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Effect of vanadium dispersion and support properties on the catalytic activity of V-SBA-15 and V-MCF mesoporous materials prepared by direct synthesis

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ABSTRACT

Two V-SBA-15 and V-MCF materials (V content *ca.* 2.5 wt.%) were prepared by direct synthesis and tested in the catalytic decomposition of dichloromethane. Their catalytic properties were compared to those of other materials with the same vanadium content, namely two mesoporous materials prepared by impregnation (V-SBA-15-i and V-MCF-i) and a non-porous one prepared by flame pyrolysis (V-SiO_2). Both direct synthesis and flame pyrolysis methods allowed a better vanadium dispersion that lead to better catalytic properties above 350 °C, due to the presence of well dispersed V species partially incorporated into silica. The higher dichloromethane conversion achieved with both V-SBA-15 and V-SBA-15-i samples, as compared to MCF samples, are ascribed to longer residence times of both reactants and products within SBA-15 mesoporous channels, in contrast to three-dimensional MCF ultra large pores facilitating diffusion. Below 350 °C, both V-SBA-15-i and V-MCF-i samples showed higher dichloromethane conversion, basically due to the presence of micro-crystalline V_2O_5 formed at the external surface of both materials.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) are used as solvents in many industrial processes, although they are often toxic/carcinogenic substances and contribute to atmospheric pollution [1–3]. During the last years, several technologies have been developed in order to reduce their environmental release, such as adsorption/absorption processes; photocatalytic degradation; hydrodechlorination and thermal incineration. Among the latter, adsorption/absorption methods are often not applicable on an industrial scale, whereas high temperature incineration produces other very toxic compounds, *e.g.* dioxins, NO_x, etc. Therefore, catalytic oxidation would be an interesting solution for Cl-VOCs abatement, making possible their decomposition at relatively low temperatures (*e.g.* 200–500 °C) [4–7].

Both supported noble metals [8,9] and metal oxides [10,11] are currently employed for the total oxidation of hazardous organic air pollutants: the former, though more active, are too expensive and undergo deactivation by chlorinated compounds in gas stream [8]; the latter, though not expensive, are by far less active. All this notwithstanding, literature reports that vanadium-based catalysts are effective towards the catalytic oxidation of several volatile organic compounds [12–15]. V-containing mesoporous silicas (*e.g.* V-SBA-15, V-MCM-41, V-MCM-48, V-MCF, etc.) with uniform pores size and high surface area are interesting catalysts for oxidation reactions, allowing a large concentration of accessible and well defined active centres (VO_x), often incorporated into the silica framework [16–20]. Although such catalysts are usually prepared by impregnation, it has been observed that V-SBA-15 materials prepared by direct synthesis exhibit larger surface area, better dispersion and reducibility of V species and superior catalytic performances in both selective and total oxidation reactions [17,18]. In the present paper, the effect is studied of both vanadium dispersion (isolated V species *versus* micro-crystalline V_2O_5) and support properties (surface area, structure, etc.) on the catalytic oxidation of dichloromethane (CH_2Cl_2), the most stable chlorinated-alkane. Two V-containing mesoporous silicas (V-SBA-15 and V-MCF), with *ca.* 2.5 wt.% V content, were prepared by direct synthesis and tested in the CH_2Cl_2 decomposition, used as a probe reaction for Cl-VOCs total oxidation. The relation between the physico-chemical properties and catalytic performance of such materials was investigated in relation to other catalysts with comparable vanadium content, namely (i) two impregnated samples (V-SBA-15-i and V-MCF-i) and (ii) a non-porous sample (V-SiO_2) prepared by flame pyrolysis (FP),

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a high temperature synthesis technique allowing a good vanadium dispersion to be achieved [21].

2. Experimental

2.1. Catalysts synthesis

V-SBA-15 sample (vanadium content about 2.5 wt.%) was prepared as reported in the literature [17,18]. SBA-15 silica obtained by following the same recipe [18], except for the addition of vanadium, was used both as blank-sample and as support of impregnated sample V-SBA-15-i. V-MCF sample (vanadium content about 2.5 wt.%) was obtained by direct synthesis, as reported earlier [19]: 4.0 g $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Sigma–Aldrich) and 2.0 g 1,3,5-trimethylbenzene (TMB, Sigma–Aldrich) as organic swelling agent were dissolved in 30.0 mL water and stirred at room temperature for 5 h. Afterwards, 9.0 g tetraethylorthosilicate (TEOS, Sigma–Aldrich) and a proper amount of ammonium metavanadate (NH_4VO_3, Sigma–Aldrich) were added to the solution. In order to obtain isolated V species incorporated into the silica framework, 0.20 M HCl was added drop-wise to the solution until pH reached a value close to 3.0, as reported in literature [20]. After stirring at 40 °C for 24 h at constant pH, the solution was transferred into a Teflon autoclave and aged at 100 °C for 24 h. The sample was then filtered off, washed with bi-distilled water and dried overnight at 100 °C under static conditions. Finally, the included surfactant was removed by calcination at 600 °C for 5 h in air. Two catalysts (V-SBA-15-i and V-MCF-i) were obtained by impregnation with NH_4VO_3 solution of SBA-15 and MCF supports, respectively, followed by drying and calcination at 600 °C in air. A non-porous catalyst (V-SiO_2) was prepared by flame pyrolysis (FP) method [21].

