

## **Thermal stability of SCR catalysts containing vanadia on silica-titania for the use in diesel applications**

C.U. Ingemar Odenbrand

*Department of Chemical Engineering II, Lund University, Institute of Technology,  
P. O. Box 124, SE-221 00 Lund, Sweden*

### **Abstract**

The effect of reaction temperature, water content, and vanadia content on the sintering of a model vanadia on silica-titania SCR catalysts has been investigated. A comparison is also made to a vanadia/titania catalyst submitted to conditions simulating at least 500 000 km driving on a diesel truck. The variation of the surface area, the crystallite size of the catalyst constituents on thermal treatment in dry and wet air was investigated. The support stabilises after 5 hours at 450 °C in wet and dry conditions. The support without vanadia sinters to a much lower degree than the complete catalyst. The vanadia crystallite size increases to fill the pores of the support. The effect of vanadia is to increase the rate of the conversion of the anatase phase of the support to rutile and to lower the transition temperature.

Keywords: Thermal stability, Vanadia based SCR catalysts, Diesel SCR catalysts

### **1. Introduction**

Today's use of the SCR technique on diesel vehicles and in other applications operating under non stationary conditions can be based on a vanadia catalyst system. A description such a system has been presented by us already in 1994 [1]. This is based on real time computerised estimations of mass flow of nitrogen oxides and of exhaust gas temperature. The function of the catalyst is monitored by a kinetic model taking into account all mass transfer and surface kinetic steps in the monolithic reactor used. The key parameter in this model is the coverage of the catalyst surface by ammonia. This value is used in the dosing strategy to regulate the amount of ammonia needed for the reduction of the nitrogen oxides.

A prerequisite for this method to be successful is a stable catalyst activity or low and predictable catalyst activity decay. The catalyst used in the system referred to above was 16 % V<sub>2</sub>O<sub>5</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The support for the catalysts used today is stabilized titania [2]. We have found only one paper [3] describing the effect of thermal treatment of a TiO<sub>2</sub>-WO<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> catalyst which is of this kind. The catalysts studied contained 1, 2 and 3 wt. % vanadia. At 600 and especially 650 °C severe decreases in

surface area were obtained. It was also shown that there was a strong effect of the vanadia content leading to a surface area loss of 87 % for the 3 % catalysts after only 30 hours at 650 °C.

There are some studies on the kinetics of the sintering of anatase though. Among these Hébrard et al. [4] describe the effect of water and oxygen on the initial sintering of anatase. They present a kinetic model based on a mechanism with the surface diffusion of hydroxyl ions as the rate-limiting step of the particle growth. With this model it was possible to explain the accelerating effect of water vapour. The calcination time used was from one to seven hours only.

In our studies on the SCR reaction, we used vanadia on silica-titania as a model catalyst [5-9]. We have found one investigation [10] on the effect of thermal treatment on similar catalysts. That paper describes characterization of monolayers of vanadia immobilized on titania-silica mixed gels. The authors show results from XRD and adsorption studies from calcination of a catalyst based on 50/50 mol. % TiO<sub>2</sub>/SiO<sub>2</sub>. The support, with the same composition as ours, was calcined for 5 hours at 600 °C. No data from other calcination times were presented. Thus there is a lack of data for a kinetic study of the sintering of this material.

Therefore an investigation of these effects was undertaken. Similarly the lack of data regarding the effect of changes in the surface area of vanadia/titania catalysts used in diesel exhausts on trucks is complete. This paper contributes to shed some light on this issue too.

## 2. Experimental

The thermal stability of the support alone and of the supported catalyst was investigated for the model catalyst. The support consisted of equimolar amounts of silica and titania and the preparation and its characterisation has been described before [11]. The support was calcined for five hours at 450 °C in a stream of dry (silica gel) air. Separate thermal treatments were performed on the support and on the catalyst. The support, about 0.8 g, was treated at 450 °C for various periods of time with a flow of 400 cm<sup>3</sup>/min of dry and wet (water pressure 22 torr, 2.9 %) air.

The vanadia catalysts were prepared from the support, calcined in a stream of dry air for 5 hours at 450 °C, by impregnation with aqueous solutions of ammonium metavanadate dissolved in oxalic acid. The amount of vanadia was 10, 20, and 30 %. The catalysts were dried at 130 °C overnight in an oven and calcined in lots of about 4 g for five hours at 500, 550 and 600 °C. One batch of the 20 % catalyst was also sintered for various times at 450 °C in 2 % water vapour. The impregnated catalysts, that were first calcined at 500 °C, were calcined a second time at 600 or 650 °C for different lengths of time to study the effect of calcination time.

The catalyst aged at Volvo was vanadia titania supported on a 400 cpsi cordierite monolith. It was made by successive dipping of slurried TiO<sub>2</sub> particles (Rhône Polenc DT(8)) to create a washcoat. Ammonium metavanadate was used for the impregnation of the washcoat. The catalyst was dried at 125 °C overnight and calcined in a stream of air at 500 °C for 2 hours. The amount of vanadia was 5.64 % of the washcoat and the amount of coating was 18.2 % in total. The aging, at Volvo, was performed in a special rig where a test cycle with 1 hour length was repeated a large number of times. The average temperature of the cycle was 470 °C, but such a high temperature as 550 °C was used for about 1000 s in each cycle. The Swedish mark 1 diesel fuel was used (< 10 ppm S).

All materials were analysed for changes in their surface area measured by adsorption of nitrogen at liquid nitrogen temperature. The equipment used was for some samples a Micromeritics Flowsorb 2300 based on a one-point measurement principle. Surface areas, total pore volumes, at a relative pressure of about 0.995, and pore size distributions were also determined on a Micromeritics ASAP 2400 instrument after degassing for 16 hours at 350 °C.

Most of the samples were also analysed by X-ray diffraction using Philips PW 1300 XRD equipment with a PW 1050 wide-angle goniometer. The crystallite sizes were estimated using line broadening along with the procedure given before [12]. The amount of anatase in the samples was calculated from the intensities of rutile ( $d=0.3245$  nm) and anatase ( $d=0.351$  nm) by the formula given by Yoganarasimhan and Rao [13].

### **3. Results and discussion**

#### **3.1 Thermal stability of the support**

The material as prepared [11] has a BET surface area of 268 m<sup>2</sup>/g, a micropore volume of 0.092, a mesopore volume of 0.446 and a macropore volume of 0.078 cm<sup>3</sup>/g. The structure consists of X-ray amorphous silica, which on calcination at 1150 °C turns into  $\alpha$ -cristoballite, and titania in the form of anatase. There is also a certain amount of a mixed oxide phase as shown by the increased  $d$  value when Ti<sup>4+</sup> is inserted into the silica matrix. The amount of this phase is not known though. The size of the cristoballite units is about 1.1 nm and the anatase 4.1 nm.

The XRD spectrum of the support, calcined at 450 °C, shows a pattern typical for anatase and contains in addition one broad peak corresponding to amorphous silica. The crystallite size of the anatase calcined in dry air is 4.0 nm and does not vary with calcination time (Table 1). Similarly the material calcined in wet conditions has a somewhat larger size of 4.2 nm and does not change with time either. The surface area for materials calcined in dry conditions, decreases by about 10 % during the first 5 hours and remains stable at  $236 \pm 6$  m<sup>2</sup>/g thereafter. In wet air a similar decrease is observed during the first hour down to  $224 \pm 19$  m<sup>2</sup>/g. No direct relationship exists between the anatase crystallite size and the surface area. There is a small decrease in surface area but no transformation of anatase to rutile which would not be expected since the transformation temperature of anatase is around 700 °C. We have not found any data for sintering of our material at 450 °C.

**Table 1. Effect of calcination time on the surface area and the anatase crystallite size of the 50/50 mol. % TiO<sub>2</sub>/SiO<sub>2</sub> support calcined at 450 °C**

| Time (hours) | S <sub>BET</sub> (m <sup>2</sup> /g) |     | Anatase crystallite size (nm) |     |
|--------------|--------------------------------------|-----|-------------------------------|-----|
|              | dry                                  | wet | dry                           | wet |
| 0            | 267                                  | 267 | 3.9                           | 3.9 |
| 1            | 266                                  | 239 | 4.2                           | 4.4 |
| 5            | 240                                  | 233 | 3.9                           | 4.2 |
| 15           | 229                                  | 219 | 3.5                           | 4.0 |
| 20           | 243                                  | 189 | 4.2                           | 4.3 |
| 40           | 232                                  | 240 | 4.2                           | 4.2 |

Nakabayashi et al. [14] characterized binary oxides, composed of TiO<sub>2</sub> and SiO<sub>2</sub> where the Ti/Si ratio was one. They prepared two materials. The first one was done by hydrolysis of mixtures of titania propoxide and silica ethoxide with water at 80 °C and the second by physical mixture of TiO<sub>2</sub> and SiO<sub>2</sub> prepared by hydrolysis separately. The mixed oxide showed small and broad peaks of anatase first at 600 °C. No rutile was observed even at 800 °C. The physical mixture showed peaks of anatase already at 400 °C. Their crystallite size increased from 8 nm at 400 °C to 27 nm at 600 °C. At 700 °C the formation of rutile was observed.

