Partial oxidation of toluene to benzaldehyde and benzoic acid over model vanadia/titania catalysts: role of vanadia species

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Abstract

Pure and K-doped vanadia/titania prepared by different methods have been studied in order to elucidate the role of vanadia species (monomeric, polymeric, bulk) in catalytic toluene partial oxidation. The ratio of different vanadia species was controlled by treating the catalysts in diluted HNO_3, which removes bulk vanadia and polymeric vanadia species, but not the monomeric ones, as was shown by FT-Raman spectroscopy and TPR in H_2. Monolayer vanadia species (monomeric and polymeric) are responsible for the catalytic activity and selectivity to benzaldehyde and benzoic acid independently on the catalyst preparation method. Bulk V_2O_5 and TiO_2 are considerably less active. Therefore, an increase of the vanadium concentration in the samples above the monolayer coverage results in a decrease of the specific rate in toluene oxidation due to the partial blockage of active monolayer species by bulk crystalline V_2O_5. Potassium diminishes the catalyst acidity resulting in a decrease of the total rate of toluene oxidation and suppression of deactivation. Deactivation due to coking is probably related to the Brønsted acid sites associated with the bridging oxygen in the polymeric species and bulk V_2O_5. Doping by K diminishes the amount of active monolayer vanadia leading to the formation of non-active K-doped monomeric vanadia species and KVO_3.
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1. Introduction

V/Ti-oxides are known to catalyse partial oxidation of hydrocarbons, selective reduction of NO_x, ammoxidation of alkylaromatics and oxidative dehydrogenation of hydrocarbons. The state of vanadia in the catalysts is non-uniform. Under dehydrated conditions V/Ti-oxides contain isolated monomeric species, polymeric species, and bulk V_2O_5 [1–7].

Benzaldehyde (BA) and benzoic acid (BAc) are the most valuable products of toluene partial oxidation formed by consecutive pathway from toluene. It is a lot of evidence that the specific rate (per m^2 of the catalyst) of toluene oxidation increases with vanadia coverage up to one monolayer, however, at higher coverage it was found to decrease [8], to be stable up to two monolayers [9,10] and to increase up to high coverage [11]. The reasons of such discrepancy could be due to the presence of impurities in the titania support,

mainly K and P [4,10], which are known to influence the structure of vanadia surface species [4,6,12,13] affecting the activity, selectivity and stability towards coking.

The treatment of V/Ti-oxides in aqueous solutions of acids and bases results in partial removal of vanadia from the surface [2,4,14–17]. The removal of bulk V_2O_5 and polymeric species has been already reported [2,18]. The coverage by vanadia species after this treatment was found in the range of 0.1–0.4 monolayer (ML) [4], but the higher than 1 ML coverage was also reported [16].

The insoluble in acids and bases vanadia was shown to catalyse oxidative dehydrogenation reactions [4], isopropanol conversion to acetone and total *o*-xylene oxidation [2]. The activity of the catalysts containing only insoluble in HNO_3 species in ammoxidation of methylpyrazine was found higher than before the HNO_3 treatment [16]. In contrast, a decrease in activity after such treatment was reported for *o*-xylene oxidation [2]. The role of insoluble species was not studied in toluene partial oxidation.

Spectroscopic information on the structure of insoluble species is quite limited [4]. Octahedral vanadium coordination

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followed from the ^{51}V NMR studies of the HNO$_3$ treated V/Ti-oxide [16]. However, isolated monomeric species with tetra-coordinated vanadium was found by Raman spectroscopy in the Eurocat V/Ti-oxide catalysts after treatment in NH$_4$OH [17]. The contradiction [16,17] could be assigned to the conditions of measurement (hydrated/dehydrated [1]) and to the different vanadia concentration in the samples remained after treatment.

Recently, we reported a detailed characterisation of the model vanadia/titania catalysts treated in diluted HNO$_3$ [18]. The present work is aimed on the elucidation of the role of different vanadia species in partial toluene oxidation regarding catalytic activity, selectivity and stability. The catalytic activity of vanadia/titania was compared within the series of the samples prepared by solid-state reaction, by impregnation and grafting. Effect of K-doping was studied for the catalysts prepared by impregnation and containing the same vanadia loading in the form of monolayer vanadia species. Bulk V$_2$O$_5$ and TiO$_2$ were also tested and characterised.

2. Experimental

2.1. Catalyst preparation

Detailed synthesis of the support and catalysts is reported elsewhere [18]. The characteristics of the mainly studied samples are presented in Table 1. A TiO$_2$ support was prepared by hydrolysis of the tetrapropylorthotitanate (>98%, Fluka). This titania was shown to possess an anatase structure and specific surface area (SSA) of 57 m^2 g^{-1}. Monolayer catalyst with 1.8 wt.% of vanadium (0.37 ML V/TiO$_2$) was prepared via a well-known grafting technique [4,5] by three-steps of VOCl$_3$ vapour deposition on the surface of the TiO$_2$, followed by hydroxylation and drying. Impregnated catalyst containing 11.1 wt.% of vanadium (2.6 ML V/TiO$_2$), was synthesised by a three-step wet impregnation with vanadium oxalate solution (prepared from V$_2$O$_5$

(>99.6%, Aldrich, SSA—9.1 m^2 g^{-1}) and oxalic acid (>97%, Fluka)). After calcination for 120 min at 723 K the SSA of these catalysts were equal to 57 and 50 m^2 g^{-1}, respectively. The amount of vanadium in the catalysts corresponds to 0.37 and 2.6 ML coverage of titania by VO$_x$ species (1 ML = 10 V − atom (nm^{-2}) [4]).

