Electronic Supplementary Information (ESI)

Mechanistic insights into NOx storage-reduction (NSR) catalyst by spatiotemporal *operando* X-ray absorption spectroscopy

Yasutaka Nagai,[*a] Akihiko Kato,[a] Masaoki Iwasaki[a] and Keisuke Kishita[b]

[a.] *Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan. E-mail: e1062@mosk.tytlabs.co.jp*

[b.] *Toyota Motor Corporation, Toyota, Aichi 471-8572, Japan*

Table of Contents

Experimental Procedures

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Catalyst preparation

0.5 wt% Rh/BaO (10 wt% as Ba)/γ-Al2O3 catalyst was prepared in the following two steps. First, the Rh/γ-Al$_2$O$_3$ catalysts were prepared by incipient wet impregnation of the aqueous solution of γ-Al$_2$O$_3$ (185 m^2/g) powder with a Rh precursor (Rhodium nitrate). The impregnated powders were dried overnight at 110 °C and calcined at 500 °C for 3 h in air. Second, the obtained sample was impregnated with an aqueous solution of a barium precursor (Barium acetate), followed by calcination at 500 °C for 3h to obtain the Rh/BaO/γ-Al$_2$O$_3$ catalyst. The catalysts for *operando* XAS measurement were pressed into disks and pulverized to 75 − 150 μm size.

Spatiotemporal operando XAS measurement

The *operando* XAS experiments were performed at the Toyota beamline (BL33XU) of SPring-8, Japan. As shown in Fig. 1a, 66 mg of pellet catalyst (sieve fraction 75 − 150 μm) was placed in a quartz capillary tube, and the length of the catalyst bed was ca. 8 mm. The capillary tube with the pellet catalyst was set in a spatial *operando* cell (Fig. 1b). The cell was designed for transition X-ray detection at high sample temperatures (*T*max ~800 °C), while minimizing dead volume. In order to measure the XAS spectra at each point in the axial direction of the catalyst bed, a window for X-ray transition, which is located between the upper and lower heating furnace, is provided in the cell. The diameter of the X-ray beam was about 0.5 mm × 0.5 mm. The NSR reaction was operated at 450 °C, and a lean stream (oxygen excess) consisting of 0% or 0.07% NO, 7% O$_2$, and He balance was introduced into the cell for 300 or 60 s, followed by a rich stream of 3% H$_2$ and He balance for 240 s. The gas flow rates of the lean and rich streams were both 100 cc/min. A time for the gas flow to pass through the catalyst bed is 60 ms. Outlet gas was monitored by a quadrupole mass analyzer. H$_2$ (*m/z* 2), N$_2$ (*m/z* 28), NO (*m/z* 30), and N$_2$O (*m/z* 44) were measured every 150 ms. H$_2$O (*m/z* 18), NH$_3$ and a fragment of H$_2$O (*m/z* 17) were also measured every *ca.* 1.2 s. The gas flowing over the sample was quickly changed from a lean to a rich atmosphere using a gas-actuated switching valve (Fig. S2†). Measurement of inlet/outlet NO concentration confirmed that the amount of the stored NOx during the lean 60 s supply with 0.07% NO corresponded to 0.050 mmol/g-catalyst (33% of the saturated NOx storage amount) and that during the lean 300 s with 0.07% NO and 0 % NO corresponded to 0.151 mmol/g-catalyst (100% NOx storage amount) and 0 mmol/g-catalyst (0% NOx storage amount), respectively.

Under the NSR operation, along with the on-line mass spectra of the outlet gas species, Rh *K*-edge XAS spectra were recorded at four positions: 1 (A), 3 (B), 5 (C) and 7 (D) millimeters from the bed front (Fig. 1a). The detailed experimental sequences for spatiotemporal *operando* XAS measurement are described in Table S1†. After the pre-treatment to refresh the nitrate and carbonate species in the entire catalyst, the X-ray beam (0.5 mm × 0.5 mm) was set at position A, and the XAS and mass spectra were measured during the NSR operation from lean to rich conditions. The same process as the above including the pre-treatment and NSR operation was also performed at each position of B, C and D. All sequences including the X-ray position, gas condition, XAS measurement, and mass measurement were fully automated. The time axis of the XAS and mass measurements was controlled by a

trigger signal. The series of 1 − 8 sequences was repeated three times, and the reproducibility of the XAS and mass data was confirmed.

