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# STRUCTURE AND THERMAL PROPERTIES OF NAPHTHALENE SULFONATED RESIN/MESOPOROUS NIOBIUM OXIDE NANOSTRUCTURED COMPOSITES

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**Abstract**. Mesoporous niobium oxide ($Nb_2O_5$) was synthesized and treated with naphthalene sulfonated formaldehyde resin (NSF) solution. These new inorganic-organic hybrid composites were characterized by different techniques. Results indicated that the pores of the nanostructured material are filled with the NSF resin with changes in the morphology and thermal properties of the mesoporous $Nb_2O_5$.

**Key words**: mesoporous materials, impregnation, naphthalene sulfonated, composites, fuel cells.

## 1. Introduction

There has been large interest in the synthesis of transition metal oxide analogues of MCM41 silicates due to the variable oxidation states and high surface acidity of many of these materials [1]. Ordered mesoporous materials containing niobium have gained much attention due to the ease of preparation and relatively high thermal stability of this material as compared to many of its Ti analogues [2, 3]. Several works in the literature focused applications of related transition metal oxides (Nb, Ti, Ta, Zr) because these structures are attractive as catalyst supports and materials for adsorption and immobilization of molecules [1, 4-8]. This ability is due to the fact that pore size characteristics of the mesostructure enable the active centers to be accessed by different species [4]. Nevertheless, the structure and properties of these nanostructured oxide transition metal materials are highly dependent on the preparation method which influences their specific applications [9].

There are many literature reports investigating the local structure of species introduced to mesoporous solids by impregnation after hydrothermal synthesis. Aqueous impregnation is one of the most widely-used procedures involved in the preparation of supported heterogeneous catalysts [10]. For example, A. Jentys and co-workers [11] have shown that impregnation of MCM-41 materials with aqueous solutions of cobalt nitrate results in small cobalt clusters being incorporated inside the amorphous mesostructure. Most of these publications have mainly addressed the structure of the oxide and metal particles incorporated into the porous structure. Although the properties of MCM-41 and SBA-15 materials have been widely investigated, only limited studies have been performed on the effect of conventional aqueous impregnation upon ordered mesoporous oxides after their exposure to aqueous solutions [12]. Most of studies have been focussed on the hydrothermal stability of the materials by assessing their structure before and after treatment in boiling water for up to 48 h. However, it is important that the pore structure integrity is retained after impregnation. It should be noted, that the data obtained under hydrothermal conditions are not immediately transferable to the evaluation of the stability of mesoporous materials in preparation procedures involving aqueous impregnation [10].

Despite numerous research works being focused on mesoporous materials, they have to replace most common microporous supports based on zeolites. One of the main reasons for this is the inherent thermal instability of the mesostructure [4]. Therefore, the modification of the composition of these materials in order to improve the structural strength and diversify the properties becomes the key step to facilitate their application. Numerous metals, metal oxides (sulfides), acid groups and organic functionalities have been incorporated by direct synthesis (one-pot method) or post-synthesis. The most widely employed method is the impregnation with solutions of simple thermally unstable precursor salts (*e.g.* nitrates, chlorides and acetates) [13, 14]. There have been only few works on the impregnation of mesoporous Nb oxide with organic materials and/or polymers, although

extensive research has been conducted on mesoporous Nb oxide impregnated with alkali fullerides [1, 15-17].

Some strategies are used to enhance proton conductivity properties of fuel cells polymer membranes. One of those forms composites by adding potencial species with the capacity to facilitate proton transportation through the matrix. Sulfonate groups can improve ion conductivity properties and can be added to basic materials by sulfonation process or by introducing polymers containing $-SO_3H$ groups as a membrane component in a simple impregnation process.

In the present work the capacity of mesoporous niobium oxide ($Nb_2O_5$) in promoting the adsorption of oligomeric sulfonated organic species such as naphthalene formaldehyde sulfonates (NSF) resins was investigated considering the system morphology and thermal behaviour. The purpose of this work was to coat the $Nb_2O_5$ mesostructure with NSF in order to obtain a new inorganic-organic hybrid material with better ionic conductivity properties and possible application as the proton conducting element in polymer membrane fuell cells. NSF resins are used as commercial products in different areas such as cement production, pigment, elastomer manufacture, textiles and mineral processing [18, 19]. The only report in the literature being focussed on the adsorption of NSFs on solid surfaces is the work of P. Jenkins *et al.* [20] who investigated the effect of naphthalene sulfonate formaldehyde condensate adsorption on the interaction between titania particles.

