

# Formation of Active Sites for Selective Toluene Oxidation during Catalyst Synthesis via Solid-State Reaction of $V_2O_5$ with $TiO_2$

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Interaction of  $V_2O_5$  with  $TiO_2$  during the preparation of V/Ti-oxide catalysts via solid-state reaction has been studied by means of *in situ* FT-Raman spectroscopy, HRTEM and XPS. This interaction results in the formation of monomeric vanadia species with vanadium in tetrahedral coordination. The bridging oxygen in the V–O–Ti bond is suggested to be responsible for the catalytic activity during the partial oxidation of toluene. The formation of the monomeric vanadia species correlates with the improved catalyst performance, characterized by reaction rate and selectivity to benzaldehyde and benzoic acid. Mechanical activation by intensive grinding of  $V_2O_5/TiO_2$  mixture via ball milling was necessary for the interaction of the oxides during the calcination. The monomeric species formation was observed at a temperature as low as 523 K. The dynamics of  $V_2O_5/TiO_2$  interaction strongly depends on the presence of moisture during the calcination. In dry oxidative atmosphere, a part of the monomeric species is rapidly formed. Then, the process slows down and becomes diffusion-controlled. During the calcination in humid oxidative atmosphere, quick amorphization of bulk crystalline  $V_2O_5$  was observed followed by slow formation of the monomeric vanadia species. © 2000 Academic Press

**Key Words:** V/Ti oxide catalysts; toluene partial oxidation; *in situ* FT-Raman spectroscopy; HRTEM.

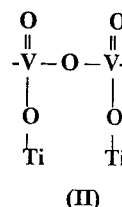
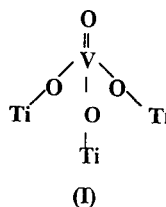
## INTRODUCTION

Vanadia/titania catalysts are widely used in selective oxidation of hydrocarbons and in selective catalytic reduction of  $NO_x$ . Dispersion of vanadia supported on  $TiO_2$  is one of the main factors controlling catalytic performance. Results of recent studies (1–4) indicate that a two-dimensional vanadia layer is the active phase in selective oxidation of hydrocarbons since it shows a higher activity and selectivity than bulk  $V_2O_5$ -crystallites. In unhydrated conditions this layer consists of different forms of  $VO_x$  species attached to the  $TiO_2$  surface (1) that can be assigned to:

- isolated monovanadate monomeric species with vanadium atom in tetrahedral coordination (I) and

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- polyvanadate polymeric species (II), which are formed at a higher loading of vanadium in the catalyst



The formation of the monomeric and polymeric species depends on the preparation method, the presence of impurities, and the conditions of catalyst pretreatment.

Among different preparation techniques a solid-state reaction of  $V_2O_5$  with  $TiO_2$ -anatase is the most attractive due to simplicity and absence of residues (5–13). The solid-state reaction includes two steps: mixing of the two oxides and calcination resulting in chemical interaction of  $V_2O_5$  with the  $TiO_2$  surface and V–O–Ti bond formation. Importance of the bridging oxygen in this bond is confirmed by a correlation between the reactivity of vanadia supported on different carriers and the appearance of the monomeric vanadia species containing this V–O–Ti bond (1). However, the mechanism and dynamics of the formation of monomeric vanadia species and the influence of mixing and calcination conditions during preparation is still not clear.

Mixing of the two oxides is usually carried out by gentle manual mixing, or by intensive grinding of  $V_2O_5/TiO_2$  mixture via ball milling. It is known that intensive grinding can result in the formation of surface defects, an increase of surface area of oxides, and can even change the ratio between different crystallographic planes (5, 6, 12). These processes affect the vanadia spreading over titania and formation of the catalytically active phases.

Calcination of  $V_2O_5/TiO_2$  mixture in oxidative atmosphere was studied earlier, but the reported results are quite contradictory. In (14, 15) no formation of vanadia species different from  $V_2O_5$ -bulk was observed in dry as well as in humid air at 673–773 K, while in (6, 8), under the same conditions, the disappearance of the bulk  $V_2O_5$  was found

and new isolated monomeric vanadia species were formed. This process was attributed to the spreading of vanadia over titania, which depends on titania crystallographic structure, atmosphere and temperature of calcination (6, 7, 11).

Our previous study on the V/Ti oxide catalysts prepared by different methods revealed an important role of the monomeric vanadia species for the selective toluene oxidation (8, 16, 17). The present study applies for the first time *in situ* FT-Raman spectroscopy for investigation of the dynamics of vanadia transformation on TiO<sub>2</sub> surface. It is important to note that FT-Raman spectroscopy is not widely used for catalytic *in situ* studies, in spite of an advantage of this technique compared to conventional Raman spectroscopy. Sample fluorescence, which may complicate the measurements, is strongly decreased because a Nd-YAG laser is used in a FT-Raman spectrometer instead of an Ar-laser in a conventional spectrometer (18–20).

In this work, the nature of vanadia species is correlated to the catalyst performance in selective toluene oxidation. The effect of grinding and the presence of water vapor during calcination on the formation of the monomeric species containing the V–O–Ti bond are considered. The catalysts are also characterized by HRTEM, XPS, and XRD techniques.

## EXPERIMENTAL

### 2.1. Catalyst Preparation

TiO<sub>2</sub> oxide (Alfa, 99.9%) with a BET specific surface area of 49 m<sup>2</sup>/g was used as a support. According to the HRTEM study titania particles are spheres of 10–100 nm with the average size about 20 nm. XRD finds a ratio of anatase to rutile phase in the support at about 89 : 11.

