PART III: MECHANISM OF THE CHLORINATED VOCS DESTRUCTION ON VO_X/TiO_2 BASED CATALYSTS

CHAPTER 7 : MECHANISM OF THE TOTAL OXIDATION OF CHLORINATED VOCS ON VO_X/TiO_2 BASED CATALYSTS

Abstract

Previous chapters demonstrated that the activity depends on several aspects of the catalyst: the acidity, the redox behavior of the VO_x sites and the retrieving of chlorine from the catalyst surface. Therefore, in order to draw a complete picture of the catalytic mechanism of the total oxidation of chlorinated VOC on VO_x/TiO_2 based catalysts, we revisit the results presented through the two first parts of the manuscript. This investigation demonstrated that the mechanism of the total oxidation of chlorinated VOCs proceeds within four steps: i) adsorption of the chlorinated VOCs on medium-strong Brønsted sites mainly located at the surface of the secondary phases, ii) VO_x redox sites give some of their lattice oxygen atoms to oxidize step-by-step the aromatic ring producing H_2O and CO_x, iii) regeneration of the VO_x reduced sites thanks to the oxidant present in the gas stream (O_2) and iv) the retrieving of chlorine from the surface thanks to its reaction with water, producing and desorbing easily HCl. Moreover, we demonstrated that the rate limiting step is the reoxidation of the reduced VO_x site. These data bring a further understanding on the fact that the catalytic activity can be improved by adding secondary phases that improve the reducibility of the VO_x phase or by increasing the oxidant strength of the gas stream that

stabilizes the vanadium oxidation level above a certain value, namely 4.87 in the case of the TsVW catalyst.

7.1. Introduction

Chapter 1, 2 and 3 demonstrated that VO_x/TiO_2 based catalysts are very efficient in the total oxidation abatement of chlorobenzene (taken as a model molecule for dioxins) from combustion exhaust gases. In particular, they proved to be highly resistant against deactivation which proceeds on other elements than V through the chlorination of the active phase or the blocking of the active sites (Chapter 2). Moreover, the addition of secondary phases leading to VO_x-WO_x/TiO_2 or VOx-MoO_x/TiO_2 formulations induces a synergetic effect (Chapter 3). This effect leads to a marked improvement of the catalyst performances. In addition, the deep investigation of the influence of co-pollutants (H_2O, CO and NO_x) on the catalysts ability to destroy chlorinated VOCs demonstrated their quite good resistance. Indeed, the presence of CO does not induce any deactivation of the catalysts while NO_x induces a huge improvement of the catalysts ability to destroy chlorinated VOCs (Chapters 5 and 6). Nevertheless, H_2O vapor negatively affects the catalyst activity when present in high concentration in the gaseous stream (Chapter 4).

However, the mechanism of the total oxidation of chlorinated VOCs on VO_x/TiO_2 based catalysts has not yet been completely depicted either in the literature or in this thesis. Therefore, the present chapter aims at drawing a clear picture of this mechanism by bringing together and by revisiting catalytic and characterization results exposed in the six previous chapters. For this purpose, this chapter focuses separately on several aspects of the catalysts that could influence their performances and that had been revealed as key parameters in Part I and II. These aspects are: the acidity, the redox behavior of the VO_x sites and the chlorine retrieving from the catalyst surface. Chapters 3, 4 and 5 indeed demonstrated the importance of Lewis

and Brønsted sites for the catalyst synthesis and for the adsorption of the chlorinated VOCs, respectively. Moreover, Chapters 4, 5 and 6 demonstrated the essential role of the redox VO_x sites for the total oxidation of chlorinated VOCs. Furthermore, Chapters 2 and 4 demonstrated the crucial impact of the retrieving of chlorine from the surface in order to regenerate the active sites.

The investigation of the role of Lewis and Brønsted sites on the performances of the VO_x/TiO_2 based catalysts was performed by compiling together the results exposed in Chapters 3, 4 and 5. These results are mainly focused on the estimation of i) the amount of Lewis and Brønsted sites, ii) the strength of these sites and iii) the influence of these two aspects on the catalytic performances.

The influence of the redox character of the catalysts will be investigated following different aspects: i) the influence of the reducibility of the VO_x sites, ii) the influence of the vanadium oxidation level of the active sites on their activity and iii) the mechanism of oxidation followed by VO_x sites to burn the chlorinated VOCs. The investigation of the influence of the reducibility is mainly based on the comparison of the extent of the variation of the V O.L. during catalytic tests in various conditions and with different formulations. The understanding of the effect of the vanadium oxidation level on the catalyst activity was fulfilled by performing the total oxidation of chlorinated VOCs in various catalytic conditions on a unique catalyst (VO_x-WO_x/TiO_2 - TsVW). All the catalytic and characterization results obtained with two series of catalytic tests under various gaseous conditions were brought together. The first series investigated the effect brought by H_2O, CO and NO_x on the catalyst performances by adding different concentrations of these co-pollutants. The second series investigated the influence of the oxidant by changing the nature and the concentration of the oxidant molecule (NO, NO_2 and O_2). The entire set of catalytic data combined with the evaluation of the vanadium oxidation level helps to reach a better understanding of the crucial influence of the V O.L. on the catalyst

activity. The understanding of the oxidation step of the complete mechanism is mainly based on the influence of different gaseous conditions on the performances as presented in Chapter 6. These results pointed out the deep influence of the oxygen concentration on the catalytic performances going in parallel with its influence on the V O.L.

The step of retrieving of chlorine from the surface is considered on the basis of the results concerning the influence of water vapor on the performances, and of literature.

Finally, the last part of this chapter brings all the observations together to draw a complete scheme of the mechanism of the complete oxidation of chlorinated VOCs on VO_x/TiO_2 based catalysts.

