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Supporting Information

Influence of reduction temperature on Pt-ZrO_2 interface for the gas-phase hydrogenation of acetone to isopropanol

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Table S1. Quantitative analysis of H_2 consumption in H_2-TPR.

Catalyst	H_2 consumption (mmol g^{-1})[a]	Mono-layers ZrO_2 reduced by H_2[b]
ZrO_2	0.018	0.7
1Pt/ZrO_2	0.021	0.8
2Pt/ZrO_2	0.029	1.1
3Pt/ZrO_2	0.061	2.3
4Pt/ZrO_2	0.066	2.5
5Pt/ZrO_2	0.069	2.6

[a]H_2 consumed at 400-500 ^oC for pure ZrO_2 and 100-300 ^oC for Pt/ZrO_2 catalysts.
[b]Calculated based on BET-SSAs.

Table S2. Pt particle size, Pt content, and specific surface area of the fresh and used catalysts.

Catalyst	D_{Pt}[a] (nm)		Pt content[b] (wt%)		SSA[c] (m^2 g^{-1})	
	Fresh	Used	Fresh	Used	Fresh	Used
3Pt/ZrO_2-100	9.3	9.6	2.9	2.8	11	11
3Pt/ZrO_2-200	9.5	9.7	2.8	2.9	12	12
ZrO_2-400	-	-	-	-	10	11
ZrO_2-450	-	-	-	-	11	10

[a]Particle size of Pt was calculated by Pt(111) XRD peak (Figs. 2A and S7A) using the Scherrer equation ("Part I: Estimation of particle size" in the last page in supporting information).
[b]Pt content was detected by ICP-AES.
[c]SSA: specific surface area.

Table S3. The turnover frequencies (TOFs) of acetone hydrogenation over the catalysts based on Pt NPs[a].

Catalyst	V_{total}[b] ($\times 10^{-4}$, cm^3)	D_{Pt}[c] (nm)	$V_{Pt\text{-}particle}$[d] (nm^3)	Amount of Pt Particles ($\times 10^{14}$)	$S_{Pt\text{-}particle}$[e] (nm^2)	S_{total} (cm^2)	Amount of Surface Pt Atoms[e] ($\times 10^{18}$)	Conv.[f] (%)	N[g] ($\times 10^{22}$)	TOF (h^{-1})
3Pt/ZrO_2-100	3.5	9.3	210	17	136	2312	3.16	8	2.04	6455
3Pt/ZrO_2-200	3.5	9.5	224	16	142	2272	3.11	11.8	3.06	9839

[a]For each catalyst, 0.25 g was used in testing experiments; [b]The total volume of Pt (V_{total}) is calculated as: Pt mass (0.25 g × Pt-loading (wt%)) is divided by the Pt density (21.45 g/cm^3); [c]The particle size is estimated from XRD patterns using Scherrer's equation; [d]The Pt particles are assumed as hemisphere, and the volume of single Pt particle is $\pi D_{Pt}^3/12$, and the surface area is $\pi D_{Pt}^2/2$; [e]The distance between the adjacent Pt atoms is 0.27 nm, and one Pt atom occupies the surface area of 0.073 ($0.27 \times 0.27 = 0.073$) nm^2; [f]The weight hourly space velocity (WHSV) = 100 h^{-1}, and 25 g acetone was fed into the reactor; [g]Amount of converted acetone (Take the converted acetone over the catalyst 3Pt/ZrO_2-100 as example: the converted benzyl alcohol in one hour is 2 g ($25 \times 0.08 = 2$ g), and the converted amount of benzyl alcohol molecule is 2.04×10^{22} (2 (g) ÷ 58 (g/mol) = 0.034 mol; $0.034 \times 6.02 \times 10^{23} = 2.04 \times 10^{22}$)).

Table S4. Reaction rates of the catalysts[a].