Two treatments of the catalysts for 25 min in excess of an aqueous solution of HNO$_3$ (1.2 N) were performed to remove some surface vanadia. After washing in deionised water, the catalysts were dried and calcined at 723 K for 30 min in air.

For the preparation of the samples by a solid-state reaction [14,19] a titania (Alfa, >99.9%) containing 89% of anatase phase and 11% of rutile was used. The SSA was found equal to 49 m^2 g^{-1}. Intensively ball-milled (1 h) physical mixtures of V$_2$O$_5$ with TiO$_2$ were calcined in air for 11 h at 723 K and then for 34 h at 773 K to obtain the 0.76, 1.6 and 3.7 ML V/TiO$_2$-ssr samples.

To study an effect of K-doping a series of V/Ti-oxide catalysts with a smaller vanadia coverage (0.2 ML) was prepared via wet co-impregnation of home made titania by aqueous solution of vanadium oxalate with potassium oxalate obtained in the reaction of K$_2$CO$_3$ (puriss, Fluka) and oxalic acid. After drying, the samples were calcined for 120 min at 723 K in air. The vanadium concentration in the samples was equal to 1.2–1.4 wt.% (0.2 ML V/TiO$_2$-K$_x$ series) and SSA was in the range of 69–77 m^2 g^{-1} corresponding to the vanadia coverage 0.19–0.24 ML.

2.2. Experimental set-up and procedure

The kinetic studies were performed in the experimental set-up described in [20]. The installation allowed a quick switch from one gas flow to another. The reactor was a quartz tube. 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 intro-

Table 1
Characteristics of the studied vanadia/titania catalysts

Catalyst	V$_2$O$_5$ content (wt.%)	SSA (m^2 g^{-1})	VO$_x$ coverage (ML)[a]	Method of preparation	K/V atomic ratio	Steady-state activity × 10^{-16} at 523 K (toluene molecule, s^{-1} m^{-2})
Catalysts on the base of the Alfa titania (SSA = 49 m^2 g^{-1})						
0.76 ML V/TiO$_2$-ssr	4.3	35	0.76	Solid-state reaction	0	0.12
1.6 ML V/TiO$_2$-ssr	8.0	32	1.6	Solid-state reaction	0	0.44
3.7 ML V/TiO$_2$-ssr	14.8	27	3.7	Solid-state reaction	0	0.29
Catalysts on the base of the home made titania (SSA = 57 m^2 g^{-1})						
0.37 ML V/TiO$_2$	3.2	57	0.37	Grafting	0	0.22
2.6 ML V/TiO$_2$	19.8	50	2.6	Impregnation	0	0.067
Catalysts on the base of the home made titania (SSA = 84 m^2 g^{-1})						
0.2 ML V/TiO$_2$-K$_0$	2.1	76	0.19	Impregnation	0	0.70[b]
0.2 ML V/TiO$_2$-K$_{0.25}$	2.1	77	0.22	Impregnation	0.25	0.56[b]
0.2 ML V/TiO$_2$-K$_1$	2.5	69	0.24	Impregnation	1	0.07[b]

[a] Monolayer is taken equal to 10 V atom nm^{-2}.
[b] Measured at 573 K.

duced into a heated evaporator by a syringe-pump. The catalyst loading corresponded to 4.0 m^2 and flow rate was 60 mL (STP) min^{-1}. Before the reaction, all the catalysts were pre-treated in oxidative atmosphere (20 vol.% O_2 in Ar) for 30 min at 673 K. Then the temperature was decreased to 523 or 573 K and the flow was switched to the reaction mixture of 2 vol.% toluene with 40 vol.% O_2 in Ar.

Gas composition was 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, CO_2) products.

Toluene conversion was calculated from the detected BA, BAc, maleic anhydride (MA) and 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. To compare the catalytic activity of the samples specific rates of the toluene oxidation referred to the total surface area were used. The conversions were below 10%. The carbon balance was within $100 \pm 5\%$.

2.3. Catalyst characterisation

Raman spectroscopic studies were performed with a Perkin-Elmer FT-Raman 2000 spectrometer. A Raman spectroscopy in situ cell [7] was attached to the same set-up as was applied for the kinetic experiments. A Nd:YAG laser, operating at 1064 nm with a 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 was measured in the flow of dry 20 vol.% O_2/Ar mixture (60 ml (STP) min^{-1}) at 363 or 523 K after pre-treatment at 673 K for 30 min. These conditions of the pre-treatment and measurement correspond to the dehydrated ones [1].

