Ircelyon
INSTITUT DE RECHERCHES SUR LA CATALYSE ET L'ENVIRONNEMENT

Quantitative *operando* IR studies involving CO: examples of catalytic hydrogenation and oxidation

frederic.meunier.2@cnrs.fr

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Content

1. *Operando* studies for Heterogeneous Catalysis:
    Why?
    Sites?
    Surface intermediates? (quantitative analyses)

2. Difficulties when using DRIFTS with CO

3. Examples of quantitative DRIFTS analyses
    Formates & the water-gas shift reaction
    Formates & methanol formation
    Carbonyls & hydrocarbon synthesis
    Carbonyls & CO oxidation

1. *Operando* studies for Heterogeneous Catalysis: why?

In many cases catalyst structure/composition evolves under reaction conditions !

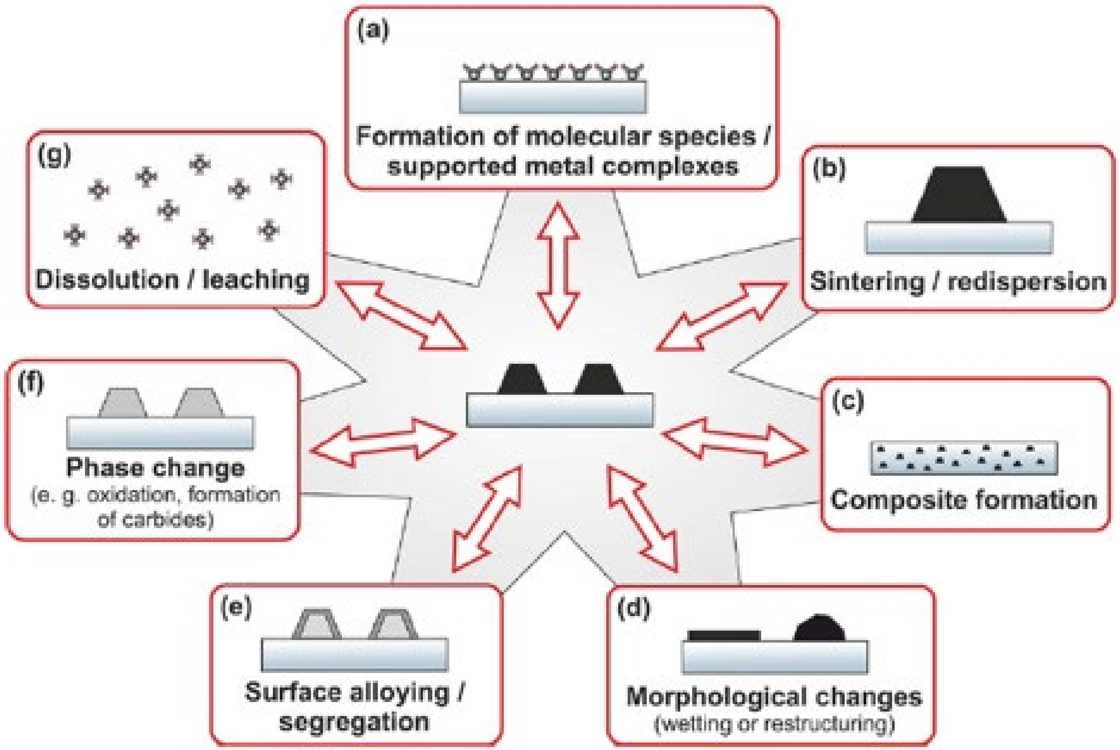
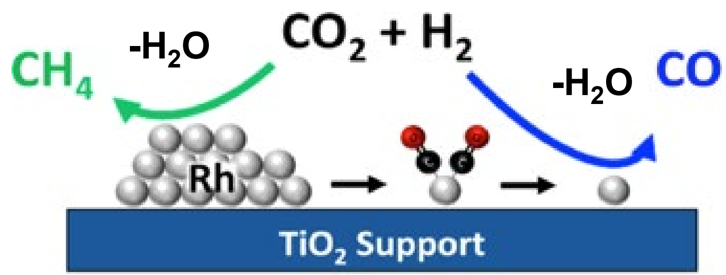


Figure 4. Examples for structural changes of supported metal nanoparticles resulting from changes of the environmental conditions (e.g. temperature, composition of the surrounding medium etc.).

Grunwaldt et al. ChemCatChem 9 (2017) 17-29

1. *Operando* studies for Heterogeneous Catalysis: sites?

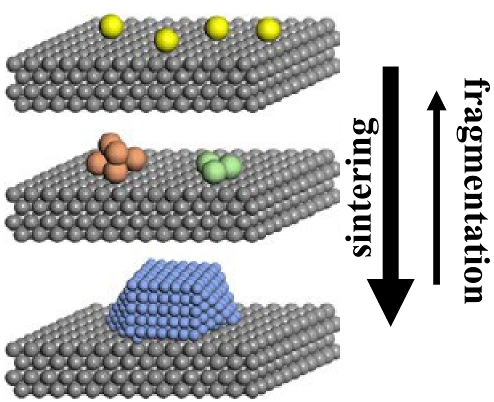
Site?
Selectivity?



Christopher et al., JACS 2015, 137, 3076

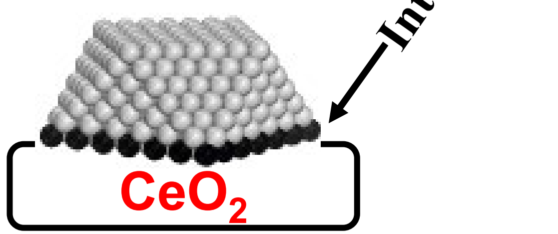
DRIFTS
gives indirect
quantitative
structural information

Activity?



Corma et al., ACS Catal. 2019, 9, 10626

CO oxidation on
Ni, Pt, Pd/CeO_2



Fornasiero, Murray et al., Science 2013, 341, 771

Low-T CO oxidation
on Pt/CeO_2

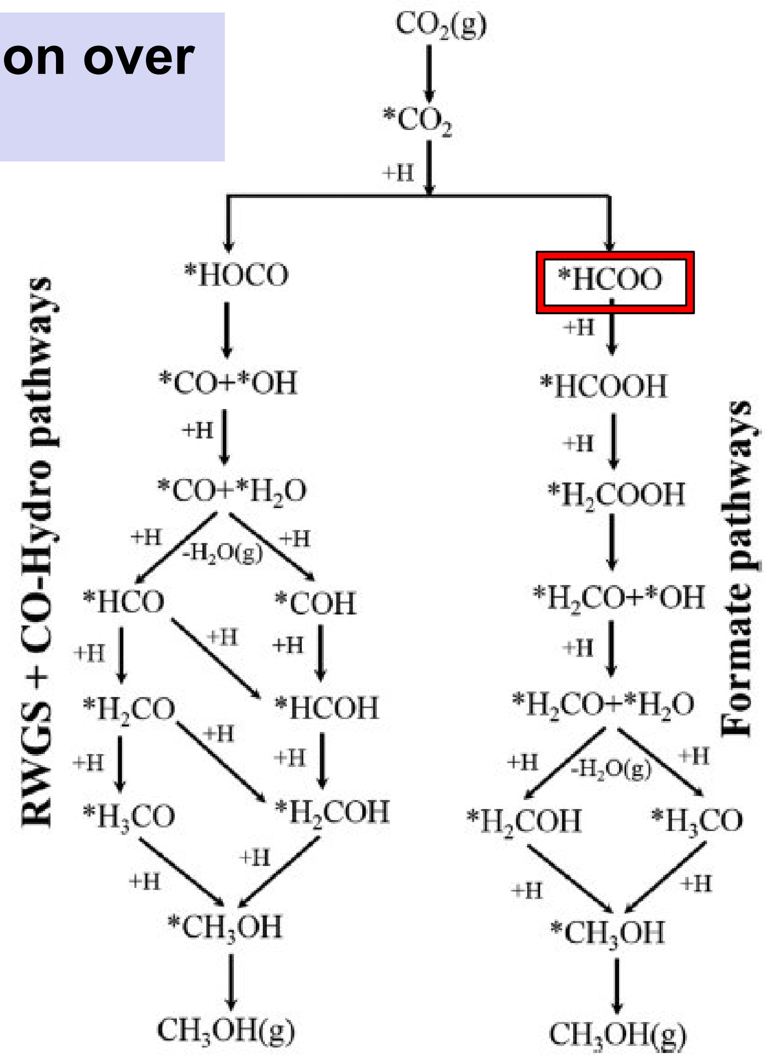
TOF Pt_{NP}
$\vee$
10^4 x TOF Pt_1

Meunier, JPCC, 2021, 25, 21810

Site nature is crucial !

1. *Operando* studies for Heterogeneous Catalysis: surface intermediates?

CO_2 hydrogenation over Cu/ZrO_2



Formate: spectator

Liu et al. , JACS 2016, 138, 12440

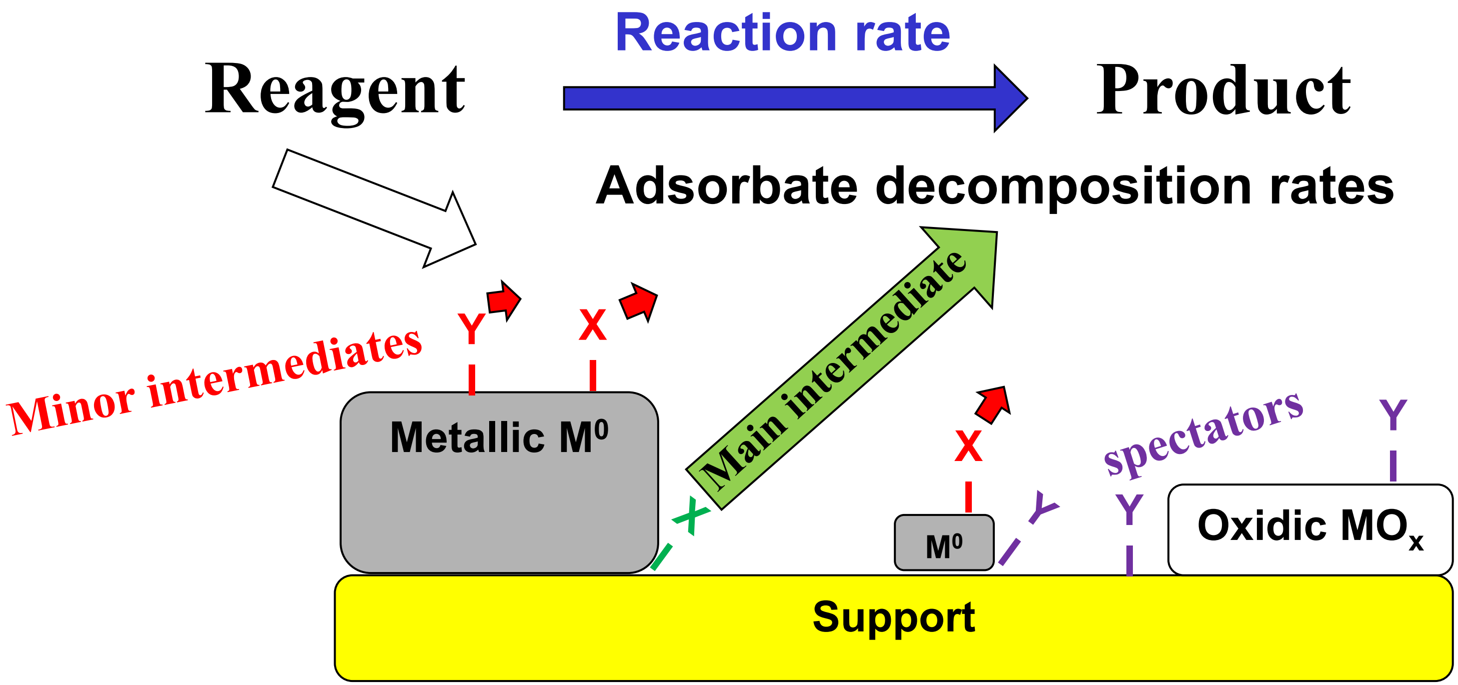
Formate: reaction intermediate

Coperet et al., ACIE 2017, 56, 2318

Formate or not formate? that is the question…

Surface intermediates?

