Electronic Supplementary Information (ESI)

Structure sensitivity of alumina- and zeolite-supported platinum ammonia slip catalysts

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Activity and selectivity calculation during *operando* X-ray absorption spectroscopy tests

The approach to ammonia conversion calculation was the same as for the laboratory catalytic tests, $X_{NH_3} = (1 - C_{NH_3}^{out}/C_{NH_3}^{in}) \cdot 100\ \%$, where $C_{NH_3}^{out}$ and $C_{NH_3}^{in}$ are ammonia concentrations at the reactor outlet and inlet, respectively. Selectivity to products was calculated according to $S_i = n_i \cdot C_i \,/ C_{NH_3}^{in} \cdot 100\ \%$, where C_i is product i concentration, and n_i – number of nitrogen atoms in the corresponding product molecule, $C_{NH_3}^{in}$ – ammonia concentration at the reactor inlet. The produced nitrogen concentration was calculated from conversion and concentrations of other products, according to the mass balance.

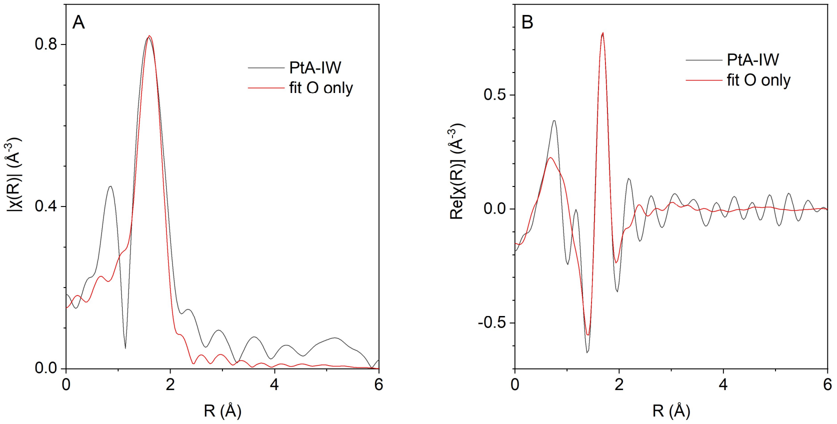

Figure S1. *Ex situ* EXAFS spectrum at the Pt L_3-edge (dark grey line) of PtA-IW sample with its fit (red line), which includes backscattering for O atoms only. A – Fourier-transformed spectrum in R-space; B – real part of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2-10 Å^{-1}; amplitude reduction factor S_0^2= 0.68.

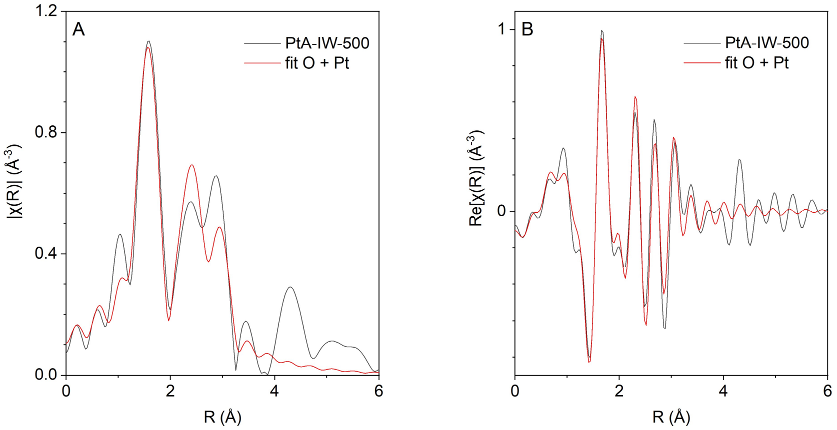

Figure S2. *Ex situ* EXAFS spectrum at the Pt L_3-edge (dark grey line) of PtA-IW sample with its fit (red line), which includes backscattering for both O and Pt atoms. A – Fourier-transformed spectrum in R-space; B – real part of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2-10 Å^{-1}; S_0^2= 0.68.

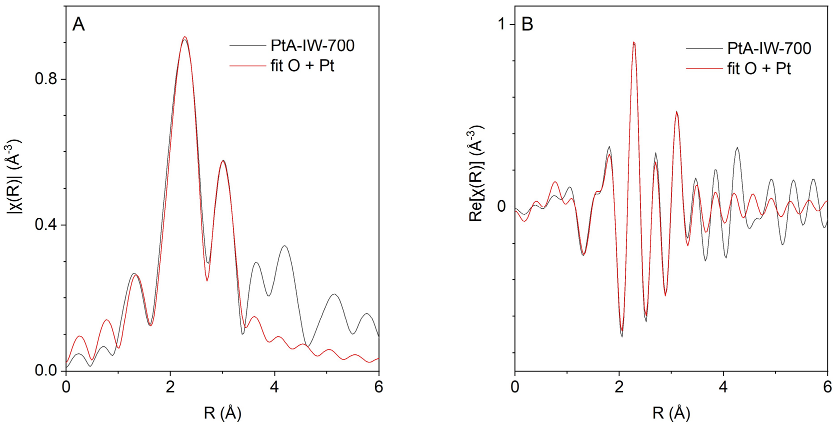

Figure S3. *Ex situ* EXAFS spectrum at the Pt L_3-edge (dark grey line) of PtA-IW sample with its fit (red line), which includes backscattering for both O and Pt atoms. A – Fourier-transformed spectrum in R-space; B – real part of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2-10 Å^{-1}; S_0^2= 0.68.

Table S1. Fitting results of *ex situ* EXAFS spectra of the PtA-IW sample at the Pt L_3-edge. Background-subtracted and k^2-weighted; k-range of 2-10 $Å^{-1}$; amplitude reduction factor $S_0^2 = 0.68$.

PtA-IW fits	Scattering atoms	R (Å)	CN	σ^2 (10^{-3} $Å^2$)	δE_0 (eV)	ρ (%)
O + Pt (metal)	Pt-Pt Pt-O	2.90 ± 0.08 2.03 ± 0.03	-1.3 ± 1.4 3.0 ± 0.6	5.6 ± 4.3	13.8 ± 2.3	2.6
O + Pt (oxide)	Pt-Pt Pt-O	3.12 ± 0.11 2.03 ± 0.03	1.5 ± 2.2 3.2 ± 0.7	6.0 ± 5.0	14.5 ± 2.8	3.0

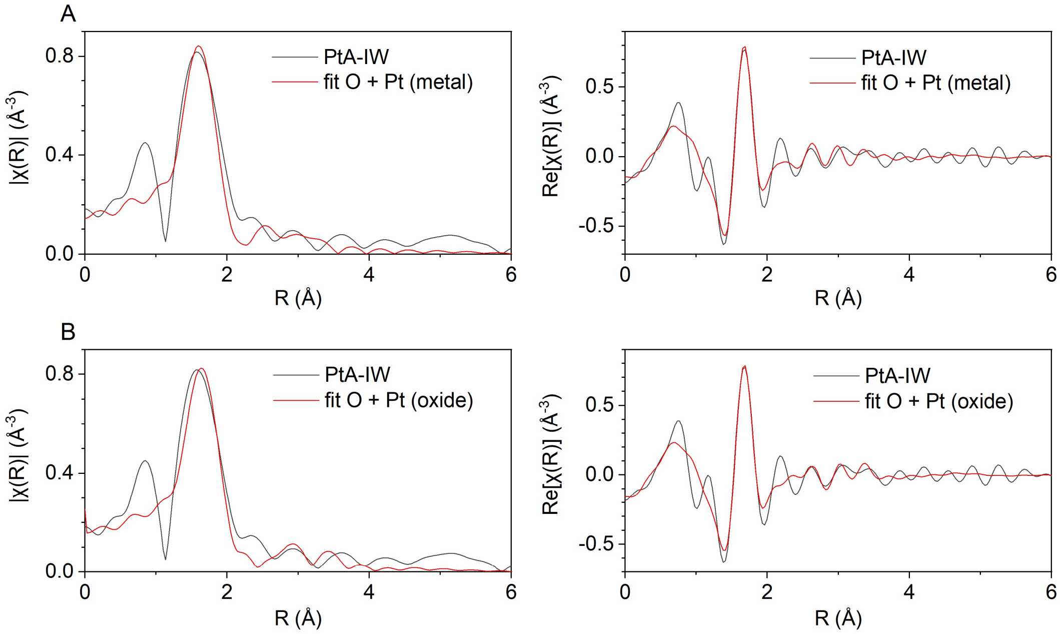

Figure S4. *Ex situ* EXAFS spectrum recorded at the Pt L_3-edge (dark grey lines) of PtA-IW sample with its fits (red lines). The fits include backscattering both for O and Pt: A – Pt from metallic structure; B – Pt from PtO_2 structure. Left – Fourier-transformed spectra in R-space; right – real parts of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2-10 $Å^{-1}$; $S_0^2 = 0.68$.

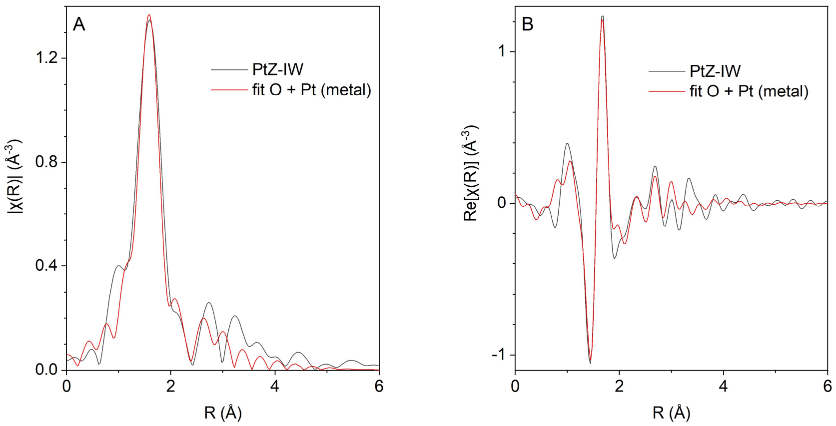

Figure S5. *Ex situ* EXAFS spectrum recorded at the Pt L_3-edge of PtZ-IW sample with its fit, which includes backscattering both for O and Pt atoms. A – Fourier-transformed spectrum in R-space; B – real part of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 Å^{-1}; S_0^2= 0.78.