Temperature programmed reduction (TPR) experiments were performed in 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.% O_2, 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 H_2 in Ar (20 ml (STP) min^{-1}) with a constant heating rate (20 K min^{-1}). The catalyst loading corresponded to 4 m^2. A thermocouple was inserted into the middle of the catalytic bed.

Pyridine temperature-programmed desorption experiments were performed with the set-up used for the TPR studies connected to the mass-spectrometer. The surface area of the catalysts placed into the reactor corresponded to 2.2 m^2. The catalysts were pre-treated in oxygen (10 vol.% O_2/He) at 673 K for 30 min and then cooled in He 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, $\geq$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 run was started. The heating rate was equal to 33.6 K min^{-1} and the total flow rate was 20 ml (STP) min^{-1}.

3. Results

3.1. Vanadia/titania catalysts prepared by solid-state reaction

An effect of vanadia concentration on the steady-state specific rates of toluene oxidation was studied for vanadia/titania catalysts prepared by solid-state reaction of V_2O_5 with TiO_2 (0.76, 1.6 and 3.7 ML V/TiO_2-ssr) (Fig. 1). It is seen that the steady-state specific activity of pure V_2O_5 and TiO_2 is much lower as compared to the activity of vanadia/titania catalysts. A deposition of vanadia on titania by solid-state reaction can result in considerable (more than 1 order of magnitude) increase of the specific activity (Fig. 1). A physical mixture of uncalcined V_2O_5/TiO_2 showed activity 2–3 times lower than after calcination indicating that calcination is an important step in preparation of an active catalyst. It should be noticed also that a two-fold increase in the concentration of vanadia from 8 to 14.8% (1.6 and 3.7 ML V/TiO_2-ssr samples) decreases the specific activity indicating that the concentration of active surface sites does not increase, but in contrast decreases.

The total selectivity to BA and BAc with vanadia/titania catalysts reaches 85–90%, while over crystalline V_2O_5 it is slightly lower (~84%) even at lower conversion. Some deactivation due to coke formation was observed without a noticeable change of the total selectivity [20]. Titania is not only less active than vanadia/titania, but also less selective providing the selectivity to BA of only 51% and no BAc formation.

FT-Raman spectra (Fig. 2) demonstrate that in the uncalcined ball-milled V_2O_5/TiO_2 mixture only V_2O_5 (994, 696 cm^{-1}) and TiO_2 (634 cm^{-1}), but no species of their interaction are present. The calcination results in a decrease of the V_2O_5 concentration and formation of monomeric (1033 cm^{-1}) and polymeric (920 cm^{-1}) vanadia species interacting with titania surface. In these species V^{5+} is tetracoordinated [1]. The obtained spectra are typical for pure V/Ti-oxides under dehydrated conditions [21,22].

An increase of the concentration of vanadia in the calcined samples from 8 to 14.8% (1.6 and 3.7 ML V/TiO_2-ssr) is accompanied by an increase in the intensity of the V_2O_5 bands (Fig. 2). The same monomeric and polymeric species are formed. The presence of bulk V_2O_5 was also found in the 0.76 ML V/TiO_2-ssr sample indicating not complete conversion of V_2O_5 to monolayer species in this sample. The difference between the intensity of the V_2O_5 band at 994 cm^{-1} before and after calcination was
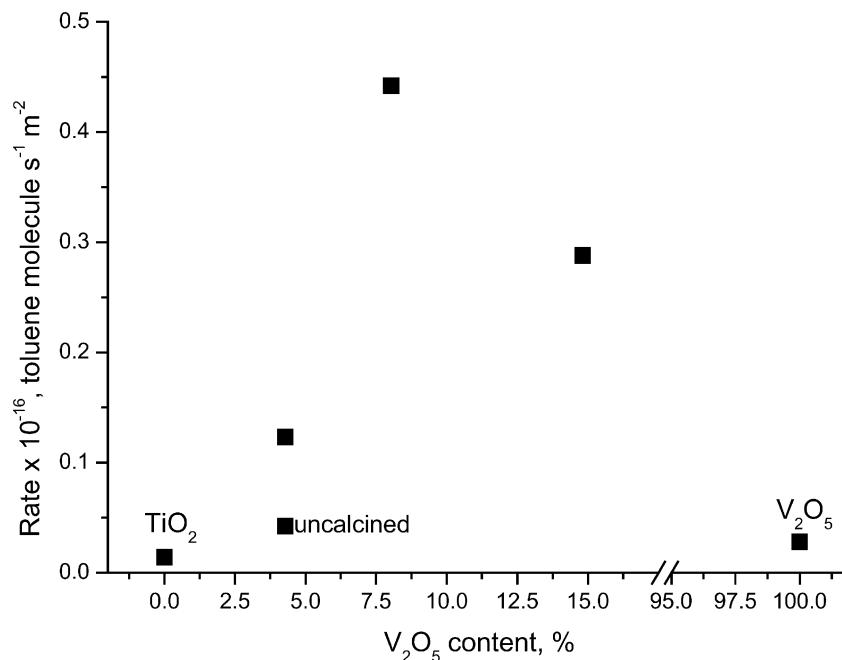
Fig. 1. Specific steady-state rates of toluene oxidation at 523 K as a function of vanadia content in vanadia/titania catalysts prepared by solid-state reaction.

used to estimate the amount of V_2O_5 interacted with the support. This value was found close to 0.9 ML for the 1.6 and 3.7 ML V/TiO_2-ssr samples, while it was 2.6 times lower for the sample with 0.76 ML V/TiO_2-ssr [20].

