

# Vanadia/titania catalysts for gas phase partial toluene oxidation Spectroscopic characterisation and transient kinetics study

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## Abstract

Formation of vanadia species during the calcination of ball milled mixture of  $V_2O_5$  with  $TiO_2$  was studied by Raman spectroscopy in situ and at ambient conditions. It is found that calcination in air leads to fast (1–3 h) spreading of vanadia over  $TiO_2$  followed by a slower process leading to the formation of a monolayer vanadia. The calcinated catalyst showed higher activity during toluene oxidation than the uncalcinated one, but the selectivity towards C<sub>7</sub>-oxygenated products (benzaldehyde and benzoic acid) remains unchanged. The activity of the catalysts is ascribed to the formation of vanadia species in the monolayer. The details of the parallel–consecutive reaction scheme of toluene oxidation are presented from steady-state and transient kinetics studies. Different oxygen species seem to participate in the deep and partial oxidation of toluene. Coke formation was observed during the reaction presenting an average composition  $C_{2n}H_{1.1n}$ . The amount of coke on the catalyst was not dependent on the calcination step and the vanadium content in the catalyst. Coke formation was seen to be responsible for the deactivation of the catalyst. ©2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Raman spectroscopy; Transient response technique; V/Ti oxide catalysts; Toluene partial oxidation

## 1. Introduction

Vanadia/titania (V/Ti) catalysts are promising materials for the selective side chain oxidation of alkyl-aromatics [1,2]. It is known that the performance of V/Ti catalysts is sensitive to the nature and coverage by vanadia species, which depend on the method of the catalyst preparation. The choice of the vanadium precursor, the temperature and time of calcination, conditions of catalyst activation and surface impurities have also been shown to be important for catalyst performance. Due to the industrial application of V/Ti catalyst in the *o*-xylene oxidation to phthalic anhydride many attempts have been made

to correlate the catalytic performance of these catalysts with their surface properties [2]. However, many questions concerning the nature of the active sites remain still open. The nature of the vanadium oxygen bond, the specific role of the terminal (V=O) and bridging (V–O–V) active sites for selective oxidation of organic compounds has been discussed intensively in literature [1–3]. No clear consensus has emerged. FT-Raman or FT-IR spectroscopy of the catalyst surface coupled with transient technique studies should provide valuable information about the catalytic cycle and the active species leading to product formation [4,5]. This knowledge seems essential for the understanding of the reaction mechanism and development of a more effective catalyst.

Catalytic toluene oxidation on vanadia/titania catalysts gives benzaldehyde and benzoic acid as the important products, however  $CO_x$  products are formed

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and their yield increases with conversion [6,7]. The kinetics of this reaction was studied previously under steady-state conditions [7–10]. Toluene interaction with the catalyst surface was investigated by FT-IR [6,11,12]. However, no results of systematical studies via transient response techniques have been reported until now in the open literature.

The present work studies the formation of different vanadia surface species during the solid state reaction of  $V_2O_5$  with  $TiO_2$  and their role in the toluene oxidation. The reaction kinetics investigation under unsteady and steady-state conditions has been carried out and the reaction scheme is proposed.

## 2. Experimental

### 2.1. Catalyst preparation

The composition of the catalysts and the preparation parameters are presented in Table 1.  $TiO_2$  support (89 wt.% anatase/11 wt.% rutile, Alfa, 99.9%) with a specific surface area of  $49 \text{ m}^2 \text{ g}^{-1}$  was used. Samples 1, 3 and 5 represent a physical mixture of  $V_2O_5$  (>99.6%, Aldrich) with  $TiO_2$  support obtained through intensive ball milling for 90 min with periodical manual mixing. Samples 2, 4 and 6 with different concentrations of vanadia were synthesised by solid state reaction [13,14]. After the ball milling of  $V_2O_5$  with  $TiO_2$  calcination in air was carried out for 11 h at 723 K and then 34 h at 773 K.

