PART II: INVESTIGATION OF THE EFFECT OF CO-POLLUTANTS (H_2O, CO, NO_X) ON THE CATALYST PERFORMANCES

Part I demonstrated that VO_x/TiO_2 catalysts, possibly "upgraded" to VO_x-WO_x/TiO_2 or VO_x-MoO_x/TiO_2, are very efficient in the total oxidation abatement of chlorobenzene (taken as a model molecule for dioxins). However, while exhaust gases inevitably contain H_2O, CO, NO_x, and SO_x the efficiency of these catalysts was attested, in our research and in the literature, only for flows containing chlorinated aromatics as single pollutant. It is thus crucial to assess whether they still succeed to oxidize chlorobenzene efficiently in the presence of co-pollutants or whether the latter induce some kind of deactivation.

H_2O is commonly regarded as a poison for the catalytic combustion of VOCs, as it could degrade the catalyst physico-chemical properties (*e.g.* reduction, decrease of the specific surface area, diminishment of the porous volume, etc…) [48,58,95,96,98,144]. However, in the case of the combustion of chlorine-containing VOCs, water could however play an additional interesting role, namely by removing Cl^- left on the surface after the oxidation of the aromatic ring [56]. It is thus crucial to investigate the influence of H_2O on the catalyst performances.

Forzatti *et al.* pointed out that all species having a "own electronic configuration" (unoccupied orbital or free electron) or a multiple bond (which is the case of CO) could be considered as a potential poison [145]. Indeed, Pattersen *et al.* demonstrated a partial deactivation of Pt, Pd and Rh based catalysts for the total oxidation of benzene in the presence of 0.9 vol.% of CO in the catalytic stream [146]. At the opposite, Van den Brink revealed that CO has no influence on the catalytic performances of a Pt/Al_2O_3 catalyst in the course of the total oxidation of chlorobenzene [61]. However, all these conflicting results are related to noble metal catalysts, referring to Forzatti, the transition metal oxides based catalysts are less sensitive to poisoning risks. Therefore, it is crucial to investigate the exact effect of CO on our catalysts and following our catalytic procedure.

The effect of NO_x on the performances of the VO_x based catalysts in the course of the total oxidation of chlorinated VOCs was never investigated. However, these catalysts were intensively explored in the field of the NO_x SCR reaction. Several authors proposed diverging hypothetical mechanisms for this reaction. Tagaki *et al.* proposed that NO adsorbs on the vanadium oxide sites, and is transformed into adsorbed NO_2 which reacts with strongly adsorbed NH_3 following a Langmuir-Hinshelwood mechanism [147]. At the opposite, Inomata [148] proposed that NO reacts in gaseous phase with strongly adsorbed NH_3 as described in a Eley-Rideal mechanism [149]. Janssen [150] and Topsøe [151] support the Eley-Rideal mechanism which does not imply the adsorption of NO on the surface of the catalyst in the catalytic conditions. However, it is well established that NO adsorption takes place only if the VO_x phase is reduced [151,152] and that the adsorption does not take place on a fully oxidized catalyst [153] or on bulk V_2O_5 [154]. However, there is only few data about the extent of the reduction required to have a significant adsorption of NO. Centeno suggested that to have an optimum adsorption of NO, the mean vanadium oxidation level must be stabilized between 3.1 and 4 [155]. Based on all these information coming from the literature, it is possible that NO adsorbs on the VO_x phases. This adsorption could lead to a competitive effect between NO and chlorinated VOCs leading to a decrease of the amount of active sites available for i) the adsorption and/or ii) the oxidation of the chlorinated VOCs. It is however very difficult to predict the influence that NO could play on the catalyst performances in the course of the total oxidation of chlorinated VOCs. Therefore, it is crucial to investigate the effect of NO in our catalytic conditions and on our catalysts.

The aim of the EPURCAT project is to design a complete catalytic system for the total oxidation of chlorinated VOCs, CO and NO_x. Therefore, the second part of the thesis aims at investigating the influence of these co-pollutants (H_2O, CO and NO_x) on the activity of the VO_x based catalysts in the course of the total oxidation of chlorinated VOCs. We have chosen to

perform this research with the three best formulations: VO_x, VO_x-WO_x and VO_x-MoO_x supported on sulfated titania. Moreover, in order to achieve this survey we decided to complete this research by investigating the effect of each co-pollutant one by one. Furthermore, the co-pollutants concentration windows investigated correspond to the industrial concentrations met in the exhaust gases from cogeneration and incineration units. The usual concentrations of H_2O, CO and NO_x in the cogeneration and combustion exhaust gases are, respectively, in the range 1-5% [40,56,72,95-98], 0.5-5% [99-101] and 100-1000 ppm [101-103].

CHAPTER 4 : MULTIPLE EFFECTS OF H_2O ON THE ACTIVITY OF VO_X BASED CATALYSTS FOR THE COMBUSTION OF CHLORINATED VOCS

Abstract

This chapter reports the investigation of the influence of H_2O on the performances of the best formulations (VO_x/TiO_2, VO_x-WO_x/TiO_2 and VO_x-MoO_x/TiO_2 catalysts) in the course of the combustion of chlorobenzene. The influence of water was investigated by varying its concentrations in the catalytic stream from 0% to 5%. Based on catalytic results, XPS, EPR and acidity measurements, we demonstrated that H_2O influences in opposite manners the chlorobenzene conversion depending on its concentration and on the kind of catalysts. The overall influence of water is the sum of three effects, two negative: i) the reduction of the vanadium phase dictated by its reducibility, itself influenced by the presence of WO_x or MoO_x, ii) the decrease of the number of strong Brønsted acid sites involved in the adsorption of the chlorobenzene; and one positive: iii) the retrieval of chlorine species from the surface through the production of HCl.

4.1. Introduction

Part I, based on a systematic screening (10 transition metal oxides supported on 4 different supports), on an investigation of the loading effect, and on the

study of the resistance against chlorinated compounds, spotlighted the very good activity of VO_x monolayer species supported on titania. Moreover, the synergetic effect brought by WO_x and MoO_x species was also demonstrated, mainly in the case of a synthesis in a unique step. However, the synthetic catalytic stream used in this first part was not representative of the real exhaust gases as it does not contain any co-pollutants present beside dioxins. It is thus crucial, now, to assess whether our best formulations are resistant to the co-pollutants or whether they induce some kind of deactivation.

Therefore, this chapter reports on our investigation of the influence of H_2O on the total oxidation of chlorobenzene on VO_x/TiO_2 catalysts possibly doped with WO_x or MoO_x. Water is indeed a very special molecule in this reaction. Firstly, water is found in exhaust gases since it is present in the combusted materials and produced during the incineration processes. Secondly, water is a product of the catalytic total oxidation of chlorobenzene as reported in equation 4-1. Thirdly, water is commonly regarded as a poison for the catalytic combustion of VOCs, as it could degrade the catalyst physico-chemical properties [48,58,95,96,98,144]. In the case of the combustion of chlorine-containing VOCs, water could however play an additional interesting role, namely by removing Cl^- left on the surface after the oxidation of the aromatic ring [56]. Finally, water could also react with chlorine to produce HCl by the Deacon reaction (Equation 4-2) and change the HCl/Cl_2 selectivity [40]. Therefore, in order to evaluate more accurately the performances of our selected catalysts in a more realistic stream and to have a better understanding of the catalytic mechanism, we decided to carry out catalytic tests in presence of different concentrations of water.

Equation 4-1: $C_6H_5Cl + 7\ O_2 \rightarrow 6\ CO_2 + 2\ H_2O + HCl$

Equation 4-2: $H_2O + Cl_2 \rightarrow 2\ HCl + ½\ O_2$

4.2. Experimental and methods

4.2.1. Preparation of the catalysts

Catalysts are supported Millennium PC100 titania. The active phase is VO_x (catalysts denoted TsV) or a combination of VO_x with WO_x (catalysts denoted TsVW) or with MoO_x (catalysts denoted TsVM). The catalysts were prepared following the procedure presented in 1.2.1. and 3.2.1. In the case of TsVM and TsVW, the impregnation was made at once from solutions containing simultaneously V and Mo, or V and W salts.

4.2.2. Catalytic tests

All catalytic tests were performed in a fixed-bed micro-reactor (PID Eng&Tech S.L, Madrid - Spain) as described at point 2.2.2.

The gas stream was composed of 100 ppm of chlorobenzene, 20 vol.% of O_2, 0-1-2-5 vol.% of H_2O and helium as diluting gas. Water was supplied by a controlled evaporator mixer (CEM from Bronkhorst HiTec) stabilized at 50 °C and flushed with 50 $ml.min^{-1}$. The reaction was run at 200 and 250 °C during 150 min at each temperature.

4.2.3. Characterization

XPS was performed following the protocol presented in 1.2.3. The following peak intensities were used for the quantitative analysis: V 2p, W 4d, Mo 3d, Ti 2p, Cl 2p, O 1s and C 1s. Accurate evaluation of the vanadium oxidation state requires to avoid vanadium reduction during time under vacuum, as observed by Nogier *et al*. [156]. Therefore a "quick XPS analysis" was performed in such a manner that for each sample a unique window with O 1s and V 2p peaks was recorded within less than 10 minutes. For the decomposition of the V $2p_{3/2}$ into V^{n+} species, we fixed the binding energy of

the O 1s at 530 eV as a reference and the gap between O 1s and V^{5+} species between 12.85 and 12.9 eV. For the evaluation of the other oxidation states, firstly, the gap V^{5+}-V^{4+} was fixed at 1.2 eV, secondly the FWHM of the two oxidation states were fixed to be equal. The surface mean vanadium oxidation state was evaluated by means of Equation 4-3.

Equation 4-3: V O.L. (XPS) = 5*atomic concentration of V^{5+} + 4*atomic concentration of V^{4+}

The bulk mean vanadium oxidation level (hereunder V O.L.) was estimated by combination of ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) and EPR measurements (Electron Paramagnetic Resonance). The ICP-AES measurements were performed as exposed in 3.2.3. The EPR spectra were recorded at 25 °C with a spectrometer JEOL JES-RE 2X equipped with a cylindrical cavity ES-UCX2 using the following settings: magnetic field (H_0), 300 mT; scan width, 250 mT; microwave frequency ν_0, 9.430-9.440 GHz; microwave radiation power (Pw), 5 mW; modulation amplitude, 0.5 mT; modulation frequency, 100 kHz; time constant, 0.01 s; scan time, 8 min. All these parameters were chosen in order to avoid saturation of the signal and were maintained constant for all the measurements. For each sample, three times, the dry catalyst was weighted to have about 100 mg of materials introduced into a 4 mm diameter EPR quartz tube, which was afterwards sealed. For each quartz tube, three times, the signal was registered. This registered signal is the first-derivative curve of the absorption signal. The data treatment (base line correction, support spectra subtraction, weight correction and double integration) was done five times for each measurements with the JEOL "esprit 330, 01.521 version" software. The amount of V^{4+} was estimated by the mean of the 45 area under the second-derivative curve integrated twice and by comparison with a series of standard mixtures of $VOSO_4$ (Merk, 99.99%) in K_2SO_4 (Aldrich 99.99%). Based on these measurements, the random error was thus limited as much as possible. However a systematic error on the value is still

possible. The vanadium mean oxidation state was evaluated by means of Equation 4-4.

Equation 4-4: V O.L. (EPR) = 5*(atomic concentration of V determined by ICP-AES - atomic concentration of V^{4+} determined by EPR) + 4*atomic concentration of V^{4+} determined by EPR

The ammonia chemisorption experiments were conducted at 35 °C, 150 °C, 250 °C and 350 °C using the static volumetric apparatus Micromeritics ASAP 2010C adsorption analyzer and using the following protocol developed in our lab. The samples (100 mg) were first degassed at 25 °C down to 0.5 Pa. The samples were heated under a pure flow of oxygen to 350 °C for 1 h and then cooled down to the analysis temperature. After evacuation of the sample at 0.5 Pa, the chemisorption analyses were performed. A first isotherm allows evaluating the volumes of ammonia physisorbed and chemisorbed at different pressures. After evacuation of the physisorbed fraction for 1 h at the analysis temperature, a second isotherm is used to determine the fraction reversibly adsorbed. The volume of ammonia chemisorbed at a given temperature is estimated by subtraction between those two isotherms.

