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High Selectivity of CO₂ Hydrogenation to CO by Controlling the Valence State of Nickel using Perovskite

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The selectivity of CO₂ hydrogenation can be significantly tuned by controlling the valence state of nickel using lanthanum-iron-nickel perovskites. Nickel with higher valence states weakens the binding of CO and increases the activation barrier for further CO hydrogenation, leading to a higher CO selectivity than the metallic nickel.

Catalytic conversion of CO₂ has attracted increasing attention in recent years, aiming at alleviating the global warming and ocean acidification.^{1–3} CO₂ hydrogenation with renewable hydrogen is proposed to utilize CO₂ as a raw material to produce valuable chemicals, such as CO, CH₄, and methanol. Ni-based catalysts are identified as one of the most promising catalysts for CO₂ hydrogenation due to their considerable catalytic activity and lower cost compared to precious metal catalysts.^{4, 5} However, Ni-based catalysts are generally favorable for the Sabatier methanation reaction for CH₄ rather than the reverse water gas shift (RWGS) reaction for CO.^{5, 6} In many cases, CO is more desirable than CH₄ as it offers more flexibility to produce oxygenates and synthetic fuels via the methanol synthesis or Fischer-Tropsch reactions.⁷ Thus, it is important to promote the selectivity of CO₂ hydrogenation to CO over Ni-based catalysts.

To date, many attempts have been made to increase the CO selectivity over Ni-based catalysts, such as alloying Ni with other metals (Cu, Pt, and Pd et al.),^{8, 9} controlling the loading of Ni,¹⁰ and using promoters like K.¹¹ However, a fundamental understanding of

the influence of the binding energies of the intermediates over Ni-based catalysts on the product selectivity is still lacking. In our previous studies, the correlation between the binding energies of key intermediates and the product selectivity for CO₂ hydrogenation was established through combined experiments and DFT calculations over several other catalysts.^{7, 12–14} For example, by simply replacing the CeO₂ or ZrO₂ supports with TiO₂ for the PtCo-based bimetallic catalysts, the ratio of CO/CH₄ was increased since the binding of C,O-bound and O-bound species at the PtCo-oxide interface was weakened.⁷ Although the mechanism of CO₂ hydrogenation is complicated and might be very different over various catalysts, it is generally accepted that CO is the key intermediate for CH₄ formation over Ni-based catalysts.^{4, 11, 15, 16} This suggests that the product selectivity of CO₂ hydrogenation can be potentially tuned by controlling the binding energies of CO on the catalysts.

It is well known that the binding energy of CO varies with the valence state of nickel, which is much weaker on oxidized nickel than that on metallic nickel.¹⁵ The weak binding energy of CO offers a potential way to promote the CO selectivity for CO₂ hydrogenation over Ni-based catalysts. However, for the supported Ni-based catalysts, nickel is more likely to be reduced to Ni⁰ under hydrogenation conditions.¹⁷ Therefore, keeping Ni at higher valence states under reaction conditions is a key challenge in promoting the CO selectivity. Perovskites with the ideal general formula of ABO₃ are known as versatile materials in which Ni ions can be located at the B sites. They could be reduced out of the perovskite lattice to form highly dispersed nanoparticles under particular environments, resulting in a strong metal support interaction (SMSI) effect.^{18, 19} These features of Ni-containing perovskites were widely investigated and the related catalysts, such as LaNiO₃, LaFe_{1-x}Ni_xO₃, and SrTi_{1-x}Ni_xO₃, were used for many reactions including dry reforming or steam reforming of methane.^{18, 20} Recently, Steiger et al. investigated the parameters for the regeneration behavior of the perovskite (LaFe_{1-x}Ni_xO₃) structure, using CO₂ hydrogenation as a probe reaction.²¹ However, to the best of our knowledge, there are no discussions about controlling the selectivity of CO₂ hydrogenation using perovskites.