Catalyst	SSA[b] (m^2 g^{-1})	T[c] (^oC)	Conv.[d] (%)	N[e](mmol)	Reaction rate ($mmol$ m^{-2} h^{-1})
3Pt/ZrO_2-100	11	60	8.0	34	12
3Pt/ZrO_2-200	12	60	11.8	50	17
ZrO_2-450	10	60	0.4	1.7	0.7

[a]For each catalyst, 0.25 g was used in testing experiments and WHSV is 100 h^{-1}; [b]Specific surface area of the catalyst; [c]Reaction temperature; [d]acetone conversion; [e]Number of converted acetone; [f]Reaction rate based on the surface area of Pt NPs.

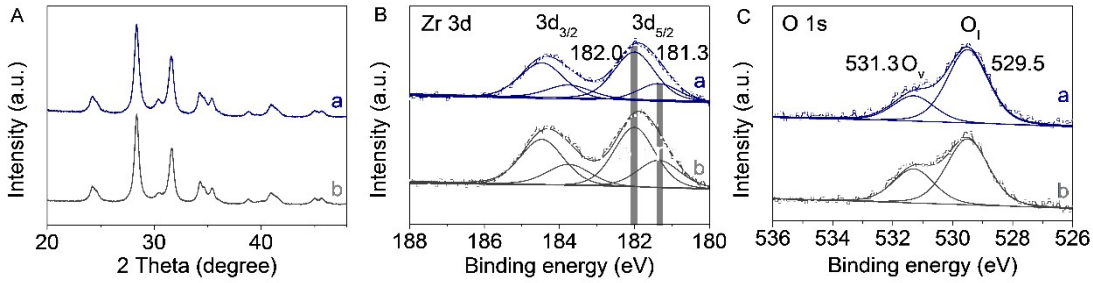

Fig. S1. XRD patterns (A), Zr 3d (B), and O 1s (C) XPS spectra of ZrO_2-400 (a) and ZrO_2-450 (b).

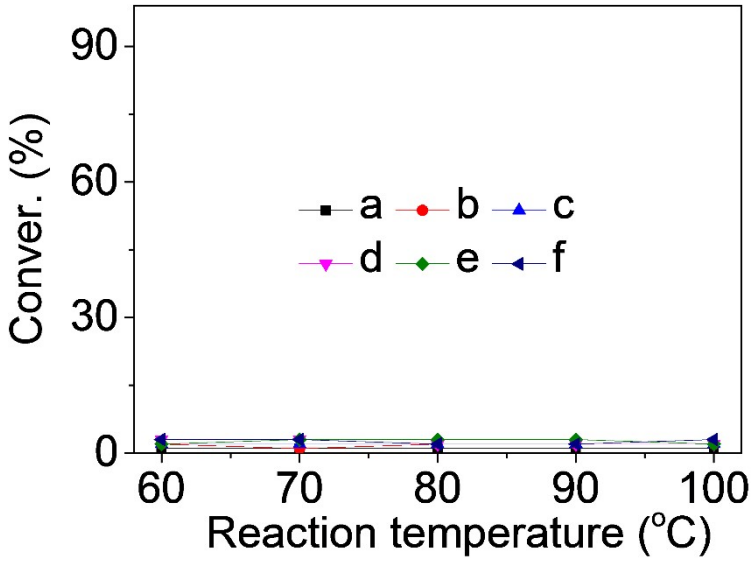

Fig. S2. Effect of reduction temperature on acetone conversion for ZrO_2 at 80 °C, H_2/acetone molar ratio of 2 and WHSV of 10 h^{-1} (IPA selectivity: 98%-99%, not shown, (a) unreduced, (b) 100 °C, (c) 200 °C, (d) 400 °C, (e) 450 °C, and (f) 500 °C).

