Anatase–rutile transformation in TiO$_2$–V$_2$O$_5$ catalyst coatings for ceramic foams

E.C. Bucharsky *, G. Schell, R. Oberacker, M.J. Hoffmann

Institute of Ceramics in Mechanical Engineering, University of Karlsruhe, Haid-und-Neu-Str. 7, D-76131 Karlsruhe, Germany

Abstract

The aim of this investigation was to study the thermal stability of TiO$_2$–V$_2$O$_5$ catalysts prepared from aqueous powder suspensions based on pigment grade anatase and sub-micron vanadia particles. Such catalysts are proposed for dip coating of ceramic foams for application in a new reactor design for the synthesis of phthalic anhydride. Catalyst mixtures with vanadia contents up to 10% were annealed in air in the temperature range from 400 to 1200 °C. The influence of temperature and vanadia content on the anatase to rutile transformation and the specific surface were monitored, employing XRD, SEM and BET measurements. Results show that the addition of V$_2$O$_5$ strongly affects the temperature of phase transformation. This process is accompanied by a large decrease of surface area. The structural changes can produce a pronounced effect on catalytic performance for the oxidation reaction of o-xylene. Possible mechanisms and the consequences for catalytic performance are discussed.
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1. Introduction

Industrial catalysts are usually made out of transition metal oxides on oxide supports.[1–3] Typically, "egg-shell" catalyst beads of millimeter size with solid, inert cores are packed into a fixed bed. A new interesting alternative is the application of ceramic foams as catalyst supports.[4–7] To achieve a sufficient specific surface, the ceramic foams have to be coated with a washcoat, on which the according catalyst is deposited. Such foams offer the possibility of improving reactor performance, especially for highly exothermic and fast chemical reaction, because heat transfer is enhanced compared with packed beds of spherical or cylindrical pellets.

An example for such reactions is the synthesis of phthalic anhydride, where usually a catalyst system containing TiO$_2$ and V$_2$O$_5$ is used. A good catalytic performance is obtained at vanadium loadings corresponding approximately to a vanadium monolayer on the TiO$_2$ surface.[8] Debated topics are both, the influence of the crystalline structure of TiO$_2$ on the catalyst performance and the influence of the active components (or even impurities) on the phase transformation. It is generally accepted that TiO$_2$ in the anatase form gives rise to superior active catalysts as compared with TiO$_2$–rutile. Thus, industrial catalysts are usually based on anatase.[8–12] But it is known that the transformation of part of it into rutile (thermodynamically favoured) leads to a decrease in surface area and to a detriment of the active 'monolayer' of vanadium on the anatase surface resulting in a degradation of the catalytic performance.[8,9] At elevated temperatures, TiO$_2$ (anatase) supported catalysts undergo an anatase–rutile phase transformation. The rate of phase transformation is strongly dependent on the presence of other ions[13–16] as oxides or fluorides enhance this transformation. A huge number of publications show, that the V$_2$O$_5$ catalyst belongs to this group and decreases the transformation temperature significantly.[17–19]

Replacing the commonly used catalyst beads by ceramic foams requires coating of the foams by a washcoat and the catalyst. Obviously, a TiO$_2$ washcoat carrying the V$_2$O$_5$ catalytic component could be a suitable solution. Coating can be realized, e.g., by dip coating of the foams using TiO$_2$–V$_2$O$_5$ particle suspensions. With respect to costs, aqueous suspensions based on pigment grade titania offer a good potential for this processing step. The coated foams have to be annealed to achieve a sufficient bonding between foam and catalyst. Enhanced

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* Corresponding author. Tel.: +49 721 608 7925; fax: +49 721 608 8891.
E-mail address: e.bucharsky@ikm.uni-karlsruhe.de (E.C. Bucharsky).

temperatures occur also during the entire service life. The exothermic phthalic anhydride reaction takes place in oxidising atmosphere between 360 and 400 °C, and involves a high heat transfer.[20]

Therefore, thermal stability of the catalyst coating is an essential requirement for production and application of ceramic foams in phthalic anhydride reactors. Prior experimental investigations on this subject were mostly carried out with special catalytic grade titania and catalyst preparation methods, which differ substantially from the regarded particle suspension dip coating process. The present investigation provides an assessment of the temperature limits during processing and application of coatings produced from suspensions containing pigment grade titania. The anatase–rutile phase transformation and the reduction in specific surface are taken as a first indicator for these limits.