Thus our material looks much like their physical mixture even if we have shown the presence of small amount of Ti-O-Si bonds [15].

Ko et al. [16] prepared a series of TiO<sub>2</sub>/SiO<sub>2</sub> mixed oxides by a coprecipitation method. After calcination for 2 hours at 500 °C the surface area was 110 m<sup>2</sup>/g for the same composition as ours. Their material did not show the presence of crystallites of anatase. Thus their mixed oxides are chemically mixed to a much larger extent than ours.

There is also a quite new study by Zelenák, et al. [17] on mesoporous silica modified with titania. The material was prepared by the sol-gel process and the thermal stability was investigated from 650 to 1000 °C. This material is composed of a mesoporous silica matrix and small titania particles. The titania was mainly located at the surface of the pore walls. Their highest amount of Ti was 30 wt. % corresponding to 20 mol. % TiO<sub>2</sub>. The material was both microporous and mesoporous with a surface area of 275 m<sup>2</sup>/g and a mesopore and a micropore volume of 0.1 and 0.06 cm<sup>3</sup>/g after 7 hours at 550 °C. We believe that this material is quite similar to our support and they showed that the titania on the pore walls strengthened the material against collapse of the pores at 850 °C. We also believe that the structure of our support is preserved to a large extent in the 10 % vanadia catalysts at least at 600 °C. Our material has a much higher pore volume as presented for vanadia catalysts below.

Baiker [10] determined the size of microcrystals of 50/50 mol. % TiO<sub>2</sub>-SiO<sub>2</sub> to be in the range of 10 to 30 nm after 5 hours at 600 °C. We obtained anatase sizes of around

4 nm after 5 hours at 450 °C. The large difference could be explained by the large gap in temperatures.

Suyama and Kato [18] studied the transformation of anatase to rutile in CVD-TiO<sub>2</sub>/SiO<sub>2</sub> powders between 800 and 1400 °C. For a 24 mol. % TiO<sub>2</sub>/SiO<sub>2</sub> material they observed a stabilizing effect of silica on the titania phase transformation. No rutile was formed until 1000 °C. Temperatures are much higher than the ones we used. The effect existed even for mechanical mixtures of TiO<sub>2</sub> and SiO<sub>2</sub>. Silica stabilizes the surface of the TiO<sub>2</sub> particles and interferes with the contact between the TiO<sub>2</sub> particles necessary for the transformation. This stabilizing effect of silica was observed by us also.

There is also a study of the sintering of titania-silica powders with 7.3 % TiO<sub>2</sub> by Mineham et al. [19]. It was performed at 1075 °C and above and showed a decrease in surface area from 310 to 21 m<sup>2</sup>/g after 100 hours. The conditions are so far from them in our study that no further remarks are made.

As stated before there is very little data on the effect of temperature and time on the sintering of TiO<sub>2</sub>-SiO<sub>2</sub>. Therefore some comparisons to the behaviour of anatase are made. Hébrard et al. [4] studied the decrease of the surface area for pure anatase up till 7 hours. At 575 °C the area decreased from 100 m<sup>2</sup>/g to 18 m<sup>2</sup>/g after 7 hours. This much more than our results at 450 °C. The comparison is thus not fair because of the large difference in temperatures. The surface area, when sintering in air, was 19 m<sup>2</sup>/g after 5 hours. In the presence of water (2666 Pa, 2.7 %) the area was reduced to 10 m<sup>2</sup>/g after 5 hours. This strong effect of the presence of water was not observed by us. Our material is less sensitive to water albeit at 450 °C. A decrease in surface area by 13 % is observed after 5 hours by us while they observed 90 % after 5 hours. The scatter in our data for the support is quite large, much larger than the vanadia catalysts shown below. This is probably caused by that the support was precalcined for 5 hours at 450 °C.

Yoganarasimhan and Rao [13] studied the transformation of anatase to rutile between 200 and 800 °C. They determined the crystallite size of anatase to 15, 23 and 87 nm at 400, 600 and 800 °C. Rutile formation was observed at 600 °C. The amount of rutile increased rapidly to 80 % at 670 °C.

The effect of the calcination time on the surface area was analysed using the kinetic model described by Schlaffer et al. [20]. This model, Power-Law equation (PLE) was originally used to study the kinetics of the ageing of alumina in steam. The model can be described by:

$$\frac{dS}{dt} = -k * S^n$$

Since the surface areas tend to stabilize at longer sintering times the GLPE [21] was also used. Then the following formula was used in the determination of the parameters:

$$\frac{dS}{dt} = -k * (S - S_{eq})^n$$

Figure 1 shows the fit to the experimental data for the support in dry and wet conditions at 450 °C for various reaction orders.

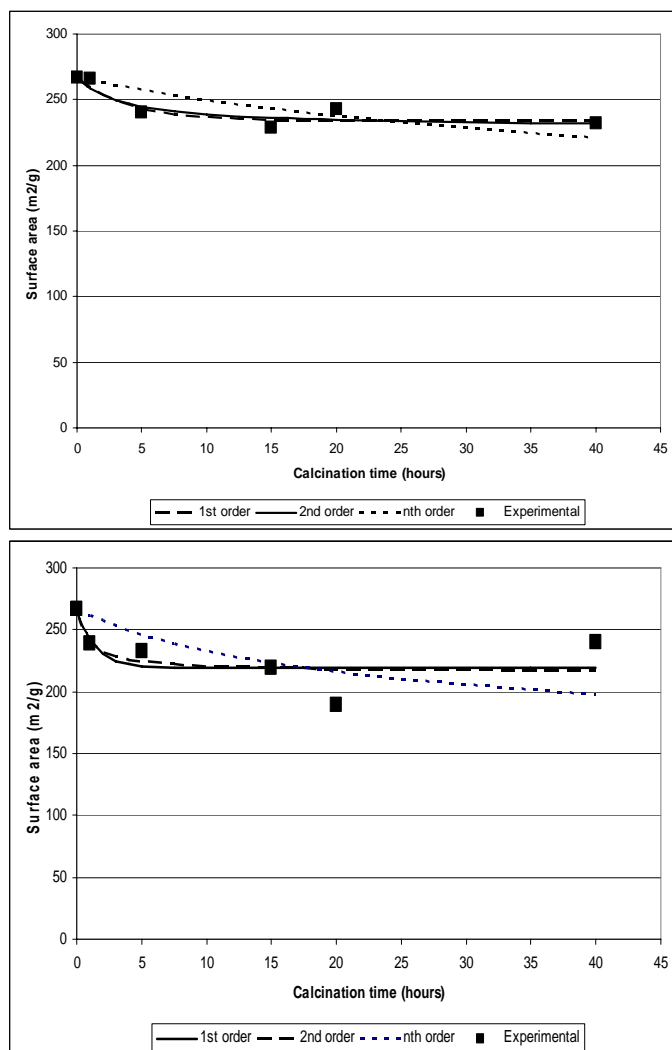


Figure 1. Comparison of experimental data to simulations by model of Fuentes (1<sup>st</sup> and 2<sup>nd</sup>) and Schlaffer (n<sup>th</sup>) in dry and wet conditions at 450 °C

Table 2 shows the result from the determination of the constants by use of the "Scientist" program and a least square regression to the differential equations above. The model that fits data best is the GLPE with first order. This is obvious from both the value of  $r^2$  and the sum of squared deviations. Thus a limiting value for the surface area of the calcined support is expected at long times. With the PLE high a value for the order, about 6, is obtained. For alumina Schlaffer obtained a value of n of 9.1 at 478 °C for silica-alumina. So high values of reaction orders are always obtained with this method.

Table 2. Results from fitting of sintering kinetics to the surface area of the support in dry conditions at 450 °C

| Model                       | GLPE    | GLPE    | PLE      |
|-----------------------------|---------|---------|----------|
| Order                       | 1       | 2       | n        |
| S <sub>eq</sub>             | 234     | 229     |          |
| Sdev                        | 4.1     | 7.5     |          |
| k                           | 0.259   | 0.00729 | 4.60e-15 |
| sdev                        | 0.145   | 0.00754 | 9.23e-14 |
| Sum of squared observations | 3.65E5  | 3.65E5  | 3.65E5   |
| Sum of squared deviations   | 166     | 198     | 663      |
| r <sup>2</sup>              | 0.99955 | 0.99946 | 0.99818  |
| n                           |         |         | 6.04     |
| sdev                        |         |         | 3.58     |

### 3.2 Effect of vanadia loading on the pore structure of the catalyst before calcination

The pore size distribution of the mesopores of catalysts, degassed for 16 hours at 350 °C (standard procedure for the measurements on ASAP 2400), showed that an increased amount of vanadia leads to a decrease in the pore volume and especially of the pores with diameters below 200 Å. The pore volume in this region decreases by about one third when the vanadia content is increased from 10 to 30 %. The average pore diameter is about 13 nm for all catalysts after degassing at 350 °C. The surface area and the pore volume are decreased in parallel as shown in Table 3.

