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On the link between CO surface coverage and selectivity to CH₄ during CO₂ hydrogenation over supported cobalt catalysts

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Abstract :

An operando IR study was carried out to investigate the loss of selectivity to higher hydrocarbons observed over cobalt-based Fischer-Tropsch catalysts when CO is replaced with CO₂. Our data unambiguously show that the structure and oxidation state of the surface of metallic cobalt remains the same whether CO₂ or CO are cofed with H₂. The selectivity to CH₄ appears to increase monotonously with decreasing surface coverage of adsorbed CO. The switch from Fischer-Tropsch synthesis to methanation using CO₂-rich feeds over metallic cobalt can therefore be assigned to surface coverage effects only.

Keywords: cobalt; carbon dioxide; Fisher-Tropsch.

1. Introduction.

The need to curb CO₂ emissions and the prospects of a future greater availability of dihydrogen produced from nuclear and renewable energies have raised interest in carbon capture and utilisation (CCU) ¹. The hydrogenation of CO₂ to methanol ², methane (Sabatier reaction) ³ and higher hydrocarbons (Fischer-Tropsch synthesis, FTS) ^{4,5,6} are all receiving renewed interests.

The production of higher hydrocarbons directly from CO₂ and H₂ is yet more difficult than that from syngas CO and H₂, especially over cobalt-based FTS catalysts that are poorly active for the reverse water gas-shift reaction (RWGS, Eq. 1) and do not readily form CO *in situ*:



Fe-based materials are highly active for RWGS, but are intrinsically less active and selective than cobalt for the synthesis of higher hydrocarbons from syngas ⁷. Thus, there is an interest in understanding better the reactivity of CO-CO₂-H₂ mixtures over cobalt surfaces.

Various groups have reported investigations of FTS using CO-CO₂-H₂ mixtures over cobalt-based materials. High selectivity to CH₄ observed with CO₂-rich feed was hypothesised to arise from a lower surface coverage of CO, which in turn would lead to a higher surface coverage with hydrogen, favouring methane formation ^{4,8}. Others have proposed that CO and CO₂ hydrogenation proceeded through different reaction pathways ⁹.

Metallic cobalt is often considered as the most active phase during CO and CO₂ hydrogenations over Co-based materials ^{7,8,10,11}. However, it was recently shown that cobalt oxides could be the main phases responsible for the formation of hydrocarbons (mostly CH₄) over Co-based catalysts used for CO₂ hydrogenation ¹². The oxidation of a fraction of metallic cobalt could thus potentially be a major cause for the increased selectivity to methane when increasing the CO₂ proportions in CO-CO₂-H₂ mixtures.

Cobalt oxidation by CO₂ is a realistic hypothesis since using CO₂ in place of CO increases the oxygen chemical potential of the feed and the concentration of water, formed through the RWGS (Eq. 1). High partial pressures of water, the main product of the FTS reaction, is known to lead to cobalt oxidation¹³. As a matter of fact, the use of CO₂ in place of CO was shown to lead to the oxidation of a part of iron carbide into iron oxide¹⁴.

The objective of this work was to investigate the surface of metallic cobalt under CO-CO₂-H₂ mixtures by *operando* diffuse reflectance spectroscopy (DRIFTS) and rationalise CO/CO₂ ratio modified the CO surface coverage and that the cobalt metallic surface was not modified, neither by reconstruction nor by oxidation.

2. Experimental

The Co(15wt.)/TiO₂ and Pt(500ppm)-Co(15wt.)/TiO₂ catalysts were in-house catalysts. Cobalt nitrates (Co(NO₃)₂, 6H₂O, Strem Chemical, 99% pure) were impregnated on the titania support (P90 Evonik Industry, 90% anatase and 10% rutile). Two successive impregnations were needed to reach the desired cobalt loading. A fraction of the same batch was further modified by impregnation of tetraamineplatinum(II) nitrates ([Pt(NH₃)₄](NO₃)₂, Alpha Aesar) to obtain 500 ppm loading of Pt. The Co(15wt.)/Siralox (5% silica-95% alumina) and Pt(500ppm)-Co(15wt.)/Siralox catalysts (supplied by IFPEN) were synthesised according to the same protocol as that used for the TiO₂-supported catalysts.

The average particle sizes were estimated from the line broadening of the Co₃O₄ main diffraction peaks ($2\theta = 36.9^\circ$) using Scherrer's equation. The XRD patterns (not shown) were recorded using the radiation Cu(K α) ($\lambda = 1.5406 \text{ \AA}$) on a Bruker D5005 diffractometer for the titania-supported catalysts and on PANalytical X'PERT Pro® for the Siralox-supported catalyst.