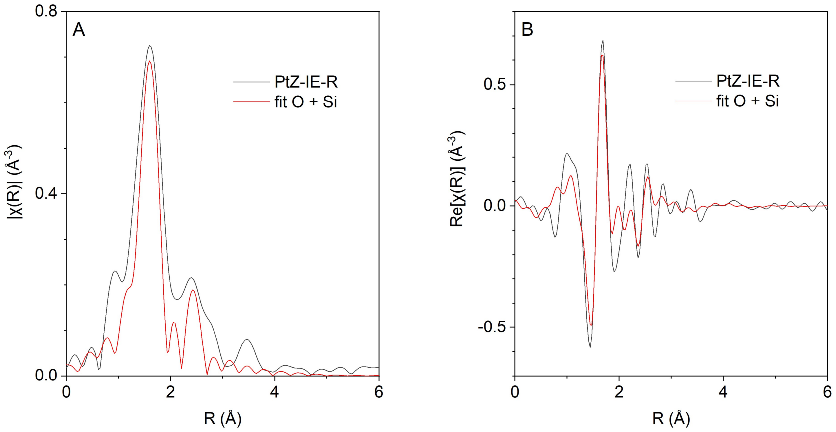

Figure S6. *Ex situ* EXAFS spectrum recorded at the Pt L_3-edge of PtZ-IE-R sample with its fit, which includes backscattering both for O and Si atoms. A – Fourier-transformed spectrum in R-space; B – real part of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 Å^{-1}; S_0^2= 0.78.

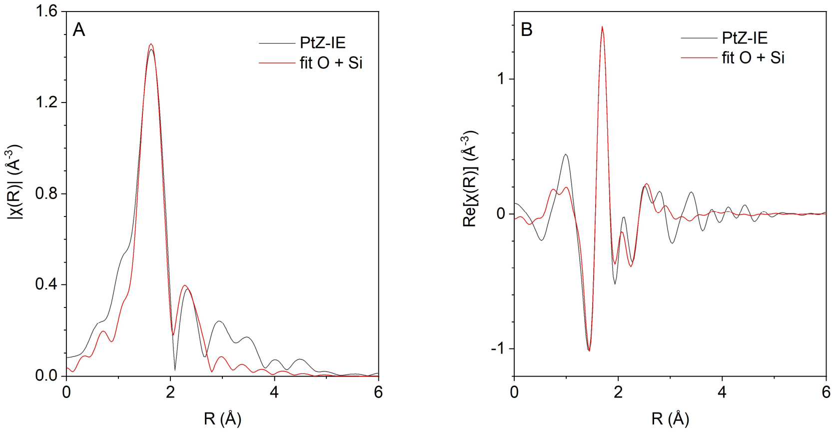

Figure S7. *Ex situ* EXAFS spectrum recorded at the Pt L_3-edge of PtZ-IE sample with its fit, which includes backscattering both for O and Si atoms. A – Fourier-transformed spectrum in R-space; B – real part of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 Å^{-1}; 0.78.

Table S2. Fitting results of *ex situ* EXAFS spectra of PtZ-IW sample at the Pt L_3-edge. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 $Å^{-1}$; S_0^2= 0.78.

PtZ-IW fits	Scattering atoms	R (Å)	CN	σ^2 (10^{-3} $Å^2$)	δE_0 (eV)	ρ (%)
O only	Pt-O	1.99 ± 0.02	3.8 ± 0.9	2.6 ± 3.2	9.1 ± 2.5	1.5
O + Pt (from oxide)	Pt-Pt	3.24 ±0.06	-1.0 ± 1.2	2.9 ± 2.4	9.1 ± 1.8	3.4
	Pt-O	1.99 ± 0.01	3.8 ± 0.7			
O + Pt, different σ^2	Pt-Pt	2.73 ± 0.05	1.8 ± 2.7	2.3 ± 2.3	8.8 ± 1.9	2.0
	Pt-O	1.99 ± 0.01	3.7 ± 0.6	6.3 ± 10.9		

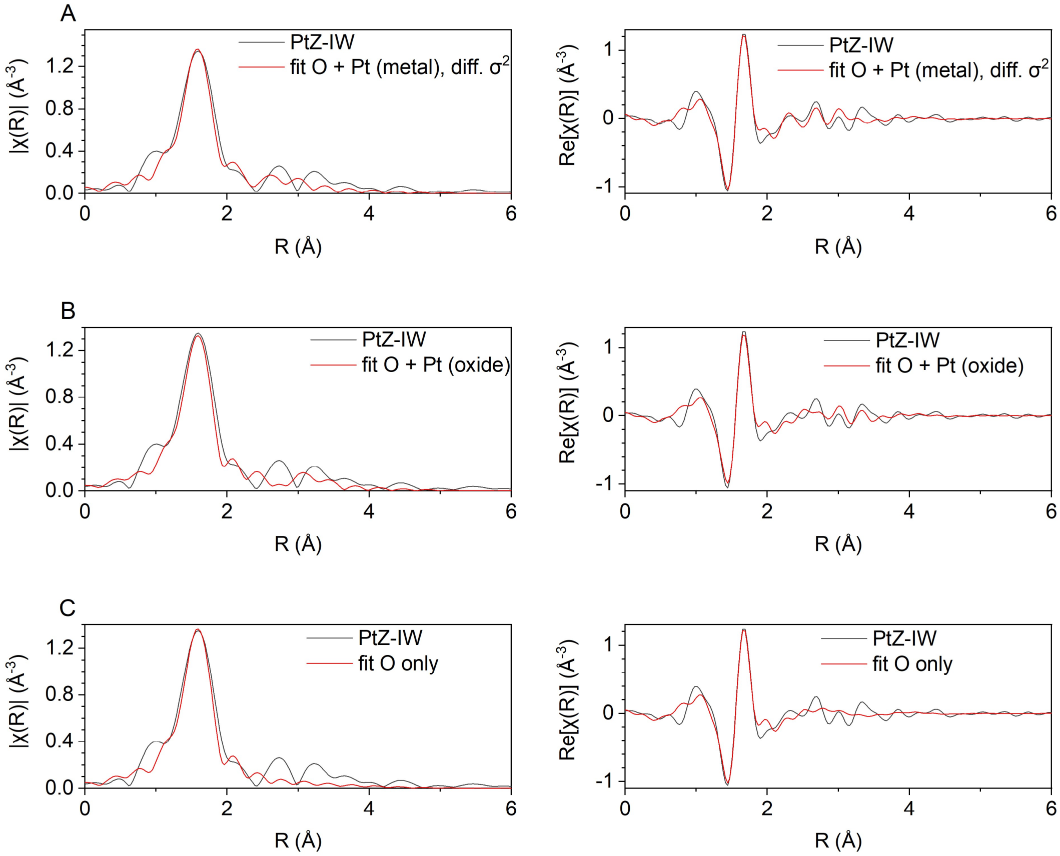

Figure S8. *Ex situ* EXAFS spectrum recorded at the Pt L_3-edge of PtZ-IW sample (dark grey lines) with its fits (red lines). A and B – fits that include backscattering both for O and Pt: A – Pt from metallic structure with different fitted variables for σ^2; B – Pt from PtO_2 structure. C – the fit which includes backscattering for O atoms only. Left – Fourier-transformed spectra in R-space; right – real parts of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 $Å^{-1}$; S_0^2= 0.78.

Table S3. Fitting results of *ex situ* EXAFS spectra of the PtZ-IE-R sample at the Pt L_3-edge. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 $Å^{-1}$; S_0^2= 0.78.

PtZ-IE-R fits	Scattering atoms	R (Å)	CN	σ^2 (10^{-3} $Å^2$)	δE_0 (eV)	ρ (%)
O only	Pt-O	1.99 ± 0.02	1.6 ± 0.4	0.7 ± 2.7	9.4 ± 2.7	10.7
O + Pt (metal)	Pt-Pt Pt-O	2.77 ± 0.05 1.99 ± 0.02	-0.4 ± 0.5 1.6 ± 0.4	1.4 ± 3.1	8.6 ± 2.7	9.6
O + Pt (oxide)	Pt-Pt Pt-O	3.04 ± 0.21 1.99 ± 0.02	-0.1 ± 0.6 1.6 ± 0.4	0.7 ± 3.0	9.1 ± 3.0	10.7

