Supplementary Information

Activity and SO₂ Resistance of Amorphous CeₐTiOₓ catalysts for the Selective Catalytic Reduction of NO with NH₃: In-situ DRIFT studies

Zhiping Zhang, Liqiang Chen, Zhibin Li, Pengying Li, Fulong Yuan, Xiaoyu Niu,* Yujun Zhu*

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, Heilongjiang University, Harbin 150080, P. R. China.

Corresponding Author

Fax (Tel): (+86) 451 8660 9650; E-mail: yujunzhu@hlju.edu.cn (YJ Zhu), niuxiaoyu2000@126.com (XY Niu)

Catalyst preparation

Crystalline phases Ce-Ti oxides catalysts with the Ce/Ti ratio of 0.3 were prepared by impregnation method and sol-gel method which were denoted as Ce₀.₃Ti-CP-1 and Ce₀.₃Ti-CP-2, respectively.

Impregnation method

Ce₀.₃Ti-CP-1 catalyst with the Ce/Ti ratio of 0.3 was prepared by Impregnation method. The commercial TiO₂ (P25) was used as the catalyst support. The catalyst was impregnated by incipient wetness with an aqueous solution containing cerium nitrate. The obtained mixture was stirred for 3 h, 40 oC rotary evaporation, then the sample was dried for 12 h at 105 oC and calcined in muffle furnace for 4 h at 500 oC to obtain the Ce₀.₃Ti-CP-1 catalyst.

Sol-gel method

Ce₀.₃Ti-CP-2 catalyst was prepared by a sol-gel method. Briefly, butyl titanate (0.10 mol)
and ethanol (0.50 mol) were mixed under vigorous stirring, and formed a transparent yellow solution. Cerium nitrate (0.03 mol) was dissolved in water (0.60 mol), acetic acid (0.30 mol) and ethanol (0.50 mol), and then added drop wisely to the above yellow solution. The obtained mixture was stirred for 6 h and placed for about three days at room temperature to form gel. Then the gel was dried for 24 h at 105 °C to remove organic solution and then calcined in muffle furnace for 4 h at 700 °C to obtain the Ce$_{0.3}$Ti-CP-2 catalyst.

Fig. S1 Activity stability test results of the Ce$_{0.3}$TiO$_x$ catalyst. (1000 ppm of NO, 1000 ppm of NH$_3$, 3% O$_2$, balance N$_2$)
Fig. S2 SO₂ tolerance of the Ce₀.₃TiOₓ catalyst at 250 °C. (1000 ppm of NO, 1000 ppm of NH₃, 3% O₂, balance N₂, GHSV=30,000 h⁻¹)

Fig. S3 SO₂ tolerance of the Ce₀.₃TiOₓ catalyst at 150 °C. (1000 ppm of NO, 1000 ppm of NH₃, 3% O₂, balance N₂, GHSV=30,000 h⁻¹)
Fig. S4 XRD patterns of the Ce-Ti mixed-oxide catalysts.

Fig. S5 NH$_3$-SCR activity over the Ce-Ti mixed-oxide catalysts (1000 ppm of NO, 1000 ppm of NH$_3$, 3% O$_2$, balance N$_2$, GHSV=30,000 h$^{-1}$).
Fig. S6 NH$_3$-TPD-MS profiles of Ce$_{0.3}$TiO$_x$ catalyst.
Fig. S7 NO+O₂-TPD-MS curves of the CeₙTiOₓ series catalysts.
Fig. S8 DRIFTS of the NH$_3$ adsorption of the Ce$_x$TiO$_x$ catalysts at 50 °C.

DRIFTS of the NH$_3$ adsorption of was performed over the Ce$_x$TiO$_x$ catalysts on a Bruker Vector FTIR spectrometer (6700) with in situ diffuse reflectance pool and high sensitivity MCT detector which cooled by liquid N$_2$. The DRIFTS spectra were recorded by accumulating 64 scans with a resolution of 4 cm$^{-1}$. Firstly, catalyst was heated to 300 °C under N$_2$ flow 40 cm$^3$/min for 60 min to remove adsorbed impurities and then cooled to 50 °C. Secondly, the sample spectra was collected by subtracting the background spectrum that was collected under a N$_2$ atmosphere. Finally, 0.8% NH$_3$/N$_2$ was introduced into diffuse reflectance pool at least 30 min to get to adsorption saturation, and the total flow rate of the feed gas was kept 25 cm$^3$/min.
Fig. S9 In situ DRIFTS of the Ce$_{0.3}$TiO$_x$ catalyst under different conditions (a) NH$_3$ + O$_2$-60 min
(b) NH$_3$ + O$_2$-60 min (the sample pretreated by SO$_2$)
Fig. S10 In situ DRIFTS of the Ce$_{0.3}$TiO$_x$ catalyst under different conditions (a) NO + O$_2$-60 min
(b) NO + O$_2$-60 min (the sample pretreated by SO$_2$)