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Vanadium-containing SBA-15 systems prepared by direct synthesis: Physico-chemical and catalytic properties in the decomposition of dichloromethane

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ABSTRACT

V_x-SBA-15 materials (vanadium content in the 0.7–4.8 wt.% range) were prepared by direct synthesis and tested in the catalytic decomposition of dichloromethane; a SBA-15 silica and a V/SBA-15 prepared by impregnation were used as reference samples. The structural and surface properties of all samples were characterized by means of complementary physico-chemical techniques. V_x-SBA-15 materials containing isolated vanadium sites were catalytically active towards dichloromethane conversion, with maximum conversion obtained by the catalyst having 2.2 wt.% vanadium. In V_x-SBA-15 materials prepared by direct synthesis, vanadium occurs mainly as isolated sites with tetrahedral coordination as far as its content does not reach the theoretical monolayer capacity (*ca.* 4 wt.%): unlike catalysts prepared by traditional impregnation method, oligomeric VOx species form only at high vanadium content.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs), used as solvents for dry cleaning and degreasing processes in industrial manufacture [1,2], are highly toxic and carcinogenic substances that contribute to photochemical smog, global warming and stratospheric ozone reduction [1–3]. After environmental legislation strictly limited their emissions, the technologies developed to control their environmental release are hydrodechlorination, adsorption/absorption, photocatalytic degradation, high temperature incineration, etc. [1,2]. Among those processes, adsorption/absorption is often not applicable at an industrial level, whereas incineration produces other toxic compounds forming at very high temperatures, like NO_x. Therefore, heterogeneous catalytic oxidation of Cl-VOCs would be a promising alternative solution, making possible pollutants destruction at the source of emission and at lower temperatures (200–500 °C) than incineration [4–7].

The two most common types of catalysts for VOCs oxidation, *i.e.* supported noble metals [8,9] and metal-oxides [10,11], have several drawbacks: the former, though very active and selective, are too expensive and undergo deactivation by chlorinated compounds in gas stream [8]; the latter are not expensive but less active, as well. All this notwithstanding, literature reports that vanadium-containing catalysts may have promising catalytic performances towards VOCs oxidation [12–15].

Ordered mesoporous SBA-15 silicas, with uniform pores size distribution and high surface area, are interesting supports for vanadium-based catalysts with plenty of accessible, isolated and well-defined active sites [16]. For instance, V-SBA-15 catalysts containing *ca.* 4 wt.% vanadium, a content corresponding to theoretical monolayer capacity [17], showed good catalytic activity and selectivity in oxidative dehydrogenation (ODH) reactions, due to high concentration of isolated or low polymeric VO_x species at the surface [17,18].

Directly adding V-precursor during SBA-15 hydrothermal synthesis should favor the entrance of vanadium into silica walls with formation of isolated sites [19,20]: this method is adopted in the present work, with the aim to prepare vanadium-containing catalysts to be tested in the decomposition of dichloromethane (CH_2Cl_2), the most stable chlorinated-alkane.

V-SBA-15 catalysts with vanadium content in the 0.7–4.8 wt.% range were prepared by direct synthesis, by slightly modifying a literature procedure [19]. Catalytic performances in dichloromethane oxidation were compared.

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2. Experimental section

2.1. Materials synthesis

Three vanadium containing SBA-15 samples (hereafter referred to as V_x-SBA-15, in which x stands for vanadium wt.%) were synthesized by slightly modifying a literature procedure [19]. In a typical synthesis, "solution I" was obtained by mixing 4 g $EO_{20}PO_{70}EO_{20}$, (Pluronic P123, Sigma–Aldrich), 0.227 g CTMACl (cetyltrimethylammonium chloride, Sigma–Aldrich), 150 mL water and hydrochloric acid (2 M) under moderate stirring at room temperature for 6 h; "solution II" was prepared by mixing H_2O_2, V_2O_5, and H_2O (molar ratios H_2O_2:V:H_2O = 1.7:0.06:106), stirring at 70 °C until the solution turned orange–brown and then cooling to room temperature.

Afterwards, "solution II" and 9.1 mL TEOS (tetraethoxysilane, Sigma–Aldrich) were added to "solution I" and stirred at room temperature for 5 h; the solid was recovered by filtration, washed with distilled water, dried overnight and calcined in oven at 500 °C for 6 h.

By following the same recipe except for the addition of vanadium precursor, SBA-15 silica was obtained and used both as blank-sample and as support of an impregnated sample, obtained by adding a NH_4VO_3 solution (nominal vanadium content 3 wt.%) to SBA-15 silica and placing the mixture in a rotary evaporator to progressively evacuate water excess; the sample was then calcined in oven at 500 °C for 6 h and will be referred to as $V_{3.0}$/SBA-15(i).

2.2. Textural characterization

Powder X-ray diffraction patterns were collected on a Philips PW3040 diffractometer using Cu Kα radiation (2θ range = 1°–10°; step = 0.02° 2θ; time per step = 1 s).

N_2 adsorption/desorption isotherms were measured at −196 °C on *ca.* 20–30 mg samples previously outgassed at 150 °C for 5 h to remove molecular water and other atmospheric contaminants (Quantachrome Autosorb 1). Samples specific surface area was calculated by using the BET method and pore size distributions were evaluated by applying the Barrett–Joyner–Halenda (BJH) algorithm to isotherms desorption branch.

