

Supplementary Materials

1 Dynamic operation window

Figure S1 displays the results of dynamic operation window test over the aged M/CZL catalysts (M = Pt, Pd and Rh). Compared with the fresh catalysts, the platforms in CO/N₂ signal and NO operation windows become narrow in all reaction conditions due to the sintering of active species. Rh/CZL-a shows the widest dynamic operation window.

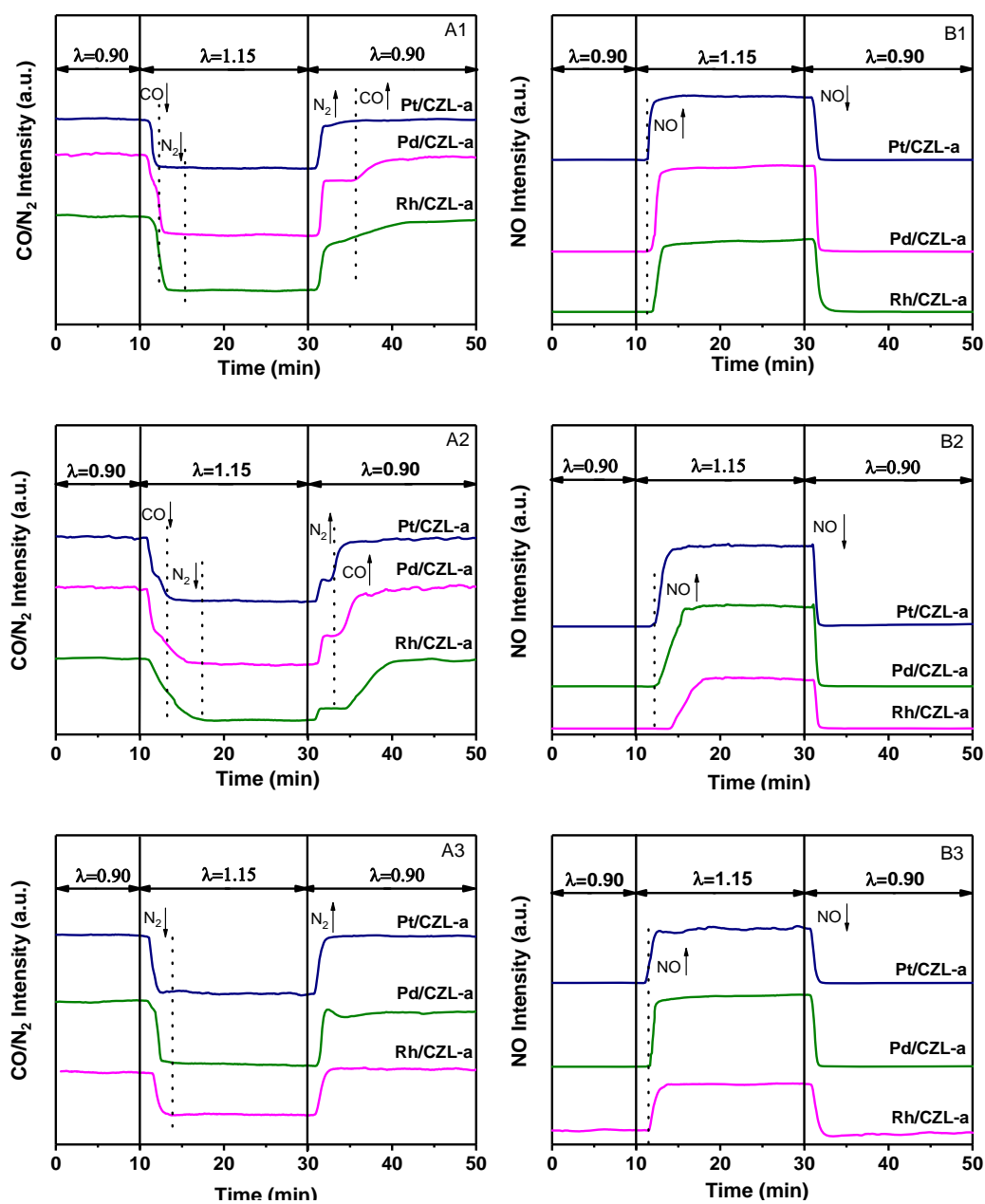


Fig. S1 Time-course curves of CO/N₂, NO over the aged M/CZL catalysts (M = Pt, Pd and Rh) in HC-CO-NO_x-O₂ condition (A1, B1), CO-NO_x-O₂ condition (A2, B2) and HC-NO_x-O₂ condition (A3, B3)

2 XPS analysis

The Ce 3d spectrum exhibits eight characteristic peaks. The Ce^{3+} $3d_{3/2}$ and $3d_{5/2}$ peaks are observed at 902.3–903.1 eV (assigned as U') and 883.8–885.1 eV (assigned as V'), respectively. The peaks attributed to U (900.3–900.8 eV), U'' (906.9–907.4 eV) and U''' (916.2–916.4 eV) arise from Ce^{4+} $3d_{3/2}$. The peaks donated as V (881.8–882.2 eV), V'' (888.2–888.8 eV) and V''' (897.7–898.1 eV) arise from Ce^{4+} $3d_{5/2}$.

