂ is uniformly surrounded by the nitrogen-rich IPOP.

As in Fig. 2A, X-ray photoelectron spectroscopy (XPS) was also collected but the Ru signal is hardly distinguishable even in the bare Ru/TiO₂ due to both the low concentration of Ru present and the overlap between the Ru 3d peak (∼279 eV for Ru 3d₅/₂ and ∼284 eV for Ru 3d₃/₂) and the C 1s peak (284.8 eV). Only adventitious carbon is found in Ru/TiO₂, while p-IPOP/Ru/TiO₂ shows signals that are consistent with a carbon framework (284.8 eV) as well as carbon atoms bonded to nitrogen atoms (286.5 eV), both of which originate from the IPOP. An additional weak signal at 290.8 eV in the p-IPOP/Ru/TiO₂ sample is attributed to the π-π conjugation of stacked aromatic rings in the IPOP. The Ti signal could be well-distinguished in the Ru/TiO₂ sample and was consistent with Ti(IV) in TiO₂ (Fig. 2B). The Ti signal in the IPOP/Ru/TiO₂ catalyst, however, is significantly attenuated and almost indistinguishable from the baseline, proving the encapsulation of the Ru/TiO₂ material within IPOP layers at least 5 to 10 nm thick that prevents the escape of photoemitted electrons.

**Scheme 1.** Schematic of the synthesis process. Synthesis of IPOP/Ru/TiO₂ by encapsulation of Ru/TiO₂ within IPOP through dispersion of the Ru/TiO₂ sample (A), addition of IPOP precursors (B), and acid-catalyzed imine network formation (C).

![Scheme 1](https://doi.org/10.1073/pnas.2114768119 Steering CO₂ hydrogenation toward C-C coupling to hydrocarbons using porous organic polymer/metal interfaces Zhou et al.)
The synthesis method could be extended to other polymer compositions starting from either ortho-phthalaldehyde (o-PA) or metaphthalaldehyde (m-PA), resulting in the formation of o-IPPOP/Ru/TiO2 and m-IPPOP/Ru/TiO2. Such a family of polymer-encapsulated samples differs in the connectivity of polymer-building units. Characterization of the samples revealed the uniform encapsulation with comparable thickness and similar morphology to the p-IPPOP/Ru/TiO2 sample (SI Appendix, Figs. S2–S4).

Fourier transform infrared (FTIR) spectroscopy confirmed the presence of hydroxyl groups in the Ru/TiO2 sample evidenced by broad vibrational modes at ∼1,635 cm⁻¹ and ∼3,350 cm⁻¹ (Fig. 2C). Such peaks are absent in the p-IPPOP/Ru/TiO2 sample, where the TiO2 surface is instead covered by p-IPPOP showing characteristic vibrations from the polymer including the C=N bond contribution at ∼1,620 cm⁻¹. Similar spectra were collected for o-IPPOP/Ru/TiO2 and m-IPPOP/Ru/TiO2 (SI Appendix, Fig. S6). We hypothesize that surface hydroxyl groups on TiO2 act as anchoring groups for IPOP growth, favoring imine condensation on the surface without any additives and resulting in uniform polymer encapsulation (21). Indeed, when TiO2 was calcined to remove hydroxyl groups, IPOP nucleated in solution (SI Appendix, Fig. S5A) (22), whereas when the TiO2 was rehydroxylated then uniform encapsulation could be achieved again (SI Appendix, Fig. S5 B and C).

Thermogravimetric analysis of the p-IPPOP/Ru/TiO2 catalyst showed minimal mass loss in airflow up to 400 °C (Fig. 2D), thus demonstrating the polymer's stability even in the presence of Ru/TiO2. The polymer started to degrade above 400 °C (23). Temperature-programmed reduction experiments of p-IPPOP/Ru/TiO2 further demonstrated the excellent stability of the sample up to 350 °C under conditions more relevant for catalytic hydrogenation (SI Appendix, Fig. S7). Similar thermal stability was also found with o- and m-IPPOP/Ru/TiO2 samples, although m-IPPOP/Ru/TiO2 started to degrade above 350 °C, likely due to a lower degree of polymerization (SI Appendix, Fig. S8).

