



Transient kinetics of toluene interaction with V/Ti-oxides in anaerobic conditions

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Abstract

Toluene interaction with the catalysts consisting of 0.35, 0.62, 0.75 and 3.7 monolayers (ML) of VO_x supported on anatase–titania, containing potassium, was studied by transient response techniques at 523–673 K. FT-Raman spectroscopy under dehydrated conditions was used to determine the state of vanadia. K-perturbed (1020 cm⁻¹) and K-doped (990 cm⁻¹) monomeric vanadia species as well as “amorphous” KVO₃ (960–940 cm⁻¹) were found at vanadia coverage less than a monolayer. Bulk V₂O₅ (994 cm⁻¹) was present only in the 3.7 ML V/TiO₂ catalyst as a dominant species. Benzaldehyde (BA), total oxidation products and surface carbon-containing species were the main products of the toluene interaction. The proposed reaction network involves five steps and two types of oxygen sites. Both the BA and CO₂ formation increased with the concentration of vanadia. The former is determined mainly by nucleophilic-lattice oxygen that is involved in the monolayer vanadia species. The latter as well as the formation of the main part of surface carbon-containing species increased much more steeply being dependent, probably, from electrophilic oxygen abundant in polymerised vanadia species and V₂O₅. The performed kinetic modelling satisfactorily describes the response curves of BA, CO₂ and toluene obtained during the toluene interaction with the pre-oxidised 0.35–0.75 ML V/TiO₂ catalysts. The presence of bulk V₂O₅ in the 3.7 ML V/TiO₂ catalyst seems to provide some change in the reaction mechanism demanding a modification of the reaction scheme.

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1. Introduction

Cyclic reduction and re-oxidation of the catalyst is one of the ways to reach an improved performance in catalytic partial oxidation reactions. This operation is industrially used in the DuPont process of butane oxidation to maleic anhydride over a vanadium–phosphorous catalyst [1]. The reason to apply this cycle was to improve the selectivity by a decrease of the concentration of surface electrophilic oxygen, which is thought to be responsible for total oxidation. The common objectives of the use of periodic operation in catalytic reactors are to provide an increased conversion, selectivity and reduced deactivation [2]. Important mechanistic information could be extracted from the transient behaviour of the

reaction after a fast change of the composition of reaction mixture over the catalyst. Modelling of the transient phenomena allows obtaining valuable kinetic constants, which often could not be determined from the steady-state experiments.

Mills et al. [3] using the TAP reactor investigated the details of the reduction kinetics of the vanadium–phosphorous catalyst by butane and its re-oxidation by oxygen. An interaction of the components of the reaction mixture with V/Ti-oxide catalysts was intensively studied for *o*-xylene oxidation [4–6] – important industrial reaction of phthalic anhydride production. This has been done also for toluene oxidation [5,7–9]. In our study [8,9], during toluene interaction with a V/Ti-oxide catalyst containing potassium it was found that benzaldehyde (BA) is formed for a long time with a very high selectivity while CO₂ is evolved only during the first moments of the reaction. This was assigned to different surface oxygen species: nucleophilic and electrophilic

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Nomenclature

C_d	concentration of sites at monolayer coverage (mol cm ⁻²)
C_g	total concentration of the gas phase (mol cm ⁻³)
C_j	mole fraction of gaseous component
C_T, C_{BA}	mole fractions of toluene and benzaldehyde in gas phase
G_d	catalyst loading (g)
k_i	rate constants (s ⁻¹)
r_i	rates of the reaction steps (s ⁻¹)
R_i	transformation rates of surface species (s ⁻¹)
R_j	transformation rates of gaseous components (s ⁻¹)
S_d	catalyst specific surface area (cm ² g ⁻¹)
V_g	reactor void volume (unoccupied by the catalyst) (cm ³)
w	total gas flow rate (cm ³ s ⁻¹)

Superscripts

m, n reaction orders

Greek symbols

$\tau (= V_g/w)$ residence time of the reactor (s)

$\theta_{YO}, \theta_{ZO}, \theta_Y, \theta_{ZOC_7H_8}, \theta_{YC_6H_5COO}$ surface fractions of the oxidised (YO, ZO) and reduced (Z, Y) sites, irreversibly adsorbed toluene and benzoate, respectively

species participating in the parallel routes of the toluene oxidation.

Steady-state kinetics of the toluene oxidation and deactivation of the pure V/Ti-oxide were also studied [10]. Low yields of the BA formation even at low conversions of toluene (2–10%) in the presence of oxygen are explained by a high rate constant of the BA transformation into benzoic acid. Oxygen-18 experiments allowed Konietzki et al. [7] to conclude that the toluene oxidation in the presence of oxygen proceeds over the microporous vanadia/silica catalyst and V₂O₅ via a Mars–van Krevelen mechanism by insertion of lattice oxygen into the products. The same mechanism could be expected for the V/Ti-oxide catalyst.