2. Experimental

Sub-micron anatase TiO_2 powder (A-ZUOK008136, 8.15 m²/g, Tronox Pigments GmbH, Germany, >99%) and vanadium oxide V_2O_5 (Merck, Germany, >99%), were dispersed in an aqueous media with a solids loading of 30 wt.% The stability of the suspensions was controlled by ζ-potential (DT1200, Dispersion Technology, USA) and viscosimetry measurements (RheoStress RS 600, Thermo Haake, Germany). At pH 5 the ζ-potential reached with −25 mV its optimum value and a well stabilized suspension could be obtained. The set of conditions is adequate for dip coating process. Oxide mixtures without and with 3, 7 and 10% V_2O_5 content were prepared by drying the suspensions under controlled temperature up to 80 °C until a constant weight of the resulting powders was reached. This covers the range of vanadia additions used in industrial catalysts of similar surface areas.[10] The powders were pulverized using a mortar and annealed for 3 h at temperatures between 550 and 1200 °C in a chamber furnace in air.

Anatase to rutile transformation, from doped and undoped TiO_2 samples, was analyzed by X-ray diffraction analysis (XRD) using a Siemens D500 diffractometer equipped with a graphite crystal monochromator using CuKα radiation. An internal Si-standard was used to correct the peaks' position. In order to obtain the lattice parameters, the data were processed by a least square fit using seven to ten diffraction peaks for rutile respectively anatase. The mass fraction of rutile (X_R) in the samples was calculated based on the relationships between the integrated intensities of the anatase (1 0 1), I_A, and rutile (1 1 0), I_R, peaks,[21,22] according to Eq. (1):

$$X_R = \frac{1}{1 + K_T(I_A/I_R)} \tag{1}$$

The constant K_T was experimentally determined, using pure anatase and defined mixtures up to a powder with an anatase–rutile ratio of 10:90. The calibration curve obtained is given in Fig. 1, resulting in $K_T = 1.2885$.

Specific surface area was determined by nitrogen adsorption at 77 K by the Brunauer–Emmett–Teller (BET) method (Flow Sorb II 2300, Micromeritics, Germany). Powder morphology
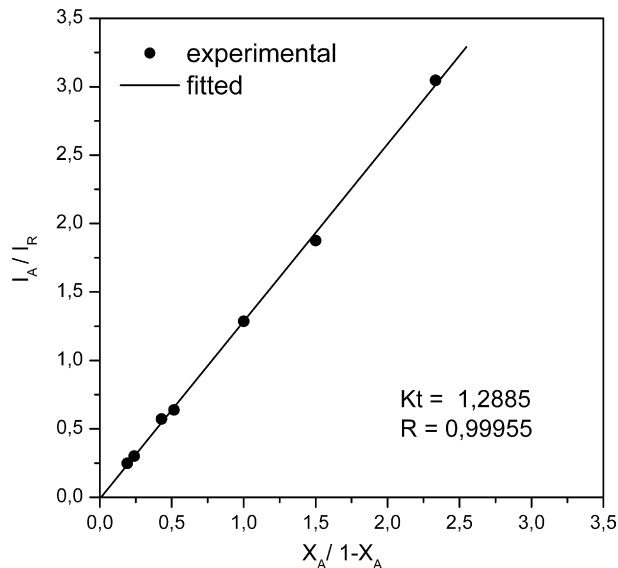

Fig. 1. Dependence of XRD peak intensities on the anatase–rutile ratio of powder mixtures.

was characterized by scanning electron microscopy (SEM) using a Stereoscan 440 (Leica, Germany).

3. Results

3.1. Preparation of the catalyst powder mixtures

Several methods exist for the preparation of vanadium as a molecular dispersion.[23–25] In the present work, the V_2O_5–TiO_2 catalyst mixtures were prepared by drying oxide slurries, which were electrostatically stabilized by varying the suspension pH.