The Rh K-edge X-ray absorption near-edge structure (XANES) spectra were collected every 100 ms. High-quality data from Rh K-edge XANES spectra were acquired using QXAS in transmission mode. The incident X-ray was monochromatized by using a servo-motor-driven Si channel-cut monochromator having a Si(220) crystal for the Rh K-edge (23.23 keV). The energy was calibrated so that the absorption edge energy for the standard (Rh foil) would be 23.23 keV. A measured XANES spectrum was normalized in the following manner. A pre-edge background was estimated by fitting in the pre-edge region to the Victoreen formula. The fitted pre-edge background was extrapolated and subtracted from the entire range of a spectrum. The background above the edge was also obtained by fitting to the Victoreen formula in the same manner as above mentioned. Normalization of an XANES spectrum was then performed so that this background curve would become one in the post-edge region.

The Rh metal fraction was evaluated by the normalized Rh K-edge XANES spectra of the sample using a liner combination fit with the reference spectra of Rh foil and Rh_2O_3 powder. The Rh reduction time, which denotes to the time for the Rh species in the $Rh/BaO/Al_2O_3$ catalyst to be completely reduced from Rh oxide (Rh_2O_3) to Rh metal, was estimated in the following. Rh reduction onset time ($t1$) and Rh reduction termination time ($t2$) were obtained by linear fitting of the variation of the Rh metal fraction (Fig. S3†). The value obtained by subtracting $t1$ from $t2$ was defined as Rh reduction time.

Table S1: Experimental sequence of the spatiotemporal *operando* XAS.

Sequence No.	X-ray position	Gas condition	Cell temperature	Rh *K*-edge XAS measurement	Mass measurement of outlet gas
1	A	Pre-treatment: 3% H_2/He (240 s) ↔ 7% O_2/He (240 s) cycling (2 times)		-	-
2	A	Lean to Rich: 0% or 0.07% NO +7% O_2/He (300 s or 60 s) → 3% H_2/He (240 s)		✓	✓
3	B	Pre-treatment: 3% H_2/He (240 s) ↔ 7% O_2/He (240 s) cycling (2 times)		-	-
4	B	Lean to Rich: 0% or 0.07% NO +7% O_2/He (300 s or 60 s) → 3% H_2/He (240 s)		✓	✓
5	C	Pre-treatment: 3% H_2/He (240 s) ↔ 7% O_2/He (240 s) cycling (2 times)	450 °C	-	-
6	C	Lean to Rich: 0% or 0.07% NO +7% O_2/He (300 s or 60 s) → 3% H_2/He (240 s)		✓	✓
7	D	Pre-treatment: 3% H_2/He (240 s) ↔ 7% O_2/He (240 s) cycling (2 times)		-	-
8	D	Lean to Rich: 0% or 0.07% NO +7% O_2/He (300 s or 60 s) → 3% H_2/He (240 s)		✓	✓

