Phase Relations in the System TiO$_2$-V$_2$O$_x$ under Oxidizing and Reducing Conditions

D. Habel, O. Goerke, M. Tovar, E. Kondratenko, and H. Schubert

The target of this work was to investigate the phase development in the catalyst system consisting of TiO$_2$ (Anatase) and V$_2$O$_5$ (Shcherbinaite) under several gas atmospheres. Thus a set of V$_2$O$_5$/TiO$_2$ specimens was prepared by ball milling and exposed to subsequent annealing in air and feed gas in the temperature range from 400 to 700 °C. The XRD-results showed that the initial phases Anatase and Shcherbinaite remain stable for all atmospheres containing oxygen. In the temperature range above 525 °C the formation of a Rutile solid solution (Rutile-ss) containing VO$_x$ species takes place. However, under reducing conditions (lower oxygen partial pressure) the reduction of V$_2$O$_5$ to V$_2$O$_3$ was found by X-ray diffraction measurements. There is no miscibility up to 1300 °C followed by the formation of V$_2$TiO$_5$ (Berdesinskiite). SEM images underline the reduction by monitoring the change in morphology with respect to the V-containing phases. TiO$_2$ remains without much alteration. The two phases V$_2$Ti$_7$O$_{17}$ and V$_2$Ti$_3$O$_9$ (Schreyerite) as described in mineralogy have not been observed in these experiments. The knowledge of phase relations helps to find the appropriate processing conditions and to understand the aging phenomena of catalysts.

1. Introduction

Polyolefins are a class of substances from petrol industry and basis of a large number of chemical products. A route to produce propene at low temperatures is the oxidative dehydrogenation of propane (ODP). One of the key steps of the ODP reaction is the induction of double bonds which is associated by removal of two hydrogen species. This hydrogen reacts at the surface with an oxygen species donated by the catalyst. Experiments with isotope labeled gases[1] proved that the oxygen does not come from the feed gas but from the catalyst. The partial oxidation may be considered as a key step in olefine processing and also as a model reaction. The common reaction path is discussed in literature as a Mars-van Krevelen mechanism.[2,3] It has been found that vanadium based systems are the most selective catalysts for the oxidation of hydrocarbons.[4]

There have been reported numerous applications of the TiO$_2$-V$_2$O$_5$ system.[5-10] Especially the Anatase-Rutile transformation was focused by many authors because it is considered to represent the major factor in catalyst

D. Habel, O. Goerke, and **H. Schubert,** Institute of Material Science and Technologies, TU Berlin, Englische Straße 20, D-10587 Berlin, Germany; **M. Tovar,** Division Structure Research, Hahn-Meitner-Institute, Glienicker Straße 100, D-14109 Berlin, Germany; **E. Kondratenko,** Leibniz Institute for Catalysis, University Rostock, Branch Berlin, Richard-Willstätter-Straße 12, D-12489 Berlin, Germany. Contact e-mail: habel@ms.tu-berlin.de.

deactivation in selective oxidation catalysis. Vejux and Courtine suggest that both the reduction of V$_2$O$_5$ and the transformation of Anatase into Rutile are activated by structural interactions at the V$_2$O$_5$-TiO$_2$ (Anatase) interface.[9]

It is known that the thermodynamically stable polymorphs of TiO$_2$ and VO$_2$ have the same rutile-type structure and form solid solutions in a wide compositional range having Rutile or pseudo-rutile structures.[11] The polymorphous Anatase to Rutile transformation may occur within a wide range of temperatures from 400 to 1200 °C,[12] though normally it takes place at 800-850 °C.[13] However, the various literature data are due to differences in chemical compositions. A review of the effects of impurities has been given by Shannon and Pask.[14,15] The Anatase-Rutile transformation can be influenced by the addition of promoters or inhibitors.[16-18] Karvinen[19] investigated the effect of trace element doping of TiO$_2$ on the crystal growth and on the Anatase-to-Rutile phase transformation of TiO$_2$. Investigators[20,21] observed that the transformation temperature is subject not only to impurities but also to grain size and processing.

