



## Abatement of model molecules for dioxin total oxidation on $V_2O_5-WO_3/TiO_2$ catalysts: The case of substituted oxygen-containing VOC

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### ABSTRACT

Dioxin oxidation is generally studied on the basis of chlorinated benzene derivative models. Oxygen containing aromatic models are however also pertinent because the impact of the central O-bridge(s) of dioxins has to be evaluated. Furan was already studied as a model for the central ring of a polychlorinated dibenzofuran (PCDF), but this paper goes further as 2,5-dimethylfuran was studied in order to better take into account the steric hindrance existing around the oxygenated moiety of the modeled pollutant. The comparison of these two model compounds highlights the fact a furan ring, whether substituted or not, tends to adsorb strongly on the catalyst surface without being readily oxidized. This phenomenon leads to the formation of a carbonaceous deposit characterized by the presence of maleate species. Selective oxidation towards maleic anhydride takes place along with total oxidation in both cases. So the substitution of two methyl groups for hydrogen atoms in furan does not change the overall behavior of the pollutant towards the catalyst. This suggests that the oxygenated moiety of a PCDF – around which the steric hindrance is comparable with 2,5-dimethylfuran – could play a decisive role in the nature of the pollutant-to-catalyst interaction. Furthermore, competition tests with chlorobenzene show that the conversion of chlorobenzene is dramatically impeded in the presence of both investigated oxygen containing models. O-driven adsorption of dioxins should be envisaged as the first step of the catalytic abatement of dioxins on V-based catalysts rather than dissociative adsorption through the chlorinated end.

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### 1. Introduction

In the recent years, stringent limits on atmospheric emission levels have been imposed by the environmental policies. In incinerators and biomass-fed cogeneration units, dioxins constitute a major concern since they are one of the most toxic and persistent pollutants [1]. Catalytic total oxidation is the most promising solution to destroy these polyaromatic and polychlorinated molecules directly at the source.

$VO_x/TiO_2$  catalysts are widely proposed for this application [2–13]. In order to study and optimize this system, researchers usually work on model molecules. The chosen model molecule should be less toxic, easier to handle than dioxins and its chemical structure should be similar to those of dioxins. Chlorobenzene or polychlorobenzene are thus frequently chosen as chlorinated aromatic VOC models [2–11,13–15]. Studies on chlorobenzene allow one to evaluate the activity of the catalysts in the oxidation of an aromatic ring, as well as their resistance against chlorine poisoning. They thus usually lead to the proposition of strategies that should

improve the performance of the catalysts in the total oxidation of dioxins (e.g.: introduction of  $WO_3$  [4]).

However, this commonly accepted strategy could be partly inappropriate. Indeed, the central moiety of a dioxin, consisting of an oxygenated ring, is not taken into account by the CI-model approach, even though it could play a crucial role in the catalytic process (adsorption of the pollutant, coking, etc.). This was indeed highlighted recently by our group [16] in a study on the total oxidation of furan. We showed that this oxygen-containing volatile organic compound (O-VOC) adsorbs strongly on V-based catalysts and that the nature of the pollutant–catalyst interaction was indeed decisively dictating the performance of the investigated catalysts. More precisely, the strong adsorption of furan on the catalyst makes the strategies based on a CI-VOC to optimize the catalyst formulations totally inappropriate or even deleterious. Furthermore, in competition tests the presence of furan as a co-pollutant in the feed leads to the formation of a carbonaceous deposit on the catalyst which hinders chlorobenzene from reaching the active sites.

The basic oxygen of furan, which dictates its adsorption on the acidic sites of the catalyst [12,17,18] is however free from any steric hindrance. This is a limitation of furan as a model, since in a polychlorinated dibenzofuran (PCDF) a steric hindrance exists around

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**Table 1**

Description of the catalyst and support; specific surface area and weight composition

Name	Support	Active phase (0.75 ML)	Doping phase (0.75 ML)	SSA (m <sup>2</sup> g <sup>-1</sup> )	V (%)	W (%)	Ti (%)
T	TiO <sub>2</sub>	–	–	49	–	–	–
TVW	TiO <sub>2</sub>	VO <sub>x</sub>	WO <sub>x</sub>	43	2.3	6.9	49.4

the oxygen bridge and may interfere in the pollutant-to-catalyst interaction. Therefore, in this paper, the total oxidation of 2,5-dimethylfuran is compared to the total oxidation of furan in order to specifically address the possible steric hindrance existing during the adsorption of a furan ring. The adsorption of both O-VOC is further investigated and the carbonaceous deposit formed in both cases is characterized. The occurrence of selective oxidation which is shown to be related to the nature of the carbonaceous deposit is also discussed and shown to be dependant on the nature of the compound that is targeted for removal. Finally, competition tests between the O-VOC models and chlorobenzene are reported in order to better understand the complex case of dioxin total oxidation.

