

## Post-synthesis deposition of V-zeolitic nanoparticles in SBA-15

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**A post-synthesis deposition of vanadium silicalite-1 zeolite nanoparticles in the pores of SBA-15 results in a highly ordered hexagonal templated silica material with V-silicalite zeolitic plugs, giving rise to an increased crystallinity of the amorphous mesoporous walls.**

Microporous zeolites with uniform and molecular sized pores have important applications as industrial catalysts and adsorbents. However, in fine chemical and biological applications the accessibility of these zeolite materials is low when bulky molecules are involved. Many mesoporous structures have been developed to overcome these difficulties.<sup>1</sup> Unfortunately, due to their poor stability and activity, the actual use of these materials is limited. However SBA-15, a mesoporous hexagonal silica with large tailorable uniform pores (3–30 nm), thick walls and a high hydrothermal stability was developed.<sup>1</sup> Due to its desirable features a lot of research has been done to activate SBA-15 with different transition metals in order to obtain large pore catalysts allowing high diffusion rates with a catalytic activity for bulky molecules. Recently plugged hexagonal templated silica (PHTS) was developed. PHTS is an SBA-15 material with extra microporous amorphous nanoparticles (plugs) in the mesoporous channels.<sup>2</sup> It has a tailorable amount of open and plugged pores and it exhibits a remarkably higher mechanical and hydrothermal stability compared to other existing mesoporous materials. Because of these improved aspects and the influence of the plugs on the diffusion behaviour, PHTS is a promising candidate for adsorbents, encapsulating media, catalysis *etc.* However, the amorphous nature of the silica walls and plugs could limit their practical applicability because of lower selectivity and adsorption capacity.

In order to overcome these disadvantages, a post-synthesis deposition method was developed to form crystalline V-activated zeolitic plugs in the mesoporous channels of the SBA-15. Nanoparticles of V-silicalite-1 zeolite were grafted on the SBA-15 channel walls influencing the specific adsorption behavior and catalytic activity.

SBA-15 was prepared by dissolving triblock copolymer EO-20PO<sub>70</sub>EO<sub>20</sub> and TEOS in a 2 M HCl solution. The solution was stirred for 7.5 hours at 45 °C, and then aged for 15 hours at 80 °C. The precipitate was filtered off, washed and calcined for 6 hours at 550 °C.

A vanadium silicalite-1 nanoparticle suspension was prepared by dissolving tetrapropylammonium hydroxide (TPAOH) 20% as a template and TEOS as a silica precursor. Afterwards, the solution of TPAOH : TEOS : H<sub>2</sub>O with molar ratio of 1 : 6.4 : 100 was heated to 80 °C. This solution was then cooled to room temperature and 0.3 g VOSO<sub>4</sub> in 30 ml of water was added under continuous stirring. Subsequently this clear solution was aged between 2 and 6 days. The resulting clear liquid containing vanadium silicalite-1 zeolite nanoparticles was diluted and acidified with 0.6 M HCl to pH 1.

The V-silicalite-1 nanoparticles were deposited in the pores of SBA-15 by means of a dry impregnation of the acidified suspension on calcined SBA-15. The ultimate product was dried for 1 day at 40 °C and subsequently calcined up to 550 °C for 6 hours.

Fig. 1 shows N<sub>2</sub> sorption isotherms of the pure SBA-15 sample and the SBA-15 after deposition of nanoparticles of vanadium silicalite-1 (denoted as SBA-VS-15). SBA-VS-15 gives rise to an isotherm with the same characteristics as the recently developed PHTS.<sup>2</sup> All prepared samples show a one-step capillary condensation, indicating uniform mesopores. In contrast with the pure SBA-15, the V-zeolitic SBA-15 exhibits a two-step desorption indicating the existence of open and plugged mesopores. The first step can be assigned to the open mesopores, the second step can be attributed to the dispersed zeolitic nanoparticles, blocking parts of the mesopores, therefore creating ink-bottle like sections within the SBA-15 mesopores.<sup>2,3</sup> By altering the amount of V-zeolitic nanomaterial impregnated in SBA-15, the ratio open/closed mesopores, the microporosity and the amount of vanadium in the sample can be varied in a wide range (Table 1). Deposition of zeolitic vanadium silicalite nanoparticles in the mesoporous channels induces an increase in micropore volume and a decrease of the mesopore volume (Table 1). The microporosity of the MFI zeolite nanoparticles in the clear suspension which have an estimated size of 4 nm<sup>4</sup> induce the increase in micropore volume between SBA and SBA-VS-15. Partial blocking of the mesopores due to the existence of vanadium silicalite nanoparticles causes a narrowing of the mesopores at distinct places resulting in a lower mesopore volume compared to the pure SBA-15. This alternation of open and narrowed sections within the mesopores can have a positive influence on the diffusion path of molecules inside the mesopores of SBA-VS. Furthermore, TGA measurements of the deposited samples before calcination revealed a weight loss over a broad temperature range (170–320 °C) due to externally adsorbed (around 200 °C) and occluded TPAOH (around 280 °C) in the zeolitic nanoparticles.<sup>5</sup> The presence of zeolite nanoparticles within the pores could not be observed by classical XRD techniques due to the small size of the dispersed nanoparticles.<sup>6</sup> As the hexagonal ordering of SBA-15 remains after deposition and no change can be