These data indicate that bulk V_2O_5 is not an active phase in toluene oxidation, since pure bulk V_2O_5 is almost not active. Therefore, an increase of the vanadium content in the samples over a certain value decreases the activity. Other methods of preparation of the catalysts were also used to understand the role of active species for catalysis.

3.2. Vanadia/titania catalysts prepared by impregnation and grafting

Specific rates of the toluene oxidation as a function of time-on-stream are shown in Fig. 3. Fig. 3a demonstrates the activity of bulk crystalline V_2O_5, 2.6 ML V/TiO_2 catalyst prepared by impregnation and the same catalyst after HNO_3 treatment. Fig. 3b shows the activity of the 0.37 ML V/TiO_2 catalyst prepared by grafting and the activity of the same catalyst after HNO_3 pre-treatment.
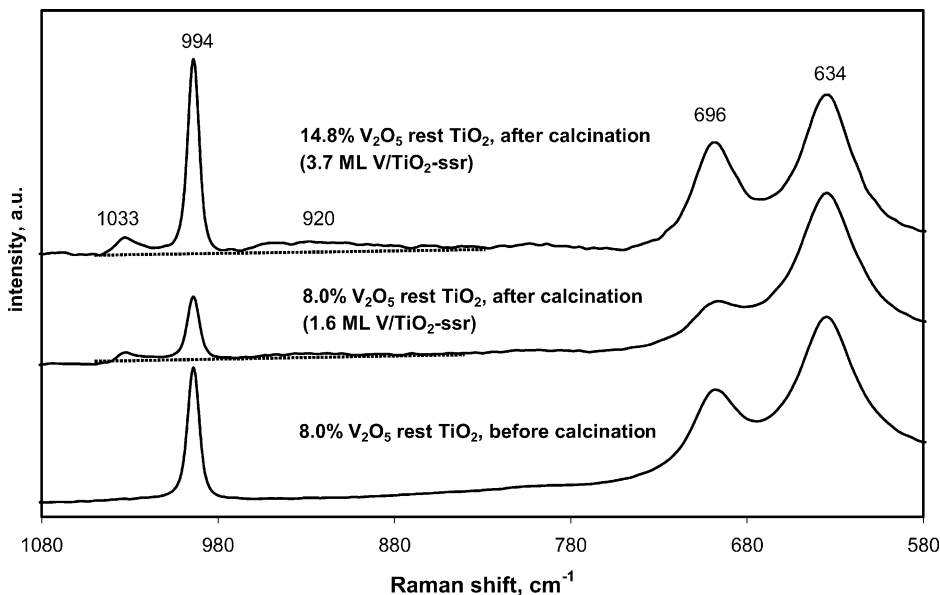

