

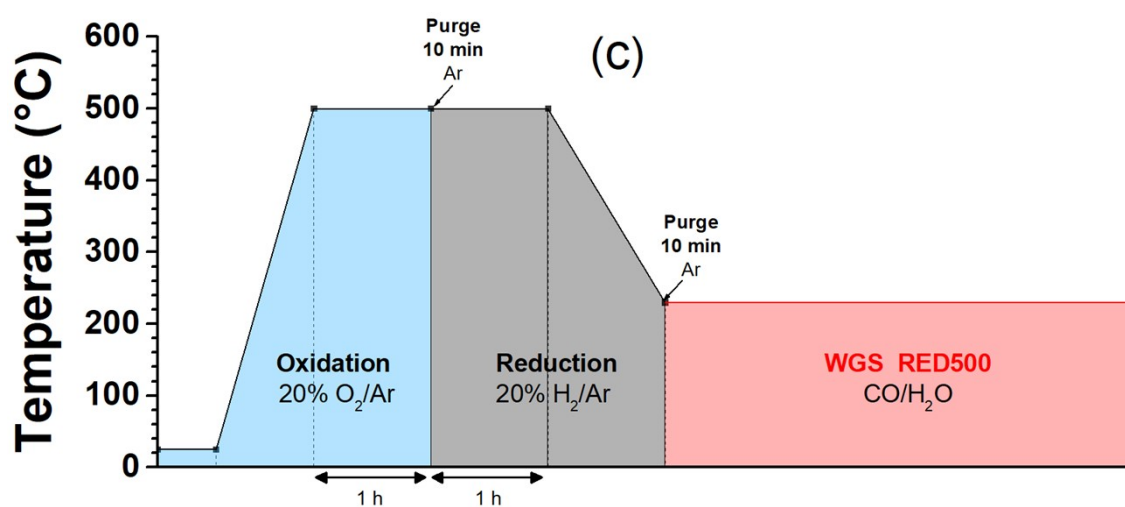
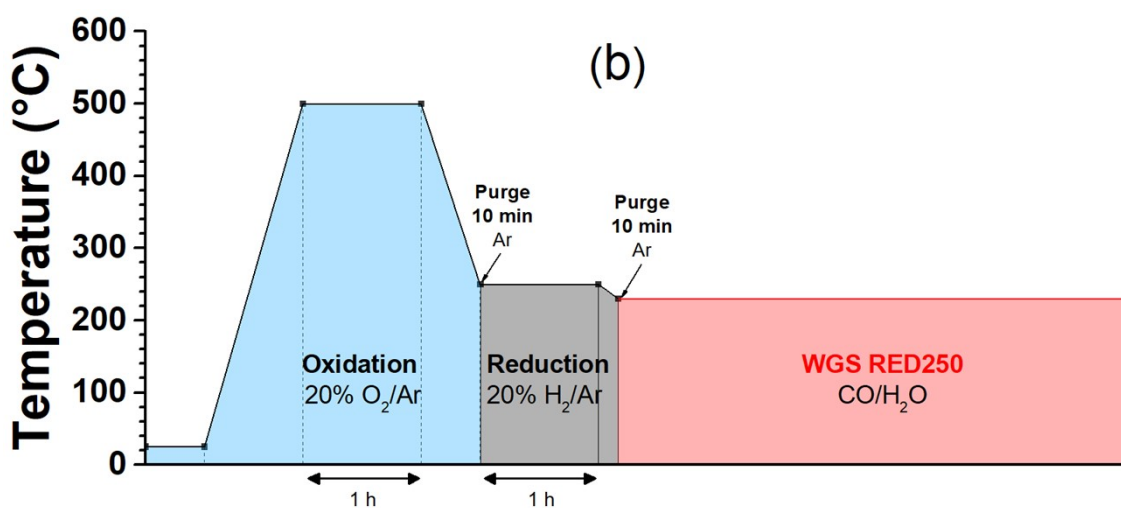
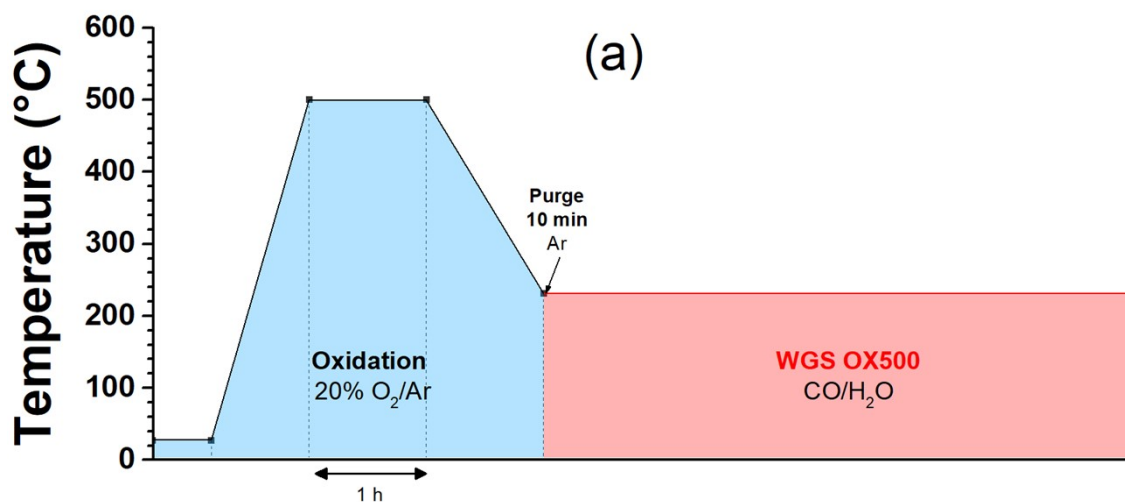
Influence of redox treatments on the low temperature water gas shift reaction over Pt/CeO₂ catalysts

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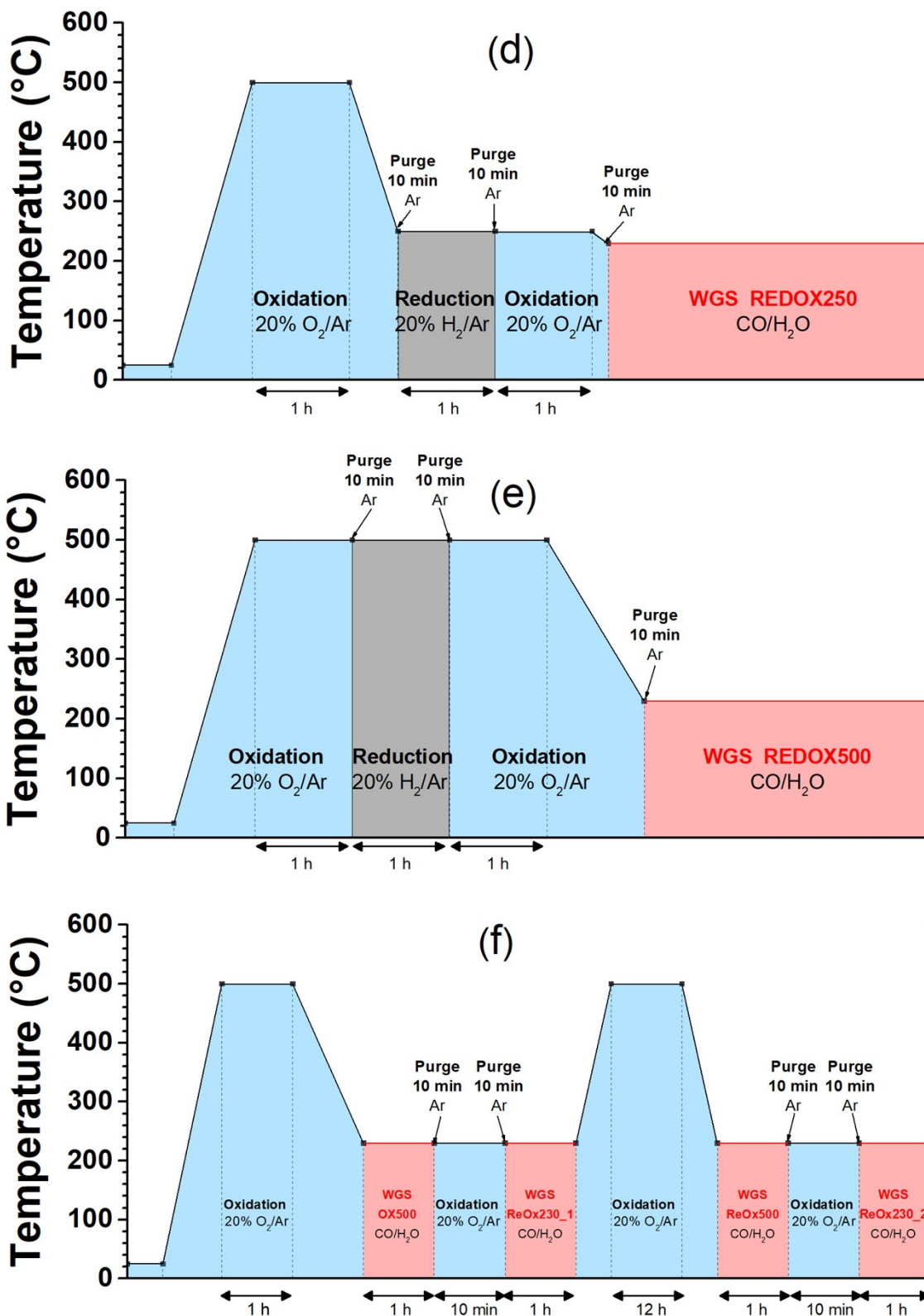


Figure S1: Scheme of the protocol used for (a) OX500, (b) RED250, (c) RED500, (d) REOX250, (e) REDOX500 pre-treatments followed by WGS reaction and (f) sequence of consecutive OX500, ReOx230_1, ReOx500 and ReOx230_2 oxidising post-treatments followed each time by WGS reaction.

