POROUS HIERARCHICAL STRUCTURES AND ADSORPTION PROPERTIES OF TiO_2 NANOTUBES/SBA-15

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ABSTRACT

A comparison study was made between the adsorptive properties of nanostructured TiO_2 and SBA-15 siliceous materials. Both systems are known to have a 1-D channel system, but substantial differences exist in terms of pore size distribution, grain orientation and aggregation state. In this work these materials have been prepared and modified to obtain more useful materials as adsorbents for removing NOx and SOx precursors from FCC gasoline. The synthesis of the basic siliceous materials (SBA-15) and the nanostructured Anatase-like TiO_2 materials was performed following general directions [1a,1b,1c] but during the synthesis an additional grafting was made using various metallic species, i.e.,M-TiO_2 and M-SBA-15(M: Fe,Ag,Cu) with distinct metal contents (0-5 %). The structural features were characterized by XRD, SEM and HRTEM methods, which confirmed the ordered pore structure of M-SBA-15 for all the metal concentrations while the TiO_2 nanostructured materials show a crystalline structure (anatase-like) and the typical nanotube morphology.. The pore diameters of TiO_2 nanotubes (NT) span in the range 8 - 15 nm and an additional porosity was obtained by promoting the NT aggregation. The properties of these materials series for adsorption of organonitrogen and organosulfur compounds from a FCC gasoline indicated a high adsorption capacity for both SBA-15 and TiO_2 (NT) having a hierarchical pore structure; these results were compared with respect to pure siliceous M-SBA-15. The hybrid M-SBA-15 materials display an increasing capacity with metal content, especially for organonitrogen compounds, while this behavior is reversed for organosulfur species. The M-TiO_2 show a more linear behavior with respect to the adsorption of organonitrogen compounds.

Keywords: NOx/SOx precursors adsorbents; Organonitrogen NOx Precursors adsorption; Hybrid TiO_2 nanotubes, Hybrid metal SBA-15.

1 INTRODUCTION

Nanostructured TiO_2 and siliceous SBA-15 type materials are known to have a 1-D channel system but different textures, with specific pore structures[1]. These materials are currently synthesized under basic or acidic conditions, respectively [1a-1c]. The post-synthesis grafting of metal species or during synthesis, using either organic functional groups or inorganic cations, may lead to hybrid materials with outstanding properties. For example, thiol- and amino- functional groups in SBA-15 were employed for removing heavy metal ions from waste water [2]; also, Titanium-substituted SBA-15 molecular sieves have been prepared at 373 K by direct synthesis under microwave-hydrothermal conditions [3];. Also, several heteroatoms (Al and Ti) have been introduced into the framework of ordered mesoporous silica under strong acidic media (pH < 0) and these materials display high catalytic activity [4] for the cracking of both small (cumene) and bulky (1,3,5-triisopropylbenzene) molecules.

Thus, in this work the synthesis of metal-grafted nanostructured TiO_2 and SBA-15 (M: Fe, Ag, Cu) was performed to design more useful materials for adsorption of noxious NOx and SOx precursors in FCC gasoline. The physicochemical properties of these materials were characterized by X-ray diffraction (XRD), Scanning and High Resolution Transmission Electron Microscopy (HRTEM) and Nitrogen adsorption (BET).

2 EXPERIMENTAL

2.1 Synthesis and Characterization

The synthesis of M-TiO_2 was realized in basic aqueous media (NaOH) using TiO_2 (anatase) and $Fe(NO_3)_3$ (1,3,5 wt. %) as raw materials, which were submitted to reaction in an autoclave at 300 ^oC (12 h); afterwards the gel is washed thoroughly with diluted HCl (0.5 N), then it is dried and calcined at 350 ^oC (6 h). The M-SBA-15 materials were prepared in acidic media (pH < 1) using a tri-block non-ionic type surfactant, i. e., Pluronic® P123, which has a low EO/PO ratio $[OE]_{20}$-$[OP]_{70}$-$[OE]_{20}$. Thus, starting with 15 ml of HCl [4M] in deionized water under stirring for 1 h, 2.12 g of TEOS (Tetraethyl-ortosilicate) were added and this mixture was heated up to 60 ºC for 48 h; after filtering an drying at 60 ºC for 12 h, the solids were calcined at 500 ^oC. The main structural features of these hybrid materials were characterized by X-ray diffraction (XRD) using a Siemens D-500 diffractometer and High Resolution Transmission Electron Microscopy (HRTEM) in a Jeol-2200 FS instrument, which is fitted with aberration corrector. A Nova (FEI) instrument was used for SEM. The surface area and pore size distribution were obtained by N_2-adsorption at 78 K (BET) in a Digisorb 2000 apparatus.

