Novel Approach for a Cerium-Base High-Efficient Catalyst with Excellent NH_3-SCR Performance

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Electronic Supplementary Information

Preparation of V_2O_5-WO_3/TiO_2, Mn/TiO_2 and Cu-SAPO-34 catalysts

In order to comprehensively evaluate the activity of CeO_2/WO_3-TiO_2 catalyst in this study, V_2O_5-WO_3/TiO_2 with 1 wt.% V_2O_5 and 10 wt.% WO_3, Mn/TiO_2 with 10 wt.% MnO_2, and Cu-SAPO-34 catalysts with a Cu loading of 1.258 wt.% were prepared as reference materials.

The V_2O_5-WO_3/TiO_2 catalyst was prepared by conventional impregnation method using NH_4VO_3 and $(NH_4)_{10}W_{12}O_{41}$ as precursors, $H_2C_2O_4 \cdot 2H_2O$ as solubility promoter, and TiO_2 as support. After impregnation, the excess water was removed in a rotary evaporator at 60 °C. The sample was dried at 100 ºC overnight and then calcined at 500 ºC for 5h in air condition.

The Mn/TiO_2 catalyst was also prepared by conventional impregnation method using $Mn(NO_3)_2$ as precursor and TiO_2 as support. After impregnation, the excess water was removed in a rotary evaporator at 60 °C. The sample was dried at 100 ºC overnight and then calcined at 500 ºC for 5h in air condition.

The Cu-SAPO-34 catalyst was prepared by liquid ion-exchange method using $CuSO_4 \cdot 5H_2O$ and H-SAPO-34 as precursors. H-SAPO-34 was firstly ion exchanged using a NH_4NO_3 solution at 80 °C for 3 h to obtain NH_4-SAPO-34. Then, Cu ion-exchange was performed by mixing the NH_4-SAPO-34 with a $CuSO_4 \cdot 5H_2O$ solution (0.1 mol/L) at 60 °C for 3 h. The solids were collected by filtration and then washed with distilled water, dried at 100 °C for 12 h and calcinated at 550 °C for 5 h, orderly.

Characterizations

The surface areas of the catalysts were obtained from N_2 adsorption/desorption analysis at -196 ^{o}C using a Micromeritics ASAP 2020. Prior to the N_2 physisorption, the catalysts were degassed at 300 ^{o}C for 4 h. Surface areas were determined by BET equation in 0.05-0.35 partial pressure range.

Powder X-ray diffraction (XRD) measurements of the samples were carried out on a computerized Bruker-AXS D8 diffractometer with Cu Kα (λ = 0.15406 nm) radiation. The data of 2θ from 20 to 80 ^{o} were collected at 8 ^{o}/min with the step size of 0.07 ^{o}.

The XPS data were obtained on a Scanning X-ray Microprobe (ESCALAB 250, Thermo-VG Scientific) using Al Ka radiation (1486.7 eV). Binding energies of Ce 3d, Ti 2p and O 1s were calibrated using C 1s peak (BE = 284.8 eV) as standard.

The H_2-TPR tests were carried out on a Micromeritics AutoChem_II_2920 chemisorption analyzer. The samples (100 mg) in a quartz reactor were pretreated at 400 °C in a flow of air (50 mL/min) for 1 h and cooled down to room temperature. Then H_2-TPR was performed in 10 vol % H_2/Ar gas flow of 50 mL/min at a heating rate of 10 °C/min.

The photos of the samples (in Fig. 1) were taken with a digital camera under the same lighting condition (natural light), at the same time. The surface morphology and elemental composition of the samples were studied using a scanning electron microscope (SEM, FEI Quanta 250F) combined with an energy dispersive X-ray (EDX) attachment. The accelerating voltage was 9.0 kV.

The NO_x-TPD was performed using the same reactor as activity tests. A typical experiment used 300 mg sample and a gas flow rate of 200 mL/min. The experiment consisted of four stages: (1) degasification of the catalyst under N_2 at 350 °C for 1 h, (2) adsorption of 500 ppm NO and 5 vol.% O_2 at 50 °C for 1 h, (3) isothermal desorption under N_2 at 50 °C, and (4) temperature-programmed desorption under N_2 at 10 °C/min up to 500 °C.

