

**Supplementary Information for**

**Controlling N<sub>2</sub>O formation in regeneration of NO<sub>x</sub> storage and  
reduction catalysts: From impact of platinum-group metal type  
to rational utilization**

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## 1. BET surface areas and noble metals dispersions

The BET specific surface area was measured by N<sub>2</sub> adsorption at 77 K with a F-Sorb 3400 apparatus. Before measurement, samples were pre-treated at 200 °C under vacuum for 4 h to eliminate the adsorbed species. Noble metals dispersions were measured using pulse CO chemisorption. A sample was oxidized in 10% O<sub>2</sub>/N<sub>2</sub> at 350 °C for 30 min and then reduced in 5.2% H<sub>2</sub>/N<sub>2</sub> at 450 °C for 20 min. After a N<sub>2</sub> purge at 450 °C for 10 min, the sample was cooled down to room temperature before the CO pulse chemisorption measurement. The dispersion of Pt (Pd or Rh) was calculated based on the CO adsorption stoichiometry of 0.8 (0.5 or 1.2).<sup>[1-3]</sup>

Table S1. BET surface areas and noble metals dispersions of each sample.

Samples	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	NM dispersions (%)
PtBaAl	120	64
PdBaAl	114	37
RhBaAl	113	32

## 2. Combined DRIFTS and FT-IR analyzer

As shown in Figure S1, the inlet gases (150 ml/min) are firstly injected into the reactor of Nicolet 6700 FT-IR Spectrometer, and then the outlet gases mixed with bypass N<sub>2</sub> (200 ml/min) are together introduced into a MKS MultiGas 2030 FT-IR analyzer. Two check valves are used to ensure the gases flow normally without backflow phenomenon. In addition, all pipes are heated to 140 °C to prevent water condensation and ammonia adsorption.

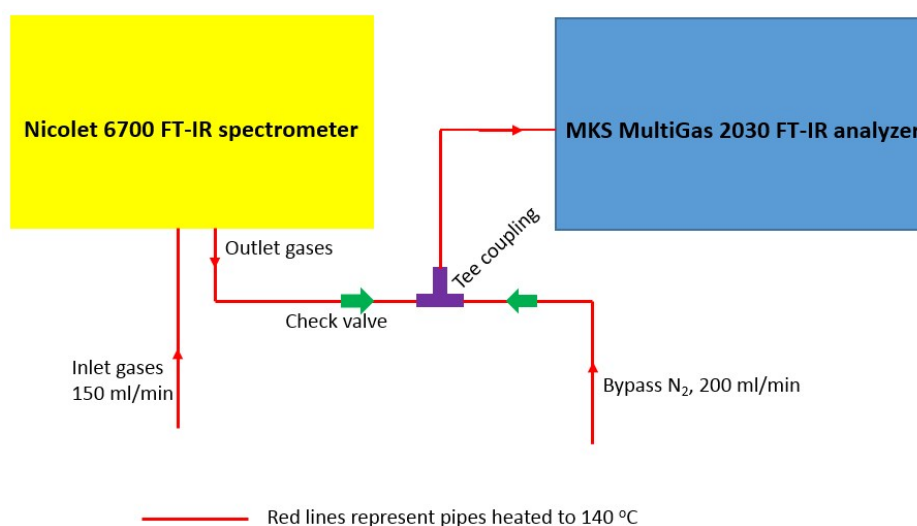


Figure S1. Schematic diagram of combined in-situ DRIFTS and FT-IR analyzer.

### Methodology of the DRIFT quantification<sup>[4]</sup>

In the DRIFTS measurements, the raw reflectance data (absorbance units) of all the spectra have been converted into Kubelka-Munk units via Nicolet OMNICTM software (Ver. 7.3).

$$f(R) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k}{s} = 2.303 \times a \times \frac{c}{s} \quad \text{S1}$$

$f(R)$ : Kubelka-Munk function;

$R$ : Absolute reflectance of the sampled layer;

k: Molar absorption coefficient;

a: Absorptivity;

s: Diffusion coefficient;

c: Concentration of absorbed species.