7.2. Experimental

7.2.1. Preparation of the catalysts

The investigated catalysts are: VO_x/TiO_2 (TV), VO_x-WO_x /TiO_2 (TVW), VO_x-MoO_x /TiO_2 (TVM), and the same formulations supported on a sulfated TiO_2 (TsV, TsVW and TsVM respectively). The entire set of catalysts was prepared in order to obtain 0.75 theoretical monolayer of each transition metal oxide dispersed at the surface of the titania supports following the experimental protocol presented in section 3.2.1.

7.2.2. Catalytic tests

All catalytic tests were performed following the experimental methods presented in sections 3.2.2., 4.2.2., 5.2.2. and 6.2.2. All gaseous conditions considered are listed in Table 7-1.

7.2.2.1. Reference test

The reference test was carried out with a gaseous stream containing 100 ppm of chlorobenzene, 20% of O_2 and He as diluting gas to obtain 200 ml min^{-1} (VVH=37000 h^{-1}) (Table 7-1, conditions 1).

7.2.2.2. Co-pollutant tests

Table 7-1: Catalytic conditions

	Catalytic conditions					
	$[C_6H_5Cl]$ ppm	$[O_2]$ ppm	$[H_2O]$ %	[CO] ppm	[NO] ppm	$[NO_2]$ ppm
1	100	200000	0	0	0	0
2	100	200000	1	0	0	0
3	100	200000	2	0	0	0
4	100	200000	5	0	0	0
5	100	200000	0	5000	0	0
6	100	200000	0	50000	0	0
7	100	200000	0	0	100	0
8	100	200000	0	0	1000	0
9	100	0	0	0	1000	0
10	100	0	0	0	4000	0
11	100	0	0	0	0	1000
12	100	0	0	0	0	2000
13	100	0	0	0	0	4000
14	100	850	0	0	0	0
15	100	1450	0	0	0	0
16	100	5000	0	0	0	0
17	100	10000	0	0	0	0

These tests were performed in order to investigate the influence of the presence of co-pollutants on the chlorinated VOCs combustion performances of the catalysts. The investigation of the effect of H_2O vapor was performed by introducing 0-1-2-5 vol.% of H_2O in the reference gas stream

corresponding to conditions 2, 3 and 4, respectively (Experimental presented in section 4.2.2.). Under conditions 5 and 6, respectively 5000 and 50000 ppm of CO were added in the reference gas stream in order to probe the influence of the latter on the catalytic performances (Experimental 5.2.2.). Under conditions 7 and 8, respectively 100 ppm and 1000 ppm of NO were added to the reference gaseous stream to investigate the influence of the NO concentration on the performances of the catalyst used in the presence of O_2 (Experimental 6.2.2.).

7.2.2.3. Investigation of the oxidant strength of NO, NO_2 and O_2

Catalytic tests were performed on the TsVW catalyst using various concentrations of different oxidant molecules (NO, NO_2, O_2), taken one by one, to further investigate their respective oxidative strength. The entire set of catalytic tests was performed on a gaseous stream containing 100 ppm of chlorobenzene and using He as a diluting gas (Experimental 6.2.2.). Tests were performed in the presence of 1000 and 4000 ppm of NO as only oxidant molecule in the stream (Table 7-1, conditions 9 and 10). Additional catalytic tests were achieved with 1000, 2000 and 4000 ppm of NO_2 corresponding to conditions 11, 12 and 13, respectively. Finally, to have a better understanding of the role and the strength of O_2 as oxidant molecule, catalytic tests were carried out in the presence of 850 ppm, 1450 ppm, 5000 ppm, 1% and 20% of O_2 matching with conditions 14, 15, 16, 17 and 1, respectively. Conditions 1 correspond to the reference conditions, namely 100 ppm of chlorobenzene and 20% of O_2.

7.2.3. Characterization

Fourier Transformed Infra Red spectra of pre-adsorbed pyridine (FTIR-pyridine) were recorded following the experimental protocol presented in 3.2.3. in order to estimate the amount of Lewis and Brønsted sites and their strength.

Ammonia chemisorption experiments were conducted at 35 °C, 150 °C, 250 °C and 350 °C following the experimental procedure 4.2.3. to estimate the amount of weak, medium and strong acid sites at the surface of the catalysts.

The mean vanadium oxidation level (V O.L.) was estimated by combination of ICP-AES and EPR measurements (experimental 4.2.3).

XPS and "quick XPS" measurements were performed following the procedure presented in 4.2.3. to estimate the atomic surface composition and the surface vanadium oxidation level.

7.3. Results and discussion

7.3.1. Influence of the acidity on the catalytic performances of the VO_x/TiO_2 based catalysts

Chapter 3 demonstrated that the surface of the catalysts is mainly covered of Brønsted acid sites. The introduction of the secondary phases (WO_x or MoO_x) induces a huge increase of the amount of Brønsted sites. Moreover, the replacement of the classical TiO_2 support by the sulfated TiO_2 induces an increase of the catalyst acidity. Both these increases of the amount of Brønsted acid sites at the surface of the catalyst take place in parallel with an increase of the catalyst performances. This beneficial effect of WO_x or MoO_x can thus be related to the increase of the number of Brønsted acid sites that they induce at the surface of the catalysts. The increase of the amount of Brønsted sites when WO_x or MoO_x are added to a VO_x based catalyst has already been reported [158,159]. The promoting effect brought by the sulfated TiO_2 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 increase of the spreading of active and secondary phases. Indeed, these Brønsted sites come from i) sulfated TiO_2 that exhibits ten times more Brønsted acid sites than the classical one and ii) VO_x and mainly the secondary phases that exhibit four times more Brønsted sites when

supported on the sulfated TiO_2 than in the case of supported on the classical TiO_2. 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. Strong Lewis sites seem to promote the better dispersion of the active and secondary phases during the impregnation. As a conclusion, Chapter 3 demonstrated that the activation effect brought by the WO_x and MoO_x secondary phases and by the sulfated TiO_2 is clearly linked to an increase of the number of Brønsted acid sites on the catalyst surface. Therefore, we can assume that the Brønsted acid sites are involved in the first step of chlorobenzene combustion reaction, namely the adsorption of the chlorobenzene on the acid sites (Brønsted) of the support and of the active and secondary phases.