Catalysts containing 18.6, 8.3, and 2.4 wt% V are prepared by mixing and grinding of V<sub>2</sub>O<sub>5</sub> (>99.6%, Aldrich) with TiO<sub>2</sub> in an agate mortar via a centrifugal ball mill (Fritsch) for 90 min with a periodical manual mixing. It is known that the presence of potassium or phosphorous elements as impurities can strongly change the properties of the V/Ti oxide catalysts (1, 2). XPS analysis did not show the presence of these elements on the catalyst surface. For comparison, other samples containing 8.3 and 2.4 wt% V were prepared by manual mixing of V<sub>2</sub>O<sub>5</sub> with TiO<sub>2</sub> without grinding and ball milling. In addition, a sample (8.3 wt% V) was prepared by careful manual mixing of V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> previously ball milled separately.

Solid-state reaction (chemical interaction of vanadia with titania) is known to take place at temperatures higher than the Tammann temperature (482 K for V<sub>2</sub>O<sub>5</sub> (5)) due to the mobility of ions in an oxide lattice (5, 6). The temperatures higher than 773 K should be avoided because of the transformation of the anatase to rutile promoted by the incorporation of vanadium cations into the crystallographic structure of titania and the formation of V<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> (2, 7, 21).

Thus, calcination of the samples in humid air was carried out for 11 h at 723 K and then for 34 h at 773 K. Humid air is defined by ambient atmosphere containing usually 2.5 kPa of water vapor. The calcination in dry oxidative atmosphere (20% O<sub>2</sub> in Ar) was performed at 673 K directly in the cell of Raman spectrometer. The gaseous Ar (99.998%) and O<sub>2</sub> (99.995%) were used as received from Carbagas (Switzerland) without purification. The BET specific surface area of the catalysts after the calcination were found to be 27 m<sup>2</sup>/g (8.3 wt% V) and 35 m<sup>2</sup>/g (2.4 wt% V).

### 2.2. Experimental Setup and Procedure

The experimental setup used for the kinetic studies has been described recently (8). The catalytic activity was measured in a plug-flow reactor. The tip of a thermocouple was inserted into the middle of the catalyst bed. Toluene (Fluka, ≥99.5%) was introduced into a hot evaporator by a syringe pump. Products in the reactor outlet were analyzed by gas chromatography and mass spectrometry. The same setup was attached to the *in situ* cell of the Raman spectrometer.

Before the reaction, the catalysts were pretreated in dry oxidative atmosphere (20 vol% O<sub>2</sub> in Ar) at 673 K during 0.5 h. The temperature was then decreased to 503 K and the flow was switched from the oxidative to the reaction mixture containing 2 vol% of toluene with 40 vol% of O<sub>2</sub> in Ar. The temperature was increased stepwise and the gas composition was determined at 503, 523, 553, and 583 K. Conversions of toluene in the whole temperature region were below 13%. At the highest conversion, the products found in the reactor outlet were benzaldehyde (BA), benzoic acid (BAc), maleic anhydride (MA), and CO<sub>x</sub> with the carbon mass balance within 100 ± 4%. The only other products identified in trace concentration were phenol, benzoquinone, and hydroquinone, which were not considered for the calculation of the conversion and selectivity.

The loading of the catalyst and the gas flow were maintained constant through the study at 0.2 g and 1 ml (STP)/s, respectively. The catalyst was diluted with quartz powder in a 1 : 1 ratio during reactor operations in kinetics studies.

### 2.3. Catalyst Characterization

The Raman spectra of the samples were recorded on a Perkin–Elmer 2000 NIR FT-Raman spectrometer with a thermal background filter. Nd-YAG laser, operating at 1064 nm with a varying power in the 10–710 mW range was used. Normally, 64 scans were averaged with a resolution of 4 cm<sup>-1</sup>. The measurement time for one scan was 11 s.

To perform *in situ* Raman measurements a special aluminum furnace was constructed (Portmann Instruments AG, Switzerland), provided with a quartz tube (8 mm external diameter, 130 mm length), where catalyst grains (0.45–1 mm) were placed. The furnace is thermally isolated and a

small hole from one side allows access of the laser beam to the catalyst. The beam passed perpendicularly to the axis of the quartz tube. The tip of the thermocouple is placed near the tube. After catalyst calcination in dry oxidative atmosphere (20 vol% O<sub>2</sub> in Ar, flow 1 ml/s) at 673 K, the catalyst was cooled in the same gas mixture down to 523 K for recording the spectrum.

Raman measurements were performed also in humid air. After calcination in air the catalyst was cooled to room temperature and placed into a Perkin–Elmer powder cell to take the spectra. The laser beam heats the surface to appreciable temperatures, leading to partial removal of adsorbed water from the catalyst (1, 10). Therefore, the influence of the laser power on the surface species has been studied. It was shown that the power of the laser beam does not affect the ratio of the V=O stretching band at 994 cm<sup>-1</sup> of bulk V<sub>2</sub>O<sub>5</sub> to the Ti–O stretching band at 634 cm<sup>-1</sup> of bulk titania.

