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A study on catalytic combustion of chlorobenzenes

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ABSTRACT

VWT and VMoT SCR catalysts have proven to be active in oxidation of chlorobenzenes, while, in the same reaction conditions, polychlorinated compounds formation, although in very low amount, limits the application of Pt–alumina catalyst in chlorinated VOC combustion. Increasing chlorination degree lowers chlorobenzene combustion rate over the most active VWT formulation. IR and activity data indicate that a common reaction mechanism involving as a first step nucleophilic substitution of chlorine atom by lattice oxygen ions occurs over these surfaces.

1. Introduction

Vanadia-based catalysts, such as vanadia–titania, vanadyl-phosphates, vanadia on silica, find widespread application in industry mainly for partial oxidation (e.g. maleic and phtalic anhydride syntheses) and for the SO_2 to SO_3 oxidation, a key step in the sulphuric acid synthesis process. Among several other research groups, the Krakow group headed by Haber performed very valuable fundamental and applied investigations concerning vanadia-based oxidation catalysts [1] which resulted in a quite satisfactory picture on the corresponding catalytic phenomena.

Vanadia–titania based catalysts, additionally containing Mo or W oxides, are also largely applied for the selective catalytic reduction of nitrogen oxides by ammonia to limit emissions of NO_x from industrial furnaces as well also diesel engines. According to several authors such catalysts allow also the simultaneous abatement of dioxins and NO_x in effluents, e.g. from waste incinerators, below the limits required by the EU directives [2–4]. Among industrial applications, vanadium rich V_2O_5–WO_3–TiO_2 catalysts (8% vanadium) are reported [5] to represent the catalyst component of Remedia® catalytic filters (W.L. Gore) working at 200 °C. Alternatively, noble-metal based catalysts (such as CK-306 and CK-307 from Topsøe [6] and EnviCat® HHC from SudChemie [7]) are used to catalytically destroy dioxins.

The catalytic oxidation and combustion of chlorobenzenes has been widely studied as model reactions of dioxin combustion in waste gases treatments. Since the work of Ross and Jones [8], several research groups studied the performances of commercial and innovative vanadia containing catalysts in VOC and Cl-VOC combustion. Our group, showed that industrial V-based catalysts are poorly active in hydrocarbons and oxygenates total oxidation, giving rise to relevant amount of CO even in the presence of large excess of oxygen. However, these catalysts retain their oxidation activity in the presence of chlorine compounds [9,10]. Amiridis et al. evaluated the catalytic oxidation of dichlorobenzene over different supported metal oxides, with respect to the V_2O_5–TiO_2 system [11]. Cr_2O_3 and V_2O_5 based catalysts have shown the highest activity, which is also affected by the nature of the support. Titania seems to be the most effective catalyst support for this application while alumina is less indicated, thus suggesting an effect of the metal–oxygen interactions. Vanadia loading is a key point for activity and it has been suggested that a single redox surface site participates in the kinetically significant steps, being the formation of crystalline V_2O_5 detrimental on oxidation activity [12]. The same authors proposed that the addition of a second transition metal oxide (i.e. WO_3, MoO_3) to the V_2O_5–TiO_2 system has no significant effect on the catalytic oxidation activity. On the other side, the addition of WO_3, and other dopants, affects the acidic properties of the catalytic surface and it has reported recently to influence the performance of vanadia based catalyst in total oxidation of chlorobenzene [13,14]. In fact, TiO_2/WO_3 catalysts are reported to be more active than the TiO_2 materials, although increasing Brønsted acidity by WO_3 introduction increases chlorinated by-products formation, such as chloromaleic anhydride. The detection

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of significant amount of this by-product can suggest a possible reaction mechanism involving hydrogen abstraction from the aromatic ring as possible initial reaction step.

The high oxidative activity of V_2O_5 supported over acidic $SiO_2/WO_3/TiO_2$ has been reported by Albonetti et al. [15]. Silica leads to a stabilization of the catalyst and favors formation of highly dispersed VO_x species, at least at low vanadia loadings.

Lewis acidity of the catalyst surface is instead proposed to be involved in another adsorption–oxidation mechanism, mainly occurring over transition metal oxide catalysts, through nucleophilic substitution of the chlorine atom to form strongly adsorbed chlorophenate species, the oxidation of aromatic ring to give carboxylate species being a later reaction step. This mechanism has been reported for chlorocarbon oxidation over V_2O_5/TiO_2 and $V_2O_5/MoO_3/TiO_2$ catalysts [16,17].

