



Experimental assessment of the bifunctional NH₃-SCR pathway and the structural and acid-base properties of WO₃ dispersed on CeO₂ catalysts



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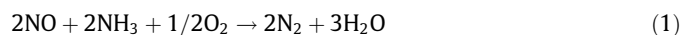
ABSTRACT

A bifunctional pathway for selective catalytic reduction (SCR) with NH₃ was established using a mixture of WO₃/ZrO₂ possessing strong acidity and CeO₂ possessing moderate redox activity. The physical mixture (tight contact) of WO₃/ZrO₂ (4.2 W/nm²) and CeO₂ provided enhanced SCR reactivity but did not improve the redox property assessed by NO oxidation. No improvement of the SCR conversion, however, was observed for mixtures of individual pellets (loose contact), suggesting the requirement of submicrometer-level proximity of the acidic sites to the redox centers. WO₃/CeO₂ (5.3 W/nm²) with intermediate acidic strength had higher SCR and NO oxidation rates than the aforementioned physical mixture of WO₃/ZrO₂ and CeO₂. The weakly basic sites (OH species) on CeO₂ were replaced stoichiometrically with strongly acidic sites on the WO₃ domains along with an increase in the W density (0–24.4 W/nm²), and monoclinic WO₃ crystallites then formed at approximately 10 W/nm². The dispersed WO₃ was in a distorted octahedral environment in all WO₃/CeO₂ samples. The intrinsic SCR reactivity was controlled by only the W surface density; the SCR rate (per surface area) increased within the polytungstate sub-monolayer region (<5–10 W/nm²) and then nearly reached a plateau. The NO oxidation rate also increased with an increase of the W density in a similar trend to the SCR rate, which is indicative of the formation of redox-active centers, rendering the synergetic enhancement of SCR reactivity. These findings and conclusions reached here provide useful guidance for new bifunctional strategies to achieve practical SCR performance.

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1. Introduction

Selective catalytic reduction (SCR) with ammonia (NH₃) is one of the most promising technologies for removing nitrogen oxides (NO_x; NO and NO₂), which cause photochemical smog, acid rain and stratospheric ozone depletion [1,2]. In a typical NH₃-SCR catalytic process, one NO molecule is reduced by one NH₃ molecule in the presence of oxygen (O₂) to produce nitrogen (N₂) and water (H₂O) via the following reaction (so-called standard SCR):



Indeed, NH₃-SCR technology has been utilized for diesel vehicles to meet stringent NO_x emission regulations as well as for power plants and other stationary sources [3,4].

V₂O₅/TiO₂ is the most widely employed catalyst in industry, and thus, extensive studies for active-site requirements and reaction mechanisms have been devoted [5–11]. The proposed reaction

mechanisms often involve two adjacent vanadium species, i.e., hydroxyl groups (V⁵⁺–OH, Brønsted acidic sites) and terminal oxygen species (V⁵⁺=O, redox sites). Topsøe et al. [6,9] suggested on the basis of in situ Fourier transform infrared (FT-IR) and online mass spectrometric studies that the reaction scheme involves the adsorption of NH₃ on the Brønsted acidic sites (V⁵⁺–OH) followed by activation of adsorbed NH₃ via reaction at the redox sites (V⁵⁺=O). The activated NH₃ reacts with gaseous or weakly adsorbed NO, producing N₂ and H₂O and leading to a partially reduced state (V⁴⁺–OH). This reduced species can be re-oxidized by oxygen to the V⁵⁺=O species. Very recently, Marberger et al. [12] identified active sites as single V⁵⁺=O species which had both V⁵⁺/V⁴⁺ redox function and Lewis acid property. They reported that NO reacts predominantly with NH₃ adsorbed on Lewis acidic sites and that nitrosamide (NH₂NO) intermediate forms alongside V⁵⁺ reduction by means of time-resolved IR and visible spectroscopies. Tronconi et al. [13] suggested the involvement of NO oxidation to the nitrite species at the V⁵⁺=O redox sites assessed by transient reactive experiments, but the equilibrium is highly unfavorable and shifts to the right only in the presence of NH₃. NH₃ that adsorbs on nearby acidic sites reacts with nitrites to give N₂ and

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H₂O via decomposition of unstable ammonium nitrite intermediates [13].

