

Supporting Information

The Electrostatic Field Effect on Catalytic Properties of Platinum Clusters Confined in Zeolite for Hydrogenation

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Table S1. The surface area and pore volumes of the samples

Samples	BET Surface Area (m ² ·g ⁻¹)	External Surface Area (t-Plot, m ² ·g ⁻¹)	Micropore volume (cm ³ ·g ⁻¹) ¹⁾	Mesopore volume (cm ³ ·g ⁻¹) ¹⁾
NaX	682	41	0.2997	0.0301
Pt _m /NaX	635	40	0.2779	0.0325
Pt _n @NaX	582	34	0.1498	0.0435

Table S2. The composition of the samples measured by X-ray fluorescence (XRF) analysis.

Catalysts	SiO ₂	Al ₂ O ₃	Na ₂ O	Cs ₂ O	CaO	La ₂ O ₃	Exchanging degree (%)
Pt _m /NaX	50.97	31.90	15.50	--	--	--	--
Pt _m /CsX	36.13	23.03	3.37	37.02	--	--	70.9
Pt _m /CaX	51.62	31.75	4.32	--	11.7	--	72.1
					3		
Pt _m /LaX	50.34	29.85	4.14	--	--	15.14	67.7

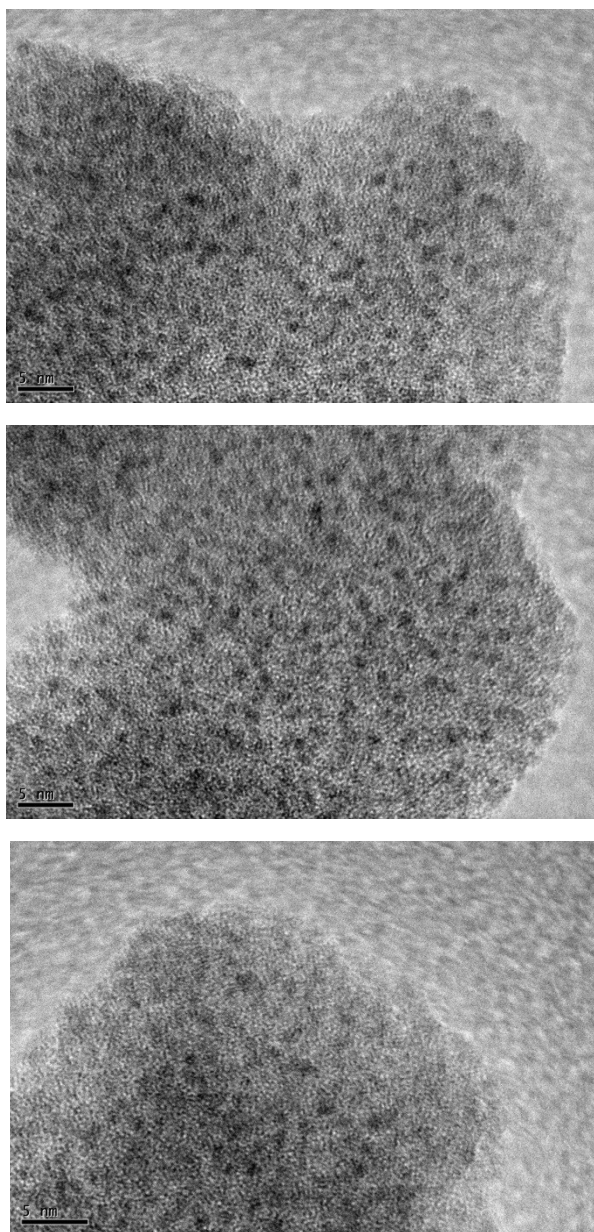


Figure S1. The results of HR-TEM images for Pt_n@NaX in different areas.

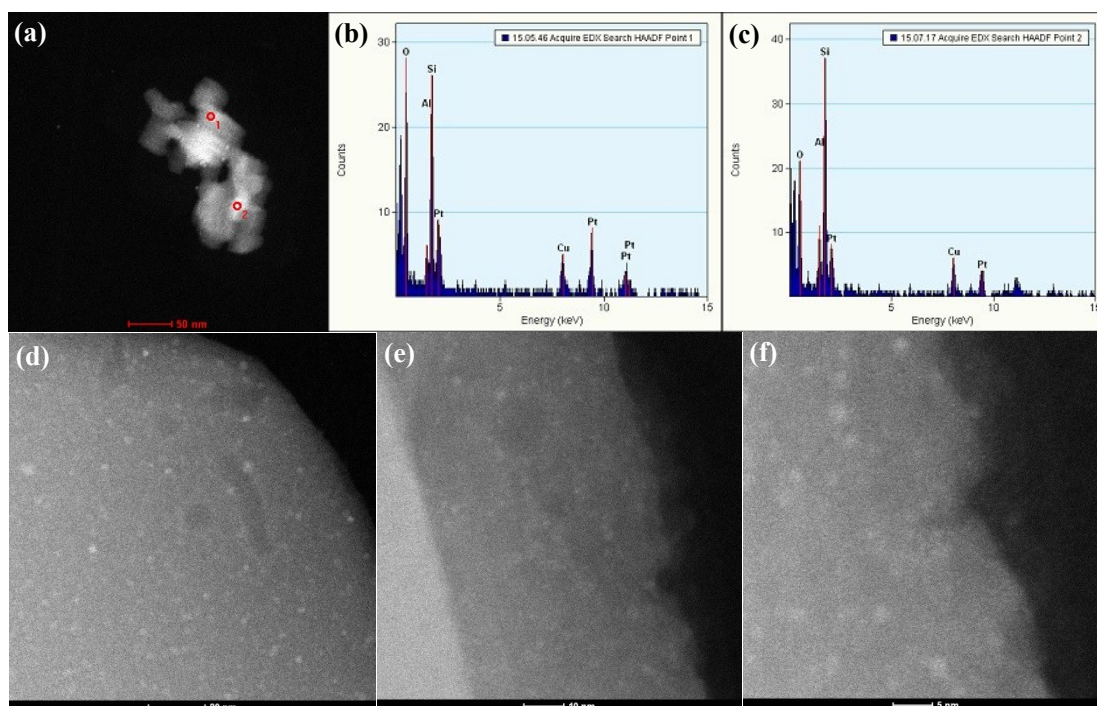


Figure S2. The HAADF-STEM results of $\text{Pt}_n\text{@NaX}$ (a) EDX spectra in area 1 (b) and area 2 (c), (d) (e) (f) Pt_m/NaX .

