

Implication of the acid–base properties of V/Ti-oxide catalyst in toluene partial oxidation

Liubov Kiwi-Minsker*, Dmitri A. Bulushev, Fabio Rainone, Albert Renken

Swiss Federal Institute of Technology, LGRC-EPFL, CH-1015 Lausanne, Switzerland

Received 15 August 2001; accepted 27 November 2001

Abstract

The work presents the effect of K-doping on V/Ti-oxides taking into account: the surface acid–base properties and the structure of surface vanadia species in respect to the catalyst performance and deactivation. The structure of active surface species determines redox properties, which are related to the catalytic performance by the Mars–van Krevelen mechanism. The reducibility of surface vanadia is studied by temperature-programmed reduction (TPR) in H₂. The molecular structure of surface vanadia is determined by FT-Raman spectroscopy in a controlled atmosphere. Surface acid–base properties are characterised via temperature-programmed desorption (TPD) of pyridine with mass spectrometric analysis of the products.

Transient response techniques with continuous monitoring of the composition of gaseous phase are applied to follow the catalyst surface transformations. Evolution of benzaldehyde (BA) formed during interaction of toluene with the pre-oxidised catalyst (without gaseous oxygen) gives information about the nucleophilicity of surface oxygen. Addition of potassium to surface vanadia leads to an increased oxygen nucleophilicity, resulting in a higher selectivity towards BA formation.

In general, increase in surface basicity decreases catalytic activity, but at the same time the catalyst deactivation due to coking is suppressed. This allows catalyst optimisation in view of a better control of the partial oxidation process. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: V/Ti-oxide catalysts; Toluene partial oxidation; K-doping; Acid–base properties; Surface vanadia species; Transient response technique

1. Introduction

Partial oxidation of toluene in gas phase to benzaldehyde (BA) and benzoic acid (BAc) is a reaction of increasing industrial interest. A high selectivity to BA and BAc is required to make this process feasible. The reaction obeys the well-known Mars–van Krevelen mechanism. The activation of toluene molecule via hydrogen abstraction is the first step, followed by consecutive steps of nucleophilic oxygen

addition [1]. Hydrogen abstraction leads to the formation of water molecule. Insertion of oxygen into the activated organic fragment results in the formation of BA. BAc is formed in a consecutive step due to a second oxygen insertion. Like in all hydrocarbon's oxidations, thermodynamics favours the formation of CO₂ and water. Therefore, BA and BAc are intermediates that can be attained by a suitable kinetic control of the reaction steps. Consequently, an effective catalyst should be able to provide a strict control of the reaction pathways, favouring steps leading to the desired products (BA, BAc), and hindering undesired by-products (CO_x). The catalyst to be used should be efficient in the following:

* Corresponding author. Tel.: +41-21-693-31-82;
fax: +41-21-693-60-91.
E-mail address: liubov.kiwi-minsker@epfl.ch (L. Kiwi-Minsker).

- An activation of C–H bond in the methyl group (known to be a rate determining step) without interaction with the aromatic ring.
- Quick insertion of oxygen into the adsorbed molecule.
- Easy desorption of the product.
- Reoxidation of the catalytic surface by gas-phase oxygen.
- Precluding the product cracking, which leads to deactivation and coking.

Therefore, an effective catalyst involves redox potential and acid–base properties. Toluene activation proceeds on the catalyst cations (Lewis acids) with subsequent nucleophilic attack by lattice oxygen ions (O^{2-} , weak basis) followed by a desorption of the oxygenated product (BA). To avoid cracking, Brønsted acidity has to be suppressed since these centres are known to be responsible for the interaction with π -electrons of the aromatic ring leading to the ring fission [2].

Catalytic studies showed that vanadia supported on TiO_2 is a suitable catalyst for the partial toluene oxidation [3–5]. It was reported that a two-dimensional vanadia layer is more active than bulk V_2O_5 [6–10]. However, the reasons for its high catalytic activity and selectivity towards partial oxidation products are not clear. The two-dimensional vanadia layer consists of two main forms of VO_x species: monomeric and polymeric (metavanadate-like), which are attached to the TiO_2 surface via V–O–Ti bond [11]. The nucleophilic oxygen of this bond seems to be responsible for BA and BAc formation. The factors determining the structure of vanadia species on titania are as follows: (i) the concentration of vanadia, (ii) the catalyst pre-treatment and (iii) the presence of additives on the titania surface.

The addition of potassium increases V/Ti-oxide basicity and changes the structure of surface vanadia [5,12–18], but the influence of K on the catalyst performance has not been studied in detail. Van Hengstum et al. [19] reported a negative effect of K addition on the activity and yield of benzoic acid. Zhu and Andersson [12] found that catalytic activity strongly decreases with an increase of the K/V ratio. The selectivity towards acidic products also decreased, while the selectivity to BA was much less affected. An increase of the selectivity to BAc [20] and to BA [17,21–23] has

been reported, when adding low amounts of K. At the same time, the catalytic activity decreased [12,20,22], remained unchanged [21] or increased [17,23]. This shows the complexity of the system, being dependent on the concentration of vanadia and potassium, nature of support, presence of impurities, order of vanadium and potassium deposition [24] as well as reaction conditions.

Moreover, one has to define the parameters, by which the catalytic activity is characterised. For example, the initial reaction rates could be in variance with the rates under steady-state after catalyst deactivation. Recently we reported the results on kinetics and modelling during toluene oxidation on pure laboratory prepared V/Ti-oxide [9]. The reducibility in hydrogen of the home-made V/Ti-oxide samples was compared with the reducibility of the catalysts, prepared from commercial titania (Aldrich), which contained small amounts of potassium as an impurity [14].