Operando DRIFTS experiments were performed using a modified high temperature DRIFT cell from Spectra-Tech fitted with KBr windows placed in a Collector II assembly described elsewhere ¹⁵. The spectrophotometer used was a Nicolet 8700 (ThermoFischer Scientific) fitted with a liquid-N₂ cooled MCT detector. The DRIFT spectra were recorded at a resolution of 4 cm⁻¹ and 16 scans were averaged. The DRIFTS spectra are reported as log (1/R), where R is the sample reflectance. This pseudo-absorbance gives a better linear representation of the band intensity against surface coverage than that given by the Kubelka-Munk function for strongly absorbing media such as those based on metals supported on oxides ¹⁶. The contribution of gas-phase CO was subtracted using a CO(g) spectrum collected under the same experimental conditions over powdered KBr.

The reaction products were measured using a 2-m path length IR transmission gas cell fitted in a Nicolet IS10 spectrophotometer from ThermoFischer Scientific. Methane, CO₂, CO and water concentrations were determined through calibration curves. All hydrocarbons other than methane were quantified altogether by integrating the IR signal between 3250-2800 cm⁻¹ after removing methane contribution, which was mostly related to methylene -CH₂- stretching vibrations. An average molar absorption coefficient equal to half that of CH₄ (which contains four C-H bonds) was used. This approximate method was sufficient to estimate trends for the selectivity to methane.

High purity gases He (99.999%), H₂ (99.999%), CO₂ (99.995%) and 5% CO/He (99.9%) from Air Liquide or Messer were used without further purification. The samples were pre-reduced *in situ* at 350 °C for 1 h, which led to the reduction of essentially all cobalt oxide phases, as indicated by other experiments realised with different reduction temperatures and contact times (not shown).

Operando DRIFTS data were then collected at 250 °C under the CO₂-H₂ mixture until steady-state was reached. Various CO-CO₂-H₂ mixtures were then used. Carbonyl desorption/reaction was also monitored after CO was removed from the feed

following steady-state under the CO-H₂ mixture, to determine carbonyl band shift as a function of coverage. The CO surface coverage obtained under the CO-H₂ mixture was used as reference to normalise that obtained under different feeds. CO DRIFTS signals are proportional to CO surface coverages in the range of low pseudo-absorbance values observed here, as in the case of transmission IR data¹⁷. The sequence was then repeated at 210 and 180 °C. The different feed compositions used are listed in Table 1. The CO_x conversions were always lower than 5 %, ensuring differential conditions.

Table 1. Gas flow rates (in mL min⁻¹) used during this study

	CO ₂	5% CO/He	H ₂	He	H ₂ /CO	H ₂ /CO ₂
CO ₂ - H ₂	15	0	45	15	-	3
CO - CO ₂ - H ₂	15	5 - 20	45	15	180-45	3
CO - H ₂	0	20	45	15	45	-

2. Results and discussion

The metal loadings measured by ICP are given were similar to the expected nominal values (Table 2).

Table 2. Metal loadings measured by ICP

	Co (wt.%)	Pt (wt. ppm)	Co particle size ^a
Co/Siralox	14. 8 ± 0.2	-	12 ± 3 nm
Pt-Co/Siralox	14. 5 ± 0.2	455 ± 20	18 ± 3 nm
Co/Titania	13. 8 ± 0.2	-	15 ± 3 nm
Pt-Co/Titania	14. 0 ± 0.2	560 ± 20	15 ± 3 nm

^a determined by XRD analysis

The *operando* DRIFTS data are only discussed for the data at 210 °C, since similar results were obtained at 250 and 180 °C (not shown). The lowest selectivity to

selectivity to CH₄ when relative surface coverage of CO only decreased by about 5%. The variation of selectivity to CH₄ with respect to relative CO surface coverage was more gradual in the case of the Co/TiO₂: methane selectivity to CH₄ was higher than 90 % only if the CO relative coverage had decreased by more than half.

These data show that a monotonous relationship existed between the relative CO surface coverage and the selectivity to CH₄ over all four catalysts. It is likely that the decrease of CO coverage led to a similar increase of hydrogen coverage, as suggested by other authors^{4,8}. The nature of the support appeared to lead to a different curve (Figure 1), possibly due to electronic effects.

For each catalyst and at each temperature the decomposition of the carbonyl band obtained under the CO-H₂ mixture was monitored following the removal of CO from the feed. This was done to determine the extent of the carbonyl band shift versus coverage for the metallic surface.

