

## Nano-particle SCR deNO<sub>x</sub> catalysts

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### Introduction

Catalysts used for cleaning flue gasses from NO<sub>x</sub> via selective catalytic reduction (SCR) with ammonia are based on anatase (TiO<sub>2</sub>) particles with a single monolayer of amorphous V<sub>2</sub>O<sub>5</sub>. If the monolayer is exceeded due to high loading, crystalline vanadia will form on the catalyst surface and cause a dramatic drop in activity and unwanted increase in SO<sub>2</sub> and NH<sub>3</sub> oxidation [1]. In the present study, very active deNO<sub>x</sub> catalyst based on anatase nano-particles containing up to 25 wt% V<sub>2</sub>O<sub>5</sub> were synthesized [2]. The catalysts were tested for SCR deNO<sub>x</sub> activity and compared to a state-of-the-art commercial catalyst. The method was further demonstrated on other supported oxide systems with V<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and CuO as the active monolayer phases supported on either anatase or tetragonal ZrO<sub>2</sub> [3].

### Materials and Methods

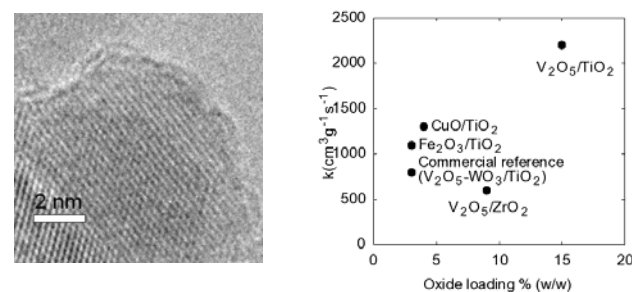
Supported catalysts with 0-25 wt% of active monolayer oxide on nano-crystals carrier were prepared by a seed-assisted sol-gel, co-precipitation procedure [2,3] using an acidic, aqueous ethanolic salt solution containing various ratios of titanium-, vanadium-, zirconium-, copper- or iron alkoxides, treated with sulfuric acid and calcined at 400°C before use. After preparation the catalysts were investigated using powder XRD, nitrogen absorption/desorption (BET surface area), TEM, AFM (atomic force microscopy) and FT-IR. 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 of 1000 ppm NO, 1100 ppm NH<sub>3</sub> and 9% O<sub>2</sub> (balanced with He) at a total flow of 280 ml min<sup>-1</sup>. Catalyst performance (as the first-order rate constant *k*) was obtained from measuring gas outlet concentrations of NH<sub>3</sub> and NO (λ = 201 and 226 nm) by UV-Vis and N<sub>2</sub>O by gas chromatography, at conversions <80%.

### Results and Discussion

XRD examination of all prepared oxide systems revealed exclusive formation of either crystalline anatase or tetragonal ZrO<sub>2</sub> carrier with no sign of crystalline forms of the active monolayer oxides. Average particle sizes were calculated from Scherrers equation to be 6-14 nm for V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> systems and 5-6 nm for Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and CuO/TiO<sub>2</sub> systems. The high degree of crystallinity was confirmed by high-resolution 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 exemplified in Fig. 1 for a 7 wt% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst. AFM height profiles further showed the average particle size to be 7 nm with a distribution from 2-14 nm of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> system, thus confirming well dispersion of particles with almost no agglomeration. BET surface area measurements of the catalysts revealed a surprising tendency as the surface area increased with higher vanadia loadings, opposite to the trend normally observed when traditional impregnation techniques is used for catalyst preparation. The BET surface area measured for the 15% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was 126 m<sup>2</sup> g<sup>-1</sup>. FT-IR measurements confirmed that the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts contained monomeric,

dimeric as well as polymeric vanadia species but no crystalline V<sub>2</sub>O<sub>5</sub>. The FT-IR spectra further indicated the TiO<sub>2</sub> and ZrO<sub>2</sub> carrier surfaces to be sulfated.

Activity measurements of the catalysts demonstrated the optimal oxide loadings to be 15 wt%, 9 wt%, 3 wt% and 4 wt% for the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and CuO/TiO<sub>2</sub> systems, respectively, with corresponding first order rate constants (*k*-values) of 2200, 600, 1100 and 1300 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>, thus comparable or considerably higher than the value of 800 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup> obtained for a commercial 3 wt% V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst (see Fig. 1). Additionally, the activities of sulfuric acid treated catalysts were found to be significantly increased compared to non-treated nano-catalysts (not shown). The selectivity of the 15 wt% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst toward N<sub>2</sub> formation was also found to be very good compared to the commercial reference catalyst, even under dry conditions, probably due to the high dispersion of surface vanadia. Thus, at 380°C the SCR selectivity (as mole N<sub>2</sub>/moles N<sub>2</sub>+N<sub>2</sub>O) was measured to be 97.1% and 98.5% under dry and humid conditions (2.5 vol% water), respectively, whereas the reference catalyst gave selectivities of 91.2% and 98.8% at analogous reaction conditions.



**Fig. 1.** HR-TEM image of 7wt% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst (left). Maximum first-order rate constants obtained in NO-SCR reactions with different catalysts as a function of oxide loadings (right).

### Significance

The work introduces a simple and versatile method for preparation of nano-crystalline oxide-based catalysts which can be applied on industrial scale. In NO-SCR the catalysts were selective and several times more active than a commercial state-of-the-art 3 wt% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst as the nano-particle texture allowed a larger part of the vanadia to remain as active monolayer. Due to their excellent catalytic performance the nano-catalysts can contribute significantly to meet future challenges in deNO<sub>x</sub> technologies for applications like, e.g. SCR-based mobile deNO<sub>x</sub>, low-temperature deNO<sub>x</sub>, and deNO<sub>x</sub> operating under poisoning conditions, for example, in biofuel fired power plants.

### References

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