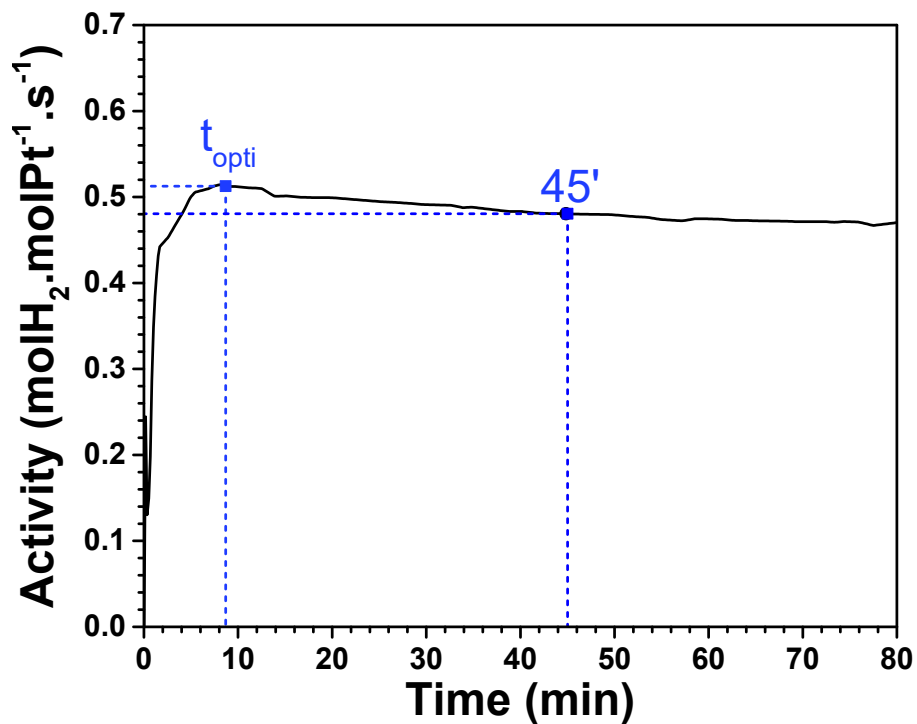


Figure S2: Evolution over time of molar activity of 0.59Pt catalyst after OX500 pre-treatment. It is maximal after minutes at t_{opti} time and then slowly decreases. The activity after 45 min on stream provides the deactivation rate.

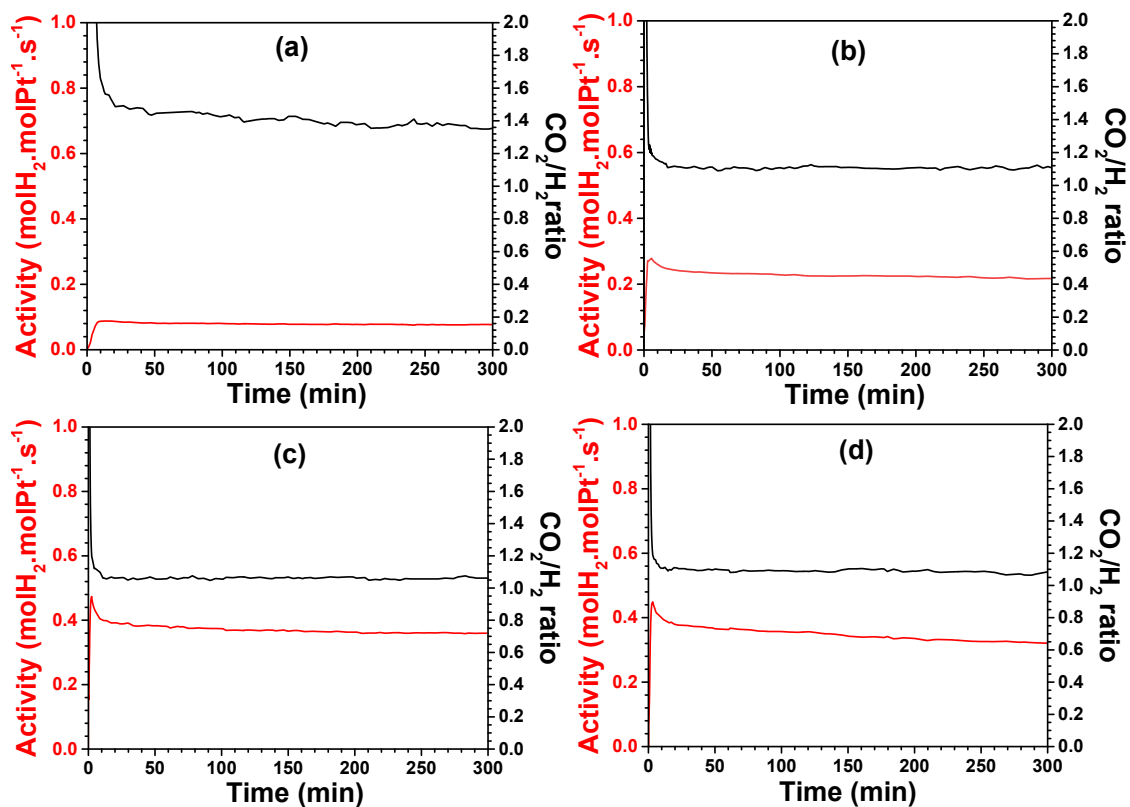


Figure S3: Evolution of molar activity and CO_2/H_2 molar ratio with time on stream for 0.10Pt catalyst after (a) OX500, (b) RED250, (c) RED500 and (d) REDOX500 pretreatments. Reaction conditions: 230 °C, $\text{H}_2\text{O}/\text{CO}/\text{Ar}/\text{He}$:33.3/8.3/54.2/4.2 vol% feed, $\text{GFSV} = 600 \text{ mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$.

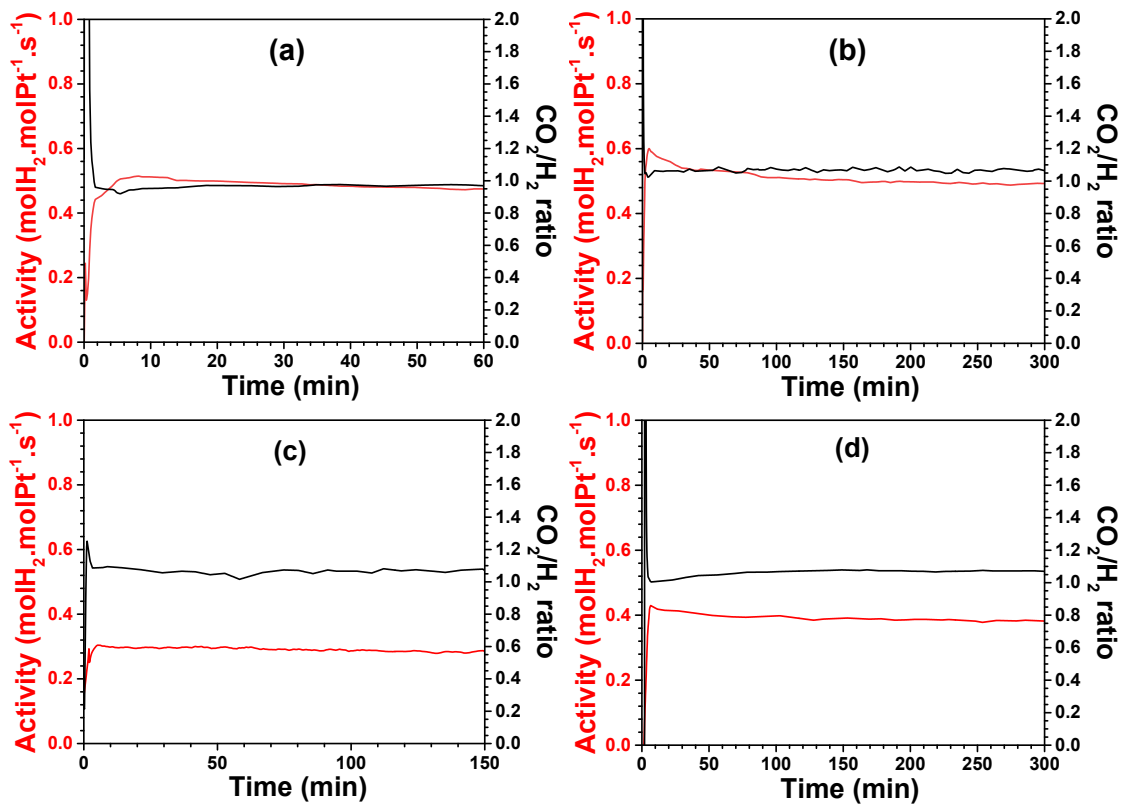


Figure S4: Evolution of molar activity and CO_2/H_2 molar ratio with time on stream for 0.59Pt catalyst after (a) OX500, (b) RED250, (c) RED500 and (d) REDOX500 pretreatments. Reaction conditions: 230 °C, $\text{H}_2\text{O}/\text{CO}/\text{Ar}/\text{He}$:33.3/8.3/54.2/4.2 vol% feed, $\text{GFSV} = 600 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$.

