

Surfactants Used in Colloidal Synthesis Modulate Ni Nanoparticle Surface Evolution for Selective CO₂ Hydrogenation

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ABSTRACT: Colloidal chemistry holds promise to prepare uniform and size-controllable pre-catalysts; however, it remains a challenge to unveil the atomic level transition from pre-catalyst to active catalytic surfaces under the reaction conditions to enable the mechanistic design of catalysts. Here we report an ambient pressure X-ray photoelectron spectroscopy (AP-XPS) study, coupled with *in situ* environmental transmission electron microscopy, infrared spectroscopy, and theoretical calculations, to elucidate the surface catalytic sites of colloidal Ni nanoparticles for CO₂ hydrogenation. We show that Ni nanoparticles with phosphine ligands exhibit a distinct surface evolution compared with amine-capped ones, owing to the diffusion of P under oxidative (air) or reductive (CO₂ + H₂) gaseous environments at elevated temperatures. The resulting NiP_x surface leads to a substantially improved selectivity for CO production, in contrast to the metallic Ni, which favors CH₄. The further elimination of surface metallic Ni sites by designing multi-step P incorporation achieves unit selectivity of CO in high-rate CO₂ hydrogenation.

INTRODUCTION

Solutions to climate change and energy sustainability of modern society require the efficient management of carbon-based fuels and chemicals.¹⁻³ Designating CO₂, one of the major greenhouse gases, as a carbon feedstock to produce commodity chemicals has garnered enormous interest, as it would provide an alternative to non-renewable petrochemical sources.^{4,5} Coupled with renewable H₂ and energy sources, heterogeneous catalytic CO₂ hydrogenation is a promising approach to closing the loop of carbon emission.⁶⁻⁸ Under atmospheric pressure, CO is one of the most appealing products from CO₂ hydrogenation via the reverse water-gas shift reaction (RWGS, CO₂ + H₂ → CO + H₂O), given its versatile role in the production of liquid hydrocarbons and oxygenates through well-established gas conversion technologies (e.g., Fischer-Tropsch synthesis and methanol synthesis).^{9,10} However, the RWGS conversion is often accompanied by the methanation reaction (CO₂ + 4H₂ → CH₄ + 2H₂O), which

generates lower-value, gaseous CH₄, making the selectivity control a central challenge of atmospheric CO₂ hydrogenation processes with minimized downstream separation cost.¹¹⁻¹³

At the core of rational catalyst design for the CO₂ hydrogenation is the atomic-level understanding of catalyst structure-property relationships. Previous theoretical and experimental studies suggested that adsorbed CO (*CO) is a key intermediate in CO₂ hydrogenation, and its strong binding often allows the subsequent methanation to produce CH₄.^{12,14,15} Guided by this principle, the synthetic tuning of metal nanoparticle sizes,¹⁶ alloy compositions,^{17,18} and metal-support interactions,¹⁹⁻²³ has been studied to improve the selectivity for CO production. For example, scaling down Ru and Pd nanoparticles to the single atom regime can suppress the CO₂ methanation.²⁴⁻²⁶ Despite enormous efforts, it is still rare to achieve unity selectivity of CO with high-rate conversion of CO₂.

Another obstacle to the mechanistic understanding of heterogeneous catalysis is the structural complexity of

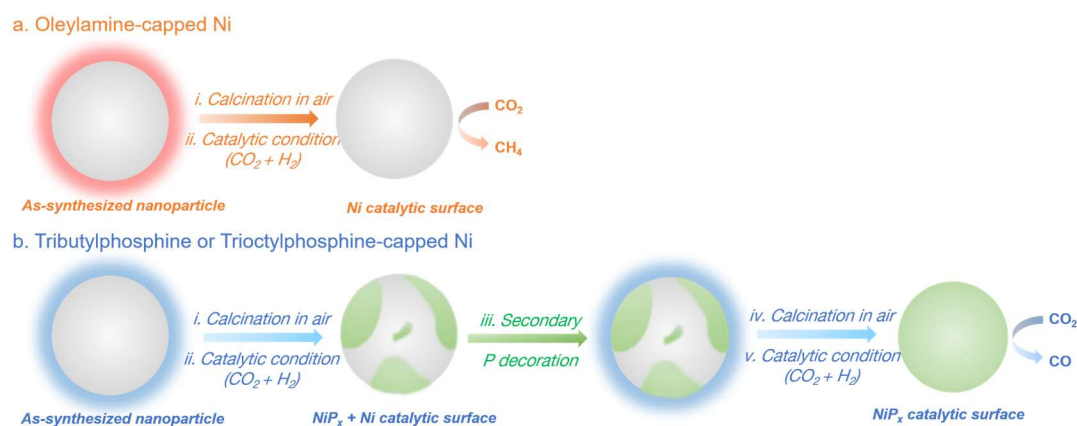


Figure 1. Schematic illustration of capping ligand governed Ni nanoparticle surface evolution. **a**, Oleilamine (OAm)-capped Ni nanoparticles provide a catalytic surface of metallic Ni after a calcination in air (to remove the bulky surfactant) and a reduction under CO₂ hydrogenation conditions. **b**, Phosphine (TOP or TBP)-capped Ni nanoparticles present a transition to generate a NiP_x dominant surface, and the surface metallic Ni site can be completely removed via a secondary phosphine treatment.