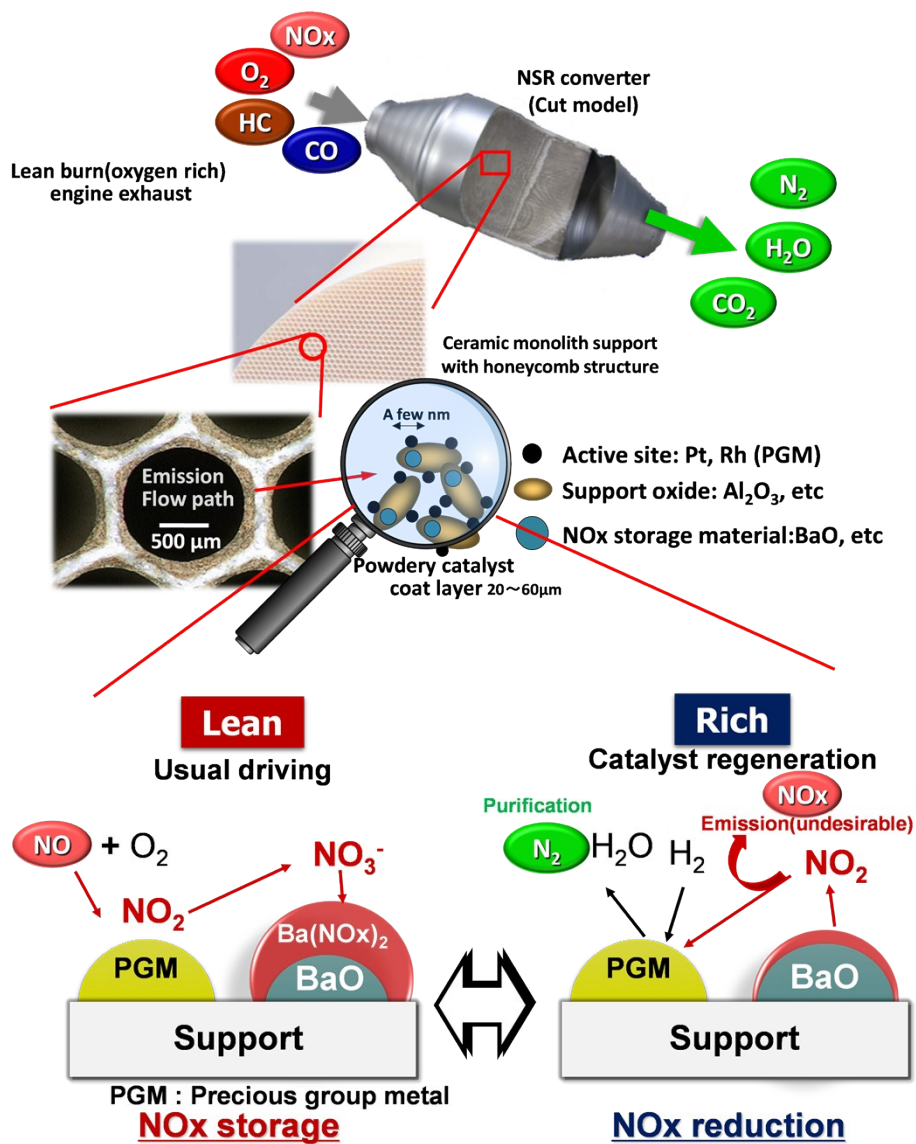Repeat the series of 1 – 8 sequences, 3 times