4.3. Results

4.3.1. Catalytic conversion of chlorobenzene

Figure 4-1 shows the evolution of the chlorobenzene conversion at 200 °C and 250 °C as a function of the water concentration in the stream for the 3 catalysts. The effect of water varies greatly with its concentration and the kind of active phases. In the case of VO_x, at 200 °C, the chlorobenzene conversion increases from 29%, obtained without water, up to 44% and 42% in the presence of 1% and 2% of water. On the contrary, in the presence of 5% of water, the chlorobenzene conversion decreases to 26%. In the case of VO_x-WO_x, the increase of the water vapor concentration progressively

induces a strong deactivation. The conversion decreases from 46% in the absence of water, to 30% and 16%, respectively, in the presence of 2% and 5% of water. The deactivation is much stronger in the case of the VO_x-MoO_x catalyst which is almost completely deactivated when 2% of water is added in the stream. This deactivation corresponds to a decrease of the chlorobenzene conversion from 48% to 8%. At 250 °C, the chlorobenzene conversions are higher but the tendencies are identical to those noticed at 200 °C.

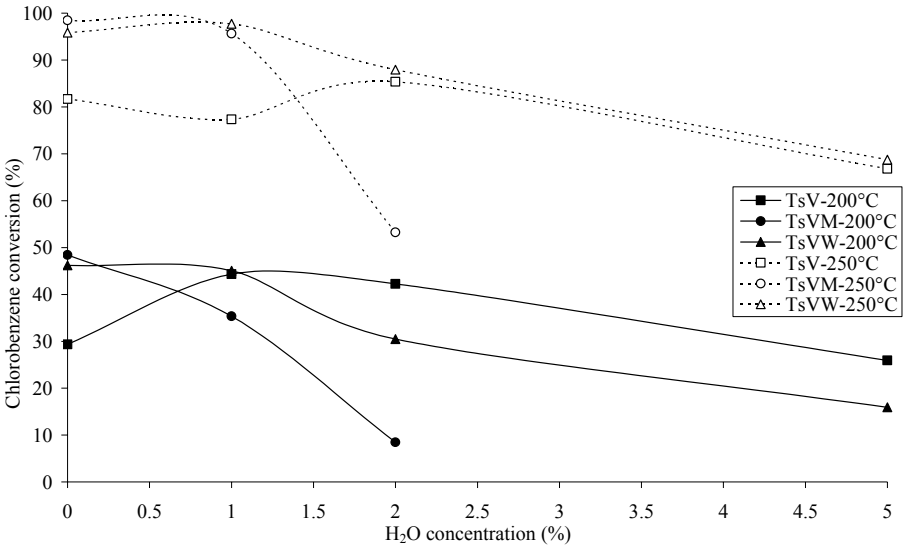

Fig. 4-1: Chlorobenzene conversion at 200 °C and 250 °C depending on the H_2O concentration (%)

4.3.2. Evaluation of the vanadium oxidation level (V O.L.)

Table 4-1 shows the estimated value of the vanadium oxidation level of the catalysts before and after catalytic test. On the one hand, the "bulk" oxidation level estimations are based on the EPR and ICP-AES results. On the other hand, the "surface" oxidation level results are obtained by

decomposition of the XPS $V2p_{3/2}$ peak. The "bulk" results (EPR-AES) show that in the "fresh" catalysts, the second phase (WO_x or MoO_x) induces a stabilization of the active phase (VO_x) at a lower oxidation level, respectively 4.907 and 4.944 for TsVW and TsVM rather than 4.980 for TsV.

Table 4-1: "bulk" and "surface" Vanadium oxidation level evaluated by EPR-ICP and XPS

	TsV		TsVW		TsVM	
	EPR	XPS	EPR	XPS	EPR	XPS
"Fresh"	4.980	4.97	4.907	4.77	4.944	4.83
0% H_2O	4.971	4.96	4.885	4.74	4.918	4.79
1% H_2O	4.958	4.89	4.867	4.70	4.859	4.67
2% H_2O	4.954	4.80	4.860	4.62	4.820	4.53
5% H_2O	4.950	4.78	4.842	4.57	-	-

For all catalysts after test, the vanadium oxidation level is lower than before the test pointing a reduction of the active phase oxidation level during the catalytic combustion. Moreover, a progressive reduction of the vanadium was observed with the increase of the water concentration. This reduction is weak in the case of VO_x which goes from 4.971 to 4.950, respectively in the absence and in the presence of 5% of water, while it is greater in the case of the combined phases. In the presence of WO_x, VO_x undergoes a reduction from 4.885 in the absence of water to 4.842 in the presence of 5% of water. VO_x was most affected in the presence of MoO_x, undergoing a reduction from 4.918 in the absence of water to 4.820 in the presence of 2% of water. The evolutions of the surface vanadium oxidation level (evaluated by XPS) are in very good agreement with the evolutions of the "bulk" oxidation level. Nevertheless, surface oxidation levels are systematically lower than "bulk" ones. Two hypotheses could account for this: (i) surface vanadium species are more affected by the stream than "bulk" ones, (ii) the deep vacuum, inherent to the XPS measurement, induces a reduction of the supported vanadium species [156].

Moreover, the investigation of the Mo and W oxidation level by XPS demonstrated that there is no modification of the mean oxidation level of both secondary phases during the catalytic tests.

4.3.3. Evaluation of the catalyst acidity

Table 4-2: Acidity of the catalysts after catalytic test determined by NH_3-chemisorption

	Catalyst	TsV				
	H_2O concentration	0%	1%		5%	
µmole NH_3/g catalyst	Weak Acid Sites (35 °C<W.A.S.<150 °C)	223	219	-4 (-2%)	220	-3 (-2%)
	Medium Acid Sites (150 °C<M.A.S.<350 °C)	102	98	-4 (-4%)	91	-11 (-10%)
	Strong Acid Sites (S.A.S.>350 °C)	75	69	-6 (-8%)	67	-8 (-10%)

	Catalyst	TsVM				
	H_2O concentration	0%	1%		2%	
µmole NH_3/g catalyst	Weak Acid Sites (35 °C<W.A.S.<150 °C)	223	221	-2 (-1%)	229	+8 (+3%)
	Medium Acid Sites (150 °C<M.A.S.<350 °C)	150	132	-18 (-12%)	78	-44 (-48%)
	Strong Acid Sites (S.A.S.>350 °C)	66	54	-12 (-17%)	46	-20 (-30%)

Table 4-2 shows the amount of acid sites determined by NH_3-chemisorption at different temperatures (35 °C-150 °C-350 °C) for the catalysts after test. Acid sites are arbitrarily classified as Strong Acid Sites (S.A.S.= those on which NH_3 is still adsorbed above 350 °C), Medium Acid Sites (M.A.S.= those on which NH_3 remains adsorbed between 150 °C and 350 °C) and Weak Acid Sites (W.A.S.= those on which NH_3 remains adsorbed only below 150 °C).

The number of W.A.S. is not significantly affected by the presence of water, but the number of M.A.S. and S.A.S. decrease with the increase of water concentration for the investigated catalysts (TsV and TsVM). The VO_x catalyst loses up to 10% of its acid sites (M.A.S. and S.A.S.) in the presence of 5% of water. The disappearance of M.A.S. and S.A.S. is even more marked in the case of the combined phase. For example, the TsVM catalyst loses, respectively, 48% and 30% of its M.A.S. and S.A.S. when 2% of water is added in the reaction stream.

4.4. Discussion

For the two combined catalysts (TsVW and TsVM), adding H_2O in the gas stream is clearly detrimental to the conversion of chlorobenzene. Within the range investigated, the activity decreases with increasing H_2O concentration. Moreover, this depressing effect has also been observed on the TsV catalyst in the presence of 5% of water. The negative effect of water on the activity of vanadium oxide-based catalysts has already been observed [48,56,72]. Nevertheless, the hypothesis proposed was based on a competitive adsorption between water and the chlorinated compound on the active sites. This hypothesis is usually only supported by catalytic results and sometimes by IR data, and never considers any possible effect of water on the physico-chemical properties of the active phase. Moreover, this hypothesis does not explain the different behaviors that we observed on three catalysts characterized by the same active phase (VO_x loaded at 0.75 monolayer on the same support).

Our characterizations pointed out the effect of water on the oxidation state of the active phase and on the acidity of the catalyst. For the three catalysts, water induces the reduction of the "bulk" and the "surface" of the VO_x phase. The degree of the reduction is progressive within the series: TsV < TsVW < TsVM. It is established that WO_x or MoO_x increase the reducibility of VO_x [157-159]. This increase of the VO_x reducibility is due to a strong

electronic interaction that operates between V and W or V and Mo oxide 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 polyhedra and/or through the conduction band of the anatase TiO_2 support as suggested by Forzatti *et al.* [158-160]. Therefore, the reduction of the vanadium phase, in the presence of water, seems to be modulated by the reducibility of the VO_x phase, which itself is dictated by the presence of WO_x or MoO_x. The progressive reduction of the active phase seems to induce the decrease of the chlorobenzene conversion with the increase of the water concentration.

The acidity characterization revealed the decrease of the number of medium and strong acid sites in the presence of water. The extent of the disappearance of the acid sites is progressive with the concentration of water and is much more marked for the combined catalyst. Based on the investigation of the acidity of the three selected catalysts in Chapter 3, their acid sites are mainly Brønsted sites. Moreover, based on the conclusions of Chapter 3 and on literature, strong Brønsted acid sites are supposed to be the adsorption sites of the chlorinated VOCs during the first step of their catalytic combustion [55,161,162]. The observed decrease of the number of M.A.S. and S.A.S. (Brønsted sites) on VO_x and MoO_x phases, thus also corresponds to a reduction of the number of chlorobenzene adsorption sites. This phenomenon perfectly accounts for the observed reduction of the chlorobenzene conversion.

Water clearly induces a negative effect on the performance of VO_x catalysts in the oxidation of chlorinated VOCs, as it induces a reduction of the active phase and a decrease of the number of acid sites. Nevertheless, TsV catalyst shows an increase of activity in the presence of the lowest water concentrations (1% and 2%). To our opinion only one hypothesis could account for this positive effect, namely the retrieval of Cl^- from the surface by H_2O through the formation of easily desorbed HCl. This phenomenon

was already reported in the case of vanadium oxide-based catalysts [52,56,87] and is governed by Equations 4-5 and 4-6, where s means surface.

Equation 4-5: $-Cl_s^- + H_2O \Leftrightarrow -OH_s^- + HCl$

Equation 4-6: $2-OH_s^- \rightarrow -O_s^{2-} + H_2O$

4.5. Conclusions

Water plays a positive role in the catalytic oxidation of chlorobenzene by removing the chlorine from the surface of the catalyst. But water vapor additionally influences negatively by two other routes. The first one is the reduction of the active phase (VO_x) which is progressive with water concentration. This reduction is modulated by the reducibility of the VO_x phase which itself is dictated by the presence of WO_x or MoO_x. The second phase (WO_x or MoO_x), on the one hand, indeed increases the reducibility of the active phase (VO_x). This effect is strongly positive for the total oxidation of chlorobenzene. But, on the other hand, it over-sensitizes the catalysts with respect to water. The second negative route by which water is diminishing the activity of the catalyst is the decrease of the amount of medium and strong Brønsted acid sites involved in the chlorobenzene adsorption during the first step of the chlorobenzene oxidation. The relative importance of the three dynamic effects (chlorine retrieval, reduction of the active phase and decrease of the number of adsorption sites) allows us to explain water influence on the VO_x based catalysts.

CHAPTER 5 : INFLUENCE OF CO ON THE PERFORMANCES OF VO_X/TiO_2 BASED CATALYSTS IN THE COURSE OF THE TOTAL OXIDATION OF CHLORINATED VOCS

Abstract

Part I spotlighted the high performances of VO_x, VO_x-WO_x and VO_x-MoO_x based catalysts for the total oxidation of chlorinated VOCs. However, it is crucial to investigate the performances of these catalysts in exhaust gases containing the co-pollutants next to dioxins (or dioxin model molecules). Therefore, this chapter investigates the effects brought by CO on the performances of the selected catalysts in the course of the total oxidation of chlorobenzene. Moreover, we investigated the influence of CO on the physico-chemical properties of the catalysts. This research pointed out the absence of influence of CO on i) the VO_x oxidation state and ii) the catalytic performances. At the opposite, we pointed out that: CO decreases the amount of medium-strong Brønsted sites at the surface of MoO_x while it increases the acidity of the WO_x secondary phase. Moreover, CO does not influence the presence of Brønsted sites on the single VO_x phase. Based on the observations of this chapter and supported by conclusions of Chapter 3 and 4, we suggested that the destruction of the chlorinated VOCs proceeds in two steps: i) the adsorption of chlorobenzene on the medium-strong

Brønsted sites, mainly at the surface of the secondary phase and ii) the combustion of the aromatic ring by the redox sites present at the surface of VO_x. This mechanism helps to understand the beneficial effect brought by a one-step synthesis that favors the intimacy between the active and the secondary phases.