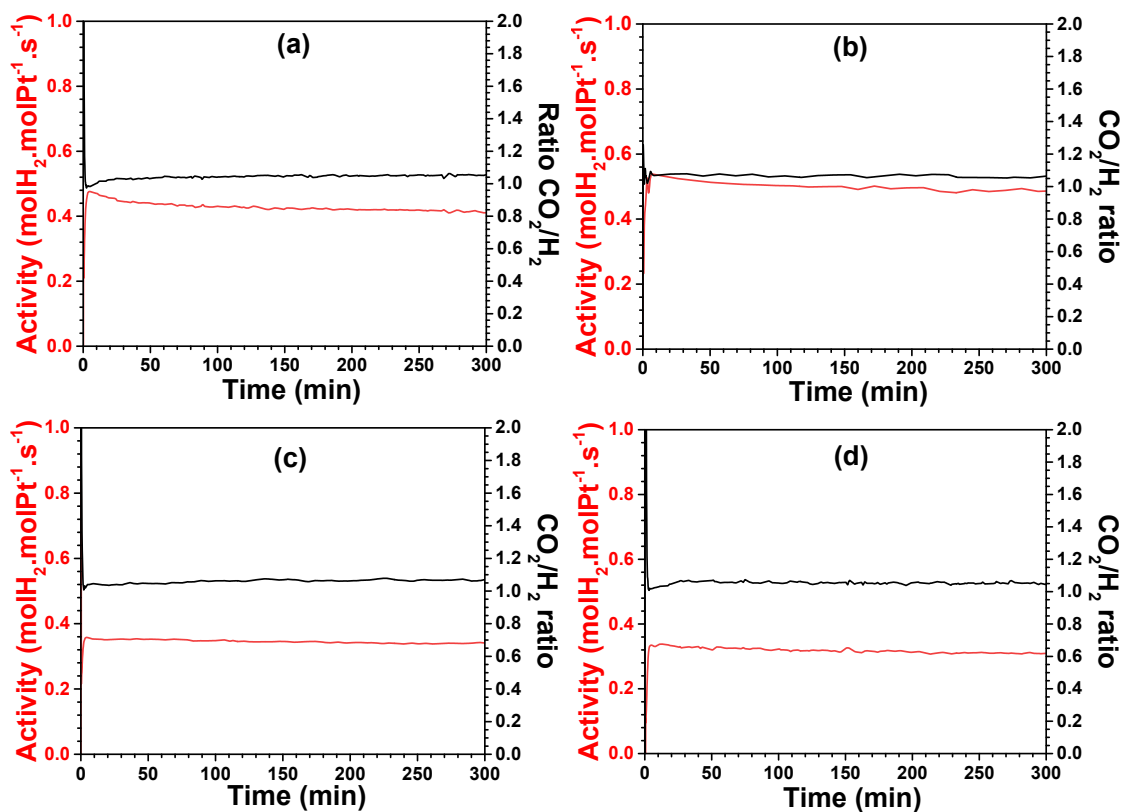


Figure S5: Evolution of molar activity and CO_2/H_2 molar ratio with time on stream for 1.06Pt catalyst after (a) OX500, (b) RED250, (c) RED500 and (d) REDOX500 pretreatments. Reaction conditions: 230 °C, $\text{H}_2\text{O}/\text{CO}/\text{Ar}/\text{He}$:33.3/8.3/54.2/4.2 vol% feed, $\text{GFSV} = 600 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$.

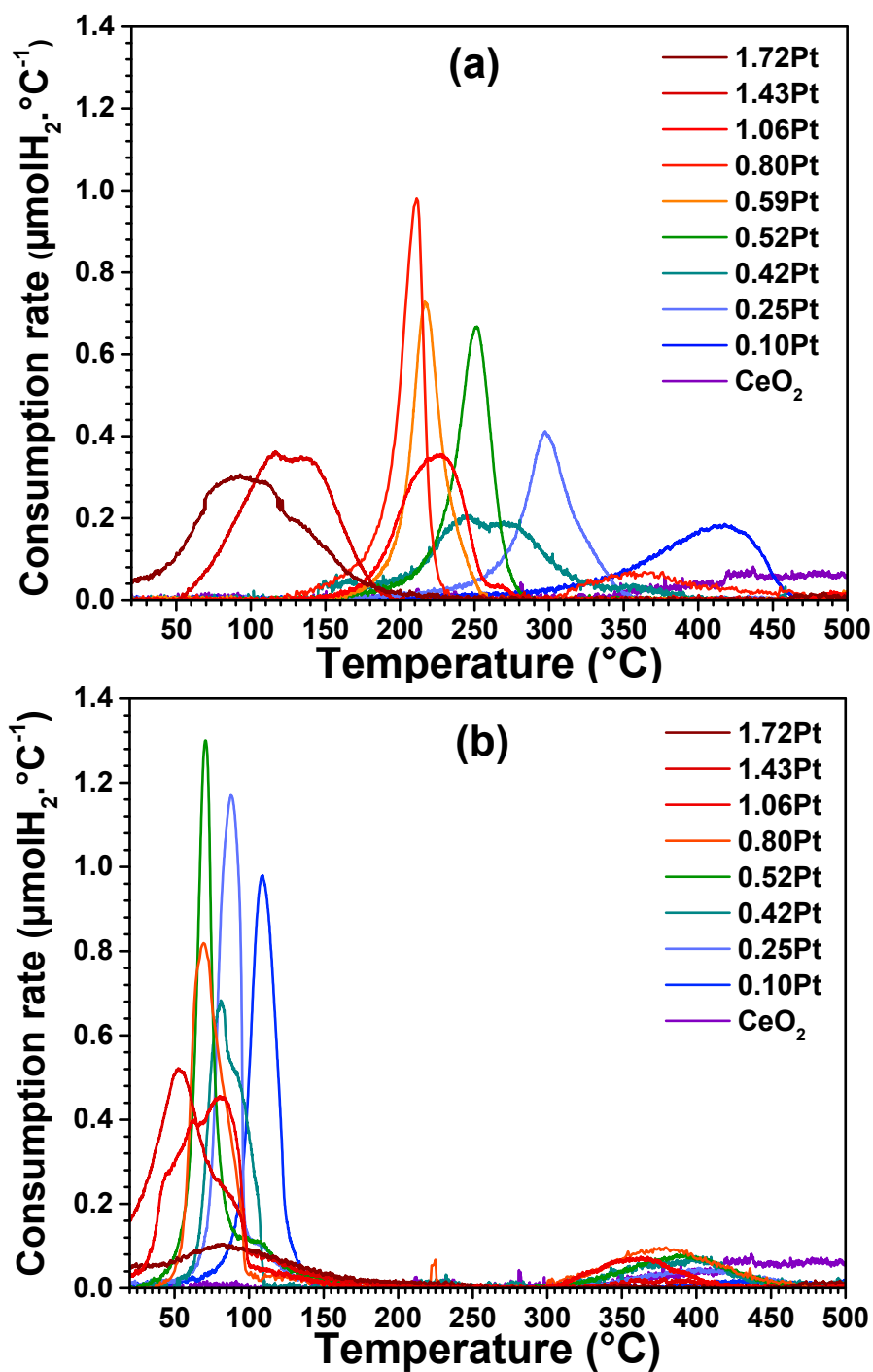


Figure S6: H₂-TPR curves recorded for different Pt/CeO₂ catalysts (a) after OX500 pretreatment (TPR1) and (b) after TPR1 followed by 1 h of oxidative treatment at 500 $^\circ\text{C}$ which is similar to REDOX500 pretreatment (TPR2).

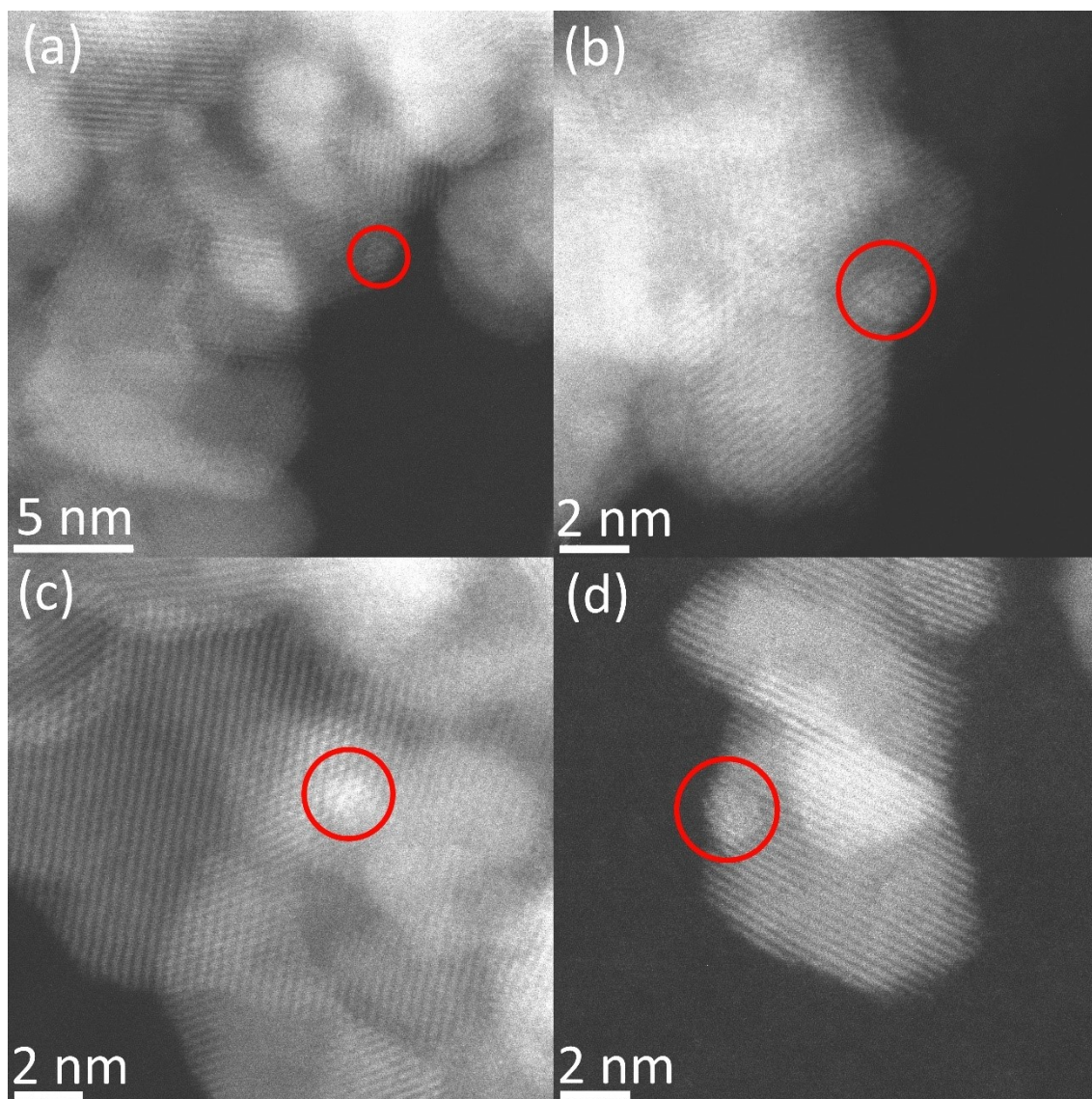


Figure S7: ADF-STEM images of 1.06Pt catalyst after RED500 pretreatment. The red circles indicate Pt NPs.