From SEM, Fig. 2, it was observed that the particles at pH 3 and pH ≥8 formed agglomerates exceeding a size of 1000 nm. When the pH was in the range between 5 and 7, the primary TiO_2 particles with a size between 200 and 700 nm remain unagglomerated. These mixtures presented a uniform distribution of V_2O_5 needle crystals on the carrier matrix, while at pH 8.0, inhomogeneous and large V_2O_5 particles were observed.

3.2. Anatase–rutile transformation during annealing of the catalyst powder mixtures

Beside the XRD patterns of anatase and rutile that could be detected in all samples, the specimens with higher V_2O_5 contents of 7 and 10% annealed at 400 °C exhibited additional reflections which correspond to V_2O_5 peaks. These peaks were weak and rather broad. When the temperature increases in the range 550–700 °C these peaks disappear and grain growth is observed. Fig. 3 shows the comparison of the peak positions of an annealed pure anatase at 1100 °C which is almost transformed into pure rutile with powder mixture containing 3 wt.% V_2O_5 annealed at 650 °C. While there is no appreciable change in the peak position of anatase (1 0 1), a significant shift of the rutile (1 1 0) peak was observed. Lattice parameters for anatase and rutile at different temperatures are depicted in Table 1 for pure TiO_2 and TiO_2 + 3% V_2O_5.
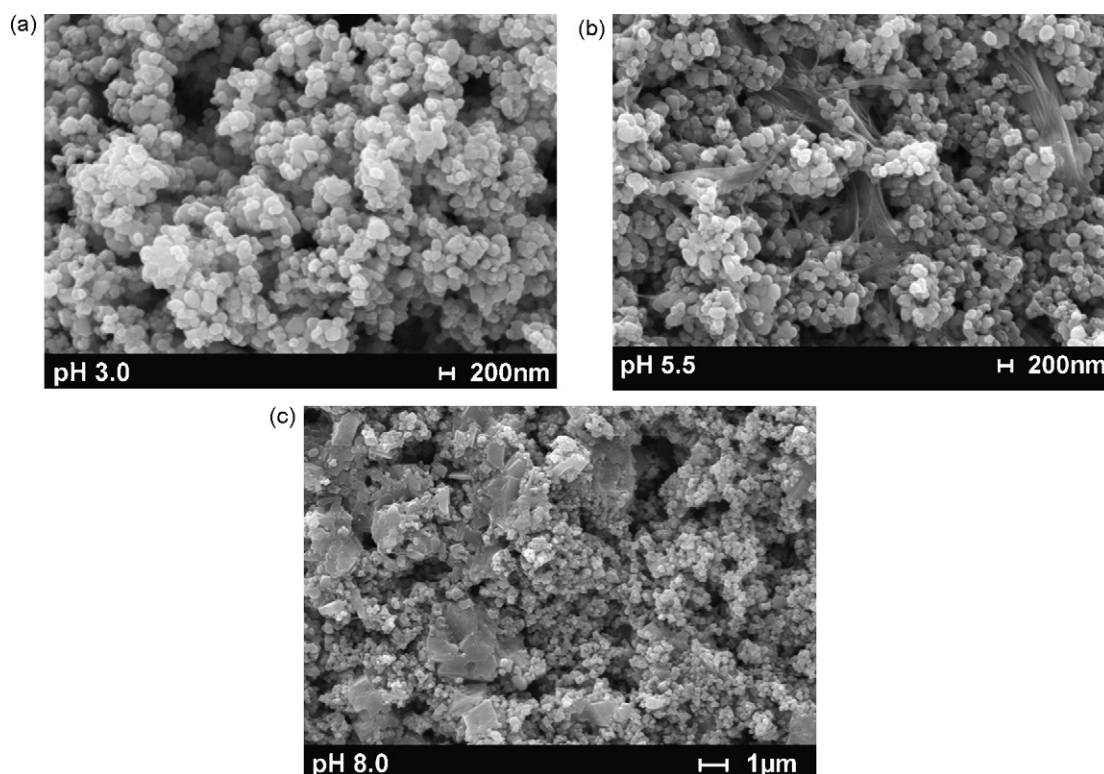
Fig. 2. SEM micrographs depicting a good distribution of 7% V_2O_5 particles at pH 5.5. At pH 8.0, bigger agglomerations of the TiO_2 particles and V_2O_5 islands were found. At pH 3.0 no V_2O_5 needles are observed.