SEM-EDX

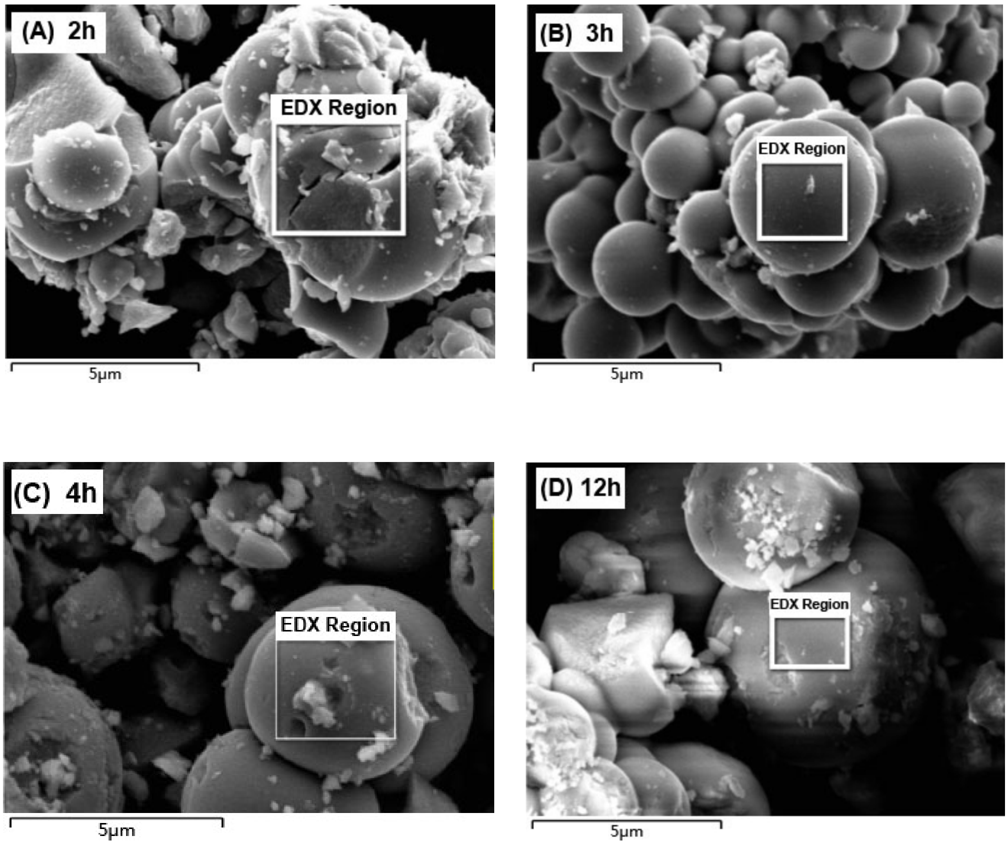

Fig. S1 SEM images and the selected regions for EDX tests of the samples with different precipitation time.

Figure S1 shows the SEM images of the samples with different precipitation time, as well as the selected regions for EDX tests. There was no obvious difference of the samples in the SEM images. All samples consisted of spherical particles with diameters varying from 1 to 5 μm. However, the EDX analysis showed a gradually increase of Ce atomic concentration with precipitation time, which confirmed the proposed formation process of the CeO_2/WO_3-TiO_2 catalyst (see the main text).

XRD patterns

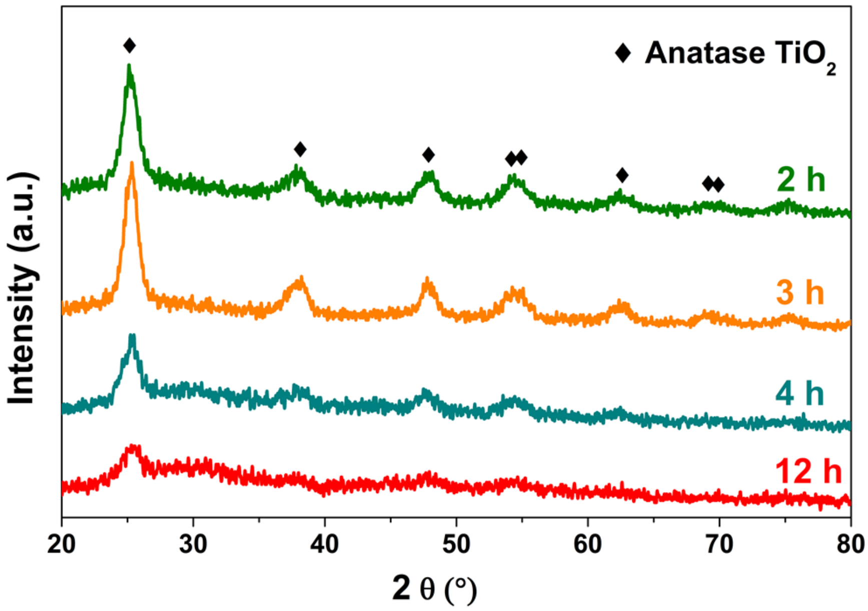

Fig. S2 XRD patterns of the samples with different precipitation time.

The description of Fig. S2 was already shown in the main text.