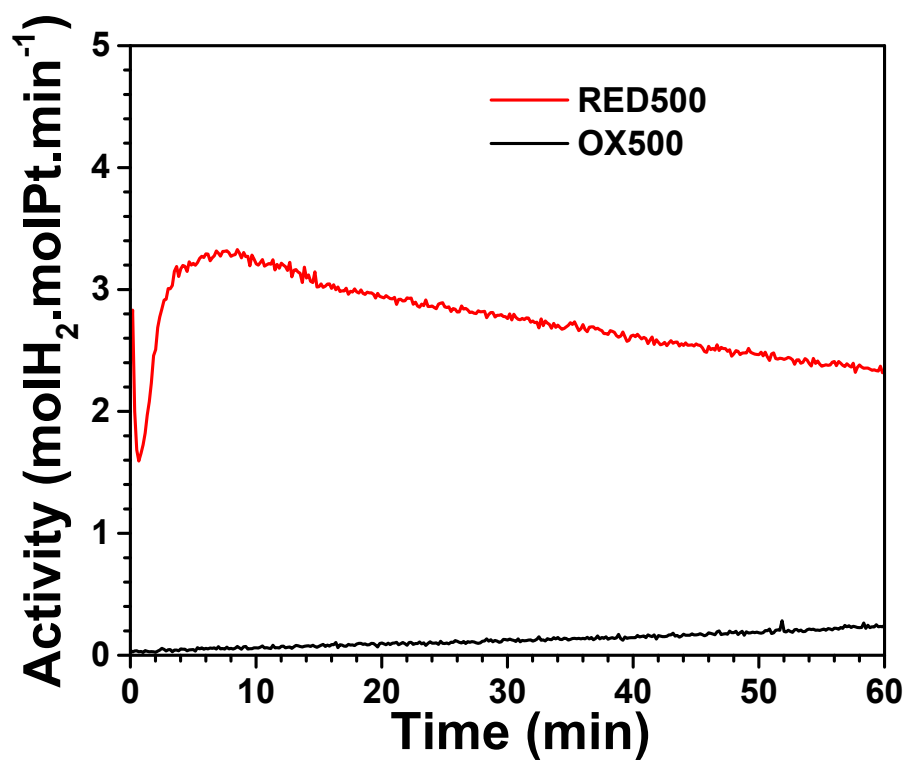


Figure S8: Evolution of molar activity during WGS reaction in the DRIFT cell for 0.10Pt catalyst after OX500 and RED500 pretreatments. Reaction conditions: T=230 °C, H₂O/CO/He:2.0/0.5/97.5 vol% feed, GHSV =1000 mL.min⁻¹.g⁻¹.

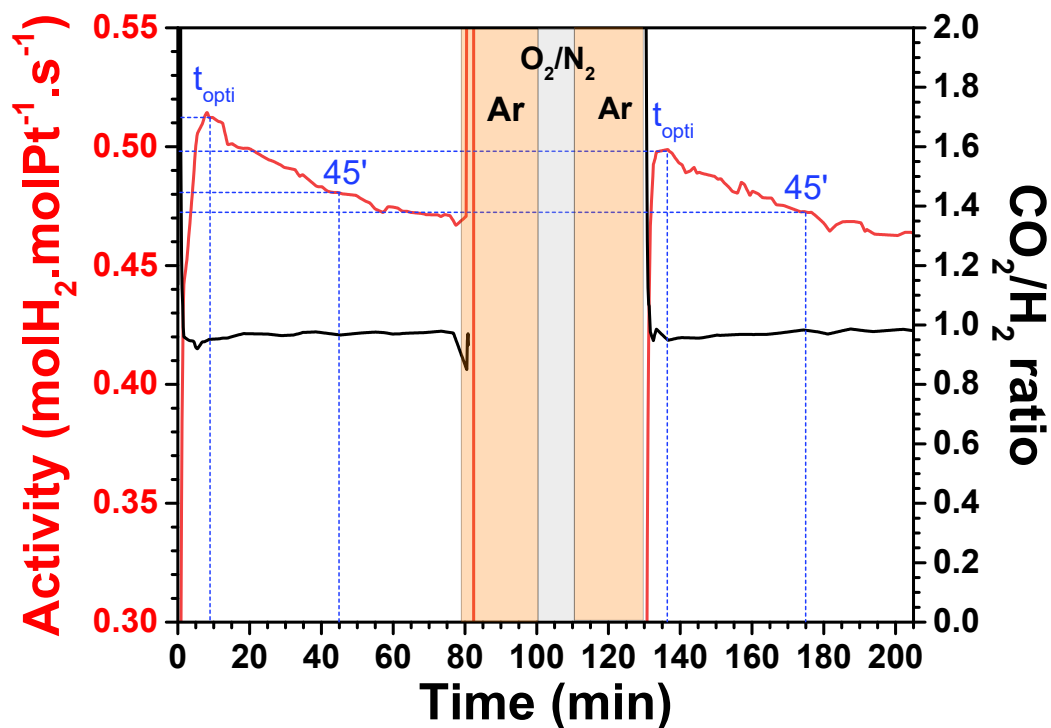


Figure S9: Evolution over time of molar activity and CO_2/H_2 ratio of 0.59Pt catalyst after OX500 pre-treatment and after 10 min under 20% O_2/Ar at 230 °C (ReOx230_1 post-treatment). The t_{opti} time corresponds to the maximal activity for each WGS reaction. The activity after 45 min on stream provides the deactivation rate.

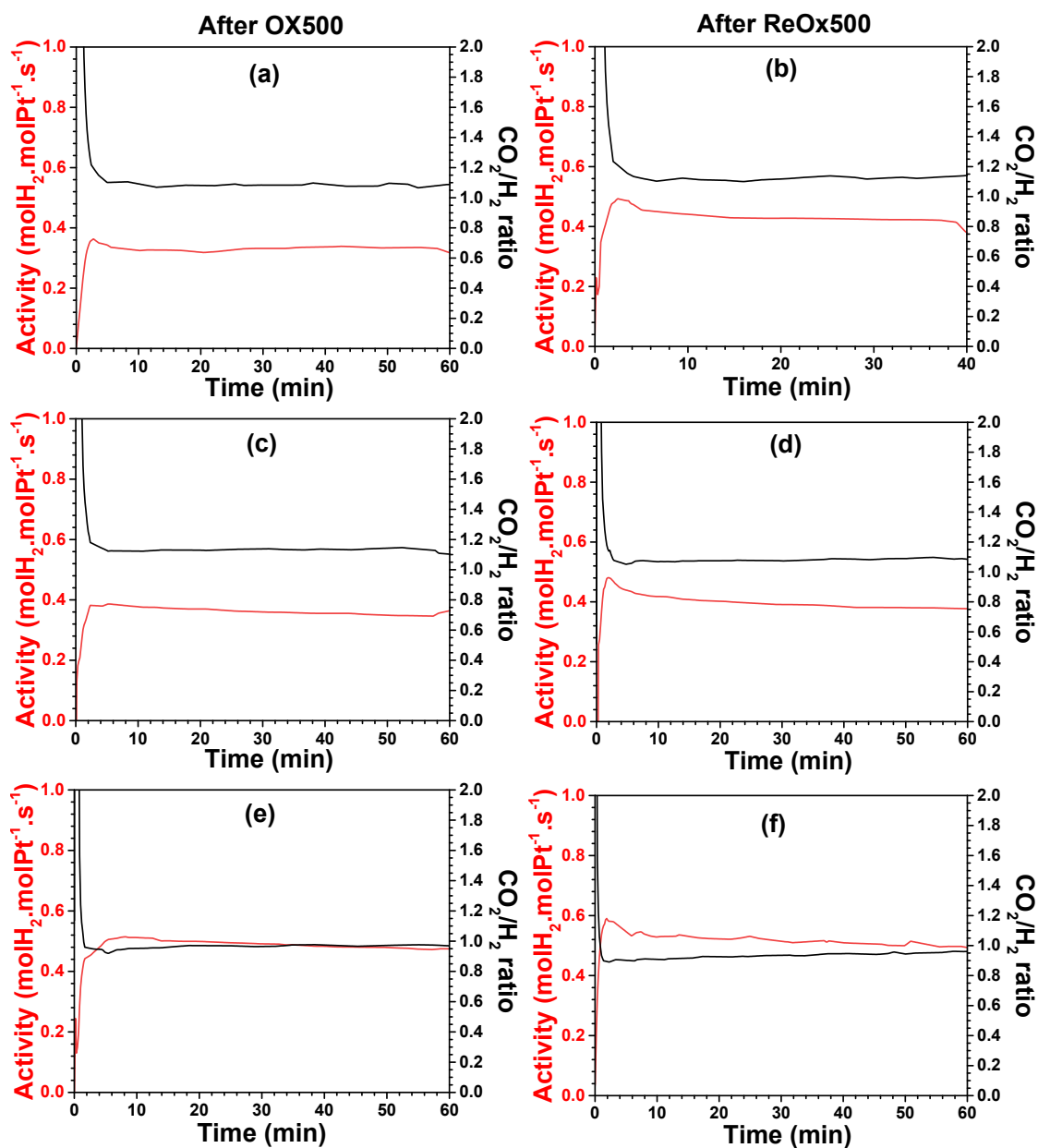


Figure S10: Evolution of molar activity and CO₂/H₂ molar ratio with time on stream after OX500 pretreatment and ReOx500 post-treatment, respectively for (a,b) 0.25Pt, (c,d) 0.42Pt and (e,f) 0.59Pt catalysts. Reaction conditions: 230 °C, H₂O/CO/Ar/He:33.3/8.3/54.2/4.2 vol% feed, GFSV = 600 mL.min⁻¹.g_{cat}⁻¹.