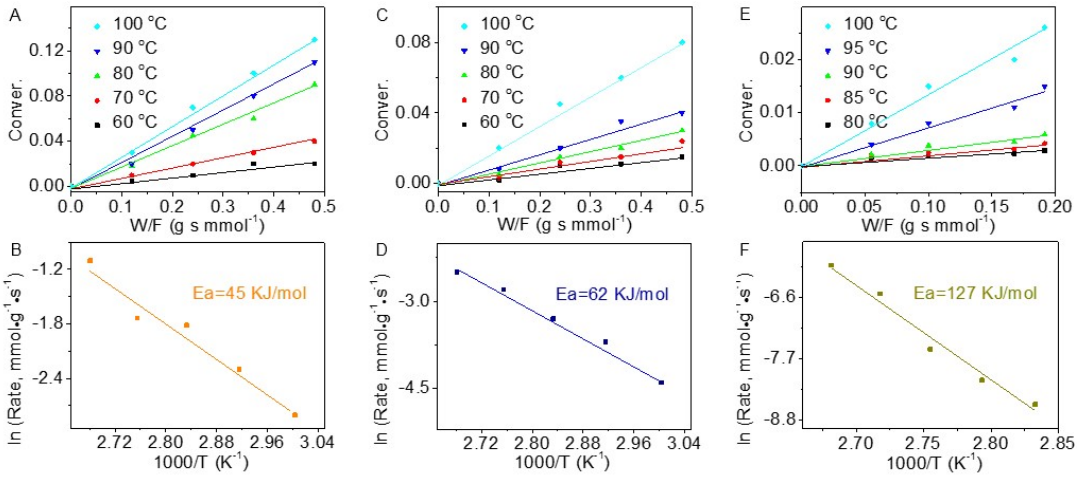

Fig. S3. Variation of the conversion of acetone to IPA against $W/F_{acetone}$ for the reduced catalysts (A) 3Pt/ZrO_2-200, (C) 3Pt/ZrO_2-100, and (E) ZrO_2-450. Ln(Rate) as a function of 1000/T for the reduced catalysts (B) 3Pt/ZrO_2-200, (D) 3Pt/ZrO_2-100, and (F) ZrO_2-450.

For reduced 3Pt/ZrO_2-200, 250 mg catalyst and 250 mg SiO_2 were loaded into the reactor. Acetone, H_2, and N_2 with molar ratio of 1/2/4 were fed into the reactor jointly. WHSV was higher than 100 h^{-1} in order to guarantee that acetone conversion is lower than 20%. We plotted the line according to W/F (X axis; W is the weight of catalyst and F is the flow rate of acetone) as well as acetone conversion (Y axis) (Fig. S3A). The slope of line is the reaction rate (unit of mmol g^{-1} s^{-1}). According to Arrhenius's formula:

$$lnk = -\frac{E_a}{R} + lnA$$

We plotted the line according to 1000/T (X axis; T is kelvin temperature) as well as the natural logarithm of reaction rate (Y axis). The slope of line is $-E_a/R$ (E_a with the unit of kJ mol^{-1}) (Fig. S3B).

For 3Pt/ZrO_2-100 and ZrO_2-450, similar method is used to calculate activation energy by tuning W/F values and reaction temperatures.

