Electronic Supplementary Information (ESI)

Operando XAFS study of catalytic NO reduction over Cu/CeO_2: effect of copper-ceria interaction under periodic operation

Yasutaka Nagai,[*a] Kazuhiko Dohmae,[a] Yusaku Nishimura,[a] Hitoshi Kato,[b] Hirohito Hirata[c] and Naoki Takahashi[a]

[a] *TOYOTA Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan. Fax: +81 561 63 6150; Tel: +81 561 71 7230; E-mail: e1062@mosk.tytlabs.co.jp*

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

[c] *TOYOTA Motor Corporation Higashi-Fuji Technical Center, Shizuoka, 410-1193 Japan*

Experimental Section

Materials and Method

6 wt% Cu/CeO_2 catalyst was prepared by the conventional wet impregnation of a commercial CeO_2 powder (S_{BET}=150 m^2/g) with $Cu(NO_3)_2$ aqueous solution. The impregnated powders were calcined at 500 °C for 1 h in air. Cu/Al_2O_3 and pure CeO_2 samples were used for comparison.

Powder X-ray diffraction patterns were collected by Ultima IV (Rigaku Co., Ltd.) diffractometer with Cu Kα radiation.

Operando XAFS measurements were performed at the TOYOTA Beamline (BL33XU) of SPring-8, Japan. The sample was pressed to a disk (10 mmϕ) and placed in an in situ cell equipped with a rapid gas switching system, allowing the gas flow to be alternated over the sample from an oxidative to reductive atmosphere. The cell was designed for transition X-ray detection at high sample temperatures (T_{max} ~800 ◦C), while minimizing dead volume. In the periodic operation, a lean stream consisting of 0.8 % O_2, 0.65 % CO, 0.15 % NO, 0.1 % C_3H_6, 3 % H_2O and the balance He and a rich stream with the same as the lean gas except for 0 % O_2 were introduced to the in situ cell cyclically every 30 seconds. For comparison, the static experiment was made using a stream with the same as the lean gas except for 0.4 % O_2. The total flow rate was 100 cc/min and a mixture of 20 mg catalyst and 50 mg BN was used. The reaction temperature was controlled from 50 to 600 °C at a rate of 10 °C/min. Mass spectra were measured by using quadrupole mass spectrometer.