### 3. Kinetic study of NO reduction by CO

In order to rule out the external mass transfer limitation, four gas hourly space velocities have been used. Figures S2-S4 present the variations in NO<sub>x</sub> consumption rates as a function of GHSV on PtBaAl, PdBaAl and RhBaAl, respectively. We chose the condition with GHSV = 750,000 h<sup>-1</sup> to ensure that the reactions are free from external mass transfer limitation.

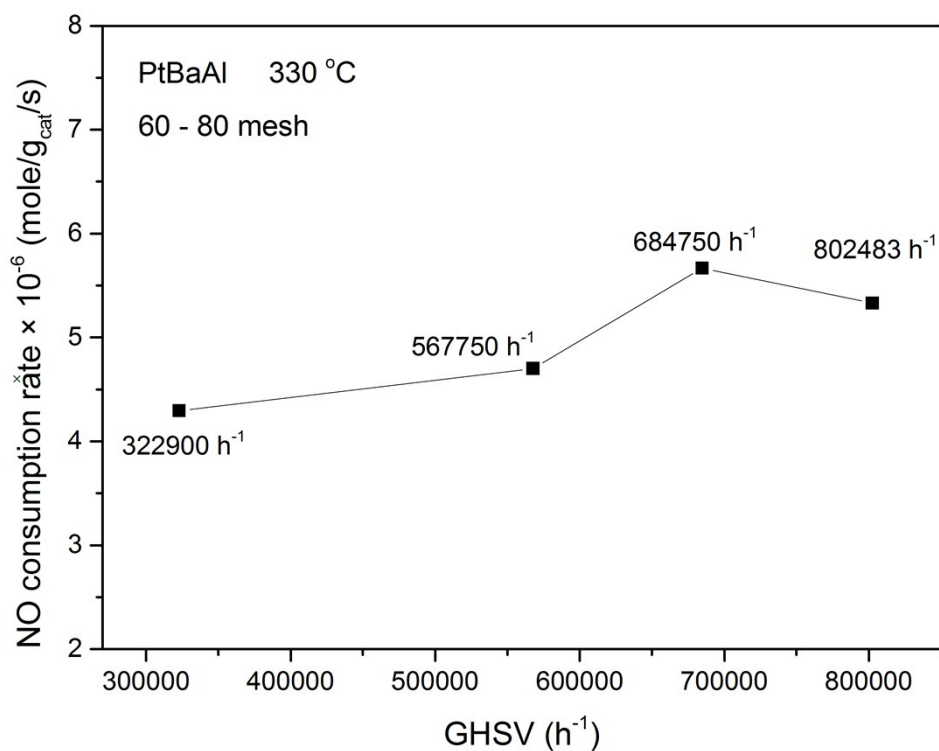


Figure S2. NO consumption rate on PtBaAl as a function of GHSV/h<sup>-1</sup> at 330 °C.