5.1. Introduction

Part I spotlighted formulations VO_x, VO_x-WO_x and VO_x-MoO_x supported on sulfated TiO_2 as the best catalysts for the total oxidation of chlorinated VOCs. However, these formulations were tested in a catalytic stream containing only chlorobenzene and oxygen. It is thus critical to investigate the performances of these catalysts in a more realistic exhaust gas from cogeneration and incineration processes. Therefore, Chapter 4 reported the influence of the presence of H_2O on the catalytic performances. In order to go further in the understanding of the ability of the selected catalysts to oxidize chlorobenzene efficiently in a real exhaust gas, we now investigate the influence of CO on them. The usual concentration of CO in the cogeneration and combustion exhaust gases is in the range: 0.5%-5% [99-101]. This research, therefore, aimed at investigating the effect brought by the presence of CO, in such concentrations, on the performances of VO_x, VO_x-WO_x and VO_x-MoO_x supported on sulfated TiO_2, in the oxidation of chlorobenzene. Moreover, we investigated the influence of the presence of CO on the physico-chemical properties of the catalysts after catalytic tests. Therefore, we performed XPS and NH_3-chemisorption measurements to have a complete view of the influence of CO, respectively on the oxidation state of the VO_x phase and on the acidity of the catalysts.

5.2. Experimental and methods

5.2.1. Preparation of the catalysts

TsV (VO_x/TiO_2), TsVW (VO_x-WO_x/TiO_2) and TsVM (VO_x-MoO_x/TiO_2) catalysts were synthesized following procedures presented in point 4.2.1 at Chapter 4.

5.2.2. Catalytic tests

All catalytic tests were performed in a fixed-bed micro-reactor (PID Eng&Tech S.L, Madrid - Spain) as described in points 2.2.2 and 4.2.2. The gas stream was composed of 100 ppm of chlorobenzene, 20 vol.% of O_2, 0, 0.5, 2.5 or 5 vol.% of CO and helium as diluting gas. The reaction was run at 200 and 250 °C during 150 min at each temperature.

5.2.3. Characterization

XPS and "quick" XPS measurements were performed following the experimental protocol presented in point 4.2.3. at Chapter 4.

Ammonia chemisorption experiments were conducted at 250 °C following the protocol presented in point 4.2.3. These measurements performed at 250 °C specifically investigate the medium and strong acid sites.

5.3. Results

5.3.1. Catalytic conversion of chlorobenzene

Figure 5-1 shows the evolution of the chlorobenzene conversion at 200 °C and 250 °C as a function of the CO concentration in the stream for the three catalysts. CO does not influence significantly the catalysts activity even at

high concentration (5%). This absence of effect is observed at 200 °C, 250 °C and for the three selected catalysts. Moreover, there is no oxidation of the introduced ppm of CO to CO_2.

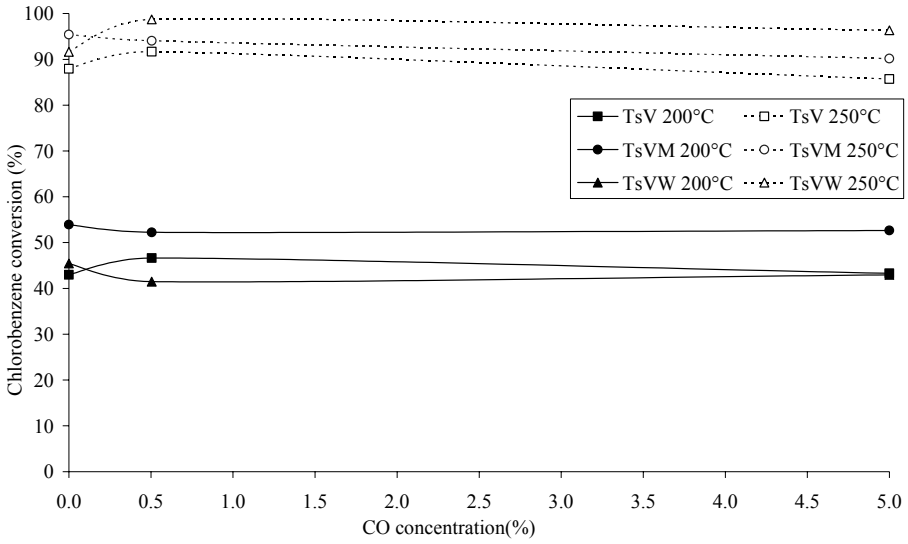

Fig. 5-1: Chlorobenzene conversion at 200 °C and 250 °C depending on the CO concentration (%)

5.3.2. Evaluation of the vanadium oxidation level (V O.L.)

Table 5-1 shows the estimated value of the vanadium oxidation level of the catalysts before and after catalytic test. The "surface" oxidation level results are obtained by decomposition of the $V2p_{3/2}$ peak from "quick" XPS measurements. As reported before, we observe a reduction of the vanadium oxidation level after catalytic test in the reference conditions (0% CO) for the three formulations. However, the extent of this reduction is deeper in the case of catalysts containing secondary phases than in the case of those containing the VO_x phase. Moreover, the reduction underwent by TsVW is even deeper than those underwent by TsVM. The introduction of 0.5 or 5%

of CO in the catalytic stream does not induce any significant modification of the vanadium oxidation level compared to the reference conditions (0% CO).

The investigation of the V/Ti, Mo/Ti, W/Ti, V/Mo and V/W ratios, determined by classical XPS measurements, does not reveal any modification of the spreading of the active and secondary phases in the presence of CO.

Table 5-1: "surface" vanadium oxidation level evaluated by "quick" XPS

	TsV	TsVM	TsVW
"Fresh"	4.97	4.83	4.77
0% CO	4.95	4.78	4.67
0.5% CO	4.95	4.83	4.62
5% CO	4.91	4.82	4.63

5.3.3. Evaluation of the catalyst acidity

Table 5-2: Acidity of the catalysts after catalytic test determined by NH_3-chemisorption (µmole NH_3/g)

	TsV	TsVM	TsVW
"Fresh"	80	100	129
0% CO	99	78	70
0.5% CO	102	55	120
5% CO	104	43	97

Table 5-2 shows the amount of medium-strong acid sites determined by NH_3-chemisorption at 250 °C for the catalysts before and after catalytic test. As a reminder, based on the results presented in Chapter 3, we know that the acidity is mainly due to Brønsted sites. The introduction of the secondary phases (MoO_x or WO_x) brought an increase of the acidity of the "fresh" catalysts. This effect was already observed in Chapter 3, which pointed out

the increase of the amount of Brønsted sites through the series: VO_x < VO_x-MoO_x < VO_x-WO_x formulations.

After catalytic test in the reference conditions, namely in the absence of CO (0% CO), the total acidity of the catalyst is modified. The variation of the number of acid sites strongly depends on the nature of the formulation: on the one hand, the TsV catalyst exhibits more acid sites after catalytic test than before it, *i.e.* 99 instead of 80 µmoles of chemisorbed NH_3 per gram of catalyst. On the other hand, TsVM and TsVW catalysts undergo a reduction of the amount of acid sites after catalytic test. TsVM after test is characterized by the chemisorption of 78 µmoles NH_3/g instead of 100. TsVW is the most affected catalyst as it undergoes a reduction of its number of acid sites from 129 µmoles NH_3/g before catalytic test down to 70 after test in the reference conditions.

The introduction of CO in the gaseous stream influences differently the catalyst acidity depending on i) the formulation of the catalyst and ii) the amount of CO in the catalytic stream. The introduction of CO in the catalytic stream does not influence significantly the acidity of the TsV catalyst recovered after reaction. Conversely, both TsVM and TsVW catalysts undergo drastic changes of their acidity in the presence of CO compared to the reference conditions. However, the influence of CO works in opposite manner on the two formulations. TsVM acidity suffers a continuous decrease of the number of acid sites with the increase of the CO concentration, *i.e.* the acidity decreases from 78 to 55 and 43 µmoles NH_3/g when the catalytic conditions go from 0 to 0.5 and 5% of CO. At the opposite, TsVW exhibits a higher amount of acid sites in the presence of CO. However, the extent of this amplification of the number of acid sites is not proportional to the CO concentration. Indeed, the introduction of 0.5% of CO induces a sharp increase of the amount of acid sites from 70, in the reference conditions, up to 120 µmoles NH_3/g, while a further increase of the CO concentration up to 5% is not followed by any additional enlargement but by a diminishment of the number of acid sites down to 97 µmoles NH_3/g.

5.4. Discussion

For the entire set of catalytic formulations (TsV, TsVM and TsVW), the addition of CO, in the investigated range of concentrations, does not induce any modification of the catalyst performances. CO can be considered as an inert molecule for the catalytic conversion of chlorinated VOCs on the VO_x/TiO_2 based catalysts. Therefore, this co-pollutant is definitely not a poison for the combustion of dioxins on our catalysts. The XPS investigation of the VO_x oxidation level before and after catalytic test and in the presence or absence of CO demonstrated that CO has no influence on it. It is thus clear that CO is also inert for the oxidation state of the active phase. At the opposite, CO influences drastically the acidity of the formulations TsVM and TsVW. On the one hand, the presence of CO induces an increase of the number of acid sites in the case of TsVW while, on the other hand, it provokes a sharp decrease of the acidity of TsVM. In spite of these observations, the acidity of the TsV formulation is not influenced by the presence of CO.

CO exclusively plays a role on the acid sites exposed at the surface of the secondary phases (MoO_x and WO_x) as demonstrated by i) the absence of influence of CO in the case of the single phase (TsV) and ii) the very different behaviors of TsVM and TsVW in front of the presence of CO. Moreover, the XPS measurements reveal that the spreading of the active phase and the secondary phases is not influenced by the presence of CO. Therefore, CO does not induce a modification of the acidity of the catalysts through a modification of the spreading of the involved phases. As a conclusion, CO directly influences the concentration of the medium-strong Brønsted sites present at the surface of MoO_x and WO_x. We have no hypothesis to explain how CO could increase or decrease the concentration of Brønsted acid sites at the surface of these secondary phases.

The strong influence of CO on the acidity of the selected formulations has no influence on the catalytic performances. Thus, the catalyst performances seem to be completely independent of its acidity. However, we demonstrated in Chapter 3 that the increase of the acidity is followed by an increase of the catalyst performances, in the case of i) the use of a sulfated support favoring the stabilization of a greater acidity and ii) the introduction of secondary phases possessing naturally more Brønsted sites. Moreover, we demonstrated in Chapter 4 that the reduction of the VO_x phase and the decrease of the number of medium and strong Brønsted sites induce a decline of the catalysts performances. Furthermore, the VO_x oxidation state is a key parameter as demonstrated in this chapter by i) the parallelism between the invariability of the VO_x oxidation state and the stability of the performances and ii) the absence of correlation between the huge variation of acidity and the stable activity. Consequently, in order to account for all our observations of the three cited chapters, we suggest that the combustion of chlorinated aromatics requires the presence of two kinds of sites: medium-strong Brønsted site and redox VO_x sites. Moreover we assume that the combustion proceeds in two steps: i) the adsorption of the chlorobenzene molecules on medium-strong Brønsted acid sites and ii) the aromatic ring combustion on the VO_x redox sites. This hypothetical mechanism is partially in agreement with those suggested by Larrubia *et al*. [68], based on a FTIR study of the adsorption of chlorinated VOCs on a VO_x-MoO_x/TiO_2 formulation. Indeed, these authors suggested that the total oxidation of chlorinated VOCs requires the presence of two sites: an acid site and a nucleophilic site. Moreover, they assume that the adsorption of the chlorinated VOCs proceeds via chlorine atom on a Lewis acid site. This adsorption takes place in a concerted mechanism with a nucleophilic substitution that forms a phenate species. This mechanism, adapted from [68], is depicted in Fig. 5-2. Furthermore, they suggested that the dechlorination step is not a crucial one while a more critical step is the full burning of the aromatic ring.