### 2.2. Experimental set-up and procedure

The kinetic studies under steady-state and transient conditions were performed in the experimental set-up presented in Fig. 1. The experimental set-up consisted of three parts: the gas supply system, the reactor and the analytical system. The gases  $O_2$  (99.995%), and Ar (99.998%) (Carba-Gas, Lausanne, Switzerland) were used without further purification. The feed was regulated through mass flow controllers. Gas mixtures (A and B) were used at a pressure of 101 kPa. Flow A contained oxygen, argon and toluene vapour. Flow B was used for the pre-treatment of the catalyst by oxygen, hydrogen or pure argon. The two gas feeds, A and B, could be interchanged from one to another by means of the Valco valves with electric actuation. Upon switching the two gas feeds, toluene reached the stationary state within 3 s in the reactor filled by quartz wool instead of the catalyst. The loading of the catalyst and the gas flow were maintained constant through the study at  $0.2 \text{ g}$  and  $1 \text{ ml s}^{-1}$  STP, respectively. The catalyst was diluted with quartz powder in a 1:1 ratio. All lines and valves were heated up to 423 K in order to avoid the condensation of the products.

A Balzers QMG-421 mass-spectrometer and a Perkin-Elmer Autosystem XL gas chromatograph were used for the gas phase analysis. Toluene and organic products were separated in a SPB-5 capillary column and analysed by a FID. As  $Ar/O_2$ ,  $CO$ ,  $CO_2$  and  $H_2O$  passed quickly through this column, they were separated in a Carboxen-1010 capillary column and analysed by a TCD. In the transient response

Table 1  
Characteristics of the studied catalysts

No.	Total V content (wt.%)	Content of V in the form of bulk $V_2O_5$ (wt.%) <sup>a</sup>	Specific surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Content of V, interacted with the support (wt.%) <sup>b</sup>	Surface concentration of V atoms interacted with the support, Monolayer <sup>c</sup>	Preparation technique
1	8.3	8.3	42	0	0	Ball milling
2	8.3	6.2	27	2.1	0.93	Ball milling, calcination
3	4.5	4.5	45	0	0	Ball milling
4	4.5	2.0	32	2.5	0.91	Ball milling, calcination
5	2.4	2.4	47	0	0	Ball milling
6	2.4	1.3	35	1.1	0.35	Ball milling, calcination

<sup>a</sup> For the samples 2, 4 and 6 determined by Raman spectroscopy.

<sup>b</sup> Determined by Raman spectroscopy.

<sup>c</sup> Monolayer is taken as equal to  $1 \times 10^{19}$  V atom  $\text{m}^{-2}$  [1].

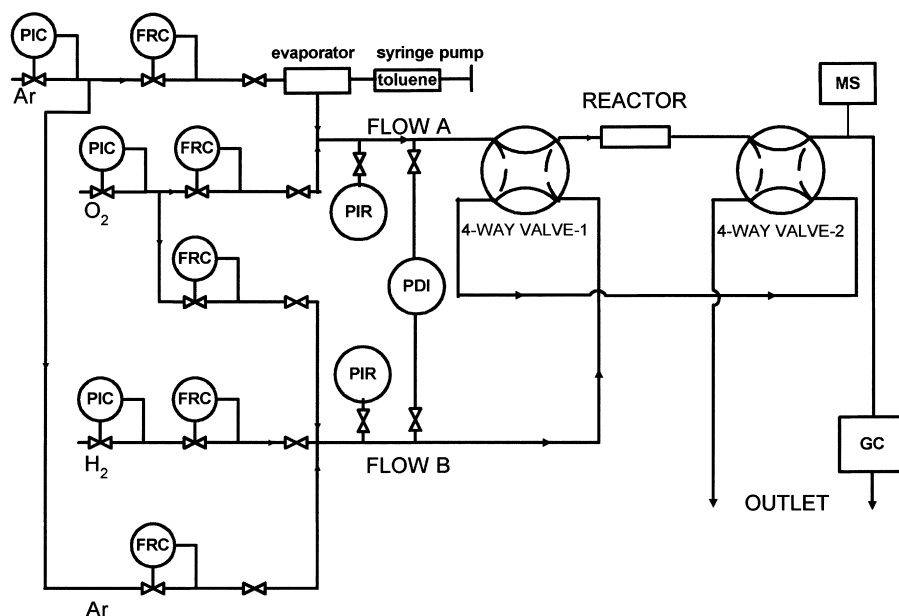


Fig. 1. Scheme of the experimental set-up for transient response and steady-state studies: PIC — pressure reducer, FRC — mass-flow controller, PIR — manometer, PDI — differential manometer, MS — mass-spectrometer, GC — gas chromatograph.

runs the mass-spectrometer was used for gas phase analysis and was calibrated by gas-chromatography technique. Calibration factors were obtained and used to assess each product concentration. Benzoic acid was determined only by gas-chromatography and its evolution was not studied in transient experiments.

