Supporting information

A superior catalyst with dual redox cycles for the selective reduction of NO_x by ammonia

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1. Catalyst preparation and catalytic tests

The Cu-Ce-Ti catalysts with different ratio of Cu/Ce/Ti were prepared by the hydrothermal method. Appropriate amounts of $Cu(NO_3)_2 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Ti(SO_4)_2$ were dissolved in deionized water at room temperature and stirred for 1 hour, then ammonia solution was added slowly to the above solution under vigorous stirring until pH is ca. 11. After stirring for 2 h, the obtained suspension was transferred to a Teflon-sealed autoclave and aged at 120 ℃ for 48 h. The obtained precipitate was filtered and washed with deionized water thoroughly. The resulting powder was dried at 120 ℃ for 12 h and then calcined in air at 500 ℃ for 6 h. In comparison, Cu-Ti, Ce-Ti and TiO_2 were also prepared by the same preparation method as described above. The state-of-the art SCR V_2O_5-WO_3/TiO_2 catalyst with 1 wt.% V_2O_5 and 5 wt.% WO_3 was also prepared by the conventional impregnation method using NH_4VO_3, $(NH_4)_{10}W_{12}O_{41}$, $H_2C_2O_4 \cdot 2H_2O$ as precursors and TiO_2 as the support. After impregnation, the sample was then dried at 120 ℃ for 12 h and calcined at 500 ℃ for 4h.

The activity measurements were carried out in a fixed-bed quartz reactor using a 0.12 g catalyst of 40-60 meshes. The feed gas mixture contained 500 ppm NO, 500 ppm NH_3, 0 or 5% H_2O, 0 or 50 ppm SO_2, 5% O_2 and helium as the balance gas. The total flow rate of the feed gas was 300 cm^3 min^{-1}, corresponding to a GHSV of 64,000 h^{-1}. The reaction temperature was increased from 150 ℃ to 400 ℃ in steps of 50 ℃. The composition of the product gas was analyzed by a chemiluminescence NO/NO_2 analyzer (Thermal Scientific, model 42i-HL) and gas chromatograph

(Shimadzu GC 2014 equipped with Porapak Q and Molecular sieve 5A columns). A molecular-sieve 5A column was used for the analysis of N_2 and Porapak Q column for that of N_2O. The activity data were collected when the catalytic reaction practically reached steady-state condition at each temperature.

2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-RB X-ray Diffractometer with Cu Kα radiation. XPS measurements were conducted on an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Mg Kα radiation, calibrated internally by carbon deposit C 1s binding energy (BE) at 284.8 eV. A least-square routine of peak fitting was used for the analysis of XPS spectra. Positron annihilation experiments were performed with a fast-slow coincidence ORTEC system with a time resolution of 196 ps full width at half maximum. A 5×10^5 Bq source of ^{22}Na was sandwiched between two identical samples. Temperature-programmed reduction (H_2-TPR) experiments were conducted on a chemisorption analyzer (Micromeritics, ChemiSorb 2720 TPx) under a 10% H_2 gas flow (50 mL min^{-1}) at a rate of 10 °C min^{-1} up to 650 °C.

The structure of catalysts was studied by the micro-Raman spectroscopy (Renisaw, InVia) under the 532 nm^{-1} excitation laser light. In situ DRIFTS experiments were performed on an FTIR spectrometer (Nicolet Nexus 870) equipped with a smart collector and an MCT detector cooled by liquid nitrogen. Prior to each experiment, the sample was pretreated at 400 ℃ for 1 h in a flow of helium and then cooled down to 200 ℃. The background spectrum was collected in flowing helium and

automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 100 mL min^{-1} total flow rate, 500 ppm NH_3 or 500 ppm NO + 5 % O_2, and helium as the balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm^{-1}.