H_2-TPR

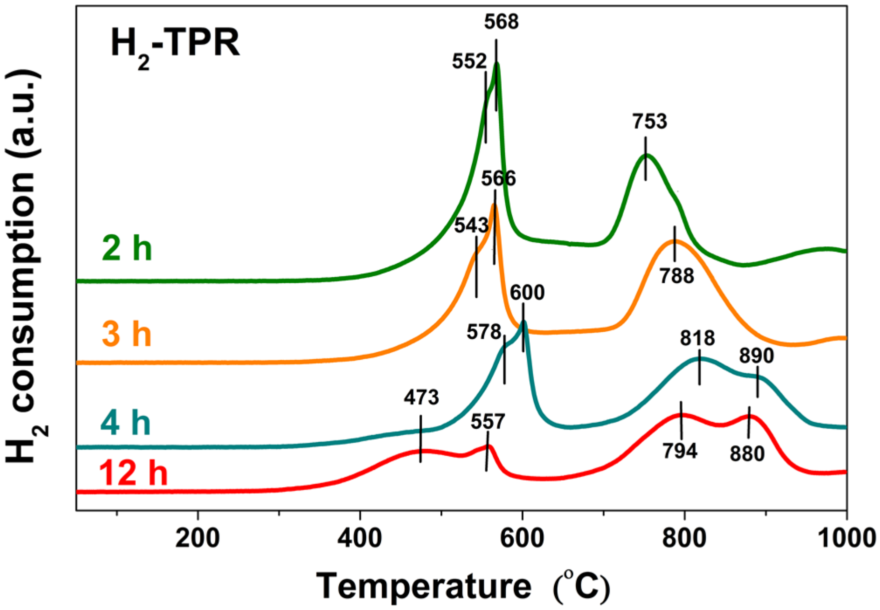

Fig. S3 H_2-TPR profiles of the samples with different precipitation time.

The H_2-TPR profiles of the samples are presented in Fig. S3. The H_2-TPR traces for the samples of 2 h and 3 h reflect multi-stage reduction process from WO_3 to WO_2

via two non-stoichiometric WO_x oxides with three peaks at 552/543, 568/566 and 753/788 °C, respectively.[S1-S3] Two TPR peaks appeared at 473 and 890/880 °C, respectively, after the addition of Ce species on the samples of 4 h and 12 h. The peaks at 473 °C can be attributed to the reduction of surface Ce^{4+} to Ce^{3+}, while the peaks at 890/880 °C might be assigned to the reduction of bulk CeO_2.[S2-S6] The H_2-TPR profiles strongly suggest an enhancement of redox property (a very important property for the NH_3-SCR reactivity in the low-temperature region) by the Ce species on the catalyst.

NH_3 conversion over the samples with different precipitation time.

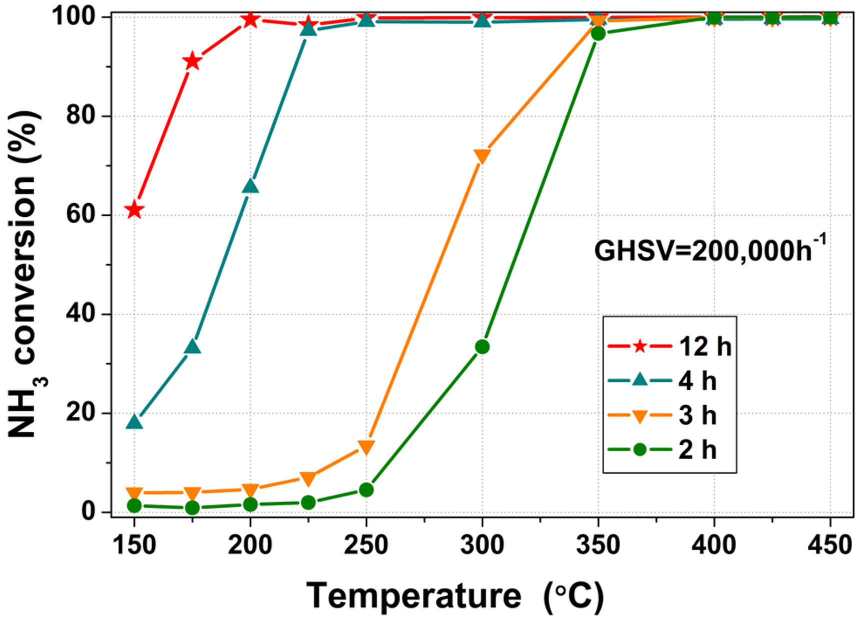

Fig. S4 NH_3 conversion over the samples with different precipitation time. Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol.%, balance N_2 and GHSV = 200,000 h^{-1}.

The description of Fig. S4 was already shown in the main text.

