



# The effect of structure of mesoporous silica and niobiosilicate on incorporation and stability of modifiers introduced by the click reaction catalyzed by different copper salts



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## ABSTRACT

The study was aimed at comparison of the stability and effectiveness of anchoring of the amine and sulfonic groups formed on mesoporous silica by the click reaction. The impact of silica dopant (niobium) and the structure of mesoporous silica (hexagonally ordered SBA-15 vs cellular foam MCF) on the properties and behavior of these surface groups was characterized in details. The modifiers stability was found to have a significant effect on the catalytic reactions in liquid phase. In order to increase the catalysts stability, the mesoporous silica and niobiosilicate were used as supports for ((3-azidopropyl)(triethoxy)silane) – AZPTES followed by the condensation with propargylamine or propargylsulfone by the click reaction performed in the presence of different copper salts used as catalysts of the process. The number of copper ions left in the material after the click reaction was also estimated.

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## 1. Introduction

Click chemistry is a relatively new approach to modification of solids with large molecules by joining two smaller units together in the presence of copper catalyst [1–4]. The reaction invented by K. Barry Sharpless in 2001 is easy to perform, occurs rapidly, does not require additional solvents and has high yields in reaction products, which could be simply isolated from reaction media [4]. One of the commonly used click reactions over Cu(I) catalyst is the 1,3-dipolar cycloaddition between azides and terminal alkynes (CuAAC – copper-catalyzed azide-alkyne cycloaddition) towards the formation of 1,4-triazole. Modification of solid samples by this technique requires a stepwise strategy in which azide or alkyl species have to be anchored previously to a support and then the immobilized species may react together with the suitable moieties to form an appropriate final molecule in the presence of copper catalyst. Several Cu catalysts have been tested in click reaction; CuI seems to be the most efficient. Other frequently used catalysts include  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ , in the presence of sodium ascorbate as a reductive agent of  $\text{Cu}^{2+}$ , CuOAc and  $\text{Cu}_2\text{O}$  [2,5–8].

Until now the click reactions have been widely applied for the synthesis of suitable triazoles, modification of peptide, DNA or pharmaceuticals, in supramolecular chemistry or nanotechnology and in dendrimer and polymer design. The supports used for immobilization of sophisticated molecules i.e. enzymes, drugs, polymers, monosaccharide or stationary phase for HPLC column, were different types of silicas such as SBA-15 or MCF, which have silanol groups available for anchoring the proper intermediate molecules [1,9–12].

Papers on the click reaction are mostly focused on the immobilization of large molecules on the support, verification of the success of this process as well as its efficiency [1,9–11]. The stability of immobilized molecules as well as the role of mesoporous silica structure and silica dopants have not been studied to the best of our knowledge. These features are very important in the context of possible applications of the aforementioned materials in catalysis and in pharmaceutical industry for the release of chemicals from mesoporous silicas. Therefore, the idea of this work was to improve the stability of amine and sulfonic species introduced into mesoporous silicas by the click chemistry method and to characterize the surface properties of modifiers anchored and their dependence on silica dopant and the structure of mesoporous material. For this purpose besides SBA-15, a material with cylindrical pores of

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6–12 nm, we used mesoporous cellular foam built of large spherical cells (24–40 nm) connected via windows (>10 nm) [13] as the supports for two kinds of propargyl modifier introduced into the porous material by the click chemistry method, i.e. propargylamine and propargylsulfone. The results of our previous study have clearly shown that niobium species incorporated into a silica support influenced the morphology of materials and their surface properties. It has been proven that in some cases niobium present in a silica matrix led to an increase in the efficiency of the modifier (e.g. imidazole) anchoring [14]. Moreover, niobium increased the stability of anchored active organic species such as organosilanes [15,16]. The niobiosilicates modified by organosilanes were also more stable in liquid phase catalytic reactions (e.g. esterification of acetic acid with glycerol [16]) reused several times without leaching of the modifier. Furthermore, niobium could increase the strength of active sites such as  $\text{HSO}_3$  groups by lengthening of O-H bonds, which makes proton extraction easier [16]. Such behavior of niobiosilicates modified by organosilanes prompted us to modify SBA-15 and MCF samples with niobium before introduction of an active phase via the click chemistry method. Such a methodology allowed us to verify the effect of Nb dopant on the efficiency of modifier inclusion and its stability.

## 2. Experimental section

### 2.1. Materials synthesis

The syntheses of SBA-15 and MCF supports were performed according to the procedure described in Ref. [13]. This route is described in details in the [Supporting Data \(S1\)](#).

The preparation of niobiosilicates, i.e. NbMCF and NbSBA-15 was modified by introducing a niobium source 10 min after TEOS addition to the synthesis gel. The niobium sources were:  $\text{Nb}(\text{OEt})_5$  (Aldrich) for MCF and ammonium niobate(V) oxalate hydrate (Aldrich) for SBA-15. The nominal Si/Nb molar ratio was 30. In NbMCF the P123/TMB weight ratio was 0.5 (P123 – Pluronic P123; TMB – 1,3,5-trimethylbenzene).

The obtained silicas and niobium doped silicas were modified with AZPTES – Az((3-azidopropyl)(triethoxy)silane) by the post-synthesis method described below. Three grams of solid sample (first dried overnight at 373 K) and 100  $\text{cm}^3$  of toluene were put together in a flask. AZPTES (1.24 g) was immersed in the solution and the mixture was stirred at 353 K for 24 h. The resulting powder was recovered by filtration, washed with 150  $\text{cm}^3$  of toluene and dried at RT.