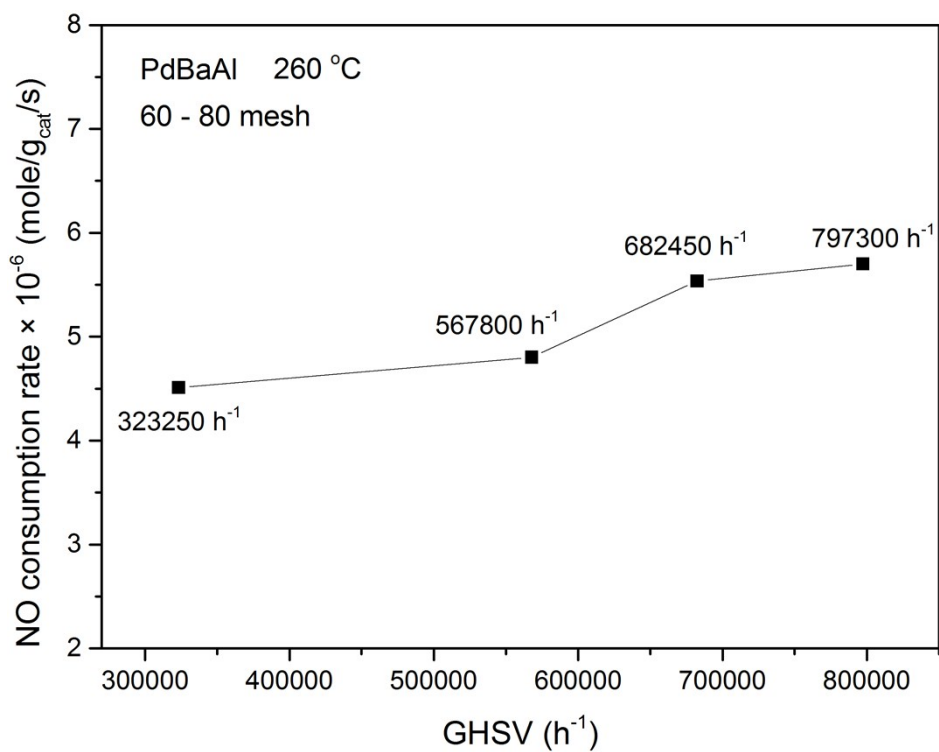


Figure S3. NO consumption rate on PdBaAl as a function of GHSV/h<sup>-1</sup> at 260 °C.

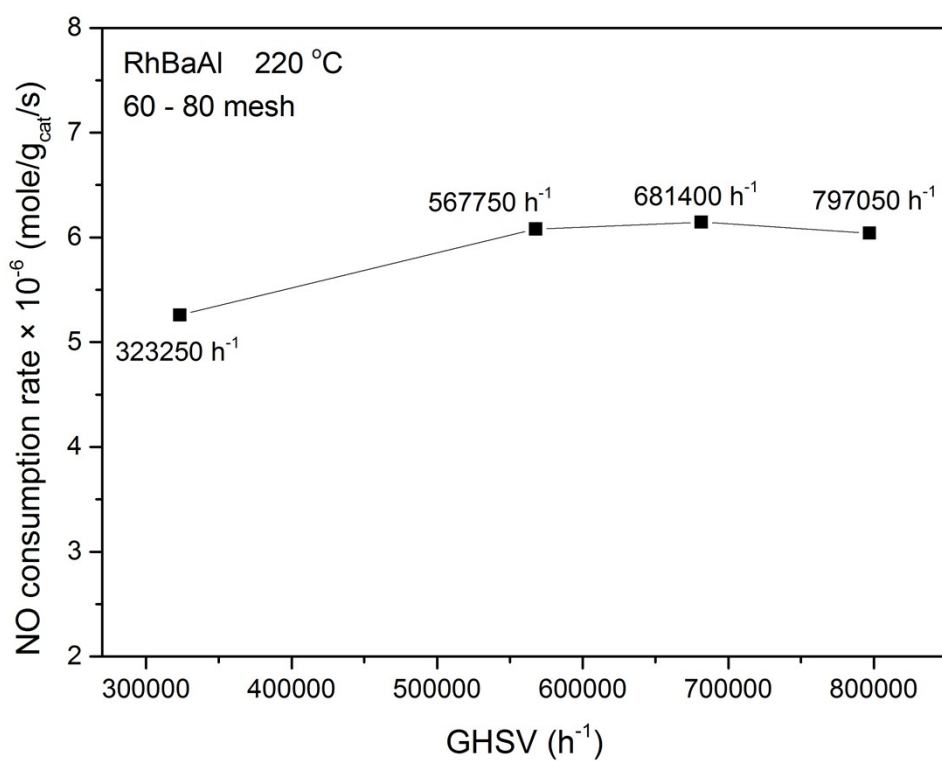


Figure S4. NO consumption rate on RhBaAl as a function of GHSV/h<sup>-1</sup> at 220 °C.

We examined the internal mass transfer limitation by measuring NO consumption

rates using the samples with four different particle sizes, see Figures S5-S7. We chose the samples with the particle size (80 – 100 mesh) that the reactions were not affected by the internal mass transfer.