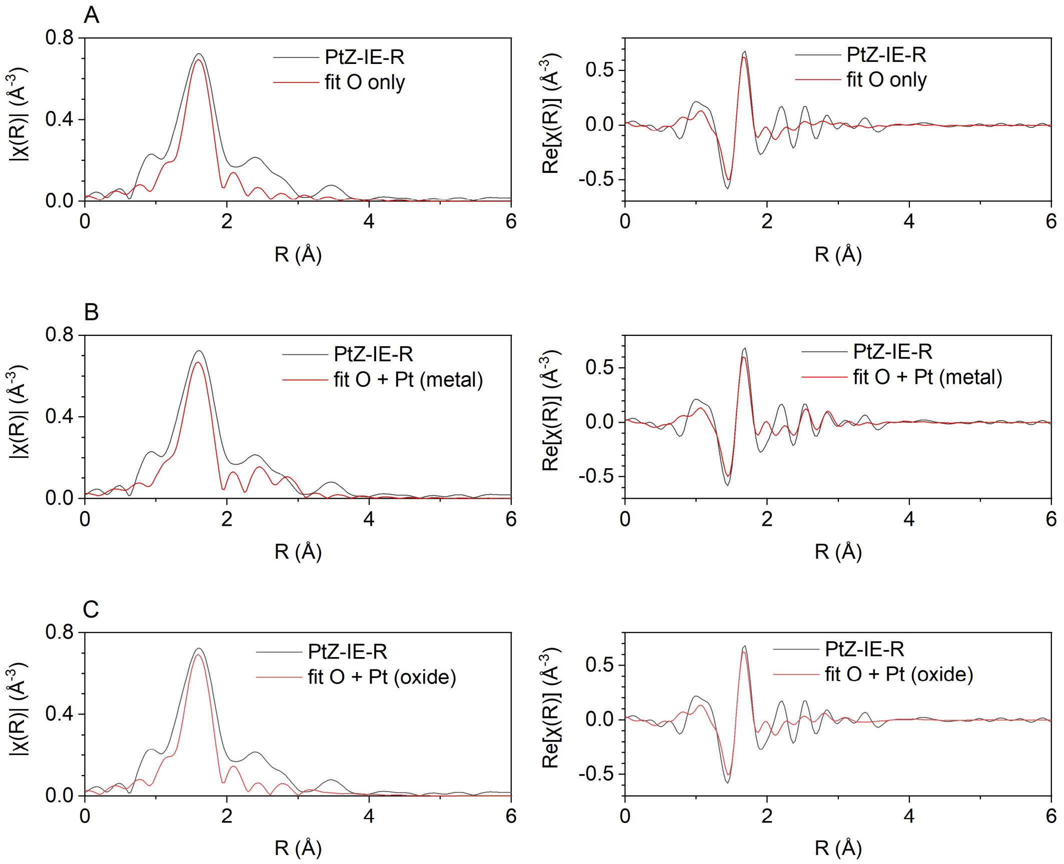

Figure S9. *Ex situ* EXAFS spectrum recorded at the Pt L_3-edge of PtZ-IE-R sample (dark grey lines) with its fits (red lines). A – the fit which includes backscattering for O atoms only. B and C – fits that include backscattering both for O and Pt: B – Pt from metallic structure; C – Pt from PtO_2 structure. Left – Fourier-transformed spectra in R-space; right – real parts of the Fourier-transform. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 $Å^{-1}$; S_0^2= 0.78.

Table S4. Fitting results of *ex situ* EXAFS spectra of PtZ-IE sample at the Pt L_3-edge. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 Å^{-1}; S_0^2= 0.78.

PtZ-IE fits	Scattering atoms	R (Å)	CN	σ^2 (10^{-3} Å^2)	δE_0 (eV)	ρ (%)
O only	O	2.03 ± 0.02	4.7 ± 0.9	4.2 ± 2.7	13.0 ± 2.3	3.0
O + Pt (oxide)	Pt-Pt	3.22 ± 0.12	0.8 ± 1.9	4.0 ± 3.0	13.2 ± 2.6	2.9
	Pt-O	2.03 ± 0.03	4.7 ± 1.0			
O + Pt (metal)	Pt-Pt	2.76 ± 0.03	-1.7 ± 1.0	3.7 ± 2.2	12.9 ± 1.7	1.9
	Pt-O	2.03 ± 0.02	4.7 ± 0.8			

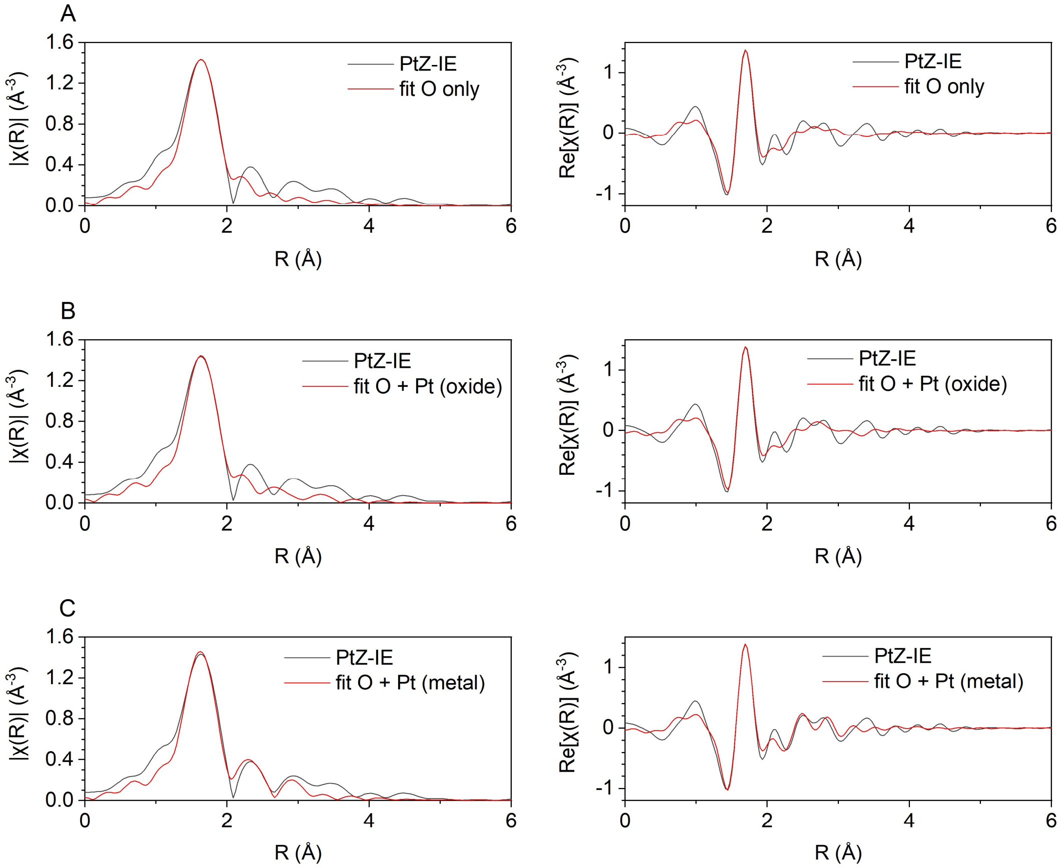

Figure S10. *Ex situ* EXAFS spectrum recorded at the Pt L_3-edge of PtZ-IE sample (dark grey lines) with its fits (red lines). A – the fit which includes backscattering for O atoms only. B and C – the fits which include backscattering both for O and Pt: B – Pt from PtO_2 structure; C – Pt from metallic structure. Left – Fourier-transformed spectra in R-space; right – real parts of the Fourier-transformation. Background-subtracted and k^2-weighted; k-range of 2.5-10.5 Å^{-1}; S_0^2= 0.78.

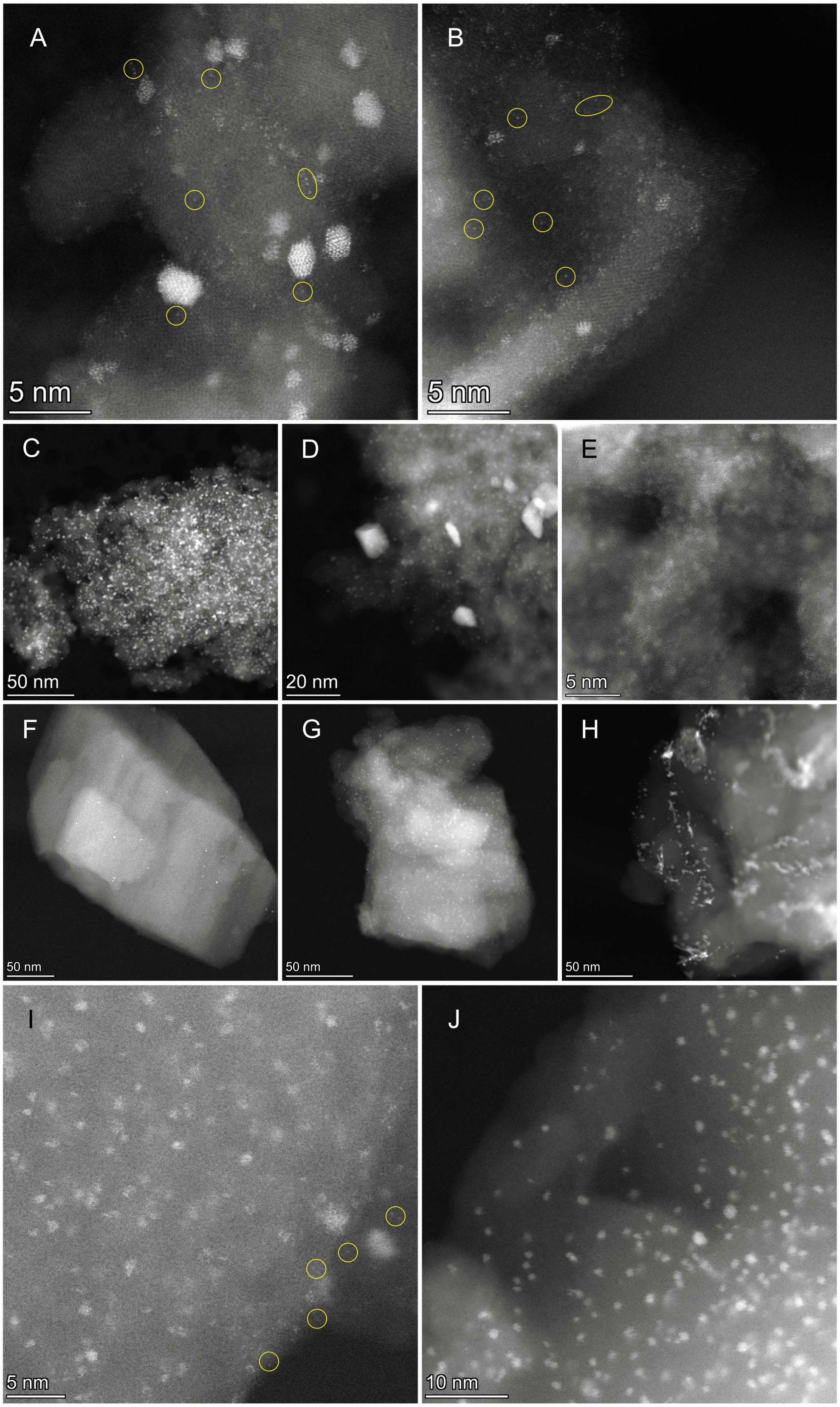

Figure S11. HAADF-STEM images of the synthesized catalysts. Alumina-supported samples: A, C – PtA-IW, B, D – PtA-IW-500, E – PtA-IW-700. ZSM-5-supported samples: F, I – PtZ-IE, G, J – PtZ-IE-R, H – PtZ-IW. Some of Pt single sites are marked with yellow ellipses.