Fig. 2. FT-Raman spectra of the vanadia/titania catalysts prepared by solid-state reaction and ball-milled vanadia/titania physical mixture (before calcination).
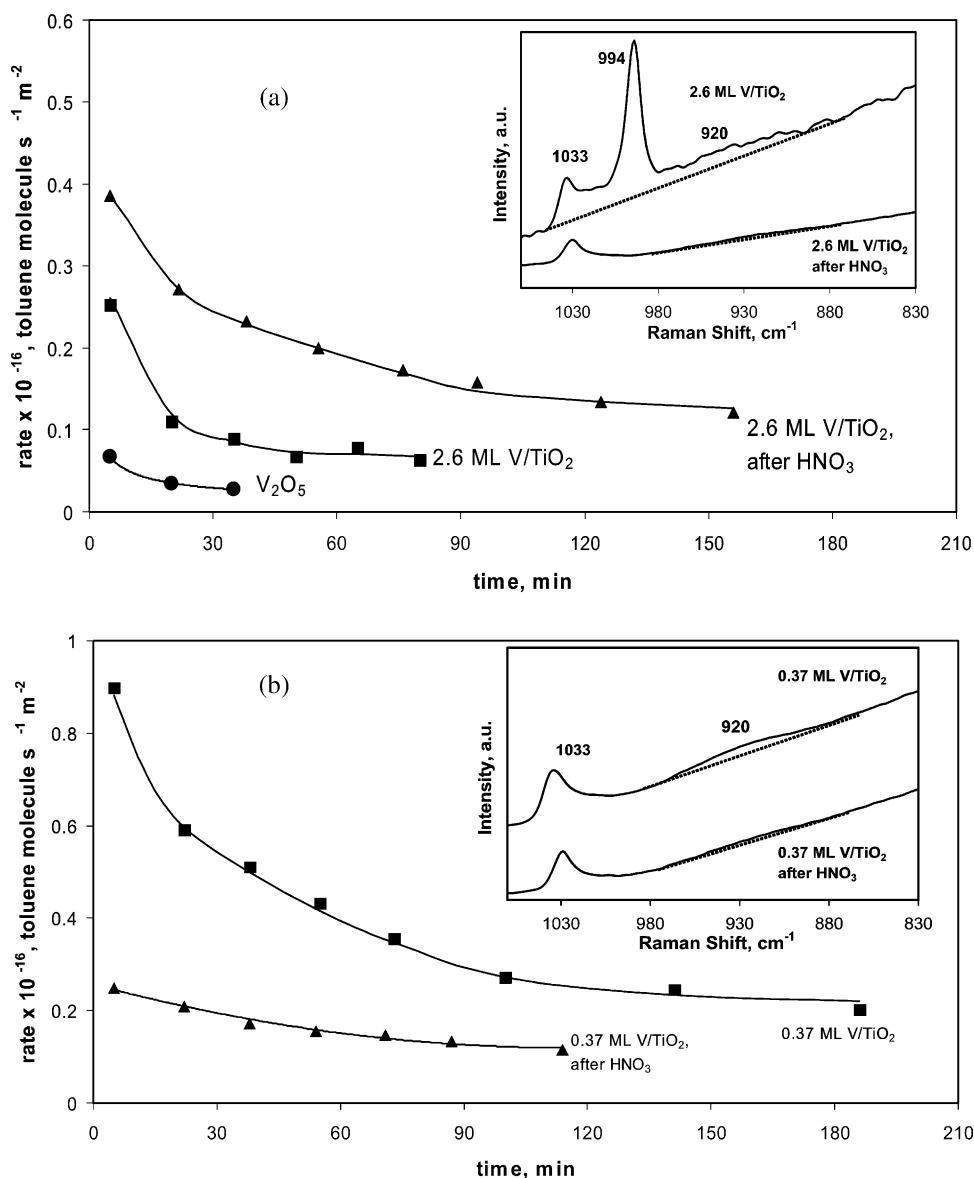
Fig. 3. FT-Raman spectra of the catalysts measured under dehydrated conditions (insets) and specific rates of toluene oxidation on time-on-stream at 523 K for: (a) 2.6 ML V/TiO$_2$ and (b) 0.37 ML V/TiO$_2$ catalysts before and after treatment in HNO$_3$.

The 2.6 ML V/TiO$_2$ catalyst after HNO$_3$ treatment possesses the activity four times higher than the bulk V$_2$O$_5$ and two times higher than the catalyst not treated in HNO$_3$ (Fig. 3a). FT-Raman spectra demonstrate that the 2.6 ML V/TiO$_2$ catalyst contains V$_2$O$_5$ (994 cm^{-1}), monomeric (1033 cm^{-1}) and polymeric (920 cm^{-1}) vanadia species (Fig. 3a, inset) similarly to the catalysts prepared by solid-state reaction (Fig. 2). Washing in HNO$_3$ completely removes bulk V$_2$O$_5$ and decreases strongly the concentration of the polymeric species. The intensity of the band associated with the monomeric species almost does not change.

These data also confirm that bulk V$_2$O$_5$ is not an active phase in the toluene oxidation over V/TiO$_2$ catalysts, because the specific activity of pure bulk V$_2$O$_5$ and the 2.6 ML V/TiO$_2$ catalyst containing V$_2$O$_5$-crystallites is lower than the one of the catalyst containing only monolayer (monomeric and polymeric) species.

The activity of the 0.37 ML V/TiO$_2$ catalyst was found to be higher than the activity of the same catalyst after the HNO$_3$ treatment (Fig. 3b). FT-Raman spectra indicate that HNO$_3$ removed almost completely the polymeric species, but not the monomeric ones (Fig. 3b, inset). The presence of small amount of polymeric species after this treatment is probably explained by equilibrium achieved between the monomeric and polymeric species during the thermal pre-treatments. The activity of the 0.37 ML V/TiO$_2$ catalyst is higher than the one of all studied catalysts with only monolayer species (Fig. 3) and is comparable with the activity of the best catalysts prepared by solid-state reaction
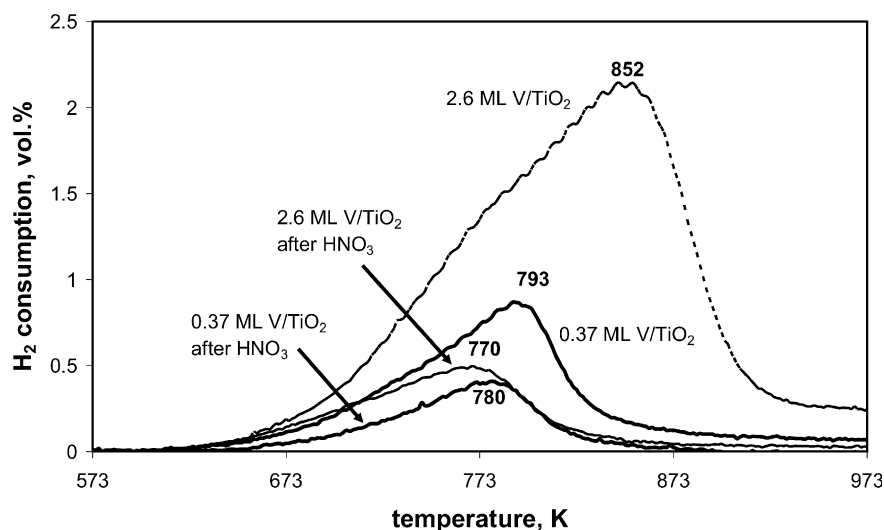
Fig. 4. TPR in hydrogen (4 vol.% H_2 in Ar) of oxidised vanadia/titania catalysts (0.37 and 2.6 ML V/TiO$_2$ taken with the same surface area) before and after treatment in HNO$_3$.