☞ Quantitatively relate surface species & product



Reaction rate >> Adsorbate decomposition rate: minor intermediate and spectators

Reaction rate ≈ Adsorbate decomposition rate : intermediate

Needed : concentrations + rate constants k + selectivity

Water-gas shift ($CO + H_2O \rightarrow CO_2 + H_2$) on MgO

K. Tamaru et al., Trans. Farad. Soc. 1970, 66 (567): 756

- Transmission IR
- Formate pre-adsorbed, concentration determined from a calibration curve
- k = decomposition rate constant at 280 °C
- Selectivity to COx from GC analysis

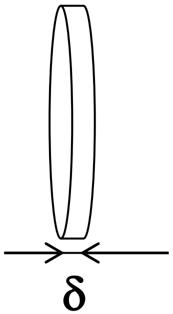
Quantitative comparison

WGS rate	Rate formate to $CO_2 + H_2$ = k . [formate] . sel.	θ
0.011 $cm^3/g\ h$	0.017 $cm^3/g\ h$	0.06
0.023	0.025	0.07
0.031	0.037	0.08

Formates: main reaction intermediates over MgO

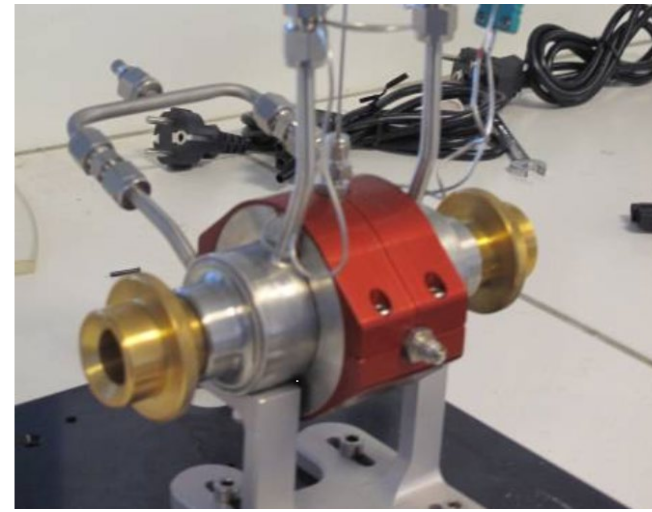
Monitoring adsorbates: Transmission IR vs. DRIFTS

Transmission IR:



More easily quantitative (δ)
Press a self-supported wafer
Pressed wafer: potential structural modification & transport limitation

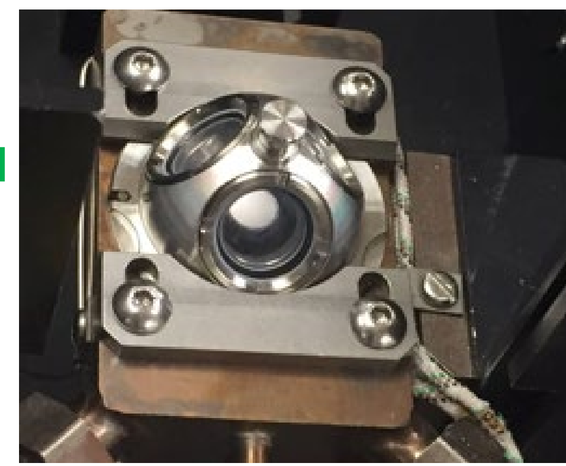
Rasmussen et al., ACS Catal. 2013, 3, 1, 86

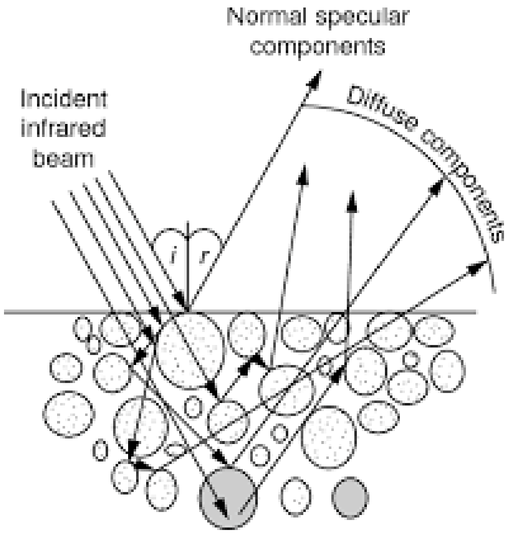


Diffuse Reflectance FTIR (DRIFTS):

Use powder or fine/gross particles
Large gas-phase signal, but can be corrected
Less easily quantitative, but possible…

Meunier et al., React. Chem. Eng. 2016, 1, 134

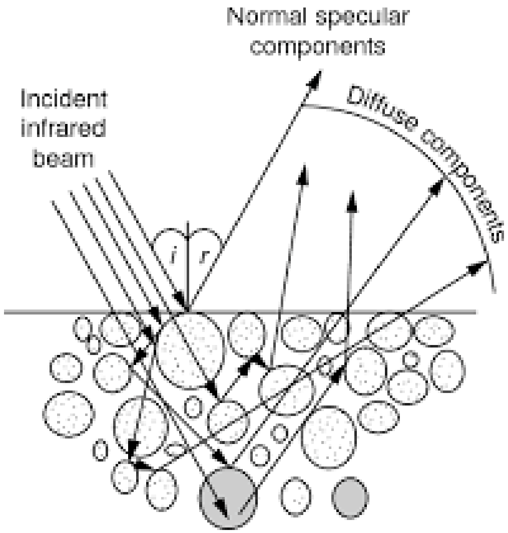




Quantitative DRIFTS

Optical path length not directly accessible

Quantitative DRIFTS



Optical path length not directly accessible

Internal standard $CaCO_3$, $BaSO_4$ (a few wt.%)

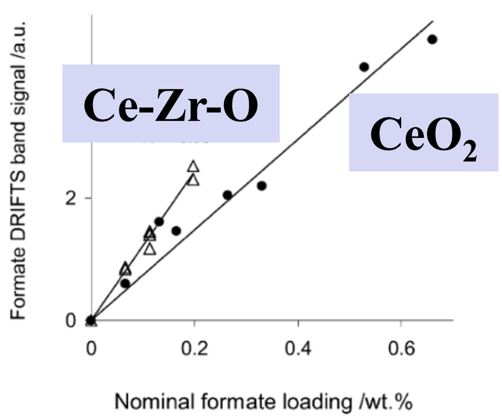
Pratsinis et al., Appl. Catal. B 2018, 226, 127

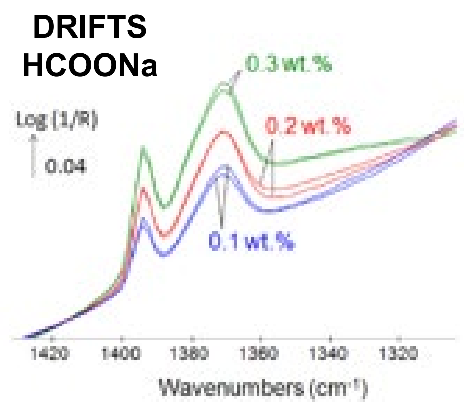
Sample structural bands (e.g. SiO_2, zeolite overtones)

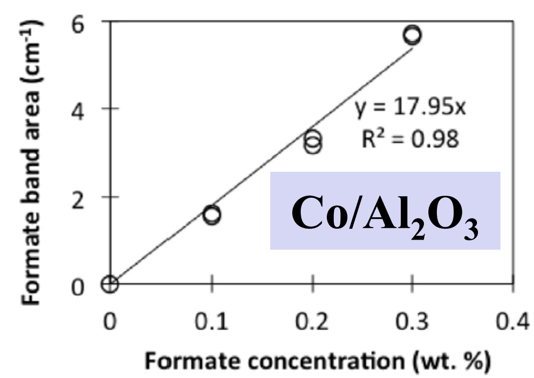
Meunier et al., MicMesMat 2016, 228, 147

D'Agostino et al., PCCP 2018, 20, 4250

Calibration curves







Meunier et al., J. Catal. 2007, 252, 18

Meunier et al., Catal. Today 2015, 259, 192

Use pseudo-Abs (= log 1/R) and not Kubelka-Munk units

Meunier et al., Anal. Chem. 2007, 79, 3912

Need transient conditions to measure reactivity "k" examples for formates seen by IR:

Methanol synthesis Cu/SiO_2 : SSITKA (^{12}C-^{13}C) and Transmission IR

Mims et al., Top. Catal. Ed. 2009, 52, 1440

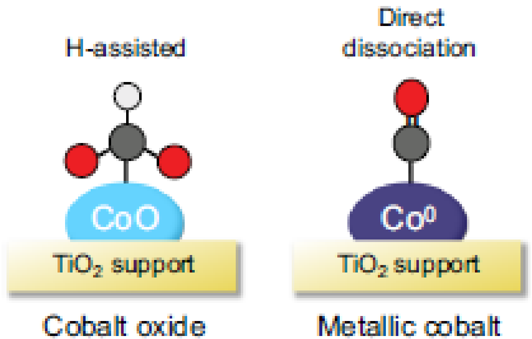
WGS – RWGS : SSITKA (^{12}C-^{13}C) and DRIFTS

Meunier et al., J. Catal. 252 (2007) 18
Efstathiou et al., Catal Today 138 (2008) 228

CO hydrogenation : Chemical transient (stop CO) and DRIFTS

Meunier et al., ACIE 2018, 57, 547

CO_2 methanation /Co^0 and CoOx : Modulation Excitation and DRIFTS



Ferri, Meirer, Weckhuysen, Nat. Comm. 2022, 13:324

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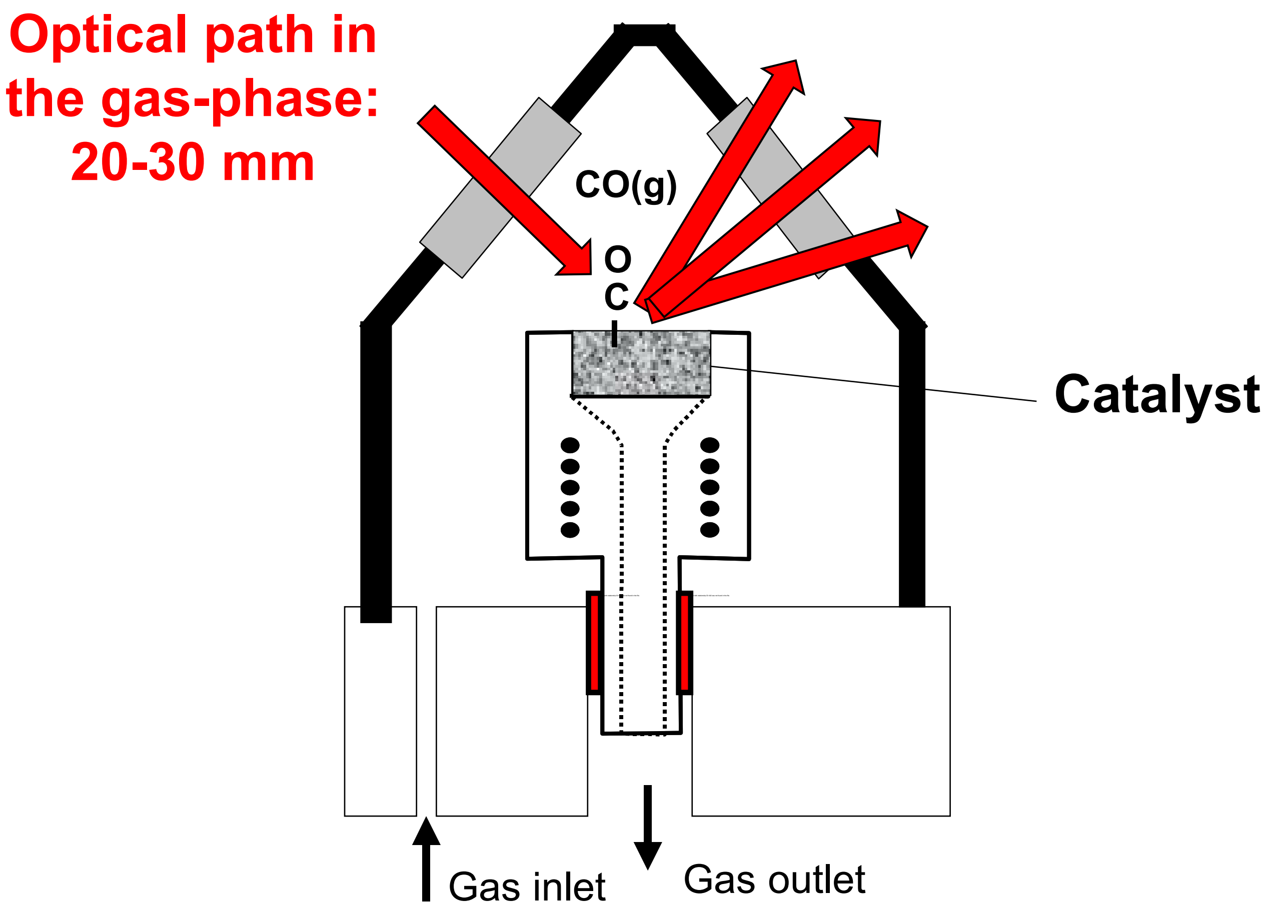
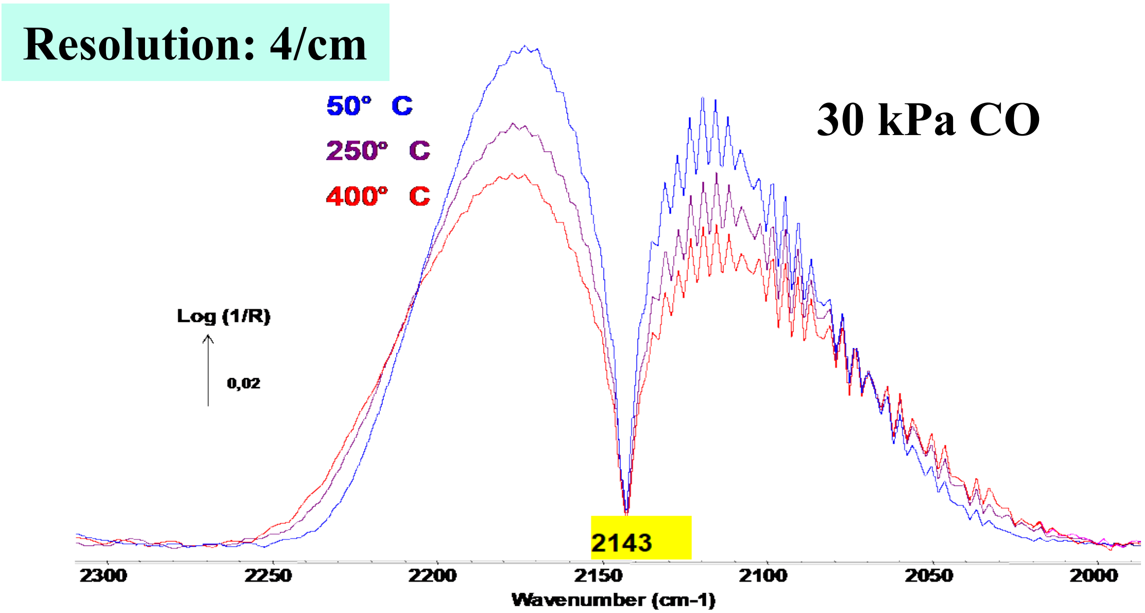
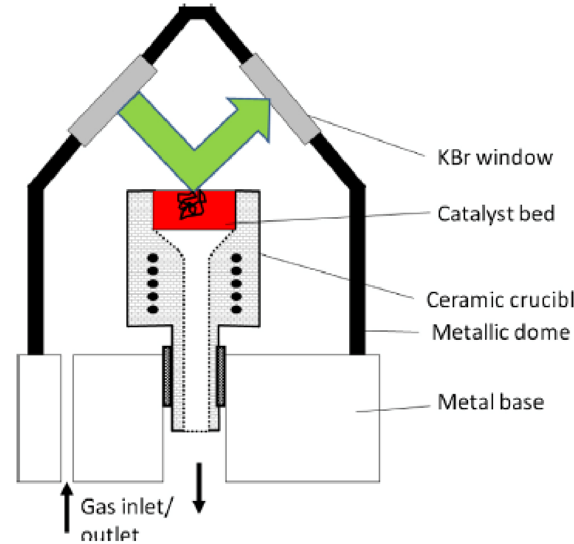
DRIFTS cell: large dead-volume