2.2 Adsorption Properties

The hybrid materials were tested for the adsorption of organonitrogen and organosulfur species at 40 ^oC, using glass flasks with moderate stirring under standard conditions. The contents of the organonitrogen species in the FCC gasoline was determined using a GC (Thermo Quest Trace 2000) fitted with a Nitrogen Phosphorous detector (NPO). In turn, the organosulfur compounds were evaluated using GC(HP) fitted with a sulfur detector (chemiluminiscence) and FID. The analyses were performed before and after adsorption and the rates were determined by the respective differences.

3 RESULTS

Figs.1and 2 illustrate the typical structural features of the hybrid M-SBA-15 materials. Basically, the XRD patterns in Fig 1 confirm the integrity of the pore arrays after grafting the metal species, i.e., from 1 to 5 wt. % Fe. Also, the XRD peak symmetry indicates a uniform pore size distribution. These features were verified in the electron microscope, i.e., the ordered pore arrays and uniform pore size, as illustrated by Fig. No. 2, where one observes the typical [001] orientation of the siliceous grains; also, the intragranular hexagonal pore arrays are very apparent from these micrographs (Fig. 2).

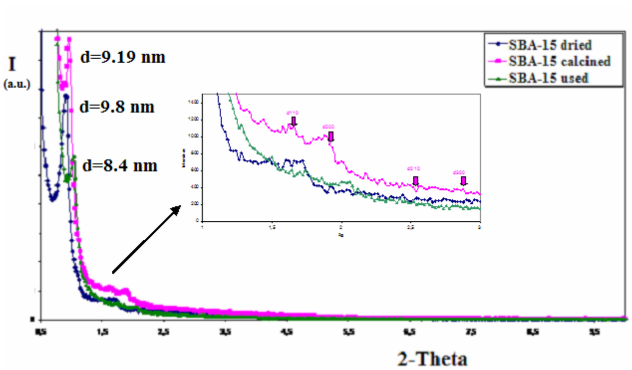

Fig. 1: XRD pattern of Hybrid SBA-15 type materials

In turn, the structural features of the M-TiO_2 type materials were confirmed (Figs. 3 – 7). The XRD pattern in Fig 3a corresponds to a typical nanostructured TiO_2 material without metals, which coincides with the typical structural features of crystalline non-nanostructured anatase (Fig. 3b), excepting that in the former case the XRD peaks are broad and display an additional low-angle peak at about 10 $^o(2\Theta)$, which is typical of the inter-sheets spacing of the TiO_2 scrolls [1b]. Also, these materials form spherical aggregates which are connected to each other as shown by Scanning Electron Microscopy images (Fig. 4), which leave wider pores in between.