The intensity of the 1033 cm<sup>-1</sup> band of the isolated monomeric vanadia species, increases with the laser power due to water desorption and reaches a saturation. In the presence of water these monomeric species could be transformed to the decavanadate species (V<sub>10</sub>O<sub>28</sub><sup>6-</sup>) with a weak characteristic band at 985–990 cm<sup>-1</sup> (7, 10). However, in the present study the sensitivity to the decavanadate species is not high enough for detection and the contribution of the hydrated species to the band at 994 cm<sup>-1</sup> can be neglected. The saturation indicates that weakly adsorbed water can be removed from the catalyst surface exposed to the laser beam within the measurement time (12 min). Therefore, the spectra in humid air were always taken at a power corresponding to the saturation. Ball milling of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> resulted in an optimal mixing of the oxides, which was con-

firmed by the linear dependence of the 994 cm<sup>-1</sup>/634 cm<sup>-1</sup> bands ratio on the weight ratio of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (8).

The investigations of surface morphology by HRTEM were carried out via transmission electron microscopes HF-2000 and JEM-2010 (maximum resolution of lines is 0.14 nm, accelerating voltage 200 kV for both). The former microscope was equipped with a Slow Scan Gatan CCD camera (1024 × 1024 pixels) able to take images at a weak intensity and minimizing the damage of the sample in the electron beam. The method of selected area diffraction (SAD) with up to 0.1 μm localization of the microdiffraction field was also used. The samples for the TEM measurements were prepared by supporting the suspension of the catalyst in ethanol on carbon films.

XPS measurements were performed in a PHI 5500 ESCA system (Perkin–Elmer) with the monochromated AlKα photon source (1486.6 eV). Spectra were calibrated against C<sub>1s</sub> 285.0 eV line. X-ray diffraction (XRD) patterns of powdered catalysts were carried out on a Siemens D5000 (θ/2θ) diffractometer with CuKα monochromatic radiation.

## RESULTS

### Catalytic Activity and Selectivity

Pure titania shows a poor activity and selectivity during toluene partial oxidation not leading to benzoic acid (BAc) and maleic anhydride (MA) formation. The toluene conversion of 1% and selectivity toward benzaldehyde (BA) of 30% was reached at 583 K. Catalytic properties of the ball-milled uncalcined and calcined V/Ti oxides at different temperatures are presented in Fig. 1. The rate of toluene oxidation over the uncalcined 2.4 wt% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>

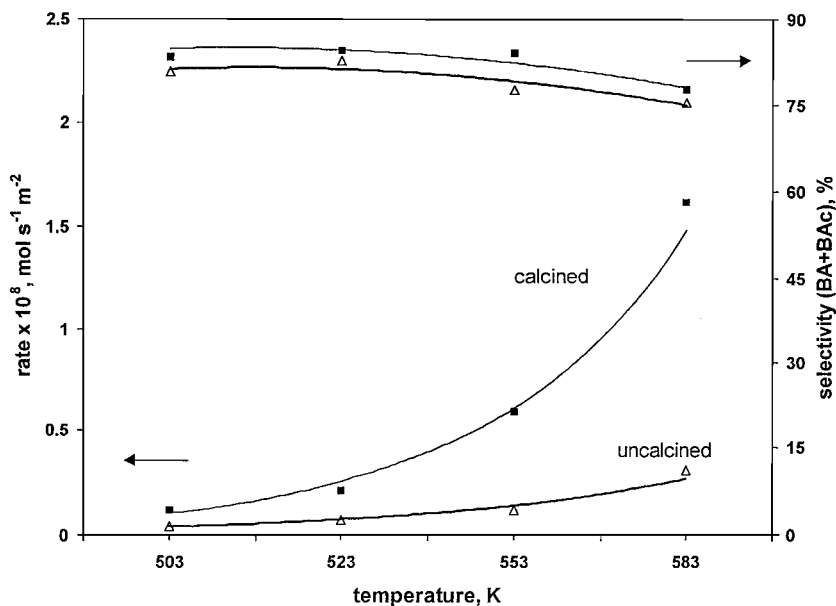


FIG. 1. Dependence of the rate of toluene oxidation and total selectivity to benzaldehyde and benzoic acid on the temperature for the calcined and uncalcined ball-milled 2.4 wt% V/TiO<sub>2</sub> catalysts (0.2 g) (2% toluene/40% O<sub>2</sub>/58% Ar, 1 ml (STP)/s).

catalyst in the whole temperature range is lower than over the calcined catalyst. The calcination in humid air leads to a 3–5 increase of the toluene oxidation rate. But the total selectivity ( $S_{(BA+BAc)}$ ) is almost not affected (Fig. 1). However, the ratio between the selectivities to BA and BAc is changed due to a higher conversion level in agreement with the mechanism reported previously (8). All catalysts, including the uncalcined one, were pretreated in oxidative dry atmosphere at 673 K for 30 min before reaction. During this pretreatment, interaction of vanadia with titania can take place leading to partial formation of active sites. The similar values for the selectivity toward BA and BAc over calcined and uncalcined catalysts, accompanied by an increase of the activity suggest that the amount, but not the nature of active sites change during the longer calcination time. Raman spectroscopy of the catalyst surface was performed to support this conclusion.

