Catalysis Today 157 (2010) 198–203

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Flame-made vs. wet-impregnated vanadia/titania in the total oxidation of chlorobenzene: Possible role of VO_x species

Bjoern Schimmoeller [a], Romain Delaigle [b], Damien P. Debecker [b], Eric M. Gaigneaux [b,*]

[a] Particle Technology Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, CH-8092 Zurich, Switzerland
[b] Université catholique de Louvain, Unité de catalyse et chimie des matériaux divisés, Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

ARTICLE INFO

Article history:
Available online 13 February 2010

Keywords:
Flame spray pyrolysis
VOC abatement
V_2O_5/TiO_2
Raman spectroscopy
XPS
Polymeric vanadia
V–O–V bonds
Dioxin

ABSTRACT

Vanadia/titania particles with a specific surface area (SSA) around 50 $m^2\,g^{-1}$ and a V_2O_5 content up to 30 wt.% (corresponding to a V surface density up to 33 V nm^{-2}) were prepared by flame spray pyrolysis as well as by classic wet-impregnation. The catalysts were characterized by nitrogen adsorption, X-ray diffraction, temperature programmed reduction, Raman spectroscopy, X-ray photoelectron spectroscopy and tested in the total oxidation of chlorobenzene. Depending on vanadia content, monomeric, polymeric and crystalline vanadia species were formed. The dispersion of the VO_x species was in general higher for flame-made catalysts. While the classic wet-impregnated catalysts already showed crystalline V_2O_5 when the V surface density reaches 8 V nm^{-2}, the flame-made ones exhibited only amorphous VO_x species up to 16 V nm^{-2}. The activity of flame-made and wet-impregnated catalysts increased with increasing V_2O_5 loading and therefore depended on the VO_x species structure: catalysts exceeding a V surface density of 8 V nm^{-2} containing high amounts of amorphous polymeric and/or crystalline VO_x species showed significantly higher activity than catalysts with lower V surface density. Wet-impregnated catalysts with numerous V–O–V bonds as involved in polymeric and crystalline VO_x species showed superior activity than FSP-made ones of similar composition. This contribution proposes a discussion aiming at understanding the role played by the different types of VO_x species in the total oxidation of volatile organic compounds on the example of chlorobenzene.

1. Introduction

Supported vanadia catalysts are used for a variety of reactions, including selective catalytic reduction (SCR) of NO_x with NH_3 [1], oxidative destruction of volatile organic compounds (VOC) or dioxins [2] or partial oxidation of o-xylene to phthalic anhydride [3]. Strong surface interactions between vanadia and titania result in amorphous monomeric (isolated) or di- and polymeric VO_x species which can be formed at sub-”monolayer” (<8–10 V nm^{-2}) coverage [4]. Exceeding this V surface density leads usually to crystalline V_2O_5 regardless of the preparation method [5–7]. Crystalline V_2O_5 is considered to have detrimental effects on catalytic activity, supported by activity data of vanadia-based catalysts for both, the total oxidation of chlorobenzene [8] and the SCR reaction [8,9] where the highest turn over frequency was measured for a V surface density <8 V nm^{-2}. Accordingly most of the tested vanadia-based catalysts deal with so called “sub-monolayer” catalysts [10–12]. In a recent review [13] on classic “sub-monolayer” wet-impregnated V_2O_5/TiO_2 catalysts for the total oxidation of VOC model molecules (e.g. benzene, chlorobenzene and furane) it was concluded that the best catalytic performance are achieved with highly dispersed, amorphous VO_x species. However, recent results on V_2O_5/TiO_2 catalysts prepared by nonhydrolytic sol-gel provided strong experimental evidence that isolated VO_x species are less active than oligomeric species [14]. Also, one recent publication [15] reported decreasing reaction temperatures at 50% conversion for a V_2O_5/TiO_2 catalyst with V surface density up to 16 V nm^{-2} (2 “monolayer”) indicating that more research on high loading (surface density) catalysts is necessary.

Recently V_2O_5/TiO_2 catalysts prepared by flame spray pyrolysis (FSP) showed a good dispersion of vanadia while retaining the amorphous VO_x species up to a V surface density of 27 V nm^{-2} [16]. These species had a strong influence on the selectivity in the selective oxidation of o-xylene, favoring amorphous species for high selectivity. Activity, however, was directly proportional to the SSA and therefore to the exposed vanadium sites but showed no dependency on the different VO_x species present [16]. This fast one-step synthesis technique allows now to tailor such V-based catalysts with specific VO_x structure and high dispersion even at high V surface density and therefore systematic studies of the influence of amorphous vs. crystalline VO_x species can be done by

---

* Corresponding author. Tel.: +32 10 47 36 65; fax: +32 10 47 36 49.
E-mail address: eric.gaigneaux@uclouvain.be (E.M. Gaigneaux).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.01.029

comparison of such flame-made V_2O_5/TiO_2 catalysts with high amorphous VO_x content vs. classic wet-impregnated materials with high amount of crystalline V_2O_5 at high V surface density.