Oliveri et al.[22] concluded that vanadium pentaoxide has a marked influence on the Anatase-to-Rutile phase transition. Vanadium oxide also has a role in favoring a decrease in the surface area of the Anatase particles. In previous investigations the formation of a Rutile solid solution was first found at 525 °C < T < 550 °C for compositions of 3 mol% < V$_2$O$_5$ < 5 mol% under oxidizing conditions. The phase field for Rutile solid solutions extends to 10 mol% < V$_2$O$_5$ < 12.5 mol% at 675 °C. For very high V$_2$O$_5$ concentrations (95 mol%) a eutectic reaction was found at 631 °C.[23]

The system TiO$_2$-V$_2$O$_3$ is used for catalytic purposes. In spite of an extended literature on catalytic reactions needing this catalyst system, no satisfactory phase diagram was available. Phase reactions were investigated by Bond and

Tahir[8] who found the Rutile formation under feed gas conditions associated with a loss of oxygen and a predominantly tetravalent V-ion. The change of the metastable Anatase to Rutile is the subject of the work of Shannon and Pask[14] who found that contaminants reduce the transformation temperature.

The present work is focused on the phase development during catalyst processing under oxidizing and reducing conditions. The resulting XRD spectra were qualitatively used to construct preliminary phase diagrams. The measurements were completed by DTA and SEM investigations.

2. Experimental

The materials for the investigation were prepared from oxidic powder mixtures of TiO_2 (Anatase modification, GL 102/10827, KRONOS International Inc., Germany) and V_2O_5 (Shcherbinaite modification, GfE Environmental Technology Ltd., Germany) by wet milling in dried cyclohexane (Merck) for 1 h in a rotary ball mill. The slurries were subsequently dried in air at 100 °C and sieved. Further thermal treatment was carried out in MgO-stabilized Zirconia (PSZ) crucibles in a box-type furnace (Nabertherm, Lilienthal, Germany). The annealing treatments for reducing conditions were proceeded in an alumina lined tube furnace (Nabertherm, Lilienthal, Germany) with an attached gas flow controller (Bronkhorst, The Netherlands). Gas mixtures were varied from air, via 40 Vol%C_3H_8/20 Vol%O_2/40 Vol% Ne, via 40 Vol%C_3H_8/60 Vol% Ne to 100 Vol% CO. The time at temperature was 4 h.

The major tool for monitoring the phase content was X-ray powder diffractometry. Thus a θ-θ-diffractometer (Bruker AXS D 5005, Karlsruhe, Germany, Cu Kα radiation) recorded diffraction patterns using a position sensitive detector (step width 0.01° 2θ, integration time 3 s). The phase analysis was carried out using the Diffrac-Plus/Search program.

Scanning electron microscopy (SEM) was applied for structural characterization of the samples. Specimens were glued onto alumina stubs, then carbon-coated and examined using a scanning electron microscope (Zeiss Cross-Beam 1540 EsB, Germany) at an accelerating voltage of 5 kV in order to avoid charging.

The weight loss was recorded by thermal gravimetric analysis (TGA, Netzsch STA 429, Selb, Germany) coupled to an infrared spectrometer (Bruker Equinox 55, Karlsruhe, Germany). The chemical composition, especially the cation stoichiometry, was determined after decomposition in an autoclave (Berghof Labortechnik DAH 406, Germany) with an ICP-OES spectrometer (inductively coupled plasma optical emission spectrometry, Jobin Yvon 39+, France).

3. Results and Discussion

3.1 Oxidizing Conditions

The low temperature part has been the subject of previous work.[23] Thus the results will be reported to the extent necessary for comparison with results from new investigations under reducing conditions. The results of the X-ray diffraction phase analysis of specimens annealed in both oxidizing as well as reducing conditions are given in Table 1.