many catalysts.²⁷ Recent advances in colloidal chemistry have allowed us to prepare monodisperse nanoparticles with well-defined surfaces and structures that are employed as simplified model systems.²⁸⁻³³ But these well-defined nanoparticle catalysts may involve surface structure evolutions sensitive to the post-treatments (e.g., the removal of surfactants through thermal annealing) and catalytic conditions. Therefore, *in situ* characterizations are required to bridge the knowledge gap between as-synthesized nanoparticle pre-catalysts and the real catalytic structures. For example, we used ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and environmental transmission electron microscopy (TEM) to probe a catalyst under reactant gases and uncovered the structural transition of monodisperse CoPd alloy nanoparticles to Pd-CoO_x quasi-core/shell structures under CO oxidation conditions.³⁴ We envision that such a multimodal, *in situ* investigation will provide unprecedented opportunities to elucidate the catalytic structures for active CO₂ hydrogenation catalysts.

This article highlights the significant impact of capping ligands on colloidal Ni nanoparticle surface evolution and reconstruction in CO₂ hydrogenation. Ni is a well-known catalyst for the CO₂ methanation reaction.³⁵ Our studies using colloidal Ni nanoparticles with different capping ligands reveal that switching from amine (oleilamine, OAm) to phosphine (tributylphosphine, TBP, or trioctylphosphine, TOP) ligands results in a drastic product selectivity change from CH₄ to CO under the same CO₂ hydrogenation conditions. Using AP-XPS and *in situ* environmental TEM, the surface evolution landscapes of the catalysts are identified under different gas conditions and temperatures. As illustrated in **Fig. 1**, in contrast to amine-capped Ni that provides conventional metallic Ni sites for CO₂ methanation, we find that phosphine-capped Ni undergoes an evident, partial transition to NiP_x under catalytic conditions, which suppresses metallic Ni surface sites and delivers a selective CO production (19.7-98.0% depending on the size of Ni nanoparticles). Furthermore, secondary phosphine modification of the Ni catalyst makes

it possible to completely eliminate the surface metallic Ni species, leading to a unit selectivity of CO (100%) with high reaction rate and durability. Density functional theory (DFT) calculations and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) validate that the NiP_x surface is beneficial to the selective CO production through the weakened *CO binding strength.

RESULTS AND DISCUSSION

Synthesis and Characterization of As-Synthesized Ni Nanoparticles. Ni nanoparticles capped with amine or phosphine ligands were synthesized by the reduction of nickel acetylacetonate (Ni(acac)₂) in the presence of OAm or TBP surfactants, according to the reported colloidal methods.^{36, 37} The obtained nanoparticles are labeled as Ni-4.2 and Ni-P-4.2, and both are highly uniform with an average size of 4.2 ± 0.4 nm as shown in the TEM images in **Fig. 2a** and **Fig. S1**. By using the bulkier ligand, TOP, instead of TBP, the sizes of Ni-P were tuned to be 8.7 ± 0.4 (Ni-P-8.7), and 12.0 ± 0.5 nm (Ni-P-12), as indicated in **Fig. S2**. The TOP functions to decrease the number of nuclei in the colloidal synthesis, allowing more atoms to be used in the particle growth to form larger nanoparticles, which is consistent with our previous report.³⁶ XRD pattern confirms the poor crystallinity of as-synthesized Ni-P nanoparticles (**Fig. S3**). Also, two P species exhibits on ³¹P solid state NMR (ssNMR) spectrum of as-synthesized Ni-P nanoparticles: organic phosphine oxide (oxidized surfactant) and phosphate PO_x. It suggests that a small amount of P could diffuse into the Ni during the colloidal synthesis of Ni-P (**Fig. S4**) and get oxidized after exposure to the air. For the subsequent catalytic testing, all as-synthesized nanoparticles were loaded onto commercial TiO₂ (P25) powders through sonication-assisted physical adsorption, with the Ni metal loading ratio controlled to be 2 wt.% (confirmed with inductively coupled plasma-optical emission spectrometer (ICP-OES)).

Catalytic Performance of Nanoparticles in CO₂ Hydrogenation. The TiO₂-supported Ni and Ni-P nanoparticles were pre-treated in air at 400 °C to remove