The main objective of the present work is to deepen the knowledge concerning the mechanism of toluene oxidation over V/Ti-oxide catalysts by studying the reaction in anaerobic conditions using transient response techniques in combination with kinetic modelling. The effect of vanadium concentration on the toluene interaction with oxidised catalysts was considered in detail especially in the range of sub-monolayer quantities. Important is that the catalysts contained potassium initially present in titania support. The reason to study these samples instead of undoped ones was that during toluene interaction with the latter gaseous products

were almost not observed, because of strong adsorption on the surface [11]. The catalysts were extensively characterised by FT-Raman spectroscopy, TPR, XPS, HRTEM [12] and ⁵¹V NMR [9]. However, until now these methods may not be used for quantitative determination of the concentration of active sites responsible for partial and total oxidation. Hence, kinetic modelling was applied in the present study as a tool for estimation of their relative concentrations.

2. Experimental

2.1. Catalyst preparation

TiO₂ (Aldrich) with the anatase structure was used as a support. It contained 0.2 wt.% of potassium as was determined by inductively coupled plasma spectrometry (ICP, Baird). Sub-monolayer catalysts with 0.27, 0.47 and 0.57 wt.% V-content were prepared by 2-, 5- and 10-steps of VOCl₃ vapour deposition on the surface of TiO₂, respectively, hydroxylation and drying (grafting technique [13]). Impregnation from aqueous solution of vanadium oxalate was used to obtain a catalyst with 2.8 wt.% of V. The catalysts were dried and then calcined in air at 723 K during 120 min. The BET specific surface area was equal to 9 m² g⁻¹. The amount of vanadium corresponds to 0.35, 0.62, 0.75 and 3.7 ML, respectively. The monolayer is taken as equal to 10 V-atom nm⁻² [14]. The presence of K was found on the surface of these catalysts by XPS [12]. It is important that K affects the structure of vanadia species, acid–base properties of the catalysts as well as reactivity of surface oxygen [9,12,14,15].

2.2. Set-up and procedure

An experimental set-up used for the transient kinetics study has been described elsewhere [16]. Toluene was introduced into a heated evaporator by a syringe-pump. Products were analysed by mass spectrometry and gas chromatography. Measurements were carried out in a tubular flow reactor made of quartz (130 × 6 mm). A thermocouple was inserted into the middle of the catalyst bed. All lines of the set-up were heated up to 413 K at least. For the transient response study the catalyst loading and the gas flow were maintained constant at 1 g and 1 cm³ s⁻¹ at standard temperature and pressure, respectively. The nitrogen response time after the switch of Ar to a 2 vol.% N₂/98 vol.% Ar mixture over the catalyst was small and close to 3 s (Fig. 1). The response of toluene over quartz particles was very similar.

All the catalysts before the reaction were pre-treated in oxidative atmosphere (20 vol.% O₂, rest Ar) at 673 K for 30 min. After this pre-treatment, the reactor was cooled in Ar, until the temperature of the reaction (523–673 K) and the flow was switched to the mixture of 2 vol.% toluene with Ar in the absence of gaseous oxygen.

Two types of transient response techniques were used: response to a step-input and response to a pulse-input. During the step-input experiments interaction of toluene with

pre-oxidised catalysts was performed for 20 min. During the pulse-input experiments, the same toluene/Ar mixture contacted with the catalyst shortly for 2.5 s and then the flow was switched back to pure Ar until no gaseous products were observed by the mass spectrometer. This cycle was repeated several times. The total amount of toluene, which passed the catalyst during the single pulse, was small and corresponded to $0.12 \text{ molecule nm}^{-2}$.

Concentration of carbon-containing species on the catalyst surface was determined after purging the reactor in Ar by transient and temperature-programmed oxidation (up to 683 K) in oxygen. The amount of these species was found by integration of the area under the carbon oxides curves obtained in this run. Relative sensitivity factors of the mass spectrometer for these products with respect to oxygen were used to determine the concentrations.

2.3. Catalyst characterisation

Raman spectroscopy measurements were performed using a Perkin Elmer FT-Raman 2000 spectrometer. An “in situ” Raman spectroscopy cell [17] was attached to the same set-up mentioned above instead of the tubular reactor. An Nd-YAG laser, operating at 1064 nm with a varying power in the range of 10–750 mW was used in the FT-Raman spectrometer. From 32 to 256 scans were averaged with a resolution of 4 cm^{-1} to obtain a spectrum. The spectra of the catalysts were taken in the dry O_2/Ar mixture at 523 K after the pre-treatment in this mixture at 673 K for 30 min implying dehydrated conditions.

3. Results and discussion

3.1. Interaction of toluene with the 0.75 ML V/TiO₂ catalyst

Fig. 1 demonstrates a typical toluene interaction with the 0.75 ML V/Ti-oxide catalyst. This catalyst was mainly

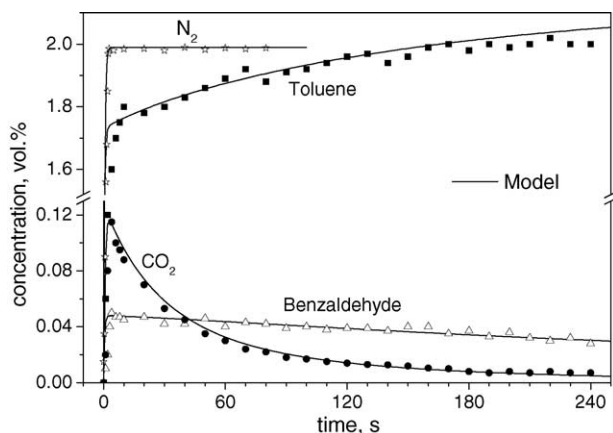


Fig. 1. Formation of products during the step-input of toluene (2.05 vol.% toluene in Ar) on the pre-oxidised 0.75 ML V/TiO₂ catalyst at 603 K. N₂ response obtained during the step-input of a 2 vol.% N₂/Ar mixture on the catalyst is shown for comparison (everywhere points – experiments, lines – modelling).

studied because it contained vanadia only in the form of surface monolayer vanadia species and no bulk crystalline V₂O₅ [12]. However, the vanadia concentration in this sample was close to the monolayer coverage implying a decrease of the possible contribution of uncovered titania sites to the reaction.