# 2. Experimental

## 2.1. Materials

Commercial niobium ethoxide and dodecylamine were purchased from Aldrich and used as supplied. Naphthalene sulfonate formaldehyde condensate (NSF) was purchased from Specco Industrial as 40 wt/v % aqueous solution.

Mesoporous oxide synthesis was carried out following the procedure previously described by Antonelli [21]. As a typical preparation, niobium ethoxide and dodecylamine were mixed and heated until complete solution homogeneity. Water and hydrochloric acid were added, followed by gradual aging to 393 K in order to obtain the stable mesoporous oxide. The as-synthesized material was dried and washed with ethanol and *p*-toluene sulfonic acid to remove the template.

## 2.2. Mesoporous Niobium Impregnation

The mesoporous material was impregnated adding the appropriate mass of mesoporous niobium oxide into different solutions (10, 5, 1 and 0.5 %) of the NSF oligomer. The dispersions were placed in an ultrasonic bath for 5 minutes and then magnetically stirred for 24 h at room temperature, followed by filtration and drying.

## 2.3. Characterization

The pristine and impregnated materials were characterized by nitrogen adsorption (BET method), wide angle X-ray scattering (WAXS), infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM) to elucidate the oxide mesopores filling process.

WAXS measurements were performed on a DMAX 2200 Rigaku diffractometer (40 kV, 40mA) with a copper X-ray tube (CuKα, wavelength λ = 1.5418 Å) and a graphite monocromator. The data were collected in the step-by-step mode of 0.05° from 1 to 40° in 2θ.

FTIR spectroscopy (Excalibur 3100, Varian) was used to ascertain the synthesis of mesoporous niobium oxide and its impregnation with naphthalene sulfonate. The specimens were prepared on potassium bromide plates. The spectra were measured over the wavenumber range 400–4000 cm$^{-1}$, with 20 scans and a resolution of 4 cm$^{-1}$.

Nitrogen isotherms at 77 K were recorded on a Micrometrics ASAP 2010 instrument. Prior to the adsorption measurements, the samples were outgassed for 5 h at 473 K. Nitrogen isotherms were obtained in both adsorption and desorption modes. The surface areas of the pure oxide and impregnated oxides were determined by the BET method. The total pore volume (TPV) was calculated from the amount of vapour adsorbed at a relative pressure ($P/P_0$) close to unity, where P and $P_0$ are the measured and equilibrium pressures, respectively. Pore size distribution curves of mesoporous $Nb_2O_5$ and $Nb_2O_5$/NSF composites were established from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method.

TEM analysis was carried out using a Hitachi H9000 transmission electron microscope. A copper grid was embedded with the powder samples of pure mesoporous niobium oxide and $Nb_2O_5$/NSF composites prepared from NSF solutions with different concentrations (0.5, 1, 5 and 10 %). The grid was placed in TEM specimen holders and the mesostructured morphology was evaluated.

The thermal behaviour of the samples was evaluated in a TA Instruments (TGA Q500 V6.7) thermogravimetric analyzer at 10° per minute in a range of 303–973 K under nitrogen atmosphere. Initial weight of the samples was approximately 10–20 mg. Before the analysis the materials were dried at 353 K during 24 h.