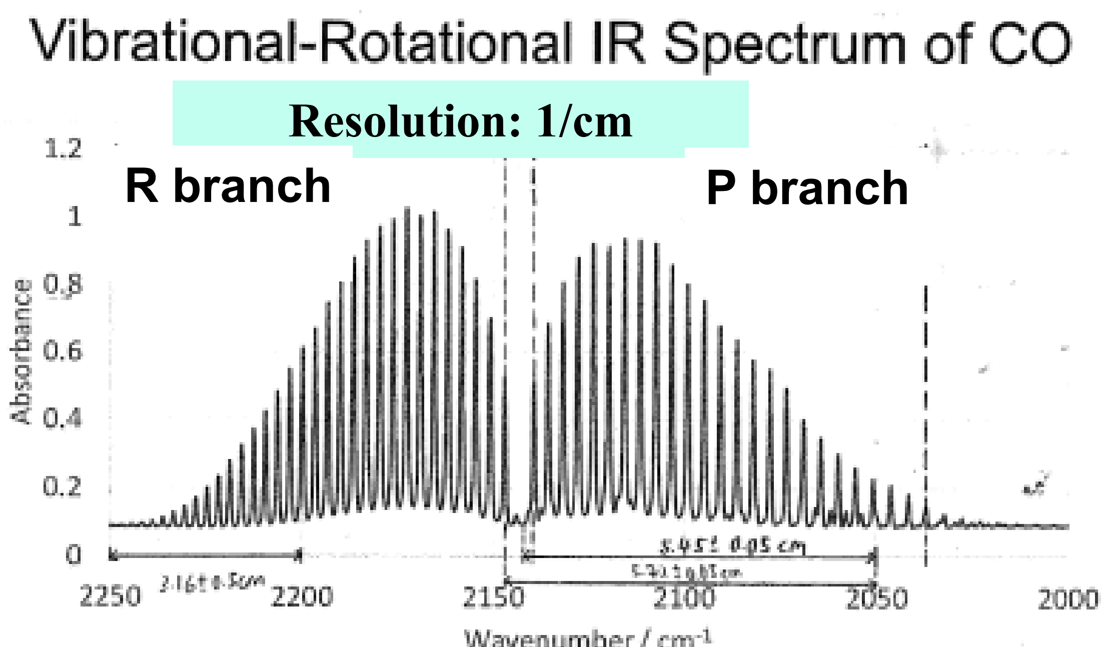


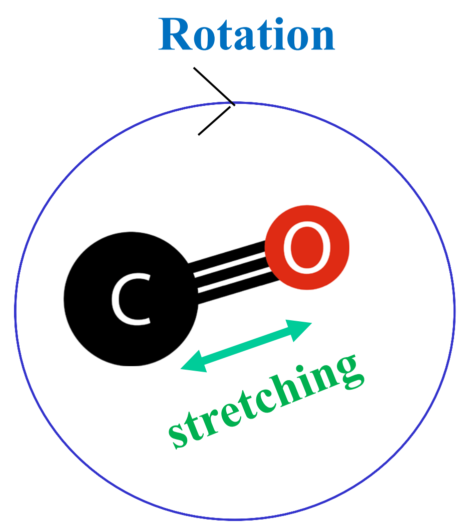
Signal from gas-phase molecules can be significant

« DRIFTS » gas-phase spectrum of CO /KBr

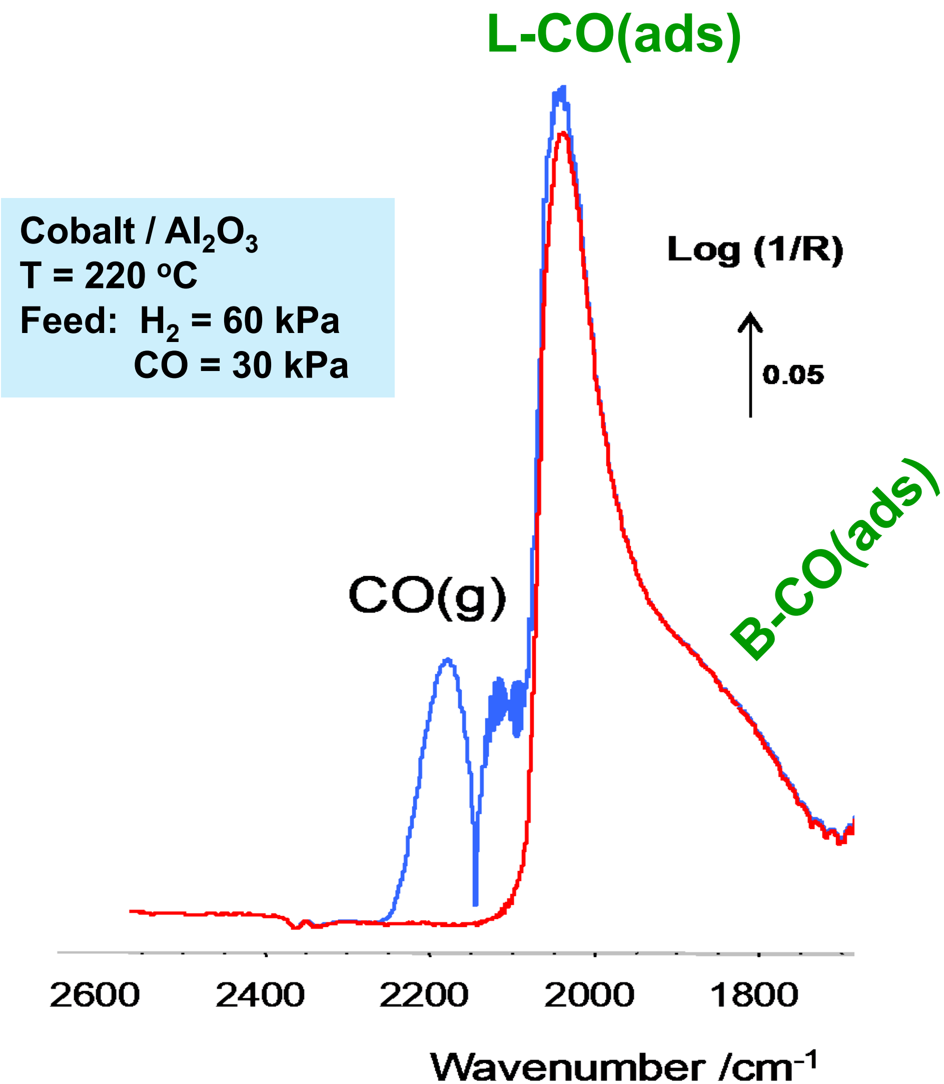








DRIFTS: gas phase-signal correction

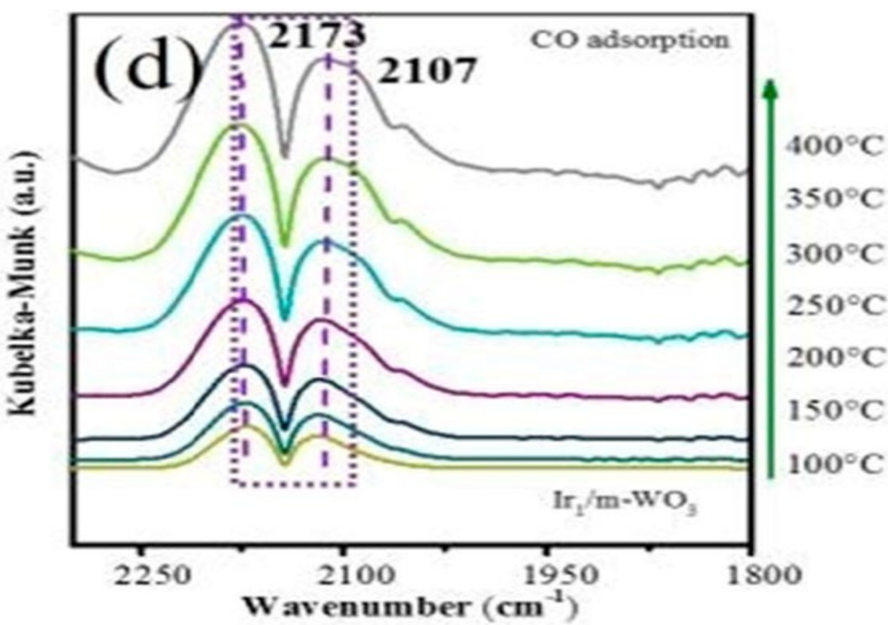


Red spectrum = Original (blue) spectrum minus CO(g) collected **under indentical conditions** over KBr