Figure S1: Schematic illustration of automotive catalytic converter and the NOx storage and reduction (NSR) mechanism.
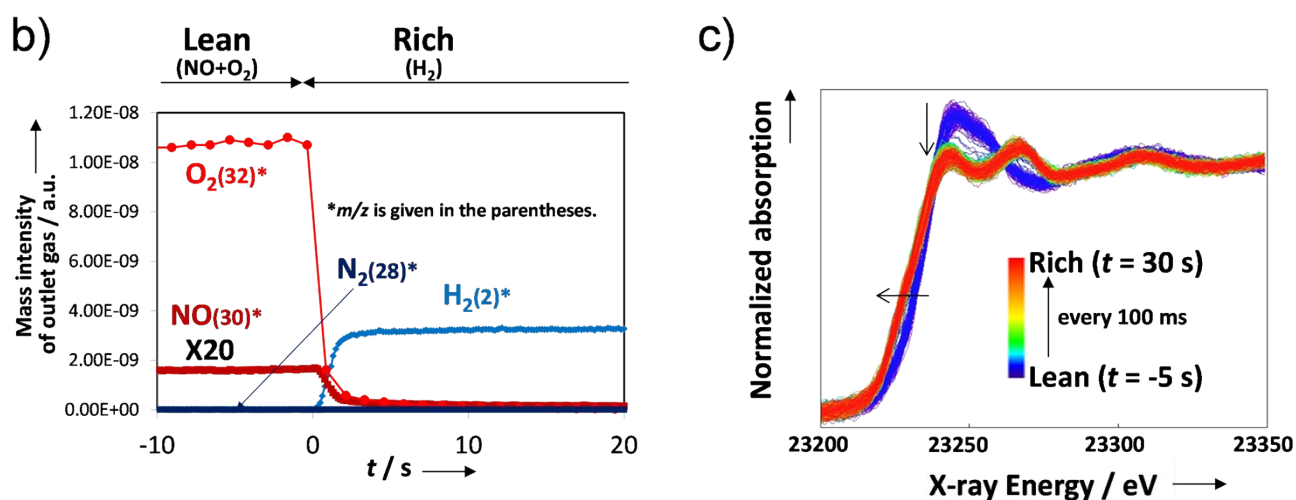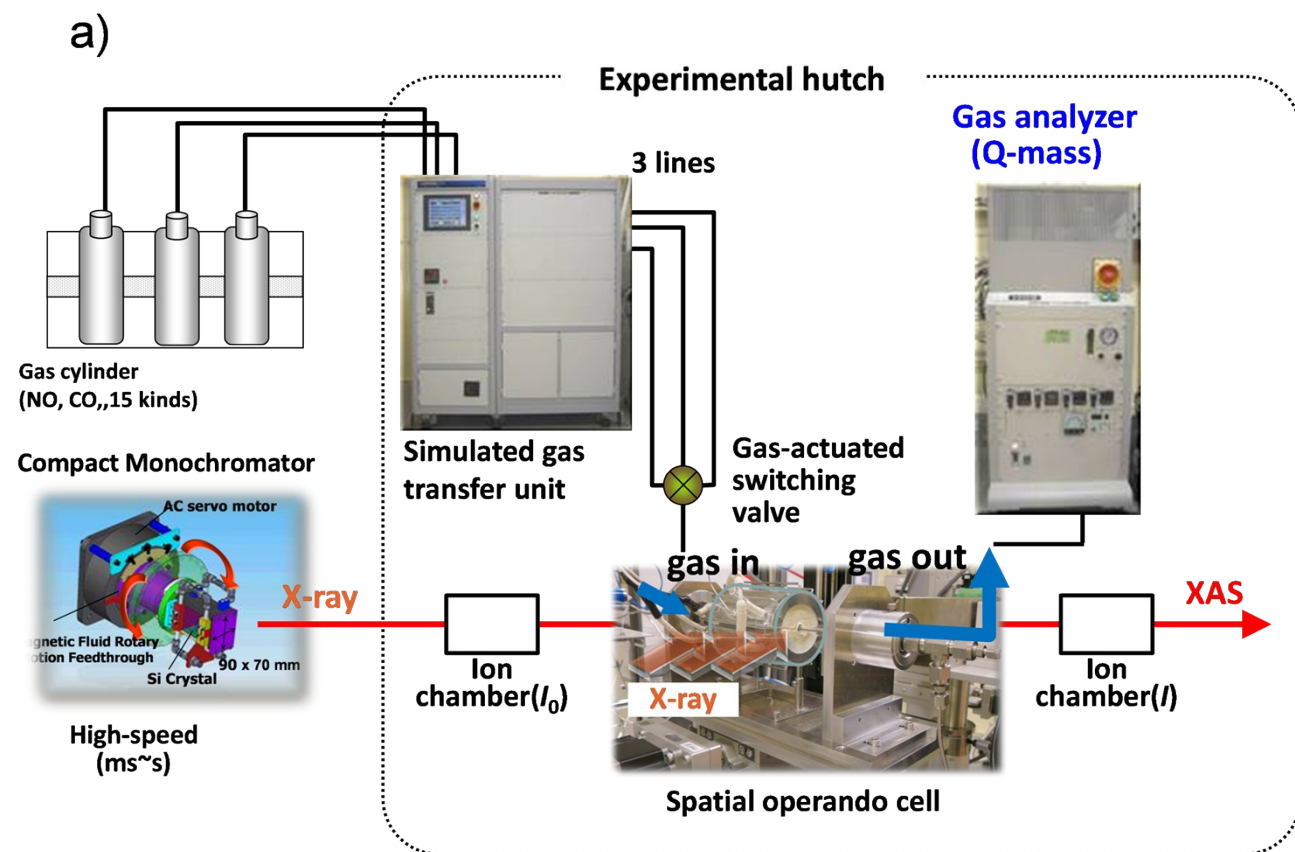
Figure S2: a) Experimental set-up for operando XAS in transition mode at Toyota beamline (BL33XU, SPring-8) . b) Quick gas changing from a lean (oxidative) to rich (reductive) atmosphere. Variations in the detected ion current in blank test. The ion current of m/z 2 (H_2), m/z 28 (N_2), m/z 