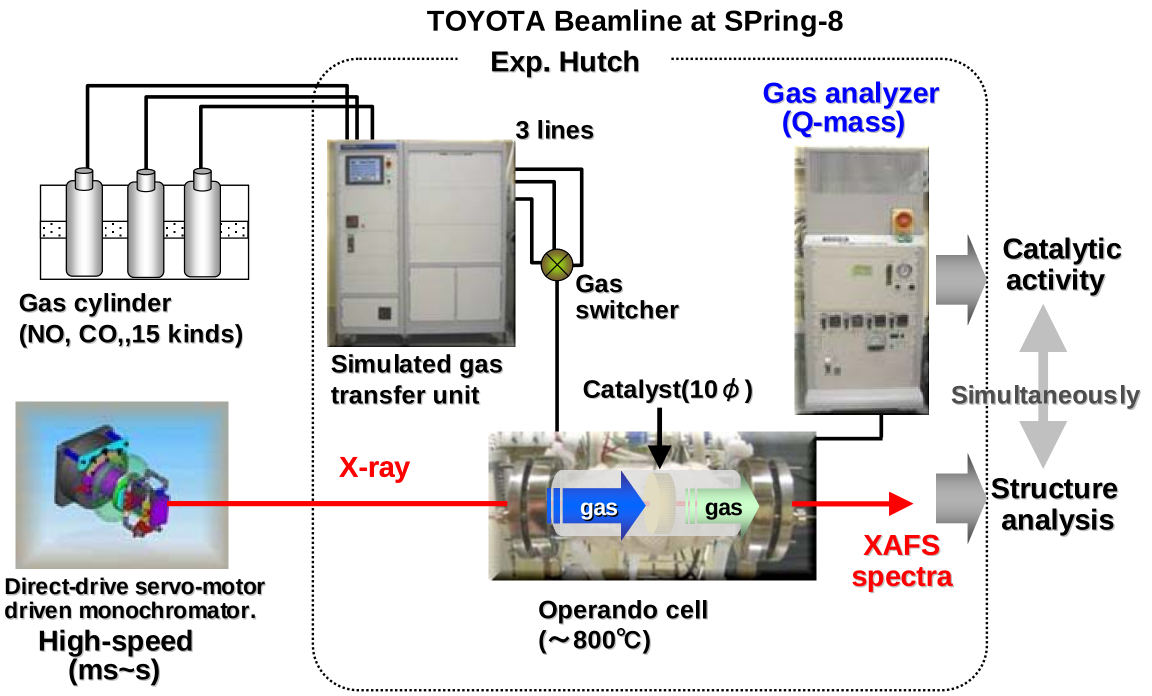
Cu and Ce *K*-edges XAFS spectra were collected every one second. The incident X-ray was monochromatized by using a servo-motor-driven Si channel-cut monochromator having a Si(111) crystal for the Cu *K*-edge (8.98 keV) or a Si(220) crystal for the Ce *K*-edge (40.45 keV). In the Cu *K*-edge measurement, higher harmonics were eliminated by utilizing the difference in the critical angle for total internal reflection on a Pt-coated mirror. An XAFS spectrum was recorded in a transmission mode. The energy was calibrated so that the absorption edge energies for standards (a Cu foil and a CeO_2 pellet) would be 8.9789 keV and 40.500 keV, respectively. Here, XAFS spectra for the standards were simultaneously measured with those for a Cu/CeO_2 catalyst. A measured XAFS spectrum was normalized in the following manner. A preedge background was estimated by fitting the spectrum in the preedge region (i.e. from −150 to −50 eV relative to the interested absorption edge) to the Victoreen formula,[S1] $\mu\, t = C/\lambda^3 - D/\lambda^4 + A$
where λ is wavelength, and C, D, and A are constants which should be determined in fitting. The fitted preedge 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 XAFS spectrum was then performed so that this background curve would become one in the postedge region. For the analysis in a XANES region, the absorption edge energy was empirically defined as the energy at which the normalized absorbance was 0.5. On the other hand, in an EXAFS region, the oscillation function $\chi(E)$ was once transformed from the space of photon energy E to that of electron wavenumber k. The $\chi(k)$ function was weighted by k^3 so as to compensate for the dampening of EXAFS oscillations at higher k. Subsequently, the k^3-weighted $\chi(k)$ in the k space ranging from 3.0 to 9.0 $Å^{-1}$ was converted into an EXAFS spectrum in the real space R like a radial distribution function by Fourier transformation.

Reference

S1 J. A. Victoreen, *J. Appl. Phys.* 1949, 20, 1141.

Figure S1: Experimental set-up for *operando* XAFS in transition mode at TOYOTA beamline (BL33XU of SPring-8) Variations in the detected ion current in blank test. of (a) the static operation and (b) the periodic operation . For the reactant gas composition, see Experimental section. The ion current of *m*/*z* 28 (CO and N_2) fluctuates under the periodic condition. This is supposed to be due to impurity of N_2 contained in a gas cylinder of 5 %O_2/He as source to make the reaction mixture.

