Controlled Alkali Doping for Enhanced Activity in LT-RWGS Catalysts

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Motivation

CO_2 valorization – CO as key intermediate for fuels & chemicals

RWGS selectivity challenge – CH_4 favored at low T, CO at high T

Catalyst design goal – Selective CO production at 200–500 °C

Objective

Alkali promotion in RWGS – Boosting CO selectivity

Mechanistic insight – Comparing Pt/TiO_2 vs. Cs-promoted system

Unveiling Cs role – Reaction pathways & surface species

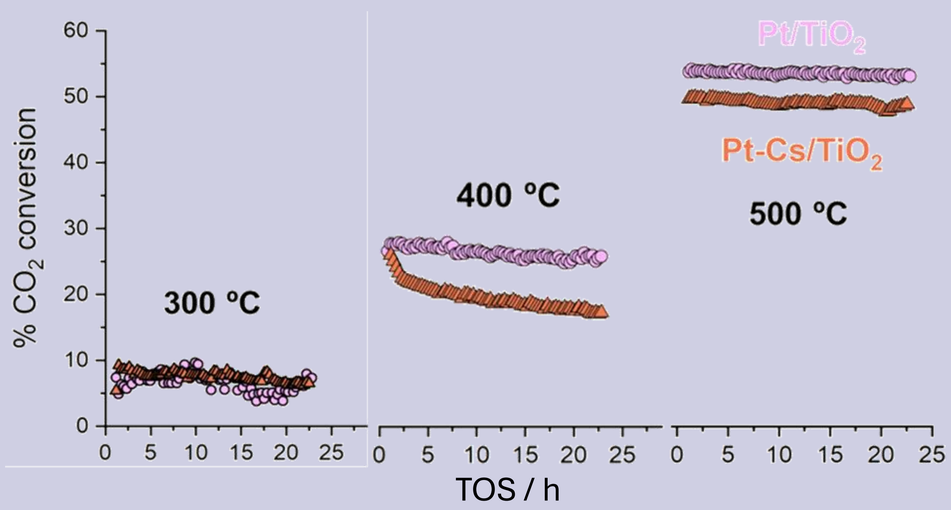
Methodology

Catalyst prep – sequential wet impregnation – Pt/TiO_2 (1 wt%) and $Pt–Cs/TiO_2$ (5 wt% Cs)

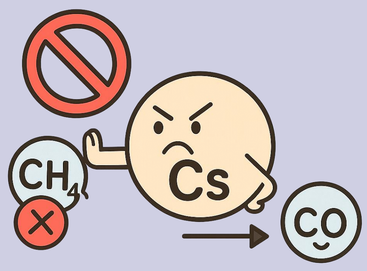
Reaction condition – 300–500 °C, 24 h/step, CO_2/H_2 = 1:4

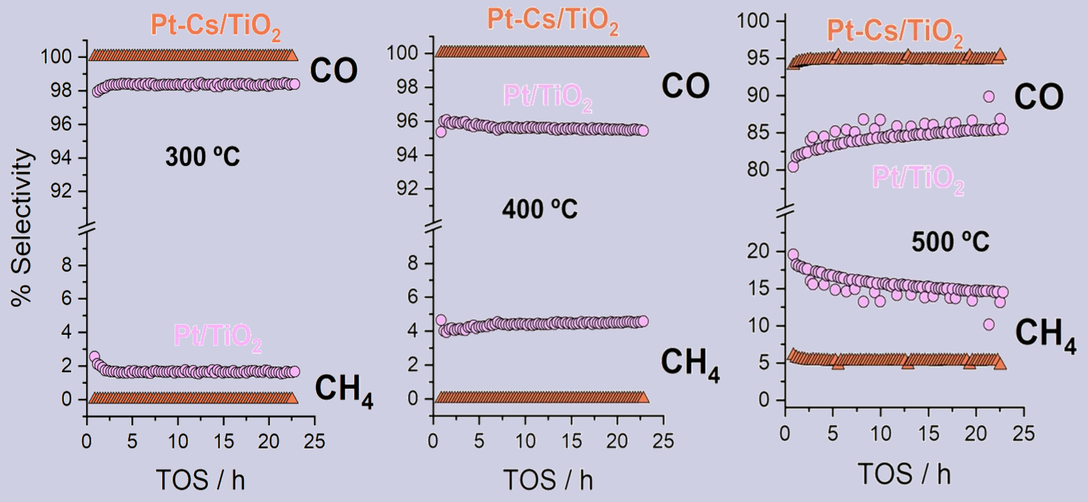
Operando DRIFTS – Surface analysis under reaction conditions and CO TPD

Catalytic activity



The CO_2 conversion shows that, when temperature is increased, the Pt/TiO_2 catalyst present a small increase in activity in comparison to the Cs doped one.