The role of different VO_x species in total chlorobenzene oxidation has been widely discussed in several papers by Gaigneaux and co-workers as well as the effect of a transition metal oxide dopant [18–21]. The authors performed benzene total oxidation as screening tests over a number of transition metal based catalysts, whose formulation has been defined in order to have a theoretical coverage of active phase spreading over titania, sulphate titania, alumina, silica supports, kept below the monolayer. Based on the work of Haber [22], the highest oxidative activity of vanadia over titania has been explained by its high dispersion on the support surface, finally governed by the difference in surface free energy. The same reactivity order has been inferred for oxidation of chloro-containing compounds, clearly not considering a possible deactivation effect of the chlorine atom in the substrate. Doping with W- or Mo-oxide the titania support hinders the subsequent spreading of vanadia phase, limiting the amount of available surface Lewis sites, although these dopants induce a synergic effect in the oxidation activity. This effect has been related to the increased Brønsted acidic sites at the catalysts surface, which are involved in the aromatic ring adsorption, as first step of the oxidation reaction.

As for noble metal based catalysts, either Pd or Pt-based, main drawbacks reported in the literature are the formation of polychlorinated by products and a possible deactivation of the catalyst at temperatures above 350 °C [23–25].

On zeolite supported Pt catalysts [26,27], Brønsted acidic sites are reported to favor 1,2-dichlorobenzene destruction, through a concerted multicenters mechanism. Over Brønsted protonic sites two dichlorobenzene molecules react to give chlorobenzene, HCl, and a second dichlorobenzene molecule adsorbed at the zeolite oxygen framework. These strongly adsorbed species are proposed to be oxidized by oxygen and water to produce CO_x and HCl, and to restore protonic zeolite sites. Also in this case significant byproduct amounts are detected.

In the open literature, total oxidation of chlorinated aromatic compounds has also been proposed over other transition metal oxide based catalysts, namely chromia based catalysts [28,29] which are well know combustion catalysts although not environmental friendly themselves due to the chromium content, ceria [30,31] and manganese based catalysts [32–36] applied for aliphatic and aromatic chlorocarbon oxidation. The manganese containing catalysts which are also active in catalytic $deNO_x$ SCR reaction, can be of interest due to the limited environmental impact of manganese and to their high oxidation activity [37,38]. However, in a previous work, we provided evidence of deactivation of bulk and alumina-supported manganese oxides by chlorine during chlorinated compounds oxidation [9]. Recent catalysts formulations seem to have at least partially overcastted this problem, since only partial deactivation has been reported in chlorobenzene oxidation in several applications, due to the formation of mixed surface phases (such as $Mn_{1.6}Cu_{1.4}O_4$ spinel phase [34]) or to an increased acidity of the catalyst surface (i.e. Mn–Zr mixed oxides [32]). Mn-based catalysts (such as the CK-395 catalyst from Topsøe [6]) are also used industrially just for abatement of halogenated hydrocarbons.

We present here our recent results on the oxidation of chlorinated aromatic compounds in vapor phase over high vanadium containing catalysts and on alternative Pt supported catalyst. Monochlorobenzene (MCB), 1,2-dichlorobenzene (1,2-DCB) and 1,4-dichlorobenzene (1,4-DCB) were chosen as model compounds to evaluate the oxidation capability of these catalysts.

Reactive adsorption of 1,2-DCB over the surface of VWT catalysts has also been studied by FT-IR spectroscopy in controlled atmosphere.

2. Materials and methods

2.1. Catalysts

Vanadia based catalysts proposed in this study have been chosen as representative of active SCR-$deNO_x$ catalysts and have been the object of previous studies carried on in our laboratory, in comparison to commercial catalysts having a similar composition.

VWT catalyst (5% wt V_2O_5 on WO_3–TiO_2) has been prepared by conventional wet impregnation method of ammonium metavanadate over support Bayertitan A-DW-1: WO_3–TiO_2, surface area 80 m^2/g, anatase, crystal size 21 nm, W content: 4.5% at. ratio. The powder has been dried at 100 °C and calcined at 500 °C [39].

VMoT catalyst (V_2O_5 on MoO_3–TiO_2, 3.5–5.5–91% wt) has been prepared by impregnation of commercial TiO_2 anatase from Rhone Poulenc (surface area 70 m^2/g) using an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NH_4VO_3. The powder has been dried at 100 °C and calcined at 450 °C.

PtA catalyst (2% wt Pt on Al_2O_3). The support is commercial γ-alumina Puralox from Sasol (surface area 160 m^2/g, Vp = 0.7 cm^3/g). Incorporation of Pt onto the support was made by incipient wetness impregnation method using aqueous solution of diamminedinitritoplatinum(II) $(Pt(NH_3)_2(NO_2)_2$, Aldrich). The white powder has been dried at 100 °C and calcined in air at 600 °C during 2 h. The metal loading, expressed as formal surface atomic density (atoms per nanometer square, at/nm^2), is 0.4 at-Pt/nm^2 [40], the mean Pt^0 particle diameter is around 16 nm.