The present work is aimed on the study of the doping of V/Ti-oxide by K taking into account the surface acid–base properties, the structure of surface vanadia species, the catalyst performance and its deactivation. The structure of surface active species determines redox properties of the oxide, which can be related to the catalytic performance by the Mars–van Krevelen mechanism. The reducibility of surface vanadia species is studied by temperature-programmed reduction (TPR) in H_2 . Surface acid–base properties are characterised via temperature-programmed desorption (TPD) of pyridine with mass spectrometric analysis of the products. This technique gives additional information as compared to the studies performed without gas-phase analysis [25–28]. The oxidation state and molecular structure of vanadia species are known to be influenced by the oxidative or reductive environment. Therefore, the molecular structure of surface vanadia is characterised by FT-Raman spectroscopy under controlled atmosphere.

Recently we have shown that transient response technique with continuous monitoring of gas-phase composition allows following the catalyst surface transformations during toluene oxidation [10]. Evolution of BA formed during interaction of toluene with the pre-oxidised catalyst (without gaseous oxygen) gives information about nucleophilicity of the surface oxygen. In the present study we applied transient and steady-state kinetics measurements to characterise

the change of the activity due to coking with time-on-stream in respect to the catalyst doping by potassium.

2. Experimental

2.1. Catalyst preparation

All catalysts in this study were synthesised in our laboratory. A TiO₂-support was prepared by hydrolysis of tetrapropyl orthotitanate (>98%, Fluka) by water at 273 K for 2 h. The precipitate was rinsed with distilled water and dried in air. The powder was calcined at 773 K overnight. To remove impurities from the surface the material was washed in 1N HNO₃ and calcined at 723 K for 1 h. Potassium and sodium (<0.01 wt.%) were not found by atomic absorption spectroscopy. Support grains have a size of 0.3–0.5 mm, and a BET surface area of 84 m²/g. Raman spectroscopy showed that the support possesses an anatase structure.

V/Ti-oxide catalysts were prepared via wet impregnation by aqueous solution of vanadium oxalate. Vanadium oxalate was synthesised from V₂O₅ (>99.6%, Aldrich) and hot aqueous solution of oxalic acid (>97%, Fluka). K-doped V/Ti-oxides were prepared via co-impregnation of vanadium oxalate and potassium oxalate prepared from the reaction of K₂CO₃ (puriss, Fluka) and oxalic acid. After drying, the samples were calcined for 120 min at 723 K in air. XPS did not show any surface impurities in the undoped catalysts. Vanadium loading was about 1.2 and 7.5 wt.%, corresponding to equivalent of 0.2 and 2 theoretical monolayers (ML) (the titania coverage by VO_x species: 1 ML = 10 V atoms/nm² [5]) and K/V

atomic ratio was varied as 0.05, 0.25, 1. The catalysts are abbreviated as xV–K_y, where *x* is the number of theoretical vanadia ML and *y* is the K/V atomic ratio. Characteristics of the catalysts are listed in Table 1.

2.2. Experimental setup and procedure

The kinetic studies under steady state and transient conditions were performed in the experimental setup recently described in [7]. The installation allowed a quick switch from one gas flow to another. The catalytic activity was measured at 573 K in a fixed-bed reactor. The reactor was a quartz tube with internal diameter of 6 mm and 130 mm length. The catalyst was diluted by quartz beads in a 1:3 weight ratio. Oxygen (99.95%), argon (99.998%) (Carbagas, Lausanne) and toluene (>99.5%, Fluka) were used as received without further purification. Toluene was introduced into a heated evaporator by a syringe pump. The catalyst loading corresponded to 4.0 m² and flow rate was set at 60 ml (STP)/min. Before the reaction, all catalysts were pre-treated in oxidative atmosphere (20 vol.% O₂ in Ar) at 673 K for 30 min. The temperature was subsequently decreased to 573 K and the flow was switched to the reaction mixture of 2 vol.% toluene with 40 vol.% O₂ in Ar. During the transient response experiments with toluene in the absence of gaseous O₂, a mixture of 2 vol.% toluene in Ar was used. The reactor was purged by Ar before the flow switch. Gas streams were analysed with a Balzers QMG-421 mass spectrometer and a Perkin-Elmer Autosystem XL gas chromatograph with two capillary columns for analysis of organic and inorganic (CO, CO₂) products.

Toluene conversion was calculated from the detected products: BA, BAc, maleic anhydride (MA) and

Table 1
Characteristics of the catalysts

Sample	V (wt.%)	K/V atomic ratio	SSA (m ² /g)	Coverage by vanadia (ML) ^a
0.2V–K ₀	1.2	0	76	0.22
0.2V–K _{0.25}	1.2	0.25	77	0.22
0.2V–K ₁	1.4	1	69	0.24
2V–K ₀	8.1	0	56	1.7
2V–K _{0.05}	7.2	0.05	50	1.5
2V–K _{0.25}	6.9	0.25	39	2.1
5V–K ₁	7.3	1	16	5.3

^a 1 ML V = 10 V atoms/nm² [5].

CO_x. Other by-products were present in trace concentrations. Selectivity was calculated as the number of moles of toluene converted into the product divided by the total number of converted toluene moles. The carbon balance was within 100 ± 5%.

The amount of irreversibly adsorbed toluene was determined by temperature-programmed oxidation (TPO) integrating the area under the concentration curves of the formed CO, CO₂. For this purpose after 20 min of the toluene interaction with the pre-oxidised catalysts and Ar purge, the mixture of 20 vol.% O₂/Ar was introduced into the reactor and the temperature was increased up to 683 K. Relative sensitivity factors of the mass spectrometer for carbon oxides with respect to oxygen were used to determine their concentration.

2.3. Catalyst characterisation

Raman spectroscopic studies were performed via a Perkin-Elmer FT-Raman 2000 spectrometer. A Raman spectroscopy cell [8] was attached to the same setup as was used for the kinetic experiments. A Nd:YAG laser, operating at 1064 nm with a varying power in the range of 10–750 mW was used in the Raman spectrometer. Sixty-four scans were taken with a resolution of 4 cm⁻¹ and averaged to obtain a spectrum. The spectrum of a catalyst in the Raman cell was measured in the flow of dry 20 vol.% O₂/Ar mixture (60 ml (STP)/min) at 523 K after pre-treatment at 673 K for 30 min. These conditions of the pre-treatment and measurement correspond to the dehydrated samples [11].