## 2. Experimental

### 2.1. Preparation of the catalyst

The support is a 70% anatase–30% rutile TiO<sub>2</sub> (Degussa P25; 49 m<sup>2</sup>/g) denoted hereafter by T (Table 1). The active phase is VO<sub>x</sub> (V) and WO<sub>x</sub> (W) is introduced as a dope [4]. The precursors of these oxides are respectively NH<sub>4</sub>VO<sub>3</sub> (Vel, 99.9%) and (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> (Aldrich, 99.99%). To obtain the impregnation solutions, the precursors are dissolved in distilled water and complexed with 2 mol of oxalic acid for 1 mol of transition metal. The impregnation solution had a pH below 3. A classical wet impregnation method was used and the amounts of precursors were calculated in order to obtain 0.75 theoretical monolayer (ML) of each transition metal oxide on the surface of the support (Table 1). The theoretical monolayer coverage was calculated based on the cross-sectional area of a unit composed of one transition metal atom and its oxygen coordination sphere. The values are 12 Å<sup>2</sup> for VO<sub>x</sub> and 15 Å<sup>2</sup> for WO<sub>x</sub> [4]. The suspension of support in the impregnation solution was stirred for 2 h at room temperature. Water was then evaporated under reduced pressure in a rotavapor at 40 °C. Afterwards, the obtained solids were dried overnight in an oven at 110 °C and then calcined at 400 °C at atmospheric pressure in air for 20 h in a muffle furnace. The obtained V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub> catalyst is hereafter denoted by TVW.

### 2.2. Catalytic tests

The catalytic tests were performed in a metallic fixed-bed microreactor made of an inconel tube of 1 cm internal diameter (PID ENG&Tech, Spain, Madrid) and operating at atmospheric pressure. The catalytic bed was composed of 200 mg of catalyst powder selected within the granulometric fraction 200–315 μm and diluted in 800 mg glass spheres that was confirmed inactive. The gas stream contained 150 ppm of furan (mixture in He; Praxair) or 100 ppm of 2,5-dimethylfuran (mixture in He; Praxair) and/or 100 ppm of chlorobenzene (mixture in He; Praxair), 20% of O<sub>2</sub> (Praxair; 99,995%) and He (Praxair; 99,996%) as diluting gas to obtain 200 ml/min (VVH = 37,000 h<sup>-1</sup>). The reaction was run from 100 to 400 °C in a step mode. At each temperature investigated, the catalyst was stabilized for 150 min. Two start-up procedures have been envisaged. In the “direct” procedure, the test is readily started from 100 °C. In the “sat” procedure (“sat” standing for saturation), the catalyst is first allowed to make contact with a con-

centrated flow of the VOC (five times more concentrated than in the test) at 100 °C for 4 h. In some cases, the procedure is stopped after this step for the purpose of characterization. Otherwise, the composition of the flow is then stabilized at the usual concentration before proceeding to the temperature-programmed catalytic test.

