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Influence of the impregnation order on the synergy between Ag and V_2O_5/TiO_2 catalysts in the total oxidation of Cl-aromatic VOC

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ABSTRACT

Silver is added to V_2O_5/TiO_2 catalysts by a wet impregnation method and the influence of the impregnation order is studied. Silver and vanadia were introduced by co-impregnation or by impregnation in 2 steps (V first or Ag first). Vanadia loading always corresponds to 2.49 wt% while 9 different loadings of silver were explored (0.02–12.5 wt%). Whatever the way of synthesis, the addition of silver to V_2O_5/TiO_2 formulation induces: (i) a decrease of the specific surface; (ii) a higher vanadium oxidation state and (iii) a decrease of the Brønsted acidity. A synergy can be evidenced for the co-impregnated Ag–V_2O_5/TiO_2 catalysts in the total oxidation of chlorobenzene. This synergy is observed for several loadings of Ag with a maximum at a loading of 0.05 wt%. This synergy can be related to the higher oxidation state of vanadium induced by silver, to the minimum decrease of the specific surface and to the absence of AgCl at the surface of the catalysts. This last aspect is confirmed via the investigation of the catalytic performances in the total oxidation of benzene. In this system, a synergy is observed for the co-impregnated catalysts and when the vanadium is impregnated first. On the contrary, no synergy was observed when silver is impregnated first. This result suggests that the synergy can be obtained only if the vanadium keeps a direct interaction with the support and if a good "degree of accessibility" of the gaseous phase to the silver species is maintained.

1. Introduction

The sustainable development and the protection of the environment need an accurate control of the gaseous emission due to human activities. These emissions can contain a wide range of different molecules [1–3]. Among these molecules, they are numerous pollutants, and dioxins are certainly one of the most problematic [4]. These pollutants are very toxic and responsible for several health problems even in very low concentrations [5]. In this context, the catalytic total oxidation of dioxins, directly at their source of emission, constitutes a relevant solution [6]. Several kinds of supports and active phases were already explored for this application [7–14]. Among these formulations, vanadium supported on titania exhibits the most interesting properties [10]. This kind of catalyst is one of the most efficient and is resistant against a chlorine poisoning effect. Nevertheless, the performances of such formulation still need to be improved in order to use less and less energy for the abatement of dioxins.

In recent works, our group has explored an innovative way to improve the performances of vanadium based catalysts: silver was added to a V_2O_5/TiO_2 formulation [15–17]. The addition of silver could potentially bring electrophilic oxygens [18,19] which are interesting species in total oxidation reactions. A synergistic effect between silver and vanadium was evidenced in the total oxidation of chlorobenzene [17] which is a classical model molecule used to mimick dioxins. This synergy was directly linked to the specific surface of the catalysts, the oxidation state of vanadium and the reaction conditions. In this study, Ag–V_2O_5/TiO_2 catalysts were synthesized by the co-impregnation of silver and vanadium. Recently, some authors studied the influence of the precise procedure of impregnation [20]. They showed that the physico-chemical properties of vanadium based catalysts doped by noble metals are directly influenced by the order of impregnation of the different elements [20,21]. The first aim of the present study is thus to evidence the influence of Ag and its order of impregnation on the physico-chemical properties of V_2O_5/TiO_2 catalysts. Catalysts prepared by two steps of impregnation (V first or Ag first) are therefore synthesized and compared to the co-impregnated catalysts.

This study is not only justified by an empirical approach. In fact, co-impregnated catalysts need special reaction conditions in order to avoid chlorination of silver at their surface during the catalytic tests [17]. The absence of chlorination is indeed a sine qua non condition to obtain a synergy between vanadium and silver. It could thus be very useful to identify a way of

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synthesis which would allow the use of Ag–V_2O_5/TiO_2 formulation in less restrictive conditions. The preparation of the catalysts by two steps of impregnation could potentially offer a solution. Indeed, different orders of impregnation could possibly induce different degrees of accessibility of the silver species. This degree of accessibility should directly influence the potential chlorination of the silver species during the catalytic tests. The second aim of this work is thus to determine if the order of impregnation influences the conditions to obtain a synergy between silver and vanadium in the total oxidation of chlorobenzene. In this context, we will assume that there is a synergy between silver and vanadium if the catalytic performances of the Ag–V_2O_5/TiO_2 catalyst are higher than the sum of the individual performances of the two corresponding reference catalysts, namely Ag/TiO_2 and V_2O_5/TiO_2.

2. Experimental

2.1. Preparation of the catalyst

Three kinds of catalysts were supported on TiO_2 (Degussa P25: 49 $m^2\,g^{-1}$; 85% anatase–15% rutile, labelled T): Ag/TiO_2, V_2O_5/TiO_2 and Ag–V_2O_5/TiO_2. Silver and vanadia were introduced by a wet impregnation method. The $AgNO_3$ precursor (Aldrich, >99%) was dissolved in distilled water while the NH_4VO_3 precursor (Vel, >99%) was dissolved in distilled water and complexed with oxalic acid (Aldrich, >99%, molar ratio vanadium:oxalic acid = 1:2 [9]). An appropriate amount of titania was then added to the solution. The suspension was mixed for 2 h at room temperature and water was evaporated in a rotary evaporator under reduced pressure at 40 °C. The material was dried overnight in an oven at 110 °C and finally calcined in air in a muffle furnace (20 h, 400 °C). The vanadia loading always corresponds to 2.49 wt% while 9 different loadings of silver were explored (0.02–12.5 wt%). The V_2O_5/TiO_2, Ag/TiO_2 and Ag–V_2O_5/TiO_2 (co-impregnation) catalysts are labelled VT, AgT-*x* and AgTV-*x*, respectively, where *x* denotes the silver content in wt%. The catalysts synthesized by two impregnation steps are labelled V-AgT-*x* and Ag-VT-*x*, corresponding respectively to Ag or V impregnated firstly.

