Catalysis Today 175 (2011) 177–182

Contents lists available at ScienceDirect

Catalysis Today

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

# Necessary conditions for a synergy between Ag and $V_2O_5$ in the total oxidation of chlorobenzene

R. Delaigle, P. Eloy, E.M. Gaigneaux*

*Institute of Condensed Matter and Nanosciences (IMCN), Division "MOlecules, Solids and reactiviTy" (MOST), Université catholique de Louvain, Belgium*

ARTICLE INFO

*Article history:*
Received 29 October 2010
Received in revised form 15 February 2011
Accepted 16 March 2011
Available online 11 May 2011

*Keywords:*
Silver
Vanadia
Chlorobenzene oxidation
Titania
Dioxin

ABSTRACT

$V_2O_5/TiO_2$ catalysts are widely developed for the total oxidation of dioxins. However, this study presents an innovative way to improve the performances of $V_2O_5/TiO_2$ catalysts by the addition of silver. Three kinds of catalysts were synthesized: $Ag/TiO_2$, $V_2O_5/TiO_2$ and $Ag–V_2O_5/TiO_2$. The vanadia loading always corresponds to a 0.75 theoretical monolayer while 9 different loadings of silver were explored (0.02–12.5%). This new kind of catalysts is tested in the total oxidation of chlorobenzene which is a classical model molecule for dioxins. The samples were characterized by BET, XPS, XRD, ICP-AES and TEM before and after catalytic tests. The specific surface decreases with the increase of the silver loading for $Ag/TiO_2$ and $Ag–V_2O_5/TiO_2$ catalysts. XPS results show that the addition of silver to a $V_2O_5/TiO_2$ formulation induces a higher oxidation state of the vanadium which should be beneficial on the performances. A synergy is indeed observed for several loadings of silver with a maximum at a loading of 0.05 wt.%. This synergistic effect between silver and vanadia can only be achieved in the total oxidation of chlorobenzene by choosing appropriate operating conditions, namely conditions avoiding AgCl formation. This synergy is directly linked to an optimal silver loading which offers the best compromise between a high oxidation state of vanadia without a significant decrease of the specific surface of the catalyst.

## 1. Introduction

The abatement of dioxins constitutes a major concern in the field of atmospheric pollution. Dioxins, which refer to polychlorinated dibenzo-furans (PCDFs) and polychlorinated dibenzo-dioxins (PCDDs), are systematically formed in all kinds of combustion processes of organic fuels in the presence of chlorinated compounds, e.g. in municipal waste incinerators or in cogeneration units [1,2]. These molecules are very toxic and responsible for carcinogenic and hormonal problems even in very low concentrations [3]. Moreover, dioxins being very stable structures, their destruction is necessary directly at the source of emission. In this context, catalytic total oxidation is the most promising solution [4]. Vanadium-based catalysts are widely developed for this application and different ways were already explored to improve the activity of $V_2O_5/TiO_2$ catalysts [5–7]. Classically, the performances of this formulation are improved by the addition of molybdenum or tungsten oxides [8–10]. These improvements lead to a higher acidity which is generally considered as a determining factor for the adsorption of the pollutant. However, these conclusions were obtained with model molecules while our group has recently shown that this approach is not fully relevant [11,12]. The oxidation of dioxins is indeed negatively influenced by the addition of these doping phases in their total oxidation on $V_2O_5/TiO_2$ catalysts [13]. Recently, some authors tried an innovative way to improve the efficiency of vanadium based catalysts by the addition of noble metals [14–17]. Synergistic effects were claimed between the noble metal and supported vanadia in the total oxidation of aromatic VOC. However, these new systems were generally not used in the oxidation of chlorinated compounds. This aspect is a major drawback regarding to the oxidation of dioxins. The potential poisoning effect of the chlorine species is indeed well known and has to be studied in this reaction. The mechanism of this synergy is actually not really understood.

To further progress in this direction, silver is added to $V_2O_5/TiO_2$ catalysts by a wet impregnation method. The addition of silver could potentially bring electrophilic oxygens [18,19] which are interesting species in a reaction of total oxidation. This new kind of catalysts is characterized by ICP-AES, XRD, $N_2$-physisorption, TEM and XPS before and after the catalytic tests. These characterizations allow to describe the effect of the addition of silver on the physico-chemical properties of $V_2O_5/TiO_2$ catalysts. These catalysts are tested in the total oxidation of chlorobenzene which is a classical model molecule for dioxins. The aim of this work is to determine whether a synergy can be achieved between silver and vanadium and which conditions are required to observe this synergy. In this context, we will assume that there is a synergy between silver and vanadium if the catalytic performances of the $Ag–V_2O_5/TiO_2$

---

* Corresponding author at: Croix du Sud 2/17, 1348 Louvain-la-Neuve, Belgium.
*E-mail address:* eric.gaigneaux@uclouvain.be (E.M. Gaigneaux).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.03.043

catalyst are higher than the sum of the performances of the two corresponding reference catalysts, namely $Ag/TiO_2$ and $V_2O_5/TiO_2$.