It is seen that the dynamics of the CO₂ and BA formation are different. CO₂ is formed during the initial time of the reaction declining quickly in time, while BA is formed for a prolonged time. This was explained earlier by participation of different oxygen species in partial and total oxidation [8]. Initial shape of the BA curve is similar to that of the toluene curve pointing out direct dependence on the toluene partial pressure. After some time in the toluene/Ar stream the BA concentration decreases with the decrease of the concentration of active surface oxygen. Small amount of CO (5–6 times less than CO₂) was also observed in products with the transient behaviour similar to CO₂.

Valuable information concerning the BA, CO₂ formation and toluene adsorption follows from the pulse-input experiments (Fig. 2). These experiments could be considered as a titration of the catalyst oxygen by toluene. The toluene curve reaches a maximum and then decreases due to the switch to Ar flow. The toluene step-down response is always close to the one over inert quartz instead of the catalyst showing that reversible adsorption of toluene is negligible. This is in accordance with the data in the presence of gaseous oxygen [10,16]. An increase of toluene amount from pulse to pulse indicates a decrease of toluene conversion. This takes place because of surface oxygen consumption and blocking of active sites by surface carbon-containing species formed in the reaction.

The BA curves are very similar in a sequence of runs (Fig. 2). This points out that a single interaction with toluene does not change noticeably the concentration of oxygen species, which are responsible for the BA formation. This confirms that these oxygen species are in large excess in accordance with the continuous run (Fig. 1). However, the total

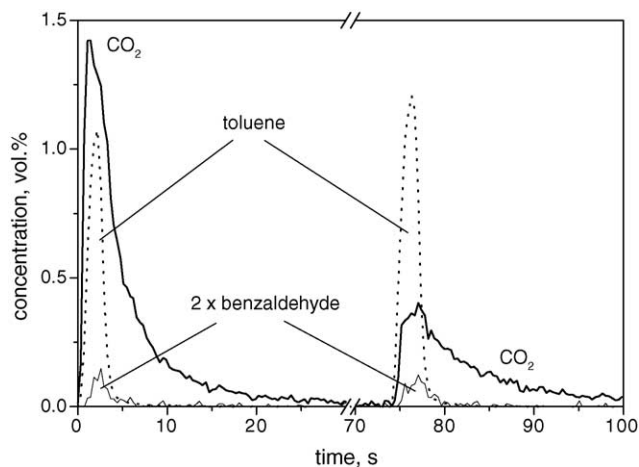


Fig. 2. Formation of products during the pulse-input of toluene on the pre-oxidised 0.75 ML V/TiO₂ catalyst at 673 K.

amount of oxygen involved in the BA formation in the experiment like that presented in Fig. 1 during 500 s at any studied temperature consists of only small fraction from a monolayer coverage (<0.1) indicating that only surface oxygen and no oxygen from the bulk of titania participates.

The CO_2 behaviour is very different (Fig. 2). When toluene is removed from the reactor, CO_2 is still produced for some time (50 s), being formed in a reaction of surface carbon-containing species with oxygen of the catalyst. The formation of CO_2 is accompanied by the water vapour formation (not shown). The re-adsorption of CO_2 may not contribute at the studied temperature range. The consecutive toluene pulses show that the reactive oxygen is present on the catalyst surface as CO_2 is formed. However, contrary to the behaviour of BA, the amount of CO_2 strongly decreases in a sequence of pulses (Fig. 2) indicating a strong decrease of the reactive oxygen concentration.

Except the formation of gaseous products, the formation of some carbon-containing species takes place on the catalyst surface. It follows from the carbon balance measurements as well as from the transient oxidation of the catalyst after its interaction with toluene (Fig. 3). CO_2 , CO, H_2O (not shown), but no BA, benzoic acid and maleic anhydride were found during oxidation of this catalyst at 603 K. Consecutive heating of the sample in oxygen up to 683 K did not provide any additional product formation indicating that all surface carbon-containing species can be removed in oxygen at 603 K. The total surface concentration of these species determined by oxidation corresponds to $2.5 \text{ C-atom nm}^{-2}$. Different benzoates were observed earlier during the toluene interaction with vanadia/titania catalysts by FTIR spectroscopy [18,19]. Coke-like species with a decreased H/C ratio with respect to toluene may be also formed [10,16,20].

