Supporting information

Pt-based catalysts for NO_x reduction from H_2 combustion engines

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S1 Experimental

S1.1 Catalyst synthesis

The catalysts (2.0 wt.% Pt/BETA and 2.0 wt.% Pt/Al_2O_3) were prepared for the study of support effect. Commercial BETA zeolite (Zeolyst) with SAR of 25 and γ-Al_2O_3 (SASOL PURALOX SBa-200) were used as supports. Following the same procedure, 2 wt.% Pt was loaded by the incipient wet impregnation. The powder sample after drying overnight was calcined at 600 °C for 8 h. The synthesized catalyst was further wash-coated onto the honeycomb monolith substrate for the flow reactor testing.

S1.2 Activity measurements

For the experiment investigating the H_2/NO ratio effect, after the standard pretreatment, a total of 20 continuous testing cycles were carried out with H_2/NO ratios of 0, 4.4, 8.8, and 13.2. This involved steadily increasing the hydrogen concentration to 2200 ppm, 4400 ppm, and 6600 ppm over five test cycles each, following the first five test cycles of 0 ppm (**Table S1**).

The three catalysts, 2 wt.% Pt/SSZ-13, 2 wt.% Pt/BETA, 2 wt.% Pt/Al_2O_3 were pre-treated for hydrothermal ageing and then subjected to five test cycles to compare their hydrothermal stability. The catalyst underwent a hydrothermal aging process at 800 °C for 2 followed by 4 hours before undergoing the standard 5 reaction cycles (**Table S1**).

Table S1 The activity test procedure and reaction conditions (GHSV=20,000 h^{-1} (STP)).

Step	H_2/NO ratio effect experiment	Conditions
1	Degreening & Pretreatment	(i) 10% O_2 in Ar for 4 h at 550 °C (ii) 10% O_2 and 5% H_2O in Ar for 30 min at 500 °C
2	Cooling	(i) Cooling from 500 °C to 80 °C in Ar (rate: 5 °C/min) (ii) keep at 80 °C for 30 min
3	Test cycle *5 *4	(i) Continuous reaction from 80 °C to 500 °C (heating rate: 5 °C/min) in the gas mixture of 500 ppm NO, 10% O_2, 5% H_2O in Ar (ii) keep at 500 °C with the same gas mixture for 20 min (iii) continuous reaction from 500 °C to 80 °C (cooling rate: 5 °C/min) in the same gas mixture (iii) repeat (i) and (ii) with 2200 ppm H_2 in the gas mixture (iv) repeat (i) and (ii) with 4400 ppm H_2 in the gas mixture (v) repeat (i) and (ii) with 6600 ppm H_2 in the gas mixture
Step	Ageing test	Conditions
1	Hydrothermal Pretreatment	(i) 10% O_2 in Ar for 4 h at 550 °C (ii) 10% O_2 and 5% H_2O in Ar for 2/4 h at 800 °C
2	Cooling	(i) Cooling from 800 °C to 80 °C in Ar (rate: 5 °C/min) (ii) keep at 80 °C for 30 min
3	Test cycle *5	(i) Continuous reaction from 80 °C to 500 °C (heating rate: 5 °C/min) in the gas mixture of 500 ppm NO, 4400 ppm H_2, 10% O_2, 5% H_2O in Ar (ii) keep at 500 °C with the same gas mixture for 20 min (iii) continuous reaction from 500 °C to 80 °C (cooling rate: 5 °C/min) in the same gas mixture