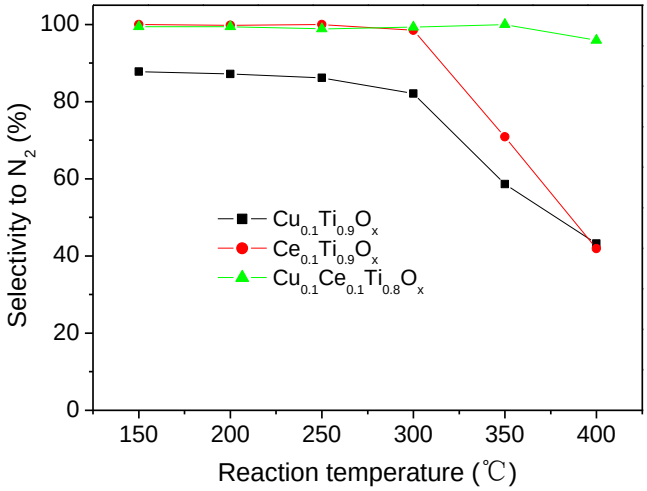

Fig. S1 N_2 selectivities of $Cu_{0.1}Ti_{0.9}O_x$, $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts (500 ppm NO, 500 ppm NH_3, 5% O_2, balance He, GHSV= 64,000 h^{-1})

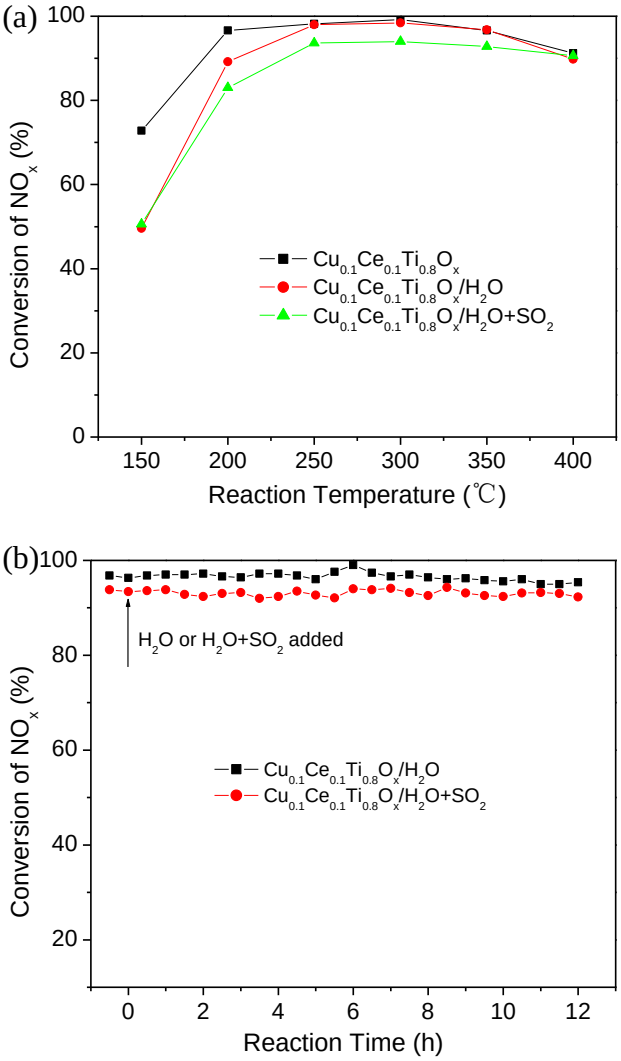

Fig. S2 NO_x conversion as a function of temperature (a) and as a function of time at 250 ℃ (b) over $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalyst in the presence of H_2O and SO_2 (500 ppm NO, 500 ppm NH_3, 5% O_2, 5% H_2O, 50 ppm SO_2, balance He, GHSV= 64,000 h^{-1}).