### Raman Spectroscopy Study

Spectrum of the uncalcined  $V_2O_5/TiO_2$  mixture after the ball milling is presented in Fig. 2a. The bands corresponding to the bulk  $V_2O_5$  (994, 694  $cm^{-1}$ ) and bulk  $TiO_2$  (634  $cm^{-1}$ ) are seen together with a much weaker band at 1020–1033  $cm^{-1}$ , corresponding to the isolated monomeric species. This band becomes more intensive after 42 h of calcination in oxidative dry atmosphere at 673 K (Fig. 2b) accompanied by a decrease of the band intensity at 994  $cm^{-1}$  corresponding to the bulk  $V_2O_5$ . A significant decrease

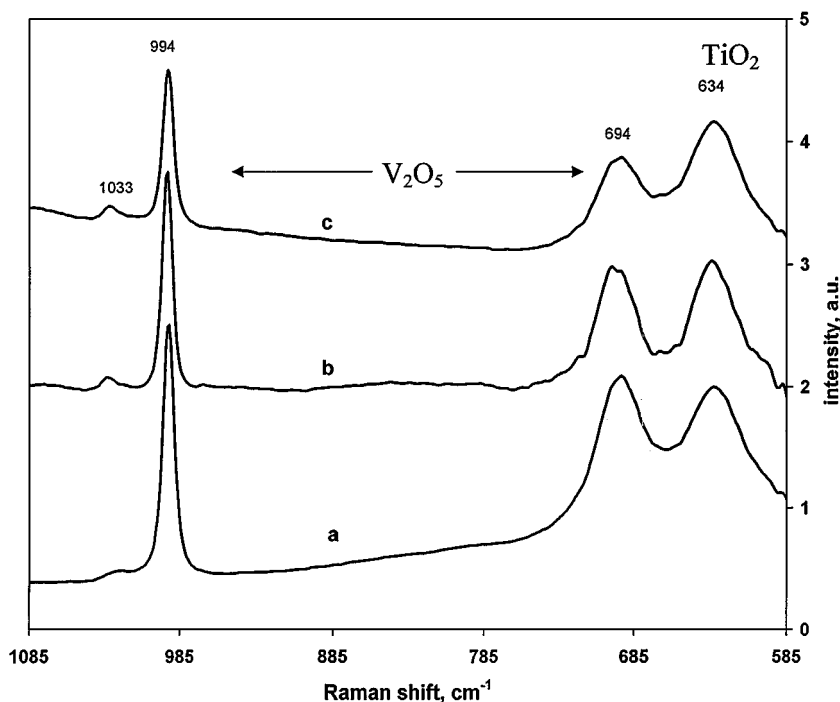


FIG. 2. FT-Raman spectra *in situ* of the ball-milled  $V_2O_5/TiO_2$  mixture (8.3 wt% V/ $TiO_2$ ) after 10 min in the dry  $O_2/Ar$  mixture at (a) 523 K, after (a) and 42 h of calcination in the dry  $O_2/Ar$  mixture at (b) 673 K, after (b) and 3 h calcination in humid air at (c) 673 K. All measurements are performed in the dry  $O_2/Ar$  mixture at 523 K.

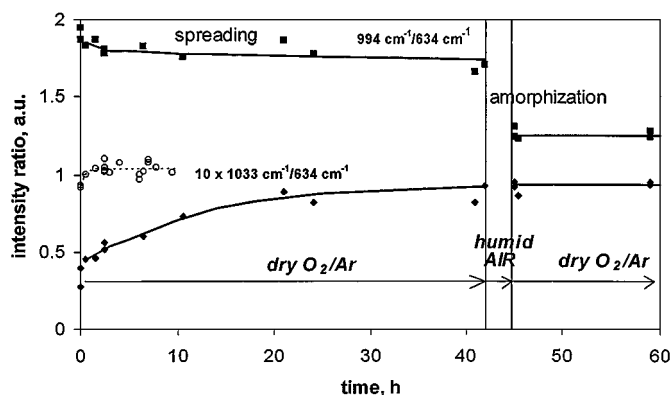


FIG. 3. Dynamics of the vanadia species transformation during the calcination of the ball-milled  $V_2O_5/TiO_2$  mixtures (8.3 wt% V/ $TiO_2$  (solid lines), 18.6 wt% V/ $TiO_2$  (dashed line)) in the dry  $O_2/Ar$  mixture (42 h), humid air (42–45 h) and the dry  $O_2/Ar$  mixture (45–58 h) at 673 K. Raman spectra are obtained *in situ* in the dry  $O_2/Ar$  mixture at 523 K.

in intensity of the  $V_2O_5$  bands (994, 694  $cm^{-1}$ ) without a change of the intensity of the monomeric vanadia species (1033  $cm^{-1}$ ) and titania (634  $cm^{-1}$ ), was observed after consecutive catalyst calcination for 3 h at 673 K in humid air (Fig. 2c). Polymeric vanadia species (region 920–940  $cm^{-1}$ ) were not observed in the spectra.

### Dynamics of Vanadia Species Transformation

It is seen in Fig. 3 (solid lines) that a part of the monomeric species (1033  $cm^{-1}$ ) is formed rapidly on the 8.3 wt%

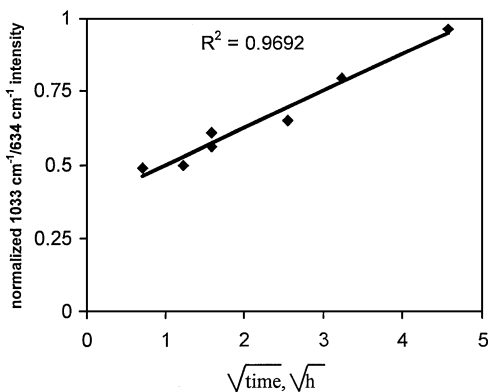


FIG. 4. Normalized intensity ratio of  $1033\text{ cm}^{-1}$  (monomeric species) to  $634\text{ cm}^{-1}$  (titania) bands on the square root of calcination time for the ball-milled 8.3 wt% V/TiO<sub>2</sub> catalyst. Conditions of the calcination and measurement are the same as described in the Fig. 3 legend.