The peaks located at 529.2–529.8 eV are assigned to the lattice oxygen (labeled as O_{latt}) while the peaks at around 531.2–531.5 eV are attributed to the surface adsorbed oxygen (labeled as O_{ads}) such as O^- or O_2^{2-} taking the forms of hydroxyl OH^- and the adsorbed molecular water.

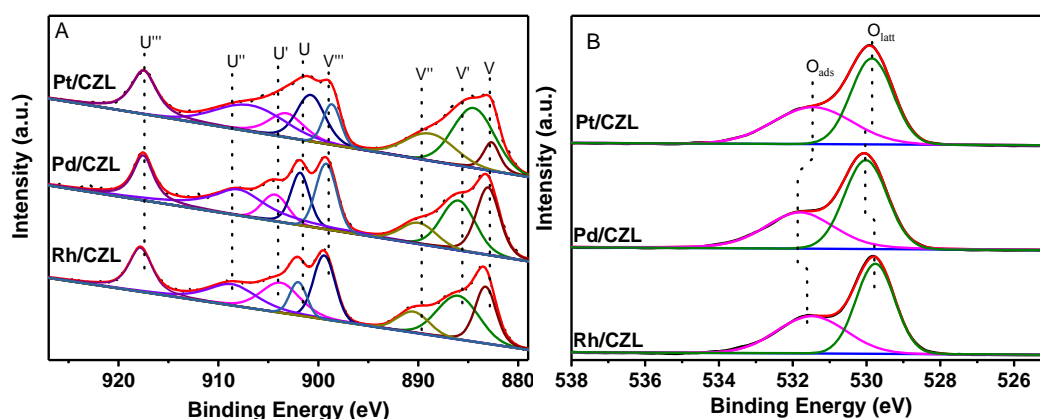


Fig. S2 Ce 3d (A), O 1s (B) XPS spectra of the fresh M/CZL catalysts (M = Pt, Pd and Rh)

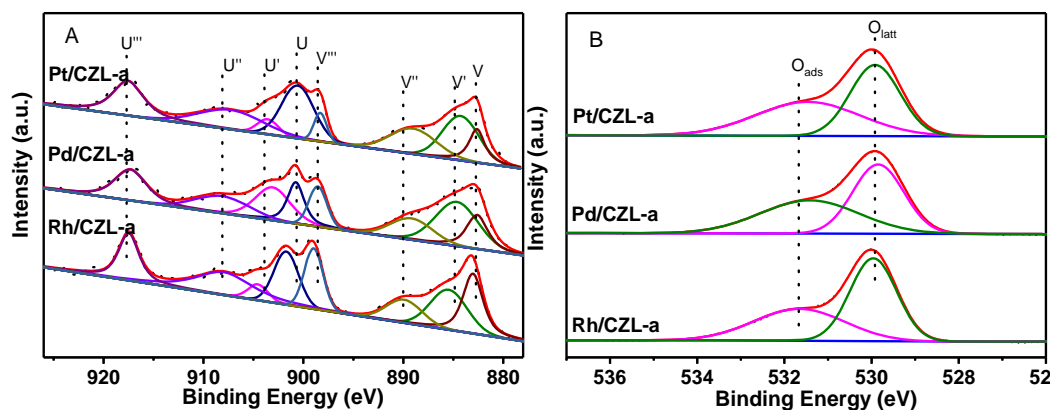


Fig. S3 Ce 3d (A), O 1s (B) XPS spectra of the aged M/CZL catalysts (M = Pt, Pd and Rh)

