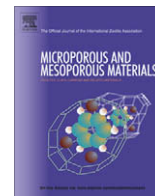Contents lists available at ScienceDirect

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Highly Ti-loaded MCM-41: Effect of the metal precursor and loading on the titanium distribution and on the catalytic activity in different oxidation processes

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ABSTRACT

Ti-MCM-41 materials have been prepared by co-condensation of tetraethylorthosilicate with two different titanium sources: titanocene dichloride and titanium isopropoxide. The hydrophobic nature of cyclopentadienyl rings has been used to enhance the interaction between the titanocene dichloride starting compound and the surfactant micelles leading to, after calcination, titanium centres finally located in the surface of the mesopores. In this way, increasing the content of titanocene dichloride in the synthesis gel causes the formation of titanium dioxide nanofibers inside the mesoporous system – clearly visible by TEM analysis – for high metal loadings. Such Ti distribution, which has not been observed when using titanium isopropoxide, confers to these Ti-MCM-41 materials a different catalytic behaviour to that of conventional Ti-MCM-41 materials for a given Ti content. Thus, samples prepared with titanocene dichloride display higher catalytic activity in the epoxidation of 1-octene and in the oxidative bromination of phenol red than samples prepared with titanium isopropoxide. Besides, in both reactions, the maximum of catalytic activity is reached for lower titanium loading when titanocene dichloride is the starting Ti source as a consequence of a better accessibility of reactants to the final Ti centres.

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1. Introduction

During the last decades, the synthesis of titanium-containing silica-based materials has been a matter of extensive research due to the great potential of these materials in catalytic oxidation processes [1]. The Shell catalyst [2] and the TS-1 zeolite [3], developed during the early seventies and eighties, respectively, are two of the most successful examples in industrial applications and the starting points in the development of a numerous family of titanium-containing silica-based catalysts, comprising from amorphous silica gels [4] to crystalline zeolites [5]. Further investigations consisted of the incorporation of titanium onto well structured silicas possessing large pores [6,7], such as the series of mesostructured M41S [8] or SBA [9] families. The main aim of these works was to overcome the diffusion problems of the zeolite micropores, which severely limits their catalytic application. In this sense, the development of the new mesostructured materials during nineties opened new opportunities to generate silica-based catalysts containing titanium as active redox sites. The first step in this research was carried out by Corma et al. [6], who reported the synthesis of a titanium-containing MCM-41 material through a direct-synthesis procedure. Later on, numerous efforts have been focused on the synthesis and preparation of new titanium-containing silica-based mesostructured materials [10–16]. For this purpose, a large variety of structure directing agents, titanium precursors and synthesis conditions have been investigated, mainly following two different strategies: co-condensation of silicon and titanium precursors [6,10] or post-synthetic functionalization by grafting procedures [17,18]. The first option leads to homogeneously dispersed titanium centres, but they can be buried inside the silica walls so that an important fraction of the loaded metal sites are not accessible. On the contrary, the second strategy ensures the accessibility to the titanium sites but lower metal dispersion degree is achieved. Obviously, the different titanium locations and environments determine their catalytic activity [19]. Combining the advantages of both synthesis procedures, high dispersion and accessibility of metal sites, is catalytically desirable. The hydrophilic–hydrophobic control of the interaction between the titanium source and the surfactant templating mesopores has resulted successful. Thus, the choice of non-ionic surfactants such as alkylene oxides and titanocene dichloride as metal source provokes the interaction between the hydrophobic cyclopentadienyl rings of titanocene with the also-hydrophobic core of the micelle [15,20,21]. This procedure has effectively been extended to other

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metal species [22], but always for non-ionic surfactants and under acid conditions.

In this work, we have applied a similar approach by using two titanium sources of different hydrophobic character – titanocene chloride and titanium tetraisopropoxide – under basic synthesis conditions and using an ionic surfactant (the conventional CTABr). The resultant materials, obtained for a huge Si/Ti molar ratio range (from 1 to 160), have been carefully characterized by means of different analysis techniques in order to determine the final location of titanium. The possible effect of the different dispersion and accessibility of reactants to titanium sites on their catalytic behaviour has been tested in the epoxidation of 1-octene and in the oxidative bromination of phenol red.