2.2. Catalytic tests

The catalytic tests were performed in a metallic fixed-bed microreactor operating at atmospheric pressure. The reactor was made of an inconel tube of 1 cm internal diameter. The catalytic bed was composed of 200 mg of catalyst powder selected within the granulometric fraction 200–315 μm and diluted in 800 mg of inactive glass spheres (diameter in the range of 315–500 μm). The gas stream contained 100 ppm of chlorobenzene (or benzene) in He (Praxair), 20% of O_2 (Praxair; 99.995%) and He (Praxair; 99.996%) as diluting gas to obtain 200 ml min^{-1} (VVH = 37,000 h^{-1}). Two different procedures were used to evaluate the catalytic activity. In the "light-off" procedure, after stabilization at 100 °C, the reaction was run from 100 to 400 °C in a step mode. In the "alternative" procedure, the stabilization step was realized at 200 °C and the catalysts performances were measured at 200 and 250 °C. The interest of this alternative will be evoked later. During the test, the catalysts were stabilized for 150 min at each temperature. In both procedures, the stabilization step corresponds to a period during which the catalytic bed as well as the gas lines are heated at the same temperature. During this step, the gas flow bypasses the catalytic reactor. At the end of this step, the gas stream is sent to the reactor and the test starts. This manner ensures that the catalytic bed and the gas are at the same temperature at the beginning of the test. The analysis of reactants and products (CO_2, CO) was continuously performed by on line gas chromatography (GC). This equipment allowed to detect potential intermediate products of the reaction like hydrocarbons and (poly-)chlorinated hydrocarbons. In both procedures, the conversion of chlorobenzene (or benzene) always corresponds to total oxidation. The selectivity of CO_2 is systematically 100% except when the conversion of chlorobenzene reached 100%. In this case, CO can sometimes be produced with, nevertheless, a selectivity never going above 5%. The conversion is defined as the ratio reactant transformed/reactant in the inlet (in %). More details of the operating conditions can be found elsewhere [9,10,12].

2.3. Characterization

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

The BET specific surface area of the catalysts was measured by nitrogen adsorption at 77 K with a Micromeritics TriStar 3000 instrument. The samples were outgassed overnight at 150 °C under vacuum before the measurement.

X-ray diffraction (XRD) measurements were performed on the catalysts with a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 0.15418 nm). The 2θ range was recorded between 5° and 75° at a rate of 0.028° s^{-1}. The ICDD-JCPDS database was used to identify the crystalline phases.

TEM measurements were performed on a JEOL 2000FX, working under an acceleration voltage of 200 kV. For the analysis, the sample was dispersed in 2-butanol (Sigma-Aldrich, > 99%) and homogenized by agitation. A droplet of the suspension was deposited on the grid and the solvent was allowed to evaporate.

Surface characterization was done with an X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra spectrometer (Kratos-Analytical, Manchester, UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). The sample powders were pressed into small stainless steel troughs mounted on a multi specimen holder. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Ti 2p, Ag 3d, V 2p, Cl 2p and C 1s again to check for charge stability as a function of time, and the absence of degradation of the samples during the analyses. Special care was taken to make sure that vanadium and silver were measured fast enough in order to avoid potential reduction under vacuum (quick XPS procedure described in [17]). The binding energy (BE) values were referred to the C–(C, H) contribution of the C 1s peak at 284.8 eV. Molar fractions [%] were calculated using peak areas normalized on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors, and transmission factors provided by the manufacturer. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). More details of the exact settings and peak analysis can be found elsewhere [16,22].

Fourier Transformed Infra Red spectra of pre-adsorbed pyridine (FTIR-pyridine) were recorded using an Equinox IFS55 spectrometer (Brücker) equipped with a DTGS detector. The absorption spectra were obtained by the recording of 100 scans between 370 and 4400 cm^{-1} with a resolution of 4 cm^{-1}. The powders were pressed into self-supporting disks (20 mg, 13 mm diameter), placed in an IR cell, and heated under a dry stream of 60 ml min^{-1} of 5% O_2 in He at 250 °C for 2 h before analysis. This special pre-treatment is used in order to avoid the reduction of the catalyst under vacuum or He at high temperature. After the cooling to room temperature, the IR cell is evacuated and the spectrum of the powder is recorded. Then, the sample is exposed to 50 mbar of pyridine for 30 min. Spectra were recorded after evacuation (7×10^{-5} Torr) for 1 h at room temperature, 200 °C and 250 °C. The amount of Brønsted and Lewis sites is determined by the integration of the area of the peaks at 1537 and 1446 cm^{-1}, corresponding respectively to