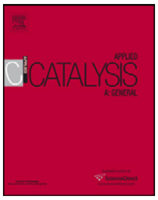
Applied Catalysis A: General 447–448 (2012) 1–6

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Effect of support on V_2O_5 catalytic activity in chlorobenzene oxidation

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ARTICLE INFO

Article history:
Received 21 May 2012
Received in revised form 23 July 2012
Accepted 15 August 2012
Available online 1 September 2012

Keywords:
Aerogel
Sulfate
Cerium
Vanadia–titania
Chlorobenzene oxidation

ABSTRACT

The present paper investigates the influence of the direct incorporation of ceria in TiO_2 aerogels support (sulfated and unsulfated) prepared by a sol–gel route on the catalytic properties of vanadia based materials in the total oxidation of chlorobenzene. ICP-AES, N_2 physisorption, XRD, DRIFTS, Raman spectroscopy, XPS, H_2-TPR and NH_3-TPD were employed for catalyst characterization. This study demonstrated that cerium oxide is present as CeO_2 form at the catalyst surface, which can improve the catalyst redox properties and so enhance the catalytic activity at high temperature (400 °C). Besides, sulfate containing vanadia–titania samples (doped or not with ceria) had their catalytic performances considerably improved (due to sulfates) at lower temperatures (range 200–300 °C). This is due to an increased global acidity and higher reactivity of redox sites thanks to the superficial interaction between (i) vanadia and sulfate, and (ii) when ceria is present, between ceria and sulfate leading to higher efficiency of catalysts in the chlorobenzene oxidation.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) are major contributors to air pollution because of their highly toxic nature [1]. A large number of methods have been applied in order to solve the problem of atmospheric release of chlorinated VOCs (typically adsorption, thermal incineration, hydrodechlorination, biological process, steam reforming, photocatalytic degradation, etc.) [2–7]. However, there is still a need for research on techniques, which are economical, more favorable and truly able to destroy the pollutants rather than merely displace and dispose them. The catalytic destruction of chlorinated VOC to CO_x, H_2O and HCl appears very promising in this context [4,6,8–12].

Supported vanadium oxide constitutes a very important class of catalytic materials resistant against chlorinated volatile organic compounds [10,12–14]. In the literature, studies indicated that the nature of the support plays a crucial role in catalytic properties since the metal oxide-support interaction affects redox, acid–base properties and dispersion of the active phase [15,16]. Titania supports seem to be the most indicated. In addition to their good mechanical, thermal, and anticorrosive properties, they favor the spreading of VO_x active phase in the form well-dispersed monolayer [17]. Furthermore, it has been shown that the addition of $SO_4{}^{2-}$ species to TiO_2 enhances the acidity and can lead to a better activity in chlorinated VOCs oxidation [10,12,18–21]. The beneficial effect of the sulfated TiO_2 is due to an increase of the amount of Brønsted acid sites which promote the adsorption of the aromatics on the support, and of strong Lewis sites which improve the spreading of VO_x phase on the surface of the catalysts [10,17].

Titania doped with CeO_2 is yet another interesting support since CeO_2 exhibits excellent redox properties due to its prominent ability to shift between Ce^{3+} and Ce^{4+} under oxidizing and reducing conditions respectively. Labile oxygen vacancies form easily and the mobility of bulk oxygen species is high [22,23]. Indeed, the mixing of the two different oxides TiO_2 and CeO_2 could bring new stable compounds that may lead to totally different physicochemical properties and catalytic behavior [24].