## 2. Experimental

### 2.1. Preparation of the catalyst

Three kinds of catalysts were supported on $TiO_2$ (Degussa P25: 49 m$^2$/g; 85% anatase–15% rutile): $Ag/TiO_2$, $V_2O_5/TiO_2$ and $Ag–V_2O_5/TiO_2$. Silver and vanadia were introduced by a wet impregnation method. The $AgNO_3$ precursor (Aldrich, >99%) was dissolved in distilled water while the $NH_4VO_3$ precursor (Vel, >99%) was dissolved in distilled water and complexed with oxalic acid (Aldrich, >99%, molar ratio vanadium:oxalic acid = 1:2 [8]). 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 reduced pressure at 40 °C. The material was dried overnight in an oven at 110 °C and finally calcined in air in a muffle furnace (20 h, 400 °C). The vanadia loading always corresponds to a 0.75 theoretical monolayer while 9 different loadings of silver were explored (0.02–12.5 wt.%). The $V_2O_5/TiO_2$, $Ag/TiO_2$ and $Ag–V_2O_5/TiO_2$ catalysts are labelled TV, AgT-*x* and AgTV-*x*, respectively, where *x* denotes the silver content in wt.%.

### 2.2. Catalytic tests

The catalytic tests were performed in a metallic fixed-bed microreactor operating at atmospheric pressure. The reactor was made of an inconel tube of 1 cm internal diameter. The catalytic bed was composed of 200 mg of catalyst powder selected within the granulometric fraction 200–315 μm and diluted in 800 mg of inactive glass spheres (diameter in the range 315–500 μm). The gas stream contained 100 ppm of chlorobenzene in He (Praxair), 20% of $O_2$ (Praxair; 99,995%) and He (Praxair; 99,996%) as diluting gas to obtain 200 ml/min (VVH = 37,000 h$^{-1}$). Two different procedures were used to evaluate the catalytic activity. In the "light-off" procedure, after stabilization at 100 °C, the reaction was run from 100 to 400 °C in a step mode. In the "alternative" procedure, the stabilization step was realized at 200 °C and the catalysts performances were measured at 200 and 250 °C. The interest of this alternative will be evoked later. In both procedures, the catalysts were stabilized for 150 min at each temperature. The analysis of reactants and products ($CO_2$, CO) was continuously performed by on line gas chromatography (GC). This equipment allowed to detect potential intermediate products of the reaction like hydrocarbons and chlorinated hydrocarbons. In both procedures, the conversion of chlorobenzene always corresponds to total oxidation. The selectivity of $CO_2$ is systematically 100% except when the conversion of chlorobenzene reached 100%. In this case, CO can sometimes be produced and its selectivity can reach up to 3%. The conversion is defined as the ratio reactant transformed/reactant in the inlet (in %). More details of the operating conditions can be found elsewhere [5,8,9].

### 2.3. Characterization

The weight percentages of V and Ag in the catalysts were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Iris Advantage apparatus from Jarrell Ash Corporation.

The BET specific surface area of the catalysts was measured by nitrogen adsorption at 77 K with a Micromeritics TriStar 3000 instrument. The samples were outgassed overnight at 150 °C under vacuum before the measurement.

**Table 1**
Specific surface area (SSA) and silver and vanadium contents (wt.%) of $Ag/TiO_2$, $V_2O_5/TiO_2$ and $Ag–V_2O_5/TiO_2$ catalysts.

| Nominal Ag loading (%) | $Ag/TiO_2$ | | $Ag–V_2O_5/TiO_2$ | | |
|---|---|---|---|---|---|
| | SSA (m$^2$ g$^{-1}$) | Ag (%) | SSA (m$^2$ g$^{-1}$) | Ag (%) | V (%) |
| 0 | 50.0 | – | 48.3 | – | 2.4 |
| 0.02 | 49.3 | n.m. | 47.0 | n.m. | 2.4 |
| 0.05 | 49.2 | 0.06 | 46.9 | 0.07 | 2.3 |
| 0.12 | 49.7 | 0.11 | 46.4 | 0.14 | 2.3 |
| 0.24 | 48.6 | n.m. | 46.3 | n.m. | 2.5 |
| 0.49 | 49.1 | 0.47 | 46.7 | 0.45 | 2.3 |
| 1.24 | 44.2 | 1.12 | 44.2 | 1.12 | 2.4 |
| 2.49 | 44.0 | n.m. | 37.8 | n.m. | 2.3 |
| 4.98 | 36.3 | 4.85 | 38.6 | 4.76 | 2.3 |
| 12.50 | 33.3 | 12.37 | 30.0 | 12.30 | 2.2 |

n.m. = not measured.

X-ray diffraction (XRD) measurements were performed on the catalysts with a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). The $2\theta$ range was recorded between 5 and 75° at a rate of 0.028° s$^{-1}$. The ICDD-JCPDS database was used to identify the crystalline phases.

TEM measurements were performed on a JEOL 2000FX, working under an acceleration voltage of 200 kV. For the analysis, the sample was dispersed in ethanol and homogenized by agitation. A droplet of the suspension was deposited on the grid and the solvent was allowed to evaporate.

Surface characterization was done with an X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra spectrometer (Kratos-Analytical, Manchester, UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). The pressure in the analysis chamber was about $10^{-6}$ Pa. The analyzed area was 700 mm × 300 mm. The pass energy of the hemispherical analyzer was set at 160 eV for the wide scan and 40 eV for narrow scans. Charge stabilization was achieved by using the Kratos Axis device. The electron source was operated at 1.8 A filament current and a bias of −1.1 eV. The charge balance plate was set at −2.8 V. The sample powders were pressed into small stainless steel troughs mounted on a multi specimen holder. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Ti 2p, Ag 3d, V 2p, Cl 2p and C 1s again to check for charge stability as a function of time, and the absence of degradation of the sample during the analyses. Special care was taken to make sure that vanadium and silver were measured fast enough in order to avoid potential reduction under vacuum. This was done by measuring these elements at first as soon as the vacuum level was low enough to allow proper XPS measurements (quick XPS procedure). The binding energy (BE) values were referred to the C–(C, H) contribution of the C 1s peak at 284.8 eV. Molar fractions (%) were calculated using peak areas normalized on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors, and transmission factors provided by the manufacturer. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). More details of the exact settings and peak analysis can be found elsewhere [16,20].