The p-IPPOP layers significantly increased the surface area of Ru/TiO2 with the introduction of both micro- and mesoporosity (SI Appendix, Fig. S9). The BET surface area increased from 56 m²/g for bare Ru/TiO2 to 222 m²/g in p-IPPOP/Ru/TiO2. The three polymer isomers were not equally porous (88 and 54 m²/g for o- and m-IPPOP/Ru/TiO2, respectively), likely because of the different conformation obtained with o-, m-, and p-phthalaldehyde in the final IPOP layers.

**CO₂ Hydrogenation on IPOP/Ru/TiO₂ Hybrid Catalysts.** The catalysts were tested for CO₂ hydrogenation to evaluate the effect of polymer layers on the catalytic performance of Ru/TiO2. CO₂ conversions were approximately the same and, in most cases, intentionally kept below 6% to compare selectivity in a kinetically controlled regime.

The reaction was initially performed at atmospheric pressure (SI Appendix, Fig. S10). The Ru/TiO2 sample produced methane with 98% selectivity, in agreement with previous reports (24–27). The p-IPPOP/Ru/TiO2 sample, however, showed dramatically different selectivity with nearly 100% CO selectivity. Such reversal in selectivity from methanation to RWGS has been previously reported in Pt and Pd catalysts modified with phosphonic acid ligands (13). However, Ru favors methanation more strongly than Pd and Pt. This change in selectivity is therefore unique for Ru nanoparticles [not to be confused with Ru single atoms (20) or clusters (28) which contain Ru⁹⁺ species] irrespective of the support nature (24–27, 29).

The catalysts were then tested at 6 bar of pressure. The increased pressure did not significantly change the product...
distribution of the Ru/TiO2 sample where methane formation was favored in 99% yield, while also producing some C2+ hydrocarbons in very low yield (Fig. 3A). However, C2+ hydrocarbon production was dramatically enhanced on the IPOP-encapsulated samples, with a pronounced steady increase in C2, selectivity from Ru/TiO2 (<1%), to o-IPOP/Ru/TiO2 (1%), to m-IPOP/Ru/TiO2 (5%), to p-IPOP/Ru/TiO2 (12%). As opposed to low pressure, all the IPOP-encapsulated samples also showed increased production of methane, with selectivity steadily decreasing from o-IPOP/Ru/TiO2 (96%), to m-IPOP/Ru/TiO2 (92%), to p-IPOP/Ru/TiO2 (64%).

When either CO2 or H2 was removed from the reactant feed and replaced by inert gas, hydrocarbon formation instantaneously ceased (SI Appendix, Fig. S11), indicating that the hydrocarbon species are produced by the conversion of CO2 and H2 on the catalyst surface. The TOFs for hydrocarbon production were calculated based on CO chemisorption measurements (Fig. 3B and SI Appendix, Table S1). CO production was significantly promoted by 50- to 80-fold on all three IPOP-encapsulated catalysts compared to the Ru/TiO2 sample, in agreement with ambient pressure experiments (SI Appendix, Fig. S10). The C1–C4 hydrocarbon yield was also enhanced by IPOP encapsulation to different degrees for the polymer isomers. Note that such enhancement in TOF and selectivity could not simply originate from physical blockage by the polymer (SI Appendix, Table S3). The α parameter, which describes the probability of C=C intermediates to form C–C bonds, was calculated from Anderson–Shulz–Flory theory and compared among catalysts (Fig. 3B) (4). It steadily increased from the Ru/TiO2 sample (α = 0.08) to the polymer-coated catalysts to a value of 0.39 for the p-IPOP/Ru/TiO2 catalyst. This result demonstrates that polymer encapsulation significantly increases the probability of C–C coupling and hydrocarbon production, which is rarely reported on Ru-based catalysts under the mild pressure conditions used in this work (2, 30–32).