(Fig. 1). These data suggest that the monomeric as well as polymeric species are active in the toluene oxidation.

To estimate the amount of vanadium removed by HNO$_3$ from the samples, TPR experiments were performed. TPR indicates that the concentration of oxygen in the catalyst able to react with H_2 decreases after the HNO$_3$ treatment (Fig. 4). Integration of the concentration profiles was used for the coverage estimations basing on the known coverage of vanadia in the 0.37 ML V/TiO$_2$ catalyst (0.37 ML). The estimation gives 0.22 and 0.16 for the HNO$_3$ treated 2.6 ML and 0.37 ML V/TiO$_2$ catalysts, respectively. This is in accordance with the measured catalytic activity (Fig. 3) showing that the higher is the concentration of monolayer species the higher is the rate of the reaction.

Thus, the specific activity order of the catalysts with the coverage less than a monolayer is the following 0.16 < 0.22 < 0.37 ML. A further increase of the vanadia concentration in the catalysts up to 2.6 ML (2.6 ML V/TiO$_2$) results in a blockage of the active monolayer vanadia species by less active bulk V_2O_5. The same order of activity was observed at a higher temperature (553 K).

Another interesting feature is that the higher is the coverage of vanadia the higher is the degree of deactivation. This may be explained by an increased contribution of the polymeric species which probably contain the sites responsible for coke formation, contrary to the monomeric species.

The shown TPR profiles (Fig. 4) reflect the reducibility of vanadia species in hydrogen. Thus, with an increase of vanadia coverage, the maximum of the TPR peak shifts to higher temperatures in line with the literature data [8,18,23,24]. The insoluble monomeric species are the species easily reducible by hydrogen ($T_{max} \leq$ 770–780 K) (Fig. 4). T_{max} for the reduction of the polymeric species is slightly higher (~800 K) [18]. The maximal rate of reduction of amorphous bulk V_2O_5 is around 850 K (Fig. 4). Crystalline bulk V_2O_5 can be reduced effectively at 950–1000 K

[6]. This reduction order of vanadia species in hydrogen agrees with the reducibility in toluene [25]. The trend of the oxidation ease of the reduced vanadia species by oxygen is the opposite. Bulk V_2O_5 after the reduction is the easiest to oxidise, while the reduced monomeric species is the most difficult for oxidation.

Hence, the monolayer species are active in toluene oxidation in aerobic conditions. To get the highest reaction rate a high surface concentration of monolayer species is needed. Bulk V_2O_5 is not necessary for activity and selectivity in the presence of oxygen. The question arises can the activity of vanadia be increased by doping? Potassium is known to improve the performance of some catalysts in different reactions [4]. This effect was supposed to be due to the change of the nature of surface vanadia species, catalyst acidity, and reducibility of the active phase.

3.3. Vanadia/titania catalysts doped with K

Effect of K-doping was studied with the catalyst containing about 0.2 ML of vanadia since it was shown above that the monolayer species are responsible for activity. It is seen in Fig. 5 that the specific activity in toluene oxidation decreases while the concentration of K increases. The activity is almost negligible when the K/V ratio is close to one, showing that active vanadia species are transformed into inactive ones.