## 3. Results and discussion

### 3.1. Physico-chemical characterization

Elementary analyses reveal a good agreement between experimental and nominal data for all catalysts (Table 1). There are no significant differences between AgTV catalysts and the corresponding AgT and TV catalysts.

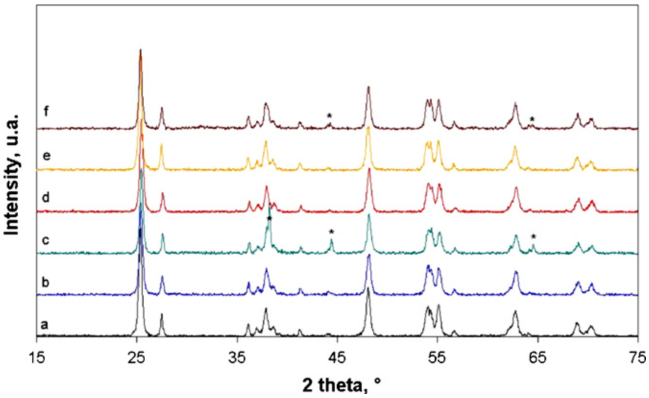

**Fig. 1.** XRD diffraction patterns obtained on (a) $TiO_2$, (b) AgT-4.98, (c) AgT-12.5, (d) TV, (e) AgTV-4.98 and (f) AgTV-12.5 catalysts after the "light-off" procedure. XRD patterns of AgT-4.98 and AgTV-4.98 are representative for all the other AgT and AgTV catalysts respectively. * = metallic silver.

A drop of the specific surface is evidenced from 1.24% of silver for $Ag/TiO_2$ catalysts as well as for $Ag–V_2O_5/TiO_2$ catalysts (Table 1). This drop is more and more pronounced with the silver loading.

The XRD patterns highlighted the diffraction lines of the anatase and rutile phases of $TiO_2$ for all catalysts (Fig. 1) while crystalline vanadia oxide was never detected for TV and AgTV catalysts. This result is in perfect accordance with former studies [5,6,16]. Schimmoeller et al. [6] showed that a wet impregnation method leads to a heterogeneous mix a vanadium species for a TV catalyst. This mixture consisted of monomeric, polymeric and small crystalline (<5 nm) vanadia species which are not detectable by XRD.

Metallic silver nanoparticles are detected for the highest loading (12.5%) of Ag for both AgT and AgTV catalysts. Such nanoparticles could be present for the lower loadings of Ag but they are probably too small and not numerous enough to be detected by XRD. This hypothesis is confirmed by TEM and XPS analyses.

The pictures obtained by TEM (Figs. 2 and 3) show metallic silver nanoparticles for an AgTV-0.12 catalyst as well as for an AgTV-12.5 catalyst. These analyses suggest that the size of the nanoparticles increases with the silver loading. Indeed, the nanoparticles are bigger for the AgTV-12.5 than for the AgTV-0.12 catalyst.