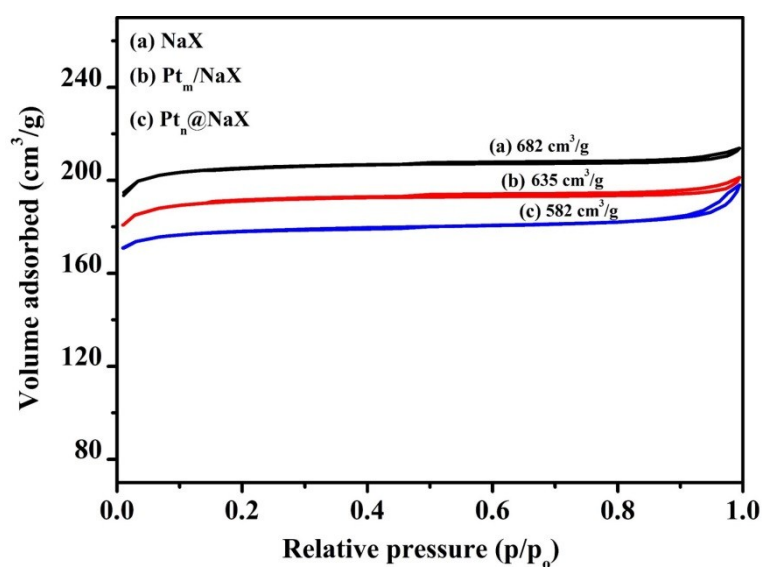


Figure S3. The N_2 adsorption/desorption isotherms of (a) NaX, (b) Pt_m/NaX , (c) $\text{Pt}_n\text{@NaX}$. (The N_2 adsorption/desorption isotherms of the three samples all display typical Langmuir-type curve (I-type) and their shapes are the same).

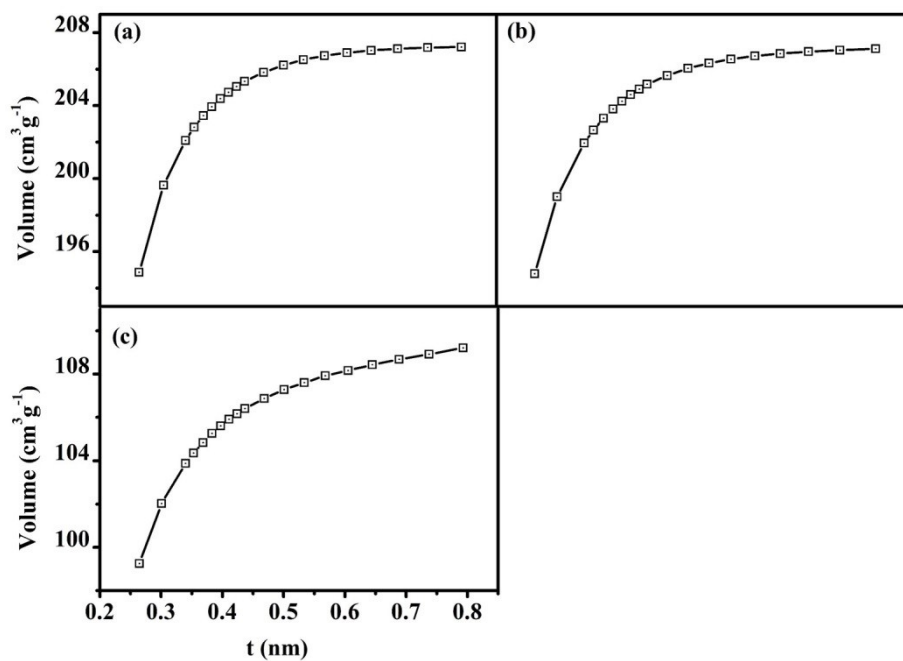


Figure S4. The t-plot curves from N₂-adsorption for (a) NaX, (b) Pt_m/NaX, (c) Pt_n@NaX.