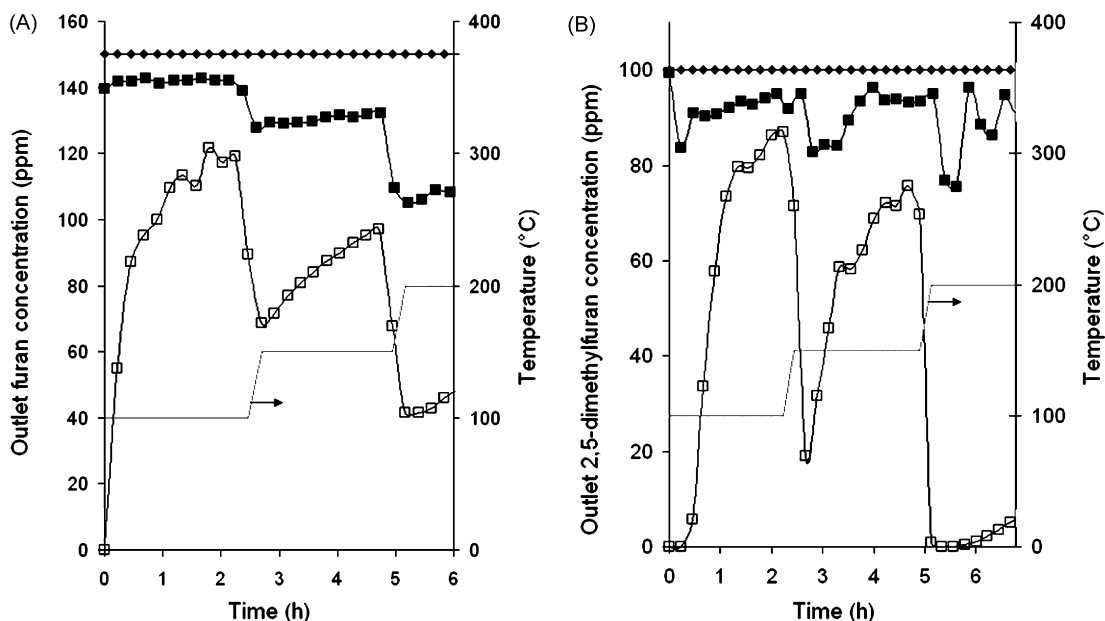
Analysis of reactants and products was continuously performed by on-line gas chromatography (GC). The CP-3800 gas chromatography apparatus from Varian equipped with four columns (one Hayesep G, one Hayesep T, one Molsieve and one CP-Sil 8CB) and three detectors (one TCD and two FIDs) was used with He as carrier gas in order to quantify furan, 2,5-dimethylfuran, chlorobenzene, O<sub>2</sub>, CO and CO<sub>2</sub> and to detect other hydrocarbons. The analytical parameters were set as to allow one analysis each 15 min and to make measured performance accurate within a range of about 1% (in relative) for the conversion of chlorobenzene and furan. To calculate the conversion at a given temperature, only the concentrations of reactants measured and averaged in the period of time from 100 to 150 min after stabilization were taken into account. The conversion is defined as the ratio reactant transformed/reactant in the inlet (in %).

### 2.3. Characterization

X-ray photoelectron spectroscopy (XPS) was performed on an SSI X-probe (SSX-100/206) spectrometer from Surface Science Instruments. The analysis chamber was operated under ultrahigh vacuum with a pressure close to 5 × 10<sup>-9</sup> Torr and the sample was irradiated with a monochromatic Al Kα (1486.6 eV) radiation (10 kV; 22 mA). Charge compensation was achieved by using an electron flood gun adjusted at 8 eV and placing a nickel grid 3.0 mm above the sample. Pass energy for the analyzer was 150 eV and the spot size was approximately 1.4 mm<sup>2</sup>. For these measurements, the binding energy (BE) values were referred to the C–(C,H) contribution of the C 1s peak at 284.8 eV. The surface atomic concentrations were calculated by correcting the intensities with theoretical sensitivity factors based on Scofield cross-sections [19]. Peak decomposition was performed using curves with an 85% Gaussian type and a 15% Lorentzian type, and a Shirley non-linear sigmoid-type baseline. The following peaks were used for the quantitative analysis: O 1s, C 1s, V 2p, Ti 2p, Cl 2p and W 4d. Based on the XPS analysis, the XPS surface ratio of a given element is defined as the atomic concentration of the element (%) divided by the atomic concentration of Ti (%).

Fourier transformed infra red spectra (FTIR) were recorded using an IFS55 Equinox spectrometer (Brücker) equipped with an MCT detector and working with a resolution of 4 cm<sup>-1</sup>. For the analysis, 3 mg of catalyst was crushed and diluted in KBr so that the catalyst accounts for approximately 1% in weight of the mixture. The sample was then compressed under a pressure of 7 ton/cm<sup>2</sup> in order to obtain a pellet of a diameter of 13 mm.