The results of Chapter 4 strengthen this hypothesis. Indeed, the acidity characterization revealed a decrease of the number of medium and strong acid sites in the presence of water. The observed decrease of the number of medium and strong acid sites on VO_x and secondary phases, takes place in parallel with a decrease of the catalyst performances. As demonstrated in Chapter 3, the acid sites are mainly Brønsted sites. Therefore, the decrease of the amount of medium and strong Brønsted sites accounts for the diminution of the catalyst performances. As a consequence of Chapters 3 and 4, medium and strong Brønsted sites thus clearly appear as the adsorption sites of the chlorinated VOCs during the first step of their catalytic combustion.

The apparently divergent data of Chapter 5 allow going further in the picture of the adsorption mechanism of chlorinated VOCs on VO_x/TiO_2 based catalysts. In Chapter 5 we saw that a strong influence of CO on the acidity of the selected formulation has no repercussion on the catalytic performances. The catalyst performance seems to be independent of its acidity. At the opposite, Chapter 5 reveals a clear dependence of the activity

to the oxidation state of active phase. Consequently, in order to account for all our observations from Chapters 3, 4 and 5, we must accept that the combustion of chlorinated aromatics requires the presence of two kinds of sites: medium or strong Brønsted sites and redox VO_x sites. One further assumption is that the combustion proceeds in two steps: i) the adsorption of the chlorobenzene molecule on a medium or strong Brønsted acid site and ii) the aromatic ring combustion on VO_x redox sites.

The necessity of having two kinds of sites (Brønsted and redox) suggests that the activity is dependent on their amounts. The dependency of the performances with the number of redox sites, i.e. the oxidation of the vanadium, is discussed and confirmed in the next section of this chapter. One should now however find an explanation accounting for the "strange" influence of CO on the performances. One hypothesis is that for each formulation, a minimal concentration of medium or strong Brønsted acid sites must be present on the catalyst surface to concentrate enough adsorbed chlorobenzene in the proximity of the active redox sites. Therefore, for a given formulation, if the amount of Brønsted sites is above this threshold of Brønsted sites, the chlorobenzene conversion turns to be completely limited by the number of redox sites. This is the case for the experiments with different concentrations of CO. Namely, although CO induces a decrease of the Brønsted acidity of the TsVM formulation, the latter still remains above the threshold, thus not bringing any variation of performances. At the opposite, if the number of acid sites is below the limit, the activity turns to be limited by the adsorption of chlorobenzene on medium or strong Brønsted sites and thus dependency between them is observed. This is the case for the addition of secondary phases or the replacement of the classical by a sulfated support for the VO_x single phase catalyst. Namely, the TV formulation is below the Brønsted sites threshold. Thus the addition of WO_x or MoO_x, or the use of a sulfated TiO_2 support boost the Brønsted acidity of the catalyst, bringing it closer to the threshold or eventually above it, inducing for both cases an improvement of the performances.

This view of the mechanism is supported by several information from literature. Döbber *et al*. suggested that the first step of the destruction of chlorinated VOCs is the adsorption of the molecule on Brønsted and/or Lewis sites [55]. Ramachandran *et al*. and Sinquin *et al.* also suggested that in the case of the total oxidation of methylene chloride, the first step is the adsorption of the chlorinated VOC on a Brønsted acid site [161,162]. Moreover, Larrubia *et al*. [68] suggested, on the basis of a FTIR study of the adsorption of chlorinated VOCs on a VO_x-MoO_x/TiO_2 formulation, that the total oxidation of chlorinated VOCs requires the presence of two sites: an acid site and a nucleophilic site. Moreover, they assumed that the adsorption of a chlorinated VOC proceeds via its chlorine on a Lewis site. This adsorption takes place through a concerted mechanism with a nucleophilic substitution that forms a phenate species. Furthermore, they suggested that the dechlorination step is not crucial while a more critical step is the full burning of the aromatic ring. These pieces of information are in agreement with our view that two types of sites are required. Our contribution concerns the understanding of a threshold of Brønsted sites at the surface of the samples or the related switch of dependency (from Brønsted sites concentration to redox sites concentration) of the performances when the catalyst crosses above the Brønsted sites threshold for any reasons.

To summarize at this stage, our works shows that the first step of the total oxidation of chlorinated VOCs is the adsorption of the molecule on a medium or strong Brønsted site. These medium or strong Brønsted sites thus generate at the surface of the catalyst a pool of adsorbed chlorobenzene molecules. These adsorbed chlorinated VOCs are therefore available for the further step, namely the oxidation of the aromatic ring on a neighboring VO_x redox site.

7.3.2. Influence of the redox sites properties on the catalytic performances of the VO_x/TiO_2 based catalysts

7.3.2.1. Reducibility of the VO_x phases

The reducibility of the VO_x monolayer of different formulations was evaluated through the investigation of the extent of the reduction undergone by the VO_x phases during the catalytic tests. The extent of the reduction was measured, on the one hand in the reference conditions and on the other hand in the presence of water vapor. Indeed, as reported in Chapters 4, 5 and 6, during the catalytic tests the VO_x active phase undergoes a reduction of its vanadium oxidation level compared to its value before test. This reduction of the V O.L. was observed on the surface and in the bulk as revealed by both XPS and the combination ICP-AES and EPR. This reduction was reported on Table 4-1, 5-1 and in Fig. 6-5 in previous chapters. In order to summarize these results, Table 7-2 exposes the average values of the V O.L. before and after catalytic test in the reference conditions and the extent of the reduction undergone during the test.