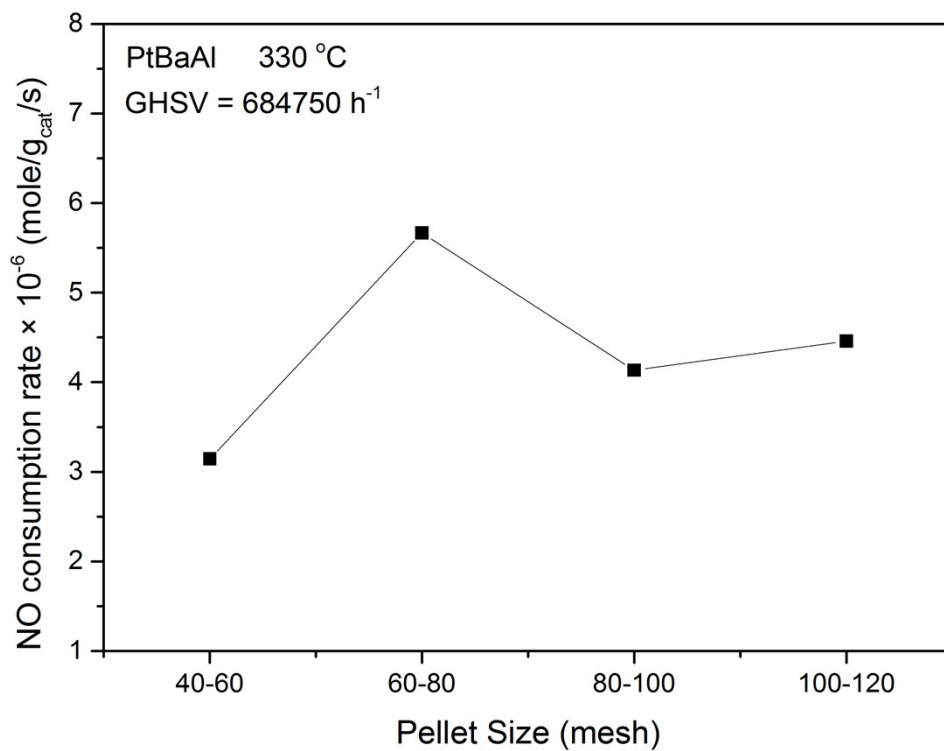


Figure S5. NO consumption rate on PtBaAl as a function of particle size at 330 °C.

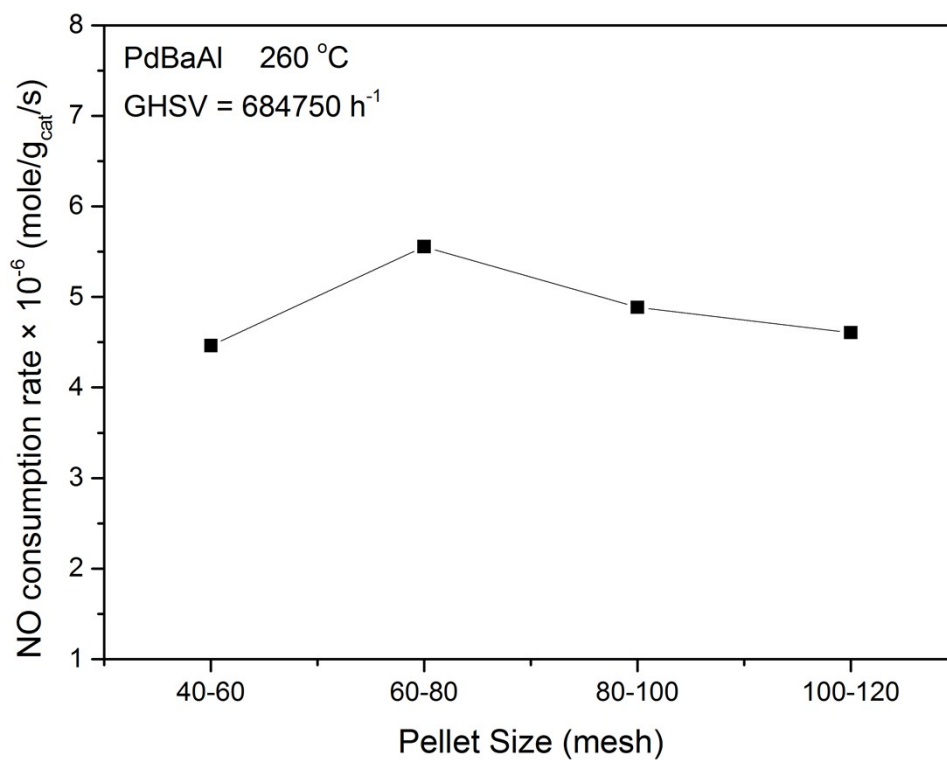


Figure S6. NO consumption rate on PdBaAl as a function of particle size at 260 °C.