The rutile fraction as calculated by Eq. (1) from the X-ray diffraction patterns of the catalyst powder mixtures is plotted in Fig. 4 as a function of the annealing temperature. Without vanadia, the onset temperature of the anatase–rutile transformation is beyond 900 °C. Partial transformation is observed in a narrow temperature interval of about 200 °C for an annealing time of 3 h. The vanadia additions cause drastic changes in the transformation behavior. Onset and end temperatures of the phase transformation decrease with increasing vanadia content. Rutile fractions of about 20, 40 and 60% are observed for additions of 3, 7 and 10% vanadia, respectively, after annealing at 650 °C. This

indicates clearly the instability of the anatase phase in this temperature range under practical conditions, where much longer exposure times need to be survived.

During heat treatment no weight change was observed in agreement with the results obtained by Vejux and Courtine,[26] Bond et al.[11] and Habel et al.[27] when the V_2O_5 content in the sample is smaller as 15 wt.%

Fig. 5 shows an Arrhenius plot for the anatase–rutile transformation. The activation energy (E_A) derived from the fitting curves is depicted in Fig. 6 as a function of the V_2O_5 concentration of the catalyst. E_A values were found to be linearly

Table 1
Lattice parameters of pure TiO_2 and TiO_2–V_2O_5 powder mixtures after 3 h annealing at different temperatures.

T (°C)	Rutile		Rutile + 3% V_2O_5	
	a (Å)	c (Å)	a (Å)	c (Å)
400	No rutile			
650			$(4582 \pm 10) \times 10^{-3}$	$(2904 \pm 40) \times 10^{-3}$
800	$(4592 \pm 4) \times 10^{-3}$	$(2951 \pm 5) \times 10^{-3}$	$(4571 \pm 4) \times 10^{-3}$	$(2921 \pm 6) \times 10^{-3}$
1100	$(4594 \pm 5) \times 10^{-3}$	$(2952 \pm 20) \times 10^{-3}$		

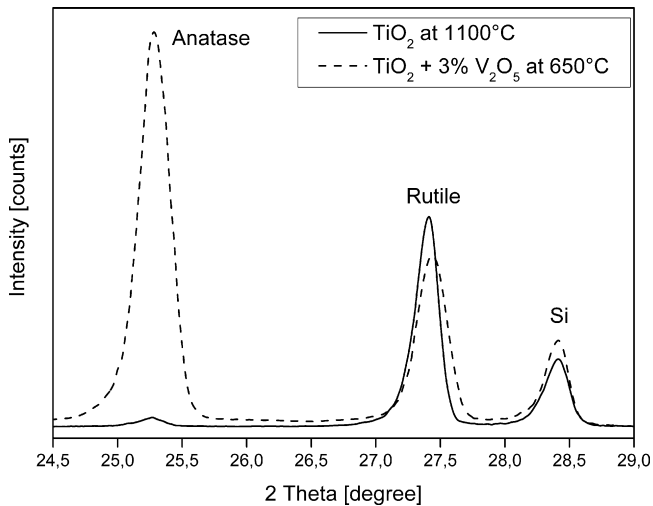| T (°C)	Anatase		Anatase + 3% V_2O_5	
	a (Å)	c (Å)	a (Å)	c (Å)
20	$(3785 \pm 2) \times 10^{-3}$	$(9525 \pm 20) \times 10^{-3}$		
400	$(3785 \pm 7) \times 10^{-3}$	$(9510 \pm 10) \times 10^{-3}$		
650			$(3788 \pm 2) \times 10^{-3}$	$(9491 \pm 4) \times 10^{-3}$
800	$(3781 \pm 7) \times 10^{-3}$	$(9515 \pm 10) \times 10^{-3}$	$(3778 \pm 20) \times 10^{-3}$	$(9469 \pm 30) \times 10^{-3}$
1100	Full anatase to rutile transformation			

Fig. 3. XRD-plot of partially transformed TiO_2 (anatase) without and with V_2O_5.

dependent on the V_2O_5 concentration in the range between 3 and 10%.

