

**PART I: DESIGN OF THE BEST CATALYST
FOR THE TOTAL OXIDATION OF
CHLORINATED VOCs**

Part I: Design of the best catalyst

CHAPTER 1 : SCREENING OF TRANSITION METAL OXIDES SUPPORTED CATALYSTS IN THE TOTAL OXIDATION OF CHLORINATED VOCs

Abstract

This chapter reports a systematic investigation (screening) of the catalytic activity of 40 different formulations of transition metal oxides-based supported catalysts in the course of the total oxidation of benzene as a model molecule for dioxin. The catalysts consisted in 10 different transition metal oxides (CrO_x , MnO_x , VO_x , SnO_x , WO_x , NbO_x , TaO_x , MoO_x , ZrO_x and BiO_x) supported on 4 different supports (2 kinds of TiO_2 , Al_2O_3 and SiO_2). A theoretical coverage of 0.75 monolayer of active phase was chosen to minimize the formation of crystallites. XPS and XRD characterizations demonstrated the better spreading of the active phases, as monolayer, on titania than on Al_2O_3 and SiO_2 . The latter induces a poor dispersion of almost all the active phases as crystallites. The variation of spreading of the active phases on the different supports is governed by the difference in surface free energy and is fully explained by the “solid-solid wetting” concept. For almost all active phases, the conversion of benzene progressively improves when the support is changed from SiO_2 to Al_2O_3 and, finally, titanias. The performances of the active phases exhibiting this behavior, are clearly dictated by their presence as well-dispersed monolayers at the surface of the support. The screening revealed CrO_x , VO_x and MnO_x

as the most active phases. The first two exhibit their best activity when spread as monolayer at the surface of TiO_2 based supports (classical behavior). At the opposite, MnO_x works best when present in the form of Mn_3O_4 crystallites poorly dispersed on the SiO_2 support.

1.1. Introduction

Cogeneration and incineration are widely used methods for generating energy and eliminating municipal, medical and hazardous wastes. These techniques have a high efficiency to simultaneously generate heat and power by minimizing the CO_2 emissions in the atmosphere [4]. However, biomass and/or wastes combustion involves the formation of many harmful organic products of incomplete combustion. Among all these compounds, PCDDs and PCDFs, also named dioxins, are the most polluting. Indeed, they are very toxic, carcinogenic and environmentally persistent organic pollutants [11-13].

Therefore, the current emission limit in Europe has been set at is $0.1 \text{ ng I-TEQ Nm}^{-3}$. A large number of methods have been applied in order to solve the problem of atmospheric release of chlorinated VOCs (typically adsorption, thermal incineration, hydrodechlorination, biological process, steam reforming, photocatalytic degradation, etc) [17,25,33-36]. However, there is still a need for research on techniques, economically more favorable and which would truly destroy the pollutants rather than merely remove them for recycling elsewhere in nature or to transfer them to a solid which would be destroyed in an additional step. The catalytic destruction of chlorinated VOCs to CO_x , H_2O and HCl/Cl_2 appears very promising in this context. It stands for a wide range of pollutants concentration, exhibits an excellent selectivity toward the formation of harmless products and it operates at relatively low destruction temperature [33,35,37,38].

Noble metal (Pt, Pd) [39-42], perovskites [43-46] and transition metals oxides (Cu, Co, V, Mn, Fe, Cr oxides) [13,47-56] based catalysts are the

major class of catalysts investigated for the catalytic combustion of VOCs (chlorinated or not). However, Van den Brink *et al.* and Crisafulli *et al.* reported the formation of polychlorinated benzene in the course of the total oxidation of chlorinated VOCs on noble metal-based catalysts [58-63]. These polychlorinated compounds are more toxic and recalcitrant than the starting molecules. This is a major drawback for the application of noble metal catalysts in the course of the total oxidation of chlorinated VOCs. Moreover, these authors demonstrated that noble metal catalysts deactivate when chlorine is present in the molecule that must be oxidized. The perovskites-based catalysts have the drawback to convert efficiently PCDD/Fs only above 500 °C, inducing a possible production of dioxins by the homogeneous route and an increase of the cost of the cleaning treatment of the exhaust gases [43,44]. Moreover, in some cases, the presence of chlorine in the VOC induces the deactivation of the perovskites. The transition metal oxides-based catalysts convert VOCs at lower temperatures than perovskites and do not produce polychlorinated compounds. Although certain formulations deactivate in the presence of chlorine, transition metal oxides-based catalysts are, in general, active at temperatures as low as 200 °C, preventing the *de novo* mechanism. Therefore, transition metal oxides seem to be the best solution for the total combustion of PCDD/Fs.

VO_x supported on TiO₂ catalysts, possibly “upgraded” to VO_x-WO_x/TiO₂ or VO_x-MoO_x/TiO₂ are the most largely used catalytic system for the combustion of chlorinated VOCs [13,28,34,49-52,56,66-72]. These catalysts were developed for the NO_x SCR with NH₃ and have proven to be active for the combustion of VOCs. However, the systematic investigation of other transition metal oxides supported on different supports was never reported. Therefore, we investigated the catalytic activity of 10 transition metal oxides (CrO_x, MnO_x, VO_x, SnO_x, WO_x, NbO_x, TaO_x, MoO_x, ZrO_x and BiO_x) supported on 4 different supports (TiO₂, TiO₂-sulfated, Al₂O₃, SiO₂). These supports were chosen with specific surface area in the same order to improve the comparison between supports. Moreover, the four supports are

characterized by the absence of microporosity and mesoporosity. This characteristic was searched in order to obtain the best spreading of the active phases as monolayer and to avoid the filling of the pores of the supports. This filling of the pores could lead to a decrease of the amount of active sites available on the surface of the catalyst and therefore to a decrease of the catalyst performances. Furthermore, the four different supports were also chosen i) to investigate the effect of the support on the stabilization of a well dispersed monolayer of active phase and ii) to investigate the support effect, namely the influence of the presence of support-active phase links. The loading in transition metal oxides was fixed to 0.75 theoretical monolayer in order to obtain a significant dispersion of the active phases by minimizing the formation of crystallites of transition metal oxides. Throughout this manuscript, we refer to the monolayer phase and give the species composing it the symbol XO_x as a convenient shorthand description. It is probable that the active oxide never forms a complete and coherent layer, and indeed it may not be necessary or even desirable that it should. Therefore, we defined a monolayer as a 2-dimensional organization of XO_x units well-dispersed at the surface of the support, this, notwithstanding the kind of chemical interactions involved between the active phase and the support. We decided to normalize the active phase loading of the catalysts in terms of monolayer and not in terms of weight percentage. This decision is supported by our interest to work with highly dispersed active phases presenting a number of available active sites as high as possible but without producing crystalline phases. However, working with four supports having quite similar specific surface area and based on the fact that the cross-sectional areas of the active phases are comparable, the amount of active phase present on the catalyst is in the same range, in terms of weight percentage, on all catalysts presented in this chapter.

The catalytic investigation was performed in two steps: i) all catalysts were tested in the total oxidation of benzene (taken as model molecule for dioxins) with the aim of investigating the intrinsic oxidative power of the

transition metal oxides by avoiding the possible deactivation effect of the presence of a chlorine atom in the molecule to be oxidized and ii) the best catalysts selected in the first step were tested in the total oxidation of chlorobenzene in order to probe their ability to convert chlorinated VOCs without deactivation.

This chapter therefore reports, for the first time, a systematic screening aiming to investigate the activity of 10 transition metal oxides supported on 4 different supports in the course of the total oxidation of benzene taken as model molecule for dioxins. The second part of the screening dedicated to the influence of the chlorinated VOCs on the catalyst performances is reported in Chapter 2 and [104]. Chapter 3 reports the investigation of the possible improvement of the resistant formulations, pointed out by the first two investigation steps, by adding secondary transition metal oxides [105].

1.2. Experimental and methods

1.2.1. Preparation of the catalysts

Catalysts are supported on 4 different commercial supports: a TiO_2 containing 70% anatase and 30% rutile (Degussa P25 - $48 \text{ m}^2/\text{g}$ - denoted hereafter TiO_2 or T), a pure anatase TiO_2 containing 1.4% sulfate (Millennium PC100 - $91 \text{ m}^2/\text{g}$ - denoted hereafter $\text{TiO}_2\text{-s}$ or Ts), a Al_2O_3 (Alfa Aesar - $66 \text{ m}^2/\text{g}$ - denoted hereafter A) and a SiO_2 (Alfa Aesar - $87 \text{ m}^2/\text{g}$ - denoted hereafter S). The four supports are characterized by specific surface area of the same order and by the absence of mesoporosity and microporosity. The Degussa P25 TiO_2 is synthesized through the oxidation of TiCl_4 which leads to the presence of chlorine traces on this support and to a certain percentage of rutile phases [106]. At the opposite, the Millennium PC100 TiO_2 is prepared via hydrolyzation and the following calcination of a titanyl sulfate which leads to the presence of a residual sulfate in the support and to a pure anatase phases [107].

Chapter 1: Screening

The active phases are CrO_x , MnO_x , VO_x , SnO_x , WO_x , NbO_x , TaO_x , MoO_x , ZrO_x or BiO_x . The supports were impregnated with solutions of precursors of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Vel, 99%); $\text{Mn}(\text{CH}_3\text{-COO})_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, >99%); $(\text{NH}_4)\text{VO}_3$ (Vel, 99.9%); $\text{Sn}(\text{COO})_2$ (Strem Chemicals, 99.9%); $(\text{NH}_4)_2\text{WO}_4$ (Aldrich, 99.99%); $\text{NH}_4[\text{NbH}_2(\text{C}_2\text{O}_4)_3]$ (Aldrich, 99.99%); $\text{Ta}[\text{OCH}(\text{CH}_3)_2]_5$ (Alfa Aesar, 99.9%); $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Aldrich, >99%); $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) or $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Vel, >99%) in distilled water and complexed with 2 moles of oxalic acid (Aldrich, 99.99%) for one mole of transition metal.

Table 1-1: Abbreviations of the entire set of catalysts

	CrO_x	MnO_x	VO_x	SnO_x	WO_x
TiO_2	TC	TMn	TV	TS	TW
$\text{TiO}_2\text{-s}$	TsC	TsMn	TsV	TsS	TsW
Al_2O_3	AC	AMn	AV	AS	AW
SiO_2	SC	SMn	SV	SS	SW

	NbO_x	TaO_x	MoO_x	ZrO_x	BiO_x
TiO_2	TN	TT	TM	TZ	TB
$\text{TiO}_2\text{-s}$	TsN	TsT	TsM	TsZ	TsB
Al_2O_3	AN	AT	AM	AZ	AB
SiO_2	SN	ST	SM	SZ	SB

All impregnation solutions had a pH below 3. A wet impregnation method was used and the amounts of precursor were calculated in order to obtain 0.75 theoretical monolayer of transition metal oxide on the surface of each support. The theoretical monolayer coverage was calculated based on the cross-section area of a unit composed of one transition metal atom and its oxygen coordination sphere. The values are $9 \text{ \AA}^2$ for SnO_x , $10 \text{ \AA}^2$ for CrO_x , $12 \text{ \AA}^2$ for VO_x , $15 \text{ \AA}^2$ for MnO_x , WO_x , NbO_x , TaO_x , ZrO_x and BiO_x and $17 \text{ \AA}^2$ for MoO_x . The suspensions of supports in the impregnation solutions (1 g of support per 100 ml of solution) were stirred for 2 h at room temperature before the solvent was evaporated under reduced pressure in a rotavapor at

45 °C. The obtained solids were dried overnight in an oven at 110 °C. Finally, the catalysts were calcined, in a muffle furnace, for 24 hours at 400 °C under air, at atmospheric pressure. The supports, that are used for comparison, followed all the synthesis steps but in the total absence of precursor. In order to validate the reproducibility of the synthesis protocol, three syntheses of the TV were performed. The three catalysts demonstrated the same physico-chemical properties and the same catalytic activity. Table 1-1 presents the list of catalysts and their annotations used throughout this chapter.

1.2.2. Catalytic tests

All the catalytic tests presented in this chapter were performed in a conventional fixed-bed reactor working at atmospheric pressure. The reactor was made of a Pyrex U-tube of 8 mm internal diameter into which the catalyst was packed. The catalytic bed was composed of 100 mg of catalyst powder selected within the granulometric fraction 200-315 μm and diluted in 400 mg of inactive glass spheres with diameters in the range 315-500 μm . This granulometric fraction of the catalyst was chosen in order to be out of the internal diffusion limits. All catalytic tests were performed with a gaseous stream containing 100 ppm of benzene and 20% of O_2 . He was the diluting gas to obtain a total stream of 100 ml min^{-1} . All gases were from Indugas and had a purity of 99.995%. The amount and granulometric fraction of catalyst and the total gaseous stream were chosen in order i) to be in true kinetic regime, namely be out of the internal and external diffusion limits and ii) to reach a VVH of 37000 h^{-1} , which corresponds to the conditions usually met in the exhaust gases from cogeneration and incineration industrial units. This VVH is calculated based on the gaseous stream and the amount of catalyst and corresponds to 7.44 $10^{-8} \text{ mole g}^{-1} \text{ s}^{-1}$ (mole of benzene per gram of catalyst and per second). The reaction was run from 100 °C to 400 °C by steps of 50 °C. At each temperature investigated, the catalyst was stabilized for 150 min in order to reach the steady state.

Chapter 1: Screening

Analysis of reactants and products was continuously performed by on-line gas chromatography (GC). The GC allowed to quantify benzene, O₂, CO, CO₂ and to detect other hydrocarbons (more details about the catalytic installation and the GC in the annex). To calculate the conversion, only the concentrations of reactants and products measured and averaged in the period of time from 100 to 150 minutes were taken into account. The conversion is calculated following equation 1-1.

Equation 1-1:

$$X\% = \frac{\text{initial benzene concentration} - \text{benzene concentration}}{\text{initial benzene concentration}} \times 100$$

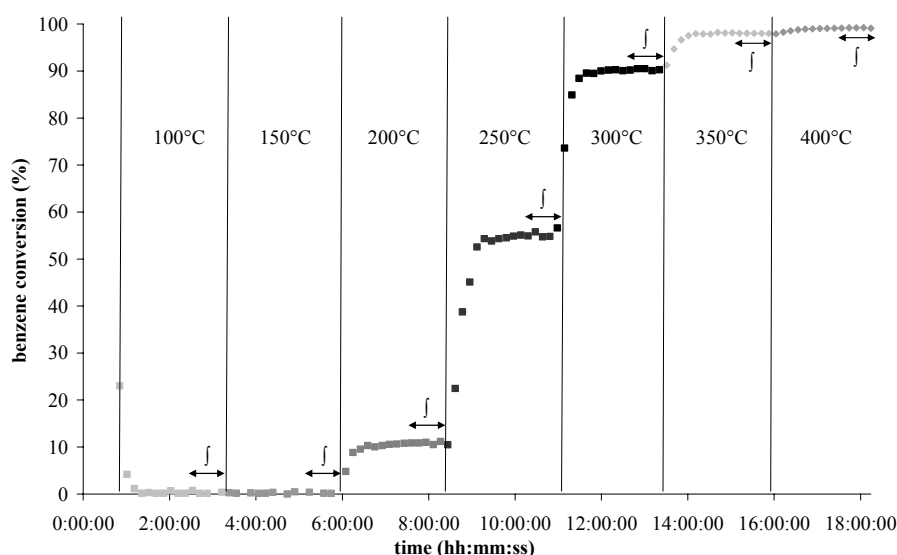


Fig. 1-1: Evolution of the benzene conversion during a catalytic test from 100 °C to 400 °C

Fig 1-1 presents the evolution of the benzene conversion as a function of the time under catalytic stream and as a function of temperature. The arrows and the $\int$ symbols represent the windows on which the catalytic conversion is

averaged to generate the light-off curve. The values of T_{50} which represent the temperature needed to convert 50% of the benzene concentration are estimated based on the light-off curves drawn as explained above. The realization of three catalytic tests on three amounts of catalyst from the same catalytic batch demonstrated the reproducibility of the catalytic test and allow us to measure the accuracy which is within a range of about 1% (in relative) for the conversion of benzene. Moreover, a catalytic test in the absence of catalyst demonstrated the inert character of the reactor in this reaction.

1.2.3. Characterization

The specific surface area, porous volume and pore size distribution analyses were performed on a Micromeritics ASAP 2000 instrument using the adsorption isotherm of nitrogen at $-196\text{ }^{\circ}\text{C}$ in the $10^{-6} < p/p_0 < 0.99$ partial pressure range. A mass of 100 mg of sample previously degassed at $180\text{ }^{\circ}\text{C}$ for 2 h under a flow of pure helium (Indugas, 99.995%) was used for the measurement. Surface area, porous volume and pore size distribution values were computed, using BET and BJH equations, from the amount of N_2 physisorbed at different relative pressures. The error of the surface area measurement is estimated at 5%.

XRD patterns of the fresh catalysts were recorded on a Siemens D5000 diffractometer using the K_{α} radiation of Cu ($\lambda=1.5418\text{ \AA}$). The 2θ range was scanned between 15° and 90° at a rate of $0.02^{\circ}\text{ s}^{-1}$. The identification of the phases was achieved by using the ICDD-JCPDS database.

XPS was performed on a SSI X-probe (SSX-100/206) spectrometer from Surface Science Instruments working with a monochromatic Al K_{α} (1486.6 eV) radiation (10 kV, 22 mA). The analysis chamber was operated under ultrahigh vacuum with a pressure close to $5 \times 10^{-9}\text{ Torr}$ ($6.67 \times 10^{-7}\text{ Pa}$). Charge compensation was achieved by using an electron flood gun adjusted at 6 eV and placing a nickel grid 3.0 mm above the sample. Pass energy for

the analyzer was 150 eV and the spot size was 1000 μm in diameter, corresponding to a full width at half maximum (FWHM) of 1.6 eV for the Au 4f_{7/2} band of a gold standard. For these measurements, the binding energy (BE) values were referred to the C-(C, H) contribution of the C 1s photopeak at 284.8 eV. The surface atomic concentrations were calculated by correcting the intensities with theoretical sensitivity factors based on Scofield cross sections [108]. Peak decomposition was performed using curves with a 85% Gaussian type and a 15% Lorentzian type, and a Shirley non-linear sigmoid-type baseline. The following peak intensities were used for the quantitative analysis: O 1s, C 1s, Al 2s, Si 2s, Cr 2p, V 2p, Mn 2p, Ti 2p, Cl 2p, Nb 3d, Mo 3d, Sn 3d, Zr 3p, W 4d, Ta 4d and Bi 4f. Based on the XPS analysis, we estimated the surface ratio active phase / support. This XPS ratio is estimated by Equation 1-2:

Equation 1-2:

$$\text{XPS ratio} = \frac{\text{atomic concentration of the metal from the active phase (\%)}}{\text{atomic concentration of the metal of support (Ti, Al, Si) (\%)}}$$

Raman was performed with a Labram spectrometer (Dilor) interfaced with an Olympus optical microscope. The excitation radiation was a He-Ne laser (632.8 nm) operated at a power of 10 mW. The 10 $\times$ objective of the microscope was used, so that a spot of about 20 μm at the surface of the sample was measured at once. Spectra were obtained by averaging 3 scans of the Raman shift range between 1200 and 200 cm^{-1} recorded in 10 s with a spectral resolution of 7 cm^{-1} . The identity of the spectra obtained at different positions of each sample was systematically verified.

1.3. Results and discussion

1.3.1. Catalytic conversion of benzene

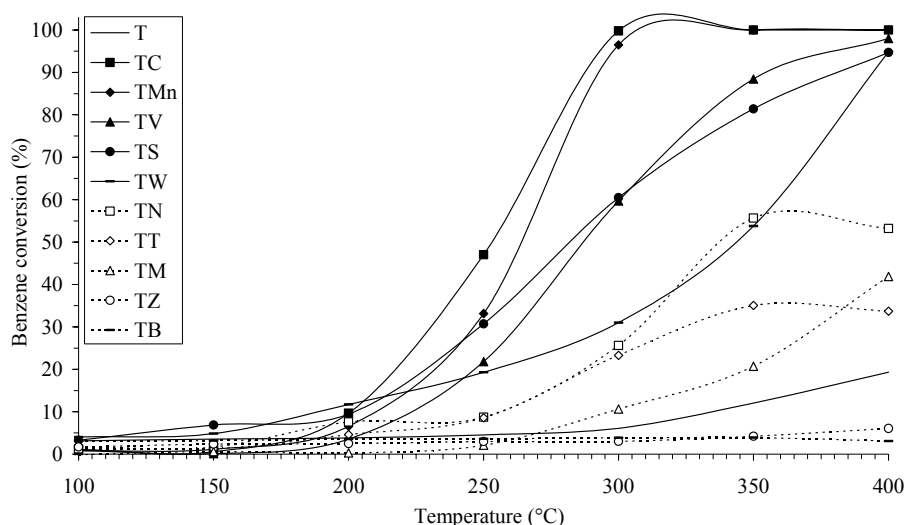


Fig. 1-2: Benzene light-off curves of the catalysts supported on TiO_2

Fig. 1-2 presents the light-off curves of the 10 catalysts supported on TiO_2 in the course of the total combustion of benzene. The TiO_2 support (T) is almost inactive up to 300 °C. At 400 °C, it converts almost 20% of the 100 ppm of benzene. The BiO_x (TB) and ZrO_x (TZ) based catalysts are completely inactive in the whole range of temperature investigated. TaO_x (TT), MoO_x (TM) and NbO_x (TN) based catalysts start to convert benzene at 300 °C to reach a conversion of, respectively, 34%, 42% and 53% at the final 400 °C temperature. WO_x (TW), SnO_x (TS), VO_x (TV), MnO_x (TMn) and CrO_x (TC) initiate the conversion of benzene at 250 °C to reach more than 95% conversion at 400 °C. TW catalyst only converts 31% at 300 °C while TS and TV convert about 60%, and TMn and TC convert almost 100% of the benzene concentration. The activity of the entire set of catalysts is

classified, based on the T_{50} (temperature needed to convert 50% of the benzene concentration), as TC (250 °C) < TMn (264 °C) < TS (282 °C) < TV (286 °C) < TN (342 °C) < TW (347 °C). TB, TZ, TT and TM convert less than 50% of the benzene concentration even at 400 °C. In the following, we focus our interest on the active phases able to convert more than 50% of the 100 ppm of benzene at 400 °C. The products observed at the outlet of the catalytic reactor are CO₂, CO and unburnt benzene. Beside CO, no other products of incomplete combustion were detected.

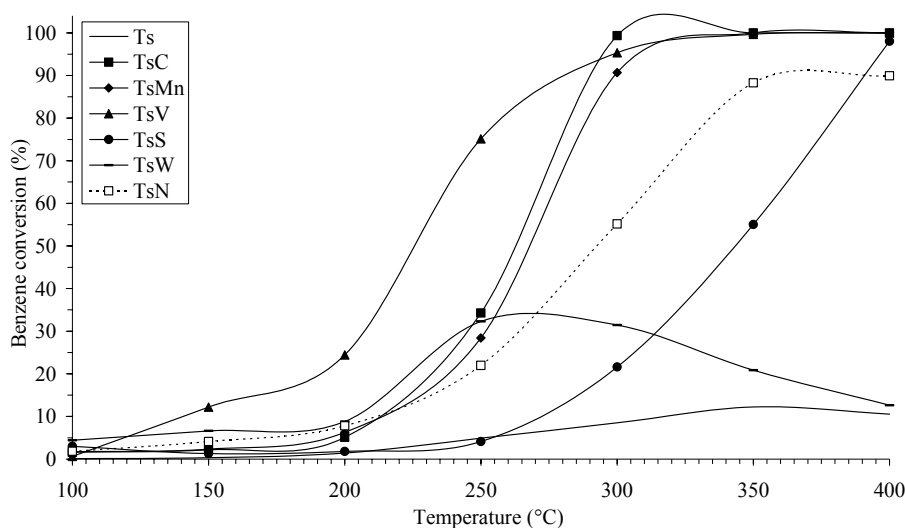


Fig. 1-3: Benzene light-off curves of the catalysts supported on sulfated TiO₂

Fig. 1-3 shows the light-off curves for the selected active phases supported on the sulfate-containing TiO₂ (Ts). The support Ts is inactive up to 300 °C and converts around 10% of benzene at 400 °C. The SnO_x (TsS) starts to convert benzene at 300 °C and reaches a steady state conversion of 98% at 400 °C. NbO_x, MnO_x and CrO_x based catalysts (TsN, TsMn, TsC) start to convert roughly 25% of benzene at 250 °C. Their activities increase with temperature to reach more than 90% conversion at 400 °C. However, at 300 °C, TsN catalyst converts only 55% while TsMn and TsC convert 91% and

99%, respectively. WO_x (TsW) and VO_x (TsV) supported catalysts initiate the benzene conversion at a temperature as low as 150 °C. However, their behavior with the increase of temperature is quite different. On the one hand, the activity of the TsW catalyst improves up to 35% with the increase of the temperature up to 250 °C, then a further increase of the temperature above 250 °C deactivates the catalyst, which converts only 13% at 400 °C. On the other hand, the activity of the TsV catalyst progresses continuously with the increase of temperature to reach 95% at 300 °C. Above 300 °C, the activity remains stable at around 100% of benzene conversion. Based on the T_{50} values, the classification of the series of catalysts is thus: TsV (230 °C) < TsC (265 °C) < TsMn (270 °C) < TsN (297 °C) < TsS (346 °C). The TsW catalyst does not appear in this classification because it never reached 50% conversion.