# 3. Results and Discussion

## 3.1. Structural Analysis

Fig. 1 shows the infrared spectra of mesoporous $Nb_2O_5$, NSF and the $Nb_2O_5$/NSF composites. The NSF resin contains an aromatic C–H stretch band at 3070 cm$^{-1}$ and aromatic ring vibration modes at 1640, 1596 and

1507 cm$^{-1}$ [22]. The sulfonate group bands related to SO group and S-phenyl vibration interactions can be observed at 1230, 1190, 1130 and 1040 cm$^{-1}$ [23]. Additionally, this spectrum contains the methylene C–H bending (scissors) at 1450 cm$^{-1}$ [22] and also around 1350 cm$^{-1}$ a band of asymmetric SO$_2$ stretch [21]. The pure niobium oxide FTIR spectrum shows a broad band around 627 cm$^{-1}$, related to the Nb–O bonds characteristic of an amorphous material as well as absorption bands at 1624 and 3416 cm$^{-1}$ for OH groups [24]. The composites spectra showed the bands at 1190 and 1040 cm$^{-1}$ related to asymmetric and symmetric stretching of the SO$_3$ group and the asymmetric SO$_2$ stretch band shifted to 1359 cm$^{-1}$, indicating the presence of NSF in the mesopores materials and on the surface of Nb$_2$O$_5$.
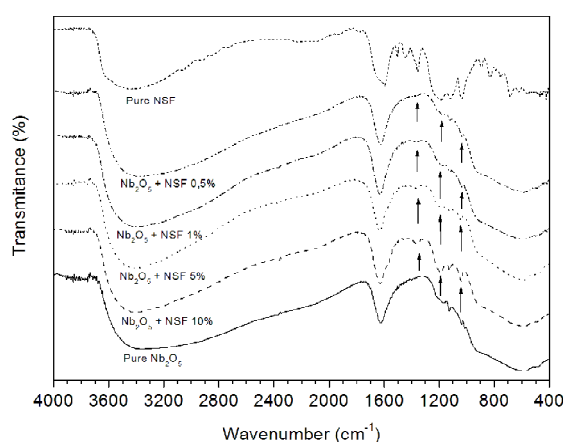


**Fig. 1**. FTIR spectra of pure Nb$_2$O$_5$, pure NSF and composites

## 3.2. Morphological Analysis

The results of specific area and pore volume of the mesoporous Nb$_2$O$_5$ and Nb$_2$O$_5$/NSF composites obtained by the nitrogen adsorption technique (BET method) are presented in Table 1. Even after impregnation of the mesoporous material with the oligomer, the composite materials showed significant porosity. The entire materials possessed pore sizes around 20 Å (2 nm).

*Table 1*

**Specific area of Nb$_2$O$_5$ and Nb$_2$O$_5$/NSF composites**

| Sample | Specific area, cm$^2$/g | Pore size, Å | Pore volume, cm$^3$/g |
|---|---|---|---|
| Nb$_2$O$_5$ | 1.106 | 21.3 | 0.78 |
| Nb$_2$O$_5$/NSF 0.5 % | 367 | 19.4 | 0.19 |
| Nb$_2$O$_5$/NSF 1 % | 419 | 19.5 | 0.21 |
| Nb$_2$O$_5$/NSF 5 % | 339 | 19.4 | 0.16 |
| Nb$_2$O$_5$/NSF 10 % | 193 | 19.4 | 0.091 |

The pure Nb$_2$O$_5$ possesses a very high specific area, which decreases when the material is treated with the naphthalene sulfonated resin. The increase of the NSF solution concentration used for impregnation decreases the pore volume of the impregnated material. This can be attributed to the interaction between the mesoporous oxide with NSF and it suggests that the pores of the nanostructured material are filled with the oligomer. This is desirable because coating the Nb$_2$O$_5$ structure with NSF can form channels enriched with SO$_3$H– groups and promote ion conductivity properties and facilitate proton exchange and its transport through the channels. The results also showed that the pores are not completely filled with the resin.