In here we test such flame-made catalysts in the abatement of chlorinated volatile organic compounds, namely chlorobenzene and study the influence of vanadia content and of the nature of VO_x species on the activity in the total oxidation. These flame-made catalysts are compared to classic wet-impregnated catalysts of similar composition.

2. Experimental

2.1. Catalyst preparation

Nanostructured vanadia/titania particles were made by FSP of appropriate precursor solutions [17]. Xylene (Fluka, >98.5%) and acetonitrile (Fluka, >99.5%) solvents were mixed (11:5 by volume) with appropriate amounts of titanium tetraisopropoxide (TTIP, Aldrich >97%) and vanadium oxo-triisopropoxide (Strem Chemicals, >98%), resulting in titanium metal concentrations of 0.67 M and a nominal V_2O_5 content of 2.3–30 wt.%). This precursor solution was fed (8 mL min^{-1}) by a syringe pump (Inotec, IER-560) through the FSP nozzle and dispersed by O_2 (4 or 5 L min^{-1}, Pan Gas, 99.5%) into a fine spray that was ignited and sustained by a premixed CH_4/O_2 flame. Particles were collected on glass microfibre filters (Whatman GF/D, 257 mm in diameter) by a vacuum pump (Busch SV 1025 B) for subsequent analysis. Details on the synthesis are described elsewhere [16,18].

For comparison, vanadia/titania reference catalysts were prepared by standard wet-impregnation of commercially available TiO_2 (TiO_2, >85 wt.% anatase, Degussa P25 (49 $m^2\,g^{-1}$)). The precursor NH_4VO_3 (Vel, >99%) was dissolved in distilled water and complexed with oxalic acid (Aldrich, >99%, molar ratio vanadium: oxalic acid = 1: 2). An appropriate amount of titania was then added to the solution. The suspension was mixed for 2 h at room temperature and water was evaporated in a rotary evaporator under reduce pressure at 40 °C. The material was dried over night in an oven at 110 °C, crushed, fractionated (0.114–0.5 mm) and finally calcined in air in a muffle furnace (20 h, 400 °C). Samples made by flame spray pyrolysis and wet-impregnation are labeled as FSP-x and WI-x, respectively, where x denotes the V_2O_5 content in wt.% (Table 1).

2.2. Catalyst characterization

The SSA ($m^2\,g^{-1}$) of the powder was determined by nitrogen adsorption (Pan Gas, >99.999%) at 77 K by the Brunauer–Emmett–Teller (BET) method with a Micromeritics Tristar 3000 (five point-isotherm, $0.05 < p/p_0 < 0.25$). Accounting for the V_2O_5 content powder density, the average particle size (d_{BET}) was calculated assuming spherical particles [18]. X-ray diffraction (XRD) was measured on a Bruker D8 Advance diffractometer (step size of 0.03°, scan speed of 0.60° min^{-1}, Cu Kα radiation). Weight content and crystal size of titania phases were obtained by Topas 2.0 software (Model AXS 2000, Bruker) [18].

Temperature programmed reduction (TPR) was used for determination of the average oxidation state after reduction (AOS) and reducibility of vanadia. Experiments were carried out on a Micromeritics Autochem II 2920 equipped with a TCD-detector by flowing vol.% H_2 in Ar (Pan Gas, >99.999%, 20 mL min^{-1}) through the sample [18].

Raman spectroscopy was performed with a Renishaw InVia Reflex Raman system equipped with a 514 nm diode (Ar-ion laser, 25 mW) laser as excitation source focused in a microscope (Leica, magnification ×50). The spectra were recorded under dehydrated conditions in an in-situ cell following the procedure described in Ref. [16].

X-ray photoelectron spectroscopy (XPS) was performed on a SSI X-probe (SSX-100/206) spectrometer from Surface Science Instruments. The analysis chamber was operated under ultrahigh vacuum with a pressure close to $5 \times 10 - 9$ Torr and the sample was irradiated with a monochromatic Al Kα (1486.6 eV) radiation (10 kV; 22 mA). Details of the exact settings and peak analysis can be found elsewhere [10].

2.3. Catalytic evaluation

The catalytic tests were performed in a metallic fixed-bed reactor operating at atmospheric pressure. The catalytic bed was composed of 200 mg of catalyst powder selected within the granulometric fraction 200–315 μm and diluted in 800 mg glass spheres checked to be inactive. The gas stream contained 100 ppm of chlorobenzene (mixture in He; Praxair), 20 vol.% O_2 (Praxair; 99.995%) and He (Praxair; 99.996%) as diluting gas to obtain 200 mL min^{-1} (VVH = 37000 h^{-1}). The reaction was run from 100 to 400 °C. More details on the operating conditions can be found elsewhere [2].