Temperature programmed desorption (TPD) was performed in a fixed bed quartz microreactor. The catalytic bed consisted of 200 mg of catalyst diluted in 800 mg of glass beads and surrounded by a layer of approximately 3 mm of glass beads. Outlet gases were analyzed by an online mass spectrometer equipped with a quadrupolar analyzer of Prisma type (Balzers). The pressure in



**Fig. 1.** Evolution of the outlet concentration of furan (A) and 2,5-dimethylfuran (B) during the catalytic tests run on TVW in the “direct” mode (□) and in the “sat” mode (■). The baseline (or inlet concentration) is given by the (◆) symbols and the straight line gives the temperature.

the chamber of analysis was  $3 \times 10^{-5}$  Pa. The catalyst was initially purged with helium at a flow rate of 110 ml/min and heated up to 450 °C at a ramping rate of 10 °C/min. After cooled down to 100 °C, the catalyst was allowed to contact a flow containing 500 ppm of 2,5-dimethylfuran or 750 ppm of furan, 20% of oxygen and He as diluting gas at a rate of 200 ml/min for 3 h. After this treatment, the system was purged with a helium flow of 110 ml/min at 100 °C during 30 min. The desorption of the products was then tracked according to a program of temperature from 100 to 450 °C in helium (flow = 110 ml/min; slope = 10 °C/min).

Thermogravimetric analysis (TGA) was performed with a TGA 851e Mettler-Toledo. Approximately 20 mg of sample were deposited in an alumina crucible located on a microbalance. The analysis was run under a 100 ml/min flow of dry air (Air Liquide, 99.99%) from 25 to 600 °C (slope of 10 °C/min).

The weight percentages of V, W and Ti in the catalysts were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Iris Advantage apparatus from Jarrell Ash Corporation (Table 1).

N<sub>2</sub> adsorption measurements have been performed at –196 °C, under a N<sub>2</sub>-partial pressure  $P/P_0 = 0.3$  on a Micromeritics ASAP 2000 in order to determine the BET specific surface area (SSA) of our catalyst and support (Table 1). Prior to the measurement, the samples were degassed under flowing N<sub>2</sub>/He (30:70, vol.%) at 120 °C for 1 h.

### 3. Results

#### 3.1. Chlorobenzene

A direct step mode procedure is suitable in order to measure the activity of the catalyst at different reaction temperature. At every given temperature, a short transition period indeed leads to a stable plateau of measured conversion. The catalyst that has been used in this work exhibits the same performance as in our former studies [3,4,16]. Small traces of maleic anhydride (MA) have been detected along with total oxidation products.

XPS characterization shows no significant Cl contamination on the post-test catalyst. A former study based on TOF-SIMS measurements showed that the Cl contamination is very low in the case of

V-based catalysts [5]. The proportion of C on the surface of the spent catalyst is not significantly higher than on the fresh one (Table 2).

#### 3.2. Furan

##### 3.2.1. Catalytic abatement

Furan adsorption on TVW is very strong [16]. In the “direct” procedure, the removal of furan occurs both through simple adsorption on the catalyst and through catalytic oxidation. At low temperature, this strong adsorption leads to prolonged instable periods during which the measurement of the actual total oxidation activity of the catalyst is impossible (Fig. 1A). This observation is also made with other V-based catalysts [16].

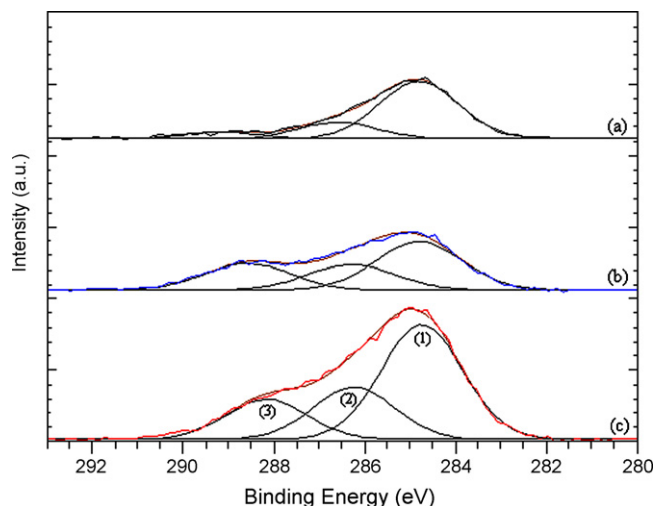
By using the “sat” procedure, it is possible to accelerate the saturation of the surface of the catalyst. After this treatment, the conversion is very stable at each temperature (Fig. 1A). A similar strategy has been applied by Paulis et al. [20] in the course of acetone abatement on manganese oxide catalysts. A carbonaceous deposit is formed during the saturation step. At each rise of temperature, a part of the deposit is burned, which is evidenced by a significant peak in the production of CO<sub>2</sub>. A progressive “cleaning” of the surface thus occurs in the course of the catalytic test. In addition to CO<sub>2</sub> and CO, significant amounts of maleic anhydride are produced in the reaction.