The carbonyl surface species over cobalt are typically converted into CH₄ rather than desorbed as CO, as signal decay is much faster under H₂ than it is under He¹¹. The evolution of the carbonyl DRIFTS band is shown for the Pt-free Co/Siralox in Figure 2, similar profiles being observed for the other samples (not shown).

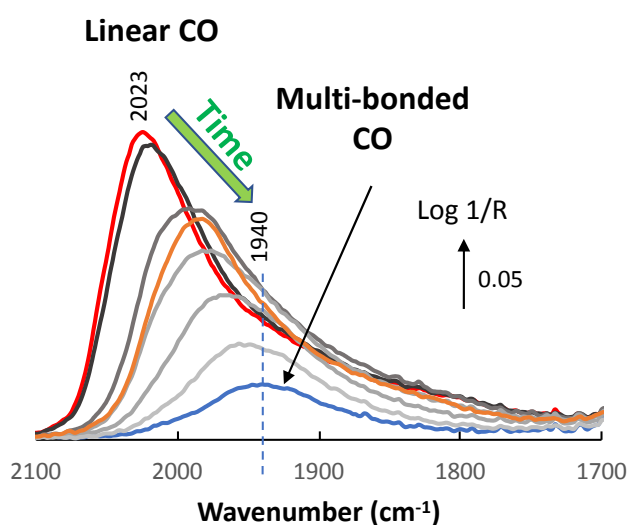


Figure 2: Evolution of the carbonyl DRIFTS band under H₂ at 210 °C following the removal of CO after steady-state under the CO-H₂ feed. The red spectrum was collected under CO+H₂ just before removing CO

The main band was located at 2023 cm⁻¹ in the presence of CO+H₂ and corresponded to linearly bound (on-top) CO (Figure 2, red spectrum). The band intensity decreased and shifted towards lower wavenumbers following CO removal. It was shown earlier that the carbonyl signal could be decomposed into two groups of bands: linear CO (bands between 2020 and 1980 cm⁻¹ related to terrace sites) and multi-bonded CO (bands below 1950 cm⁻¹ related to isolated sites, e.g. B5-type sites). The linear CO were shown to be spectator species, whereas multi-bonded CO were reaction intermediates leading to hydrocarbon formation¹¹. The interconversion of the linear and multi-bonded CO species through surface diffusion was proposed to be fast.

The observed band evolution reported in Figure 2 can be explained as follows. The carbonyls at ca. 1940 cm⁻¹ corresponded to multi-bonded species and were readily converted into hydrocarbons, mostly methane in the absence of gas-phase CO. These sites were then readily replenished by linear carbonyl surface-diffusing from the terrace sites. Globally, this resulted in a decay and shift (because of decreased dipole-dipole interaction on the terraces) of the linear CO signal and a slower decay and absence of shift of the signal of multi-bonded CO, which are isolated from each other and not lead to dipole-dipole coupling interactions¹¹.

The plots of the main carbonyl DRIFTS band position versus the total band area are given in Figure 3 for the Pt-free samples. The data points represented by coloured crosses were measured under various CO-CO₂-H₂ mixtures, while the blue thick line is associated with the data collected following CO removal described in Figure 2. All

the data points collected under the various feeds fell exactly of the CO removal line, which was related to the metallic cobalt surface obtained under the CO+H₂ mixture.

These data indicate that feed composition only affected the relative CO surface coverage and that the metal surface structures and oxidation states were identical whatever the CO-CO₂-H₂ mixture used.