Mechanistic Studies of CO2 Hydrogenation at IPOP/Metal Interfaces. Kinetic parameters, including apparent activation energy and reaction rate orders, were collected and are summarized in Table 1. Apparent activation energy for CH4 or CO formation (Ea,CH4 and Ea,CO) at 6 bar on Ru/TiO2 was 88 ± 1 and 69 ± 4 kJ mol−1, respectively (SI Appendix, Fig. S12), the former in line with previous reports (20, 27, 32, 33), while the latter is not usually reported for Ru catalysts. Since RWGS and methanation would rarely contribute to the TOF of CO2 conversion, the activation energy for CO production (Ea,CO) is expected to be lower than that for CH4 production (Ea,CH4). Consistently, it was lower than Ea,CH4 in all cases, as expected. The coupled reaction was also characterized by a higher-order reaction with respect to CO2 pressure (pCO2). The apparent activation energy for CO2 hydrogenation was carried out under 20 sccm 75% H2, 6% CO2, at temperatures of 220, 230, 240, and 250 °C. Rate order measurements were carried out at 250 °C, 6 bar total pressure. To calculate CO2 rate order, H2 pressure was kept at 75% while CO2 pressure was varied from 15 to 25% with 1% interval. To calculate H2 rate order, CO2 pressure was kept at 15% while H2 pressure was varied from 45 to 80% with 4% interval.

Table 1. Apparent activation energy and partial reaction orders of the different catalysts

| Catalyst | E_a CH4, kJ·mol⁻¹ | E_a CO, kJ·mol⁻¹ | R_CO ∝ p_CO² | R_CH4 ∝ p_H2 | R_CO ∝ p_CO² | R_CH4 ∝ p_H2 |
|----------|------------------|------------------|----------------|----------------|----------------|----------------|
| Ru/TiO2  | 69 ± 4           | 88 ± 1           | −0.5 ± 0.1     | 1.6 ± 0.1     | 0.4 ± 0.1     | 0.7 ± 0.1     |
| o–IPOP/Ru/TiO2 | 74 ± 7        | 58 ± 1           | −0.4 ± 0.1     | 1.1 ± 0.1     | 1.3 ± 0.1     | 0.5 ± 0.1     |
| m–IPOP/Ru/TiO2 | 88 ± 2         | 61 ± 1           | −0.5 ± 0.1     | 1.1 ± 0.1     | 1.4 ± 0.1     | 0.7 ± 0.1     |
| p–IPOP/Ru/TiO2 | 90 ± 2         | 69 ± 2           | −0.4 ± 0.1     | 1.3 ± 0.1     | 1.5 ± 0.1     | 0.5 ± 0.1     |

For apparent activation energy calculation, CO2 hydrogenation was carried out under 20 sccm 75% H2 + 25% CO2, 6 bar total pressure, at temperatures of 220, 230, 240, and 250 °C. Rate order measurements were carried out at 250 °C, 6 bar total pressure. To calculate CO2 rate order, H2 pressure was kept at 75% while CO2 pressure was varied from 15 to 25% with 1% interval. To calculate H2 rate order, CO2 pressure was kept at 15% while H2 pressure was varied from 45 to 80% with 4% interval.