3. Results

3.1. Characterization of structural properties of catalysts

Table 1 shows the structural characterization data of all tested catalysts. For FSP-made catalysts (2.3–13.5 wt.% V_2O_5) the SSA of ≈55 $m^2\,g^{-1}$ ($d_{BET} \approx 28$ nm) is almost constant, independent of the vanadia loading. At 17.5 wt.% the produced particles slightly decreased in SSA (49 $m^2\,g^{-1}$) probably due to the slightly increased production rate (higher V_2O_5 content) resulting in higher particle

Table 1

Vanadia content, BET and TPR results for all tested V_2O_5/TiO_2 catalysts from different preparation methods.

Sample ID	Nominal V_2O_5 content[a] in wt.%	SSA in $m^2\,g^{-1}$	V surface density[b] in V nm^{-2}	AOS[c]
FSP-2.3	2.3	52.6	2.9	3.4
FSP-4.5	4.5	56.2	5.3	3.4
FSP-8.5	8.5	55.6	10.1	3.8
FSP-13.5	13.5	55.1	16.2	3.6
FSP-17.5	17.5	49	23.5	3.6
FSP-30	30	60	32.8	4.1
WI-2.3	2.3 (1.94)	48	3.1	3.4
WI-4.3	4.3 (4.55)	46.2	5.9	3.7
WI-8.2	8.2 (7.92)	45.6	11.4	3.8
WI-13.2	13.2 (13.22)	44.9	18	3.7
WI-19.5	19.5	36	26.8	4.1

[a] number in brackets state the real wt.% V_2O_5 measured by ICP-MS analysis

[b] calculated for the initial SSA (48 $m^2\,g^{-1}$) before impregnation and measured V_2O_5 content by ICP for WI catalysts

[c] oxidation state after reduction, assuming V^{5+} before reduction

concentrations favoring coagulation and sintering. To avoid further decrease of the SSA at higher vanadia contents [16] the dispersion gas feed rate was increased from 4 to 5 L min^{-1} oxygen for the 30 wt.% V_2O_5 catalysts resulting in higher cooling rates. This slowed down coagulation and sintering causing a higher SSA of 60 $\text{m}^2\,\text{g}^{-1}$. For the wet-impregnated (WI) catalyst the initial SSA (48 $\text{m}^2\,\text{g}^{-1}$) slightly decreased to 46 m^2g^{-1} with increasing the vanadia content from 2.3 to 13.2 wt.% during the impregnation and calcination procedure. The V surface density was calculated based on the final SSA of the flame-made catalysts and on the initial SSA of the P25 support for the wet-impregnated. The values of the V surface density (V nm^{-2}) for FSP and WI are fairly comparable (Table 1) despite the difference in SSA. Average oxidation states (AOS) after reduction of both, flame-made and WI catalysts, were in the range of 3.4–3.8 after reduction and comparable at given content, indicating almost similar reducibility of the present VO_x species. Low loadings, however, showed a slightly higher reducibility than high loadings indicated by the lower AOS. Reported values for the FSP-made catalysts are similar to the ones observed in previous studies [16,18].

XRD of the flame-made V_2O_5/TiO_2 analysis showed more than 98% (w/w) anatase with respect to the TiO_2 phase and no crystalline V_2O_5 up to 13.2 wt.% (16.2 V nm^{-2}, not shown) in agreement with previous studies [16].

Broad XRD reflections indicating nanosized anatase crystals of ≈32 nm which correspond well to the calculated average BET-diameter and indicate thus the predominance of monocrystalline non porous particles [16]. Only at very high loadings of 30 wt.% crystalline V_2O_5 was detected by XRD (Fig. 1) contributing a fraction of 2 wt.% and a calculated crystal size of 14 nm. Diffraction lines, however, attributed to crystalline VO_2 (*, $2\Theta = 14.2, 28.4, 33.4, 43.7^\circ$) were detected already at 17.5 wt.% and got more pronounced in the 30 wt.% sample resulting in approximately 10 wt.% VO_2 (12 nm) in the latter sample. VO_2 formation in FSP-made V_2O_5/TiO_2 was reported before and is due to the very high cooling rates in the flame, allowing the formation of thermodynamically less stable crystal phases [16]. Increasing, however, the flame enthalpies by increasing the liquid feed rate (similar to the one used in this study) and decreasing dispersion gas (3 L min^{-1}) induced the disappearance of VO_2 in those catalysts reported before [16] due to longer residence time in the hot temperature range. Apparently with 4 and 5 L min^{-1} dispersion gas it was not possible to extend the residence time in the hot temperature zone long enough in order to prevent VO_2 formation.