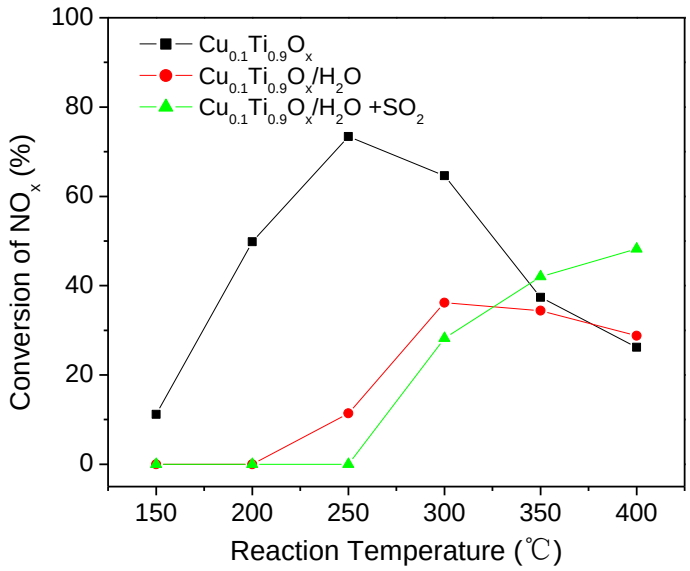

Fig. S3 The effects of H_2O and SO_2 on the activity of $Cu_{0.1}Ti_{0.9}O_x$ catalysts (500 ppm NO, 500 ppm NH_3, 5% O_2, 5% H_2O, 50 ppm SO_2, balance He, GHSV=64,000 h^{-1}).

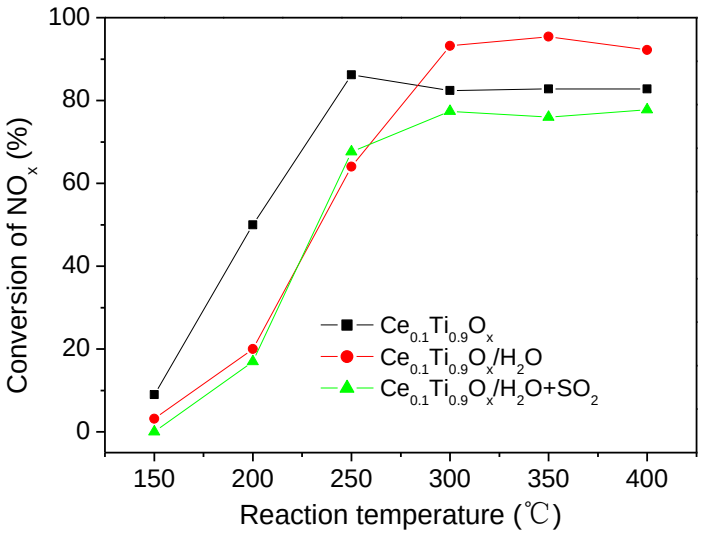

Fig. S4 The effects of H_2O and SO_2 on the activity of $Ce_{0.1}Ti_{0.9}O_x$ catalysts (500 ppm NO, 500 ppm NH_3, 5% O_2, 5% H_2O, 50 ppm SO_2, balance He, GHSV=64,000 h^{-1}).

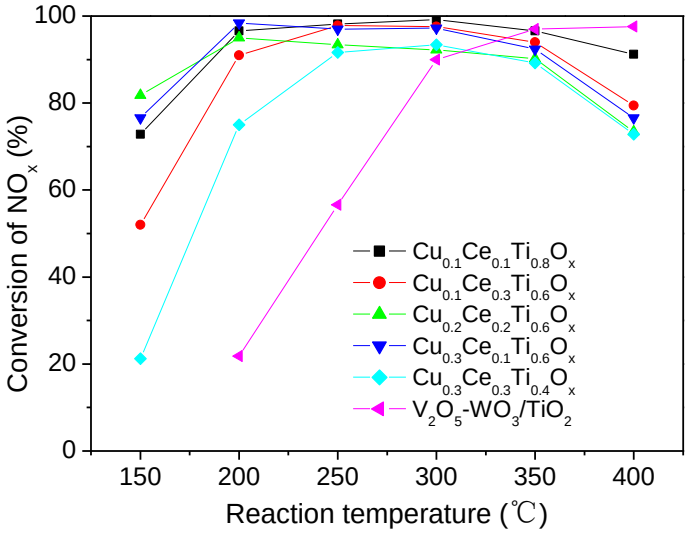

Fig. S5 Comparison of NH_3-SCR activity of Cu-Ce-Ti catalysts with that of V_2O_5-WO_3/TiO_2 (500 ppm NO, 500 ppm NH_3, 5% O_2, balance He, GHSV=64,000 h^{-1}).