Fig. 3. Catalytic reactivity of Ru/TiO2 and IPOP/Ru/TiO2 samples. (A) Conversion and product distributions for CO2 hydrogenation at 250 °C, 30 sccm 75% H2 + 25% CO2, 6 bar total pressure and (B) corresponding reaction TOFs for different catalysts. Transition-state enthalpy and entropy, respectively, for (C) methanation and (D) RWGS pathways of different catalysts.
pathways share similar intermediate steps (28, 34, 35), close values for the activation energies are reasonable. \( E_{\text{CH}_4} \) for IPOP-coated catalysts also showed values between 58 and 69 kJ mol\(^{-1}\). On the other hand, the activation energies for CO formation were quite different (75 to 92 kJ mol\(^{-1}\)), which suggests that IPOP encapsulation induces changes in the RWGS pathway. The transition-state enthalpy values increased from Ru/TiO\(_2\) to \( \alpha-\), \( \mu-\), and p-IPOP/Ru/TiO\(_2\) with a concomitant similar trend in the activation entropy values increasing from very negative for Ru/TiO\(_2\) \(-180 \pm 7\) J mol\(^{-1}\) K\(^{-1}\) to less and less negative for \( \alpha-\), \( \mu-\), and p-IPOP/Ru/TiO\(_2\) samples \(-141 \pm 14, -117 \pm 4, \) and \(-101 \pm 5\) J mol\(^{-1}\) K\(^{-1}\), respectively, thus highlighting how the transition state is less strongly adsorbed on the Ru surface but has higher degree of freedom potentially by interacting with the IPOP layers. Such favorable entropic contribution induced by polymer encapsulation compensates for the milder increase in transition-state enthalpy and explains the significantly increased \( \text{CO} \) production in the IPOP-encapsulated catalysts. Moreover, the trend strongly suggests that the IPOP layers distinguishably affect the reaction pathway and energy landscape through active interactions with the transition states in a manner analogous to previous reports (36).

The rate of methane production over Ru/TiO\(_2\) catalyst showed moderate dependence on \( \text{CO}_2 \) \(+0.7 \pm 0.1\) and weak dependence on \( \text{H}_2 \) \(+0.4 \pm 0.1\) (SI Appendix, Figs. S14 and S15), suggesting that the Ru surface is mostly covered by hydrogen instead of carbon species (33, 37). The rate orders for RWGS reaction are very different from those of methanation, with strong dependence on \( \text{CO}_2 \) \(+1.6 \pm 0.1\) and negative dependence on \( \text{H}_2 \) \(-0.5 \pm 0.1\). The notably more negative hydrogen rate order compared to methanation indicates that the two reactions proceed through competitive pathways. It has been reported that a high C/H ratio on the Ru surface is favorable for the \( \text{CO}_2 \) reaction, whereas a low ratio leads to methane formation (2, 31, 38). The low C/H ratio indicated by the \( \text{CO}_2 \) and \( \text{H}_2 \) production results obtained for this sample at 2,070 cm\(^{-1}\) and 1,966 cm\(^{-1}\), and its intensity positively correlated with increasing \( \text{CO} \) partial pressure. This observation suggests that \( \text{CO} \) adsorption can be increased with external pressure, thus making the sample more reactive, which is consistent with the hydrocarbon production results obtained for this sample at higher pressure (Fig. 34 and SI Appendix, Fig. S10).

Finally, operando DRIFT spectra were collected under reaction conditions at 6 bar of pressure (Fig. 4 B and C). For Ru/TiO\(_2\) (Fig. 4B), multiple species were formed upon the introduction of \( \text{CO}_2 \) together with contributions from gaseous \( \text{H}_2\text{O} \), which appear as sharp peaks due to their rotational components. The broad features at 1,880 to 2,070 cm\(^{-1}\) are attributed to CO adsorption on Ru sites as described above. The two bands at 1,472 cm\(^{-1}\) and 1,556 cm\(^{-1}\) are assigned to the \( \text{OCO} \) stretching vibration of bicarbonate and formate species, respectively (8, 42–45), while the peak at 1,622 cm\(^{-1}\) slightly originates from \( \text{Ti}-\text{OH} \) as a result of surface hydration (8). The reactivity of the formate species is under debate. However, based on the fact that peak intensities at 1,880 to 2,070 cm\(^{-1}\) were not affected by the notable accumulation of formate species, we surmise that formate species are only partially dissociated and hydrogenated to \( \text{CO} \), which then migrates onto Ru sites to produce methane (45). Overall, these IR signatures are in line with prior literature (8, 25, 42–45), suggesting that \( \text{CO}_2 \) hydrogenation is facilitated through the formate pathway over Ru/TiO\(_2\) interfaces.