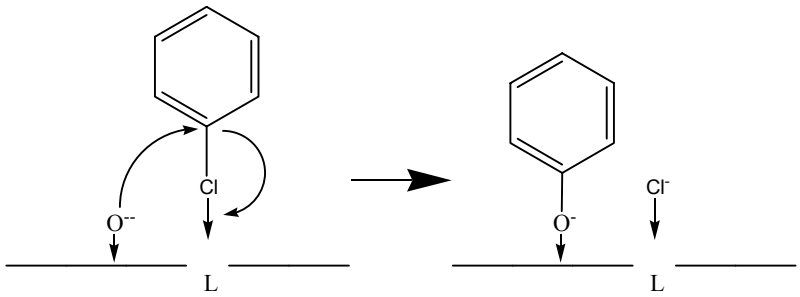

Fig. 5-2: First step of the mechanism of combustion of chlorinated aromatics suggested by Larrubia *et al.*

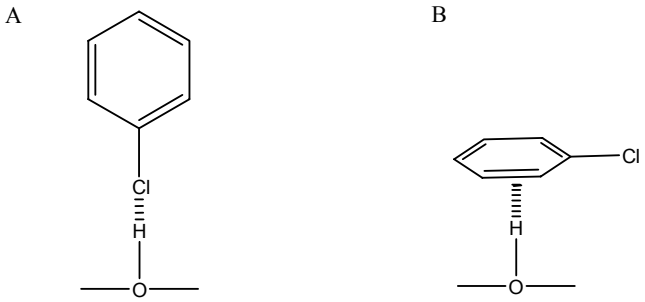

Fig. 5-3: Two possible ways of chlorobenzene adsorption of Brønsted acid site

Our hypothesis differs from the mechanism presented by Larrubia *et al*. as we suggested that the adsorption of the chlorobenzene molecules proceeds on medium-strong Brønsted sites. Fig. 5-3 presents two ways of chlorobenzene adsorption on Brønsted acid sites. In both cases the adsorption is based on the presence of strong hydrogen bonds between the hydrogen atom from the Brønsted site and the chlorine atom (case A) or between the hydrogen atom and the π orbital of the aromatic ring (case B). Both ways of adsorption were demonstrated in the literature [42,163,164]. This is in agreement with Sinquin *et al*. [162] and Ramachandran *et al*. [161] who both suggested that the adsorption sites of chlorinated VOCs are Brønsted sites. For that reason, based on our results, we presume that, for each formulation, a minimal concentration of medium-strong Brønsted acid

sites is necessary to provide enough adsorbed chlorobenzene to the active redox sites. Therefore, if the amount of Brønsted sites is over the limit value, the chlorobenzene conversion is completely limited by the redox sites. At the opposite, if the number of acid sites is below the limit, the activity is limited by the adsorption of chlorobenzene on medium-strong Brønsted sites in the neighboring of redox sites. In the case of this study of the influence of CO on VO_x supported on sulfated TiO_2, the amount of medium-strong Brønsted sites is always above the limit values.

The medium-strong Brønsted sites generate at the surface of the catalyst a pool of adsorbed chlorobenzene molecules. The Brønsted sites being mainly localized on the surface of the secondary phases as demonstrated in chapter 3, the pool of adsorbed chlorobenzene is thus essentially limited to these secondary phases (MoO_x and WO_x). At the opposite, the redox sites for the oxidation of the aromatic ring are mainly localized at the surface of VO_x. It is thus crucial to have the best intimacy between the secondary phases and the active phases in order to improve the accessibility of the adsorbed chlorobenzene to the redox sites. This conclusion is in very good agreement with the conclusions of Chapter 3 that pointed out the importance of synthesizing the binary formulations in a unique step to obtain the best performances. This one-step synthesis improves the spreading of small-size domains of VO_x and secondary phases in very good intimacy.

5.5. Conclusions

We investigated the influence of CO, in concentrations comparable to those in exhaust gases, on the catalytic performances of TsV, TsVM and TsVW in the course of the combustion of chlorobenzene. This research pointed out the absence of influence of CO on i) the VO_x oxidation state and ii) the catalytic performances. At the opposite, we pointed out the various influences of CO on the amount of medium-strong Brønsted sites present at the surface of the catalyst. CO decreases the amount of acid sites at the

surface of MoO_x while it increases the acidity of the WO_x secondary phase. However, CO does not influence the presence of Brønsted sites on the TsV formulation. The absence of variation of the catalytic performances whereas there is variation of the catalyst acidity, brings us to the hypothesis of the pool of adsorbed chlorobenzene on the medium-strong Brønsted acid sites. The number of medium-strong Brønsted acid sites must be above a limit value to provide enough adsorbed molecules to the redox sites. In the case of this investigation of formulation supported on TiO_2, the amount of adequate acid sites is always above the limit value.

Additionally, we suggested that the destruction of chlorinated VOCs proceeds in two steps: firstly the adsorption of chlorobenzene on the medium-strong Brønsted sites, mainly at the surface of the secondary phase; afterwards the so-formed pool of adsorbed chlorobenzene provides the aromatic rings for the second step, namely their combustion by the redox sites present at the surface of VO_x. Therefore, the beneficial effect of performing the synthesis of the binary formulations in a unique step resides in the increase of the intimacy between both the active and the secondary phases. The intimacy favors the accessibility of the adsorbed chlorobenzene to the redox sites, improving the combustion of chlorobenzene.

CHAPTER 6 : UNDERSTANDING THE ACTIVATION MECHANISM INDUCED BY NO_X ON THE PERFORMANCES OF VO_X/TiO_2 BASED CATALYSTS IN THE TOTAL OXIDATION OF CHLORINATED VOCS

Abstract

The influence of NO_x on the performances of VO_x/TiO_2, VO_x-WO_x/TiO_2 and VO_x-MoO_x/TiO_2 catalysts is investigated in the combustion of chlorobenzene. NO proves to induce an increase of the chlorobenzene conversion. However, the effect only happens if O_2 is present and is maximized when the catalyst contains WO_x or MoO_x. The mechanism suggested understood from numerous tests in different gaseous conditions is: 1) NO gets oxidized to NO_2, mainly on WO_x and MoO_x, 2) afterwards, NO_2 assists O_2 in the reoxidation step (as described by Mars-van Krevelen) of the VO_x phase thus speeding up the oxidation cycle. The latter macroscopically corresponds to the observed increase of chlorobenzene conversion. Moreover, plotting all the catalytic activity data versus the mean vanadium oxidation level clearly depicts, for the first time, the strong dependence between them. Under a mean vanadium oxidation level of 4.82 the catalyst

is inactive while above 4.87 the activity is stabilized at a high level of conversion independent of the vanadium oxidation level.

6.1. Introduction

Part I reported that VO_x/TiO_2 catalysts, possibly "upgraded" to VO_x-WO_x/TiO_2 or VO_x-MoO_x/TiO_2, which have been developed for the NO_x Selective Catalytic Reduction with NH_3, are very efficient in the total oxidation abatement of chlorobenzene (taken as a model molecule for dioxins) from combustion exhaust gases. In particular, they have proved to be highly resistant against the deactivation which proceeds on other elements than V through the chlorination of the active phases as demonstrated in Chapter 2. However, while exhaust gases inevitably contain H_2O, CO and NO_x, the efficiency of these catalysts was attested in the literature only for flows containing chlorinated aromatics as single pollutant. It is thus crucial to assess whether VO_x/TiO_2 based catalysts still succeed to oxidize chlorobenzene efficiently in the presence of co-pollutants or whether the latter induce some kind of deactivation. The usual concentrations of H_2O, CO and NO_x in the cogeneration and combustion exhaust gases are, respectively, in the range 1-5% [40,56,72,95-98], 0.5-5% [99-101]and 100-1000ppm [101-103]. This research therefore aimed at investigating the effect brought by NO as co-pollutant on the performances of VO_x, VO_x-WO_x and VO_x-MoO_x supported on sulfated TiO_2 in the oxidation of chlorobenzene.

This chapter investigates the influence of the presence of NO by introducing different concentrations of NO in the gaseous stream. This chapter aims at further understanding the mechanism of chlorinated VOC combustion. This chapter also reports the deep investigation of the influence of the vanadium oxidation state on the catalyst activity, which allows highlighting, for the first time, the clear dependence between them.

Taking into account the concentration of NO in real exhaust gases from cogeneration units, 1000 ppm of NO were introduced in the gaseous stream in order to evaluate the catalyst activity under more realistic conditions. To have a better understanding of the role of NO in the catalytic mechanism and of the interaction of NO with the catalyst, we changed the concentrations of NO and O_2 in the stream. In particular, to probe the ability of NO to substitute O_2 as oxidant in the process, some tests with NO but without O_2 were carried out. In addition, the reversibility of the possible effect brought by NO was addressed by cycling, at different temperatures, the concentration of NO incorporated in the gas feed. Moreover, the activity of the catalysts in the catalytic oxidation of NO to NO_2 was investigated in order to have a better comprehension of the underlying mechanism brought by the presence of NO. Furthermore, to evaluate the strength of the different potential oxidant molecules (NO, NO_2 and O_2), tests were carried out in the presence of various concentrations of each oxidant taken one by one. In parallel to this investigation of the catalytic mechanism, the vanadium oxidation level of the catalysts was estimated by the combined use of ICP-AES and EPR measurements. All catalytic and characterization results are considered together to develop the mechanism of activation by NO and to have a better understanding of the influence of the vanadium oxidation level on the catalyst activity.

6.2. Experimental and methods

6.2.1. Preparation of the catalysts

The catalysts TsV (VO_x/TiO_2), TsVW (VO_x-WO_x/TiO_2) and TsVM (VO_x-MoO_x/TiO_2) were synthesized following the experimental procedure presented at point 4.2.1 in chapter 4.

6.2.2. Catalytic tests

All catalytic tests were performed in a fixed-bed micro-reactor (PID Eng&Tech S.L, Madrid - Spain) as described at point 2.2.2 and 4.2.2. The measured performances were accurate within a range of about 1% (in relative) for both the conversions of chlorobenzene and NO. The gas analyzers (GC, Horiba and Oldham) allowed to quantify O_2, CO_2, CO, NO and total NO_x. The measured performances were accurate within a range of about 1% (in relative) for the conversion of chlorobenzene and NO.

6.2.2.1. Conventional tests

Table 6-1: Catalytic conditions

	Concentrations			
Conditions	**$[C_6H_5Cl]$ (ppm)**	**$[O_2]$ (ppm)**	**[NO] (ppm)**	**$[NO_2]$ (ppm)**
1	100	200000	0	0
2	100	200000	100	0
3	100	200000	1000	0
4	100	0	1000	0
5	100	0	4000	0
6	100	0	0	1000
7	100	0	0	2000
8	100	0	0	4000
9	100	850	0	0
10	100	1450	0	0
11	100	5000	0	0
12	100	10000	0	0
13	0	200000	1000	0

The conventional tests regroup the reference test, the tests performed in order to investigate the effect of the NO concentration in the presence of O_2 and the tests performed in order to estimate the effect of the O_2 concentration in the presence of NO. The reference test was carried out with a gaseous stream containing 100 ppm of chlorobenzene and 20% of O_2 (Table 6-1,

conditions 1). Under catalytic conditions (2) and (3), 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 performance of the catalyst used in the presence of O_2. To investigate the influence of the O_2 concentration, the catalysts performances were compared under conditions (3) and (4), *i.e.* in the presence of 1000 ppm of NO. Under conditions (4), the catalytic test was operated without O_2.

6.2.2.2. Reversibility test

Additional tests were specifically adapted in order to probe the reversibility of the possible effect of NO. Therefore, tests during which the concentration of NO was cycled were performed at 200 and 250 °C. At each temperature, the catalysts were submitted to three periods of 150 min with different gaseous conditions (see Table 6-1): firstly the reference conditions (1), *i.e.* 100 ppm of chlorobenzene and 20% of O_2 diluted in He, were applied, then conditions (3) were applied by suddenly incorporating 1000 ppm of NO in the reference gas; finally, conditions (1) were applied again by suddenly stopping the addition of NO in the feed.

6.2.2.3. NO oxidation test

Specific tests were performed in order to investigate the ability of TsV, TsVW and TsVM catalysts to oxidize NO to NO_2. Catalytic tests were carried out at 200 and 250 °C in the total absence of chlorobenzene on 200 mg of catalyst. The stream was composed of 1000 ppm of NO, 20% of O_2 and He as diluting gas (table 6-1, conditions 13). The NO consumption and the possible NO_2 production were followed by two gas analyzers: Horiba PG250 and an Oldham OX-PX12 gas analyzer which allowed quantifying NO_2 specifically.

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

To further investigate the respective oxidative strength of NO, NO_2 and O_2, catalytic tests were performed on the TsVW catalyst using various concentrations of these different oxidant molecules taken one by one. The entire set of catalytic tests was performed on a gaseous stream containing 100 ppm of chlorobenzene and using He as a diluting gas to obtain a total stream of 200 ml min^{-1}. Tests were performed in the presence of 1000 and 4000 ppm of NO as unique oxidant molecule in the stream (table 6-1, conditions 4 and 5). Additional catalytic tests were achieved with 1000, 2000 and 4000 ppm of NO_2 (table 6-1, conditions 6-8). 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 (table 6-1, conditions 9-12 and 1).

6.2.3. Characterization

The "bulk" mean vanadium oxidation level (hereunder V O.L.) was estimated by combination of ICP-AES and EPR measurements as reported at point 4.2.3. of chapter 4.

6.3. Catalytic results

6.3.1. Conventional tests

Fig. 6-1 exposes the chlorobenzene conversion performances of the three selected catalysts at 200 °C and 250 °C for all the conventional tests (Table 6-1, conditions 1-4).