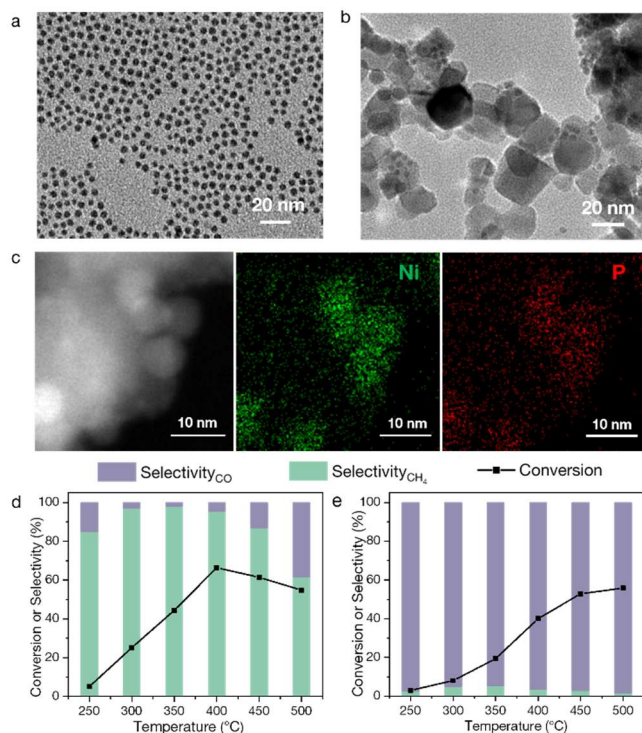


Figure 2. **a, b**, TEM images of as-synthesized Ni-P-4.2 nanoparticles (**a**) and TiO₂-supported Ni-P-4.2 after calcination (**b**). **c**, STEM HAADF image and EELS mapping of the TiO₂-supported Ni-P-8.7 after calcination. **d, e**, Catalytic performances of the TiO₂-supported Ni-4.2 (**d**) and Ni-P-4.2 (**e**) catalysts for CO₂ hydrogenation as a function of temperature (1 vol.% CO₂ + 4 vol.% H₂ + 95 vol.% N₂ with a space velocity of ~30,000 mL g_{cat}⁻¹ h⁻¹ at ambient pressure).

the organic ligands (noted as pretreatment in the following discussion). The calcination in an oxidative gas environment has been widely used to remove surfactants with long hydrocarbon chains for colloidal nanocatalysts, but often causes surface oxidation of nanoparticles. The calcined samples were subsequently annealed in reductive gas conditions (1 vol.% CO₂ + 4 vol.% H₂ + 95 vol.% N₂, same as the CO₂ hydrogenation experimental conditions) at 400 °C to activate the nanoparticle surface for catalytic reactions {Experimental section in Supporting Information (SI)}. The TEM image in **Fig. 2b** confirms that the supported nanoparticles well preserve their sizes and morphologies after the pretreatment. For the Ni-P sample after calcination, we can confirm its amorphous structure based on aberration corrected scanning TEM high-angle annular dark field (STEM HAADF) images (**Fig. S5**). The amorphous structure is also verified by the XRD patterns of Ni-P after calcination, where only very weak and broad peaks of NiO were observed due to surface oxidation of nanoparticles (**Fig. S3**). We also used STEM electron energy loss spectroscopy (EELS) 2D elemental mapping to analyze the Ni-P sample after the calcination, which clearly indicates incorporation and homogeneous distribution of P in the treated sample (**Fig. 2c**).

Fig. 2d and **2e** summarize the catalytic performance of Ni-4.2 and Ni-P-4.2 for ambient-pressure CO₂ hydrogenation. The Ni-4.2 exhibits a typical methanation catalyst

behavior,^{38,39} with CO₂ being selectively converted into CH₄ at temperatures lower than 400 °C. Although high temperature is known to favor CO production, the CO selectivity over Ni-4.2 catalyst is still lower than 40% at 500 °C. A significantly improved selectivity towards CO was observed on Ni-P-4.2 catalysts, which was consistently in the range of 94.0-98.0% at 250-500 °C. The Ni-P-4.2 catalyst delivers a high conversion of CO₂ at 40.0% at 400 °C. Moreover, there is little product selectivity change for both Ni-4.2 and Ni-P-4.2 catalysts when the CO₂ conversion is lowered by tuning the feed gas space velocity and reaction temperature (**Fig. S6** and **S7**). Based on the kinetic measurements, we observed the apparent activation energy for Ni-P-4.2 was 43.4 ± 1.7 kJ mol⁻¹, lower than that for Ni-4.2 catalyst (68.8 ± 1.0 kJ mol⁻¹). (**Fig. S8**).⁴⁰ These results suggest that the Ni and Ni-P provide distinct catalytic sites, which enables the selectivity modulation of CO₂ hydrogenation product.

Environmental TEM characterization. To unveil the possible nanoparticle size, morphology, and dispersity changes during the reaction, we carried out *in situ* environmental TEM measurement on TiO₂-supported Ni-P-4.2 nanoparticles with a gas cell simulating both the pretreatment and catalytic conditions (**SI**). As shown in **Fig. 3**, the Ni-P nanoparticles can be readily distinguished from the TiO₂ support due to their Z contrast difference. Although the gas-cell configuration and heating-induced sample shifting limit the environmental TEM resolution, it is evident that nanoparticle size, morphology, and dispersity are well maintained at the elevated temperatures, regardless of the oxidative or reductive conditions. It is further corroborated by *ex situ* TEM images of the used catalyst in **Fig. S9a**. In addition, the STEM HAADF image indicates that the used Ni-P catalysts preserve their amorphous nanoparticle structure (**Fig. S9b**). Previous studies reported that metallic nanoparticles, such as Ru, can be disintegrated into single atoms or clusters due to strong metal-support interactions, which promote the CO selectivity in CO₂ hydrogenation.¹⁶ Our *in situ* and *ex situ* TEM studies enable us to exclude size and morphology changes in our catalytic materials, and indeed motivate us to further reveal the molecular-level active surface sites for Ni-P catalysts using AP-XPS.