On the other hand, operando DRIFT spectra on p-IPOP/Ru/TiO\(_2\) catalyst were notably different. We wish to first emphasize that control experiments with similar conditions were performed with both TiO\(_2\) and p-IPOP encapsulated TiO\(_2\), and the resulting spectra (SI Appendix, Fig. S25) were notably different from Fig. 4 B and C, which confirms that Fig. 4 B and C represent the unique interface between Ru, IPOP, and TiO\(_2\), denoted as (IPOP)Ru(TiO\(_2\)). It was found that a broad band centered at ~1,910 cm\(^{-1}\) quickly emerged upon the introduction of \( \text{CO}_2 \) together with a weak peak at 2,052 cm\(^{-1}\). As the \( \text{CO}_2 \) concentration in the DRIFT cell slowly accumulated, the band at 1,910 cm\(^{-1}\) gradually evolved and two peaks could be clearly distinguished at steady state at 1,962 cm\(^{-1}\) and 1,901 cm\(^{-1}\), which we attribute to CO adsorbed on Ru surface and at the interface [CO-(IPOP)Ru(TiO\(_2\))]_3, respectively. Given the
measured CO₂ reaction orders under reaction conditions, it is reasonable to postulate that CO partial pressure rapidly increases as CO₂ accumulates, which leads to an increase of *CO coverage and the consequent increase in IR absorption intensity and shift of the IR band position to higher wavenumbers. The peak at 2,052 cm⁻¹, which did not notably change position, is assigned to (CO)ₙ-Ru⁺, which is known to be coverage-insensitive (40). No distinctive features for carbonates, bicarbonates, and formates were discerned between 1,700 and 1,450 cm⁻¹, and broad bands of relatively low intensity (compared to gaseous water contributions) at 1,513 and 1,610 cm⁻¹ were instead observed. We propose that Lewis acid–base interactions between CO₂ and imine groups on the IPOP are responsible for these contributions, given that active sites are surrounded by imino groups in IPOP that can form adducts with CO₂ (19) and that CO₂ can be efficiently activated by Schiff base-modified metals catalysts (18). Interactions between a weak Lewis acid (CO₂) and a weak base (imine) are generally weak. Indeed, instead of strong IR bands in the region 1,700 to 1,450 cm⁻¹, only a broad feature ranging from 1,700 to 1,550 cm⁻¹ over o-IPOP/Ru/TiO₂ was found, and no peaks could be distinguished from m-IPOP/Ru/TiO₂ (SI Appendix, Fig. S18). We hypothesize that steric hindrance in the imine bond of the ortho isomer dictates a weaker interaction with CO₂ that becomes progressively stronger as the steric hindrance is released moving to the meta and para isomer. Moreover, the absence of formate intermediates on all encapsulated samples also strongly corroborates the observed transition-state entropic favor induced by IPOP. We hypothesize that the introduction of polymer chains replaces the Ru/TiO₂ interface with a polymer/Ru interface, and the *HCOOˣ are no longer abundant on the catalyst surface. Instead, RWGS is likely facilitated from adsorbed CO₂ through N–CO₂ interactions, which has lower configurational entropy in the initial state, resulting in less negative entropic changes.

In situ X-ray absorption near-edge structure and extended X-ray absorption fine structure (EXAFS) data (SI Appendix, Figs. S19 and S20) indicate that Ru is completely oxidized to RuO₂, and the in situ EXAFS data show that Ru foil, RuO₂ powder, and p-IPOP/Ru/TiO₂ after oxidative pretreatment, reductive pretreatment, and under reaction conditions (250 °C, 75% H₂ + 25% CO₂). Dark traces are fits; thicker light traces are experimental data; dotted traces are imaginary components of the Fourier transform. Data offset for clarity. (E) Comparison of scattering paths of in situ EXAFS from p-IPOP/Ru/TiO₂ after oxidative pretreatment and under reaction conditions (250 °C, 75% H₂ + 25% CO₂). Dark traces are fits; thicker light traces are experimental data; dotted traces are fitted scattering paths. (F) Schematic drawing of the reaction intermediates and pathways over Ru/TiO₂ (right) or p-IPOP/Ru/TiO₂ (left) catalysts. Note that atoms are not drawn to scale.