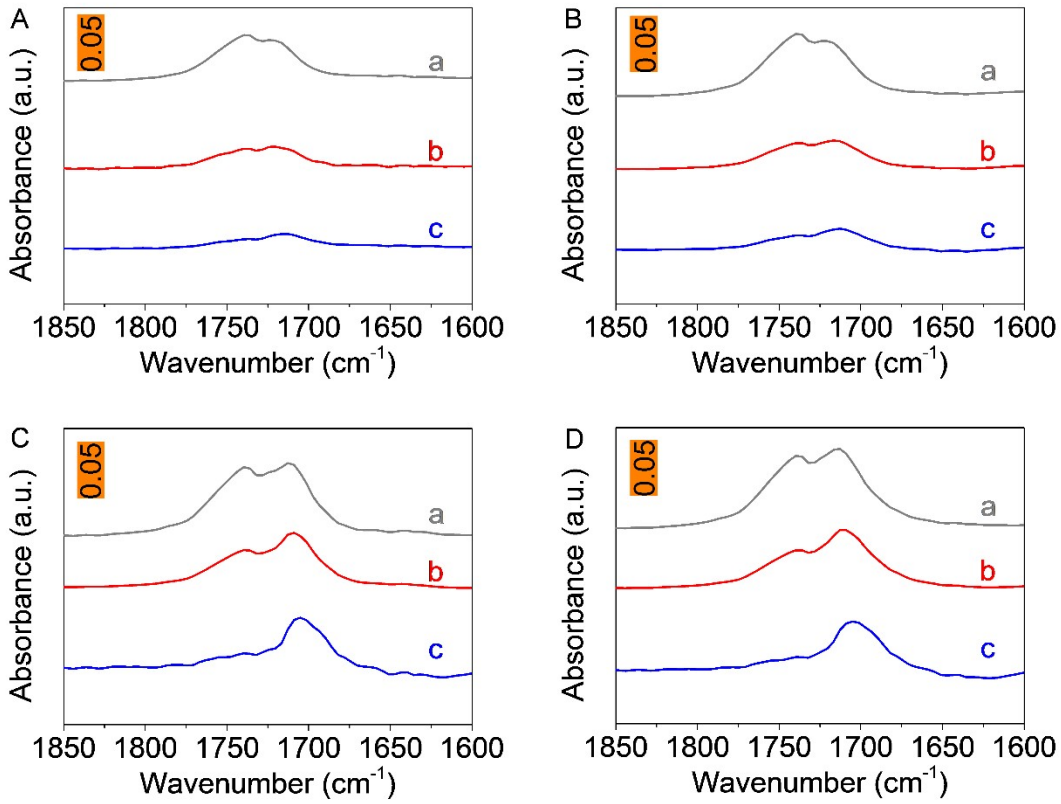

Fig. S4. *In-situ* FT-IR spectra of acetone adsorbed on (A) unreduced ZrO_2, and ZrO_2 reduced at (B) 400, (C) 450, and (F) 500 °C (Line a: purging for 5 min; line b: purging for 10 min; line c: purging for 20 min).

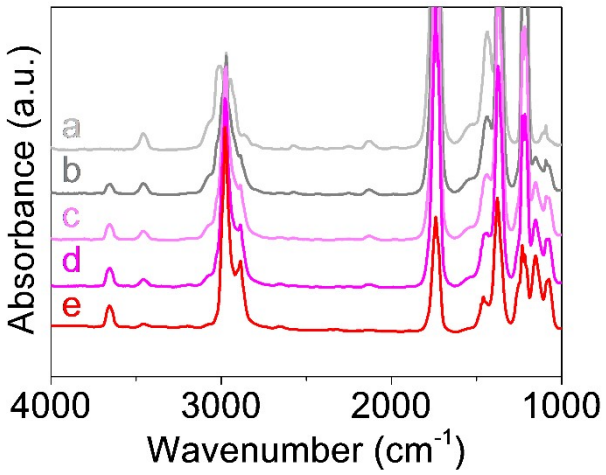

Fig. S5. *In-situ* FT-IR spectra of acetone hydrogenation on 3Pt/ZrO_2-200 (Line a: introducing acetone at room temperature; line b: reaction at 80 °C for 1 min; line c: reaction at 80 °C for 5 min; line d: reaction at 80 °C for 10 min; line e: reaction at 80 °C for 30 min).