A similar bifunctional mechanism has been proposed for metal-exchanged (Fe, Cu) zeolite because they possess both strong acidity on the zeolites and high redox ability on the ion-exchanged metals [14,15]. Further, improvements of standard SCR reactivity were reported by mechanical mixing of H-zeolite and CeO₂ based catalysts (CeO₂-ZrO₂ or Mn-Ce/CeO₂-ZrO₂) by Stakheev et al. [16–18]. They suggested these enhancements are attributed to fast SCR reaction process ($\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$) caused by NO₂ formation on the CeO₂ catalysts because of negligible standard SCR activities on the individual catalysts and because of high NO oxidation performance on the CeO₂ catalysts. A definitive understanding of such bifunctionality, however, has not been achieved simply because it is difficult to differentiate and quantify the contributions of each site to SCR catalysis.

Recently, tungsten (W), niobium (Nb), and molybdenum (Mo) oxides dispersed on cerium (Ce) containing oxides have attracted great attention because these composite oxides exhibit high SCR activity as well as excellent N₂ selectivity at practical temperatures of diesel exhausts [19–36]. These catalyst systems are based on non-toxic elements and include WO₃-CeO₂ [19–24], WO₃-CeO₂-ZrO₂ [25–27], WO₃-CeO₂-TiO₂ [28–31], Nb₂O₅-CeO₂ [32,33], Nb₂O₅-CeO₂-ZrO₂ [34], Nb₂O₅-WO₃-CeO₂-TiO₂ [35], and MoO₃-CeO₂-ZrO₂ [25,36] compositions. The requirements for the acidic and redox sites, as proposed for V₂O₅ and zeolite catalysts, may also account for the emergence of SCR reactivity on these materials because the oxides of group 5 and 6 elements often act as acidic catalysts, and CeO₂ exhibits high redox properties known as O₂ storage and release function used in automotive catalysts. Peng et al. [22] proposed two independent functions composed of acidic and redox catalytic cycles over WO₃-CeO₂ in which Ce₂(-WO₄)₃ provides Brønsted acidic sites for strong NH₃ adsorption, and cubic fluorite CeO₂ acts as an NH₃-activation site, but no synergetic effect of CeO₂ redox performance by WO₃ domains was observed from temperature-programmed reduction (TPR) by H₂. In contrast, a recent study revealed that dispersed WO₃ greatly promotes the redox performance (NO oxidation reactivity) of CeO₂ via the formation of redox-active centers near their interface [37]. Such synergetic activation on the redox sites may also account for the enhanced SCR reactivity on the WO₃/CeO₂ catalysts, but at the same time, such the synergetic activation complicates the assessment of the bifunctional reaction pathway assumed in Scheme 1a.

Here, we report direct evidence for the bifunctional pathway of the NH₃-SCR reaction using mixtures of WO₃/ZrO₂ and CeO₂ as acidic and redox materials, respectively (Scheme 1b). Such a methodological approach can assess the functional contributions

of the acidic and redox sites and evaluate the significance of their spatial proximity. We also examined the effect of the W surface density (0–24.4 W/nm²) on the acidic and redox properties, on the structure, and thus on the SCR reactivity for the WO₃/CeO₂ catalysts by means of temperature-programmed desorption (TPD) by several probe molecules (NH₃, CO₂, NO_x, O₂), as well as of spectroscopic investigations with ¹H magic-angle spinning (MAS) nuclear magnetic resonance (NMR), Raman, X-ray diffraction (XRD), and W L₁- and L₃-edge X-ray absorption near-edge structure (XANES) techniques. These systematic but comprehensive characterizations illustrate the type and genesis of the acidic and redox-active centers on WO₃/CeO₂ and provide universal interpretation of bifunctional SCR pathway.