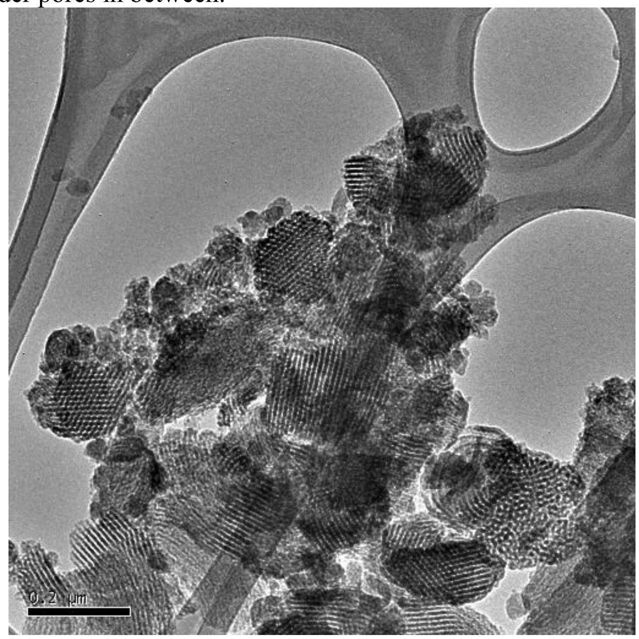

Fig. 2: Typical HRTEM image of Hybrid M-SBA-15 type materials

A closer observation by HRTEM confirms the tubular shape of the individual particles as well as the presence of the metal phase, as illustrated in Fig. 5, for the case of Fe-TiO_2, which shows some contrast features which are attributed to iron oxide particles dispersed on the tubular TiO_2 phase. However, the location of small metal or metal oxide particles into the tubular channel system may be ambiguous if one uses the bright field electron microscopy images (Fig. 5) because the slight contrast difference between the dispersed iron oxide species and the TiO_2 matrix. In order to distinguish further these differences, we used dark field imaging techniques, and a selected dark field image is displayed on Fig. 6. This micrograph shows a clear profile region corresponding to a dispersed Fe-oxide phase. Thus, the iron oxide phase appears now distinctly contrasted with respect to the TiO_2 tubular matrix. Apart the bright zone corresponding to an iron oxide particle there are regular straight lines running along the nanotubes walls, which might indicate the presence of intercalated iron-oxide species into the rolled foils of the TiO_2 nanotubes.

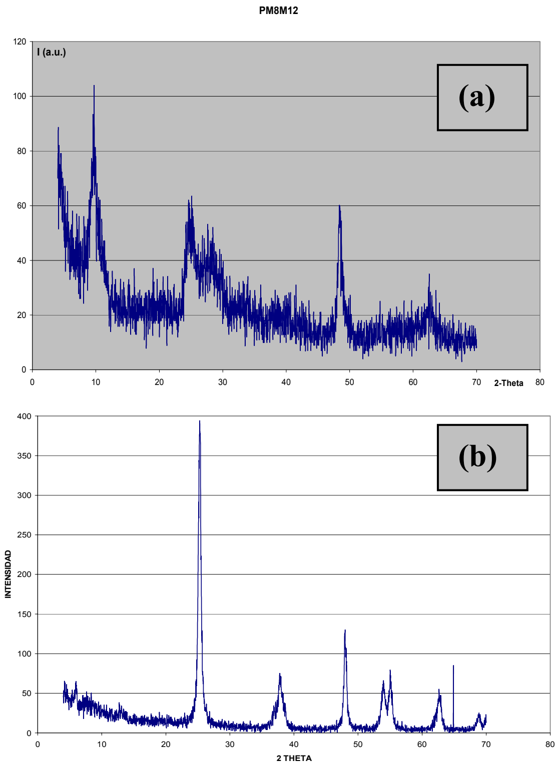

Fig. 3: XRD patterns of (a) nanostructured TiO_2 and (b) normal crystalline Anatase.

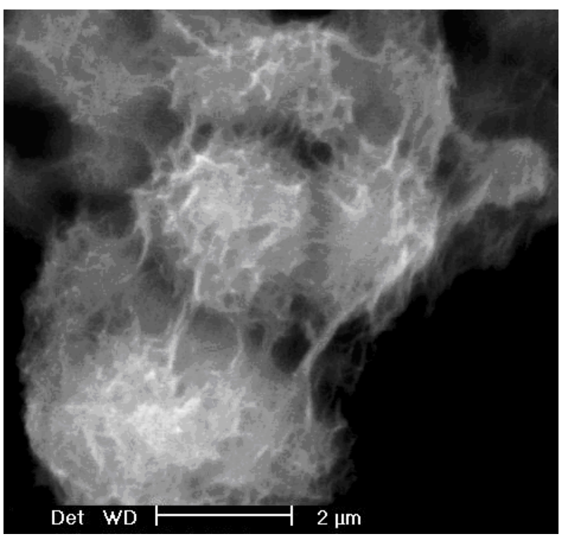

Fig. 4: Typical SEM image showing the hierarchical pore structure in TiO_2 –NT (without metals).

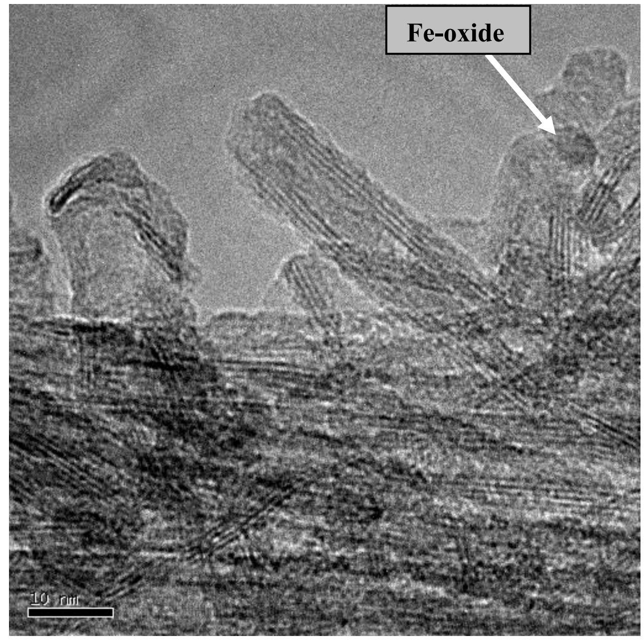

Fig. 5: Typical HRTEM bright-field image of the hybrid Fe-TiO_2 materials.

