Promoter effect of V_2O_5/TiO_2 catalyst on deNOx activity and N_2O 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_2O, whose greenhouse effect is 310 times larger than CO_2, has been issued due to the new regulatory trend [1]. N_2O is known to be an undesirable product of SCR system (e.g. V_2O_5/TiO_2 catalyst), especially at higher temperature than 300°C.

Here we aimed at finding the optimum condition to prepare V_2O_5/TiO_2 SCR catalyst with excellent deNOx activity and minimized N_2O formation by changing the various parameters such as promoters and the order of impregnation.V_2O_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 method and the type 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_2O_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_2O_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, 500ppm 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_2O 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_2O concentration result indicated no difference between Group A and Group B. Accordingly, N_2 selectivity was also higher when V_2O_5 was firstly impregnated.

N_2O concentration after SCR reaction was demonstrated in **Figure 1. (b).** V_2O_5/TiO_2 sample meant 5wt% V_2O_5/TiO_2 catalyst which was used as reference. Although W and Ce promoted V_2O_5/TiO_2 catalysts showed the highest NOx conversion over all temperature range, the formation of N_2O during SCR reaction exceeded reference catalyst (V_2O_5/TiO_2) especially above 350 °C. However, Mn and Zr promoted V_2O_5/TiO_2 catalysts demonstrated least N_2O 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.

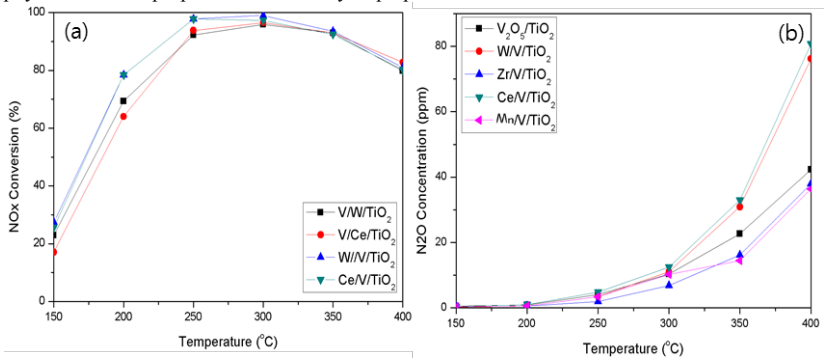

Figure 1. (a) NOx conversion of Group A and Group B with promoter Ce and W **(b)** N_2O concentration of Group A catalysts.

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_2O formation of V_2O_5/TiO_2 SCR catalyst, which provides the valuable information to develop a novel SCR catalyst with excellent activity as well as minimized N_2O selectivity.

References

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