

Effect of potassium doping on the structural and catalytic properties of V/Ti-oxide in selective toluene oxidation

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Abstract

Small addition of potassium to V/Ti-oxide catalyst (K:V=0.19), consisting of 3.7 monolayer VO_x, increased activity and selectivity in partial oxidation of toluene. In order to elucidate the nature of vanadia species formed on the surface of V/Ti-oxide upon potassium doping, the catalysts were studied by transient kinetics method. The transient product responses during toluene oxidation by the oxygen present in the catalyst were compared for K-doped and non-doped samples. The formation of CO₂ decreased and formation of benzaldehyde increased with addition of potassium. This suggests a lower surface concentration of electrophilic oxygen (O⁻, O₂⁻), which is usually responsible for the deep oxidation, and a higher concentration of nucleophilic oxygen (O²⁻), responsible for the partial oxidation.

The catalysts were characterised by means of HRTEM, FT-Raman spectroscopy and ⁵¹V NMR. Potassium addition introduces a disorder in the crystalline structure of bulk V₂O₅ particles resulting in better spreading of V₂O₅ over TiO₂ surface. The interaction of V₂O₅ with TiO₂ was facilitated upon K-doping, leading to the increased formation of monomeric vanadia species, which are the active sites in toluene partial oxidation to benzaldehyde. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Multiphase catalysts are used in industrial processes of selective oxidation. Synergetic effect due to mixing several oxides have been reported by Prof. Delmon and Collaborators [1] involving (1) bifunctional catalysis, (2) formation of new active compounds due to interaction between the two phases, (3) contamination of one phase by an element of the other one and (4) remote control. Vanadia supported on titania is a

multiphase catalyst used for selective oxidation. Chemical interaction between phases of V₂O₅ and TiO₂ is known to lead to the formation of a two-dimensional vanadia layer [2–4]. In unhydrated conditions, this layer consists of isolated surface monomeric species, in which vanadyl (V=O) is connected with three titanium cations via bridging V–O–Ti oxygens, and surface polymeric species, in which vanadyl is attached to a titanium cation via bridging V–O–Ti oxygen and connected via bridging V–O–V oxygens to other vanadyls. The two-dimensional layer is considered as the active phase in selective catalytic oxidation, because activity/

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selectivity of the individual bulk oxides, V_2O_5 and TiO_2 , is low. The surface interaction of vanadia with titania can be enhanced by introduction of alkali promoters.

Toluene selective oxidation on V/Ti-oxide catalysts is known to give two valuable products: benzaldehyde (BA) and benzoic acid (BAc). The products of deep oxidation, CO_2 and CO, are also formed in accordance to a parallel-consecutive scheme proposed earlier [5]. No clear mechanism of potassium influence on the catalyst performance is available up to now in the literature. van Hengstum et al. [6] reported a negative effect of K addition on the activity and maximal yield of benzoic acid. Other authors observed an increase of the selectivity to BA [8–10] adding a low concentration of promoter. At the same time, the catalytic activity decreased [7,9], did not change [8] or even increased [10]. Published works used different experimental conditions like (a) concentration of vanadium and potassium on the titania surface, (b) consequence of vanadium and potassium deposition [4,11] and (c) different potassium salt precursors.

It is well-known that the addition of potassium affects the acid–base properties of the V/Ti-oxide catalyst increasing its basicity [3,4]. Raman [3] and NMR [12,13] studies showed that the increase of the basicity decreases the ability of the monomeric species to associate into the polymeric species. Different types of oxygen species are known to be present on the oxide surface. Besides structural (lattice) nucleophilic oxygen species (O^{2-}), electrophilic anion radical oxygen species (O^- , O_2^-) with high reactivity were detected [14]. According to [14,15], (O^{2-}) species are mainly responsible for partial oxidation of hydrocarbons, while (O^- , O_2^-) species are suggested to be involved in deep oxidation, leading to CO_x product formation. The hindrance of the electrophilic species formation and facilitating of the formation of the nucleophilic O^{2-} species promoted by K has been reported in the literature [16].

Concentration of monomeric vanadia species correlates positively with the catalytic activity [5,17]. However, no solid confirmations of this correlation have been reported until now. Dynamic equilibrium of different surface oxygen species with gaseous oxygen complicates the identification of different type vanadia species, if gaseous oxygen is present. We have shown recently [17] that the transient product responses dur-

ing the toluene oxidation over pre-oxidised catalysts in absence of gaseous oxygen give the information concerning the initial reactivity of the catalyst. Therefore, the effect of potassium doping on V/Ti-oxide catalyst was studied in this work by the transient response method. The catalysts were also characterised by HRTEM, FT-Raman spectroscopy and ^{51}V NMR.