6.3.1.1. Reference test

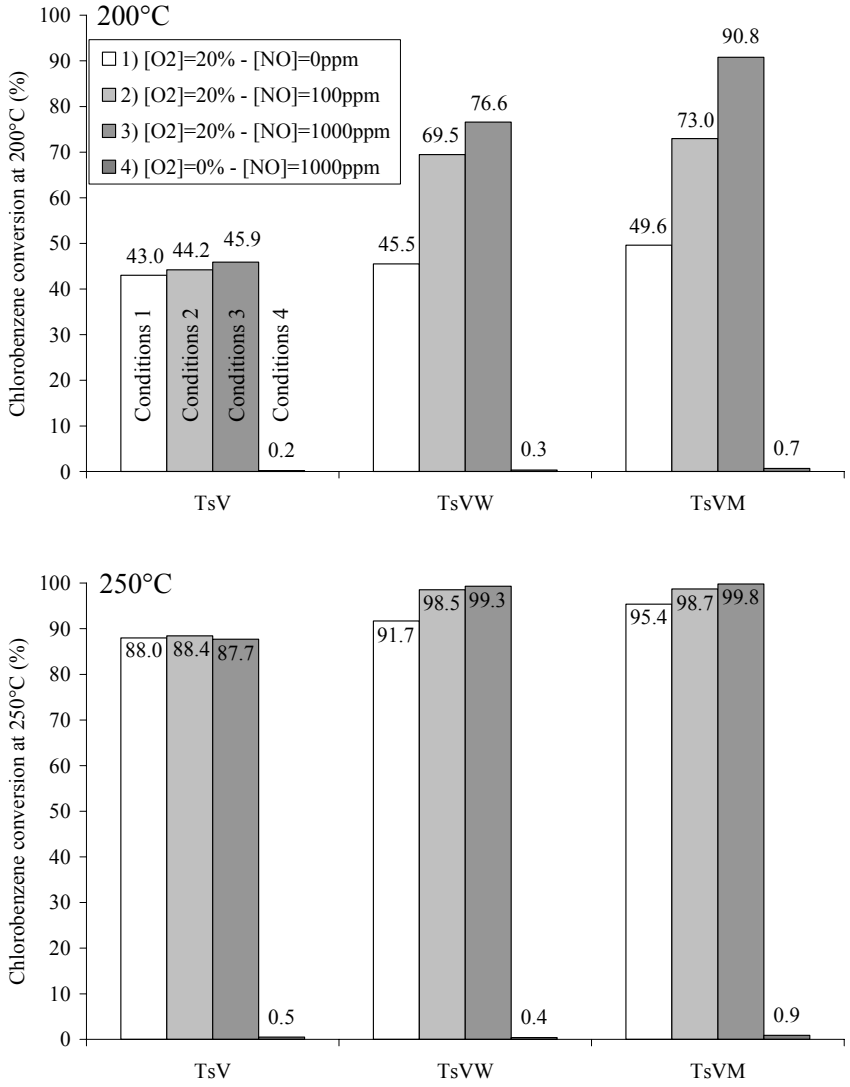

Fig. 6-1: Catalytic results in terms of percentage of chlorobenzene conversion at 200 °C and 250 °C for the entire set of conventional tests; conditions 1: [O_2] = 20%, [NO] = 0 ppm; conditions 2: [O_2] = 20%, [NO] = 100 ppm; conditions 3: [O_2] = 20%, [NO] = 1000 ppm; conditions 4: [O_2] = 0%, [NO] = 1000 ppm.

The results of the reference test, *i.e.* 100 ppm of chlorobenzene, 20% of O_2 and no NO (conditions 1), at 200 and 250 °C, are shown in Fig. 6-1. The TsV catalyst, containing VO_x as only active phase, converted 43.0% and 88.0% of the chlorobenzene at 200 and 250 °C, respectively. The addition of a second phase, WO_x or MoO_x, to the VO_x active phase induced an enhancement of the activity at 200 °C, respectively from 43.0% to 45.5% (TsVW catalyst) and to 49.6% (TsVM catalyst). This improvement of activity was also observed at 250 °C as the chlorobenzene conversion increased from 88.0% to 91.7% (TsVW catalyst) and to 95.4% (TsVM catalyst). The beneficial effect of adding MoO_x or WO_x in VO_x/TiO_2 catalysts has already been reported and discussed in Chapter 3 and [86,93,165,166].

6.3.1.2. Effect of the NO concentration in the presence of O_2

Fig. 6-1 compares the catalytic performances for the test realized in the presence of 20% of O_2 but in the absence of NO (Table 6-1, conditions 1) and for the tests realized in the simultaneous presence of 20% of O_2 and of, respectively, 100 and 1000 ppm of NO in the gaseous stream (Table 6-1, conditions 2 and 3).

At 200 °C, in the case of the VO_x supported phase (TsV), the introduction of 100 and 1000 ppm of NO in the gaseous stream induced only a slight increase of the activity, respectively +1.2% and +2.9%. But the presence of NO induced a dramatic increase of activity when WO_x or MoO_x were present. For the TsVW catalyst, the chlorobenzene conversion increased from 45.5% to 69.5% (+24.0%) when 100 ppm of NO were added in the stream, and to 76.6% (+31.1%) when 1000 ppm of NO were added. The strongest effect of the addition of NO in the gaseous flow was observed for the catalyst containing simultaneously VO_x and MoO_x. For this catalyst, adding 100 or 1000 ppm of NO induced an increase of, respectively, +23.4% and +41.2% of the catalyst activity with the conversion of chlorobenzene going from 49.6% in absence of NO to 73.0% and 90.8% in the presence of

100 and 1000 ppm of NO, respectively. As a summary of these results, it turns out that i) NO brings a positive effect on the catalytic conversion of chlorobenzene on VO_x based catalysts, ii) this positive effect is progressive with the NO concentration and iii) is stronger on the VO_x-WO_x and VO_x-MoO_x catalysts than on the single VO_x active phase.

At 250 °C, although attenuated (in terms of conversion) likely because the conversion was close to 100% for all catalysts (the kinetic seems to be the same), almost identical tendencies were observed. The addition of NO did not induce any significant modification of the chlorobenzene conversion (+0.4% and -0.3%) in the case of the TsV catalyst. For the TsVW and TsVM catalysts, the introduction of NO in the stream is followed by a slight increase of the activity: respectively +6.8% and +3.3% of conversion in the presence of 100 ppm and +7.6% and +4.4% in the presence of 1000 ppm.

Under all tested conditions (100 or 1000 ppm of NO, 200 °C or 250 °C) and for all catalysts, NO was recovered at the reactor outlet in a concentration of exactly 100 or 1000 ppm. It is thus crucial to understand here that no global consumption of NO occurs during any experiment.

6.3.1.3. Effect of the O_2 concentration in the presence of NO

Fig. 6-1 gives the activity in terms of chlorobenzene conversion for the three catalysts in the presence of 1000 ppm of NO but in the absolute absence of O_2 in the feed (Table 6-1, conditions 4). Under these conditions, the conversion of chlorobenzene always remained below 1% at both 200 and 250 °C. It must however be mentioned that for the three catalysts, during the first 5 minutes of reaction, more than 50% of the chlorobenzene was converted. But after this short period of time, the conversion sharply decreased down to about 0.5%. These behaviors and performances are obviously different from those observed in the simultaneous presence of O_2 and NO in the feed. It is thus clear that the huge positive effect that NO is able to induce on the ability of VO_x/TiO_2, VO_x-WO_x/TiO_2 and VO_x-

MoO_x/TiO_2 catalysts to oxidize chlorobenzene, is only possible when O_2 is present in the gaseous stream.

6.3.2. Reversibility test

Fig. 6-2 presents the evolution of the chlorobenzene conversion during the cycling of the NO concentration for the three catalysts (TsV, TsVW and TsVM). For the TsV catalyst, containing VO_x as only active phase, the introduction of 1000 ppm of NO in the gaseous stream induced a slight increase of activity in an extent similar to the difference of activity between the performances in the reference test and the performances in the test with 1000 ppm (Fig. 6-1 conditions 1 and 3 and Fig. 6-2). Moreover, the increase of activity was progressive during the first 60 min of contact with NO, after what the conversion remained at a constant level.

After 150 min under conditions 3, stopping the NO input induced a progressive decrease of the chlorobenzene conversion down to the level of activity observed during the first stage of the cycle (conditions 1). In the case of the TsVW and TsVM catalysts, the activity increased rapidly when the gaseous composition was switched from the reference conditions (1) to conditions 3 corresponding to the addition of 1000 ppm of NO. This enhancement of conversion was progressive during the first 45-60 min and was followed by a stabilization of the activity at a level of performances similar to those obtained by applying conditions 3 from the very beginning of the experiment (see Fig. 6-2 and Fig. 6-1). After the sudden removal of NO from the stream, the activity of the catalyst rapidly went back to a level of conversion as obtained under the reference conditions. Similar effects were obtained at 250 °C.

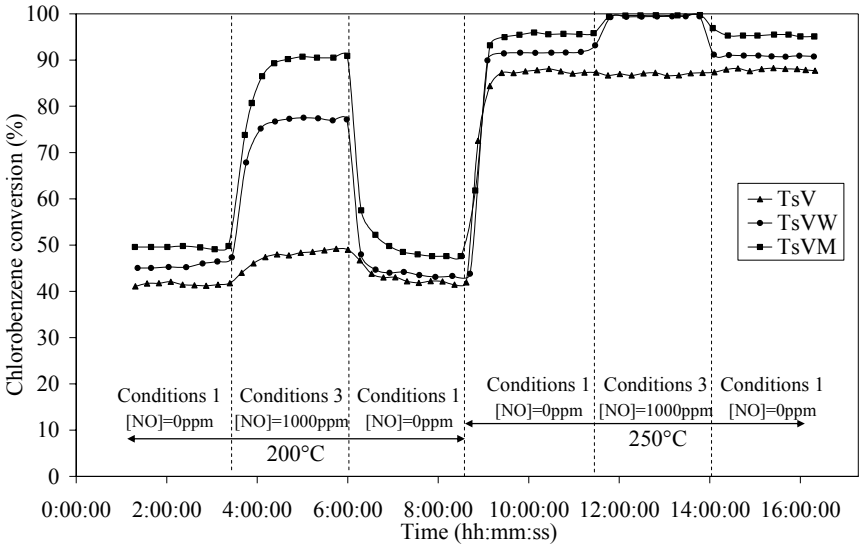

Fig. 6-2: Chlorobenzene conversion on TsV, TsVW and TsVM catalysts during the cyclic test with sudden addition and retrieval of 1000 ppm of NO in the gaseous stream

The effect of NO on the performances of VO_x/TiO_2, VO_x-MoO_x/TiO_2 and VO_x-WO_x/TiO_2 catalysts in the oxidation of chlorobenzene is thus clearly reversible.

6.3.3. NO oxidation test

Fig. 6-3 presents the results of the catalytic activity of the three catalysts for the conversion of 1000 ppm of NO in the presence of 20% of O_2 and in the total absence of chlorobenzene, at 200 °C and 250 °C. At 200 °C, the TsV catalyst converted 3.8% of the NO while the combined catalysts containing WO_x (TsVW) or MoO_x (TsVM) converted 17.5% and 19.5% respectively. The presence of the WO_x and MoO_x phases in the catalyst thus improved the NO conversion by more than a factor 4.

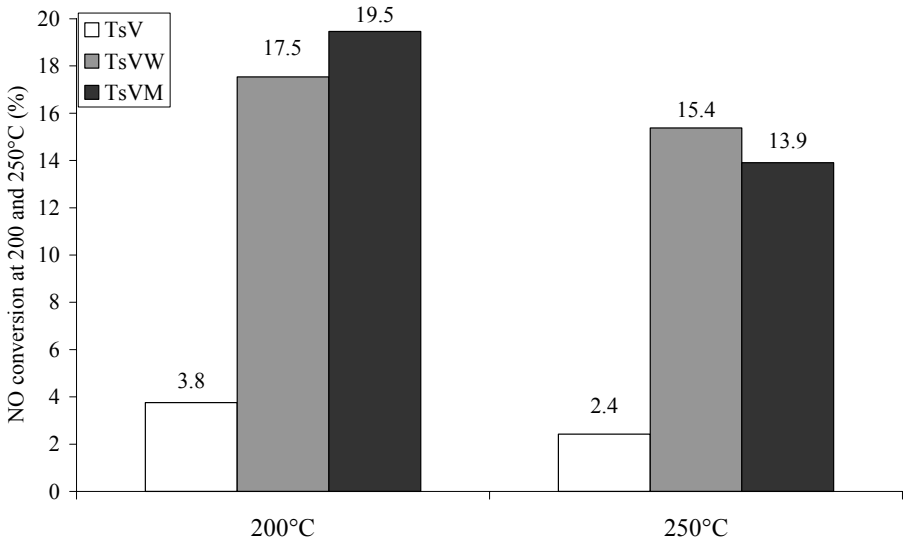

Fig. 6-3: Percentage of NO oxidation at 200 °C and 250 °C on TsV, TsVW and TsVM

Moreover, the three catalysts converted NO to NO_2 with a selectivity of 100%. At 250 °C, the activities for the three catalysts were slightly weaker than those observed at 200 °C: TsV converted 2.4%, while TsVW and TsVM converted respectively 15.4% and 13.9%. However, the selectivity to NO_2 at 250 °C was maintained at 100% as observed at 200 °C for all catalysts.