The pore volume of the 10 % catalyst is 0.680 cm<sup>3</sup>/g. When 10 % extra vanadia is introduced a calculated loss of pore volume of 0.030 cm<sup>3</sup>/g is obtained if the density of solid vanadia [22] is used. If the porosity of the vanadia layer is 0.5 the loss in pore volume should be 0.060 cm<sup>3</sup>/g. The experimental value is 0.051 for the 20 % catalyst. Thus the correspondence is reasonable. For the 30 % catalyst the calculated values are 0.060 and 0.120 respectively while the experimental value is 0.246. Thus a blocking off of some of the smaller pores could explain the large decrease for this catalyst.

### 3.3 Thermal stability of the vanadia catalysts calcined for 5 hours in dry air

Table 3 shows the results for the catalysts containing 10 to 30 % vanadia calcined in dry air at respective temperature for five hours. The support has a surface area of 227 m<sup>2</sup>/g after calcination at 450 °C. After impregnation the calcined surface areas (Flowsorb) are 184, 176 and 143 m<sup>2</sup>/g for 10 to 30 % vanadia. The calcination for 5 hours at 500 °C and above caused a decrease in surface area for all samples except for a 10 % catalyst for which it increased by 15 %.

It is obvious that the surface area decreases with an increased amount of vanadia on the catalyst at all temperatures. It is also clear that the decrease is largest from 550 to 600 °C. There is also a large effect on the crystallite size of the anatase phase. The catalyst with 10 % vanadia increases its anatase size from 4 to 18 nm between 350 and 600 °C. The 30 % increases from 4 to 29 nm in the same range. This change is

not reflected in a corresponding change in surface area. It should be pointed out that the uncertainty in the crystallite size determinations has been determined to be 24 % which means that the observed change is significant.

At 20 % vanadia crystalline vanadia is present at 600 °C. At 30 % vanadia all samples calcined at or above 500 °C contain crystalline V<sub>2</sub>O<sub>5</sub>. The sizes of the vanadia crystalline domains vary with temperature in an irregular manner. The measurements using the ASAP 2400 yields surface areas about 7 to 12 % larger than the Flowsorb. This is as expected since the degassing procedure is more thorough on the ASAP.

**Table 3. Effect of calcination temperature in dry conditions on the surface area and the crystallite size of vanadia and titania in catalysts with 10, 20 and 30 % vanadia treated for 5 hours**

| Vanadia content (%) | Temperature (°C) | S <sub>BET</sub> ASAP 2400 (m <sup>2</sup> /g) | Average pore diameter (nm) | V <sub>pore</sub> <sup>2</sup> (cm <sup>3</sup> /g) | S <sub>BET</sub> Flowsorb (m <sup>2</sup> /g) | V <sub>2</sub> O <sub>5</sub> size (nm) | Anatase size (nm) |
|---------------------|------------------|--|----------------------------|---|---|---|-------------------|
| 10                  | 350 <sup>1</sup> | 208  | 13.2                       | 0.680   | 184   |   | 4.1               |
| 10                  | 500              |  |                            |   | 212   |   | 5.5               |
| 10                  | 550              |  |                            |   | 173   |   | 11.7              |
| 10                  | 600              |  |                            |   | 144   |   | 17.8              |
| 20                  | 350 <sup>1</sup> | 191  | 13.0                       | 0.629   | 176   |   | 4.4               |
| 20                  | 500              |  |                            |   | 145   |   | 7.5               |
| 20                  | 550              |  |                            |   | 137   |   | 12.1              |
| 20                  | 600              |  |                            |   | 113   | 28.3                                    | 21.8              |
| 30                  | 350 <sup>1</sup> | 139  | 12.4                       | 0.434   | 143   |   | 4.2               |
| 30                  | 500              |  |                            |   | 96  | 12.0                                    | 20.2              |
| 30                  | 550              |  |                            |   | 58  | 23.4                                    | 25.8              |
| 30                  | 600              |  |                            |   | 38  | 15.8                                    | 28.5              |

<sup>1</sup> The samples where the temperature 350 °C is given were only degassed at 16 hours before nitrogen adsorption measurements

<sup>2</sup> Pore volume of pores with diameters between 1.7 and 300 nm

When vanadia was added to the support the surface area decreased from 227 to 184, 176 and 143 m<sup>2</sup>/g for 10, 20 and 30 % vanadia measured after degassing at 350 °C for 16 hours. If the vanadia was deposited as a monolayer this would cover 30, 60 and 90 % of the surface area of the support.

A comparison can be made to the data of Baiker et al. [10] for their monolayer vanadia on 50/50 mol. % TiO<sub>2</sub>/SiO<sub>2</sub> catalyst. After 5 hours at 600 °C they determined the surface area to around 100 m<sup>2</sup>/g compared to 128 m<sup>2</sup>/g in our investigation for the 10 % catalyst. The content of vanadia is not given by them, it is only stated that the catalyst is monolayer. Thus no crystallinity of the vanadia is reported by them. The



presence of crystalline anatase was observed in materials with 20 or higher amount of TiO<sub>2</sub>. The 50 % material is quite crystalline as is ours.

Saleh et al. [23] describe the calcination of 7 % vanadia on titania. The surface area was about 9.5 m<sup>2</sup>/g decreasing by 36 % to 6.1 m<sup>2</sup>/g at 570 °C after 2 h. Our decrease after 5 h is 6 % at 550 °C and 22 % at 600 °C. They report that there is no formation of crystalline vanadia as long as the support is not covered completely.

The XRD studies reported here show that all samples except the 30 % one calcined for five hours at 500 °C contain only amorphous vanadia. At 550 °C the 10 and 20 % catalysts were amorphous but the 30 % contained crystalline phases. At 600 °C both 20 and 30 % catalysts contained crystalline V<sub>2</sub>O<sub>5</sub>. A calculation of the monolayer coverage using the lower area after the sintering showed that all samples which show XRD crystallinity contained vanadia in amounts exceeding one monolayer. This is in agreement with results of Saleh et al.

Madia et al. [3] studied the thermal stability of vanadia-tungsta-titania SCR catalysts. The vanadia loading was 1, 2 or 3 % only. The ageing procedure was 1) 100 h at 550 °C, 2) 100 h 550 °C + 30 h 600 °C and 3) 100 h 550 °C + 30 h 600 °C + 15 h 650 °C. The support had a surface area of 85 m<sup>2</sup>/g before ageing and decreased to 63 m<sup>2</sup>/g after ageing 3. 1 and 2 % vanadia catalysts behaved similarly. The 3 % one aged much more rapidly though. Its fresh area was 73 m<sup>2</sup>/g and decreased to 14 m<sup>2</sup>/g after ageing 3. The crystallite sizes increased from 18 nm for the fresh material via 23 and 27 to 55 nm after ageing 1 to 3. Our material had an anatase size of only 18 nm after 5 h at 600 °C (ageing 2). The difference is probably caused by the much shorter time in our experiment.

Our catalysts, first calcined at 500 °C for five hours, were calcined further for up to 46 hours at 600 and 650 °C. The results (Flowsorb) are collected in Table 4. Again we observe a rapid decrease in surface area during the first few hours of calcination and sometimes stabilization after about 20 hours. An increased amount of vanadia on the catalyst increases the rate of sintering of the catalyst. A 10 % catalyst loses about 50 % of its surface area in 46 hours at 600 °C while at 650 °C the loss is 80 %.

**Table 4. Effect of calcination time on the surface area of the catalysts treated in dry conditions at 600 and 650 °C**

| Time (hours) | Surface area calcined at 600 °C (m <sup>2</sup> /g) |                                    |                                    | Surface area calcined at 650 °C (m <sup>2</sup> /g) |                                    |                                    |
|--------------|---|------------------------------------|------------------------------------|---|------------------------------------|------------------------------------|
|              | 10 % V <sub>2</sub> O <sub>5</sub>                  | 20 % V <sub>2</sub> O <sub>5</sub> | 30 % V <sub>2</sub> O <sub>5</sub> | 10 % V <sub>2</sub> O <sub>5</sub>                  | 20 % V <sub>2</sub> O <sub>5</sub> | 30 % V <sub>2</sub> O <sub>5</sub> |
| 0            | 212   | 145                                | 96                                 | 212   | 145                                | 96                                 |
| 1            | 169   | 117                                | 54                                 | 134   | 109                                | 37                                 |
| 5            | 128   | 97                                 | 36                                 | 85  | 54                                 | 16                                 |
| 24           | 95  | 67                                 | 25                                 | 45  | 15                                 | 7                                  |
| 46           | 97  | 57                                 | 26                                 | 34  | 10                                 | 7                                  |

Figure 2 shows the fit to the GLPE model with n=2 at 600 and 650 °C. The fit is quite good for all experiments ( $r^2 > 0.997$ ).