2. Experimental

2.1. Catalyst preparation

TiO_2 (Aldrich, 99.9%) with a perfect anatase structure and average particle sizes of 100 nm was used as a support. Catalysts were prepared by impregnation from aqueous solution of vanadium oxalate. The content of vanadium in the catalysts was 2.8 wt.%. The amount of vanadium in the catalysts corresponds to 3.7 monolayer coverage of VO_x containing 10^{19} V atoms/ m^2 in a monolayer [4]. The catalyst doped by potassium was prepared by impregnation from aqueous solution of vanadium oxalate with potassium phosphate. Concentration of potassium in this catalyst was equal to 0.4 wt.%, which corresponds to an atomic K:V ratio of 0.19. The catalysts were dried and then calcined in air at 723 K for 2 h before use. XPS analysis showed the same atomic V:Ti ratio on the surface of the K-doped and pure V/Ti-oxide. Phosphorous was not found on the catalyst surface. The BET specific surface area of the catalysts was $9\text{ m}^2/\text{g}$.

2.2. Set-up and procedure

Experimental set-up used for the transient kinetics studies has been described in [5,17]. Toluene (Fluka, $\geq 99.5\%$) was introduced into a heated evaporator by a syringe-pump. Products were analysed by ‘on line’ mass spectrometry and gas chromatography. Measurements of the steady-state catalytic activity were carried out in a plug-flow reactor. The tip of a thermocouple was inserted into the middle of the catalyst bed. The catalyst loading and the gas flow were maintained constant through the study at 1 g and 1 ml (STP)/s, respectively.

All catalysts were pre-treated in oxidative atmosphere (20 vol.% O_2 , rest Ar) at 673 K for 0.5 h before reaction. The temperature was subsequently

decreased to 523 K and the flow was switched to the reaction mixture of 2 vol.% toluene with 40 vol.% O₂ in Ar. The conversion and selectivity were determined at 523, 553, 583 and 623 K by the analysis of gas composition in the reactor outlet. During reaction, the temperature was increased step-wise.

Transient response experiments of the pre-oxidised catalysts with toluene in absence of gaseous O₂ were performed at 573 K. After the standard catalyst pre-treatment mentioned above, the reactor was purged by Ar and flow switched to the mixture of 2 vol.% toluene in Ar.

Irreversibly adsorbed toluene on the catalyst surface was determined by catalyst oxidation in oxygen at 573 K after the purging the reactor by Ar. Consecutive oxidation during heating the catalyst up to 673 K resulted in the additional formation of CO_x and H₂O, but the amount never exceeded 10% from total.

2.3. Catalysts characterisation

The Raman spectra were recorded in air on a Perkin-Elmer 2000 NIR FT-Raman Spectrometer. Nd-YAG laser at 1064 nm with a power range of 10–710 mW was used. Usually 64 scans were collected and averaged with a resolution of 4 cm⁻¹. It was shown in our recent publication [5] that the presence of water in ambient air during the measurements did not influence the intensity of the V=O stretching vibration (994 cm⁻¹), characteristic for bulk V₂O₅.

Investigation of the surface morphology by HRTEM was carried out via a HF-2000 transmission electron microscope (maximum resolution of lines is 0.14 nm, accelerating voltage up to 200 kV). Slow Scan Gatan CCD camera (1024×1024 pixels) allowed to register weak images and to minimise the transformation of

the sample in the field of electron beam [18]. The samples for HRTEM measurements were prepared by supporting the catalyst suspension from ethanol on carbon films.

Solid state ⁵¹V NMR wide line and magic angle spinning (MAS) studies were performed by means of a Bruker MSL-400 spectrometer at 102.2 MHz. MAS spectra were recorded at the rotation frequencies of 10–15 kHz in the MAS probe, produced by NMR Rotor Consult ApS, Denmark. The rotors were made from silicon nitride (5 mm). Repetition time of 0.1–1 s and the angle for radio-frequency pulse of about $\pi/12$, corresponding to a pulse duration of 2 μ s were used. Chemical shifts were referenced against VOCl₃.