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

Fig. 6-4 compares the chlorobenzene conversion obtained at 200 °C and 250 °C with the TsVW catalyst, in the presence of different concentrations of various oxidant molecules (NO, NO_2 and O_2) taken one by one (table 6-1 conditions 4-12 and 1). These catalytic tests were performed in order to have a better understanding of the catalytic mechanism and more precisely in order to evaluate the strength of the different potential oxidant molecules.

Fig. 6-4 presents the chlorobenzene conversion as a function of the concentration of atomic oxygen that could be released by the oxidant molecule to the catalyst. In the case of NO and NO_2, as these molecules are able to give only one oxygen atom per molecule, the concentration of oxygen atom on the X axis is equal to the concentration of the molecules in the reaction feed. In the case of O_2, due to the fact that each O_2 molecule is able to give 2 atoms of oxygen, the concentration of oxygen atom represented on the X axis is the double of the concentration of molecular O_2. It is important to note here that the total combustion of the 100 ppm of chlorobenzene present in the stream requires 1400 ppm of atomic oxygen (700 ppm of O_2) as shown in Equation 6-1:

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

The use of NO as unique oxidant has already proved to be inefficient for the total combustion of chlorobenzene as shown in section 6.3.1.3. and Fig. 6-1. Fig. 6-4 shows that this fact remains true, even when the concentration of NO was increased up to 4000 ppm in the stream. As a conclusion, NO is definitely not able to play the role of oxidant in the catalytic combustion of chlorobenzene.

At the opposite, the use of NO_2 as unique oxidant, revealed that this molecule is able to induce a huge conversion of chlorobenzene. The increase of the NO_2 concentration from 1000 to 2000 and 4000 ppm induced a progressive enhancement of the chlorobenzene conversion from 5.1 to 87.5 and 92.1% at 200 °C. At 250 °C, the chlorobenzene conversion improved from 1.5 to 93.8 and 92.6% in parallel with the increase of the concentration from 1000 to 2000 and 4000 ppm of NO_2. Moreover, at the outlet of the reactor, between 200 and 1100 ppm of NO were detected depending on the temperature and the amount of NO_2 introduced in the stream. Other nitrogen containing compounds, in particular N_2, were never detected. The production of NO and the absence of other nitrogen containing compounds confirm the fact that each NO_2 molecule is able to liberate only one atom of

oxygen, available for the catalytic reaction, while simultaneously generating one molecule of NO.

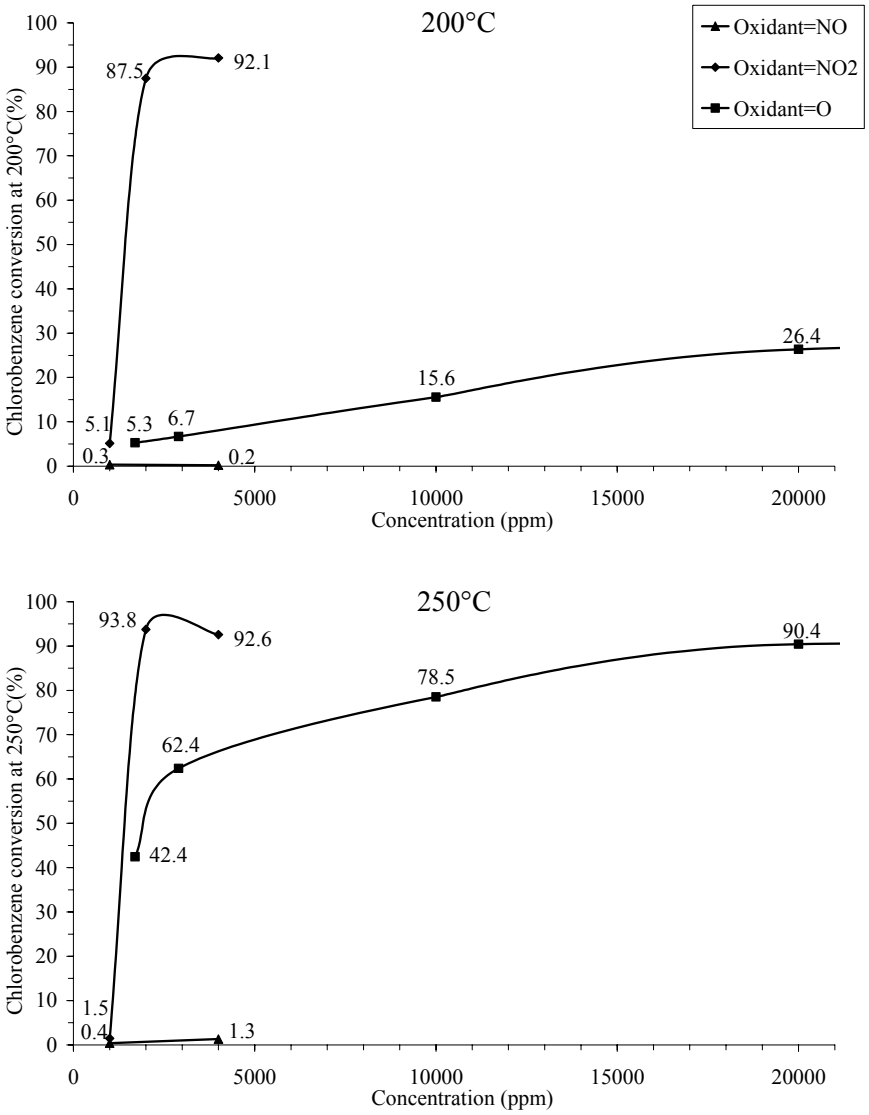

Fig. 6-4: Chlorobenzene conversion as a function of the concentration of oxidant

The use of O_2 showed that it is able to induce a conversion of chlorobenzene, which is stable with time-on-stream. The increase of the atomic oxygen concentration within the series: 1700, 2900, 10000, and 20000 ppm induced a continuous enhancement of the chlorobenzene conversion from 5.3 to 6.7, 15.6 and 26.4%. As a reminder, in the reference conditions, 20% of O_2, corresponding to 400000 ppm of atomic oxygen, led to 45.5% of conversion. At 250 °C, the progressive improvement of the conversion, going in parallel to the increase of the atomic oxygen concentration, was also observed. The conversion went from 42.4 to 62.4, 78.5 and 90.4% when the atomic concentration went from 1700 to 20000 ppm (Fig. 6-4). As a reminder, in the reference conditions, *i.e.* in the presence of 400000 ppm of atomic oxygen, the chlorobenzene conversion was 91.7%.

The results at both temperatures show that the dissociation of O_2 molecules into monoatomic O^* seems to be a limiting factor. While at the opposite, the dissociation of NO_2 into $NO + O^*$ seems to be quicker. Indeed, the presence of 4000 ppm of NO_2 was enough to induce a conversion higher than that induced by the presence of 400000 ppm of atomic oxygen (20% of O_2).

6.4. Characterization results

6.4.1. Evolution of the mean V O.L. during conventional tests

The evaluation of the mean Vanadium Oxidation Level (hereunder denoted V O.L.) was performed by combination of ICP-AES and EPR analyses. Fig. 6-5 presents the V O.L. for the three catalysts (TsV, TsVW, TsVM) after tests carried out in conditions 1, 2, 3 and 4 (Table 6-1).

In the case of the TsV catalyst, the V O.L. after the test in conditions 1, corresponding to the reference test *i.e.* in the presence of 20% O_2 and in the absence of NO, was equal to 4.971. In order to compare the effect of the different gaseous conditions, the evolution of the vanadium oxidation level

(oxidation or reduction) is compared to the oxidation level stabilized in the reference conditions. The introduction of 100 and 1000 ppm of NO in the reaction feed induced a slight reoxidation of the vanadium phase, compared to the V O.L. in the reference conditions, up to 4.983 (+0.003) and 4.984 (+0.004). At the opposite, in the presence of 1000 ppm of NO but in the total absence of oxygen (conditions 4), the vanadium phase underwent a reduction down to 4.924 (-0.056).

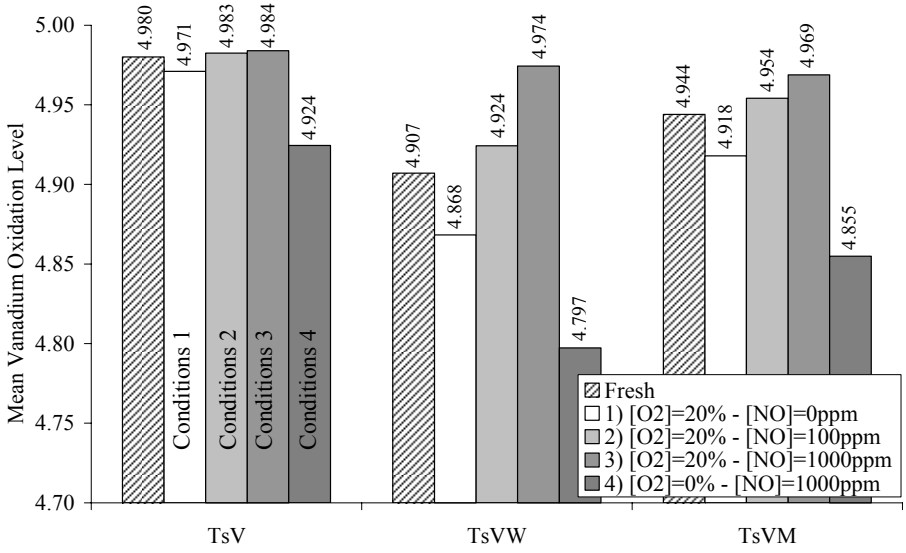

Fig. 6-5: Mean vanadium oxidation level of the TsVW catalyst before catalytic test (Fresh) and after catalytic test in the presence of 1000 and 4000 ppm of NO

After the catalytic test on TsVW in reference conditions 1, the V O.L. was estimated to 4.868. The presence of the WO_x phase induced the stabilization of the V O.L. at a lower value than in the case of the single vanadium phase. The addition of 100 and 1000 ppm of NO in the stream induced an increase of the V O.L., referring to the V O.L. stabilized in the reference conditions, up to 4.924 (+0.056) and 4.974 (+0.106), respectively. The increase of the V O.L. was more than 20 times more important than that observed in the absence of the WO_x phase. At the opposite, in the presence of NO but in the

absence of O_2, the vanadium phase underwent a deep reduction down to 4.797 (-0.071).

In the presence of the MoO_x phase, the vanadium phase was stabilized, under reference conditions, at a value of 4.918. Similarly to the effect of the presence of WO_x, the presence of the MoO_x phase caused the stabilization of the vanadium phase at a lower level than in the case of the single phase as already reported in Chapter 4 and 5. As in the case of the presence of WO_x, the addition of NO in the stream induced a deep reoxidation of the VO_x phase used in the presence of MoO_x, up to 4.954 (+0.036) and 4.969 (+0.061). Compared to the evolution of the V O.L. in the case of the single phase, the presence of the MoO_x phase increased the sensitivity of the vanadium phase to the effect of NO by a factor 10. On the contrary, in conditions 4, the vanadium phase was reduced down to 4.855 (-0.063).

For all catalysts, the introduction of NO in the presence of oxygen induced a stabilization of the vanadium phase at a higher value than in the reference conditions. The extent of this reoxidation was progressive with the increase of the amount of NO introduced in the gaseous stream. Moreover, this reoxidation of the vanadium phase was strongly affected by the presence of the second phase (WO_x or MoO_x). The reoxidation of the vanadium phase was, respectively, 20 and 10 times more important in the presence of WO_x and MoO_x phases than in the case of their absence.

For the three catalysts, the absence of oxygen in the gaseous stream, although 1000 ppm of NO were flowed on the catalyst, causes a deep reduction of the vanadium phase. The extent of this reduction was quite similar for the three catalysts.