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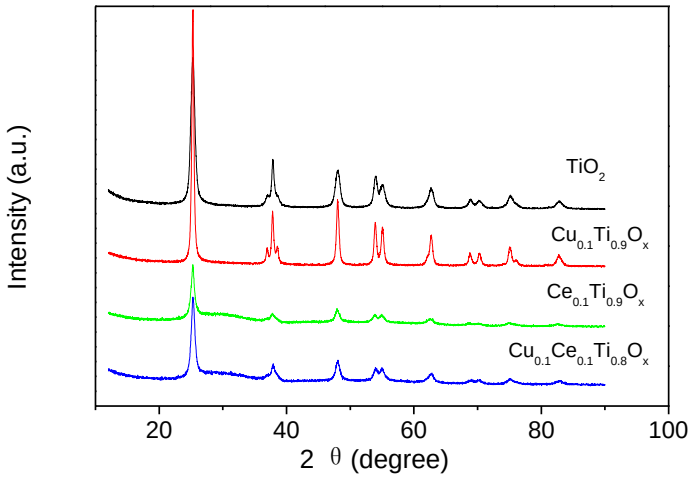

Fig. S6 XRD patterns of TiO_2, $Cu_{0.1}Ti_{0.9}O_x$, $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$.

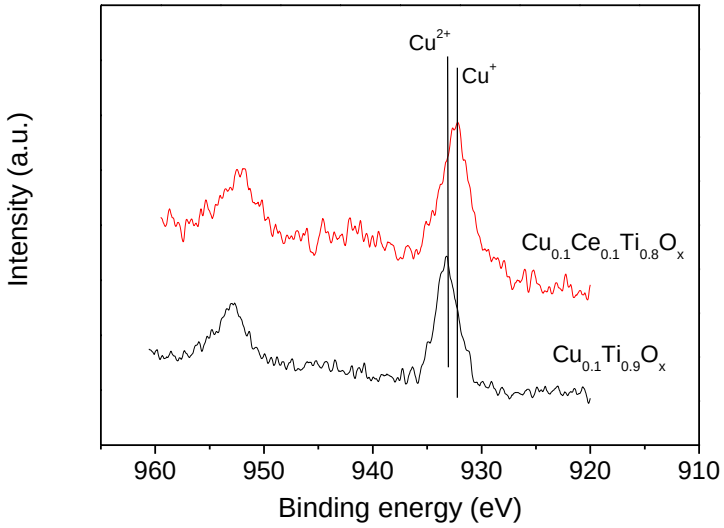

Fig. S7 Cu 2p XPS spectra of $Cu_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts.

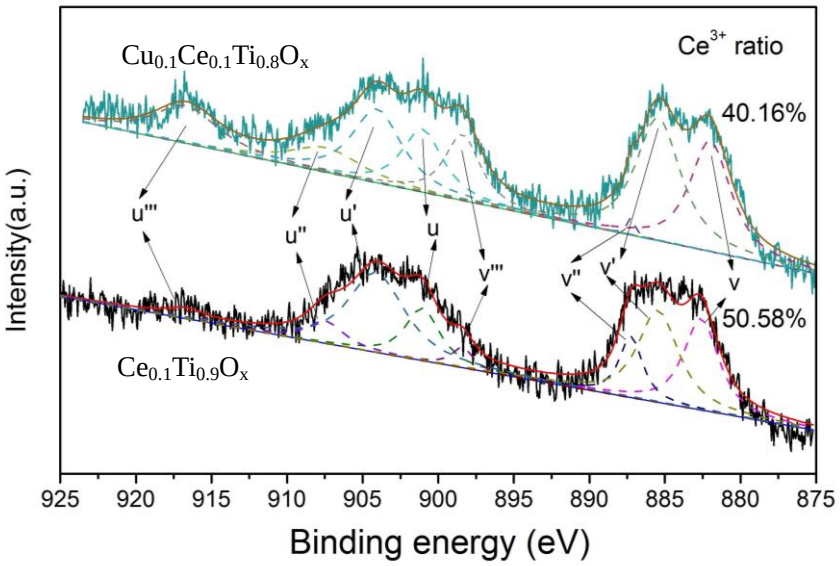

Fig. S8 Ce 3d XPS spectra of $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts.