The XRD profiles for VWT and VMoT catalysts agree with those of the support anatase. The absence of peaks due to other oxide indicates that active species are well dispersed over the surface or that, if present, they should be in form of amorphous clusters. UV–vis–NIR spectra as well as FT IR skeletal spectra are consistent with a vanadia content near the monolayer (Fig. S1 in Supporting Information) [41,42].

2.2. Catalytic tests

The catalytic tests were carried out using 500 mg of catalysts powder in a flow reactor operating at atmospheric pressure in the 100–450 °C range (total gas flow rate 350 ml/min, 500 ppmv CVOC vapor, helium carrier, 10% oxygen, dry conditions). The inlet and outlet gases were analyzed by GC equipped with TCD and FID detectors and by GC–MS. HCl and Cl_2 have been determined by ionic chromatography, after bubbling the effluents in NaOH water solution. Chlorine balance was generally approximately fulfilled, unless otherwise specified. Blank experiments showed no reactions in the considered temperature range.

Activation energies for the different organic compounds oxidation are in the range 90–70 kJ/mol.

Chlorobenzene (MCB), 1,2-dichlorobenzene (1,2-DCB) and 1,4-dichlorobenzene (1,4-DCB) reactants were from Sigma–Aldrich.

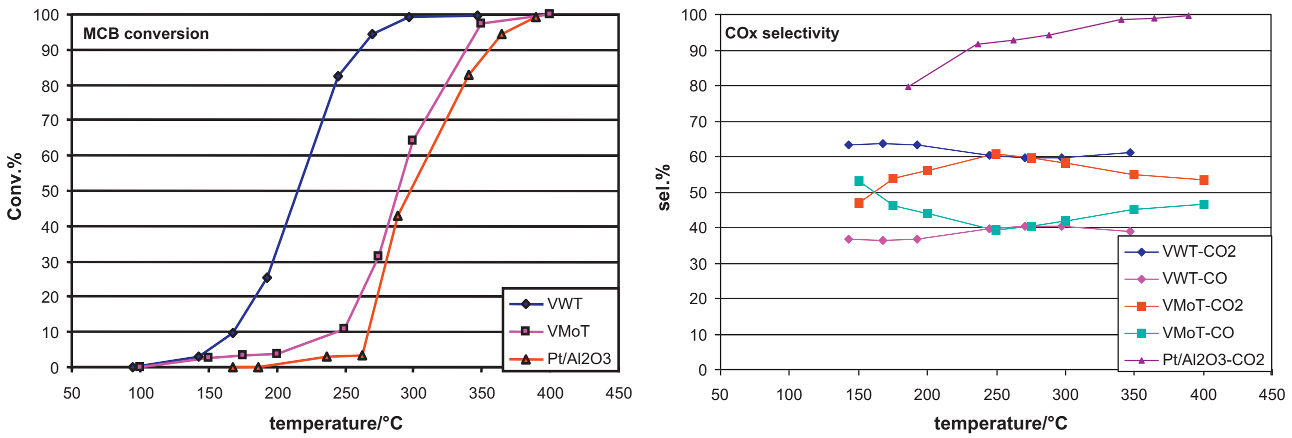


Fig. 1. MCB conversion and selectivity to CO_x as a function of the temperature. 500 ppmv VOC vapor, helium carrier, excess oxygen (dry conditions). GHSV = 42,800 h^{-1}.

2.3. *FT IR experiments*

Adsorption and *in situ* IR experiments have been performed by using a conventional gas manipulation apparatus connected to the IR cell under static conditions and by transmission method. Self supporting disks of pure powder (30 mg) have been heated in air at 500 °C and briefly outgassed at the same temperature directly in the IR cell, then cooled to room temperature under vacuum (10^{-4} mbar) prior to any adsorption experiments. This activation step is common to all the experiments discussed in the text. 1,2-DCB adsorption has then been performed at room temperature, over the activated catalyst surface. Two different experimental procedures are then applied:(i) the catalyst has been heated in the presence of 1,2-DCB vapor (from room temperature to 500 °C, static conditions) to allow the analysis of both adsorbed species and gas phase species in the IR cell. Only at the highest reaction temperature (i.e. 400 °C) air was admitted in the IR cell and the sample was heated again at 400 °C in the presence of air; (ii) after 1,2-DCB adsorption at room temperature, the sample has been outgassed at room temperature, and up to 200 °C and surface species IR spectra have been collected (in vacuum).

IR spectra of catalysts surface and gas phase species were recorded on a Thermo Nicolet Nexus FT instrument (OMNIC^{TM} software, 100 scans, DTGS detector).

3. Results and discussion

3.1. *Catalytic activity*

Over the VWT catalyst, Chlorobenzene conversion starts around 150 °C, reaches 95% at 270 °C and is complete around 300 °C (Fig. 1), in good agreement with data reported by Amiridis et al. which found over 3% wt V_2O_5/TiO_2 catalyst MCB conversion exceeding 80% at 300 °C in conditions close to our experimental set up [16]. During the overall catalytic test, selectivity to CO_x fulfils the carbon balance, selectivity to CO_2 and CO being close to 60% and 40% respectively.