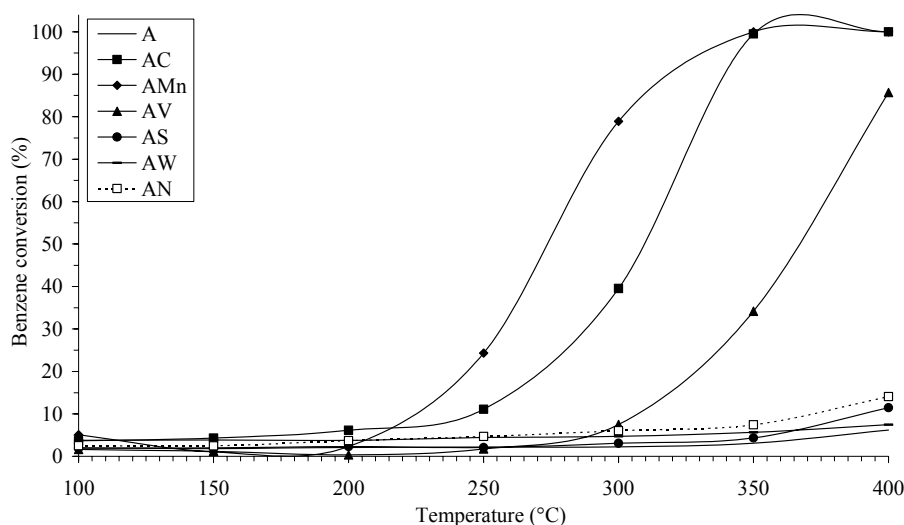


Fig. 1-4: Benzene light-off curves of the catalysts supported on Al_2O_3

Fig. 1-4 presents the light-off curves for the catalysts supported on Al_2O_3 (A). The fresh support A is more or less inactive in the whole temperature window investigated. It converts less than 6% of benzene at the highest

temperature. Similarly to the fresh support, WO_x , SnO_x and NbO_x based catalysts (AW, AS, AN) are almost inactive in the entire temperature range: they convert, respectively, 7.5, 11.5 and 14% of the benzene at 400 °C. At the opposite, the benzene conversion obtained with the VO_x supported on Al_2O_3 (AV) starts at 350 °C with 34% of conversion and reaches 86% at 400 °C. CrO_x and MnO_x based catalysts (AC, AMn) begin to convert, respectively, 11% and 24% of benzene at 250 °C. Moreover, they convert 40% and 79% at 300 °C and both reach total conversion at 350 °C. Based on the T_{50} values, the catalysts are ordered as follows: AMn (275 °C) < AC (310 °C) < AV (367 °C). The AS, AN and AW catalysts are not able to convert more than 14%, even at 400 °C.

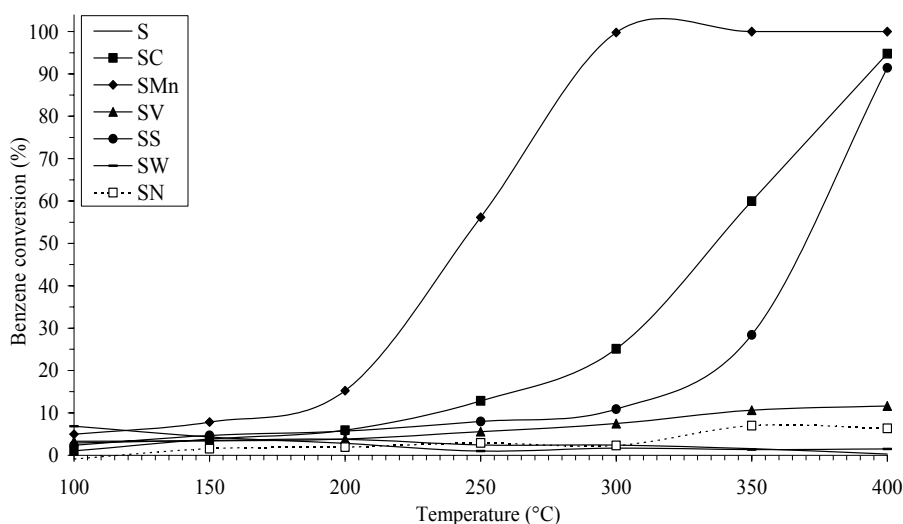


Fig. 1-5: Benzene light-off curves of the catalysts supported on SiO_2

Fig. 1-5 shows the light-off curves of the catalysts supported on SiO_2 (S). SiO_2 is completely inactive in the entire range of temperature tested. As the fresh support, WO_x , NbO_x and VO_x catalysts supported on SiO_2 (SW, SN and SV) are more or less inactive up to 400 °C: they convert between 2 and 12% of benzene at the highest temperature. At the opposite, the SnO_x

supported on SiO₂ catalyst (SS) converts 11%, 28% and 91% of benzene at 300, 350 and 400 °C, respectively. The SC catalyst (CrO_x on SiO₂) starts to convert benzene at 250 °C and converts, respectively, 25%, 60% and 95% at 300, 350 and 400 °C. The most active phase is MnO_x, which begins to convert benzene at 200 °C and converts 100% at a temperature as low as 300 °C. The T₅₀ classification of the SiO₂ supported catalysts is: SMn (242 °C) < SC (336 °C) < SS (370 °C). The SN, SV and SW catalysts are not able to convert more than 12%, even at 400 °C.

To extract trends from this huge amount of catalytic data, we only focused on the catalysts that induced a benzene conversion of at least 50%. Considering this, the 16 best combinations of active phases and supports based on the T₅₀ were: TsV (230 °C) < SMn (242 °C) < TC (250 °C) < TMn (264 °C) < TsC (265 °C) < TsMn (270 °C) < AMn (275 °C) < TS (282 °C) < TV (286 °C) < TsN (297 °C) < AC (310 °C) < SC (336 °C) < TN (342 °C) < TsS (346 °C) < TW (347 °C) < AV (367 °C) < SS (370 °C). Among these 16 pointed best catalysts, 6 involve the TiO₂ support, 5 involve the sulfated TiO₂, 3 involve the Al₂O₃ support, and 2 involve the SiO₂ support. Moreover, among the 10 best formulations, 8 correspond to active phases supported on titania (T or Ts). It is thus clear that the best supports for the synthesis of catalysts active in the total oxidation of benzene are those based on titania. From the point of view of the best active phase, among the 16 pointed best formulations, 4 involve MnO_x, 4 involve CrO_x, 3 involve VO_x, 2 involve SnO_x, 2 involve NbO_x and 1 involves WO_x. Moreover, among the 10 very best catalysts, 8 are based on MnO_x, VO_x or CrO_x as active phase. These last three oxides thus clearly appear as the best active phases for the total oxidation of benzene.

The further investigation of the catalytic results of the three best active phases (MnO_x, CrO_x and VO_x) proves that the importance of the active phase support contacts strongly depends on the considered active phase. The activity of the VO_x phase is quite dependent on the nature of the support. The values of T₅₀ for the VO_x based catalysts indeed vary in a range of more

than 170 °C, *i.e.* from 230 °C (TsV) to 286 °C (TV), 367 °C (AV) and more than 400 °C in the case of the silica support (SV). To a smaller extent, the activity of the CrO_x based catalysts also depends on the nature of the support. The T₅₀ values indeed vary in a range of about 90 °C: from 250 °C (TC) to 265 °C (TsC), 310 °C (AC) and 336 °C for the SC catalyst. At the opposite, the activity of the MnO_x based catalysts is almost independent from the nature of the support. The performances of these catalysts indeed only vary within a range of T₅₀ as narrow as 30 °C: from 242 °C (SMn) to 264 °C (TMn), 270 °C (TsMn) and 275 °C (AMn). Summarizing, VO_x and CrO_x based catalysts present what we term hereafter a “conventional” behavior: the support has a deep impact on the activity of these active phases. On one extreme, titania supports induce the best performances for the active phases, but on the other extreme, SiO₂ support induces their lowest activity. MnO_x based catalysts, at the opposite, exhibit what we term a “non conventional” behavior: the support has a weak impact on the catalytic performances and MnO_x works much better in the total combustion of benzene when impregnated on SiO₂ than on titania or alumina.

1.3.2. XRD results

Table 1-2 presents the nature of the crystalline phases that were detected by the XRD analysis on several formulations. The entire set of catalysts was synthesized in order to have a 0.75 theoretical monolayer. Therefore, the detection of bulk phase by XRD reveals a poor homogeneity of the coverage by the active phase, namely its poor dispersion, and suggests that the active phase is not present as a monolayer at the surface of the support. At the opposite, the absence of XRD peaks of active phase suggests the establishment of a well-dispersed oxide, and likely the formation of a homogeneous coverage of the active phase as a monolayer.

Table 1-2: Identification of the crystalline phases detected by XRD

	CrO_x	MnO_x	VO_x	SnO_x	WO_x
TiO₂	-	-	-	SnO ₂	-
TiO₂-s	-	-	-	SnO ₂	WO ₃
Al₂O₃	-	-	-	SnO ₂	WO ₃
SiO₂	Cr ₂ O ₃	Mn ₃ O ₄	V ₂ O ₅	SnO ₂	WO ₃

	NbO_x	TaO_x	MoO_x	ZrO_x	BiO_x
TiO₂	-	-	-	-	Bi ₂ O ₃
TiO₂-s	-	-	-	-	Bi ₂ O ₃
Al₂O₃	-	-	MoO ₃	-	Bi ₂ O ₃
SiO₂	-	-	MoO ₃	ZrO ₂	Bi ₂ O ₃

On the classical TiO₂ support, the active phase of SnO_x and BiO_x formed SnO₂ and Bi₂O₃ crystallites. In the case of the sulfated TiO₂, the SnO_x, WO_x and BiO_x active phases are present as bulk SnO₂, WO₃ and Bi₂O₃. The formulations based on MoO_x, SnO_x, WO_x and BiO_x and supported on Al₂O₃ exhibit the presence of crystallites of MoO₃, SnO₂, WO₃ and Bi₂O₃. On the SiO₂ support, we detected bulk phases of V₂O₅, Cr₂O₃, Mn₃O₄, ZrO₂, MoO₃, SnO₂, WO₃ and Bi₂O₃, *i.e.* for all active phases excepted NbO_x and TaO_x. These results were confirmed by the Raman measurements which pointed out the presence of new vibration bands due to polymeric species in the same samples as the samples that exhibit new X-ray diffraction peaks.

The presence of bulk active phases depends on the nature of both the active phase and the support. On the one hand, certain active phases induce the formation of crystallites independently of the nature of the support, *e.g.* SnO_x, WO_x and BiO_x. These active phases are present in a bulk state on all kinds of support (both titanias, Al₂O₃ and SiO₂). On the other hand, certain supports favor the production of crystallites by the transition metal oxides whatever the nature of the concerned active elements. While on the titania supports, we observe only 2 or 3 active phases in bulk state, Al₂O₃ and SiO₂ induce, respectively, the crystallization of most of the 10 investigated active

phases (4 for Al_2O_3 and 8 for SiO_2). At the opposite of titanias, Al_2O_3 and, even more, SiO_2 supports, prevent the homogeneous spreading of the active phase in the form of a well-dispersed monolayer but promote the formation of poorly dispersed crystallites of active phase. This observation is strengthened by the observations of Bond *et al.* [109] who compared VO_x monolayer supported on TiO_2 , Al_2O_3 and SiO_2 . They pointed out the preferential spreading of VO_x on TiO_2 rather on Al_2O_3 . Moreover, they demonstrated the formation of V_2O_5 crystallites on SiO_2 , even below the theoretical monolayer coverage.

As a conclusion, the nature of the support deeply influences the tendency of the active phases to spread as monolayer coverage or to generate crystallites and bulk phases.

1.3.3. XPS results

Different authors developed quantitative models for prediction and interpretation of surface ratios of a binary system (phase A on a support S). These models were specifically developed for the interpretation of the dispersion of a phase A at the surface of a phase S in the case of heterogeneous catalysts. These models were developed by Moulijn *et al.* [110], Fung *et al.* [111], Defosse *et al.* [112], Kuipers *et al.* [113] and Sheng *et al.* [114]. The difference between these models resides mainly in the assumption of the kind of arrangement of phase A on the surface of the support S (layers, shell structure, small blocks, etc...). Nevertheless, in the case of a modification of the experimental phase A / support S ratio, at constant overall concentration, all these models lead to the same conclusions. An increase of the phase A / support S ratio is synonym of an increase of the spreading of phase A on the surface of the support S, which could lead to the formation of a uniformly dispersed monolayer. At the opposite, a decrease of the phase A / support S ratio indicates a decrease of

the homogeneity of the coverage, which could lead to the formation of separate blocks (crystallites) of A almost independent from the support S.

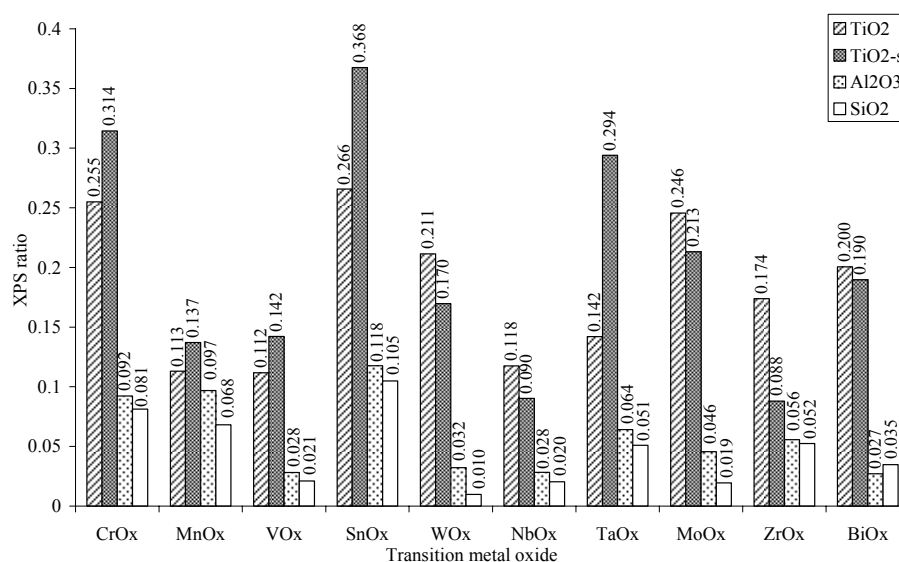


Fig. 1-6: XPS ratio active phase / support for the entire set of catalysts

For a selected active phase, the syntheses were done in order to impregnate the same loading (0.75 theoretical monolayer) on the different supports. Therefore, in a series of 4 catalysts based on the same active phase but supported on 4 different supports, a modification of the active phase / support ratio indicates a difference of spreading of the active phase. Fig. 1-6 presents the XPS active phase / support ratio for the 10 active phases supported on the 4 different supports. For the CrO_x active phase: the catalysts based on titania supports show a value in the range 0.25 - 0.31, while for those supported on Al₂O₃, the ratio is three times lower with a value of about 0.09. The ratio is even lower in the case of the SiO₂ support, as it decreases down to 0.081. It is thus clear that the CrO_x phase spreads better on titania than on Al₂O₃ and even better than on SiO₂. The better spreading of the active phase on the titania supports than on Al₂O₃ and on

SiO₂ is observed for the entire set of active phases. However, the difference in spreading on the titanias compared to the other supports depends on the active phases. On the one hand, CrO_x, VO_x, SnO_x, WO_x, NbO_x, TaO_x, MoO_x, ZrO_x and BiO_x show values of dispersion between 3 and 15 times higher on titania supports than on Al₂O₃ and SiO₂. On the other hand, MnO_x shows a value of dispersion on Al₂O₃ that is quite similar to those observed on titania supports. Moreover, the dispersion is less than 2 times better on titania supports than on SiO₂. It is thus clear that the behavior of the MnO_x phase is completely different to that of the other active phases.

1.3.4. Discussion of the active phase spreading

The XPS results are in excellent agreement with the XRD observations. Both techniques point the progressive preferential spreading of the active phase on the support within the series: SiO₂ < Al₂O₃ < titania supports. Titania clearly induces a spreading of the entire set of active phase as a well-dispersed monolayer at its surface. At the opposite, SiO₂ favors the agglomeration of the active phase as crystallites. Al₂O₃ has an intermediate behavior between titania and SiO₂, as it induces an intermediate spreading avoiding, in the majority of cases, the formation of crystallites. Comparison of XPS data before and after catalytic test demonstrated the absence of significant modification between the two sets of experiments. There is thus no clear trend for the active phases to spread or crystallize during the catalytic tests. This influence of the support on the spreading of the active phase is strongly governed by the “solid-solid wetting” concept developed by Haber *et al.* [115,116]. The spreading of one oxide over the surface of a second oxide can be considered to proceed principally through three possible ways: i) transport by surface diffusion in a concentration gradient, ii) gas-phase transport and redeposition on the support surface, and iii) solid-solid wetting with a gradient of the surface free energy as the driving force. Haber *et al.* [115,116] and Knözinger *et al.* [117] have proven that the migration of the active phase ions over the surface of the support cannot be due only to

the spreading under the influence of the concentration gradient or the gas-phase transport. The gas-phase transport is rather unlikely at a temperature as low as the calcination and reaction temperatures used here, namely 400 °C. The surface diffusion by itself could not induce the spreading because, in such a case, the migration would take place independently of the nature of the support [115]. The only other driving force, which may cause the spreading of the active phase over the surface of the support, is the difference in surface free energy. The spreading of the active phase over the surface of the support is thus the manifestation of a general phenomenon of wetting of one solid by another solid (solid-solid wetting), which is fully analogous to wetting of solids by liquids. The overall free energy change (ΔF) of the process is given by Equation 1-3, where γ_{Ag} and γ_{Sg} are the specific surface free energies of the oxides A and the support S, respectively in equilibrium with the gas phase. γ_{AS} is the specific free interaction energy between the oxide and the support, and ΔA_A , ΔA_S and ΔA_{AS} are the absolute values of surface area changes of the oxide A, the support S and the interface between these two, respectively.

$$\text{Equation 1-3: } \Delta F = \gamma_{Ag} \Delta A_A - \gamma_{Sg} \Delta A_S + \gamma_{AS} \Delta A_{AS}$$

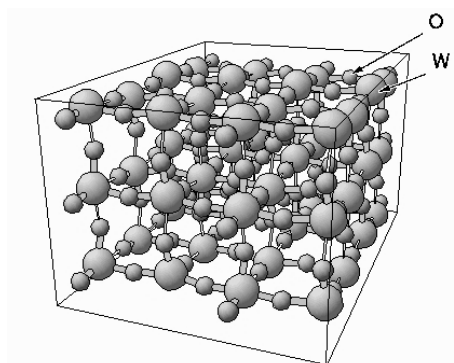
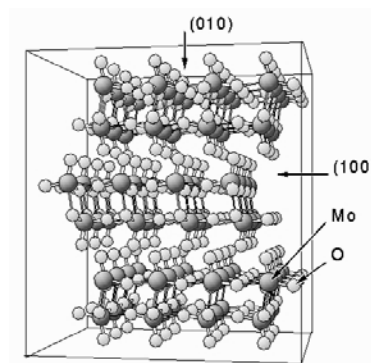
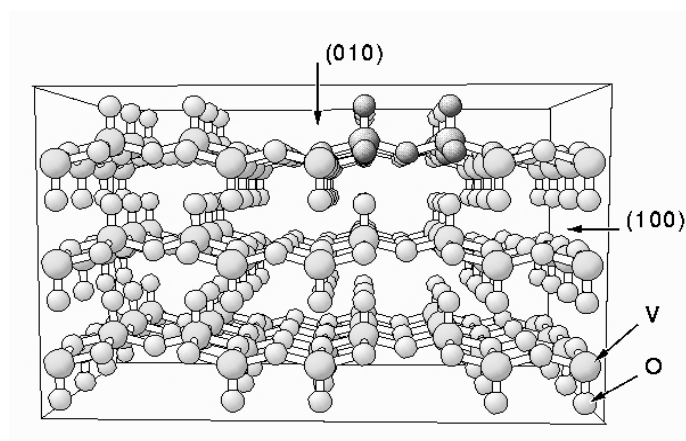
For the spreading to occur, the overall free energy change must be negative. Therefore, such spreading will take place if the surface free energy of the support S in equilibrium with the gaseous phase is higher than the sum of the surface free energy of the phase A in equilibrium with the gas and the free energy of adhesion of the phase A on the support S as demonstrated in Equation 1-4.

$$\text{Equation 1-4: } \gamma_{Sg} \Delta A_S > \gamma_{Ag} \Delta A_A + \gamma_{AS} \Delta A_{AS}$$

Knözinger *et al.* showed that the spreading of MoO_3 , WO_3 and V_2O_5 occurs to a large extent on TiO_2 and to a smaller extent on Al_2O_3 while it does not take place on SiO_2 . These results are in very good agreement with our XPS and XRD results, which revealed the same classification of the three

supports. Haber *et al.* proved that the extent of this phenomenon of spreading of the active phase by solid-solid wetting depends on the crystal planes of the given solid. In certain cases, the wetting could take place only on certain crystal planes of the support and not on others. For example, Haber *et al.* proved that the wetting of V_2O_5 takes place on the surface of anatase- TiO_2 but not on the surface of rutile- TiO_2 [116]. This difference of behavior between anatase and rutile TiO_2 could be a key factor to understand the difference of XPS values of dispersion on TiO_2 (70% anatase - 30% rutile) and on TiO_2 -sulfated (100% anatase).

Beside the difference in spreading of the same oxides on different supports, Knözinger *et al.* explained the difference in spreading of different oxides on the same support. These authors pointed out the increasing spreading of the oxides on TiO_2 within the series: $WO_3 < MoO_3 < V_2O_5$ [117]. This classification could be predicted by the structural characteristics of the three oxides based on the layer structure and, even more, on the cleavability of the oxides. Indeed, in WO_3 , each W atom is surrounded by six O atoms in distorted octahedral coordination as shown in Fig. 1-7. Moreover, each O atom is shared by two W atoms. Due to these structural characteristics, WO_3 has a very low cleavability. The structure of MoO_3 corresponds to an intermediate situation between octahedral and tetrahedral coordination as shown in Fig. 1-8. It can thus be described as being composed of MoO_4 tetrahedral connected via remote O atoms to form chains. This layer structure cleaves relatively easily in the (010) plane. This cleavage generates layers characterized by a thickness of two Mo atoms and their surrounding O atoms. V_2O_5 has a structure quite similar to the MoO_3 structure, the major difference being the distance between the most remote O atoms as shown in Fig. 1-9. Therefore, V_2O_5 can easily be cleaved parallel to the (010) plane generating layers of one V atom of thickness [117].

Fig. 1-7: Atomic structure of WO_3 Fig. 1-8: Atomic structure of MoO_3 Fig. 1-9: Atomic structure of bulk V_2O_5

The epitaxy could also play a role in the stabilization of a well-dispersed phase of oxide A at the surface of the support S. Indeed, the value of γ_{AS} depends on the intimacy between both phases. This value can thus be minimized if an epitaxy is possible between oxide A and support S [118]. However, the development of an epitaxy between phases requires highly controlled synthesis pathway which is not achieved in our synthesis protocol. Moreover, in the case of the TiO_2 support and the VO_x , MoO_x and WO_x

oxides, the literature exposed cases of epitaxy between rutile TiO_2 and not anatase TiO_2 . These epitaxial cases were observed only at low-range scale ordering between VO , VO_2 and V_2O_3 and rutile TiO_2 [118-122]. Moreover, there is no clear evidence that an epitaxial phenomenon is possible between an oxide phase with V^{4+} or V^{5+} and an anatase TiO_2 phase. Based on these information, it seems that the spreading is not governed by the epitaxial phenomenon in our case.

The better spreading of the entire set of active phases on titania supports than on Al_2O_3 and SiO_2 , demonstrated by the XPS and XRD results, is thus in very good agreement with previous observations of the literature. Moreover, the differential spreading of the active phases on the different supports is governed by the difference in surface free energy and could be completely understood based on the “solid-solid wetting” concept developed by Haber [115].

1.3.5. Discussion active phase spreading - activity

The XPS and XRD measurements pointed out the better spreading of all the active phases on the titania supports than on the others. These measurements also revealed the better spreading on Al_2O_3 than on SiO_2 . In parallel to this spreading of the active phases as well-dispersed monolayer in the case of the titania supports, the catalytic tests revealed that, for each transition metal oxide, the titania supported formulations are the most active. The activity within the series based on the same active phase and on the 4 different supports decreases when going through the series Titania $\rightarrow$ Al_2O_3 $\rightarrow$ SiO_2 . This rule is true for all the active phases, except for the MnO_x based catalysts, which show the best activity for the SiO_2 supported catalyst. We can thus assume that, on the one hand, almost all the active phases work better when stabilized as a homogeneously well-dispersed monolayer spread at the surface of the support. Therefore, among the best formulations, are those based on VO_x and CrO_x phases working as monolayer homogeneously

spread at the surface of the titanias. On the other hand, MnO_x phase works best as crystallites of Mn_3O_4 heterogeneously poorly dispersed on the supports, which happens preferentially on SiO_2 . To be fully validated, however, this hypothesis would necessitate further investigation, for example, checking the influence of the loading on the dispersion and on the performances: Chapter 2 and [104].