3.2. Structure of vanadia species

The Raman spectra of the oxidised catalysts measured under dehydrated conditions are shown in Fig. 4. As it was mentioned the titania used as a support contained potassium,

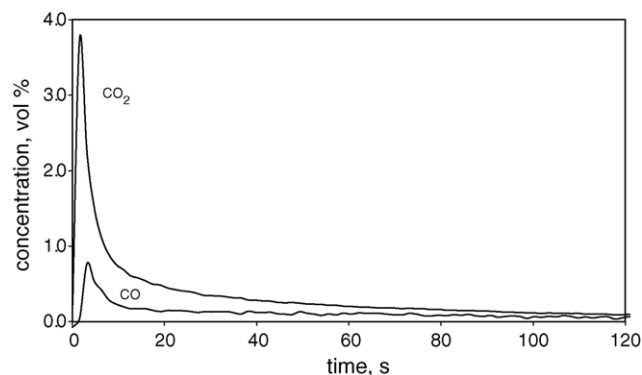


Fig. 3. Formation of products during the step-input of a 20 vol.% O_2/Ar mixture on the 0.75 ML V/TiO₂ catalyst at 603 K after 20 min of the toluene interaction (Fig. 1) and Ar purge.

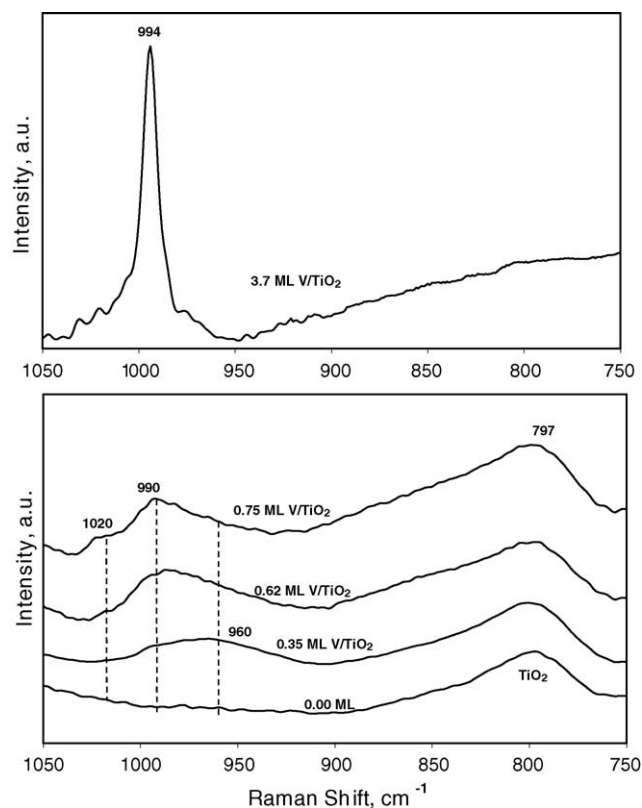


Fig. 4. FT-Raman spectra of the V/TiO₂ catalysts and TiO₂ measured in the 20 vol.% O_2/Ar mixture at 523 K under dehydrated conditions.

which was not removed after vanadia deposition. XPS analysis showed that the K/V surface atomic ratio in the 0.35, 0.62 and 0.75 ML V/TiO₂ catalysts corresponded to 1, 0.57 and 0.47, respectively [12].

The presence of K-impurities provided the difference in the Raman spectra of the catalysts with respect to the ones obtained for the pure V/Ti-oxides [17,21]. For the sub-monolayer catalysts the following bands are present: 1020, 980–1000 and 940–960 cm^{-1} . They are assigned to the K-perturbed, K-doped monomeric vanadia species and bulk “amorphous” KVO_3 , respectively, basing on the FT-Raman and TPR study of the catalysts intentionally doped by potassium [12,15]. Vanadium in all of these species is tetra-coordinated. Contrary to the sub-monolayer catalysts the 3.7 ML V/TiO₂ catalyst contained bulk V_2O_5 as a dominant species, which is characterised by a very intensive and narrow band at 994 cm^{-1} (Fig. 4). The monolayer vanadia species in this catalyst must exist also, but are not clearly seen in the spectra, because of the strong V_2O_5 band. The presence of bulk crystalline vanadia (V_2O_5) in this catalyst was also confirmed by HRTEM and ^{51}V NMR spectroscopy [9].

An important fact is that the FT-Raman study shows that different vanadia (oxygen) species exist on the surface of the studied catalysts. The shape of the V=O bands region (900–1050 cm^{-1} , Fig. 4) is dependent on the concentration of vanadia and indicates that the ratio of different vanadia