30 (NO) and m/z 32 (O_2). c) Serial time-resolved Rh K-edge XANES spectra of Rh/BaO/Al$_2$O$_3$ under the lean to rich condition.
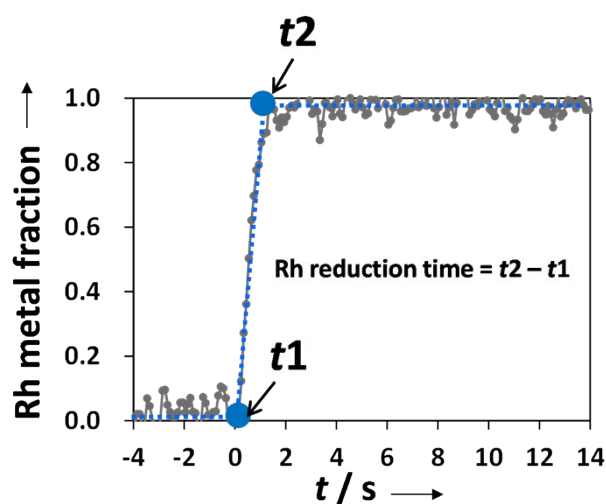
Figure S3: Calculation method of Rh reduction time. Rh reduction start time (*t*1) and Rh reduction end time (*t*2) were obtained by linear fitting of the variation of the Rh metal fraction. The value obtained by subtracting *t*1 from *t*2 was defined as Rh reduction time.
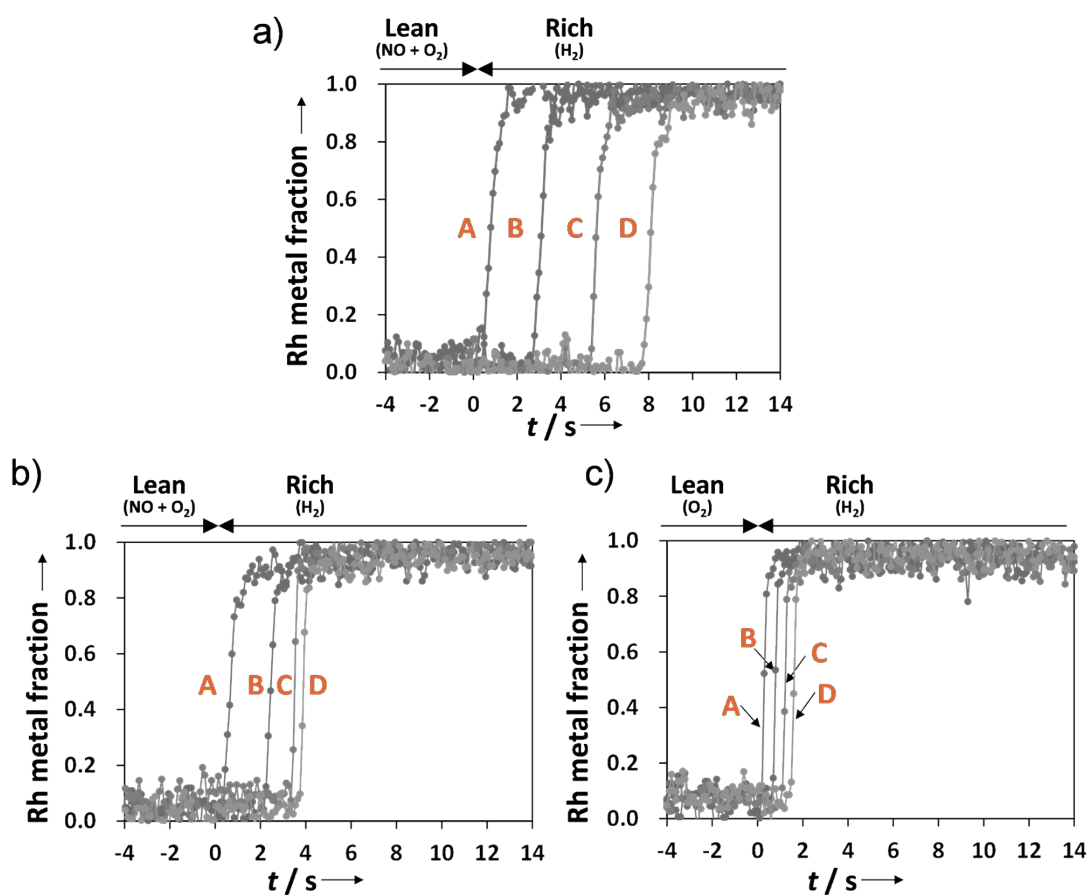