Fig. 2a shows the WAXS curves of the NSF, Nb$_2$O$_5$ and Nb$_2$O$_5$/NSF composites. NSF is an amorphous material which presents a broad bimodal amorphous halo at higher angles (2θ > 10°). Curiously a broad diffraction peak with low intensity was detected at low angles, suggesting some degree of structural order probably due to the aromatic rings stacking. For Nb$_2$O$_5$ and Nb$_2$O$_5$/NSF composites, the low angle scattering peaks characteristic of mesoporous materials have a small shift on 2θ position and increase of intensity with impregnation. The curves also show a broad peak at the high-angle region, demonstrating that the materials possess an amorphous structure. These all data indicate that mesoporous Nb$_2$O$_5$ retained its overall mesostructure when treated with NSF. Fig. 2b presents the high intensity samples peaks (around 1.500 cps) at the angles between 2.00 and 4.35 (2θ). The incorporation of NSF in Nb$_2$O$_5$ structure shifted the peaks to small angles, which can be attributed to changes in average interplanar distances of the nanoporous oxide, with the influence on its morphological structure. Table 2 presents the basal distances obtained by WAXS. The difference observed on basal distance seems to be related to the concentration of NSF solutions used during impregnation. It suggests that the NSF molecules can permeate through Nb$_2$O$_5$ structure, being adsorbed by the inorganic material. In the composite prepared with the lower concentrated NSF solutions (0.5 and 1 %) the intensity of the diffraction peaks is higher, suggesting changes in the Nb$_2$O$_5$ morphology and better array of the oxide structure. The WAXS results also proved the interaction between the inorganic material and the NSF resin due to the new morphological behavior.

TEM analysis was used to evaluate the pore structure and the pore shape of the mesoporous materials before and after impregnation. Fig. 3 shows TEM micrographs of the mesoporous Nb$_2$O$_5$ and Nb$_2$O$_5$/NSF composites obtained by impregnation with different solutions of NSF. It can be seen that all materials have nanoporosity. In samples impregnated with NSF, it is not easy to detect the pore structure due to physical interaction between inorganic and organic materials. A higher

resolution was applied to those samples treated by NSF. Transmission electron micrographs of these materials conrmed the presence of 20 Å pores detected by nitrogen adsorption. The samples were nearly uniform which is consistent with other mesoporous materials prepared *via* the ligand-assisted templating approach.

The nitrogen adsorption and TEM results are thus in agreement, showing that the inorganic material adsorbs more resin when a more concentrated solution is employed for impregnation. By nitrogen adsorption, the higher concentration of the oligomer solution results in the material lowest surface area; and by TEM, it is difficult to detect the structure of the sample with the lowest surface area.

*Table 2*

**Interplanar distance of $Nb_2O_5$ and $Nb_2O_5$/NSF composites**

| Sample | $2\theta$ | d, Å |
|---|---|---|
| $Nb_2O_5$ | 2.60 | 33.9 |
| $Nb_2O_5$/NSF 10 % | 2.45 | 36.0 |
| $Nb_2O_5$/NSF 5 % | 2.40 | 36.8 |
| $Nb_2O_5$/NSF 1 % | 2.35 | 37.5 |
| $Nb_2O_5$/NSF 0.5 % | 2.3 | 38.4 |