1.4. Conclusions

We have investigated the catalytic activity of 40 different formulations, based on 10 different transition metal oxides supported on 4 different supports, in the course of the total oxidation of benzene as a model molecule for dioxin. The entire set of catalysts was synthesized in order to have a theoretical coverage of 0.75 monolayer in each catalyst to minimize the formation of crystallites. This investigation pointed a “conventional behavior” consisting in a progressive improvement of the conversion of benzene by the active phases when we change from SiO_2 support to Al_2O_3 and finally titania supports.

The XPS, XRD and Raman characterizations demonstrated the better spreading as monolayer of the active phase at the surface of titanias than on Al_2O_3 and SiO_2 . The latter induces a heterogeneous dispersion of almost all the active phases as crystallites. The variation of spreading of the active phase on the different supports is governed by the difference in surface free energy and is fully explained by the “solid-solid wetting” concept.

The higher activity of the catalysts supported on titania based supports is clearly related to the spreading of the active phases on the surface of those supports. Indeed, the active phases usually show the best catalytic activity when present as well-dispersed monolayer on the surface of the support. Among the most active catalysts, this behavior particularly applies for the CrO_x and VO_x based ones. Sulfated TiO_2 favors this behavior even more than classical TiO_2 thanks to its higher anatase content. MnO_x constitutes an

Chapter 1: Screening

exception to the conventional behavior described. XPS, XRD and catalytic results reveal that MnO_x works best as crystallites of Mn_3O_4 . SiO_2 thus turns out to be the most adequate support for MnO_x as promoting the crystallization of impregnated oxides.

CHAPTER 2 : NATURE AND RESISTANCE OF THE CrO_x , VO_x AND MnO_x SUPPORTED CATALYSTS IN THE TOTAL OXIDATION OF BENZENE AND CHLOROBENZENE

Abstract

Chapter 1 reported that CrO_x , VO_x and MnO_x supported catalysts are very efficient in the combustion of VOCs. However, the nature of the active species (isolated-polymeric species homogeneously dispersed or crystallites heterogeneously dispersed) and their resistance in the course of the combustion of chlorinated VOCs has not been clearly depicted yet. Therefore, we investigated the activity of catalysts with different loading in CrO_x , VO_x or MnO_x supported on TiO_2 in the total oxidation of benzene and chlorobenzene. In the benzene case, the performances increase within the series $\text{VO}_x < \text{CrO}_x < \text{MnO}_x$. XRD, XPS and ToF-SIMS demonstrated that CrO_x and VO_x work best as homogeneously dispersed species while MnO_x must be in crystalline Mn_3O_4 form to be active, confirming the observations of Chapter 1.

In the case of chlorobenzene, the very good resistance of VO_x catalysts is correlated to the absence of chlorine on their surface. Conversely, a huge deactivation of MnO_x catalysts was found while CrO_x catalysts exhibited an

intermediate behavior. The deactivation extent is related to the number of Cl atoms present at the surface per metal atom. But it is also correlated to the kind of chlorinated species: CrO_x deactivation is due to the presence of chlorobenzene or of chlorinated intermediates of its oxidation that slightly block the active sites. Mn_3O_4 deactivates as being covered by a layer of chlorides and oxychlorides of manganese. A regeneration of this catalyst under helium or diluted oxygen is possible through the removal of the chlorinated layer thus restoring the Mn_3O_4 activity.

2.1. Introduction

Over the last decade, environmental legislation has imposed more rigid limits for atmospheric emission levels. In particular, the release of volatile organic compounds (VOCs) has received much attention. Among VOCs, chlorinated ones are the most polluting. Polychlorinated dibenzo-dioxins and dibenzo-furans (PCDDs and PCDFs), also named dioxins, are very toxic, carcinogenic and environmentally persistent organic pollutants [11-13]. They are systematically formed in all incineration processes in presence of hydrocarbons and chlorinated compounds, like in municipal and medical wastes incinerators or in biomass-fed cogeneration units.

A huge number of methods have been applied in order to fix the problem of the chlorinated VOCs atmospheric release (typically adsorption, thermal incineration, hydrodechlorination, biological process, steam reforming, photocatalytic degradation, etc). The catalytic destruction of chlorinated VOCs to CO_x , H_2O and HCl/Cl_2 appears very promising in this context. Indeed, among all the cited methods, the catalytic destruction is the most viable and economical approach. It stands for a wide range of pollutants concentration, exhibits an excellent selectivity toward the formation of harmless products and operates at relatively low destruction temperature [37,38].

CrO_x [53,123-125], VO_x [28,34,49,56,66-71] and MnO_x [47,54,126-129] based catalysts are reported to be very efficient in the catalytic destruction of VOCs. In Chapter 1, we pointed out from a screening of 40 catalyst formulations, CrO_x , VO_x and MnO_x based catalysts as the three best active phases in the course of the total oxidation of benzene [130]. These phases thus appear as good candidates to catalyze the total oxidation of chlorobenzene, taken as model molecule for dioxins, from combustion exhaust gases. However, the nature of the best active species of these three oxides (submonolayer, monolayer or bulk) has not been clearly determined yet. Moreover, the resistance of these active phases to possible deactivation by chlorinated reactants (chlorobenzene) and/or products (Cl_2 , HCl) has not been fully investigated yet.

This chapter therefore aims at i) evaluating the nature of the best active phase (submonolayer, monolayer or bulk) for the three catalysts (CrO_x , MnO_x and VO_x) supported on TiO_2 , ii) evaluating their resistance to deactivation in the course of the oxidation of chlorinated VOCs and iii) in the case of the occurrence of a deactivation, investigating the reasons and its mechanism.

Our approach consisted in the comparison of CrO_x , VO_x and MnO_x supported on TiO_2 catalysts with different loadings in active metal oxides in the course of the oxidation either of benzene or of chlorobenzene. In a first step, the comparison of the behaviors of the differently loaded catalysts in the total oxidation of benzene together with XPS and XRD characterizations allows to determine the nature of the best active phases (submonolayer, monolayer or bulk) for each catalyst. In the particular case of the MnO_x supported catalysts, further experiments using commercial bulk manganese oxides were made to gain further insight on the nature of the active phase. Moreover, this investigation points out the best catalyst for the combustion of non-chlorinated VOCs. In a second step, the comparison of the catalysts activity in the total oxidation of benzene and chlorobenzene gives clues on the possible deactivation undergone by the three catalysts in the presence of

chlorinated VOCs. Indeed, in the course of the total oxidation of chlorinated VOCs, the catalysts could deactivate following several mechanisms: i) blocking of the catalytic active sites by the reactants or the intermediates, ii) structural changes and iii) formation of metal volatile chlorides or oxychlorides [129]. Furthermore, this investigation reveals the best active phase for the total oxidation of chlorinated VOCs. In a third step, physico-chemical characterizations (XPS and ToF-SIMS) of the catalysts before and after catalytic tests, together with deactivation-regeneration cycles, allow to have a full understanding of the possible deactivation mechanism of the active phases.

2.2. Experimental and methods

2.2.1. Preparation of the catalysts

Catalysts are supported on Degussa P25 titania and the active phase is CrO_x (catalysts denoted by TCr) or VO_x (catalysts denoted by TV) or MnO_x (catalysts denoted by TMn). The catalysts were prepared following the experimental protocol presented in 1.2.1. and controlling the amount of precursor in order to obtain 0.125, 0.25, 0.5, 0.625, 0.75, 1 and 4 theoretical monolayers of CrO_x on the surface of the TiO_2 support. The obtained catalysts are hereunder denoted TCr-X with X being the number of theoretical monolayers, *e.g.* the catalyst with 0.125 monolayer of CrO_x is denoted TCr-0.125. In the case of the VO_x containing catalysts, the syntheses were performed in order to obtain 0.5, 0.75, 1, 1.5, 2, 3 and 4 theoretical monolayers (catalysts hereunder denoted TV-X). The syntheses of the MnO_x supported catalysts were realized to obtain 0.25, 0.5, 0.75, 1 and 4 theoretical monolayers (catalysts hereunder denoted TMn-X). ERACHEM Comilog provided $\alpha\text{-MnO}_2$, $\beta\text{-MnO}_2$ and Mn_3O_4 pure phases.

2.2.2. Catalytic tests

The catalytic tests were performed in a metallic fixed-bed micro-reactor (PID Eng&Tech S.L, Madrid - Spain) operated at atmospheric pressure and fully computerized. The reactor was made of inconel with an internal diameter of 8 mm and a height of 300 mm, into which the temperature is checked by an inconel covered thermocouple. The catalytic bed was composed of a layer of inert glass wool surmounted by 200 mg of catalyst powder selected within the 200-315 μm granulometric fraction and diluted in 800 mg of inactive glass spheres with diameters in the range 315-500 μm . For all kinds of performed catalytic tests, He was used as diluting gas to obtain a total stream of 200 ml min^{-1} . All gases were from Indugas and had a purity of 99.995%. The amount of catalyst and the total gaseous stream were chosen in order to be in the same conditions as in the reactor presented in chapter 1, namely with a VVH of 37000 h^{-1} corresponding to $7.44 \cdot 10^{-8}$ mole $\text{g}^{-1} \text{s}^{-1}$ (mole of benzene or chlorobenzene per gram of catalyst and per second). In these conditions the catalytic test is performed in a true kinetic regime avoiding the internal and external diffusion limitation. At each temperature investigated, the catalyst was stabilized for 150 min in order to reach the steady state. Analysis of reactants and products and catalysts performance evaluation were performed as described in the protocol 1.2.2.

2.2.2.1. Benzene and chlorobenzene total oxidation test

The reaction was run from 100 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ by step of 50 $^{\circ}\text{C}$. At each temperature, the catalyst was stabilized for 150 min in order to reach the steady state. The benzene combustion tests were made with a gaseous stream containing 100 ppm of benzene, 20% of O_2 and He as diluting gas. The combustion of chlorobenzene was performed with the same concentrations of VOC (100 ppm of chlorobenzene) and oxygen (20% of O_2), measuring the activity at the same temperatures.

2.2.2.2. *Reversibility test*

Additional tests were adapted in order to probe specifically the reversibility of the possible deactivation in the case of the chlorinated VOCs. Therefore, tests were performed during which the gaseous stream was switched from the conventional catalytic conditions to a regeneration stream and then switched back to the conventional catalytic conditions after a certain time. Practically the reversibility tests started with a conventional chlorobenzene oxidation test (100 ppm of chlorobenzene and 20% of O₂) from 100 °C to 300 °C by steps of 50 °C, then the gaseous stream was suddenly replaced by a stream of i) pure He or ii) 20% O₂ in He and maintained at 300 °C for 4 hours. Subsequently, the gaseous stream was switched back to the conventional conditions and the activity was then measured at 300 °C for a further 11 hours.

2.2.3. **Characterization**

X-ray diffraction (XRD) patterns were recorded following the protocol presented at point 1.2.3. The extent of the presence of crystalline (bulk) transition metal oxides in the samples was estimated through the ratio between the area of the Cr₂O₃ (104, 2 θ =33.586° and d=2.666 Å), V₂O₅ (001, 2 θ =20.279° and d=4.379 Å) or Mn₃O₄ (103, 2 θ =32.315° and d=2.768 Å) diffraction peaks and the TiO₂ anatase (101, 2 θ =25.302° and d=3.520 Å) one.

X-ray photoelectron spectroscopy (XPS) was performed following the experimental presented at point 1.2.3. of chapter 1.

Positive and negative static-ToF-SIMS (Time of Flight - Secondary Ion Mass Spectrometry) measurements were performed with a ToF-SIMS spectrometer from Phi-Evans in order to investigate the nature of the surface chemistry and to assess if there is a production of oxychloride of metal. The catalyst powder was pressed with spatula on a silvered double side tape (SPI

5070). The sample was bombarded with a pulsed primary 15 keV $^{69}\text{Ga}^+$ liquid metal ion beam. Secondary ions were accelerated to 3 keV before being 270° deflected by three electrostatic hemispherical analyzers (TRIFTTM). To increase the detection efficiency of ions at high m/z values, a post-acceleration of 7 keV was applied at the detector entry. A 600 pA DC primary ion was pulsed at 11 kHz repetition rate with a pulse width of 22 ns, finally electrostatically bunched down to 1 ns to increase mass resolution, and raster over a $120\text{ }\mu\text{m} \times 120\text{ }\mu\text{m}$ surface area. With a data acquisition of 5 min, the total fluence was $\sim 1.4 \times 10^{12}\text{ Ga}^+/\text{cm}^2$ ensuring static conditions. Charge effects were compensated by means of a 24 eV pulsed electron flood gun. To prevent variation of the surface potential, a stainless steel grid (non-magnetic) with 2 mm mesh was put onto the sample surface. In these experimental conditions, the mass resolution ($m/\Delta m$) was about 2000 at m/z 48 (^{48}Ti). To obtain statistical data, experiments were repeated four times on different areas of the same sample. The semi-quantitative results were obtained by the mean of the 4 results of percentage obtained on the same sample following the equation:

$$\text{Relative intensity (\%)} = \left[\frac{\text{peak area of the ion of interest}}{\text{sum of peaks areas } 10 < m/z < 1000} \right] * 100$$

2.3. Results and discussion

2.3.1. Evaluation of the nature of the active phases (submonolayer, monolayer or bulk)

We classify the nature of the active phase into three different systems: submonolayer, monolayer and bulk. The submonolayer nature characterizes an active phase highly dispersed at the surface of the support but without being in sufficient amount to cover completely the support. It corresponds to isolated species or polymeric species which do not cover the entire surface of the support. The monolayer nature describes an active phase highly

dispersed at the surface of the support and being in sufficient amount to cover the entire surface of the support. Finally, the bulk nature characterizes an active phase poorly dispersed that forms crystallites heterogeneously disposed at the surface of the support. In order to investigate the nature of the best active phases, catalytic tests and characterizations were performed on CrO_x , VO_x and MnO_x supported on TiO_2 catalysts with different loadings in active metal oxides.

2.3.1.1. Benzene combustion test

Fig. 2-1, 2-2 and 2-3 present the benzene light-off curves, respectively for the TCr, TV and TMn catalysts with different loadings. Fig. 2-4 shows for the three families of catalysts the evolution of the T_{50} (temperature needed to achieve the conversion of 50% of the benzene concentration) as a function of the theoretical loading (expressed in terms of monolayers).

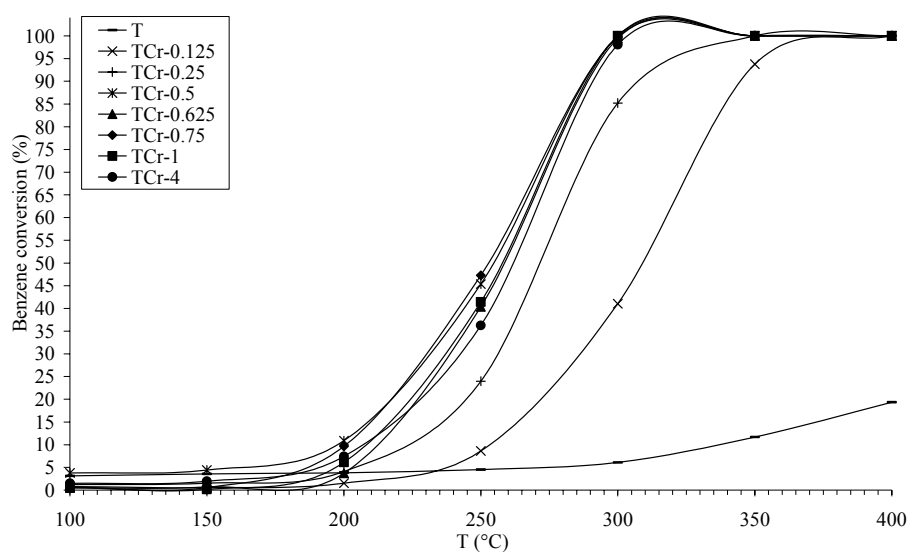


Fig. 2-1: Light-off curves of the benzene conversion on the CrO_x on TiO_2 catalysts

The TiO_2 support (T) exhibits a very low activity, *e.g.* it converts less than 20% of benzene at 400 °C. In the case of the CrO_x based catalysts, the progressive increase of the CrO_x loading from 0.125 up to 0.5 monolayer induces a progressive increase of the activity (Fig. 2-1 and 2-4). However, a further increase of the loading above 0.5 monolayer of CrO_x is not followed by a further increase of activity but by a stabilization of the activity up to a loading of 1 theoretical monolayer. Finally, the increase of loading from 1 to 4 monolayers provokes a slight decrease of the benzene conversion which corresponds to a weak increase of the T_{50} . The optimum theoretical loading within the CrO_x family is thus 0.75 monolayer corresponding to a T_{50} of 252 °C.

Fig. 2-2 presents the light-off curves for the catalysts of the TV family. The increase of the VO_x loading from 0.5 to 2 induces a gradual enhancement of the catalysts activity. Conversely, the further increase of the loading above 2 monolayers leads to a decrease of the catalysts activity, which corresponds to an increase of the T_{50} (Fig. 2-4). The best performances are obtained with the TV-2 catalyst, which converts 50% of the benzene charge at 246 °C.

The increase of the MnO_x loading leads to a progressive increase of the catalytic combustion of benzene up to the highest coverage of MnO_x , *i.e.* 4 theoretical monolayers (Fig. 2-3). This enhancement of the catalyst activity corresponds to a progressive decrease of the T_{50} as observed in Fig. 2-4. The highest activity is thus observed with the highest loading of MnO_x phase, namely 4 monolayers. TMn-4 catalyst converts 50% of the benzene concentration at 215 °C.

The comparison of the best catalyst of each family, in terms of the lowest T_{50} , allows to classify them in progressive activity: $\text{TCr-0.75} < \text{TV-2} < \text{TMn-4}$. As a conclusion, the best catalyst for the combustion of the non-chlorinated VOCs is the catalyst most loaded with MnO_x , *i.e.* TMn-4.

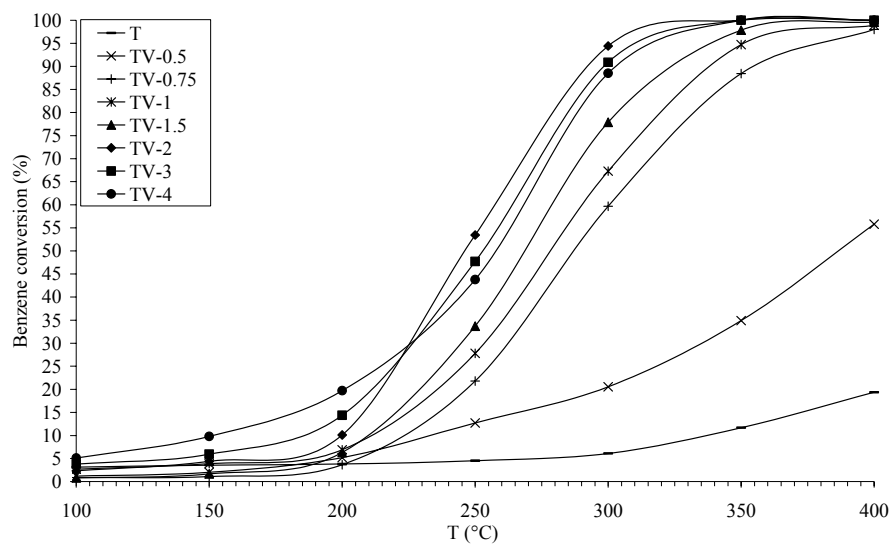


Fig. 2-2: Light-off curves of the benzene conversion on the VO_x on TiO_2 catalysts

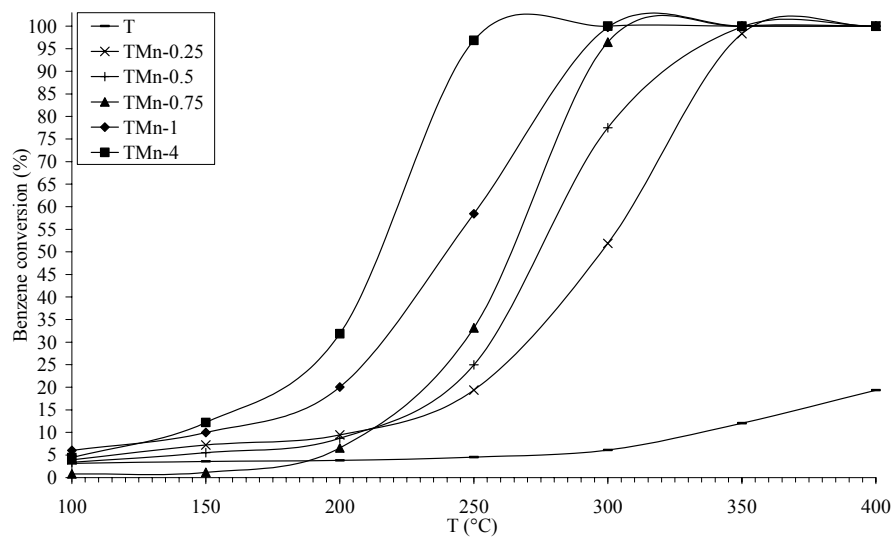


Fig. 2-3: Light-off curves of the benzene conversion on the MnO_x on TiO_2 catalysts

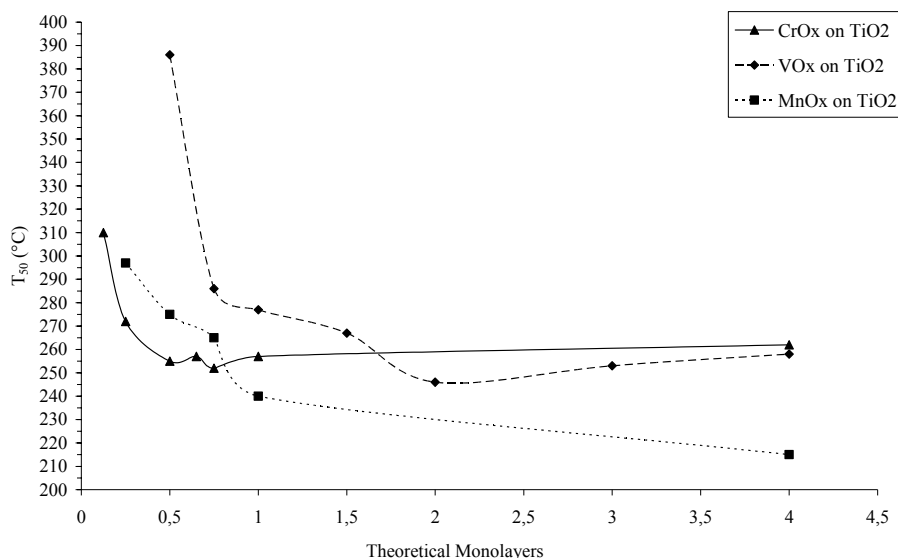


Fig. 2-4: Evolution of the T_{50} for the benzene combustion as a function of the theoretical loading in terms of monolayers for the three active phases (CrO_x , VO_x and MnO_x)

2.3.1.2. Characterizations

XPS and XRD measurements were performed on the post-mortem catalysts in order to determine the kind of dispersion of the best active phases for the three families of catalysts (CrO_x , VO_x , and MnO_x).

Fig. 2-5 presents, as a function of the theoretical coverage in terms of monolayers, i) the atomic concentration of Cr, V and Mn detected on the surface of the catalyst by XPS and ii) the intensity ratio between the XRD peaks of the crystalline bulk transition metal oxides and the bulk TiO_2 anatase, as defined in the experimental section.

The increase of the loading of CrO_x from 0.125 to 0.5 monolayer induces a sharp increase of the atomic concentration of Cr detected by XPS on the

surface of the catalyst (Fig. 2-5). The further increase of the loading provokes a less marked increase of the surface concentration of Cr. The MnO_x based catalysts show a similar behavior: the increase of the theoretical loading induces a progressive increase of the concentration of Mn detected at the surface, but the increase depends on the loading. Below 1 monolayer, the atomic concentration of Mn sharply increases and above 1 monolayer the increase is less sharp. The VO_x catalysts exhibit a quite similar behavior: the increase of the loading induces a progressive increase of the atomic concentration of V on the surface of the catalyst. However, in the case of the VO_x based catalyst, the break of the curve for the transition between the high and the low loadings is not clearly established. Nevertheless, one can reasonably assess that this transition occurs between 1 and 2 monolayers.

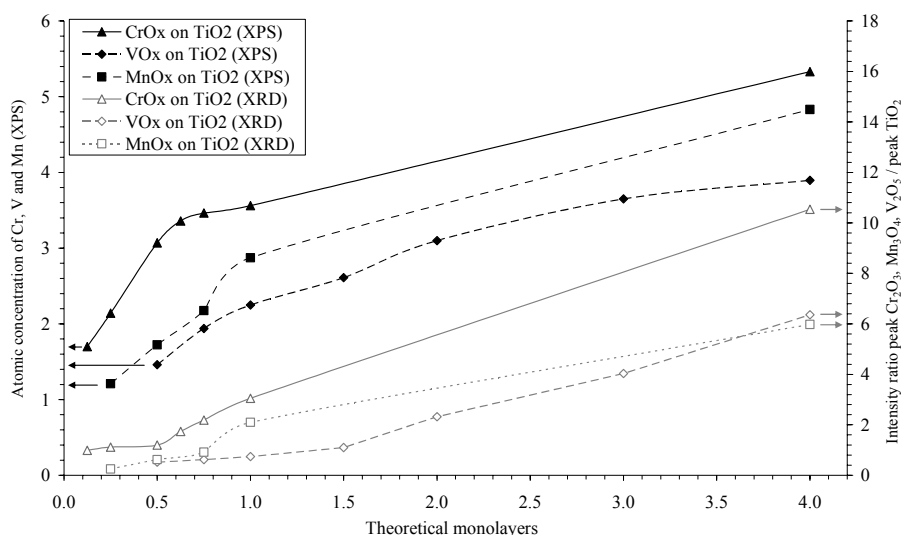


Fig. 2-5: Evolution of the atomic concentration (%) of Cr, V and Mn quantified by XPS and of the percentage bulk transition metal oxides (Cr_2O_3 , V_2O_5 and Mn_2O_3) / bulk TiO_2 detected by XRD as a function of the theoretical loading in terms of monolayers

For the three families of catalysts (CrO_x , VO_x , and MnO_x), the increase of the loading brings a slight increase of the XRD intensity ratio between bulk transition metal oxide and bulk titania up to a determined loading. The further increase of the loading induces a sharper increase of the intensity ratio. The transition occurs at a different loading depending on the type of catalyst: 0.5, 1.5 and 1, respectively for CrO_x , VO_x , and MnO_x based catalysts. These transition values are roughly similar to the values at which the bulk transition metal oxides are clearly detected on the diffractogram. Indeed Cr_2O_3 , V_2O_5 and Mn_3O_4 bulk phases appear above a loading of 0.75, 1.5 and 1 monolayers, respectively.