Under air and oxygen containing feed gas, the initial phases Anatase and Shcherbinaite remained stable up to about 500 °C. The specimens annealed at 600 °C contain a Rutile solid solution (Rutile-ss) generated by the Anatase-Rutile transformation.

X-ray diffraction measurements of the air-treated specimens show no Perlite-like decompositions and also no indication for glass formation. Instead a Shcherbinaite structure (V_2O_5) with shifted peak intensities and peak heights was found. Thus a direct solidification of the melt to solid of the same composition took place.

The Anatase-Rutile transformation occurs at much lower temperatures in the vicinity of V_2O_5 compared to the transformation of pure TiO_2. The XRD results as depicted in Fig. 1 show the existence of a Rutile solid solution.

Table 1 Phase composition of TiO_2-V_2O_5 samples annealed at 500 and 600 °C under several atmospheres

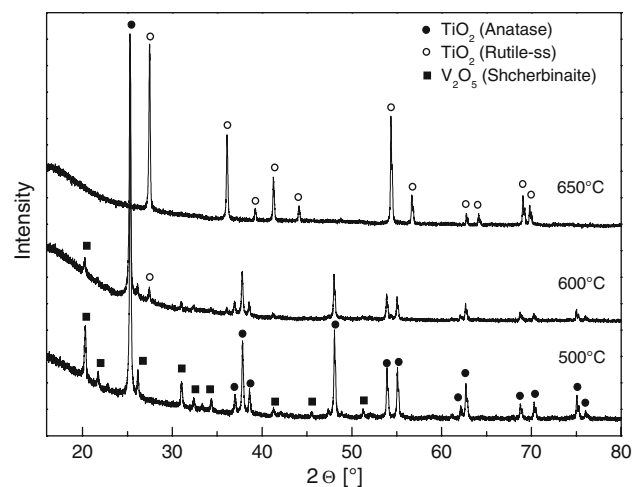| Atmosphere	Gas	Phase composition	
		500 °C	600 °C
Oxidizing	21 O_2 : 79 N_2 (air)	Anatase Shcherbinaite (V_2O_5) No Rutile	Anatase Shcherbinaite (V_2O_5) Rutile-(ss)
Catalytic/feedgas	40 C_3H_8 : 20 O_2 : 40 Ne	Anatase Shcherbinaite (V_2O_5) Rutile-(ss)	Anatase Shcherbinaite (V_2O_5) Rutile-(ss)
Reducing	40 C_3H_8 : 60 Ne 100 CO	Anatase Karelianite (V_2O_3) No Rutile	Anatase Karelianite (V_2O_3) No Rutile

Fig. 1 XRD-diffractogram of the formation of Rutile-(ss) under oxidizing conditions
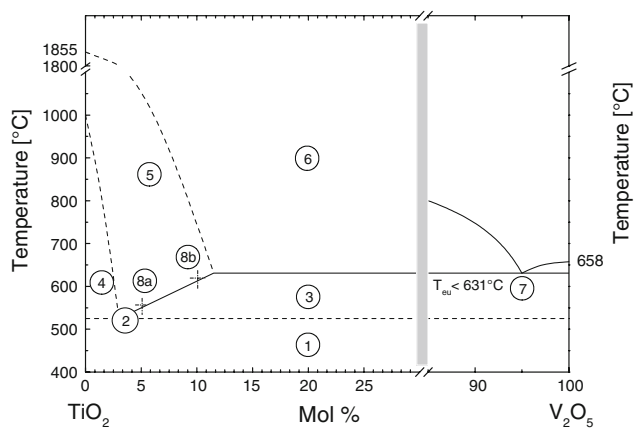
Fig. 2 Phase diagram of the system TiO$_2$-V$_2$O$_5$ under oxidizing conditions: (1) Anatase (TiO$_2$)+ Shcherbinaite (V$_2$O$_5$); (2) begin of Rutile-(ss) transition at 3-5 mol% V$_2$O$_5$ and approx. 525 °C; (3) Rutile-(ss) + V$_2$O$_5$; (4) Anatase + Rutile-(ss); (5) Rutile-(ss); (6) Rutile-(ss) + V$_2$O$_5$ eutectic liquid; (7) rapidly solidified eutectic liquid at 95 mol% V$_2$O$_5$ and 631 °C; (8a and b) Points determined by DTA