Table 7-2: Mean vanadium oxidation level (V O.L.) of the catalyst before and after reference test

	TsV	TsVW	TsVM
Mean V O.L. before test	4.977	4.861	4.906
Mean V O.L. after reference test	4.967	4.831	4.875
Δ V O.L.	-0.010	-0.030	-0.031

Table 7-2 shows that the V O.L. before test depends on the formulation. In the TsV catalyst, the VO_x phase is stabilized at a value close to the fully oxidized V^{5+} state as having a V O.L. of 4.977. The presence of the secondary phases WO_x or MoO_x stabilizes the VO_x phase at a lower vanadium oxidation level, namely 4.861 and 4.906, respectively. The stabilization of the vanadium oxidation level at a lower value in the presence of secondary phases was already reported by Forzatti *et al*. [159]. These

authors demonstrated that the introduction of WO_x in a VO_x/TiO_2 formulation induces i) a decrease of the vanadium oxidation level and ii) an increase of the reducibility of the VO_x phase. This increase of the VO_x reducibility is due to a strong electronic interaction that operates between VO_x and WO_x or VO_x and MoO_x surface species and the TiO_2 support. The electronic interactions lead to the formation of free electrons and may operate through oxygen bridging of the polyhedral structure and/or through the conduction band of the anatase TiO_2 support as suggested by Forzatti *et al.* [158-160].

Table 7-2 additionally shows that the extent of the reduction undergone during the catalytic test also depends on the formulation. The single VO_x phase (TsV) undergoes a slight reduction of -0.010, while VO_x-WO_x (TsVW) and VO_x-MoO_x (TsVM) undergo a deeper reduction: -0.030 and -0.031, respectively. The extent of the reduction of the VO_x phase is thus 3 times deeper in the case of the presence of WO_x or MoO_x. This conclusion is in good agreement with the conclusion of Chapter 4, which pointed out the effect of water on the oxidation state of the active phase. For the three catalysts, water induces the reduction of the "bulk" and of the "surface" of the VO_x phase. The degree of the reduction increases within the series: TsV < TsVW < TsVM. The reduction of the vanadium phase, in the presence of water, thus seems to be governed by the reducibility of the VO_x phase, which itself is dictated by the presence of WO_x or MoO_x. Moreover, the increase of the reducibility in the case of the addition of WO_x or MoO_x to a VO_x phase was already demonstrated based on H_2-TPR [157-159]. Our study has the advantage to investigate the reducibility of the catalyst under working conditions: it clearly demonstrates that the VO_x phase undergoes a reduction under the reference conditions.

From another point of view, the introduction of the WO_x or MoO_x secondary phases to VO_x/TiO_2 formulation (equivalent loading of VO_x and WO_x or MoO_x in terms of monolayer impregnated in a unique step) have shown to induce a synergetic effect. Namely, the performances of the binary catalysts

are higher than the sum of those obtained for VO_x/TiO_2 and WO_x/TiO_2 or MoO_x/TiO_2. As an example, in the case of formulations supported on sulfated TiO_2, the synergetic effect is revealed as the activity of the VO_x/TiO_2 formulation at 200 °C increases from 29% to 46% and 48% in the case of the addition of WO_x or MoO_x, respectively, while the activity of WO_x/TiO_2 and MoO_x/TiO_2 are only 8% and 5% respectively. This synergetic effect is exposed in details in Chapter 3. It is crucial to observe that the increase of conversion within the series: TsV < TsVW < TsVM and the extent of the synergetic effect both go in parallel with the increase of the reducibility of the VO_x phases, namely TsV < TsVW < TsVM, as reported above. There is thus a clear relationship between the reducibility of the VO_x phase and its activity in the course of the total oxidation of chlorinated VOCs. This relationship is supported by several authors, who reported that the increase of performance, in the SCR reaction of VO_x/TiO_2 based catalysts when adding WO_x or MoO_x in their formulation, is due to the increase of the reducibility of the VO_x phase [140,142,157-159,171-173].

Table 7-3: chlorobenzene conversion at 200 °C and 250 °C on the three selected catalysts

Chlorobenzene conversion (%)	TsV	TsVW	TsVM
200 °C	29	46	48
250 °C	81	92	95

The increase of reducibility should be regarded as an increase of the ability of the VO_x phase to transfer its lattice oxygen to a reactant. Moreover, an increase of reducibility usually goes in parallel with an increase of the ability of the active phase to get reoxidized by an oxidant present in the stream. We thus assume that the catalytic mechanism includes a step in which the active phase transfers some of its lattice oxygen atoms to oxidize the VOC molecule.

7.3.2.2. Influence of the vanadium oxidation level on the catalyst activity

The columns entitled X%-CLB of Table 7-4 report the chlorobenzene conversion of TsVW, respectively at 200 °C and 250 °C for the entire set of catalytic conditions. The last column of Table 7-4 gives the mean V O.L., estimated by combination of ICP-AES and EPR measurements.

