

New Titania Materials with Improved Stability and Activity for Vanadia-Based Selective Catalytic Reduction of NO_x

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ABSTRACT

Selective Catalytic Reduction (SCR) of NO_x using reductants such as urea continues to be of high interest to meet impending regulations. Vanadia supported on anatase titania is a well-established catalyst for stationary and heavy-duty-diesel truck deNO_x applications. However, traditional anatase titania-based materials are regarded to have limited thermal stability in the most demanding applications such as those where the SCR catalyst is located downstream of a regenerating DPF, in which the catalyst could be exposed to very high temperatures. More recently, state-of-the-art titania-based vanadia catalysts have shown good cold-start performance and are capable of surviving accelerated aging treatments of up to 64 hrs at 670°C [1], good performance in a configuration upstream of a DOC/DPF [2], good low temperature NO_x conversion on par with Cu-zeolite SCR catalysts and superior resistance to sulfur poisoning [3]. We report here new, highly engineered titania-based materials with substantially improved stability and/or activity compared to the state-of-the-art commercial titania-based vanadia SCR catalysts. New synthetic approaches were used to prepare catalyst support materials that are predominantly anatase TiO₂ in composition. The thermal and hydrothermal stabilities of the new materials were characterized using a combination of x-ray powder diffraction with Rietveld Refinement, transmission and scanning electron microscopies, and N₂ porosimetry. Vanadia-loaded catalysts in powder form were thermally- or hydrothermally-aged and evaluated for NO conversion activity and selectivity in model-gas bench-scale reactors using NH₃ as the reductant, and were compared to commercial titania-based vanadia powders. The new materials fall into two classes. In the first,

the materials exhibit substantially improved thermal stability, anatase phase stability and higher porosity, while exhibiting deNO_x activity comparable to commercial materials. In the second class, the activity and stability of the new materials can be tuned to yield higher deNO_x activity, particularly after exposure to high temperatures, while maintaining crystal phase stability and porosity at least as good as that of state-of-the-art commercial titania-based vanadia catalysts. In a bench test under severe conditions that simulate lifetime catalyst exposure, no detectable vanadium is lost from the new catalysts to the vapor phase. The new, highly engineered materials should provide the catalyst formulator with new options to achieve robust and active SCR systems.

INTRODUCTION

The selective catalytic reduction (SCR) of nitrogen oxides produced during combustion processes using reductants such as NH₃ has been a commercially successful technology for over 30 years [4]. Over the last several years there has been extensive development of SCR catalysts for mobile-source applications. Titania-based vanadia catalysts have been employed widely on a commercial basis in stationary-source applications for many years, and more recently in heavy duty diesel mobile-source applications [5]. Recent SAE papers on titania-based vanadia catalysts have shown that these catalysts offer good cold-start performance, and are capable of surviving accelerated aging treatments of up to 64 hrs at 670°C [1], good performance in a configuration upstream of a DOC/DPF [2] and superior resistance to sulfur poisoning [3].

However, it is commonly accepted that the main limitation of titania-based vanadia catalysts is a relative lack of thermal durability relative to zeolite-based catalysts [6]. The titania

catalysts are typically mostly comprised of anatase titania from the sulfate process as the catalyst support, present at greater than 80 wt%. The active catalytic functionality is based on vanadia, present at low amounts, typically 0.5 to 3 wt%. Other oxides such as tungsta and silica are also added in relatively low amounts as promoters and stabilizers. Silica enhances the thermal stability of anatase, and tungsta enhances the catalytic activity of vanadia.

The main mechanisms for loss in activity after high temperature exposure are typically thought to involve all of the catalyst components. With regard to the support, anatase titania undergoes thermal sintering, which causes a loss in the surface area and pore volume of the support. At suitably high temperatures, the anatase titania undergoes a transformation in crystal structure to the less active rutile form. With regard to the active phase, vanadia undergoes rearrangement that can ultimately lead to bulk three-dimensional structures that are less active than well-dispersed surface vanadia. Finally, with regard to the promoters, tungsta also can migrate and ultimately crystallize to form a less effective phase.

In actual application, there also is concern over the potential loss of vanadia to the environment, and the subsequent possible toxicity of such vanadia. This loss can potentially occur via two mechanisms, one of which involves the physical attrition of the whole catalyst [7] and one which involves the possible loss of vanadia to the vapor phase in a very hot gas exhaust stream. Thus, it is desired to develop a better understanding of the mechanisms that underlie the loss in activity associated with high temperature exposure, and to further improve the performance of titania-based vanadia catalysts.