3. Results

3.1. Catalyst performance

The data on the activity and selectivity in toluene oxidation for the V/Ti-oxide catalyst with and without addition of K are presented in Table 1. No deactivation was observed during 90 min on stream at 573 K for all catalysts under the study. Addition of K (0.4 wt.%) to the V/Ti-oxide results in the increase of the conversion approximately 1.5 times at 553 K and 2 times at 583 K. The total selectivity towards partial oxidation products ($S_{(BA+BAc)}$) for the doped catalyst is also higher.

The transient responses (product evolution) when toluene reacts with pre-oxidised catalysts are shown in Fig. 1. The transient CO_x formation over the K-doped catalyst (Fig. 1b) is lower than for the undoped one (Fig. 1a). The total amount of oxygen involved in the CO_x formation is equal to 4.5×10^{17} atoms O/m²

Table 1

Catalytic properties of the 2.8 wt.% V/TiO₂ catalysts (1 g) at 553 and 583 K in toluene oxidation (2 vol.% toluene, 40 vol.% O₂ in Ar, 1 ml (STP)/s)^a

| Catalyst | Temperature (K) | Conversion (%) | $S_{(BA+BAc)}$ (%) | S_{BA} (%) | S_{BAc} (%) | S_{MA} (%) | S_{CO_x} (%) |
|-----------------------|-----------------|----------------|--------------------|--------------|---------------|--------------|----------------|
| Undoped | 553 | 8.1 | 50.5 | 25.9 | 24.6 | 16.3 | 33.2 |
| Doped with 0.4 wt.% K | 553 | 12.2 | 60.7 | 22.4 | 38.3 | 13.0 | 26.3 |
| Undoped | 583 | 16.9 | 41.2 | 14.9 | 26.3 | 20.6 | 38.2 |
| Doped with 0.4 wt.% K | 583 | 32.5 | 53.0 | 10.7 | 42.3 | 17.2 | 29.8 |

^a BA: benzaldehyde; BA_c: benzoic acid; MA: maleic anhydride.

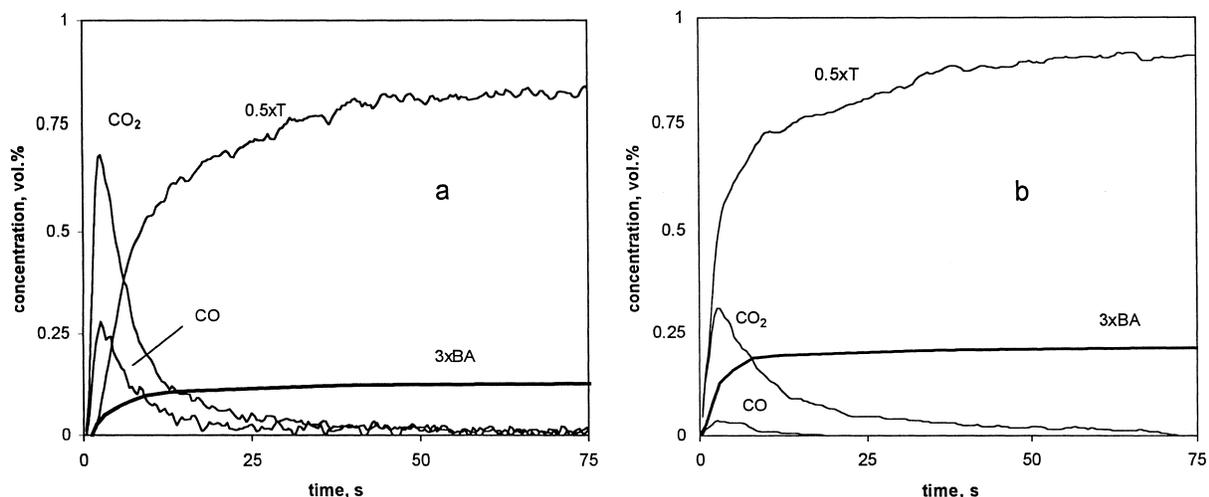


Fig. 1. Toluene interaction (2 vol.% toluene in Ar, 1 ml/s, 573 K) with the pre-oxidised undoped (a) and doped by K (b) V/Ti-oxide catalysts (1 g).

for the undoped catalyst and is 1.7 time less for the K-doped one. At the same time, the evolution of BA is 1.5–2 times higher over the K-doped catalyst compared to the undoped catalyst. These data suggest that the potassium addition decreases the concentration of electrophilic oxygen species (O_2^- , O^-), responsible for deep oxidation [17], while the concentration of nucleophilic oxygen (O^{2-}), responsible for BA formation is increased.