Table 7-4: Catalytic conditions, chlorobenzene conversion at 200 °C and 250 °C and V O.L. for TsVW

	Catalytic conditions						X%-CLB		V
	$[C_6H_5Cl]$ ppm	$[O_2]$ ppm	$[H_2O]$ %	[CO] ppm	[NO] ppm	$[NO_2]$ ppm	200 °C	250 °C	O.L.
0	-	-	-	-	-	-	-	-	4.907
1	100	200000	0	0	0	0	45.5	95.1	4.868
2	100	200000	1	0	0	0	45.1	97.7	4.867
3	100	200000	2	0	0	0	30.5	88.0	4.860
4	100	200000	5	0	0	0	15.9	68.7	4.842
5	100	200000	0	5000	0	0	41.5	98.7	4.863
6	100	200000	0	50000	0	0	43.0	96.3	4.871
7	100	200000	0	0	100	0	69.5	98.5	4.924
8	100	200000	0	0	1000	0	76.6	96.7	4.974
9	100	0	0	0	1000	0	0.3	0.4	4.797
10	100	0	0	0	4000	0	0.2	1.3	4.737
11	100	0	0	0	0	1000	5.1	1.5	4.788
12	100	0	0	0	0	2000	87.5	93.8	4.949
13	100	0	0	0	0	4000	92.1	92.6	4.996
14	100	850	0	0	0	0	5.3	42.4	4.841
15	100	1450	0	0	0	0	6.7	62.4	4.846
16	100	5000	0	0	0	0	15.6	78.5	4.850
17	100	10000	0	0	0	0	26.4	90.4	4.854

The upper part of Table 7-4 (rows 1-8) presents the results of the experiments achieved in order to investigate the resistance of the VO_x-WO_x/TiO_2 catalyst (TsVW) in front of the co-pollutants (H_2O, CO, NO). In

the presence of 20% of O_2, the addition of co-pollutants in the stream induce huge changes i) in the chlorobenzene conversion and ii) on the vanadium oxidation level, depending on the nature and the concentration of the co-pollutant.

The introduction and the increase of the water concentration from 0 to 1, 2 and 5% induces a progressive decrease of the catalytic performances, *e.g.* the conversion at 200 °C decreases from 45.5 to 45.1, 30.5 and 15.9%, respectively (rows 1-4). In parallel, the increase of the water concentration induces a progressive decrease of the V O.L. (rows 1-4) from 4.868 to 4.867, 4.860 and 4.842 respectively. The presence of 5000 or 50000 ppm of CO in the stream does not induce any significant modification neither of the activity nor of the V O.L. (rows 1;5;6).

Contrary to the effect of water, increasing the concentration of NO in the stream induces a progressive increase of the chlorobenzene conversion and of the V O.L. (rows 1;7;8). Indeed, the chlorobenzene conversion at 200 °C improves from 45.5 to 69.5 and 76.6% when the concentration of NO in the catalytic stream is changed from 0 to 100 and 1000 ppm. In parallel to this improvement of activity, the vanadium oxidation level increases from 4.868 to 4.924 and 4.974. The mechanism of this positive effect was exposed in Chapter 6.

The results of this first set of experiments indicate a parallel evolution of the V O.L. and of the catalyst activity: i) increase of vanadium oxidation level means enhancement of catalytic performances in the presence of NO, ii) steadiness of the vanadium oxidation level in the presence of CO means stability of the chlorobenzene conversion and iii) decrease of the vanadium oxidation level means deactivation in the presence of H_2O.

The bottom part of Table 7-4 (rows 9-17) presents the results of the experiments aiming at investigating the influence of the presence of various concentrations of three different oxidants (NO, NO_2 and O_2), taken one by

one. Therefore this part of the table presents the chlorobenzene conversion and the vanadium oxidation level of the TsVW catalyst after test performed in the corresponding conditions.

In the absence of oxygen, the increase of the concentration of NO in the catalytic stream induced a severe drop of chlorobenzene conversion to less than 1% both at 200 °C and 250 °C (rows 9;10). This complete deactivation of the catalyst takes place in parallel to a deep reduction of the VO_x phase compared to the vanadium oxidation state before catalytic test. Indeed, the V O.L. decreased from 4.907, before test, to 4.797 and 4.737 after catalytic test, respectively in the presence of 1000 and 4000 ppm of NO. This investigation reveals that NO is not able to stabilize the catalyst at an adequate vanadium oxidation level to induce a stable conversion.

In the case of the use of NO_2 as oxidant, the increase of the concentration causes a gradual improvement of the chlorobenzene conversion (rows 11-13). However, in the presence of the lowest concentration of NO_2, *i.e.* 1000 ppm, the catalyst underwent a strong reduction passing from 4.907 to 4.788, respectively before and after test. This strong reduction is observed in parallel with a very weak catalyst activity corresponding to only 5.1% of chlorobenzene conversion at 200 °C. Nevertheless, a further increase of the NO_2 concentration up to 2000 and 4000 ppm induces a huge progressive increase of the catalyst performances and of the oxidation state of the VO_x phases. Indeed, the activity improves up to 87.5 and 92.1% at 200 °C while the reoxidation of the catalyst goes up to 4.949 and 4.996. In the presence of these two highest concentrations of NO_2, the vanadium phase of the catalyst thus clearly underwent a strong reoxidation in front of the V O.L. before catalytic test.

The lasts rows of Table 7-4 illustrate the catalytic activity and the evolution of the V O.L. before and after catalytic test in the presence of different concentrations of oxygen in the gaseous stream adjusted in the range 850-200000ppm (conditions 14-17 and 1). Under all the oxygen concentrations

investigated, the V O.L. was reduced in front of its value before catalytic test. However, the increase of the oxygen concentration induced a slight progressive decrease of the extent of this reduction from 4.841 to 4.846, 4.850, 4.854 and 4.868 when the concentration was increased from 850 to 1450, 5000, 10000 and 200000 ppm of atomic oxygen. In parallel, the activity of the TsVW catalyst progresses continuously from 5.3 to 6.7, 15.6, 26.4 and 45.5% when the oxygen concentration goes progressively from 850 to 200000 ppm of O_2. The results at both temperatures show that the oxygen concentration is a limiting factor, at least, up to the reference conditions *i.e.* in the presence of 20% of O_2.

