**Tuning CO₂ hydrogenation selectivity on Ni/TiO₂ catalysts via sulfur addition**

Carole Le Berre, Andrea Falqui, Alberto Casu, Tekalign T. Debela, Mathias Barreau, Christopher H. Hendon and Philippe Serp

In the context of CO₂ valorization, the possibility of shifting the selectivity of Ni catalysts from CO₂ methanation to reverse water gas shift reaction could be economically attractive provided that the catalyst presents sufficient activity and stability. Remarkably, the addition of sulfur (0.2–0.8% w/w) to nickel on a Ni/TiO₂ catalyst induces a complete shift in the catalyst selectivity for CO₂ hydrogenation at 340 °C from 99.7% CH₄ to 99.7% CO. At an optimal Ni/S atomic ratio of 4.5, the productivity of the catalyst reaches 40.5 mol⁻¹CO mol⁻¹Ni h⁻¹ with a good stability. Density functional theory (DFT) calculations performed on various Ni surfaces reveal that the key descriptor of selectivity is the binding energy of the CO intermediate, which is related to the local electron density of surface Ni sites.

**Introduction**

Efficient CO₂ conversion using green H₂ coming from renewable sources represents a potential way to limit global CO₂ emission. Useful CO₂-derived C₁ building blocks, such as formic acid, carbon monoxide, methanol and methane, can be obtained from the catalytic hydrogenation of CO₂. Among these C₁ building blocks, CO, which can be used as a syngas component to be subsequently transformed into liquid fuels via Fischer–Tropsch synthesis (FTS), and CH₄, which represent a pillar of the power-to-gas technology, are particularly attractive. On supported nickel catalysts, the reaction leads to methane formation (Sabatier reaction). Noble metal-based catalysts are usually preferred for CO production via the reverse water gas shift reaction (RWGS). Considering the low cost of nickel compared to noble metals, shifting the selectivity of Ni catalysts from methanation to RWGS could be economically attractive provided that the catalyst presents sufficient activity and stability.

It was recently reported that supported Ni single atoms could be active for the RWGSR, unravelling structure sensitivity in Ni-catalyzed CO₂ hydrogenation (decreasing CO adsorption strength with decreasing particle size). However, such catalysts present the drawback of being difficult to prepare at high metal loadings and on a large scale for industrial use. Another way to shift the selectivity of Ni towards CO is to modify its valence state such as in perovskites, since the CO binding energy is much weaker on oxidized than on metallic-Ni. At 400 °C, a LaFe₀.₅Ni₀.₅O₃ catalyst allows a STY of 8.7 mol⁻¹CO mol⁻¹Ni h⁻¹ with a selectivity of 96.6%. Modifications in the Ni electronic structure can also be achieved by pretreating conventional Ni supported catalysts. For example, it has been demonstrated that the selectivity of Ni/SiO₂ catalysts was found to change from CH₄ to CO after a CO₂ hydrogenation cycle from 100 to 800 °C, due to the formation of Ni₃C presenting a lower CO adsorption energy than metallic Ni. The formation of alloys or intermetallic compounds is also an efficient way to tune the metal d-band center, which proves to be instructive in assessing the binding energy of σ-donor intermediates, such as CO.
Sulfur has long been identified as a poison for Ni catalysts in CO-methanation, due to the quick and irreversible formation of inactive NiS sites that lead to the loss of catalytic activity due to geometric and electronic surface restructuring, terminally affecting the electronic properties of the Ni sites. For CO−methanation, on conventional supports such as alumina or silica, the presence of traces of sulfur impurities (H2S, SO2) in the feed gas, or the use of a sulfate precursor during catalyst preparation (the methanation being conducted without sulfur impurities), also results in a drastic activity decrease. Thus, a Ni/SiO2 catalyst prepared from Ni sulfate without sulfur impurities, also results in a drastic activity decrease. Thus, a Ni/SiO2 catalyst prepared from Ni sulfate showed negligible activities for CO2 hydrogenation because of the formation of inactive Ni3S2 during catalyst preparation. Interestingly, a higher tolerance of Ni catalysts to sulfur poisoning was evidenced when using a reducible support such as CeO2 due to the thermodynamically favorable formation of the Ce2O2S phase that restricts the formation of nickel sulfide. In addition, infrared studies on the effect of sulfur poisoning on the CO adsorption by Ni catalysts have shown that the strength of CO adsorption to surface nickel atoms was weaker on pre-sulfided catalysts. Strong reduction or even blocking of CO adsorption upon sulfur addition to Ni(111) was also reported. Finally, it is worth mentioning that (Fe, Ni)S clusters of natural enzymes, such as carbon monoxide dehydrogenase, efficiently and reversibly catalyze the reduction of CO2 to CO. Additionally, recent DFT calculations have shown the potentiality of the sulfur-deficient FeS(001) surface for CO2 activation and reduction.

