



# Insight into the interaction of calcium species with mesoporous silica and niobosilica



Maciej Trejda\*, Dorota Kryszak, Maria Ziolk

Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89b, PL-60-780 Poznań, Poland

## ARTICLE INFO

### Keywords:

SBA-15  
Niobium  
Structural promoter  
Basicity  
Calcium

## ABSTRACT

SBA-15 mesoporous materials were modified with calcium species (up to 40 wt% of Ca) using calcium acetate and calcium nitrate salts. Niobium species were also incorporated into the SBA-15 support. The structure and surface properties of final materials were examined using XRD, N<sub>2</sub> adsorption/desorption, XRF, UV-vis, FTIR as well as cyclization and dehydration of 2,5-hexanedione. The impact of niobium species on stability of mesoporous solids was investigated. It was found that niobium stabilizes the structure of the support upon its modification with calcium salts. The procedure applied in this work allowed obtaining basic catalysts with high surface area of Ca content up to 40 wt%.

## 1. Introduction

Market demand and legislation are the driving force behind development of fuels that are alternative to fossil ones [1]. They can be produced by the transesterification of triglycerides with short chain alcohols. Although homogeneous catalysts such as sodium or potassium hydroxide are conventionally applied, the heterogenization of this process is desirable and welcome. Despite the high activity of sodium and potassium hydroxides their application is a troublesome issue because of the problems with separation and production of a large amount of wastewater [2–4]. In this context solid materials which can be applied as catalysts in different processes requiring basic centres are still of great interest [5]. It should be mentioned that solid base materials have the added advantage of being usually not toxic, easy to separate, not causing corrosion and diminishing pollution [5].

The synthesis of ordered mesoporous materials such as MCM-41 [6,7] or SBA-15 [8,9] was an important discovery in the context of the process heterogenization. These solids are characterized by high surface area and the presence of regular channels with the pore diameter ca. 4–10 nm. Such a structure allows incorporation of large number of active centres at preserved good dispersion. Moreover, the channels of above-mentioned materials can serve as “nanoreactors” for bulk molecules enabling diffusion of substrates and products to/from the active centres. This is an important issue especially in the liquid phase processes. Both MCM-41 and SBA-15 materials have been previously applied as supports for calcium species [10–15]. The catalysts obtained have been used in different processes, mainly in transesterification [10,12–16] or sorption [11]. However, the introduction of larger

amount of calcium oxide via impregnation of mesoporous silica led to changes in the support structure, which was demonstrated by decreased surface area of the final material. For example SBA-15 materials containing 10% of CaO [15] and 14% of CaO [10] (obtained from calcium acetate monohydrate) exhibited surface area of 207 m<sup>2</sup>g<sup>-1</sup> and 7.4 m<sup>2</sup>g<sup>-1</sup>, respectively. For mesoporous silica impregnated with calcium nitrate tetrahydrate the surface area was 110–140 m<sup>2</sup>g<sup>-1</sup> and 36–45 m<sup>2</sup>g<sup>-1</sup> for 20% of CaO and 40% of CaO, respectively [16].

As mentioned above, the modification of mesoporous silica based supports with alkali metals can result in disturbances to the structure. However, this problem can be reduced by the alterations to the preparation procedure, e.g. the use of structure promoters. It has been found that the addition of niobium into the MCM-41 structure protects the solid from the disordering caused by the treatment with alkali metal solution (Li, Na, K, Rb, Cs) [17]. It is reasonable to expect a similar effect in the case of calcium. Nevertheless, the concentration of metals applied in [17] was not high (0.5 mmol per 1 g of support). It would give ca. 2 wt% of metal when calculated for calcium. Thus, the aim of our work was to increase the resistance of mesoporous structure of SBA-15 upon exposition to alkali (calcium source) solution in high amount, by the incorporation of a structure promoter (niobium species) to the mesoporous silica matrix. In this work we estimated the interaction of calcium species with mesoporous silica and niobosilica of SBA-15 type using a high Ca loadings (20 wt% and 40 wt%). For this purpose two calcium salts (calcium acetate monohydrate and calcium nitrate tetrahydrate) were applied. The positive role of niobium was evidenced even for the highest Ca loading.

\* Corresponding author.

E-mail address: [tmaciej@amu.edu.pl](mailto:tmaciej@amu.edu.pl) (M. Trejda).

## 2. Experimental

### 2.1. Materials

All chemicals and materials used were collected from commercially available sources and used without further purification. Pluronic P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)), tetraethyl orthosilicate – TEOS (> 98%), ammonium niobate(V) oxalate, calcium nitrate tetrahydrate (> 99%), calcium acetate monohydrate (> 99%), 2,5-hexanedione (> 98%) were purchased from Sigma-Aldrich. HCl (35%) was procured from Chempur, silica from Degussa, Nb<sub>2</sub>O<sub>5</sub> from Alfa Aesar and 2,5-hexanedione (GC grade) from Fluka.

### 2.2. Synthesis of SBA-15 and NbSBA-15

SBA-15 and NbSBA-15 materials were prepared via hydrothermal synthesis. The synthesis was performed in polypropylene bottle (PP). The synthesis procedure was as follows. To the PP bottle Pluronic P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (8 g), HCl (17.52 g) and water (282.5 g) were added. After the surfactant was dissolved, TEOS (17.054 g) was added dropwise. For Nb containing samples, ammonium niobate(V) oxalate was also added to the gel (10 min after TEOS addition) keeping Si/Nb molar ratio 30. Final mixture was stirred at 313 K for 20 h and then heated at 373 K under static conditions for 24 h. The product was washed with water (1000 ml) and dried at RT. The template was removed by calcination at 823 K for 8 h (temperature ramp 1 K min<sup>-1</sup>).