The peaks for both Anatase and Shcherbinaite diminished and simultaneously the Rutile phase appears however with slightly altered peak positions. This indicates the formation of a Rutile solid solution in which the V$_2$O$_5$ is dissolved. Details can be seen in the report of the earlier work.[23]

Based on the X-ray diffraction results a working phase diagram was deduced and is shown in Fig. 2.

The straight lines indicate the stable equilibria, while the dotted lines show the metastable equilibrium under the given conditions. For the low temperature phase Anatase no solid solution with Shcherbinaite was found (cf. field 1). If it exists the solubility will be small. A continuous melt regime, a eutectic reaction and an extended field of Rutile-(ss) belong to the stable part. Point 8a and 8b were obtained as a result of DTA measurements and affirm the run of the tie-line. Since Anatase is a metastable phase, no pronounced reaction enthalpy ΔH occurs. High temperature XRD patterns showed a continuous reaction from Anatase to Rutile in the temperature range from 500 up to 650 °C (Fig. 1).

3.2 Reducing Conditions

The TiO$_2$-V$_2$O$_5$ (V$_2$O$_3$) system is applied for olefin catalysis, which is associated with compositions of reduced oxygen partial pressure. Under these conditions the previous starting phase V$_2$O$_5$ is reduced to V$_2$O$_3$. From the standpoint of application, a partial pressure low enough to form V$_2$O$_3$ is considered as reducing. Thus a series of several gas mixtures was tested. Specimens of various TiO$_2$-V$_2$O$_5$ starting compositions were exposed to the different gas compositions. The results of the subsequent X-ray inspection are shown in Fig. 3 and Table 1, respectively.

For gas atmospheres with a substantial amount of oxygen the initial phases TiO$_2$ (Anatase) and V$_2$O$_5$ (Shcherbinaite)
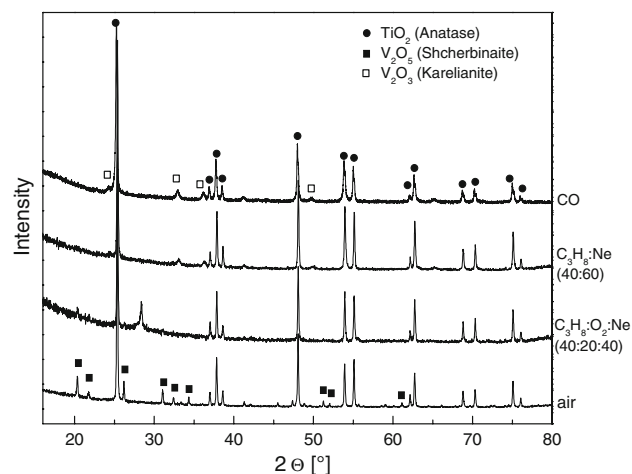

Fig. 3 XRD-diffractogram of 90 mol% TiO$_2$-10 mol% V$_2$O$_5$ samples annealed at 500 °C under several atmospheres

remained stable (cf. Fig. 4a, b). TiO$_2$ is characterized by nearly spherical and homogenous particles of about 100 nm whereas V$_2$O$_5$ shows large orthorhombic structured particles. The TiO$_2$ reflection at $2\theta = 25.3°$ were found for all gas compositions, the peak became a bit broader for CO annealing (cf. Fig. 3). Since the Ti-ion may have a different state of valence, the increasing peak width is attributed to defects. V$_2$O$_5$ reacted with TiO$_2$ to form the Rutile-(ss) at elevated temperatures, as long as the feed gas contained free oxygen (cf. Table 1). For a feed gas of propane plus only an inert gas (Ne) as well as for CO the fine needle-like V$_2$O$_3$ Karelianite phase was found (cf. Fig. 4c, d).