In that latter case, a high sulfur vacancy density is expected to improve the catalytic activity of FeS-containing catalysts for the RWGS. However, to the best of our knowledge, there are no discussions in the literature about controlling the extend of sulfidation (x). Our findings suggest that despite sulfur being a traditional poison for the Sabatier reaction on Ni, the incorporation of sulfidation offers one unique avenue to tune catalyst selectivity.

Results and discussion

Two Ni catalysts supported on the reducible oxide TiO2 were first compared. The first one (10% Ni/TiO2) was prepared by the incipient-wetness impregnation method from nickel nitrate using TiO2-P25 as a support (a mixture of TiO2 rutile (80%) and anatase (20%) phases). The second one (10% Ni−S/TiO2) was prepared similarly but the calcination was performed in the presence of SO2, resulting after reduction in a sulfided catalyst. The catalytic performance using a flow reactor is shown in Fig. 1, and the results obtained after the reaction reached a steady-state at 260 and 340 °C are summarized in Table 1.

It is noticed that at temperatures as low as 260 °C, the 10% Ni/TiO2 catalyst produces selectively CH4 (SCH4 = 98.7%) with a high activity (56.5 molCH4 molNi−1 h−1), while CO is selectively produced on 10% Ni-S/TiO2 (SCO = 98.3%) at a lower rate (6.5 molCO molNi−1 h−1).

As CH4 selectivity can increase at high CO2 conversion, we also run the 10% Ni/TiO2 catalyst at lower conversion (Fig. S1†). Under these conditions (higher F/W ratio), the CO2 conversion at 260 °C (4.3%) is similar to that obtained with Ni-S/TiO2 (7.5%), and the Ni/TiO2 catalyst is still very selective for CH4 (SCCH4 > 94%). The temperature increase (up to 400 °C) significantly affects the CO2 conversion, but not the selectivity (Fig. S2†). This sulfided catalyst shows interesting performances compared to other nickel catalysts active for the RWGS reported in the literature (Table S1†). Indeed, a selectivity of 99.1% and a CO2 conversion rate of 60.6 molCO molNi−1 h−1 were obtained, which are similar to those obtained on a Ni/SiO2 catalyst presenting a nickel carbide-like phase obtained after surface modification upon exposure to CO2/H2 or CH4 atmospheres at high temperature.22 The F/W ratio was further increased to 33,000 mL g−1 h−1 without impact on the selectivity (Fig. S3, Table S1†). As expected, the CO2 conversion decreased with the increase in F/W because of the shorter contact time and the
We independently study by XRD the reaction of the TiOSO₄·xH₂O reference compound under the conditions used for catalyst reduction. The data obtained (Fig. S9†) point to the complete transformation of TiOSO₄·xH₂O into anatase TiO₂ under these reducing conditions.

HRSTEM-HAADF analysis of the 10% Ni–S/TiO₂ catalyst provided better-defined information from a spatial point of view and highlighted the rare presence of small-sized nanoparticles at the edges of wider crystalline domains. While the structures of the latter are compatible with TiO₂, local Fourier analysis performed on these small nanoparticles (<5 nm) showed a sufficiently clear structural projection resulting in finding different sets of interplanar distances and angular relationships that could be ascribed to distinct phases of nickel sulfide, namely NiS, NiS₂ and Ni₃S₄ (Fig. 3).

