Phosphate-Containing CeO₂-ZrO₂ Solid for NH₃-SCR Catalysis: Effects of Oxygen Vacancies on NOₓ Adsorption and Activity

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Introduction

As oxygen is one of the essential reactants in the standard SCR reactions, the ability of restoring and releasing oxygen is an important factor to determine the SCR activity of the catalyst. Ceria catalyst presents an innate prospect because of the easier redox cycles from Ce³⁺ to Ce⁴⁺. The surface oxygen has been reported to be highly active in the NH₃/NO oxidation reaction, leading to the decrease in NH₃-SCR performance as the consequence of over-oxidation of NH₃ [1]. The high mobility of lattice oxygen was essential for a catalyst with high NH₃-SCR activity [1, 2, 3]. Recently, we reported that oxygen vacancies on ceria catalyst facilitated the electron and/or oxygen transfers on catalyst and therefore promoted the nitrite/nitrate formation and decomposition on catalyst [4]. However, the role of surface/lattice oxygen and oxygen defects on NH₃-SCR reaction pathway was not clarified clearly.

In the present study, zirconium phosphate @ CeₓZrO₂ (ZP/CₓZₐ, x=0.25, 0.5) samples are pre-treated by O₂ (ZP/CₓZₐ-O₂), N₂ (ZP/CₓZₐ-N₂) and H₂ (ZP/CₓZₐ-H₂) to study the effects of the surface/subsurface/lattice oxygen and/or oxygen vacancies on NOₓ adsorption and NH₃-SCR reaction.

Materials and Methods

CeₓZrO₂ powders were synthesized by the precipitation method followed by spray drying. ZPCₓZ₁ₓ powders were prepared by impregnating zirconyl chloride octahydrate and ammonia phosphate on CeₓZrO₂ powders. The catalysts were characterized by SCR activity measurement, X-ray photoelectron spectroscopy (XPS), O₂ shut-off/on test, NO, NO temperature programmed desorption (NOₓ-TPD) and diffuse reflectance infrared Fourier transformed spectra (DRIFTS) of NH₃/NOₓ adsorption. Samples were tested in 500 ppm NO, 500 ppm NH₃, 5% O₂, 5% H₂O and N₂ balanced with a high gas hourly space velocity (GHSV) of 3 × 10⁴ h⁻¹.

Results and Discussion

From Fig 1, NO conversions of the catalysts pre-treated by N₂ and O₂ at temperatures lower than 400 °C are very similar. However, the activity of ZP/CₓZₐ-H₂ decreases significantly both at the low and the high temperatures. The NOₓ-TPD profiles are shown in Fig 2. N₂ pretreatment leads to more nitrates/nitrites adsorbed on ZP/CₓZₐ catalyst and the decomposition temperature of these ad-NOₓ species are almost the same. It is interesting that the H₂ pretreatment results in sharp increase in nitrite species adsorbed on catalysts. Both ad-nitrates and ad-nitrites species on ZP/CₓZₐ catalyst are reduced by N₂ treatment. A large increase in nitrites on H₂ treated ZP/CₓZₐ catalyst is observed. Therefore, it can be concluded that NO adsorbed on ceria catalyst are firstly oxidized to nitrates by surface oxygen, and then oxidized to nitrates by subsurface/lattice oxygen. H₂ treatment generates subsurface and lattice oxygen vacancies on catalyst. H₂-treated catalyst in oxidizing atmosphere can adsorb gaseous oxygen on oxygen vacancies to form active surface oxygen and consequently react with gaseous or ad-NO to generate ad-nitrates on catalyst. The formation of NH₄NO₃ can not promote the dNOₓ efficiency on ceria catalyst at high temperatures. And NH₄NO₃ species are found to be more important intermediates in NH₃-SCR reaction, consisting with our previous results in [4].

Significance

We found that NO adsorbed on ceria catalyst are firstly oxidized to nitrates by surface oxygen, and then oxidized to nitrates by subsurface/lattice oxygen. NH₄NO₃ rather than NH₄NO₃ species are more important intermediates in NH₃-SCR reaction on ceria catalyst. Oxygen vacancies lead to more strongly ad-nitrite species on ceria catalyst.

References