VMoT also shows a good oxidation activity, although at definitely higher temperatures: at 300 °C conversion is around 65%, reaching 100% at 350 °C, thus 50 °C higher than in the previous case: indeed we can notice that vanadium content is lower in this catalyst than in VWT catalyst (3.5% vs. 5% wt). On the other side, selectivity to CO_2 is slightly higher (above 60%) than in the previous case, while CO formation is reduced.

Conversion of MCB has also been tested over the Pt-containing catalyst, a powerful oxidation catalyst. TEM analysis showed the presence at the surface of rather large Pt particles (about 15 nm diameter) [40] which should be less prone to polychlorinated products formation [23]. Following a pre-oxidation step in He–oxygen mixture, MCB conversion starts to be significant at 250 °C and is complete at 400 °C, thus at temperatures in any case higher than VWT and VMoT catalysts. The main C-containing product is CO_2, being selectivity to CO always below 10%, as expected for a combustion catalyst. However, the product analysis by GC mass-spectrometry shows formation of dichlorobenzene isomers, and also traces of polychlorinated aromatic compounds, in agreement with data previously reported by Van den Brink et al. for Pt based catalysts, regardless support composition [23,43]. The by-products formation can be calculated with a selectivity around 1% in a temperature range 250–300 °C and decreases at total MBC conversions. We must notice that, in the same reaction conditions, over VWT catalyst no polychlorinated benzenes formation could be detected by GC mass analysis of organic products. Indeed, polychlorinated compounds formation, together with quite high temperatures required for MCB combustion, limit Pt-based materials applications in Cl-VOC combustion.

VWT catalyst is also active in 1,2-DCB combustion, reaching 90% conversion of organic reactant around 300 °C, with almost complete selectivity to CO_x (Fig. 2). From 1,2-DCB and chlorobenzene conversion, HCl is the only chloro-containing reaction product, detected at the highest conversions. These data agree with results reported by us for 1,2-DCB conversion over other impregnated and commercial VWT systems at different vanadia loadings [9,39].

In the low temperature range, 1,2-DCB conversions over both VWT and VMoT catalysts are completely consistent. At increasing temperature, however, a higher activity of the former catalyst can be detected: this behavior can be interpreted assuming that, although the adsorption and reaction first steps of the oxidative activity likely follow a similar path, the VO_x content, higher in the VWT catalyst, is responsible for the aromatic ring deep oxidation occurring at temperatures above 200 °C, as discussed also in the IR section. In contrast with findings from Albonetti et al. [13] we do not find any evidence of byproducts formation i.e. chloro-maleic anhydride, over the VWT formulation catalyst. A possible explanation can be found in the different reaction conditions: although we worked in dry conditions, thus the most favorable to allow chlorinated by products formation, GHSV are high and, on the other side, 1,2-DCB concentration has been kept as low as 500 ppmv.

Pt catalyst, tested in the same conditions, shows a low activity, limited at 30% 1,2-DCB conversion around 300 °C, in agreement with the behavior described by us for a commercial Cat-ox catalyst [2]. During this catalytic run, no total DCB conversion could be reached even above 400 °C. It has to be noted that the catalyst we used is the same which has been previously used for MCB

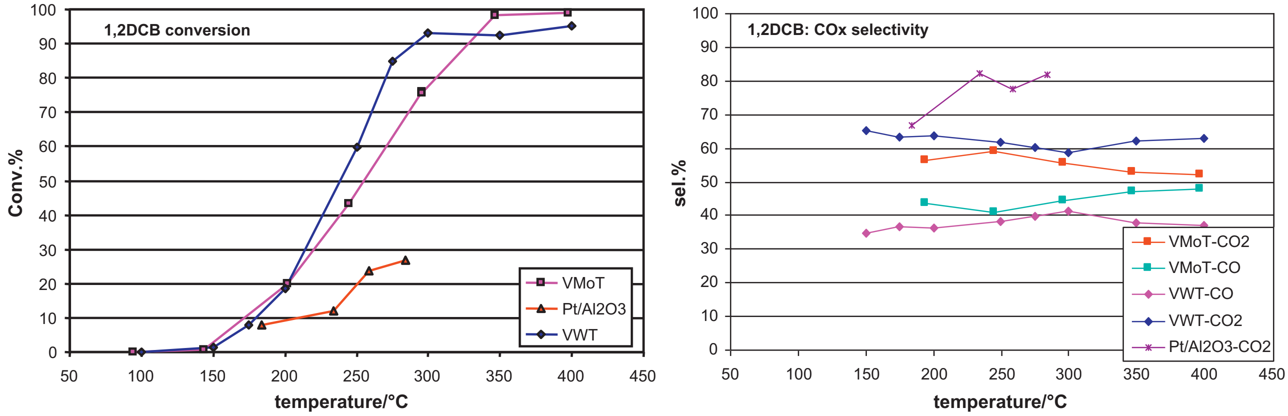


Fig. 2. 1,2-DCB conversion and selectivity to CO_x as a function of the temperature. 500 ppmv VOC vapor, helium carrier, excess oxygen (dry conditions). GHSV = 42,800 h^{-1}.