To understand the structural transformation of the catalyst during the sulfidation, XRD analyses were performed (Fig. S10†). The Ni diffraction peaks of the 10Ni/TiO₂ catalyst (2θ = 44.5°, 51.9°, and 76.3°) correspond to the (111), (200), and (220) crystal faces of Ni. For the 10Ni–S/TiO₂ catalyst, these peaks are much wider and less intense, but still present (2θ = 44.3°, 51.9°, and 76.3°). Given the low occurrence and the small size of many of the crystalline nickel sulfide nanoparticles observed by HRSTEM-HAADF analysis, the presence of a crystalline sulfided phase (NiS, NiS₂ or Ni₃S₄) could not be clearly detected by XRD, but the wide peaks observed could also fit some peaks of Ni sulfide phases. Finally, the presence of amorphous nickel sulfide nanoparticles cannot be ruled out from STEM and XRD analyses.

The Ni crystallite size measured by XRD was 16.5 and 9.2 nm for the 10% Ni/TiO₂ and 10% Ni–S/TiO₂ catalysts, respectively, which is in good accordance with the STEM-HAADF measurements. XPS analyses were performed just after reducing the samples at 400 °C. Fig. S11 presents the high-resolution Ni 2p, S 2p and Ti 2p spectra of the two samples. The Ni 2p spectra are composed of two spin–orbit doublets (2P₃/₂ and 2P₁/₂) and shakeup satellites. For the 10% Ni/TiO₂ catalyst (Fig. 4a), Ni is present as Ni⁰ (main peak at

<table>
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<th>Catalyst</th>
<th>CO₂ conv. (%)</th>
<th>Sᵢ₄H (%)</th>
<th>CH₄ (%)</th>
<th>STY (%)</th>
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<tr>
<td>10Ni/TiO₂</td>
<td>79.1 (99.7)</td>
<td>98.7 (99.7)</td>
<td>1.3 (0.3)</td>
<td>56.5 (72.1)</td>
</tr>
<tr>
<td>10Ni–S/TiO₂</td>
<td>7.5 (29.2)</td>
<td>1.7 (0.3)</td>
<td>98.3 (99.7)</td>
<td>6.3 (25.2)</td>
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* The values between parentheses are the values obtained at 340 °C. ‡ In molCH₄ mol⁻¹ h⁻¹ for 10Ni/TiO₂ and in molCO mol⁻¹ h⁻¹ for 10Ni–S/TiO₂. Reaction conditions: 200 mg catalyst, F/W = 16.500 mL g⁻¹ h⁻¹, H₂/CO₂ = 4, P = 6.1 bar.
852.6 eV)\textsuperscript{,43} NiO (multiplet-split peaks at 853.7 and 855.8 eV)\textsuperscript{,44} and possibly Ni(OH)\textsubscript{2} (855.8 eV)\textsuperscript{,45,46} The presence of a significant amount of Ni\textsuperscript{0} can explain the high selectivity for methane obtained with this catalyst. The Ni 2p\textsubscript{3/2} core-level spectrum of the 10% Ni–S/TiO\textsubscript{2} catalyst is significantly different (Fig. 4b), showing a very small contribution of Ni\textsuperscript{0} (852.6 eV) and an intense peak at 856.3 eV, which could arise from Ni(OH)\textsubscript{2}, NiS (855.7 eV),\textsuperscript{47} Ni\textsubscript{3}S\textsubscript{2} (855.7–856.1 eV)\textsuperscript{,48,49} and/or NiS\textsubscript{2} (855.7–855.9 eV)\textsuperscript{,50,51} The Ni/S surface atomic ratios of the 10% Ni–S/TiO\textsubscript{2} catalyst allow the calculation of an atomic% of S related to Ni of 7.6% (in good accordance with the values obtained from elemental and EDX analyses) that precludes the exclusive formation of NiS. For the S 2p spectrum, the peak at 162.1 eV corresponds to divalent ions (S\textsuperscript{2−}) involved in metal–sulfur bonds,\textsuperscript{52} which could correspond to NiS\textsubscript{2} (161.6 eV), Ni\textsubscript{3}S\textsubscript{2} (162.2 eV) and/or NiS\textsubscript{2} (162.4 eV).\textsuperscript{51,52} The peak at 168.9 eV is associated with sulfate species resulting from surface oxidation of NiS\textsubscript{x} species.\textsuperscript{51,54} The high-resolution Ti 2p\textsubscript{3/2} XPS spectra of the 10% Ni/TiO\textsubscript{2} and 10% Ni–S/TiO\textsubscript{2} catalysts are shown in Fig. 4c. For 10% Ni/TiO\textsubscript{2}, the Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} peaks centered at binding energies of 459.3 and 465.2 eV (Fig. S10\textsuperscript{†}) are typical of the Ti\textsuperscript{4+}–O bonds in TiO\textsubscript{2}. In 10% Ni–S/TiO\textsubscript{2}, the envelop of the Ti 2p\textsubscript{3/2} peak is broader due to the presence of surface oxygen vacancies (O\textsubscript{v}).\textsuperscript{47} The attribution of the 458.3 eV component to titanium(IV) oxysulfate species must be excluded on the basis of XPS measurements over the TiO\textsubscript{SO\textsubscript{4}}•xH\textsubscript{2}O reference compound (Fig. S12\textsuperscript{†}). The formation of O\textsubscript{v} upon sulfidation/reduction was confirmed by Raman analyses (Fig. S13\textsuperscript{†}). The lowest frequency vibrational mode \(\text{E}_\text{g}(1)\) at 140 cm\textsuperscript{−1} characteristic of TiO\textsubscript{2} in 10% Ni/TiO\textsubscript{2} shows pronounced broadening and blue-shift (149 cm\textsuperscript{−1}) in 10% Ni–S/TiO\textsubscript{2}.
Theoretical calculations proposed that the broadening and blue-shift resulted from the presence of localized lattice defects associated with surface Ov. The formation of Ov on TiO$_2$ leads to the creation of unpaired electrons or cationic Ti$^{3+}$ centers observable by EPR.