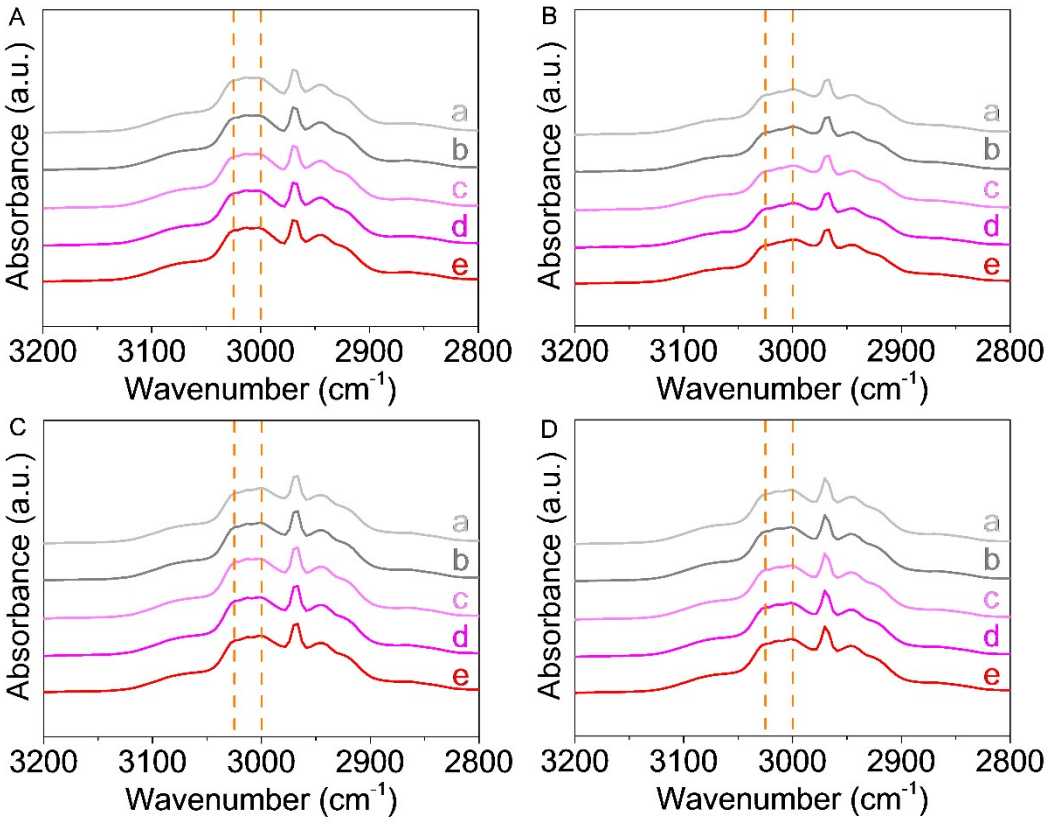

Fig. S6. *In-situ* FT-IR spectra of acetone hydrogenation on (A) unreduced ZrO_2, and ZrO_2 reduced at (B) 400, (C) 450, and (D) 500 °C (Line a: introducing acetone at room temperature; line b: reaction at 80 °C for 1 min; line c: reaction at 80 °C for 5 min; line d: reaction at 80 °C for 10 min; line e: reaction at 80 °C for 30 min).

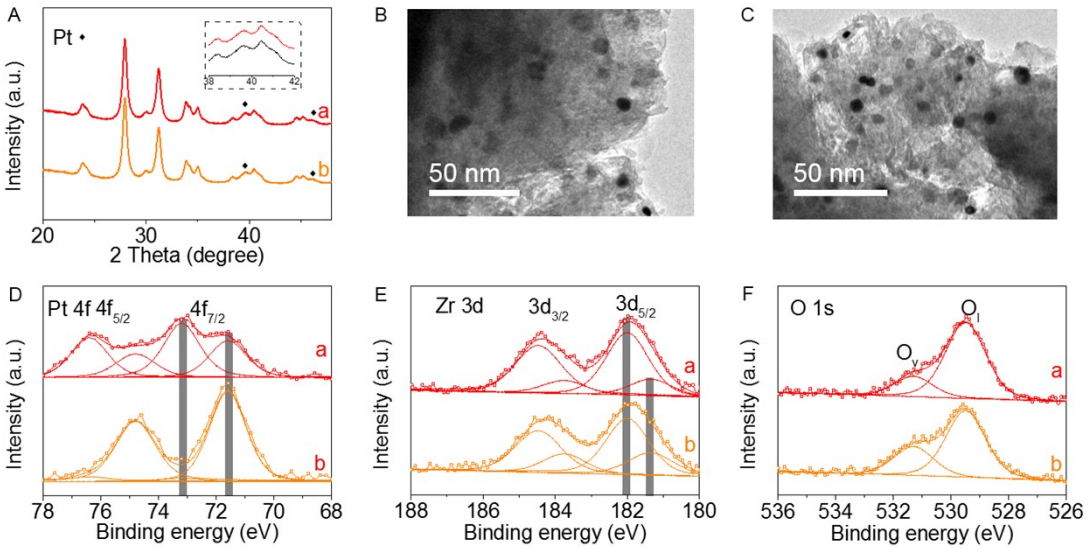

Fig. S7. (A) XRD patterns of used 3Pt/ZrO_2-100 (a), and 3Pt/ZrO_2-200 (b). TEM images of used 3Pt/ZrO_2-100 (B), and 3Pt/ZrO_2-200 (C). (D) Pt 4f, (E) Zr 3d, and (F) O 1s XPS spectra of used 3Pt/ZrO_2-100, (a) and 3Pt/ZrO_2-200 (b).

