Nano-particle Vanadia-Anatase SCR deNO$_X$ Catalysts

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Introduction

Traditional V_2O_5/TiO_2 SCR deNO$_X$ catalysts used for flue gas cleaning are limited by the surface area of the anatase carrier, since only up to one monolayer of vanadia on the carrier is acceptable. Increased vanadia loading leads to decreased deNO$_X$ activity and unwanted increased oxidation of NH_3 and possible SO_2 in flue gas [1].
In the present work nano-particle anatase-based catalysts with higher surface area are synthesized and these nano-V_2O_5/nano-TiO_2 catalysts with vanadia loading in the range of 0-25 wt% are tested for SCR deNO$_X$ activity and compared to an industrial reference catalyst.

Materials and Methods

Supported catalysts containing up to 25 wt% V_2O_5 on nano-crystallic anatase were prepared by a modified sol-gel procedure [2] using an acidic, aqueous ethanolic salt solution containing various ratios of titanium- and vanadium alkoxides and calcined at 400°C before use. Afterwards, the catalysts were characterized by X-ray powder diffraction (XRD), nitrogen absorption/desorption (BET surface area) and transition electron microscopy (TEM).

NO-SCR reactions were performed with 50 mg fractionized (180-295 μm) samples containing 2-10 mg catalysts diluted in silica with a reaction mixture containing 690 ppm NO, 760 ppm NH_3 and 6.9 % O_2 (balanced with He) at a total flow of 145 ml/min. Catalyst performance (expressed as the first-order rate constant k) was obtained from measuring gas outlet concentrations of NH_3 and NO (λ = 201 and 226 nm) by UV-Vis at conversions <80%.

Results and Discussion

XRD examination of all prepared V_2O_5/nano-TiO_2 catalysts revealed exclusive formation of crystalline anatase carrier containing amorphous vanadia with a calculated average particle size of 12-14 nm based on the Scherrer equation. Only for catalysts with high V content corresponding to ≥15 wt% V_2O_5 did another crystalline – possibly mixed vanadia-titania phase – appear. The high degree of crystallinity was confirmed by TEM where anatase particles with average sizes about 9 nm containing an outer shell of amorphous vanadia of about 0.2 nm thickness was clearly identified, as shown in Fig. 1 for a catalyst containing 7 wt% V_2O_5. Additionally, BET surface areas of the catalysts were found to be significantly increased when modified with the nano-sized vanadia layer, thereby allowing the catalysts to possess higher theoretical monolayer coverage of vanadia (Table 1).

The influence of the vanadia content on the maximal first-order rate constant obtained using the prepared V_2O_5/nano-TiO_2 catalysts in the NO-SCR reaction are shown in Fig. 1. As can be seen from the figure the maximum loading of vanadia on the nano-particle TiO_2 carrier leading to a maximum activity seems to be around 15 wt% corresponding to about a monolayer, which is much higher than 1-3 wt% usually utilized in commercial catalysts. For comparison the activity (k-value) of an industrial 3 wt% reference catalyst is also given on the figure. It is seen that the activity of the developed nano-catalyst is around twice of the industrial reference, both obtained at 380°C.

Table 1. Characteristics of support and a selected catalyst

Material	BET area* (m^2/g)	Theoretical V_2O_5 monolayer (wt%)
nano-TiO_2	73-89	10.6-12.9
11.8 wt% V_2O_5/nano-TiO_2	129	18.7

* Calculated from N_2 desorption isotherms.

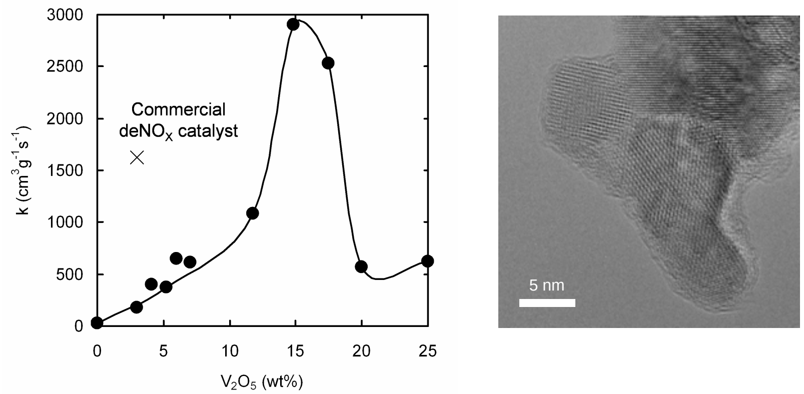

Figure 1. Influence of the vanadia content on the maximal first-order rate constant obtained using the V_2O_5/nano-TiO_2 catalysts in the NO-SCR reaction (left) (activity of reference catalyst inserted). TEM image of unused 7 wt% V_2O_5/nano-TiO_2 catalyst (right).

Significance

Vanadia-anatase SCR catalyst based on crystalline support provide a significant higher catalytic activity towards conversion of NO$_X$ than traditional industrial catalysts, as the nano-particle texture of the catalyst allows a larger part of the vanadia to remain as active monolayer. Thus a more efficient deNO$_X$ catalyst may be obtained by applied nano-supported catalyst technology.

References

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2. Hari-Bala, Guo, Y., Zhao, X., Zhao, J., Fu, W., Ding, X., Jiang, Y., Yu, K., Lv, X., and Wang, Z., *Mater. Lett.* 60, 494 (2006).