The EPR spectrum of 10% Ni–S/TiO$_2$ (Fig. S14†) shows a broad EPR resonance line at $g = 2.156$, which could arise from surface exposed Ti$^{3+}$ sites but also from Ni$^{3+}$ species. The presence of a significant amount of Ov on the 10% Ni–S/TiO$_2$ catalyst can be of importance for the CO$_2$ hydrogenation reaction. Indeed, it has been proposed that on Ni/TiO$_2$ catalysts, the presence of Ti$^{3+}$ species, which likely altered the SMSI between Ni and the support, allows the enhancement of CO$_2$ hydrogenation activity. It is also known that Ni$^{3+}$–Ov–Ti$^{3+}$ interfacial sites on Ni/TiO$_2$ catalysts serve as dual-active sites to efficiently catalyse the WGSR.

The TPR profiles of the supported nickel catalysts are shown in Fig. S15†. They indicate a different metal–support interaction in the two catalysts. The reduction temperature maxima (RTM) peaks were located at 510 °C for 10% Ni/TiO$_2$ and 460 °C for 10% Ni–S/TiO$_2$. Similar differences in RTM have been reported for Ni/Al$_2$O$_3$ and NiSO$_4$/Al$_2$O$_3$ catalysts.

Also, the shape of the TPR curve for the 10% Ni–S/TiO$_2$ catalyst is less symmetrical, which indicates a less uniform state of the nickel species in this catalyst. The reduction peak of the 10% Ni–S/TiO$_2$ catalyst begins at 360 °C, which may explain the slight catalyst deactivation observed when the RWGS is carried out at 400 °C (Fig. S2†).

Together, the 10% Ni/TiO$_2$ catalyst presents several features of a good methanation catalyst: relatively large particle size and predominance of Ni(0). The 10% Ni–S/TiO$_2$ catalyst contains significant amounts of Ov on the support, which are active for CO$_2$ activation. This catalyst contains few Ni$^{0}$ for H$_2$ activation (H$_2$ heterolytic dissociation can also occur on sulfided catalysts†), and significant amounts of amorphous and crystalline NiS$_2$ species. As it has been shown that the strength of CO adsorption to surface Ni atoms was weaker for pre-sulfided catalysts, we can propose that this is the origin of the high selectivity for the RWGS catalyst observed for the Ni–S/TiO$_2$ catalyst.