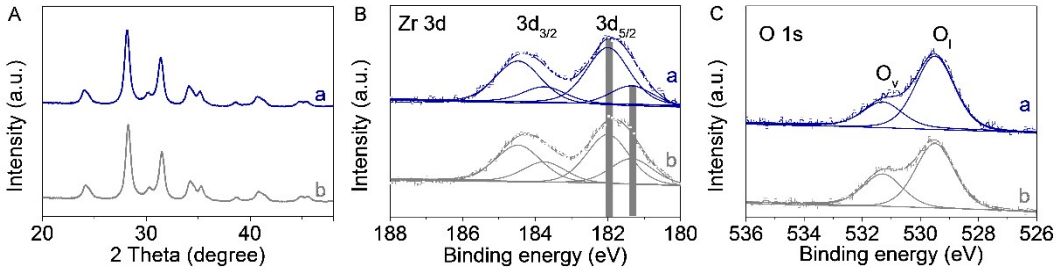

Fig. S8. (A) XRD patterns, (B) Zr 3d XPS spectra, and (C) O 1s XPS spectra of used ZrO_2-400 (a) and ZrO_2-450 (b).

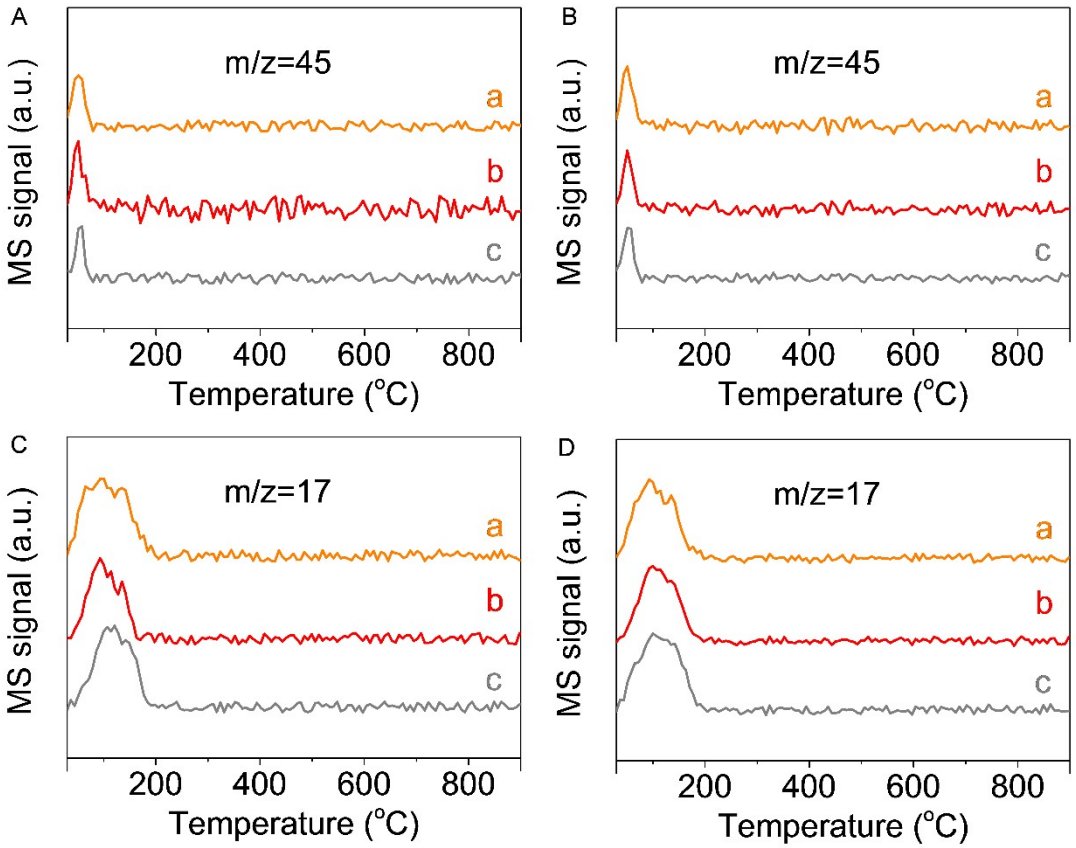

Fig. S9. IPA-TPD-MS profiles of (A) fresh, and (B) used catalysts. NH_3-TPD-MS profiles of (C) fresh, and (D) used catalysts. ((a) 3Pt/ZrO_2, (b) 3Pt/ZrO_2-100, (c) 3Pt/ZrO_2-200).

Part I: Estimation of particle size

In this work, the diffraction peaks of Pt and ZrO_2 are overlapped, but the XRD patterns could be fitted using PEAKFIT program and the particle sizes could be estimated [1] using Scherrer equation based on Pt(111) peaks at 39.6°. As shown in Fig. IA,B, FWHMs (full width at half maximums) are 0.89, 0.87, 0.88, and 0.86° for reduced 3Pt/ZrO_2-100, used 3Pt/ZrO_2-100, reduced 