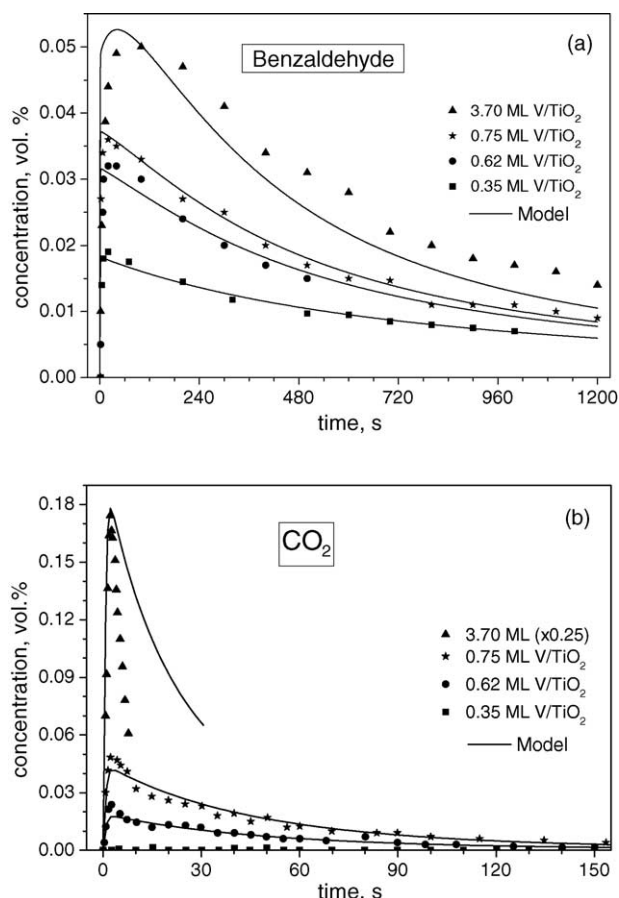


Fig. 5. Dependences of the benzaldehyde (a) and CO₂ (b) formation on time during the step-input of a 2 vol.% toluene/Ar mixture on the pre-oxidised V/Ti oxide catalysts at 573 K (points – experiments, lines – modelling).

species changes. This fact will be used for kinetic modelling of the toluene interaction with these catalysts.

3.3. Effect of the vanadia coverage on the toluene interaction

The BA and CO₂ formation in transient conditions are compared during the toluene interaction with the pre-oxidised catalysts containing different vanadia concentrations (from 0.35 to 3.7 ML) at the same temperature (573 K) (Fig. 5). No gaseous products were detected during the interaction of toluene with the titania support. Small amount of benzoic acid was found only for the 3.7 ML V/TiO₂ catalyst at higher temperatures. Maleic anhydride has never been observed during the toluene interaction.

For all the sub-monolayer catalysts, the ratio of the amount of oxygen atoms removed from the catalyst in the form of gaseous products (including water) to the amount of vanadium atoms in the sample at 523–673 K was lower than 0.6 during the first 500 s of the interaction. Hence it was concluded that bulk-surface oxygen diffusion processes do not contribute to the reduction of these catalysts. For the 3.7 ML V/TiO₂ catalyst this ratio was not higher, however if to relate

the amount of the removed oxygen to the amount of the vanadium in the monolayer (10 V-atom nm⁻²) the ratios reached 1.2 and 1.7 at 633 and 673 K, respectively. These high values indicate that oxygen of the bulk V₂O₅ is involved in the toluene interaction with this catalyst.

The BA formation is observed at the coverage by vanadia as low as 0.35 ML and increases with the vanadia content (Fig. 5a). Strong increase of the vanadia content from 0.75 to 3.7 ML results in only a small increase of the BA formation. These data point out that the monolayer vanadia species are mainly active in the BA formation and bulk V₂O₅ possesses a lower activity.

Carbon dioxide is not observed on the catalyst with the lowest concentration of vanadia (0.35 ML) (Fig. 5b). Formation of CO₂ is not directly proportional to the vanadia coverage being strongly increased for the catalyst containing bulk V₂O₅ particles (3.7 ML). Another type of oxygen, probably, electrophilic mainly abundant on the surface of the bulk V₂O₅ seems to participate in the CO₂ formation. The absence of this type of oxygen results in 100% BA selectivity for the 0.35 ML V/TiO₂ catalyst.

A total concentration of the surface carbon-containing species determined by oxidation after 20 min of the toluene interaction increases with the vanadia content, but as well as the CO₂ formation is not directly proportional to it (Fig. 6). It only slightly increases until 0.35 ML of V and then increases drastically with the increase of the VO_x concentration reaching 7.4 C-atom nm⁻² for the 3.7 ML V/TiO₂ catalyst. This increase is, probably, provided by the appearance of electrophilic oxygen sites associated with polymerised vanadia species. At low coverage, vanadia species interact mainly with titania surface, while at high they interact each other forming polymerised vanadia and V₂O₅.

A formation of the CO_x products increases strongly with the temperature, while the concentration of the surface

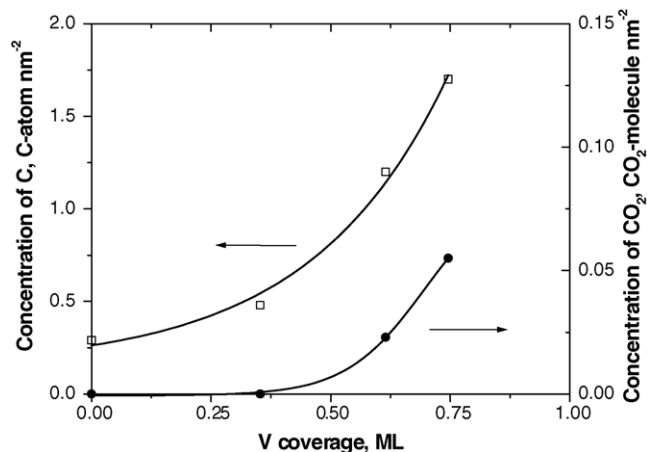


Fig. 6. Total amounts of CO₂ and surface carbon-containing species formed during 20 min of the toluene interaction with the pre-oxidised V/Ti oxide catalysts at 573 K on the vanadia coverage (concentration of surface carbon-containing species is determined by temperature-programmed oxidation after the toluene interaction).