The results of this second set of experiments confirm the observations of the first set of catalytic tests, indicating the parallel evolution of the V O.L. and of the catalyst activity: i) the use of NO as single oxidant induces a complete deactivation of the catalyst going simultaneously with a deep reduction of the vanadium, ii) the increase of the concentration of NO_2 as single oxidant provokes an almost complete reoxidation of the VO_x phase going in parallel with a very high activity and iii) the decrease of the concentration of O_2 from the reference conditions down to its total absence was followed by both a strong decrease of the catalyst activity and a decrease of the mean oxidation level of vanadium.

All these results from the two sets of catalytic investigation clearly demonstrate the existence of a strong correlation between the catalyst activity and the mean vanadium oxidation level. In order to investigate further this connection, Fig. 7-1 compiles all the catalytic and characterization results of the TsVW catalyst investigated in seventeen different catalytic conditions. This figure plots the catalyst activity of the TsVW catalyst, in terms of chlorobenzene conversion at 200 °C and 250 °C, as a function of the mean vanadium oxidation level estimated by the combination of ICP-AES and EPR measurements of the catalysts after the reaction.

The fitting of the catalytic results as a function of the vanadium oxidation level demonstrates that the V O.L. is the key factor determining the catalyst performances. The fact that the results of 17 catalytic tests, performed in very different gaseous conditions, fit all together proves that the catalytic conditions do not directly induce the catalyst activity. The catalytic conditions influence the performances of the catalyst through the stabilization of the VO_x phase at a certain vanadium oxidation level, and the vanadium oxidation level is the parameter that directly governs the catalytic performances. Therefore, the catalyst could exhibit the same catalytic performances independently of the catalytic conditions if these conditions lead to stabilize the VO_x at the same vanadium oxidation level.

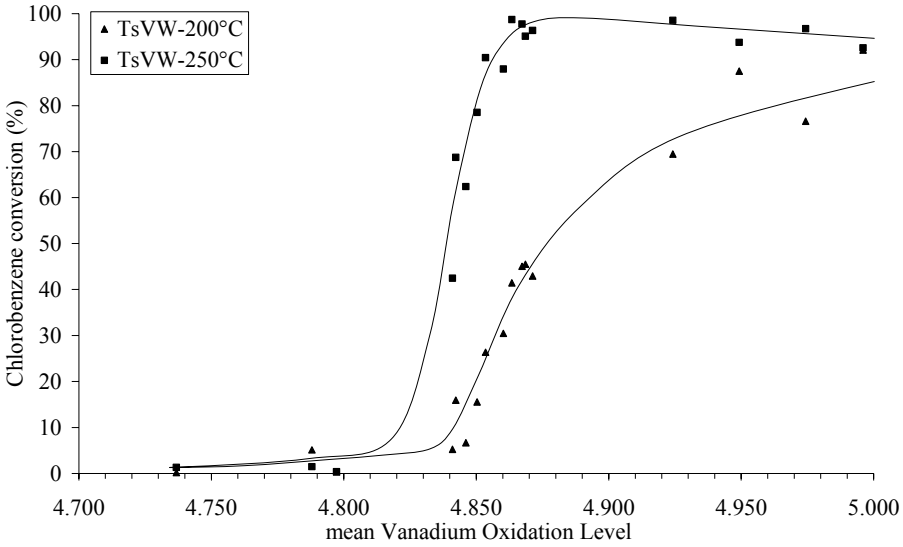

Fig. 7-1: Chlorobenzene conversion at 200 °C and 250 °C as a function of the vanadium oxidation level

The curve at 250 °C could be divided into 3 parts: i) V O.L.<4.82 the VO_x species are almost inactive for the total oxidation of chlorobenzene, ii) 4.82<V O.L.<4.87 the activity increases very sharply with the increase of the V O.L., and iii) 4.87<V O.L. the activity is maintained at a high level

independently of the V O.L. This figure precisely answers the question of the relationship between the V O.L. and the catalyst activity. It shows that in the case of the TsVW catalyst, to have a good catalyst, its vanadium oxidation level must be stabilized above an adequate value that we estimated as 4.87.

7.3.2.3. Understanding of the oxidative step of destruction of chlorinated VOCs on VO_x/TiO_2 based catalysts

The investigation of the influence of the VO_x reducibility on the catalytic performances reveals that the increase of the reducibility of the VO_x induces an improvement of the catalyst activity. This result demonstrates that the increase of the ability of the VO_x phase to give its lattice oxygen atoms is beneficial for the total oxidation of the chlorinated VOCs. It is thus clear that the mechanism of the oxidation of chlorinated VOCs on VO_x/TiO_2 catalysts contains a step consisting in the transfer of lattice oxygen atoms to a reactant. The observation of the reduction of the VO_x phase during the catalytic process as exposed at point 7.3.2.1. indeed confirms this view.

In the investigation of the strength of O_2 as an oxidant molecule on the TsVW catalyst, we observed that the increase of the oxygen concentration induces an enhancement of the catalyst activity. This observation reveals that the oxygen concentration in the catalytic stream is a limiting factor for the catalytic reaction as shown in Fig. 6-4. The activity increases up to a concentration of 20% of O_2. Moreover, Table 7-4 and Fig. 6-8 show that the catalyst undergoes a reduction of its vanadium oxide phase in all tests *i.e.* for all concentrations up to 20% of O_2. However, the progressive increase of the atomic oxygen concentration induces the stabilization of the vanadium in an oxidation state gradually higher in front of the oxidation level in the presence of the smallest oxygen concentration. These results demonstrate that VO_x takes oxygen from the gaseous stream to reoxidize the reduced VO_x sites. This fact, in parallel with the fact that the VO_x sites give lattice oxygen atoms, demonstrates that the catalyst "breathes" during the catalytic

process. The VO_x phase cyclically gives lattice oxygen to a reactant and then is reoxidized by the oxidant present in the gaseous stream.