All catalysts were pre-treated in  $O_2$  (20 vol.%  $O_2$ , rest Ar) at 673 K for 0.5 h (oxidised catalyst) before the reaction. The temperature afterwards was decreased as necessary and the flow was switched to the mixture of 2 vol.% toluene plus 40 vol.%  $O_2$  in Ar. To prepare a reduced catalyst the oxidised catalyst was treated by  $H_2$  (10 vol.%  $H_2$  in Ar) at 673 K for 0.5 h. The interaction of toluene (2 vol.% toluene in Ar) with the oxidised catalyst (or reduced catalyst) was also studied. In these experiments the cooling of the reactor until the necessary temperature was performed in the mixture of 20 vol.%  $O_2$  in Ar, or in 10 vol.%  $H_2$  in Ar for the oxidised and the reduced catalysts, respectively. The reactor was purged by Ar for 10 min to eliminate  $O_2$  or  $H_2$  from the gas phase before the toluene introduction.

To calculate conversion and selectivities, benzaldehyde, benzoic acid, maleic anhydride, CO and  $CO_2$  were taken into account. Phenol, benzoquinone,

hydroquinone in trace concentrations were not considered. Conversion was defined as the sum of the number of moles of toluene converted into reaction products divided by the initial number of moles of toluene. The product selectivity was calculated as the number of moles of toluene converted into the product divided by the total number of the moles of converted toluene.

### 2.3. Catalyst characterisation

The Raman spectra of the samples were recorded on a Perkin-Elmer 2000 NIR FT-Raman spectrometer with a resolution of  $4\text{ cm}^{-1}$ . A Nd-YAG laser, operating at 1064 nm with a varying power output in the range of 10–250 mW was used. As the measurements were performed in air, the question of water absorption and its influence on the surface V species should be taken into account [3,15,16]. The laser beam can heat the samples to appreciable temperatures leading to partial removal of water from the catalyst. Therefore, the influence of the laser power on the V species was studied for different catalysts. It was shown that the power of the laser beam does not influence the

ratio of the intensity of the V=O stretching band at  $994\text{ cm}^{-1}$  (characteristic for the bulk  $\text{V}_2\text{O}_5$ ) to the Ti–O stretching band at  $634\text{--}638\text{ cm}^{-1}$  for the titania. Thus, a linear dependence of this ratio on the weight ratio of  $\text{V}_2\text{O}_5$  to  $\text{TiO}_2$  in the catalyst was obtained with the correlation factor of 0.9982. The ratio of the intensities of the Raman bands  $994$  to  $634\text{--}638\text{ cm}^{-1}$  was used for the estimation of the content of V in the bulk  $\text{V}_2\text{O}_5$  and the content of V strongly interacting with the titania surface (Table 1). The latter value is equal to the difference of the  $\text{V}_2\text{O}_5$  concentration present initially in the sample and its concentration left after the calcination.

To perform in situ Raman measurements a quartz tube with the catalyst was placed into a special furnace with a small hole allowing access of the laser beam to the catalyst. After heating in the  $\text{O}_2/\text{Ar}$  mixture for a certain period of time at  $673\text{ K}$ , the catalyst was cooled to  $523\text{ K}$  and the spectrum was taken at a laser power of  $250\text{ mW}$ .

Specific surface areas of the catalysts used were determined by nitrogen adsorption ( $77.4\text{ K}$ ) employing BET method via Sorptomatic 1900 (Carlo-Erba).

For the temperature-programmed oxidation (TPO) experiments the set-up shown in Fig. 1 was used. The pre-treated sample was exposed to the reaction mixture at  $523\text{ K}$  until the steady-state was reached. Then the reaction mixture was switched to the flow of  $\text{O}_2$  and the reactor was heated with a rate of  $50\text{ K min}^{-1}$ . Effluents were continuously analysed using the quadrupole mass-spectrometer.