Temperature-programmed reduction (TPR) experiments were performed via a Micromeritics AutoChem 2910 analyser with a quartz plug-flow reactor. Hydrogen concentration was determined by a Thermostar 200 quadrupole mass spectrometer (Pfeiffer Vacuum). The catalysts were pre-treated in oxidative atmosphere (2 vol.% O₂, rest He) at 673 K for 30 min, and then cooled down to 323 K. After purging with Ar, the reactor was heated up in a mixture of 4 vol.% of H₂ in Ar (20 ml (STP)/min) with a constant heating rate (20 K/min). The thermocouple was inserted into the middle of the catalytic bed. The catalyst loading corresponded to 11 μmole of vanadium. The maximal conversion of hydrogen at the temperature peak maximum (*T*_{max}) was lower 10%.

Pyridine temperature-programmed desorption experiments were performed with the setup used for the TPR studies connected to the mass spectrometer. The surface area of the catalysts placed into the reactor corresponded to 2.2 m². The catalysts were pre-treated in oxygen (10 vol.% O₂/He) at 673 K for 30 min and then cooled in He (>99.999%) to reach the adsorption temperature (473 K). Helium was saturated with pyridine (2.4–3.1 vol.%) by passing through a flask with liquid pyridine (Fluka, ≥99.8%) at room temperature. Pulsed chemisorption was performed until the surface was saturated and after purging with He for 3 min, the temperature-programmed desorption was started. The heating rate was equal to 33.6 K/min and the total flow rate was 20 ml (STP)/min. Experiments with the reactor filled with quartz wool without the catalyst showed no adsorption of pyridine.

The *BET surface area* (SSA) of the support and the catalysts were measured using N₂ adsorption–desorption at 77 K by a Sorptomatic 1990 (Carlo Erba) instrument.

3. Results and discussion

3.1. Catalyst characterisation

BET specific surface areas of the catalysts are reported in Table 1. The catalysts with vanadia surface coverage of 0.2 and 2–5 ML with different addition of K were investigated. The BET surface area decreased with increasing amount of vanadia supported on titania being 76 m²/g for 0.2 ML and 56 m²/g for 2 ML of vanadia. Doping by K slightly decreased the SSA of 0.2 ML V/TiO₂ samples, but the introduction of K into high loading catalysts (2 ML) drastically decreased the SSA down to 16 m²/g for K/V = 1. This result can be explained by the increased wetting of the titania surface by supported vanadia upon K-doping as reported earlier [17]. Strong decrease of SSA for the 1 ML V/TiO₂ catalyst was also reported by Zhu and Andersson [12], but at the K/V atomic ratio higher than 1. This decrease of SSA was explained by the formation of rutile and potassium titanate phases.

The effect of K-doping on the structure of surface vanadia was studied via FT-Raman spectroscopy under controlled oxidative atmosphere (dehydrated conditions). Rutile bands were not found in the FT-Raman

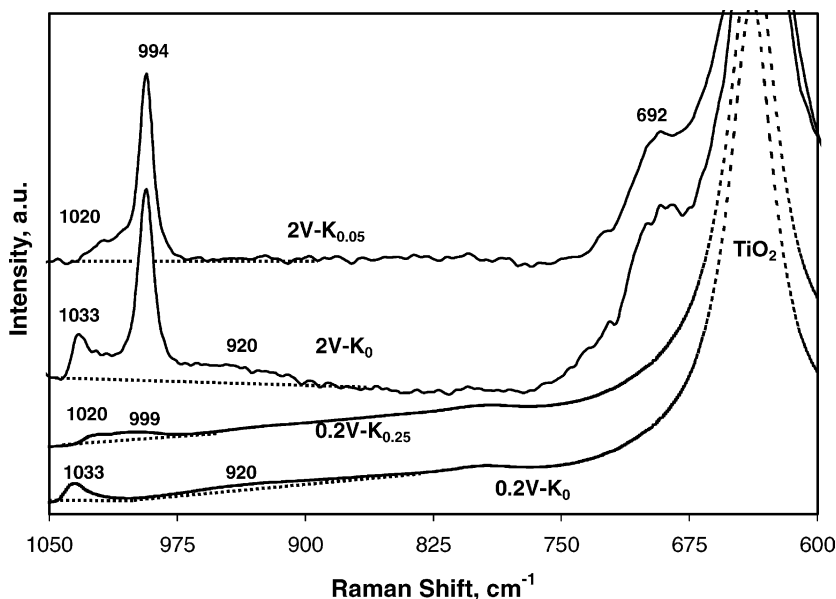


Fig. 1. FT-Raman spectra of the catalysts with different vanadia and K content measured under dehydrated conditions.

spectra for these samples. The form, in which vanadia is present on the titania surface, depends on the vanadia surface concentration, the K-concentration and the K/V ratio. The spectra are presented in Fig. 1. The undoped $0.2V-K_0$ and $2V-K_0$ catalysts contain isolated monomeric species (1033 cm^{-1}) and polymeric metavanadate-like species (920 cm^{-1}). In both of these species V^{5+} is tetracoordinated [11,13]. At a vanadium content of 2 ML, the bulk crystalline V_2O_5 is formed on the surface as seen from the Raman spectrum of the catalyst without K (bands at 994 and 692 cm^{-1} , Fig. 1).

Doping by K affects the composition of surface species for both samples in a similar way. The band at 920 cm^{-1} assigned to the polymeric metavanadate-like species disappears, the band at 1033 cm^{-1} (monomeric species) shifts to 1020 cm^{-1} and a new band appears at 999 cm^{-1} . The shift of the high-frequency band (1033 cm^{-1}) indicates a distortion of the monomeric species structure accompanying by the lengthening of the V=O bond due to the presence of K [13, 14,16,29]. The band at 1020 cm^{-1} is assigned to the K-perturbed monomeric species. The increase of the V=O bond length is not significant and corresponds to 0.007 \AA calculated using an equation proposed by

Hardcastle and Wachs [29]. An electrostatic interaction like $(\text{Ti}-\text{O}-)_3\text{V} = \text{O}^{\delta-} \dots \text{K}^{\delta+}-\text{O}$ may be the cause of the observed perturbation [14].

