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Evaluation of PCDD/F oxidation catalysts: Confronting studies on model molecules with tests on PCDD/F-containing gas stream

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ABSTRACT

Titania supported vanadium oxide is a renowned catalyst for the abatement of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) from gas effluents. To develop more active formulations, researchers mainly rely on lab-scale experiments on “PCDD/Fs-mimicking substances”, like (chloro)-benzene. Using such model compounds is convenient whereas handling PCDD/Fs in the laboratory is potentially hazardous and complicated. Recent studies, however, challenged some foremost conclusions of model compound based studies, starting from the observation that different model compounds gave contrasted results. Thus the present work aims at confronting some of these dubious conclusions with direct experimental tests on PCDD/Fs. One reference V_2O_5/TiO_2 catalyst and three modified formulations ($V_2O_5/TiO_2–SO_4$, $V_2O_5–MoO_3/TiO_2$, and $V_2O_5–WO_3/TiO_2$) have been evaluated. A dedicated apparatus was used which allows safe and reliable tests on a mixture of PCDD/Fs congeners. Some of the previously proposed catalyst improvement strategies actually prove to be disadvantageous in the removal of PCDD/Fs. In particular, MoO_3- and WO_3-modified catalysts were significantly less active than the reference catalyst. These observations show that conclusions from model compound based studies must be drawn with care and should ideally be confronted with tests on the actual target pollutants.

1. Introduction

Polyaromatic and polychlorinated compounds including polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are persistent pollutants – commonly referred to as dioxins – which are generated during biomass or waste combustion processes i.e. in incinerators (Gao et al., 2009), in industrial furnaces (Yu et al., 2010), in cogeneration units (Consonni et al., 2005), in metallurgy (Ba et al., 2009), etc. Their emission must be maintained below stringent legal limit values. Treating gases containing PCDD/Fs from industrial or domestic gas effluents has often been based on adsorption using activated carbon or lignite cokes (Buekens and Huang, 1998). Yet, there is a tendency in emission codes to limit total dioxin output, i.e. residues included, rather than output via off-gases only. This leaves two options: either a thermal treatment of the solid residues (Hagenmaier et al., 1991) or else in-line destruction using suitable catalysts (Hiraoka et al., 1991).

Heterogeneous catalysts are widely applied in the abatement of many kinds of atmospheric pollutants, including aromatics and chlorinated pollutants (Delaigle et al., 2009). The development of improved catalytic formulations, highly active and selective even at low temperature, is a topical field of research. For the destruction of PCDD/Fs, V_2O_5/TiO_2 catalysts are especially acknowledged (Everaert and Baeyens, 2004). V_2O_5/TiO_2 catalysts indeed offer high total oxidation activity and excellent resistance against chlorine poisoning (Delaigle et al., 2009). As far as industrial applications are concerned, V_2O_5/TiO_2 catalysts are known to be the basis for the efficient Shell de-dioxin system (Liljelind et al., 2001) and of many other patented catalytic solutions (Naoaki et al., 1999; Yukihiro, 2002; Masaki et al., 2003; Soung et al., 2005; Hou et al., 2009).

As dioxins are highly toxic, their manipulation in laboratories is delicate and often restricted by legal aspects. In consequence, most studies published with the aim of developing efficient catalysts for the total oxidation of dioxins rely on the use of model compounds. Usually, benzene and (poly)-chlorobenzene are employed to eval-

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uate both (i) the ability of the catalyst to complete the oxidation of aromatics to CO_2 and H_2O (and HCl or Cl_2) and (ii) their resistance against chlorine poisoning.

These model compounds based approaches have prompted progress in developing more active formulations for the total oxidation of organic air pollutants. Vanadia was identified as the best active oxide, combining high oxidation potential with high resistance against chlorine poisoning (Cho and Ihm, 2002; Bertinchamps et al., 2006b). Titania was evidenced as the best support for this active phase (Bertinchamps et al., 2006b). New preparation routes were proposed including hydrolytic (Kruse et al., 2009) or non-hydrolytic (Debecker et al., 2010a,b) sol–gel routes, grafting methods (Santacesaria et al., 2004), flame spray pyrolysis (Schimmoeller et al., 2010), etc. Active V_2O_5/TiO_2 formulations were further improved by adding solid promoters including metals like Pt (Garetto et al., 2009) and Ag (Debecker et al., 2008b) or transition metal oxides like MoO_3, WO_3, ZnO_2, etc. (Krishnamoorthy et al., 1998; Masaki et al., 2003; Bertinchamps et al., 2006c; Albonetti et al., 2007) in the formulation.

A difficult problem in such an approach, however, is that of judging the adequacy of model compounds (benzene and (poly)-chlorobenzenes) in mimicking target pollutants (dioxins). This issue was raised recently and independently by two groups. Lee and Jurng on the one hand noticed that the energy of activation for the destruction of some dioxin congeners was very different from the energy of activation of one of the most commonly used model, namely 1,2-dichlorobenzene (Lee and Jurng, 2008). Thus they suggested that this model compound was not suitable for studying V_2O_5/TiO_2 catalysts. On the other hand, Gaigneaux and co-workers – after having reported repeatedly on the total oxidation of benzene and chlorobenzene (Bertinchamps et al., 2005, 2006a,b,c, 2007, 2008) – described the total oxidation of furan and furan derivatives (used to mimic the central moiety of PCDF) (Debecker et al., 2007, 2008a). It was found that the “improvements” designed to increase the activity towards (chloro)-benzene were in fact deleterious for the removal of furan. In other words, the choice of the model compound may affect the conclusions of laboratory studies that aim at assessing improved catalytic formulations.