It is important to point that for each family of catalysts, the fracture in the curve of the XPS atomic concentration as a function of the theoretical coverage and in the curve of the XRD intensity ratio as a function of the coverage is observed at the same theoretical loading (Fig. 2-5). The rupture occurs at 0.75, 1.5 and 1, respectively, for the CrO_x , VO_x and MnO_x based catalysts.

2.3.1.3. Discussion

The catalytic tests demonstrated that the activity of the three families of catalysts is highly dependent of the loading in active phases. CrO_x and VO_x phases prove to have the best activity at submonolayer and monolayers theoretical coverage, respectively at 0.5 and 2 monolayers, while MnO_x phase proves to be the most active in the case of the highest loading, *e.g.* 4 theoretical monolayers, and it seems that its activity would have further increased for higher loadings. To investigate further the relationship between the loading of transition metal oxides and the catalyst activity, two additional plots were drawn.

Fig. 2-6 presents the catalyst activity in terms of T_{50} as a function of the atomic surface concentration of Cr, V and Mn detected by XPS. For both CrO_x and VO_x based catalysts, the T_{50} decreases with the increase of the

atomic concentration up to roughly 3%. Above an atomic concentration of 3%, a stabilization or an increase of the T_{50} was observed, thus meaning that the catalysts become less active. For both active phases, the activity is thus clearly not directly correlated to the amount of active phase on the surface of the catalyst. At the opposite, in the case of the MnO_x based catalysts, the T_{50} decreases continuously with the increase of the atomic concentration of Mn. This result points out the direct correlation between the amount of active phase of the catalyst and its activity.

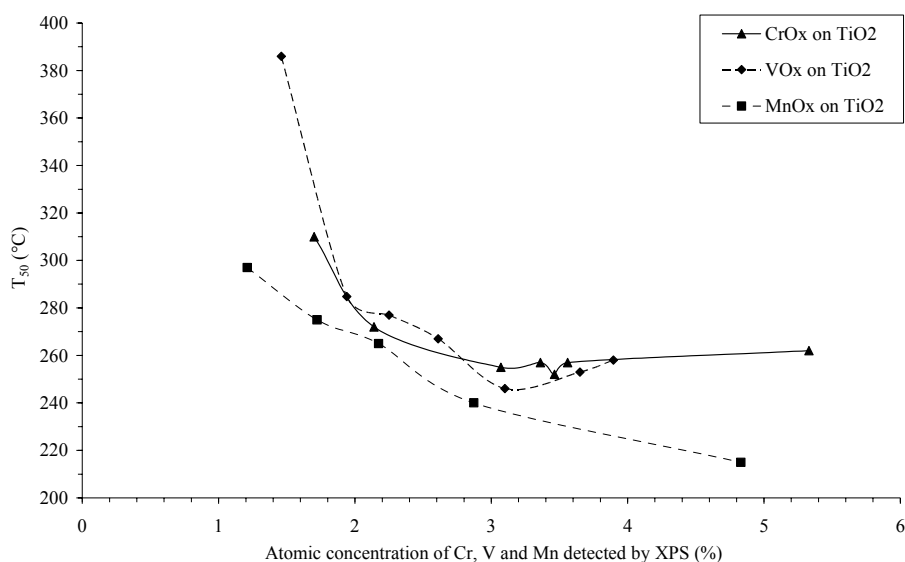


Fig. 2-6: Evolution of the T_{50} for the benzene combustion as a function of the atomic concentration of Cr, V and Mn quantified by XPS

Fig. 2-7 shows the T_{50} of the catalysts as a function of the XRD intensity ratio between bulk transition metal oxide and bulk titania peaks. In the case of the CrO_x based catalysts, the curve clearly splits into two parts: i) at low loadings, the T_{50} decreases sharply with a tiny increase of the ratio up to about 1.2% that is obtained for a loading of 0.5 monolayer and ii) above 1.2%, the increase of the amount of Cr_2O_3 detected by XRD does not induce

any further increase of activity. The curve of the VO_x based catalysts is split into three parts: i) the T_{50} dramatically drops with a tiny increase of the ratio up to 0.7%, which is obtained with a loading of 1 monolayer, ii) above 0.7%, the T_{50} decreases continuously with the increase of the amount of bulk V_2O_5 detected up to 2.3% that is obtained for a loading of 2 monolayers and iii) above 2.3%, the increase of the amount of V_2O_5 detected induces an increase of T_{50} showing that the TV catalyst becomes less active for higher loadings. At the opposite, a continuous decrease of T_{50} is observed when the ratio evaluating the extent of the presence of bulk Mn_3O_4 increases up to the highest loading of Mn_3O_4 investigated.

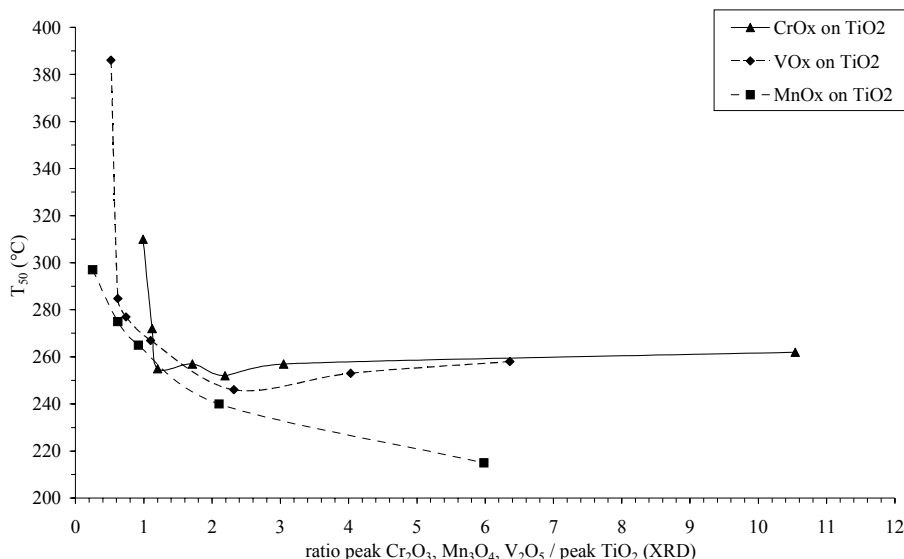


Fig. 2-7: Evolution of the T_{50} for the benzene combustion as a function of percentage bulk transition metal oxides (Cr_2O_3 , V_2O_5 and Mn_2O_3) / bulk TiO_2 detected by XRD

In chapter 1, we investigated the influence of the nature of the support on the performances of the active phases [130]. The active phases (CrO_x , VO_x and MnO_x) supported on various supports (TiO_2 , TiO_2 -s, Al_2O_3 and SiO_2) were tested in the course of the total oxidation of benzene and characterized by

XPS and XRD. These characterizations pointed out that the spreading of the active phase on the support is strongly governed by the “solid-solid wetting” phenomenon. This phenomenon depends on the difference in surface free energy and leads to the formation of monolayer or bulk of active phase depending on the couple active phase - support. Moreover we demonstrated that the activity of a catalyst depends on the nature of the support but in an extent largely depending on the element constituting the active phase. In the case of the VO_x and CrO_x based catalysts, the activity strongly depends on the nature of the support and therefore on the quality of the spreading as monolayer of these phases on the support. While in the case of the MnO_x based catalysts, the activity is almost independent of the nature of the support and the best performances are observed on the SiO_2 support, which does not favor the homogeneous spreading of the active phase and favors the formation of crystallites of Mn_3O_4 .

In the case of the CrO_x based catalysts, i) the absence of enhancement of the activity with the increase of the theoretical loading above 0.5 monolayer, ii) the absence of linear correlation between the atomic concentration of Cr on the surface and the activity, iii) the absence of influence of the amount of bulk Cr_2O_3 on the activity and iv) the influence of the nature of the support on the active phase activity prove that the active phase is a submonolayer of CrO_x . This CrO_x submonolayer corresponds to the presence of highly dispersed CrO_x isolated or polymeric species covering partially the surface of the support.

For the MnO_x based catalysts, i) the continuous enhancement of the activity with the increase of the theoretical loading, ii) the direct relationship between the atomic concentration of Mn and the activity, iii) the linear continuous improvement of the activity with the amount of Mn_3O_4 detected by XRD and iv) the absence of influence of the nature of the support on the active phase activity demonstrate that the nature of the active phase is bulk Mn_3O_4 . Moreover, catalytic tests performed on pure manganese oxides phases (α - MnO_2 , β - MnO_2 and Mn_3O_4) demonstrated, at equivalent amount

of active phase introduced in the reactor, that the activity of the TMn-4 ($T_{50}=215$ °C) catalyst is quite similar to the activity of the pure Mn_3O_4 ($T_{50}=212$ °C). α - MnO_2 ($T_{50}=244$ °C), β - MnO_2 ($T_{50}=265$ °C) demonstrated quite a different activity than the TMn-4 catalyst.

In the case of the VO_x based catalysts, i) the loss of activity with the increase of the theoretical loading above 2 monolayers, ii) the absence of direct correlation between the atomic concentration of V on the surface and the activity, iii) the negative influence of the increase of the amount of bulk V_2O_5 on the activity and iv) the deep influence of the nature of the support on the active phase activity attest that the active phase is a monolayer of VO_x . This monolayer corresponds to the formation of a homogeneous coverage of the entire surface of the support by highly polymeric species.

Based on the activity in the oxidation of benzene and on the XPS and XRD characterizations, the nature of the phase in the most active catalysts strongly depends on the metal oxides: while CrO_x and VO_x work best as submonolayer and monolayer species, respectively, MnO_x requires to be present in the form of bulk Mn_3O_4 to be active. These results confirm the conclusions presented in Chapter 1.

2.3.2. Evaluation of the deactivation in the presence of chlorinated VOCs

2.3.2.1. Chlorobenzene combustion test

Table 2-1 presents the performances, in terms of T_{50} , in the course of the oxidation of benzene and chlorobenzene for three selected samples from each family (TCr-0.125, TCr-0.5, TCr-4, TV-0.75, TV-2, TV-4, TMn-0.25, TMn-0.75 and TMn-4). Additionally, Table 2-1 shows the ΔT_{50} referring to the formula: $\Delta T_{50} = T_{50}^{chlorobenzene} - T_{50}^{benzene}$.

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A negative value of ΔT_{50} means that the catalyst converts more easily chlorobenzene than benzene. Thus, a negative or a zero value indicates that the catalyst does not suffer any deactivation in the presence of chlorinated species (chlorobenzene or the chlorinated products of its oxidation). At the opposite, a positive value of ΔT_{50} means that it is more difficult to convert chlorobenzene than benzene. Therefore, a positive value of ΔT_{50} indicates that the catalyst undergoes a kind of deactivation when placed in the presence of chlorinated species.

Table 2-1: Catalytic results in terms of T_{50} (°C) for the benzene and chlorobenzene combustion for selected catalysts from the three families

	T_{50} (°C) benzene	T_{50} (°C) chlorobenzene	ΔT_{50} (°C)
TCr-0.125	310	307	-3
TCr-0.5	252	262	10
TCr-4	262	266	4
TV-0.75	286	284	-2
TV-2	246	247	1
TV-4	258	260	2
TMn-0.25	297	370	73
TMn-0.75	265	320	55
TMn-4	215	302	87

Generally, the catalysts of the TCr family show slightly positive ΔT_{50} values meaning that CrO_x based catalysts only suffer a slight deactivation in the presence of chlorinated species.

In the case of the TV family, ΔT_{50} values are close to zero. The behavior of the VO_x based catalysts thus appears generally unchanged when reacted in the presence of chlorinated VOCs instead of in the presence of non-chlorinated ones. VO_x based catalysts thus exhibit a total resistance against any deactivation due to chlorinated species.

At the opposite, the MnO_x based catalysts exhibit very positive ΔT_{50} values within the range 50-90 °C, pointing out the occurrence of a deep deactivation when reacted in the presence of chlorinated VOCs.

On the one hand, within each family of catalysts, the classification of the catalysts as a function of their performances in the combustion of chlorobenzene and of their loading in active phase is identical to the corresponding classification made in the combustion of benzene. The effect of the chlorinated species thus seems to be independent of the loading in active phases. Consequently, the best catalyst within each family remains the same as pointed from the catalytic tests using benzene: namely TCr-0.5, TV-2 and TMn-4. On the other hand, the presence of the chlorine atom in the molecule of interest has an impact, which dramatically depends on the transition metal oxides used as active phase. A very good resistance of VO_x catalysts was observed, while a huge deactivation of MnO_x and an intermediate behavior of CrO_x were found. Therefore, in the case of the combustion of chlorinated VOCs, the ranking of the best catalysts becomes, from the less to the most active, $\text{TMn-4} < \text{TCr-0.5} < \text{TV-2}$. TV-2, the best catalyst identified in the combustion of chlorobenzene, abates 50% of the chlorobenzene concentration at a temperature as low as 247 °C. As in the combustion of benzene, the products detected at the outlet of the reactor are only CO_2 and CO. Polychlorinated hydrocarbons or partially oxidized hydrocarbons were never detected.

2.3.2.2. Characterizations

XPS quantification of the atomic concentration of Cr, V, Mn and Cl on the surface of the catalysts was performed after catalytic test on chlorobenzene. These measurements were performed with the purpose of identifying the origin of the resistance mechanism of VO_x catalysts to chlorinated species and of the origin of the deactivation of CrO_x and MnO_x catalysts. XPS measurements on post-mortem TV-0.75, TV-2 and TV-4 do not reveal any presence of Cl on the surface of the catalysts. Consequently, it must be

concluded that the amount of Cl at the surface of the catalysts after test is below the detection limit of the XPS (0.01% of atomic concentration). Identical measurements on CrO_x and MnO_x based catalysts demonstrate the presence of Cl on the surface of the entire set of samples. Fig. 2-8 and 2-9 present, respectively, the atomic concentrations of Cr, Cl and Mn, Cl. Additionally, both figures present the atomic concentration ratio chlorine / transition metal. The atomic concentration of Cl, detected on the surface of the CrO_x based catalysts, increases with the increase of the atomic concentration of Cr (Fig. 2-8). The corresponding Cl/Cr ratio is roughly 0.035 and is rather independent of the loading in active phase. This mean value of 0.035 indicates that there is about 1 Cl atom for 30 Cr atoms at the surface of the catalyst. Moreover, the independence of the ratio from the loading reveals that the chlorinated species interact with the CrO_x phase whatever its nature, namely whether it is crystalline or not.

As in the case of the CrO_x catalysts, the atomic concentration of Cl detected on the surface of the MnO_x catalysts increases with the increase of the amount of Mn on the surface (Fig. 2-9). However, the Cl/Mn ratio is between 5 and 9 times higher than the Cl/Cr ratio and is dependent on the loading in MnO_x . At the lowest loading, the Cl/Mn ratio is about 0.175 while at the two highest loadings this ratio is roughly 0.275. The 0.275 ratio corresponds approximately to the presence of 2 Cl atoms for 7 atoms of Mn exposed on the surface. Moreover, the evolution of the Cl/Mn ratio shows that chlorine tends to affect more severely the bulk Mn_3O_4 phases than the submonolayer phases.

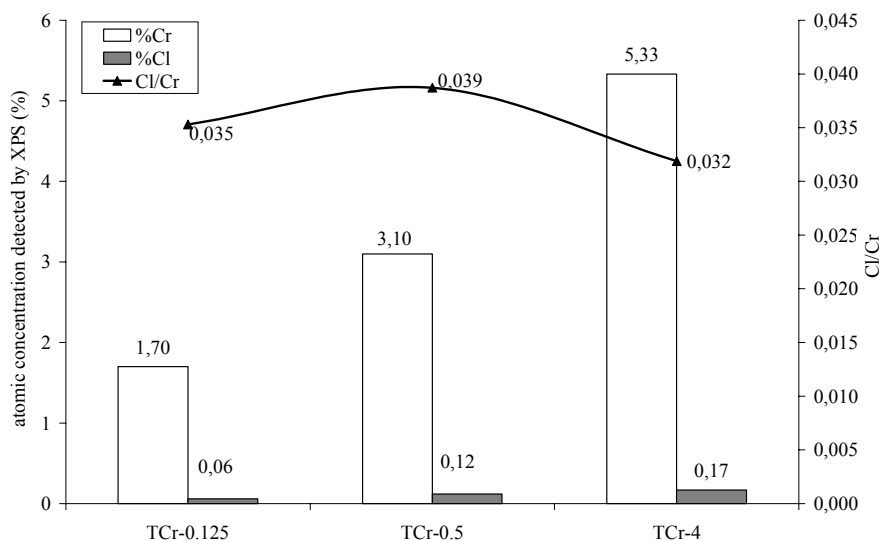


Fig. 2-8: Atomic concentration of Cr and Cl and Cl/Cr ratio detected on the surface by XPS measurements for TCr-0.125, TCr-0.5 and TCr-4 catalysts

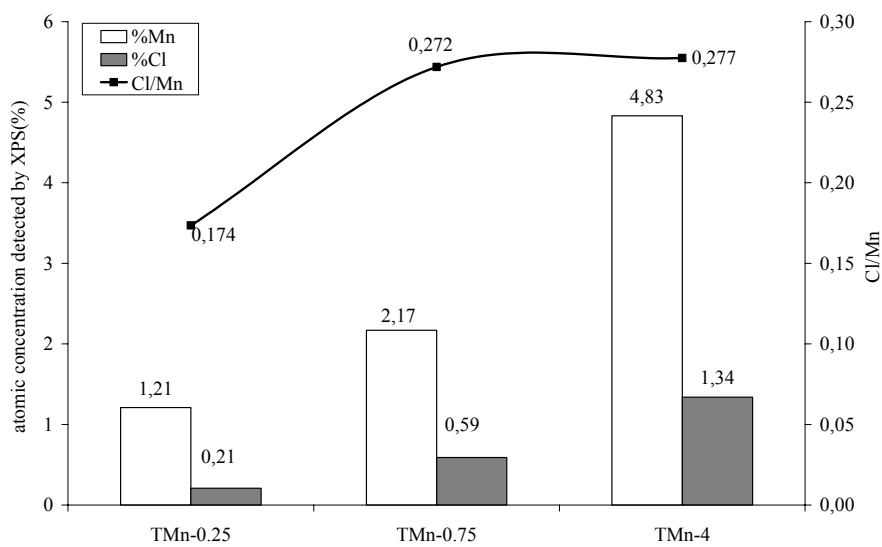


Fig. 2-9: Atomic concentration of Mn and Cl and Cl/Mn ratio detected on the surface by XPS measurements for TMn-0.25, TMn-0.75 and TMn-4 catalysts

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ToF-SIMS measurements were performed on T, TV-4, TCr-4 and TMn-4 before and after catalytic combustion of chlorobenzene in order to have a better understanding of the nature of the chlorinated species at the surface of the used catalysts. ToF-SIMS blank measurements were performed on the TiO₂ support which was submitted to the impregnation steps but in the absence of metal oxide precursor in the solution.

The measurements of the blank TiO₂ and the fresh TV-4, TCr-4 and TMn-4 catalysts reveal the presence of some peaks corresponding to chlorine containing fragments. The characteristic negative peaks appear at the m/z 35, 37, 47, 49, 51, 53, 70, 72, 74, 115, 117, 134, 136 and 138 and correspond to $^{35}\text{Cl}^-$, $^{37}\text{Cl}^-$, $^{35}\text{ClC}^-$, $^{37}\text{ClC}^-$, $^{35}\text{ClO}^-$, $^{37}\text{ClO}^-$, $^{35}\text{Cl}_2^-$, $^{35}\text{Cl}^{37}\text{Cl}^-$, $^{37}\text{Cl}_2^-$, $^{35}\text{ClTiO}_2^-$, $^{37}\text{ClTiO}_2^-$, $^{35}\text{Cl}_2\text{TiO}^-$, $^{35}\text{Cl}^{37}\text{ClTiO}^-$ and $^{37}\text{Cl}_2\text{TiO}^-$. To simplify the treatment of these results, the different chlorine isotopes of a same kind of fragment were summed and the sum served to calculate the relative intensities presented in Table 2-2. The considered fragments are thus: Cl^- , ClC^- , ClO^- , Cl_2^- , ClTiO_2^- and Cl_2TiO^- . The ToF-SIMS investigates the samples surface from uppermost monolayer to 40 Å of depth following the number of atoms presents in the considered ions. The investigated depth is inversely proportional to the number of atoms in the fragments, *e.g.* the mean emission depths of fragments of number of atoms equal to 1, 3 and 4 are respectively 9.3, 4.9 and 3.0 Å [131]. The decrease of the mean emission depth from 9.3 to 3.0 Å (factor of roughly 3) leads to a decrease of the amount of detected fragments by ToF-SIMS by a factor of roughly 100. Therefore the detected relative intensity of a fragment depends on i) the concentration of the precursor of the fragment at the surface of this catalyst, ii) the number of atoms of the fragment and iii) the probability to be ionized. The disparity within the number of atoms in the fragments (from 1 to 4), observed in our case, could induce a variation by a factor 3 of the mean emission depth between the Cl^- and the Cl_2TiO^- fragments. This decrease of the mean emission depth leads to a decrease of the detected intensity by a factor of

more than 100. This should be carefully taken into account in the interpretation of the ToF-SIMS data.

Table 2-2 presents the relative intensity of each chlorinated fragments detected by ToF-SIMS on all samples. A high amount of chlorine containing fragments is detected at the surface of the TiO_2 with a total relative intensity of 19.4%. The total relative intensity decreases down to 0.9 and 1.4%, respectively in the case of the fresh TV-4 and TCr-4 catalysts. In the case of the TMn-4 fresh catalyst the total relative intensity goes down to a value of 11.2%. The presence of chlorine containing fragments in the support is explained by the synthesis protocol used by Degussa producing its TiO_2 P25 from chlorinated titanium precursors, which could lead to a concentration of Cl up to 3000 ppm in this commercial product [106]. The ToF-SIMS demonstrated that these chlorine atoms are present at least partially as TiO_yCl_z . The decrease of the amount of chlorinated containing fragments in the samples TV-4, TCr-4 and TMn-4 is explained by the coverage of the support by the active phases (masking effect). Indeed, the ToF-SIMS measurement investigates the samples in a depth of less than 40 Å for atomic ions (Cl^- isotopes). Therefore, the difference in the extent of the decrease of the chlorinated fragments concentration of the TV-4, TCr-4 and TMn-4 with respect to the TiO_2 support is clearly related to the difference of dispersion of the active phase. The very low chlorine containing fragments concentration of the TV-4 catalyst is linked to a very good dispersion of the VO_x forming continuous layer(s) at the surface of the support. In the same way, the low concentration of chlorinated fragments is in good agreement with the layer coverage of the support by CrO_x . At the opposite, the TMn-4 catalyst shows a high concentration of chlorine containing fragments that is definitely connected to the very bad dispersion of the MnO_x phases on the support. From our XRD observations, it turns out that MnO_x phase indeed tends to readily form crystallites at the surface of the support starting from low loadings. These crystallites do not have a “masking” effect as efficient as a continuous layer of active phase, leaving large spots of support

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uncovered with, as a consequence, huge remaining chlorinated fragments from the support exposed and detected by ToF-SIMS.