With increase of K content a distortion of the monomeric species structure becomes stronger. The length of the V=O bond increases by 0.017 \AA with respect to the monomeric species in pure V/Ti-oxide. A part of the bridging Ti-O-V=O sites could be substituted by K-O-V=O sites as reported earlier [16]. Hence, the Raman band at 999 cm^{-1} is assigned to this K-doped monomeric species.

The disappearance of the 920 cm^{-1} band indicates that K inhibits the formation of the polymeric metavanadate-like species leading to the formation of the K-doped monomeric species (999 cm^{-1}). This result is in accordance with the result of Courcot et al. [15] attained by ^{51}V solid-state NMR. They reported that the formation of the polymeric species takes place at a higher vanadia loading in K-doped samples than in undoped ones.

The bands characteristic for V_2O_5 (994 , 692 cm^{-1}) seen for the 2 ML V/TiO₂ catalysts were not changed upon addition of a low amount of potassium ($K/V = 0.05$). Thus, K interacts first with surface species and then at higher K/V ratios a bulk KVO_3 is

formed instead of V_2O_5 . The K-doped monomeric species and KVO_3 were the main vanadia forms observed in the $5V-K_1$ and $0.2V-K_1$ catalysts [14].

The surface acid–base properties of the studied catalysts were characterised via TPD of pyridine. Chemisorption of pyridine is commonly used as a probe for the presence of Lewis and Brønsted acid sites on a catalyst surface [25–28]. Brønsted acid sites are associated with hydroxyl groups and interact with pyridine molecule forming pyridinium ion (PyH^+), while Lewis acid sites (metal cations) coordinatively bind pyridine (PyL).

The pyridine TPD profiles are shown in Fig. 2. In order to facilitate quantitative comparison between different catalysts the loading was adjusted to the same surface area. From the pure titania support pyridine desorbs without decomposition since pyridine is weakly adsorbed as seen from the peak maximum at 573 K. It is known that pyridine interacts with titania surface forming only PyL and no PyH^+ species [25,26]. Therefore, the peak at 573 K is assigned to Lewis acid sites. The observed broadness of this peak suggests the existence of Lewis acid sites of different strength. The total amount of pyridine in this peak corresponds to 0.08 ML of pyridine supposing that $1 \text{ ML} = 10 \text{ Py molecules/nm}^2$.

Deposition of 0.2 ML vanadia on titania results in a slight decrease of the intensity of this peak without any change in the shape and position of peak maximum. This could be explained by pyridine adsorption mainly on the titania sites not covered by vanadia. However, appearance of new vanadia sites showing Lewis acidity with the strength close to titania Lewis acid sites is also possible in accordance with the FTIRS data [25,26]. Additionally, removal of pyridine in the form of oxidised products (CO_2 , CO , H_2O and probably N_2 , N_2O , NO in much smaller concentrations) takes place with a peak maximum at 740 K. PyH^+ ions stable to evacuation were observed by FTIRS at temperatures as high as 573 K [26] and 673 K [27]. Formation of the oxidised products indicates that surface oxygen of a vanadia species strongly interacts with the adsorbed pyridine resulting in the ring fission. This oxygen species is assigned to the electrophilic type [1]. Similar picture is observed in the TPD of ammonia [18] with a broad TPD peak and oxidation of adsorbed ammonia at high temperatures.

Doping by K at $K/V = 0.25$ does not result in any change of the 573 K peak, while the peak of the oxidised products becomes much smaller (Fig. 2a). This indicates that K interacts mainly with vanadia blocking some of the Brønsted acid sites responsible for the strong adsorption of pyridine. Raman spectroscopy shows that the K-doped monomeric species are observed instead of the polymeric metavanadate-like species upon addition of potassium (Fig. 1). Hence, the sites responsible for pyridine oxidative decomposition are assigned to hydroxyl groups attributed to the polymeric vanadia species. Increase of the K/V ratio up to 1 results in strong decrease of the concentration of weakly adsorbed pyridine showing that surface Lewis acid sites are also affected by K. This observation is in line with the effect of alkali doping on Lewis acidity of an oxide surface already reported in [30].

Increase of vanadia concentration from 0.2 to 2 ML does not change the total amount of adsorbed pyridine. The main difference is that the ratio between weakly adsorbed pyridine (removed from the surface without decomposition) and strongly adsorbed (removed via oxidation products) substantially diminishes (Fig. 2b). As it follows from the Raman results (Fig. 1) these catalysts contain bulk crystalline V_2O_5 , which is known to possess Brønsted acidity [11,31]. Additionally, the concentration of monolayer species and the ratio of the polymeric to the monomeric species in the $2V-K_0$ catalyst should be higher than in the $0.2V-K_0$ case, due to the higher vanadia concentration. Increase of the Brønsted acidity in the sample should provide an increase of the strongly adsorbed pyridine, which is removed from the surface in the form of CO_x and nitrogen containing products. The peak of the weakly adsorbed pyridine decreases and slightly shifts to the lower temperature 564 K (Fig. 2b) as compared with the 0.2 ML V catalyst (Fig. 2a) indicating a decrease in the concentration and strength of the Lewis acid surface sites. This peak is assigned to the monolayer vanadia Lewis acid sites. However, some contribution from titania Lewis acid sites is not excluded [5].