Herein, this study demonstrates how the selectivity of CO₂ hydrogenation can be tuned by changing the valence state of nickel using different lanthanum-iron-nickel perovskites. The catalytic performance using a flow reactor is shown in Fig. S1 and S2 (ESI[†]) and results obtained after the reaction reached a

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[†] Electronic Supplementary Information (ESI) available: Experimental details, specific surface area, activity curves, H₂-TPR curves, additional XRD patterns, TEM figures, and XPS spectra. See DOI: 10.1039/x0xx00000x

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steady-state at 14 hours at 673 K are summarized in Table 1. It is noticed that LaNiO_3 mainly produces CH_4 rather than CO while very little CH_4 is formed over $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$. Table S1 (ESI[†]) compares the catalytic performance of a series of perovskites with different Fe/Ni ratios. LaFeO_3 shows poor activity with the lowest CO_2 and H_2 conversions. After doping Ni into the perovskites their activity is significantly increased, indicating that Ni-related species should be responsible for the production of CH_4 or CO over the Ni-containing perovskites. It is known that the selectivity of CO_2 hydrogenation over Ni-based catalysts often varies with CO_2 conversion, which depends on the gas space velocity and temperature. Here the CO_2 conversion of LaNiO_3 was controlled at a similar level with $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$, i.e. 18.1%, and the selectivity is also listed in Table 1. It can be seen that even at similar CO_2 conversion LaNiO_3 still shows a much higher selectivity of CH_4 (71.4%) compared to $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ (3.2%).

Table 1: Summary of flow reactor data for CO_2 hydrogenation over LaNiO_3 and $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ (calculated by averaging data points in 12–14 h on stream, $\text{CO}_2/\text{H}_2/\text{Ar} = 5/10/25 \text{ mL min}^{-1}$).

Catalyst		LaNiO_3^a	$\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3^a$	LaNiO_3^b
Conversion (%)	CO_2	39.7	16.3	18.1
	H_2	75.5	11.4	28.4
TOF ($\text{mol mol}_{\text{Ni}}^{-1} \text{ min}^{-1}$)	CO_2	0.20	0.15	1.03
	H_2	0.75	0.21	3.19
Yield (%)	CO	3.2	15.8	5.1
	CH_4	36.5	0.5	12.9
Selectivity (%)	CO	8.0	96.6	28.2
	CH_4	92.0	3.2	71.4

^a 100 mg catalyst, $T = 673 \text{ K}$. ^b 15 mg catalyst, $T = 623 \text{ K}$.

Fig. 1 shows the TEM images and particle size distributions of the spent catalysts. In Fig. 1a and d the Ni-related particles can be found on the surface of both spent catalysts, while no such particles are observed on the fresh catalysts (Fig. S3, ESI[†]), indicating that Ni ions were exsolved from the perovskite lattice to form surface nanoparticles. The magnified images in Fig. 1b and e reveal that the nanoparticles are closely attached to the perovskite host. The size distributions of the nanoparticles are shown in Fig. 1c and f. The average particle size in the spent LaNiO_3 and $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ are 6.5 and 4.5 nm, respectively. However, according to the general view of the catalysts derived from perovskites, the particles on the surface usually interact strongly with the support and their properties are significantly influenced by their parent lattice.^{18, 21} Thus, the oxidation states of Ni in the nanoparticles are still unknown.

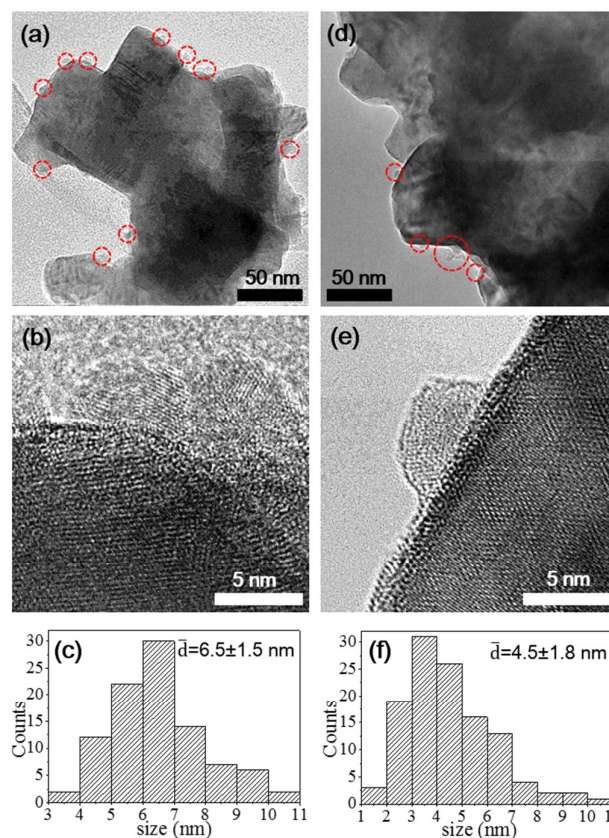


Fig. 1 TEM images and particle size distributions of the spent catalysts (a–c) LaNiO_3 ; (d–f) $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$.