### 3. Results and discussion

#### 3.1. Catalytic activity and selectivity

The selectivity for different products as a function of temperature (constant flow rate) is presented in Fig. 2 (catalyst 4). The conversion changed with the temperature from 1.7 to 18%. It is seen that the selectivity to benzaldehyde (BA) drops with temperature and the selectivity to benzoic acid (BAc) passes through a maximum. The selectivity to maleic anhydride (MA) increases, when the selectivity to BAc decreases. Constant selectivity to BA and BAc at low temperatures ( $<505\text{ K}$ ) points out to a parallel route of the formation of BA and  $\text{CO}_x$  products. At higher temperatures  $\text{CO}_x$  products can be mainly formed by consecutive oxidation of BAc. The presented behaviour corresponds to the parallel–consecutive mechanism (Fig. 3) which is in line with the results reported in [10].

To make conclusions about the role of vanadium concentration on titania and influence of the calcination, the steady-state reaction rates obtained after 20 min of the toluene oxidation are compared at  $523\text{ K}$  on the catalysts 2, 4, 5, 6 and pure titania (Fig. 4). At these conditions no maleic anhydride was observed and the reaction was limited by the steps 1–3 of the parallel–consecutive scheme (Fig. 3). Conversions were low in all cases and did not exceed 6%. As it is seen from Fig. 4 the total rate of the toluene conversion on the ball milled pure titania (without V) is 3.4 times lower than the one on the uncalcinated

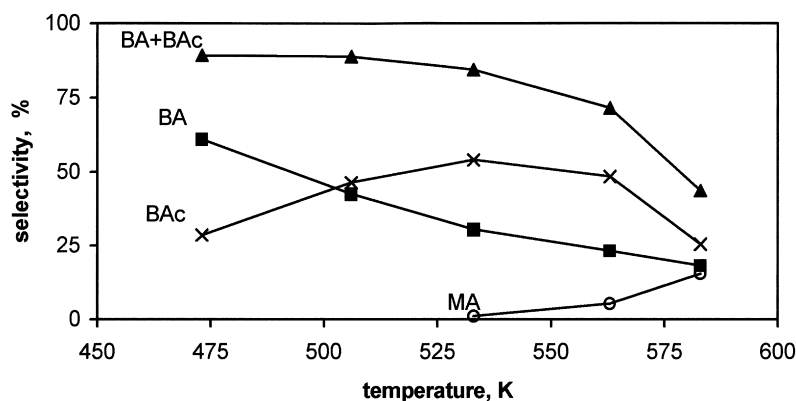


Fig. 2. Dependence of the selectivity on the temperature for the calcinated 4.5 wt.%  $\text{V/TiO}_2$  catalyst (4). BA — benzaldehyde, BAc — benzoic acid, MA — maleic anhydride.

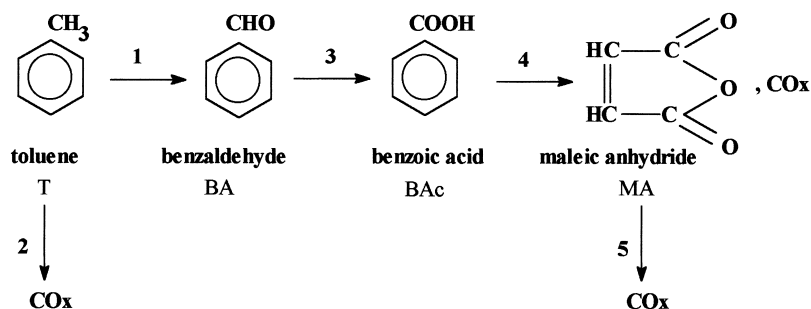


Fig. 3. Reaction network for the toluene oxidation.

catalyst 5. Only BA, CO<sub>2</sub> and H<sub>2</sub>O were observed in the products. The selectivity to BA on the titania under these conditions was close to 50%.

The selectivity towards BA and BAc reaches 85% for the catalyst 5. Calcination of this catalyst in air (catalyst 6) leads to a 2.6 times increase of the total rate. However, the selectivity keeps on the same level. The observed increase in activity may be due to higher amount of active sites. The close values of the selectivity obtained for the calcinated and noncalcinated samples at 523 K suggest that the nature of the active sites does not change strongly with calcination.