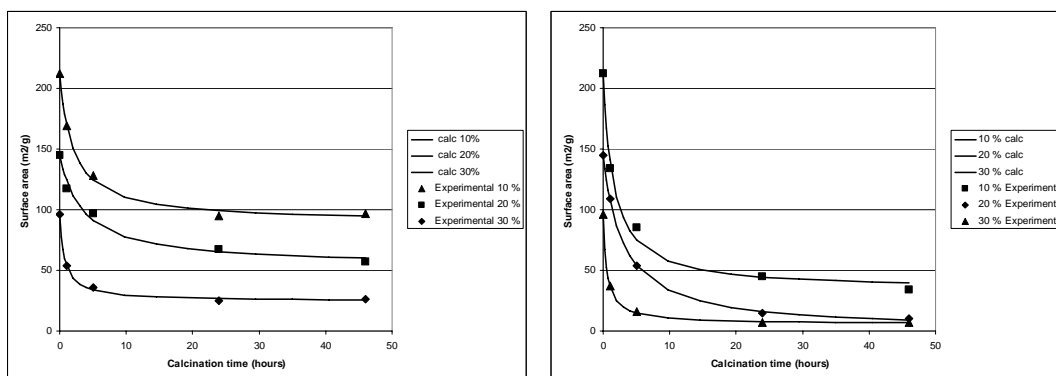


Figure 2. Comparison between calculated and experimental values of the surface area of catalysts calcined at 600 (left) and 650 (right) °C

**Table 5. Results from the fitting of sintering data using the GLPE model with n=2 in dry conditions**

| Temperature     | 600 °C  |         |         | 650 °C  |         |         |
|-----------------|---------|---------|---------|---------|---------|---------|
| Vanadia content | 10 %    | 20 %    | 30 %    | 10 %    | 20 %    | 30 %    |
| k               | 0.00410 | 0.00314 | 0.0191  | 0.00376 | 0.00232 | 0.0207  |
| sdev            | 0.00059 | 0.00109 | 0.0023  | 0.00081 | 0.00005 | 0.0012  |
| $S_{eq}$        | 89.7    | 53.8    | 24.6    | 34.1    | 0.157   | 5.96    |
| sdev            | 3.1     | 6.1     | 1.2     | 6.3     | 0.176   | 0.67    |
| $R^2$           | 0.99965 | 0.99798 | 0.99940 | 0.99759 | 0.99993 | 0.99975 |

The results show that the equilibrium surface area is strongly and systematically (except for the value for the 20 % catalyst at 650 °C) decreasing with increased vanadia content and with an increased temperature. At 650 °C a total collapse of the pore system is predicted for the 20 % catalysts. This value is not realistic; a finite surface area would be expected.

The textural properties was investigated by adsorption/desorption studies of nitrogen with ASAP 2400. Figure 3 shows results from measurement of the pore volume at 600 °C. It is clear that the decrease in pore volume, presented as  $v_{cum}$ , is considerable and is increasing with time, temperature and vanadia content. The pore volumes after 1 hour are 0.67, 0.68 and 0.39 cm<sup>3</sup>/g for 10, 20 and 30 % vanadia catalysts. At 600 °C there is a decrease of the pore volume with 30, 46 and 58 % after 46 hours.

For the 10 % catalyst almost all pores has diameters below 200 Å.

The 20 % on the other hand has a much larger portion of pores larger than 200 Å. When the vanadia content is 30 % there is a larger amount of pores below 400 Å already after 1 hour. As the time is increased the volume is decreased and the size is shifted towards larger diameters. There is an unexpected effect after 46 hours where the volume is increased compared to the value at 24 hours. The size of most of the pores is larger than 600 Å though.

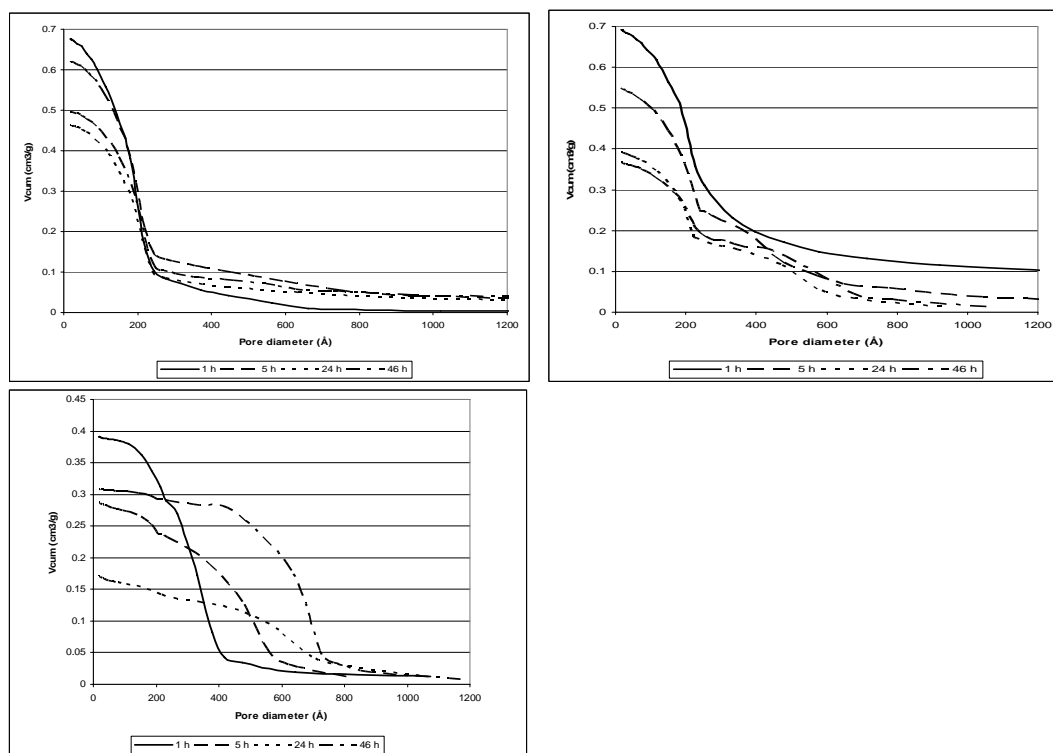


Figure 3. Changes in pore volume structure during calcination at 600 °C in dry conditions for 10, 20 and 30 % catalysts

The textural structure studies of the monolayer catalysts of Baiker et al. [10] showed that they had a pore volume of only 0.2 cm<sup>3</sup>/g after calcination at 600 °C for 5 hours. Ours was over 0.6 cm<sup>3</sup>/g at the same time for the 10 % catalyst.

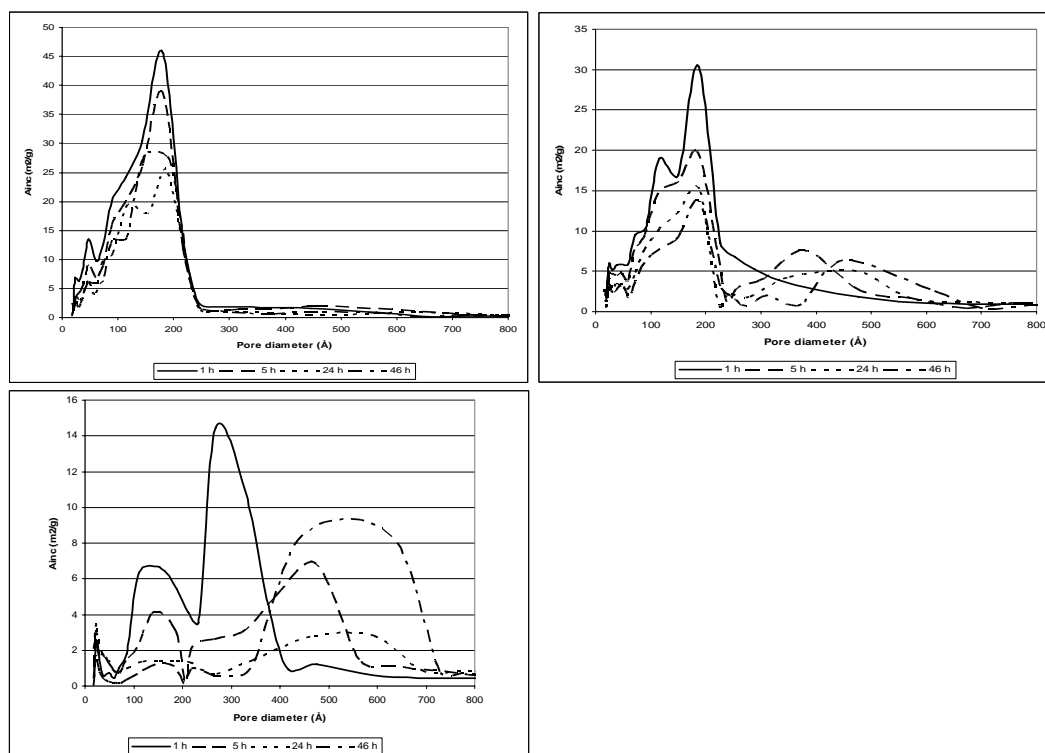


Figure 4. Changes in pore area distribution during calcination at 600 °C in dry conditions for 10, 20 and 30 % catalysts

The incremental pore area distribution,  $A_{inc}$ , shows that the area is present in smaller pores in catalysts with low vanadia contents and in larger ones at high contents (Figure 4). The 10 % catalyst has one major peak at 200 Å with a shoulder at 100 Å at 1 hour. As time is increased the area is decreases but the size remains the same. The 20 % catalyst on the other hand shows 2 clear peaks at 100 and 200 Å. The largest peak, after 1 hour, is again at 200 Å. The area is shifting to larger pores with time and after 46 hours 3 peaks at 100, 200 and 460 Å are observed. The areas of the low diameter ones and the high one are about the same.