2.2. Catalysts characterization

The main textural properties of all the prepared samples were obtained as follows: (i) BET (Brunauer–Emmett–Teller) specific surface area (S_{BET}) was measured by N_2 adsorption/desorption isotherms at −196 °C on *ca.* 30 mg sample previously outgassed at 150 °C for 5 h to remove molecular water and other atmospheric contaminants (Quantachrome Autosorb 1); (ii) Pores Size Distributions (PSDs) were calculated by either applying the Barrett–Joyner–Halenda (BJH) algorithm to isotherms desorption branch (SBA-15 materials) or according to the modified Broekhoff de Boer (BdB) method using Hill's approximation for the adsorbed layer thickness (MCF materials) [22]; (iii) powders X-ray diffraction (XRD) patterns were collected on a Philips PW3040 diffractometer, using Cu Kα radiation (2θ range = 0.8–10°; step = 0.02° 2θ; time per step: 1 s).

Samples morphology was studied by Transmission Electron Microscopy (TEM, JEM 2011 operating at 200 kV); V-content was determined by EDS analysis (Oxford 7353 probe on a LEO 1450 VP microscope): for each sample, 5 different spots with a 10–50 nm diameter, were selected in representative zones of the sample, and then an average V-content was calculated. For H_2-TPR (Temperature Programmed Reduction) experiments, *ca.* 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 using a Thermal Conductivity Detector (TCD); a gas condenser operated at −196 °C and placed prior the TCD was used to remove water possibly formed by reduction.

Micro-Raman spectra were collected at ambient conditions on a Renishaw micro-Raman system, equipped with an Ar laser (514.5 nm). For infrared (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. To study surface dehydroxylation, samples were outgassed for 1 h at 150 and 500 °C before collecting IR spectra. To study surface acidic properties, ammonia was dosed at room temperature on samples outgassed at 150 and 500 °C: in a typical experiment, increasing pressures of ammonia (0.01–20 mbar range) were dosed on each sample and adsorption reversibility was checked by prolonged evacuation (about 30 min) at room temperature.

2.3. Catalytic activity

Catalytic tests were carried out in a continuous quartz tubular reactor (7 mm i.d.) heated by an electric furnace, as reported elsewhere [18]. In a typical experiment, *ca.* 70 mg catalyst was activated before each run in air (flowing rate: 41 mL min^{-1}) at 500 °C for 1 h. The gas flow was then switched from air to the reactive mixture (1000 ppm CH_2Cl_2 in air, VVH = 21,000 h^{-1}) and catalytic activity was investigated 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_x detection, was equipped with a succession of a Porapak-Q (for backflush) and a MS-5A columns, and a thermal conductivity detector (TCD). 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 ratio of moles of *i*th product over moles of converted CH_2Cl_2, normalized to the respective stoichiometric coefficients.

3. Results and discussion

3.1. Catalytic activity in CH_2Cl_2 decomposition

Fig. 1a and b reports the main catalytic results for the CH_2Cl_2 oxidative decomposition in the 200–500 °C temperature range and Table 1 reports both conversion and selectivity values measured at 500 °C. Pure silica SBA-15 was tested as blank sample, showing no conversion (not reported) [18]. As a whole, all the catalysts showed: (i) stable conversions in the explored temperatures range (maximum reaction time tested = 2 h); (ii) almost constant conversion and selectivity values, in that after reaction the samples were reactivated at 500 °C and several reaction–reactivation cycles were repeated: the obtained data were completely reproducible. In agreement with literature [23,24], Cl-containing by-products were mostly HCl, the most thermodynamically favoured compound at high temperature, and, to a minor extent, Cl_2, but only at low temperatures.

Fig. 1a shows that conversion increases with increasing temperature in all cases, but the following differences are observed from

Table 1
Dichloromethane conversion (%) and CO_2 selectivity (%) obtained with V-SBA-15, V-SBA-15-i, V-MCF, V-MCF-i and V-SiO_2 catalysts during catalytic tests under aerobic conditions at 500 °C.

Sample	CH_2Cl_2 conversion (%)	CO_2* selectivity (%)
V-SBA-15	68	95
V-SBA-15-i	31	48
V-MCF	52	75
V-MCF-i	23	45
V-SiO_2	43	65

* CO_2 was the only product measured in aerobic conditions with our experimental set up; the "missing products" could involve coke and/or adsorbed compounds.