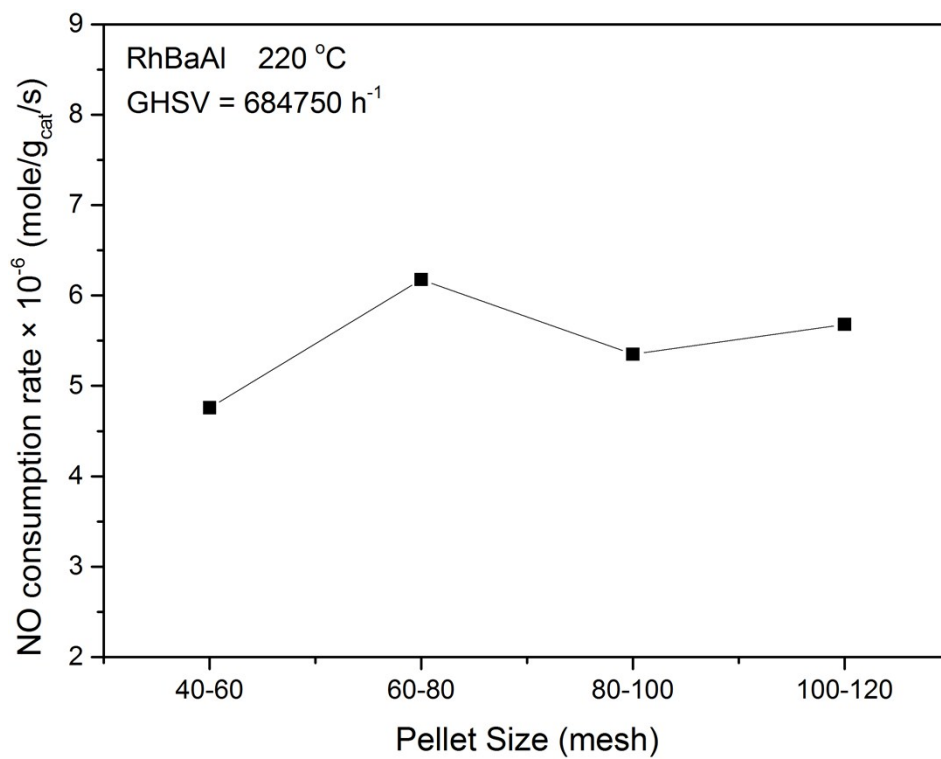


Figure S7. NO consumption rate on RhBaAl as a function of particle size at 220 °C.



#### 4. NSR activity tests

The NO<sub>x</sub> stored amount in lean periods, and the amount of N<sub>2</sub>O and NH<sub>3</sub> formed in rich periods on these samples at 150 – 300 °C were calculated based on equations S2-S4.

$$\text{Lean NO}_x \text{ storage} = \frac{\left( \int_0^t ([\text{NO}_x]_{\text{in}} - [\text{NO}_x]) dt - \int_t^{t'} [\text{NO}_x] dt \right)}{60 \frac{\text{s}}{\text{min}} V_m \times m_{\text{cat}}} \times F \quad \text{S2}$$

$$\text{Rich N}_2\text{O formation} = \frac{\int_{t'}^{t''} [\text{N}_2\text{O}] dt}{60 \frac{\text{s}}{\text{min}} V_m \times m_{\text{cat}}} \times F \quad \text{S3}$$

$$\text{Rich NH}_3 \text{ formation} = \frac{\int_{t'}^{t''} [\text{NH}_3] dt}{60 \frac{\text{s}}{\text{min}} V_m \times m_{\text{cat}}} \times F \quad \text{S4}$$