The 30 % catalyst has 3 peaks already after 1 hour, at 150, 300 and 460 Å. The one at 300 Å is the largest. After 46 hours the area in small pores has almost completely disappeared while there is a major fraction of the area in a range of pore sizes from 350 to 750 Å. The maximum of the distribution is at 560 Å.

Baiker et al. [10] showed the most frequent pore radius to be 1.8 nm while ours was 10 nm for the 10 % vanadia catalyst.

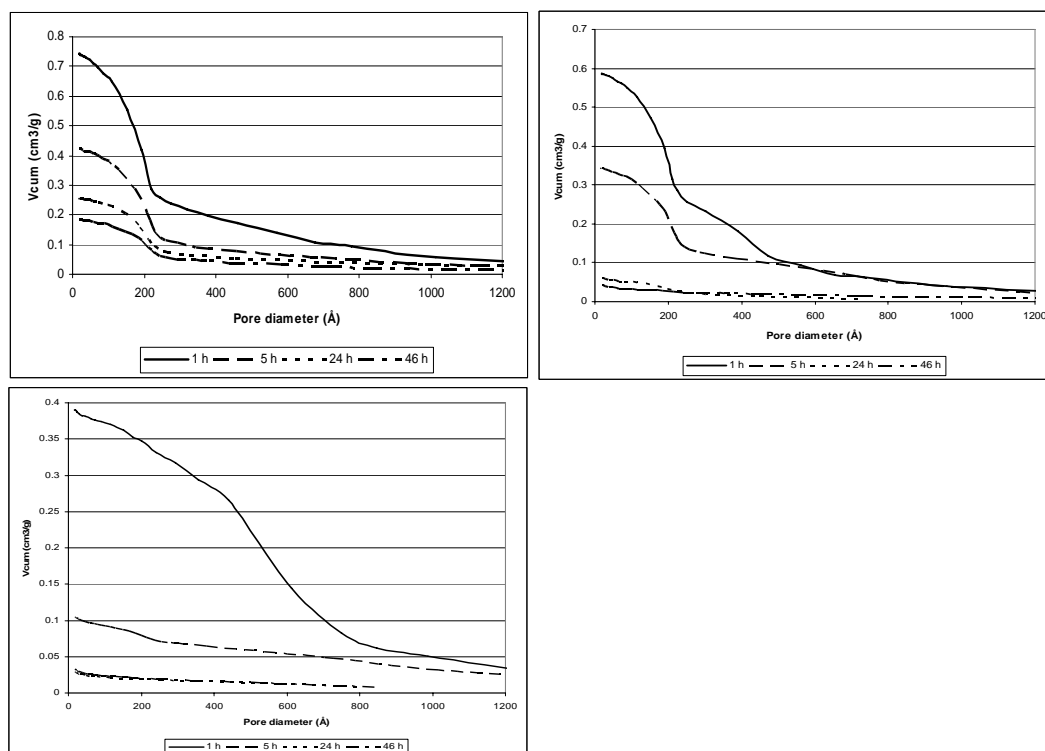


Figure 5. Changes in pore volume distribution during calcination at 650 °C in dry conditions for 10, 20 and 30 % catalysts

At 650 °C the changes are more drastic (Figure 5). After 1 hour the cumulative pore volumes are 0.74, 0.58 and 0.39 cm<sup>3</sup>/g for 10 to 30 % catalysts. There is a very rapid decrease in pore volume with time being 0.18, 0.05 and 0.03 cm<sup>3</sup>/g at 46 hours.

The 10 % catalyst does not change the size of the pores much and has about half its pores below 200 Å at all calcination times.

When the vanadia content is increased to 20 % the pore volume is shifting to larger pore sizes. About half of the pore volume is above 250 Å and 1/6 above 500 Å for 1 and 5 hours. At higher times the decrease in pore volume is so large that it is hard to see if the shift to larger pores continues.

The 30 % material loses about 75 % of its pore volume between 1 and 5 hours. At 1 hour half of its pores are larger than 550 Å. After 5 hours half of the pore volume is in pores larger than 700 Å. After 24 and 46 hours the material has lost 90 % of its pore volume.

Thus there is a general trend of increasing pore sizes with temperature and vanadia content. The use of these catalysts at 600 and especially 650 °C cannot be recommended.

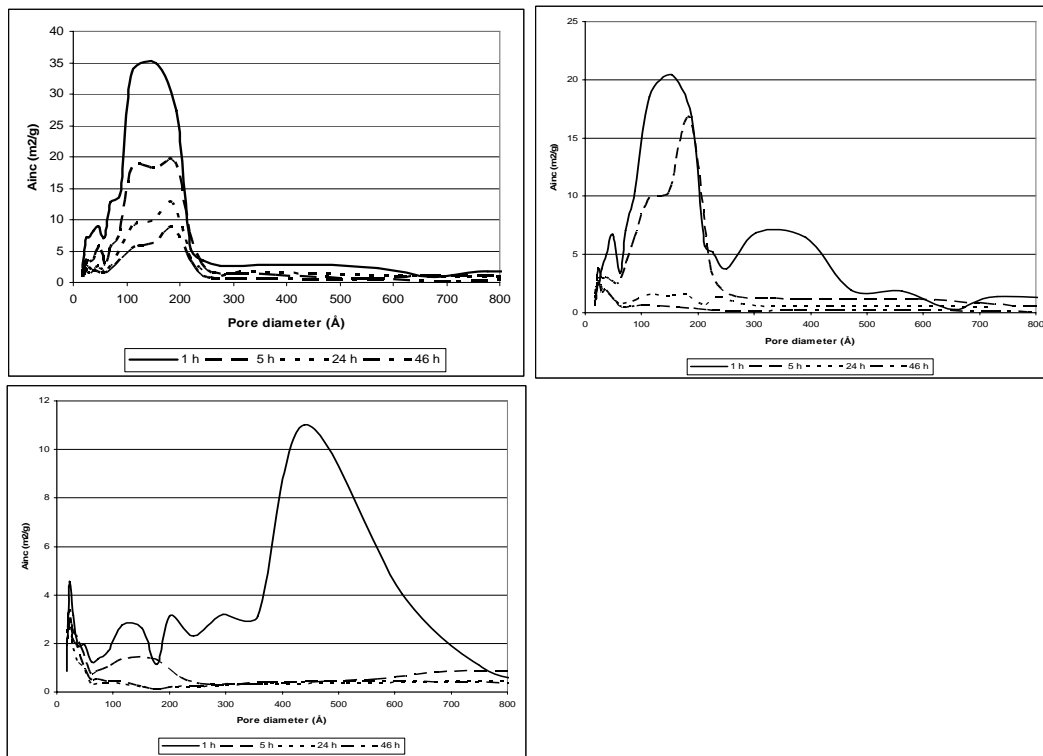


Figure 6. Changes in pore area distribution during calcination at 650 °C in dry conditions for 10, 20 and 30 % catalysts

The pore area distributions show that the 10 % catalyst has a pore system with a maximum in the distribution at around 180 Å. This structure is retained during the course of calcination even if the magnitude of the surface area decreases. For the 20 % catalyst there is more of a bidisperse area pore size distribution after 1 hour of calcination (Figure 6). The pore size of the most common pores is the same but a new peak appears at 350 Å. As time increases the incremental pore area decreases rapidly and the peak at 350 Å disappears. At 30 % vanadia the effect is even more pronounced. Now there are five peaks at 20, 140, 210, 300 and 470 Å after 1 hour. The peak at 20 Å is probably present in the other two materials as well but appears clearly in the 30 % material because the other peaks have become so small. Now the peak at the largest pore size is the dominant one. There is also a tendency of shifting the largest peak to larger sizes with increasing calcination time (not so clearly visible in Figure 6).

According to Schaper [24] it is possible to determine the activation energy for the sintering of a metal oxide by using the formula:

$$\left( \frac{S_0 - S_t}{S_0} \right)^\gamma = \beta * \frac{\exp\left(\frac{-E_a}{R * T}\right)}{T} * t$$

In this work we have determined  $\gamma$  to 3. Figure 7 shows the results for the different catalysts sintered in dry conditions. The activation energies determined were 220, 139

and 157 kJ/mol for 10, 20 and 30 %  $V_2O_5$ . This trend of decreasing values shows the catalytic effect of vanadia on the sintering of anatase in the support. The value for 10 % vanadia was determined from the surface areas from the two highest temperatures only since the  $S_0$  value of this material, shown in Table 2 as the value at 350 °C, is lower than the value at 500 °C. Again the 20 % catalyst does not follow the general trend. The same is true for the decrease in surface area as shown in Figure 3.