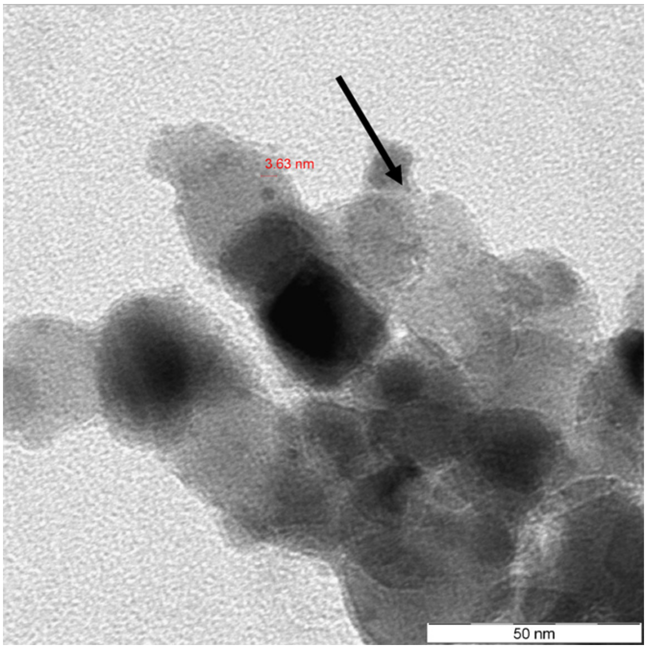

**Fig. 2.** TEM picture of AgTV-0.12 catalyst. The arrow indicates silver nanoparticle.

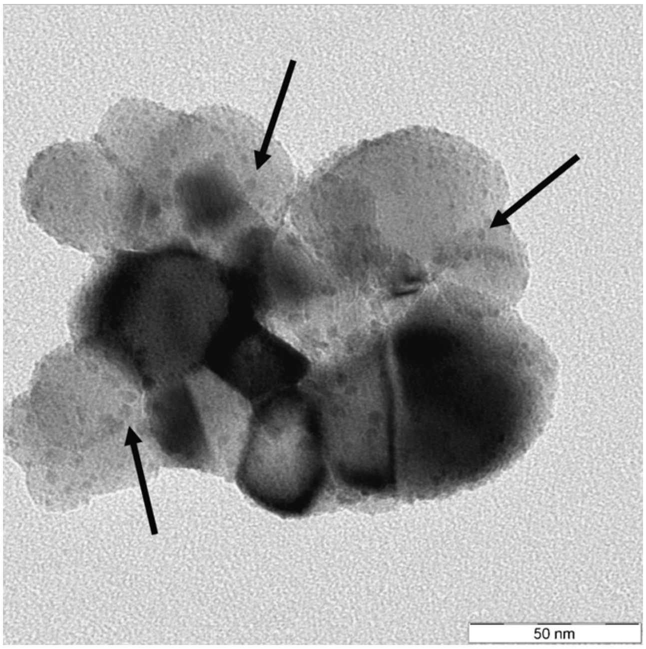

**Fig. 3.** TEM picture of AgTV-12.5 catalyst. The arrows indicate silver nanoparticles.

The XPS binding energies of Ag, V and Ti are summarized in Table 2. The binding energy of titanium (459.0 eV) corresponds to $Ti^{4+}$ for all catalysts [8,21]. This result is in agreement with XRD analyses. The silver binding energy (368.0 eV) corresponds to the metallic state for all catalysts [22,23]. The slight differences observed inside a series of catalysts are essentially due to the silver loadings. Indeed, a higher silver loading induces bigger nanoparticles, whereas Schnippering et al. [24] have shown that the binding energy of metallic silver is directly linked to the size of the nanoparticles. The binding energy precisely shifts to a higher value with an increase of the size of the nanoparticles. The XPS peak of AgTV-12.5 (Fig. 4), which is a representative sample for silver containing catalysts, clearly shows that there is only one kind of silver. We can thus assume that silver is present only in the metallic state. This information is crucial because it means that silver does not form

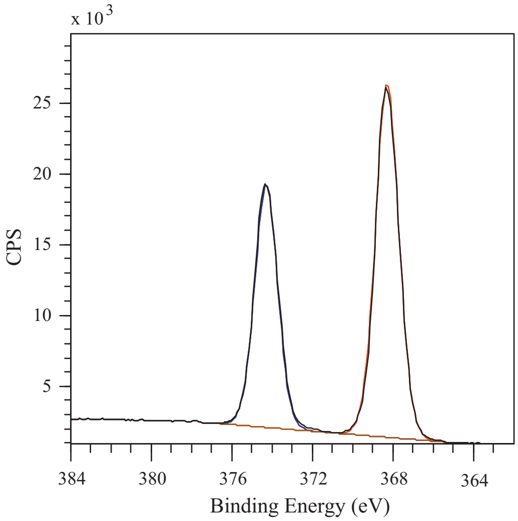

**Fig. 4.** XPS Ag $3d_{5/2}$ peak of AgTV-12.5 catalyst. The doublet shape and location of this peak are representative for all $Ag/TiO_2$ and $Ag–V_2O_5/TiO_2$ catalysts.

**Table 2**
Binding energy (BE) of Ag, V and Ti and proportion of $V^{5+}$ and $V^{4+}$ determined by XPS for all the catalysts.

| Ag nominal loading (%) | Ag/$TiO_2$ catalysts | | Ag–$V_2O_5$/$TiO_2$ catalysts | | | | |
|---|---|---|---|---|---|---|---|
| | BE Ti 2 $p_{3/2}$ (eV) | BE Ag $3d_{5/2}$ (eV) | BE Ti 2 $p_{3/2}$ (eV) | BE Ag 3 $d_{5/2}$ (eV) | BE V 2 $p_{3/2}$ (eV) | Proportion of $V^{5+}$ (%) | Proportion of $V^{4+}$ (%) |
| 0 | 458.8 | – | 459.0 | – | 517.0 | 61 | 39 |
| 0.02 | 458.9 | 367.8 | 459.1 | 368.2 | 517.3 | 73 | 27 |
| 0.05 | 458.8 | 367.8 | 459.0 | 368.2 | 517.4 | 70 | 30 |
| 0.12 | 458.8 | 367.8 | 459.0 | 368.2 | 517.2 | 75 | 25 |
| 0.24 | 458.8 | 367.8 | 458.9 | 368.4 | 517.4 | 78 | 22 |
| 0.49 | 458.8 | 368.0 | 459.1 | 368.4 | 517.4 | 81 | 19 |
| 1.24 | 458.9 | 368.0 | 459.1 | 368.4 | 517.3 | 85 | 15 |
| 2.49 | 458.9 | 368.1 | 459.0 | 368.4 | 517.3 | 84 | 16 |
| 4.98 | 458.9 | 368.0 | 459.0 | 368.4 | 517.4 | 93 | 7 |
| 12.50 | 458.8 | 368.2 | 459.1 | 368.3 | 517.3 | 95 | 5 |

any mixed oxide with vanadium. The absence of mixed oxide is catalytically interesting. Mixed V–Ag oxides (as silver vanadates) indeed, lead essentially to the partial oxidation of aromatic compounds [25], which has to be avoided in our case. The binding energy of vanadium (517.3 eV) corresponds to $V^{5+}$ [21,26]. However, the peak of vanadium is composed of a mixture of $V^{4+}$ and $V^{5+}$ for all AgTV catalysts as well as for TV catalyst. The decomposition of this peak shows that the addition of silver to $V_2O_5$/$TiO_2$ formulation induces a higher oxidation state of the vanadium. The proportion of $V^{5+}$ indeed increases with the silver loading (Table 2). This result suggests that AgTV catalysts should be more efficient than the TV reference catalysts. Indeed, $V_2O_5$/$TiO_2$ catalysts react in the oxidation of chlorobenzene following a Mars and Van Krevelen mechanism [20] (Fig. 5). In this mechanism, a higher oxidation state of vanadium induces better catalytic performances [5,20]. At corresponding V content, AgTV catalysts are thus potentially more efficient than the TV one in the total oxidation of chlorobenzene. Catalytic tests should allow to verify this hypothesis.

