

On the impact of the choice of model VOC in the evaluation of V-based catalysts for the total oxidation of dioxins: Furan vs. chlorobenzene

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Abstract

V-based catalysts, widely developed for the catalytic abatement of dioxins, are usually studied and optimized by investigating the oxidation of model chlorinated aromatic compounds (e.g. chlorobenzene). Even though the oxygenated function included in the central aromatic ring of the molecular structure of a dioxin could influence major aspects of the catalytic process, it has never been taken into account in the reported works. In this study, furan is chosen as a model for the central oxygenated ring of a polychlorinated dibenzo furan (PCDF) and its oxidation is compared to the case of chlorobenzene. The strategy was to check systematically if the improvements of formulations enlightened from our previous investigation on chlorobenzene also remain beneficial with furan. It turned out that the use of a sulfate containing TiO_2 as support for the active VO_x phase as well as the doping of the formulation with Mo or W oxides had very different impacts in the two cases. Some improvement strategies prove to be inefficient or deleterious in the case of furan. Competition tests further suggest that the adsorption behavior of dioxin could be better imitated by furan than by chlorobenzene. These observations highlight, in the case for which working with the target pollutant is difficult (as with dioxins), that the choice of the model molecule is critical.

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1. Introduction

In the field of atmospheric pollution, it is evident that polychlorinated hydrocarbons, and in particular dioxins, constitute a major concern. The word “dioxin” collectively refers to polychlorinated dibenzo furans (PCDF) and polychlorinated dibenzo dioxins (PCDD). Dioxins are very stable structures consisting in three aromatic cycles. The central ring includes one (PCDF) or two (PCDD) oxygen atoms and the external cycles are substituted with chlorine atoms at various positions (Fig. 1). These compounds are formed during incineration and combustion processes [1]. As a response to their high persistence and their subsequent toxicity, catalysis is the most promising solution since it allows to directly destroy these pollutants at the source of emission [1–3]. Moreover, the catalytic total oxidation can exhibit an excellent selectivity

towards harmless products and can operate at relatively low destruction temperature [2,4–6].

For this application, two families of catalysts have been developed. Noble metal-based catalysts are highly active [7–10] but suffer from high cost and low stability toward the produced HCl and Cl_2 [2,11–13]. Moreover, they also catalyze the further poly-chlorination of the pollutants [14]. Transition metal-based catalysts are the alternative. In particular, vanadia-based catalysts are recognized as active and stable in a chlorine-containing environment [2,15,16]. Indeed, Bertinchamps et al. showed that their activity in benzene oxidation was the same as in chlorobenzene oxidation [17]. So, V-based formulations constitute a promising solution for dioxin total oxidation and efforts are made to improve their formulation. A large number of fundamental works have been done in order to understand the oxidation mechanism that is involved during total oxidation of dioxins on V-based catalysts. However, very few authors have reported works realized directly on real dioxins [18–20]. Real dioxins are usually not used in mechanistic studies because they are hard to handle and of course very toxic. Model volatile organic compounds (VOC) are thus often used. The chosen

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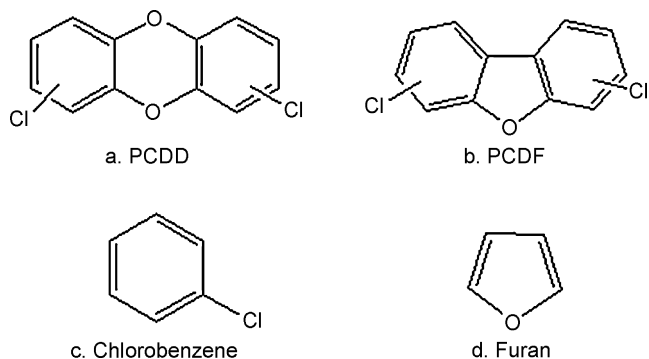


Fig. 1. Molecular structures of PCDD, PCDF, chlorobenzene and furan.

models need to be structurally similar to dioxins, less toxic and easier to handle. Even if they always differ in some ways from the target compound, model compounds prove to be essential in order to test and optimize the proposed formulations. Classically the authors want to evaluate the activity of the catalyst in the oxidation of an aromatic ring, as well as its resistance to chlorine poisoning. Therefore, simple chlorinated aromatic compounds (e.g. chlorobenzene) are very often chosen [1,11,12,15,17,21–25]. As interesting lines to optimization of the catalysts for such model VOCs, it has been found that titania supports are able to spread the vanadia very well on their surface, which leads to high activity [22,24]. Sulfate containing TiO_2 are also claimed to be even more efficient [15,17,24]. Additionally, several authors have shown that other transition metal oxides (essentially MoO_x , WO_x) can act as dope for the active phase of VO_x [11,17,21,23,26–29].