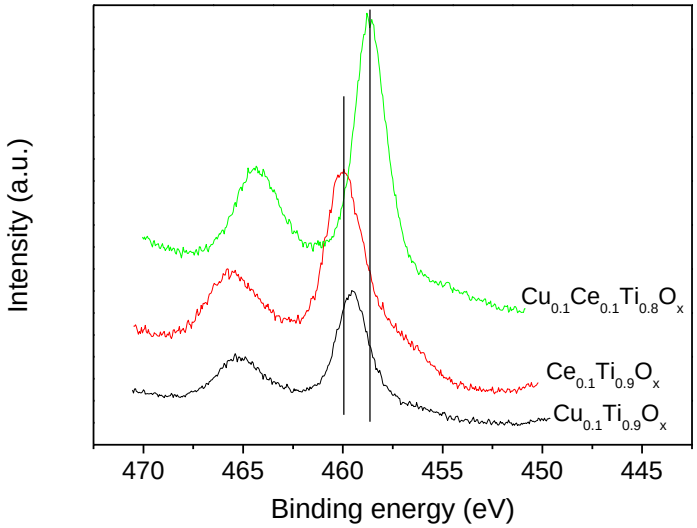

Fig. S9 Ti 2p XPS spectra of $Cu_{0.1}Ti_{0.9}O_x$, $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts.