DRIFTS: gas phase-signal misinterpretation

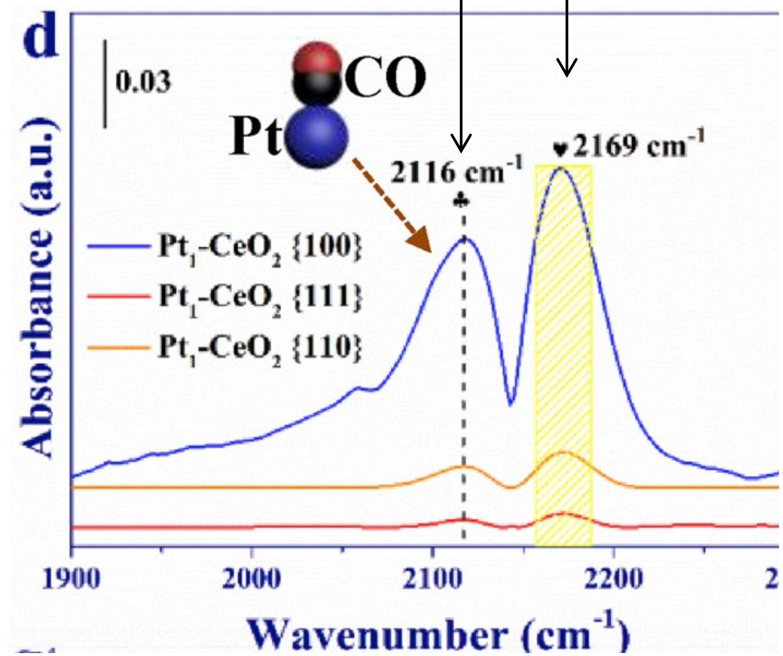
$Ir^{\delta+}$-CO

Ir^{0}-CO



Pt_1-CO

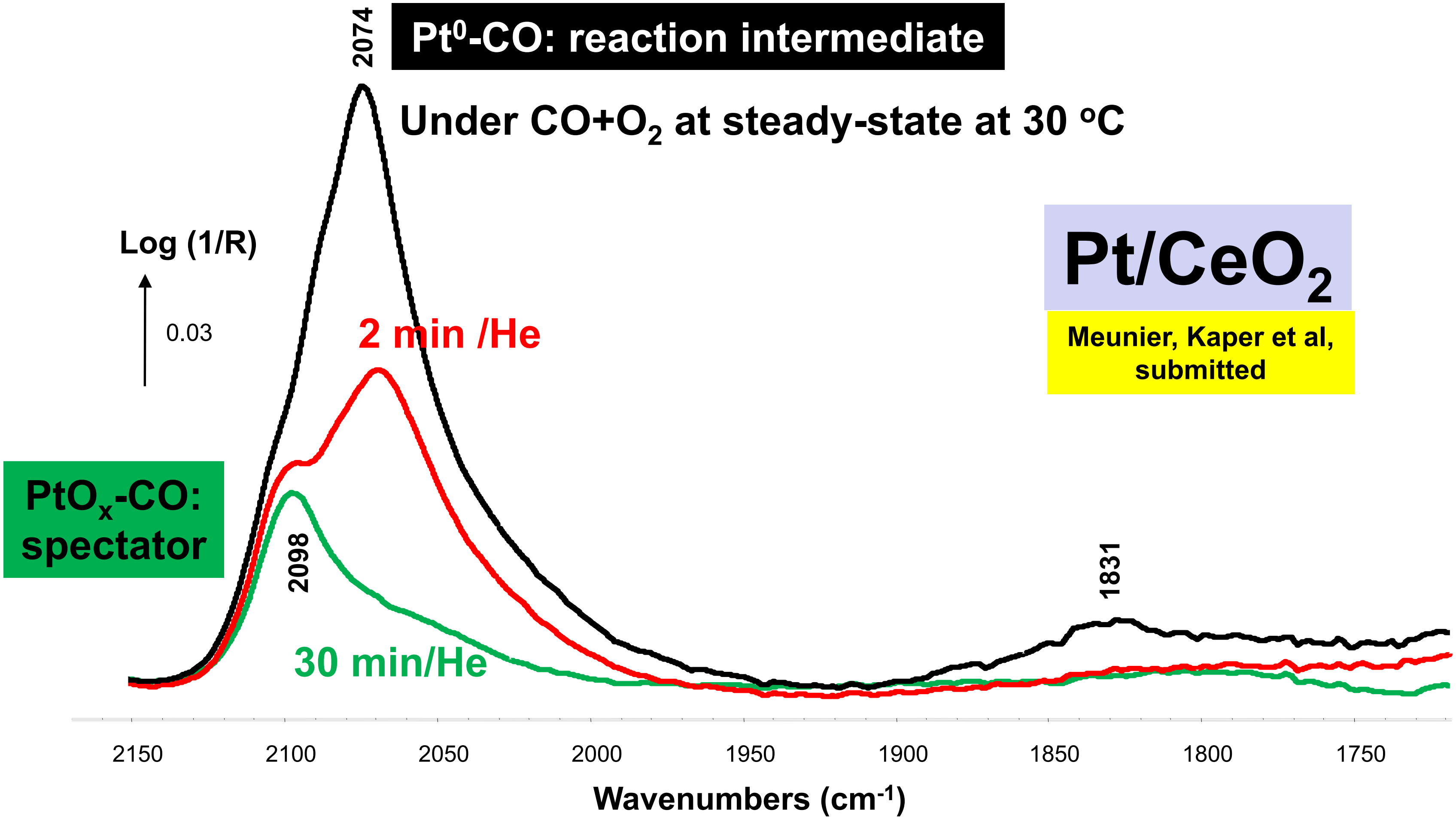
CO(g)



Meunier, JPCC, 2021, 25, 21810

Solution: remove CO(g) from the cell ?

DRIFTS gas-phase signal: removing CO not an ideal solution



Pt/CeO_2

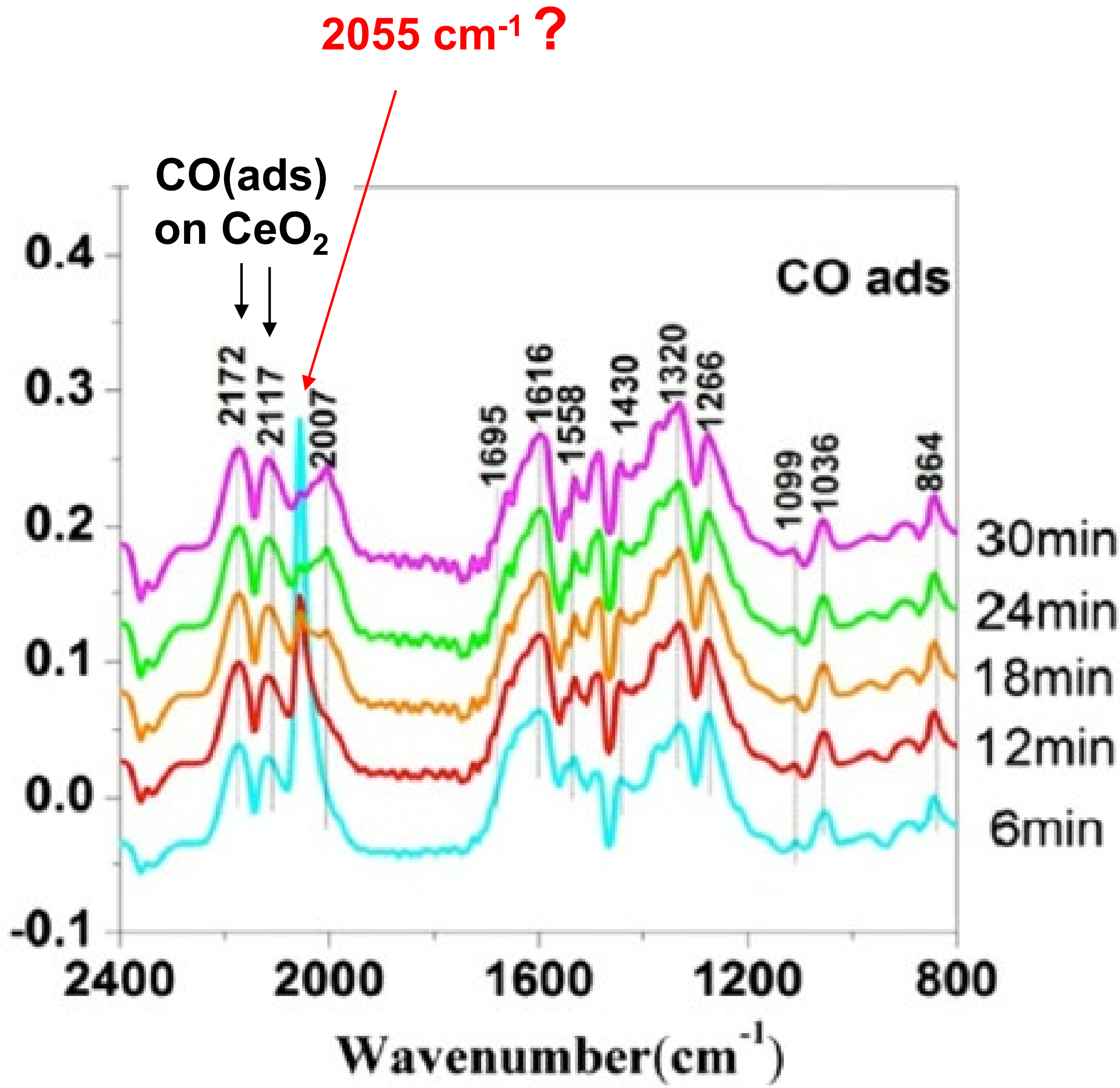
Meunier, Kaper et al, submitted

Pt^0-CO reacts with O from ceria at RT

Safonova et al., ACIE 2015, 54, 8728

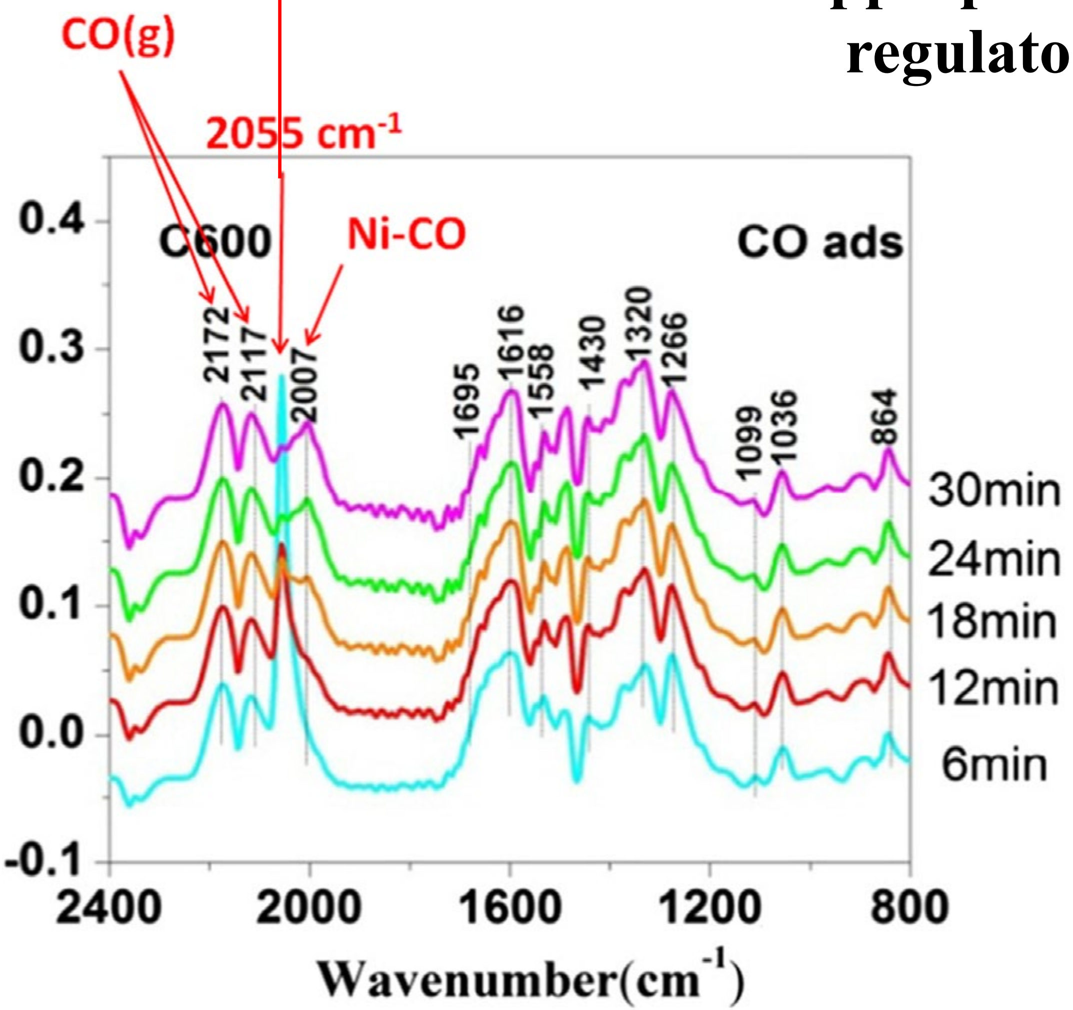
DRIFTS: more gas phase signal misinterpretation and ?