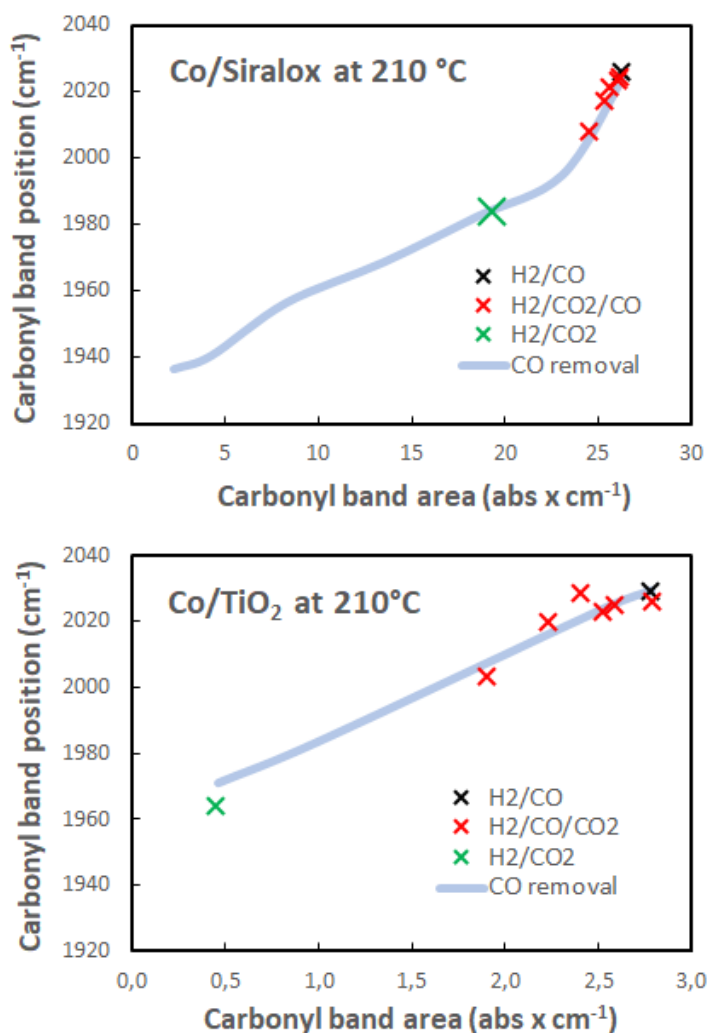


Figure 3: Positions of the main carbonyl DRIFTS band versus the band total area measured at 210 °C over (Top) Co/Siralox and (Bottom) Co/TiO₂ under various CO and CO₂-containing feed. The blue thick lines are the data corresponding the band decomposition following CO removal as shown in Figure 2.

It should be stressed that the plots giving carbonyl band position versus band areas are highly sensitive to the structure of the surface. A chlorine-modification induced by the presence of 50 ppm of trichloroethylene over a similar cobalt catalyst led to a plot shift of more than 60 cm^{-1} ¹⁸. In the present case, all data points are located on the same CO removal line pertaining to metallic cobalt within 5 cm^{-1} , which is the estimated precision of the measure.

While our data show that the state of the surface of metallic cobalt is not modified by varying feed composition in terms of CO/CO₂ proportions, we need to stress that some CoOx phases may still have been present under reaction conditions. Those were shown to lead mostly to methane formation¹². These authors proposed that two reaction pathways occurred, one through CO(ads) on metallic cobalt and one through carbonate/formate on CoOx. Formates were in fact also observed on our catalysts and their reactivity will be discussed in a subsequent paper.

Our data unambiguously show that the structure and state of the surface of metallic cobalt remains the same whether CO₂ or CO are cofed with H₂. The selectivity to CH₄ appears to increase monotonously with decreasing surface coverage of CO. The switch from Fischer-Tropsch synthesis to methanation using CO₂-rich feeds over metallic cobalt can therefore be assigned solely to surface coverage effects (Figure 4). Our results clearly indicate that high CO coverage is a key requirement to obtain high selectivity for FTS synthesis in the presence of CO₂, which acts as a diluent.

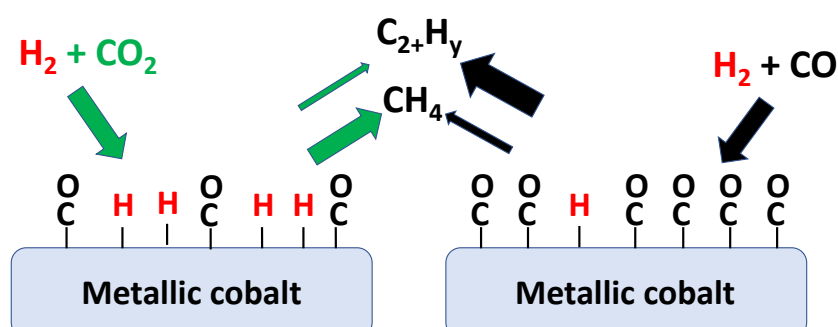


Figure 4: Schematic representation of the state of the surface under reaction conditions. The CO surface coverage under CO-H₂ is very high, limiting methanation. In contrast, CO surface coverage is much lower under CO₂-H₂, leading to increased selectivity to methane. The structure of the surface remains intact for all CO-CO₂-H₂ mixtures.

Notes and references

There are no conflicts to declare. PB collected and analysed all the data. FCM validated and supervised data analysis. YS and DF acquired funds and conceptualized the project. FCM drafted the manuscript that was reviewed and edited by all authors.

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