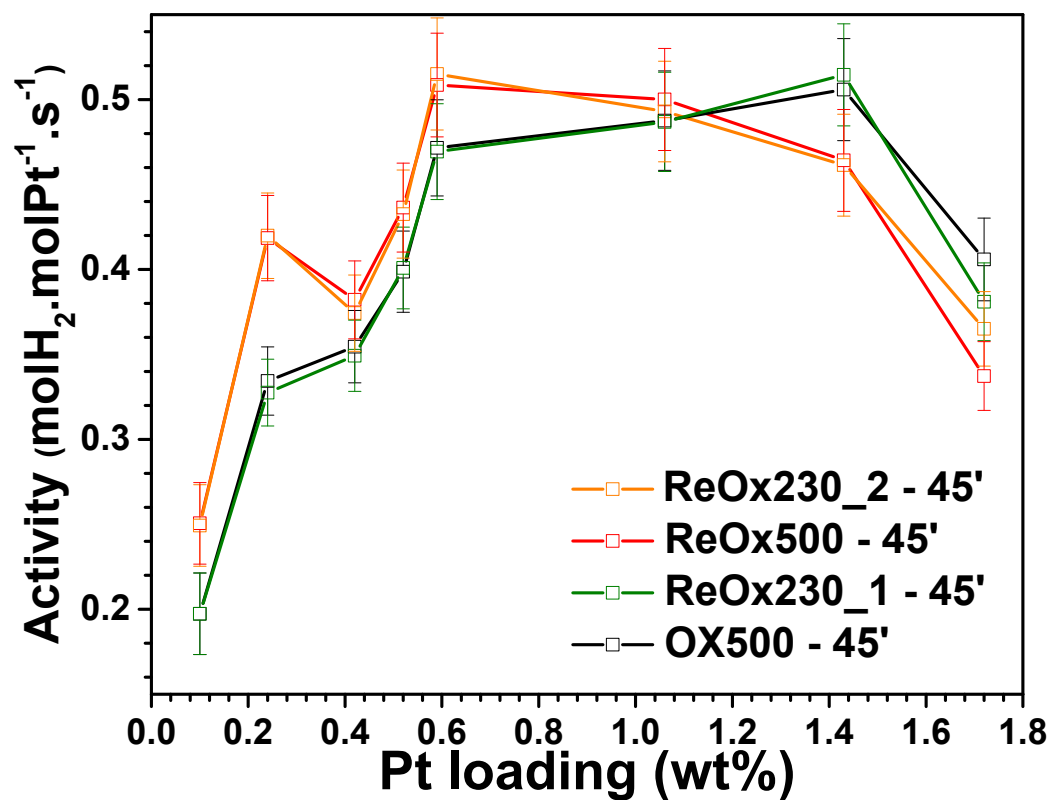


Figure S11: Evolution with Pt loading of molar activity at 45 min on stream after OX500 pretreatment and after ReOx230_1, ReOx500 and ReOx230_2 post-treatments.

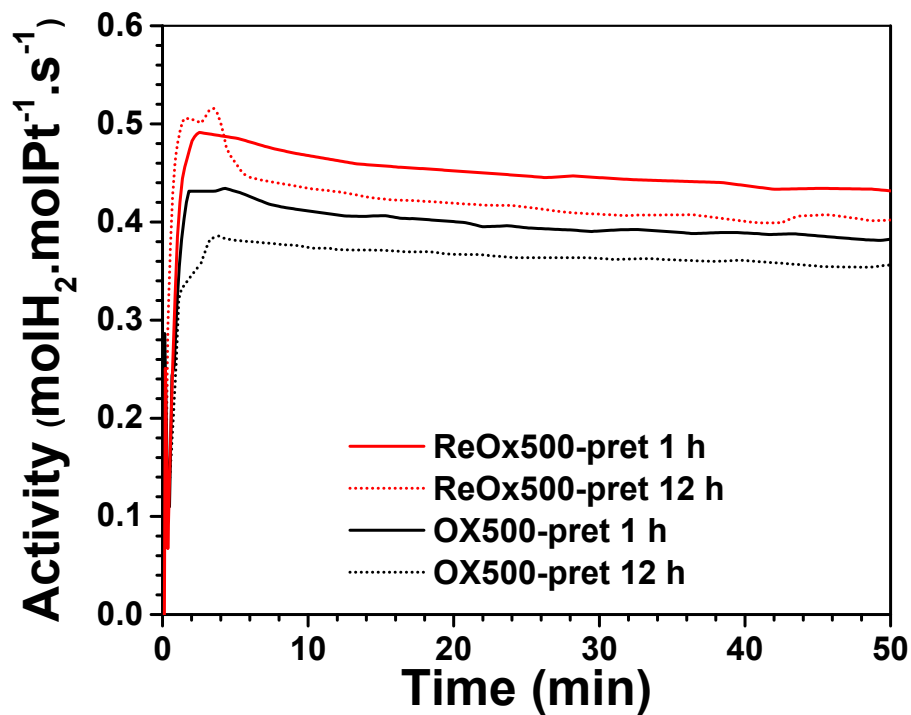


Figure S12: Evolution of molar activity with time on stream for 0.52Pt catalyst after 1 h or 12 h oxidative pretreatment at 500 °C (OX500-pret 1 h and OX500-pret 12 h) and after a first testing and oxidative post-treatment at 500 °C for 12 h (ReOx500-pret 1 h and ReOx500-pret-12 h). Reaction conditions: 230 °C, H₂O/CO/Ar/He:33.3/8.3/54.2/4.2 vol% feed, GFSV = 600 mL.min⁻¹.g_{cat}⁻¹.

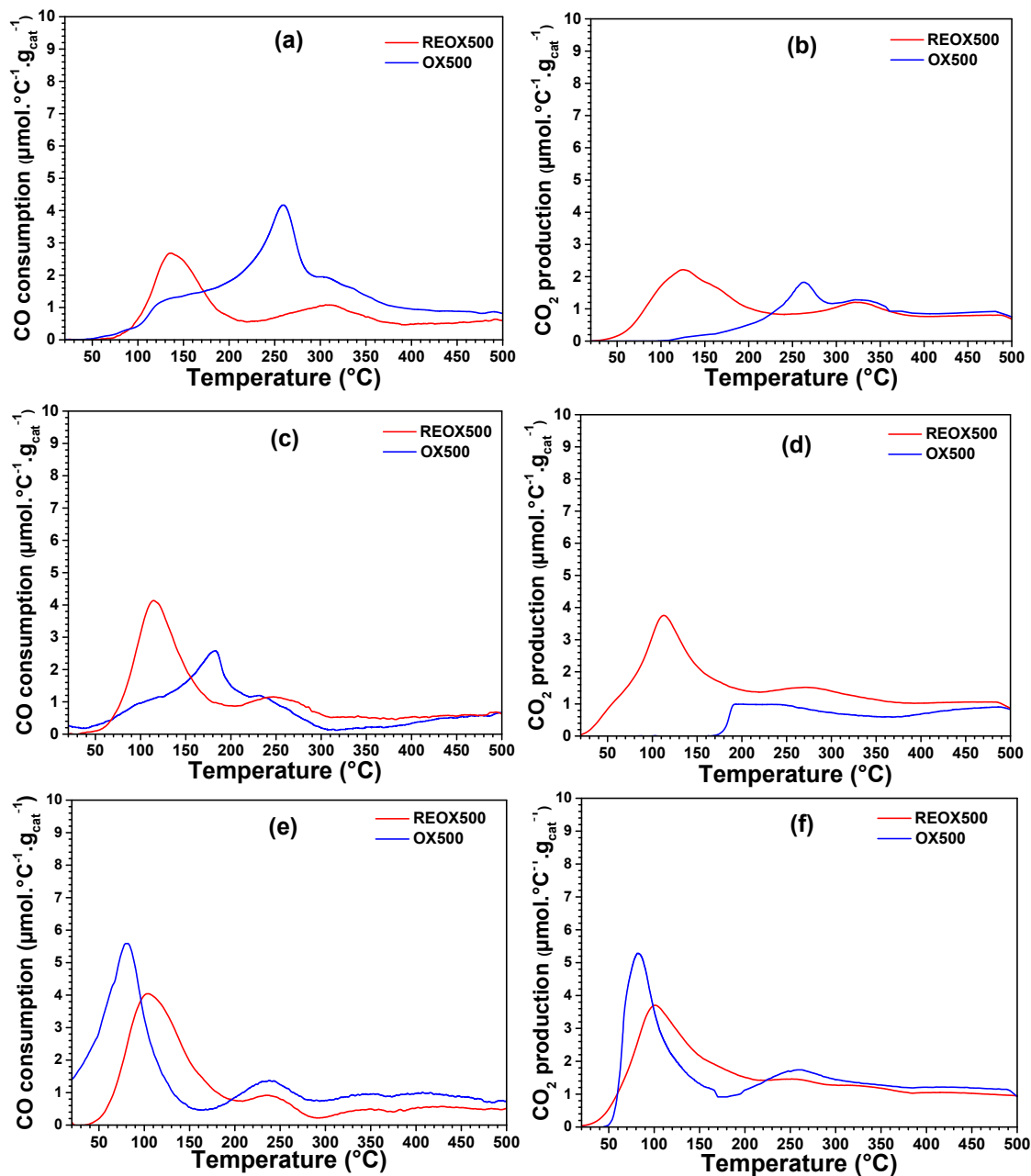


Figure S13: Evolution of CO consumption and CO_2 production with temperature during CO-TPR analysis under 1%CO/He after OX500 pretreatment and after 120 min of WGS reaction followed by ReOx500 post-treatment for (a,b) 0.10Pt, (c,d) 0.52Pt and (e,f) 1.43Pt catalysts.