Surface evolution of Ni-P nanoparticles under the pretreatment and catalytic conditions. Given that the low conductivity of TiO₂ support can cause severe charging effect and the Ni-P concentration is too low in TiO₂-support catalysts, we used unsupported Ni-P nanoparticles for AP-XPS measurements (Experimental section in **SI**). The as-synthesized Ni-P-4.2 nanoparticles show an intense C 1s XPS signal originating from the surfactant layer on the nanoparticles (**Fig. S10**). It also presents metallic Ni 2p_{3/2} (at binding energy BE = 852.6 eV) and P 2p_{3/2} (BE = 129.3 eV) peaks (**Fig. 4a**).^{41,42} An additional P 2p signal at 132.1 eV is assigned to the oxidized phosphine ligands attached on the nanoparticle surface.⁴³ To elucidate the surface evolution of catalyst, we monitored the Ni-P-4.2 AP-XPS spectra while exposing the sample in a sequence of different gaseous environments that mimic the pretreatment (0.1 mbar of O₂ and 0.4 mbar of N₂ at 400 °C) and reaction conditions (0.1 mbar of CO₂ and 0.4 mbar of H₂ at 100 °C,

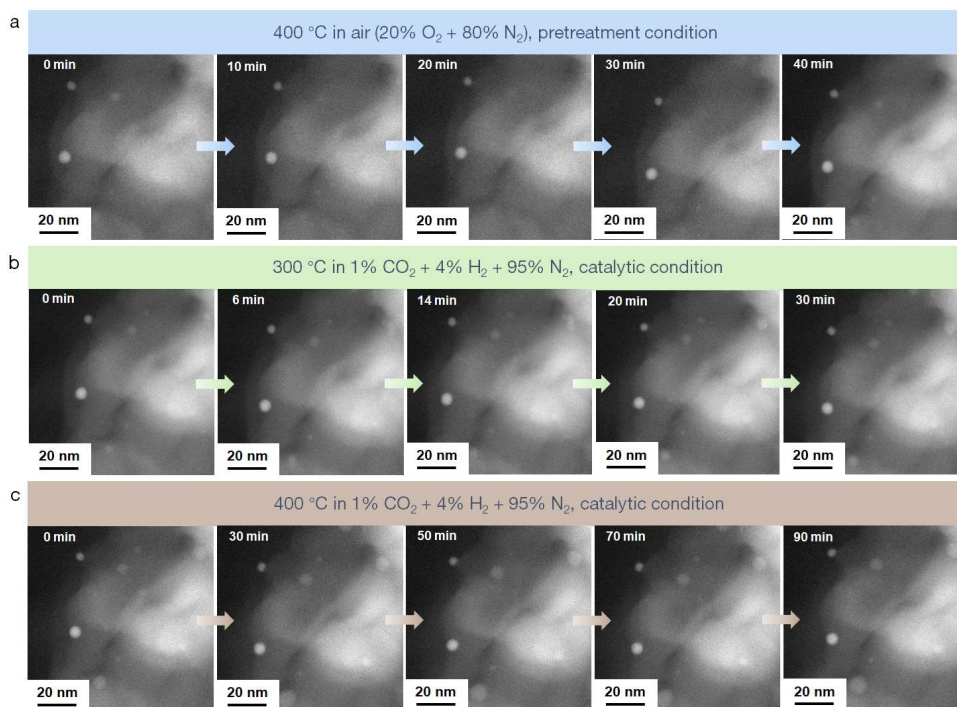


Figure 3. *In situ* observation of the structures of Ni-P-4.2 nanoparticles supported on TiO₂ during the pretreatment and the catalytic reactions. TEM images collected at (a) 400 °C in air (20 vol.% O₂ + 80 vol.% N₂, 1 atm) for 40 minutes, (b) 300 °C in reductive environment (1 vol.% CO₂ + 4 vol.% H₂ + 95 vol.% N₂, 1 atm) for 30 minutes, and (c) 400 °C in reductive environment (1 vol.% CO₂ + 4 vol.% H₂ + 95 vol.% N₂, 1 atm) for 90 minutes.

200 °C, 300 °C, and 400 °C). There is almost no C signal that can be detected after the pretreatment, indicating the hydrocarbon chain of organic ligand is decomposed and removed (**Fig. S10**). The oxidative pretreatment leads to the dominant NiO surface in the Ni-P sample, evidenced by NiO fingerprint signals at 853.7 eV in the Ni 2p spectrum and at 529.1 eV in the O 1s spectrum (**Fig. 4a**).⁴⁴ It is worth noting that the P 2p signal vanishes after the pretreatment, also confirming the surface dominance of NiO. Such a NiO surface is maintained in the CO₂ hydrogenation reaction gases at low temperatures (100 °C and 200 °C).