S1.4 Results

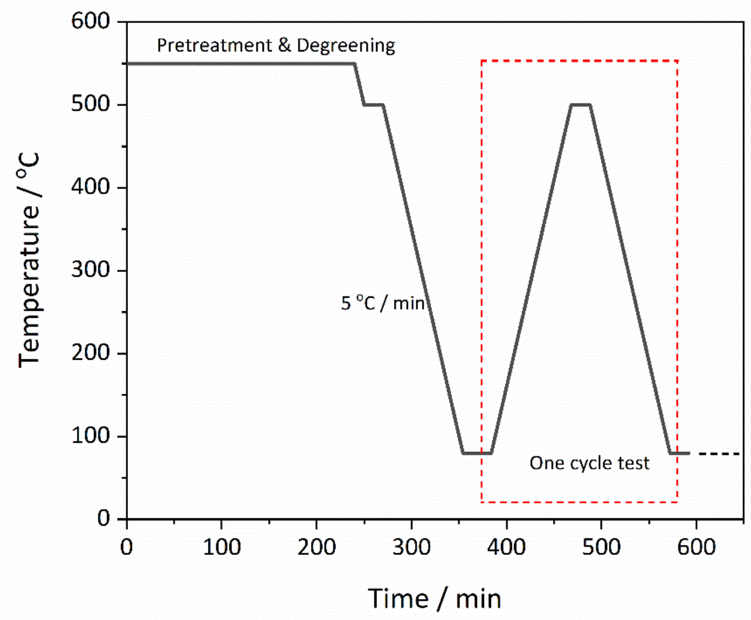

Fig. S1 The activity test procedure (GHSV=20,000 h^{-1} (STP); gas inlet: 10 % O_2, 5 % H_2O, 500 ppm NO, varying H_2 concentration balanced in Ar; T: 80-500 °C; heating rate: 5 °C/min). Five cycles are repeated.

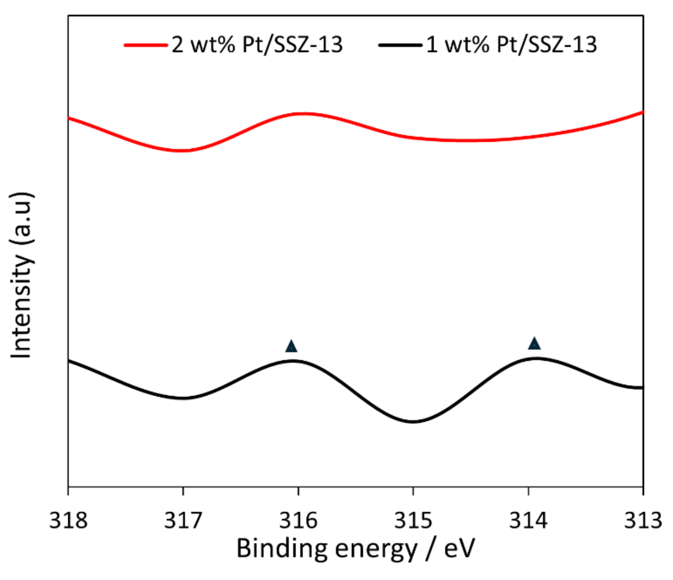

Fig. S2 X-ray photoelectron spectrum (XPS) spectra of the Pt $4d_{5/2}$ regions for 2.0 wt.% Pt/SSZ-13 and 1.0 wt.% Pt/SSZ-13 de-greened catalysts.

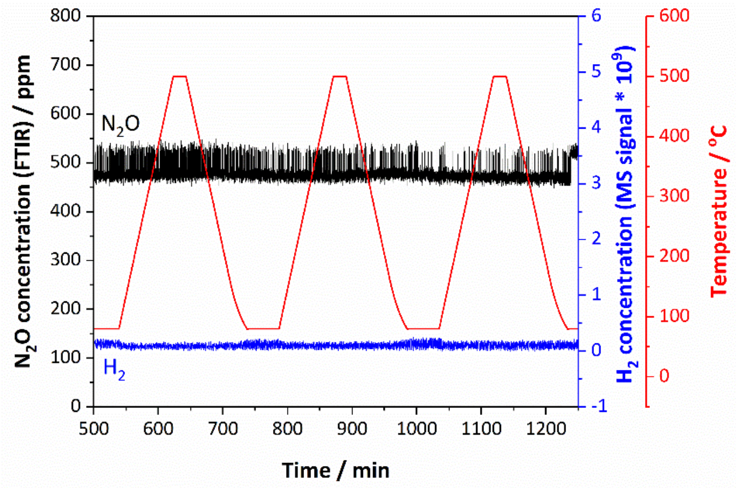

Fig. S3 The activity test result of N_2O reduction by H_2 on 1 wt.% Pt/SSZ-13 catalyst (GHSV=20,000 h^{-1} (STP); gas inlet: 10 % O_2, 5 % H_2O, 500 ppm N_2O, 5000 ppm H_2 balanced in Ar; T: 80-500 °C; heating rate: 5 °C/min).