V/TiO<sub>2</sub> catalyst during first 0.5 h of calcination in dry oxidative atmosphere and then the process slows down. Linear dependence of the normalized  $1033\text{ cm}^{-1}/634\text{ cm}^{-1}$  intensity on the square root of time (Fig. 4) suggests a diffusion-controlled formation of the monomeric species. This process is accompanied by a small decrease of the intensity of the  $994\text{ cm}^{-1}$  band.

Consecutive calcination in humid air for 3 h did not influence the concentration of the monomeric species. The concentration of the crystallite bulk V<sub>2</sub>O<sub>5</sub> decreased, indicating its transformation into another form. Since no new bands appeared during calcination in humid air, amorphization of V<sub>2</sub>O<sub>5</sub> crystalline phase promoted by water vapor can be suggested. The amorphization seems to be irreversible since no change of the intensities of all bands took place upon consecutive calcination in dry air for 13 h.

Increasing V<sub>2</sub>O<sub>5</sub> concentration by a factor of 2.2 in the oxide mixture increases the rate of the monomeric species formation (Fig. 3, dashed line). Achievement of the saturation in the monomeric species takes place within 0.5–1 h for the 18.6 wt% V catalyst compared to 25–40 h for the 8.3 wt% V catalyst. However, approximately the same saturation concentration is reached for the both catalysts independently of the pretreatment in humid air at 673 K.

Figure 5 (solid lines) shows a plot of the intensities of the 994 and  $1033\text{ cm}^{-1}$  bands as a function of time of calcination in humid air. It is seen that the intensity of the band  $994\text{ cm}^{-1}$  (V<sub>2</sub>O<sub>5</sub>) decreases strongly during the first 3 h of calcination. Formation of the monomeric species as well as other new species does not accompany this process. The formation of the monomeric species is a slow process (Fig. 5). In accordance with the Raman *in situ* results (Fig. 3) the disappearance of V<sub>2</sub>O<sub>5</sub> during the calcination in humid air can be ascribed to the amorphization of V<sub>2</sub>O<sub>5</sub>, which is promoted by water vapor.

### Effect of Oxides Mixture Grinding

To study an effect of grinding on the formation of vanadia surface species, a mixture of V<sub>2</sub>O<sub>5</sub> with TiO<sub>2</sub> (2.4 and 8.3 wt% V) without ball milling was calcined in humid air for 6 h at 723 K, followed by 15 h at 773 K and then for 20.5 h in the dry O<sub>2</sub>/Ar flow at 673 K *in situ* in the Raman cell. Raman spectra were taken after different periods of calcination. No formation of the monomeric and/or polymeric species was observed. Only peaks corresponding to the V=O bond of bulk V<sub>2</sub>O<sub>5</sub> and to the Ti–O bond of TiO<sub>2</sub> were found. Therefore, grinding seems necessary for the chemical interaction of oxides during the calcination resulting in the formation of the monomeric species. No conclusion concerning amorphization of V<sub>2</sub>O<sub>5</sub> during calcination is possible, because an intimate mixing of these two oxides, necessary for the reliable Raman measurements, is doubtful.

Very slow interaction of the two oxides during the calcination was observed in the sample (8.3 wt% V) prepared by careful mixing of V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> ball milled separately. It is seen in Fig. 5 (dashed line) that the interaction with the formation of the monomeric species proceeds at least with one order lower rate than in the case of the oxide mixture ball milled simultaneously (Fig. 5, solid line). *In situ* Raman measurements were performed to prove that the low concentration of the monomeric species is not due to the presence of water vapor during measurement and calcination. The concentration of the monomeric species did not change after several hours of the calcination in the dry oxidative atmosphere at 673 K.

### XRD and XPS Studies

Uncalcined and calcined catalysts were studied by XRD and XPS methods. XRD measurements showed three

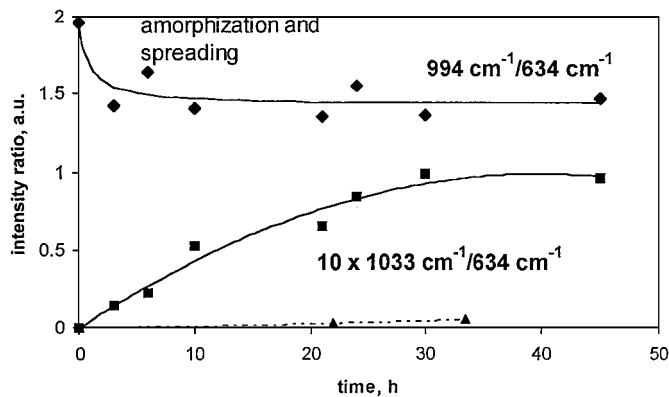


FIG. 5. Dynamics of the vanadia species transformation during the calcination (humid air for 11 h at 723 K and 34 h at 773 K) of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> mixtures (8.3 wt% V/TiO<sub>2</sub>) after simultaneous ball milling of the two phases (solid lines) and separate ball milling and careful mixing of the two phases (dashed line). Measurements are performed in humid air.

TABLE 1

**Binding Energies (BE) for  $V2p_{3/2}$  and Surface Atomic Percentage of Vanadium in the Bulk  $V_2O_5$  and in the Ball-Milled 8.3 wt% V/TiO<sub>2</sub> Catalyst after Different Calcination Times in Humid Air**

Catalyst	Calcination time, h	BE $V2p_{3/2}$ , eV	V/(V + Ti), atomic surface ratio, %
$V_2O_5$	0	517.1	100
8.3 wt% V/TiO <sub>2</sub>	0	517.7	19.2
8.3 wt% V/TiO <sub>2</sub>	1	517.4	18.8
8.3 wt% V/TiO <sub>2</sub>	45	517.6	22.8

crystallographic phases in the uncalcined mixture:  $V_2O_5$ , TiO<sub>2</sub> (anatase) and TiO<sub>2</sub> (rutile). Calcination did not lead to the formation of new phases or to changes in the rutile/anatase ratio.