In order to understand the correlation between the binding energy of CO and the product selectivity, we calculated the CO adsorption energies ($E_a$) for Ni(111), Ni$_3$S$_2$(001), NiS(100) and NiS$_2$(111) surfaces using the spin-polarized DFT. We sampled several plausible CO binding modes to various facets of the Ni-S$_2$ systems (Fig. S16 and Table S2†), and show the most stable CO-bound configurations in Fig. 5. We find the binding energies to be $-1.57$, $-1.47$, $-0.73$, and $-1.20$ eV for Ni(111), Ni$_3$S$_2$(001), NiS(100), and NiS$_2$(111) surfaces, respectively. The results indicate that the Ni(111) surface binds CO most strongly. The addition of sulfur leads to weakening of the CO binding. The CO binding energy is inversely proportional to the degree of sulfidation. We can understand this through examination of the Ni d-band center. Since CO is both a σ-donor and π-acceptor, the CO bond energy should be reduced as the metal d-states are occupied, as the d-center is a descriptor for σ-accepting ability. Thus, a downward shift of the d-band center is considered favorable because it correlates with the decrease in adsorption energies of typical catalytic σ-donor and π-acceptor poisons, such as CO, resulting in the turnover of surface active sites.

In our case, the calculated Ni d-band centers are $-0.30$, $-1.14$, $-1.34$, and $-1.37$ eV for Ni(111), Ni$_3$S$_2$(001), NiS(100), and NiS$_2$(111) surfaces, respectively. This trend supports the hypothesis that sulfidation is one route to affecting CO-binding energies, thereby affecting the catalytic preference to form CO over CH$_4$. We also considered possible CO$_2$ binding sites on the Ni$_3$S$_2$ systems (Fig. S17†), but did not include the energetics of these species in this study. Instead, we focus on the CO binding energy as an energetic descriptor for selectivity.
Finally, as the Ni/S atomic ratio could have an influence on both activity and selectivity, we used different pre-sulfided catalysts showing sulfur atomic percentage related to nickel between 4.5 and 15% (based on elemental and ICP analyses) to evaluate its impact. Fig. 6 shows the catalytic performances of these catalysts for the RWGSR performed at 340 °C. In the investigated range, the atomic% of sulfur related to Ni significantly affects the catalyst activity, with an optimum value at 4.5%, but has no influence on selectivity.

Conclusions

In summary, we have demonstrated a facile strategy to tune the selectivity of a Ni/TiO2 catalyst in the CO2 hydrogenation reaction. Calcination of the Ni/TiO2 catalyst under SO2–air mixtures allows after reduction a sulfided Ni–S/TiO2 catalyst to be obtained. The sulfided catalyst contains significant amounts of O, to activate CO2, metallic nickel or sulfided Ni (ref. 67) for H2 activation and significant amounts of amorphous and crystalline NiS species. Compared to the Ni/TiO2 catalyst that produces selectively CH4 in the 260–400 °C temperature range, the Ni–S/TiO2 catalyst is less active but selectively produces CO in the same temperature range, while maintaining a good stability below 340 °C. According to DFT calculations, the key descriptor of selectivity is the CO binding energy to the Ni surface, which is related to the position of the d-band centre of the Ni species. Notably, while sulfur has long been identified as a poison for Ni catalysts in CO-methanation, we have demonstrated that its association with Ni on a reducible support such as TiO2 allows the production of a precious metal-free RWGSR catalyst.

Experimental section

Catalyst preparation

The Ni catalysts were prepared by using an impregnation method. Ni(NO3)2·6H2O (99.9% Strem Chemical) was dissolved in water, where TiO2·P25 (99.5%, Aerosol, Aldrich) was then added. The desired quantity of Ni(NO3)2·6H2O to reach a 10% w/w was used. The mixture was stirred for 4 h. The water was evaporated to obtain the catalyst, which was dried at 120 °C overnight, and calcined at 500 °C for 6 h under air to produce the calcined 10% Ni/TiO2 catalyst. A similar procedure was followed to prepare the 10% Ni–S/TiO2 catalyst, but in that case the calcination was performed in the presence of SO2–air mixtures obtained by mixing SO2 with air, with the SO2 concentration in the gas–air mixture being in the range of 0.2–5 g m−3. The amount of nickel deposited on each support was determined by inductively coupled plasma (ICP) analyses.