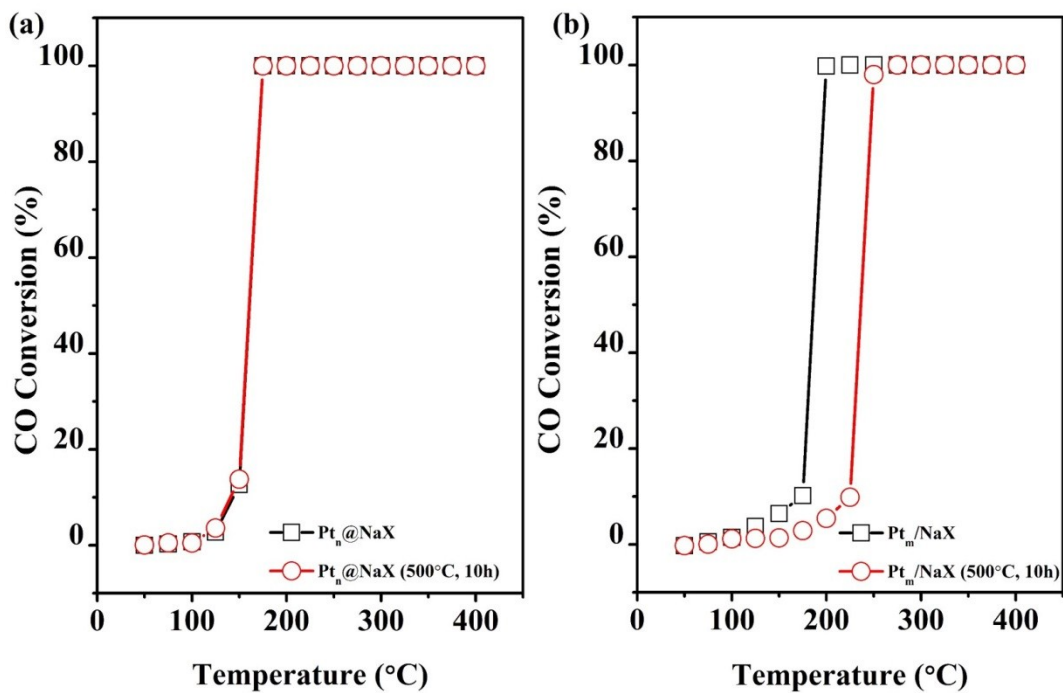


Figure S5. (a) The CO conversion over Pt_n@NaX and (b) Pt_m/NaX after the prolonged time of 10 h reaction at 500°C.

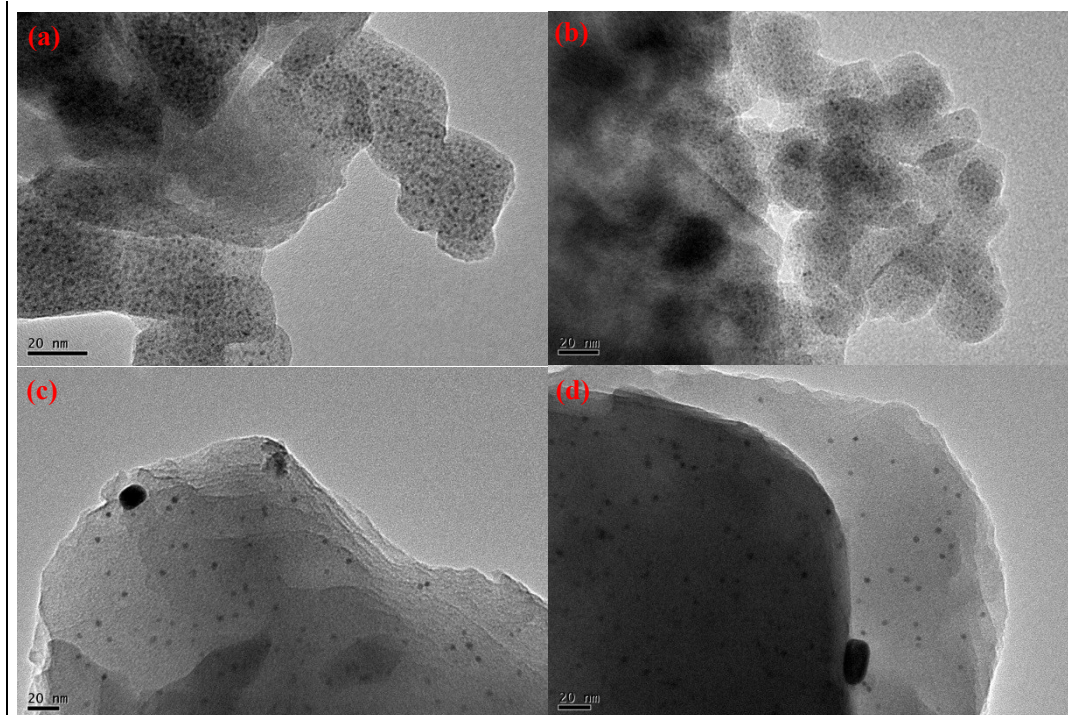


Figure S6. (a), (b): The HR-TEM images for Pt_n@NaX after the prolonged time of 10 h reaction at 600°C in different areas; (c), (d): The HR-TEM images for Pt_m/NaX after the prolonged time of 10 h reaction at 600°C in different areas.

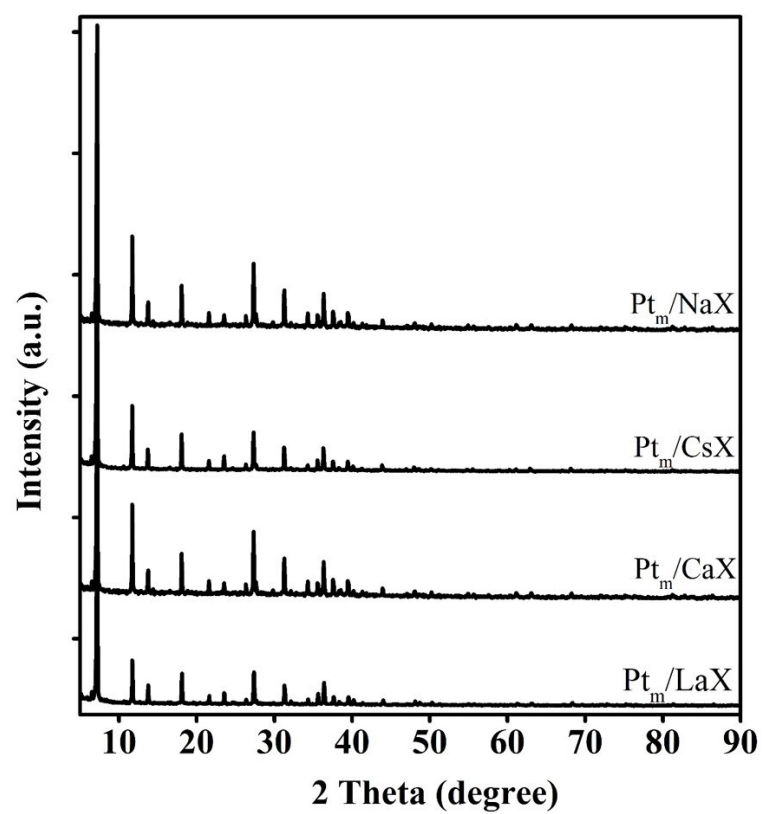


Figure S7. The results of X-ray diffraction patterns of Pt_m/MX (M = Na⁺, Cs⁺, Ca²⁺, La³⁺).