From the mass carbon balance toluene seems to be partially irreversibly adsorbed on the catalyst. The concentration of the irreversibly adsorbed toluene was determined by catalyst oxidation as described above. CO₂ is the main product of this oxidation and its evolution is presented in Fig. 2. It is seen that the amount of the formed CO₂ is significantly higher for the undoped catalyst (Fig. 2). CO and H₂O formation (not shown in Fig. 2) proceeds with the same pattern as

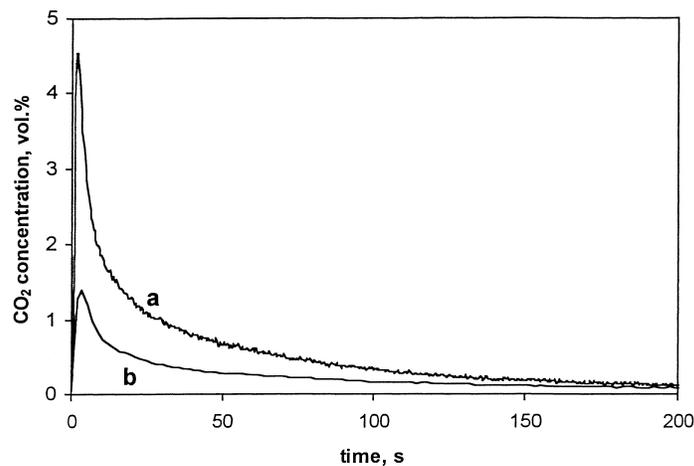


Fig. 2. CO₂ evolution during oxygen interaction (20 vol.% O₂ in Ar, 1.2 ml/s, 573 K) with the undoped (a) and doped by K (b) V/Ti-oxide catalysts (1 g) after 20 min of their interaction with toluene.

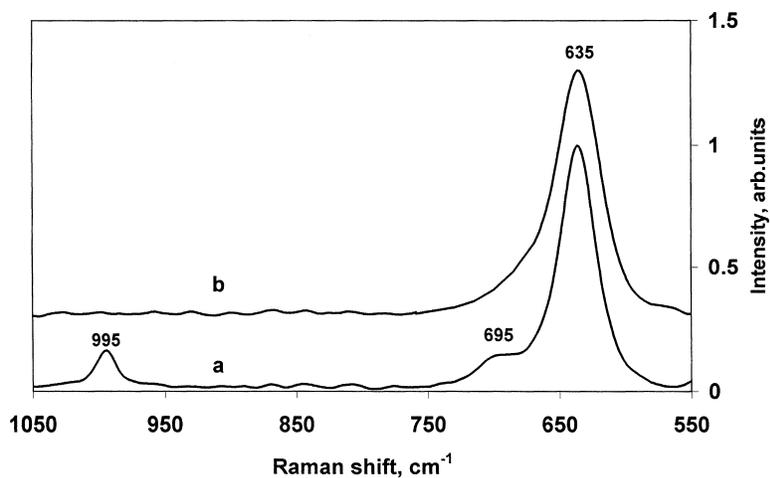


Fig. 3. Raman spectra of the undoped (a) and K-doped (b) V/Ti-oxide catalysts.

CO₂. Total amount of carbon removed from the catalyst at 573–673 K is 2.5 higher for the undoped catalyst than for the K-doped one and corresponds to 7.4×10^{18} atom C/m².

3.2. Catalyst morphology

Raman spectra of the V/Ti-oxide catalysts are presented in Fig. 3. Bands characteristic for crystalline