Doubling the vanadia content (sample 4) increases four times the reaction rate. The selectivity towards BA and BAc is only slightly higher. These data also indicate an increase of the total amount of active sites,

which can participate in the conversion of toluene, but not a modification in their nature. The following increase of the concentration of vanadium up to 8.3 wt.% (sample 2) does not result in the increase of the reaction rate (Fig. 4). Thus, at a certain value of V content a saturation of the concentration of the active sites is reached. The presence of the excess of bulk V<sub>2</sub>O<sub>5</sub> does not provide an increase of the amount of the active sites and, hence, the contribution of the bulk V<sub>2</sub>O<sub>5</sub> to the total rate of toluene oxidation is not essential.

### 3.2. Raman spectroscopy characterisation

To understand the effect of calcination on the vanadia surface species formation, the calcination step was followed by Raman spectroscopy. It is seen in Fig. 5(a)

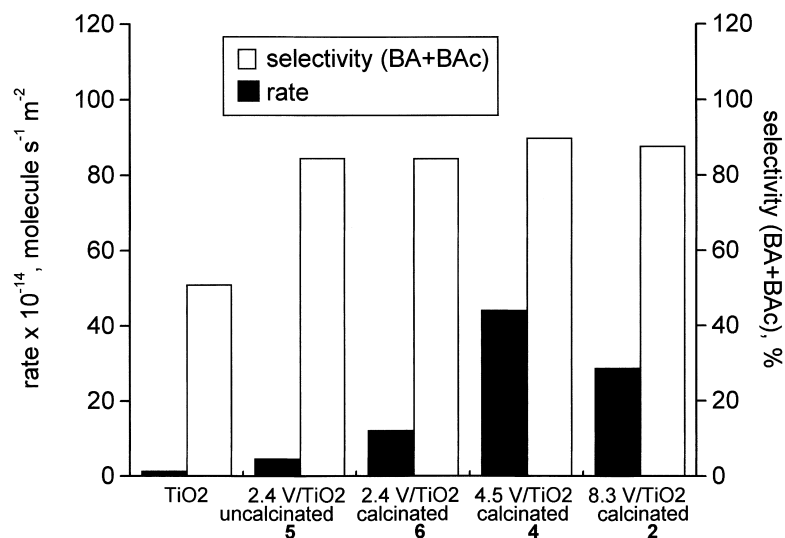


Fig. 4. Rate of toluene transformation and selectivity to BA and BAc for different catalysts at 523 K. Conversion is lower than 6%.

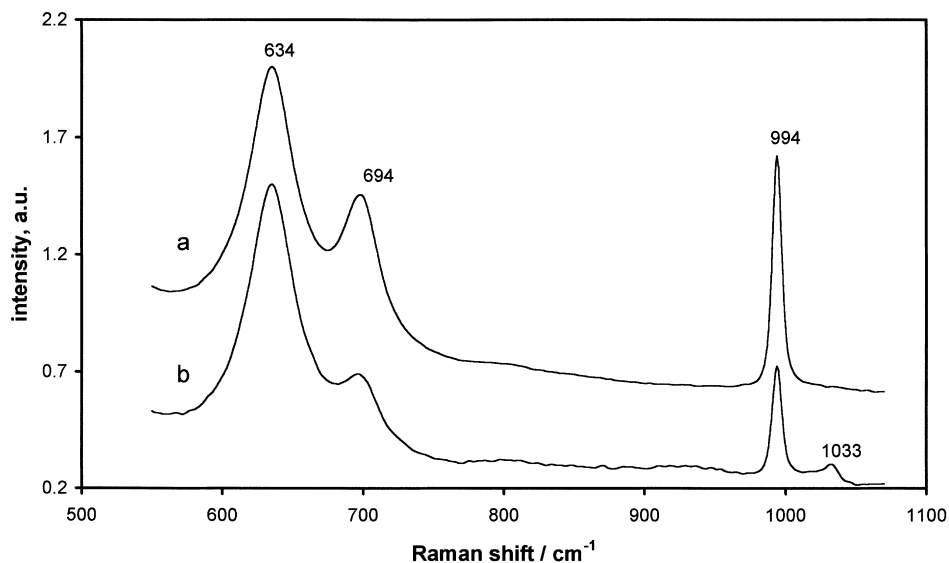


Fig. 5. Raman spectra of the ball milled physical mixture of  $V_2O_5$  with  $TiO_2$  (4.5 wt.% V) before (a) and after calcination for 11 h at 723 K and 34 h at 773 K (b). Measurements at ambient conditions.

and (b) that the calcination in air of the ball milled mixture of 4.5 wt.% V/ $TiO_2$  results in the appearance of a band at  $1033\text{ cm}^{-1}$ , corresponding to the V=O vibration in tetrahedrally co-ordinated vanadia species (monomeric species) and, probably, a very broad band at  $920\text{--}930\text{ cm}^{-1}$  corresponding to the V=O vibration in polymeric species [17]. At a constant intensity of the band of  $TiO_2$  ( $634\text{ cm}^{-1}$ ) the intensities of the bands

of vanadia ( $V_2O_5$ ) at  $994$  and  $694\text{ cm}^{-1}$  decrease with the time of calcination. These data are in line with the results reported earlier [13].