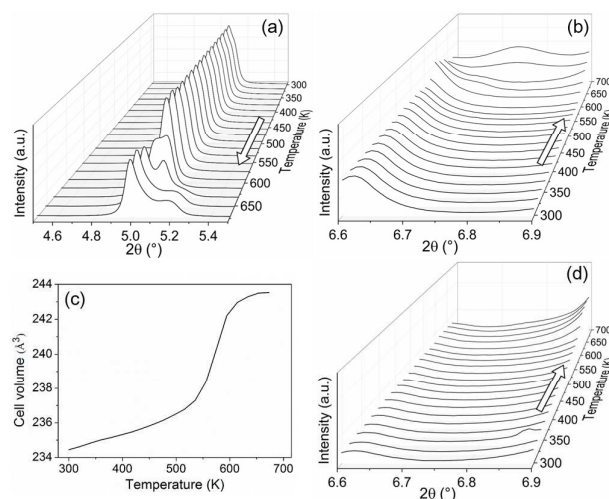


Fig. 2 Results of the *in-situ* XRD measurements during the temperature ramping stage, (a) and (b) patterns of LaNiO_3 ; (c) and (d) lattice expansion and patterns of $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$. Fig. b and d show regions where Ni diffraction peaks would be expected.

To understand the structural evolution of the catalysts, *in-situ* XRD experiments for LaNiO_3 and $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ under reaction conditions were performed. Fig. 2a shows the strongest diffraction peak around $2\theta = 5.0^\circ$ of LaNiO_3 as a function of temperature from 300 to 673 K. It can be seen that the peaks start to slightly shift to lower angle position at 553 K

due to the exsolution of Ni ions and the phase transformation from LaNiO_3 to $\text{LaNiO}_{2.5}$ takes place at about 625 K. In Fig. 2b the diffraction peaks of metallic Ni centered at $2\theta = 6.8^\circ$ start to appear at 653 K, right after the phase transformation. These results suggest that a portion of the Ni ions in the LaNiO_3 perovskite is converted into metallic Ni under reaction conditions.²¹ In the case of $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$, its perovskite structure is still maintained after the reaction (Fig. S4, ESI[†]). In Fig. 2c there is an abrupt volume expansion occurred between 520 and 615 K on top of the upward-sloping background line from the thermal effect, demonstrating that there are Ni^{3+} ions coming out of the perovskite lattice.^{19, 21} However, it should be noted that the diffraction peak of metallic Ni is almost invisible in the XRD patterns in Fig. 2d. The H_2 -TPR results (Fig. S6, ESI[†]) are also consistent with that the $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ perovskite is able to stabilize Ni in the oxidized states until a higher temperature range than LaNiO_3 . When changing the atmosphere to H_2 +He at 673 K, the strongest diffraction peak in both catalysts are without further change (Fig. S5, ESI[†]), demonstrating that the changed structures are stable to endure such a reaction condition.

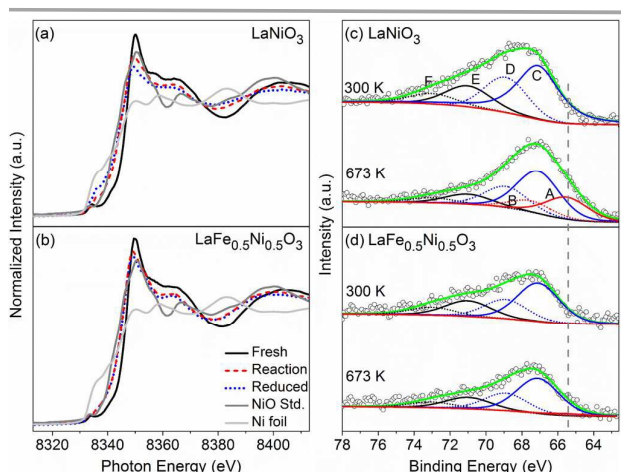


Fig. 3 *In-situ* XANES spectra of Ni K-edge of (a) LaNiO_3 and (b) $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$. *In-situ* AP-XPS spectra of Ni 3p of (c) LaNiO_3 and (d) $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ at 300 K and 673 K, peak A and B correspond to the $3p_{3/2}$ and $3p_{1/2}$ of Ni^0 , peak C and D correspond to the $3p_{3/2}$ and $3p_{1/2}$ of Ni^{2+} , peak E and F correspond to the $3p_{3/2}$ and $3p_{1/2}$ of Ni^{3+} .