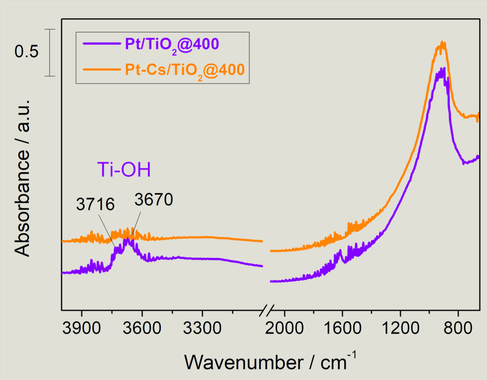


$Pt–Cs/TiO_2$ outperforms unpromoted catalyst
At 500 °C – Pt/TiO_2 loses ~20% CO selectivity; $Pt–Cs/TiO_2$ only ~5%
Stable CO selectivity at low T – 100% maintained with Cs promotion

Operando DRIFTS

Reaction conditions: 50 mL min^{-1} of H_2/CO_2 = 4, 1 bar, 150 - 350 ºC

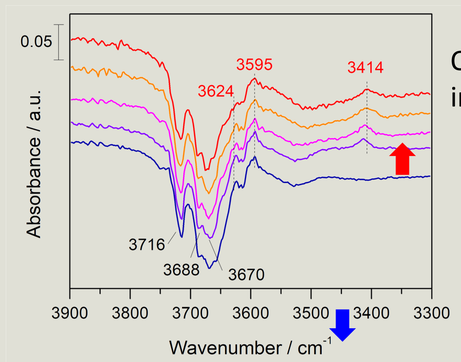
Spectras after activation under H_2/Ar



Cs neutralize –OH surface groups

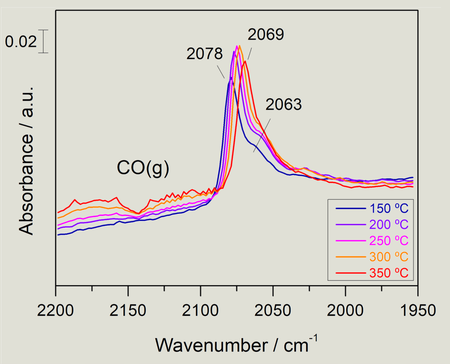
This involve a change in reaction mechanism compared to Pt/TiO_2

Pt/TiO_2

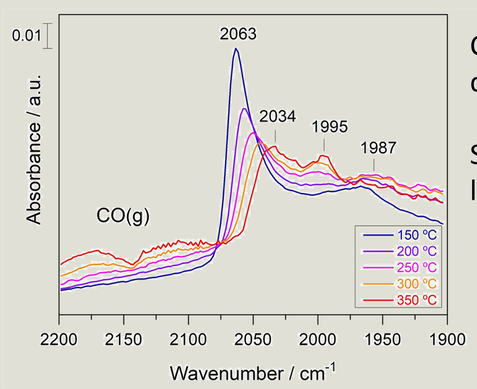


Oxygen vacancies formation in TiO_2 involving a redox mechanism

Electron transfer from TiO_2 to Pt – CO redshift & vacancy formation
CO dissociation on Pt – C deposits & CH_4 formation