EXPERIMENTAL

MATERIALS

The compositions of some commercial catalysts, as well as the developmental catalysts of interest in this paper, are given in Table 1. In this Table and throughout the text, the nomenclature is used that “CA” refers to commercial catalyst “A”, and “DA” refers to developmental catalyst “A”.

Table 1. Compositions of Commercial and Developmental Catalysts

Material	Composition, wt%			
	TiO ₂	SiO ₂	WO ₃	ZrO ₂
CA	90	0	10	0
CB	81	10	9	0
CC	90	10	0	0
DA	73.4	4.5	8.2	13.8
DB	88	8	4	0
DC	90	4	6	0
DD	86	8	6	0

Catalyst powders were aged in muffle furnaces either by calcination in static air or by treatment in slowly flowing air (~21% O₂, 100 sccm) with 10 vol. % H₂O introduced via metering pump. To a first approximation, the degree of sintering should not depend on the gas flow rate, only the moisture and oxygen partial pressures (see below).

METHODS

The structure and stability of titania-based catalysts and the changes that occur during exposure to elevated temperatures were investigated by various means. The methods employed consist of x-ray diffraction analysis (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), nitrogen porosimetry (N₂ BET/BJH) and catalytic evaluation of activity for the reaction of NO with NH₃ (deNO_x). All samples were tested as pure powders.

XRD

Samples were evaluated for crystal structure, phase composition and crystallite size in the following manner. The samples were prepared for XRD by pressing into spherical XRD PW1812/00 holders and then analyzed using a Panalytical X'Pert Pro™ MPD diffractometer equipped with a sealed Cu x-ray tube and an X-Celerator position sensitive detector. Instrument conditions were set at 45kV, 40mA, 0.008°2θ/step and 50 second dwell time. Phase identifications are performed through search-match of the experimental patterns with both the ICDD and ICSD databases. The Rietveld method was used for quantitative phase composition analysis by X-Ray diffraction. Although the Rietveld method also yields crystallite size data, these were also obtained from single (1,0,1) peaks using the full-width at half- maximum via the Scherrer formula as employed in the Panalytical High Score software. For crystals less than 1000 Å in size, there was good agreement between the Scherrer and Rietveld methods, and the former values were used in the analysis of crystal growth kinetics. The instrument broadening value used for calculation was from the LaB6 standard (NIST profile standard material).

TEM

The samples were prepared for TEM analysis by dipping holey, carbon coated Cu TEM grids directly into the provided powder. The grids were then viewed in the TEM at magnifications ranging from 50 to 400,000X. Analysis was performed using a JEOL 2000FX II TEM operated at 200kV. During the imaging process particular attention was given to characterizing phase size and distribution. Images were collected with a Gatan MultiScan™ CCD camera.

N₂ Porosimetry

Samples were evaluated for nitrogen porosimetry using Micromeretics TriStar™ units. The samples were outgassed

overnight at 150°C under flowing nitrogen. They were then cooled to room temperature for the adsorption measurement. Adsorption/desorption curves were measured at liquid nitrogen temperature. Surface area was determined using the BET method, and pore volumes were measured using the BJH method on the adsorption branch.

Catalytic Evaluation

For the SCR evaluation, steady-state measurements were made in a small quartz reactor. A 0.1 g sample of each vanadia-loaded catalyst powder was pelletized and meshed to -24/+40 mesh, and was loaded into the reactor to determine the conversion of NO in the presence of NH₃. A flowing stream that contained 5% O₂, 5% H₂O, 500 ppm NH₃, 500 ppm NO with the balance N₂ was passed over the catalyst at a typical total flow rate of 65 L/hr. The cylindrically-shaped powder bed dimensions were typically 6.3 mm diameter and ~5 mm height, so that the GHSV was ~400,000 hr⁻¹. This high space velocity was used so that these very active catalysts could be easily differentiated, with conversions typically in the range of 50-80% at 350°C. Occasionally, a 0.2 g sample was used (GHSV ~ 200,000 hr⁻¹). Gas analysis was accomplished using an Ametek Proline Mass Spectrometer and a Nicolet FTIR spectrophotometer. Catalyst bed temperatures were measured by K-type thermocouples inserted into a thermocouple well, the tip of which was in contact with the bed. Baseline gas composition was measured at the beginning of each run in bypass mode. Activities are reported either as conversion (%) or rate, $r = -\ln(1 - (\text{conv.}/100))$, and these were measured over the temperature range 250°C to 450°C.