### *3.2. Catalytic tests with the "light-off" procedure*

Ag/$TiO_2$ catalysts are all almost inactive with the "light-off" procedure (Fig. 6). These catalysts exhibit a very poor activity even at the highest silver loading. The AgTV catalysts with the lowest loadings, from 0.02 to 0.1% of silver, present the same activity as the TV reference catalyst (Fig. 6). The highest loadings of silver in the AgTV catalysts lead to similar or even weaker performances than the TV catalysts (Fig. 7). Considering the physico-chemical properties of AgTV catalysts (higher oxidation state of V) and their expected beneficial effect on a Mars and Van Krevelen driven reaction, these catalytic results are disappointing. The lower performances of AgTV-4.98 and AgTV-12.5 can easily be explained by their lower specific surfaces compared to the TV reference catalyst. The performances of vanadia based catalysts for such a reaction can be linked to the specific surface [27]. This parameter can be limiting for the adsorption of the molecule of interest. However, we cannot exclude the potential influence of the surface acidity on this step of the reaction. This property could be determining and should be studied in further works as they were previously investigated in the case of Mo (or W) doped TV catalayst [5,9]. At this stage, we can assume that the adsorption of chlorobenzene is more limited for these two catalysts. In this case, the potential benefit of a higher oxidation state of vanadium is likely counterbalanced by their lower specific surface. However, this explanation cannot account for all AgTV catalysts and thus one question still remains: why is there no improvement of the catalytic activity in the light-off mode? This question can be answered by characterizing the used catalysts. This will allow to understand what does happen during the catalytic test.

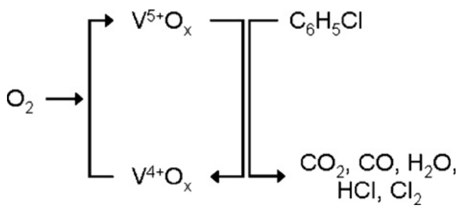

**Fig. 5.** Scheme of the chlorobenzene oxidation.

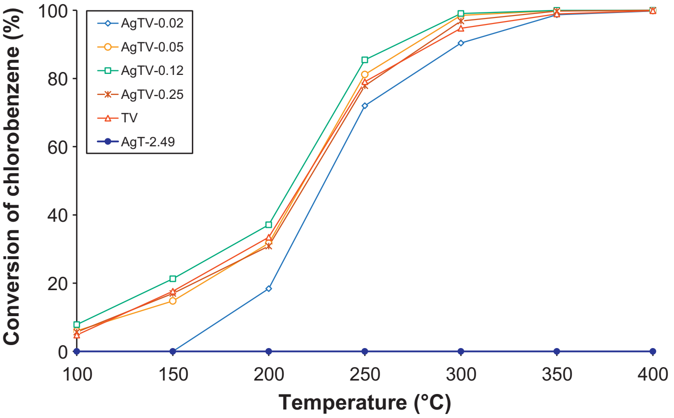

**Fig. 6.** Catalytic performances of TV, AgT-2.49, AgTV-0.02, AgTV-0.05, AgTV-0.12 and AgTV-0.24 in the total oxidation of chlorobenzene with the light-off procedure. The catalytic performances of AgT-2.49 catalyst are representative for all the AgT catalysts.

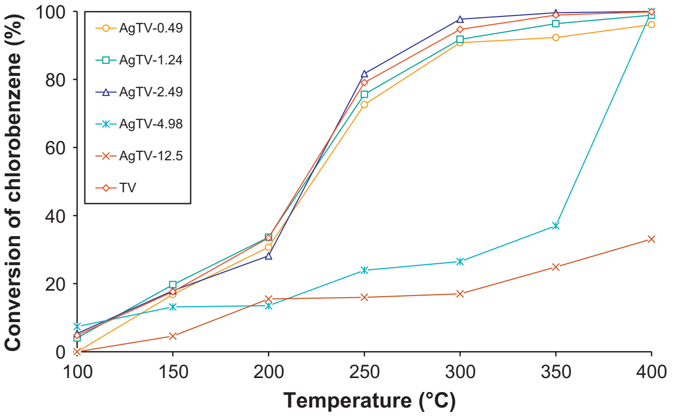

**Fig. 7.** Catalytic performances of TV, AgTV-0.49, AgTV-1.24, AgTV-2.49, AgTV-4.98 and AgTV-12.5 in the total oxidation of chlorobenzene with the light-off procedure.