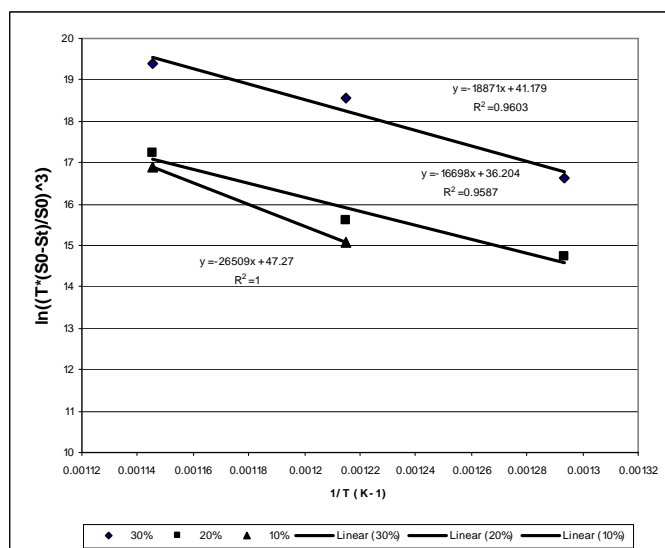


Figure 7. Determination of activation energies for calcination in dry conditions for 10, 20 and 30 % vanadia catalysts at temperatures between 500 and 600 °C

### 3.4 Effect of calcination time on the changes in crystalline structure as determined by XRD after treatment at 650 °C

If the catalyst, during short periods of time, experiences unusually high temperatures it is important to know if that destroys it completely. Therefore studies at 650 °C were performed for up to 46 hours. The XRD analysis (Table 6) showed that the rate of transformation of anatase to rutile was much larger at 650 than at 600 °C. After 24 hours only 11 % rutile was formed at 600 °C while 79 % was formed at 650 °C for the 30 % vanadia catalyst.

**Table 6. Crystallite sizes of phases detected by XRD after calcination at 650 °C in dry conditions**

| Size of anatase domain (nm) at vanadia content (%)         |       |       |       |
|--|-------|-------|-------|
| Time (hours)   | 10    | 20    | 30    |
| 0  | 5.5   | 7.5   | 20.2  |
| 1  | 17.7  | 26.0  | 47.4  |
| 5  | 26.0  | 34.9  | 66.0  |
| 24   | 23.1  | 39.4  | 86.9  |
| 46   | 43.7  | 68.5  | 51.9  |
| Size of rutile domain (nm) at vanadia content (%)          |       |       |       |
| Time (hours)   | 10    | 20    | 30    |
| 0  | nd    | nd    | nd    |
| 1  | nd    | 18.7  | Nd    |
| 5  | 55.0  | 59.9  | 66.3  |
| 24   | 41.6  | 41.6  | 66.3  |
| 46   | 71.7  | 68.8  | 78.4  |
| Size of vanadia domain (nm) at vanadia content (%)         |       |       |       |
| Time (hours)   | 10    | 20    | 30    |
| 0  | nd    | nd    | 12.0  |
| 1  | 40.3  | 35.6  | 30.9  |
| 5  | nd    | nd    | 40.3  |
| 24   | 29.1  | 45.1  | 52.8  |
| 46   | 26.3  | 40.3  | 63.1  |
| Rutile fraction of TiO <sub>2</sub> at vanadia content (%) |       |       |       |
| Time (hours)   | 10    | 20    | 30    |
| 0  | 0.000 | 0.000 | 0.000 |
| 1  | 0.000 | 0.036 | 0.000 |
| 5  | 0.362 | 0.348 | 0.470 |
| 24   | 0.615 | 0.659 | 0.791 |
| 46   | 0.645 | 0.629 | 0.742 |

nd= No peak found

The results at 650 °C (Table 6) show that the anatase phase is present in all samples. Its size increases with an increased sintering time and with an increased vanadia content. No rutile is present before calcination at 650 °C at any vanadia content. The onset of the transformation of the anatase to rutile is faster for the 20 % catalyst than for the other ones. Rutile is always observed already after 1 hour for this catalyst but only after 5 hours for the other ones. The final rutile fraction seems to be 0.67 with a standard deviation of 0.06 independent of the vanadia content.

Our 10 % catalyst is just exceeding the monolayer capacity after 5 hours at 600 °C. At 650 °C the same is true already after 1 hour. This is why we observe vanadia crystallites by XRD at this early time.

The presence of other phases of the material can also be compared to the results of Baiker et al. [10]. Our findings of an amorphous silica phase and a crystalline anatase phase are observed by them also.

Madia et al. [3] calcined their 3 % catalyst based on tungsta-titania for 15 h at 650 °C and found an anatase size of 55 nm. Our results, for a 10 % catalyst, show after 24 h a size of 23 nm. The sintering is increased by the presence of vanadia so our smaller size must mean that our titania-silica supported catalyst is more stable to sintering than theirs. We also observed crystallites of vanadia with a size of 29 nm. They do not have any crystalline vanadia because of the low content of V<sub>2</sub>O<sub>5</sub>.



Bond and Sárkány [25] early discovered the enhancing effect of vanadia on the sintering of anatase.

### 3.5 Calcination of 20 % $V_2O_5/SiO_2-TiO_2$ in 2 % water vapour at 450 °C

In order to simulate the effects of thermal degradation under diesel exhaust conditions a sintering study was performed, in water vapour, at 450 °C. This is about the maximal useful mean temperature for a SCR catalyst of the vanadia type. The results of the growth in crystallite size during sintering for up to 333 hours are shown in Figure 8. Both the anatase phase and the  $V_2O_5$  phase increase in size with sintering time. The anatase crystallites are around 21 nm in the unsintered material increasing to about 47 nm in the most sintered material. The increase follows a logarithmic time. There also exists a linear relationship between the BET surface area and the crystallite size of anatase.

The size of the  $V_2O_5$  crystallites is around 25 nm in the unsintered material, but they increase more rapidly in size with time. There seems to be a limit of about 100 nm for the size of the  $V_2O_5$  crystallites even if the scatter in data is large at longer sintering times and for some samples. A trend of decreasing size of the vanadia crystallites is observed after 100 to 150 hours.

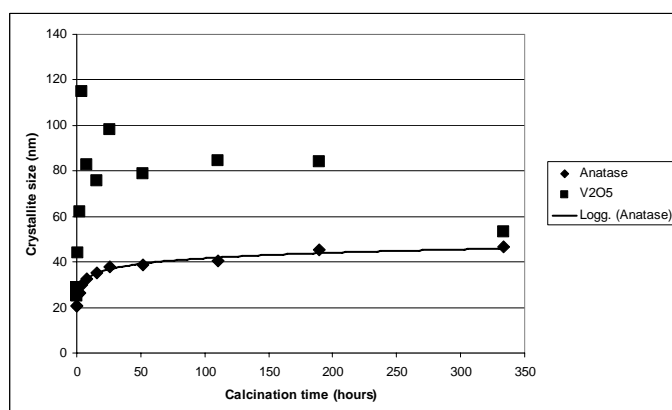


Figure 8. Effect of calcination time on the crystallite sizes of anatase and vanadium pentoxide as determined by XRD for 20 %  $V_2O_5/SiO_2-TiO_2$  in wet conditions.

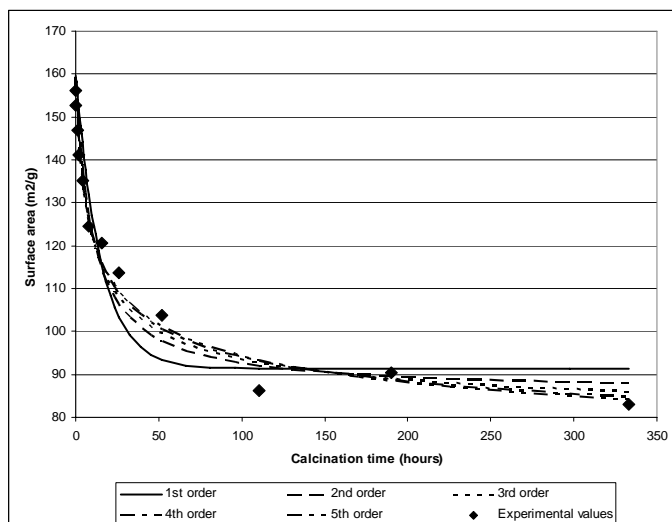


Figure 9. Effect of calcination time on a 20 %  $V_2O_5/SiO_2-TiO_2$  catalyst at 450 °C in wet conditions

The surface area is rapidly decreasing from about 160 to 100  $m^2/g$  after 52 hours. A further much slower decrease is observed up till 333 hours. The data would suggest a limiting value of the surface area after some time. A fit to the model of Fuentes is shown in Table 7. It is obvious that the higher the reaction order the better is the fit. A higher order also yields a lower equilibrium surface area. A fit to the PLE is also shown. For this model the 95 % confidence range for the rate constant contains negative values, which should exclude this model.