The FT-Raman spectrum of the undoped 0.2 ML V/TiO$_2$-K$_0$ catalyst (Fig. 5, inset) is similar to the one of the 0.37 ML V/TiO$_2$ catalyst (Fig. 3b, inset) and demonstrates the presence of the monomeric as well as polymeric species. Doping by small amount of K results in the lengthening of the V=O bond in the monomeric species (1020 cm^{-1}, K-perturbed monomeric species) [6,27]. The bond length increases 0.007 Å as was calculated using an equation proposed by Hardcastle and Wachs [27].
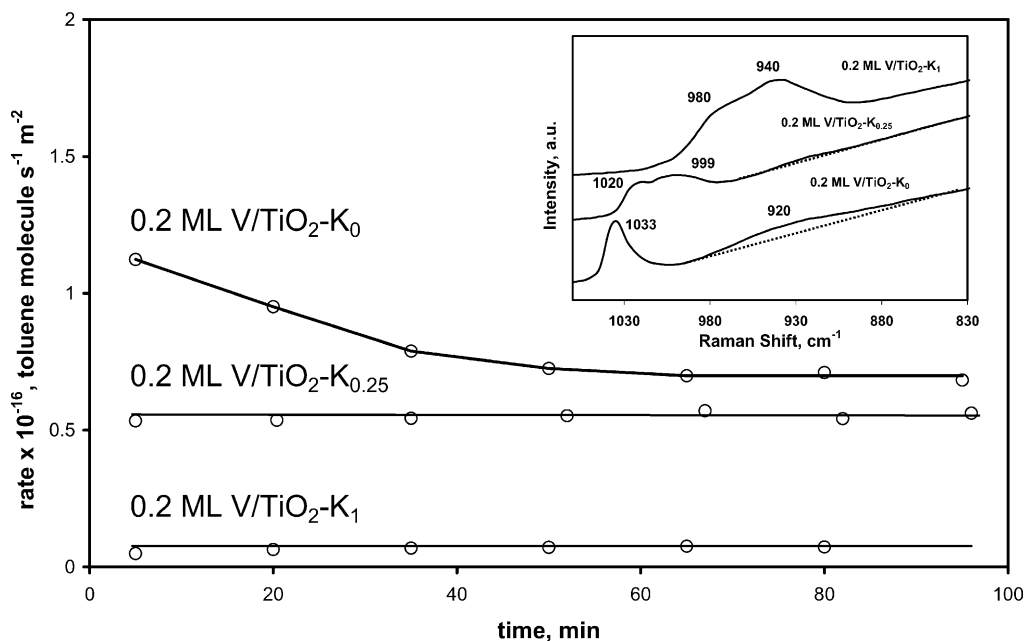
Fig. 5. Specific rates of toluene oxidation over vanadia/titania catalysts with different K/V ratio on time-on-stream at 573 K. FT-Raman spectra of the catalysts measured under dehydrated conditions (inset).

The polymeric vanadia species are almost not present in the studied K-doped samples being transformed to K-doped monomeric species (990 ± 10 cm^{-1}). A part of the bridging Ti–O–V=O fragments could be substituted by K–O–V=O fragments as reported earlier [13]. This provides more strong lengthening of the V=O bond (0.017 Å). Additionally, KVO_3 is formed (940 cm^{-1}).

Only KVO_3 and K-doped monomeric species are present in the catalyst with K/V = 1. A correlation with the catalytic activity data indicates that these vanadia species are almost not active in toluene oxidation (Fig. 5), while the activity of the K-perturbed monomeric species is very similar to the one of the undoped monomeric species. Important is that the increase in the V=O bond length and weakening of this bond taking place by K-doping do not provide any increase in the toluene oxidation rate. In contrast, this rate decreases (Fig. 5).

Deactivation is not observed for the studied K-doped catalysts. This fact could be correlated with the one that the polymeric species probably containing the sites for coke formation are not present in the K-doped catalysts. To find the evidence of the Brønsted acidity of the polymeric species pyridine TPD experiments were performed (Fig. 6).

It is known that pyridine interacts with TiO_2 surface forming only adsorbed species on Lewis acid sites and no
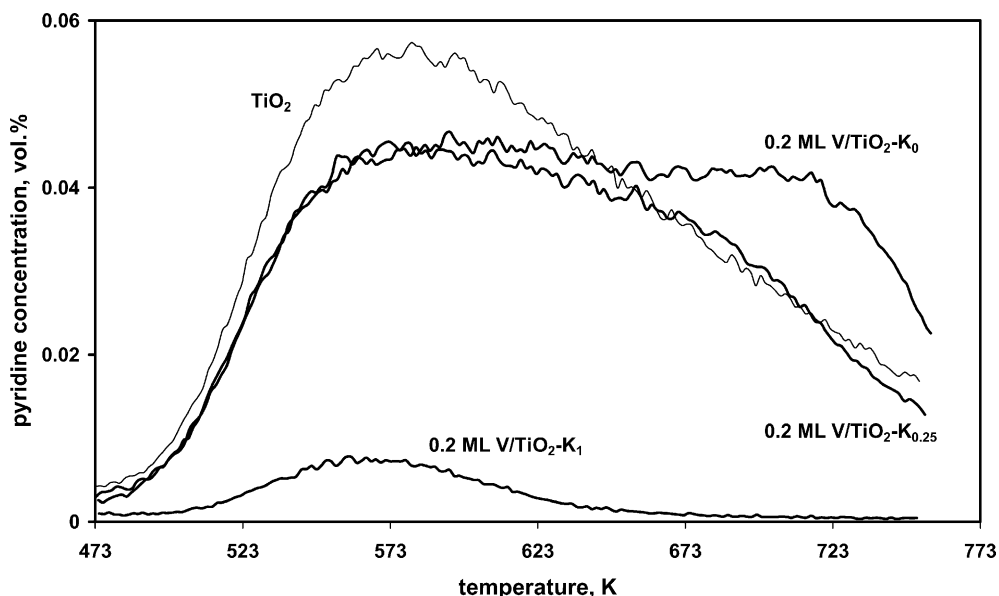

Fig. 6. Pyridine TPD from TiO_2 and vanadia/titania catalysts with different K/V ratio taken with the same surface area.

species associated with Brønsted acid sites [28,29]. Hence, the observed pyridine TPD profile from TiO_2 with a maximum at 573 K should be related to the Ti^{4+} Lewis acid sites.