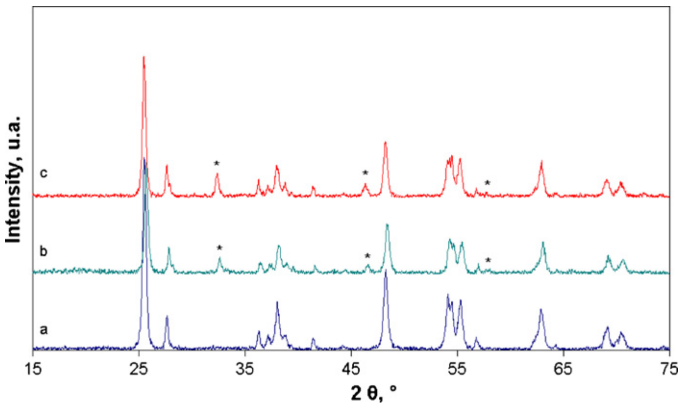

**Fig. 8.** XRD diffraction pattern obtained on (a) $V_2O_5/TiO_2$, (b) AgTV-4.98 and (c) AgTV-12.5 catalysts after the "light-off" procedure. * = AgCl.

**Table 3**
Chorine concentration at the surface of the $V_2O_5/TiO_2$ and $Ag–V_2O_5/TiO_2$ catalysts determined by XPS after the "light-off" procedure.

| Ag nominal loading (%) | Cl (at.%) |
|---|---|
| 0 | 0 |
| 0.02 | u.l.d. |
| 0.05 | u.l.d. |
| 0.12 | 0.15 |
| 0.24 | 0.15 |
| 0.49 | 0.15 |
| 1.24 | 0.54 |
| 2.49 | 0.95 |
| 4.98 | 1.15 |
| 12.50 | 1.32 |

u.l.d. = under limit of detection.

### 3.3. Post-test analyses

All spent catalysts were therefore analyzed by XRD and XPS. XRD measurements evidence the presence of AgCl at the surface of AgTV catalysts with the highest silver loadings (4.98 and 12.5%) while no chlorine species were detected for the TV catalyst (Fig. 8). The presence of Cl is confirmed by XPS at the surface of all AgT and AgTV catalysts after light off tests (Table 3). Only catalysts with the lowest Ag contents did not reveal Cl at their surface as likely under the limit of detection of the equipment. These results indicate that the chlorine function of chlorobenzene reacts with silver during the catalytic test. This chlorination could happen at the adsorption of the pollutant. The first step of the oxidation of chlorobenzene is the adsorption of the molecule by a nucleophilic substitution of the chlorine function [28]. This substitution leads to the formation of $Cl^-$ which could then react with silver. This chlorination could be considered as a poisoning effect which could impede silver to play its potential promoting effect on the vanadium active phase.

XPS analyses showed that AgTV and AgT catalysts are already chlorinated during the first step of the light-off procedure at 100 °C. AgTV-0.24 and AgTV-2.49 catalysts were thus used in a light-off mode from 100 to 250 °C in order to induce this Cl poisoning. The performances of these catalysts were then evaluated during 10 h at 250 °C. Their performances did not change during these 10 h suggesting that Ag is entirely chlorinated from the very beginning of the test. These two tests confirmed that the chlorination would essentially impede silver to play its promoting effect. The catalytic performances of AgT and AgTV catalysts can thus probably be correlated with two parameters: the drop of specific surface for the highest loadings of silver and the formation of AgCl at their surface during the tests.

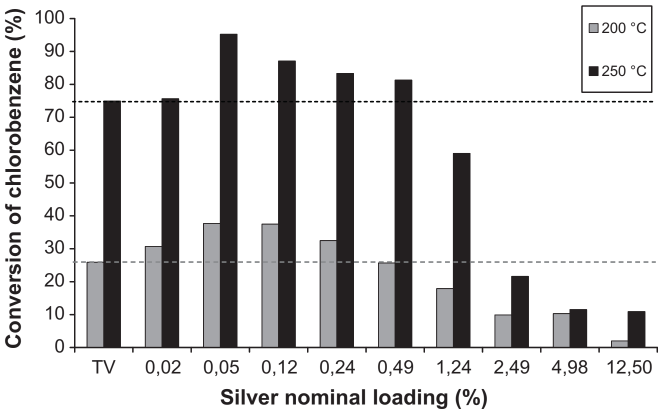

**Fig. 9.** Catalytic performances of TV and AgTV catalysts in the total oxidation of chlorobenzene with the "alternative" procedure. The grey and black dotted lines correspond to the expected performances "TV + AgT-*x*" at 200 and 250 °C respectively. There is a synergy if the performances of the AgTV catalyst are higher than these performances.

In order to verify the hypothesis of a poisoning effect by chlorine, we need to work in operating conditions which permit to avoid or to limit this chlorination. We identified these conditions by considering the following details. Two kinds of chlorinated species can be produced in the total oxidation of chlorinated aromatic molecules: HCl and $Cl_2$. In the total oxidation of chlorinated hydrocarbons, it is known that the relative production of these species depends on the temperature [29,30]. HCl is essentially produced under 200 °C while $Cl_2$ is essentially produced above 200 °C. Moreover, several studies showed that HCl reacts better with Ag than $Cl_2$ [29]. Finally, the reaction/adsorption between Ag and $Cl_2$ is favoured under 100 °C [31,32].

The hypothesis is thus that (i) at the temperature at which the light off procedure starts (namely 100 °C), HCl is the chlorinated species mainly formed and Ag is already chlorinated; (ii) if we work directly at a temperature higher than 100 °C, we should promote the production of $Cl_2$ in conditions unfavorable for its reaction with Ag. We thus decided to define an "alternative procedure" of test for which the measurement starts directly at 200 °C. Thanks to this "alternative" procedure, we should limit or avoid the chlorination of silver during the catalytic tests.