Figure S4: Temporal dependence of the Rh metal fraction in the $Rh/BaO/Al_2O_3$ catalyst from lean to rich condition. a) 100% NOx storage, b) 33% NOx storage, c) 0% NOx storage. The Rh metal fraction was evaluated by the Rh *K*-edge XAS spectra of the sample using a liner combination fit with the reference spectra of Rh foil and Rh_2O_3 powder.
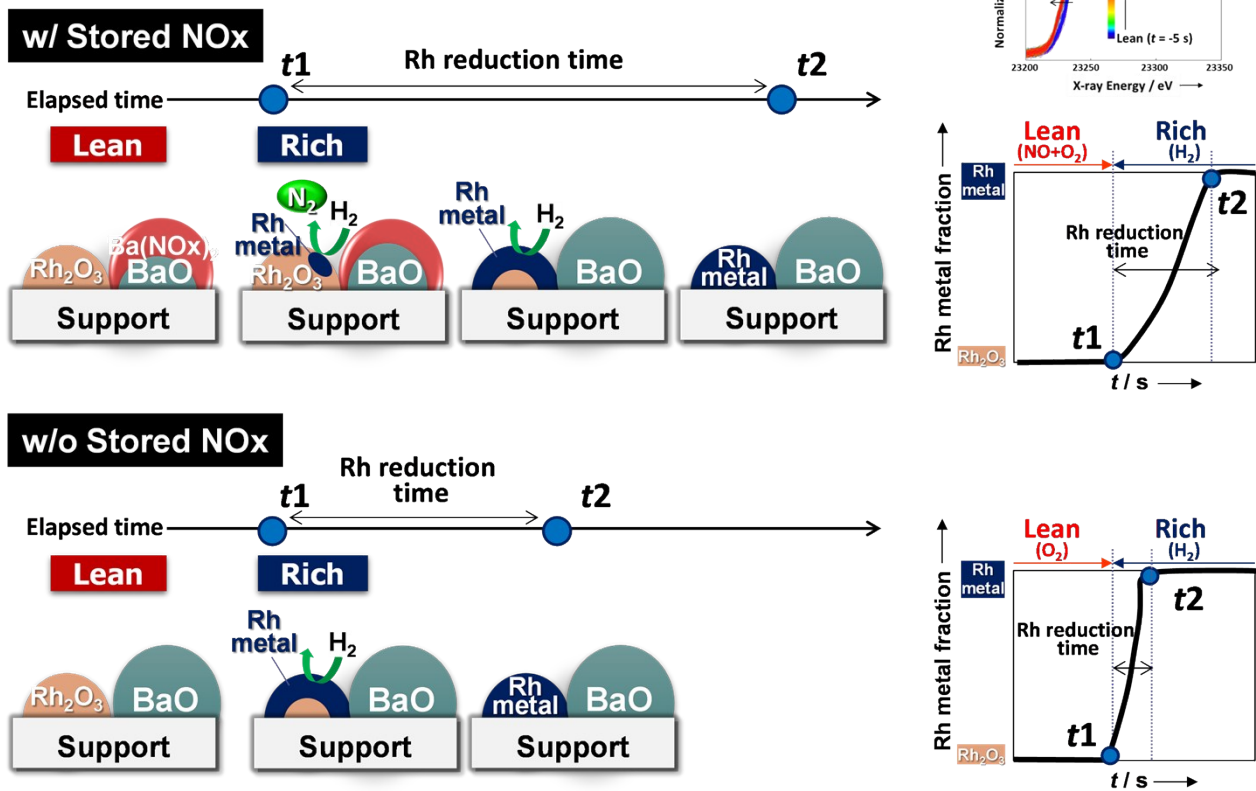
Figure S5: Schematic illustration of Rh reduction time for Rh/BaO/Al₂O₃ catalyst with or without stored NOx.