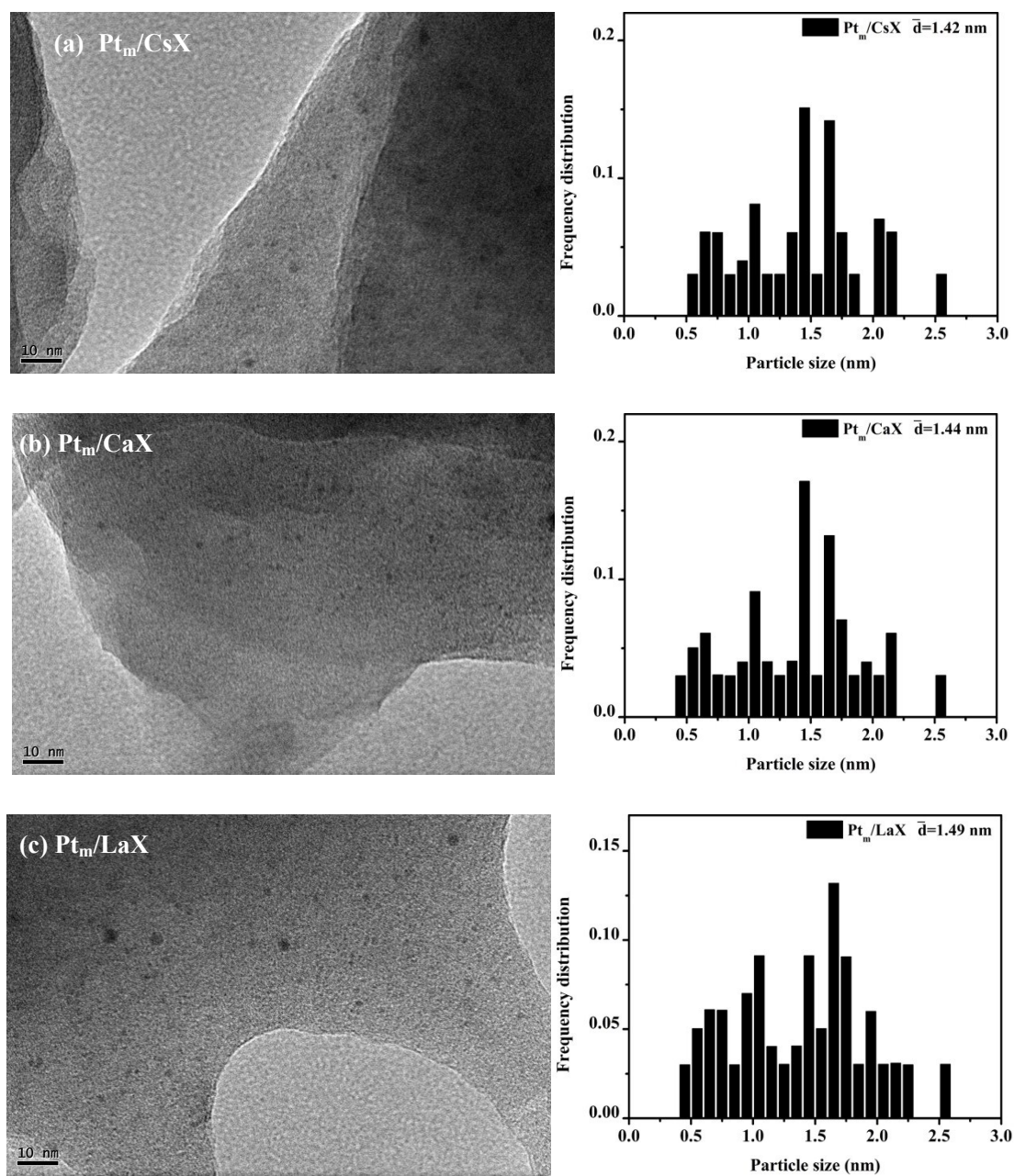


Figure S8. The results of HR-TEM images of (a) Pt_m/CsX, (b) Pt_m/CaX, (c) Pt_m/LaX.