XPS measurements showed the presence of vanadium, titanium, oxygen, and carbon as the main elements on the catalyst surface. Calcination did not change the position of the  $V2p_{3/2}$  peak maximum (Table 1) corresponding to the  $V^{5+}$ -state. The V atomic surface concentration was the same before and after calcination for 1 h. A 20% increase of the V atomic surface concentration due to the vanadia spreading over titania took place after 45 h of calcination in humid air. This increase should be assigned to the formation of the isolated monomeric species as detected by Raman spectroscopy (Fig. 5, solid line).

#### HRTEM Studies

Characteristic platelates of  $V_2O_5$  and round-shaped particles of titania are observed by HRTEM for the uncalcined 8.3 wt% V/TiO<sub>2</sub> catalyst after intensive ball milling. The sur-

face of TiO<sub>2</sub> does not contain any layers and/or small vanadia particles. After the calcination in humid air except of the platelates of  $V_2O_5$ , some small particles of  $V_2O_5$  are observed on the titania surface (Fig. 6). Moreover, a thin layer (<2 nm) with a disordered structure is seen (electron beam of low intensity was applied). It is not clear if this is a vanadia thin layer or a contamination layer, which may be formed inside the electron microscope. It is known that a reduction of the  $V_2O_5$  phase under the electron beam of high energy in vacuum takes place (22, 23). To identify the nature of the thin layer on the titania surface a HRTEM study at the electron beam of high energy (200 kV) was performed and compared with the behavior of the  $V_2O_5$  particle surface.

It is seen in Fig. 7 that under the influence of electron beam of high intensity (200 kV) a crystallization of the disordered thin layer takes place with the formation of a new phase with the lattice parameters of about 0.2 nm. It is assigned to the tetragonal vanadia phase ( $VO_2(T)$ ) with the lattice parameters of  $a = b = 1.19$  nm,  $c = 0.768$  nm, and  $d(600) = 0.192$  nm (24). Planes of (200) of the anatase and (060) of the thin  $VO_2(T)$  layer are parallel to each other (Fig. 7), indicating an epitaxial interaction of  $VO_2(T)$  with the anatase. This layer is not observed on some places of the anatase surface. Moreover, its thickness does not depend on the crystallographic orientation of the anatase planes.

Platelates of  $V_2O_5$  with the dimensions of 100–1000 nm have a perfect structure with characteristic lattice parameters of 0.58, 0.44, and 0.34 nm (25). No layers were found on the  $V_2O_5$  surface by HRTEM at low intensity of the electron beam. However, under the electron beam of 200 kV a thin crystalline layer (less than 2 nm) is observed (Fig. 8). The structure of this layer is close to that of tetragonal vanadia— $VO_2(T)$  (24). The layer is formed on the (100)

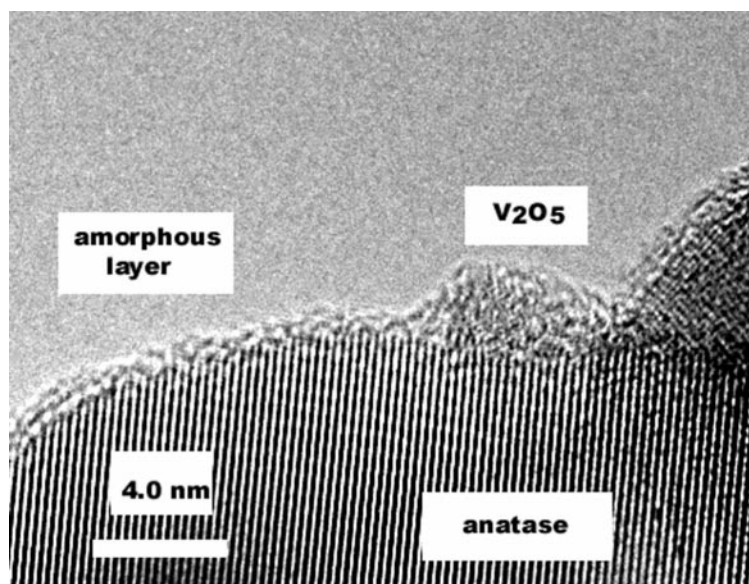


FIG. 6. HRTEM image of the ball-milled 8.3 wt% V/TiO<sub>2</sub> catalyst after the calcination in the conditions described in the Fig. 5 legend.