In-situ X-ray absorption near-edge structure (XANES) measurements were performed to further understand the evolution of Ni ions in the perovskites. The XANES spectra of Ni K-edge for the two catalysts are shown in Fig. 3a and b. Ni in reduced oxidation states can be identified by the decreased white line in the spectra. The compositions are estimated by a linear combination fitting method and summarized in Table S2 (ESI[†]). The results indicate that metallic Ni exists (11%) in LaNiO_3 under reaction conditions, and its amount further increases to 41% when cutting off CO_2 in the stream. In contrast, the Ni-related species in $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ are almost without metallic Ni under both reaction and reduced conditions. As mentioned above, the Ni in supported catalyst is easy to be reduced to the metallic state. Here, a comparison between the Ni K-edge spectra of $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ and Ni/ZrO_2 under reaction condition is given in Fig. S7 (ESI[†]). It can be

seen that $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ truly has the ability to maintain Ni in a higher valence state than the supported catalyst.

The aim of *in-situ* ambient pressure X-ray photoelectron spectroscopy (AP-XPS) experiments was to detect the oxidation states of surface Ni. They were carried out under 10 mTorr pressure of reactants ($\text{CO}_2/\text{H}_2 = 1/2$) and the Ni 3p spectra are adopted in this work since the Ni $2p_{3/2}$ and La $3d_{3/2}$ spectra strongly interfere with each other.²² The Ni 3p spectra in Fig. 3c and d show changes in valence states between the catalyst at 300 K and during the reaction at 673 K. The spectra of LaNiO_3 -300 K and $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ -300 K show co-existence of Ni^{3+} and Ni^{2+} , with their $3p_{3/2}$ peaks appearing at approximately 70.9 and 67.0 eV, respectively.²²⁻²⁵ The Ni^0 $3p_{3/2}$ peak as indicated by the dashed line (65.5 eV) is absent in both fresh catalysts.^{25, 26} For the spectrum of LaNiO_3 -673 K, the overall peak shifts to a lower binding energy range (Fig. S8, ESI[†]) due to a decrease in the intensity peaks assigned to Ni^{3+} and Ni^{2+} , together with the appearance of the Ni^0 peaks. In contrast, such a peak shift does not occur obviously between the two spectra of $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$. The intensity of the peaks assigned to Ni^{3+} decreases in the spectrum of $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ -673 K compared to that of $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ -300 K. However, the peaks attributed to Ni^0 are very weak in $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ -673 K. As summarized in Table S3 and S4 (ESI[†]), the peak area of Ni^0 in the spectrum of LaNiO_3 -673 K accounts for 29.1% of the total peak area, while it is only 3.0% of the total peak area of $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ -673 K. It should be noted that some metallic Ni might come from the Ni nanoparticles over the $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ surface. However, Ni in the nanoparticles of this sample should likely be in a mixed states of metallic Ni and Ni ions, as the nanoparticles strongly interact with the perovskite support²⁰ and the electronic properties of Ni in the nanoparticles should also be modified. Based on the *in-situ* XRD, XANES, and AP-XPS results, it is suggested that $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ is able to maintain the surface Ni species at a higher valence state in the reducing atmosphere.