The change of the band intensities for different V species with time of calcination in air is presented in Fig. 6. It is seen that the ratio of the intensities of the band corresponding to the bulk vanadia ( $994\text{ cm}^{-1}$ ) to the band corresponding to the bulk

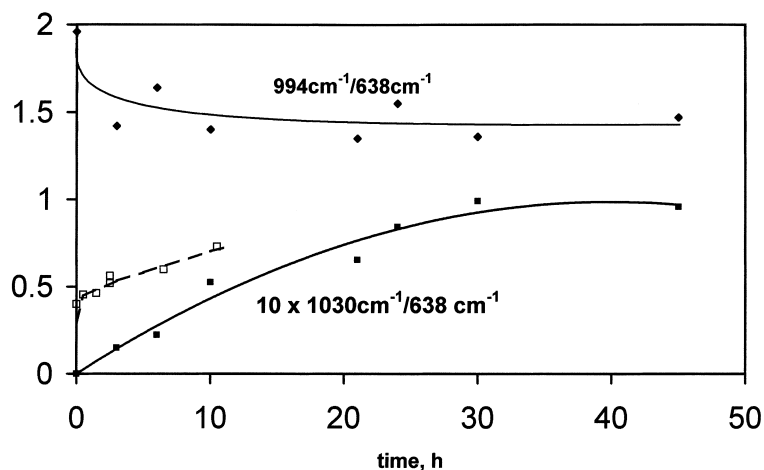


Fig. 6. Dependence of the transformation of different vanadia species on the calcination time for the ball milled physical mixture containing 8.3 wt.% V in  $TiO_2$ . Solid lines — calcination in air, measurements at ambient conditions, dashed lines — calcination in the  $O_2/Ar$  mixture (dry atmosphere), measurements at 523 K.

titania ( $638\text{ cm}^{-1}$ ) decreases with the time of calcination. This decrease is accompanied by the increase of the concentration of the tetrahedrally co-ordinated vanadia species ( $1030\text{ cm}^{-1}$ ). The relative amount of bulk vanadia decreases more quickly in the initial period of the calcination than the appearance of the tetrahedrally co-ordinated species takes place. Relatively fast spreading of the bulk vanadia over titania support seems to proceed first, as also reported by Haber et al. [13]. It can be ascribed to the formation of a thin layer of disordered  $\text{V}_2\text{O}_5$  with a several monolayer thickness. Formation of the thin vanadia layer, occupying large part of titania was observed earlier by high resolution electron microscopy [18]. The second process occurs slower and corresponds to the formation of the monolayer vanadia species.

Table 1 shows that catalysts 2 and 4 have different total V concentration but the same amount of V interacting with the support including the thin vanadia layer and the monolayer species. This amount is close to the full physical monolayer taken as  $1 \times 10^{19}$  atom  $\text{V m}^{-2}$  [1]. The smaller concentration of the interacting vanadia in the sample 6 (Table 1) is, probably, a reason for the lower activity of this catalyst, compared to the catalysts 2 and 4.

An in situ Raman study was performed to understand the nature of vanadia species in the uncalcinated catalyst. It was mentioned that every catalyst including the uncalcinated sample was pre-treated in the  $\text{O}_2/\text{Ar}$  mixture at 673 K for 30 min before the reaction. The main difference between the catalyst calcination in air and catalyst pre-treatment in the  $\text{O}_2/\text{Ar}$  mixture is the absence of water vapour. It can be seen from

Fig. 6 that during the short pre-treatment in dry atmosphere ( $\text{O}_2/\text{Ar}$  mixture) a certain part of the monolayer species ( $1030\text{ cm}^{-1}$ ) is formed much rapidly (dashed line) than during the calcination in ambient air (solid line).