Rh oxidation state(XAFS)

Lean (NO+O$_2$) Rich (H$_2$)

Rh metal fraction

A B C D

Time / s

Rich 1 s

Evolution profile(Mass)

Lean (NO+O$_2$) Rich (H$_2$)

Mass intensity of outlet gas / a.u.

Inlet NO level

N_2(28)*

NO(30)*

H_2(2)*

Time / s

Rich 1 s

Rich 0 s

ca. 8 mm

A B C D

NOx storage and reduction state in catalyst bed

Front Rear

$Ba(NOx)_2$

Rh oxidation state

A B C D

Rh_2O_3

Gas atmosphere

A B C D

H_2 O_2+NO

Rich 1 s

ca. 8 mm

A B C D

Front Rear

$Ba(NOx)_2$

N_2

NOx

NO

H$_2$ reacts with stored NOx

A B C D
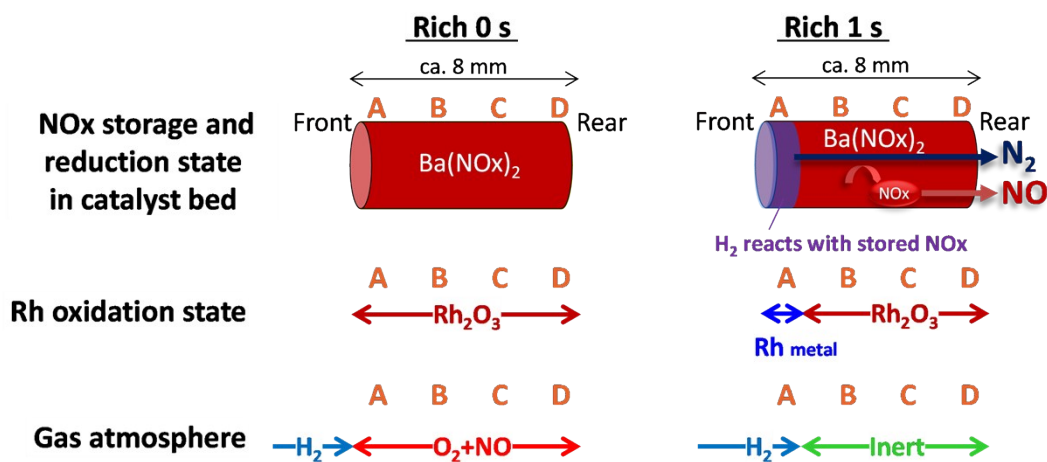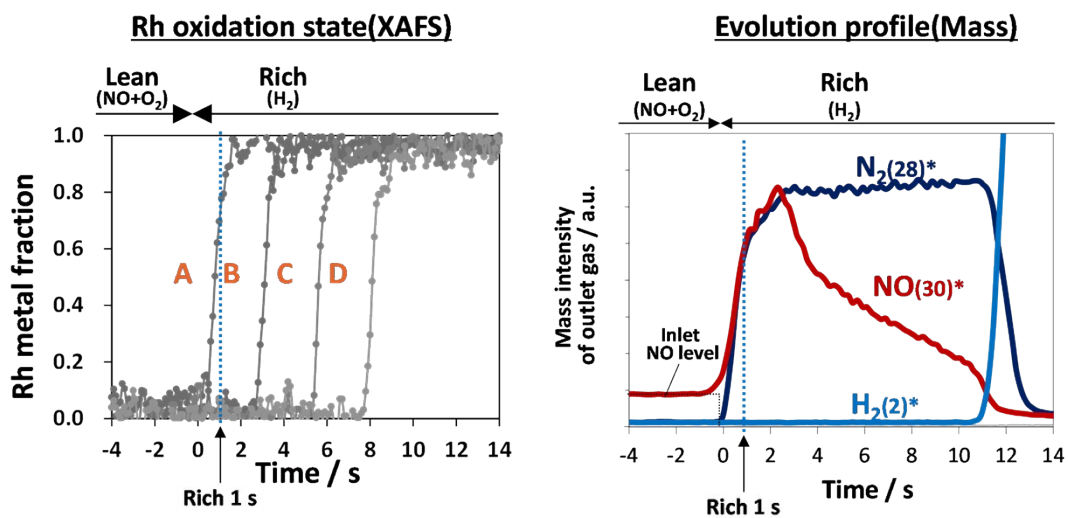
Rh metal Rh_2O_3