Table 2-2: Relative intensity of the chlorinated fragments detected by ToF-SIMS for the T, TCr-4, TV-4 and TMn-4 before and after catalytic test of combustion of chlorobenzene (% and 95% confidence limits)

Catalyst		Cl ⁻	ClC ⁻	ClO ⁻	Cl ₂ ⁻
T	fresh	18.72 ±0.368	0.044 ±0.002	0.396 ±0.015	0.040 ±0.001
	after test	0.632 ±0.038	0.012 ±0.003	0.015 ±0.001	0.008 ±0.001
TV-4	fresh	0.828 ±0.071	0.011 ±0.001	0.017 ±0.001	0.008 ±0.000
	after test	0.632 ±0.038	0.012 ±0.003	0.015 ±0.001	0.008 ±0.001
TCr-4	fresh	1.203 ±0.055	0.035 ±0.012	0.035 ±0.002	0.036 ±0.001
	after test	1.168 ±0.098	0.016 ±0.002	0.028 ±0.002	0.028 ±0.002
TMn-4	fresh	10.88 ±0.571	0.038 ±0.003	0.144 ±0.019	0.063 ±0.007
	after test	38.96 ±0.423	0.035 ±0.004	0.304 ±0.014	0.188 ±0.006

Catalyst		ClTiO ₂ ⁻	Cl ₂ TiO ⁻	TOTAL
T	fresh	0.206 ±0.006	0.032 ±0.000	19.44
	after test	0.043 ±0.007	0.004 ±0.000	0.714
TV-4	fresh	0.053 ±0.001	0.005 ±0.001	0.922
	after test	0.043 ±0.007	0.004 ±0.000	0.714
TCr-4	fresh	0.068 ±0.012	0.013 ±0.002	1.390
	after test	0.044 ±0.004	0.009 ±0.002	1.293
TMn-4	fresh	0.068 ±0.009	0.013 ±0.003	11.21
	after test	0.072 ±0.004	0.032 ±0.002	39.59

For TV-4 and TCr-4 catalysts, after test in the presence of 100 ppm of chlorobenzene, the relative intensities of chlorine containing fragments decrease in front of the values found for the fresh samples. Moreover, in both cases, no new chlorine containing fragments are detected. The decrease of concentration could be explained by two hypotheses: i) during the catalytic test the dispersion of the active phase (VO_x and CrO_x) at the surface

of the support increases slightly, ii) a slight amount of the chlorine containing compounds is lost at the highest temperatures at which the reaction is run.

At the opposite, in the case of the TMn-4 catalyst, the sum of the relative intensities of all the chlorine containing fragments increases by a factor of roughly 3.7 in front of the values before catalytic test, to reach about 40%. Moreover, the amount of the chlorine-titanium containing fragments detected is above the concentrations observed at the surface of the blank support. This observation proves that the increase of the concentration of the chlorine containing fragments is not due to a change in the dispersion of the active phase (MnO_x) on the surface of the support, more precisely a sintering, but to the occurrence of a true chlorination of the catalyst.

The chlorination of the TMn-4 catalyst involves the support as an increase of the relative intensity of the TiO_yCl_z fragments is observed. This is in agreement with a previous reference observing such a chlorination of the support of a MnO_x active phase in the course of the total oxidation of chlorinated VOC [129]. However, it also involves the active phases as new chlorinated fragments were observed by ToF-SIMS in the case of the TMn-4 catalyst after chlorobenzene test. These appears at m/z 106, 108, 125, 127, 129, 141, 143, 145, 160, 162, 164, 166, which corresponds to $^{35}\text{ClMnO}^-$, $^{37}\text{ClMnO}^-$, $^{35}\text{Cl}_2\text{Mn}^-$, $^{35}\text{Cl}^{37}\text{ClMn}^-$, $^{37}\text{Cl}_2\text{Mn}^-$, $^{35}\text{Cl}_2\text{MnO}^-$, $^{35}\text{Cl}^{37}\text{ClMnO}^-$, $^{37}\text{Cl}_2\text{MnO}^-$, $^{35}\text{Cl}_3\text{Mn}^-$, $^{35}\text{Cl}_2^{37}\text{ClMn}^-$, $^{35}\text{Cl}^{37}\text{Cl}_2\text{Mn}^-$, $^{37}\text{Cl}_3\text{Mn}^-$. For reasons evoked above, one only considers ClMnO^- , Cl_2Mn^- , Cl_2MnO^- , Cl_3Mn^- fragments summing the contribution from the different isotopes. The sum of these fragments represents a relative intensity of roughly 0.3% while the Cl^- relative intensity represents 39%. However, the number of atoms of these fragments is up to 4 times higher than those of Cl^- , inducing a decrease of the mean emission depth. As discussed above, this also leads to a decrease of the detected intensity by a factor of more than 100 [131]. We can thus conclude that the chlorinated manganese species are present at the surface of

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the catalyst at relatively high concentration and that they are probably the major way of immobilization of chlorine atom at the surface of the catalyst.

Table 2-3: Relative intensity of the chlorinated fragments detected by ToF-SIMS for the TMn-4 catalysts after classical test, before regeneration and after both kinds of regeneration: i) pure He and ii) 20% of O₂ in He (% and 95% confidence limits)

TMn-4	Cl ⁻	ClC ⁻	ClO ⁻	Cl ₂ ⁻	ClMnO ⁻	ClTiO ₂ ⁻
After CBZ classic test	38.96 ±0.423	0.035 ±0.004	0.304 ±0.014	0.188 ±0.006	0.049 ±0.003	0.072 ±0.004
Before regeneration	43.59 ±1.211	0.059 ±0.004	0.579 ±0.065	0.395 ±0.036	0.093 ±0.016	0.151 ±0.028
After He regeneration	31.75 ±1.320	0.042 ±0.004	0.313 ±0.050	0.108 ±0.019	0.075 ±0.017	0.098 ±0.024
After O₂ regeneration	21.46 ±1.163	0.034 ±0.003	0.175 ±0.028	0.060 ±0.012	0.043 ±0.009	0.081 ±0.018

	Cl ₂ Mn ⁻	Cl ₂ TiO ⁻	Cl ₂ MnO ⁻	Cl ₃ Mn ⁻	TOTAL
After CBZ classic test	0.053 ±0.002	0.032 ±0.002	0.044 ±0.008	0.127 ±0.017	39.86 ±0.517
Before regeneration	0.140 ±0.026	0.083 ±0.016	0.106 ±0.021	0.409 ±0.080	45.60 ±1.225
After He regeneration	0.048 ±0.012	0.029 ±0.007	0.034 ±0.009	0.046 ±0.012	32.54 ±1.432
After O₂ regeneration	0.031 ±0.007	0.020 ±0.005	0.022 ±0.004	0.026 ±0.006	21.95 ±1.233

Therefore, the ToF-SIMS measurements prove that the MnO_x active phase undergoes a deep chlorination leading to the formation of manganese chlorides (MnCl_x) and manganese oxychlorides (MnCl_yO_z) in the course of the catalytic oxidation of chlorobenzene. This is in agreement with literature

as the formation of oxychlorides of manganese (MnCl_yO_z) was suspected by Döbber *et al.* and Liu *et al.* in the course of the total oxidation of low molecular weight chlorinated VOCs [83,129]. These authors suppose that the reaction of HCl or Cl_2 with the MnO_x phases induces the formation of the oxychlorides of manganese at temperatures above 200 °C.

2.3.2.3. Discussion

The catalytic tests pointed out the resistance of the VO_x based catalysts in the presence of chlorinated-VOCs. This resistance is borne out by the absence of chlorine on the surface of the catalyst after combustion of chlorobenzene, as revealed by the XPS and ToF-SIMS measurements. At the opposite, in the case of the MnO_x catalysts, high values of ΔT_{50} revealed their deep deactivation in the presence of chlorinated VOCs. This deactivation goes in parallel with the high atomic concentration of chlorine detected on the surface by XPS (2 Cl atoms for 7 Mn atoms) and with the ToF-SIMS measurements evidencing the formation of manganese chlorides (MnCl_x) and manganese oxychlorides (MnCl_xO_y) in the course of the catalytic oxidation of chlorobenzene. The catalytic results demonstrated the intermediate behavior of the CrO_x based catalysts, which underwent a slight deactivation with a mean ΔT_{50} around 4 °C only. This slight deactivation is supported by the low concentration of chlorine detected on the surface: XPS pointed out the presence of only 1 Cl atom for 30 Cr atoms on the surface of the catalyst while ToF-SIMS revealed the absence of oxychlorides or chlorides of chromium (CrO_yCl_z or CrCl_x) at the surface of the catalyst. This matches up thermodynamic aspects as in the case of our catalytic tests, the formation of oxychlorides of chromium is not favored as the reaction of HCl or Cl_2 and O_2 with CrO_x to produce CrO_yCl_z requires temperatures above 550 °C [132-138]. Therefore, in the case of the CrO_x based catalysts, the decrease of activity in the combustion of chlorinated VOCs in front of the combustion of non-chlorinated ones must thus be regarded as due to the

blocking of the active sites adsorbed by the reactant (chlorobenzene) or oxidized chlorinated intermediates.

The difference in resistance to deactivation of the various families of samples is clearly related to the difference in the chlorine atoms / transition metal atoms ratios detected by XPS and by the detection by ToF-SIMS of the occurrence of a formation of chlorides and oxychlorides species. The resistance of the VO_x based catalysts must be correlated to the absence of chlorine on their surface, the presence of less chlorine on CrO_x makes it less deactivated than MnO_x which presents more chlorine. However, the kind of chlorine at the surface of the catalyst, which is different in both cases, must also be considered as possibly influencing the resistance to deactivation of the catalyst. On the one hand, the deactivation of the CrO_x based catalyst is linked to the presence of chlorine as chlorobenzene or chlorinated intermediates of its oxidation on the surface of the catalyst but not on the production of chlorides or oxychlorides. On the other hand, the deactivation of the MnO_x based catalyst is related to the formation of chlorides and oxychlorides of manganese. Moreover, this formation of oxychlorides of manganese is linked to a progressive decrease, with time-on-stream (2-3h), of the catalyst activity up to a stable conversion. Döbber *et al.* [129] and Liu *et al.* [83] suppose that the active phase, at stable conversion, is the oxychloride of manganese but without proving the presence of such compounds. The formation of these chlorides and oxychlorides of manganese is now clearly demonstrated by our ToF-SIMS investigation.

2.3.3. Investigation of the reversibility of the deactivation mechanism

2.3.3.1. Reversibility tests

The CrO_x and MnO_x based catalysts are deactivated during the catalytic combustion of chlorinated VOCs. TMn-4 is the catalyst mostly affected by the presence of chlorine in the VOC that must be oxidized. Therefore, additional catalytic tests were achieved in order to further investigate the

mechanism of the deactivation occurring during the catalytic combustion of chlorinated VOCs and its possible reversibility. This should also permit to point out possible guidelines to regenerate the catalyst. Fig. 2-10 presents the evolution of the activity of the TMn-4 catalyst in the chlorobenzene conversion, as a function of time, during two reversibility tests. The regeneration was performed at 300 °C during 4 h under two different gaseous streams: i) pure He or ii) 20% of O₂ in He.

The first part of the test is equivalent for both tests independently of the subsequent regeneration. During the first 20 minutes, a slight decrease of the concentration of chlorobenzene at the outlet of the reactor was observed. This decrease of concentration corresponds to an apparent conversion as it is linked to the adsorption of chlorobenzene on the catalyst surface and not to its destruction. TMn-4 does not exhibit any catalytic activity neither at 100 °C nor at 150 °C. At the beginning of the stage at 200 °C, the catalyst converts roughly 20% of the chlorobenzene; however, the catalyst activity progressively decreases down to less than 10% of conversion. The same deactivation of the TMn-4 catalyst during time on stream occurs, even more severely, at 250 °C and 300 °C. At 300 °C, the catalyst activity starts roughly at 85% of conversion and stabilizes around 50% at the end of the 150 minutes of the temperature stage.

After regeneration under pure He, the catalyst starts to convert about 85% of the chlorobenzene. This value of conversion is equal to the conversion observed in the first part of the test at 300 °C before the regeneration step. After what, the conversion decreases very sharply to more or less 40%, value at which the catalyst remains for the last 9 hours of the catalytic test.

After the regeneration under 20% of O₂, the catalyst converts more than 98% of the chlorobenzene during approximately 40 minutes. This value of conversion is almost twice the conversion observed, at stability, in the first stage at 300 °C. Afterward, the catalyst undergoes a progressive deactivation with a corresponding decrease of the conversion down to

roughly 50%. The catalyst activity is stabilized at 50% for the 8 last hours of the catalytic test.

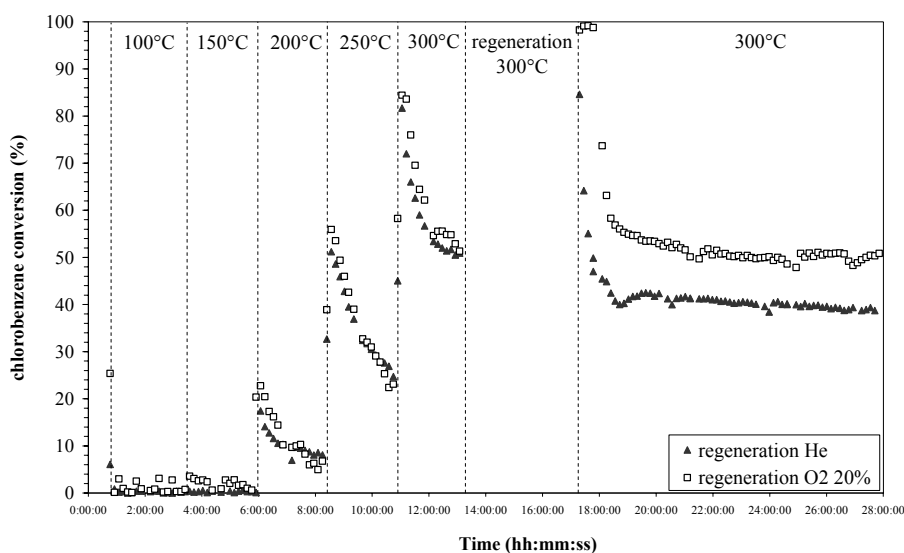


Fig. 2-10: Time evolution of the chlorobenzene conversion on the TMn-4 catalyst for the reversibility tests ($\square$ regeneration with 20% of O_2 , $\blacktriangle$ regeneration with pure He)

Both regenerations induce the restoration of the catalytic activity to a level of conversion at least equal to the beginning of the first stage at 300 °C. These catalytic results point out the reversibility of the deactivation provoked by chlorobenzene. Moreover, the stream containing 20% of O_2 induces a stronger regeneration than that observed in the case of pure He. This stronger regeneration brings the catalyst to a higher stage of activity. Indeed, after the regeneration under O_2 , the catalyst converts more chlorobenzene than at the beginning of the first step at 300 °C.

2.3.3.2. ToF-SIMS characterization

Table 2-3 presents the relative intensity of each chlorine containing fragment (notwithstanding isotopic speciation) detected by ToF-SIMS on the TMn-4 catalyst after a classical test (100-400 °C), before regeneration (after test 100-300 °C), after 4 hours of regeneration at 300 °C under He and after regeneration at 300 °C under a stream containing 20% of O₂ diluted in He. The sum of all relative intensities of the chlorine containing fragments represents 39.9% in the case of the post-mortem catalyst after a classical test (100-400 °C). The catalyst before regeneration, corresponding to an aborted classical test (100-300 °C), presents a huger relative intensity (45.6%) than after a classical test up to 400 °C (39.9%). This observation demonstrates that the chlorination of the catalyst is higher at 300 °C than at 400 °C. This fact could be explained by, at least, two hypotheses: i) the increase of the volatility of the chlorine containing compounds with temperature and ii) the increase of the oxidative strength of the catalytic stream with the increase of temperature. The increase of the volatility of the chlorine containing molecules (TiCl_yO_z, MnCl_x and MnCl_yO_z) with the temperature leading to a decrease of the amount of the chlorinated compounds on the surface of the support leading to the decrease of the relative intensity detected by ToF-SIMS. The more efficient activation of the oxygen in the regeneration stream with temperature would favor the reoxidation of the manganese phase. This reoxidation would reduce the amount of chlorinated species at the surface of the catalyst and therefore the amount of chlorinated species detected by ToF-SIMS.

For both regenerations (pure He and 20% O₂), the relative intensity of all the chlorine containing fragments decreases in front of the values before regeneration. For the value of the total concentration of chlorinated fragments, the value decreases from 45.6% before regeneration to 32.5% and 21.9%, respectively after pure He regeneration and O₂ regeneration. Another aspect concerns the fact that the regeneration under He clears away

73% of the compounds containing manganese and chlorine (MnCl_x and MnCl_yO_z) while the regeneration under O_2 retrieves 84% of the same compounds. This demonstrates that both regenerations retrieve the chlorides and oxychlorides of manganese preferentially to the other chlorine containing compounds, namely Cl^- and Cl_2 . Moreover, the entire set of ToF-SIMS results shows that the regeneration under O_2 retrieves more chlorine containing compounds than the regeneration under pure He.

2.3.3.3. Discussion

The specific test, performed to probe the reversibility of the deactivation undergone by the MnO_x based catalyst in the course of the total oxidation of chlorobenzene, proves that this phenomenon is reversible. These observations are in good agreement with the observations of Döbber *et al.* [129]. They prove that the deactivation of the MnO_x based catalyst during the combustion of chloromethane is reversible. The original catalyst activity is restored after regeneration with a stream of air or N_2 at temperatures above 300 °C. In our case, the regeneration is more efficient in the case of the stream containing 20% of O_2 than under a pure He stream. The ToF-SIMS measurements reveal that the regeneration is directly linked to the decrease of the concentration of chlorine containing compounds at the surface of the catalyst. Moreover, the retrieving of the compounds containing simultaneously manganese and chlorine is preferentially obtained in the course of the regeneration rather than other chlorinated fragments. Furthermore, the regeneration of the catalyst activity above its initial activity at 300 °C is explained by the retrieving of roughly 85% of the MnCl_x and MnCl_yO_z fragments by the stream containing 20% of O_2 . This regeneration cleans the catalyst surface from the chlorinated manganese compounds, revealing the original Mn_3O_4 active phase. Moreover, the presence of O_2 , as oxidant, in the regeneration stream favors the retrieving of a fully oxidized active phase.

All these results demonstrate that the deactivation of the MnO_x based catalysts in the course of the total oxidation of chlorinated VOCs is linked to the chlorination of the surface of the active phase leading to the formation of a layer of MnCl_yO_z and/or MnCl_x on the Mn_3O_4 active phase. The stable activity observed after the deactivation step is probably linked to the intrinsic activity of the layer of oxychloride and/or chloride of manganese. Furthermore the reversibility of the deactivation process is closely correlated to the reduction of the surface concentration in oxychloride and chlorides of manganese. The retrieving of the chlorinated species releases the original surface of the Mn_3O_4 active phase inducing the improvement of the catalyst up to its high activity observed in the case of the non-chlorinated VOCs.

2.4. Conclusions

We investigated the activity of catalysts containing different loadings of CrO_x or VO_x or MnO_x active phase in the course of the total oxidation of either benzene or chlorobenzene. The investigation of the activity in the combustion of benzene showed that the performances of the active phases increase within the series $\text{VO}_x < \text{CrO}_x < \text{MnO}_x$. The catalytic results combined with XRD, XPS and ToF-SIMS analyses demonstrate that the nature of the active phase in the most active catalysts strongly depends on the metal oxides: while CrO_x and VO_x work best as submonolayer and monolayer species respectively, MnO_x must be in a crystalline bulk Mn_3O_4 form to be active.

The catalytic results on chlorobenzene combined with XPS and ToF-SIMS measurements pointed out that the presence of the chlorine atom in the molecule of interest has a different impact dramatically depending on the transition metal oxides used. The very good resistance of the VO_x catalyst is correlated to the absence of chlorine on its surface after catalytic conversion of chlorobenzene. Conversely, a huge deactivation of MnO_x catalysts was found while CrO_x catalysts exhibited an intermediate behavior. Therefore,

the activity progresses within the series: $\text{MnO}_x < \text{CrO}_x < \text{VO}_x$ and the best catalyst for the combustion of chlorobenzene is a monolayer of VO_x . The extent of the deactivation of the CrO_x and MnO_x catalysts is dictated by the amount of chlorine on their surfaces. The huge deactivation of the MnO_x catalysts corresponds to the presence of 2 atoms of Cl per 7 atoms of Mn, while the weak deactivation of the CrO_x catalysts is linked to the presence of 1 atom of Cl only per 30 atoms of Cr. The deactivation is not only linked to the amount of chlorine on the surface but also to the kind of chlorine at the surface of the catalyst. On the one hand, the deactivation of the MnO_x based catalyst is correlated to the formation of a layer of chlorides and oxychlorides of manganese, which covers the active phase of Mn_3O_4 . After the covering of the active phase, the layer of chlorides or oxychlorides detected by ToF-SIMS becomes the phase that converts the chlorobenzene but at a lower rate than the oxide phases. A regeneration of the catalyst under pure He or under 20% of O_2 is efficient to remove the chlorinated manganese layer from the surface of the Mn_3O_4 active phase. Therefore, the deactivation by chlorination of the active phase is reversible. On the other hand, the deactivation of the CrO_x based catalyst is linked to the presence of chlorine as chlorobenzene or chlorinated intermediates of its oxidation that block the active sites of the catalyst.

CHAPTER 3 : IMPROVEMENT OF THE VO_x/TiO₂ FORMULATION BY ADDITION OF TRANSITION METAL OXIDES FOR THE TOTAL OXIDATION OF CHLORINATED VOCs

Abstract

This chapter reports a systematic investigation of the effect of adding secondary phases on the activity of VO_x/TiO₂ based catalysts in the course of the total oxidation of benzene and chlorobenzene as model molecules for dioxins. The catalysts consisted in binary formulations VO_x-secondary phases (CrO_x, MnO_x, SnO_x, WO_x, NbO_x, TaO_x, MoO_x, ZrO_x or BiO_x). Three impregnation orders of both phases were investigated (1-2, 2-1 and 1,2 both together). Catalysts synthesized in a unique step demonstrated the best activities for the oxidation of benzene. Moreover, WO_x and MoO_x phases induce a synergetic effect with VO_x. XPS demonstrated that this effect resides in the absence of mutual spreading between both phases, preventing the VO_x coverage by the secondary phase and promoting the stabilization of contacts VO_x-TiO₂. The investigation of different loading ratios WO_x/VO_x and MoO_x/VO_x on the total oxidation of chlorobenzene was performed on binary formulations supported on classical TiO₂ or on sulfated TiO₂. For both supports and both binary formulations, the optimum ratio is equal to 1. This ratio is the highest that prevents the presence of crystallites of MoO_x or

WO_x, which seems to be detrimental for the catalyst activity. Moreover, the resistance of the formulations in front of the chlorinated VOCs and the better activity of the formulations supported on sulfated TiO₂ were proven. The activation effects brought by WO_x, MoO_x and by sulfated TiO₂ are linked to the increase of the number of Brønsted acid sites as proven by FTIR with adsorbed pyridine. Moreover, the strong Lewis sites present on the sulfated TiO₂ promote the dispersion of the active and secondary phases. Furthermore, these investigations pointed out the role play by Brønsted sites in the adsorption of VOCs and chlorinated VOCs aromatics.

3.1. Introduction

In order to fulfill the Kyoto protocol, it is now crucial to promote the use of energy production systems that can significantly reduce the CO₂ emissions. Therefore, the energy efficient systems such as combined heat and power (CHP) systems and biomass-fed cogeneration units are considered for a wider application in the future [5]. In parallel, incineration of wastes is expected to be more appealing as it reduces the mass and volume of wastes and produces energy. However, these two combustion processes have the huge drawback of producing many organic products of incomplete combustion including Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzo Furans (PCDFs) also named dioxins. These compounds are very toxic, carcinogenic and environmentally persistent organic pollutants [11-13]. Therefore, environmental legislation has imposed strict emission limits in order to fix the problem of the atmospheric emission of these Chlorinated Volatile Organic Compounds (Cl-VOCs). The catalytic destruction of chlorinated VOC to CO_x, H₂O and HCl/Cl₂ appears very promising in this context. Indeed, it stands for a wide range of pollutants concentrations, exhibits an excellent selectivity toward the formation of harmless products and it operates at relatively low destruction temperature [33,35,37,38].

Chapter 1 spotlighted the very good activity of VO_x, CrO_x and MnO_x based catalysts in the course of the total oxidation of chlorine-free aromatic VOC (benzene). These formulations supported on TiO₂ convert efficiently benzene at temperatures as low as 250-300 °C [130]. Moreover, we pointed out the positive effect of supporting VO_x on a sulfated TiO₂. In Chapter 2, the subsequent investigation of these formulations in the course of the total oxidation of a chlorinated VOC (chlorobenzene) pointed out the perfect resistance of the VO_x based catalysts in the presence of chlorine while MnO_x based catalysts deeply deactivated and CrO_x based ones exhibited an intermediate behavior [104]. These studies clearly pointed out the VO_x supported on TiO₂ catalysts as the most promising formulation for the total oxidation of chlorinated VOCs.

In the case of the SCR of NO_x with NH₃, VO_x/TiO₂ had their performances improved when “upgraded” to VO_x-WO_x/TiO₂ or VO_x-MoO_x/TiO₂ [69,87,93,94]. Based on the fact that the good catalysts for SCR are also efficient in the oxidation of chlorinated VOCs, several authors suspected that the addition of WO_x or MoO_x would also be beneficial for the performances of VO_x/TiO₂ in the chlorinated VOCs oxidation [52,87-90]. This was indeed proven experimentally [13,28,34,49-52,70-72].

Nevertheless, the systematic investigation of transition metal oxides other than WO_x and MoO_x as secondary phases was never reported for the improvement of the combustion activity of the VO_x active phase supported on TiO₂. Therefore, we investigated the catalytic activity of binary catalysts containing VO_x as the main active phase and a secondary phase of transition metal oxide (CrO_x, MnO_x, SnO_x, WO_x, NbO_x, TaO_x, MoO_x, ZrO_x and BiO_x) both impregnated on TiO₂. In a first step we investigated the total combustion of benzene on binary formulations characterized by an identical loading in active and secondary phases, namely 0.75 theoretical monolayer. In this part we paid attention to the influence of the impregnation order on the catalytic performances. Therefore, three impregnation protocols were followed: i) impregnation of the VO_x phase precursor and calcination

followed by the impregnation of the secondary phase precursor and calcination, ii) impregnation of the secondary phase precursor and calcination followed by the impregnation of the VO_x phase precursor and calcination and iii) impregnation of both phase precursors simultaneously and calcination. The difference of performances was correlated with the tendency of each phase to spread on the support accordingly to the impregnation protocol. This tendency was evaluated by XPS and XRD.