Hence, taking into account the Raman spectroscopy data, the nearly independence of the selectivity on the vanadium content and the calcination step (Fig. 4), it is possible to suggest that the catalysis in the toluene oxidation is mainly due to the fact that monolayer species are present.

### 3.3. Catalyst deactivation and coke formation

The process of catalyst deactivation with time on stream was studied and is presented for the catalyst 4 in Fig. 7. The conversion of toluene decreases from 8 to 3.4%, while the selectivity to BA and BAc does not change. The surface coke concentration determined by the TPO method after 20 min of reaction was  $1.2 \times 10^{19}$  atom  $\text{C m}^{-2}$ . After 75 min it increases up to  $1.5 \times 10^{19}$  atom  $\text{C m}^{-2}$ . The selectivity to BAC decreases with the coke accumulation, while the selectivity to BA increases. These features are typical for a consecutive reaction and could be explained by the decrease of the partial pressure of BA with the conversion leading to a decrease of the rate of the BAC formation.

The maximal rate of the coke burning in oxygen was reached at a temperature close to 623 K. The main products observed were  $\text{CO}_2$ , CO and water. The average composition of the coke was determined equal

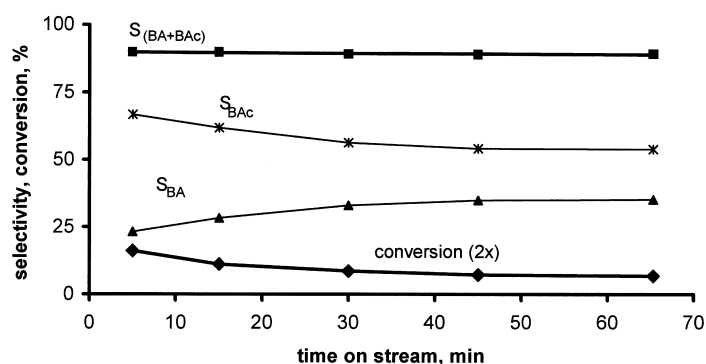


Fig. 7. Dependence of the selectivities and conversion on the time on stream for the calcinated 4.5 wt.%  $\text{V/TiO}_2$  (4) at 523 K.

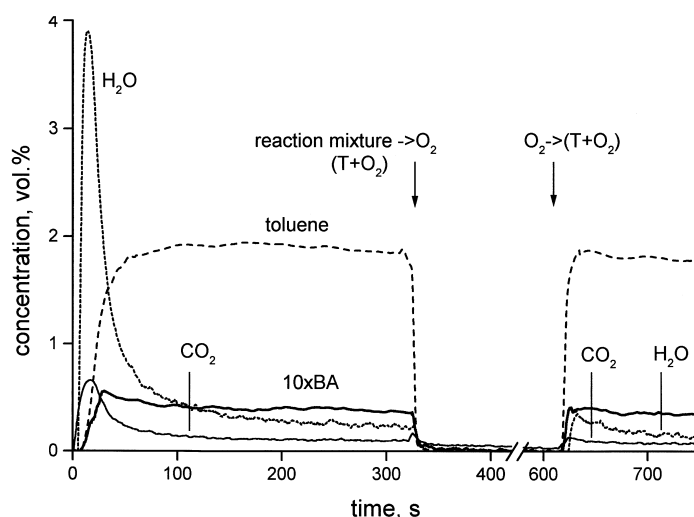


Fig. 8. Response curves, obtained during the switch of the oxygen containing mixture to the reaction mixture, back and again to the reaction mixture on the calcinated 4.5 wt.% V/TiO<sub>2</sub> (4) at 523 K.

to C<sub>2n</sub>H<sub>1.1n</sub>. The concentration of the coke formed in the reaction during 20 min on the samples 1, 2, 4, 5 and 6 during the first 20 min of the reaction was found to be in the range 1.0–1.4 × 10<sup>19</sup> atom C m<sup>-2</sup>. So, it was almost independent on V concentration. The concentration of the coke accumulated on the surface of the pure titania was determined to be two times lower. TPO experiments showed that it was burned in oxygen at higher temperature if compared to vanadia containing catalysts. Hence, vanadia sites promote the coke oxidation as well as the coke formation.