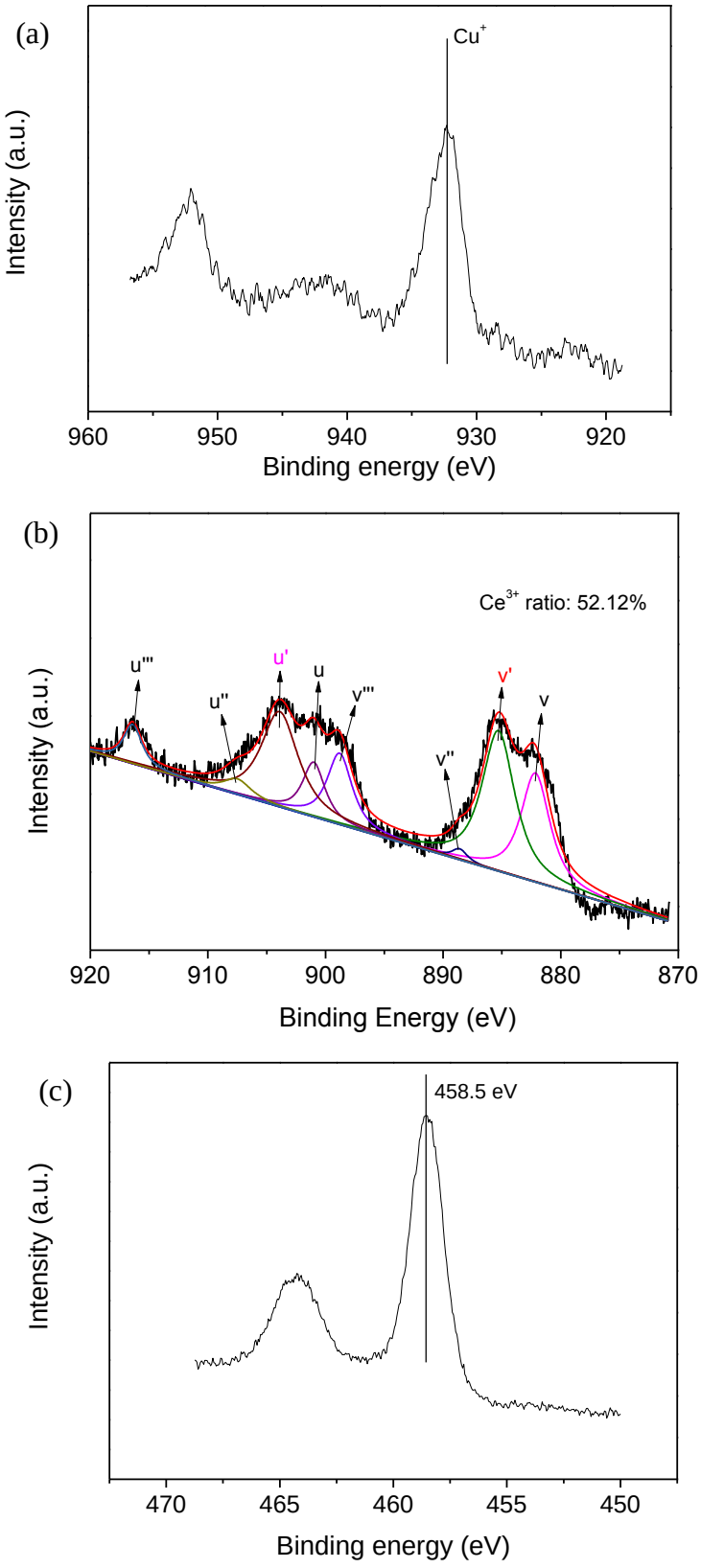

Fig. S10 Cu 2p(a), Ce3d(b) and Ti2p(c) XPS spectra of the used $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalyst.

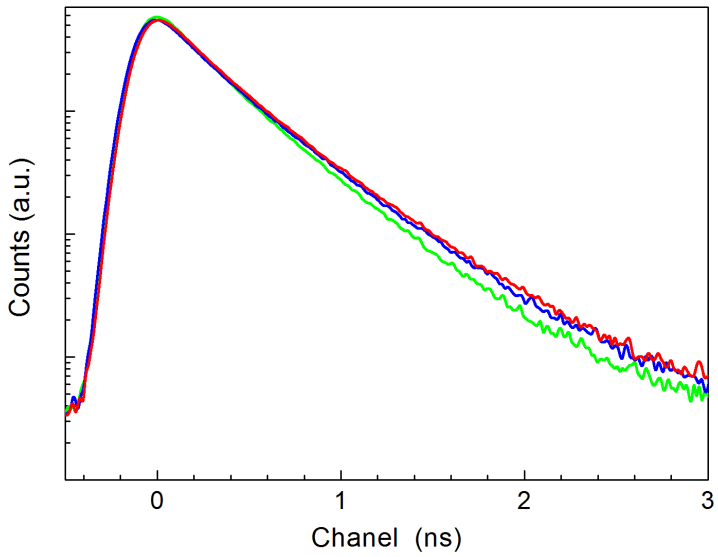

Fig. S11 The lifetime spectra of $Cu_{0.1}Ti_{0.9}O_x$(–), $Ce_{0.1}Ti_{0.9}O_x$(–) and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ (–)catalysts.

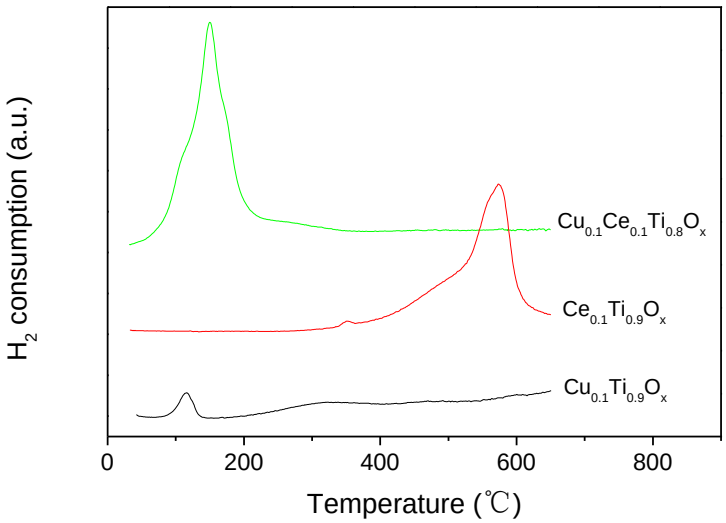

Fig. S12 H_2-TPR profiles of $Cu_{0.1}Ti_{0.9}O_x$, $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts.