##### 3.2.2. Adsorption of furan and characterization of the deposit

The catalyst that has been in contact with furan at low temperature (<250 °C) acquires a characteristic dark brown colour. This fact

**Table 2**  
XPS ratios

TVW	Tested molecule	C/Ti	V/Ti	W/Ti
Fresh	–	1.10	0.14	0.15
Post-test	Chlorobenzene	1.12	0.15	0.13
	Furan	1.12	0.14	0.15
	2,5-Dimethylfuran	1.14	0.14	0.15
Saturated	Furan	1.24	0.16	0.15
	2,5-Dimethylfuran	2.43	0.14	0.15



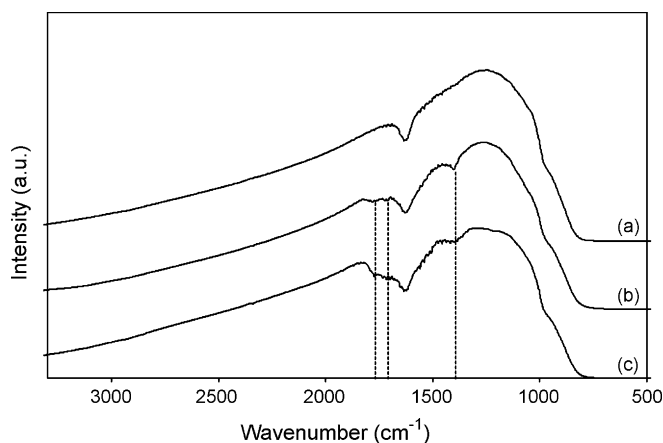
**Fig. 2.** XPS C 1s peak of (a) fresh TVW, (b) TVW after saturation step with furan and (c) TVW after saturation step with 2,5-dimethylfuran. (1) (2) and (3) are respectively the C-(C,H), C-O and C=O contributions.

was also observed by Spoto et al. who attributed the phenomenon to the fast reaction of the heterocycles on the acidic sites of the catalyst and to their subsequent oligomerization [18].

After saturation in the reactor the catalyst has been characterized. Thermogravimetric analyses show that a loss of 2.3 wt% can be attributed to the carbonaceous deposit formed by furan adsorption on TVW. Furthermore, TPD shows that under He and with increasing temperature, only CO and CO<sub>2</sub> desorb from a saturated sample.

XPS characterization confirms the presence of a high carbon surface content on the saturated catalyst. Indeed, the C/Ti ratio is higher than that obtained on a fresh catalyst (Table 2). In addition, the shape of the peak is significantly modified (Fig. 2). A larger proportion of carbon species linked to oxygen atom(s) (C=O at 288.9 eV and C-O at 286.6 eV) and a smaller proportion of carbon species linked to carbon or hydrogen (at 284.8 eV) can be detected.

On the saturated catalyst, FTIR spectra (Fig. 3) reveal the presence of bands at 1400, 1710 and 1770 cm<sup>-1</sup> which can be attributed to maleic anhydride and maleate species [12,21,22]. This is in agreement with our previous observation that maleic anhydride was produced during the oxidation of furan. It is also in agreement with the conclusions of Larrubia et al. who observed the same species on similar catalysts after the adsorption of various aromatic pollutants,



**Fig. 3.** FTIR spectra of (a) fresh TVW (b) TVW after saturation step with furan and (c) TVW after saturation step with 2,5-dimethylfuran.

including dibenzofuran [12]. The presence of maleic anhydride and maleate species can also account for the more marked XPS contribution of O-linked carbon (Fig. 2).