Addition of K to the 2 ML V catalyst with $K/V = 0.25$ results in the decrease and shift of the pyridine TPD peak to the lower temperature region (537 K) since K decreases the strength and the amount of monolayer vanadia Lewis acid sites. Increase of K concentration up to $K/V = 1$ leads to the formation of the catalyst which does not adsorb pyridine. The sample

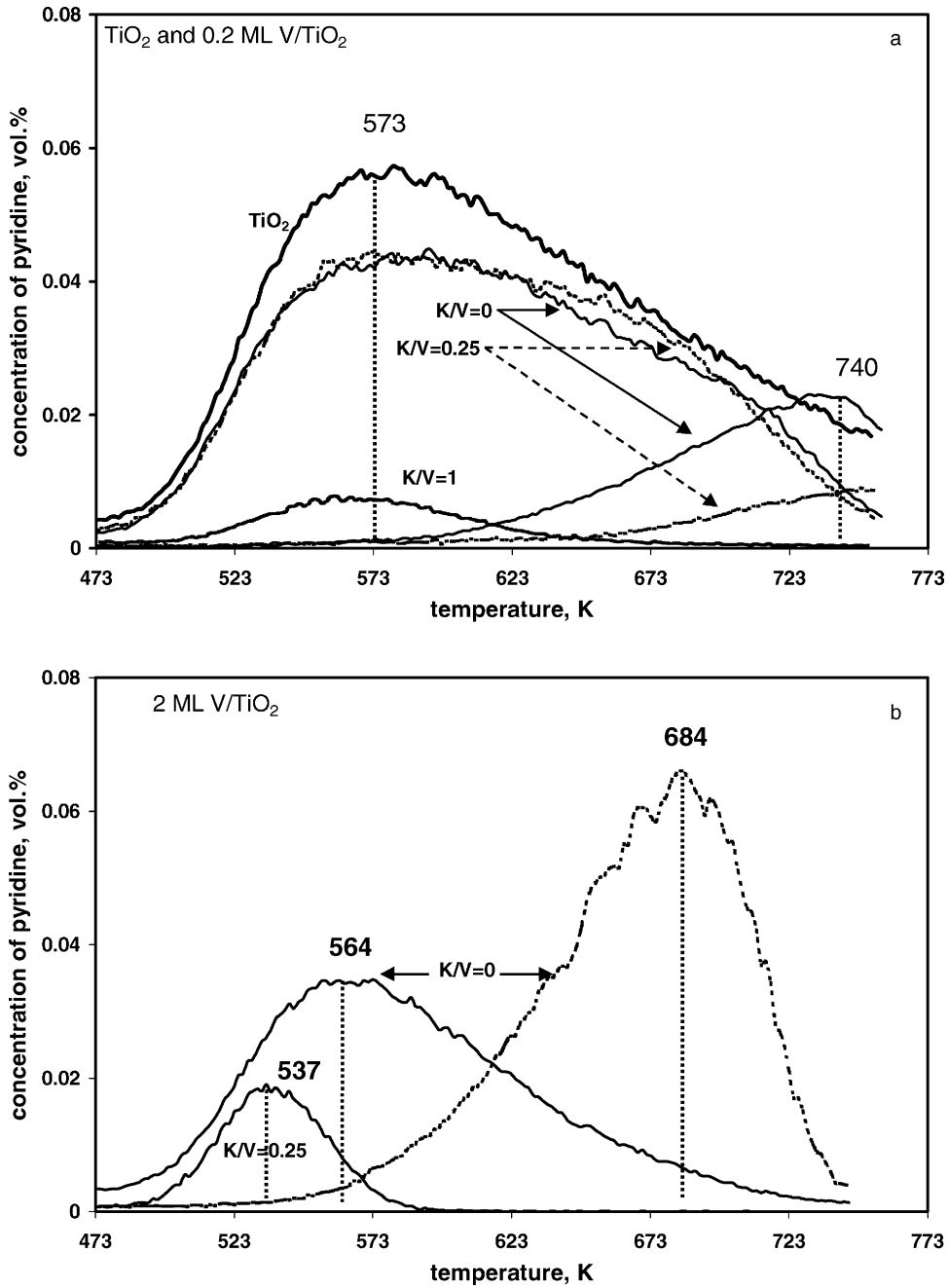


Fig. 2. TPD of pyridine from the catalysts with different vanadia and K content taken with the same surface area equal to 2.2 m² (peaks at 684 and 740 K correspond to pyridine removed from the surface in the form of CO, CO₂ and nitrogen containing products, determined as a sum of CO and CO₂ concentrations divided by 5).

was shown to contain mainly the K-doped monomeric and amorphous KVO_3 species [14].

The assignment of the TPD peak maxima: 537–573 K due to the monolayer vanadia and titania Lewis acid sites, 684 K due to the V_2O_5 Brönsted sites and 740 K to the monolayer vanadia Brönsted sites is similar to the one reported by Khader [31] for vanadia/alumina catalysts based on TPD and FTIRS of ammonia. TPD peaks of ammonia from vanadia/titania catalysts are usually broader [18] than the ones from the vanadia/alumina catalysts. This complicates their assignment for the vanadia acid sites. However, in general the similar decrease of the intensity of the ammonia TPD peaks upon K-doping was observed by Lietti et al. [18].

The effect of K-doping on the reducibility of surface vanadia was studied by TPR in hydrogen. Only the reducibility of monolayer vanadia upon K-doping was considered, since monolayer species are active in toluene oxidation [8,9]. The TPR profile of the sample 0.2V-K_0 (Fig. 3) shows one peak at 767 K. The monomeric and polymeric species are reduced by hydrogen at the same temperature [11,32]. Doping of vanadia by K results in a considerable change in the TPR profiles. Vanadia in the $0.2\text{V-K}_{0.25}$ catalyst is reduced at higher temperatures as compared to the V/Ti-oxide without K. The broadness of the

TPR peak for the catalyst with $\text{K/V} = 0.25$ indicates the reduction of multitude of surface vanadia species. This result is in line with a variety of vanadia forms found on the surface of $0.2\text{V-K}_{0.25}$ catalyst by Raman spectroscopy. The shift of the T_{max} to higher temperatures for the K-doped catalysts was reported earlier [19], but no relation was found for the reduction and the structure of surface vanadia species. The reported results [14] allow proposing the following trend for T_{max} of reduction of vanadia species: monomeric, polymeric < K-perturbed monomeric < K-doped monomeric < amorphous KVO_3 .