Temperature-programmed reduction (H_2-TPR) analysis was conducted to investigate the reduction behavior of $Cu_{0.1}Ti_{0.9}O_x$, $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts. As illustrated in Fig.S12, $Cu_{0.1}Ti_{0.9}O_x$ shows a hydrogen consumption peak at 120 ℃, which is attributed to the reduction of CuO particles being in strong interaction with the TiO_2.[1,2] The reduction peak is significantly lower than that of the bulk and unsupported CuO, which is reduced at about 300℃.[3] $Ce_{0.1}Ti_{0.9}O_x$ exhibited two reduction peaks at around 350 and 570 ℃. The former small peak is probably assigned to the reduction of the surface oxygen of ceria and the second reduction peak is due to the reduction of Ce^{4+} to Ce^{3+}.[1,4] Interestingly, the $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalyst possesses an intense peak centering around 150 ℃ and the reduction peak starts at lower temperature compared with $Cu_{0.1}Ti_{0.9}O_x$ catalyst.

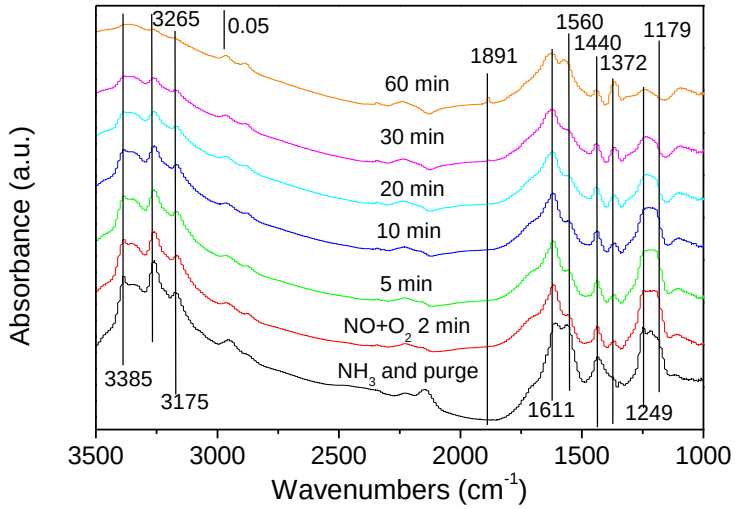

Fig. S13 In situ DRIFTS of $NO+O_2$ reacted with pre-adsorbed NH_3 species at 200 ℃ over $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalyst.

The DRIFT spectra of $NO+O_2$ adsorption over $Cu_{0.1}Ti_{0.9}O_x$, $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts at 200℃ was investigated. Several distinct bands at 1891, 1625, 1601, 1585, 1375, 1274, 1235 and 1218 cm^{-1} were observed, which were respectively assigned to the gas phase or weakly adsorbed NO (1891 cm^{-1}),[5] adsorbed NO_2 (1601, 1625 cm^{-1}),[5,6] bidentate nitrate (1585 cm^{-1}),[7,8] bridging nitrate (1274, 1235 and 1218 cm^{-1})[7,8] and M-NO_2 nitro compounds (1375 cm^{-1}).[10]

In the case of NH_3 adsorption over these three catalysts, the bands at 1611, 1249 and 1179 cm^{-1} can be assigned to the coordinated NH_3 on Lewis acid sites,[10, 11] and that at 3385, 3265 and 3175 cm^{-1} can be ascribed to the N-H stretching vibration modes of the coordinated NH_3.[11] The ionic NH_4^+ bound to Brønsted acid sites(1440 cm^{-1})[8] was also observed over $Ce_{0.1}Ti_{0.9}O_x$ and $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$ catalysts, with the N-H stretching vibration modes of NH^{4+} (2959 cm^{-1}).[12] The peak at 1560 cm^{-1} can be

assigned to the scissoring vibration mode of NH_2 species.[9]

The reactivity of adsorbed NH_3 species towards $NO+O_2$ was evaluated by the time-dependent changes of the IR spectra at 200 °C and the results are shown in Fig. S13. After the catalyst was exposed to NH_3 for the 60 min and purged with helium, the adsorbed NH_3 on Lewis acid sites (3385, 3265, 3175, 1611, 1249 and 1179 cm^{-1}),[10, 11] and ionic NH_4^+ bound to Brønsted acid sites(1440 cm^{-1})[8] were observed clearly. Switching the feed gas to NO + O_2 resulted in the decreases of both adsorbed NH_3 and ionic NH_4^+ peak intensities, indicating that both the coordinated NH_3 and NH_4^+ participated in the reduction of NO_x.

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