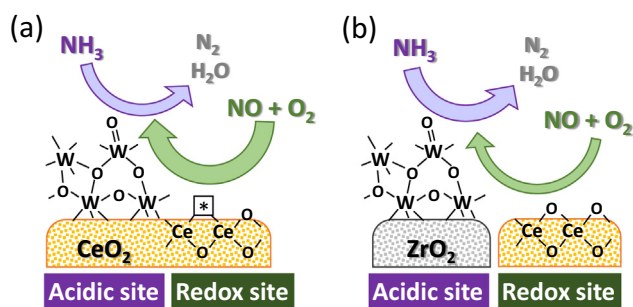
2. Experimental methods

2.1. Catalyst preparation

Two series of WO₃/CeO₂ with various W surface densities were prepared using two CeO₂ supports with different surface areas (136 and 75 m²/g). The CeO₂ support with a low surface area was obtained by pre-calcining the high surface area one at 873 K in flowing air for 10 h. These CeO₂ powders were impregnated by incipient wetness method using aqueous ammonium metatungstate solutions ((NH₄)₆H₂W₁₂O₄₀, Strem Chemicals, 99.9%) containing the desired amount of WO₃ and treated in static ambient air at 383 K overnight. Then, they were treated in flowing dry air at 823 K (4.8 K/min) for 3 h. The W loading amounts were varied from 2 to 31.5 wt% WO₃, which gave a wide range of W surface densities (0.8–24.4 W/nm²). The W surface densities were calculated using the surface area of each W loaded sample. The WO₃/ZrO₂ were also prepared in a similar manner to WO₃/CeO₂. ZrO₂ powders (Daiichi Kigenso Kagaku Kogyo, RC-100, 114 m²/g) were impregnated using an aqueous solution of (NH₄)₆H₂W₁₂O₄₀ and treated using the same protocols as for WO₃/CeO₂. The W loadings with 10–15 wt% WO₃ gave W surface densities of 2.6–4.2 W/nm².

2.2. Catalyst reactivity measurement

The NH₃-SCR and NO oxidation reactions were carried out in a fixed-bed flow reactor operating at atmospheric pressure (Best Sokki, CATA-5000). The reactant gasses were metered using mass flow controllers to give the desired reactant compositions (balance N₂), and the total gas flow was set to be constant (10 L/min). The inlet gas temperature was controlled using a programmable temperature controller. The catalyst samples (0.5–5 g) were pelleted and sieved to retain particles with diameters of 0.5–1.0 mm and were placed on a quartz wool, which was held on the quartz fixed-bed reactor (id = 7 or 13 mm). To measure the mixing effect of WO₃/ZrO₂ and CeO₂, pellet mixtures were prepared by homogeneous mixing of individual pellets (0.5–1.0 mm), and the powder mixtures were prepared by physical mixing of the two powders using a mortar and then pelleted to 0.5–1.0 mm. NO reduction and NO oxidation conversions under steady-state conditions were estimated from the inlet and outlet NO/NO_x concentrations measured by a chemiluminescent analyzer (Best Sokki, Bex-8900C). For rate measurements in the NH₃-SCR and NO oxidation reactions, NO conversions were kept well below 18% in the SCR reaction and below 16% in the NO oxidation reaction by changing the residence times. No formation of N₂O was observed by a non-dispersive infrared N₂O analyzer (Best Sokki, Bex-8900C) in any samples under all the reaction conditions, suggesting that NO was selectively converted to N₂ and NO₂ under NH₃-SCR and NO oxidation conditions, respectively. NH₃ and O₂ concentrations were also measured by a microwave ammonia analyzer and paramagnetic oxygen analyzer, respectively (Best Sokki, Bex-8900C).



Scheme 1. Schematic representation of bifunctional pathways of NH₃-SCR reaction by acidic sites on WO₃ domain and by redox sites on CeO₂ using WO₃/CeO₂ (a) and the physical mixture of WO₃/ZrO₂ and CeO₂ (b). The widths of the arrows represent the abilities of NH₃ and NO activation on acidic and redox sites, respectively; for WO₃/CeO₂ (a), redox-active centers forms on CeO₂ near WO₃ domains.

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