**Table 7. Results from fitting of the surface areas of a 20 % catalyst calcined at 450 °C in wet conditions**

| Reaction order          | 1       | 2       | 3        | 4        | 5        | n         |
|-------------------------|---------|---------|----------|----------|----------|-----------|
| k                       | 6.70e-2 | 1.37e-3 | 1.71E-05 | 1.46E-07 | 1.01E-09 | 1.57e-16  |
| 95% Range (Univariate): | 3.2e-2  | 6.0e-4  | 6.70E-06 | 4.37E-08 | 2.28E-10 | -8.40E-16 |
|                         | 10.2e-2 | 2.1e-3  | 2.75E-05 | 2.49E-07 | 1.79E-09 | 1.15E-15  |
| Seq                     | 91.3    | 86.0    | 76.8     | 65.9     | 54.9     |           |
| 95% Range (Univariate): | 81.5    | 77.7    | 68.5     | 56.7     | 44.7     |           |
|                         | 101.1   | 94.3    | 85.0     | 75.1     | 65.0     |           |
| $r^2$                   | 0.99608 | 0.99817 | 0.99883  | 0.99909  | 0.99922  | 0.99859   |
| n                       |         |         |          |          |          | 7.62      |
| 95% Range (Univariate): |         |         |          |          |          | 6.29      |
|                         |         |         |          |          |          | 8.94      |

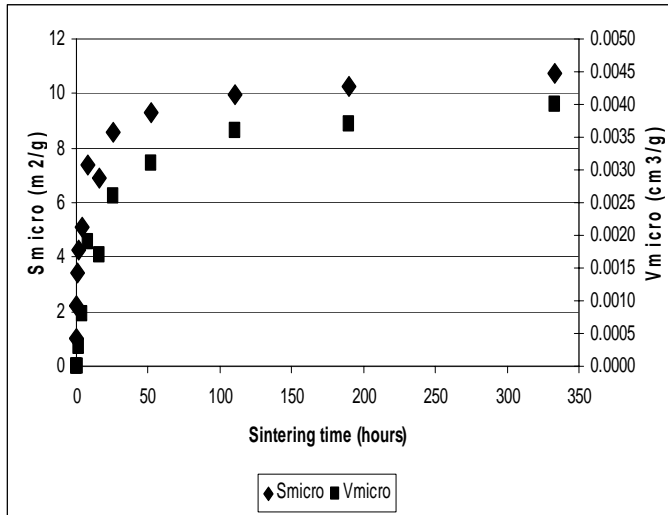


Figure 10. Effect of sintering time on the micropore structure for 20 %  $V_2O_5/SiO_2-TiO_2$  at 450 °C evolved during calcination in wet conditions

Figure 10 shows the effect of calcination time on the microporosity. There is a large increase, about 10 times, in micropore area with increasing sintering time up to 333 hours. A micropore volume is created and its magnitude increases from 0 to 0.004  $cm^3/g$ . The microporosity can be created by partial filling of small mesopores or by direct formation of new pores. It is not possible to draw any conclusions about the mechanism of pore formation from the measurements presented here.

Zelenák et al. [17] observed a micropore volume of 0.06  $cm^3/g$  after 7 h at 550 °C for the material with 30 %  $TiO_2$ . Their material has a higher micropore volume than ours, 0.0019  $cm^3/g$  at 7 h, and this is probably caused by, amongst other things, the difference in preparation methods. Our material had 20 % vanadia on the support and as we demonstrated the vanadia is creating new micropores so the properties could be different for a number of reasons.

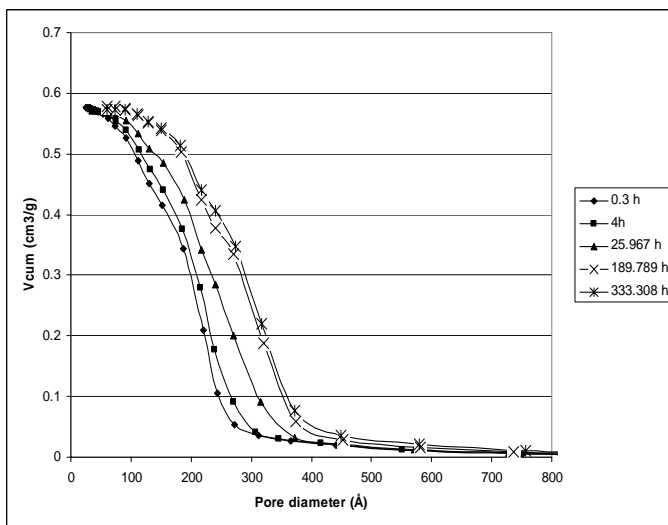


Figure 11. Change in pore volume distribution at various calcination times in wet conditions at 450 °C

The cumulative pore volume (Figure 11) shows that the total pore volume remains constant at about  $0.58 \text{ cm}^3/\text{g}$  in wet conditions for the 20 % catalyst. There is a shift towards larger pore sizes though. The 20 % vanadia catalyst should give a volume of  $0.0595 \text{ cm}^3 \text{ V}_2\text{O}_5$  catalyst for each gram of catalyst. As seen in Figure 11 this amount can only be present in the mesopore structure if the size of the particles is below  $250 \text{ \AA}$  ( $25 \text{ nm}$ ) at 0.3 hours. This is about the size present at this time (Figure 8). After 190 hours the pore volume at  $800 \text{ \AA}$  pore diameter is around 0.01. Thus there is no room for the large vanadia particles shown in Figure 8 inside the mesoporous structure. So what must happen is that during the sintering vanadia is transported towards the catalyst particle outer surface and accumulates in the macropores, the volume of which has been showed to be  $0.08 \text{ cm}^3/\text{g}$  for the support [11].

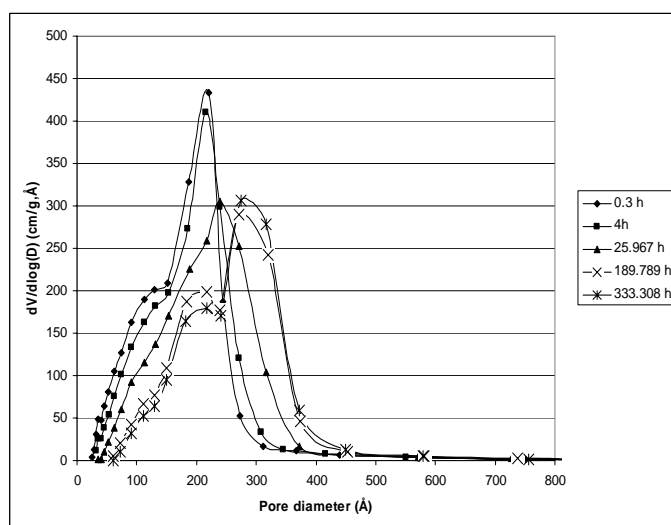


Figure 12. Change in pore volume distribution at various calcination times in wet conditions at  $450 \text{ }^\circ\text{C}$

In Figure 12 the pore volume distribution is shown a various calcination times. At 0.3 hours there are two peaks at  $100$  and  $220 \text{ \AA}$ . As time increases the volume in the low sizes region decreases at the same time as it increases in the large size region. After 33 hours the size of the largest pores has increased to  $330 \text{ \AA}$ .

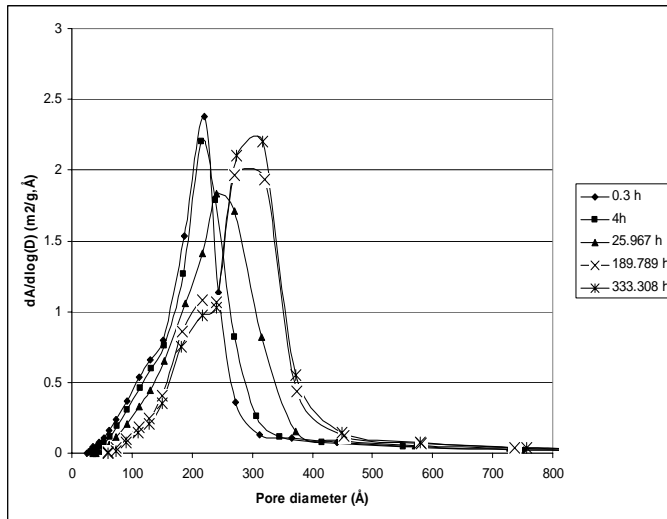


Figure 13. Change in pore area distribution at various calcination times in wet conditions at 450 °C

The surface area distribution (Figure 13) peaks at around 100 Å after 0.3 hours. As the time is increased there is a continuous shift of the maximum towards larger pore diameters. At 333 hours the maximum is at around 330 Å. Simultaneously the total surface area is decreased by about 50 %.