As a consequence, there is a need to confront the results of classical model compound based catalytic studies with tests on the real PCDD/F-containing gas stream. For that purpose, a dedicated experimental set-up must be developed as it was done in the recent years by the Chang group (Yang et al., 2008; Chang et al., 2009). A PCDD/F-containing gas stream generating system coupled with appropriate analytic facilities allows direct assessment of the performances of given catalysts in the PCDD/F removal (see Scheme S1 in supplementary information). The system was adopted to generate a gas stream with relatively stable and predictable dioxin concentration for evaluating the effectiveness of catalysts developed for dioxin removal. The gas stream generation system and reactor are installed in a hood operating below atmospheric pressure and the exhaust gas stream is treated with active carbon (AC) adsorption. Leak-checks are performed before each test for ensuring the safety of the operators and the reliability of experimental results.

Table 1
Specific surface area (N_2-physisorption) and composition (ICP-AES) of the catalysts.

	SSA_{BET} ($m^2\ g^{-1}$)	V_2O_5 (%)	MoO_3 (%)	WO_3 (%)
V_2O_5/TiO_2	46	4.6	–	–
$V_2O_5/TiO_2–SO_4$	69	7.0	–	–
$V_2O_5–MoO_3/TiO_2$	45	3.8	4.3	–
$V_2O_5–WO_3/TiO_2$	43	3.5	–	7.5

In the present paper, one reference V_2O_5/TiO_2 catalyst and three “improved” formulations (Table 1) as studied earlier in the Gaigneaux group are now evaluated in the total oxidation of a complex mixture of 17 dioxin congeners. The objective is to confront the catalytic activity towards PCDD/Fs with the performance previously reported for model compounds. The catalyst based on a sulphated titania support ($V_2O_5/TiO_2–SO_4$) was shown to markedly outcompete the reference catalyst in the total oxidation of benzene and chlorobenzene yet this positive effect was very much limited for the abatement of furan (Debecker et al., 2007). The Mo- or W-modified samples ($V_2O_5–MoO_3/TiO_2$ and $V_2O_5–WO_3/TiO_2$) were clearly more active than the reference V_2O_5/TiO_2 catalyst in the total oxidation of benzene and chlorobenzene (Bertinchamps et al., 2006c). In contrast, such modification was reported to be inefficient (Krishnamoorthy et al., 1998) in the total oxidation of 1,2-dichlorobenzene. Mo- and W-modified catalysts were significantly less active than the reference V_2O_5/TiO_2 sample in the total oxidation of furanic compounds (Debecker et al., 2007, 2008a).

2. Experimental

The catalysts were prepared by a classical wet impregnation method as described in (Debecker et al., 2007). Supports used are a commercial titania (Degussa P25, 49 $m^2\ g^{-1}$) and a sulphated titania (Millenium PC100, ca. 1.4 wt.% of sulphate, 82 $m^2\ g^{-1}$). The V loading in terms of theoretical V_2O_5 monolayer (ML) was always kept constant at 0.75 ML. In modified samples, the additive (MoO_3 or WO_3) was co-impregnated with V oxide so as to have also 0.75 ML of Mo or W oxide. All catalysts were calcined at 400 °C for 20 h in static air.

Catalytic tests on PCDD/F-containing gas streams were conducted in a fixed-bed tubular reactor in borosilicate glass. Abatement efficiencies were evaluated at 200 °C and under slightly negative pressure. The reaction time is 2 h for each run. The catalytic bed was composed of 1 g of catalyst beads (200–315 μm) diluted in 4 g of inactive glass powder (315–500 μm). The gas stream contained 21% O_2, 79% N_2 and a mix of 17 PCDDs/PCDFs (Table 2). The gas flow rate was controlled at 60 L h^{-1} (1 atm, 25 °C, GHSV = 37 000 h^{-1}). These experimental conditions were chosen identical to those used in previous model compounds based studies by the Gaigneaux group. The method to obtain the PCDD/Fs mixture and the analytical method to quantify PCDD/Fs is described elsewhere (see Scheme S1 in supplementary information and reference (Yang et al., 2008)). The 17 target PCDD/F compounds are collected simultaneously and analyzed with HRGC/HRMS. The removal efficiency is defined as ratio “(concentration in the inlet – concentration in the outlet)/concentration in the inlet * 100%”.

3. Results and discussion

3.1. Reliability of the tests on dioxins

The stability of inlet PCDD/F concentrations provided by the PCDD/F-containing gas stream generating system is shown in Table 2. In this study, only seventeen 2,3,7,8-substituted PCDD/Fs were analyzed. The Relative Standard Deviation (RSD) of average total inlet PCDD/F concentrations is calculated with three tests. The characteristics of each PCDD/F congener, such as melting points (227–326 °C) and vapor pressures (8.96×10^{-9}-8.25×10^{-13} mmHg), are quite different. However, the RSD value for each substituted PCDD/F remains reasonably low and the RSD of the total inlet PCDD/F concentrations is below 10%, indicating that PCDD/F-containing streams can be stably and steadily generated for testing.