Once treating the sample in the CO₂ hydrogenation reaction gases at 300 °C, the NiO surface is reduced, as indicated by the downshift of Ni 2p peak to 852.6 eV and the disappearance of the O 1s peak at 529 eV (**Fig. 4a**). Interestingly, we observed that the Ni 2p at this condition showed a satellite peak with BE ~ 6.2 eV higher, which is clearly larger than that of the metallic Ni (~ 5.7 eV). It is established that NiP_x often presents an indistinguishable Ni 2p main peak with metallic Ni, but its satellite features are sensitive to P content in NiP_x.⁴⁵ Therefore, the Ni-P-4.2 surface species under CO₂ hydrogenation reaction is primarily NiP_x rather than metallic Ni. It is also confirmed by the re-emergence of P 2p signals at elevated temperatures, with two peaks corresponding to NiP_x and PO_x species. The P 2p signal intensity is further increased at 400 °C, demonstrating the further enrichment of P content on the surface. In contrast, oleylamine-capped Ni-4.2 presents a typical NiO feature under oxidative pretreatment condition and a metallic Ni surface under reductive CO₂ hydrogenation condition (**Fig. S11**).

The surface structure under different conditions is associated with the robustness of P against ligand removal in the calcination, and its migration and redistribution within the Ni-P nanoparticles. This process produces the NiP_x surface in the reductive gas condition of CO₂ hydrogenation, which probably underpins the distinct catalytic property compared to metallic Ni. While the NiP_x is proposed as the active catalytic species for CO production, we still observed a certain portion of CH₄ in the product (2-6%) over Ni-P-4.2 catalyst. Considering that P is solely from the phosphine ligand bound to the nanoparticle, we hypothesize that such a monolayer P source cannot completely remove the surface metallic Ni sites in the catalyst, causing the undesirable methanation reaction. This point was corroborated by using Ni-P-8.7 and Ni-P-12 nanoparticles. With a larger size, the P source from the monolayer of phosphine ligands becomes further inadequate in the metal phosphorization. As a result, the CO selectivity decreases to 70.0% and 19.7% for Ni-P-8.7 and Ni-P-12 catalysts, respectively (**Table S1**).

Secondary P modification to optimize the catalyst selectivity. The used Ni-P catalyst was stirred in the solution of TOP (1 mM in ethanol) to allow for the secondary phosphine ligand binding. Followed by the similar treatment (calcination in air to remove organic hydrocarbon and then in reductive gas), the secondary P incorporation was designed to phosphorize the remaining surface metallic Ni, as described in **Fig. 4b**. Results from ICP analysis identified that the secondary P modification result in the increase of P content in the Ni-P catalysts (from 29.0% to 38.1%), as presented in **Table S2**. The resulting