6.4.2. Evolution of the mean V O.L. during the tests investigating the oxidant strength

Figures 6-6, 6-7, 6-8 and 6-9 present the evaluation of the vanadium oxidation level (V O.L.) of the TsVW catalyst, before and after catalytic tests on 100 ppm of chlorobenzene and in the presence of various concentrations of the three different oxidants (NO, NO_2 and O_2), taken one by one.

Fig. 6-6 presents the V O.L. before and after catalytic test in the presence of 1000 or 4000 ppm of NO (conditions 4 and 5). The introduction and the increase of the concentration of NO in the catalytic stream induced a progressive reduction of the VO_x phase compared to the vanadium oxidation state before catalytic test. 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.

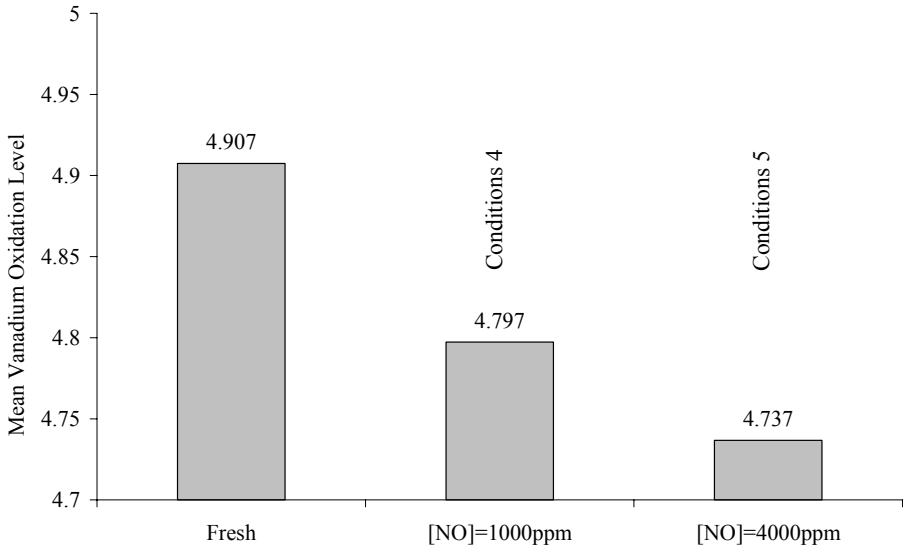

Fig. 6-6: Mean vanadium oxidation level of the TsVW catalyst before catalytic test (Fresh) and after catalytic test in the presence of 1000 and 4000 ppm of NO

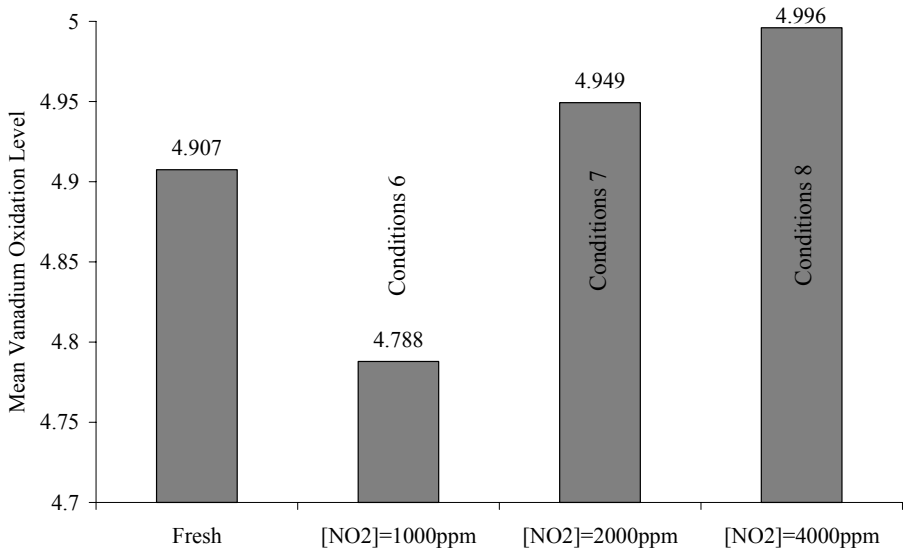

Fig. 6-7: Mean vanadium oxidation level of the TsVW catalyst before catalytic test (Fresh) and after catalytic test in the presence of 1000, 2000 and 4000 ppm of NO_2

Fig. 6-7 shows the V O.L. before and after catalytic test with a gaseous stream containing 100 ppm of chlorobenzene and 1000, 2000 or 4000 ppm of NO_2 (conditions 6-8). In the presence of the lowest concentration of NO_2, *i.e.* 1000 ppm, the catalyst underwent a strong reduction from 4.907 to 4.788, respectively before and after test. However, a further increase of the NO_2 concentration up to 2000 and 4000 ppm induced a significant progressive reoxidation of the catalyst up to 4.949 and 4.996.

Fig. 6-8 illustrates the evolution of the V O.L. before and after catalytic test in the presence of different concentrations of atomic oxygen, from 1700 to 2900, 10000, 20000 and 400000 ppm of atomic oxygen in the gaseous stream (conditions 9-12 and 1). Under all the atomic oxygen concentrations investigated, the V O.L. was reduced compared to its value before catalytic

test. However, the increase of the oxygen atomic concentration induced a slight progressive decrease of the extent of the reduction of the VO_x phase from 4.841 to 4.846, 4.850, 4.854 and 4.868 when the concentration was increased from 1700 to 2900, 10000, 20000 and 400000 ppm of atomic oxygen.

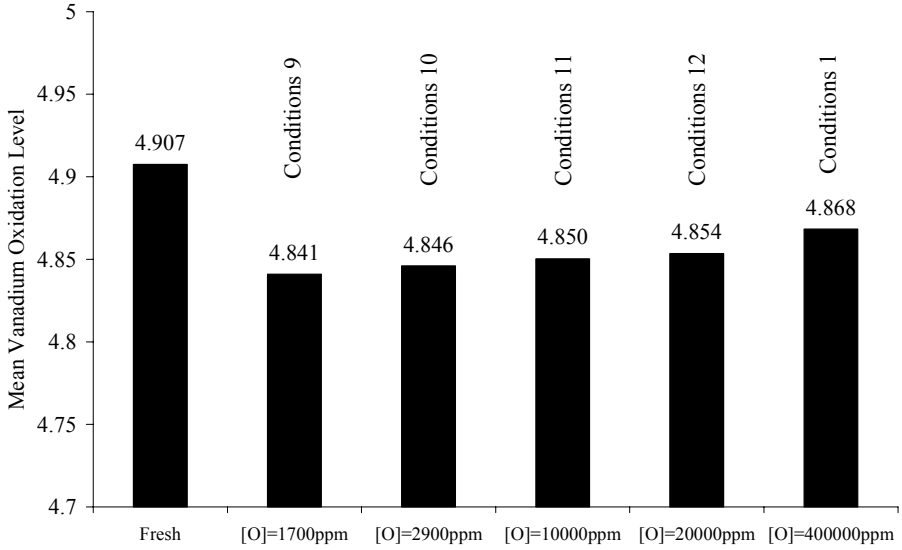

Fig. 6-8: Mean vanadium oxidation level of the TsVW catalyst before catalytic test (Fresh) and after catalytic test in the presence of 1700, 2900, 10000, 20000 and 400000 ppm of atomic oxygen

Fig. 6-9 compares the evolution of the V O.L. in the TsVW catalyst as a function of the concentration of equivalent atomic oxygen possibly released by the different oxidants (NO, NO_2 and O_2). The comparison of the behaviors of the different oxidants shows that NO is not able to oxidize the catalyst, while O_2 is able to stabilize the V O.L. at a value close to that of the fresh catalyst and NO_2 induces a strong reoxidation. These results clearly point out the higher oxidant strength of NO_2 than O_2.

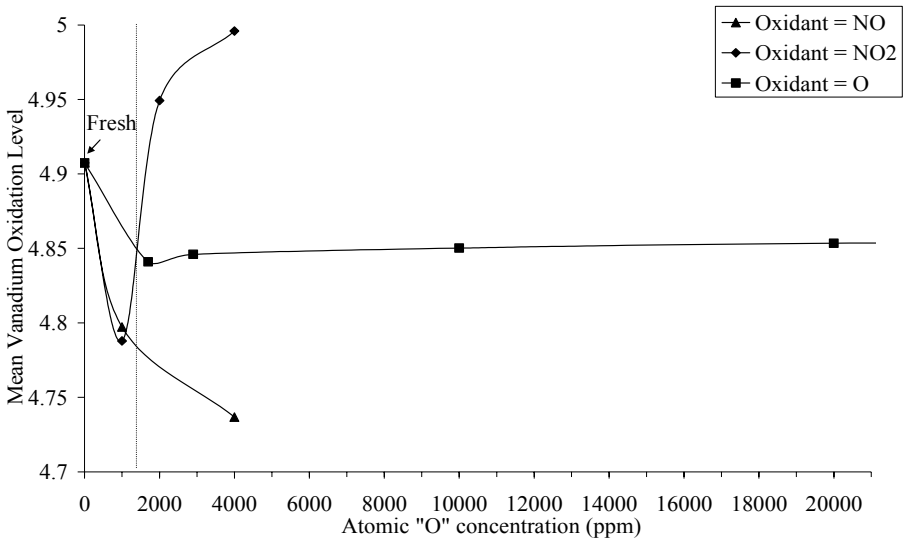

Fig. 6-9: Mean vanadium oxidation level of the TsVW catalyst as a function of the concentration of oxidant (NO, NO_2, atomic O)

6.5. Discussion

6.5.1. Classical mechanism

In the investigation of the strength of O_2 as an oxidant molecule on the TsVW catalyst, we observed that the increase of the concentration of atomic oxygen induces an enhancement of the catalyst activity. This observation reveals that the dissociation of O_2 into activated O^* 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. Simultaneously it was found that the catalyst undergoes a reduction of its vanadium oxide phase for all the investigated concentrations of O_2, *i.e.* up to 20% of O_2. However, the extent of this reduction decreases gradually when the concentration of O_2 in the feed increases.

Furthermore, in conditions 4, *i.e*. in the absence of O_2 but in the presence of 1000 ppm of NO (which is unable to reoxidize the catalyst as proven in section 6.4.2. and Fig. 6-6), during a very short period of time (more or less 5 minutes), the catalysts induce a limited conversion of chlorobenzene. This limited conversion is followed by a sharp decrease of the activity down to less than 1% of conversion at stabilization as shown in Fig. 6-1. This absence of stable conversion was correlated to the strong reduction of the catalysts in the corresponding conditions as shown in Fig. 6-5.

The conjunction of these results reveals that: i) the catalyst gives some of its lattice O_2 to perform the oxidation of 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 oxygen concentration in the stream facilitates the reoxidation of the catalyst. It is thus clear that the conversion of chlorobenzene occurs in two steps (Figure 10 A), as classically described by the Mars and van Krevelen mechanism [167]. 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 O_2 from the gaseous stream.

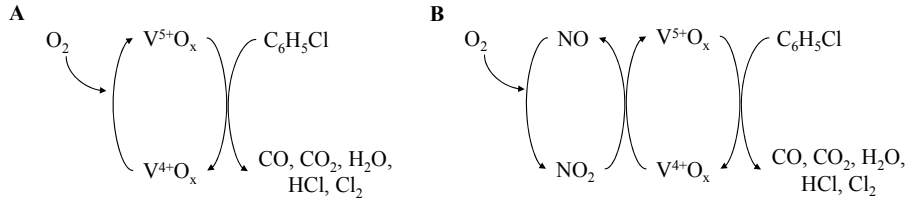

Fig. 6-10: Scheme of the chlorobenzene oxidation in the absence (A) or presence (B) of NO

6.5.2. NO activation mechanism

The investigation of the NO influence at different concentrations on the catalyst activity has shown a series of phenomena that are summarized

hereafter. For the three catalysts, adding NO in the gaseous stream is clearly beneficial for the conversion of chlorobenzene. Within the range investigated, this enhancement of activity increases with increasing NO concentration. Moreover, this beneficial effect of NO is much more important when WO_x or MoO_x is associated to the VO_x active phase. However, the effect is only possible if some O_2 is present in the stream. In the absence of O_2, the activity decreases very rapidly down to less than 1% of chlorobenzene conversion. Moreover, the enhancement of activity brought by the presence of NO quickly disappears when NO is suddenly removed from the stream. Finally, all this occurs without any global consumption of NO during any catalytic test.