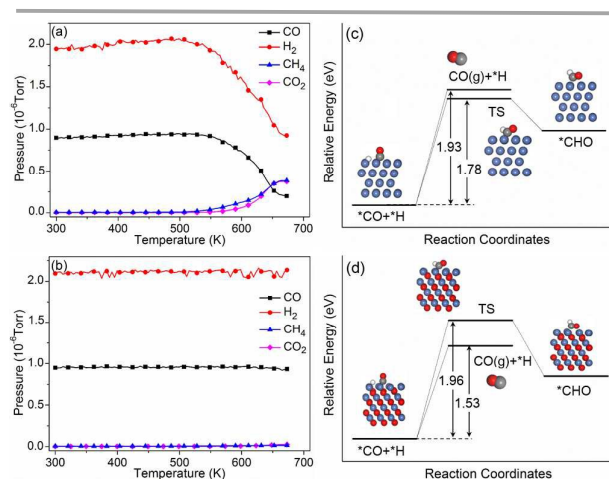


Fig. 4 The partial pressures of CO, H_2 , CH_4 , and CO_2 during the CO hydrogenation reaction for (a) LaNiO_3 and (b) $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$. Potential energy diagram for the reaction routes of $^*\text{CO}+\text{H}$ on $\text{Ni}(111)$ and $\text{NiO}(111)$. The DFT optimized geometries of $^*\text{H}$, $^*\text{CO}$, transition states (TS), and $^*\text{CHO}$ on $\text{Ni}(111)$ and $\text{NiO}(111)$, are shown as insets in (c) and (d), Ni: blue, O: red, C: gray, H: white.

Density functional theory (DFT) calculations combined with the CO hydrogenation experiments were carried out to understand how

the valence states of Ni control the selectivity of CO₂ hydrogenation. Fig. 4a and b show the CO, H₂, CH₄, and CO₂ partial pressures during the CO+2H₂ reaction on LaNiO₃ and LaFe_{0.5}Ni_{0.5}O₃. LaNiO₃ is active for the further hydrogenation of the CO product; both CO and H₂ start to react at 525 K, and their pressures keep decreasing with a simultaneous increase in the CH₄ pressure. In contrast, LaFe_{0.5}Ni_{0.5}O₃ is inactive for CO hydrogenation in the entire temperature range. The results confirm that CO is a key intermediate for CO₂ hydrogenation to CH₄ and its reactivity is quite different over LaNiO₃ and LaFe_{0.5}Ni_{0.5}O₃.

DFT calculations were performed to correlate the binding energy of CO with the product selectivity by using Ni(111) and NiO(111) model surfaces simulating Ni oxidation states. According to previous studies, the RWGS + CO-Hydro pathway with key intermediates of CO and CHO is employed.^{7, 11, 12, 27, 28} The optimized geometries and binding energies of CO and CHO species are shown in Fig. S9 and Table S5 (ESI[†]), respectively. According to the RWGS + CO-Hydro mechanism, the formed *CO either desorbs to produce gas phase CO or undergoes subsequent hydrogenation reaction to form CH₄. As shown in Fig. 4c the hydrogenation of *CO to *CHO on Ni(111) has an activation barrier (*E*_a) of 1.78 eV, while the formation of CO should overcome a desorption energy (*E*_d) of 1.93 eV, which is equal the BE of *CO on Ni(111). Such a strong binding makes the desorption of *CO difficult and thus it is more favorable for its further hydrogenation to *CHO and subsequently to CH₄. On the other hand, the hydrogenation of *CO to *CHO on NiO(111) has an *E*_a of 1.96 eV, while the *E*_d for CO is only 1.53 eV. Thus, the *CO desorption is more favorable than its hydrogenation to *CHO on the NiO(111) surface. Overall, the DFT calculations predict that the NiO(111) surface should be more selective than Ni(111) for CO production, consistent with the experimental results.

In conclusion, the combined *in-situ* experimental and theoretical investigations have shown that by changing the valence state of Ni, the product selectivity of CO₂ hydrogenation can be tuned over lanthanum-iron-nickel perovskites. LaNiO₃ shows high selectivity toward CH₄, whereas CO is preferentially formed on LaFe_{0.5}Ni_{0.5}O₃. According to the *in-situ* XRD, XANES, and AP-XPS analysis, metallic Ni is formed over LaNiO₃ under reaction conditions, while the Ni-related species present higher valence states in LaFe_{0.5}Ni_{0.5}O₃. DFT calculations reveal that CO binds weakly on NiO(111) where *CO desorption is more favorable over its further hydrogenation to CH₄, leading to a much higher CO selectivity. This correlates well with the experimental results that Ni-related species in higher valence states could produce more CO. These findings establish new correlations between the catalytic performance and structural properties of Ni-based catalysts and provide catalyst synthetic strategies for controlling the metal oxidation state to achieve the selectivity in CO₂ hydrogenation reactions.