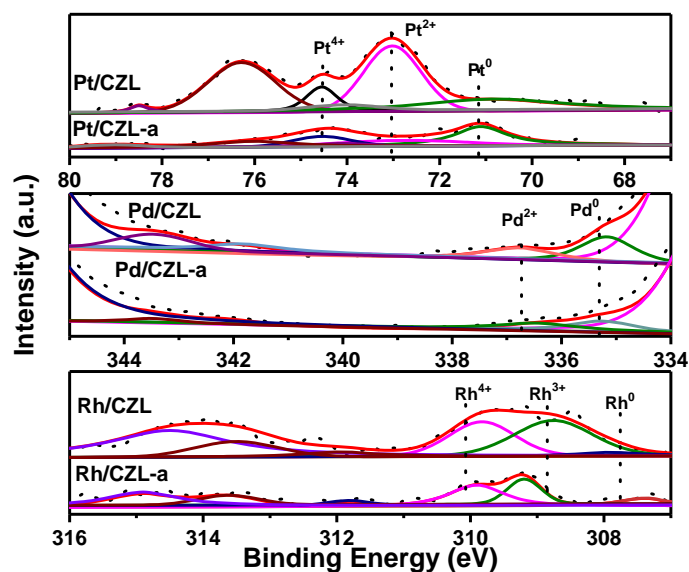


Fig. S4 Pt 4f, Pd 3d and Rh 3d XPS spectra of fresh and aged M/CZL catalysts (M = Pt, Pd and Rh)

3 H₂-TPR

Table S1 H₂ consumption of H₂-TPR peaks for fresh M/CZL catalysts (M=Pt, Pd and Rh)

Catalyst	peak α		peak β		Total H ₂ cons. ($\mu\text{mol/g-cat}$)	Theoretical value ^{a)} ($\mu\text{mol/g-cat}$)
	Tem.	H ₂ cons.	Tem.	H ₂ cons.		
	(°C)	($\mu\text{mol/g-cat}$)	(°C)	($\mu\text{mol/g-cat}$)		
Pt/CZL	23	390.3	53	217.0	607.3	25.6–51.3
Pd/CZL	96	325.9	105	171.4	497.3	47
Rh/CZL	93	228.9	135	165.9	394.8	72.9–97.2

Notes: a) The Theoretical value is defined as the hydrogen consumption for reducing the PMO_x to PM^0 , and it is calibrated by the quantitative reduction of CuO to the metallic copper

4 Chemical composition

Table S2 Surface elemental composition of fresh and aged M/CZL catalysts (M=Pt, Pd and Rh)

Catalyst	Surface composition (at. %)				
	Ce 3d	Zr 3d	La 3d	O 1s	M
Pt/CZL	4.5	13.2	1.4	54.3	0.14
Pd/CZL	4.5	12.9	1.3	53.0	0.14
Rh/CZL	4.6	13.3	1.4	55.3	0.17
Pt/CZL-a	3.8	13.2	4.2	57.8	0.08
Pd/CZL-a	3.8	12.6	3.8	56.2	0.14
Rh/CZL-a	4.0	12.7	3.1	52.5	0.10

5 HR-TEM and EDS mapping

Figure S5 shows the HR-TEM images and STEM-EDS mapping analysis of aged Pt/CZL-a, Pd/CZL-a and Rh/CZL-a catalysts calcined at 1100 °C. It could be seen that the CZL mixed oxides are obviously sintered in all catalysts. The PM nanoparticles suffer from the agglomeration and the particle size is significantly increased, especially in Pt/CZL-a catalyst, which is also confirmed by the EDS mapping. The signal of Pt is gathered, indicating the undesirable distribution of PtO_x species.