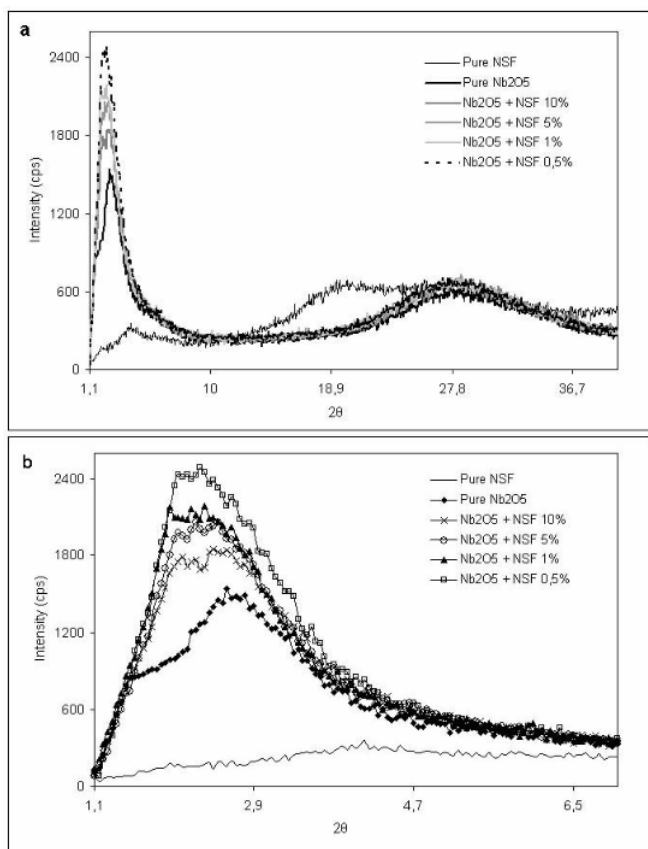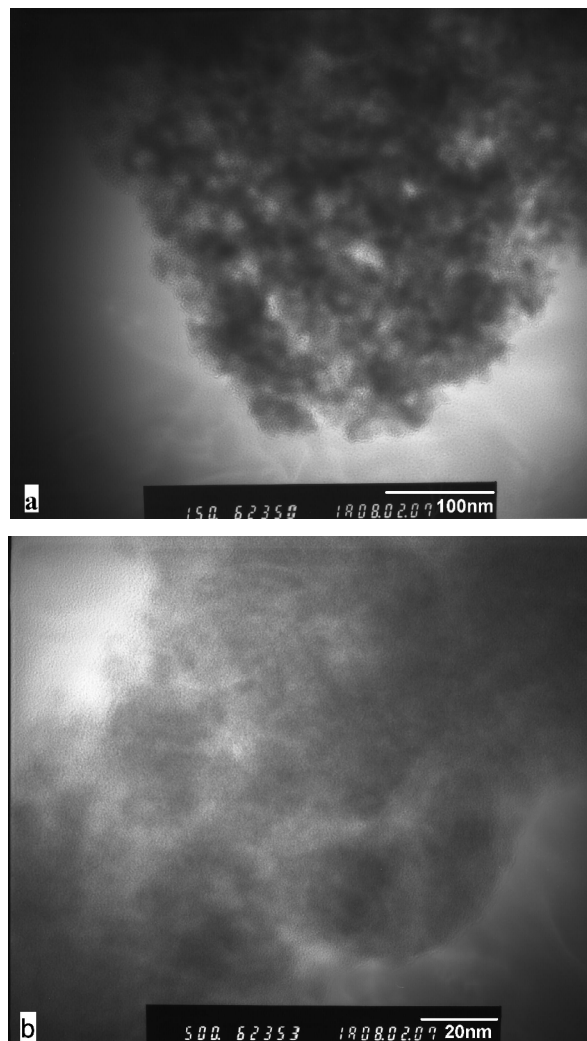**Fig. 2**. WAXS curves of $Nb_2O_5$ and $Nb_2O_5$/NSF composites



**Fig. 3**. TEM micrographs of pure $Nb_2O_5$ (a) and composite of $Nb_2O_5$/NSF 10 % (b)

## 3.3. Thermal Stability

Decomposition temperatures of all materials were determined from the temperature peak maximum in the TGA derivative of the curves presented in Fig. 4. Complete TGA data are shown in Table 3. In all TGA curves, the weight lost beginning at 298 K was attributed to elimination of water from the hydrophilic materials. Although the materials were dried this loss of weight related to the presence of water was due to the absorbed humidity while preparing the sample.

The TGA curves in Fig. 4 and results of Table 3 show that mesoporous $Nb_2O_5$ has a degradation temperature at 725 K besides the weight loss related to water loss starting at room temperature. This decomposition can be attributed to the beginning of the mesopore collapse and also to the possible presence of residual dodecylamine used as a template in the oxide synthesis. The NSF degradation curve presents the water

*Table 3*

**TGA data of Nb$_2$O$_5$, NSF and Nb$_2$O$_5$/NSF composites**

| Sample | Temp$_1$, K | Weight loss$_1$, % | Temp$_2$, K | Weight loss$_2$, % | Residual mass at 973 K, % |
|---|---|---|---|---|---|
| NSF | 391 | 1.8 | 485 | 13.5 | 68 |
| Nb$_2$O$_5$ | 452 | 2.7 | - | - | 72 |
| Nb$_2$O$_5$/NSF 0.5% | 457 | 2.4 | - | - | 71 |
| Nb$_2$O$_5$/NSF 1% | 462 | 2.4 | 573 | 0.23 | 72 |
| Nb$_2$O$_5$/NSF 5% | 464 | 2.9 | 581 | 2.5 | 73 |
| Nb$_2$O$_5$/NSF 10% | 485 | 4.0 | 595 | 3.7 | 67 |



