



## Novel vanadium-containing mesocellular foams (V-MCF) obtained by direct synthesis

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### ABSTRACT

This work reports the preparation and characterization of novel V-containing mesocellular foams (MCF) obtained by direct synthesis: their physico-chemical properties were investigated by means of complementary techniques and comparison was made with V-containing MCF prepared by (traditional) impregnation method, figuring out the main differences in both textural and surface features of the two types of materials. Catalytic tests showed that V-MCF prepared by direct synthesis are more active towards dichloromethane decomposition, due to the presence of isolated vanadium sites, as detected by means of (complementary) spectroscopic techniques. Direct synthesis allows the formation of acidic V–OH groups and favours the incorporation of highly reducible tetrahedral vanadium species that are well dispersed inside silica walls. On the contrary, impregnation brings about an overall decrease of surface hydroxyls and preferential formation of highly acidic sites, most probably related to extra-framework VO<sub>x</sub> species, that are reduced at a higher temperature than isolated vanadium sites.

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### 1. Introduction

Ordered mesoporous materials with uniform and well-defined pores have been extensively studied since their discovery in the early 90s [1–3] because of their potential applications in several fields, like catalysis, adsorption, gas separation and storage, enzyme immobilization, host–guest systems etc. [4–8].

Ordered mesoporosity silicas are commonly prepared by using organic templates as pore directing agents: among the different kinds of mesoporous silicas, SBA-15 has many potential and actual applications in virtue of its relatively large pores (5–30 nm in diameter), high specific surface area (600–1000 m<sup>2</sup> g<sup>-1</sup>), thick walls and good hydrothermal and thermal stability [9–13]. The two-dimensional hexagonal system (*P6mm*) of SBA-15 is obtained by using an amphiphilic tri-block copolymer (namely Pluronic P123, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) as structure directing agent under strong acidic conditions. If micro-emulsions of tri-block copolymers are used as colloidal templates, siliceous mesocellular foams (MCF) may be prepared [14]: in such a case, a swelling agent is added to the synthesis mixture, e.g. 1,3,5-trimethylbenzene (TMB) that dissolves into the hydrophobic core of Pluronic P123 micelles, thus favouring the formation of the three-dimensional MCF network,

characterized by uniform spherical cells (up to 50 nm in diameter) interconnected through small windows [14].

It has also been observed that a phase transition from highly ordered SBA-15 *P6mm* hexagonal system to MCF system [15–17] may occur by adding TMB to Pluronic P123 copolymer (i.e. TMB/P123 mass ratio >0.3) [14].

Their three-dimensional porous network renders MCF valuable materials in the field of heterogeneous catalysis, by facilitating the diffusion of both reactants and products, unlike other monodimensional mesoporous systems leading to severe mass transfer limitations (e.g. MCM-41) [18,19]. All this notwithstanding, only a few papers deal with the incorporation of catalytically active metals in their framework by impregnation [20,21]. This work reports a new direct synthesis method for the preparation of MCF containing highly dispersed vanadium species that are known to be effective in many oxidation reactions, from oxidative dehydrogenation (ODH) of alkanes [22,23] to oxidation of volatile organic compounds (VOCs) [24–29], e.g. the decomposition of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), the most stable chlorinated-alkane.

It must be pointed out that direct incorporation of vanadium into a silica matrix is feasible over a limited pH range (around 3.0), since in such conditions mainly isolated tetrahedral V<sup>5+</sup> and/or square pyramidal (VO<sup>2+</sup>) ions occur [30–32]. The main advantage of direct synthesis with respect to impregnation [33] is the possibility to introduce vanadium inside silica walls and to obtain highly dispersed and reactive sites. Gao et al. [30] previously

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observed that V-containing SBA-15 obtained by direct synthesis at pH = 3.0 exhibited highly dispersed vanadium species incorporated inside silica walls, whereas at lower pH values (e.g. pH = 2.0) some extra-framework VO<sub>x</sub> species formed, as well. This is the first report on V-MCF materials prepared by direct synthesis.

All prepared samples were tested as catalysts for dichloromethane decomposition, used as a probe reaction, and their physico-chemical properties were characterized by transmission electron microscopy, N<sub>2</sub> sorption isotherms at –196 °C, H<sub>2</sub>-temperature programmed reduction and several spectroscopic techniques, with the aim to figure out the effects of different synthesis procedures on the: (i) textural properties of the materials; (ii) surface hydroxyls population and surface hydration/dehydration behaviour; (iii) presence of different V-environments that could affect its reduction behaviour, a parameter of vital importance for applications as redox catalysts.

## 2. Experimental section

### 2.1. Materials synthesis

Two V<sub>x</sub>-MCF materials, *x* standing for the vanadium content expressed as wt.%, were prepared as follows: 4.0 g tri-block copolymer Pluronic P<sub>123</sub> (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, Sigma–Aldrich) and 2.0 g 1,3,5-trimethylbenzene (TMB, ACS reagent 98%, Sigma–Aldrich) were dissolved in 30.0 mL bi-distilled water (Carlo Erba) and stirred at room temperature for 5 h. Afterwards, 9.0 g tetraethylorthosilicate (TEOS, ACS reagent 98%, Sigma–Aldrich) and an appropriate amount of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>, ACS reagent 99%, Sigma–Aldrich) were added to the solution. 0.20 M HCl solution (obtained by diluting 37% HCl, Sigma–Aldrich) was then added drop-wise to the mixture until pH reached a value close to 3.0. After stirring at 40 °C for 24 h at constant pH, the solution was transferred into a 150 mL Teflon autoclave and aged at 100 °C for 24 h in order to increase both cells and windows size of the foam.