carbon-containing species is almost independent on it in the range 573–673 K. It corresponds to $1.7\text{--}2.5\text{ C-atom nm}^{-2}$ for the 0.75 ML V/TiO₂ catalyst and $7.4\text{--}9.5\text{ C-atom nm}^{-2}$ for the 3.7 ML V/TiO₂ catalyst. This may indicate that the coverage by surface carbon-containing species is close to saturation value after 20 min in the toluene stream at any studied temperature. An increase of the temperature is favourable for the aromatic ring fission and formation of carbon oxides. Surface carbon-containing species were also found to be formed on the 0.75 ML V/TiO₂ catalyst reduced in H₂ for 1 h at 673 K, but their total concentration ($0.7\text{ C-atom nm}^{-2}$) was much lower as compared to the oxidised catalyst ($2.1\text{ C-atom nm}^{-2}$).

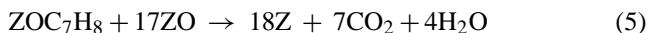
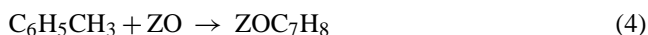
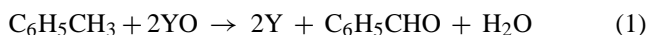
3.4. Kinetic modelling of the toluene interaction with the pre-oxidised catalysts

A simulation of the toluene interaction with the pre-oxidised 0.75 ML V/TiO₂ catalyst at different temperatures (Figs. 1, 5, 7) as well as with the 0.35, 0.62, 3.7 ML V/TiO₂ catalysts at 573 K (Fig. 5) was performed.

The kinetic model is based on the following results and assumptions:

- (1) Two different oxygen sites nucleophilic and electrophilic are responsible for the BA and CO₂ formation, respectively [22]. The presence of potassium impurities in the catalysts strongly complicates the assignment of the reactivity to certain vanadia species. Hence the oxygen sites were arbitrary denoted as YO (nucleophilic) and ZO (electrophilic).
- (2) The total amount of reactive oxygen species was accepted to be equal to the vanadium concentration for the sub-monolayer catalysts and the initial YO/ZO concentration ratio independent on the temperature.
- (3) Concentrations of reversibly adsorbed toluene, H₂O, CO₂, BA as well as of an intermediate of BA formation can be neglected.
- (4) Adsorbed benzoates [10,18,19,23] and other carbon-containing species [10,16,18,20] may be present on the surface of V/Ti-oxides in reaction conditions. Benzoates are formed in the reaction of BA with oxygen of the catalyst [18].
- (5) Two processes of the CO₂ formation fast and slow could exist. If toluene adsorbs with a ring parallel to the surface a strong interaction of carbon atoms with the surface takes place [22,24]. In the fast process toluene interacts simultaneously with several oxygen sites accompanying by ring fission. In the slow process CO₂ may be formed in a surface reaction of irreversibly adsorbed toluene with oxygen of the catalyst as follows from the pulse-input experiments (Fig. 2). CO formation is small and can be neglected.
- (6) Diffusion of oxygen from the bulk of titania is not important for the sub-monolayer catalysts in the studied temperature range.

There were tested about 20 different reaction schemes. One of the key points in the choice of the reaction scheme was its simplicity reached by the use of minimal amount of reasonable steps and intermediates. The proposed kinetic scheme includes five irreversible steps, which may not be considered as elementary:



The following kinetic equations for the reaction steps (1)–(5) were applied:

$$r_1 = k_1 C_T \theta_{\text{YO}}^m, \quad r_2 = k_2 C_{\text{BA}} \theta_{\text{YO}}, \quad r_3 = k_3 C_T \theta_{\text{ZO}}^n,$$

$$r_4 = k_4 C_T \theta_{\text{ZO}}, \quad r_5 = k_5 \theta_{\text{ZOC}_7\text{H}_8} \theta_{\text{ZO}}$$

respectively.

In the equations, r_i , k_i are the rates and rate constants of the reaction steps, C_T , C_{BA} are the mole fractions of toluene