### 3.4. Catalytic test with the "alternative" procedure

$Ag/TiO_2$ catalysts are still inactive with the alternative procedure (not shown). XPS and XRD post-test analyses revealed that the chlorination of silver is still effective. On the contrary, $Ag–V_2O_5/TiO_2$ catalysts exhibit higher performances with the alternative procedure than with the light-off one. A synergy is observed for several silver loadings, 0.05, 0.12, 0.24 and 0.49%, with a maximum at 0.05 wt.% (Fig. 9). This $Ag–V_2O_5/TiO_2$-0.05 catalyst destroys 95.2% of chlorobenzene at 250 °C while $V_2O_5/TiO_2$ and $Ag/TiO_2$-0.05 catalysts remove 74.9% and 0% respectively.

Along the alternative procedure, the formation of AgCl at the surface of the AgTV catalysts has been avoided or limited thanks to the stabilization step at 200 °C. XRD patterns did not reveal AgCl while XPS measurements on used catalysts detected chlorine only for the three highest loadings. In this case, the quantity of chlorine detected at the surface of AgTV-2.49, AgTV-4.98 and AgTV-12.5 is significantly less important than after the light-off procedure. The atomic chlorine concentrations for these catalysts correspond to 0.65, 0.80 and 1.20% respectively. The weak activity of these three catalysts via the alternative procedure can thus be linked to their low specific surface and their chlorination as compared to the other catalysts.

One could wonder why this chlorination is still effective in the case of AgT catalysts while it is limited for AgTV catalysts. This difference could be explained by their behavior during the catalytic test. All AgT catalysts are inactive with the alternative procedure. However, the adsorption of the molecule at the surface of the catalysts cannot be excluded. During this step, Ag would be chlorinated (as explained in Section 3.3) and would become therefore inactive for the oxidation of chlorobenzene. At the opposite, the adsorption of chlorobenzene would preferably occur on the vanadium phase (because adsorption is acidity driven and vanadia is more acidic than metallic silver) avoiding the chlorination of silver. Moreover, AgTV are very efficient with this alternative procedure. The oxidation of chlorobenzene leads to the formation of $H_2O$ which can react with the chlorine species following the Deacon reaction [33,34]. This reaction will clean the surface of the catalyst from adsorbed chlorine species. This cleaning could explain why chlorination is avoided or limited for the AgTV catalysts and not for AgT catalysts.

In the end, the hypothesis concerning the potential poisoning effect of the chlorine function is confirmed by the correlation between these physico-chemical characterizations and the catalytic performances. The addition of silver inducing a higher oxidation state of vanadium leads to higher performances if we are able to avoid Ag chlorination. However, the physico-chemical characterizations on the fresh and spent catalysts do not explain why there is a synergy during the test. Considering that Ag could generate electrophilic oxygens [18,19], these species could improve the oxidation step of $V^{4+}$ to $V^{5+}$ in the Mars and Van Krevelen mechanism (Fig. 5). This improvement will maintain the vanadium in a higher oxidation state and induce higher catalytic performances. Ag could thus be considered as a promoter of the oxidation of $V^{4+}$ to $V^{5+}$ and the high amount of $V^{5+}$ detected on fresh catalysts could be considered as an indication of such a mechanism during the calcination step of the synthesis.

Finally, the synergy between silver and vanadium can only be observed in appropriate operating conditions. Moreover, the AgTV catalysts for which a synergistic effect is observed correspond to silver loadings which induce a high oxidation state of vanadium (Table 2) without inducing a too marked drop of the specific surface (Table 1).

## 4. Conclusion

Silver is added to a $V_2O_5/TiO_2$ catalyst in order to improve its performances in the total oxidation of chlorobenzene. The physico-chemical characterizations of Ag–$V_2O_5/TiO_2$ showed that the specific surface decreases with the increase of the silver loading while the oxidation state of the vanadium increases. These catalysts exhibited disappointing performances in the light-off procedure because of a chlorination of silver that occurs during the test. A synergistic effect between silver and vanadia has however been achieved in the total oxidation of chlorobenzene by choosing appropriate operating conditions, namely impeding AgCl formation. These conditions are achieved by not operating the catalysts below 200 °C, thus avoiding the formation of HCl that would otherwise deactivate the catalysts by inducing Ag chlorination. Moreover, the synergy is observed at optimal silver loadings which correspond to a good compromise between using enough Ag to maintain a high oxidation state of vanadia, but not too much Ag, which would bring a detrimental decrease of the catalyst specific surface.

## Acknowledgements

The authors gratefully acknowledge the *Fonds National de Recherche Scientifique* (*FNRS*) of Belgium and the *Fonds Special de la Recherche* (*FSR*) of the Université catholique de Louvain for financial support and R. Delaigle's PhD fellowship. The involvement of the authors in the "Inanomat" IUAP network sustained by the "Service public fédéral de programmation politique scientifique" (Belgium) is also acknowledged. The group of heterogeneous catalysis (formerly *Unité de catalyse et chimie des matériaux divisés*) also acknowledges its involvement in the Cost Action D41 sustained by the European Science Foundation.