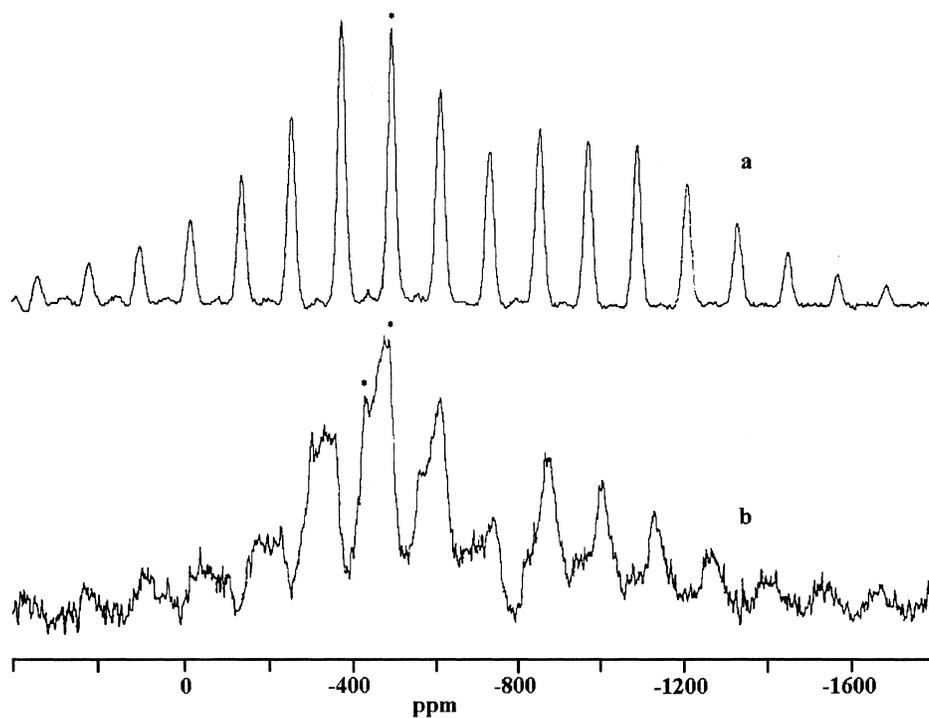


Fig. 4. ⁵¹V NMR MAS spectra of the undoped (a) and K-doped (b) V/Ti-oxide catalysts.

bulk V_2O_5 ($995, 695\text{ cm}^{-1}$) and TiO_2 (635 cm^{-1}) are seen in the spectrum of the undoped catalyst (Fig. 3a). K-doping results in the disappearance of the V_2O_5 characteristic bands from the spectrum (Fig. 3b). This effect may be due to amorphization of the crystalline V_2O_5 and/or to phase transformation of V_2O_5 into another species, which may not be detected by Raman spectroscopy.

NMR technique is known to be sensitive to the local environment of the V nuclei [12,19,20]. Fig. 4 presents the ^{51}V NMR MAS spectra of the K-doped (b) and undoped (a) V/Ti-oxides. The main part of V in the undoped catalyst is in the state of V_2O_5 ($\sigma_1 \sim \sigma_2 = 250\text{ ppm}$, $\sigma_3 = 1270\text{ ppm}$, $\sigma_{iso} = 612\text{ ppm}$) (Fig. 4a). Potassium addition strongly changes the spectra. Analysis of the side bands shows that there are at least two different states of V (Fig. 4b). Narrow bands with the isotropic shift of $\delta = -552\text{ ppm}$ are assigned to potassium metavanadate (KVO_3) [12,20]. The positions of the other bands correspond to crystalline V_2O_5 . However, they are broader compared to the bands of perfectly crystallised V_2O_5 and are assigned to V_2O_5 with partially disordered structure. Hence, the introduction of K into V/Ti-oxide introduces disorder in the bulk V_2O_5 and leads to the formation of KVO_3 .

HRTEM study of the catalysts showed the presence of bulk V_2O_5 particles on both doped and undoped catalysts. The V_2O_5 particles on the TiO_2 surface seem

to be in the form of wetting drops. For the K-doped catalyst (Fig. 5b) the contact angle of the V_2O_5 particle with TiO_2 is smaller than for the undoped catalyst (Fig. 5a), indicating the increased wetting of titania surface by V_2O_5 upon K-doping. Another observation concerns the pattern of the K-doped catalyst. The surface of titania is covered by a thin amorphous layer with a thickness of about 1 nm (Fig. 5b). This layer has a higher contrast than the contrast of titania and V_2O_5 phases, allowing to suppose the formation of amorphous vanadia. Similar thin layer was observed earlier [21].

4. Discussion

4.1. Transient response experiments without gaseous oxygen

It is known that nucleophilic oxygen species (O^{2-}) are responsible for partial oxidation, while electrophilic oxygen species (O^- , O_2^-) are involved in the deep oxidation leading to CO_x and H_2O formation [14,15]. Bulk V_2O_5 has been reported to be low active in selective toluene oxidation [22]. Hence, the activity of V/Ti-oxide catalysts is assigned to the vanadia monolayer [5,22]. As it was mentioned above, this monolayer consists of mono- and polymeric vanadia species. Oxygen of the monomeric species (bridging oxygen in V–O–Ti bond) has nucleophilic character and oxygen in polymeric species has electrophilic character. Transient responses of BA and CO_2 correlate with the presence of nucleophilic and electrophilic oxygen species, respectively. The K-doping leads to an increase of the surface concentration of the monomeric species and decrease of the polymeric species one. This conclusion is based on the transient product responses during toluene oxidation over pre-oxidised catalyst in absence of oxygen (Fig. 1) and on spectroscopic data [3,12].

