Promoter effect of V$_2$O$_5$/TiO$_2$ catalyst on deNOx activity and N$_2$O formation in the selective catalytic reduction of NO with NH$_3$

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Introduction
Nitrogen oxides (NOx) cause the photochemical smog, acid rain, ozone depletion and greenhouse effect. Therefore, a great deal of studies has been performed to reduce NOx by using various catalytic systems such as selective catalytic reduction (SCR) or NOx storage-reduction catalyst. Recently, N$_2$O, whose greenhouse effect is 310 times larger than CO$_2$, has been issued due to the new regulatory trend [1]. N$_2$O is known to be an undesirable product of SCR system (e.g. V$_2$O$_5$/TiO$_2$, catalyst), especially at higher temperature than 300°C.

Here we aimed at finding the optimum condition to prepare V$_2$O$_5$/TiO$_2$ SCR catalyst with excellent deNOx activity and minimized N$_2$O formation by changing the various parameters such as promoters and the order of impregnation V$_2$O$_5$/TiO$_2$ catalysts with various promoters, for example, W [2], Zr, Zn, Ga, Mo, Mn, Cr and Ce were prepared. In addition, we changed the sequence of impregnation between promoters and vanadium precursor, and also introduced co-impregnation method. Thus, the effect of loading of promoters on the activity and the selectivity during SCR reaction was extensively investigated.

Materials and Methods
We used ammonium metavanadate (99% Sigma Aldrich) dissolved in diluted oxalic acid solution. Each promoter precursor was also dissolved in diluted water. The loading of V$_2$O$_5$ and promoter was fixed to 5 and 3wt%, respectively. The sequence of impregnation was controlled and catalysts were divided into 3 groups. Group A was designated as promoter/V/TiO$_2$ which vanadium was first impregnated on TiO$_2$ then promoter was introduced on V/TiO$_2$. Group B was designated as V/promoter/TiO$_2$, and the impregnation sequence is opposite to that of Group A. Finally, co-impregnation method was used in Group C. For example, Group A catalysts were prepared by mixing vanadium precursor solution and TiO$_2$ support in a rotary evaporator. After drying at 105°C for 12h, promoter precursor solution was added to V$_2$O$_5$/TiO$_2$ in a rotary evaporator again. After a series of impregnation process, catalysts were dried and then calcined at 400°C for 4 h in air. We applied N$_2$ adsorption-desorption, ICP, XRD NH$_3$, TPD, Raman, XPS, DRIFT and H$_2$ TPR to investigate the physicochemical properties of various catalysts. SCR reaction test was performed with 500ppm NO, 5000ppm NH$_3$, 2vol.% O$_2$ and balanced with N$_2$. FT-IR gas-phase cell was used to quantitatively measure the NOx, NH$_3$ and N$_2$O in the product.

Results and Discussion
Textural and structural properties of each catalyst did not show noticeable differences despite of changes in impregnation method. All XRD patterns, which revealed TiO$_2$ phase only, indicated the formation of highly dispersed vanadia and promoter oxides. In addition, N$_2$ adsorption-desorption results showed that addition of promoters on catalysts cause slight decrease in surface area. However, there was not significant change of N$_2$ adsorption-desorption curves, implying that the order of impregnation did not affect textural characteristics significantly.

According to SCR reaction result, the order of impregnation affected the NOx conversion, especially below 300°C. Comparing two promoters (W and Ce) added catalysts, Group A samples (W/V/TiO$_2$ and Ce/V/TiO$_2$) showed much higher NOx conversion, moreover, the gap between V/Ce/TiO$_2$ and Ce/V/TiO$_2$ was maximized at 200°C by 20% (Figure 1 (a)). However, N$_2$O concentration result indicated no difference between Group A and Group B. Accordingly, N$_2$ selectivity was also higher when V$_2$O$_5$ was firstly impregnated.

N$_2$O concentration after SCR reaction was demonstrated in Figure 1. (b). V$_2$O$_5$/TiO$_2$ sample meant 5wt% V$_2$O$_5$/TiO$_2$ catalyst which was used as reference. Although W and Ce promoted V$_2$O$_5$/TiO$_2$ catalysts showed the highest NOx conversion over all temperature range, the formation of N$_2$O during SCR reaction exceeded reference catalyst (V$_2$O$_5$/TiO$_2$) especially above 350°C. However, Mn and Zr promoted V$_2$O$_5$/TiO$_2$ catalysts demonstrated least N$_2$O formation as well as excellent NOx conversion above 350°C.

We investigated characteristics of reduction behavior and morphology of the vanadia species in the catalysts by using the combination of Raman and H$_2$ TPR. In addition, the various surface states of the catalysts such as surface concentration and acidity were analyzed with XPS, NH$_3$ TPD and DRIFT. The combination of performance and characterization results allowed us to obtain the relationship between activity/selectivity and physicochemical properties of the catalysts prepared with various methods.

Figure 1. (a) NOx conversion of Group A and Group B with promoter Ce and W (b) N$_2$O concentration of Group A catalysts.

Significance
It is concluded that the preparation parameters such as promoter element and the order of impregnation has significant impact on the deNOx activity and N$_2$O formation of V$_2$O$_5$/TiO$_2$ SCR catalyst, which provides the valuable information to develop a novel SCR catalyst with excellent activity as well as minimized N$_2$O selectivity.

References