a)



b) static

c)periodic

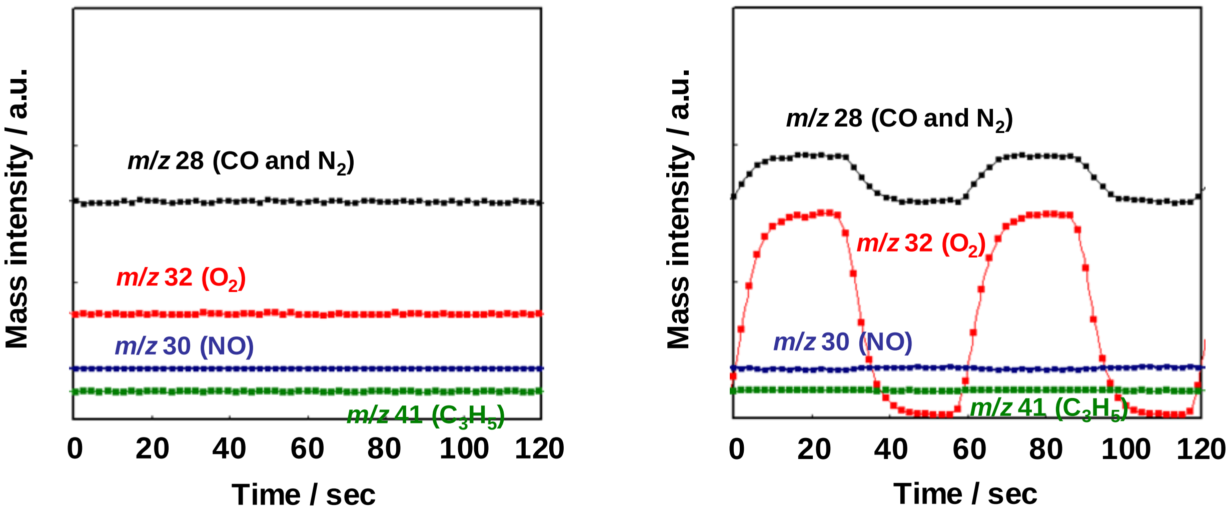


Figure S2: Serial time-resolved (a) Cu and (b) Ce *K*-edges XAFS spectra of Cu/CeO$_2$ catalysts under the static operation. Inset: Magnified view of XANES region. The first EXAFS spectrum at the start of measurement for (c) Cu and (d) Ce *K*-edges.