Here,  $\int_0^t [\text{NO}_x] dt$  was the integration area of inlet NO<sub>x</sub> introduced to the reactor in the lean period and  $\int_0^t [\text{NO}_x] dt$  was the integration area of NO<sub>x</sub> measured in the lean period.  $\int_t^{t'} [\text{NO}_x] dt$  was the area of NO<sub>x</sub> measured in the delay1 period. ‘F’ (L·min<sup>-1</sup>) was the total flow rate.  $V_m = 22.4 \text{ L} \cdot \text{mol}^{-1}$ ,  $m_{\text{cat}} = 0.25 \text{ g}$ . In addition, 0 – t, t – t’ and t’ – t’’ was the time corresponding to lean, delay1 and rich period, respectively.

Table S2. Lean NO<sub>x</sub> storage, and rich N<sub>2</sub>O and NH<sub>3</sub> formation on PtBaAl, PdBaAl and RhBaAl at 150, 200, 250 and 300 °C, respectively.

Samples	Temperature (°C)	Lean NO <sub>x</sub> storage (umol/g <sub>cat</sub> )	Rich N <sub>2</sub> O formed (umol/g <sub>cat</sub> )	Rich NH <sub>3</sub> formed (umol/g <sub>cat</sub> )
PtBaAl	150	45.17	0.30	0.05
	200	54.03	0.42	0.45
	250	89.66	1.04	2.09
	300	103.01	0.15	12.36
PdBaAl	150	62.95	0.21	0.03
	200	61.49	3.30	0.32
	250	48.15	3.15	1.05
	300	60.69	0.87	4.80
RhBaAl	150	30.35	0.16	1.10
	200	39.34	0.18	1.42
	250	50.92	0.12	6.34
	300	55.37	0.12	9.20

## 5. Normalization of CO adsorption on PGM-BaO/Al<sub>2</sub>O<sub>3</sub>

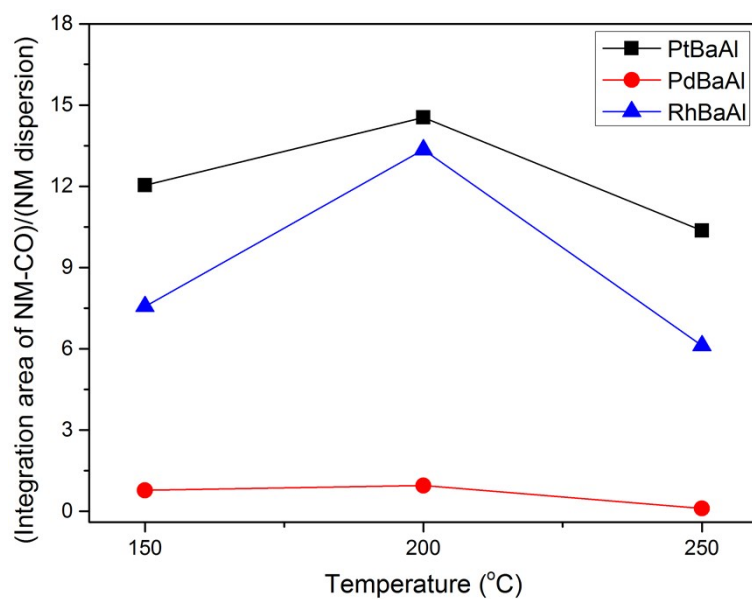


Figure S8. Normalization of CO adsorption on Pt, Pd and Rh metals during CO/NO co-adsorption at 150, 200 and 250 °C. The normalization is defined that integration area of PGM-CO IR band is

divided by PGM dispersion.

As shown in Figure S8, CO adsorption on noble metals of these catalysts decreases in the order: PtBaAl > RhBaAl > PdBaAl at 150, 200 and 250 °C. PdBaAl has the weakest CO adsorption, implying CO adsorption behavior may be less detrimental to NO reduction on PdBaAl than PtBaAl.

## References

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- [4] L. Wang, W. Li, S.J. Schmieg, D. Weng, *J. Catal.* 324 (2015) 98-106.