Fig. 4. Mechanistic studies of CO₂ hydrogenation on Ru/TiO₂ and p-IPOP/Ru/TiO₂. (A) DRIFT spectra of CO adsorption on Ru/TiO₂ and p-IPOP/Ru/TiO₂ under different temperature and conditions as indicated in the colored bar on the right. Operando DRIFT spectra under CO₂ hydrogenation conditions (250 °C, 20 sccm 75% H₂ + 25% CO₂, 6 bar total pressure) of (B) Ru/TiO₂ and (C) p-IPOP/Ru/TiO₂ catalysts. (D) In situ EXAFS of Ru foil, Ru₂O₃ powder, and p-IPOP/Ru/TiO₂ after oxidative pretreatment, reductive pretreatment, and under reaction conditions (250 °C, 75% H₂ + 25% CO₂). Dark traces are fits; thicker light traces are experimental data; dotted traces are imaginary components of the Fourier transform. Data offset for clarity. (E) Comparison of scattering paths of in situ EXAFS from p-IPOP/Ru/TiO₂ after reductive pretreatment and under reaction conditions (250 °C, 75% H₂ + 25% CO₂). Dark traces are fits; thicker light traces are experimental data; dotted traces are fitted scattering paths. (F) Schematic drawing of the reaction intermediates and pathways over Ru/TiO₂ (right) or p-IPOP/Ru/TiO₂ (left) catalysts. Note that atoms are not drawn to scale.
Fig. 5. Study of stability and versatility of the IPOP coating approach. (A) Continuous measurement of CO₂ hydrogenation performance of p-IPOP/Ru/TiO₂ at 250 °C, 30 sccm 75% H₂ + 25% CO₂, 6 bar total pressure. (B) STEM image and (C–E) corresponding EDS maps of several elements in the p-IPOP/Ru/TiO₂ catalyst after the catalytic test reported in A. (F) N 1s and (G) Ti 2p XPS spectra of p-IPOP/Ru/TiO₂ before and after catalytic tests. (H) Comparison of CO₂ hydrogenation performance over several Ru-based oxide-supported catalysts either bare or encapsulated within p-IPOP layers.
resemble that of RuO₂ after the oxidation pretreatment and then readily reduced back to metallic state after reduction and also remained metallic during CO₂ hydrogenation. Indeed, the best-fit model of the EXAFS data (Fig. 4D) after oxidation was one that included only Ru–O and Ru–(O)–Ru single scattering paths from RuO₂ (SI Appendix, Table S2). However, for p-IPOP/Ru/TiO₂ after reduction and under reaction conditions (Fig. 4E), it was found that a metallic Ru–Ru path alone does not fully describe the original data, as a misfit persists around R = 2 Å for both datasets. An Ru–O scattering path that was initially included to account for Ru–TiO₂ interface sites (46, 47) did not improve the fit. Besides, the fitted Ru–O bond (2.19 Å) is significantly longer than theoretical (2.00 Å) or experimental (1.98 Å) values (46). Given that 50% of the Ru atoms are at the Ru particle surface and surrounded by IPOP (SI Appendix, Additional Materials and Methods), Ru–N and Ru–C paths were then considered, and it was found that Ru–C path at 2.22 Å produced the most reasonable fit with the smallest ΔE and reduced χ² (SI Appendix, Table S2). Such Ru–C bonding at 2.22 Å is longer than Ru–C carbide bonds (1.98 Å) and instead in agreement with Ru–π bonds in organometallic compounds such as in ruthenocene (2.22 Å) (48). Therefore, we hypothesize that the abundant benzene rings in IPOP are adsorbed face-on onto Ru surfaces, determining the change in reaction selectivity observed for the reaction. Such Ru–C bond most certainly modifies the electronic states of Ru particles as well as break down Ru ensemble size via geometric effects.