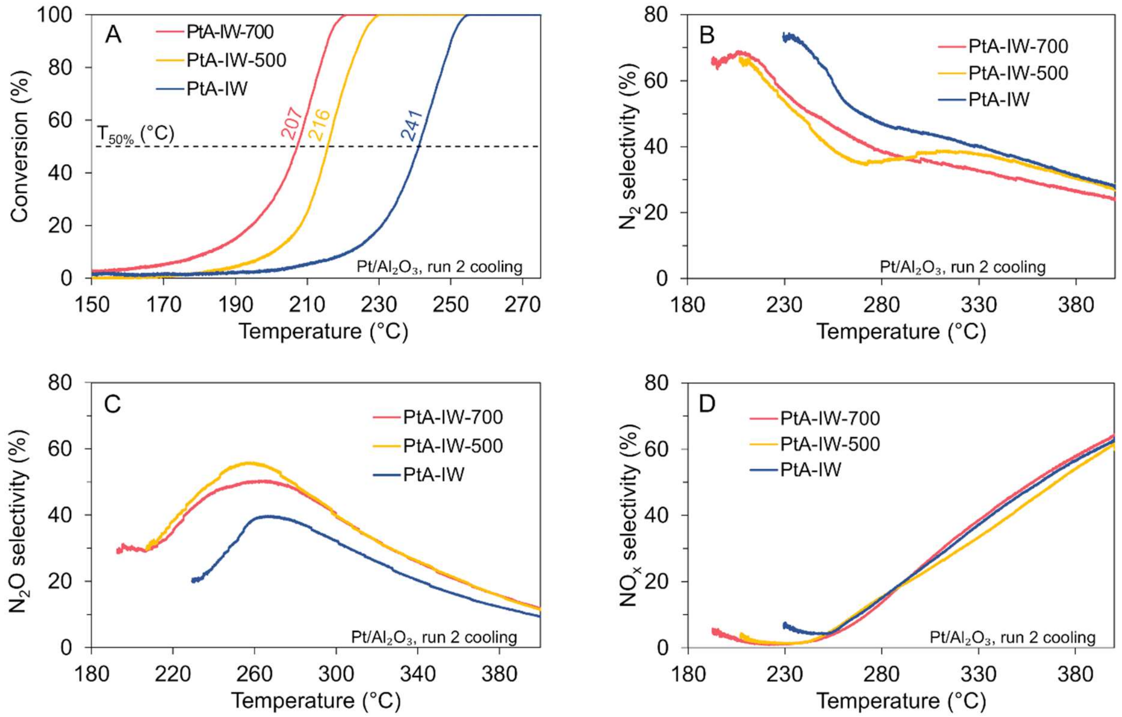

Figure S12. Catalytic tests results for the alumina-supported catalysts during the second cooling in reaction mixture. A – conversion; B – selectivity to N_2; C – selectivity to N_2O; D – selectivity to NO_x. Red line – PtA-IW-700; orange line - PtA-IW-500; blue line – PtA-IW. Reaction feed – 500 ppm NH_3, 13 % O_2 in N_2. Flow –1050 cm^3/min. Gas hourly space velocity GHSV = 63,000 cm^{-1}. Loading – 25 mg of 2 wt. % Pt catalyst. Heating rate of 3 °C/min.

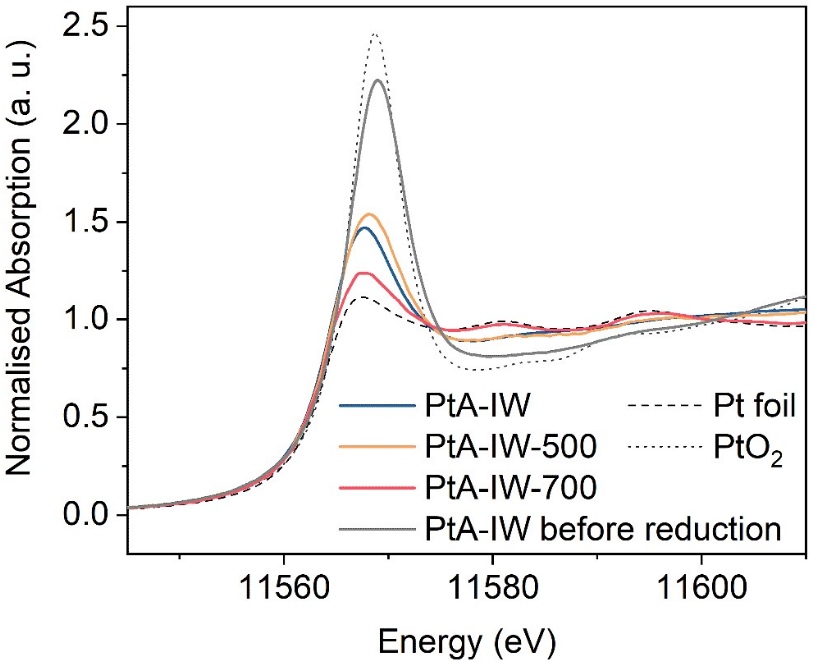

Figure S13. *Ex situ* XANES spectra recorded at the Pt L_3-edge of the alumina-supported catalysts together with the spectra of Pt foil and PtO_2. Red line – PtA-IW-700; orange line - PtA-IW-500; blue line – PtA-IW; grey line - PtA-IW before reduction; black dotted line – PtO_2; black dashed line – Pt foil.

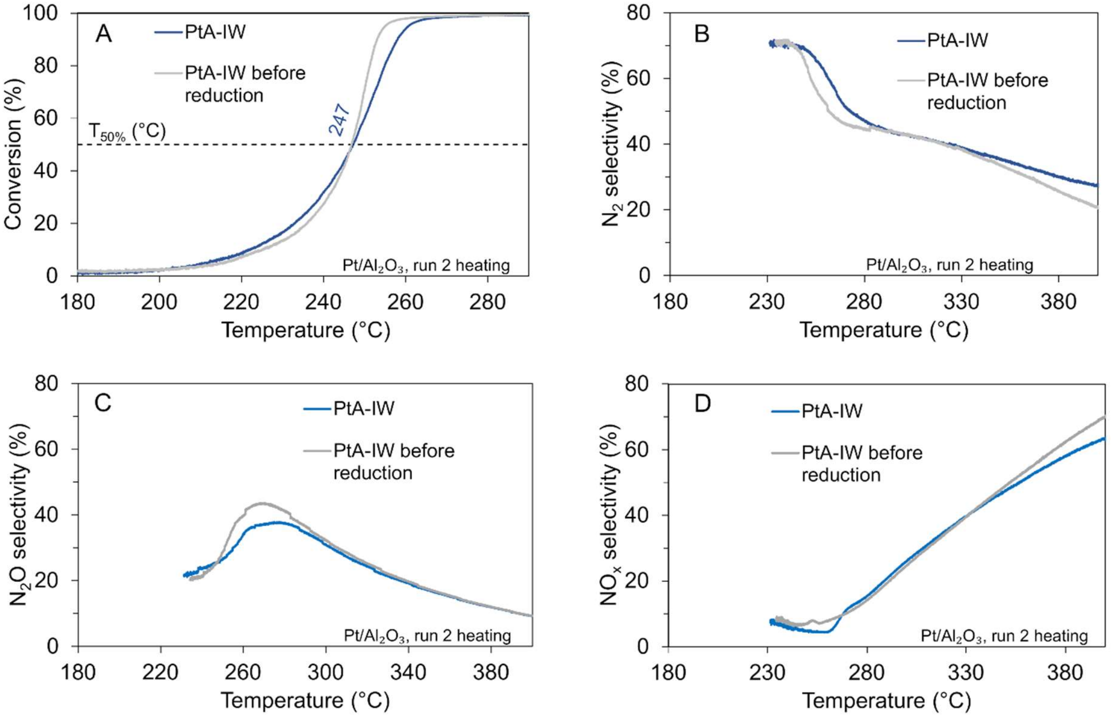

Figure S14. Catalytic tests results for PtA-IW catalyst compared with the same sample before reduction during the second light-off in reaction mixture. A – conversion; B – selectivity to N_2; C – selectivity to N_2O; D – selectivity to NO_x. Blue line – PtA-IW; grey line – the same catalyst before reduction. Reaction feed – 500 ppm NH_3, 13 % O_2 in N_2. Flow –1050 cm^3/min. GHSV = 63,000 cm^{-1}, 25 mg of 2 wt. % Pt catalyst. Heating rate – 3 °C/min.

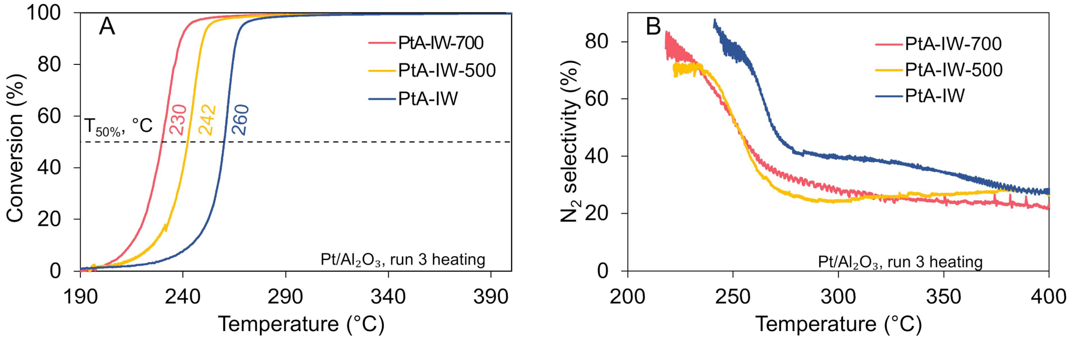

Figure S15. Catalytic tests results for the alumina-supported catalysts during the third heating in reaction mixture containing water and CO_2. A – conversion; B – selectivity to N_2. Red line – PtA-IW-700; orange line - PtA-IW-500; blue line – PtA-IW. Reaction feed – 500 ppm NH_3, 13 % O_2, 5 % H_2O, and 10 % CO_2 in N_2. Flow –1050 cm^3/min. Gas hourly space velocity GHSV = 63,000 cm^{-1}. Loading – 25 mg of 2 wt. % Pt catalyst. Heating rate of 3 °C/min.