As a result of DTA and X-ray measurements a phase diagram for the system TiO$_2$-V$_2$O$_3$ under reducing conditions has been proposed (Fig. 5).

For the temperature of interest for catalysis up to 600 °C no other phase than TiO$_2$ and V$_2$O$_3$ were observed. This indicates a total miscibility gap.

Because V$_2$O$_3$ is isostructural with Al$_2$O$_3$ the analogy with the well investigated oxidic systems Al$_2$O$_3$-TiO$_2$ and Al$_2$O$_3$-SiO$_2$ suggest the intermediate phase of the type M$^{3+}_2$M$^{4+}_1$O$_5$. Examples are Al$_2$TiO$_5$ (aluminum-titanate), an anisotropic low expansion phase as well as Al$_2$SiO$_5$ (aluminum-silicate).

The annealing of a TiO$_2$-V$_2$O$_5$ material at 1300 °C under CO gives a new set of reflection belonging to the phase V$_2$TiO$_5$ (Berdesinskiite) which was described from Bernhardt et al.[24] The lowest temperature for the formation of this phase was determined to be 1300 °C. However, thermal treatment at lower temperatures up to 700 °C did not give indication for the presence of such an intermediate phase. Thus one must assume a eutectic reaction at higher temperatures; however, there was no further investigation.

3.3 Catalytic Conditions

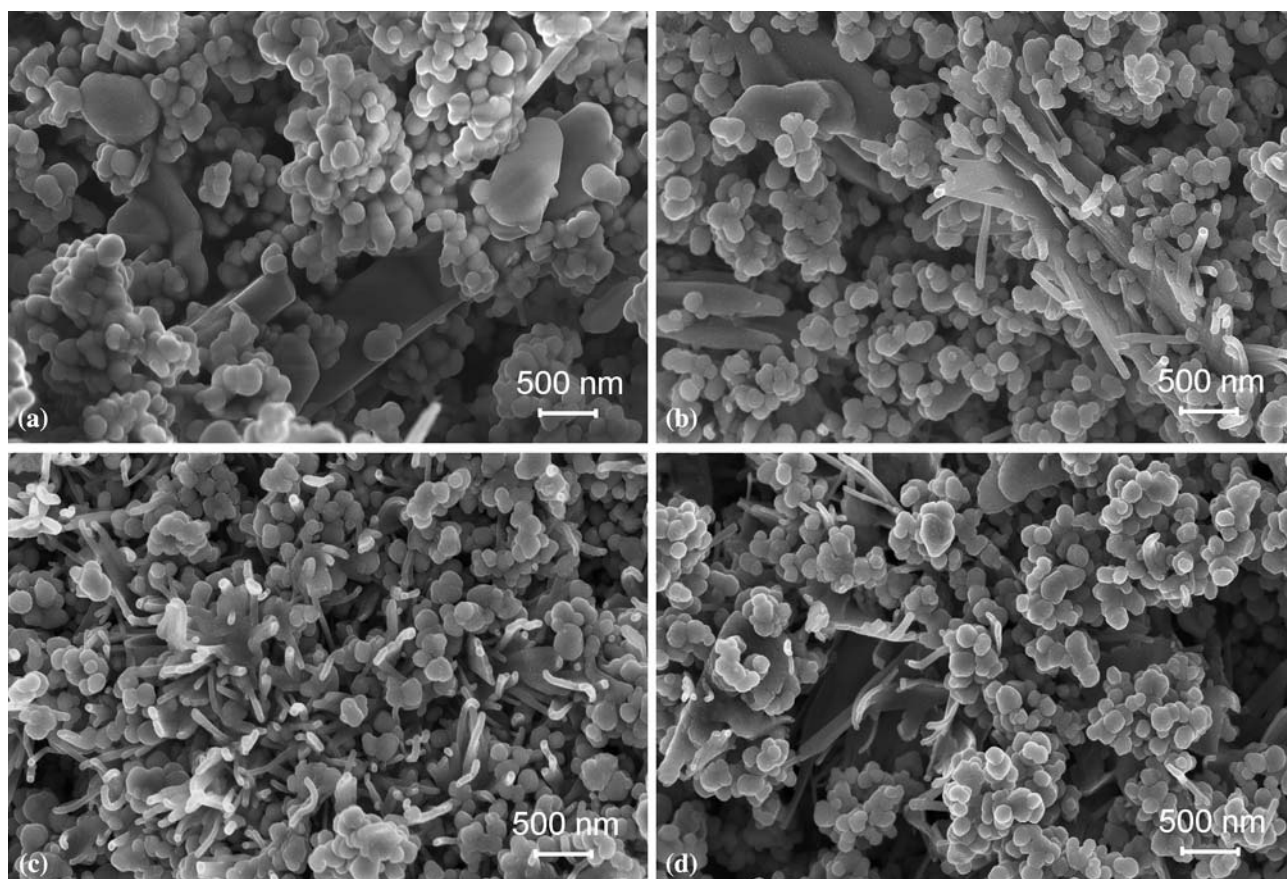When a catalyst system is formed the first heat treatment takes place in air at around 500 °C. This temperature is not