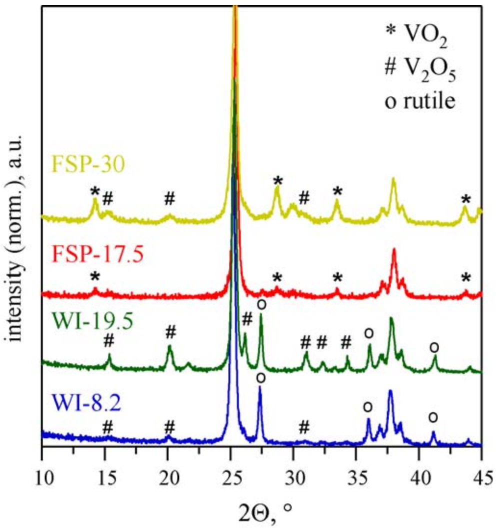

Fig. 1. XRD diffraction patterns of the high V surface density FSP- and WI catalysts.

In case of the WI catalysts crystalline vanadia was detected for loadings ≥8.2 wt.% (≥11.4 V nm^{-2}, Fig. 1) following the classic "monolayer" theory of wet-made V_2O_5/TiO_2 catalysts [3]. The crystalline V_2O_5 content increased from 3.3 wt.% (WI-8.2), 6.6 wt.% (WI-13.2) to 12.5 wt.% for the highest vanadia content (WI-19.5) as determined by TOPAS 2.0 software indicating that half or more of the nominal content is present as crystalline V_2O_5. The initial anatase weight fraction (85 wt.%) of the P25 was preserved for all catalysts.

The structure of the present VO_x species was analyzed by Raman spectroscopy under dehydrated conditions at 300 °C. The FSP-made catalysts showed no indication of crystalline V_2O_5 species up to 17.5 wt.% loading (23.5 V nm^{-2}, not shown), more than two times the theoretical "monolayer", in agreement with previous studies [16,18]. Only peaks at 1033 cm^{-1} attributed to V=O stretching modes of monomeric (isolated) VO_x species [19] and the broad band around 920 cm^{-1} of V–O–V bridges indicating polymeric VO_x species were detected [20–22]. Due to the high cooling rates in the flame and extremely short residence times in the hot temperature zone, FSP-made V_2O_5/TiO_2 exhibit a high amount of stable, amorphous VO_x species at very high vanadium surface density [16]. At 30 wt.% vanadia loading (33 V nm^{-2}, Fig. 2) crystalline V_2O_5 was formed as indicated by the peak at 998 cm^{-1} [23] in agreement with XRD analysis (Fig. 1). Due to the dominant Raman shifts and scattering arising from the TiO_2 support and additional overlapping with V_2O_5 bands, detection of discrete major VO_2 bands expected at 191, 258 and 35 cm^{-1} [24] was not possible for the FSP-17.5 and FSP-30 samples.

The wet-impregnated catalyst (Fig. 2), on the other hand, showed already traces of crystalline V_2O_5 at relative low (4.5 wt.%) vanadia loadings (<5.9 V nm^{-2}), namely below the theoretical "monolayer", indicated by the small peak at 998 cm^{-1} which got more intense at higher V_2O_5 loadings. Thus the on-set of crystalline formation is reached at much lower V coverage for the wet-impregnated catalysts compared to the FSP-made ones. Usually such low contents don't necessarily lead to a formation of crystalline species [3]. This indicates that the dispersion of the VO_x species on catalysts obtained by the herein used

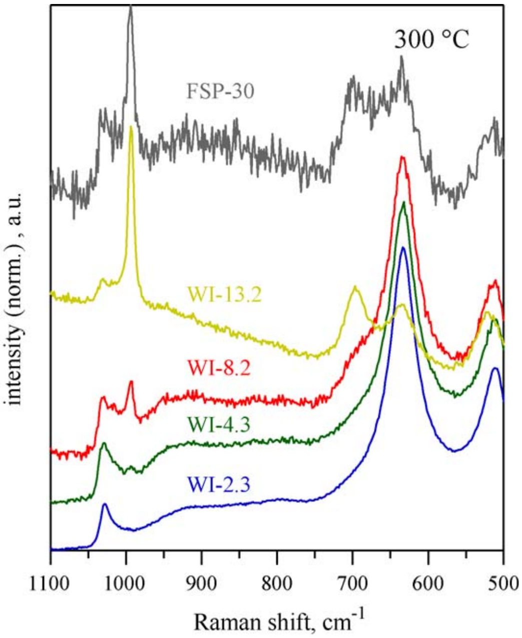

Fig. 2. Raman spectra of the WI catalysts and the FSP-30 catalyst. WI catalysts show the on-set for crystalline V_2O_5 already at low V surface density of 6 V nm^{-2} (WI-4.3). FSP-made V_2O_5/TiO_2 showed crystalline bands only for the FSP-30. Spectra were recorded under dehydrated conditions at 300 °C.