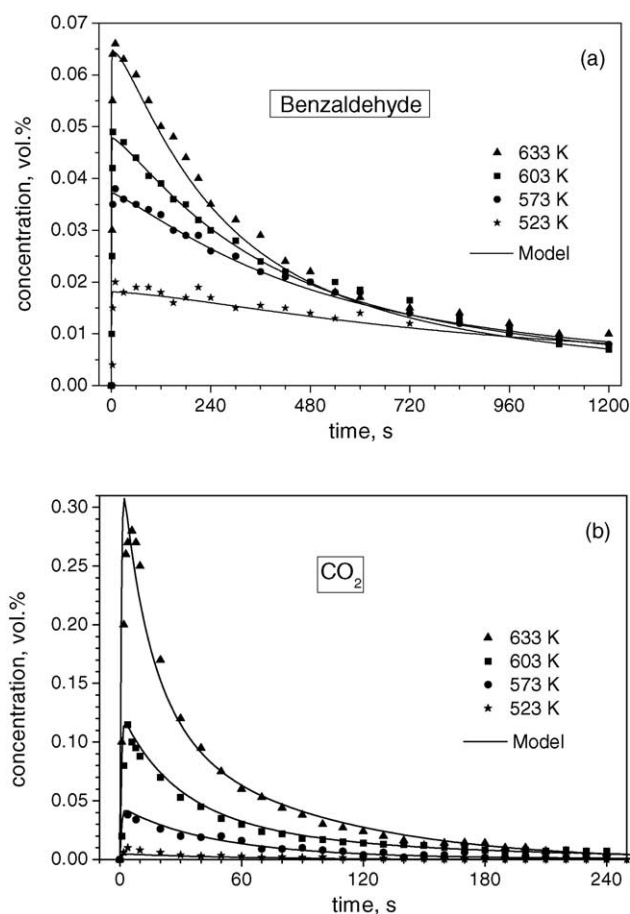


Fig. 7. Transient experimental (points) and modelling data of the BA (a) and CO₂ (b) formation obtained during the step-input of toluene (2 vol.%) on the pre-oxidised 0.75 ML V/Ti-oxide catalyst at different temperatures.

Table 1

Rate constants at 603 K and activation energies (with 95% confidence limits) for the reaction steps of the toluene interaction with the pre-oxidised sub-monolayer catalysts

	T → BA (1)	BA → benzoate (2)	T → CO ₂ (3)	T → irreversibly adsorbed T (4)	Irreversibly adsorbed T → CO ₂ (5)
k_i (s ⁻¹)	0.07	0.51	0.91	0.3	0.0012
$E_{a,i}$ (kJ/mol)	36.0 ± 1.6	6.3 ± 0.7	106.7 ± 1.8	0	231 ± 7

T – toluene, BA – benzaldehyde.

and benzaldehyde in gas phase, θ_{YO} , θ_{ZO} , θ_Z , θ_Y , $\theta_{ZOC_7H_8}$, $\theta_{YC_6H_5COO}$ are surface fractions of the oxidised (YO, ZO) and reduced (Z, Y) sites, irreversibly adsorbed toluene (ZOC_7H_8) and benzoate (YC_6H_5COO), respectively, m and n are the reaction orders.

The balance of active surface sites corresponds to

$$\theta_{YO} + \theta_{YC_6H_5COO} + \theta_Y = \theta_{YO}^0,$$

$$\theta_{ZO} + \theta_{ZOC_7H_8} + \theta_Z = \theta_{ZO}^0$$

where $\theta_{YO}^0 + \theta_{ZO}^0 = \theta_{ML}$ is a fraction of active sites equal to the vanadia coverage (ML) for the sub-monolayer catalysts.

The first step involves an interaction of toluene with nucleophilic-lattice oxygen atoms of the catalyst (YO) taking place with the BA formation. It may include several elementary steps. The dissociative adsorption of toluene taking place with the breakage of the C–H bond in the methyl group can be expected as rate limiting analogously to the *o*-xylene interaction [4]. This adsorption may demand two surface sites. It leads to the formation of adsorbed benzyl ($C_6H_5CH_2-$) [18,25] or benzyloxy ($C_6H_5CH_2O-$) species located on one vanadium surface atom and hydroxyl group on the other. In accordance, the best description of the experimental data at different temperatures was reached with $m=2$, which indicates the necessity of two oxygen sites for this reaction. The description with $m=1$ can be reached only in a much smaller time interval. The concentration of benzyl, benzyloxy species and hydroxyl groups should be negligible in the studied conditions in accordance with the transient response data. The necessity of two oxygen sites in the first step of alkanes interaction with V_2O_5 was shown by the density functional theory calculations [26,27]. In the Step (2), BA reacts with the YO site with the benzoate (YC_6H_5COO) formation.

Electrophilic oxygen (ZO) is responsible for the CO₂ formation (Steps (3)–(5)) taking place by fission of the aromatic ring. Toluene may be adsorbed with a ring parallel to the surface on an ensemble of several ZO sites followed by the fast CO₂ formation. In accordance, the best description is reached with $n=3$. Earlier [6], it was concluded that there are

two different adsorption sites for *o*-xylene adsorption on the V/Ti-oxide surface, which include from 2 to 4 oxygen atoms. Toluene may also interact with a single ZO site forming irreversibly adsorbed toluene ZOC_7H_8 or coke of unclear nature (Step (4)). This irreversibly adsorbed toluene reacts slowly with another ZO site forming the total oxidation products (Step (5)).

The reactor was considered of continuous stirred tank type (CSTR) because the conversion of toluene was low, the residence time of the reactor was small and the modelling using this approach described satisfactorily the N₂ response after the switch of Ar to a nitrogen/argon mixture (Fig. 1, N₂). Thus, the following equations were applied:

$$\frac{dC_j}{dt} = \frac{1}{\tau}(C_j^f - C_j) + A_R R_j(C, \theta)$$

$$\frac{d\theta_i}{dt} = R_i(C, \theta)$$

$$t = 0, \quad C_j = C_j^0, \quad \theta_i = \theta_i^0$$

$$\text{where } A_R = \frac{G_d S_d C_d}{V_g C_g}.$$

The third-order semi-implicit Runge–Kutta method for stiff equations with a step-size adjustment strategy was used to solve the system of differential nonlinear equations [28]. The consequence of the modelling steps was the following:

- (1) The reactor void volume (V_g) was estimated via the N₂ response simulation (Fig. 1). It was found equal to 2 cm³.
- (2) For the 0.35 ML V/TiO₂ catalyst, when no CO₂ formation was observed at 573 K (Fig. 5), it was accepted that only the YO sites with the concentration θ_{YO}^0 equal to the coverage of VO_x (θ_{ML}) are present initially. The rate constants – k_1 and k_2 (Table 1) as well as the order – $m=2$ were found.
- (3) At the same temperature for the 0.75 ML V/TiO₂ catalyst, with the kinetic parameters obtained in the previous modelling step the initial concentration of YO (θ_{YO}^0) was determined (Table 2). The initial concentration of ZO (θ_{ZO}^0) was taken as a difference between the total cover-

Table 2

Initial coverage by active nucleophilic (YO) and electrophilic (ZO) oxygen in the pre-oxidised V/TiO₂ catalysts estimated by kinetic modelling

	0.35 ML V/TiO ₂	0.62 ML V/TiO ₂	0.75 ML V/TiO ₂	3.7 ML V/TiO ₂
θ_{YO}^0	0.35	0.51	0.60	0.98
θ_{ZO}^0	0.00	0.11	0.15	0.43

- age of VO_x (θ_{ML}) and θ_{VO}^0 . The rate constants – k_3 , k_4 , k_5 (Table 1) as well as the order $n = 3$ were found.
- (4) For the 0.62 ML V/TiO₂ catalyst, θ_{VO}^0 and θ_{ZO}^0 were found by the same way as for the 0.75 ML V/TiO₂ catalyst, the same constants and reaction orders were used for calculations.
 - (5) For the 0.75 ML V/TiO₂ catalyst the rate constants were determined at different temperatures. The activation energies ($E_{a,i}$) were found using Arrhenius plots (Table 1).

The calculated rate constants for the reaction steps at 603 K as well as the activation energies are presented in Table 1. The highest rate constant corresponds to the transformation of toluene to CO₂ on the ZO sites (Step (3)). The Step (5) has the lowest rate constant and contributes to the CO₂ formation more strongly at high temperatures. The proposed model satisfactorily describes the products (Fig. 7) and toluene (Fig. 1) response curves in the temperature range 523–633 K.

This model was used to describe the toluene interaction with four catalysts containing different amount of vanadia (Fig. 5). It follows from the Raman study (Fig. 4) that the ratio of different vanadia species changes with the vanadia content. In accordance, the kinetic modelling showed that it is not possible to simulate satisfactorily the experimental data for the different sub-monolayer catalysts keeping the same $\theta_{\text{VO}}^0/\theta_{\text{ZO}}^0$ ratio.

For the 3.7 ML V/TiO₂ catalyst, new bulk V₂O₅ species different from those observed for the sub-monolayer catalysts are formed in large excess (Fig. 4). For this catalyst the main part of oxygen in vanadia is not accessible by toluene, as it is located in the bulk of V₂O₅ particles. Therefore, the initial concentrations of active sites for modelling were chosen in a way to reach the maxima attained by the experimental CO₂ and BA curves. The obtained initial concentrations of the active oxygen sites for that catalyst are shown in Table 2.

With the obtained kinetic parameters (Tables 1 and 2), a good description of the kinetic data is reached for all the sub-monolayer catalysts (Fig. 5). However, the proposed reaction model demands a modification to describe the toluene interaction with the 3.7 ML V/TiO₂ catalyst. It is seen, for example, that the experimental CO₂ response is much narrower than the simulated one (Fig. 5). The reason is that this catalyst contains V₂O₅, which may participate in the reaction either directly or by providing of oxygen by diffusion to the monolayer vanadia sites reduced by toluene. It follows from the simulation that the total concentration of reactive oxygen for this catalyst is higher than the monolayer coverage (Table 2). In accordance, the experimental amount of oxygen removed from this catalyst exceeded the monolayer at 633 and 673 K.

This consideration is also in line with the data obtained for the same catalysts pre-reduced in hydrogen at 673 K. After such a treatment some formation of BA was still observed during the toluene interaction with the 3.7 ML V/TiO₂ catalyst [8], but was not with the sub-monolayer

catalysts. Hydrogen is known to reduce easier the monolayer species than the bulk V₂O₅ [12,21], hence some oxygen, which may not be removed from the vanadia particles in hydrogen, participates in the interaction with toluene.

4. Conclusions

In the vanadia/titania catalysts containing potassium, vanadia species are present in the K-perturbed, K-doped monomeric vanadia species [12], “amorphous” KVO₃ and at a coverage higher than the monolayer also in the V₂O₅ form. The pre-oxidised sub-monolayer catalysts were found to be efficient in the BA formation from toluene in anaerobic conditions. The selectivity could reach up to 100%.

The benzaldehyde formation is probably determined by nucleophilic-lattice oxygen, involved in the monolayer vanadia species. Electrophilic oxygen, formed at a higher concentration of vanadia, is responsible for the formation of carbon oxides and main part of surface carbon-containing species. The proposed kinetic model was used to estimate the rate constants, reaction orders, activation energies and relative amount of active oxygen sites. It satisfactorily describes the transient behaviour of benzaldehyde, CO₂ and toluene for the sub-monolayer catalysts in the temperature range 523–633 K. The model demands a modification to simulate kinetics of the toluene interaction with the 3.7 ML V/TiO₂ catalyst explained by the presence of V₂O₅ in excess. This V₂O₅ provides oxygen participating in the interaction with toluene.

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