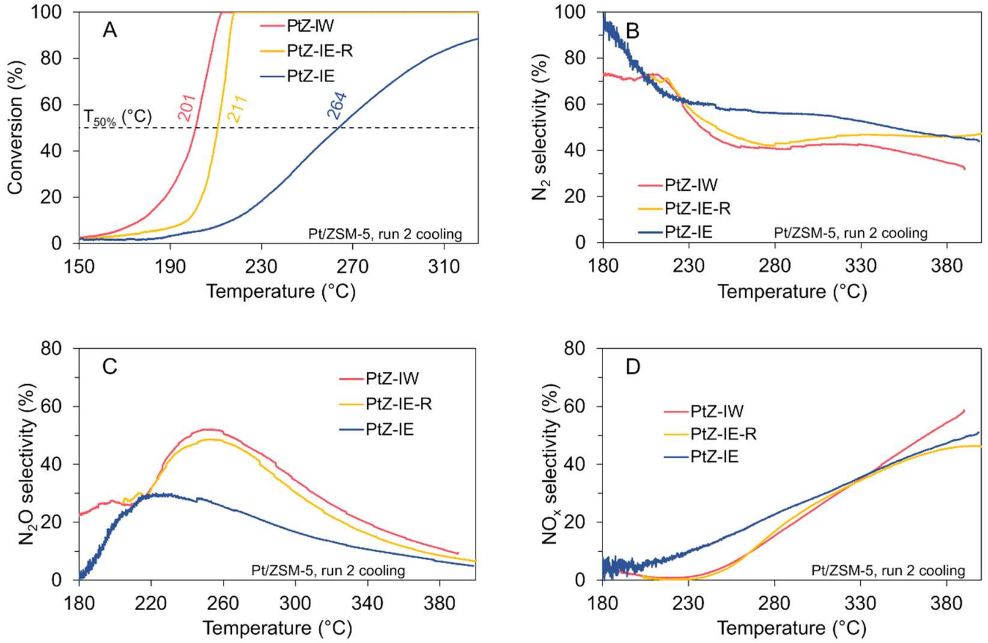

Figure S16. Catalytic tests results for the zeolite-supported catalysts during the second cooling in the reaction mixture. A – conversion; B – selectivity to N_2; C – selectivity to N_2O; D – selectivity to NO_x. Red line – PtZ-IW; orange line - PtZ-IE-R; blue line – PtZ-IE. Reaction feed – 500 ppm NH_3, 13 % O_2 in N_2. Flow –1050 cm^3/min. GHSV = 63,000 cm^{-1}. 50 mg of 1 wt. % Pt catalyst. Heating rate – 3 °C/min.

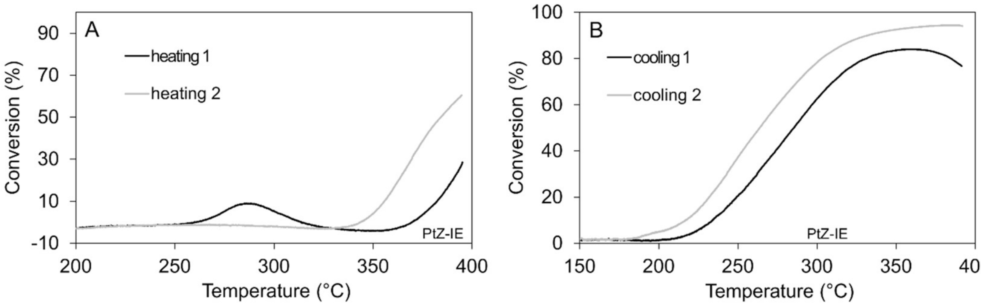

Figure S17. Ammonia conversion for PtZ-IE during the first and the second catalytic cycle in the reaction mixture. A – heating; B – cooling. Reaction feed – 500 ppm NH_3, 13 % O_2 in N_2. Flow –1050 cm^3/min. GHSV = 63,000 cm^{-1}. 50 mg of 1 wt. % Pt catalyst. Heating rate – 3 °C/min.

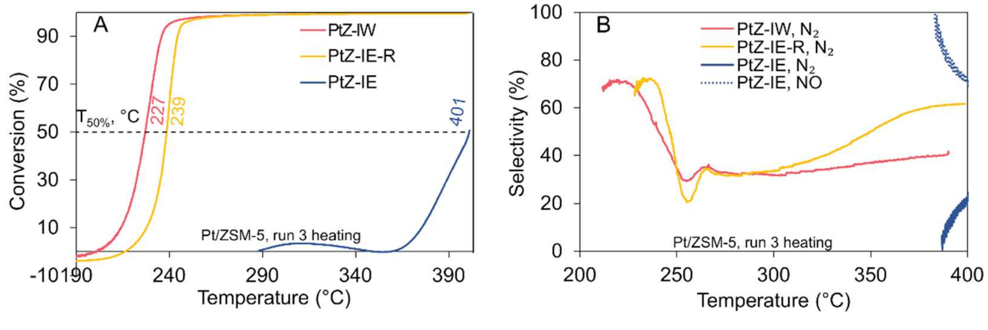

Figure S18. Catalytic tests results for the zeolite-supported catalysts during the second cooling in the reaction mixture. A – conversion; B – selectivity to N_2 (and to NO for PtZ-IE). Red line – PtZ-IW; orange line - PtZ-IE-R; blue line – PtZ-IE. Reaction feed – 500 ppm NH_3, 13 % O_2, 5 % H_2O, and 10 % CO_2 in N_2. Flow –1050 cm^3/min. GHSV = 63,000 cm^{-1}. 50 mg of 1 wt. % Pt catalyst. Heating rate – 3 °C/min.

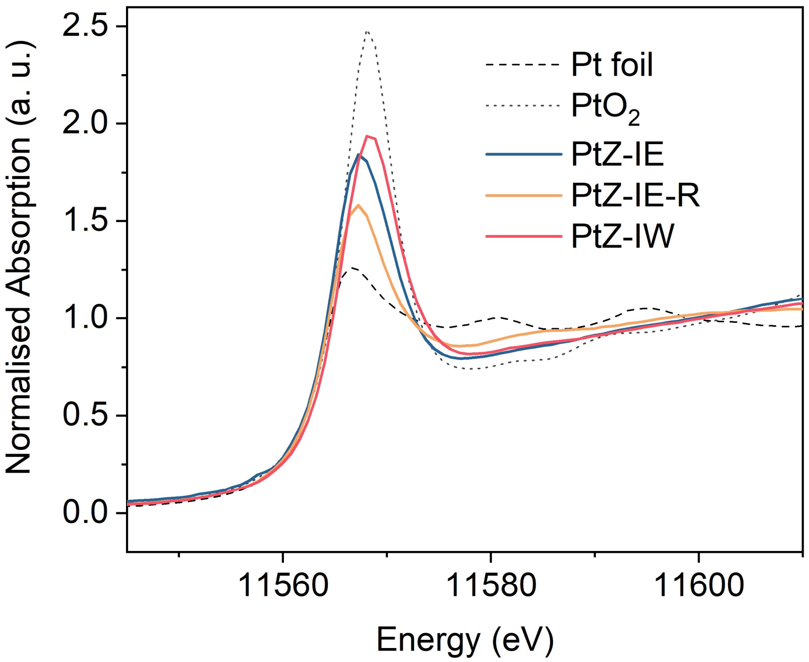

Figure S19. *Ex situ* XANES spectra recorded at the Pt L_3-edge of the zeolite-supported catalysts together with the spectra of Pt foil and PtO_2. Red line – PtZ-IW; orange line - PtZ-IE-R; blue line – PtZ-IE; black dotted line – PtO_2; black dashed line – Pt foil.

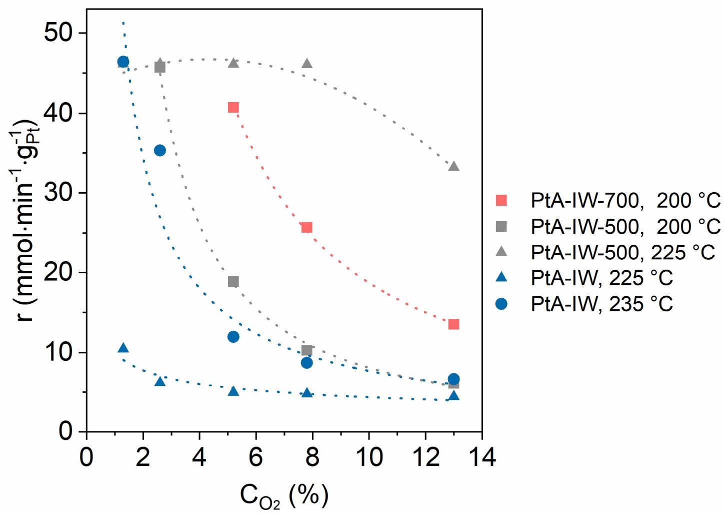

Figure S20. Integral reaction rates of ammonia oxidation at varying oxygen concentrations. The concentration of NH_3 was 500 ppm in all cases, and the concentration of O_2 varied from 1.3 to 13 %. GHSV = 63,000 cm^{-1}. Loading – 25 mg of 2 wt. % Pt catalyst. Heating rate of 3 °C/min.