conversion and then submitted to a pretreatment in air at high temperature: likely some deactivation phenomena already started during the first run and could not be recovered by reactivation in air. Following high temperature treatment of Pt/alumina in oxidative environment, Van den Brink et al. reported the formation of PtIV species, less active in combustion but more active in chlorination [23]. The GC–MS analysis of the products once again revealed polychlorinated benzene formation, up to tetrachlobenzene isomers.

The behavior of the VWT and VMoT catalysts in 1,4-DCB conversion is described in Fig. 3: the former catalyst resulted to be the most active in DCB oxidation. Selectivities to CO_x are consistent with previous results.

Comparing activity results in deep oxidation of chlorobenzenes, reported in Figs. 1–3 for VWT and VMoT catalysts, both suited for Cl-VOC combustion, some remarks can be proposed.

As for the VWT catalyst, the increased chlorination degree (from MCB to 1,2-DCB) corresponds in our conditions to a slight decrease in oxidation rate, in agreement with results reported by Amiridis et al. and Weber et al. [16,44] and related to the electronic effect of the chlorine atoms towards the aromatic ring system.

Studying benzene oxidation over vanadium oxide, Haber et al. [45,46] pointed out the importance of steric arrangement of the substrate molecule at the oxide surface towards partial and total oxidation pathways. Both benzene and toluene can adsorb with the ring parallel or perpendicular to the surface, at the bridging or vanadyl oxygen sites. The preferential, most stable, perpendicular adsorption of toluene at the bridging oxygen should lead to the oxygenate products formation, whose desorption is favored by the weakening of V–O–V sites. On the other hand, the side-on (parallel) adsorption of the aromatic ring, leads to a stronger interaction with surface oxygen, resulting in total oxidation, thus CO_x formation. Electrophilic attack of molecular oxygen on the benzene aromatic ring, perpendicular to the ring plane, is needed to achieve the total oxidation of benzene oxidized fragments [45,46]. In partial agreement with this picture, in dichlorinated benzenes combustion, the presence of a second chlorine atoms could limit the side-on adsorption of the aromatic ring at the oxide surface.

1,4-DCB complete conversion over VWT catalyst occurs in the range 300–350 °C, thus at temperatures similar to 1,2-DCB conversion, although in the range 200–300 °C 1,4-DCB conversion is slightly higher than 1,2-DCB conversion, pointing out a possible isomer effect of the second chlorine atom (conversions values almost within the experimental uncertainty). This effect has been discussed by several other groups over similar catalysts and reported results are somehow conflicting. In particular, Lichtenberger et al. reported that the rate of chlorobenzenes oxidation decreases from the *meta* to *para* and to the *orto* isomer in relation to electronic effects [16]. The presence of a second chlorine atom in different position affects the rate of nucleophilic substitution which is proposed to be the first step of the reaction mechanism. If we consider chlorobenzenes combustion over VMoT catalyst, chlorobenzenes total conversion is reached at 350 °C but, apparently, below this temperature, DCB conversion rates are slightly higher than MCB conversion rate. A possible explanation can be proposed considering that, over the less active VMoT oxidation catalyst, an increase of the reactant molecular weight and, starting from a perpendicular adsorption of the aromatic ring, two adjacent chlorine atoms, working as “grafting points” at the surface can facili-