N_2O production over the samples with different precipitation time.

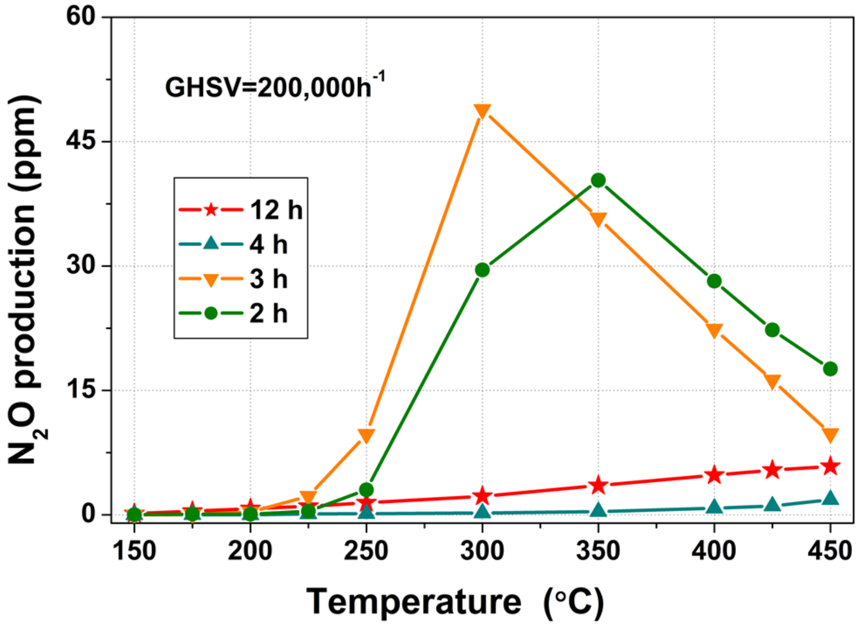

Fig. S5 N_2O concentrations over the samples with different precipitation time. Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol.%, balance N_2 and GHSV = 200,000 h^{-1}.

The description of Fig. S5 was already shown in the main text.

Influences of H_2O and CO_2

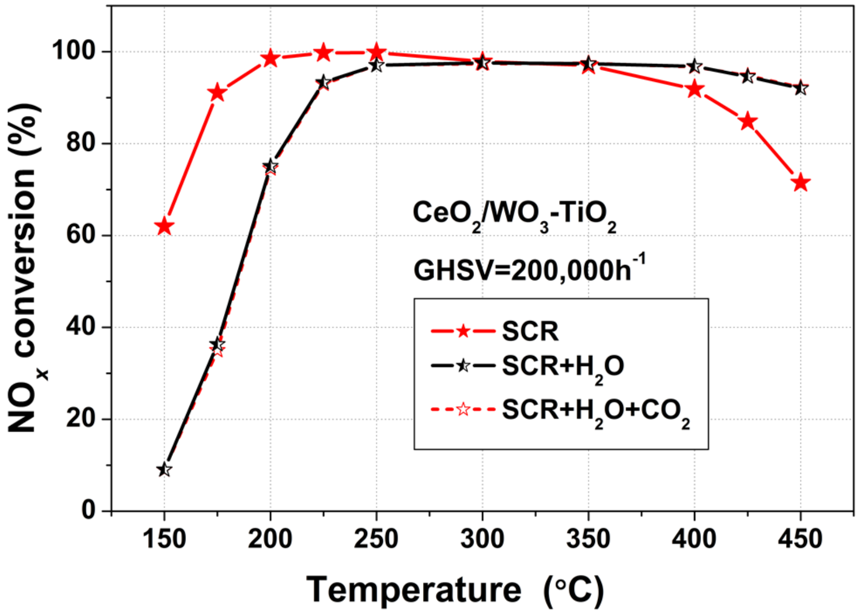

Fig. S6 Influences of H_2O and CO_2 on the NO_x conversion over CeO_2/WO_3-TiO_2

catalyst. Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol.%, [H_2O] = 5 vol.% (when used), [CO_2] = 5 vol.% (when used), balance N_2 and GHSV = 200,000 h^{-1}.

The effects of H_2O and CO_2 on NO_x conversion over the CeO_2/WO_3-TiO_2 catalyst were tested under a GHSV of 200,000 h^{-1} (Fig. S6). The existence of 5% H_2O induced a decrease of low temperature activity while an enhancement of high temperature activity. Over 90% NO_x conversion could still be obtained from 225 to 450 °C (Fig S6). The NO_x conversion under the coexistence of 5 % CO_2 and 5 % H_2O was almost the same as that with only 5 % H_2O in the feeding gas, suggesting that no synergistic inhibition effect between CO_2 and H_2O was present on the SCR activity.

References

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