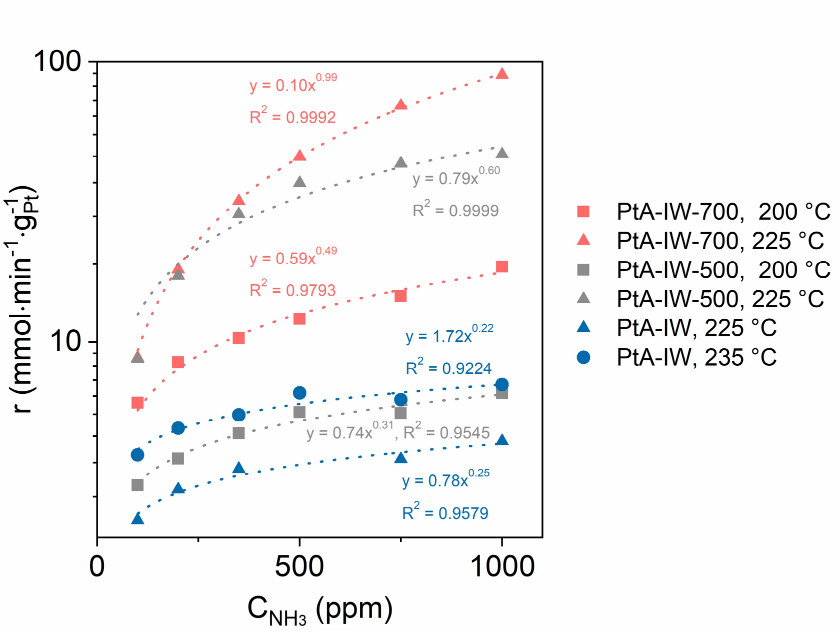

Figure S21. Integral reaction rates of ammonia oxidation at varying ammonia concentrations. The concentration of O_2 was 13 % in all cases, and the concentration of NH_3 varied from 100 to 1000 ppm. GHSV = 63,000 cm^{-1}. Loading – 25 mg of 2 wt. % Pt catalyst. Heating rate of 3 °C/min.

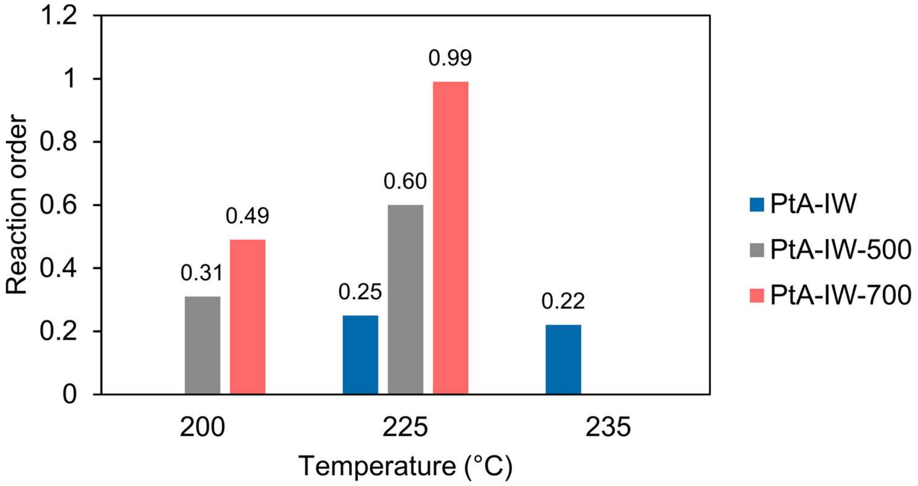

Figure S22. Reaction orders of ammonia in ammonia oxidation over Pt/Al_2O_3 catalysts with different particle sizes of Pt. The reaction orders were calculated from the results presented in Figure S21.

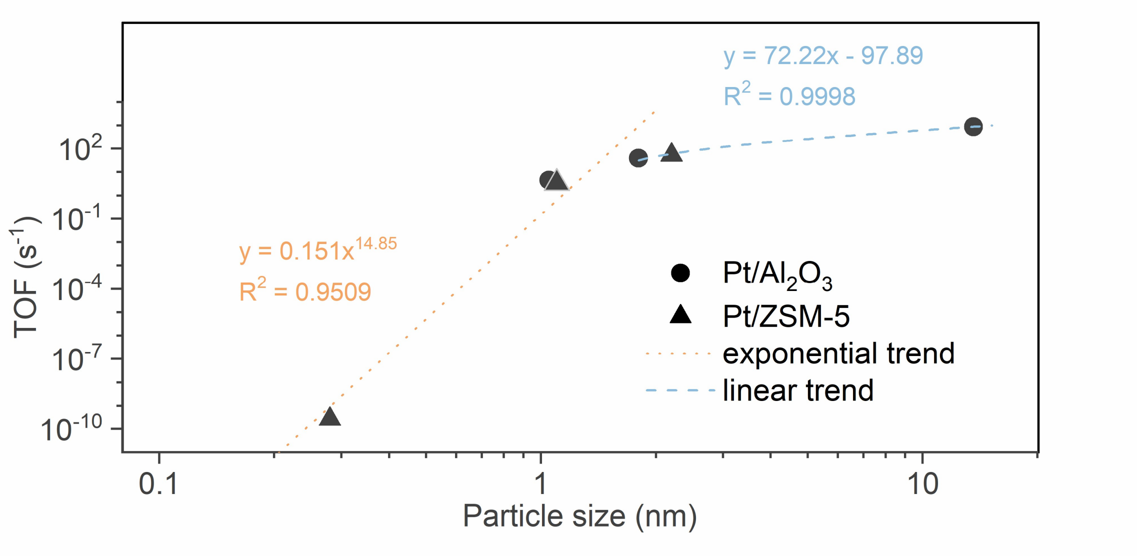

Figure S23. Dependence of TOF for ammonia oxidation on Pt particle size at 190 °C, calculated for data measured during heating in reaction mixture (500 ppm NH_3 and 13 % O_2 in N_2). Flow – 1050 cm^3/min. GHSV = 63,000 cm^{-1}. Loading – 50 mg of 1 wt. % Pt catalyst for Pt/ZSM-5, 25 mg of 2 wt. % Pt catalyst for Pt/Al_2O_3. Heating rate – 3 °C/min. Note the logarithmic scale of the y-axis while inspecting the trend linearity above 2 nm.

In order to compare TOFs in analogous conditions, the values of chemical reaction rate at 190 ° for all samples C during heating in the reaction mixture were determined. These TOF values were extrapolated from linear regressions plotted in Arrhenius coordinates that are shown in fig S19. For calculations 4 conversion points in the range 5-20 % conversion were selected for each sample. Each conversion value used in calculations was averaged from several data points collected at a certain temperature ±0.5 K and is listed in table S5.

TOF was calculated according to the formula:

$$TOF = \frac{X_{NH_3} \cdot C_{NH_3}^{in} \cdot F}{22.4 \cdot 10^6 \cdot 10^2 \cdot n_{surf}}$$

where: X_{NH_3} – ammonia conversion (%); $C_{NH_3}^{in}$ – ammonia concentration at reactor inlet (ppm); F – flow of reaction feed (L/s); 22.4 – normal molar volume (mol/L); 10^6 and 10^2 – ppm and percent conversion factors respectively; n_{surf} – number of surface Pt atoms in a catalyst sample (mol). Number of surface atoms was calculated by the formula:

$$n_{surf} = \frac{(m_{cat} \cdot w_{Pt} \cdot D)}{10^2 \cdot 195}$$

where m_{cat} – mass of a catalyst sample tested (g), w_{Pt} – Pt loading in a sample (%), 10^2 – percent conversion factor, D – Pt dispersion (fraction of 1). Pt dispersion was calculated based on an assumption that Pt particles were of hemispherical shape using the atomic parameters of Pt described in literature. [1, 2] The specific formula used is

$$D = \frac{1.02}{d}$$

where *d* is the particle diameter in nm.

Particle size used in calculations corresponded to the bigger fraction determined with TEM for samples PtA-IW-500, PtA-IW-700, PtZ-IW, since this fraction was predominant. For the other three samples, the predominant fraction showed particle sizes lower than 1 nm, which corresponded to full dispersion, according to the model used. Hence, dispersion equal to 1 was used in the case of PtZ-IE sample which had the predominant fraction of single sites. For PtA-IW-500 the particle diameter used in calculations was chosen as 1.1 nm as the average of the higher size fraction detected with TEM (1.7 nm) and the size of one Pt crystal cell unit (~0.4 nm) representing its highly disperse fraction. For PtZ-IE-R with slightly higher dispersion, the particle diameter chosen for calculations was 1.05 nm.

Table S5. Source data for Arrhenius plots for the tested catalysts and the results of TOF determination at 190 °C (in the rows marked with “extrapolated”).