CeO_2



? = $Ni(CO)_4$

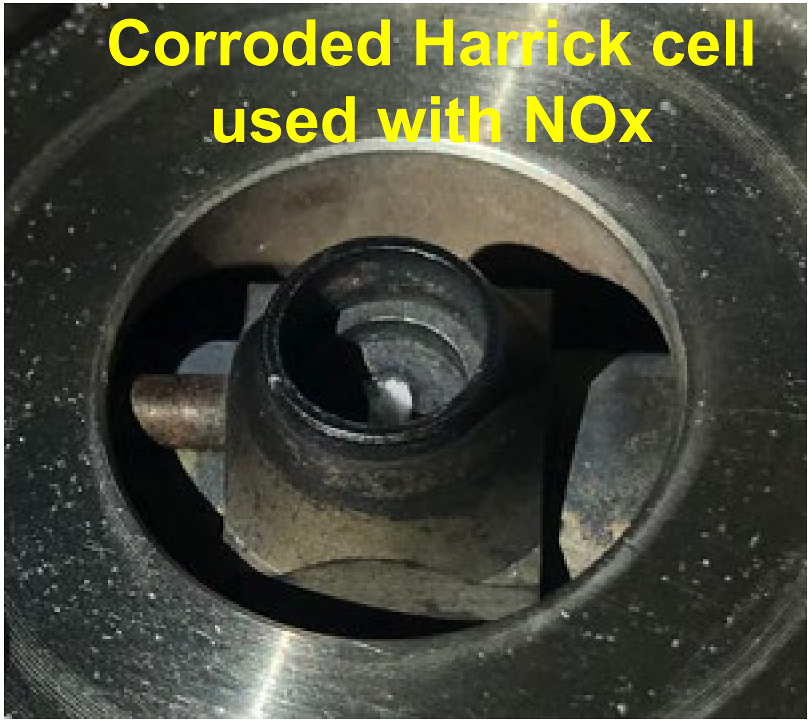
Inappropriate alloy for cylinder, regulator, lines, IR cell ?

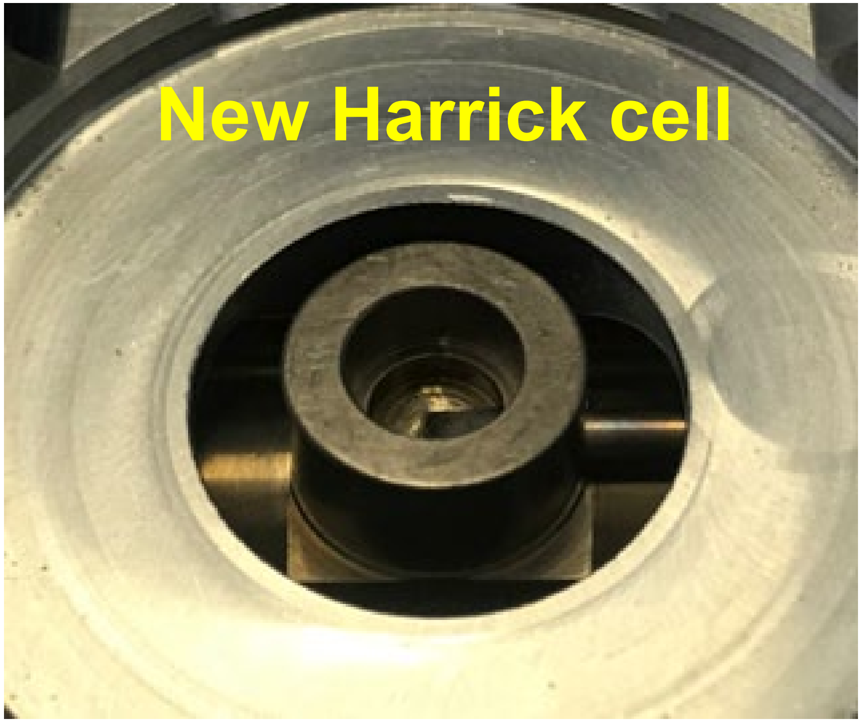


Not looking at CeO_2, but actually at Ni/CeO_2 !

J. Catal. 372 (2019) 388

Corroded DRIFTS cell: *in situ* formation of $Ni(CO)_4$





5 ppm of $Ni(CO)_4$ formed *in situ* only if the cell had been:
- **reduced above 300 °C**
- **and then used with CO at low T**
- **in the absence of O_2**

Retractation note: Meunier et al. Topic Catal. 2021, 64, 1054

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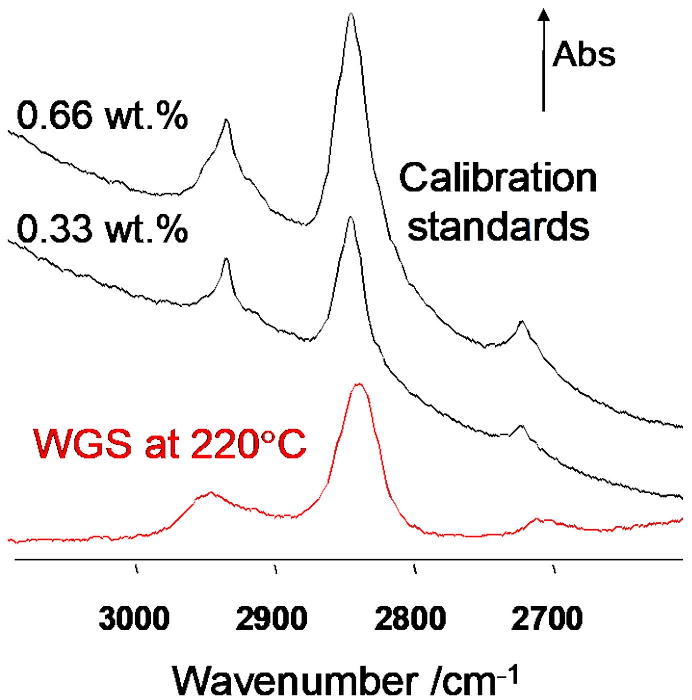
Pt/CeO_2 WGS: Formate DRIFT signal calibration

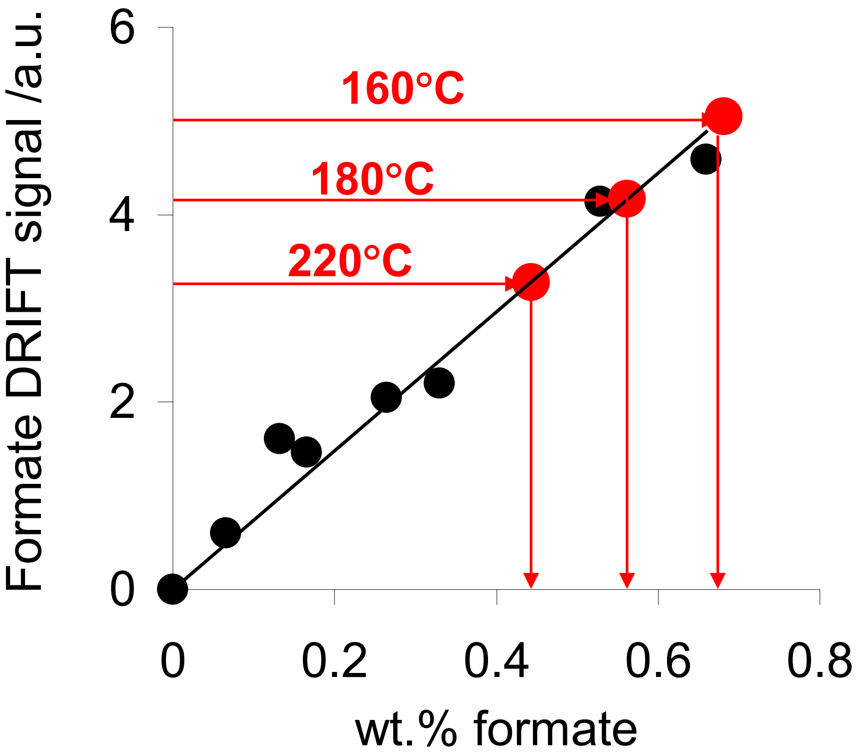
$CO + H_2O \rightarrow CO_2 + H_2$

J. Catal. 252 (2007) 18

Anal. Chem. 79 (2007) 3918

Na-formate deposition (by IWI) over the CeO_2 support. Spectra recorded at 100°C under Ar