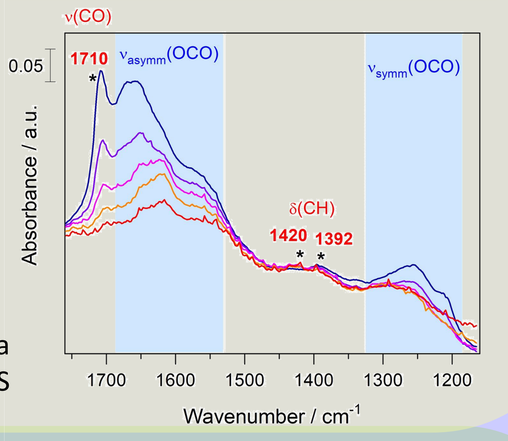


$PtCs/TiO_2$



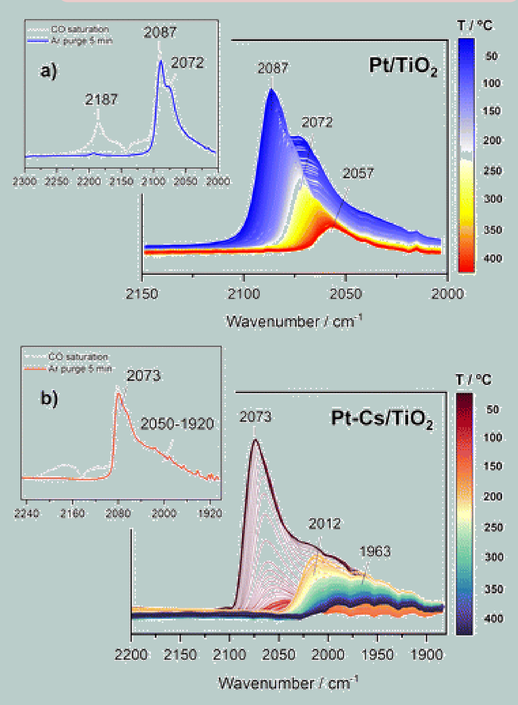
CO desorption from Pt – Clean surface & delayed C deposition – this explains the better selectivity to CO

Small Pt clusters stabilized by Cs – Possible frustrated lewis pairs (FLPs) formation



Oxygenated intermediates (1710, 2840 cm^{-1}) – involving a Formyl/acyl route in RWGS

Operando DRIFTS CO TPD



•Pt/TiO_2:

Intense CO bands at 2087 and 2012 cm^{-1} vanish with temperature increase.

A 2057 cm^{-1} residual band indicates CO dissociation and carbon deposition.

A 2187 cm^{-1} band (Ti^{4+}–CO) appears initially, linked to acidic Lewis sites.

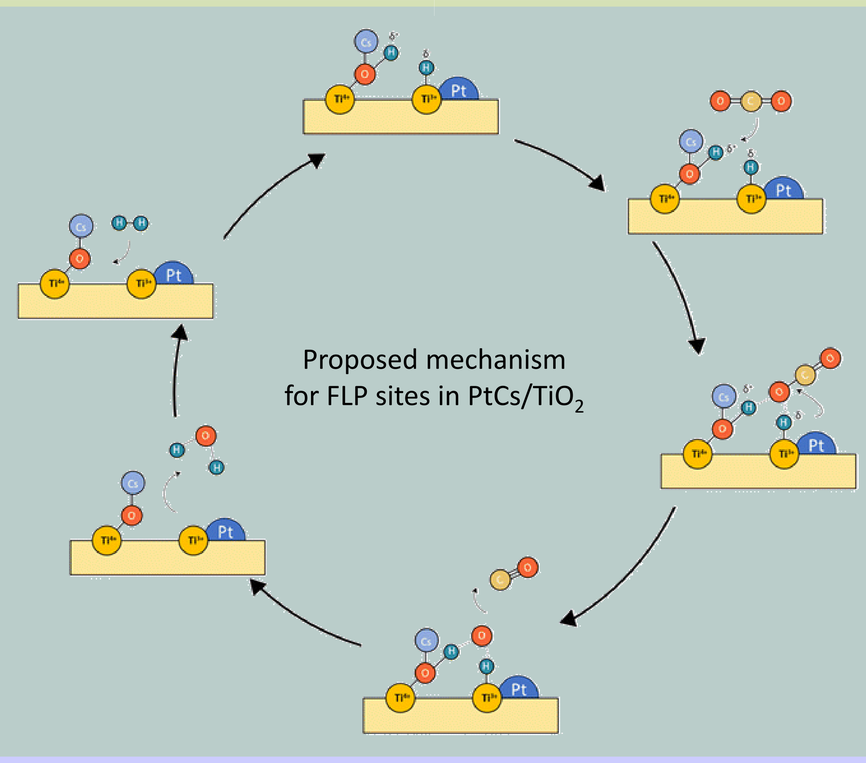
•$Pt–Cs/TiO_2$:

No 2187 cm^{-1} band → Acidic sites neutralized by Cs.

CO completely desorbs by 150 °C.

A broad 2050–1920 cm^{-1} band (small Pt clusters) reappears and remains up to 400 °C.

Cs prevents CO dissociation and stabilizes ultrasmall Pt particles.



Proposed mechanism for FLP sites in $PtCs/TiO_2$

Conclusion

The addition of Cs has been shown to enhance CO selectivity at low temperatures by inhibiting CO dissociation and suppressing carbon deposition on Pt particles.
The proximity of Cs to small Pt clusters promotes the formation of frustrated Lewis pairs (FLPs), enabling an alternative reaction pathway for CO formation.
The detection of oxygenated intermediates, such as –CHO species, on $PtCs/TiO_2$ catalysts suggests the involvement of a distinct formyl/acyl reaction route.

Acknowledgments

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