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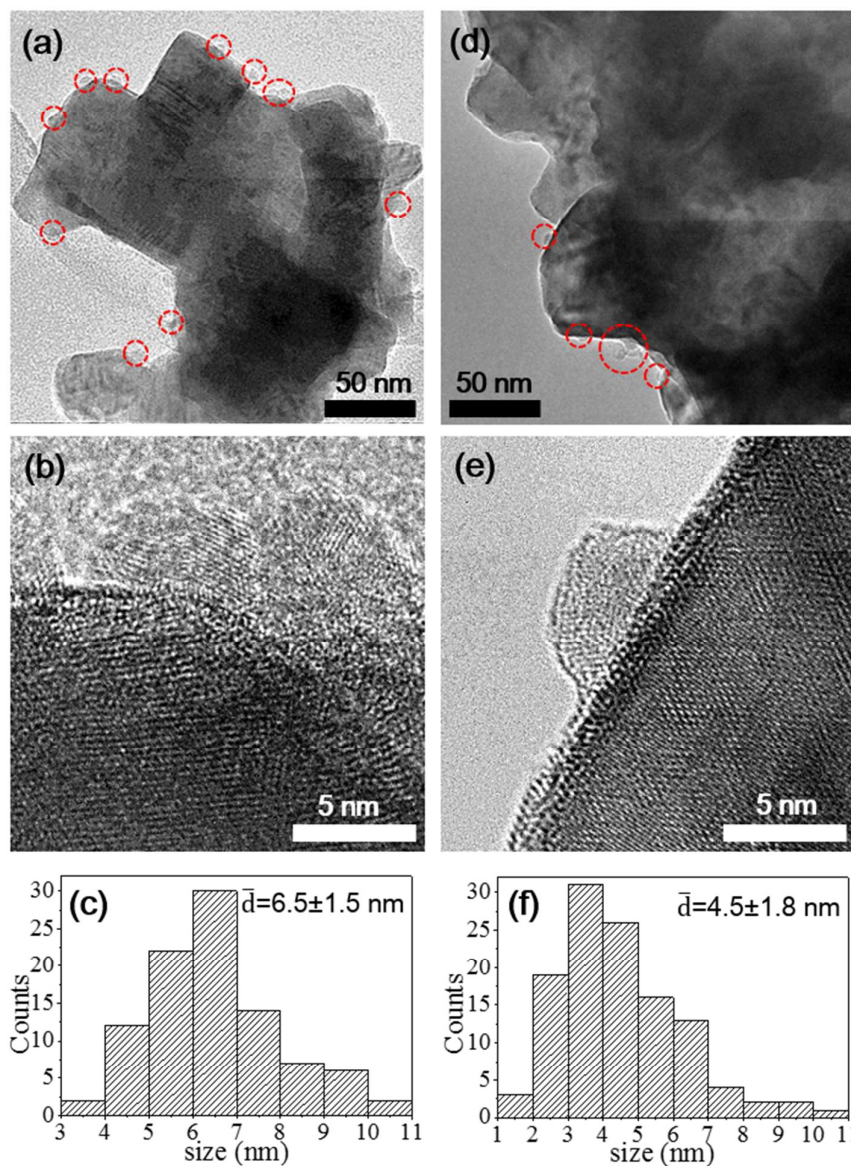


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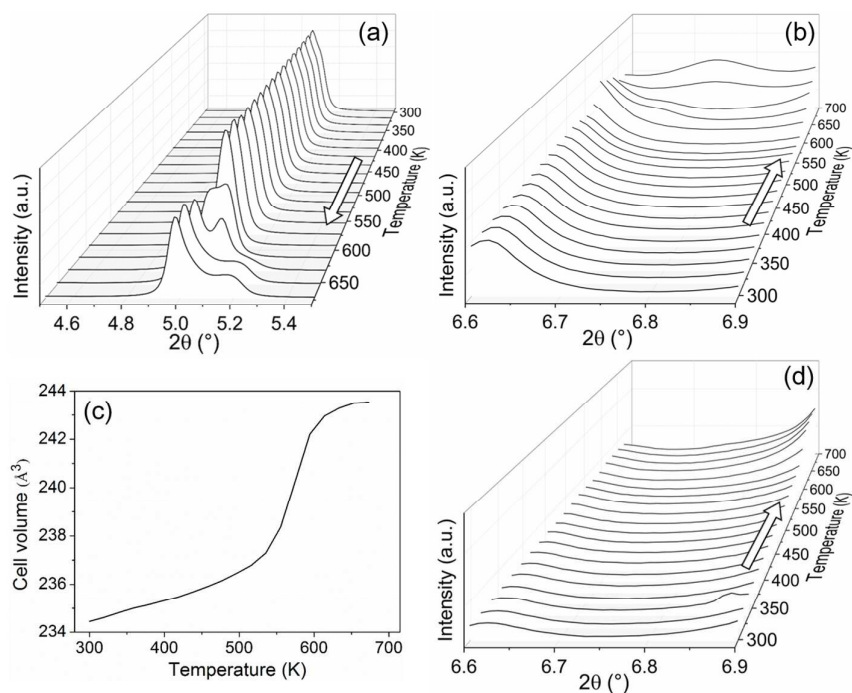