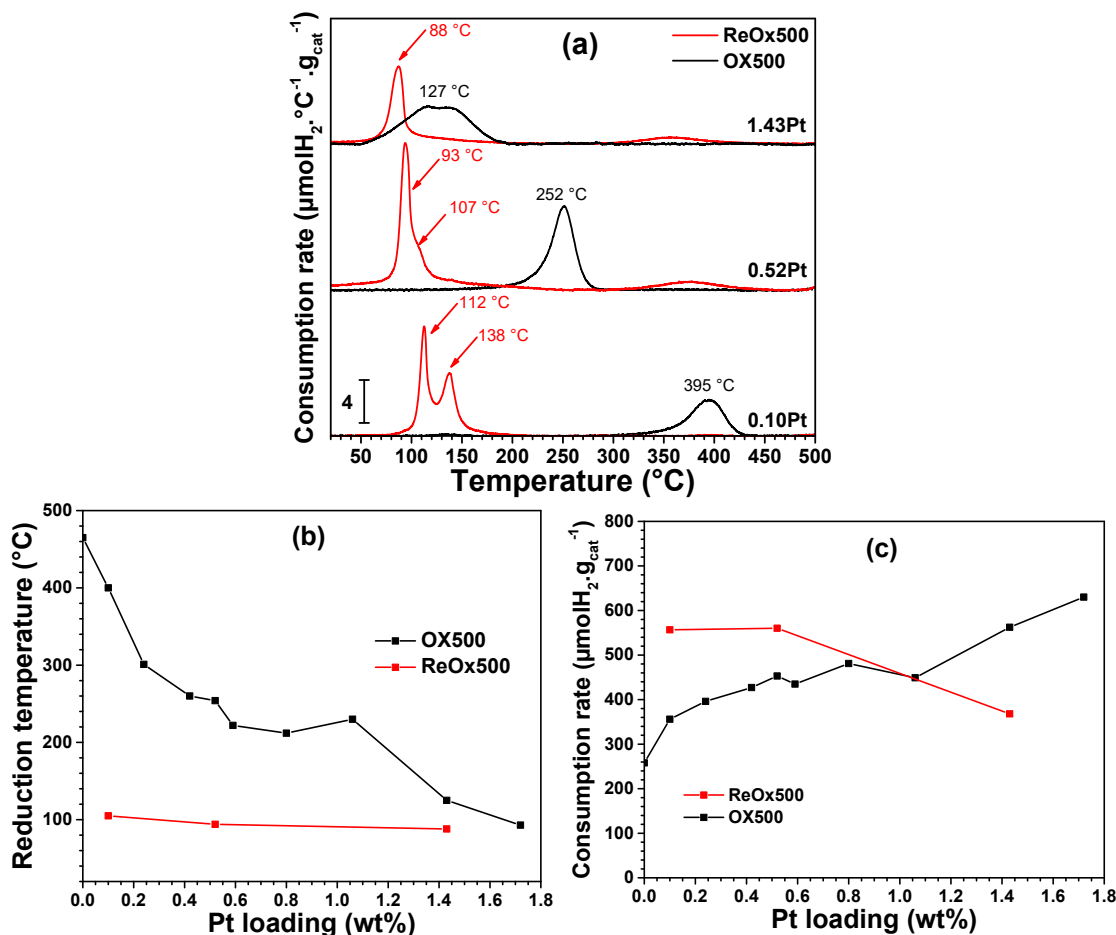


Figure S14: (a) H₂-TPR curves of 0.10Pt, 0.52Pt and 1.43Pt catalysts, (b) evolution of reduction temperature and (c) evolution of H₂ consumption rate with Pt loading after OX500 pretreatment and ReOx500 post-treatment.

H₂-TPR analysis after OX500 pretreatment and after ReOx500 post-treatment were compared: for 0.10Pt, 0.52Pt and 1.43Pt catalysts, the reduction temperature (temperature at the peak maximum) decreases after ReOx500 post-treatment especially for the LPC catalysts (Figure S12a and b). The values reached are close to that 1.43Pt catalyst after OX500 pretreatment. Furthermore, H₂ consumption is observed at room temperature for the three catalysts (Table S4). The H₂ consumption rate was compared after OX500 and ReOx500 (Figure S12c). As shown by the much lower consumption rates required for the reduction of PtO to Pt⁰ than the determined values (Table S4), it corresponds mostly to surface reduction of CeO₂. This parameter was significantly higher for 0.10Pt and 0.52Pt catalysts after ReOx500 while it was lower for the 1.43Pt catalyst. The increase in reducibility of CeO₂ suggests a higher reducibility of PtO_x species than after OX500 leading to the formation of Pt⁰ NPs capable of dissociating H₂. Thus, the PtO_x species formed upon reoxidation of Pt⁰ NPs from WGS reaction are different from those present

after the OX500 pretreatment. Despite the redispersion observed by STEM-ADF analysis, the ReOx500 post-treatment does not lead to the regeneration of PtO_x species strongly anchored to CeO₂ surface and poorly reducible, thus confirming the irreversibility of the structural modifications of Pt species.

For LPC catalysts, ReOx500 post-treatment increases the H-spillover on CeO₂ surface. Thus, it seems to increase the number of Pt⁰ NPs. However, CeO₂ sintering (decrease in surface area) could occur for HPC catalysts during WGS reaction and/or TPR measurement after ReOx500 leading to a lower reduction rate.

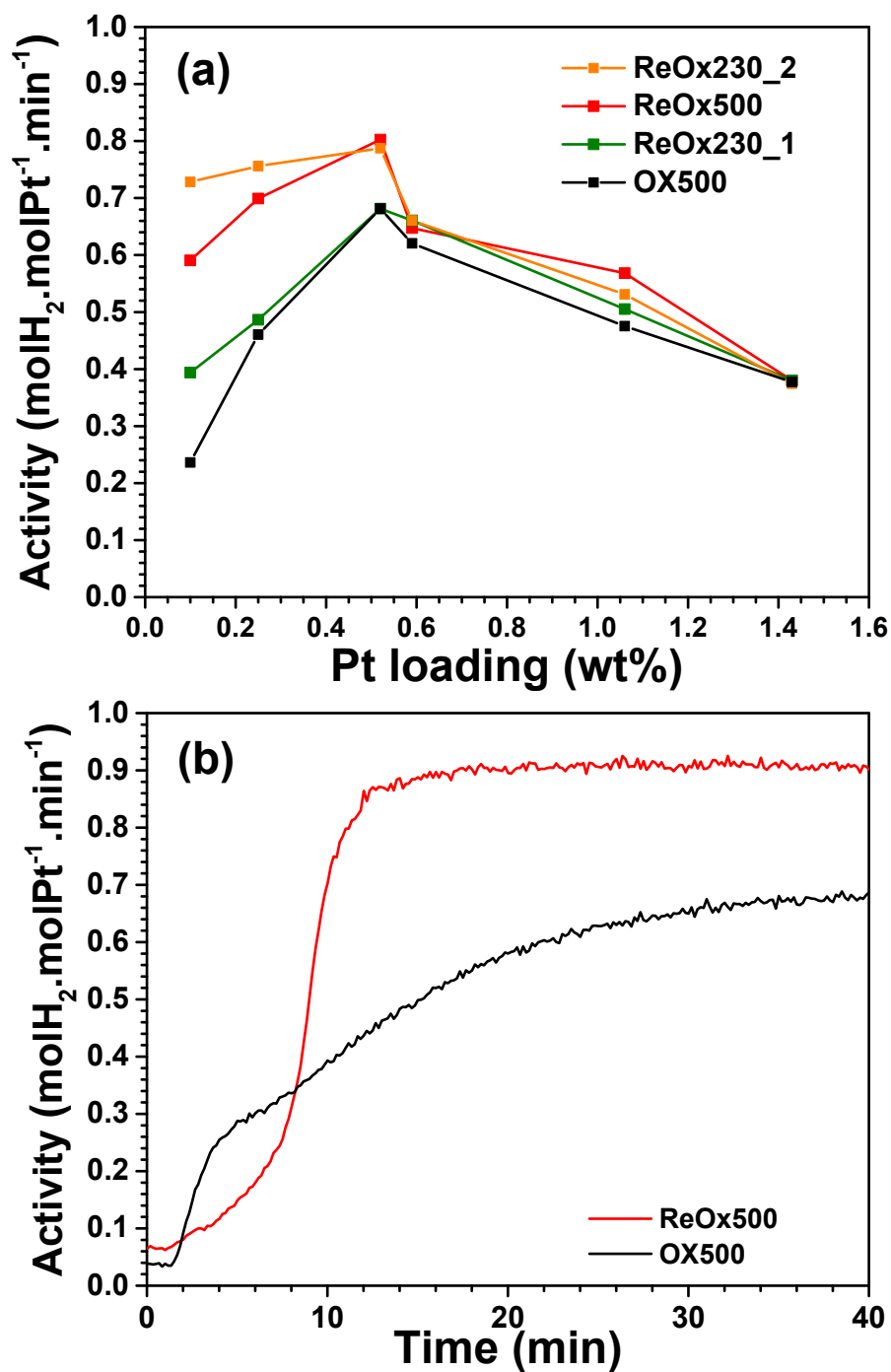


Figure S15: (a) Evolution with Pt loading of molar activity at steady state after OX500 pretreatment, after ReOx230_1, ReOx500 and ReOx230_2 post-treatments in the DRIFTS cell and (b) evolution of molar activity with time on stream for 0.52Pt catalyst after OX500 pretreatment and ReOx500 post-treatment. Reaction conditions: 230 °C, H₂O/CO/Ar/He:33.3/8.3/54.2/4.2 vol% feed, GFSV = 600 mL.min⁻¹.g_{cat}⁻¹.