A B C D

H_2 Inert

Figure S6: Schematic illustration of NOx storage and reduction behavior for the case of 100% NOx storage.
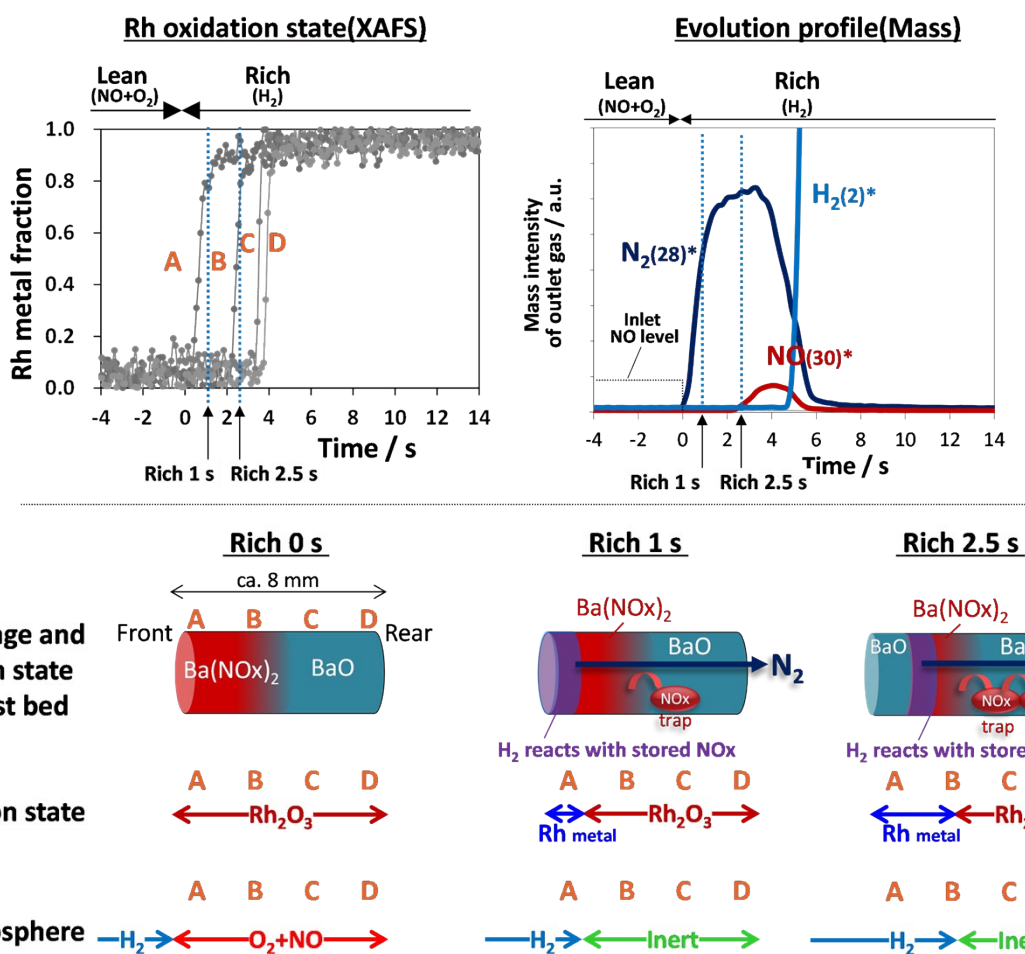
Figure S7: Schematic illustration of NOx storage and reduction behavior for the case of 33% NOx storage.