### 3.4. Transient kinetics study

The coke formation influences strongly the transient behaviour observed in the reaction (Fig. 8). After a switch of the O<sub>2</sub>/Ar mixture to the toluene/O<sub>2</sub>/Ar mixture over the oxygen pre-treated catalyst (673 K), toluene does not immediately evolve into the gas phase, but adsorbs irreversibly. Large evolution of water points out that some coke is formed with the decrease in H/C ratio with respect to toluene as also was seen by the TPO study. Irreversibly adsorbed toluene does not lead to the BA formation. Benzaldehyde is seen to appear only when toluene appears in the gas phase. A back switch of the reaction mixture to the oxygen containing mixture (after 330 s)

shows that the formation of BA stops almost completely when toluene is removed from the gas phase. It suggests only a small reversible adsorption of BA under reaction conditions. Toluene is removed from the reactor quickly confirming that the concentration of reversibly adsorbed toluene is also rather small.

During the second introduction of the toluene/O<sub>2</sub> mixture at 625 s (Fig. 8) no initial significant evolution of water and CO<sub>2</sub> was observed. The concentrations of CO<sub>2</sub>, BA and water quickly reach the steady-state values. The oxygen introduction did not disturb strongly the steady-state of the catalyst. Therefore, the initial transient behaviour of the oxidised catalyst is explained by the coke formation.

To check whether the products of the reaction can be obtained with the participation of the oxygen of the catalyst (structural or lattice oxygen) the introduction of the toluene/Ar mixture on the oxidised catalyst 2 was performed (Fig. 9). The CO<sub>x</sub> products are formed quickly without an induction period. Their concentration reaches a maximum and quickly decreases. This can be explained by the decrease of the amount of oxygen, which can participate in deep oxidation. The total amount of CO<sub>x</sub> formed is small comparing to the value of oxygen monolayer and is equal to 5 × 10<sup>16</sup> molecule m<sup>-2</sup>. It points out that there is only a small fraction of the sites containing oxygen



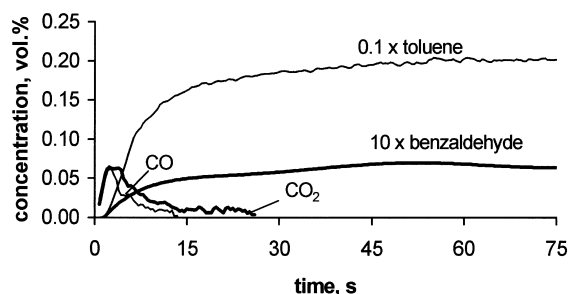


Fig. 9. Response curves obtained during the toluene introduction on the oxidised calcinated 8.3 wt.% V/TiO<sub>2</sub> (2) at 523 K.

(<2%), which can participate in the CO<sub>x</sub> formation at this temperature.

Benzaldehyde is formed simultaneously with the appearance of toluene in the gas. A decrease of the BA formation was observed only after 13–15 min. The BA formation was also observed on the catalyst pre-reduced by hydrogen for 30 min at 673 K. These data suggest that weakly chemisorbed, more mobile oxygen interacts with toluene and forms CO<sub>x</sub>. Structural oxygen seems to be responsible for the BA formation. This consideration is in line with published results [19,20]. However, it is not clear whether different oxygen species are responsible for parallel routes of BA and CO<sub>x</sub> formation in the presence of gaseous oxygen. A further investigation by means of steady-state isotopic transient kinetics analysis (SSITKA) [21] is necessary.

#### 4. Conclusions

1. Calcination in air of the V/Ti oxide catalysts prepared by ball milling provides fast (1–3 h) spreading of vanadia over the titania support followed by slow formation of the monolayer vanadia (30–45 h). After calcination the catalyst shows higher activity in the toluene oxidation, but the selectivity towards BA and BA<sub>c</sub> formation does not change.
2. Monolayer vanadia species formation is responsible for the catalytic activity.
3. A parallel–consecutive scheme of the toluene transformation is presented.
4. Coke formation was observed under the reaction conditions leading to the catalyst deactivation.

The average composition was determined to be C<sub>2n</sub>H<sub>1.1n</sub>.

5. Structural oxygen species of the monolayer vanadia are supposed to participate in toluene oxidation to BA in the absence of gaseous oxygen.

#### Acknowledgements

The authors gratefully acknowledge the financial support of EU committee in the framework of Inco-Copernicus contract. Performance of some experiments by F.-R. Balestra is highly appreciated.

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