3.2. Toluene interaction with pre-oxidised catalysts

In order to elucidate the structure/activity relationship of vanadia species formed on the surface of V/Ti-oxide upon K-doping, the catalysts were studied by transient kinetics method. Catalyst loading was taken to have the same total surface area. The transient responses of products during toluene oxidation by the surface oxygen of pre-oxidised catalyst in the absence of gaseous oxygen allow the comparison of the surface reducibility by toluene molecules. This technique is probably the only one, which gives an access to the reduction process of active sites (the first step in the Mars–van Krevelen mechanism)

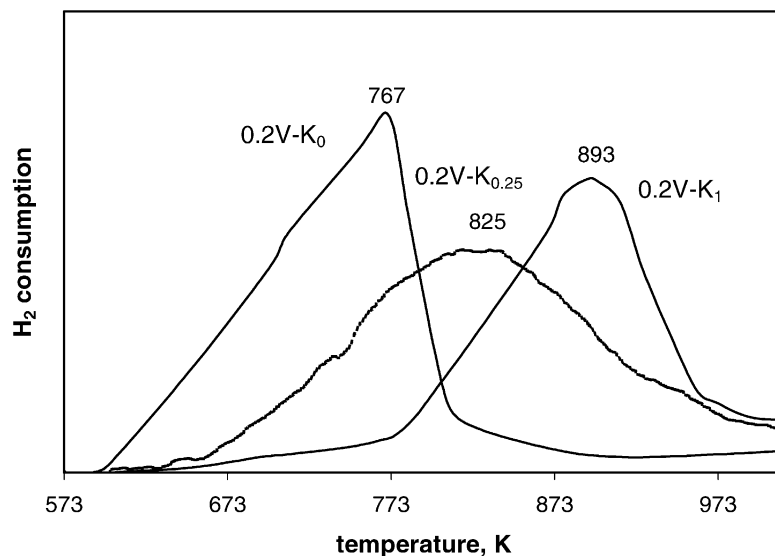


Fig. 3. TPR profiles of the 0.2 ML V/TiO₂ catalysts with different K/V ratio.

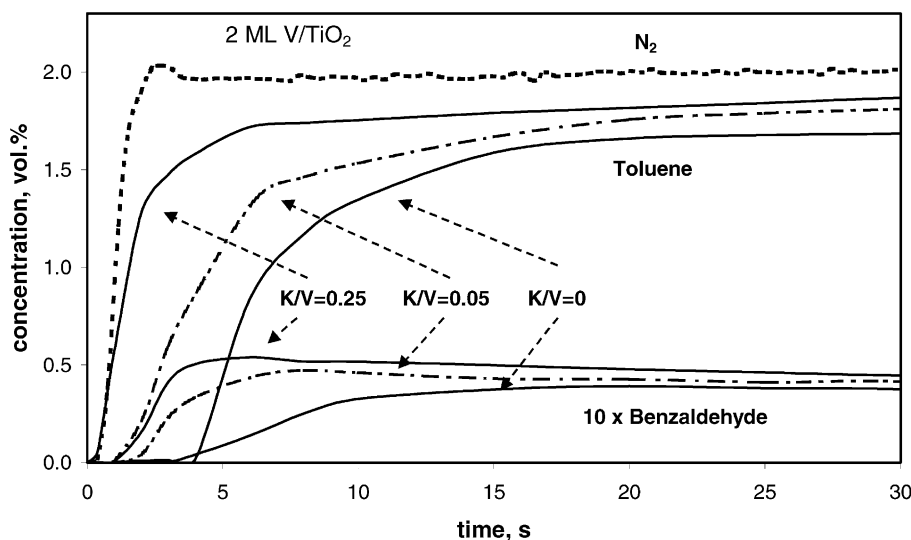


Fig. 4. Transient response curves obtained at 573 K after the switch of the Ar flow to the 2 vol.% toluene/98 vol.% Ar flow over the pre-oxidised catalysts containing 2 ML of vanadia and different K/V ratios (catalyst loading corresponds to 4.0 m^2).

separated from the step of the reoxidation (the second step in the Mars–van Krevelen mechanism). The responses of toluene and BA for K-doped and undoped samples were compared with the response of inert gas (N_2) (Fig. 4). The conversion of toluene is equal to the difference between the response curves of inert gas and toluene. Among the products only BA, CO, CO_2 and H_2O were observed, but no MA and BAc.

It is seen that with addition of K, the conversion of toluene decreases while the formation of BA increases (Fig. 4). Toluene is converted mainly to irreversibly adsorbed products that were determined after transient experiments in TPO runs (Table 2). Formation of these products decreases with K concentration and this provides a disappearance of the

delay for the toluene and BA evolution observed in Fig. 4. The irreversibly adsorbed toluene was transformed by oxygen during TPO into CO_x over the 0.2 ML V/TiO₂ catalysts and to CO_x , BAc and MA over the 2 ML V/TiO₂ ones. It is seen from Table 2 that an increase in vanadia coverage from 0.2 to 2.0 ML in the undoped catalysts increases the amount of irreversibly adsorbed products. This fact can be explained by the higher coverage of titania by vanadia, providing an increase of the Brønsted acidity. This favours benzene ring fission resulting in CO_x and coke formation.

The increase of strongly adsorbed pyridine (removed in the form of oxidised products) with vanadia concentration was observed in the pyridine TPD runs (Fig. 2). Potassium diminishes the acidity and decreases the concentration of electrophilic oxygen by transforming it to more stable nucleophilic oxygen species [15]. This leads to a higher initial selectivity to BA over K-doped V/Ti-oxides (Fig. 4). The selectivity towards BA formation after 30 s was 12, 22 and 34% for the K/V ratios of 0.0, 0.05 and 0.25, respectively. No adsorption of toluene and product formation was found for the catalysts with $\text{K/V} = 1$ containing mainly the K-doped monomeric species and KVO_3 .