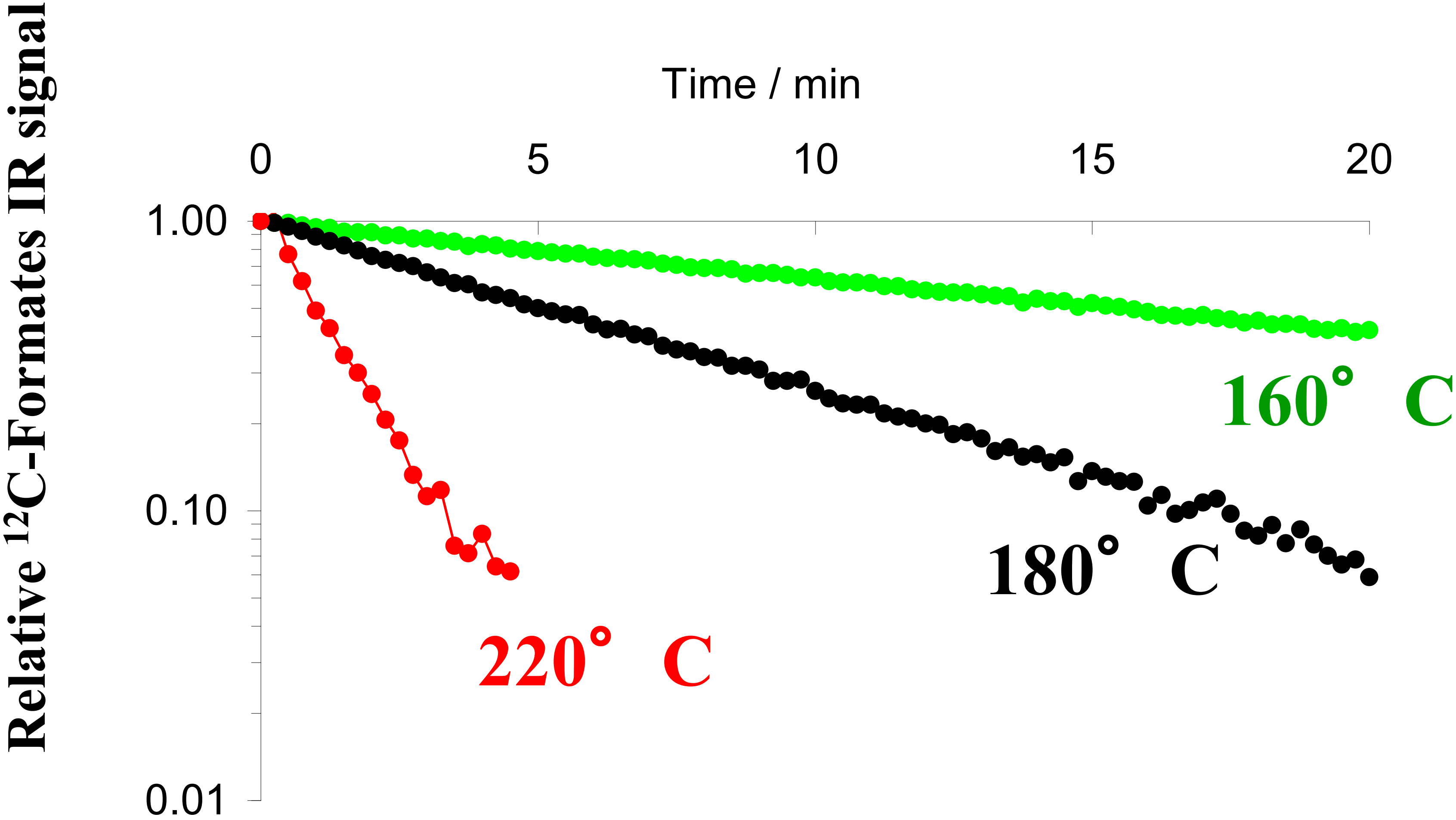




Formate concentrations can be determined accurately

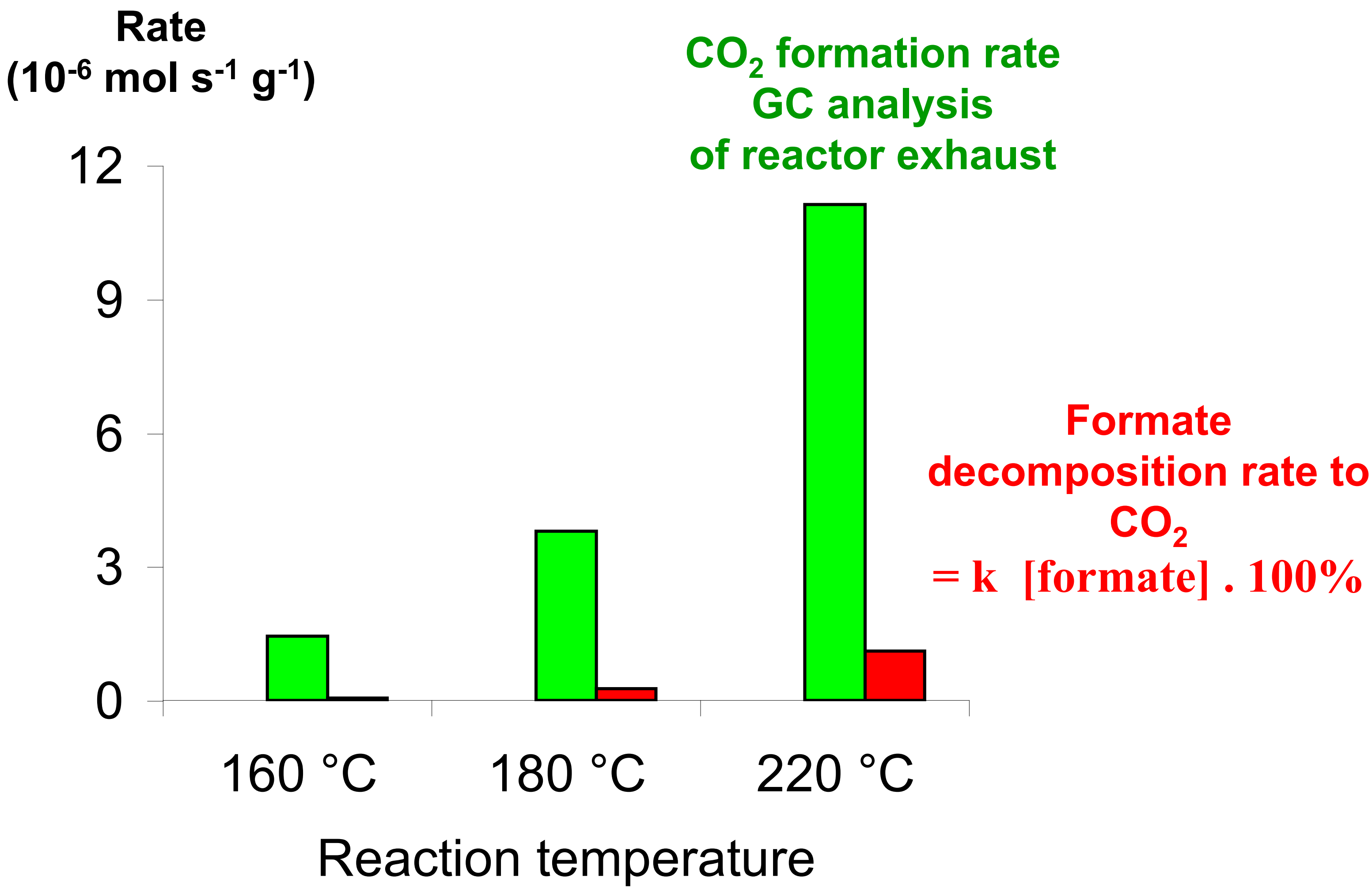
DRIFTS: Formate exchange over Pt-CeO_2

$$2\%\ ^{12}CO + 7\%\ H_2O \rightarrow 2\%\ ^{13}CO + 7\%\ H_2O$$



Slope = k

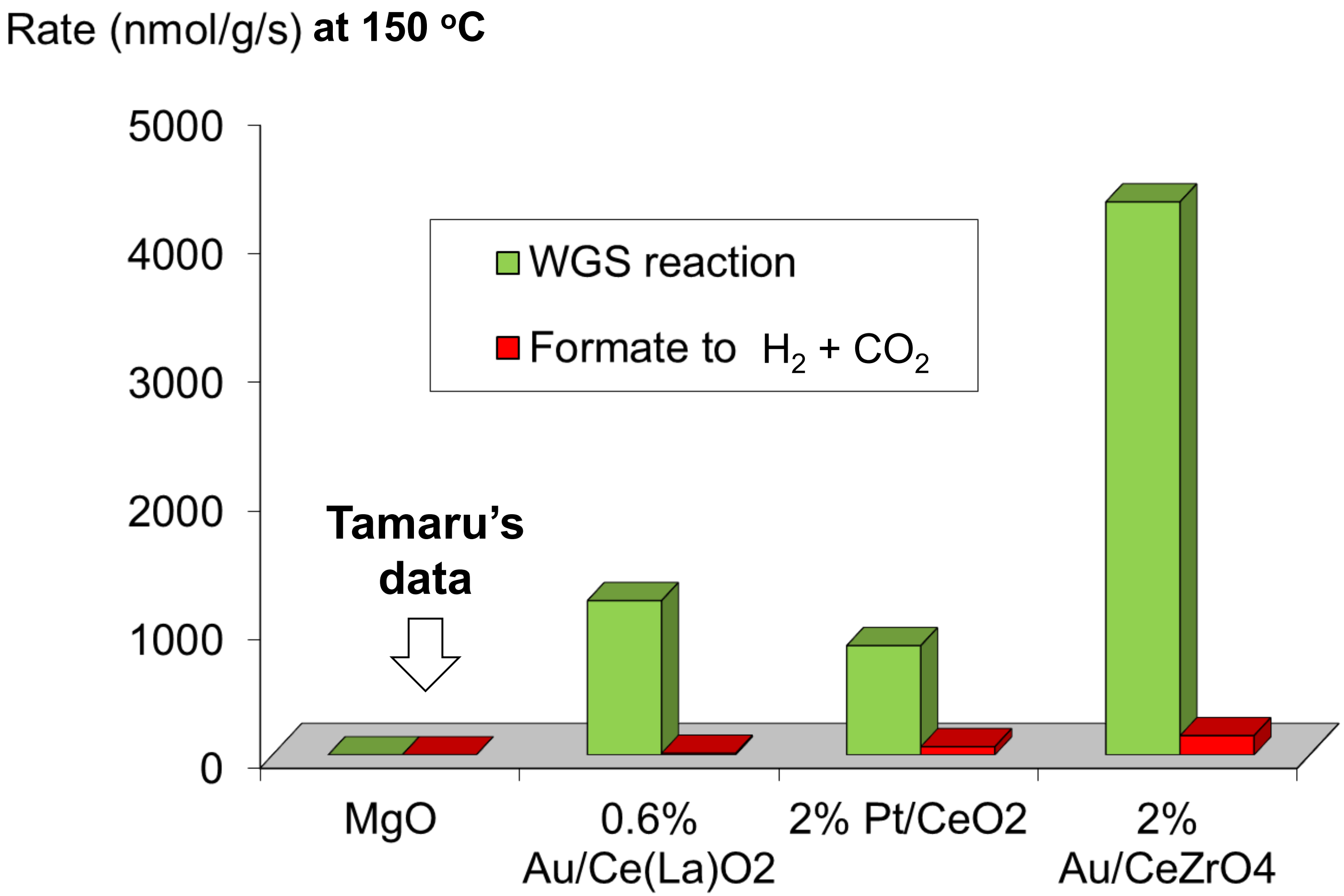
Pt/CeO_2: rate of CO_2 formation vs. rate of formate decomposition



Formates seen by IR: minor (not main) intermediates

25

MgO vs highly active WGS catalysts



Formates seen by IR: minor (not main) intermediates on the best low-temperature WGS catalysts

Burch, Goguet, Meunier, Appl Catal A 409-410 (2011) 3

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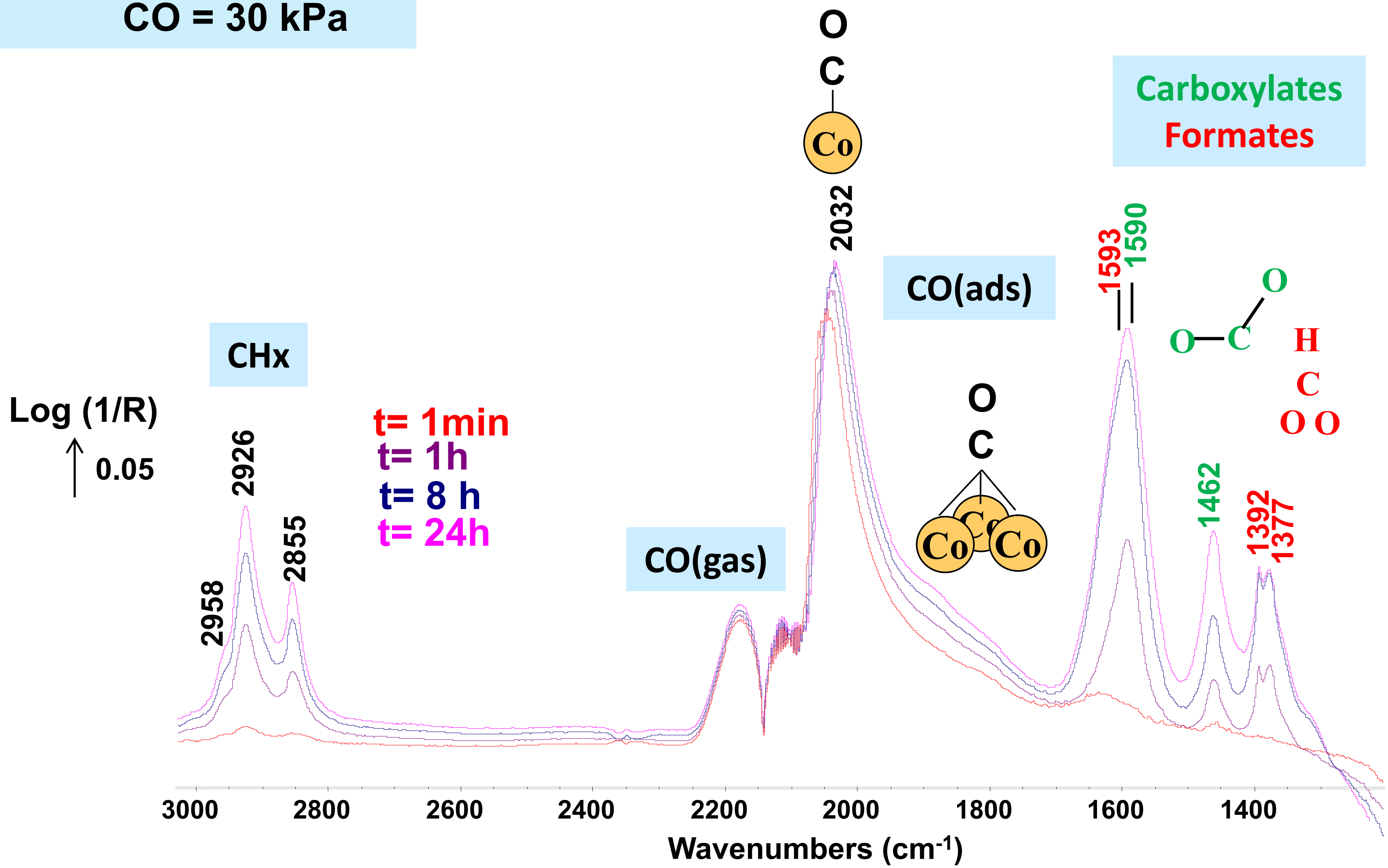
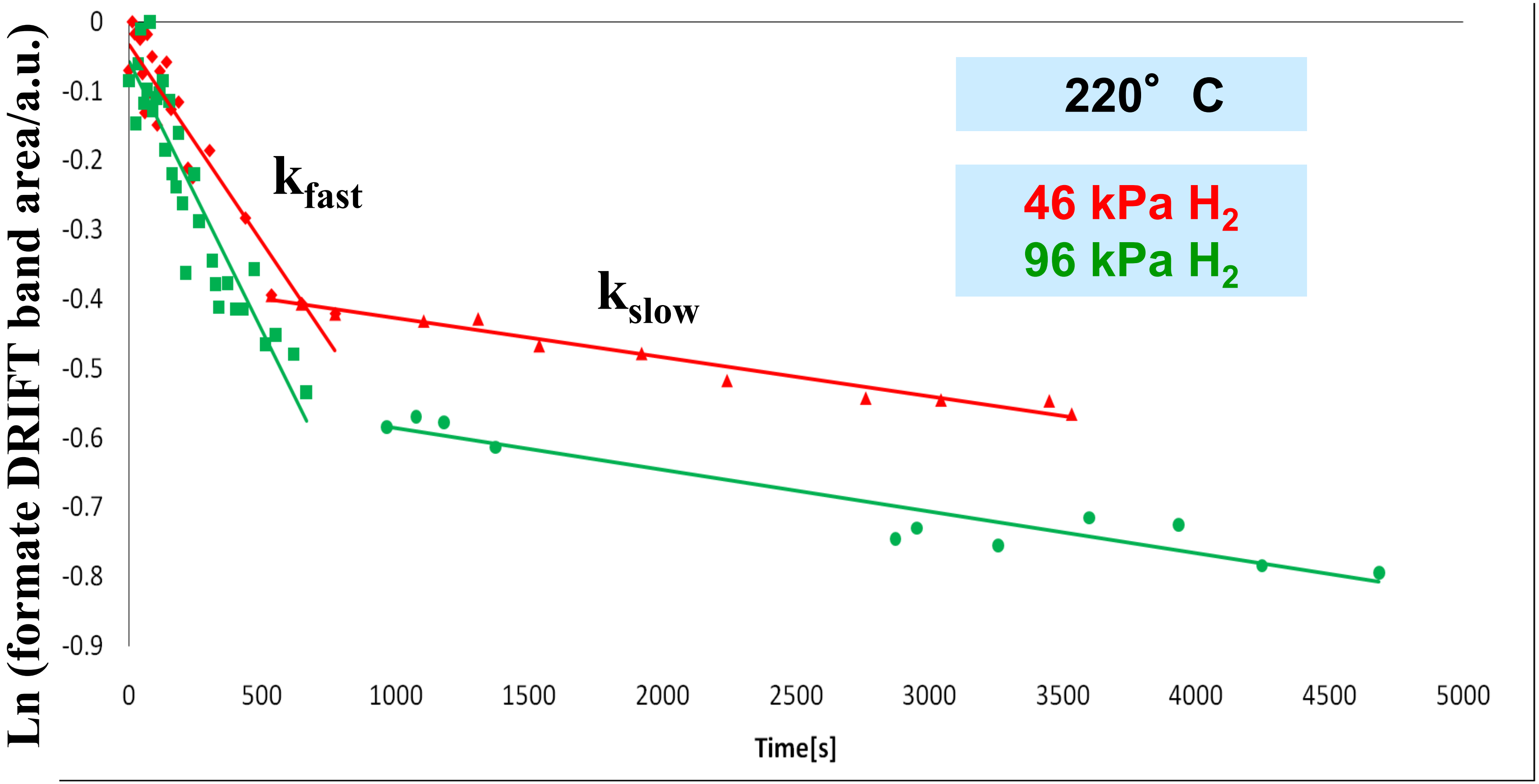
CO hydrogenation on Co/Al_2O_3