A 1% Pt/TiO2 catalyst was also prepared for comparative purposes by using the impregnation method from tetraammineplatinum(II) nitrate.

Catalyst characterization

The structural and textural properties of the catalysts were evaluated using different characterization techniques. The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size distribution of the samples were measured using a Quantachrome Autosorb instrument with N2 automatic injection. This method permits the N2 adsorption/desorption isotherms to be obtained at −196 °C. All the samples were pretreated under vacuum at 90 °C for 1 h to remove adsorbed water, then at 250 °C for 10 h for all other physisorbed species.

For the Temperature-Programmed Reduction (TPR) experiment (Micromeritics AutoChem 2920 Analyzer), the catalyst (100 mg) was introduced in a U-shaped tube and placed in an oven. Firstly, it was heated to 200 °C (10 °C min−1) for 1 h. After the reactor cooled to room temperature, an argon flow (30 mL min−1) swept the sample for 30 minutes. In the second step, the catalyst was reduced under a gaseous mixture of 10% H2/Ar (30 mL min−1) with a heating ramp of 10 °C min−1 to 850 °C. The amount of hydrogen consumed was monitored using a TCD. The peaks of hydrogen consumption were obtained as a function of the temperature.

The distribution, shape and size of the metal particles were obtained using a JEM 1011 transmission electron microscope (TEM). High-resolution analyses were conducted by using a JEM 2100F equipped with a field emission gun (FEG) operating at 200 kV with a point resolution of 2.3 Å and a JEM-ARM200F Cold FEG operating at 200 kV with a point resolution of >1.9 Å.

The crystalline structure of the samples was determined using a D8 Advance Bruker diffractometer (XRD). The surface of a sample to a depth of 1 to 10 nm was observed by X-ray Photoelectron Spectroscopy (XPS) using a Thermo Scientific K-alpha spectrometer equipped with an aluminum monochromatic source (Al Kα, hν = 1486.6 eV). Raman measurements were recorded with a Raman Horiba Jobin Yvon Labram HR 800 spectrometer in backscattering geometry using an optical objective 100 (NA 0.9). The wavelength of the incident laser was 532 nm, and its power was set to 1 mW. EPR data were recorded using an Elexys E 500 Bruker spectrometer, operating at a microwave frequency of ≈9.5 GHz. All spectra were recorded using a microwave power of 10 mW across a sweep width of 1500 G (centred at 3100 G) with a modulation amplitude of 2 G. Experiments were carried out at 10 K using a liquid helium cryostat.

Catalytic tests

The catalytic tests of CO2 hydrogenation were performed using a continuous-flow stainless steel fixed bed reactor (height = 300 mm, e.d. = 9.52 mm, i.d. = 7.9 mm) under a total pressure of 6.1 bar. 200 mg of catalyst with a particle size in the 100–200 μm range were mixed with 1800 mg of SiC (Alfa Aesar). Before the catalytic test, the catalyst was reduced in situ at 400 °C for 4 h under a 1/4 mixture of N2/
H₂, at atmospheric pressure. Then, experiments were performed at a constant F/W ratio (molar flow of reactant per mass of catalyst) of 16.500 mL (g h)⁻¹. Catalytic tests were performed under a N₂/H₂/CO₂ gas mixture of 1/4/1 at 260, 300 and 340 °C and 6.1 bar. The composition of the reactant/product mixture was analyzed using an on-line gas chromatograph (500 Clarius) equipped with two TCDs: one with argon as the gas vector to quantify H₂, CH₄, and CO, and another with helium to quantify CO₂. The GC is equipped with two Shincarbon columns (1/8, 2.0 mm, 80/100), and recorded the formation of methane and conversion of H₂ and CO₂ every 8 min.