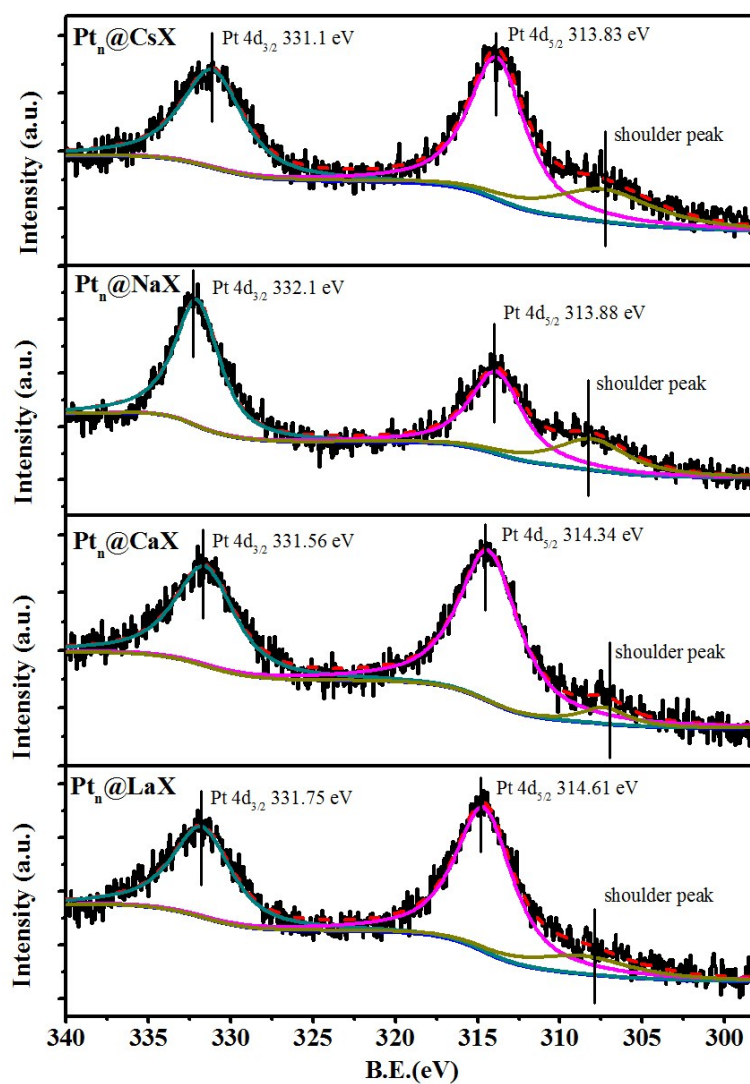


Figure S9. The Pt4d in-situ XPS results of Pt_n@MX (M=Cs⁺, Na⁺, Ca²⁺, La³⁺).

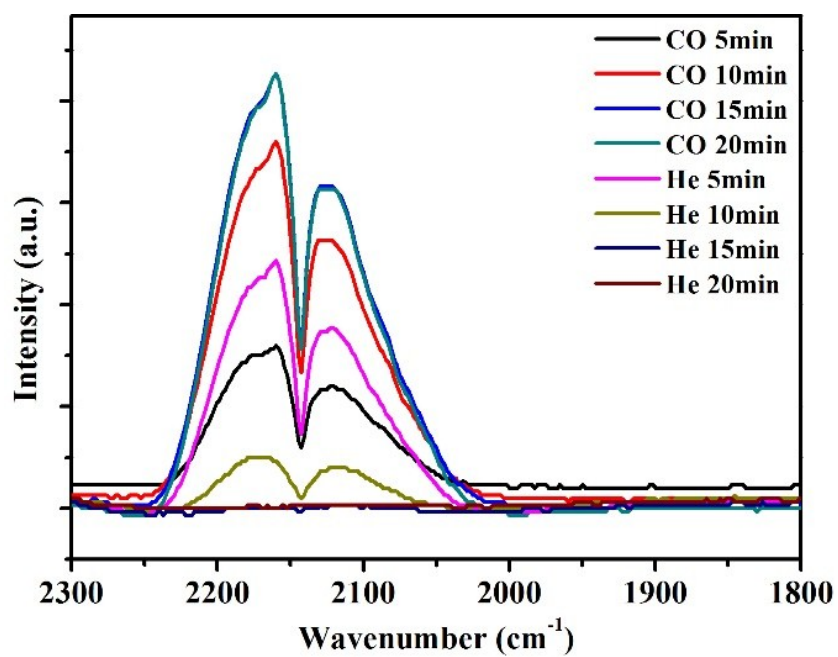


Figure S10. The in-situ DRIFTS of CO adsorption on pure NaX zeolite crystals.