### 2.3. Modification with calcium

Mesoporous supports were impregnated (incipient wetness impregnation) with calcium acetate monohydrate or calcium nitrate tetrahydrate. Prior to the modification, the mesoporous silica was outgassed in an evaporator flask for 1 h at 353 K. Then the material was filled with such an amount of the aqueous solution of calcium nitrate or calcium acetate which filled only the pores of the support. The amount of calcium in the solution was sufficient to obtain 20 wt% or 40 wt% of this metal in the final product. The mixture was located in an evaporator flask, rotated and heated at 353 K for 1 h (first 15 min without evaporation). The impregnated powder was dried at 373 K for 12 h and calcined at 973 K (temperature ramp 1 K min<sup>-1</sup>).

### 2.4. Characterization methods

The materials prepared were characterized using different techniques: XRD, N<sub>2</sub> adsorption/desorption, XRF, UV–vis and FT-IR spectroscopies.

#### 2.4.1. X-ray diffraction (XRD)

XRD measurements were carried out on a Bruker AXS D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) with a step of 0.02° or 0.05° in the small-angle and wide-angle range, respectively.

#### 2.4.2. N<sub>2</sub> adsorption/desorption

N<sub>2</sub> adsorption/desorption isotherms were obtained in Micromeritics ASAP 2020 apparatus at 77 K. The samples were pretreated in situ under vacuum at 573 K. Their surface area was calculated by the BET method. The volume of mesopores was determined from BJH, whereas the micropore surface area and micropore volume were determined by the t-plot method.

#### 2.4.3. X-ray fluorescence (XRF)

X-ray fluorescence using MiniPal-Philips instrument was applied to determine the real molar ratio of Si/Nb in materials prepared. The calculations were performed using calibration curve based on reference

mixtures of silica and metal oxide Nb<sub>2</sub>O<sub>5</sub>. The calibration curve consisted of 10 points related to different Si/Nb molar ratio in the range from 3 to 300. The metal concentration in a given sample was established by the amount of emitted X-ray radiation related to the values in the calibration curves.

#### 2.4.4. UV–vis spectroscopy

UV–vis spectra were recorded on a Varian-Cary 300 Scan UV–visible spectrophotometer with an integrated sphere CA-30I. The solids, dehydrated at 673 K for 2 h, in the form of powders were placed into a cell equipped with a quartz window. The Kubelka-Munk function (F(R)) was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of SPECTRALON as a reference.

#### 2.4.5. FTIR spectroscopy

Infrared spectra were recorded with a Bruker Vector 22 FTIR spectrometer. The 1 mg of sample was mixed with 200 mg of KBr. 70 mg of this mixture was used to prepare a pellet for measurement.

### 2.5. Cyclization and dehydration of 2,5-hexanedione

The catalysts were tested in 2,5-hexanedione (2,5-HDN) dehydration and cyclization as the probe reaction. A tubular, down-flow reactor ( $\varnothing$  8 mm; length 80 mm) was used for 2,5-HDN cyclization that was carried out at atmospheric pressure, using nitrogen as the carrier gas. The catalyst bed (0.05 g, 2 mm height in the reactor) was first activated for 2 h at 673 K (heating rate 15 K min<sup>-1</sup>) under nitrogen flow (40 cm<sup>3</sup> min<sup>-1</sup>). Subsequently, a 0.5 cm<sup>3</sup> of 2,5-hexanedione was passed continuously into the catalyst at 623 K. The substrate was delivered with a pump system (KD Scientific) and vaporized before being passed through the catalyst with the flow of nitrogen carrier gas (40 cm<sup>3</sup> min<sup>-1</sup>). The reaction products were collected for 30 min downstream of the reactor in a cold trap (liquid nitrogen + 2-propanol) and analyzed by gas chromatography (SRI 310C, DB-1 column 30 m, temperature of column 373 K) with TCD detector. Helium was applied as a carrier gas.

## 3. Results and discussion

Two series of calcium containing materials were prepared. The first group was obtained using calcium acetate monohydrate as Ca precursor and is denoted as (A20) or (A40) depending on the metal content (wt %), e.g. Ca(A20)/SBA-15. The second group was based on calcium nitrate tetrahydrate and is labelled as (N20) or (N40) according to the Ca content. Moreover, two supports, i.e. SBA-15 and NbSBA-15 were chosen for investigation. The application of the latter was aimed at improving the structure of final material.

### 3.1. Texture/structure characterization

The X-ray diffraction patterns of both supports, i.e. SBA-15 and NbSBA-15 are presented in Fig. 1. They are typical of mesoporous materials with hexagonally ordered pores regular in size. The presence of peak at 2 theta ca. 0.99° and 0.93° for SBA-15 and NbSBA-15, respectively, is related to (100) and assigned to regular in size channels. The position of this peak is related to the distance between the material walls. Thus it can be associated with pore diameter. A lower value of (100) recorded for NbSBA-15 points out that the pores in this material are a little bit wider. The next two peaks in the ranges 1.55°–1.65° and 1.80°–1.90° are assigned to the regular arrangement of channels inside the support thus can verify the level of pore ordering. The impregnation of SBA-15 and NbSBA-15 with both calcium acetate monohydrate and calcium nitrate tetrahydrate (20 wt% of Ca) leads to a decrease in the peak intensity at ca. 1° and a shift of this peak to higher values of 2 theta. The later phenomenon is typical of impregnated mesoporous samples and should be related to the coating of channels with a new

Download English Version:

<https://daneshyari.com/en/article/5441763>

Download Persian Version:

<https://daneshyari.com/article/5441763>

[Daneshyari.com](https://daneshyari.com)