Table 2

Concentration of irreversibly adsorbed products removed by TPO in the form of CO and CO_2 after toluene interaction with the pre-oxidised catalysts for 20 min (C atom/nm^2)

Coverage by vanadia (ML)	K/V atomic ratio			
	0	0.05	0.25	1
0.2	4.3	–	3.7	0.35
2	7.8	6.8	3.5	0

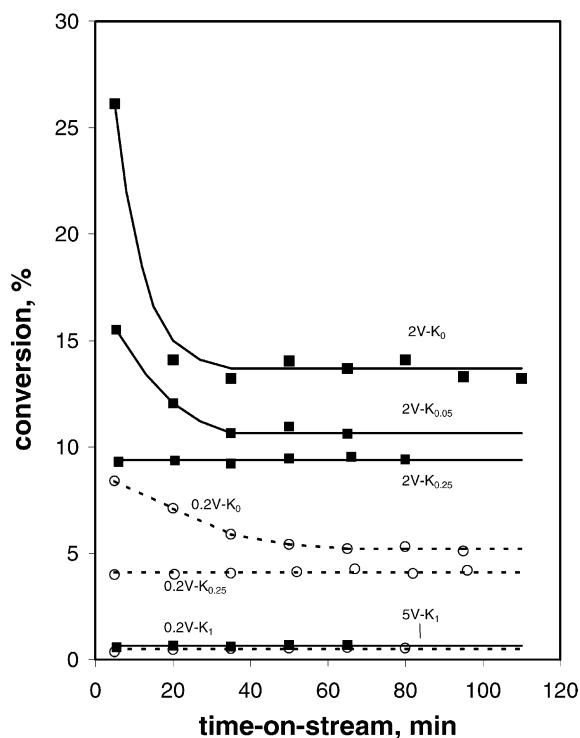


Fig. 5. Dependence of the conversion of toluene on time-on-stream for the catalysts with different vanadia and K content (2 vol.% toluene/40 vol.% O₂/58 vol.% Ar, 573 K, catalyst loading corresponds to 4.0 m²).

3.3. Catalyst deactivation and steady-state activity

The dynamics of the catalyst activity with time-on-stream is presented in Fig. 5. The activity, characterised by toluene conversion at constant temperature referred to the same catalyst surface area, is seen to depend on the total coverage by vanadia and on the K-doping. The undoped 2 ML V/Ti-oxide catalyst possesses the highest initial and steady-state activity, but quickly deactivates. It is seen that the conversion decreases reaching a steady-state within ~60 min. The deactivation decreased with addition of K and was not observed at K/V = 0.25 for the catalysts with vanadia coverage of 0.2 and 2 ML. The activity of the 2V-K₀ catalyst higher than in the case of 0.2V-K₀ could be assigned to the higher concentration of the monolayer species.

Low activity (conversion lower than 0.7%) is observed for the catalysts with the K/V ratio equal to one. These catalysts as was mentioned above contain mainly the K-doped monomeric species and KVO₃, but do not contain the undoped monomeric/polymeric species and V₂O₅ [14]. Lower activity of the 2V-K_{0.05} catalyst than the activity of the 2V-K₀ sample correlates with the transformation of a part of the monomeric/polymeric species into the K-doped species found by Raman spectroscopy (Fig. 1). Different activity (Fig. 5) but similar intensity of the V₂O₅ band (994 cm⁻¹) for these two samples (Fig. 1) indicates that bulk V₂O₅ does not play an important role for the catalytic activity. However, deactivation is observed only for the samples containing the polymeric and/or V₂O₅ species, which possess some Brönsted acidity in accordance with the pyridine TPD data (Fig. 2). Potassium interacts with Brönsted acid sites decreasing the adsorption ability of aromatic and unsaturated products, which can block the catalyst surface [9].

Hence, the results suggest that alkali doping causes the decreased acidity (Fig. 2) by transformation of some monolayer vanadia species into K-doped and KVO₃ ones. As a result the catalyst activity decreases, but at the same time the catalyst deactivation could be completely suppressed (Fig. 5). This allows a better control of the oxidation process.

3.4. Reaction pathways: coking, partial and total oxidation

In a recent publication [9] devoted to the deactivation kinetics of V/Ti-oxide in toluene partial oxidation, a reaction network was suggested for low conversions (<15%) and is shown in Fig. 6. BA (1), BA_c (2), MA (3) are formed via consecutive pathway. Benzyl species, a possible intermediate of this pathway [33,34], could be provided by toluene adsorption via methyl group and abstraction of one hydrogen atom from the toluene molecule [35].

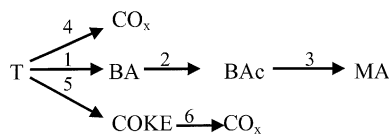


Fig. 6. Reaction network.

3.4.1. Toluene activation

The activation of C–H bond in the methyl group of toluene is believed to be the rate-determining step of the overall process. It should occur through the interaction of σ or σ^* C–H orbital with the d-type orbitals of a vanadium cations (V^{5+}) at the catalyst surface. This interaction involves the electron transfer from toluene to the surface cations (Lewis acid sites) and should be more difficult when vanadia is doped by K because K is an electron-donating additive. Neither toluene adsorption nor products evolution were observed in the transient experiments when the catalysts contained $K/V = 1$. Almost no acidity was found by pyridine adsorption at this K/V ratio. The K-doped monomeric and KVO_3 species present in this catalyst [14] probably cannot activate toluene molecules. Additionally the reduction of these species is complicated as follows from the TPR study (Fig. 3). It was shown by DRIFTS that toluene could be activated by the monomeric species while another type of vanadia species, containing oxygen for an insertion (polymeric and V_2O_5) is necessary [36]. Thus, the monomeric species seems to possess the Lewis acidity suitable for toluene activation.

The results of the present work show that the activity in toluene oxidation in the presence of oxygen (Fig. 5) is almost absent when the monomeric species (pure or K-perturbed ones) are not found in the catalysts. Hence, the monomeric species can be responsible for the activity in the toluene oxidation. This is also in line with the results obtained for the catalysts prepared by solid-state reaction, when the increased catalytic activity correlated with the higher concentration of the monomeric species [8]. In these catalysts the polymeric species were not found, while bulk V_2O_5 was observed. Hence, the presence of the polymeric species is not so crucial for the catalyst activity.