Average composition of the irreversibly adsorbed toluene was found to correspond to $C_{2n}H_{1.1n}$ [5]. The smaller the amount of CO_2 formed during the reaction of toluene over the pre-oxidised catalyst, the smaller is the amount of irreversibly adsorbed toluene on the catalyst surface. This suggests that the same sites are responsible for the CO_2 formation and also for irreversible adsorption of toluene. Both

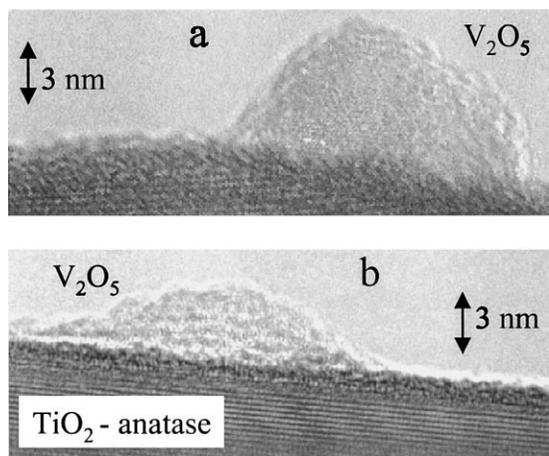
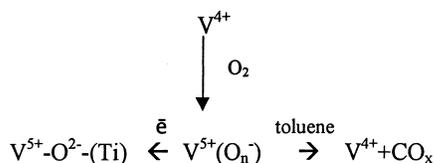


Fig. 5. HRTEM pattern of the undoped (a) and K-doped (b) V/Ti-oxide catalyst.

processes occur via the aromatic ring fission induced by the electrophilic oxygen. To be effectively attacked, toluene should be adsorbed on the catalyst with the ring parallel to the surface. A similar approach has been reported earlier for the toluene interaction with the V_2O_5 (010) surface [23]. Thus, the observed decrease of the irreversibly adsorbed toluene concentration on the K-doped catalyst agrees with the decrease in the electrophilic oxygen concentration.

4.2. Steady-state experiments with gaseous oxygen

From our studies [17], it follows that the adsorption of oxygen on the V^{4+} sites in the reduced isolated vanadia species does not lead to immediate catalyst re-oxidation with direct formation of nucleophilic oxygen species. Intermediate electrophilic oxygen species $V^{5+}(O_n^-)$ ($n=1$ or 2) are formed, which could be either transformed by electron transfer into the bridging nucleophilic V–O–Ti oxygen, active in partial oxidation, or removed from the catalyst in the form of the CO_x products.



Potassium, being an electron-donating additive to vanadia, should facilitate the process of the electron transfer to the electrophilic species accompanied by the formation of the nucleophilic species. Thus, the concentration of ($V^{5+}(O_n^-)$) sites, active in the deep oxidation, decreases along with the reaction rate. This agrees with the change of the catalytic selectivity due to K-doping in the presence of gaseous oxygen (Table 1).

The K-doping introduces disorder in the structure of the V_2O_5 particles. This improves wetting of the titania surface and facilitates spreading of V_2O_5 over titania. The particles have a better interfacial contact to each other. This has a positive effect in the partial oxidation since it facilitates interaction of V_2O_5 with TiO_2 , leading to V–O–Ti bond formation.

However, it should be noted that at a high concentration of potassium, the active vanadia species would

transform into inactive KVO_3 [6] decreasing the catalytic activity [6,7]. This has to be considered during the optimisation of the catalyst formulation.

5. Conclusions

1. Doping of the V/Ti-oxide by potassium increases the catalyst activity and selectivity of toluene partial oxidation to BA and BAc.
2. Transient responses of products during toluene oxidation over the pre-oxidised catalysts without gaseous oxygen show a decrease of CO_2 and increase of BA evolution upon K-doping. This suggests an increase of the relative surface concentration of the isolated monomeric species (with nucleophilic oxygen in the V–O–Ti bond), which are the active sites in partial oxidation.
3. According to the Raman spectroscopy, ^{51}V NMR and HRTEM studies, the K-doping introduces a disorder in the crystalline structure of V_2O_5 , increasing wetting of the titania surface by V_2O_5 and leading to a better contact of the oxides to each other. V_2O_5 interacts more favourably with TiO_2 , resulting in a higher relative surface concentration of the isolated monomeric vanadia species.

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