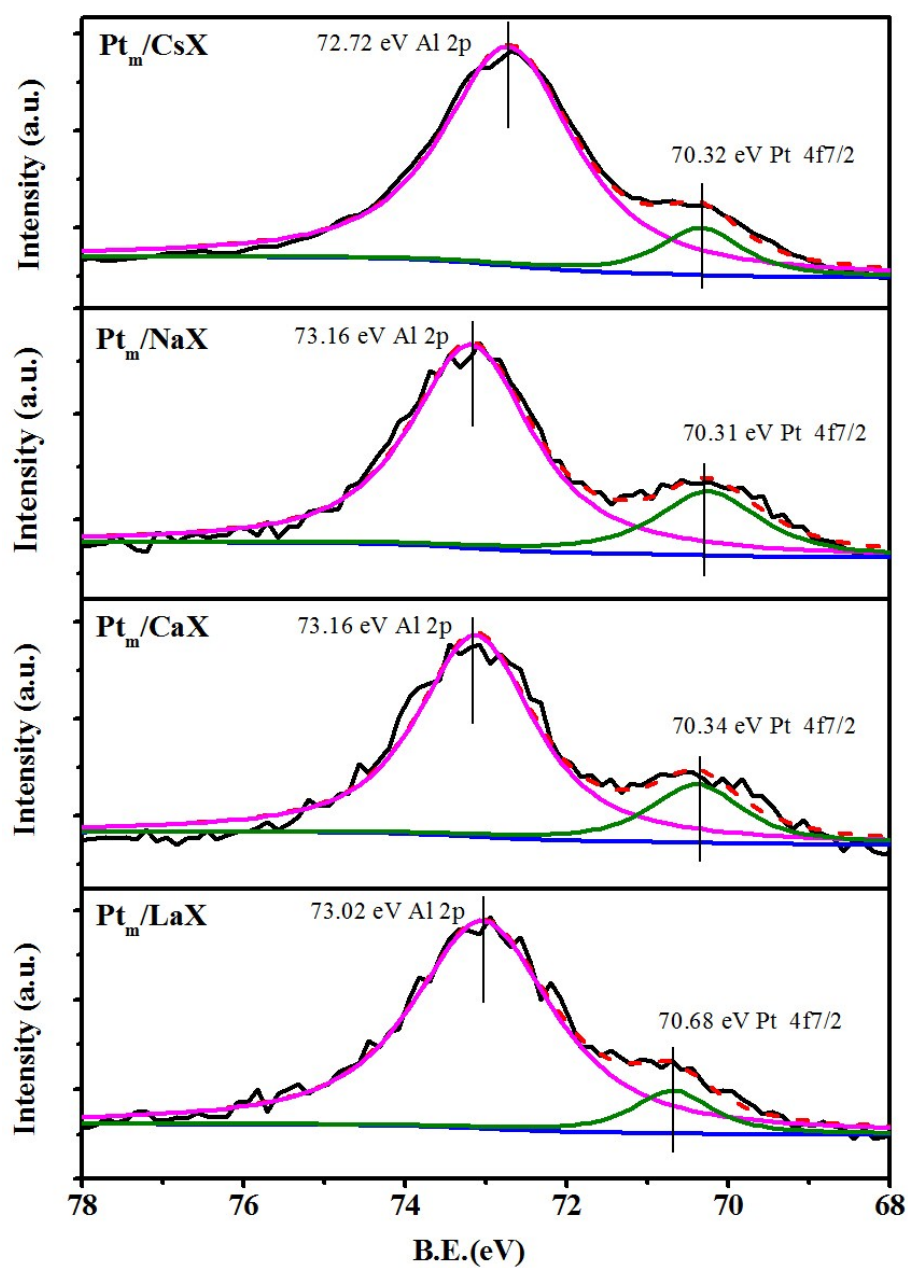


Figure S11. The Pt4f in-situ XPS results of Pt_m/MX (M=Cs⁺, Na⁺, Ca²⁺, La³⁺)

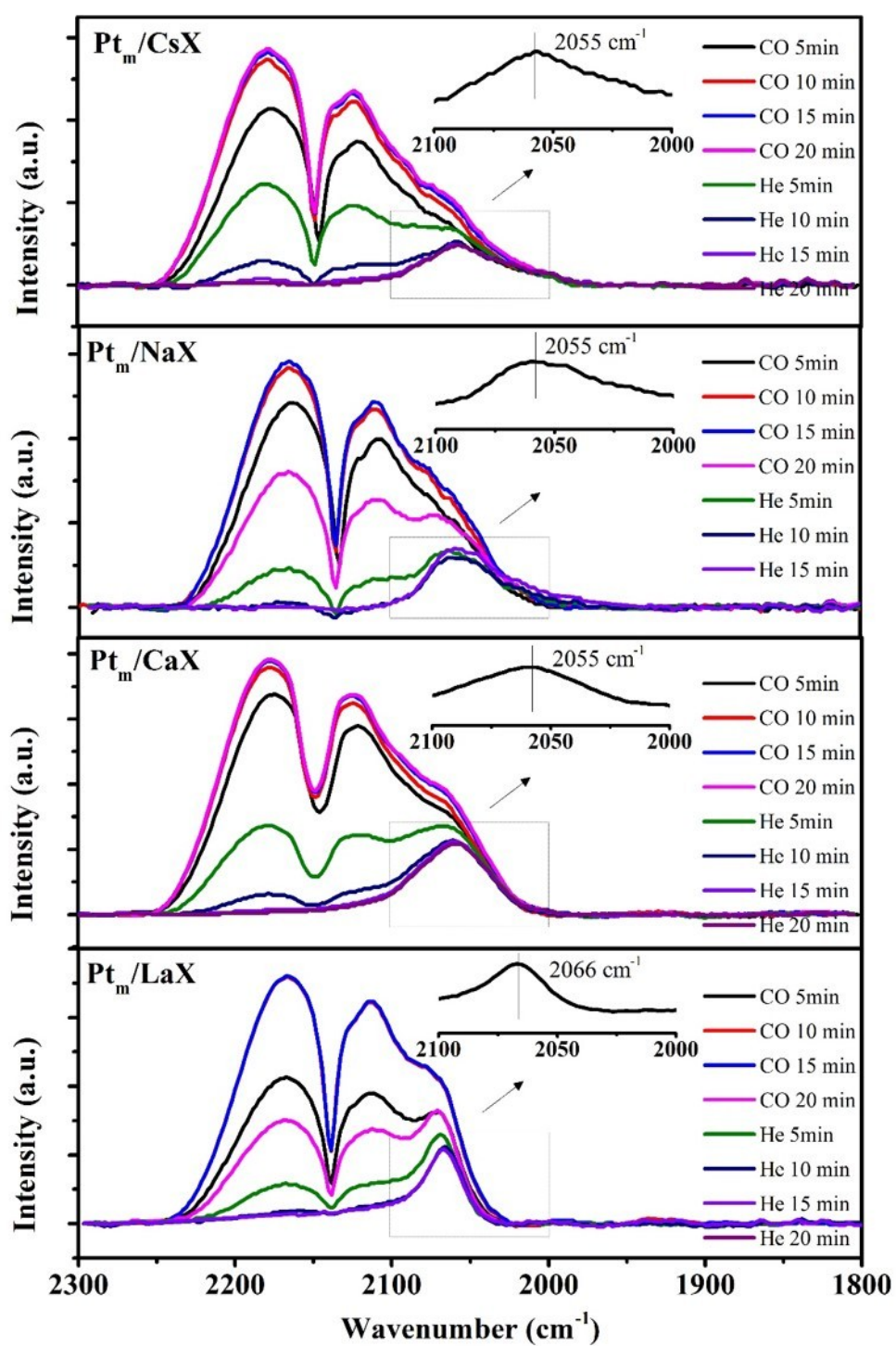


Figure S12. The in-situ DRIFTS of CO adsorption on Pt_m/MX (M=Na⁺, Cs⁺, Ca²⁺ or La³⁺) after the adsorption of CO in 25 mL·min⁻¹ for 10 min and then purged in 50 mL·min⁻¹ flowing He for various times.