3.4.2. Product desorption

Another key factor in the catalyst performance in toluene partial oxidation, is to drive the reaction towards the formation of BA as a main product and to desorb it without further transformation and over-oxidation [37]. This should be largely influenced by the surface acid–base properties with more favourable BA desorption from basic surface. This is in line with the experimental results obtained in the absence of oxygen (Fig. 4).

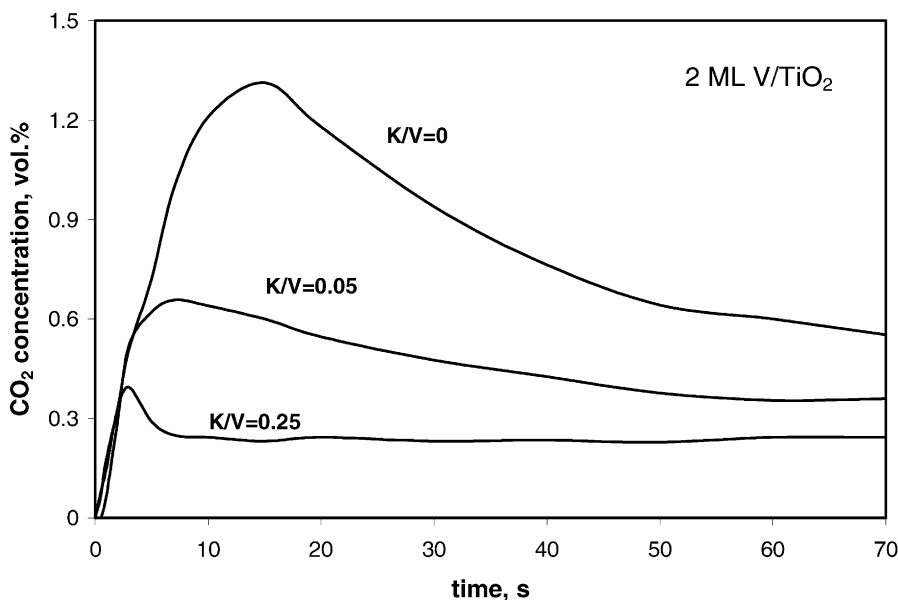


Fig. 7. Transient response curves of CO_2 obtained at 573 K after the switch of the 20 vol.% O_2 /80 vol.% Ar mixture to the 2 vol.% toluene/40 vol.% O_2 /58 vol.% Ar one over the catalysts containing 2 ML of vanadia with different K content (catalyst loading corresponds to $4.0 m^2$).

In the presence of oxygen, the total selectivity to BA, BAc and MA, corresponding to the consecutive route via BA was found very similar (80–90%) for the 2 ML V/TiO₂ catalyst independently on the presence of K in the range 0–1. It seems also that BAc is more easily transformed to MA on the K-doped samples in accordance with the data of Zhu and Andersson [12]. This result can be understood taking into account that more basic surface can retain BAc for a longer time, which favours the consecutive oxidation of this product with MA and CO_x formation [7,38].

3.4.3. Coking and total oxidation

The products blocking the surface are denoted in Fig. 6 as COKE (5) and imply all the products responsible for deactivation of the catalyst. Among them are benzoic acid and the products of coupling [9] formed via benzyl species [34]. Some of the COKE species are oxidised by gaseous oxygen to CO_x (the path 6) under the reaction conditions. Another part of CO_x is formed in parallel to BA by the path 4 and results in the maximum of the CO₂ response curve in the presence of oxygen (Fig. 7). Toluene adsorption with aromatic ring in parallel to the surface may be responsible for this pathway via interaction with electrophilic oxygen leading to the ring destruction [39]. It is seen in Fig. 7 that the maximum disappears upon K-doping. Therefore, one may speculate that upon alkali doping, decreasing Lewis and Brønsted acidity, formation of CO_x via the path 4 may be decreased.

4. Conclusions

The conclusions of the present study can be summarised as follows:

1. The vanadia molecular structure in the catalysts containing 0.2 and 2.0 ML of vanadia supported on titania was characterised by FT-Raman spectroscopy and compared with the molecular structure of K-doped samples with atomic ratios $0.05 < K/V \leq 1$. Isolated monomeric vanadia, polymeric metavanadate-like species and bulk V₂O₅ are formed with increasing vanadia loading. Upon K addition the K-perturbed and K-doped monomeric

surface species with increased length of the V=O bond as well as KVO₃ were formed. Disappearance of the metavanadate-like polymeric species and undoped monomeric species was observed upon K-doping.

2. Acid–base properties were characterised by TPD using pyridine. Two main forms of adsorbed pyridine were detected: (i) weakly held species associated with pyridine molecularly coordinated to vanadium and/or titanium cations (Lewis acid sites) desorbed without any transformation; (ii) strongly adsorbed species associated with pyridinium ion (PrH⁺) formed on the Brønsted acid sites of monolayer vanadia and bulk V₂O₅. These species are removed at higher temperatures in the form of oxidised products. The surface concentration of both species decreases upon K-doping. At an atomic ratio $K/V > 0.25$, strongly adsorbed pyridine was not detected.
3. TPR in H₂ data provide evidence that K-doped vanadia species could be reduced at a higher temperature than the undoped ones. These data correlate with lower activity of K-doped catalysts as compared with the undoped ones.
4. Transient responses during toluene interaction with the pre-oxidised catalysts in the absence of oxygen allow characterisation the relative surface concentration of electrophilic/nucleophilic oxygen species upon K-doping. Potassium addition decreases the concentration of electrophilic oxygen species (O₂⁻, O⁻), responsible for the total oxidation. But concomitantly the concentration of nucleophilic oxygen (O²⁻) increased, leading to higher selectivity towards BA formation. The transformation of the monomeric species, responsible for toluene activation, into K-doped monomeric and KVO₃ species decreases the catalytic activity.
5. Coke formation, determined by TPO, was observed to decrease upon K-doping as well as deactivation of the catalyst with time-on-stream. Suppression of the deactivation provides an improved control of the oxidation process.

Acknowledgements

The authors gratefully acknowledge the Swiss National Science Foundation for the financial support.

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