Vanadium Volatility

A test was developed to quantify the amount of vanadium lost to the vapor phase during exposure of the catalyst to reaction gases at elevated temperature [19]. The same reactor tubes used for catalytic evaluation were loaded with 0.2 g catalyst powder that was pelletized and meshed to -24/+40 mesh. The reactor was heated to 750°C, maintained at that temperature for 4 hr, and the same reactant stream described above (which contained water and oxygen each at 5 vol%) was flowed over the catalyst bed at 32.5 L/hr (GHSV ~ 100,000 hr⁻¹). Vanadium deposited downstream was recovered and quantified using ICP analysis. The detection limit for this method was 2.5 µg V/g catalyst.

RESULTS AND DISCUSSION

BENCHMARKING OF COMMERCIAL CATALYSTS-EFFECT OF VANADIA AND TEMPERATURE

Commercially-available, titania-based catalysts span a range of compositions, and three were chosen for this study as

shown in Table 1. While the sintering and crystal chemistry of titania-based materials have been reported in the literature, it was necessary to establish relevant baseline performance data for this study with vanadia levels in the commercially realistic 1-3 wt% V₂O₅ range.

Shown in Fig. 1 are catalyst surface areas as a function of thermal exposure temperature at constant time (for 6 hrs in air) for titania-based vanadia catalysts, and Fig. 2 shows the crystal phases that are observed for 3 wt% V₂O₅ catalysts after exposure at 800°C.

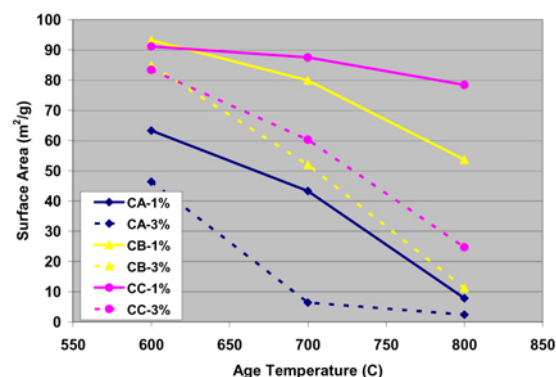


Figure 1. Effect of age temperature (6 hr in air) on commercial materials loaded with either 1% or 3% vanadia.

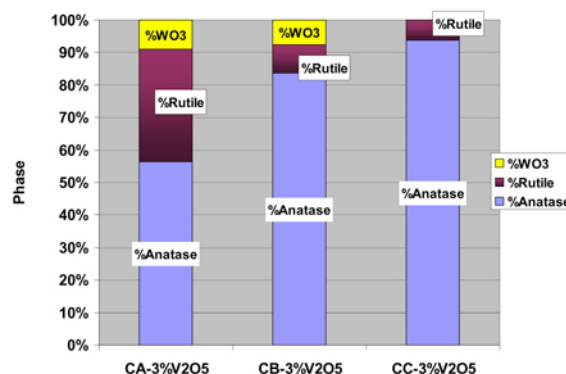


Figure 2. Crystal chemistry of commercial materials with 3 wt% vanadia after thermal treatment at 800°C for 6 hr in air.

These results reveal several features that are consistent with previous studies. That is, the catalyst surface area, extent of transformation of anatase into rutile and crystallization of tungsta are strongly dependent on both temperature and vanadia level. The relative ranking for the surface area and anatase-phase stability of these materials follows the order:

$$\text{CC (Ti/Si)} > \text{CB (Ti/Si/W)} > \text{CA (Ti/W)}$$

The catalytic activity for NO conversion at 350°C of the materials is represented in Fig. 3. While the responses are relatively complex functions of temperature and vanadia loading, several observations can be made.