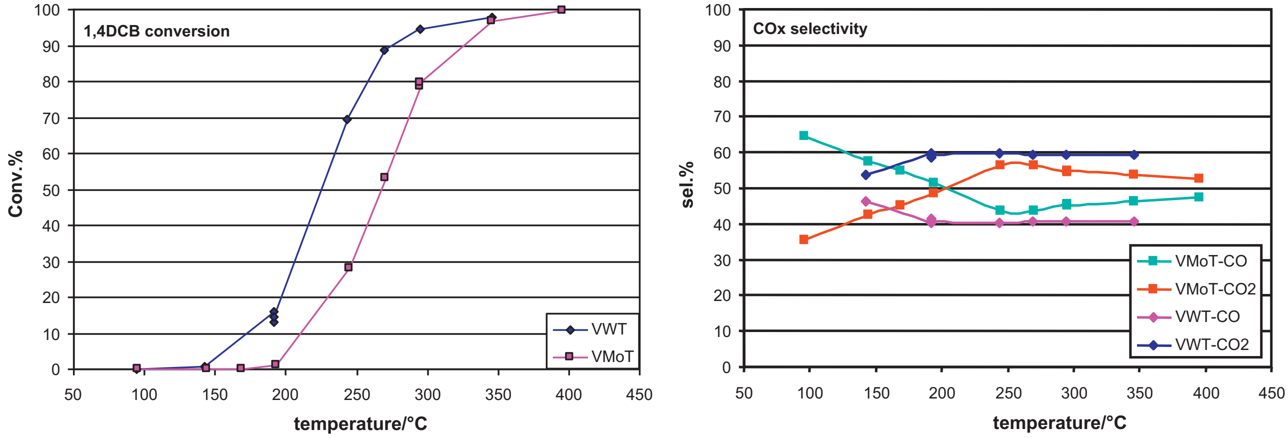


Fig. 3. 1,4-DCB conversion and selectivity to CO_x as a function of the temperature. 500 ppmv VOC vapor, helium carrier, excess oxygen (dry conditions). GHSV = 42,800 h^{-1}.

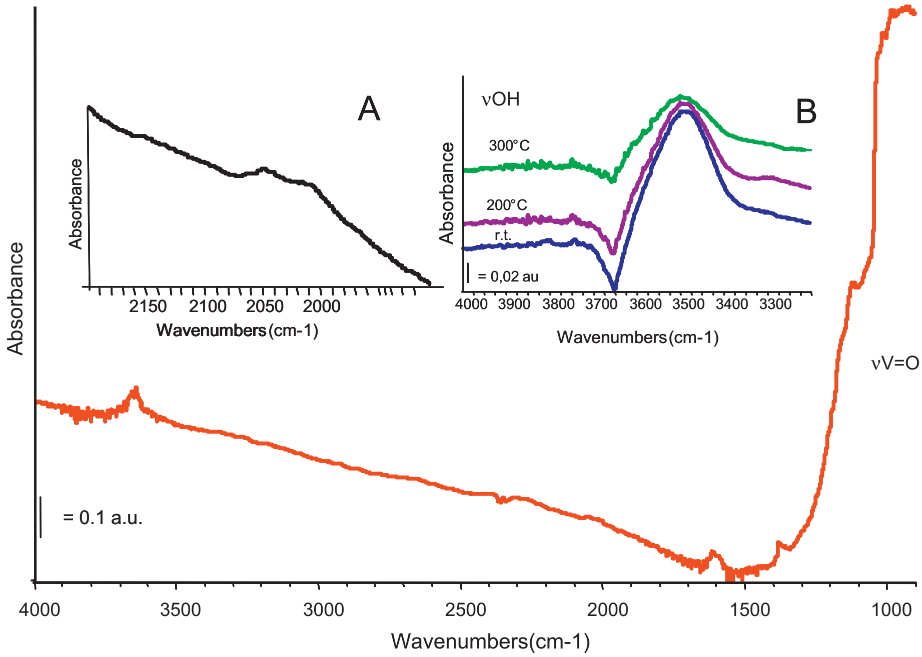


Fig. 4. FT IR spectrum of the activated VWT surface, after heating in air and outgassing at 500 °C. Inset (A): enlargement of the overtones region. Inset (B): subtraction spectra recorded after 1,2-DCB adsorption at room temperature and at increasing temperature (static conditions), OH stretching region. The activated surface spectrum has been subtracted.

tate the reactive adsorption rate, through successive nucleophilic substitution.

The similar high conversions we detected in the high temperature range are affected by kinetics limitations, however we had some spectroscopic indications of the aromatic ring resisting oxidation up to temperatures above 300 °C over these surfaces (see next paragraph), thus we cannot exclude the effect of the common organic substrate structure, oxidation of the aromatic ring becoming a kinetically relevant step [16,17].

3.2. *FT IR studies*

FT IR experiments have been carried out investigating adsorption and heating of 1,2-DCB at the VWT catalyst surface, both in the presence of 1,2-DCB vapor (static conditions, Figs. 4 and 5) and in vacuum (Fig. 6). The activated VWT surface spectrum, after heating in air at 500 °C and outgassing in vacuum at the same temperature, shows at the cut-off limits weak and sharp bands due to wolframil and vanadyl stretching modes (about 1040 cm^{-1}), whose overtones fall around 2000 cm^{-1} (enlargement in Fig. 4, inset A). The detection of such quite well resolved overtone bands at frequencies similar to those observed for the binary systems VT and WT is consistent with the assignation to isolated V=O and W=O species, interacting with the support. These low coordination species have been reported to behave as Lewis sites [47,48]. Weak bands at 1350 cm^{-1} and 1600 cm^{-1} are due to sulphate impurities from the support titania and residual carboxylate species, respectively. In the high frequency region, a broad band due to OH stretching mode can also be detected, pointing out the only partial dehydroxylation of the surface.

At first, 1,2-DCB adsorption at room temperature is molecular, involving OH groups of the support which appear as negative bands in the subtraction spectra (Fig. 4, inset B). The same negative feature can be detected also at increasing temperature.