Furthermore, in conditions 9, *i.e.* in the absence of oxygen but in the presence of 1000 ppm of NO (which is unable to reoxidize the catalyst as proven in Chapter 6 and Fig. 7-4), during a very short period of time (more or less 5 minutes), the catalysts induce a limited conversion of chlorobenzene. This limited conversion then sharply goes down to less than 1% of conversion after stabilization as shown in Table 7-4. This absence of stable conversion is linked to the impossibility for the catalyst to be regenerated (reoxidized) due to the absence of oxidant in the catalytic stream. This demonstrates the incapacity of the catalyst to sustain a stable conversion without being reoxidized by an oxidant from the gaseous stream.

Changing the nature of the oxidant present in the gaseous stream (from O_2 to NO_2) induces a modification of i) the catalytic activity and ii) the VO_x oxidation level. Indeed, the change from a moderate oxidant (O_2) to a stronger oxidant of the reduced VO_x sites (NO_2) is beneficial for the activity. This observation also confirms that the mechanism contains a step of reoxidation of the VO_x reduced sites and that the catalyst breathes during the catalytic process.

All the previous observations are consistent with the relationship between the VO_x level and the improvement of the catalyst activity demonstrated at point 7.3.2.2. Indeed, we demonstrated that the increase of the VO_x oxidation state induces an increase of the catalytic performances. Actually, the increase of the mean oxidation level goes in parallel with the increase of the amount of lattice oxygen atoms that could be transferred to induce the combustion of the chlorobenzene. This enhancement of the quantity of lattice oxygen atoms available accounts for the observed improvement of the conversion of the chlorinated VOCs.

This entire set of results, namely: i) the catalyst gives lattice oxygen atoms to perform the oxidation of the chlorobenzene (inducing the observed reduction of the VO_x phase in the absence of an efficient oxidant in the feed), ii) the increase of the ability of the catalyst to gives its lattice oxygen atoms (increase of the reducibility) induces an increase of the catalyst performances, iii) the increase of the oxygen concentration in the stream facilitates the reoxidation of the catalyst, iv) the choice of a stronger oxidant for the VO_x reduced sites (NO_2 instead of O_2) leads to an increase of the vanadium oxidation level and of the activity and v) the increase of the amount of lattice oxygen atoms available for the oxidation of the chlorinated VOCs improves the conversion, demonstrates that the oxidation of chlorinated VOCs proceeds via a Mars and van Krevelen mechanism [167].

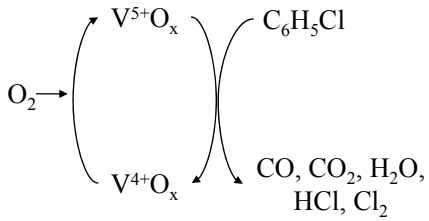

Fig. 7-2: Scheme of the Mars and van Krevelen proceeding at the surface of the VO_x/TiO_2 based catalyst

This mechanism occurs in two steps following the scheme of Fig. 7-2. In the first step, the $V^{5+}O_x$ phase gives some of its lattice oxygen atoms to oxidize chlorobenzene which leaves behind reduced $V^{4+}O_x$ species. In the second step, these $V^{4+}O_x$ species are reoxidized by the oxidant present in the gaseous stream (O_2 or NO_2). The limitation of the chlorinated VOCs destruction in the case of a limited concentration of oxygen and the stabilization of the VO_x phase at a lower oxidation state reveal that the second step of the mechanism is limitative.

Equation 7-1: $C_6H_5Cl + 7\ O_2 \rightarrow 6\ CO_2 + 2\ H_2O + HCl$

The oxidation of one chlorobenzene molecule requires 14 atoms of oxygen as demonstrated in Equation 7-1. We can thus assume that the total oxidation of a chlorobenzene molecule requires either the intervention of more than one VO_x site or the occurrence of more than one cycle (reduction-oxidation) by the active VO_x site. We presume that both situations take place at the surface of the catalyst, even if we can assume that the first situation must be predominant. This assumption is based on the fact that the reoxidation of the reduced VO_x sites is a limiting step. It is thus more probable that the chlorobenzene molecule is oxidized step by step by neighboring VO_x sites. Each neighboring VO_x sites gives some of its lattice oxygen atoms to finally achieve the total oxidation of the chlorobenzene molecule.

7.3.3. Influence of the retrieving of chlorine from the catalysts surface

Chapters 2 and 3 demonstrated that VO_x based catalysts are resistant to the presence of chlorine atom in the molecule that must be oxidized. Indeed, the ToF-SIMS measurements demonstrated (Table 2-2) that there is not more chlorine on the surface of the used VO_x based catalysts than on the fresh one. Such suggested that the easy retrieving of the chlorine from the surface of VO_x catalysts is far from being observed for all formulations. Indeed in the case of other oxides, like CrO_x and MnO_x, the presence of chlorine in the molecule that must be oxidized induces a deactivation of the catalyst through, on the one hand, a blocking of the active sites, and on the other hand, the formation of oxychlorides. These results demonstrated that the retrieving of the chlorine from the surface of the catalyst is a crucial step of the total oxidation of chlorinated VOCs on VO_x based catalysts. The fact that the chlorine retrieving is not a significant rate limiting step was suggested by Amiridis *et al* [56] based on the fact that, even under dry conditions, VO_x based catalysts are very active.

However, Chapter 4 demonstrated that water vapor can play a positive role in the destruction of the chlorinated VOCs. TsV catalyst shows indeed an increase of activity in the presence of the lowest water concentrations (1% and 2%). Only one hypothesis could account for this positive effect, namely the retrieving of Cl^- from the surface by H_2O through the formation of easily desorbed HCl. This phenomenon was reported by Lomnicki *et al*. in the case of the use of vanadium oxide-based catalysts in the course of the total oxidation of trichlorophenol [52,87]. Moreover, this is strengthened by Amiridis *et al*. who proposed the same mechanism in the case of the total oxidation of dichlorobenzene on transition oxides based catalysts [56]. They suggested that this positive effect is governed by Equations 7-2 and 7-3, where s means surface.