### 3.3. 2,5-Dimethylfuran

#### 3.3.1. Catalytic abatement

In the “direct” procedure, the measured removal efficiency at a given reaction temperature is first very high and then decreases rapidly without reaching a stable level (Fig. 1B). This shows that 2,5-dimethylfuran adsorbs strongly on our catalyst and progressively saturates its surface. The same observations were made in the case of furan abatement (Section 3.2.1). It means that the two methyl groups do not provoke sufficient steric hindrance to block the access of the heterocycle to the acidic sites of the catalyst. This information is crucial because the steric hindrance that occurs in the structure of a PCDF is comparable. As a consequence, the oxygenated moiety of the dioxin may indeed play an important role in its adsorption. The behavior of a dioxin would thus be better modeled by the behavior of a furan molecule, or by a substituted furan, than by a chlorobenzenic derivative.

With the “sat” procedure, the initial stability of the removal efficiency is improved (Fig. 1B). When the temperature is raised we observe, after a peak in the production of CO<sub>2</sub>, an overall increase in 2,5-dimethylfuran removal. Maleic anhydride is also detected in the effluent. But unlike in the case of furan, the use of the “sat” procedure does not lead to exploitable activity measurements. After the saturation of the catalyst, the conversion remains too unstable to draw rigorous light-off curves. This suggests that the carbonaceous deposit in the case of 2,5-dimethylfuran adsorption is less stable than in the case of furan.

The precise reasons for this unsuccessful stabilization of the catalyst are however unclear but explanations can be proposed by looking at what discriminates 2,5-dimethylfuran from furan. Firstly, the oxygen atom in 2,5-dimethylfuran is more basic than in furan because of the two methyl groups [23] and its adsorption on the catalyst should be even stronger. Secondly, as is observed when comparing the reactivity of pyridine and 2,5-dimethylpyridine on acidic materials [24] one could state that 2,5-dimethylfuran still access Brønsted sites but that the steric hindrance provoked by the methyl groups prevents it from accessing Lewis sites. Thirdly, the presence of methyl groups in the position 2 and 5 of the furan ring could impede certain types of reaction (e.g.: oligomerization) of the adsorbed molecules. Overall, the reactivity of the two compounds on the surface can be assumed to be dissimilar eventually leading to carbonaceous deposits which differ in their nature and stability.

#### 3.3.2. Adsorption of 2,5-dimethylfuran and characterization of the deposit

The catalyst saturated with 2,5-dimethylfuran has a dark brown colour like those saturated with furan, which is characteristic of a carbonaceous deposit. This deposit accounts for a loss of 3.2% of the weight of the saturated TVW during TGA. Under TPD analysis, no product other than CO or CO<sub>2</sub> desorbs. Infrared spectroscopy, as in the case of furan-saturated catalyst, shows the occurrence of maleic anhydride and maleate species (Fig. 3). Furthermore, the XPS C/Ti ratio was significantly increased by the adsorption of 2,5-dimethylfuran (Table 2), and the shape of the C 1s peak indicates an amount of carbon linked to oxygen larger than in the case of the fresh catalyst (Fig. 2). The characterizations thus indicate that the nature of the carbonaceous deposit formed by the saturation of the catalyst with 2,5-dimethylfuran and with furan is quite similar.

However, the production of maleic anhydride during the reaction is much less abundant for 2,5-dimethylfuran abatement than for furan abatement. In addition, the shape of the C 1s peak is dif-

ferent (Fig. 2). Namely, the proportion of the C doubly linked to O versus C simply linked to O is comparatively higher in the deposit formed by furan adsorption. These two elements tend to indicate that the formation of maleic anhydride or maleate species is less favored from 2,5-dimethylfuran than from furan. The presence of the two methyl groups seems to affect the transformations that the furan ring undergoes on the catalyst surface (this will be further discussed in the next section). Nevertheless, the methyl substitution of the furan ring obviously does not affect the adsorption behavior of the model compounds.

### 3.4. Selective oxidation product

Maleic anhydride (MA) is found as a byproduct in the total oxidation of VOCs on V-based catalysts. In the case of furan abatement, the proportion of MA with respect to the products of total combustion is high. It is impossible to discuss this in terms of selectivity because, during a test run with the sat procedure, the products formed from the entering reactants are accompanied by molecules arising from the desorption and/or reaction of adsorbed molecules present in the deposit formed during the saturation step. However, it is worth mentioning that the concentration of MA in the outlet flow reaches several ppm. A peak of production/desorption of MA is observed at 200 °C with an outlet concentration above 50 ppm. From 350 °C only total oxidation products are detected. In the case of 2,5-dimethylfuran, the production of MA is also observed but as a rule the amounts are five times smaller than during furan oxidation. During chlorobenzene oxidation only traces of MA are detected.