The different response coefficients determined from the GC calibration allowed us to calculate the molar fractions (χ) of the different molecules considered during the methanation reaction, as follows:

\[ X_A = \left( \frac{\text{Area of A signal}}{\text{Area of N}_2 \text{ signal}} \times \text{N}_2 \text{ flow} \right) \times \frac{1}{k_A} \]

With \( a = \text{CO}_2, \text{CH}_4, \text{H}_2, \text{CO} \) and \( k = \) response coefficient. The conversion rates of the reagents were then calculated as follows:

\[ \text{CO}_2 \text{ conversion} (\%) = \left( 1 - \frac{X_{\text{CO}_2}}{X_{\text{CO}_2} + X_{\text{CH}_4} + X_{\text{CO}}} \right) \times 100\% \]

\[ \text{H}_2 \text{ conversion} (\%) = \left( 1 - \frac{\text{H}_2 \text{ Output flow}}{\text{H}_2 \text{ Input flow}} \right) \times 100\% \]

With \( \text{H}_2 \) output flow = dry flow output \( x_{\text{H}_2} \).

\[ \text{Dry flow output} = \left( \frac{\text{CO}_2 \text{ input flow}}{X_{\text{CO}_2} + X_{\text{CH}_4} + X_{\text{CO}}} \right) \]

\[ \text{CH}_4 \text{ yield} (\%) = \left( \frac{\text{CH}_4 \text{ output flow}}{\text{CO}_2 \text{ input flow}} \right) \times 100\% \]

\[ \text{CH}_4 \text{ output flow} = \text{dry flow output} \times x_{\text{CH}_4}. \]

\[ \text{CO yield} (\%) = \% \text{CO}_2 \text{ conversion} - \text{CH}_4 \text{ yield} (\%) \]

\[ \text{CH}_4 \text{ selectivity} (\%) = \left( \frac{\text{CH}_4 \text{ yield} (\%)}{\% \text{CO}_2 \text{ conversion}} \right) \times 100\% \]

\[ \text{CO selectivity} (\%) = \left( \frac{\text{CO yield} (\%)}{\% \text{CO}_2 \text{ conversion}} \right) \times 100\% \]

We expressed the percentage of \( \text{CO}_2 \) consumed by unit of time and by mole of metal, which corresponds to the STY.

**Computational details**

First-principles calculations were performed using spin-polarized DFT as implemented in the Vienna ab initio simulation package (VASP), version 5.4.4. The projected augmented plane wave (PAW) approach with a plane-wave kinetic energy cutoff of 500 eV, and the revised Perdew–Burke–Ernzerhof (RPBE) exchange–correlation functional were employed. The Methfessel–Paxton method with broadening of 0.1 eV was used for the slabs, while Gaussian-smearing with 0.01 eV was used for the CO molecule.

Ni(111), Ni₃S₂(001), NiS(100), and NiS₂(111) surfaces were used to model the slab geometry. A vacuum space of 20 Å was used along the c-direction (perpendicular to the slabs) to ensure no significant interaction between adjacent cells occurred. For each surface, several competing binding modes were examined, and the most stable was presented. The others are available in the ESI. Structural optimization was performed until the average force was <0.03 eV Å⁻¹ and the total energy converged within 10⁻⁵ eV per atom. A Monkhorst-Pack K-point sampling of 3 × 3 × 1 was used for the slab geometry, while only the Γ-point was used for the free CO molecule. The adsorption energy is defined as \( E_a = E_{\text{tot}} - E_{\text{pristine}} - E_{\text{mol}}, \) where \( E_{\text{tot}}, E_{\text{pristine}} \), and \( E_{\text{mol}} \) are the calculated energy of the slab with adsorbate, the pristine slab, and the CO molecule in the gas phase, respectively.

The d-band center was computed by aligning the mean d-states from the density of states to the Fermi level, following the method presented elsewhere.

**Author contributions**

Dr. Carole Le Berre: catalyst synthesis and characterization and catalytic experiments, data elaboration and interpretation, writing original draft; Dr. Andrea Falqui and Dr. Alberto Casu: electron microscopy studies, data elaboration and interpretation; Prof. Christopher H. Hendon and Dr. Tekalign Debela: modeling studies, data elaboration and interpretation; Dr. Mathias Barreau: XPS studies; Prof. Philippe Serp: conceptualization and supervision of all the activities. All the authors contributed to the result discussion and review & editing of the manuscript.

**Conflicts of interest**

The authors do not have any conflict of interests to be declared.

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