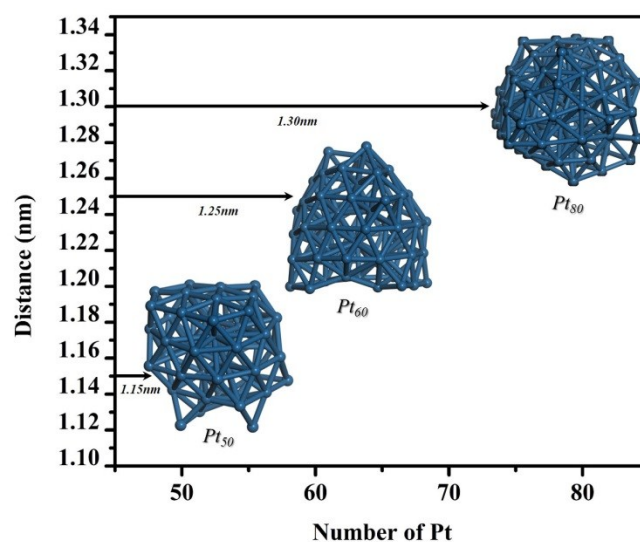


Figure S13. The optimized structure and size of the platinum clusters with different platinum atoms (Pt_{50} , Pt_{60} , Pt_{80}) by VASP using DFT calculations.

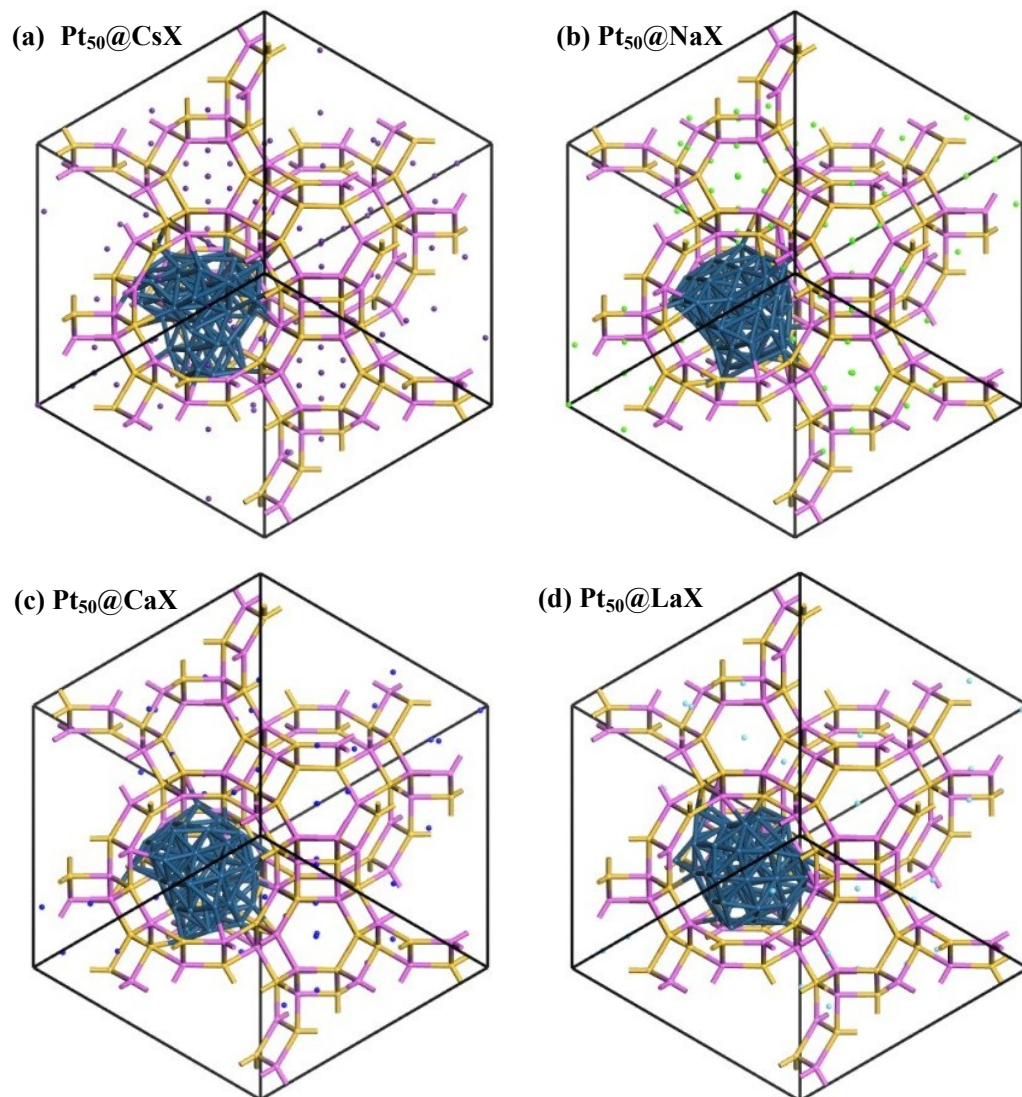


Figure S14. The optimized structures of the four models (a) $\text{Pt}_{50}@\text{CsX}$, (b) $\text{Pt}_{50}@\text{NaX}$, (c) $\text{Pt}_{50}@\text{CaX}$, (d) $\text{Pt}_{50}@\text{LaX}$.