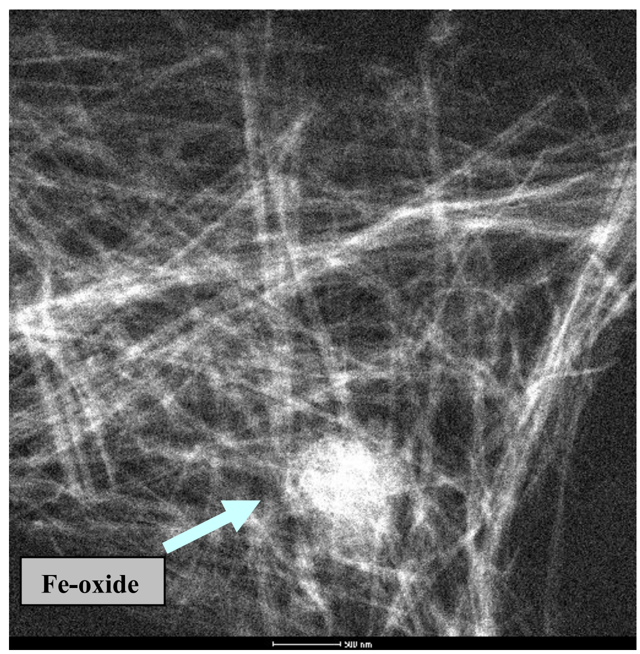

Fig. 6: Typical Dark-Field HRTEM image of hybrid Fe-TiO_2 materials.

Table 1: Adsorption properties of M-SBA-15 materials

		% REMOTION		
wt. % Cation	Cation	N_{basic}	$N_{non-basic}$	**Sulfur**
1%	Fe	30.3	92.9	30.7
	Ag	40.3	86.2	22.2
	Cu	32.7	91.9	31.3
2.00%	Fe	10.9	96.3	16
	Ag	8	55.7	15.4
	Cu	24.7	88.2	8.7
5.00%	Fe	30.4	100	14.6
	Ag	45	79.2	15.4
	Cu	19.7	97	16.9
Pure SBA-15	None	37.2	92.9	18.7

The adsorption properties of the mesoporous materials are presented in Table No. 1. Here one observes the total capacity of some materials for retaining organonitrogen and organosulfur compounds, which are normally found in FCC gasoline, i.e. Quinoline, Carbazol, Thiophene, DBT, etc.

One observes from Table No. 1 that pure siliceous SBA-15 (without metals) has a high potential for adsorption of organonitrogen compounds but the Fe-SBA-15 materials display further this property; the total capacity of hybrid SBA-15 compounds is proportional to the Fe content, especially for organonitrogen compounds, while this behavior is reversed for organosulfur species.

In conclusion, the general structural features of hybrid M-TiO_2 and M-SBA-15 type materials were determined by means of X-Ray diffraction techniques. The formation of nanoscrolls of TiO_2 with anatase-like structure was verified and these structures define a pore size distribution around 8 nm, but in turn the nanotubes create bigger aggregates with spherical shape, which aggregate with each other to create additional porosity (hierarchical pore structures) between the spheres. These are hierarchical pore structures that might be useful for the rapid diffusion of chemical species. The influence of these structures on the adsorption properties of pure and metal-loaded (M: Fe,Ag,Cu) TiO_2-NT and SBA-15 type materials was illustrated by the adsorption properties of the M-SBA-15 materials, which display a high capacity for adsorbing organonitrogen and organosulfur compounds from FCC gasoline. Thus, the capacity of these materials for removing pollutants precursors species in motor fuels is clearly shown in this work. The organonitrogen and organosulfur compounds are precursors of noxious species when they are converted into NOx and SOx in the motor vehicles. On the other hand, iut was shown that the proper use of HRTEM methods (Dark Field) allowed it to identify the dispersed metal oxide phases (i.e., Fe-oxide) that form along the edges in the space between the sheets of the scrolls forming the TiO_2-NT structures,. Also, some Fe oxide islands were detected by these techniques, which might contribute further to the catalytic and adsorptive properties of the hybrid materials, with respect to the more finely dispersed iron oxide phase.

4. REFERENCES

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