Ni-P-4.2 and Ni-P-8.7 catalysts showed a 100% selectivity for the CO

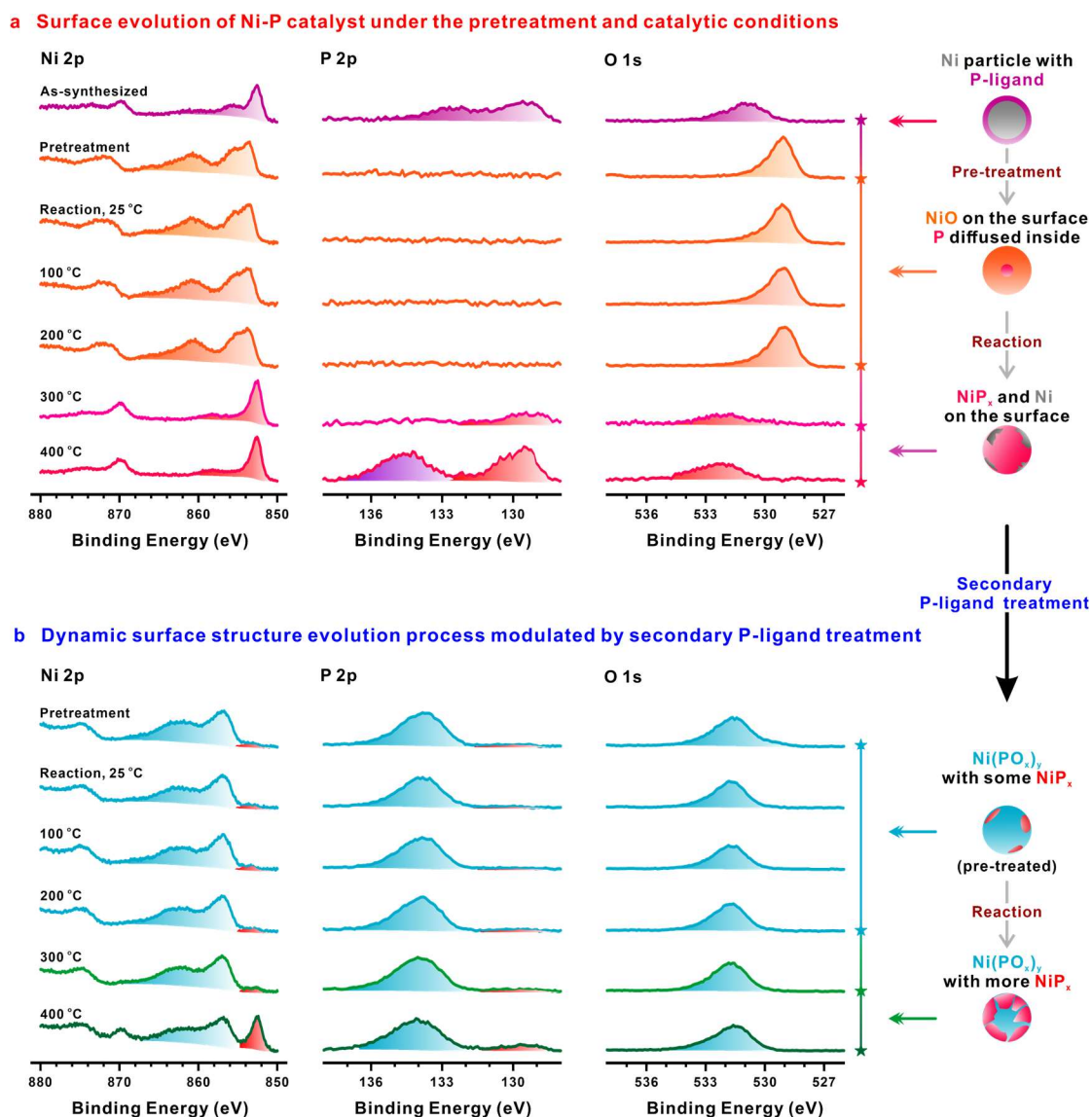


Figure 4. Surface evolution of Ni-P nanoparticles. **a, b**, AP-XPS measurements of the Ni-P-4.2 nanoparticles in different conditions from as-synthesized Ni-P-4.2 catalyst (**a**) and secondary P-treated catalyst (**b**). Ni 2p, P 2p and O 1s spectra were obtained under 0.5 mbar of mixtures of O₂ and N₂, or under 0.1 mbar of CO₂ and 0.4 mbar of H₂, at different temperatures. The spectra were acquired in normal emission geometry using a monochromated Al K α emission source (h ν = 1486.6 eV).

product (**Fig. 5a**). Even for Ni-P-12, CH₄ product was substantially prohibited (CO selectivity increased from 19.7% to 88.9%), which confirmed the efficacy of secondary P incorporation. We also found that the obtained catalyst was highly durable. With a 38.8% conversion of CO₂ and a 100% selectivity for CO product, the Ni-P-8.7 exhibits a CO production rate of 4.8 mmol g_{cat}⁻¹ h⁻¹ at 400 °C and well maintains the performance in a 150-hour stability test (**Fig. 5b**).

Fig. 4b summarizes the AP-XPS spectra of the Ni-P-4.2 sample related to secondary P modification process. A major change we observed in the oxidative conditions at 400 °C is that Ni 2p signal is at 857 eV, which is clearly different from the original Ni-P-4.2 sample (BE = 852.6 eV).⁴⁶ Meanwhile, the NiP_x peak in the P 2p spectra

substantially attenuates, while a strong PO_x signal is detected. The O 1s spectrum shows a peak at BE 531.7 eV, much higher than that of NiO. These changes clearly demonstrate that the surface is dominated by Ni(PO_x)_y species, after the secondary P incorporation. The excess amount of P enables the effective metal phosphorization that couples with the oxidation process to generate Ni(PO_x)_y. It is also found that the oxidized sample still has a small proportion of NiP_x on the surface, with weak peaks at lower BE regions on both Ni 2p and P 2p spectra. Bypassing the NiO formation, the secondary P treated Ni-P-4.2 sample displays unaltered spectra under reductive CO₂ hydrogenation condition from room temperature to 300 °C. The transformation from Ni(PO_x)_y to NiP_x can be observed at 400 °C, which generates more active sites for CO₂-to-CO

selective conversion. The direct comparison of the APXPS spectra of Ni-P catalyst before and after secondary P modification allows us to conclude that the incorporation of P, left by phosphine ligand decomposition, is the cornerstone to minimize the surface metallic Ni sites and thus to optimize CO product selectivity.

It is worth highlighting that AP-XPS is critical to elucidate the surface evolution of catalyst under pretreatment and reaction conditions, which cannot be achieved by ex situ characterizations. For example, *ex situ* XRD results of Ni-P after the pretreatment and catalysis (including secondary P treatment) show only weak peak of NiO due to surface oxidation in air, while the information pertaining to the transition from NiO or NiPO_x to NiP_x under reductive

catalytic condition at high temperatures were missed (**Fig. S3**). Ex situ ³¹P ssNMR can only identify PO_x signals for the used Ni-P catalysts (both without and with secondary P-treatment). The signal from NiP_x is not observed, which is probably due to oxidation to NiPO_x or the paramagnetism of the species (**Fig. S12, 13**).