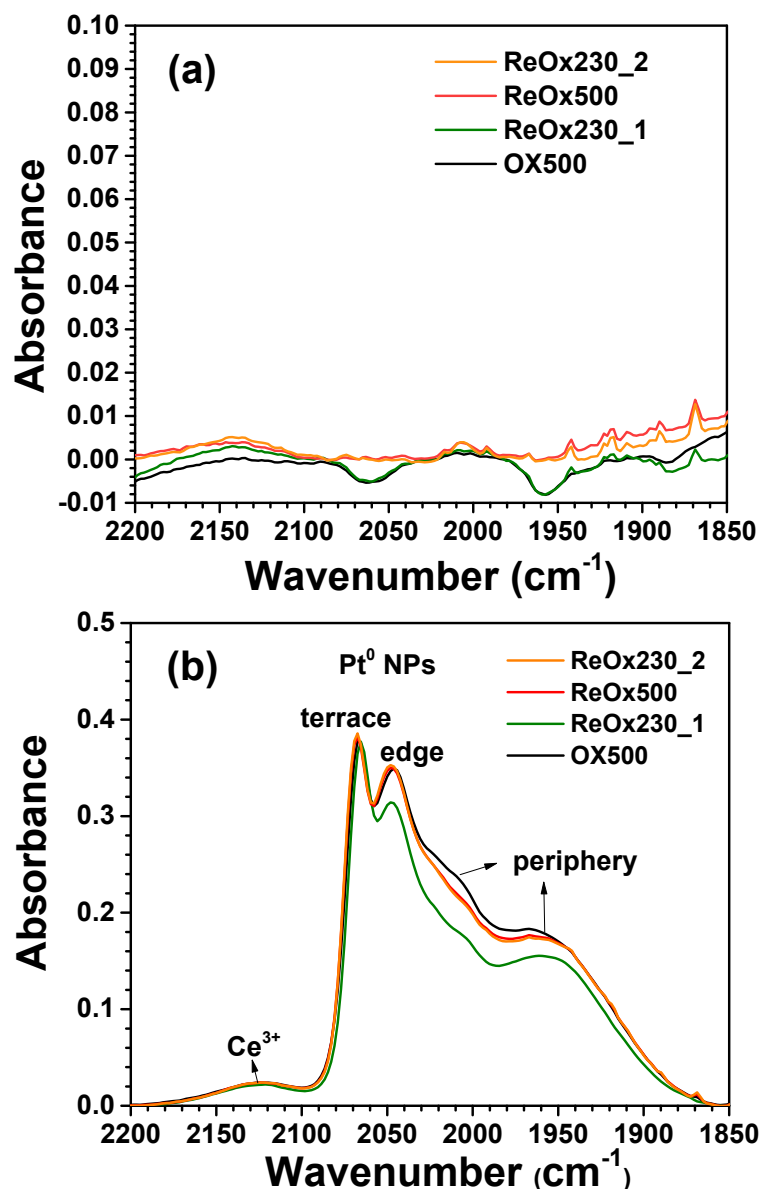


Figure S16: *operando* DRIFTS spectra between 2200 and 1850 cm⁻¹ of (a) 0.10Pt and (b) 1.43Pt catalysts recorded after OX500 pretreatment, ReOx230_1, ReOx500 and ReOx230_2 post-treatments. Reaction conditions: T=230 °C, P_{CO} = 5 mbar, P_{H2O} = 20 mbar, GHSV =1000 mL.min⁻¹.g⁻¹. The background corresponds to the spectrum of KBr powder recorded at 230 °C and the ν(CO)_{gas} signal is subtracted.

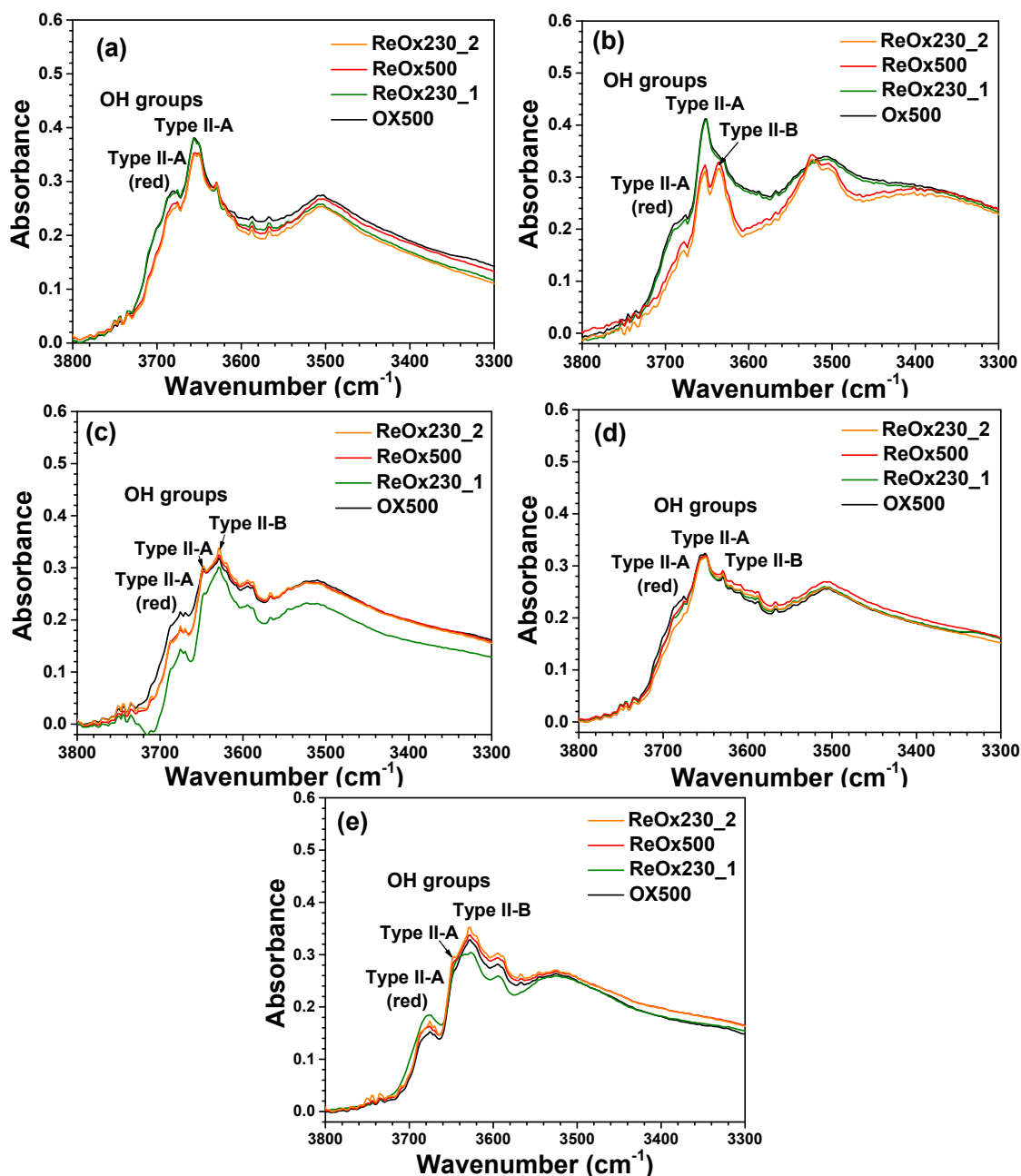


Figure S17: *operando* DRIFTS spectra between 3800 and 3100 cm⁻¹ of (a) 0.10Pt, (b) 0.25Pt, (c) 0.52Pt, (d) 1.06Pt and (e) 1.43Pt catalysts recorded after OX500 pretreatment, ReOx230_1, ReOx500 and ReOx230_2 post-treatments. Reaction conditions: T=230 °C, P_{CO} = 5 mbar, P_{H₂O} = 20 mbar, GHSV = 1000 mL.min⁻¹.g⁻¹. The background corresponds to the spectrum of KBr powder recorded at 230 °C.