Fig. 4 SEM images of 90 mol% TiO$_2$-10 mol% V$_2$O$_5$ samples annealed at 500 °C under several atmospheres: (a) air; (b) C$_3$H$_8$: O$_2$: Ne; (c) C$_3$H$_8$: Ne; (d) CO
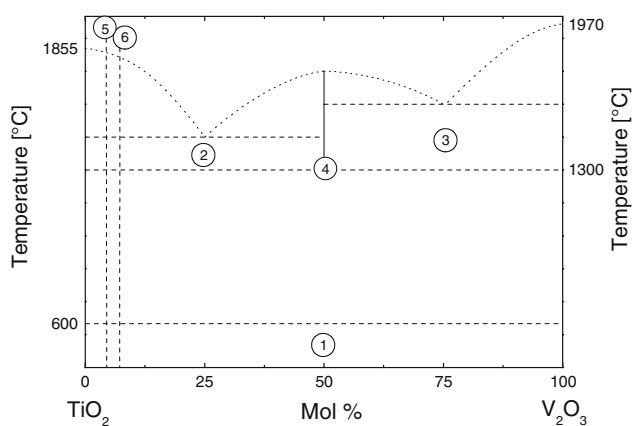
Fig. 5 Phase diagram of the system TiO$_2$-V$_2$O$_5$ (V$_2$O$_3$) under reducing conditions: (1) Anatase (TiO$_2$) + Karelianite (V$_2$O$_3$); (2) TiO$_2$ + V$_2$TiO$_5$; (3) V$_2$TiO$_5$ + V$_2$O$_3$; (4) V$_2$TiO$_5$ (Berdesinskiite); (5) V$_2$Ti$_7$O$_{17}$; (6) V$_2$Ti$_3$O$_9$ (Schreyerite)

yet high enough to enable the Rutile-(ss) formation which starts between 525 and 550 °C.[23] In service much lower oxygen partial pressure than in during formation occurs and the vanadium ion reduces to its trivalent state. This reaction

needs the release of oxygen. As shown above, the titania remains generally unchanged with respect to the X-ray results. Thus the overall reaction of a titania-vanadia couple going from the oxidizing (processed under 525 °C) to the reducing condition may be seen as:

$$\text{support} \quad TiO_2 \ \rightarrow TiO_2$$

$$\text{active compound} \quad V_2O_5 \ \rightarrow \ V_2O_3 \ + \ O_2$$
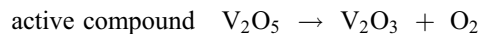
i.e., for the low temperature regime no interactions between support and active compound occur. For higher temperature the formation of the Rutile-(ss) takes place, which decomposes under reducing conditions (cf. Table 1).