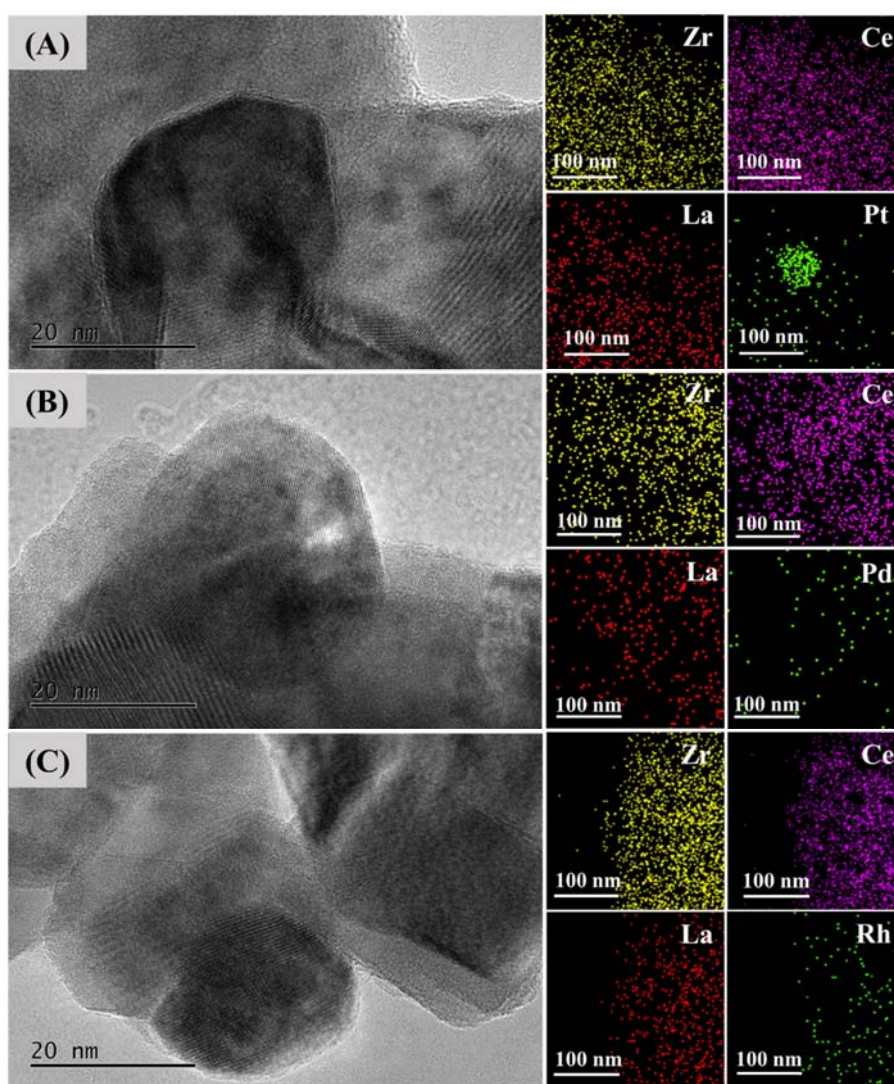


Fig. S5 HRTEM images and EDS elemental mapping images of catalysts (A: Pt/CZL-a, B: Pd/CZL-a, C: Rh/CZL-a)

6 CO adsorption

For the DRIFTS spectra in Fig. S6, Pt/CZL and Pt/CZL-a catalysts show a linear CO peak at 2050 cm^{-1} . Pd/CZL and Pd/CZL-a catalysts show a bridge carbonyl adsorbed on Pd sites at 1985 cm^{-1} and an atop carbonyl adsorbed on Pd at 2085 cm^{-1} . Rh/CZL and Rh/CZL-a catalysts show geminal dicarbonyl peak at 2085 cm^{-1} and 2010 cm^{-1} and a linear CO peak at 2050 cm^{-1} . Compared with the fresh catalysts, the peak intensity in aged M/CZL catalysts decrease obviously, furthermore, the precious metals dispersion of aged catalysts measured at room temperature drop sharply, the sequence are as follows: Rh/CZL-a(14%) > Pd/CZL-a (6.2%) > Pt/CZL-a (2.1%), which suggests the aggregation of PMO_x species. Especially for the Pt/CZL-a catalyst, the CO adsorption peak at 2055 cm^{-1} almost disappears, moreover, the precious metal dispersion of Pt/CZL decreases from 59.4% to 2.1%.

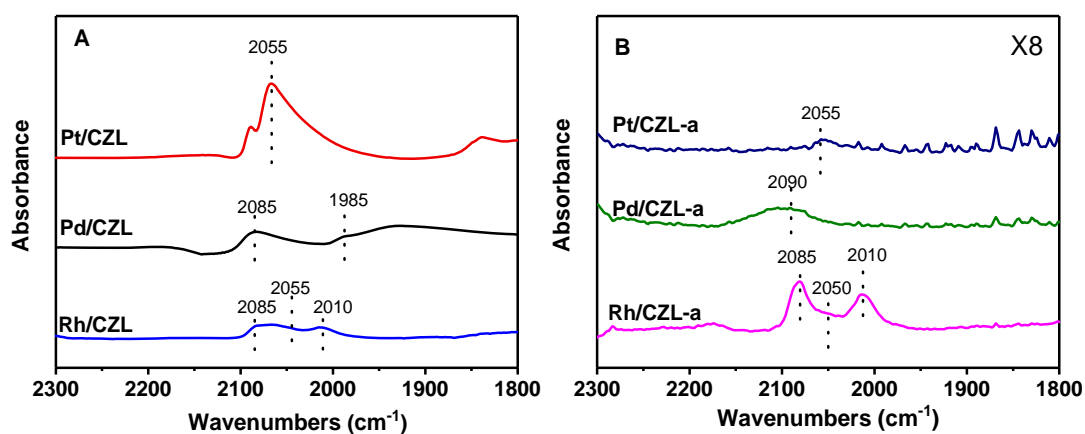


Fig. S6 CO adsorption DRIFTS spectra of M/CZL catalyst (M = Pt, Pd and Rh): (A) fresh catalysts; (B) aged catalysts