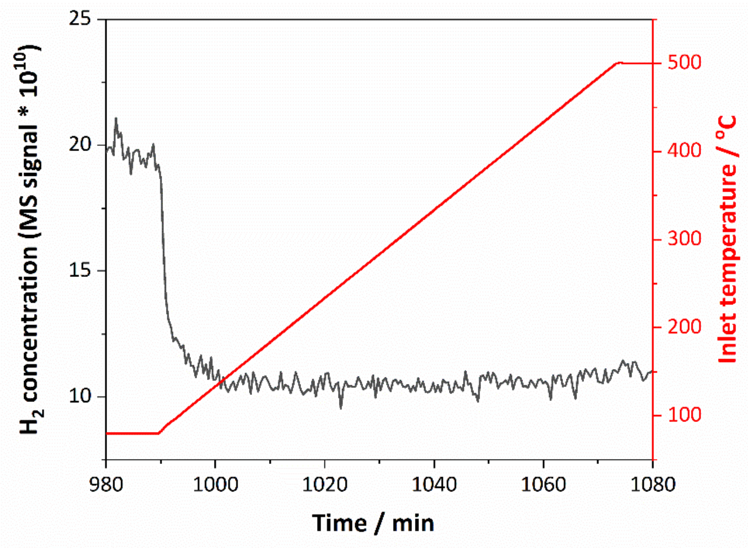

Fig. S4 H_2 intensity profiles measured by MS on 2 wt.% Pt/SSZ-13 (GHSV=20,000 h^{-1} (STP); gas inlet: 10% O_2, 5% H_2O, 500 ppm NO, 4400 ppm H_2 balanced in Ar; T: 80-500 °C; heating rate: 5 °C/min).

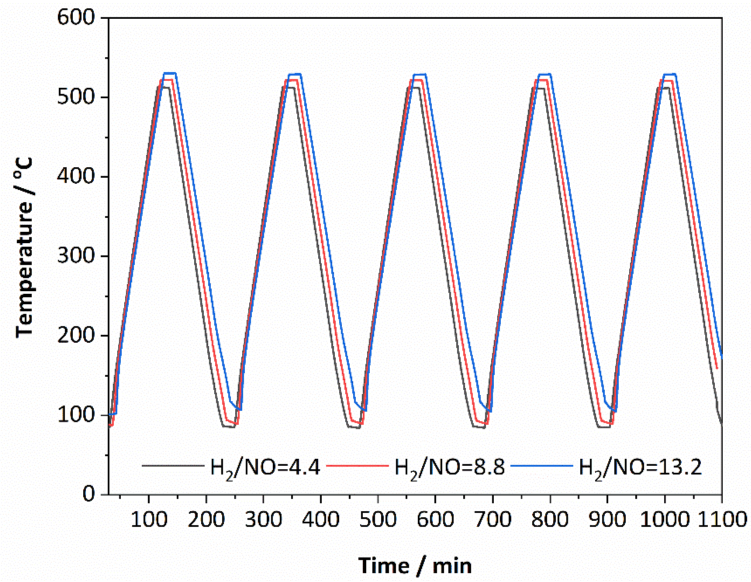

Fig. S5 The catalyst temperature comparison of 2 wt.% Pt/SSZ-13 catalyst with different H_2/NO (GHSV=20,000 h^{-1} (STP); gas inlet: 10 % O_2, 5 % H_2O, 500 ppm NO, 2200 /4400/6600 ppm H_2 balanced in Ar; T: 80-500 °C; heating rate: 5 °C/min).