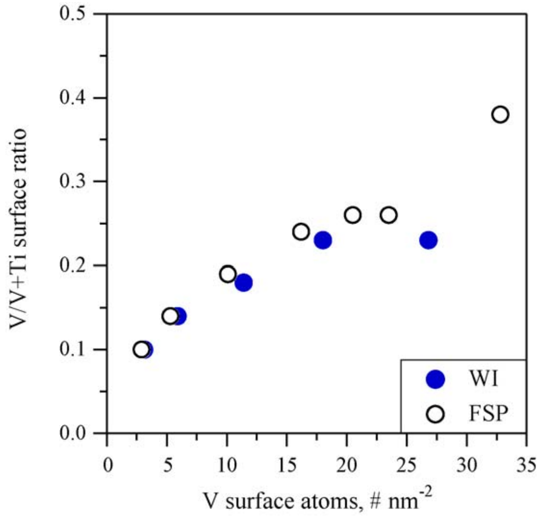

Fig. 3. V/V + Ti surface ratio determined from XPS analysis for the WI- and FSP-made catalysts. FSP-made V_2O_5/TiO_2 showed higher dispersion compared to WI samples at V surface density >6 V nm^{-2}.

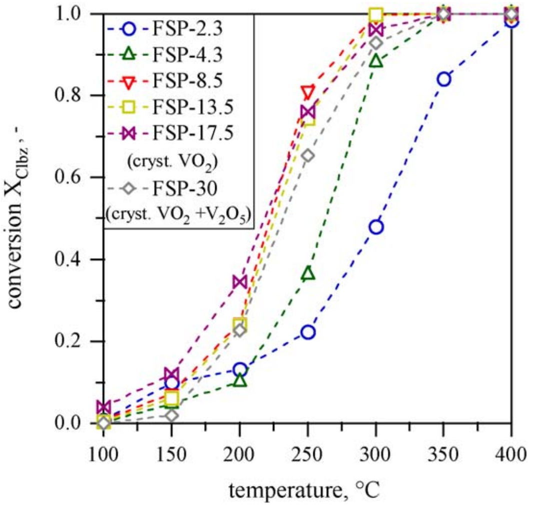

Fig. 4. Light off curves for the FSP-made V_2O_5/TiO_2 catalysts in the total oxidation of chlorobenzene. 100 ppm of chlorobenzene, 20 vol.% O_2, total flow 200 mL min^{-1}.

wet-impregnation procedure is less homogeneous. This could probably be attributed to the relative low calcination temperature of 400 °C. At higher loadings (≥8.5 wt.%) the Raman results for the WI catalysts are in agreement with XRD analysis (Fig. 1) as clear crystalline V_2O_5 bands are detected at 998 and 699 cm^{-1}.

All catalysts were analyzed by XPS in order to determine the V atomic surface concentration. In Fig. 3 the V/V + Ti ratio of both, FSP-made and wet-impregnated catalysts is shown in dependence of the V surface coverage. Up to 6 V nm^{-2} FSP-made and WI catalysts show similar surface concentration of vanadium. Considering the synthesis of the WI catalysts and the fact that vanadium has almost no solubility in TiO_2 after treatment at 400 °C [25] the XPS results corroborate, that for the flame-made catalysts vanadia is located dominantly on the titania surface. The TiO_2 nucleates first in the flame and then the VO_x species condensate on top of it creating a core (TiO_2) shell (VO_x) type structure as stated already earlier [16,18,26,27]. Above 6 V nm^{-2} the slope decreases. At the same time the surface concentration of the wet-impregnated catalysts is slightly lower compared to the FSP-made ones indicating a better dispersion of the V for the flame-made samples at such high contents [28]. Around 13.5 wt.% (16 V nm^{-2}) the increase in the surface ratio is noticeably leveling off. At 30 wt.% a significant increase in the surface concentration can be seen again due to the formation of VO_2 and V_2O_5 crystals likely grown in a more tower like structure [29], covering a large part of the surface of TiO_2 and thus dominating the XPS signal.

3.2. Catalytic performance

Temperature dependency of the conversion of chlorobenzene (X_{Clbz}) (light off curves) for the FSP-made and WI catalysts tested is shown in Figs. 4 and 5, respectively. For both preparation methods the conversion at a given temperature (>200 °C) increases with increasing vanadia content of the catalysts, indicating a higher activity of the catalysts with higher V_2O_5 content. This relation between the vanadia content and the activity was already reported for classic SCR reactions [11] with comparable catalyst systems and for VOC abatement with V_2O_5/Al_2O_3 catalysts [30]. The investigated vanadia content however is usually very low and the surface coverage does not exceed 8–10 V atoms per nm^2 constituting the class of so-called "sub-monolayer" catalysts. Recently V_2O_5/TiO_2 catalysts with >10 V nm^{-2} were reported for the total oxidation of chlorobenzene showing a maximum in activity for 16 V nm^{-2} surface density [15]. A similar V surface density was reported for highly active V_2O_5/TiO_2 catalysts in the oxidative dehydrogenation of propane [31].