The production of maleic anhydride from furan is not surprising. As an oxide involved in the Mars and van Krevelen oxidation mechanism, the vanadium oxide surface bears both nucleophilic and electrophilic oxygen species [25,26]. So, not only the total oxidation but also the selective oxidation may occur. V-based catalysts have been extensively studied for their ability to catalyze the formation of MA from butane or butadiene [27–29] and furan has been identified as one of the last intermediates in the reaction mechanism [29]. Reaction of furan on supported  $V_2O_5$  catalyst is a shortcut to the production of MA through the selective route.

The formation of MA from 2,5-dimethylfuran can be envisaged with furan as an intermediate following oxidative demethylation of the aromatic ring. Demethylation of an aromatic ring can occur on several kinds of catalysts [30–32] and is also a common reaction in the catabolism of living organisms against toxic xenobiotics [33,34]. After adsorption through the ether function on an acidic site, the C–H bond of the methyl groups may react with the empty orbital of a  $V^{5+}$  and subsequent nucleophilic addition of a bridging oxygen ion to the carbon atom of the  $-CH_2$  group may be performed [28]. Demethylation is completed after the further oxidation towards a carboxylic function which is then eliminated in the form of  $CO_2$  [32]. From thus obtained furan, the well-known production of MA is now possible. The fact that additional steps are needed in order to complete the selective oxidation route accounts for the better selectivity in the total oxidation route in the case of 2,5-dimethylfuran oxidation on V-based catalysts.

It is noteworthy that various organic compounds react on V-based catalysts to give at least traces of MA. C4 hydrocarbons [27,29,35] are the obvious substrates. Benzene [28,36] and its methylated or chlorinated derivatives [16,28,37] as well as higher polyaromatics [38] can also be converted to MA on  $V_2O_5$  surfaces. So the cleavage of the aromatic ring and reconstitution on MA is common. But Larrubia et al. [12] also measured the production of MA from the oxidation of propane on a  $V_2O_5-WO_3/TiO_2$  catalyst. So building MA from lower hydrocarbon is also possible. In conclusion, the partial degradation of 2,5-dimethylfuran and subsequent reconstruction of MA from various adsorbed species cannot

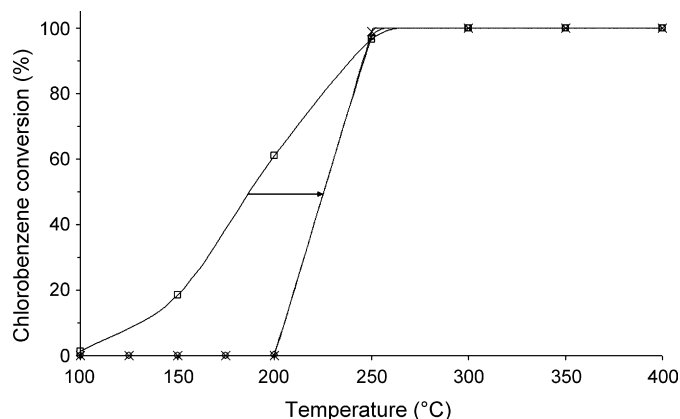


Fig. 4. Chlorobenzene light-off curves ( $\square$ ) alone, ( $\circ$ ) in competition with furan and ( $\times$ ) in competition with 2,5-dimethylfuran on TVW.

be ruled out. Further insights on these two possible pathways could be gained by following the labeled  $O^{18}$  atom of 2,5-dimethylfuran during the reaction.

### 3.5. O-VOC versus Cl-VOC competition tests

Fig. 4 shows the light-off curves obtained in the course of the total oxidation of chlorobenzene alone and in the presence of furan or 2,5-dimethylfuran in the “direct” procedure. In this procedure, no rigorous light-off curve can be drawn when the abatement of the O-compounds alone is concerned (cfr. Sections 3.2.1 and 3.3.1). The complete removal of the O-model – that can be determined rigorously – has however been observed at 250 °C. As long as furan or 2,5-dimethylfuran is present in the reactant flow, the chlorobenzene conversion is totally inhibited. Since furan or 2,5-dimethylfuran adsorption is fast and produces a carbonaceous deposit on the surface, the active sites are blocked and chlorobenzene cannot reach them. Above 250 °C, namely when the total conversion of the O-containing co-reactant is reached, the total oxidation of chlorobenzene starts and reaches the level that was measured in a test with chlorobenzene alone. 250 °C was previously identified as the ignition temperature of the deposit above which furan is readily destroyed after adsorption, does not accumulate anymore on the surface and leaves active sites free to adsorb and further oxidize chlorobenzene [16].