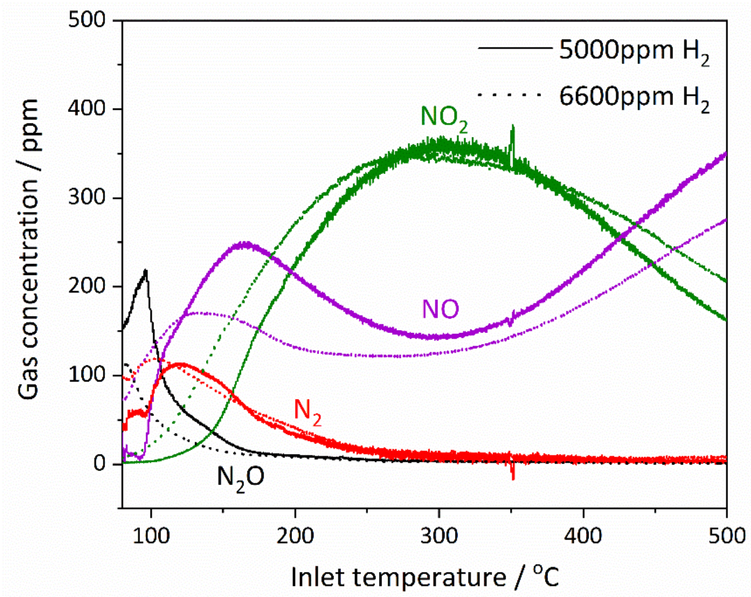

Fig. S6 NO, NO_2, N_2O, and N_2 concentrations of H_2-SCR on 1 wt.% Pt/SSZ-13 with H_2/NO ratio of 10 and 15 (GHSV=20,000 h^{-1} (STP); gas inlet: 10% O_2, 5% H_2O, 500 ppm NO, 5000/6600 ppm H_2 balanced in Ar; T: 80-500 °C; heating rate: 5 °C/min).

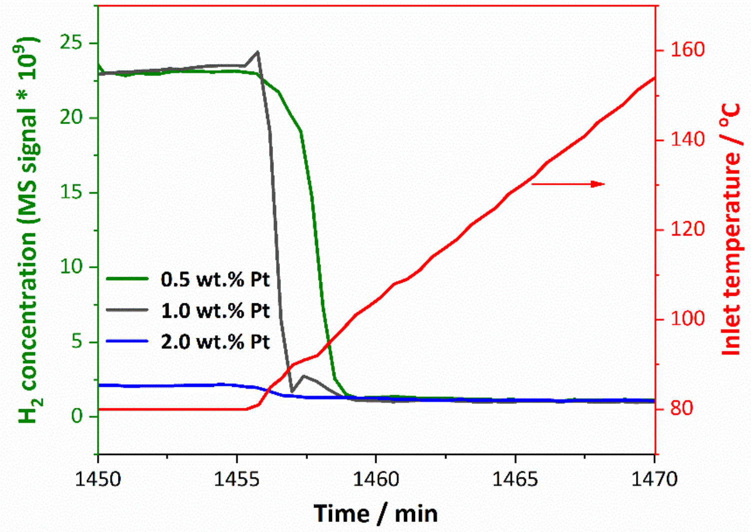

Fig. S7 H_2 Intensity profiles measured by MS on Pt/SSZ-13 catalysts with different Pt loadings (GHSV=20,000 h^{-1} (STP); gas inlet: 10% O_2, 5% H_2O, 500 ppm NO, 5000 ppm H_2 balanced in Ar; T: 80-500 °C; heating rate: 5 °C/min).