The WI catalysts steadily increase in activity with increasing vanadia content reaching a maximum around 18 V nm^{-2} (WI-13.2, Fig. 5), namely more than two times the "theoretical monolayer", before the activity decreases at higher loading (WI-19.5, Fig. 5), consistent with a former study [15]. The flame-made FSP-8.5 and FSP-13.2 catalysts on the other hand, follow the same trend but exhibit the activity maximum at lower loadings (FSP-8.5) before it decreases at higher loadings. Overall, the best catalytic activity was measured for the WI-13.2 catalyst with high amounts of polymeric/crystalline V_2O_5 species as confirmed by XRD (Fig. 1) and Raman (Fig. 2), reaching almost full conversion (98.5%) at 250 °C.

4. Discussion

4.1. Possible role of VO_x species

Looking at the results presented in this study, several explanations can be considered: For both the wet-impregnated

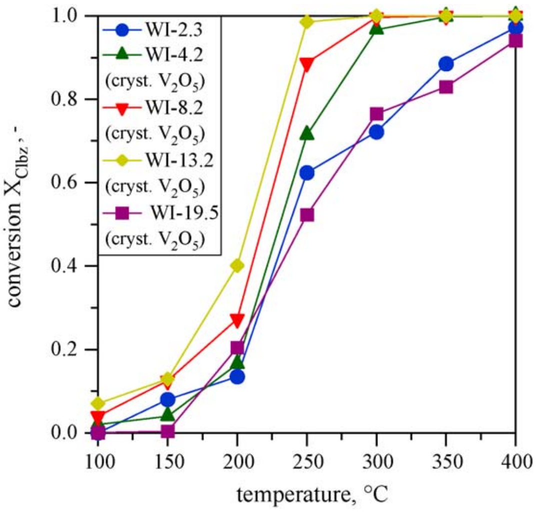

Fig. 5. Light off curves for the WI-made V_2O_5/TiO_2 catalysts in the total oxidation of chlorobenzene. 100 ppm of chlorobenzene, 20 vol.% O_2, total flow 200 mL min^{-1}.

and flame-made catalysts, the samples with low V_2O_5 loading (<4.3 wt.%), corresponding to dominantly monomeric VO_x species as confirmed by Raman analysis, show inferior activity compared to the ones at higher V surface density (Figs. 4 and 5). Obviously the increasing amount of di-, polymeric and/or crystalline V–O–V bonds formed at higher loadings induce a higher activity in the total oxidation of chlorobenzene rather then well spread isolated VO_x species as in the SCR reaction reported by Krishnamoorthy et al. [8]. Recently it was shown that in the total oxidation of benzene on nonhydrolytic sol-gel catalysts indeed the polymeric VO_x species are more active than isolated monomeric species [14]. Krishnamoorthy et al. studied low surface coverage ($<8\ \mathrm{V\ nm^{-2}}$) V_2O_5/TiO_2 catalysts in the total oxidation of chlorobenzene, too [8]. Interestingly no correlation between V surface density and TOF was observed. Light off curves, however, showed increasing activity with increasing vanadia loading indicating that probably the amount of the increasing di- or polymeric VO_x species is likely responsible for the increase in activity. In fact, several authors have reported high activity at relatively high ($>8\ \mathrm{V\ nm^{-2}}$) V surface density for different reactions including oxidative dehydrogenation of propane [31], oxidation of toluene to benzaldehyde [32] and oxidation of o-xylene [33].

At first glance all herein presented results seem to indicate towards the polymeric and crystalline V_2O_5 species containing dominantly V–O–V bonds as an active species for the total oxidation of chlorobenzene. Indeed neither a high amount of well dispersed amorphous (monomeric) VO_x species (Fig. 3) nor the presence of crystalline VO_2 (Fig. 1, FSP-17.5 and FSP-30) have a positive effect on activity (Fig. 4) for the flame-made catalysts when compared to the WI ones (Fig. 5). The latter show always a superior activity at comparable catalyst composition. The only (measured) difference in this study is the presence and amount of crystalline V_2O_5 for FSP-made vs. wet-impregnated catalysts (Figs. 1 and 2) and higher VO_x species dispersion of the flame-made catalysts (Fig. 3). Additionally the available surface area and therefore number of V surface sites cannot be called for explaining the differences in activity, as all catalysts have almost the same SSA. This is in contrast to studies on selective oxidation of o-xylene where the activity depended mainly on the SSA (available V sites) and not on the structure of those VO_x sites [16].

On the other hand crystalline species have been always considered to be less active than mono- or polymeric VO_x species. The herein presented results could indeed suggest that the difference in activity of the WI compared to the FSP catalysts is related to an actual difference in the amount of di- and polymeric VO_x species in relation to the amount of crystalline species present on the surface of the TiO_2. The higher dispersion and lower activity, however, of the FSP catalysts, due to the surface growth of VO_x on single TiO_2 particles in the flame confirmed by Raman [16] and XPS (Fig. 3), corroborate a higher amount of less active mono- and dimeric species for the FSP catalysts compared to the wet-impregnated ones. With increasing vanadia loading ($>16\ \mathrm{V\ nm^{-2}}$ or 2 "theoretical monolayers") the flame-made catalysts show no enhancement in the activity anymore (Fig. 4) since the additionally formed V–O–V bonds are not close enough to the TiO_2 support. While on the WI samples due to the lower dispersion more 2D polymeric VO_x species, V–O–V bonds influenced by the TiO_2, could have formed already at low V surface density (WI-4.3, $6\ \mathrm{V\ nm^{-2}}$) and additional TiO_2 surface becomes available favoring the formation of 2D polymeric structures in close proximity of the titania at high loadings up to $18\ \mathrm{V\ nm^{-2}}$ which in turn increases the activity (Fig. 5).