The obtained solid was filtered off, washed with bi-distilled water and dried overnight at 100 °C under static conditions. Finally, the occluded organic phase was removed by 5 h calcination at 600 °C in air. The two samples will be referred to as V<sub>2.5</sub>-MCF and V<sub>4.5</sub>-MCF, respectively.

A synthesis in more acidic conditions was attempted as well (pH < 2.0), but chemical analysis (EDS measurements, Table 1) showed the absence of vanadium in the final material, as reported in literature [30].

A purely siliceous MCF was synthesized according to a literature method [17] at a pH of about 2.0, with the aim to obtain a material that could be used both as reference blank sample and as support of two samples obtained by wet impregnation, hereafter referred to as V<sub>2.5</sub>-MCF(i) and V<sub>4.5</sub>-MCF(i), respectively. Impregnated samples were obtained by adding appropriate amounts of NH<sub>4</sub>VO<sub>3</sub> solution to the MCF silica support and placing the mixture in a

rotary evaporator, in order to progressively evacuate water excess; the obtained solids were then calcined in oven at 600 °C for 5 h.

### 2.2. Materials characterization

Powders morphology was studied by transmission electron microscopy (TEM, JEM 2011 operating at 200 kV).

V-contents reported in Table 1 were determined by energy dispersive X-ray spectroscopy (EDS) analysis onto 10–50 nm diameter spots (Oxford 7353 probe on a LEO 1450 VP microscope).

N<sub>2</sub> adsorption/desorption isotherms were measured at –196 °C on ca. 30 mg samples previously outgassed at 150 °C for 5 h to remove molecular water and other atmospheric contaminants (Quantachrome Autosorb 1). Specific surface area was calculated according to the BET (Brunauer–Emmett–Teller) method and pores size distributions (PSDs) were evaluated according to the modified Broekhoff de Boer method, using the Hill's approximation for the adsorbed layer thickness (BdB-FHH) [33].

For infra-red (IR) measurements, samples were studied either in pellets, obtained by mixing powders with optical grade KBr, or pressed into (thin) self-supporting wafers. The latter were pre-treated under high vacuum (residual pressure < 10<sup>–3</sup> 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<sup>–1</sup> resolution on a Bruker Equinox 55 FT-IR spectrophotometer, equipped with a MCT detector. To study hydroxyls population, wafers were outgassed for 1 h at 150, 300, and 500 °C and the corresponding IR spectra were recorded at room temperature. On samples outgassed at 150 and 500 °C, CO adsorption was studied at the nominal temperature of liquid nitrogen: IR spectra were recorded after CO dosage (0.01–15.0 mbar equilibrium pressure range) and after prolonged evacuation, to verify reversibility of the interaction.

Magic angle spinning (MAS) NMR spectra were registered on a Bruker Avance spectrometer. <sup>29</sup>Si MAS NMR and cross polarized (CP) <sup>1</sup>H–<sup>29</sup>Si CP-MAS NMR spectra were recorded at 99.4 MHz into 7 mm zirconia rotors spun at 5 kHz. <sup>29</sup>Si MAS NMR spectra were obtained using a 2.5 μs excitation pulse and a 10 s recycle delay. For CP-MAS experiments, the setting of Hartmann–Hahn conditions was made using 3-(trimethylsilyl)-1-propanosulfonic sodium salt: proton π/2 pulse duration, contact time and recycle delay were 7 μs, 5 ms and 5 s, respectively. <sup>1</sup>H and <sup>51</sup>V MAS NMR spectra were recorded in 4 mm zirconia rotors spun at 12 kHz. For <sup>1</sup>H MAS NMR spectra, a 90° pulse duration of 3.8 μs and a recycle delay of 5 s were used; a special attention was made to carefully clean the rotor with ethanol in order to avoid spurious proton signals. The probe signal was subtracted from the total free induction decay. <sup>51</sup>V MAS NMR spectra were acquired at 131.5 MHz with 0.5 s recycle delay and pulse duration of 3.7 ms. Chemical shifts were measured by making reference to (i) tetramethylsilane (TMS), for both silicon and proton, and (ii) NH<sub>4</sub>VO<sub>3</sub>, for vanadium.

**Table 1**  
Samples properties, as derived by both EDS analysis and N<sub>2</sub> adsorption/desorption isotherms at –196 °C.

Sample code	Synthesis method	V-content <sup>a</sup> (wt.%)	S <sub>bet</sub> (m <sup>2</sup> g <sup>–1</sup> )	V <sub>p</sub> <sup>b</sup> (cm <sup>3</sup> g <sup>–1</sup> )	V <sub>micro</sub> <sup>c</sup> (cm <sup>3</sup> g <sup>–1</sup> )	D <sub>c</sub> <sup>d</sup> (nm)	D <sub>w</sub> <sup>d</sup> (nm)
V2.5-MCF	Direct	2.6	925	1.00	0.17	16	6
V4.5-MCF	Direct	4.4	740	0.87	0.13	16	6
V2.5-MCF(i)	Impregnation	2.5	645	1.75	0.06	23	12
V4.5-MCF(i)	Impregnation	4.7	530	1.63	0.05	23	12
MCF	Ref. [17]	–	685	2.10	0.08	25	13

<sup>a</sup> As measured by EDS analysis.

<sup>b</sup> V<sub>p</sub> total porous volume.

<sup>c</sup> V<sub>micro</sub> = microporous volume, as measured according to the *t*-plot method.

<sup>d</sup> Diameters of cells (D<sub>c</sub>) and windows (D<sub>w</sub>) as determined from adsorption and desorption branches of N<sub>2</sub> isotherms (BdB-FHH method).

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