3.3. Change of specific surface and particle morphology during annealing of the catalyst powder mixtures

The specific surface area of the starting powder mixtures is mainly in the range of 8–10 m²/g (Fig. 7). Only the catalyst powder with the highest V_2O_5 content has a slightly higher surface of 11 m²/g, probably caused by a different morphology of the active vanadia phases on the anatase surface. The surface area of pure TiO_2 begins to decrease at around 650 °C. At 900 °C, where the onset of anatase–rutile phase transformation is detected, the specific surface has already decreased to one-third of its initial value. The reduction in specific surface area during annealing is dramatically accelerated by V_2O_5 additions. Higher amounts of V_2O_5 result in lower specific surface areas at a given annealing temperature.

Pure TiO_2 starting powder is shown in Fig. 8a, in comparison with the TiO_2 powder (anatase form, Fig. 8b) and the mixture
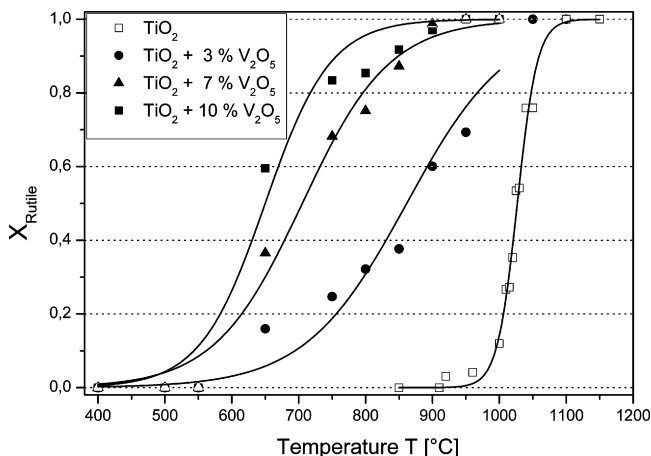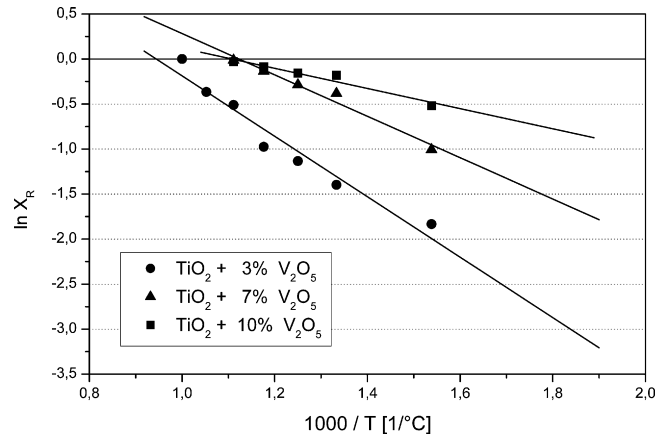

Fig. 5. Arrhenius plot of the rutile fraction as function of the annealing temperature for various V_2O_5 concentrations.
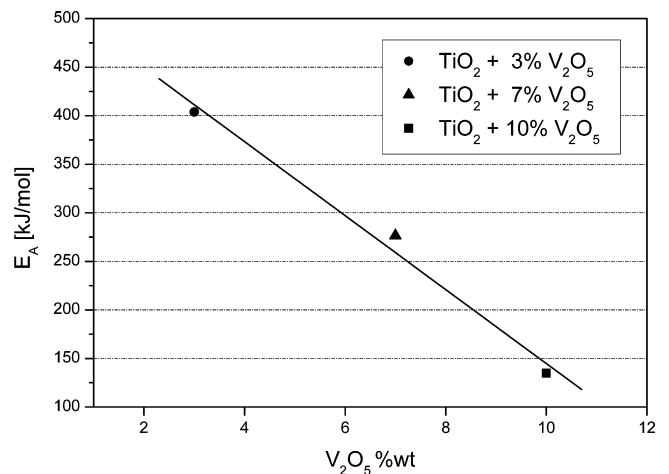

Fig. 6. Dependence of the activation energy for phase transformation E_A on the V_2O_5 content of the catalyst powders.