CeO_2–TiO_2 mixed oxide was studied in various applications, either as support or as catalyst, such as catalytic wet air oxidation reactions of organic compounds [25], NO removal [26] and Diesel soot combustion [27]. Huang et al. introduced CeO_2 to V_2O_5/TiO_2 formulations and demonstrated that V_2O_5/CeO_2–TiO_2 catalysts exhibit higher activity than V_2O_5–TiO_2 in the selective catalytic reduction (SCR) of NO to N_2 with NH_3 (NO conversion is 99.2% at 165 °C) [28]. Xu et al. successfully developed a CeO_2/TiO_2 catalyst by impregnation method for the NH_3-SCR of NO_x in the temperature range of 275–400 °C [29] (NO conversion greater than 92%). Similarly, Gao et al. proposed a Ceria titania mixed oxide system, prepared by sol gel route, as very efficient catalyst for the SCR process in the temperature range of 300–400 °C (NO_x conversion

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0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.08.034

exceeds 95%) [30]. Besides, Shan et al. developed CeO_2/TiO_2 catalyst by homogeneous precipitation method for NH_3-SCR of NO_x [31]. The catalyst exhibited good catalytic performance (over 90% NO_x conversion from 250 to 450 °C).

Based on the fact that the good catalysts for SCR are also efficient in the oxidation of chlorinated VOCs and motivated by the favorable characteristics of ceria-based mixed oxides, we thus investigate in this study the direct incorporation of cerium species in the TiO_2 support (sulfated or not sulfated) and hope to achieve a good activity of the supported vanadia in the total oxidation of chlorobenzene.

V_2O_5/TiO_2, $V_2O_5/TiO_2–SO_4^{2−}$, $V_2O_5/TiO_2–CeO_2$ and $V_2O_5/TiO_2–SO_4^{2−}–CeO_2$ catalysts were synthesized by impregnation method. The amount of vanadia oxide is fixed to be small (2 wt.%) due to the requirement in the industrial practice in order to limit the oxidation of SO_2 to SO_3 as much as possible in the case of the elimination of Cl-VOCs from sulfur bearing fuels [32].

The supports (TiO_2, $TiO_2–SO_4^{2−}$, $TiO_2–CeO_2$ and $TiO_2–SO_4^{2−}–CeO_2$) were elaborated by a one step sol–gel method and transformed into aerogels using a supercritical drying process [12]. The structural, textural, acidic and redox properties of the catalysts have been characterized by ICP-AES, XRD, N_2-physisorption, DRIFTS, Raman spectroscopy, NH_3-TPD and H_2-TPR.

2. Experimental

2.1. Catalysts preparation

Four kinds of TiO_2 supports (TiO_2, $TiO_2–SO_4^{2−}$, $TiO_2–CeO_2$ and $TiO_2–SO_4^{2−}–CeO_2$) were prepared via sol–gel method as follows: Titanium (IV) isopropoxide (Aldrich, 98%), as precursor, with anhydrous ethanol (Aldrich, 98%), as solvent, was chemically modified by adding acetylacetone (Fluka, 99%) according to a molar ratio acetylacetone/Ti = 1 in order to control hydrolysis and condensation reaction rates. This solution was maintained for 1 h under stirring. To obtain mixed ceria titania oxide, cerium nitrate (Aldrich, 99.5%) was added to the organic mixture according to a molar ratio Ce/Ti = 0.1. To obtain sulfated supports, sulfuric acid (Fluka, 96%) was added according to a molar ratio S/Ti = 0.2. Homogenous gels are obtained by hydrolysis and condensation after HNO_3 supply. The amount of distilled water added corresponded to the molar ratio H_2O/Ti = 10. The gels were, thereafter, transformed into aerogels by drying under supercritical conditions of ethanol (P = 63 bars, T = 243 °C) and are denoted Ti, TiS, TiCe and TiSCe. Then, corresponding catalysts with theoretical vanadia loading of 2 wt.% were synthesized by impregnating 2 g of support with 4 ml of an acetone solution of vanadyl acetylacetonate (Fluka, 95%). The obtained wet solids are then dried in an oven at 60 °C for 24 h. Finally, catalysts are calcined for 12 h at 500 °C under flowing O_2 (30 ml/min) and denoted respectively VTi, VTiS, VTiCe and VTiSCe.