The subtraction spectra in Fig. 5A and B evidence the IR bands due to surface species arising from 1,2-DCB adsorption at room

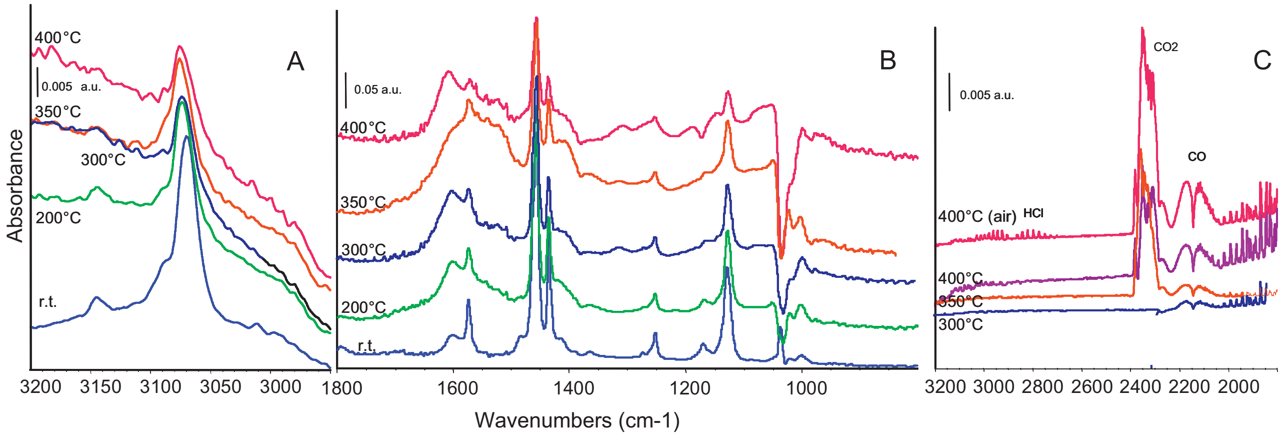


Fig. 5. (A and B) FT IR subtraction spectra of the surface species arising from 1,2-DCB adsorption at the VWT surface at room temperature and increasing temperatures, recorded in the presence of 1,2-DCB vapor (static conditions). The activated surface spectrum has been subtracted. (C) FT IR spectra of the corresponding gas phase species at increasing temperatures.

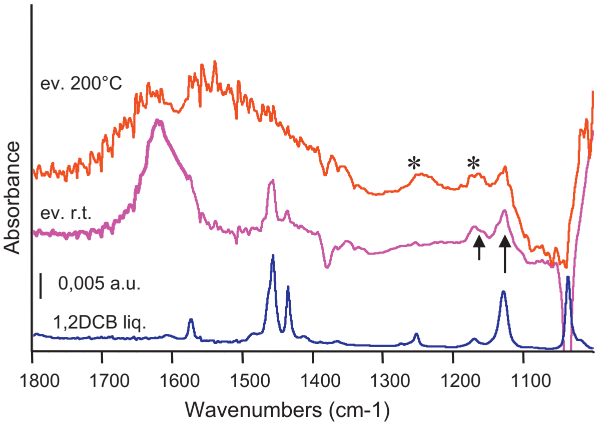


Fig. 6. FT IR subtraction spectra of the surface species arising from 1,2-DCB adsorption at VWT catalyst surface, after outgassing at room temperature and at 200 °C. Liquid 1,2-DCB reference spectrum is reported for comparison.

temperature and after heating in static conditions. No air or oxygen have been admitted in the IR cell during this experiment.

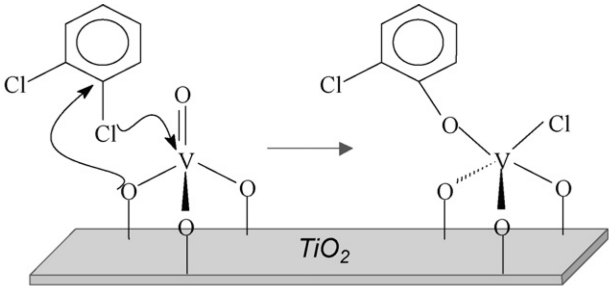
In the high frequency region, a main band at 3070 cm^{-1} with small components at higher frequency, can be assigned to the aromatic ring stretching modes (Fig. 5A). The split of this band, although very weak, has been previously assigned to the co-existence of two adsorbed species of similar structure [17].

Peaks at 1600, 1573, 1456 and 1434 cm^{-1}, sharp, are due to the aromatic ring breathing modes (8a, 8b, 19a, and 19b vibrational modes, respectively). The "substituent sensitive" bands (C–Cl stretching modes) are observed at 1168 and 1127 cm^{-1}. The reported frequencies, although shifted with respect to the gas phase 1,2-DCB, are very close to the corresponding bands in the liquid phase spectrum, as expected for a molecular interaction. At lower frequencies, bands due to vanadyl and wolframyl species are also perturbed and shifted by the interaction with the organic reactant, a further evidence that these species are active in the adsorption processes.