## References

[1] K. Everaert, J. Baeyens, J. Degreve, Environ. Sci. Technol. 37 (2003) 1219–1224.
[2] E. Finocchio, G. Busca, M. Notaro, Appl. Catal. B: Environ. 62 (2006) 12–20.
[3] E.C. Rada, M. Ragazzi, V. Panaitescu, T. Apostol, Chemosphere 62 (2006) 404–410.
[4] K. Everaert, J. Baeyens, Waste Manage. (Oxf.) 24 (2004) 37–42.
[5] R. Delaigle, D.P. Debecker, F. Bertinchamps, E.M. Gaigneaux, Top. Catal. 52 (2009) 501–516.
[6] B. Schimmoeller, R. Delaigle, D.P. Debecker, E.M. Gaigneaux, Catal. Today 157 (2010) 198–203.
[7] 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.
[8] F. Bertinchamps, C. Gregoire, E.M. Gaigneaux, Appl. Catal. B: Environ. 66 (2006) 1–9.
[9] F. Bertinchamps, C. Gregoire, E.M. Gaigneaux, Appl. Catal. B: Environ. 66 (2006) 10–22.
[10] D.P. Debecker, R. Delaigle, K. Bouchmella, P. Eloy, E.M. Gaigneaux, P.H. Mutin, Catal. Today 157 (2010) 125–130.
[11] D.P. Debecker, F. Bertinchamps, N. Blangenois, P. Eloy, E.M. Gaigneaux, Appl. Catal. B: Environ. 74 (2007) 223–232.
[12] D.P. Debecker, R. Delaigle, P. Eloy, E.M. Gaigneaux, J. Mol. Catal. A: Chem. 289 (2008) 38–43.
[13] D.P. Debecker, R. Delaigle, P.C. Hung, A. Buekens, E.M. Gaigneaux, M.B. Chang, Chemosphere 82 (2011) 1337–1342.
[14] D. Andreeva, T. Tabakova, V. Idakiev, A. Naydenov, Gold Bull. 31 (1998) 105–106.
[15] T.F. Garetto, M.S. Avila, C.I. Vignatti, V.V. Rao, K. Chary, C.R. Apesteguia, Catal. Lett. 130 (2009) 476–480.
[16] D.P. Debecker, C. Faure, M.E. Meyre, A. Derre, E.M. Gaigneaux, Small 4 (2008) 2096–12096.
[17] D.P. Debecker, R. Delaigle, M.M.F. Joseph, C. Faure, E.M. Gaigneaux, Stud. Surf. Sci. Catal. 175 (2010) 805–809.
[18] V.V. Kaichev, V.I. Bukhtiyarov, M. Havecker, A. Knop-Gercke, R.W. Mayer, R. Schlogl, Kinet. Catal. 44 (2003) 432–440.
[19] X. Bao, M. Muhler, T. SchedelNiedrig, R. Schlogl, Phys. Rev. B 54 (1996) 2249–2262.
[20] F. Bertinchamps, M. Treinen, N. Blangenois, E. Mariage, E.M. Gaigneaux, J. Catal. 230 (2005) 493–498.
[21] J. Nogier, M. Delamar, P. Ruiz, B. Delmon, J.P. Bonnelle, M. Guelton, L. Gengembre, J.C. Vedrine, M. Brun, P. Albers, K. Seibold, M. Baerns, H. Papp, J. Stoch, L.T. Andersson, J. Kiwi, R. Thampi, M. Gratzel, G.C. Bond, N. Verma, J.C. Vickerman, R.H. West, Catal. Today 20 (1994) 109–123.
[22] M.S. Park, M. Kang, Mater. Lett. 62 (2008) 183–187.
[23] W. Su, S.S. Wei, S.Q. Hu, J.X. Tang, J. Hazard. Mater. 172 (2009) 716–720.
[24] M. Schnippering, M. Carrara, A. Foelske, R. Kotz, D.J. Fermin, PCCP 9 (2007) 725–730.
[25] F. Rosowski, S. Altwasser, C.K. Dobner, S. Storck, J. Zühlke, H. Hibst, Catal. Today 157 (2010) 339–344.
[26] G. Silversmit, D. Depla, H. Poelman, G.B. Marin, R. De Gryse, J. Electron. Spectrosc. Relat. Phenom. 135 (2004) 167–175.
[27] B. Schimmoeller, H. Schulz, A. Ritter, A. Reitzmann, B. Kraushaar-Czametzki, A. Baiker, S.E. Pratsinis, J. Catal. 256 (2008) 74–83.
[28] J. Lichtenberger, M.D. Amiridis, J. Catal. 223 (2004) 296–308.
[29] S.K. Agarwal, J.J. Spivey, J.B. Butt, Appl. Catal. A: Gen. 82 (1992) 259–275.
[30] K. Ramanthan, J.J. Spivey, Combust. Sci. Technol. 63 (1989) 247–255.
[31] B.V. Andryushechkin, K.N. Eltsov, V.M. Shevlyuga, Surf. Sci. 433 (1999) 109–113.
[32] B.V. Andryushechkin, K.N. Eltsov, V.M. Shevlyuga, C. Tarducci, B. Cortigiani, U. Bardi, A. Atrei, Surf. Sci. 421 (1999) 27–32.
[33] S. Krishnamoorthy, J.A. Rivas, M.D. Amiridis, J. Catal. 193 (2000) 264–272.
[34] S. Lomnicki, J. Lichtenberger, Z.T. Xu, M. Waters, J. Kosman, M.D. Amiridis, Appl. Catal. B: Environ. 46 (2003) 105–119.