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Catalysts based on pillared clays for the oxidation of chlorobenzene

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ABSTRACT

The aim of this work was to reveal the main factors which affect the oxidation of chlorobenzene (PhCl) over palladium and platinum supported on alumina pillared clays. The catalysts were prepared by wet impregnation of an alumina-pillared montmorillonite (Al-PILC) with palladium and platinum solutions and characterized by several physicochemical techniques before and after the catalytic tests. During oxidation of PhCl over the catalysts, the formation of carbon dioxide along with small quantities of carbon monoxide, $PhCl_x$ and coke was found. The nature of the supported metal, the temperature, the metal loading, the support, and the time on stream, are factors affecting the combustion of PhCl.

1. Introduction

Volatile Organic Compounds (VOCs), which often represent a serious environmental problem, can be produced from a variety of industrial and commercial processes, including printing, metal decorating, paint drying, metal degreasing, manufacturing of organic compounds and polymers and food processing [1]. Chlorinated VOCs (Cl-VOCs) are considered important environmental pollutants due to their toxicity and high stability. As a result of their widespread application in industry, their production and hence their emission into the environment are increasing rapidly. As Cl-VOCs have always been considered among the most hazardous organic compounds emitted into the environment, the decomposition and removal of these pollutants have always been subjects of great importance [2–4].

While the methods commonly employed in removing gaseous pollutants from industrial gas streams, wet scrubbing and adsorption, are relatively efficient in removing several gaseous pollutants, their efficiency towards Cl-VOCs is very limited [5]. A large number of methods have been applied in order to solve the problem of releasing Cl-VOCs into the atmosphere: e.g. thermal incineration, hydrodechlorination, biological processes, steam reforming and photocatalytic degradation [6]. Thermal incineration, usually above 1000 °C, is the most extensively used method to remove VOCs from industrial air streams. Besides the high cost, due to the high temperatures necessary, it involves additional fuel, high operating costs and the use of temperature-resistant materials. Moreover, the incineration process is always associated with the formation of a wide range of toxic byproducts, such as NO_x, and partial oxidation products, such as phosgene ($COCl_2$), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) [2,3,7,8]. A well-managed incineration process is feasible but expensive, due to the advanced pollution control devices needed to prevent the emission of dioxins, for example [9]. Cost analysis has clearly shown that thermal incineration technologies should be dedicated to high flow rates or VOC contents [10].

Catalytic combustion is a promising air abatement technology for treating VOCs under moderate flow rates. The major advantage of catalytic combustion is that very dilute pollutants (<1%), which cannot be thermally combusted without additional fuel, can be treated efficiently. Thus, catalytic combustion offers environmental advantages, since it is an energy-efficient, low-cost process and operates at much lower temperatures, thus preventing the formation of NO_x [8,11]. The low operating temperatures (<500 °C) and high selectivity into harmless products, such as CO_2, H_2O and HCl/Cl_2, make it an attractive option [12–16]. Catalytic combustion has broader application for end-of-pipe pollution clean-up than thermal combustion [2]. For catalysts, there are two points to be considered. As the industrial catalytic reactors have to be operated at high space velocities, the use of highly active catalysts is needed [17]. It must be also taken into account that the treated pollutants are emitted from various industrial sectors, thus another important

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characteristic of these catalysts is the capability to remove all the contaminants present in the stream simultaneously [18]. Catalytic combustion has been widely applied to the destruction of Cl-VOCs [2,3,19–22]. However, the interaction of the catalysts with chlorine is the main problem in the design of catalytic systems for Cl-VOCs combustion. The optimal catalyst for this reaction should be active, stable and above all, highly selective towards CO_2, H_2O and HCl; limiting the formation of other environmentally hazardous organic compounds [23].

Catalysts based on noble metals (Pt, Pd) [8,9,12,19,22–24] and transition metals (Cu, Co, V, Mn, Fe, Cr) [8,25–27] are used in the combustion of VOCs. Noble metals are effective catalysts for combustion reactions, but can easily form inorganic chlorides that could also cause chlorination of organic compounds besides their oxidation [28]. Van den Brink et al. [19] and de Jong et al. [9] showed that the combustion of PhCl over 2% Pt/γ-Al_2O_3 produced a significant amount of $PhCl_x$, in addition to the expected combustion products. Similarly, the combustion of PhCl carried out by Scirè et al. over 0.5% Pt supported on several zeolites also produced $PhCl_x$ [23]. Becker and Förster [22] and Oliveira et al. [8] showed the formation of $PhCl_x$ in the combustion of PhCl when using Pd supported catalysts. Giraudon et al. reported the formation of polychlorinated by-products with Pd supported on perovskites [24] and nanostructured TiO_2 and ZrO_2 [12]. These polychlorinated by-products are more toxic and recalcitrant than the starting molecule. Despite these drawbacks, Pd and Pt catalysts have been investigated and commercially applied in the combustion of Cl-VOCs [1,29–31].