T = 220°C
Feed: H_2 = 60 kPa
CO = 30 kPa

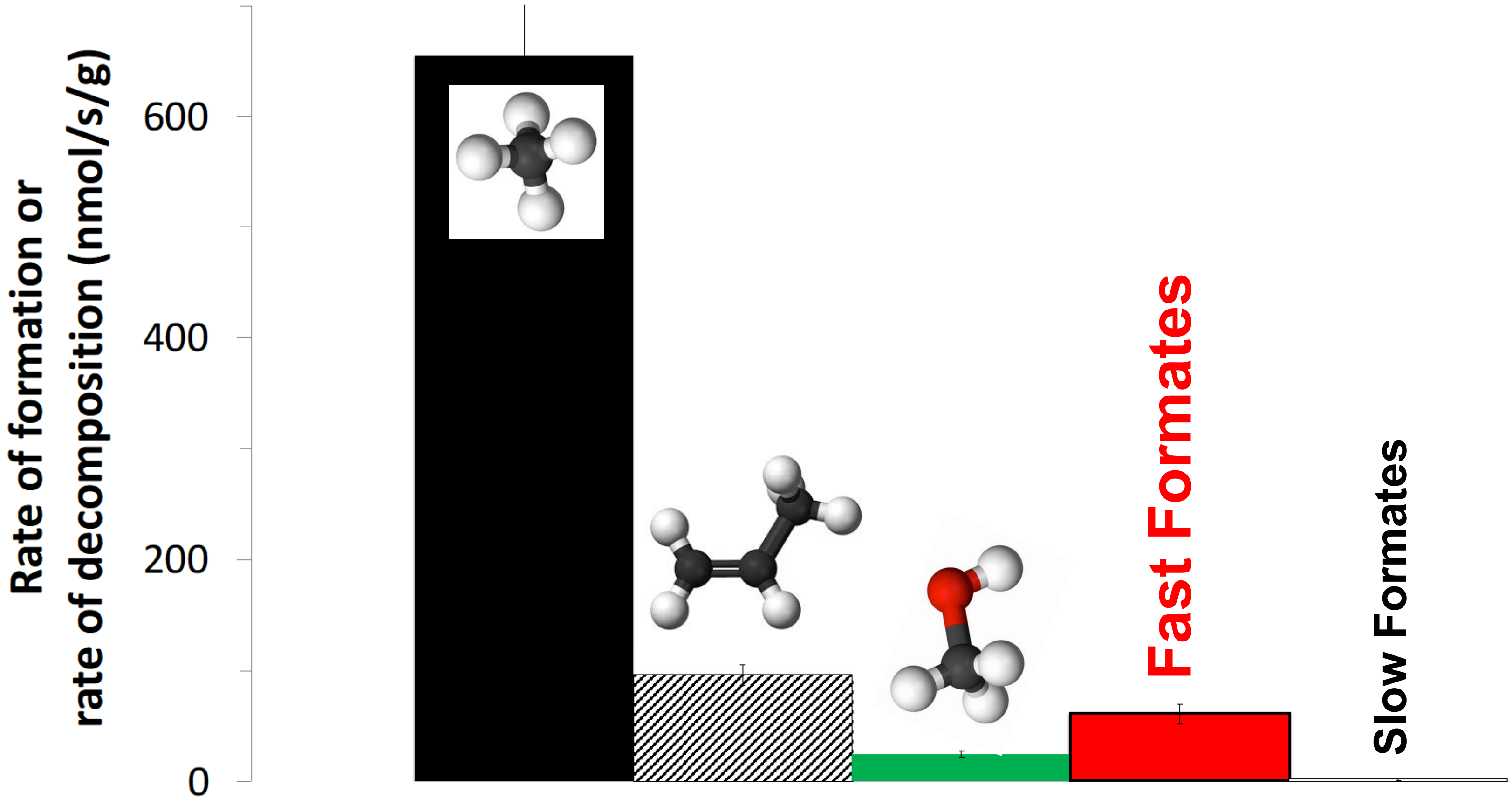


Formate decomposition in H_2 after CO removal



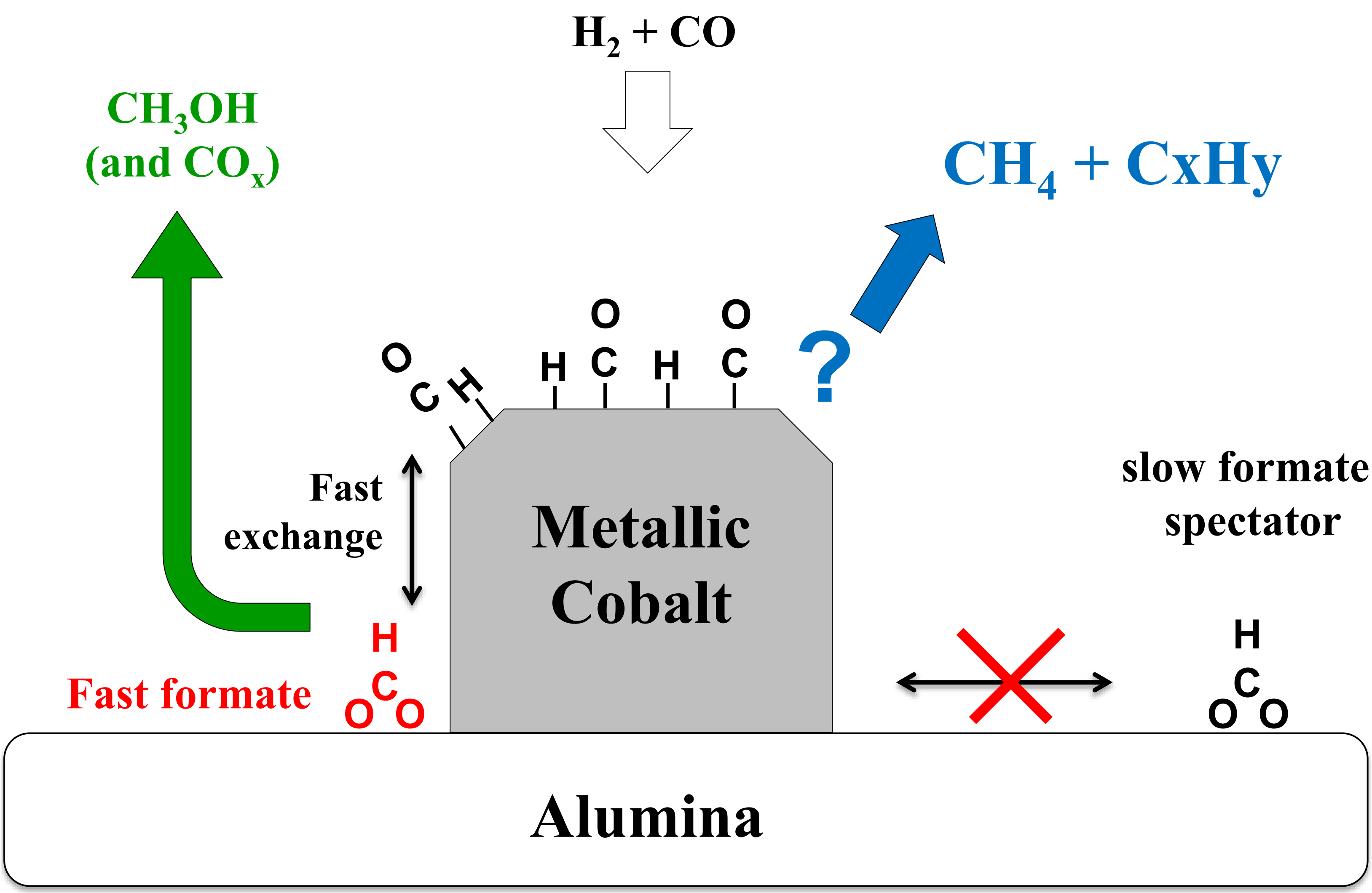
Two types of formates: fast and slow, yet exhibiting identical IR spectra

Rates of product formation (*at steady-state*) and decomposition rates of formates (*transient*) at 220 °C



Fast formates: potential reaction intermediate in the formation of methanol, but not for CH_4 and propene

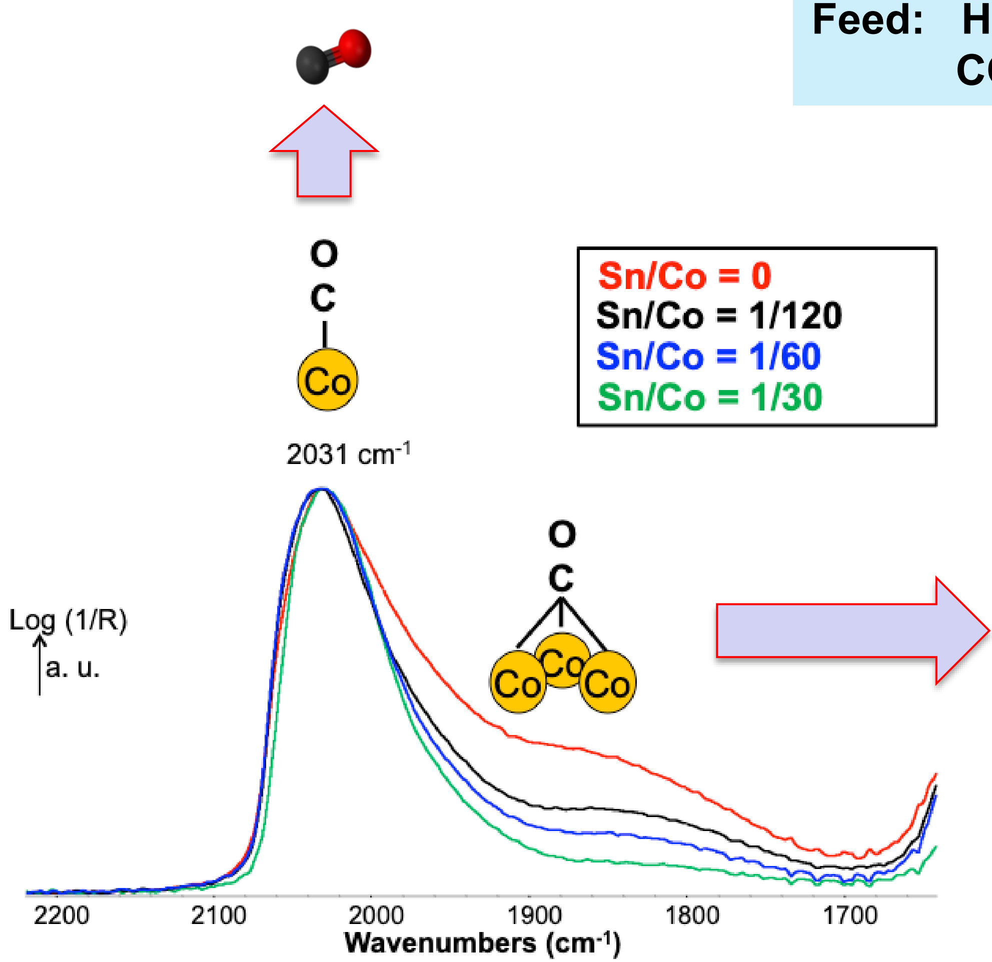
Suggested simplified reaction model:

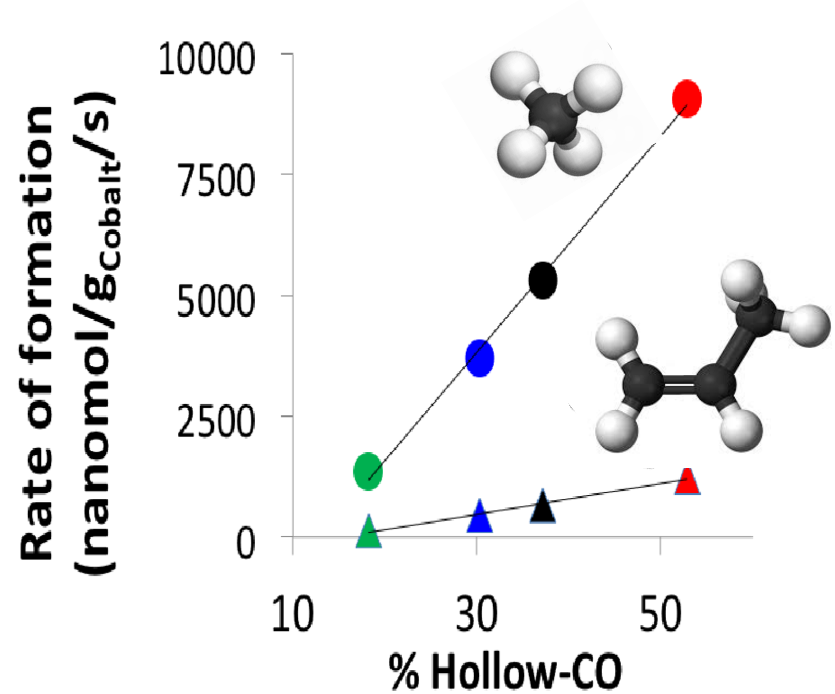


Catal. Today 259 (2016) 192

CO + H_2: quantitative *operando* DRIFTS

T = 220 °C
Feed: H_2 = 60 kPa
CO = 30 kPa

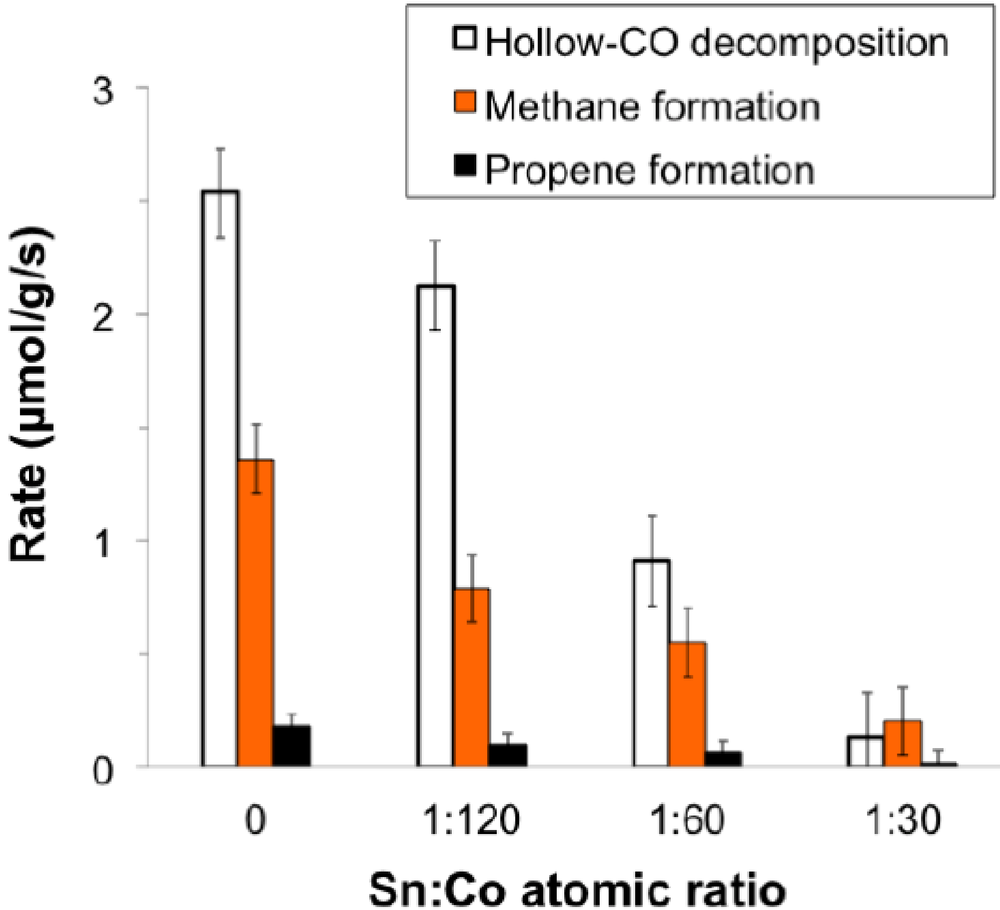




Only Hollow CO relates to C_xH_y

CO + H_2: quantitative *operando* DRIFTS

T = 220 °C
Feed: H_2 = 60 kPa
CO = 30 kPa



Hollow CO: can account for all the formation of C_xH_y

ACIE 57 (2018) 547

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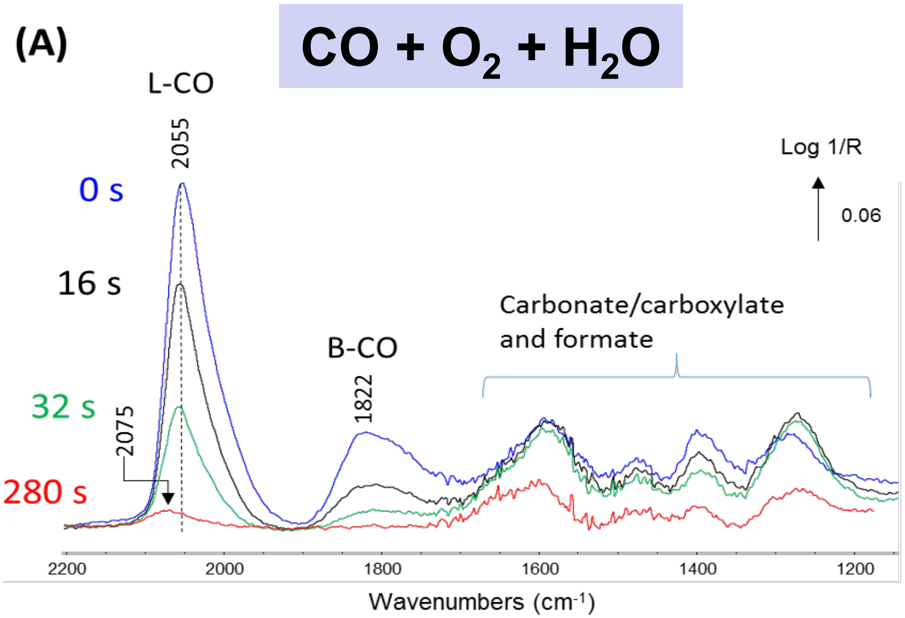
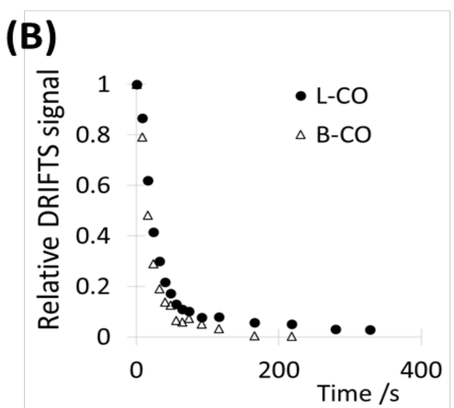
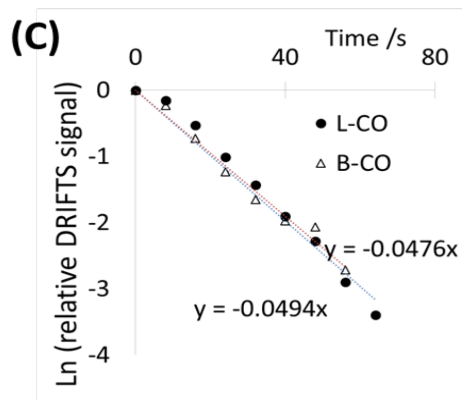
Pt/CeO_2 : quantitative *operando* DRIFTS at 30°C







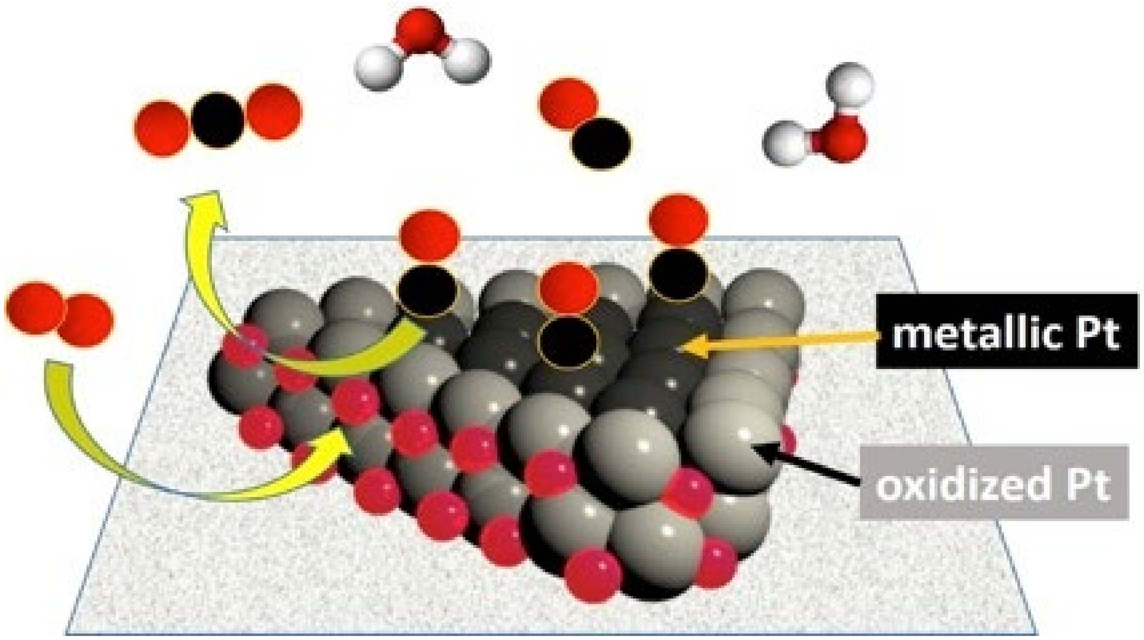
Carbonyl (L+B) decomposition rate	6.1 ± 3	µmol/ (s g_{cata})
Rate of CO_2 production	4.0 ± 0.4	µmol/ (s g_{cata})

Pt°-CO: can account for all the formation of CO_2

ACIE 2021, 60, 3799

$CO + O_2$ ($+H_2O$) on Pt/CeO_2 at RT: quantitative *operando* DRIFTS + NAP-XPS

IR: CO on metallic Pt is main reaction intermediate
Kinetics: partial positive orders for CO (+0.35) and O_2 (+0.2): oxidised Pt?
IR and NAP-XPS: large fraction of Pt (> 50%) is oxidised at steady-state



Synergy between Metallic and Oxidised Pt Sites

ACIE 2021, 60, 3799

Conclusions

- Possible to match rates product formation & surface intermediate decomposition using quantitative DRIFTS in transient analyses

- Need to remove gas-phase signals in DRIFTS

- Ceria-supported Pt^{o}-CO readily reacts at RT in He

- Watch out for $Ni(CO)_4$

Acknowledgements

DRIFTS: Julian Ross, John Breen, Haoguang Li, F. Thibault-Starzyk, A. Travert, M. Rivallan

WGS: Daniele Tibiletti, Alex Goguet, Robbie Burch, Chris Hardacre, Dave Thompsett

Cobalt-FTS: Anaelle Paredes-Nunez, Davide Lorito, Yves Schuurman, Paul Hazemann

CO oxidation: Luis Cardenas, Helena Kaper