To account for all these observations, a reaction mechanism based on the classical Mars and van Krevelen mechanism, but enclosing an additional step, is suggested. In the reference test, namely without NO, the conversion of chlorobenzene occurs in two steps (Figure 10 A), as described in section 6.5.1. The proposed additional step is that NO would react with O_2 (when present) at the surface of the catalyst to produce NO_2 (figure 10 B). The NO_2 thus formed *in situ* would then assist (or replace, at least partially) O_2 to reoxidize the reduced $V^{4+}O_x$ as in the second step of the Mars and van Krevelen mechanism. NO_2 being a stronger oxidant than O_2, as shown by the results of the investigation of the strength of the different plausible oxidants in sections 6.3.4. and 6.4.2., its participation in the reoxidation step of the $V^{4+}O_x$ sites would thus induce a speeding up of the reaction cycle. This speeding up would thus macroscopically correspond to the observed increase of the chlorobenzene conversion.

This 3-step mechanism proposed for the oxidation of chlorobenzene on VO_x based catalysts in the presence of O_2 and NO, not only accounts for the activation of the catalyst by NO, but also accounts for several others of our catalytic and characterization observations and is supported by several elements from the literature.

1° The observed increase of the conversion of chlorobenzene is well explained by the 3-step mechanism which involves NO_2 as a powerful oxidant for the regeneration of the $V^{4+}O_x$ reduced sites. The enhancement of the activity due to the speeding up of the reoxidation step of the Mars and van Krevelen mechanism in the presence of *in situ* produced NO_2 is strengthened by our observations and those of Koebel *et al.* [168]. With the purpose to reinforce the hypothesis of activation through the *in situ* production of NO_2, we investigated the influence of NO_2 in the total absence of O_2 (6.3.4. and [169]). As pointed out in Fig. 6-4, NO_2 can induce, in the total absence of O_2, the total oxidation of chlorobenzene during the entire catalytic test. Moreover, NO_2 induces a huger conversion of chlorobenzene than O_2, *e.g.* 4000 ppm of NO_2 induce 92.1% of conversion at 200 °C while only 26.4% are reached in the presence of 10000 ppm of O_2. Furthermore, Fig. 6-9 shows that NO_2 is a stronger oxidant than O_2. In fact, 4000 ppm of NO_2 stabilize the vanadium phase at a V O.L. of 4.996 while 10000 ppm of O_2 only succeed to stabilize the V O.L. at a value of 4.854. These results are in good agreement with the observations of Koebel who showed that the oxidation of the vanadia reduced sites in the case of VO_x based catalysts devoted to the SCR reaction proceeds faster with NO_2 than O_2 at temperatures below 300 °C.

2° The proposed mechanism elucidates the occurrence of an activity enhancement brought about by NO while no NO consumption was observed during any catalytic tests. Our mechanism indeed proposes that first, NO gets oxidized to NO_2 on the surface of the catalyst, thanks to the presence of O_2 in the stream. Then the *in situ* generated NO_2 gives one of its oxygen atoms to oxidize $V^{4+}O_x$ species while giving back NO. Such a "NO cycle" indeed fits quite well with the absence of NO consumption. Moreover, the envisaged donation of one atom of oxygen by NO_2 to the reduced vanadium site, leading to the formation of NO, was confirmed by the results of the tests performed with different concentrations of NO_2 but in the total absence of O_2. The results of these tests presented in section 6.3.4. indeed show that the

use of NO_2 as a single oxidant leads to a stable conversion of the chlorobenzene and to the liberation of NO. The concentrations of NO at the outlet are in good agreement with the amount theoretically needed to induce the observed chlorobenzene conversion. As a conclusion, the proposed "NO cycle" fits very well with the absence of NO consumption while the conversion is enhanced.

3° The absence of conversion when the gaseous stream contains only NO and no O_2 could also be explained by the proposed 3-step mechanism. In the presence of NO and absence of O_2, during a very short period of time (more or less 5 minutes), the VO_x phase gives some of its lattice oxygen atoms inducing a limited conversion of chlorobenzene and leading to the formation of reduced $V^{4+}O_x$ sites. The next step of the mechanism, which is the reoxidation of the so-formed reduced $V^{4+}O_x$ sites, requires the presence of oxidizing species. The presence of NO alone, which is not able to play the role of oxidant by itself, induces the end of the chlorobenzene conversion. The inefficiency of NO to reoxidize the reduced vanadium sites and to sustain a catalytic activity was demonstrated in sections 3.4. and 4.2. which pointed out i) the absence of chlorobenzene conversion even if the catalytic stream contains up to 4000 ppm of NO and ii) the deep reduction of the vanadium phase leading to the deactivation of the catalyst when NO is used as single oxidant molecule. NO, according to the proposed 3-step mechanism, must be oxidized *in situ* to NO_2 thanks to O_2 to induce the "NO cycle" and to further induce the reoxidation step of the $V^{4+}O_x$ sites by NO_2. The 3-step mechanism involving the oxidation of NO to NO_2 thanks to O_2 to induce the reoxidation of the $V^{4+}O_x$ sites explains well the absence of sustainable conversion in the presence of NO without O_2.

4° Another of our observations is that the enhancement of activity brought by NO is much more marked for the catalysts containing WO_x and MoO_x than for that containing only VO_x. This observation is explained by the preferential oxidation of NO to NO_2 occurring mainly on the surface of the WO_x and MoO_x phases. This hypothesis is demonstrated by the catalytic

tests of NO oxidation exposed in section 3.3. The oxidation of 1000 ppm of NO in the presence of 20% O_2 was probed on the three catalysts. The WO_x and MoO_x containing catalysts oxidize roughly 20% of the NO at 200 °C while the VO_x catalyst oxidizes less than 4% of it. In both cases NO is converted to NO_2. Moreover the preferential oxidation of NO on the WO_x and MoO_x phases is strongly supported by the observations of Dawody *et al.* [170] who showed that 400 ppm of NO could be oxidized to NO_2 in the presence of 8% of O_2 at a temperature as low as, roughly, 140 °C on WO_x and MoO_x containing catalysts. The VO_x phase is also shown to be able to oxidize NO to NO_2 but at a higher temperature (170 °C) and to a lower extent. The preferential oxidation of NO to NO_2 on the surface of WO_x and MoO_x explains very well the effect of NO on the conversion of chlorobenzene, which is stronger in the case of the VO_x-MoO_x/TiO_2 and VO_x-WO_x/TiO_2 catalysts than in the case of VO_x/TiO_2 ones.

5° The thermodynamic equilibrium between NO and the produced NO_2 (mainly on the surface of the WO_x and MoO_x phases) depending on temperature explains the less marked influence of NO at 250 °C than at 200 °C. We spotlighted that at 250 °C the observed activity of the three catalysts to oxidize NO to NO_2 is reduced compared to the activity observed at 200 °C (section 3.3 and Fig. 6-3). This observation is confirmed by Dawody *et al*. who showed that above 220 °C, the oxidation of NO decreases in the case of the WO_x and MoO_x phases due to the thermodynamic equilibrium concentration. The equilibrium between NO_2 and NO + ½ O_2 strongly depends on the temperature. Therefore, at a fixed concentration of O_2 and for a chosen catalyst, the increase of the temperature induces a decrease of the concentration of NO_2 produced in the stream. The corresponding decrease of NO_2 production at 250 °C is certainly a key factor to understand the lower positive effect of NO at 250 °C than at 200 °C.

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

The behavior of the catalysts was investigated under numerous different catalytic conditions, precisely in the presence of different concentrations of various oxidant molecules taken one by one or in combinations. The modification of the gaseous stream conditions induced changes in the catalytic activity and, in parallel, in the mean vanadium oxidation level stabilized on the catalyst. The decrease of the concentration of O_2 as in the reference conditions down to the total absence of O_2 was followed by a strong decrease of the catalyst activity and by a decrease of the mean oxidation level. At the opposite, the addition of NO to a catalytic stream containing O_2 was followed by an enhancement of the chlorobenzene conversion parallel to a reoxidation of the V O.L. Furthermore, the replacement of O_2 by NO_2 as a stronger oxidant has induced a drastic improvement of the catalyst activity and the stabilization of the V O.L. very close to the fully oxidized species V^{5+}.

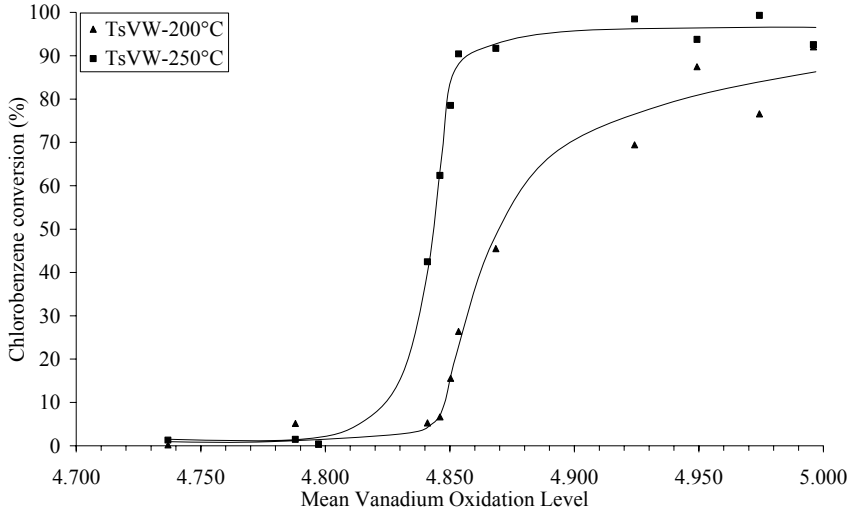

Fig. 6-11: Evolution of the chlorobenzene conversion at 200 °C (▲) and 250 °C (■) as a function of the mean vanadium oxidation level of the TsVW catalyst

All these results clearly demonstrate the existence of a strong relationship between the catalyst activity and the mean vanadium oxidation level. In order to investigate further this connection, Fig. 6-11 brings together all the catalytic and characterization results of the TsVW catalyst, which was investigated in twelve different catalytic conditions. This figure plots the catalyst activity of 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. 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, for the first time, the major question, which is the relationship between the V O.L. and the catalyst activity. It shows that to have a good catalyst, its vanadium oxidation level must be stabilized above 4.87 in the case of the TsVW catalyst. Moreover, this plot confirms that the activity of the VO_x based catalyst is strongly dependent of the mean vanadium oxidation level. These observations are in agreement with the proposed mechanism (Mars and van Krevelen) which logically supports an enhancement of the activity with the increase of the vanadium oxidation level. Actually, the increase of the mean oxidation level goes in parallel with the increase of the amount of lattice oxygen that could be transferred to induce the combustion of the chlorobenzene. Consequently, an increase of the mean oxidation level induces, logically, an enhancement of activity. However, this investigation goes further by plotting the exact relationship between the mean oxidation level and the activity. This exact relationship proves that: i) below the relatively high vanadium oxidation value of about 4.82, the catalyst is inactive and ii) an increase of the oxidation level above a certain value (about 4.87 in this case) does not further enhance the catalyst activity.

6.6. Conclusions

In classical conditions, *i.e*. in the presence of O_2 and in the absence of NO, we established that the concentration of O_2 in the stream is a limiting factor for the total oxidation of chlorobenzene. Moreover, we demonstrated that the chlorobenzene conversion proceeds following a classical Mars and van Krevelen mechanism on VO_x based catalysts.

In the presence of O_2, the increase of the NO concentration induces a dramatic enhancement of the chlorobenzene conversion on VO_x/TiO_2, VO_x-WO_x/TiO_2 and VO_x-MoO_x/TiO_2 catalysts. We demonstrated that, in the presence of NO and O_2, the oxidation of chlorobenzene follows a mechanism in 3 steps. In the first one, the vanadia phase gives its lattice oxygen to oxidize the chlorobenzene following a Mars and van Krevelen mechanism. In parallel, in a second step, NO is oxidized into NO_2 principally on the WO_x and MoO_x doping phases. The *in situ* produced NO_2 is able to replace or assist O_2 for the reoxidation of the reduced vanadia sites, which stands for the third step. This third step leads to the regeneration of the reduced vanadia sites which could then give again their lattice oxygen atoms and to the liberation of NO in the same amount as had been introduced in the stream. We demonstrated that the strength of NO_2 to reoxidize the reduced vanadium sites is significantly stronger than the strength of O_2 while NO is unable to induce any reoxidation of these reduced sites. The higher oxidation power of NO_2 than of O_2, for the reoxidation of the vanadia reduced sites, induces a speeding up of the Mars and van Krevelen mechanism.

The reconciliation of the catalytic results and of the catalysts mean vanadium oxidation level, estimated by the combination of ICP-AES and EPR measurements, pointed out, for the first time, the clear relationship between them. The activity of the VO_x based catalyst in the total oxidation of chlorobenzene is strongly governed by the mean vanadium oxidation level.

In order to obtain a most active VO_x based catalyst, the V O.L. must be stabilized above a certain oxidation level value that we evaluated to be at 4.87.