In summary (Fig. 4F), kinetic and spectroscopic characterization demonstrates that CO₂ hydrogenation on Ru/TiO₂ mainly produces formate intermediates that are precursors for CH₄, leading to high methanation selectivity. The encapsulation by IPOP overlayer suppressed the reactivity of the Ru/TiO₂ interface while introducing polymer/Ru surface interfaces, whose selectivity is dominated by *CO intermediates (49). Moreover, IPOP overlayers also greatly reduced *H coverage, which compensated for the decreased number of Ru sites and increased C–C coupling probability and selectivity toward C₂ hydrocarbons. We envision that, to further enhance C–C coupling while suppressing methanation, future works should be dedicated to developing new methodologies that can selectively block Ru–TiO₂ interfacial sites without sacrificing Ru–Ru terrace sites.

Stability and Applicability. CO₂ conversion only slightly decreased and hydrocarbon yield increased and stabilized over the course of 3 d on the p-IPOP/Ru/TiO₂ catalyst (Fig. 5A), demonstrating the stability of the sample. STEM and EDS mapping confirmed that the Ru particle size did not appreciably change and that the Ru/TiO₂ was still encapsulated by polymer layers after catalysis (Fig. 5 B–E). XPS analysis also confirmed that no appreciable change was discerned between the fresh and spent catalyst in the N 1s region (Fig. 5F) and that Ti 2p signals were still undistinguishable from the baseline (Fig. 5G), demonstrating maintained encapsulation. IR spectra demonstrated that the imine groups remained stable under catalysis conditions (SI Appendix, Fig. S23). Excellent stability was also found for c-IPOP/Ru/TiO₂ and m-IPOP/Ru/TiO₂ catalysts (SI Appendix, Figs. S21–S23). In summary, the IPOP-coated catalysts demonstrated excellent stability during continuous catalytic tests, with no degradation or decomposition of the IPOP layers.

As a proof of concept of the versatility of the IPOP coating to affect the reactivity of supported catalysts, a series of IPOP-coated Ru catalysts was synthesized using oxide supports including Al₂O₃, WO₃, SiO₂, and ZrO₂ (SI Appendix, Fig. S24) and evaluated for CO₂ hydrogenation. All the corresponding Ru/oxide catalysts produced predominantly methane as product (Fig. 5H), in agreement with previous reports (24, 30, 32, 34, 50), with Ru/ZrO₂ being the only exception and showing prominent RWGS selectivity of 78% possibly due to either strong metal support interactions (51) or Ru redispersion (52). Nevertheless, in all cases it was found that IPOP encapsulation significantly promoted CO production through RWGS pathway and, more importantly, much increased C₂ hydrocarbon selectivity. In analogy to the Ru/TiO₂ case, the enhanced CO and C₂ production was attributed to the IPOP effect on the Ru surface reactivity and intermediate stability. The fact that product selectivity is also dependent on the nature of the oxide suggests that the support still plays a crucial role in affecting the Ru reactivity through metal–support interactions (28, 34, 53).

Conclusions

We have demonstrated that the CO₂ hydrogenation reaction on supported Ru catalysts is tuned using polymer encapsulation. Specifically, while methanation is predominant over Ru/TiO₂ catalysts, encapsulating the catalyst in imine-based porous polymer layers dramatically altered the reaction selectivity, with notably enhanced CO and C₂ hydrocarbons selectivity. Specifically, the TOFs for CO and C₂ hydrocarbon production are increased by 80- and 10-fold, respectively. The different kinetic parameters and transition-state entropic gain induced by the IPOP layers suggest that these layers promote different reaction pathways at the polymer/metal interface, as confirmed by operando DRIFTS. Given its stability and versatility, we believe the approach of tuning active sites by polymer encapsulation has potential to be applied to a wide range of heterogeneous catalysts. We also envision that the polymer functionality can be systematically designed to interact with specific intermediates and guide novel reaction pathways in complex reaction networks.

Materials and Methods

Synthesis of Hybrid p-IPOP/Ru/Oxide Catalysts and Postsynthesis Treatments.