In a second step, we concentrated on the two best binary formulations prepared by the best impregnation protocol and studied the influence of the secondary phase loading on the performances in the reaction of total oxidation of chlorinated VOCs (chlorobenzene). Therefore, fixing the loading of VO_x at 0.75 theoretical monolayer, we synthesized various formulations characterized by ratios of loading secondary phases / VO_x of 0, 0.3, 1, 2, 3 and 6. This was done on the classical TiO₂ P25 from Degussa but also on a sulfated TiO₂. This investigation brought information on i) the resistance of the formulations in front of the presence of chlorine in the molecule that must be oxidized, ii) the best ratio of loading secondary phases / VO_x and iii) the interest of supporting the binary formulations on a sulfated TiO₂. The catalytic activity of these formulations was correlated with XRD and ICP-AES measurements.

Finally, in order to have a better understanding of the mechanism of the activation brought by the secondary phases and of the reasons dictating the optimal performances of one of the two supports, we investigated the acidity of the catalyst. As suggested by Larrubia *et al.* [68], the acidity of the catalyst could indeed play a crucial role in the adsorption of the VOCs on the surface of the catalyst. This investigation of the catalysts acidity was done by FTIR analysis with adsorbed pyridine on a series of selected catalysts. Moreover, the strength of the Lewis and Brønsted sites present at the surface of our catalysts was assessed by performing the pyridine desorption at increasing temperature.

3.2. Experimental and methods

3.2.1. Catalysts preparation

Catalysts are supported on two different TiO₂ supports Degussa P25 and Millennium PC100. The active phase is VO_x (V) and the secondary phases (X) are WO_x (W), MoO_x (M), NbO_x (N), CrO_x (C), TaO_x (T), MnO_x (Mn), SnO_x (S), ZrO_x (Z) or BiO_x (B).

Four groups of catalysts were synthesized (see Fig. 3-1). The first group corresponds to reference catalysts containing only one secondary phase loaded at 0.75 monolayer on TiO₂ P25 (catalysts denoted TX). The second group is subdivided into three families corresponding to three different synthesis pathways varying by the impregnation order. The catalysts are supported on TiO₂ P25. They contain the VO_x active phase loaded at 0.75 theoretical monolayer and a secondary phase (transition metal oxides) at the same loading (0.75 theoretical monolayer). The first and second families correspond to a synthesis pathway in two impregnation steps. In the case of the first family (catalysts denoted TV-X), the catalyst synthesis proceeds following these steps: i) impregnation of the VO_x phase precursor followed by drying and a calcination step and ii) impregnation of the secondary phase precursor followed by drying and a calcination step. In the case of the second family (catalysts denoted TX-V), the synthesis pathway is the following: i) impregnation of the secondary phase precursor followed by drying and a calcination step and ii) impregnation of the VO_x phase precursor followed by drying and a calcination step. The third family (catalysts denoted TVX) corresponds to a synthesis in a unique impregnation step: the VO_x and the secondary phase precursors were impregnated simultaneously followed by drying and a calcination step. The abbreviations of all catalysts from families 1 and 2 are presented in Table 3-1.

Table 3-1: Abbreviations of the catalysts from families TX, TV-X, TX-V and TVX

	WO _x	MoO _x	NbO _x	CrO _x	TaO _x	MnO _x	SnO _x	ZrO _x	BiO _x
TX	TW	TM	TN	TC	TT	TMn	TS	TZ	TB
TV-X	TV-W	TV-M	TV-N	TV-C	TV-T	TV-Mn	TV-S	TV-Z	TV-B
TX-V	TW-V	TM-V	TN-V	TC-V	TT-V	TMn-V	TS-V	TZ-V	TB-V
TVX	TVW	TVM	TVN	TVC	TVT	TVMn	TVS	TVZ	TVB

The third group is composed of four series of catalysts: two supported on TiO₂ P25 (T) with formulations VO_x-WO_x (VW) or VO_x-MoO_x (VM) and two supported on TiO₂-SO₄ PC100 (Ts) containing the same combinations. For all catalysts, the amount of VO_x phases was fixed at 0.75 monolayer and the impregnation of the two oxides was performed in a unique step. Each series contains six catalysts differing by the ratio of the loadings in secondary phase and in VO_x. The investigated ratios (calculated on the basis of the number of theoretical phase involved versus the number of theoretical monolayer VO_x (ML) involved namely 0.75) are 0 (reference, catalyst containing only VO_x and no MoO_x or WO_x), 0.3 (0.25 ML of MoO_x or WO_x and 0.75 ML of VO_x), 1 (0.75 ML of MoO_x or WO_x and 0.75 ML of VO_x), 2 (1.5 ML of MoO_x or WO_x and 0.75 ML of VO_x), 3 (2.25 ML of MoO_x or WO_x and 0.75 ML of VO_x) and 6 (4.5 ML of MoO_x or WO_x and 0.75 ML of VO_x). The obtained catalysts are hereunder denoted TVX-Y or TsVX-Y with X being W in the case of catalysts having WO_x as secondary phase or M in the case of catalysts having MoO_x, and Y being the ratio of loadings. *E.g.* the catalyst containing 0.25 monolayer of MoO_x and 0.75 monolayer of VO_x is denoted TVM-0.3 while the catalyst containing 1.5 monolayer of WO_x and 0.75 monolayer of VO_x is denoted TVW-2. The fourth group is composed of the corresponding reference catalysts synthesized with only the secondary phases loaded at the corresponding concentrations, namely 0.25, 0.75, 1.5, 2.25 and 4.5 theoretical monolayers. Fig. 3-1 gives an overview of the notations of the catalysts from the four groups and Table 3-2 presents the entire set of catalysts from groups 3 and 4 and gives their abbreviations used

through this chapter. All syntheses were performed following the experimental protocol presented in 1.2.1.

Table 3-2: Abbreviations of the catalysts from families TW-Y, TM-Y, TVW-Y, TVM-Y, TsVW-Y and TsVM-Y

			Second phase / VO _x phase ratio (ML/ML)		
Support	Active phase	Second phase	0	0.3	1
TiO₂ P25	VO _x	WO _x	TVW	TVW-0.3	TVW-1
	-	WO _x	-	TW-0.3	TW-1
	VO _x	MoO _x	TVM	TVM-0.3	TVM-1
	-	MoO _x	-	TM-0.3	TM-1
TiO₂-s PC100	VO _x	WO _x	TsVW	TsVW-0.3	TsVW-1
	VO _x	MoO _x	TsVM	TsVM-0.3	TsVM-1

			Second phase / VO _x phase ratio (ML/ML)		
Support	Active phase	Second phase	2	3	6
TiO₂ P25	VO _x	WO _x	TVW-2	TVW-3	TVW-6
	-	WO _x	TW-2	TW-3	TW-6
	VO _x	MoO _x	TVM-2	TVM-3	TVM-6
	-	MoO _x	TM-2	TM-3	TM-6
TiO₂-s PC100	VO _x	WO _x	TsVW-2	TsVW-3	TsVW-6
	VO _x	MoO _x	TsVM-2	TsVM-3	TsVM-6

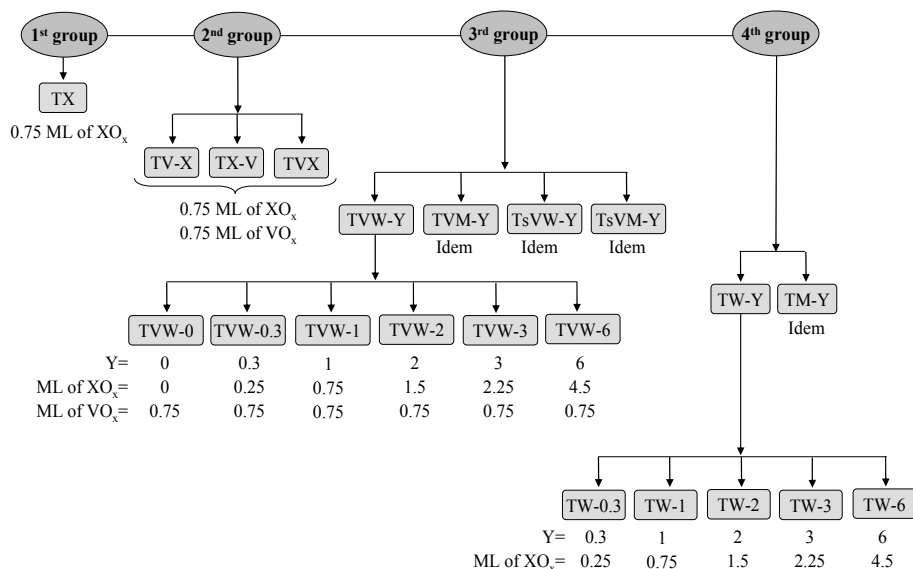


Fig. 3-1: Overview of the abbreviations of the catalysts

3.2.2. Catalytic tests

The tests on catalysts of the first and second groups were performed in a conventional fixed-bed reactor system following the experimental method exposed in 1.2.2. In the case of the catalysts of the second group, we calculated the theoretical activities of the catalysts containing two oxides based on the activity measured for the catalysts of the first group. For TVX (or TV-X or TX-V), this theoretical activity thus corresponds to the sum of the activities of TV and TX, limited to 100% if the sum surpasses 100% of conversion. Based on the theoretical conversions at each temperature, theoretical light-off curves were drawn. These theoretical curves are denoted as TV+TX on the figures.

The third group of catalysts was tested in a fixed-bed micro-reactor (PID Eng&Tech S.L, Madrid - Spain) following the procedure presented in 2.2.2.

and 2.2.2.1. The reaction was run at 200 and 250 °C for 150 min at each temperature.

For both kinds of tests, analysis of reactants and products was continuously conducted as presented in 2.2.2.

3.2.3. Characterization

The specific surface area, porous volume and pore size distribution analyses were performed as exposed in the protocol presented in 1.2.3.

X-ray diffraction (XRD) patterns were recorded following the experimental protocol presented in 2.2.3.

X-ray photoelectron spectroscopy (XPS) was performed following the experimental procedure exposed in 1.2.3. Based on the XPS analysis, we estimated the V/Ti, X/Ti and V/X surface ratios that correspond to the ratio of the atomic concentration detected on the surface. For example, the V/Ti ratio is estimated by the formula:

$$V / Ti = \frac{\text{atomic concentration of V (\%)}}{\text{atomic concentration of Ti (\%)}}$$

Inductively Coupled Plasma-Atomic Emission Spectrometry measurements (ICP-AES) allowed estimating the weight percentage of V, W, Mo and Ti. These measurements were performed on an Iris Advantage apparatus from Jarrell Ash Corporation.

Fourier Transformed Infra Red spectra of pre-adsorbed pyridine (FTIR-pyridine) were recorded using an Equinox IFS55 spectrometer (Brücker) equipped with a DTGS detector. The absorption spectra were obtained by the recording of 100 scans between 370 and 4400 cm⁻¹ with a resolution of 4 cm⁻¹. The powders were pressed into self-supporting disks (20 mg, 13 mm

diameter), placed in an IR cell, and heated under a dry stream of 60 ml min⁻¹ of 5% O₂ in He at 250 °C for 2 h before analysis. This special pre-treatment is used in order to avoid the reduction of the catalyst under vacuum or He at high temperature. After cooling to room temperature, the IR cell is evacuated and the spectrum of the powder is recorded. Then, the sample is exposed to 50 mbar (5000 Pa) of pyridine for 30 min. Spectra were recorded after evacuation ($7 \cdot 10^{-5}$ Torr - $9.33 \cdot 10^{-3}$ Pa) for 1 h at room temperature, 200 °C and 250 °C. The amount of Brønsted and Lewis sites is determined by the integration of the area of the peaks at 1537 and 1446 cm⁻¹, corresponding respectively to pyridine adsorbed on Brønsted sites and Lewis sites. The amount of acid sites is given in arbitrary unit (A.U.).

3.3. Results and discussion

3.3.1. Investigation of the effect brought by a secondary phase

3.3.1.1. Conversion of benzene on the TX family (1st group)

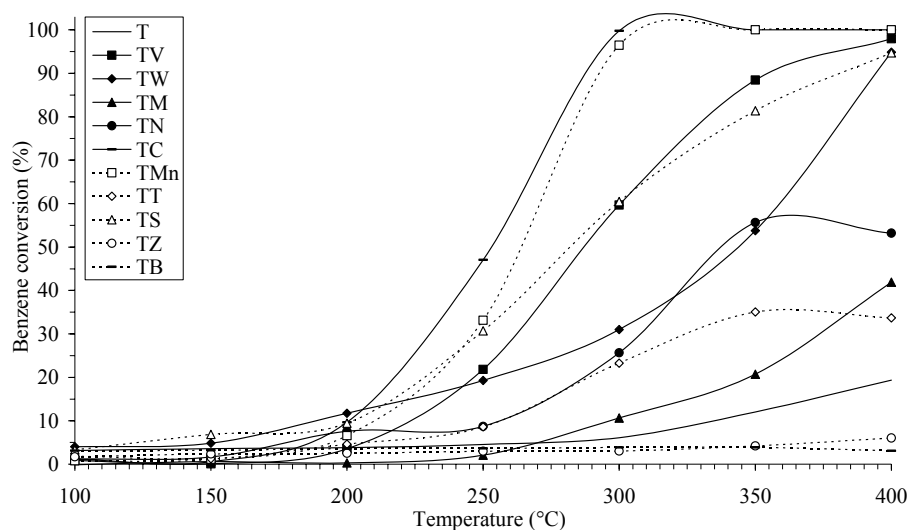


Fig. 3-2: Benzene light-off curves on the TX family

Fig. 3-2 presents the light-off curves of the 10 single-phase catalysts supported on TiO₂ in the course of the total combustion of benzene (Fig. 3-2 is identical to Fig. 1-2). This figure is presented here in order to serve as reference for comparison with the binary catalysts containing the active phase and a secondary phase.

3.3.1.2. Conversion of benzene on TV-X family (2nd group-VO_x then secondary phases)

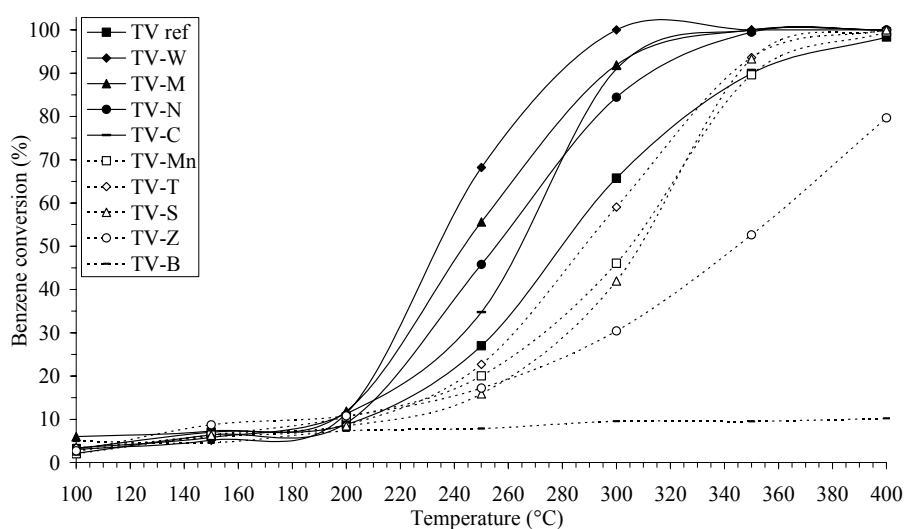


Fig. 3-3: Benzene light-off curves on the TV-X family

Fig. 3-3 presents the light-off curves of the 10 catalysts of the TV-X family in the combustion of benzene. The reference catalyst (TV ref), corresponding to a unique synthesis of the VO_x phase followed by a second impregnation without precursor, converts 27, 66, 90 and 98% of benzene at 250, 300, 350 and 400 °C, respectively. Based on the light-off curve and the T₅₀ of this reference catalyst, the catalysts are gathered into two groups. These groups differ by the kind of influence of the secondary phase on the activity of the VO_x based catalysts. On the one hand, for the series of

catalysts TV-T, TV-Mn, TV-S, TV-Z and TV-B, the activity is lower compared to the activity of the reference catalyst (TV ref). Thus, the presence of the secondary phases TaO_x, MnO_x, SnO_x, ZrO_x or BiO_x clearly has a negative impact on the VO_x performances. On the other hand, for the series TV-C, TV-N, TV-M and TV-W, the activity of the catalysts is better than that of TV-ref. The VO_x active phase thus clearly benefits from the presence of the CrO_x, NbO_x, MoO_x and WO_x secondary phases. Among the beneficial secondary phases, MoO_x and WO_x induce more than a doubling of the catalytic performances of TV-ref. Indeed, the TV-M and TV-W convert 56 and 68% of benzene at 250 °C instead of 27% for the reference catalyst (TV ref).

3.3.1.3. Conversion of benzene on TX-V family (2nd group-secondary phase then VO_x)

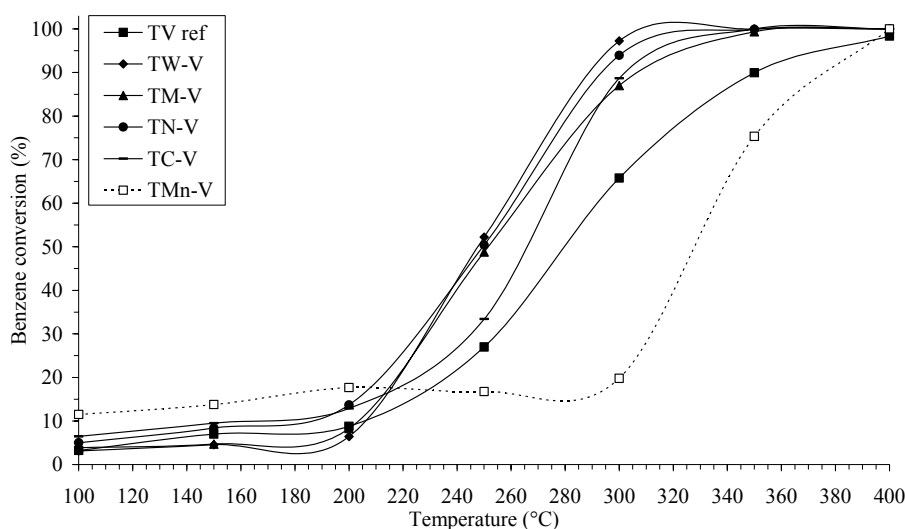


Fig. 3-4: Benzene light-off curves on the TX-V family

Based on the results exhibited by the catalysts of the TV-X family, only the catalysts containing secondary phases that improve the activity of the VO_x phase were further investigated. MnO_x containing catalysts were also

investigated as this phase has proven to be very active when used as unique phase on the catalyst as shown in 3.3.1.1. and [104].

Fig. 3-4 presents the benzene light-off curves of 5 selected catalysts of the TX-V family. The catalytic performances of the TMn-V formulation are lower than those of the TV ref catalyst. Consequently, as already observed for the TV-Mn catalyst, the presence of the MnO_x phase on the TMn-V catalyst induces a decrease of activity of the VO_x active phase, and this, independently of the order of impregnation. At the opposite, the presence of the CrO_x , NbO_x , MoO_x and WO_x secondary phases induces a positive effect on the performances of the VO_x active phase. TC-V induces a slighter improvement than the three other formulations. At 250 °C, the bests formulations TN-V, TM-V and TW-V convert 50, 49 and 52%, respectively, instead of 27% for the TV ref catalyst. The performances of the best catalysts from the TX-V family differ from the catalytic activity of the same formulations belonging to the TV-X family by two major facts: i) the variation of activities between formulations are lower in the case of TX-V than of TV-X and ii) the catalytic performances are weaker in the case of TX-V than of TV-X.

3.3.1.4. Conversion of benzene on TVX family (2nd group-simultaneous impregnation)

Fig. 3-5 presents the benzene light-off curves for the five selected formulations. The presence of MnO_x in the TVMn formulation induces a decrease of the catalytic performances compared to the TV ref. The negative effect of MnO_x has already been observed in the case of TV-Mn and TMn-V. However, the extent of the activity decrease is smaller in the case of simultaneous impregnation or the VO_x precursors. At the opposite, the four other secondary phases bring an improvement of the catalyst ability to oxidize benzene efficiently. Based on the benzene conversion at 250 °C, the enhancement of activity increases within the series TVC, TVN, TVM and TVW. Indeed, the binary formulations containing CrO_x (TVC), NbO_x

(TVN), MoO_x (TVM) and WO_x (TVW) convert, respectively, 44, 59, 67 and 72% of the benzene charge at 250 °C. As a comparison, TV-ref converts only 27% of the benzene at this temperature.

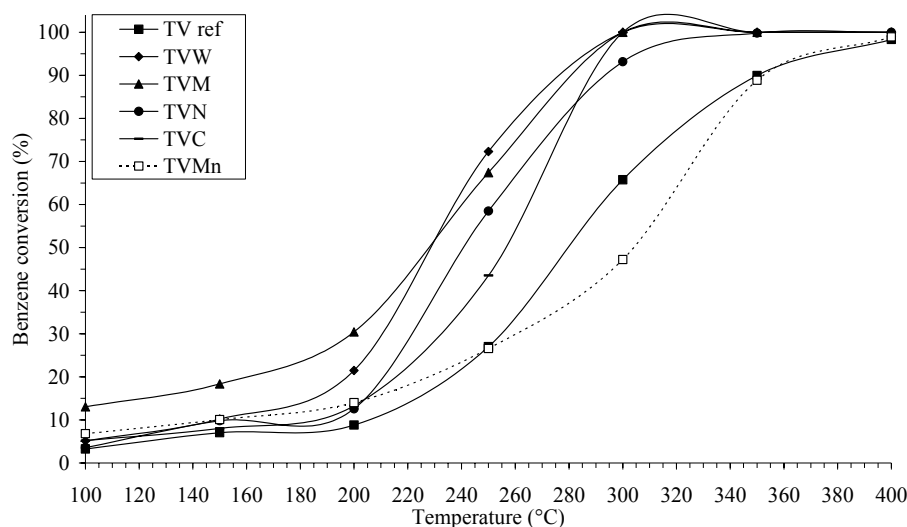


Fig. 3-5: Benzene light-off curves on the TVX family

The TVX catalysts exhibit a dispersion of the catalytic activities close to those observed in the case of the TV-X family and larger than those observed in the case of the TX-V family. In addition, the catalytic performances of the TVX catalysts are better than those observed in the case of both families of catalysts synthesized in two steps (TV-X and TX-V).

3.3.1.5. XPS characterization

Different authors developed quantitative models for prediction and interpretation of surface atomic ratio of a binary system of a phase A at the surface of a phase B. These models were developed by Moulijn *et al.* [110], Fung *et al.* [111], Defosse *et al.* [112], Kuipers *et al.* [113] and Sheng *et al.* [114]. The difference between these models mainly resides in the

assumption of the kind of arrangements used by phase A on the surface of phase B (layers, shell structure, small blocks, etc...). Nevertheless, in the case of a constant concentration of phase A, all these models lead to the same conclusion: an increase of the phase A / support S ratio indicates an improvement of the spreading of phase A on the surface of support S, which could go to the formation of a uniform monolayer. At the opposite, a decrease of the phase A / support S ratio indicates a decrease of the homogeneity of the coverage of the surface of S by phase A, which could lead to the formation of separate blocks (crystallites) of A almost independent of support S. This theory can be implemented to a system with three components: the active phase VO_x (V), the secondary phase (X) and the TiO₂ support (Ti). In our case, all the catalysts discussed present constant loadings of V and X on the surface of Ti. Therefore, an increase of the V/Ti or X/Ti ratio can be correlated to a better spreading of the selected phase (V or X) on the surface of the support. Respectively, a decrease of the V/Ti or X/Ti ratio can be correlated to a poorer spreading of V or X on the support. However, such a decrease of the V/Ti or X/Ti ratio could also be related to a more pronounced coverage of the selected phase (V or X) by the other one (X or V), implying that the ratios should be regarded with much care. Table 3-3 presents the surface atomic concentrations (V, X, Ti) determined by XPS and the ratios (V/Ti, X/Ti and V/X). This Table also shows the progressive ranking of the ratios V/Ti, X/Ti and V/X for the different synthesis pathways. The analysis of these rankings allows to construct good pictures of the surface of the different formulations.

The five combinations VO_x-XO_x exhibit three different behaviors in terms of XPS observations. The first group contains VO_x-MoO_x and VO_x-WO_x based catalysts. In this group, the V/Ti ratio progresses within the series: TX-V < TVX < TV-X. The X/Ti ratio increases through the series: TVX < TV-X < TX-V. Moreover, the TX-V formulation shows the lowest V/X ratio. The highest value of V/Ti in the case of the TV-X synthesis pathway suggests that i) VO_x spreads completely on the bare TiO₂ support and ii) VO_x is

poorly covered by the secondary phases. The fact that TX-V formulation shows the lowest V/Ti ratio, the lowest V/X ratio and the highest X/Ti ratio points out that i) the presence of the secondary phase prevents the good dispersion of VO_x on the support, ii) the VO_x phase does not spread on the secondary phase (MoO_x and WO_x) and iii) the secondary phase spreads better on the bare surface. Moreover, the TVX formulation, showing an intermediate value of V/Ti, an intermediate value of V/X and the lowest value of X/Ti, points out that the spreading of the VO_x phase on TiO₂ is better than the spreading of the MoO_x and WO_x phases. As a conclusion, this group is characterized by i) a marked tendency of all phases (VO_x, MoO_x and WO_x) to spread on the support, ii) the better spreading of VO_x than of MoO_x and WO_x on TiO₂ and iii) the near absence of spreading of VO_x on the secondary phases or of the secondary phase on VO_x. This absence of mutual spreading for VO_x and the secondary phases leads to a marked tendency to have more poorly dispersed phases in the case of samples prepared through an impregnation in two steps, whatever the order of impregnation.