Samples morphology was studied by both transmission electron microscopy (TEM, JEM 2011 operating at 200 kV) and field emission scanning electron microscopy (FE-SEM, ZEISS ultra); V-content was determined by EDS analysis on 10–50 nm diameter spots (Oxford 7353 probe on a LEO 1450 VP microscope).

For H_2-TPR experiments, 100 mg sample was placed in a quartz micro-reactor, then contacted with reducing flowing gas (5% molar H_2 in Ar, 40 ml min^{-1}) and heated in the 20–1000 °C temperature range (heating rate: 10 °C min^{-1}), while recording H_2 consumption by using a thermal conductivity detector (TCD); a gas condenser operated at −196 °C and placed prior TCD was used to remove water possibly formed by reduction.

2.3. Spectroscopic characterization

Micro-Raman spectra were collected at ambient conditions on a Renishaw Micro-Raman system, equipped with an Ar laser (514.5 nm).

For IR measurements, powder samples were pressed into thin, self-supporting wafers and pre-treated under high vacuum (residual pressure < 10^{-3} mbar) using a standard vacuum frame, in a quartz cell equipped with KBr windows. Fourier transform-IR (FT-IR) spectra were collected at 2 cm^{-1} resolution on a Bruker Equinox 55 FTIR spectrophotometer, equipped with a MCT detector. Surface Brønsted and Lewis properties were studied by means of NH_3 adsorption at room temperature: before dosing ammonia, wafers were outgassed for 1 h at 150 and 500 °C, to follow the degree of surface hydration; in a typical experiment, increasing equilibrium pressures of NH_3 (0.01–20.0 mbar range) were dosed and adsorption reversibility was checked by evacuating for 30 min at room temperature.

Diffuse reflectance (DR) UV–vis spectra were recorded on a CARY-500 UV–vis-NIR spectrophotometer (Varian Instruments) equipped with an integrating sphere: *ca.* 200–300 mg powders were studied both as such (after calcination and exposure to atmospheric moisture) and after outgassing for 3 h at 250 °C (dehydrated samples), a temperature ensuring dehydration without vanadium reduction phenomena expected at higher temperature.

2.4. Catalytic activity test

Catalytic tests were performed on a continuous reactor, a quartz U-tube with inner diameter = 7 mm, heated by an electric furnace; temperature was measured by a thermocouple placed in proximity of the middle of catalytic bed. Before each run, 70 mg catalyst was activated in air (flowing rate = 41 mL min^{-1}) as temperature was increased to 500 °C (heating rate = 5° min^{-1}) and kept at 500 °C for 1 h. The gas flow was then switched from air to the reactive mixture obtained by co-feeding 14 mL min^{-1} of a mixture containing 3000 ppm CH_2Cl_2 in N_2 and 27 mL min^{-1} of either pure N_2 or air (reactive mixture composition: 1000 ppm CH_2Cl_2 in either N_2 or O_2/N_2, VVH = 21,000 h^{-1}). Then, catalytic activity was measured in the 200–500 °C temperature range.

The outlet gas composition was analyzed by an on-line gas chromatograph (PERICHROM, PR 2100) with two detection lines: the former, for analysis of organic compounds, was equipped with a capillary column and a flame ionization detector (FID); the latter, for CO and CO_2 detection, was equipped with a succession of a Porapak-Q (for back-flush) and a MS-5A columns, and a thermal conductivity detector (TCD). The flowing gas after reaction was passed through an HCl trap made of zeolite beads in order to avoid possible corrosion of the chromatograph column and detector.

The percentage of dichloromethane conversion was calculated as moles of CH_2Cl_2 converted over moles of CH_2Cl_2 fed. The selectivity to each *i*th product was calculated as the ratio between moles of produced *i*th species and moles of converted CH_2Cl_2, normalized to the respective stoichiometric coefficients.

3. Results and discussion

3.1. Materials textural properties

Table 1 gathers the main textural properties of all samples, as derived from both powder XRD patterns and N_2 physisorption isotherms.

All XRD patterns in Fig. 1 exhibit the main diffraction peak due to $d_{(100)}$ reflection of SBA-15 hexagonal space group *p6mm*; corresponding inter-reticular distances (d_0) and unit cell parameters ($a_0 = 2d_0/\sqrt{3}$) are reported in Table 1. At higher 2θ angles, $d_{(110)}$ and $d_{(200)}$ reflections are not observed, indicating that the adopted procedure leads to less ordered materials than traditional SBA-15 synthesis: this is due to the fact that the presence of vanadium peroxo-species in the reaction medium does not permit to perform the hydrothermal treatment usually carried out to obtain long-range order materials [19,21].

Analysis of both XRD patterns and data in Table 1 shows that $d_{(100)}$ peak shifts to lower 2θ angles as V loading increases and, correspondingly, the unit cell parameter a_0 increases, probably due to vanadium entering silica walls. The maximum value of a_0 = 8.75 nm obtained with $V_{4.8}$-SBA-15 sample is not much