Equation 7-2: $$-Cl_s^- + H_2O \Leftrightarrow -OH_s^- + HCl$$

Equation 7-3: $$2-OH_s^- \rightarrow -O_s^{2-} + H_2O$$

Although these results suggest that the retrieving of the chlorine from the surface of the VO_x based catalyst is one of the steps of the mechanism of the total oxidation of chlorinated VOCs, they also show that it influences only slightly the rate of the total oxidation.

7.4. Mechanism of the total oxidation of chlorinated VOCs on VO_x/TiO_2 based catalysts

One can now compile all the pieces of understanding that we have acquired to build the complete mechanism of the total oxidation of chlorinated VOCs on VO_x/TiO_2 based catalysts. This proceeds thus in four steps. The first step is the adsorption of the chlorinated VOCs on medium or strong Brønsted acid sites. These sites are mainly located at the surface of the WO_x and MoO_x secondary phases. Their main role it to create a pool of adsorbed chlorinated VOCs at the surface of the catalyst. This stage is followed by

the attack of a redox site in order to induce the step-by-step oxidation of the aromatic ring of the chlorinated VOCs by the redox sites present at the surface of the active VO_x phase. This second step, namely the oxidation of the aromatic ring, proceeds via a Mars and van Krevelen mechanism. Several VO_x sites are probably involved in order to oxidize completely the aromatic ring by transferring some of their lattice oxygen atoms to the hydrocarbon. This step leads to i) the formation of CO_x and H_2O and ii) the reduction of the active phase. The third step of the total oxidation of chlorinated VOC is the regeneration of the VO_x sites through their reoxidation by the oxidant present in the gas stream, namely O_2 or by the O* oxygen atoms produced by the decomposition of the O_2 molecules on the surface of the catalyst. These active sites when reoxidized can play again their oxidant role in the combustion of either fragments of the same aromatics or of a new molecule. The last step is the retrieving of the chlorine from the catalyst surface. This step is performed by the reaction of water, whether produced during the third step or initially present in the effluent gas, with the chlorine on the surface easily desorbing HCl.

In this mechanism, the third step, namely the reoxidation of the reduced VO_x sites, is the rate limiting step. In order to improve this step, several properties of the VO_x active sites can be optimized. The best activity is obtained when: i) the reducibility of the VO_x redox sites is increased and ii) the vanadium oxidation level is stabilized under working conditions above a mean value, namely around 4.87 in the case of the TsVW catalyst. The reducibility is improved by introducing secondary phases as WO_x and MoO_x in the catalyst formulation. The vanadium oxidation level can be stabilized at a high value by performing the catalytic destruction of the chlorinated VOCs in a stream as oxidant as possible. This increase of the oxidant strength of the stream can by obtained by i) increasing the oxygen concentration, ii) introducing a stronger oxidant (NO_2) or iii) generating *in situ* a stronger oxidant than O_2, namely by introducing NO which then generate NO_2 in the reactor (Chapter 6).

The proposed mechanism requires the presence of two sites: a medium or strong Brønsted acid site and a redox VO_x site. However, these two sites are mainly located on two different phases. The medium or strong Brønsted sites are principally located on the surface of the secondary phases while the redox active sites are essentially present on VO_x. Therefore, the beneficial effect of performing the synthesis of the binary formulations in a unique step resides in the maximization of the intimacy between both the active and the secondary phases. Such intimacy favors the accessibility of the adsorbed chlorobenzene to the redox sites, improving the combustion of chlorobenzene.

7.5. Conclusions

The separate investigation of several aspects of the catalysts that could influence their performances allows us to draw a complete picture of the catalytic mechanism. These aspects are: the acidity, the redox behavior of the VO_x sites and the retrieving of the chlorine from the catalyst surface. This investigation demonstrated that the mechanism of the total oxidation of chlorinated VOCs proceeds within four steps. The first one is the adsorption of the chlorinated VOCs on medium or strong Brønsted sites. These sites are mainly located at the surface of the secondary phases. The so-formed pool of adsorbed chlorobenzene provides the aromatic rings for the second step. The second and third steps of the destruction are the oxidation of the aromatic ring by several VO_x redox sites and the regeneration of the reduced sites as described by a classical Mars and van Krevelen mechanism [167]. In the second step, the VO_x redox sites give some of their lattice oxygen atoms to oxidize step-by-step the aromatic ring producing H_2O and CO_x. This step is followed by a regeneration step, namely the reoxidation of the VO_x reduced sites thanks to the oxidant present in the gas stream (O_2). The fourth step of the mechanism is the retrieving of the chlorine from the surface thanks to its reaction with water, liberated in the previous step or initially present in the feed, producing HCl.

The third step, namely the reoxidation of the reduced VO_x site is the rate limiting step of the mechanism. The catalytic performances can thus be improved by tuning the redox properties of the VO_x phases. The addition of the secondary phases that improves the reducibility of the VO_x phases promotes the conversion. Also, the increase of the oxidant strength of the gas stream promotes the activity through the increase of the vanadium oxidation level. The best performances are obtained when vanadium is maintained at an oxidation level of more than a certain value that we estimated as 4.87 in the case of the TsVW catalyst.

Furthermore, the beneficial effect of performing the synthesis of the binary formulations in a unique step is understood as residing in the increase of the intimacy between both the active and the secondary phases. The intimacy favors the accessibility of the adsorbed chlorobenzene, present as a pool on the secondary phases, to the redox VO_x sites, improving the combustion of chlorobenzene.