with 7 wt.% V_2O_5, both after heat treatment at 800 °C. Without V_2O_5 doping the particles grow slightly in size, compared to the as received powder. The increase in particle size corresponds to the reduction in specific surface area of 20–30%. Under the
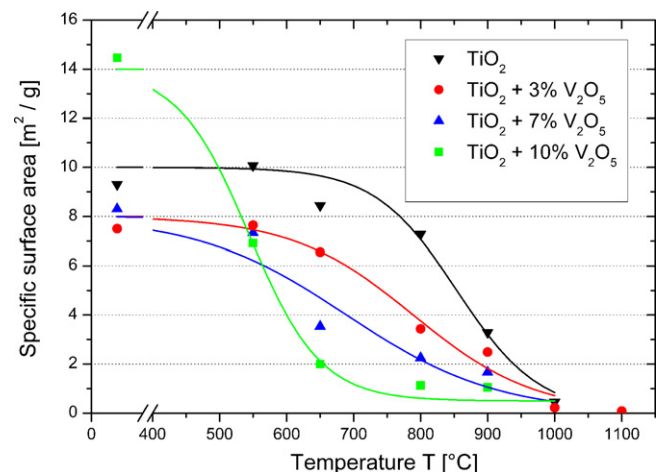

Fig. 4. Effect of annealing temperature on the rutile transformation fraction for different V_2O_5 doping concentrations and for pure TiO_2 powder.

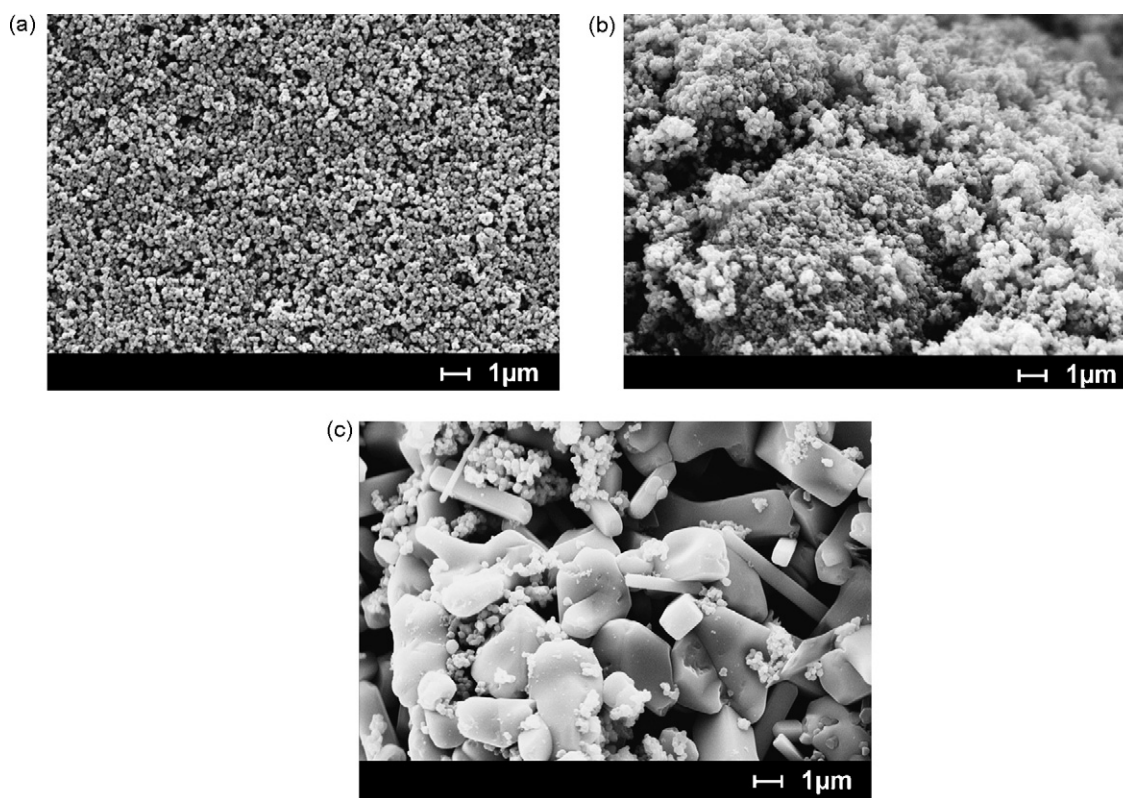Fig. 7. Dependence of specific surface area on annealing temperature.