In the 1700–2000 cm^{-1} frequency region, bands due to combination and overtones of the aromatic ring can be detected at 1950, 1914 and 1793 cm^{-1} (not reported here) coincident with the same bands reported for liquid 1,2-DCB and stable upon heating. This effect has been explained considering the aromatic ring adsorption at the surface to be perpendicular, interacting mainly through its Cl substituents [17].

Heating in the presence of 1,2-DCB and without oxygen allowed us to study the role of the lattice oxygen species in the organic molecule oxidation [49]. Between 200 °C and 300 °C, below the sharp bands due to residual organic molecules, broad and complex absorptions grow around 1600, 1520 and 1400 cm^{-1}, due to a mixture of carboxylate and carbonate species formed by aromatic ring oxidation. These broad bands reach the maximum intensity around 350 °C, then are somehow reduced in intensity. Another component is growing, quite complex, around 1300 cm^{-1}, which can be assigned to phenate and chlorophenate species formation [17,48]. Negative bands due to surface vanadyl and wolframyl, appear clearly in the subtraction spectra, the higher the temperature, the more negative the peaks, thus indicating the consumption of these species during DCB oxidation.

Correspondingly, we observe CO (at 300 °C) and CO_2 (between 300 and 400 °C) formation in the gas phase (Fig. 5C). Some shift at higher frequencies could be detected for the main band in the CH stretching region only upon heating, showing that interaction through the aromatic ring occurs at the catalyst surface at high temperature.



Scheme 1. Reactive 1,2-DCB adsorption.

At 400 °C, traces of HCl can also be detected in the gas phase (see the fine rotational band structure in the 2700–3000 cm^{-1} region, in Fig. 5C), but only after admission in the IR cell of humid air at the same temperature an extensive HCl release could be detected and a corresponding faster decomposition of the carboxylate and carbonate species occurs at the surface.

In order to further evaluate the reactive adsorption of 1,2-DCB at the catalyst surface another set of experiments has been performed, by adsorbing it at room temperature and after outgassing at room temperature and increasing temperature. Results are reported in Fig. 6.

Beside the molecular adsorption involving OH groups, already described above, reactive adsorption occurs. In fact, analyzing the spectra of chemisorbed surface species, resistant outgassing, new bands appear already at room temperature in the low frequency region around 1140 and 1160 cm^{-1}, suggesting the presence of another aromatic species, possibly adsorbed phenate/chlorophenate (↑ in Fig. 6). At 200 °C 1,2DBC bands almost disappear and two broad bands around 1170 and 1260 cm^{-1} are detectable, together with a broad absorption at higher frequency, likely due to a mixture of carboxylate and di-phenate species (* in Fig. 6). This effect arises from an almost irreversible chlorine nucleophilic substitution step in the 1,2-DCB molecule [17,50]. In agreement with data previously reported for catalytic combustion of alkylic chlorinated compounds [51] the formation of strongly adsorbed alkoxy/phenoxy species is suggested to be the first reactive step in the CVOC catalytic oxidation reaction reactions, followed by the aromatic ring oxidation.

1,2-DCB conversion has been previously studied by us over a $V_2O_5–MoO_3–TiO_2$ catalyst. Over this surface the nucleophilic substitution step seems to be very fast and occurs already at room temperature, leading to the detection of sharp and strong bands due to adsorbed phenate species, while over the VWT catalyst phenate formation becomes significant only at increasing temperature.

These data, together with literature data [16,17,52], provide thus an evidence for an interaction of chlorobenzene through the chlorine atoms with Lewis surface sites, followed by an irreversible step of nucleophilic substitution to give rise to chlorophenate species (Scheme 1). The adsorbed species are likely precursor of carboxylate formation, and CO_x evolution at the highest temperatures.

4. Conclusions

VWT and VMoT SCR catalysts are active in oxidation of several aromatic Cl-VOC while polychlorinated compounds formation, although in very low amount, limits the application of Pt–alumina catalyst in chlorinated VOC combustion. The limiting effect of increasing chlorination degree on chlorobenzene combustion is evident over the most active VWT, likely related to electronic effects. Over the less active VMoT formulation, steric effects could explain the different reaction rates at least in the low temperature range.

IR data reveal that over both VWT and VMoT surfaces 1,2-DCB adsorbs through chlorine atom substitution by lattice oxygen, giving rise to adsorbed chlorophenate. Further evolution of the surface species at increasing temperature leads to adsorbed carboxylate likely precursors of CO_x products. Thus a common reaction mechanism involving as a first step nucleophilic substitution of chlorine atom by lattice oxygen ions occurs over these surfaces.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2010.10.097.

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