The role of NiP_x catalytic sites. *In situ* DRIFTS was used to understand the CO₂ hydrogenation pathways over Ni and Ni-P catalysts under flow reaction conditions. Once the model reaction gas (2 vol.% CO₂ + 8 vol.% H₂ + 90 vol.% N₂) is fed into the cell at room temperature, both Ni and Ni-P catalysts display the characteristic bands of bicarbonate (1381, and 1689 cm⁻¹) that results from the reaction

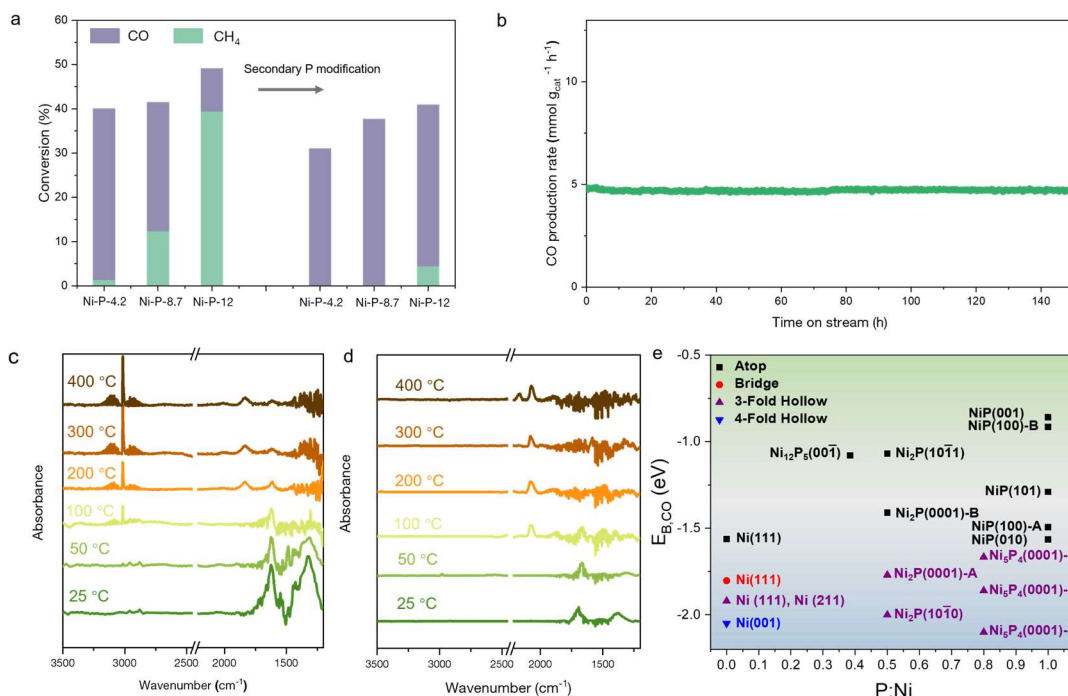


Figure 5. Catalytic performance and the NiP_x site properties. **a**, comparison of activity and selectivity on various catalysts before and after secondary P modification (1 vol.% CO₂ + 4 vol.% H₂ + 95 vol.% N₂ at ambient pressure, 400 °C). **b**, catalytic stability of secondary P modified Ni-P-8.7 (1 vol.% CO₂ + 4 vol.% H₂ + 95 vol.% N₂ at ambient pressure, 400 °C). **c**, **d**, *In situ* DRIFT spectra following exposure to feeding gas at 50 °C and subsequent stepwise heating to 400 °C under the same flow for Ni-4.2 (**c**) and Ni-P-4.2 (**d**). **e**, DFT calculation results of CO binding energies on Ni and various NiP_x surfaces.

between CO₂ and the hydroxyl group on the TiO₂ support (**Fig. 5c and 5d**).⁴⁷ The bicarbonate peak intensity gradually decreases along with the rise of temperature, while new peaks attributed to adsorbed formate species appear at 2980 and 2939 cm⁻¹.¹⁷ Formate has been claimed as a possible intermediate for CO₂ methanation in previous reports.^{12,48} The similar feature of bicarbonate-to-formate transition on our Ni and Ni-P catalysts suggests that formate is an intermediate for both CO and CH₄ formation, but not the key to determine the catalyst selectivity. Most interestingly, we found a very different CO adsorption behavior over the Ni and Ni-P catalysts. On Ni, a peak at 1845 cm⁻¹ is detected at 300 °C, which is correlated with multi-centered *CO on multifold hollow Ni sites (**Fig. 5c**).¹² This multi-centered *CO band is accompanied by a gaseous CH₄ peak (at 3017 cm⁻¹) whose intensity increases with the temperature.²¹ In contrast to the Ni catalyst, the primary

*CO on Ni-P is linear *CO on the atop site with a stretching band at 2,071 cm⁻¹ (**Fig. 5d**).²⁰ In addition, the adsorbed CO molecules diffusing from the Ni to the Ti sites can be identified at 2168 cm⁻¹ at 400 °C for Ni-P catalyst, but the gaseous CH₄ peak is negligible.^{49,50}

We also investigated the *CO binding strength on Ni and Ni-P catalysts by using temperature-programmed desorption (TPD) DRIFTS. The CO-saturated samples were flushed with Ar under a series of temperatures with TPD DRIFTS spectra being recorded. As shown in **Fig. S14**, Ni-P showed a complete CO desorption at room temperature. The multi-centered *CO is much more stable and still present on the surface of Ni at 450 °C and 500 °C. Based on these results, it is clear that Ni-P catalyst can effectively decrease the binding strength of *CO by diminishing multi-centered CO adsorption. It is also in an excellent agreement with the catalytic performance of Ni and Ni-P catalysts; i.e., Ni-P is

favorable for the CO desorption and avoids the deep hydrogenation (methanation) to produce CH₄.