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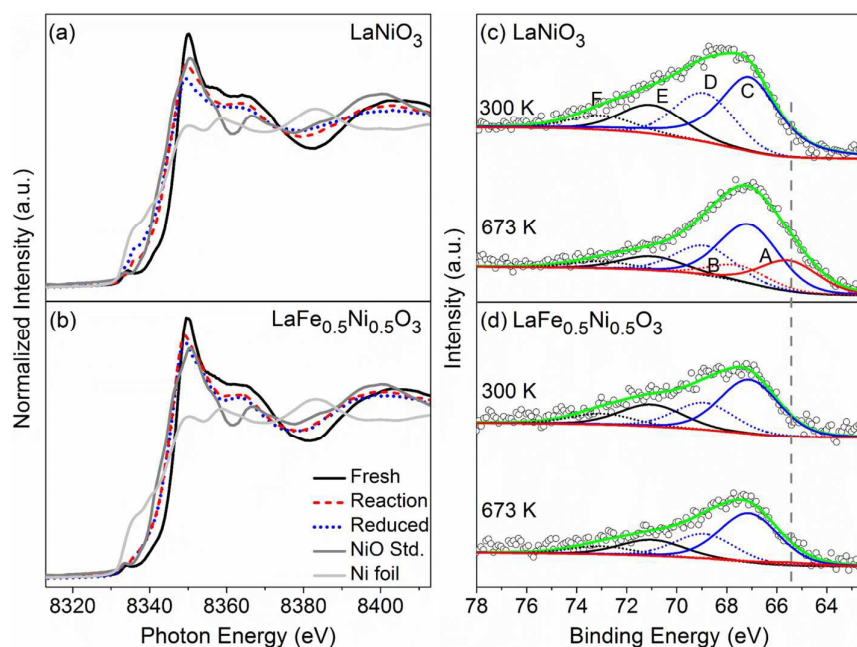


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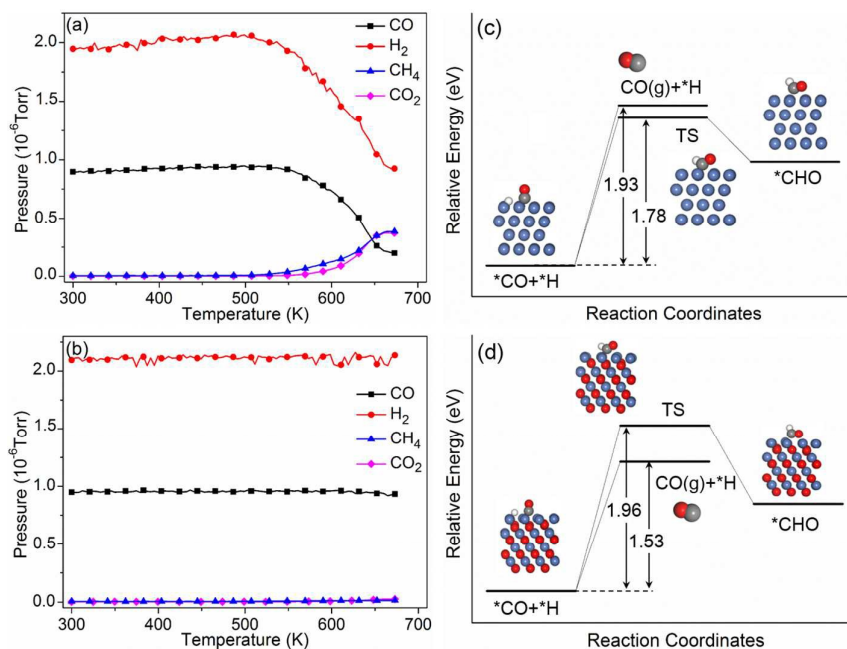


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Table of contents entry

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