For encapsulation targeting ~15 nm overlayer thickness, 500 mg of Ru/TiO₂ catalysts (detailed synthesis of Ru nanoparticles and Ru/TiO₂ catalysts can be found in SI Appendix, as well as characterization techniques) together with 290 mg of phthalaldehyde (either ortho-, meta-, or para-) were added into 30 mL of 1,4-dioxane and sonicated for 20 min until full dispersion/dissolution. Five hundred milligrams of 1,3,5-Tris(4-aminophenyl)benzene (TAPB, 97%; TCI) was separately dissolved in 30 mL 1,4-dioxane. The two solutions were then mixed and vigorously stirred for 30 min under room temperature to promote adsorption of organic monomers onto inorganic substrates. Five milliliters of acetic acid was then added as Bronsted acid catalyst for imine condensation. The polymerization was allowed to proceed for 90 min, after which products were collected by centrifugation and subsequently washed with methanol in a Soxhlet extractor for 12 h. The samples were finally dried at 80 °C under dynamic vacuum conditions for 12 h.

The synthesis process to prepare p-IPOP/Ru/Al₂O₃, p-IPOP/Ru/ZrO₂, and IPOP/Ru/SiO₂ is the same as above, except that 500 mg of either Ru/Al₂O₃, Ru/ZrO₂, or Ru/SiO₂ (5 g (due to high density and low surface area) of Ru/WO₃) was used, respectively.

Catalytic Measurements.

Catalytic experiments were conducted in a custom-made stainless-steel reactor with an internal diameter of 1 cm. Approximately 20 mg of Ru/TiO₂ or 100 mg of IPOP/Ru/TiO₂ were physically mixed with SiC to reach a total mass of 300 mg and loaded into the reactor in between two layers of granular acid-washed quartz. Prior to reaction, the catalysts were activated by oxidation at 250 °C in 5% O₂/Ar atmosphere for 30 min and subsequent reduction at 250 °C in 5% H₂/Ar atmosphere for another 30 min. After pretreatments, the reactant gas mixture (75% H₂ + 25% CO₂) was fed into the reactor at the flow rate of 30 mL min⁻¹, and the system was gradually pressurized to a total pressure of 6 bar. For steady-state measurements, the reactant gas mixture was carried through the reactor in Ar condition at 250 °C, with gas-hourly space velocity adjusted to maintain CO₂ conversion lower than 5%. All products remained in the gaseous phase and thus continuously analyzed by a GC system equipped with a Hayesep D column and a molecular sieve 5A column. CO and all hydrocarbons were quantified using flame

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Steering CO₂ hydrogenation toward C–C coupling to hydrocarbons using porous organic polymer/metal interfaces
ionization detector, while H2 and CO2 consumption was measured using thermal conductivity detector.

Apparent activation energy measurements were carried out under similar conditions, with 3:1 H2:CO2 6 bar total pressure, varying temperature from 220 °C to 230 °C, 240 °C, and 250 °C while maintaining CO2 conversion less than 5%.

Rate-order experiments were carried out at 250 °C with constant total flow rate. To obtain rate orders for H2, the concentration of CO2 in the reactant feed was kept at 15%, while the concentration of H2 was gradually increased from 4:5 to 80% with 4% increments and Ar as balance component. Similarly, to obtain rate order for CO2, the concentration of H2 in the reactant feed was kept at 75%, while the concentration of CO2 was gradually increased from 15 to 25% with 1% increments and Ar as balance component. Throughout all kinetic measurements, the conversions for H2 and CO2 were always kept below 5%.

CO2 conversion was calculated by the equation

\[ \text{CO2 conversion} \% = \frac{\text{CO2 in} - \text{CO2 out}}{\text{CO2 in}} \times 100\% \]

where CO2 (in) and CO2 (out) denote moles of CO2 at the inlet and outlet, respectively.

Selectivity distribution of individual products was calculated by equation

\[ C_{CH_2O} \text{ Selectivity} % = \frac{x \times C_{CH_2O}\text{out}}{C_{CH_2O}\text{in} - C_{CH_2O}\text{out}} \times 100\% \]

where C_{CH_2O} denote moles of possible products, such as CO, CH3OH, CH4, and other hydrocarbons in the outlet.

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