DFT simulations demonstrate that the P incorporation in Ni effectively alters the CO binding energy ($E_{B, CO}$). Given the fact that our Ni-P catalyst has an amorphous structure, we simulated a series of Ni-P surfaces, including Ni₂P (0001)-(2 terminations, A and B), Ni₂P (10 $\bar{1}$ 0), Ni₂P (10 $\bar{1}$ 1), Ni₅P₄ (0001)-(3 terminations, A, B, and C), NiP (001)-(2 terminations, A and B), NiP (010), NiP (100), NiP (101), and Ni₁₂P₅ (00 $\bar{1}$) surfaces, to encompass possible adsorption sites for CO. These results were compared to the CO adsorption models on the Ni (001), Ni (111), and Ni (211) surfaces. $E_{B, CO}$ for the most stable adsorption site is aggregated in **Fig. 5e** against the P:Ni ratio and tabulated in **Table S3** (calculated structures are shown in **Fig. S15-S30**). CO adsorption on Ni surfaces is strongest in the hollow sites with binding energies of -2.05 eV, -1.92 eV, and -1.92 eV on Ni (001), (111), and (211) respectively, which are consistent with previous DFT calculations.⁵¹⁻⁵⁴ After the P is incorporated, the $E_{B, CO}$ is strongly surface dependent, varying from -2.05 eV on Ni₅P₄ (000 $\bar{1}$) to -0.86 eV on NiP (001), with most presenting a lower $E_{B, CO}$ than Ni. More importantly, we found that $E_{B, CO}$ is strongly dependent on the coordination number of surface adsorption sites. The average $E_{B, CO}$ of singly coordinated CO molecules over NiP_x is -1.21 ± 0.27 eV, which is much lower than that of the multi-coordinated CO adsorption being -1.91 ± 0.14 eV. Indeed, P primarily acts to reduce the CO binding strength by acting as a temperature stable means of breaking up multi-coordinated binding sites to leave singly coordinated binding sites as the remaining option. Experimentally, this was demonstrated by the appearance and dominance of atop site (singly coordinated) in the infrared at 2071 cm⁻¹ on the NiP_x rather than the multi-coordinated CO at 1845 cm⁻¹ (computed infrared frequency is shown in **Table S3**). Moreover, the improvement of CO selectivity with the second P incorporation step, which would further break up the Ni multi-binding sites, is consistent with this conclusion.

CONCLUSION

In summary, we report a full description of the surface evolution of colloidal Ni nanoparticles under the CO₂ hydrogenation conditions, by combining the AP-XPS and complementary *in situ* spectroscopic and microscopic probes. The mono-layer phosphine ligands encapsulating Ni nanoparticles results in P incorporation in the real catalyst at the elevated temperature, which diffuses into the interior of the nanoparticles under oxidative gas atmosphere, leaving a NiO surface, and returns the nanoparticle surface to form NiP_x under reductive CO₂ hydrogenation conditions. Such a ligand-induced surface evolution is responsible for the significantly improved selectivity to CO production owing to the decreased *CO adsorption strength over the NiP_x surface, while amine-capped Ni remains a CO₂ methanation catalyst. Furthermore, the secondary P modification drives a deeper phosphorization of surface Ni sites under the reaction conditions, which generates a catalyst with a 100% CO selectivity in CO₂ hydrogenation. Given the fact that phosphine is one of the most representative surfactants in the colloidal nanoparticle library, we anticipate that the P diffusion and incorporation effect will likely modulate many other nanoparticle catalyst

properties, providing a new controlling knob for governing reaction that are critical to energy and environmental sustainability.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge at <http://pubs.acs.org>. Experimental section, additional TEM and STEM HAADF images, XRD patterns and ssNMR spectra of all samples, additional catalysis and AP-XPS results, CO-TPD spectra, ICP-OES results, and DFT calculated structures and calculation results.

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Notes

The authors declare no competing interest.

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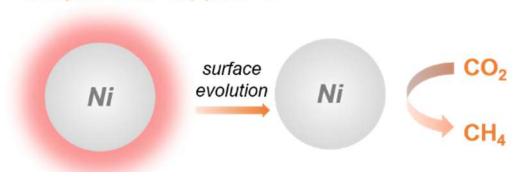
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Oleylamine-capped Ni



Tributylphosphine or Trioctylphosphine-capped Ni