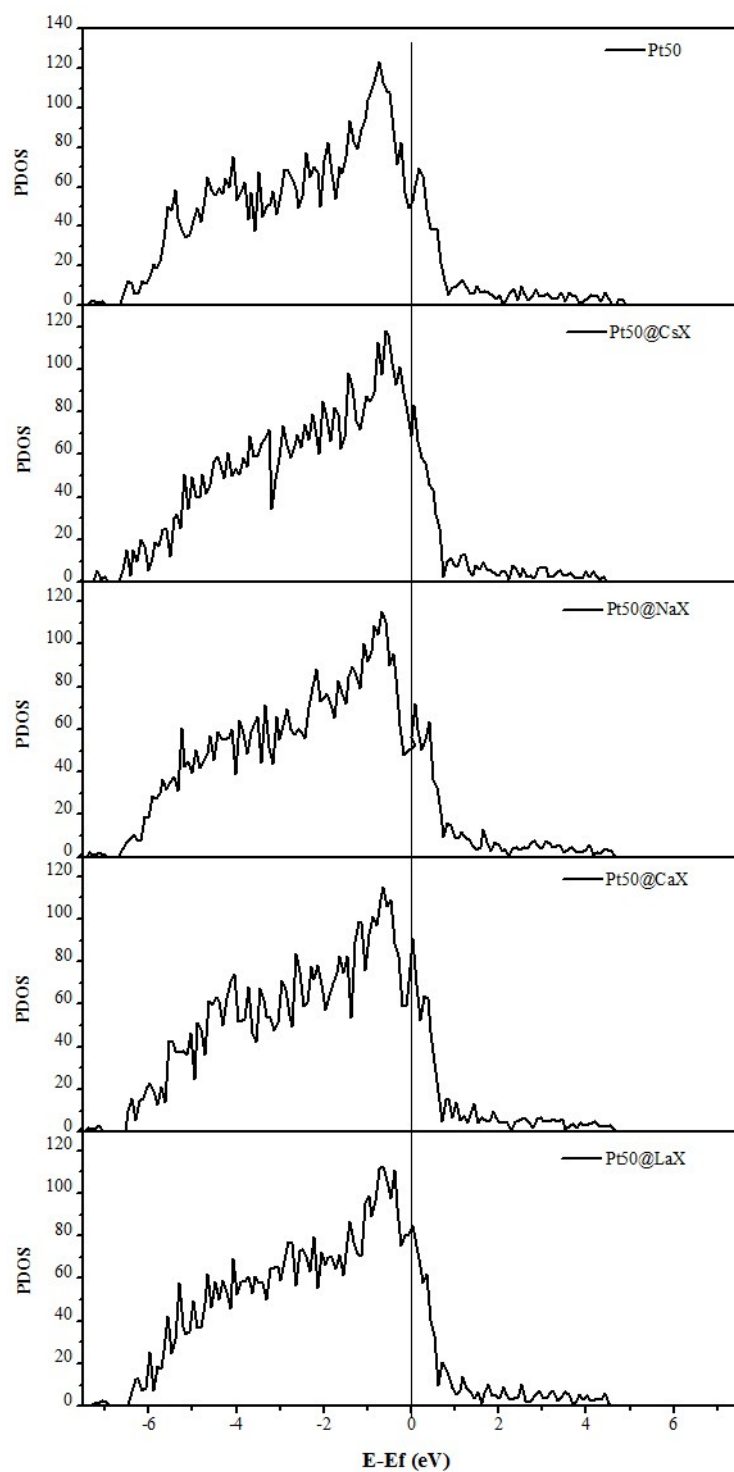


Figure S15. The partial density of states (PDOS) of the four samples ($\text{Pt}_{50}@\text{LaX}$, $\text{Pt}_{50}@\text{CaX}$, $\text{Pt}_{50}@\text{NaX}$, $\text{Pt}_{50}@\text{CsX}$) with PBE method

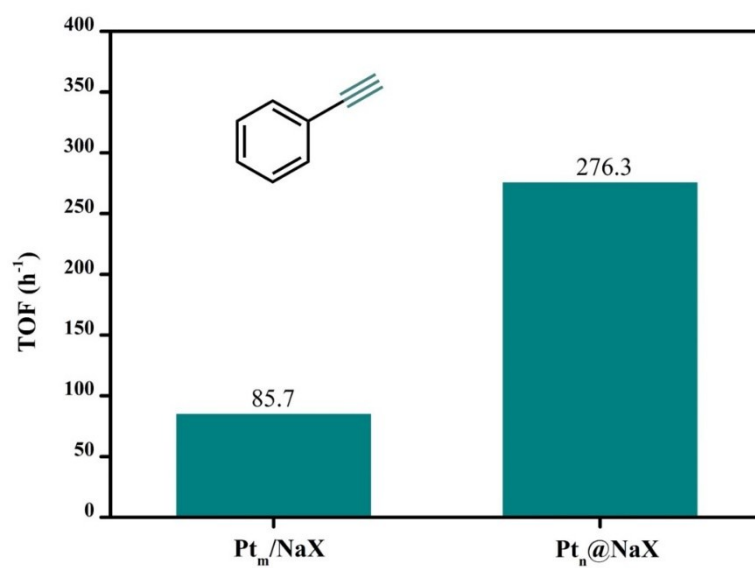


Figure S16. The TOF values of phenylacetylene hydrogenation over Pt_m/NaX and $Pt_n@NaX$. (T=50°C; P=0.5 MPa; Catalyst=40 mg; Substrate=400 μ L). The TOF is defined as the number of converted molecule of reactant per hour per atom of Pt. All the TOF values for the reaction are measured at conversions less than ~20.0%.