### 3.6 Deactivation studies at Volvo in real diesel exhaust gases

In Figure 14 is shown the results from sintering in a motor rig at Volvo Truck Corporation for a 5.6 %  $V_2O_5/TiO_2$  catalyst on a monolith. The test driving has been performed under conditions which would simulate normal driving for at least 500 000 km with a heavy duty truck. The cordierite monolith has a surface area of only 0.49  $m^2/g$ . When the active material is applied and after 2 hours of calcination at 500 °C the area is 13.6  $m^2/g$ . When it is deactivated the area drops to 7.7 and 6.9  $m^2/g$  after 890 and 2299 hours. The decrease is as shown before faster at short times and seems to level off at longer times.

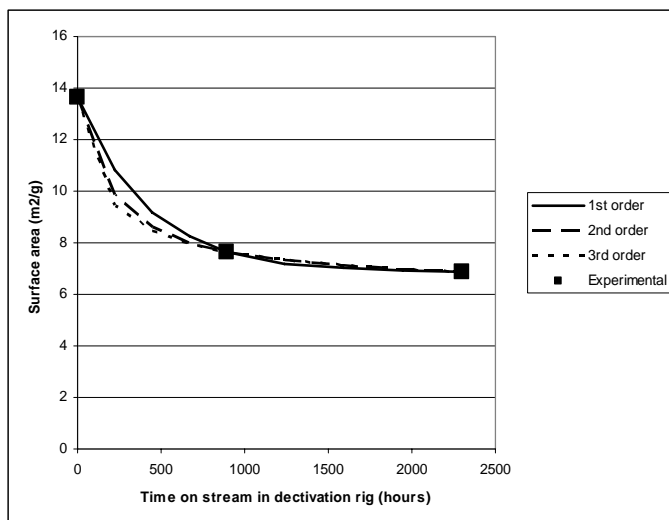


Figure 14. Effect of time on stream in the deactivation rig of the 5.6 %  $V_2O_5/TiO_2$  monolithic catalyst

Since there are so few data it is not very easy to say which reaction order fits the data best. From the figure one can conclude that data from around 300 hours have been very useful in separating the models. Table 7 gives the result from the fitting.

**Table 7. Results from fitting the data from deactivation at Volvo to the model of Fuentes**

| Reaction order | 1        | 2        | 3        |
|----------------|----------|----------|----------|
| k              | 0.002372 | 0.000644 | 0.00011  |
| sdev           | 9.91e-7  | 7.64e-7  | 2.21e-7  |
| k/sdev         | 0.0004   | 0.0012   | 0.0020   |
| $S_{eq}$       | 6.8457   | 6.2562   | 5.4895   |
| sdev           | 0.000548 | 0.001091 | 0.001743 |
| $S_{eq}/sdev$  | 0.0001   | 0.0002   | 0.0003   |
| $r^2$          | 1        | 1        | 1        |

Table 7 shows that the best fit is obtained using a 1<sup>st</sup> order equation. All have a  $r^2$  equal to one but the 1<sup>st</sup> order model has the lowest value for parameters divided by their standard deviation (sdev). An  $r^2$  of 1 is expected when two parameters, k and  $S_{eq}$  are determined from only 3 data point one of which is the starting value at zero time in the fit of the differential equation. The  $S_{eq}$  value of 6.85 is almost the same as the experimental value at 2299 hours which is 6.87. A further decrease in surface area would be expected for longer times so higher orders than 1 are more likely. It is clear that more data are needed to make a firm conclusion of the effect of longer times on stream. The experimental data show that there is only a small decrease in surface area between 890 and 2299 hours and the model which predicts a higher equilibrium surface is always the one with the lowest order.

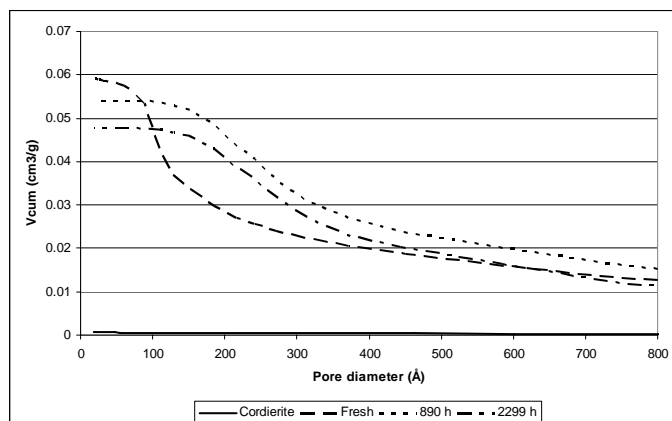


Figure 15. Cumulative pore volume at various time of stream in deactivation test at Volvo

The cordierite has a very small,  $0.3 \text{ m}^2/\text{g}$ , BET surface area and pore volume,  $0.001 \text{ cm}^3/\text{g}$ . When vanadia/titania is added the surface area increases to  $13.6$  and the pore volume to  $0.059$ . These values are still low in comparison to normal catalysts but it should be remembered that the amount of washcoat is  $18 \%$  only. Thus the values are quite reasonable.

As an effect of thermal deactivation the pore volume is decreasing continuously with time to  $0.037 \text{ cm}^3/\text{g}$  after  $2299 \text{ h}$  (Figure 15). The size of the pores is also changing being larger at longer times. In the fresh catalyst  $50 \%$  of the pores are less than  $180 \text{ \AA}$  in diameter. After  $2299 \text{ h}$   $50 \%$  are smaller than  $500 \text{ \AA}$ . The change in size distribution is largest between the fresh condition and the condition after  $890 \text{ h}$  of use.

### 3.7. Comparison of reduction of surface area in different conditions

It is interesting to compare surface area prediction during different conditions for the materials studied. The data given in Table 8 are based on fitting the data to the model of Fuentes with  $n=2$ . It is clear that the catalyst used at Volvo is the most stable one when it comes to loss of surface area during the first hours on stream. The model predicts a reduction of its surface area by  $54 \%$  at equilibrium though. This is more than for the treatment of the support at  $450 \text{ }^\circ\text{C}$ . The higher temperature in the deactivation rig and the content of vanadia does explain this difference. The consequence of calcination in wet conditions is a faster reduction in area in the beginning but just a small difference at equilibrium. Next in stability comes the  $20 \%$  catalyst in wet conditions at  $450 \text{ }^\circ\text{C}$ . It reaches the  $30 \%$  reduction after  $18 \text{ h}$  and  $46 \%$  at equilibrium. This catalyst contains about  $3$  times the amount of vanadia of the Volvo one. This will cause a large acceleration in sintering which was also observed. Finally the  $10 \%$  catalysts, with a composition not so far from the Volvo one, calcined at  $600$  and  $650 \text{ }^\circ\text{C}$  show a very severe surface area reduction. It is reduced by  $58$  and  $84 \%$  at  $600$  and  $650 \text{ }^\circ\text{C}$  at equilibrium respectively. These high temperatures, even if the conditions are dry, lead to a very rapid sintering. Thus one has to avoid these temperatures or to introduce a stabilising agent in the catalyst.

Table 8. Comparison of sintering behaviour for different materials and conditions

| Catalyst/conditions  | Time for 10 % reduction (hours) | Time for 30 % reduction (hours) | $S_{eq}/S_0$ |
|----------------------|---------------------------------|---------------------------------|--------------|
| Volvo catalyst       | 100                             | 200                             | 0.46         |
| Support / 450 °C dry | 6                               | -                               | 0.86         |
| Support / 450 °C wet | 2                               | -                               | 0.81         |
| 20 % / 450 °C wet    | 2                               | 18                              | 0.54         |
| 10 % / 600 °C dry    | 0.6                             | 2.3                             | 0.42         |
| 10 % / 650 °C dry    | 0.4                             | 0.9                             | 0.16         |

#### 4. Conclusions

It has been shown that there is a large effect of the content of vanadia on the sintering of the catalyst. Higher amounts accelerate the sintering. This is also observed as a lowering of the activation energy of the process. It has also been shown that temperatures at or above 600 °C should be avoided by any means since they cause rapid and severe surface area losses. The sintering of our 20 % catalyst at 450 °C in wet conditions is much more severe than that used at Volvo. This is so even if the temperatures in the deactivation rig are higher. This is probably caused by the 3 times higher loading of vanadia.

Pore size distributions show that the size of pore increase as the surface area decreases. This holds for all materials investigated. Some materials showed creation of very large mesopores the distribution of which could be bi or tridisperse. It is possible to use the model of Fuentes to simulate the decrease in surface area with time for all materials. It has been shown though that in some cases there is need for more experimental data. The use of the simpler model of Schlaffer has not been so successful.

XRD showed the model catalysts to be composed of an amorphous silica phase and an anatase phase. The appearance of crystalline phases of vanadia is observed at 500 °C and above in dry conditions depending of the vanadia content. Rutile is formed after 5 hours at 650 °C. XRD crystallite size determinations have shown the expected increase in the size of the anatase regions when the surface area is reduced. For the 20 % catalyst in wet conditions there is a clear linear relationship between BET surface area and the size of the anatase crystallites. The vanadia crystallites are increasing to an extent that they cannot be present in the mesopores. They are transported toward the catalyst particle surface and are accumulated in the macropores.

#### 5. Acknowledgements

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