Decisive factor in determining NO selective catalytic reduction with NH_3 over WO_3/CeO_2 catalysts

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Introduction

Selective catalytic reduction by ammonia (NH_3-SCR) is one of the most promising methods to remove lean burn NO_x emission. Thus, a large variety of oxide based SCR materials have been proposed in addition to zeolite based catalysts. Among them, WO_3-CeO_2 has gotten a great attention due to free from toxic elements as well as high activity in a wide range of temperature [1]. However, a major factor in determining high catalytic activity is still unclear in spite of being quite important topic for further development of the catalyst performance.

In this study, several characterizations and model reactions were conducted, and we propose the following three essential factors probably contributing SCR activity; a) strong acid sites, b) redox sites, and c) the vicinity of these two sites.

Materials and Methods

Tungsten is loaded by impregnation of ammonium metatungstate solution onto CeO_2 and ZrO_2 (as a reference) supports. Catalytic activities were measured using fixed bed flow reactor under steady state condition. In addition to NH_3-SCR reaction, NO oxidation reaction in the absence of NH_3 is tested to evaluate redox ability. As characterizations, NH_3-TPD, O_2-TPD, ^{1}H MAS NMR, W-L edge XAFS, Raman, TEM, XPS, and XRD were conducted.

Results and Discussion

WO_3/CeO_2 showed a high SCR conversion compared to pure CeO_2 and WO_3/ZrO_2 which have negligible activities (Fig.1a). It suggests that both Ce and W are necessary to exhibit the SCR activity. Raman, TEM, W-XAFS and XRD characterizations showed loaded W is highly dispersed over CeO_2 support. CO_2-TPD and ^{1}H NMR found that weak basic OH sites on CeO_2 surface were decreased with WO_3 loading amount. Meanwhile, NH_3-TPD (Fig.1b) suggests strong acid sites are created on WO_3/CeO_2. However, since WO_3/ZrO_2 possesses strong acidity as well, the acid sites would not be the sole cause of the high activity.

O_2-TPD spectra (Fig. 1b) shows a certain amount of O_2 can be desorbed from WO_3/CeO_2, implying that WO_3/CeO_2 has a high redox ability. To clarify this presumption, the effect of W density on SCR as well as NO oxidation activities were investigated (Fig.1c). Judging from the fact that not only SCR reaction but also NO oxidation rates increased with W density (up to 4-6 atom/nm^2), loaded W would promote the redox ability over surface Ce sites because loaded W itself does not have a function to be able to oxidize NO to NO_2 (see WO_3/ZrO_2 in Fig. 1d).

Finally, we examined the possibility of bifunctionality between the redox sites and the acid sites by physical mixing of pure CeO_2 and WO_3/ZrO_2. The SCR activity was greatly increased with mixture of the two powders within intrapellet, whereas no activity improvement was observed when mixing individual pellets (separated interparticle, 500-900 μm). The fact that NO oxidation conversions of the two samples were equivalent means that the redox ability remains unchanged by the ways of making pellets. Hence, the bifunctionality of strong acidity and redox ability would be required to progress SCR reaction. Considering the reactant of SCR reaction, the role of W acid sites would be adsorption and activation of NH_3, whereas Ce redox sites would activate NO_x. Also, the vicinity of the two sites is important, suggesting that the reaction mechanism cannot be expressed only by sequential reaction step on the each site but contains a certain steps to which both the sites would concurrently contribute. The detailed mechanism is investigating especially focusing on the synergetic effect of the two sites.

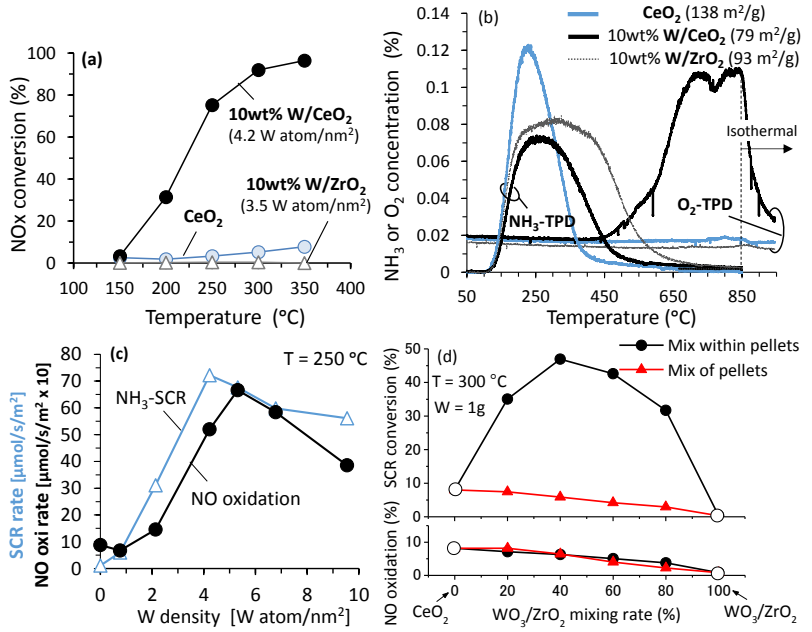

Fig.1. a) SCR conversion (0.03% NO, 0.04% NH_3, 8% O_2, 10% CO_2, 8% H_2O); b) NH_3- and O_2-TPD spectra of W/CeO_2, W/ZrO_2 and CeO_2; SCR and NO oxidation versus c) W density of W/CeO_2 and d) mixing rate of CeO_2 and W/ZrO_2 (0.06% NO, 0.06 or 0% NH_3, 10% O_2).

Significance

As key factors in determining NH_3-SCR reaction over WO_3/CeO_2, a) strong acidity, b) redox ability, and c) the vicinity of the above two function sites are important. The loaded WO_3 would not only create acid sites but also promote redox ability over Ce sites. A certain distance between the acid sites and the redox sites is necessary to develop the NH_3-SCR reaction.

References

1. a) L. Chena, J. Li, M. Gea, R. Zhuc, *Catal. Today* **2010**, *153*, 77; b) W. Shan, F. Liu, H. He, X. Shi, C. Zhang, *Chem. Commun.* **2011**, *47*, 8046.