The second group includes CrO_x and NbO_x containing catalysts. The TX-V synthesis pathway leads to the highest value of V/Ti and V/X and the lowest value of X/Ti. These observations reveal that VO_x spreads well on the surface of pre-existing CrO_x or NbO_x layers. Moreover, the high values of X/Ti in both cases of TVX and TV-X samples points out the equal tendency of the secondary phases to spread on both the support and the VO_x phase. As a conclusion, this group is characterized by i) the good spreading of both phases (VO_x and secondary phases) on the support and ii) a mutual spreading of both phases, VO_x and secondary phases, on each other.

The third group corresponds to formulations containing simultaneously VO_x and MnO_x phases. In this case, the three synthesis pathways lead to, more or less, the same values of V/Ti, thus pointing out that the VO_x spreading is independent on the impregnation order. This observation is linked to the poor spreading of MnO_x on the TiO₂ support, which leaves in all cases the

support almost uncovered, as demonstrated in Chapter 2 and [104], for VO_x. However, the secondary phase spreading is the best when the MnO_x layer is supported first and is the worst when the synthesis is based on a simultaneous impregnation. As a conclusion, this last group is characterized by i) a very weak spreading of the secondary phase on the support and ii) a good spreading of the VO_x on the TiO₂ support independently of the impregnation order.

Table 3-3: XPS atomic concentrations, XPS ratios and classification of the formulations depending on the XPS ratios

		Ti	V	X	<i>V/Ti</i>	<i>X/Ti</i>	<i>V/X</i>
VO_x	TV	17.36	1.94	-	<i>0.112</i>	-	-
MoO_x	TV-M	17.23	1.64	3.14	<i>0.095</i>	<i>0.182</i>	<i>0.523</i>
	TM-V	16.83	1.21	3.17	<i>0.072</i>	<i>0.188</i>	<i>0.381</i>
	TVM	17.44	1.53	2.08	<i>0.088</i>	<i>0.119</i>	<i>0.736</i>
WO_x	TV-W	15.86	1.71	2.28	<i>0.108</i>	<i>0.144</i>	<i>0.750</i>
	TW-V	16.13	1.47	2.50	<i>0.091</i>	<i>0.155</i>	<i>0.586</i>
	TVW	15.28	1.54	2.18	<i>0.101</i>	<i>0.143</i>	<i>0.706</i>
CrO_x	TV-C	14.25	1.89	3.98	<i>0.133</i>	<i>0.280</i>	<i>0.475</i>
	TC-V	14.17	1.97	3.95	<i>0.139</i>	<i>0.279</i>	<i>0.499</i>
	TVC	15.15	1.78	4.37	<i>0.117</i>	<i>0.288</i>	<i>0.407</i>
NbO_x	TV-N	15.74	1.92	2.29	<i>0.122</i>	<i>0.145</i>	<i>0.838</i>
	TN-V	15.43	2.82	1.85	<i>0.183</i>	<i>0.120</i>	<i>1.520</i>
	TVN	15.11	2.17	2.18	<i>0.144</i>	<i>0.144</i>	<i>0.995</i>
MnO_x	TV-Mn	17.12	2.17	2.41	<i>0.127</i>	<i>0.141</i>	<i>0.900</i>
	TMn-V	16.75	2.15	2.84	<i>0.128</i>	<i>0.170</i>	<i>0.757</i>
	TVMn	17.51	2.15	2.09	<i>0.123</i>	<i>0.119</i>	<i>1.029</i>

		V/Ti	X/Ti	V/X
VO _x	TV	-	-	-
	TV-M			
MoO _x	TM-V	TX-V<TVX<TV-X	TVX<TV-X<TX-V	TX-V<TV-X<TVX
	TVM			
	TV-W			
WO _x	TW-V	TX-V<TVX<TV-X	TVX<TV-X<TX-V	TX-V<TVX<TV-X
	TVW			
	TV-C			
CrO _x	TC-V	TVX<TV-X<TX-V	TX-V<TV-X<TVX	TVX<TV-X<TX-V
	TVC			
	TV-N			
NbO _x	TN-V	TV-X<TVX<TX-V	TX-V<TVX<TV-X	TV-X<TVX<TX-V
	TVN			
	TV-Mn			
MnO _x	TMn-V	TVX<TV-X<TX-V	TVX<TV-X<TX-V	TX-V<TV-X<TVX
	TVMn			

3.3.1.6. XRD characterization

The XRD analysis points out, for all the formulations, the absence of crystallites of VO_x phase or of secondary oxide phase. The only exceptions are the samples containing WO_x for which WO₃ crystallites are observed. The fast formation of crystallites of WO₃ supported on TiO₂ was observed at a theoretical loading as low as 0.75 monolayer in Chapter 1 at point 1.3.2. The relative intensity of the diffraction peaks corresponding to WO₃ increases within the series: TW < TW-V < TV-W < TVW. This reveals that the presence of VO_x in the catalyst formulation favors the crystallization of WO_x as WO₃. Moreover, the presence of a pre-existing VO_x layer further favors the formation of WO₃ crystallites. Finally, the simultaneous impregnation of VO_x and WO_x induces the greatest production of WO₃ crystallites.

3.3.1.7. *Specific surface area measurment*

The analyses of the TiO₂ support, TV and TV-X, TX-V, TVX catalysts before and after catalytic tests were performed in order to investigate the possible variation of the specific surface area. These measurements demonstrated that i) all fresh catalysts have a specific surface area which is not significantly different from the fresh support surface area and ii) the catalytic test does not induce any significant modification of the surface area.

3.3.1.8. *Discussion*

On the one hand, the presence of secondary phases like TaO_x, MnO_x, SnO_x, ZrO_x or BiO_x has a negative impact on the VO_x performances. On the other hand, the addition of WO_x, MoO_x, CrO_x or NbO_x on the VO_x based catalyst induces an improvement of the activity independently of the synthesis pathway and the impregnation order. Moreover, the WO_x and MnO_x secondary phases induce the hugest activation effect on the VO_x phase. Thus, the addition of a secondary phase on the VO_x/TiO₂ formulation brings a positive or negative effect depending strongly on the nature of the secondary phases. At the opposite, the synthesis pathway does not modify the kind of influence (positive or negative). Amiridis *et al.* [50] and Economidis *et al.* [139] observed, in the case of the SCR reaction, the same kind of increase or decrease of the performances of the VO_x/TiO₂ formulation when it is doped with transition metal oxides. They observed a decrease of the performances in the case of the introduction of SnO_x or MnO_x in the catalyst formulation. At the opposite, they showed an activity improvement in the case of the addition of NbO_x, WO_x or MoO_x in the catalyst formulation. Those influences are the same as the ones observed here with the same kind of formulations but on another reaction: the total oxidation of benzene.

To go further in the understanding of the effect brought by the addition of the secondary phases to the VO_x phase, theoretical light-off curves (TV+TX) were drawn. These curves are used to understand whether the improvement of the catalyst activity brought by the secondary phase is due to a simple addition of activities of each phase reached individually or whether the improvement or deactivation is due to an interaction between phases. These interactions could lead to modifications of the properties and of the activity of the VO_x phase. Fig. 3-6, 3-7 and 3-8 present the activity of TV, TX, TV-X, TX-V, TVX and the theoretical curve TV+TX in the case of MnO_x, WO_x and MoO_x as secondary phase.

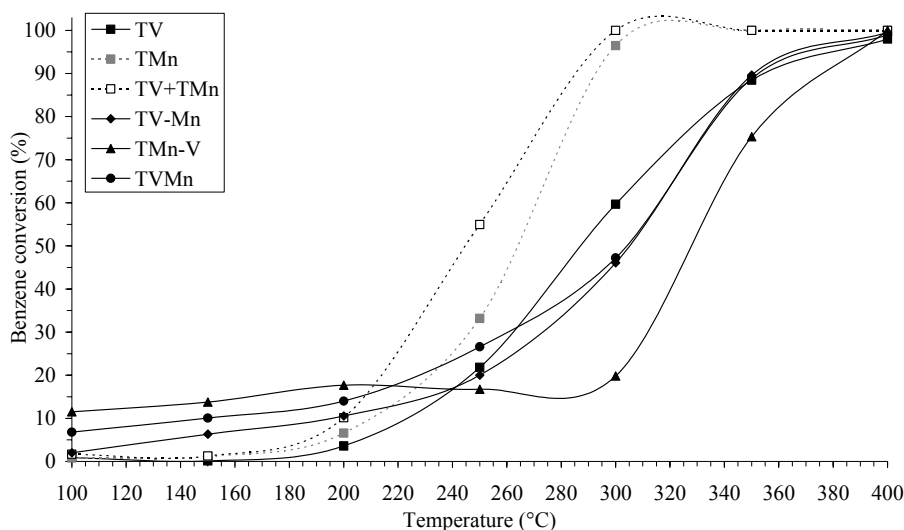


Fig. 3-6: Benzene light-off curves on TV, TMn, TV+TMn, TV-Mn, TMn-V and TVMn

Fig. 3-6 reveals, as already mentioned, that the presence of MnO_x induces a decrease of the catalyst activity compared to the TV reference. Moreover, this figure points out that the activities of the binary formulations are lower than the theoretical activity TV+TMn. Identically, TaO_x, SnO_x, ZrO_x and BiO_x secondary phases induce a decrease of the conversion in front of the

TV reference catalyst and of the theoretical light-off curves (TV+TX). Concerning CrO_x and NbO_x secondary phases, they induce an improvement of the activity of the binary catalysts in front of the TV reference, but they lead to a lower conversion of benzene than the theoretical activity predicted (TV+TX). In the case of these secondary phases, the improvement of the activity is due to partial summation of the effect brought independently by the VO_x and the secondary phases. It is thus clear that in these cases, there is no constructive but a slight destructive interaction between the active phase and the secondary phases. At the opposite, the introduction of MoO_x or WO_x secondary phases in the catalyst formulation induces an improvement of the catalyst activity supposing the theoretical activity predicted, as shown in Fig. 3-7 and 3-8.

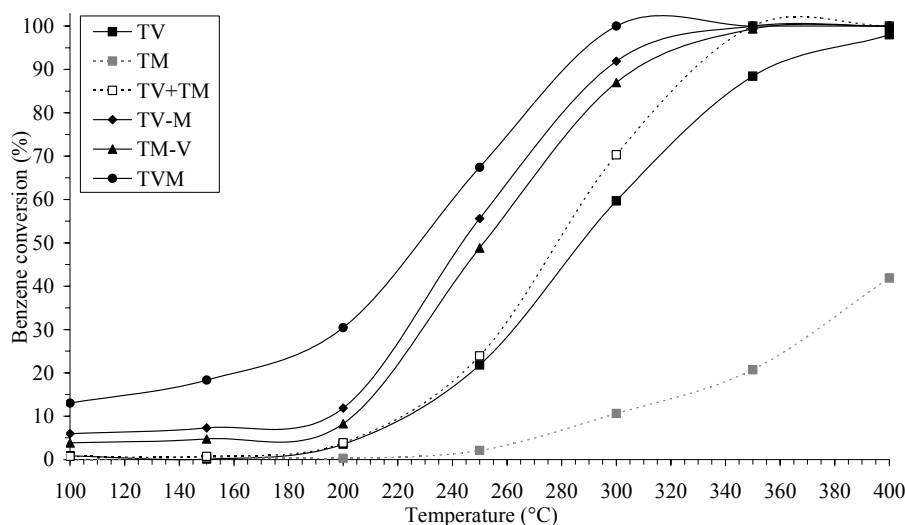


Fig. 3-7: Benzene light-off curves of TV, TM, TV+TM, TV-M, TM-V and TVM

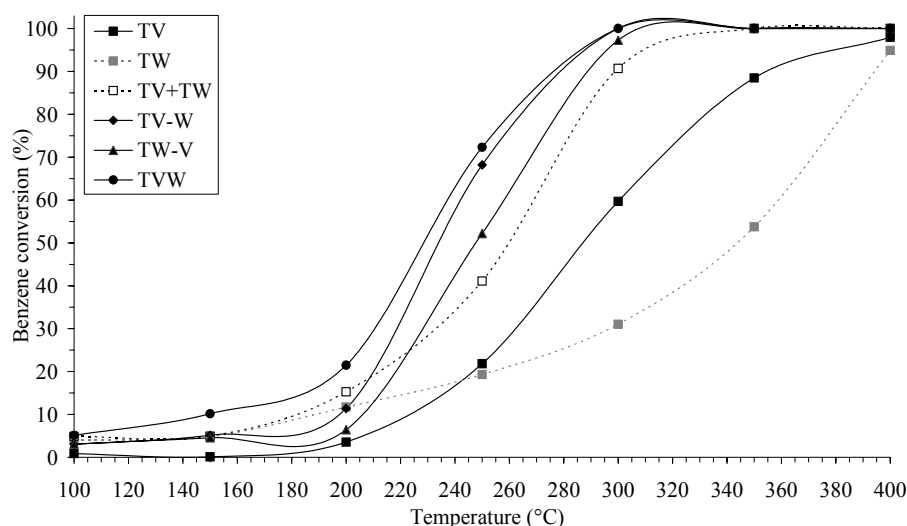


Fig. 3-8: Benzene light-off curves of TV, TW, TV+TW, TV-W, TW-V and TVW

It is thus clear that these two secondary phases induce a synergetic effect with VO_x . This synergetic effect is huger in the case of syntheses involving simultaneous impregnation of both metal precursors. This is likely due to the fact that thanks to such a protocol, the contacts between both phases (VO_x and secondary phase) are promoted.

We pointed out that the kind of influence (positive or negative) strongly depends on the nature of the secondary phase but only weakly on the synthesis pathway and the impregnation order. On the contrary, the extent of the activation brought by the addition of the activating phases (WO_x , CrO_x , MoO_x , NbO_x) is clearly related to the nature of the secondary phase but also to the impregnation order. The synthesis based on the simultaneous impregnation brings the most beneficial effect, while the syntheses in two steps bring a weaker improvement. Moreover, the improvements brought by the secondary phases are superior when VO_x is impregnated and followed by the secondary phase (TV-X) than in the opposite case (TX-V).

The standardization and the decrease of the performances, observed on the TX-V family compared to the TV-X family, are directly correlated to the impregnation order. The impregnation of VO_x in a second step can promote the formation of a layer of VO_x covering the surface of the previously deposited secondary phase and the surface of the support. The external surface of the catalyst (support + secondary phase + VO_x) is thus mainly composed of VO_x. This similarity of the external surface of the TX-V catalysts, mainly composed of VO_x, compared to the different surfaces of the TV-X catalysts mainly composed of different XO_x, can account for the standardization of the activity.

However, the nature of the secondary phase present at the surface of the support before the impregnation of the VO_x precursor (TX-V) can also influence the spreading of VO_x on its own surface. This effect is governed by the “solid-solid wetting” which depends on the evolution of the surface free energy [104,115-117]. Depending on the nature of the two solids, this effect leads, on the one hand, to a homogeneous well-dispersed monolayer of VO_x or, on the other hand, to the formation of badly dispersed VO_x. In the case of TN-V and TC-V, the XPS measurements demonstrated that the impregnation of VO_x in second promotes the formation of a layer of VO_x covering the surface of the previously deposited secondary phase. At the opposite, pre-existing MoO_x (TM-V) and WO_x (TW-V) layers are not covered by VO_x phases impregnated after.

In these cases of the MoO_x and WO_x phases, VO_x is only stabilized on the surface of the remaining exposed areas of bare support. This stabilization on a lower surface of bare support, on the one hand, eventually promotes the formation of intimate VO_x-TiO₂ contacts but on the other hand, as concentrating VO_x species at local places favors the system towards the crystallization. Therefore, the slighter activation brought by the secondary phases in the case of the TX-V family than in the case of the TV-X family is also due to an active phase-support effect. Indeed, as we demonstrated in Chapter 1 and 2, VO_x based catalysts work best as monolayer of VO_x well

dispersed on the surface of a TiO₂ support. As a conclusion, in the case of the MoO_x and WO_x secondary phase, the synthesis of the VO_x on an already partially covered TiO₂ induces the spreading essentially on the surface of the support. This fact, on the one hand, favors the activity by promoting VO_x-support contacts but on the other hand, reduces the activity by preventing the best spreading of the VO_x phase.

NbO_x and CrO_x phases promote the spreading of the VO_x on them and thus decrease the VO_x-support contacts. Therefore, for the TX-V syntheses, we observe a decrease of the activity in front of the TV-X syntheses. The impregnation order of the latter family promotes the formation of VO_x-support interactions. These interactions lead to an overall improvement of the activity. However, as demonstrated by XPS, the CrO_x and NbO_x phases spread on the surface of the pre-existing VO_x layer. This fact induces a reduction of the number of VO_x sites present at the external surface of the catalyst. This reduction leads to a slighter activation than in the case of the catalysts synthesized in one single impregnation step.

This most pronounced activating effect observed in the case of the syntheses performed with a simultaneous impregnation is explained by two facts: i) VO_x is homogeneously dispersed on the surface of the support as observed by XPS and ii) this kind of impregnation leads to an increase of the quality and numbers of contacts between the two phases, leading to an increase of the possible interactions between them.

As a conclusion, the addition of selected transition metal oxides to the VO_x/TiO₂ formulation induces an improvement of the catalyst activity. This enhancement of the catalyst performances is greater when the precursors of the two oxides are impregnated simultaneously. This synthesis pathway promotes i) the stabilization of the VO_x active phase as a well-dispersed layer at the surface of the TiO₂, which induces a higher activity and ii) the good intimacy between VO_x and the secondary phases.

The best performances are observed on the binary formulations VO_x-MoO_x and VO_x-WO_x characterized by a simultaneous impregnation. XPS demonstrated that these formulations are characterized by i) the spreading of the VO_x phase at the surface of the TiO₂ support, ii) the absence of spreading of the secondary phases on the VO_x layer and iii) an intimacy between the VO_x and the secondary phases. The almost absence of spreading of the secondary phases on VO_x prevents the covering of the active sites. Moreover, we demonstrated that these binary phases show a synergetic effect. Furthermore, these catalytic and XPS results pointed out the importance of a contact between the VO_x phases and the TiO₂ support. The presence of these contacts seems to be crucial to reach the best activity. It is thus clear that the best performances are obtained with a VO_x layer in contact with the TiO₂ support and in proximity of WO_x or MoO_x phases.

3.3.2. Influence of the secondary phase / VO_x ratio and of the support

In order to go further in the understanding of the synergetic effect detected in the two most performing systems (TVW and TVM synthesized in a unique step), we studied the influence of the ratio of loadings secondary phases / VO_x on the catalyst performances. Therefore, five VO_x-WO_x formulations and five VO_x-MoO_x catalysts supported on TiO₂ were synthesized with various loading ratios, namely 0.3, 1, 2, 3 and 6. In addition, a TV catalyst was synthesized to serve as reference.

Chapter 1 pointed out the positive effect of supporting VO_x on a sulfated TiO₂. Therefore, we synthesized the same ten formulations supported on a sulfated TiO₂ (Millennium PC 100). Furthermore, to work in more realistic conditions, we performed this second round of catalytic tests on chlorobenzene. The chlorobenzene is a more adequate molecule than benzene to model dioxin because it contains a chlorine atom, as in the dioxin molecules.

3.3.2.1. Catalytic results

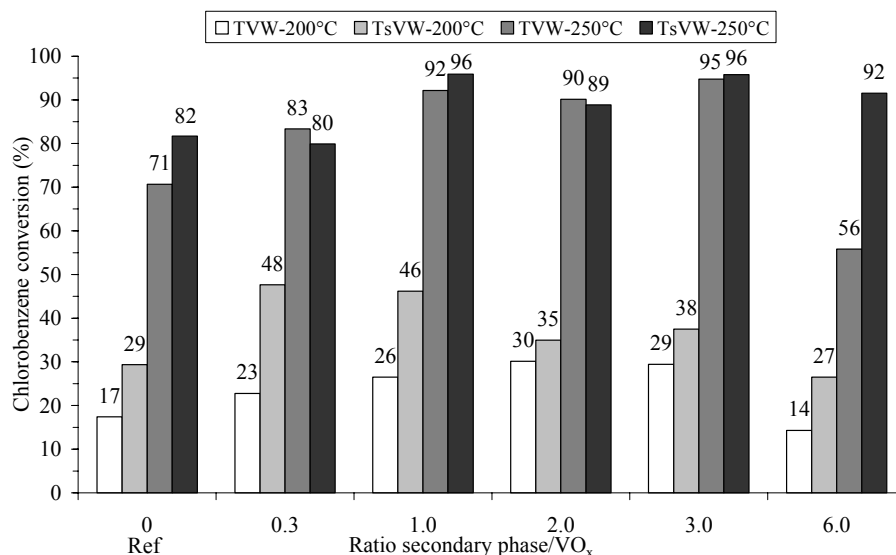


Fig. 3-9: Chlorobenzene conversion on TVW-Y and TsVW-Y families at 200 and 250 °C

Fig. 3-9 and 3-10 present the chlorobenzene conversion at 200 °C and 250 °C for the formulations based on VO_x-WO_x and VO_x-MoO_x, respectively. The introduction of WO_x in the catalyst formulation induces an overall improvement of the chlorobenzene conversion in front of the reference activity (Fig. 3-9). This improvement was already observed in the case of the combustion of benzene in points 3.3.1.2, 3.3.1.3. and 3.3.1.4. This activation appears on the formulations supported on both classic (T) or sulfated TiO₂ (Ts) and at both 200 °C and 250 °C. However, the extent of this activation varies with the WO_x/VO_x ratio. The increase of the ratio, from 0 to 0.3 and 1, induces a progressive overall improvement of the performances of the catalyst. For example, the conversion of the TVW catalyst at 250 °C goes from 71%, in the case of the reference catalyst, to 83% and 92%, respectively for ratios 0.3 and 1. The further increase of the

amount of WO_x up to a ratio equal to 2 and 3 induces a stabilization of the catalytic performances. Finally, for the ratio of 6, a deactivation of the catalyst is observed. Based on the catalytic results at both temperatures and for both families of catalysts (supported on T and on Ts), we can conclude that the WO_x/VO_x ratio equal to 1 is the best compromise to have the hugest activity. Furthermore, this series of catalytic tests pointed out the overall better activity of the formulations supported on Ts than on T. The Ts formulations exhibit a conversion more than twice higher than the conversion exhibited by the formulations supported on the classical TiO₂. This was already observed in the case of the single VO_x active phase in the course of the total oxidation of benzene in Chapter 1.

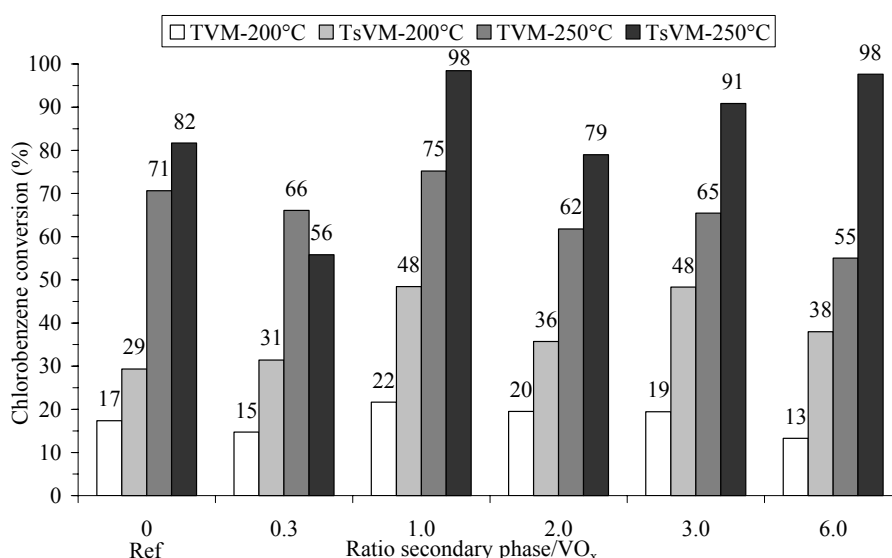


Fig. 3-10: Chlorobenzene conversion on TVM-Y and TsVM-Y families at 200 and 250 °C

Fig. 3-10 presents the catalytic performances at 200 °C and 250 °C of the 10 formulations containing VO_x and MoO_x. The impregnation of 0.25 monolayer of MoO_x in addition to the 0.75 monolayer of VO_x (MoO_x/VO_x

ratio of 0.3) induces an overall decrease of the catalyst activity in front of the reference catalyst. Nevertheless, the further increase of the ratio to a value of 1 induces a significant enhancement of the conversion of chlorobenzene at both temperatures and for both supports. At a ratio of 2, a decrease of the extent of the activation brought by MoO_x is observed in front of the overall activation observed with the MoO_x/VO_x ratio equal to 1. Nevertheless, the further increase of the ratio to 3 leads, on the one hand, to an increase of the activity compared to the performances of the catalysts characterized by a ratio of 2 but, on the other hand, to a decrease of the activity in front of the chlorobenzene conversion of the catalyst with a ratio of 1.