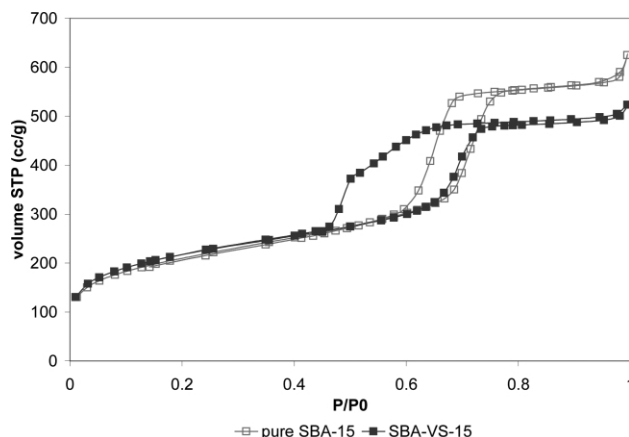
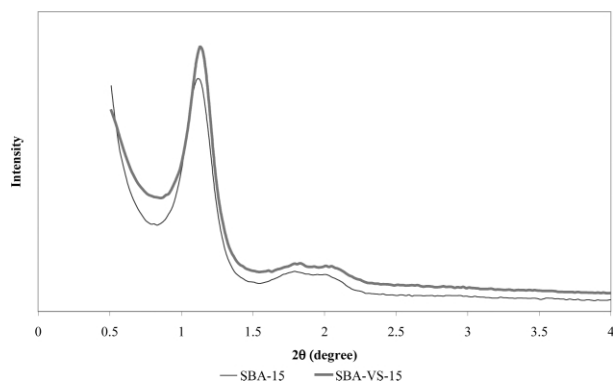


Fig. 1 N<sub>2</sub> Sorption of pure SBA-15 and SBA-15 after deposition of zeolite nanoparticles (SBA-VS-15).

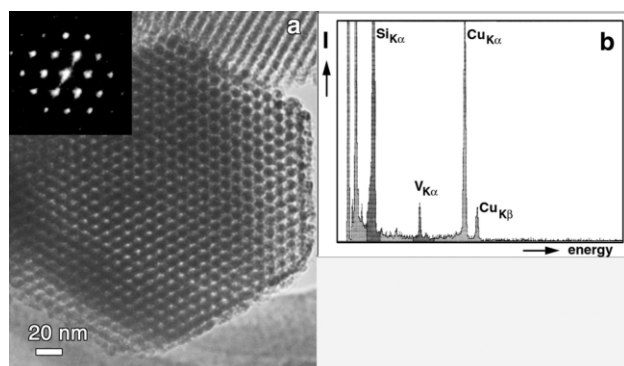
**Table 1** Structural properties of SBA-15 before and after deposition of different amounts of zeolitic vanadium silicalite nanoparticles in the mesoporous channels of SBA-15<sup>a</sup>

Sample	Deposited amount of clear suspension/ml	$V_{\text{tot}}$ /ml/g	$V_{\mu}$ /ml/g	Open/closed	Amount of vanadium/mmol/g	TGA % weight loss (190–320 °C)
SBA-1		0.71	0.10			
SBA-VS-1	10	0.64	0.14	0.34	0.09	10
SBA-2		0.88	0.11			
SBA-VS-2	15	0.76	0.17	0.20	0.14	17

<sup>a</sup>  $V_{\text{tot}}$  = total pore volume (micropores and mesopores),  $V_{\mu}$  = micropore volume,  $V_{\text{meso}}$  = mesopore volume, open/closed = ratio of open mesopores to closed mesopores. The amount of vanadium was determined colorimetrically. % weight loss describes the weight lost by the uncalcined samples determined by TGA between 190 and 320 °C under oxygen flow.



**Fig. 2** XRD Spectra of the pure SBA-15 and SBA-15 after deposition of the zeolite nanoparticles.



**Fig. 3** (a) Real space image and corresponding [0001] ED pattern of SBA-VS-15 ; (b) EDX analysis of the region shown in (a), taken from several areas of the particle with a probe size of around 50 nanometres. The Cu peaks result from the use of copper support grid.

observed in the overall  $d$ -spacing, this indicates a good distribution of the nanoparticles in the SBA mesopores (Fig. 2). Using ED and TEM however (Fig. 3), changes in  $d$ -spacing in the diffraction pattern, of about 5% difference from the ones of pure SBA-15, are deduced in small distinct areas of the mesopores. Moreover, SBA-

VS-15 shows a different contrast in these distinct areas in comparison with the pure SBA-15. EDX analysis shows vanadium concentrations only in areas where the contrast and the  $d$ -spacing changes are detected. The V-concentration is variable but  $V/Si \approx 1.5\%$ . In good agreement with the  $N_2$  adsorption data, the TEM results confirm the existence of small distinct microporous zeolitic vanadium silicalite plugs inside the mesopores of SBA-15.

In conclusion, a new type of V-activated PHTS material was synthesised in a fast and simple way. Post-synthesis deposition of zeolitic V-activated nanoparticles inside the mesoporous channels of SBA-15 resulted in a combined micro- and mesoporous material with both open and plugged mesopores. This new material is important for adsorption and catalytic activation purposes, since the presence of the zeolitic nanoparticles in the mesoporous channels will influence the diffusion behaviour of molecules in mesoporous templated silicas.

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