Fig. 8. Microstructure of (a) pure TiO_2 anatase powder prior to annealing, (b) pure TiO_2 after annealing at 800 °C for 3 h and (c) pure TiO_2 plus 7% V_2O_5, after annealing at 800 °C for 3 h.

same annealing conditions, the powder mixture containing 7% V_2O_5 (Fig. 8c) develops extremely coarse, faceted crystals of up to 4 μm besides a small amount of particles with a size similar to that of the starting powder. The reduction in specific surface of about 80% is in a good qualitative correlation with this bimodal particle size distribution. The fraction of rutile of about 80%, as detected by XRD, correlates to the fraction of coarse particles. This indicates a coupled mechanism of phase transformation and grain growth.

Another observation was a change in the colour of the samples. The starting powder mixture changes from pale orange to brown-grey as the annealing temperature and V_2O_5 content is increased.

4. Discussion

Our experiments confirm earlier findings[11,12,27–29] that V_2O_5 additions favour the anatase–rutile phase transformation in TiO_2 supported catalyst powders. As V_2O_5 loading increases in the composition range from 3 to 10%, the temperature required to render transition to rutile is decreased in the range 900 °C > T > 600 °C. The calculated activation energy decreases linearly from 400 to 150 kJ/mol between 3 and 10% V_2O_5. In parallel to phase transformation, the specific surface area of the powders is reduced and a colour change from pale orange to brown-grey is perceived.

For the partially transformed titania a bimodal particle size distribution was observed. Probably, the coarse particle frac-

tion corresponds to the transformed rutile, the fine fraction to the residual anatase phase. This indicates that particle growth occurs in combination with phase transformation. The change in particle size is adequate to explain the drastic reduction of specific area.
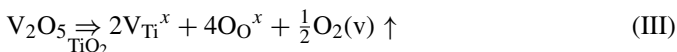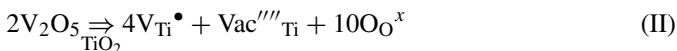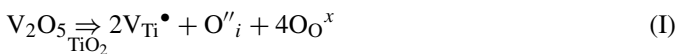
4.1. Influence of temperature and V_2O_5 content on anatase–rutile phase transition

Different mechanisms can lead to the accelerated transformation of anatase to rutile by the V_2O_5 additions. Our X-ray diffraction studies reveal the presence of microcristalline V_2O_5 for annealing temperatures of 400 °C which disappear already at 550 °C, where no measurable transformation has yet occurred. Within the precision of measurement, the lattice parameters of the TiO_2 anatase phase remain unchanged during annealing and, independent whether V_2O_5 is present in the powder mixture or not. The rutile lattice parameters however are significantly smaller for the V_2O_5 containing mixtures. As the XRD-measurement technique used allows no precision lattice parameter determination, a solid solution formation in the anatase phase cannot completely be ruled out. However, solution of V-ions in the rutile lattice is much more significant and seems to occur to a much higher extent. Our observations agree with findings of Habel et al.[27] from precision lattice parameter measurements. They concluded that no alloying between anatase and V_2O_5 has taken place. Gasior et al.[29] have reported unchanged lattice parameters in anatase, when the samples were calcined

at 600 °C in nitrogen atmosphere. In these conditions the incorporation of V(IV) occurs very fast with simultaneous anatase to rutile transformation.

Saleh et al.[30] reported that the presence of crystalline V_2O_5 appears to be essential for the formation of a solid solution from the supported vanadia phase and TiO_2. They observed that as the content of rutile rises, the crystalline V_2O_5 phase is diminished. After heat treatment at 650 °C a considerable amount of the rutile phase was present. For samples heat treated at 700–750 °C, they inferred by Raman spectroscopy studies, that most of V_2O_5 is incorporated into the titania (rutile) support as $V_xTi_{1-x}O_2$.