2. Experimental

2.1. Synthesis of Ti-MCM-41 materials

Titanium-contained mesoporous MCM-41 molecular sieves were prepared following the method proposed by Pang et al. [23] for the synthesis of pure silica MCM-41 materials, which here is modified by adding titanocene dichloride (Cp_2TiCl_2, Aldrich) or titanium isopropoxide ($Ti(OiPr)_4$, Alfa-Aesar) as metal precursors. In a typical synthesis, 2.5 g of hexadecyl trimethylammonium bromide (CTABr, Aldrich) and 8 g of dimethyl amine (DMA, 40% wt in water, Aldrich) were dissolved in 95 g of deionised water – milliQ grade – at room temperature. The mixture was then homogenized until complete dissolution, and proper amounts of the titanium and silicon sources (TEOS, Aldrich) were then added. The amount of the titanium precursor was increased to give gels with Si/Ti molar ratios between 160 and 1. The molar composition of the synthesis gel was: 120 H_2O:1.5 DMA:0.15 CTABr:1 SiO_2:x TiO_2, where x was varied from 0.00625 to 1. After the addition of the silicon precursor, the suspension was stirred for four additional hours before being hydrothermally aged at 110 °C for 48 h in a PTFE-lined stainless-steel autoclave under static conditions. The material was then recovered by filtration and dried overnight at room temperature. The removal of the surfactant occluded in mesopores was carried out by calcination in static air conditions at 550 °C during 5 h.

The samples have been called Ti-MCM-41-Cp-X or Ti-MCM-41-OR-X for the materials prepared with titanocene dichloride and titanium isopropoxide, respectively, where X denotes the Si/Ti molar ratio of the starting gel.

2.2. Characterization of the samples

Textural properties were evaluated by nitrogen adsorption–desorption isotherms performed at −196 °C in a TriStar Unit (Micromeritics). Specific surface area values were estimated by B.E.T. method and the total pore volume was assumed to be that recorded at p/p_0 = 0.985 for each sample. Pore sizes distributions were calculated through the B.J.H. method applying the K.J.S. correction and using the adsorption branch values of the isotherms. X-ray diffraction patterns were collected on a Philips X'pert unit fitted with an accessory for low angle experiments, using the Kα line of copper and in two different 2θ ranges from 0.5° to 10° for the evaluation of the mesoscopic ordering, and from 5° to 50° when searching the presence of crystalline titanium dioxide phases. In both cases, the assays were recorded with a step size of 0.01°. Diffuse Reflectance UV–Vis spectra (DR UV–Vis) were recorded under ambient conditions on a VARIAN CARY-500 spectrophotometer equipped with a diffuse reflectance accessory in the wavelength range from 200 to 600 nm. Transmission electron microscopy (TEM) microphotographs were collected on a PHILIPS TECNAI-20 electron microscope operating at 200 kV. Raman spectra were recorded at room temperature using a LabRam HR spectrometer fitted with a Jobin–Yvon CCD detector and an excitation line at 632.8 nm from an Helium Neon laser (source power: 11 mW). Titanium content was determined by ICP-atomic emission spectroscopy. The samples (100 mg) were dissolved in aqueous hydrofluoric acid. After dissolution, the sample was transferred into 1 l calibrated flask and diluted with water. An absorption standard solution of Ti (1000 µg ml^{-1} in water) was used for the calibration of the equipment.

Table 1
Phyico-chemical properties of titanium-functionalized MCM-41 materials.

Ti Source	Metal loading		Textural properties			Structural properties		
	Si/Ti[a] (molar)	Ti[b] (% wt.)	Sg[c] ($m^2 g^{-1}$)	Vp[d] ($cm^3 g^{-1}$)	Dp[e] (Å)	d_{100}[f] (Å)	a_0[g] (Å)	wt[h] (Å)
Cp_2TiCl_2	160	0.5	1081	0.89	27	42	48	21
	80	1.1	1036	0.88	26	42	49	23
	40	2.1	923	0.82	26	43	49	23
	20	3.9	836	0.75	25	43	49	24
	10	6.6	792	0.72	25	42	49	24
	5	15.2	717	0.71	24	42	48	24
	2	28.5	455	0.49	22	–	–	–
	1	36.3	350	0.57	–	–	–	–
$Ti(OiPr)_4$	160	0.5	1075	0.88	26	41	47	21
	80	1.1	993	0.86	26	40	47	21
	40	2.0	975	0.79	26	40	47	21
	20	4.0	895	0.83	27	42	48	21
	10	7.4	798	0.82	28	41	47	19
	5	12.4	618	0.69	23	41	47	24
	2	26.6	290	0.23	20	–	–	–
	1	35.5	80	0.08	–	–	–	–

[a] Initial composition of the synthesis gel.
[b] Final titanium content after calcination.
[c] Surface area estimated by the B.E.T. method.
[d] Total pore volume recorded at p/p_0 = 0.985.
[e] Mean pore size evaluated by the B.J.H. method applying the K.J.S. correction.
[f] Interplanar spacing calculated through the Bragg law.
[g] Unit cell size calculated assuming hexagonal geometry.
[h] Pore wall thickness calculated as $a_0 - Dp$.