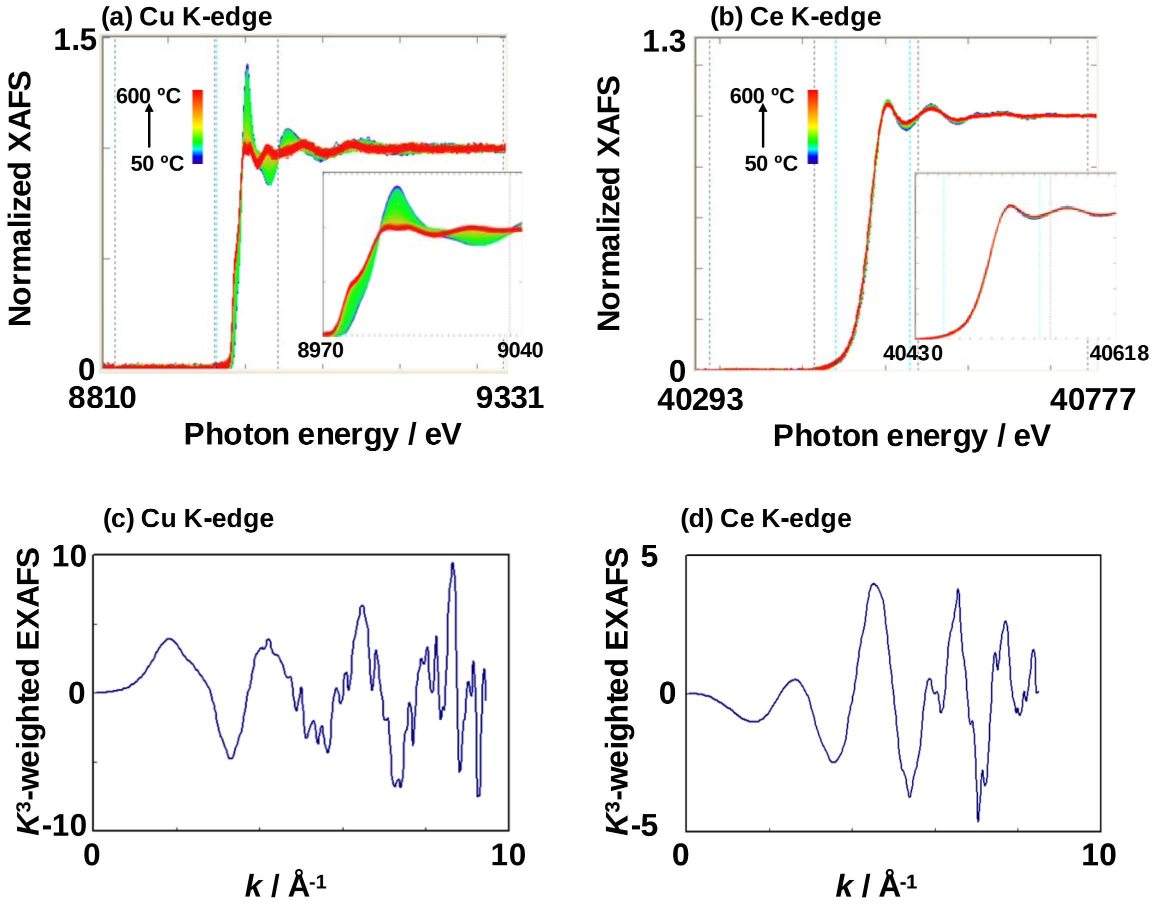


Figure S3: Temperature dependences of NO conversion of Cu/CeO$_2$ catalysts under the periodic operation: (a) raw data, (b) average of 60 seconds.

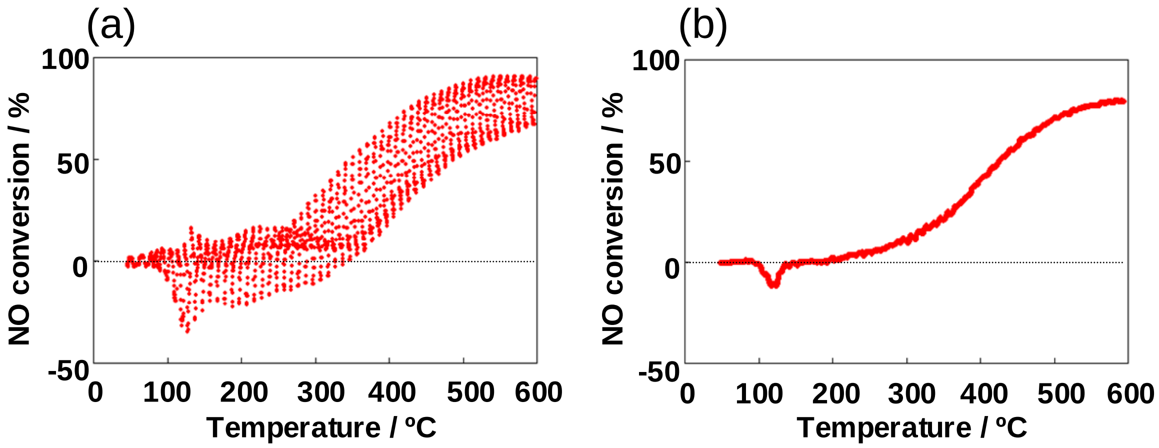


Figure S4: The result of *operando* XAFS analysis for CeO_2 under (a) static and (b) periodic operations. Energy shifts of Ce *K*-edge and color map representations of Fourier-transformed k^3x data of Ce *K*-edge EXAFS as a function of temperature. (c) Temperature dependences of average NO conversion of 60 seconds.