In other words, the most active species could be those involved in V–O–V bonds that are directly connected to the support or not too distant from a V–O–Ti bond. The active V–O–V bonds would thus be those keeping a sufficient interaction with the support. This explanation would hence suggest a lower activity of the monomeric and isolated species, which consist only in V–O–Ti bonds (and not of V–O–V), and the big crystals, for which a big part of the V–O–V bonds are too far away from the support, to be influenced positively. In the opposite, the more active species would correspond to the polymeric species, namely those containing V–O–V bonds and sitting directly on the support, preferably as a 2D structure, but could also include the small amorphous 3D structures and the crystals little enough to keep a good interaction with the support.

The link between this interpretation and the catalytic results is quite clear. The catalysts with the lowest loading of vanadia, whatever the kind of synthesis, have only or essentially monomeric species and are the least active ones. In the same way, the highest loading of vanadia (FSP-30 and WI-19.5) lead to the biggest crystals observed in this study and showed a lower activity as compared to the most active catalysts which are those with an intermediate loading of vanadia (WI-13.2 and FSP-8.5). These intermediate samples contain essentially polymeric species and small 3D structures (amorphous bodies or little crystals) which are probably equally responsible of this high activity.

5. Conclusions

V_2O_5/TiO_2 catalysts with different vanadia loadings and comparable SSA were prepared by flame spray pyrolysis and classic wet-impregnation synthesis. For the first time (to the best of our knowledge) vanadia/titania catalysts exceeding a V surface density of $8\ \mathrm{V\ nm^{-2}}$ were evaluated in detail for the total oxidation of chlorobenzene. The flame-made catalysts showed in contrast to the wet-impregnated catalysts no indication of crystalline V_2O_5 species even at high ($>8\ \mathrm{V\ nm^{-2}}$) V surface density. VO_x species dispersion was found to be better for the FSP-made catalysts especially for $>6\ \mathrm{V\ nm^{-2}}$. Activity in the catalytic total combustion of chlorobenzene increased with increasing vanadia loading at constant SSA independent of the preparation method, indicating an activity dependency on the structure and amount of VO_x species present on the TiO_2 surface. Indeed V–O–V bonds in close proximity of the titania could be considered as the most active species. In contrast to earlier studies, higher loadings leading to polymeric and/or crystalline VO_x species seem to be beneficial in the abatement of chlorinated VOCs. Additionally the beneficial role of the TiO_2 support for the catalytic activity up to a critical V surface density of around $18\ \mathrm{V\ nm^{-2}}$ can be concluded.

This study exemplifies again that, even though V_2O_5/TiO_2 catalysts have a long history, the active species as well as catalytic mechanisms which are responsible for good catalytic performance of such catalysts are yet not completely understood. Further research is necessary in which effects like surface acidity, average oxidation state and possible vanadia crystal size effects should be analyzed in more detail.

Acknowledgements

The authors gratefully acknowledge financial support by ETH Research Grant TH-41 06-1 and the Université catholique de Louvain for the financial support provided by a FSR project. D.P. Debecker acknowledges the FNRS for its Research Fellow position. R. Delaigle thanks the FRIA for its PhD Student position. The involvements of the Unité de catalyse et chimie des matériaux divisés in the « Inanomat » IUAP network sustained by the « Service public fédéral de programmation politique scientifique » (Belgium) and in the Cost Action D41 sustained by the European Science Foundation are also acknowledged. The Unité de catalyse et chimie des matériaux divisés is involved in the European Multifunctional Materials Institute (EMMI) built from the former FP6-NoE "FAME".

References

[1] I.E. Wachs, G. Deo, B.M. Weckhuysen, A. Andreini, M.A. Vuurman, M. deBoer, M.D. Amiridis, J. Catal. 161 (1996) 211–221.

[2] D.P. Debecker, F. Bertinchamps, N. Blangenois, P. Eloy, E.M. Gaigneaux, Appl. Catal. B-Environ. 74 (2007) 223–232.

[3] B. Grzybowska-Swierkosz, Appl. Catal. A-Gen. 157 (1997) 263–310.

[4] G. Deo, I.E. Wachs, J. Haber, Crit. Rev. Surf. Chem. 4 (1994) 141–187.