From the standpoint of crystal chemistry two questions have to be discussed:

What is the crystal chemistry of the Rutile solid solution?

Various investigations have shown a simple solid state reaction without weight change or change in chemistry. Hence, associated XPS measurements of Hess et al.[23] showed a basically unchanged state of valence of the vanadium ion slightly under 5 for the starting mixture as well as the reacted Rutile-(ss). The solid solution of TiO$_2$ with V$_2$O$_5$ takes place without change in valency, chemistry and weight. The difference in charge of the dopand V^{5+} to

the host Ti^{4+} can be compensated by either introducing interstitial oxygen ions or by introducing cation vacancies. Since Rutile is a generally ionic structure interstitial oxygen ions are very unlikely. An XRD investigation by Tovar et al. conducted a Rietveld refinement showed that the Ti sites are not fully occupied (to be published). Thus the defect model shows a substitution of Ti^{4+} ions by higher valent V^{5+} ions which causes a number of cation vacancies. The anionic sublattice is fully occupied.

Why is there no alloying of TiO_2 with V_2O_3?

Considering the size of the ionic radii as given by Shannon and Prewitt[25] the V^{3+} ion shows a much larger ion radius as compared to V^{5+} and Ti^{4+}. Therefore the excessive mismatch is supposed to be the major reason for non-miscibility.

This finding is quite different from the alloying behavior of zirconia. The literature reports about a number of possible dopands, e.g., yttria and magnesia, which all are showing a lower or equal charge than 4^+.[26,27] Hence, for zirconia no alloying with quinquevalent oxide is observed (no reaction with vanadium-, niobium- or tantalum-pentoxide), unless a previous doping with a metal oxide of lower charge has created oxygen vacancies. However, the Rutile and the Fluoride structures are following different rules. The work of M. Lerch (priv. comm.) also underlined that anionic vacancies are not typical for either Rutile or Anatase.

4. Summary

- The investigation for oxidizing conditions showed a eutectic reaction for high vanadia concentrations (95 mol% V_2O_5, 631 °C). For higher temperatures the presence of a melt solution has to be recognized which enhances the reactions and leads to significant grain growth.
- The eutectic melt does neither form a perlite-like structure nor an amorphous phase. Instead direct crystallization of the mixed melt to a solid solution in the Shcherbinaite structure was observed.
- The transformation of Anatase with lower amounts of V_2O_5 to form a Rutile solid solution occurred with only small DTA signals. Since Anatase is a metastable structure no significant ΔH at a specific temperature was found. Instead the reaction proceeds continuously on heating. The ΔT signal was very small but the specimens were through a transformation.
- The phase field of the Rutile-(ss) starts at temperatures above 525 °C and a composition of approximately 4 mol% of V_2O_5. The large extension was observed at the eutectic temperature and reaches more than 10 mol%.
- For reducing conditions the V_2O_5 modification is not stable. Instead a reduction to form V_2O_3 was found. However, this experiment did not show any tetravalent vanadium species.
- The system TiO_2-V_2O_3 is characterized by an entire miscibility gap at low temperatures.

- For the temperatures of interest for catalysis this miscibility gap indicates a separation between active compound and support.
- The analogy to the Al_2O_3-TiO_2 and the Al_2O_3-SiO_2 system suggested the presence of a $Me^{3+}_2Me^{4+}_1O_5$-type intermediate phase (aluminum-titanate, aluminum-silicate), which however was not observed at lower temperatures.
- At higher temperatures the formation of a new phase V_2TiO_5 (Berdesinskiite) under CO was observed.

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