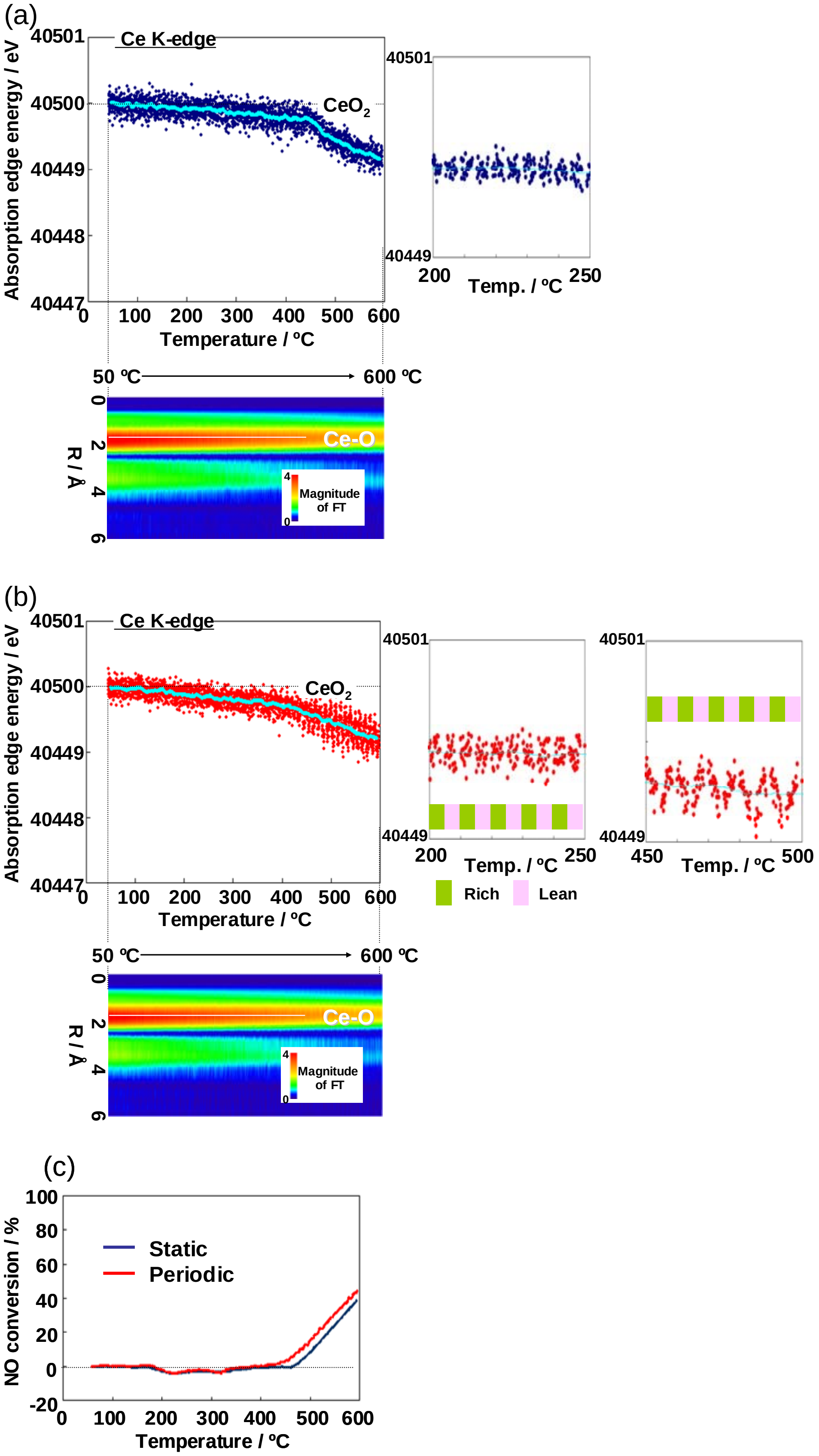


Figure S5: The result of *operando* XAFS analysis for Cu/Al_2O_3 under (a) static and (b) periodic operations. Energy shifts of Cu *K*-edge and color map representations of Fourier-transformed k^3x data of Cu *K*-edge EXAFS as a function of temperature. (c) Temperature dependences of average NO conversion of 60 seconds.