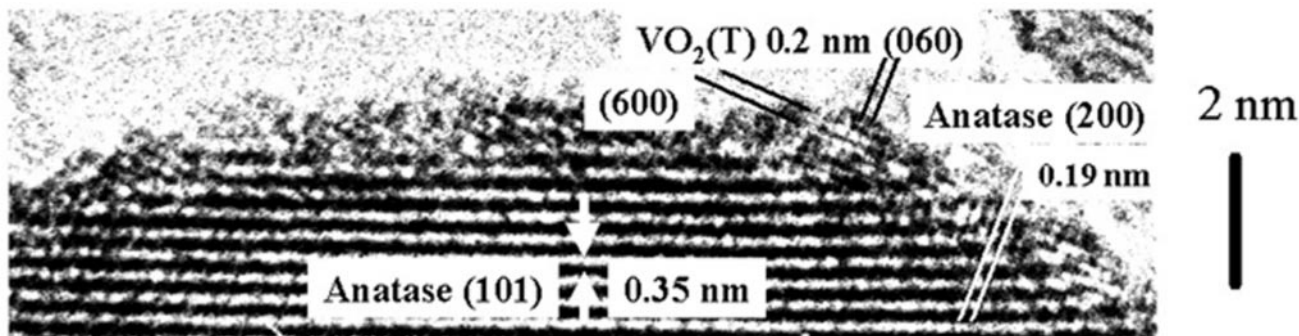


FIG. 7. HRTEM image of the ball-milled 8.3 wt% V/TiO<sub>2</sub> catalyst after the calcination in the conditions described in the Fig. 5 legend.

plane of V<sub>2</sub>O<sub>5</sub> in a way that the planes with close lattice parameters (020) of V<sub>2</sub>O<sub>5</sub> and (060) of VO<sub>2</sub>(T) are stacked. Thus, the same surface phase of VO<sub>2</sub>(T) is formed on the surface of the bulk V<sub>2</sub>O<sub>5</sub> and in the thin amorphous layer on the V/Ti oxide catalyst under the influence of the electron beam of high intensity. This study proves that the thin layer that is observed on the TiO<sub>2</sub> surface has to be assigned to amorphous V<sub>2</sub>O<sub>5</sub>, but not to a contamination.

Therefore, the electron microscopy data suggest that no interaction of vanadia with titania takes place without thermal treatment even after intensive grinding of the oxide mixture. After the calcination in humid air a thin amorphous layer of vanadia was found on the surface of TiO<sub>2</sub>. This thin layer can be the result of partial amorphization of crystalline V<sub>2</sub>O<sub>5</sub> promoted by water and temperature induced spreading of amorphous V<sub>2</sub>O<sub>5</sub> over titania.

## DISCUSSION

The results of Raman spectroscopy showed that the monomeric species are formed during the calcination of

the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> at 673–773 K only after intensive grinding of the oxide mixture. The interaction is almost absent when the oxides are ball milled separately and mixed. This result excludes the gas-phase transport of the intermediates from the vanadia surface to the titania one. Important factors facilitating the interaction are due to the increased interface area between V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> and, probably, their mechanical activation during ball milling leading to defects formation (5, 7). In spite of the fact that the surface defects were not found by HRTEM, the activation of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> mixture can be suggested from the Raman data. Fast formation of the monomeric species was observed in dry atmosphere even at the temperature as low as 523 K. This temperature is only slightly higher than the Tammann temperature of bulk V<sub>2</sub>O<sub>5</sub>. The difference in mixing procedure is probably a reason for the contradictory results reported in the literature concerning the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> interaction (6, 8, 14, 15). Hence, the *intensive* grinding is a necessary step during the preparation of the V/Ti oxide catalysts by solid-state reaction.

The calcination of the ball-milled mixtures in oxidative dry atmosphere was found to consist of two processes. The first process is a fast and the second is a slower diffusion-controlled formation of the monomeric species (Fig. 4). The similar dynamics of the bulk V<sub>2</sub>O<sub>5</sub> disappearance in dry atmosphere was earlier observed by XRD (6). The fast initial process was explained by amorphization of bulk V<sub>2</sub>O<sub>5</sub>. The diffusion-controlled process was assigned to diffusion of defects (vacancy type) through the vanadia monolayer and their subsequent refilling with fresh vanadium ions at the interface between the monolayer and the amorphous V<sub>2</sub>O<sub>5</sub>. The present Raman study does not confirm amorphization of V<sub>2</sub>O<sub>5</sub> in dry conditions.

In contrast, fast amorphization of crystalline bulk V<sub>2</sub>O<sub>5</sub> takes place in the presence of water vapor. Simultaneous formation of the thin layer of V<sub>2</sub>O<sub>5</sub> with a disordered structure was observed (Fig. 6). Similar vanadia layers have been earlier found by HRTEM on the surface of the catalysts prepared by impregnation (21, 23). Our data from XPS (Table 1) and Raman spectroscopy (Fig. 3, after 45 h) indicate that the thin amorphous layer of V<sub>2</sub>O<sub>5</sub> does not cover a large surface of the TiO<sub>2</sub>.

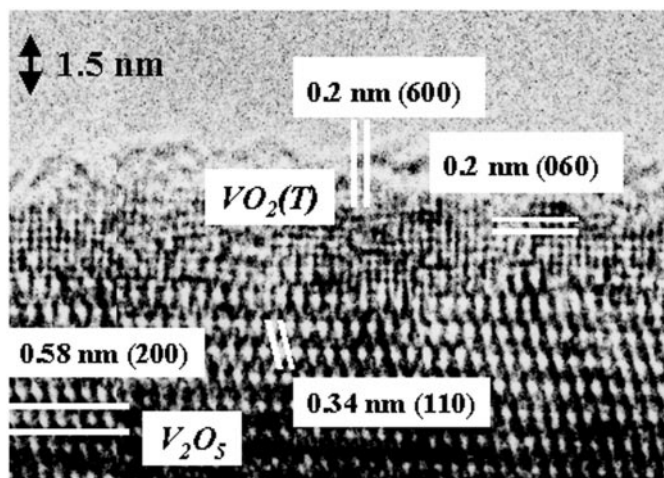


FIG. 8. HRTEM image of the V<sub>2</sub>O<sub>5</sub> region of the ball-milled 8.3 wt% V/TiO<sub>2</sub> catalyst after the calcination in the conditions described in the Fig. 5 legend.