The amine modified samples were synthesized using several procedures. In the first of them 1.5 g of azide modified sample (first dried overnight at 373 K) was added to a flask together with 50  $\text{cm}^3$  of toluene, CuI (0.235 g) (Aldrich) and propargylamine (0.825 g) (Aldrich). The mixture was kept under stirring at 318 K for 26 h. After that time the modified sample was filtered, washed with hot water (300  $\text{cm}^3$ ), acetone (150  $\text{cm}^3$ ), methanol (50  $\text{cm}^3$ ) and THF (250  $\text{cm}^3$ ) [9]. The obtained material was brown after drying at RT. The samples obtained by this method were denoted by (CuI) in the symbol.

In another procedure 1.00 g of Az/SBA-15 dried overnight at 373 K was mixed together with  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$  (0.025 g) (Aldrich) or  $\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$  (0.024 g) (Aldrich), propargylamine (0.55 g), THF (7  $\text{cm}^3$ ), distilled water (14  $\text{cm}^3$ ) and ethanol (14  $\text{cm}^3$ ). The solution was stirred at 333 K for 24 h. Then acetone (115  $\text{cm}^3$ ) was added to the cooled mixture. Afterwards, the solution was filtered, and the filter cake was washed with distilled water (200  $\text{cm}^3$ ) and acetone (115  $\text{cm}^3$ ) and finally dried in air at RT. The samples obtained by this method were denoted by ( $\text{CuSO}_4$ ) or ( $\text{Cu}(\text{NO}_3)_2$ ) in the symbol of material, depending on the copper salt used.

In the next procedure, 0.2 g of Az/SBA-15 dried overnight at 373 K was added to a flask together with  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$  (0.005 g),

sodium ascorbate (0.005 g) (Aldrich), propargylamine (0.042  $\text{cm}^3$ ), THF (1.4  $\text{cm}^3$ ), ethanol (2.8  $\text{cm}^3$ ) and distilled water (2.8  $\text{cm}^3$ ). The mixture was stirred at 333 K for 24 h. Then 23  $\text{cm}^3$  of acetone were added to the cooled down mixture. The obtained solution was filtered and the filter cake was washed with 23  $\text{cm}^3$  of acetone. The product was dried at RT.

The modification with propargylsulfone was performed as follows. First, the sulfone modifier was synthesized according to the modified procedure described in Ref. [17]. The difference was the prolongation of the time of reaction media mixing to 24 h. Moreover, the cooled mixture was stirred for additional 24 h and then placed in a fridge in order to increase the efficiency of crystallization of propargylsulfone modifier. The obtained sulfone was placed in a flask together with 1.00 g of AZPTES modified sample (first dried overnight at 373 K),  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$  (Aldrich), sodium ascorbate (Aldrich), THF, distilled water and ethanol. The reaction mixture was stirred at 333 K for 24 h. Then acetone was added to the cooled mixture. Afterwards the solution was filtered and the filter cake was washed with two portions of acetone (the total amount of acetone was the same as the amount added to the cooled mixture) and dried in air at RT. The reactants used for sample modification depended on the nitrogen amount detected by elemental analysis of AZPTES modified silica or niobium doped silica. For 1 mmol of N incorporated into the 1.00 g of sample the amounts of reactants used were as follows: 0.418 g of sulfone modifier, 0.058 g of  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ , 0.56 g of sodium ascorbate, 7  $\text{cm}^3$  of THF, 14  $\text{cm}^3$  of EtOH, 14  $\text{cm}^3$  of water, 117  $\text{cm}^3$  of acetone.

### 2.2. Characterization of materials

The obtained samples, i.e. mesoporous supports, materials after AZPTES modification and click reaction, were examined by several analytical techniques such as:  $\text{N}_2$  adsorption/desorption, XRD, elemental analysis, ICP-OES, SXF, XPS, FT-IR, DTA/TG,  $^{13}\text{C}$  MAS NMR and UV-Vis. These techniques are precisely described in Refs. [14,18,19] and in the [Supporting Data \(S2\)](#).

In order to reduce the copper content in samples obtained, MCF and NbMCF modified with 1,2,3-triazol-4-ylmethanamine, were treated with ethylenediaminetetraacetic acid - EDTA (Aldrich) solution. At first, 100 mg of solid sample was placed in a flask together with 20  $\text{cm}^3$  of EDTA solution (50 mg of EDTA was dissolved first in 200  $\text{cm}^3$  of distilled water). Then, the mixture was stirred for 1 h at RT (room temperature). After that, the solid was removed from the mixture by filtration and dried at RT. The obtained dried sample was then prepared for ICP-OES analysis according to the procedure described in [Supporting Data \(S2\)](#).

In order to verify the interaction of copper species with Nb-OH groups in niobiosilicates, the NbMCF sample was treated with CuI in 50  $\text{cm}^3$  of toluene solution for 26 h at 318 K. After that, the solid was removed from the mixture by filtration, washed with 100  $\text{cm}^3$  of toluene and dry at 373 K for 12 h. The experiments of pyridine adsorption combined with FTIR measurements on NbMCF before and after treating with CuI were then performed.

## 3. Results and discussion

Two mesoporous silicas, hexagonally arranged SBA-15 and mesoporous cellular foam MCF, were doped with niobium using a one-pot synthesis method. The samples obtained were functionalized with ((3-azidopropyl)(triethoxy)silane - AZPTES) in which azide species were used as functional groups for both amine or sulfone modifiers anchored by the click reaction. In the click reaction the presence of copper species (as a catalyst) is required for joining azide groups with alkyl ones. As a result of this process a five-membered ring is formed. In our study, the SBA-15-type materials modified

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