Effect of support

To examine the effect of support, Pt was loaded onto Al_2O_3 and two different zeolites (BETA and SSZ-13) for performance comparison. It is well known that SSZ-13 zeolite has excellent high-temperature hydrothermal stability and low-temperature activity, so the three catalysts were subjected to high-temperature hydrothermal treatment to study the stability of their performance. Specific pre-treatment conditions can be found in the Experimental section of the **SI**. It should be noted that Pt/BETA and Pt/Al_2O_3 are freshly degreened samples, while the Pt/SSZ-13 sample has been previously tested for its effect on hydrogen concentration (**Fig. 7**) and multiple other cycles. Comparing the activities of the three catalysts in **Fig. S8**, the two zeolite-based catalysts exhibited similar N_2 production (105 ppm), but the degreened Pt/BETA has a higher NO conversion (blue line). On the contrary, although more NO was converted on the Pt/Al_2O_3 catalyst, the majority of NO was oxidised to form NO_2, with only a small portion reduced to form N_2. After two hours of hydrothermal treatment, the performance of Pt/SSZ-13 improved from the original experiment in **Fig. 7** regarding the elevated NO conversion and unchanged N_2 production. The BETA zeolite sample began to show degradation of its performance after 2 hours of hydrothermal ageing, as evidenced by a lowering of N_2 production at low temperatures and simultaneously more N_2O generation. However, at higher temperatures, the N_2 production increased. Moreover, the results in **Fig. S9** demonstrate that after another 4 hours of hydrothermal ageing (6 hours in total), the Pt/BETA further increased the N_2 formation at higher temperatures. However, it is observed a decrease in the overall catalyst activity in the NO performance at high temperatures. The SSZ-13-supported sample received less influence on the performance, reflecting its good hydrothermal durability, but interestingly also more nitrogen was produced for the 6 h aged sample. The summarize, the two zeolite samples are similar concerning N_2 generation, but they are superior to the Al_2O_3 catalyst for H_2 SCR performance. However, SSZ-13 are well known to be very robust support for aftertreatment catalysts, compared to both beta and ZSM-5 [1,2] and is, therefore, the focus of this work.

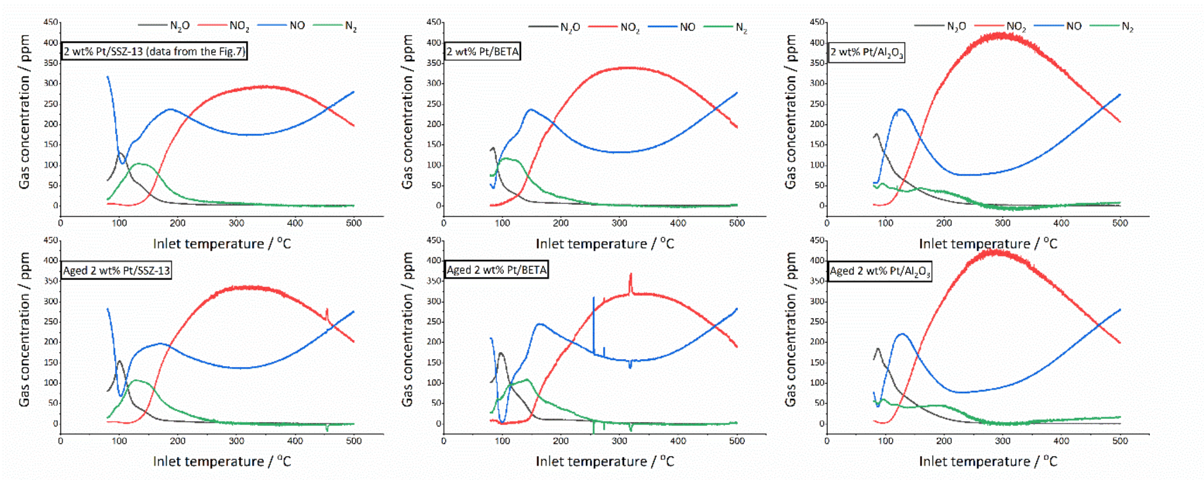

Fig. S8 NO, NO_2, N_2O, and N_2 concentrations of H_2-SCR on 2 wt.% Pt/SSZ-13; 2 wt.% Pt/BETA; 2 wt.% Pt/Al_2O_3 and hydrothermal aged 2h samples. (GHSV=20,000 h^{-1} (STP); gas inlet: 10% O_2, 5% H_2O, 500 ppm NO, 4400 ppm H_2 balanced in Ar; T: 80-500 ℃; heating rate: 5 ℃/min).