This confirms that the oxygenated function of a heterocycle has an extremely higher affinity for V-based catalysts than (chloro)benzene derivatives. The fact that these observations are valid for both furan and 2,5-dimethylfuran should be highlighted. Indeed this higher affinity is not diminished by the presence of the two methyl groups. The intermolecular competition between chlorobenzene and a furan ring is won by the latter even when the oxygen is neighbored by two substituting groups. Besides, the steric hindrance that occurs in the case of 2,5-dimethylfuran is similar to that found in a PCDF. This allows suggesting that the central oxygenated ring of a dioxin should also win the intramolecular competition against the chlorinated moieties. The oxygen bridges found in the dioxin could thus decisively dictate the adsorption behavior of the pollutant.

On the other hand, the commonly accepted model approach uses Cl-models for which the adsorption through the chlorine atom is the rate-limiting step [13]. If a dioxin adsorbs easily through its O-moieties and not through its Cl-ends, then the optimization strategies that are proposed, mainly aiming at the promotion of the adsorption of the Cl-model, are not valuable in the ultimate application to dioxin catalytic abatement. Weber et al. reported

that in industrial plants, dioxin removal proceeds, like in the case of furan and 2,5-dimethylfuran, under two distinct regimes: in the lower temperature regime, removal mainly proceeds through adsorption and in the higher temperature regime catalytic oxidation is dominant [39]. Furthermore, Liljehund et al. [40] noted that the adsorption of dioxins is reversible. This means that, unlike in the course of chlorobenzene abatement, the dissociative adsorption through the chlorine atom should not be considered as the initial step of dioxin abatement.

It is worth mentioning that these observations also apply to other V-based catalyst formulations. Catalysts with Mo instead of W and catalysts supported on sulfate-containing TiO<sub>2</sub> have also been studied in our laboratory and the comparison of their properties and performance is described in Ref. [16]. The data on TVW that are discussed in this paper, i.e. inhibited conversion of chlorobenzene during competition, strong adsorption of furan and substituted furan, carbonaceous deposit formation, maleate species, MA production, etc., have been proved experimentally to be also valid for this wider range of V-based catalysts.

#### 4. Conclusions

V-based formulations typically proposed as total oxidation catalysts for PCDF and PCDD abatement have been studied in the course of the oxidation of various pollutant model molecules. Chlorobenzene is often used for testing the performance of the catalyst in the removal of an aromatic structure and checking its resistance towards chlorine poisoning. However, our results show that models with an O-containing ring, like furan and 2,5-dimethylfuran are needed in order to better mimic the adsorption behavior of the real target pollutant. Indeed, the affinity of the oxygenated moiety of the dioxin is likely to be similar to that of the furan ring. In addition, we show that the potential steric hindrance that occurs in a PCDF and that is modeled in 2,5-dimethylfuran by the two methyl groups does not inhibit the strong adsorption of the pollutant.

Partial oxidation also occurs on V-based catalysts in addition to the desired total oxidation route. Studying O-VOC as model compounds allowed us to raise the question of the production of significant amounts of harmful molecules like maleic anhydride while aiming at the removal of other pollutants. Maleic anhydride is significantly produced from furan and to a lower extent from 2,5-dimethylfuran. In the ultimate case of a PCDF, the problem of partial oxidation towards MA is expected to be more limited although our work, along with other studies on various pollutants, suggests that this issue should be addressed carefully.

In the course of intermolecular competition, the O-containing models win against the Cl-containing model. As this is also true with 2,5-dimethylfuran against chlorobenzene, it should also be the case in the course of the intramolecular competition that occurs during dioxin abatement. The nature of the pollutant-to-catalyst interaction would thus be decisively dictated by the presence of an O-moiety. This information is crucial for further studies on the evaluation and/or optimization of catalyst formulations for the purpose of dioxin abatement.

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