Molecules like chlorobenzene are useful models for dioxins. However, one should bear in mind that the central aromatic ring of a dioxin molecule is oxygenated. In a PCDF this ring is a furan (Fig. 1). This essential characteristic is not taken into account when a simple chlorinated VOC like chlorobenzene is chosen as a model. Nevertheless this moiety can influence major aspects of the catalytic process (adsorption of the pollutant, coking, etc.) as it is suggested from the DRIFTS study of Larrubia and Busca [30] on the adsorption of various compounds on a $\text{VO}_x\text{-WO}_x/\text{TiO}_2$ catalyst. Taralunga [31] also intended to take this oxygenated moiety of dioxins into account when investigating the oxidation of benzofuran in addition to the oxidation of dichlorobenzene over zeolite and noble metal-based catalysts. To our knowledge though, no other reported study did investigate the importance of this central ring in the catalytic abatement of dioxins on V-based catalysts. Improvements of the catalyst formulations are proposed but they are never checked in the perspective of an oxygenated model. We thus, propose a comparative study of the oxidation of chlorobenzene – as a chlorinated aromatic model molecule – and the oxidation of furan—as an oxygenated aromatic model molecule.

It should be noted that the issue of the total oxidation of oxygenated VOC is already well documented in the literature. Studies on ketones [32–38], alcohols [38–41] or esters [42–44] total oxidation show that O-compounds are quite easily destroyed and that the behavior of the VOC differ with their

structure. In this paper, the total oxidation of an aromatic O-compound is addressed. Even though it can be expected that our catalyst would destroy furan easily, this remained to be checked. Also, the basic oxygen of furan is likely to play an important role in the adsorption of the pollutant on the acid VO_x/TiO_2 based catalyst. Since the adsorption of this polar group (similar to those present in PCDD and PCDF) can influence major aspects of the catalytic process it is important to have a better insight on this matter.

Besides, the main goal of this comparative study is to check the beneficial effect brought by “improved” formulations of V-based catalysts in the case of the oxidation of furan. In particular, two parameters of the formulation are studied: (i) the use of a sulfate containing TiO_2 support instead of the classical TiO_2 support and (ii) the use of Mo and W oxides as doping phases of the active phase of vanadium. Therefore, the catalytic performances of V-based catalysts supported on two different supports and possibly upgraded with MoO_x or WO_x are investigated in the oxidation of chlorobenzene and furan. Also, in addition to the one-pollutant tests, the respective behaviors of the two models are investigated in the course of a competition test, namely a test involving both pollutant models simultaneously.

The observed performances are correlated with the results of various characterizations. FTIR analysis with adsorbed pyridine allowed us to study the acidity of the catalysts. As suggested by Larrubia and Busca [30], the acidity of the catalyst should indeed play a crucial role in the adsorption of the VOCs on the surface of the catalyst. The tendency of the various impregnated oxides to spread on the supports is considered thanks to XPS and XRD analysis. The weight loadings (ICP-AES) and the surface area (N_2 adsorption) are also measured.

2. Experimental

2.1. Preparation of the catalysts

Catalysts are supported on two different TiO_2 supports: a 70% anatase-30% rutile TiO_2 (Degussa P25: 48 m^2/g , denoted hereafter T) and a pure anatase TiO_2 containing 1.4% wt of sulfate (Millenium PC 100: 91 m^2/g , denoted hereafter Ts).

The active phase is VO_x (V) and the secondary phases are MoO_x (Mo) and WO_x (W). The precursors of these oxides are respectively NH_4VO_3 (Vel, 99.9%); $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Aldrich, >99%); and $(\text{NH}_4)_2\text{WO}_4$ (Aldrich, 99.99%). To obtain the impregnation solutions, the precursors are dissolved in distilled water and complexed with 2 moles of oxalic acid for 1 mole of transition metal. All impregnation solutions had a pH below 3. A classical wet impregnation method was used and the amounts of precursor were calculated in order to obtain 0.75 theoretical monolayer of transition metal oxide on the surface of each support. The theoretical monolayer coverage was calculated based on the cross sectional area of a unit composed of one transition metal atom and its oxygen coordination sphere. The values are 12 \AA^2 for VO_x , 17 \AA^2 for MoO_x and 15 \AA^2 for WO_x [24]. The suspension of support in the

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