Sample	Conversion, %	T, °C	$1/T \cdot 10^3$, K^{-1}	TOF, s^{-1}	ln(TOF)
Pt/Al_2O_3					
PtA-IW	5.1	213.9	2.05	29.7	3.39
	9.8	223.0	2.02	57.4	4.05
	14.7	229.0	1.99	86.3	4.46
	19.5	233.1	1.98	113.0	4.73
	Extrapolated:	190.0	2.16	4.8	1.57
PtA-IW-500	5.2	193.0	2.15	50.0	3.91
	10.1	202.0	2.11	97.8	4.58
	14.6	207.0	2.08	141.5	4.95
	19.9	211.0	2.07	192.7	5.26
	Extrapolated:	190.0	2.16	39.3	3.67
PtA-IW-700	5.2	178.9	2.21	371.2	5.92
	9.9	187.4	2.17	712.3	6.57
	14.9	192.5	2.15	1070.5	6.98
	19.8	196.2	2.13	1426.4	7.26
	Extrapolated:	190.0	2.16	884.4	6.78
Pt/ZSM-5					
PtZ-IE	7.0	353.7	1.60	30.5	3.74
	11.3	357.1	1.59	66.3	4.19
	15.9	360.5	1.58	96.1	4.56
	19.2	362.8	1.57	116.3	4.79
	Extrapolated:	190.0	2.16	$2.4 \cdot 10^{-10}$	-22.16
PtZ-IE-R	5.0	208.9	2.08	31.4	3.45
	10.0	215.0	2.05	62.2	4.13
	14.9	218.5	2.03	92.6	4.53
	19.4	220.9	2.02	121.1	4.80
	Extrapolated:	190.0	2.16	3.3	1.18
PtZ-IW	6.6	192.9	2.15	77.4	4.35
	9.9	195.7	2.13	116.1	4.75
	15.2	199.2	2.12	178.8	5.19
	20.1	201.5	2.11	236.2	5.46
	Extrapolated:	190.0	2.16	53.5	3.98

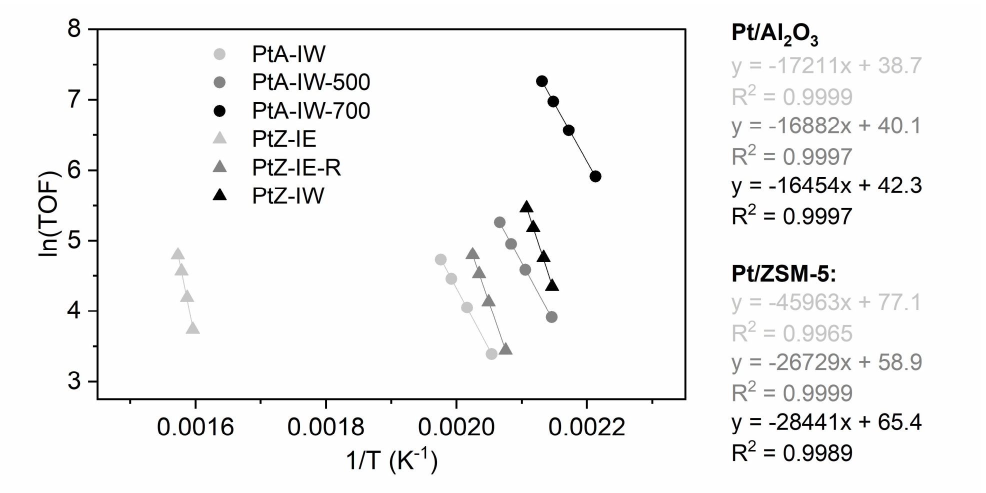

Figure S24. Arrhenius plots for the tested catalysts. Feed – 500 ppm NH_3, 13 % O_2 in inert; GHSV = 63,000 h^{-1}. The conversions used for reaction rates calculation did not exceed 20 % (see table S5 or details).

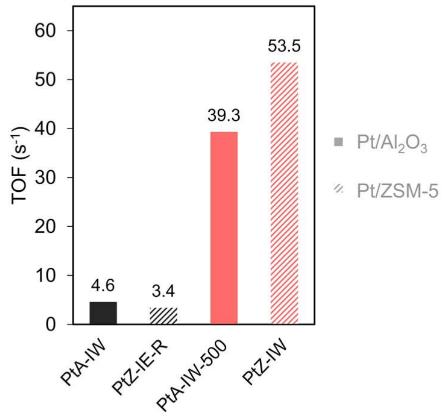

Figure S25. TOF comparison over alumina- and zeolite-supported samples with similar particle sizes. Full bars represent alumina-supported catalysts and dashed bars signify zeolite-supported catalysts. Samples with similar Pt particle sizes are marked with the same colour. Based on the data of the second heating in reaction mixture containing 500 ppm NH_3 and 13 % O_2 in N_2. Flow –1050 cm^3/min. GHSV = 63,000 cm^{-1}. Loading – 50 mg of 1 wt. % Pt/ZSM-5 catalysts and 25 mg of 2 wt. % Pt/Al_2O_3 catalysts.

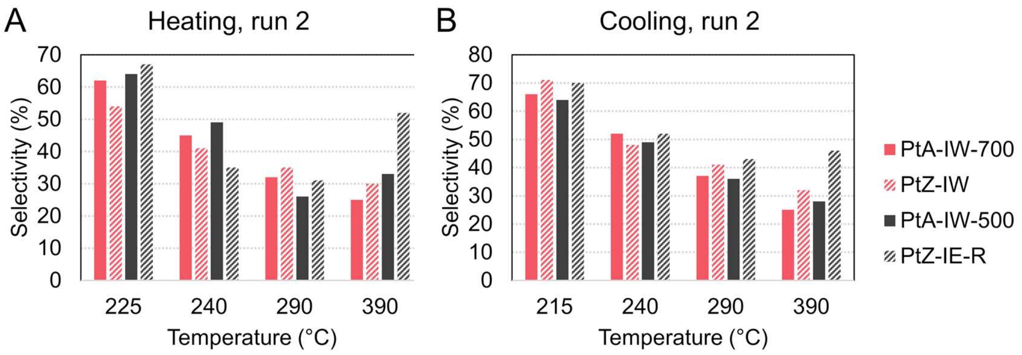

Figure S26. Selectivity comparison of alumina- and zeolite-supported samples (full and dashed bars respectively). Catalysts of similar light-off temperatures are marked with the same colour. Based on the data of the second heating (A) or cooling (B) in reaction mixture containing 500 ppm NH_3 and 13 % O_2 in N_2. Flow –1050 cm^3/min. GHSV = 63,000 cm^{-1}. Loading – 50 mg of 1 wt. % Pt/ZSM-5 catalysts and 25 mg of 2 wt. % Pt/Al_2O_3 catalysts.

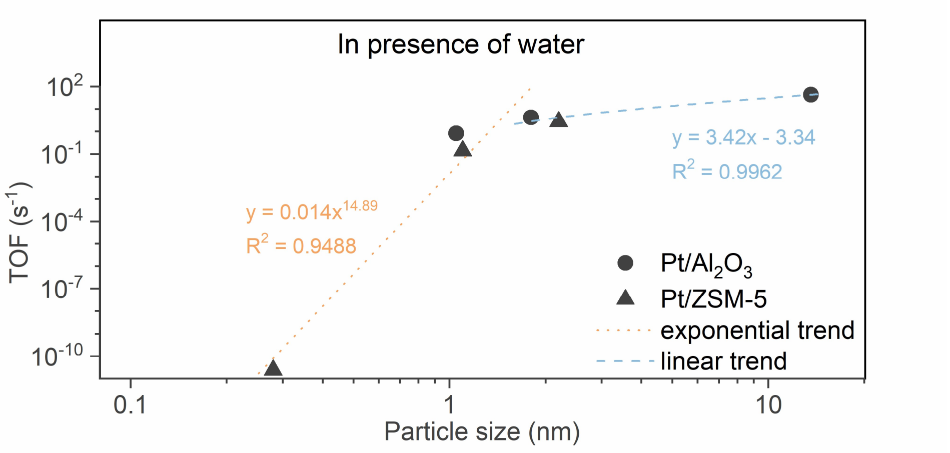

Figure S27. Dependence of TOF for ammonia oxidation on Pt particle size at 190 °C in presence of water, calculated for data measured during heating in water-containing reaction mixture (500 ppm NH_3 and 13 % O_2 , 5 % H_2O, and 10 % CO_2 in N_2). Flow – 1050 cm^3/min. GHSV = 63,000 cm^{-1}. Loading – 50 mg of 1 wt. % Pt catalyst for Pt/ZSM-5, 25 mg of 2 wt. % Pt catalyst for Pt/Al_2O_3. Heating rate – 3 °C/min. Based on light off data presented in figs. S15, S18.

Table S6. Source data for Arrhenius plots for the tested catalysts and the results of TOF determination in presence of water at 190 °C (in the rows marked with “extrapolated”).

Sample	Conversion, %	T, °C	1/T · 10^3, K^{-1}	TOF, s^{-1}	ln(TOF)
Pt/Al_2O_3					
PtA-IW	5.0	233.4	0.00198	29.3	3.38
	10.0	243.6	0.00194	58.7	4.07
	15.0	249.1	0.00192	87.9	4.48
	19.8	252.3	0.00190	116.3	4.76
	Extrapolated:	190	0.00216	0.83	-0.190
PtA-IW-500	4.9	216.8	0.00204	49.3	3.90
	7.5	221.4	0.00202	72.6	4.29
	10.0	224.9	0.00201	96.7	4.57
	14.9	229.6	0.00199	144.5	4.97
	16.9	231	0.00198	163.6	5.10
	Extrapolated:	190	0.00216	4.2	1.44
PtA-IW-700	5.0	208.2	0.00208	357.9	5.88
	10.0	214.3	0.00205	721.7	6.58
	15.0	218.2	0.00204	1077.5	6.98
	20.0	221	0.00202	1436.9	7.27
	Extrapolated:	190	0.00216	43.5	3.77
Pt/ZSM-5					
PtZ-IE	7.4	373.1	0.00155	43.0	3.76
	10.0	375.4	0.00154	57.8	4.06
	12.3	377.3	0.00154	71.8	4.27
	14.8	379.2	0.00153	86.9	4.47
	20.0	382.8	0.00152	124.1	4.82
	Extrapolated:	190	0.00216	$2.42 \cdot 10^{-11}$	-24.4
PtZ-IE-R	5.0	223.5	0.00201	31.2	3.44
	10.2	228.0	0.00200	63.7	4.15
	14.7	230.6	0.00199	91.6	4.52
	18.0	232.1	0.00198	112.0	4.72
	20.0	232.7	0.00198	125.5	4.82
	Extrapolated:	190	0.00216	0.14	-1.97
PtZ-IW	4.9	209.6	0.00207	57.2	4.05
	9.9	214.0	0.00205	117.0	4.76
	12.4	215.6	0.00205	146.2	4.98
	14.9	216.9	0.00204	175.0	5.17
	19.1	218.9	0.00203	224.7	5.42
	Extrapolated:	190	0.00216	2.8	1.01

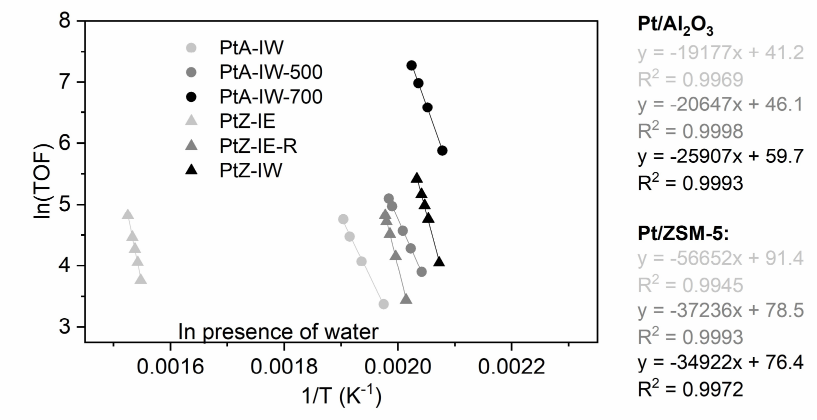

Figure S28. Arrhenius plots for the tested catalysts in the presence of water. Feed – 500 ppm NH_3, 13 % O_2, 5 % H_2O, and 10 % CO_2 in inert; GHSV = 63,000 h^{-1}. The conversions used for reaction rates calculation did not exceed 20 % (see table S5 or details).