Lastly, doubling the loading of MoO_x in the formulation from 2.25 (ratio 3) to 4.5 (ratio 6) monolayers diminishes the catalyst activity. As a conclusion, the best performances were obtained on the catalysts with the identical loading of VO_x and MoO_x . Furthermore, the replacement of the classical TiO_2 by a sulfated TiO_2 induces an overall increase, by about a factor 2, of the catalyst performances at both temperatures (200 °C and 250 °C).

3.3.2.2. XRD results

Fig. 3-11 and 3-12 present the XRD diffractograms obtained on the TW-Y, TVW-Y and TsVW-Y families and on the TM-Y, TVM-Y and TsVM-Y families, respectively. Fig. 3-11 presents the diffractograms obtained on formulations containing WO_x . For the entire set of formulations, the diffractograms do not exhibit any diffraction peaks corresponding to VO_x crystalline phases. For all families, at the ratio 1, the apparition of very broad peaks is observed, corresponding to the beginning of the formation of WO_3 crystallites. For higher ratios, the presence of diffraction peaks becomes very clear confirming the formation of crystallites of WO_3 at loading of 1.5 monolayer (ratio 2) and above.

Fig. 3-12 points out the absence of crystallites of VO_x on the entire set of formulations. Diffraction peaks attributed to MoO_3 become visible for a

MoO_x/VO_x ratio of 2 (TVM-Y and TsVM-Y). In the case of the TM-Y family (containing only MoO_x), the ratio must however be increased to 3 to observe the diffraction peaks characteristic of MoO₃ crystallites. The presence of the VO_x phases thus clearly promotes the formation of crystallites of MoO₃ on both supports (T and Ts), which consequently appear at lower loadings than in the absence of VO_x. However, at the highest loading (ratio 6 corresponding to 4.5 monolayers of MoO_x), the Full-Width Half-Maximum of the MoO_x diffraction peaks (FWHM) are smaller in TM-Y family than in the case of TVM-Y and TsVM-Y. This observation suggests that the quality of the MoO₃ crystals is affected by the presence of the VO_x.

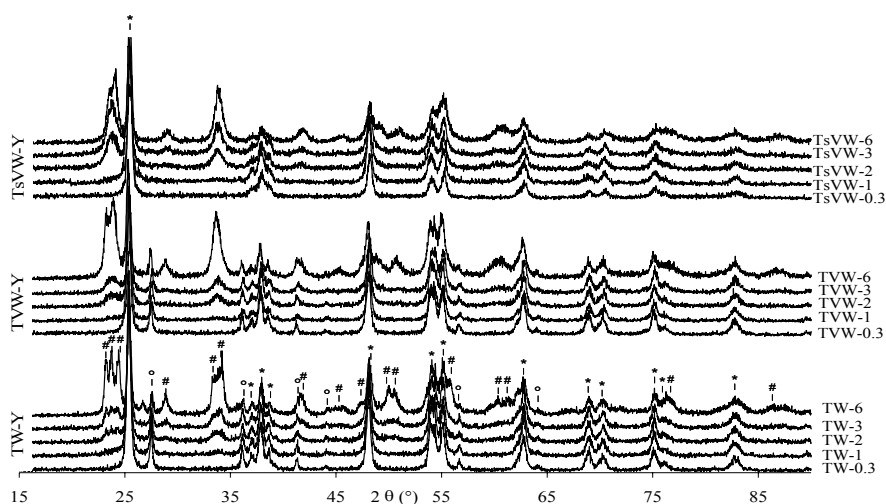


Fig. 3-11: X-Ray diffraction patterns of the TW-Y, TVW-Y and TsVW-Y families (*=TiO₂ anatase, °=TiO₂ rutile, #=WO₃)

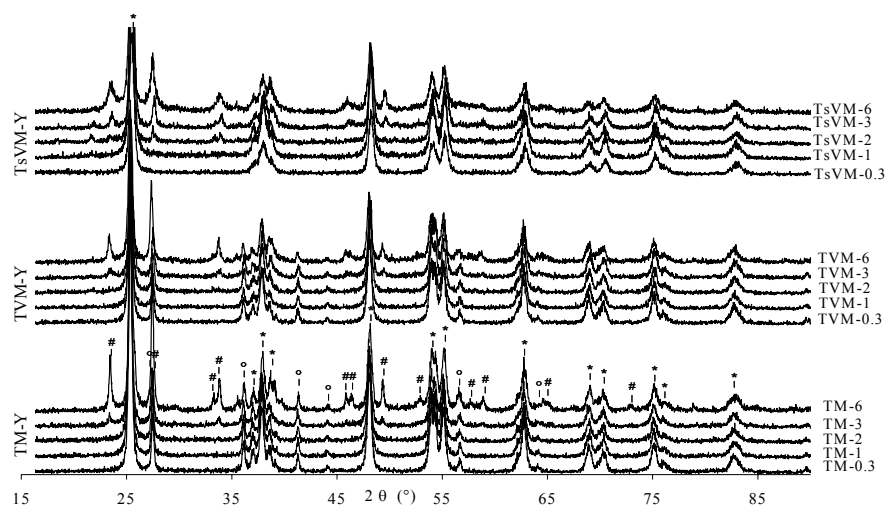


Fig. 3-12: X-Ray diffraction patterns of the TM-Y, TVM-Y and TsMV-Y families (*=TiO₂ anatase, °=TiO₂ rutile, #=MoO₃)

3.3.2.3. Discussion

Both WO_x and MoO_x secondary phases promote the total oxidation of chlorobenzene on VO_x/TiO₂ based catalysts as it was observed in the case of the benzene combustion (see sections 3.3.1.1, 3.3.1.2 and 3.3.1.3). Indeed, the various formulations containing only VO_x or VO_x-WO_x and VO_x-MoO_x, supported either on classical TiO₂ or on a sulfated one, are all resistant to the presence of chlorine atom in the molecule that must be oxidized. This observation completes the previous results showed in Chapter 2, which pointed out the complete resistance of the VO_x based catalysts in the course of the total oxidation of chlorinated aromatics. Moreover, the extent of the activation effect is deeply influenced by the secondary phase/VO_x loadings ratio. For both secondary phases (MoO_x and WO_x), the most marked activation is observed in the case of a ratio equal to 1, namely when 0.75 monolayer of WO_x is impregnated simultaneously to 0.75 monolayer of VO_x. As pointed out by XRD, the formulations of ratio 1 are characterized by the highest amount of secondary phases that can be stabilized at the

surface of the catalyst without producing crystallites. It is thus clear that the improvement of the catalyst activity goes in parallel with the increase of the loading in secondary phase at the condition that these phases are still present as well-dispersed phase (non-crystalline). When these phases form crystallites, a smaller improvement is brought by the secondary phases

As exposed in the introduction, the catalytic formulations usually employed for the total oxidation of chlorinated aromatics are identical to those used in the SCR reaction. Therefore, the formulations are based on formulations VO_x-WO_x and VO_x-MoO_x with weight concentration ratios wt.%MoO₃ / wt.% V₂O₅ and wt.% WO₃ / wt.% V₂O₅ of about 5 and 10, respectively [25,52,66,69,71,87,90,140-143]. To compare our best formulations (ratio equal to 1 in terms of theoretical coverage) to these ratios (in terms of oxides phases weight), we performed ICP-AES analysis of the formulations TV, TsV, TVM, TsVM, TVW and TsVW. The weight percentages of V, W, Mo, the X/V and V/X ratios, the weight percentages of V₂O₅, WO₃, MoO₃ and the XO_y/V₂O₅ ratios determined by ICP-AES are presented in table 3-4.

Table 3-4: ICP-AES weight concentrations and ICP-AES ratios

	V%	W%	Mo%	X/V	V/X
TV	2.76	-	-	-	-
TVM	2.06	-	5.41	2.63	0.38
TVW	2.02	6.30	-	3.11	0.32
TsV	4.42	-	-	-	-
TsVM	3.50	-	8.07	2.31	0.43
TsVW	2.87	9.38	-	3.27	0.31
	V ₂ O ₅ %	WO ₃ %	MoO ₃ %	XO _y /V ₂ O ₅	
TV	4.92	-	-	-	
TVM	3.68	-	8.15	2.21	
TVW	3.61	7.94	-	2.20	
TsV	7.88	-	-	-	
TsVM	6.24	-	12.15	1.95	
TsVW	5.12	11.82	-	2.31	

The ratio in terms of weight XO_y/V₂O₅ calculated for both TVM-1 and TVW-1 (and their equivalent on Ts support) is about 2. Therefore, our research points out that the amount of secondary phases could be reduced by a factor 2 to 5 in the case of an application in chloro-aromatics oxidation. In a commercial point of view, this would lead to a reduction of the metallic inventorying of the catalyst by diminishing the amount of MoO_x or WO_x in the catalyst formulations without any drawback on the activity; on the contrary, the performances were optimal for slightly lower concentrations of MoO_x or WO_x.

The entire set of catalytic tests demonstrated the better performances of the formulations supported on the sulfated TiO₂ compared to the classical one. The same observation was previously done in the case of the catalyst containing only VO_x in the course of the total oxidation of benzene (Chapter 1). Therefore, these new results prove that the positive effect brought by the sulfated TiO₂ remains in the case of the chlorinated VOC. Moreover, this positive effect of the support also promotes the performances in the case of the catalysts improved by MoO_x and WO_x secondary phases.

3.3.3. Investigation of the effect brought by the secondary phases and sulfated TiO₂

To have a better understanding of the origin of the beneficial effect gained by the addition of MoO_x and WO_x as secondary phases and by the sulfated support, we performed characterizations. TV, TVM, TVW, TsV, TsVM and TsVW formulations with a XO_x/VO_x ratio of 1 (in terms of theoretical monolayer) and synthesized in a unique step were selected for the following. The nature and the strength of the acid sites were investigated by FTIR measurements after pyridine adsorption. Indeed, as suggested by Larrubia *et al.* [68], the acidity of the catalyst could play a crucial role in the adsorption of the VOCs on the surface of the catalyst.

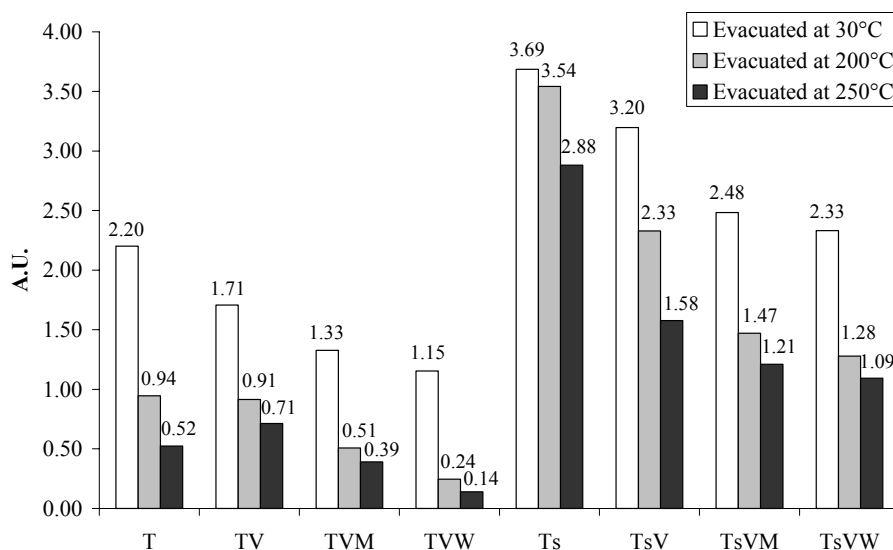


Fig. 3-13: Amount of Lewis sites detected by FTIR-pyridine on T, TV, TVM, TVW, Ts, TsV, TsVM and TsVW

Fig. 3-13 and 3-14 present the amount of Lewis and Brønsted sites, respectively, for the T, TV, TVM, TVW and Ts, TsV, TsVM, TsVW formulations. In Fig. 3-13, for the formulations based on the classical TiO₂ (T), a decrease of the amount of Lewis sites with the addition of the VO_x phase is observed. A further decrease is observed with the introduction of a secondary phase (TVM or TVW). The samples based on the combination VO_x-WO_x correspond to the lowest amount of Lewis sites on the surface of the catalyst. For all TiO₂ supported catalysts, the increase of the evacuation temperature of pyridine induces a huge decrease of the amount of adsorbed pyridine on acid Lewis sites, revealing that the Lewis sites of these catalysts are mainly weak Lewis sites. In the case of the bare support, the amount of strong Lewis sites (measured after evacuation at 250 °C) represents about 25% of the total Lewis sites (measured after evacuation at 30 °C). Sulfated TiO₂ (Ts) exhibits twice more Lewis sites than the classical support. However, the same observations as in the case of the T support are made: i)

the number of Lewis sites decreases with the introduction of VO_x, WO_x and MoO_x and ii) the lowest amount is observed in the case of the VO_x-WO_x formulation. However, in this case of the Ts support, the extent of the reduction of the amount of pyridine adsorbed on Lewis sites at 250 °C compared to 30 °C is lower than in the case of the T support. For the bare support, the amount of strong Lewis sites (measured after evacuation at 250 °C) represents about 80% of the total Lewis sites (measured after evacuation at 30 °C). These results pointed out i) the twice higher amount of Lewis sites on the sulfated TiO₂ than on the classical TiO₂ support and ii) the strengths of the Lewis sites present at the surface of the sulfated TiO₂ are stronger than those of conventional TiO₂.

Moreover, all these observations point out that Lewis acid sites are mainly present on the surface of the TiO₂ based supports. At the opposite, VO_x and secondary phases either do not exhibit any Lewis sites on their surface or exhibit less Lewis sites than the supports. Therefore, the decrease of the number of Lewis sites when VO_x, MoO_x and WO_x phases are present is due to a coverage effect of the support by these phases. Moreover, the highest decrease of the amount of Lewis sites in the case of the VO_x-WO_x combination is due to its best spreading on TiO₂ based supports as already discussed in section 3.1.7.

Fig. 3-14 presents the amount of Brønsted sites at the surface of the same formulations as those presented in Fig. 3-13. The T support exhibits almost no Brønsted sites. The impregnation of VO_x, MoO_x and WO_x induces an increase of the amount of Brønsted sites. The binary formulations present more acid Brønsted sites than catalysts containing VO_x only and the TVW exhibits the highest amount of acid sites. The decrease of the amount of adsorbed pyridine with the temperature of evacuation reveals the strengths of the Brønsted sites. Indeed, the amount of strong Brønsted sites (measured after evacuation at 250 °C) counts for 39% of the total amount of Brønsted sites (measured after evacuation at 30 °C). The Ts support exhibits almost ten times more Brønsted sites than the non-sulfated one (T). As in the case

of T, the impregnation of VO_x, MoO_x and WO_x or combinations of them induces a sharp increase of the amount of Brønsted sites. However, in the case of Ts, the introduction of these phases induces the presence of around four times more Brønsted sites than in the case of the T support. Nevertheless, the amount of strong Brønsted sites (measured after evacuation at 250 °C) counts for 35% of the total amount of Brønsted sites (measured after evacuation at 30 °C). The percentage of strong acid sites is almost equivalent to the amount of 39% observed in the case of the T support.

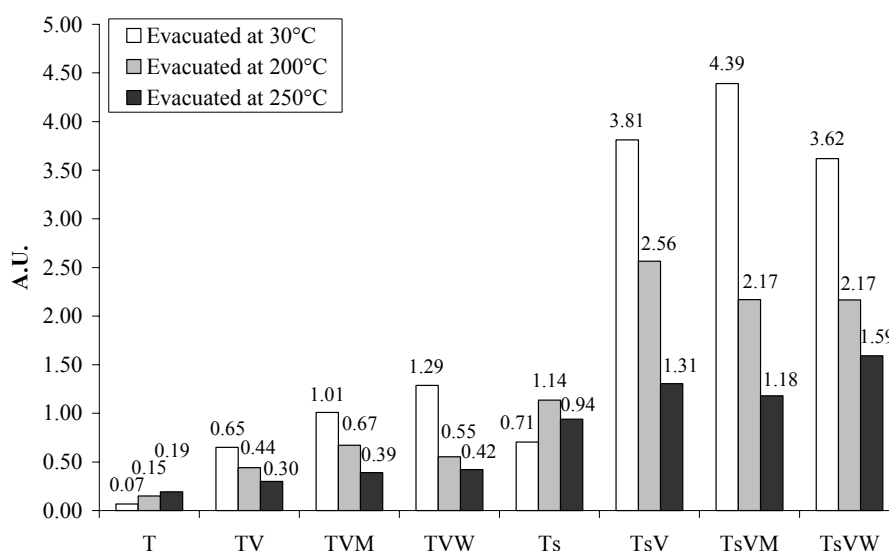


Fig. 3-14: Amount of Brønsted sites detected by FTIR-pyridine on T, TV, TVM, TVW, Ts, TsV, TsVM and TsVW

All these observations point out that, while the classical support does not exhibit any Brønsted sites, the sulfated one exhibits some of them. VO_x, MoO_x and WO_x phases present a huge amount of Brønsted sites on their surface. The equivalent percentage of strong acid Brønsted sites present on both supports confirms that Brønsted sites are present on the surface of the

VO_x, MoO_x and WO_x phases but almost not on the surface of the support. However, the amount of Brønsted sites is 4 times bigger in the case of Ts than of T support. This fact can possibly be related to a better spreading of the active and secondary phases on the sulfated support than on the conventional one. The better spreading of the active and secondary phases on the sulfated support can be related to the difference of Lewis sites characteristic of the support, *i.e.* the presence of stronger Lewis sites on the sulfated TiO₂. Indeed, we demonstrated that VO_x, WO_x and MoO_x cover the Lewis sites of the support. Thus, we can assume that, during the synthesis, oxide phase precursors are stabilized on the Lewis sites of the support. This stabilization of the active and secondary phase precursors on the Lewis sites promotes the formation of a uniform layer of these phases on the support. Therefore, the presence of 2 times more Lewis sites on the sulfated TiO₂ than on the conventional support favors the spreading of the oxides as layers. Moreover, the higher strength of the Lewis sites present at the surface of Ts can also promote the better spreading of the VO_x, WO_x and MoO_x phases. This improvement of the spreading leads to the exposition of a larger surface of VO_x, MoO_x and WO_x at the surface of the catalyst, with as a consequence a bigger amount of acid Brønsted sites observed at the surface of the samples based on these phases.

The catalytic results pointed out the beneficial effect of i) introducing WO_x or MoO_x in the catalyst formulation and ii) supporting the active phase on a sulfated TiO₂. The beneficial effect of WO_x or MoO_x can partially be related to the increase of the number of Brønsted acid sites that they induce at the surface of the catalysts. The promoting effect brought by sulfated TiO₂ is also due to an increase of the amount of Brønsted acid sites. However, this activation effect is mainly an indirect promotion going through the modification of the active and secondary phases. Indeed, the sulfated support, showing more and stronger Lewis sites, improves the spreading of the VO_x, WO_x and MoO_x phases. This improvement of the spreading favors

the exposure of more Brønsted acid sites at the surface of the active and secondary phases, which brings about an enhancement of performances.

These results allow a deeper understanding of the spreading of the VO_x and secondary phases on the surface of the support in relation with the synthesis pathway and impregnation order. The better spreading of the VO_x on a bare support of TiO₂ than on a pre-existing layer of secondary oxides can, now, be explained by the variation in the amount of Lewis sites on the surface of the catalyst. Therefore, in the case of a pre-existing layer of WO_x or MoO_x, the absence of Lewis sites on these phases prevents the spreading of VO_x on them. Moreover, these phases force VO_x to spread on the remaining bare parts of the support that exhibit Lewis sites.

The spreading of the active phase or of the secondary phases on the support or on each other is governed by “solid-solid wetting”. This preferential wetting depends on the evolution of the surface free energy during the synthesis pathway. In the case of the impregnation of VO_x, MoO_x and WO_x precursors, the presence of Lewis sites on the support promotes the spreading of these phases. This promotion of the spreading is linked to the positive evolution of the free energy happening when a layer of active or secondary phase covers these Lewis sites.

3.4. Conclusions

We investigated the catalytic influence of nine transition metal oxides as secondary oxides on the activity of the VO_x supported on TiO₂ catalysts in the course of the total oxidation of benzene. Moreover, we considered three synthesis pathways and impregnation orders for the preparation of these binary catalysts (VO_x-XO_x): i) impregnation of the VO_x and then impregnation of the secondary phases, ii) impregnation of the secondary phases and then of the VO_x and iii) simultaneous impregnation of VO_x and secondary phases in a unique step. We demonstrated that the nature of the influence (positive or negative) is related to the nature of the secondary

phases. While TaO_x, MnO_x, SnO_x, ZrO_x or BiO_x have a negative impact on the VO_x performances, WO_x, MoO_x, CrO_x or NbO_x have a positive influence on the VO_x based catalyst activity in the course of the oxidation of benzene. At the opposite, the extent of the activation brought by the secondary phases strongly depends on the synthesis pathway and impregnation order. We proved that the best activities are observed in the case of the catalysts synthesized in a unique step. Moreover, we pointed out that the WO_x and MoO_x phases are the only secondary phases that induce a synergetic effect with VO_x for the oxidation of benzene. VO_x-MoO_x and VO_x-WO_x supported on TiO₂ are well-known formulations used for the total oxidation of chlorinated VOCs. The use of these formulations is due to a fortuitous discovering made by using these formulations for the NO_x SCR with NH₃. Nevertheless, the systematic investigation of transition metal oxides other than WO_x and MoO_x as secondary phases was never reported for the improvement of the combustion activity of the VO_x active phase supported on TiO₂. Therefore, we investigated the catalytic activity of binary catalysts containing VO_x as the main active phase and various secondary phases of transition metal oxides. This investigation pointed out the same catalysts as those discovered empirically. The XPS measurements demonstrated that the VO_x phase spreads well on the surface of the bare TiO₂. However, the spreading of the VO_x and the secondary phases on the support and on each other depends on the couple VO_x-secondary phase and on the couple secondary phase-TiO₂. We suggested that the beneficial effect of the presence of WO_x and MoO_x resides in the absence of mutual spreading between VO_x and the secondary phases. This fact prevents the coverage of VO_x by the secondary phases and promotes the stabilization of the VO_x-TiO₂ support intimate contacts. At the opposite, the other secondary phases and VO_x spread on each other. This leads to a decrease of the VO_x-support interactions and to a reduction of the number of active VO_x sites exhibited at the surface of the catalyst. Moreover, we demonstrated that the beneficial effect brought by the impregnation in a unique step is due to an increase of

the quantity and quality of the contacts between the two phases (VO_x and secondary phase).

We subsequently investigated, for the two secondary phases bringing a synergetic effect (WO_x and MoO_x), the influence of the ratio of loadings secondary phase / VO_x on the total oxidation of chlorobenzene. This investigation was performed on VO_x-MoO_x and VO_x-WO_x formulations supported on a classical TiO₂ and on a sulfated one (Ts). We demonstrated the resistance of all the formulations in front of the chlorine present in the molecule that must be oxidized. Moreover, this investigation pointed out the better activity of these formulations supported on sulfated TiO₂ than supported on the classical one. Furthermore, this research showed that the formulations characterized by a loading ratio secondary phase / VO_x equal to 1 are the most efficient for converting chlorobenzene. This fact is true independently of the kind of support (T or Ts) and of the nature of the secondary phase (WO_x or MoO_x). These formulations are characterized by the highest loading of secondary phases characterized by the total absence of crystallites in the case of MoO_x or by the presence of a very weak amount of crystallites in the case of WO_x.

The IR investigation with pyridine as a probe molecule on selected formulations (TV, TVM, TVW, TsV, TsVM and TsVW) brought key information about the amount of Brønsted and Lewis sites on the surface of the catalysts. These results demonstrated that the beneficial effect of the sulfated TiO₂ is due to an increase of the amount of Brønsted sites on the surface of the catalysts. These Brønsted sites come from i) sulfated TiO₂ that exhibits ten times more Brønsted acid sites than the classical one and ii) the VO_x and the secondary phases that exhibit four times more Brønsted sites when supported on sulfated TiO₂ than in the case of supported on classical TiO₂. The increase of the amount of Brønsted sites exhibited by the VO_x and secondary phases is due to a better spreading of these phases on the surface of the sulfated support. The better spreading is correlated to the presence of a high number of strong Lewis sites on the surface of the

sulfated support. These strong Lewis sites seem to promote the better dispersion of the active and secondary phases during the impregnation. As a conclusion, we demonstrated that the activation effect brought by the sulfated TiO₂ is clearly linked to the increase of the number of Brønsted acid sites on the catalyst surface. The WO_x and MoO_x secondary phases also seem to have an influence on the amount of Brønsted sites at the catalyst surface. Therefore, we can assume that the Brønsted acid sites are involved in the first step of the benzene and chlorobenzene combustion reaction. This step is the adsorption of the aromatics on the acid sites (Brønsted) of the support and of the active and secondary phases.

Practically, to synthesize the best catalyst, we must i) use a support that exhibits Brønsted acid sites to promote the adsorption of the aromatics, ii) use a support that exhibits a huge number of strong Lewis sites in order to improve the spreading of VO_x and secondary phases, iii) add secondary phases that do not exhibit Lewis sites but a huge number of Brønsted sites, iv) perform the impregnation of both precursors simultaneously in a unique step and v) introduce the secondary phase at the highest possible loading but avoiding its tendency to form crystallites of secondary phase.