3Pt/ZrO_2-200, and used 3Pt/ZrO_2-200, respectively, so their particle sizes are calculated to be 9.3, 9.6, 9.5, and 9.7 nm (Table S2 in SI), respectively, being close to each other.

Moreover, the histograms of the Pt particle sizes based on TEM results are exhibited in Fig. IC-F, showing ~8-10 nm Pt particle sizes and corresponding well with XRD results.

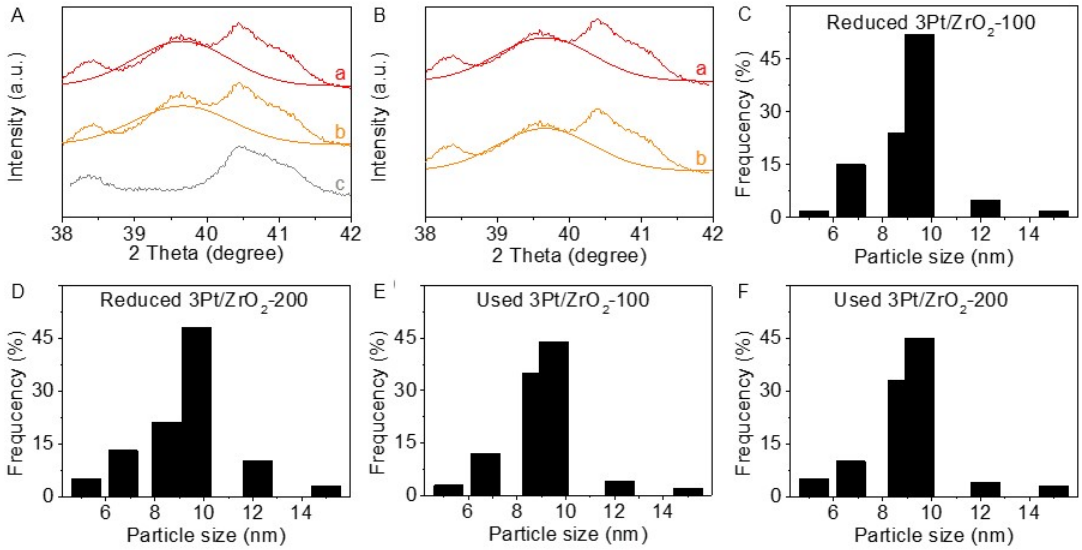

Fig. I. Particle sizes of the catalysts. (Fitted XRD patterns of reduced (A) and used (B) catalysts (a: 3Pt/ZrO_2-100, b: 3Pt/ZrO_2-200, c: ZrO_2-450); particle size distributions of Pt nanoparticles for reduced 3Pt/ZrO_2-100 (C), reduced 3Pt/ZrO_2-200 (D), used 3Pt/ZrO_2-100 (E), and used 3Pt/ZrO_2-200 (F)).

[1] K. Liu, Y. Zhao, J. Wang, Q. Xue, G. Zhao, Catal. Sci. Technol., 2020, **10**, 8445.