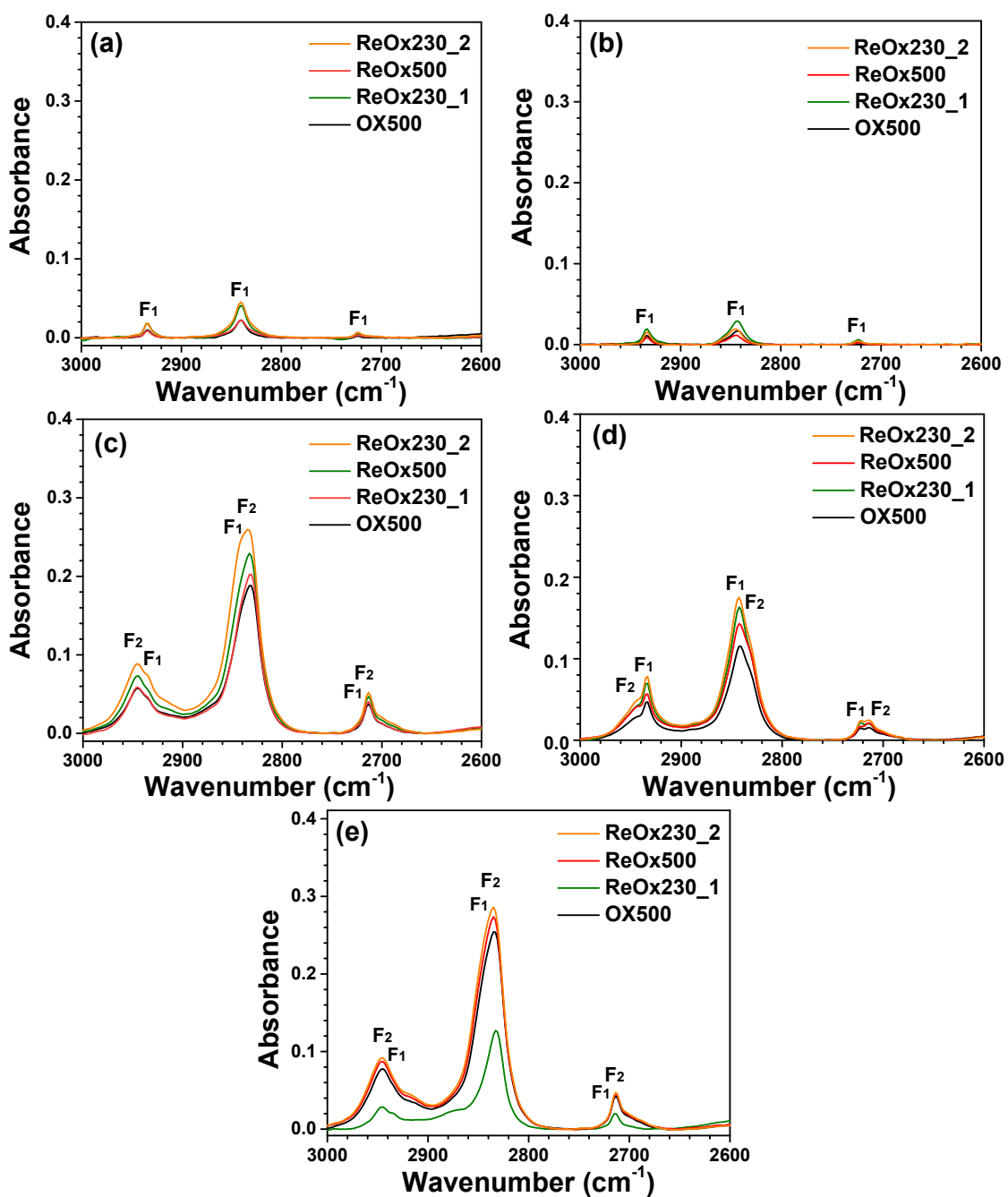


Figure S18: *operando* DRIFTS spectra between 3000 and 2600 cm^{-1} of (a) 0.10Pt, (b) 0.25Pt, (c) 0.52Pt, (d) 1.06Pt and (e) 1.43Pt catalysts recorded after OX500 pretreatment, ReOx230_1, ReOx500 and ReOx230_2 post-treatments. Reaction conditions: $T=230\text{ }^{\circ}\text{C}$, $P_{\text{CO}} = 5\text{ mbar}$, $P_{\text{H}_2\text{O}} = 20\text{ mbar}$, $\text{GHSV} = 1000\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. The background corresponds to the spectrum of KBr powder recorded at $230\text{ }^{\circ}\text{C}$. F1 and F2: bridged formates.

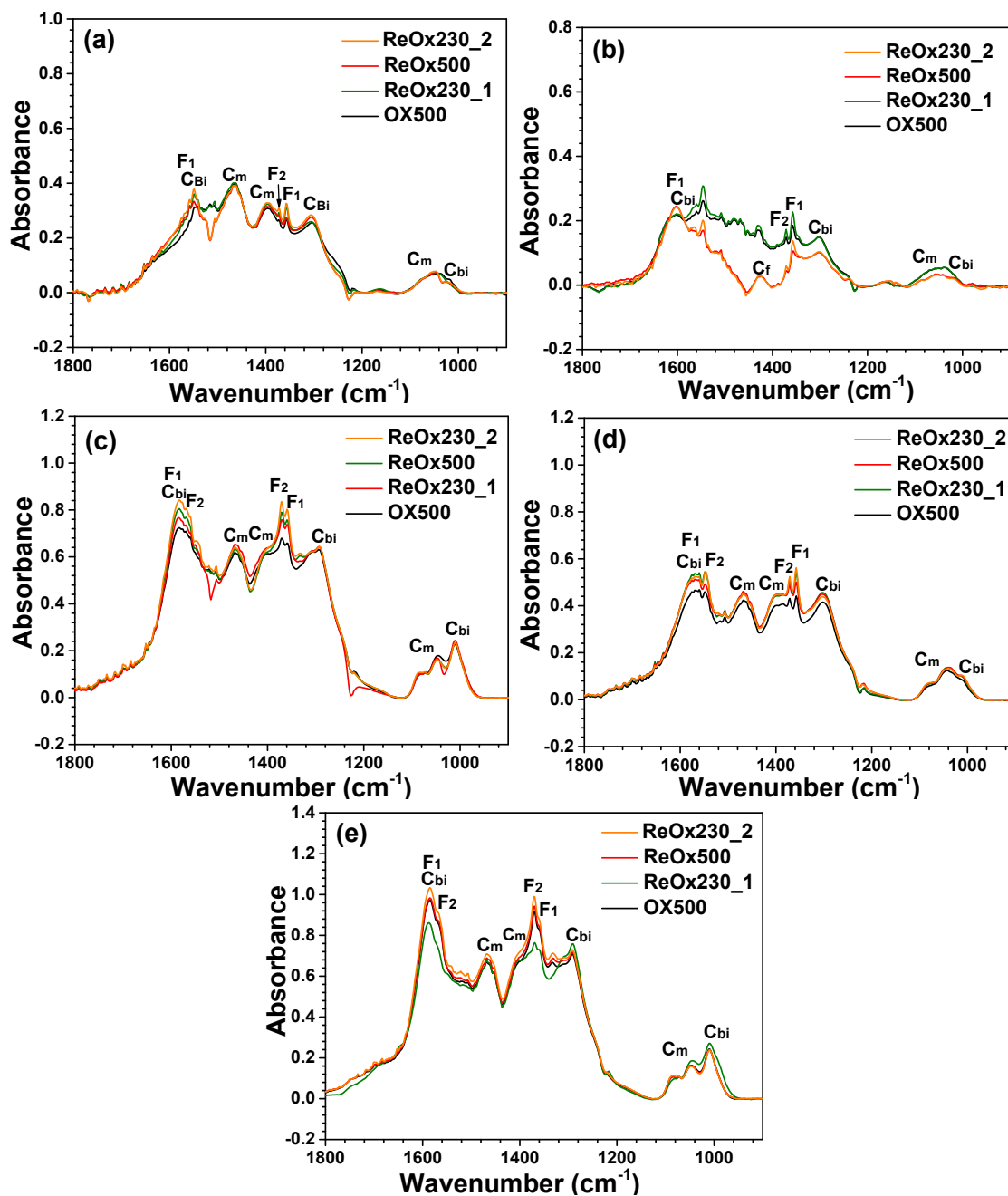


Figure S19: *operando* DRIFTS spectra between 1800 and 800 cm^{-1} of (a) 0.10Pt, (b) 0.25Pt, (c) 0.52Pt (d) 1.06Pt and (e) 1.43Pt catalysts recorded after OX500 pretreatment, ReOx230_1, ReOx500 and ReOx230_2 post-treatments. Reaction conditions: $T=230\text{ }^{\circ}\text{C}$, $P_{\text{CO}} = 5\text{ mbar}$, $P_{\text{H}_2\text{O}} = 20\text{ mbar}$, $\text{GHSV} = 1000\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. The background corresponds to the spectrum of KBr powder recorded at $230\text{ }^{\circ}\text{C}$. Cbi: bidentate carbonate, Cm: monodentate carbonate, F1 and F2: bridged formates.

Table S1: H₂ consumption rate during H₂-TPR analysis determined between RT and 500 °C and theoretical H₂ consumption to reduce PtO into Pt⁰.

Catalyst	H ₂ consumption rate (μmolH ₂ .g _{cat} ⁻¹)		
	TPR1	TPR2	PtO +H ₂ → Pt ⁰ + H ₂ O
CeO ₂	258	258	0
0.10Pt	357	491	5
0.25Pt	396	485	13
0.42Pt	427	400	22
0.52Pt	455	457	27
0.80Pt	480	463	41
1.06Pt	449	446	54
1.43Pt	562	600	73
1.72Pt	631	670	88

Table S2: Relative deviations of molar activity measured during WGS reaction at 230 °C after OX500, RED250, RED500, REDOX500 pretreatments. They are calculated from

Catalyst	Relative deviation of molar activity (%)				
	OX500	RED250	REDOX250	RED500	REDOX500
0.10Pt	7	16	20	19	18
0.59Pt	7	11	8	2	6
1.06Pt	6	4	5	2	4

the maximal activities at t_{opti} and the activities at 45 min as follows:

$$\frac{a(t_{opti}) - a(45')}{a(t_{opti})}$$

Table S3: Relative deviations (%) of molar activity measured during WGS reaction at 230 °C after ReOx230_1, ReOx500 and ReOx230 post-treatments in comparison with activity after OX500 pretreatment. They are calculated from the maximal activities at t_{opti} and the activities at 45 min as follows:

$$\frac{a_{OX500}(t_{opti}) - a_{OX500}(45')}{a_{OX500}(t_{opti})}, \frac{a_{ReOx230}(t_{opti}) - a_{OX500}(t_{opti})}{a_{OX500}(t_{opti})} \text{ and } \frac{a_{ReOx230}(45') - a_{OX500}(45')}{a_{OX500}(45')}$$

$$\frac{a_{ReOx500}(t_{opti}) - a_{OX500}(t_{opti})}{a_{OX500}(t_{opti})} \text{ and } \frac{a_{ReOx500}(45') - a_{OX500}(45')}{a_{OX500}(45')}$$

Catalyst	Relative deviation of the molar activity (%)							
	OX500		ReOx230_1		ReOx500		ReOx230_2	
	45'	t_{opti}	45'	t_{opti}	45'	t_{opti}	45'	t_{opti}
0.10Pt	-6	0	0	41	27	38	26	
0.25Pt	-11	-1	-2	31	25	28	26	
0.42Pt	-7	0	-2	25	8	13	6	
0.52Pt	-10	-3	1	29	9	7	9	
0.59Pt	-5	-3	0	18	8	9	9	
1.06Pt	-8	-3	0	1	3	3	1	
1.43Pt	-6	-5	-1	-7	-6	-8	-8	
1.72Pt	-4	-6	-6	-13	-17	-19	-19	

Table S4: H₂ consumption rates at room temperature (RT) and total values determined between RT and 500 °C during H₂-TPR analysis. They are calculated from the integration of the consumption rate.

Catalyst	Consumption rate ($\mu\text{molH}_2\cdot\text{g}_{\text{cat}}^{-1}$)				
	PtO +H ₂ → Pt ⁰ + H ₂ O	RT		Total	
		OX500	ReOx500	OX500	ReOx500
0.10Pt	5	<1	46	357	510
0.52Pt	27	<1	3	455	560
1.43Pt	73	6	7	562	367