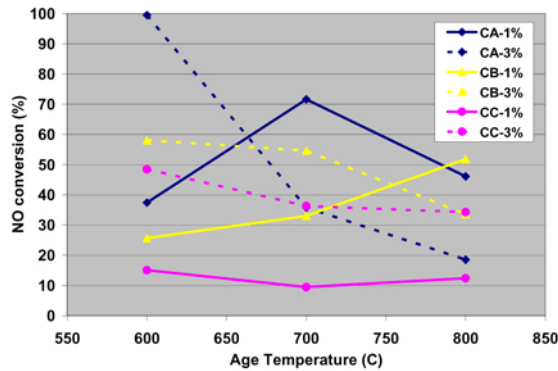


Figure 3. Effect of Age Temperature and Vanadia Level on NO Conversion at 350°C, GHSV ~ 400,000 hr⁻¹.

For the most part, the conversion is higher for the higher vanadia level; further, when averaged over the full range of temperatures and vanadia levels, the relative ranking for activity of these materials follows the order:

$$CA (Ti/W) > CB (Ti/Si/W) > CC (Ti/Si).$$

This order is exactly the opposite of that observed for the stability of these materials; therefore, it is apparent that a trade-off will likely have to be made between stability and activity. One possible goal would be to develop a material with the optimum activity of CA and the optimum stability of CC.

While the catalytic behavior in Fig. 3 appears to be complex, one means of simplifying and possibly rationalizing the results involves the concept of the extent of the surface coverage of the titania support with the supported oxides (Si, W and V). The surface density of supported oxides, ρ_{surf} (metal atoms/nm²) is given [8] as:

$$\rho_{surf} = (A \cdot x / MW) / (S \cdot 10^{18}) \quad (1)$$

where A is Avogadro's number, x is the supported oxide mass fraction, MW is the molecular weight of the supported oxide and S is the support surface area (m²/g). Thus, the lower the support surface area, the higher the surface density of supported oxide. The ρ_{surf} in turn likely affects the chemical nature of the supported phase.

Literature values for the complete, or monolayer coverage, $\rho_{surf, monolayer}$, of the surface of pure silica (6 Si atoms/nm²) [9], tungsta on titania (4.5 W atoms/nm²) [10] or vanadia on

titania (7.1 V atoms/nm²) [11] were obtained. The fractional monolayer coverage, $f_{m, i}$, with respect to oxide (i) is:

$$f_{m, i} = \rho_{surf, i} / \rho_{surf, monolayer, i} \quad (2)$$

and the total fractional monolayer coverage Tf_m is the sum of the $f_{m, i}$ for each supported oxide in the case that there are multiple supported oxides (e.g., Si, W, V).

$$Tf_m = \sum_i f_{m, i} \quad (3)$$

Shown in Fig. 4 are the results for NO conversion results from Fig. 3, re-plotted against the logarithm of the total fractional monolayer. This approach allows the vanadia level, the levels of other promoters/stabilizers and the catalyst surface area to be condensed into one parameter. It can be seen that the curves exhibit the classic “volcano” shape often encountered in catalysis, and the maximum in activity for each material occurs in the range of 2-3 Tf_m .

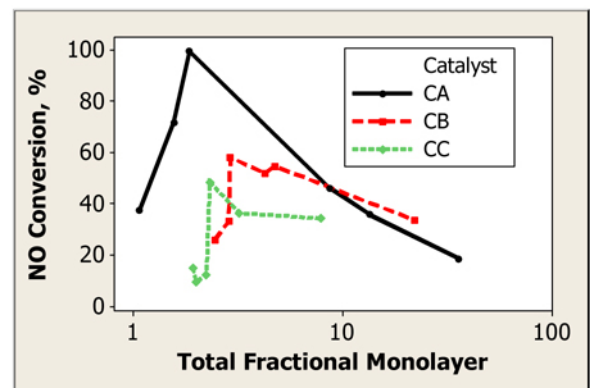


Figure 4. NO conversion as a function of total fractional monolayer for commercial catalysts with either 1 wt% or 3 wt% vanadia, GHSV ~ 400,000 hr⁻¹.

In this case, an explanation that is consistent with the literature is that at low fractional monolayer coverage, the vanadate species are isolated and less active than when present as surface polymeric species. At high fractional monolayer coverage, the vanadates form larger, three dimensional structures that have less available surface for reaction. At intermediate coverage, the active polymeric vanadate species have maximum surface area. Thus, control of the support surface area and catalyst and promoter levels in the appropriate range is imperative for the design of improved catalysts.

STABILITY- ANATASE TITANIA SINTERING