The effect of water on the surface vanadia species transformation was observed earlier (7, 10). The monomeric vanadia species were found to transform reversibly into the species with the structure close to the polymeric (decavanadate) species. After the interaction of the humid atmosphere with the catalyst the consecutive calcination in dry atmosphere even for 13 h does not result in any change of the  $V_2O_5$  and monomeric species concentration (Fig. 3 after 45 h). Hence, the presence of water initiated the amorphization of bulk  $V_2O_5$ , but a reversibility of this process was not found.

Two types of hydroxyl groups are known to be present on the titania surface (26, 27). Bridging acidic hydroxyl groups can be removed from the catalyst surface at temperatures lower than isolated basic groups [27]. Desorption of water at elevated temperatures leads to the removal of weakly adsorbed acidic hydroxyl groups, resulting in the formation of basic bridging oxygen (Ti–O–Ti).

Hydrated surface of  $V_2O_5$  possesses Brønsted acidic sites of medium strength (1, 2). The reaction of water vapor with  $V_2O_5$  is known to lead to mobile and even volatile (at temperatures higher than 900 K) oxyhydroxide compounds of  $VO(OH)_3$ -type (5, 28). Thus, the hydrated acidic species on the  $V_2O_5$  surface together with basic bridging oxygen and isolated hydroxyl groups on the titania surface can be considered as intermediates in the solid-state reaction of  $V_2O_5$  with  $TiO_2$ .

Heating in dry atmosphere leads to a more favorable interaction of the hydrated vanadia with the basic bridging oxygen (Ti–O–Ti) and fast formation of the monomeric vanadia species (Fig. 9). The process of the interaction of the hydrated vanadia species with the terminal basic hydroxyl groups (Fig. 9) is slow and apparently diffusion controlled.

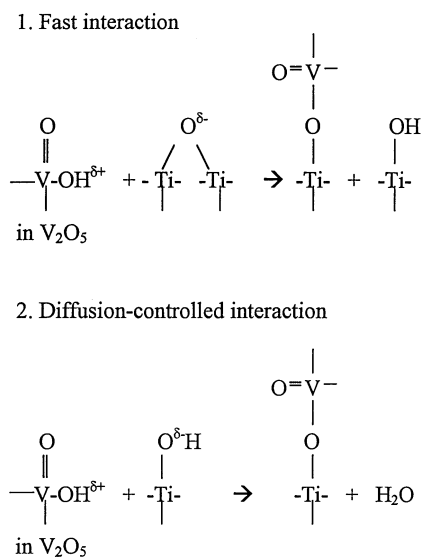


FIG. 9. Scheme of the active oxygen formation (V–O–Ti) during the calcination of the  $V_2O_5/TiO_2$  mixture.

The concentration of these groups on the titania surface is relatively low and they are located at large distances from each other. Formation of some amount of the monomeric species also could diminish the further diffusion of the hydrated species.

Heating in humid air leads to a higher concentration of the hydrated vanadia than in dry atmosphere. In contrast, the bridging oxygen (Ti–O–Ti) concentration becomes lower. Acidic hydroxyl groups, which are formed instead of the bridging oxygen sites on the titania surface decrease the mobility of the hydrated vanadia species over the titania toward more basic hydroxyl groups.

Increase of the  $V_2O_5$  concentration from 8.3 wt% up to 18.6 wt% results in an increase of the interaction rate between the two oxides, but the same saturation limit for the monomeric species concentration is valid. The effect of vanadia spreading is of importance for the catalytic reactions. After several hours under *o*-xylene oxidation conditions, the  $V_2O_5/TiO_2$  mixture reached the catalytic performance of the best catalysts prepared by impregnation or grafting (29). This confirms the conclusion that the nature of the active vanadia species does not depend strongly on the preparation technique (1). The present Raman spectra show the formation of the monomeric vanadia species of high concentration in the  $V_2O_5/TiO_2$  catalyst calcined in humid air for a long time and the monomeric vanadia species at low concentration in the case of the catalyst pretreated in dry atmosphere for a short time. Correlation between the concentration of these species and catalytic activity in the toluene oxidation takes place. Almost the same selectivity  $S_{(BA+BAc)}$  on the both catalysts indicates the same active sites in calcined and uncalcined pretreated catalysts. Taking into account the earlier consideration of the reactivity of different vanadia species (1), the activity during the toluene selective oxidation is assigned to V–O–Ti sites of the isolated monomeric vanadia species.

Hence, vanadia concentration, water vapor presence, and grinding are important for an optimization of the catalyst calcination time and activation process.

## CONCLUSIONS

1. Isolated monomeric vanadia species are formed during solid-state interaction of  $V_2O_5$  with  $TiO_2$  and are suggested to be the active sites in toluene selective oxidation.
2. Intensive grinding was found to promote solid-state interaction of  $V_2O_5$  with  $TiO_2$  and is shown to be a necessary step in the catalyst preparation.
3. The dynamics of the monomeric vanadia species formation strongly depends on the vanadia concentration and the presence of water vapor during the calcination step.
4. During the calcination in oxidative dry atmosphere a part of the monomeric species is formed quickly followed by a slower step that is diffusion controlled.



5. During the calcination in oxidative humid atmosphere amorphization of  $V_2O_5$  takes place first, resulting in the formation of the thin (<2 nm) vanadia layer with disordered structure. The amorphization process is followed by slow formation of the monomeric vanadia species.

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