[5] C.R. Dias, M.F. Portela, Catal. Rev. -Sci. Eng. 39 (1997) 169–207.

[6] A. Gervasini, P. Carniti, J. Keranen, L. Niinisto, A. Auroux, Catal. Today 96 (2004) 187–194.

[7] I.E. Wachs, Catal. Today 27 (1996) 437–455.

[8] S. Krishnamoorthy, J.P. Baker, M.D. Amiridis, Catal. Today 40 (1998) 39–46.

[9] J. Lichtenberger, M.D. Amiridis, J. Catal. 223 (2004) 296–308.

[10] D.P. Debecker, R. Delaigle, R. Eloy, E.M. Gaigneaux, J. Mol. Catal. A-Chem. 289 (2008) 38–43.

[11] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B-Environ. 18 (1998) 1–36.

[12] G.C. Bond (Ed.), and J.C. Vedrine (Ed.), Catal. Today 20 (1994) 1-184.

[13] R. Delaigle, D.P. Debecker, F. Bertinchamps, E.M. Gaigneaux, Top. Catal. 52 (2009) 501–516.

[14] D.P. Debecker, K. Bouchmella, R. Delaigle, P. Eloy, C. Poleunis, P. Bertrand, E.M. Gaigneaux, P.H. Mutin, Appl. Catal. B-Environ. 94 (2010) 38–45.

[15] F. Bertinchamps, C. Poleunis, C. Gregoire, P. Eloy, P. Bertrand, E.M. Gaigneaux, Surf. Interface Anal. 40 (2008) 231–236.

[16] B. Schimmoeller, H. Schulz, A. Ritter, A. Reitzmann, B. Kraushaar-Czametzki, A. Baiker, S.E. Pratsinis, J. Catal. 256 (2008) 74–83.

[17] L. Mädler, H.K. Kammler, R. Mueller, S.E. Pratsinis, J. Aerosol Sci. 33 (2002) 369–389.

[18] B. Schimmoeller, H. Schulz, S.E. Pratsinis, A. Bareiss, A. Reitzmann, B. Kraushaar-Czarnetzki, J. Catal. 243 (2006) 82–92.

[19] D.A. Bulushev, L. Kiwi-Minsker, F. Rainone, A. Renken, J. Catal. 205 (2002) 115–122.

[20] D.E. Keller, T. Visser, F. Soulimani, D.C. Koningsberger, B.M. Weckhuysen, Vib. Spectrosc. 43 (2007) 140–151.

[21] N. Magg, B. Immaraporn, J.B. Giorgi, T. Schroeder, M. Baumer, J. Dobler, Z.L. Wu, E. Kondratenko, M. Cherian, M. Baerns, P.C. Stair, J. Sauer, H.J. Freund, J. Catal. 226 (2004) 88–100.

[22] G.T. Went, S.T. Oyama, A.T. Bell, J. Phys. Chem. 94 (1990) 4240–4246.

[23] F. Roozeboom, M.C. Mittelmeijerhazeleger, J.A. Moulijn, J. Medema, V.H.J. Debeer, P.J. Gellings, J. Phys. Chem. 84 (1980) 2783–2791.

[24] G.I. Petrov, V.V. Yakovlev, J. Squier, Appl. Phys. Lett. 81 (2002) 1023–1025.

[25] D. Habel, J.B. Stelzer, E. Feike, C. Schroder, A. Hosch, C. Hess, A. Knop-Gericke, J. Caro, H. Schubert, J. Eur. Ceram. Soc. 26 (2006) 3287–3294.

[26] W.J. Stark, K. Wegner, S.E. Pratsinis, A. Baiker, J. Catal. 197 (2001) 182–191.

[27] P.F. Miquel, and J.L. Katz, 6th International Symposium on Preparation of Catalysts - Scientific Bases for the Preparation of Heterogeneous Catalysts, (1994), Proceedings, 207-216.

[28] F. Bertinchamps, C. Gregoire, E.M. Gaigneaux, Appl. Catal. B-Environ. 66 (2006) 1–9.

[29] G.C. Bond, J.P. Zurita, S. Flamerz, P.J. Gellings, H. Bosch, J.G. Vanommen, B.J. Kip, Appl. Catal. 22 (1986) 361–378.

[30] R.S.G. Ferreira, P.G.P. de Oliveira, F.B. Noronha, Appl. Catal. B-Environ. 29 (2001) 275–283.

[31] H. Poelman, B.F. Sels, M. Olea, K. Eufinger, J.S. Paul, B. Moens, I. Sack, V. Balcaen, F. Bertinchamps, E.M. Gaigneaux, P.A. Jacobs, G.B. Marin, D. Poelman, R. De Gryse, J. Catal. 245 (2007) 156–172.

[32] M. Sanati, L.R. Wallenberg, A. Andersson, S. Jansen, Y.P. Tu, J. Catal. 132 (1991) 128–144.

[33] G. Centi, Appl. Catal. A-Gen. 147 (1996) 267–298.