Noble metals deposited on conventional supports like Al_2O_3, SiO_2, and TiO_2 have been studied as catalysts for the combustion of Cl-VOCs. Pillared InterLayered Clays (PILCs) are also good supports due to their high surface area, special surface acidity and thermal stability. In spite of being added-value materials from natural products and having very interesting properties, there is very little information in the literature about transition metal oxides and noble metal catalysts supported on PILCs for the catalytic combustion of chlorobenzene (PhCl). The advantage of using PILCs with respect to other supports is that, starting from natural, inexpensive clay minerals, it is possible to develop new materials with a microporous structure that can be controlled during the intercalation process, and create catalytic sites by incorporating metal cations. The possibility of catalyst design and the control of active site distribution are the two main reasons for choosing pillared clays as stable and selective catalysts in sustainable combustion reactions [32].

In this study the main factors affecting the combustion of PhCl related to the type of catalysts prepared are examined. The use of the catalytic series Pd/Al-PILC and Pt/Al-PILC in PhCl combustion, the comparison between the two series, the detailed study of the products obtained and the study of the stability of a selected catalyst are original in this study.

2. Experimental

2.1. Catalyst preparation and characterization techniques

The catalysts were prepared from an alumina-pillared montmorillonite which has been described in detail in a previous work [33]. The starting material was a montmorillonite from Tsukinuno, supplied by The Clay Science Society of Japan. The clay mineral was pillared with alumina, according to a conventional pillaring procedure, for use as a support in all the sample preparations. Supported metal catalysts were prepared by wet impregnation of the support with solutions of palladium (palladium(II) nitrate solution, 10 wt.% in 10 wt.% HNO_3, Sigma–Aldrich) and platinum salts ($[Pt(NH_3)_2](NO_2)_2$, Strem Chemicals). The metal salt/clay slurries were evaporated to dryness under reduced pressure in a rotary evaporator and the resulting solids dried at 120 °C for 16 h before being calcined in air at 500 °C for 4 h to form the final supported catalysts. The catalysts had metal loadings of 0.1, 0.5, 1 and 2 wt.%, and are referred to hereinafter as *wt.Met*, where *wt.* indicates the metal content and Met the metallic phase (Pd or Pt). The raw clay is referred to as Na-Mont, and the alumina pillared clay as Al-PILC. The catalytic series are referred to as Pd/Al-PILC and Pt/Al-PILC.

The physicochemical characterization of the catalysts included chemical analysis, nitrogen physisorption at −196 °C, carbon dioxide physisorption at 0 °C, X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), CO and H_2 chemisorption at 35 °C, NH_3 chemisorption at 70 °C, and temperature-programmed reduction (TPR). Details of the experimental conditions are given elsewhere [33].

2.2. Catalytic performance

Chlorobenzene (PhCl) oxidation was carried out on an automated bench-scale catalytic unit (Microactivity Reference, PID Eng&Tech). The reactor was a tubular, fixed-bed, downflow type, with an internal diameter of 0.9 cm and a length of 30 cm. Catalyst samples were mixed with an inert material (glass spheres with diameters in the range 315–500 μm), at a weight ratio of 1:4 to dilute the catalyst bed and avoid hot spot formation. The catalytic bed was composed of 200 mg of catalyst powder selected within the 200–315 μm granulometric fraction and diluted in 800 mg of inactive glass spheres with diameters in the range 315–500 μm. The PhCl concentration in the feed was 0.01% (Praxair; PhCl-helium, 0.2–99.8%) and the oxygen-to-hydrocarbon molar ratio was 2000 (Praxair; 99.995%), with helium as diluting gas (Praxair; 99.996%), up to a total feed flow of 200 cm^3/min. Space velocities (GHSV), calculated at standard temperature and pressure and based on the volume of the catalytic bed, were about 22,000 h^{-1}. Before and after the reaction, stabilization stages of 1.5 h were carried out in by-pass mode at 100 and 25 °C, respectively, to investigate the evolution of the concentration of the various reagents and products. After the first stabilization stage, the reaction was run from 100 to 400 °C in 50 °C steps. At each temperature considered, the catalyst was stabilized for 150 min in order to ensure steady-state conversion.

The reactants and the reaction product streams were analyzed on-line using a Varian CP-3800 gas chromatograph system equipped with three detectors (one TCD and two FIDs). Analysis of the gases was performed by separating them into a four-column system (Hayesep Q, Hayesep T, Molsieve 13X and CP-Sil 8CB). The parameters of the GC system allowed an analysis approximately every 35 min (each injection lasts 28 min). All tubes and injection valves in the GC were heated at 190 °C to prevent condensation of products. The identification and quantification of the $PhCl_x$ was carried out by injecting in the GC a liquid PhCl mixture of known composition from Sigma–Aldrich (40621-U-DL 152/2006 Chlorobenzene mixture). The analytical standard, which contained the same concentration (100 μg/cm^3) of each component in methanol, included: PhCl, 1,2-$PhCl_2$, 1,3-$PhCl_2$, 1,4-$PhCl_2$, 1,2,4-$PhCl_3$, 1,2,4,5-$PhCl_4$, $PhCl_5$ and $PhCl_6$. The retention times of all peaks, except the one ascribed to methanol, were compared and identified as specific congeners of $PhCl_x$. The denomination 1,2,*x*,5-$PhCl_4$ represents both 1,2,3,5-$PhCl_4$ and 1,2,4,5-$PhCl_4$ isomers, because these compounds could not be separated on our GC. PhCl conversion was calculated from the disappeared reagent as well as from the products obtained. Only the data measured after 2–2.5 h of reaction time were taken into account.