The shift to smaller lattice parameters in the rutile unit cell indicates a replacement of Ti-ions by smaller V-ions resulting in the formation of a rutile solid solution in which V_2O_5 is dissolved. Habel et al.[27] proposed three different defect models for the formation of this rutile solid solution:

$$V_2O_5 \underset{TiO_2}{\Rightarrow} 2V_{Ti}^{\bullet} + O''_i + 4O_O{}^x \qquad (I)$$

$$2V_2O_5 \underset{TiO_2}{\Rightarrow} 4V_{Ti}^{\bullet} + Vac''''_{Ti} + 10O_O{}^x \qquad (II)$$

$$V_2O_5 \underset{TiO_2}{\Rightarrow} 2V_{Ti}{}^x + 4O_O{}^x + \tfrac{1}{2}O_2(v)\uparrow \qquad (III)$$

In reducing atmospheres vanadium(IV) is favored[27,29,31] while under oxidizing condition as used in our work, vanadium(V) species are more probably present.[31,32] A type (3) defect model with a consequent weight loss[19,33] is unlikely under such conditions. We also did not observe any considerable weight loss during annealing.

Even if there is no apparent change in the XRD-patterns of the anatase phase in presence of V_2O_5, the heat treatment may promote diffusion of V(V) into titania crystal structure to some extent, leading to a deformation of the lattice. These defects can act as nuclei for $V_xTi_{1-x}O_2$ phase genesis, which is almost identical to pure rutile phase. Rey et al.[32] conclude, that since vanadium oxide species are closely interacting with the titania support, a higher V_2O_5 loading results in a higher surface density of nuclei for the phase transition from anatase to rutile. This promotional effect of vanadium oxide in anatase to rutile transformation has also been reported in[28,30] and appears to be accompanied by grain growth.

An interesting finding is, that the V_2O_5 spreads rapidly over the titania surface, already at temperatures as low as 450 °C. Oxidising conditions and well developed anatase crystal planes favour spreading.[34] In addition, a eutectic liquid is formed at 631 °C in the system TiO_2–V_2O_5 under oxidising conditions. Both, the surface nuclei and the liquid phase could explain the observed acceleration of phase transition. The dramatic grain growth observed during annealing above 650 °C makes a liquid phase mechanism more likely. Such mechanism could be grain growth controlled by liquid film migration, as observed in sintering of various metal and oxide systems.[35,36] A higher surface density of rutile nuclei would not inevitably cause grain growth.

4.2. Possible consequences for the catalytic system performance

The consequences of the phase transformation for the catalytic performance in o-xylene oxidation does not only depend on the crystallographic structure of the TiO_2 support itself. For catalysts prepared under the same conditions on anatase and rutile, the yield of phthalic anhydride are approximately similar[37] when rutile supports indicate comparable specific surface area and contaminations. However the phase transition is accompanied by a dramatic decrease in specific surface area. In addition, as the formation of the solid solution starts, the available amount of free vanadia on the TiO_2 support is decreased. Thus the onset temperature for phase transformation respectively the formation of the solid solution has therefore to be regarded as maximum temperatures for calcination and therefore for application of the catalyst systems. It has been shown that the formation of a solid solution affects unfavourably total activity and selectivity on the partial oxidation products.[38]

As these temperatures decrease with the vanadia content, the V_2O_5 addition should be not higher, as required for maximum selectivity and yield. The monolayer content corresponds to 0.145 wt.% of V_2O_5/m^2 of TiO_2 surface,[39] which means about 1.27 wt.% in our materials.

5. Conclusions

An attractive method for coating ceramic foams with V_2O_5–TiO_2 catalyst has been developed. Investigated suspension parameters allow us to obtain good particle dispersion in water for different V_2O_5 contents, which are suitable to produce catalytic washcoats by dip coating.

The anatase–rutile transformation temperature of these catalysts, which can be regarded as an upper limit for calcination and service temperature, depends strongly on the presence and concentration of V_2O_5. This temperature decreases with increasing V_2O_5 content. Phase transformation is accompanied by a drastic reduction of specific surface. The upper temperature limit is about 600 °C. The formation of a eutectic melt at 631 °C is assumed to be the responsible mechanism which controls transformation and grain growth by liquid film migration. Anatase is transformed to a rutile–V_2O_5-solid solution by this mechanism.

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