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 the peak maximum. In the presence of vanadia this peak should be related to titanium as well as to vanadium Lewis acid sites in accordance with FTIRS data [28,29]. However, the presence of more strongly adsorbed pyridine (723 K) is evident in the TPD profile of the undoped catalyst. This pyridine is removed from the surface in the form of CO and CO_2 as was shown by mass-spectrometry. Pyridinium ion was found by FT-IRS to be stable to evacuation at 673 K [30]. Hence, the TPD peak at 723 K is associated with strong Brønsted acid sites, which are not present on the surface of TiO_2 and K-doped catalysts, where almost no polymeric species was found (Fig. 5, inset). Only small amount of pyridine can adsorb on the catalyst with K/V = 1 showing no acidity of such sample. This catalyst, as was mentioned, contains the K-doped monomeric species and KVO_3, but does not contain the polymeric species and V_2O_5 with Brønsted acidity. Additionally, K-doping makes vanadia species more difficult to reduce than the undoped ones as was shown by TPR [6,26].

The average total selectivity to BA and BAc was lower with the K-doped catalysts. It decreases from 82 to 65% after K doping (K/V = 0.25) in spite of the conversion with K-doped catalyst was lower. K-doping decreases mainly the selectivity of BAc formation in favour of maleic anhydride and CO_x formation. Similar effect of potassium on vanadia species, catalytic activity, reducibility and acidity was observed at much higher vanadia loading (2 ML) [6,26].

4. Discussion

The comparison of the specific activity in toluene oxidation of the samples with different vanadia content indicated that vanadia/titania catalysts could be one order of magnitude more active as compared to pure bulk TiO_2 and V_2O_5 (Fig. 1). This suggests that considerably more active vanadia species are formed upon interaction of vanadia with titania. FT-Raman spectroscopy finds the polymeric and monomeric species in the active and selective catalysts independently on the method of preparation (Figs. 2 and 3, insets). The specific activity of the catalysts is controlled by the surface concentration of the monolayer vanadia species.

The presence of V_2O_5 is not necessary for catalysis in aerobic conditions. Moreover, at high vanadia coverage V_2O_5 blocks the active monolayer sites of toluene oxidation, decreasing the activity. This is in line with literature data for partial toluene [8] and o-xylene [31] oxidation as well as selective catalytic reduction of NO by NH_3 [32].

It should be mentioned that in anaerobic conditions toluene can be oxidised by the oxygen of the catalyst [33]. However, the reactivity of the 2.6 ML V/TiO_2 and

0.37 ML V/TiO_2 catalysts was found different. Gaseous BA and CO_x formation is observed only for the 2.6 ML V/TiO_2 catalyst, but not for the 0.37 ML V/TiO_2 one. In the latter case, DRIFTS studies found that adsorbed BA as well as CO_x formation intermediates are formed and retained on the surface, but either gas phase oxygen or oxygen of the bulk V_2O_5 are necessary for their desorption [33].

In the presence of oxygen both the monomeric and polymeric vanadia species oxidise toluene effectively to BA and BAc. The total BA and BAc selectivity is very similar independently on the concentration of vanadia. However, the polymeric species probably contain acid hydroxyl groups associated with the V–O–V bridges [1], which are responsible for coking and deactivation of the catalyst. Similar bridges exist in V_2O_5 also introducing Brønsted acidity [26]. This correlates with the increase of deactivation with vanadia coverage (Fig. 3) and with the effect of K-doping decreasing deactivation (Figs. 5 and 6). The polymeric species are not present in the K-doped catalysts and in accordance the deactivation of these catalysts is not observed (Fig. 5).

Insoluble in HNO_3 vanadia species was shown to consist mainly of the monomeric species, which do not possess Brønsted acidity [4]. Upon K-doping the V=O bond in the monomeric species becomes slightly longer (K-perturbed monomeric species) probably because of electrostatic interaction of vanadyl oxygen with K-cations on the surface. This seems not to affect the activity of the monomeric species in toluene oxidation. At high K/V ratios the formation of the K-doped monomeric and KVO_3 species instead of polymeric species takes place, which are almost not active in toluene oxidation (Fig. 5). Moreover, their presence results in decreased selectivity to BAc, which is retained on the basic surface for a longer time being transformed to maleic anhydride and CO_x via consecutive surface reactions.

5. Conclusions

Monomeric and polymeric (monolayer) vanadia species are responsible for the catalytic activity in partial toluene oxidation over V/Ti-oxides independently on the methods of their preparation. Bulk V_2O_5 and TiO_2 possess considerably lower activity and their presence in big excess should be avoided.

Polymeric species and V_2O_5 are responsible for coke formation and deactivation of vanadia/titania catalysts in toluene oxidation. This effect is probably due to acid hydroxyl groups associated with bridging oxygen.

Bulk V_2O_5 and polymeric vanadia could be selectively removed by diluted HNO_3 from the catalyst, while monomeric vanadia species are retained on the titania surface.

Catalyst deactivation can be suppressed by doping with potassium, which interacts with Brønsted acidic sites on the catalyst surface. At the same time activity decreases due to diminished amount of monolayer species, which are par-

tially transformed into inactive K-doped monomeric and KVO_3 species.

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