2.2. Characterization of catalysts

The elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) allowing estimating the weight percentage of S, V and Ce. These measurements were performed on a Horiba Jobin Yvon apparatus, Model Activa.

Specific surface area and pore volume measurements of the samples were done by N_2 physisorption at 77 K using a Micromeritics ASAP 2020 apparatus. The samples were outgassed in vacuum during 6 h at 200 °C prior the nitrogen physisorption.

X-ray diffraction patterns (XRD) were obtained using a MRD PRO PANalytical X'Pert PRO instrument with CuKα radiation (λ = 1.5418 Å) at the rate of 0.02°/s from 5 to 70 °C.

Total acidity was evaluated by temperature-programmed desorption of ammonia (TPD/NH_3) using a quadrupole Balzers QMC 311. Before NH_3 desorption, the samples were pre-treated under He flow (60 ml/min) at 200 °C for 1 h. NH_3 adsorption was performed under ambient conditions by flowing 0.5% NH_3 in He over the catalyst until saturation and then desorption of NH_3 by temperature-programmed treatment under He from 50 to 500 °C using a heating rate of 10 °C/min.

In situ diffuse reflectance infrared spectroscopy (DRIFTS) spectra were recorded on a Bruker IFS 55 spectrophotometer equipped with a Thermo Spectra Tech reacting cell at a spectral resolution of 4 cm^{-1} and accumulating 200 scans. Samples were treated in situ at 500 °C with helium (5 °C/min, flow: 30 cm^3/min).

Temperature programmed reduction (TPR) experiments were performed in a dynamic apparatus using 5% H_2 in helium flowing at 60 ml/min. Experiments were carried out in the range 30–800 °C. The inlet and outlet gas compositions were measured using a quadrupole mass spectrometer QMC 311 Balzers coupled to the reactor.

X-ray photoelectron spectra (XPS) were collected on a SSI X probe spectrometer (model SSI 100, Surface Science Laboratories, Mountain View, CA, USA) equipped with a monochromatized AlK_α radiation (1486 eV). The samples powders, pressed in small stainless steel troughs of 4 mm diameter, were placed on an insulating home made ceramic carousel. The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyser lens was 55°. The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. The C1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale. Data treatment was performed with the CasaXPS program (Casa Software Ltd., UK) and some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non linear baseline.

Raman spectra were measured with a Dilor Instrument S.A. spectrometer with the 632 nm line of Ar ion laser as excitation source under ambient conditions. The number of scans is 10 and the time of accumulation is 10 s per scan.

2.3. Catalytic test

Catalytic tests were performed with 200 mg of catalyst (200–315 μm) diluted in 800 mg of inactive glass spheres with diameters in the range 315–500 μm in a metallic fixed-bed micro-reactor (PID Eng&Tech, Madrid, Spain) operating at atmospheric pressure and fully monitored by computer. The gas stream was composed of 100 ppm of chlorobenzene, 20 vol.% of O_2 and helium as diluting gas to obtain 200 ml/min (space velocity (VVH) = 37,000 h^{-1}). The reaction was run from 100 to 400 °C in a step mode with a 150 min plateau at each temperature investigated. Analysis of reactants and products was continuously performed by on line gas chromatography (GC).

3. Results and discussion

Theoretical and experimental chemical compositions of the investigated samples VTi, VTiS, VTiCe and VTiSCe are compared in Table 1. The results indicate that vanadium and cerium were successfully incorporated in the catalysts. For sulfated samples, differences between the theoretical and the experimental sulfur ratio could be attributed to the loss of some of the sulfur during calcinations [12].

The surface areas and pore diameters of Ti, TiS, TiCe and TiSCe supports (as references) and VTi, VTiS, VTiCe and VTiSCe catalysts, calcined at 500 °C are given in Table 2. All solids are classified as mesoporous materials (pores between 2 and 50 nm). It can be seen from this table that the specific surface area of TiO_2 support