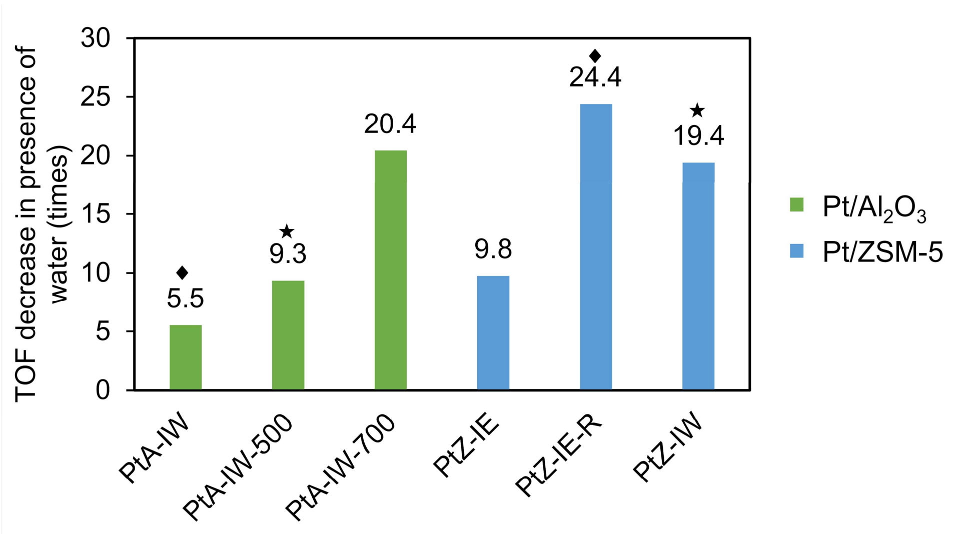

Figure S29. Comparison of TOF decrease in water-containing reaction mixture for alumina- and zeolite-supported catalysts. Based on TOF data presented I figs. S23 and S27. Two groups of catalysts with similar Pt particle size on different supports are marked with either a diamond or a star.

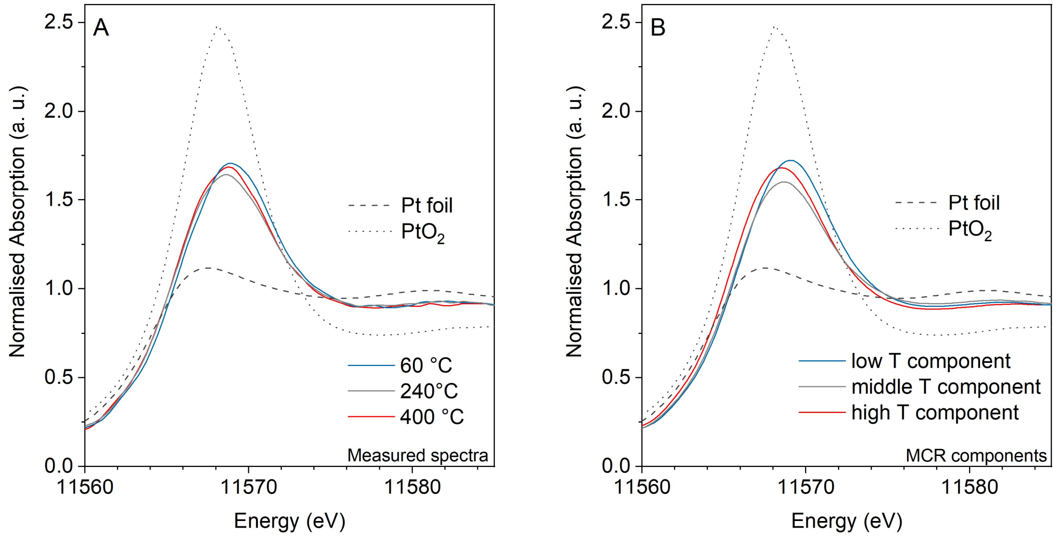

Figure S30. Comparison of Pt foil and PtO_2 XANES spectra at the Pt L_3-edge with: A – the XANES spectra of PtA-IW-500 measured at three different temperatures during the light-off (energy profiles of the contour plot in fig. 6); B – MCR-resolved spectral components from the QEXAFS dataset for the same sample (are shown in fig.7).

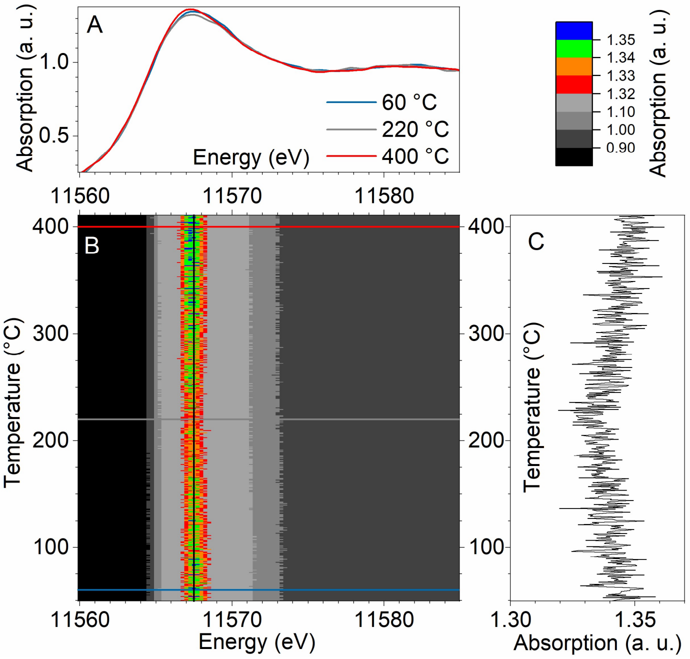

Figure S31. Contour plot of PtA-IW-700 *operando* Pt L_3-egde XANES spectra measured during the light-off in the reaction mixture (500 ppm NH_3 and 10 % O_2 in inert). A – spectra with three most distinct whiteline shapes (energy profiles from the contour plot). B – the contour plot. C – absorption profile at the energy close to maximum absorption (11567.5 eV). Flow – 75 cm^3/min (corresponds to a GHSV of about 127,000 h^{-1}). Heating rate – 5 °C/min. 2 wt. % Pt catalyst of 100-200 µm sieved fraction was loaded into a 1.5-mm-diameter quartz capillary to form a bed length of ~ 5 mm.

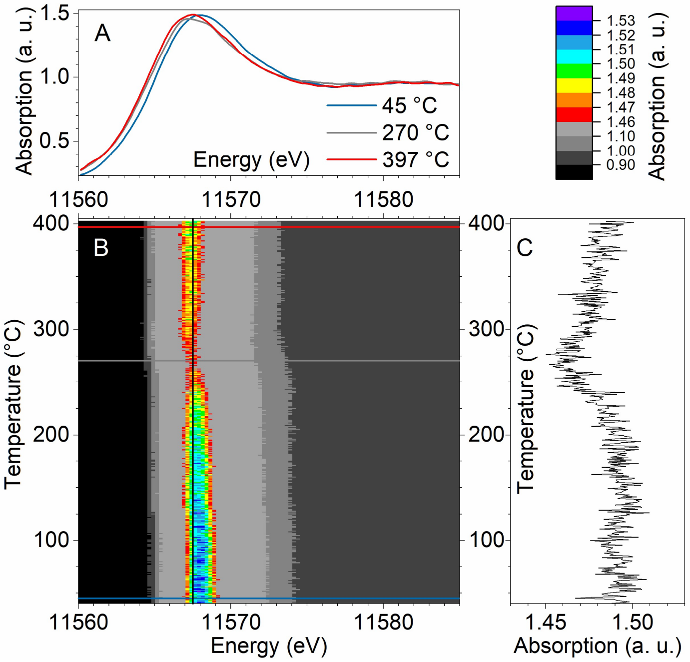

Figure S32. Contour plot of PtZ-IW *operando* Pt L_3-edge XANES spectra measured during the light-off in the reaction mixture (890 ppm NH_3 and 10 % O_2 in inert). A – spectra with three most distinct whiteline shapes (energy profiles from the contour plot). B – the contour plot. C – absorption profile at the energy close to maximum absorption (11567.5 eV). Flow –70 cm^3/min (corresponds to a GHSV of about 120,000 h^{-1}). Heating rate – 5 °C/min. 1 wt. % Pt catalyst of 100-200 µm sieved fraction was loaded into a 1.5-mm-diameter quartz capillary to form a bed length of ~ 5 mm.

References

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2 A. Boubnov, S. Dahl, E. Johnson, A. P. Molina, S. B. Simonsen, F. M. Cano, S. Helveg, L. J. Lemus-Yegres and J.-D. Grunwaldt, *Appl. Catal. B*, 2012, **126**, 315-325.