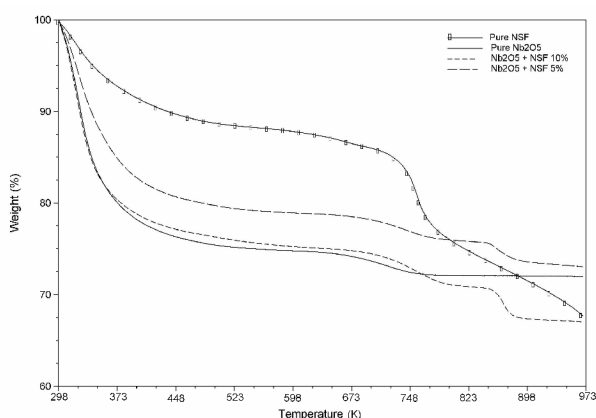**Fig. 4.** TGA curves of Nb$_2$O$_5$, NSF and Nb$_2$O$_5$/NSF composites

loss temperature and two more degradation temperatures, one at around 664 K which can be attributed to the sulfonic acid groups [25] and at 758 K attributed to NSF chain degradation. When Nb$_2$O$_5$ is impregnated with different concentrations of NSF, instead of three steps of weight loss predicted from individual materials, only two degradation temperatures are observed. Although these degradation maximum temperatures are close to those of NSF, they were shifted to higher temperatures, indicating the influence of the inorganic material on the thermal stability of the encapsulated organic component. The interaction between nanocomposite components dislocates the second degradation stage of NSF to higher temperatures. Increasing the NSF solution concentration increases the material decomposition temperatures. When the impregnation was carried out with the NSF 0.5 % solution, the nanocomposite did not show a second temperature weight loss, although it still showed the increase of thermal stability attributed to the interaction between the two materials. This interaction brings a significant delay in the sulfonic acid groups degradation when Nb$_2$O$_5$ is treated with NSF 10 %. The increase of the materials stability can be attributed to the presence of NSF in the mesoporous and to the surface of the niobium oxide, forming physical interactions. It seems that the inorganic component protects NSF molecules from degradation promoting better thermal stability. This is

another evidence that the nanoporous materials of Nb$_2$O$_5$ are filled with NSF.

## 4. Conclusions

When mesoporous Nb$_2$O$_5$ is treated with solutions of different concentrations of naphthalene sulfonated olygomer, a hybrid inorganic-organic composite is formed. The presence of NSF on Nb$_2$O$_5$ pores and the interaction between them was observed by FTIR, WAXS, BET, TEM and TGA. An increase of the oligomer solution concentration during the impregnation step increases the rate of mesoporous oxide impregnation, decreasing its surface area, but with retention of porosity and pore characteristics. A striking enhancement of thermal stability of both organic and inorganic phases takes place by the interaction of the composite components. This may be important in designing composite materials with higher thermal stability. The incorporation of sulfonic acid groups of NSF in the mesoporous Nb$_2$O$_5$ can also enhance the ionic conductivity properties. Thus this new composite may be useful in the fabrication of fuel cell composite membranes where this property is crucial.

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**СТРУКТУРА І ТЕРМІЧНІ ВЛАСТИВОСТІ НАФТАЛІН-СУЛЬФОВАНА СМОЛА/ МЕЗОПОРИСТИЙ ОКСИД НІОБІЮ НАНОСТРУКТУРНОГО КОМПОЗИТУ**

***Анотація***. *Синтезовано мезопористий оксид ніобію ($Nb_2O_5$), який оброблено розчином нафталін-сульфованої формальдегідної смоли (НСФС). Нові неорганічні-органічні композити досліджено різними методами. Показано, що пори наноструктурного матеріалу заповнені НСФС, змінюють морфологію і термічні властивості мезопористого $Nb_2O_5$.*

***Ключові слова****: мезопористі матеріали, імпрегнація, нафталін-сульфований, композити.*