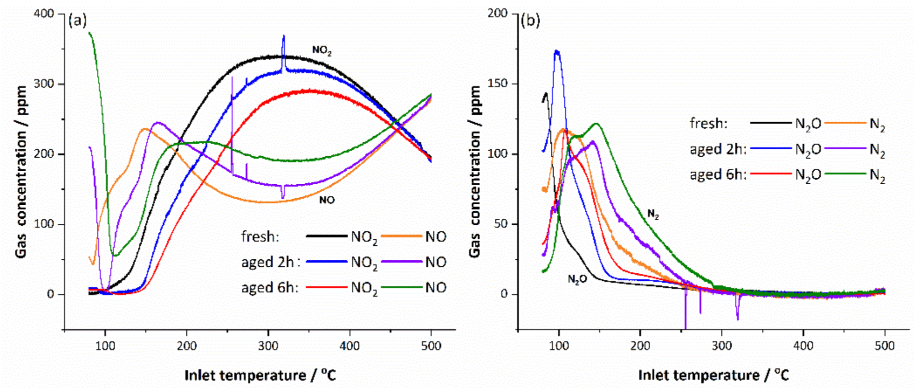

Fig. S9 NO, NO_2, N_2O, and N_2 concentrations of H_2-SCR on 2 wt.% Pt/BETA (fresh), hydrothermally aged for 2h and 6 (2+4) h. (GHSV=20,000 h^{-1} (STP); gas inlet: 10% O_2, 5% H_2O, 500 ppm NO, 4400 ppm H_2 balanced in Ar; T: 80-500 ℃; heating rate: 5 ℃/min).

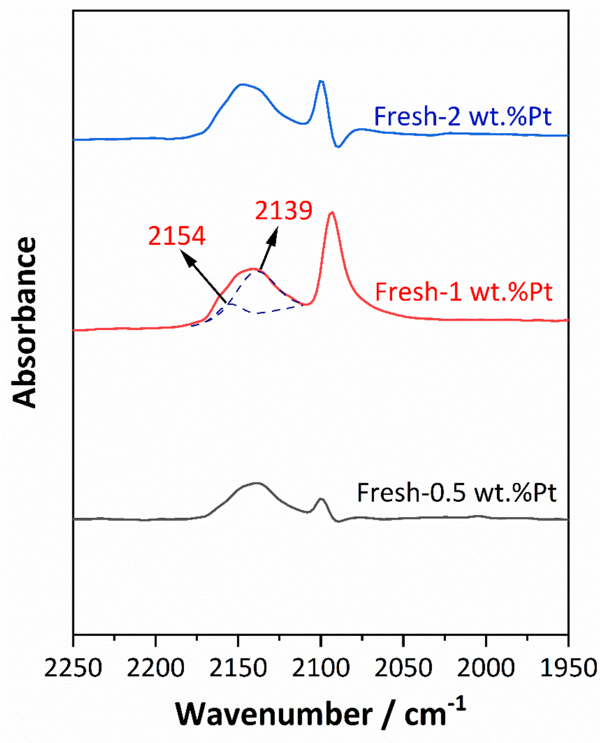

Fig. S10 CO DRIFTS spectra performed on 0.5 wt.%/1.0 wt.%/2.0 wt.% fresh Pt/SSZ-13 catalysts.

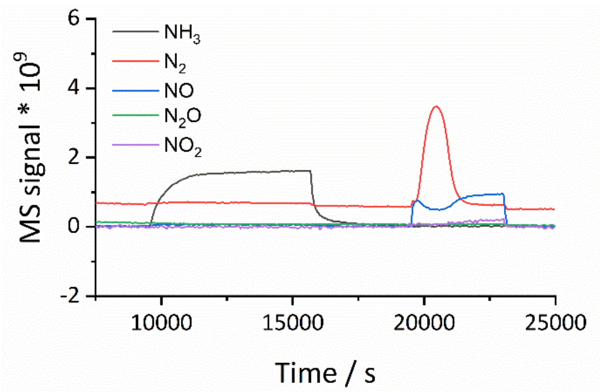

Fig.S11 MS signal of NH_3, N_2, NO, N_2O, NO_2 for In-situ DRIFTS experiment for NH_3-NO reaction

S1.5 References

1 F. Gao and J. Szanyi, *Appl Catal A Gen*, 2018, **560**, 185–194.

2 S. Mohan, P. Dinesha and S. Kumar, *Chemical Engineering Journal*, 2020, 384.