Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)

METAL-ORGANIC HYBRIDS OBTAINED BY FUNCTIONALIZATION OF MESOPOROUS SILICA

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Ordered mesoporous silica materials (MS) were modified with n-propyl-salicylaldimine and acetylacetone by two-steps post-synthesis method. The results were compared with those of amorphous silica gel functionalized by the same procedure. These materials were tested for their metal (Cu, Co, and Mn) adsorption capacity in order to obtain the efficient oxidation catalyst based on the metal complex covalently bonded on modified mesoporous silica. The MS material was synthesized by direct synthesis using a triblock copolymer, Pluronic P123, as a structure directing agent. The MS support and functionalized materials exhibited the structure (XRD patterns and N_2 adsorption-desorption isotherms) and morphology (SEM images) characteristics of the ordered mesoporous sieves. The functional groups grafted on the support surface were identified by FTIR spectra and their amounts by elemental analysis and ATG measurements. The obtained hybrids presented the high adsorption capacity for Cu and Co cations and the very weak adsorption capacity for Mn cations. The obtained metal-organic hybrids were tested in oxidation of cyclohexene with hydrogen peroxide.

INTRODUCTION

Since the discovery of ordered mesoporous silica a variety of ordered mesoporous materials have been synthesized under a wide range of pHs using cationic, anionic, nonionic surfactants[1-4]. In view of the extensive applications as molecular sieves, catalysts, adsorbents and sensors, the production of novel structures and novel synthesis procedures for them were developed. Many research efforts have focused on functionalization of organic groups onto the surface of the mesoporous silica materials by direct incorporation of organic groups through co-condensation of siloxane and organosiloxane precursors or by grafting (post-synthesis reaction) the organic groups onto the surface of the mesoporous silica[5-8].

Well-ordered mesoporous silica materials with larger pore size and better stability in comparison with the M41S mesoporous materials were synthesized by employing of commercially available nonionic poly (ethylene oxide-propylene oxide-ethylene oxide) (EOn–POm–EOn) triblock copolymer in acidic conditions. These novel mesoporous materials denote SBA-n silicas, exhibit two or three-dimensional hexagonal or cubic pore architectures[5-8]. However, SBA-n silicas limit its practical application especially in catalysis owing to the lack of active sites on the wall. Therefore, efforts have been made on the surface modification in order to increase its catalytic potential. The introduction of heteroatoms into the framework is one of the most effective ways to realize catalytic activity. Direct-synthesis and post

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synthesis grafting are two typical methods that have been practiced for the introduction of heteroatoms. The direct-synthesis method [9-12] involved the addition of metal precursors to the synthesis gel before hydrothermal treatment. The incorporation of transition metals such as Co and Mn into the framework of SBA-n silicas has not been successful because of the strongly acidic synthesis conditions. In the post-synthesis method the heteroatom is grafted as a metal complex through covalent bonding of ligands to the inorganic support [13-16]. Herein, we present the results on synthesis, characterization and properties of mesoporous silica modified with n-propylsalicylaldimine and acetylacetone by the two-steps post-synthesis method. The metal (Cu, Co, and Mn) adsorption capacity of functionalized mesoporous support (MS) was evaluated, by AAS, in order to obtain catalysts for oxidation reactions in liquid phase. The results are compared with those of amorphous silica functionalized by the same procedure. The synthesized materials were characterized by XRD, N_2 adsorption-desorption, FTIR, TEM and SEM techniques. The obtained metal-organic hybrid materials were tested, as catalysts, in oxidation with hydrogen peroxide of cyclohexene.

RESULTS

Various techniques were used in order to evaluate the physicochemical characteristics of solids. As, XRD patterns of the NH_2-MS and SA-MS exhibits XRD reflections similar to that of the SBA-16 mesoporous molecular sieves (Fig. 1). Morphology and porous structure of mesoporous support are presented in Figures 2.
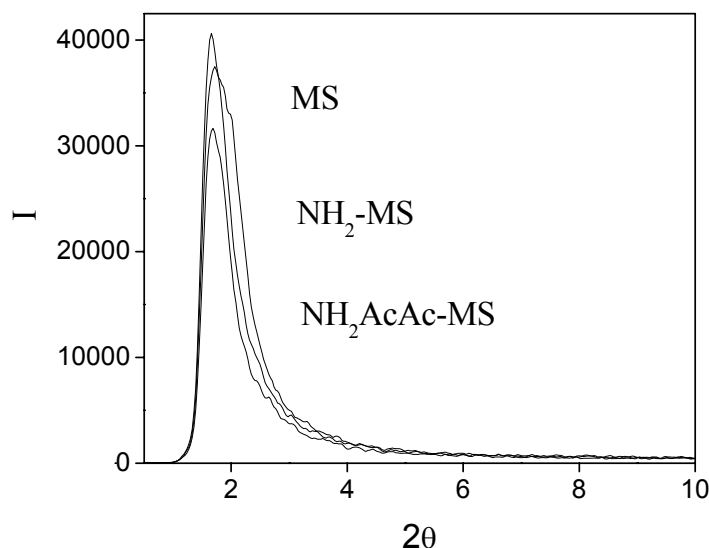

Fig. 1 – Powder X-ray diffraction patterns of calcined mesoporous silica materials.
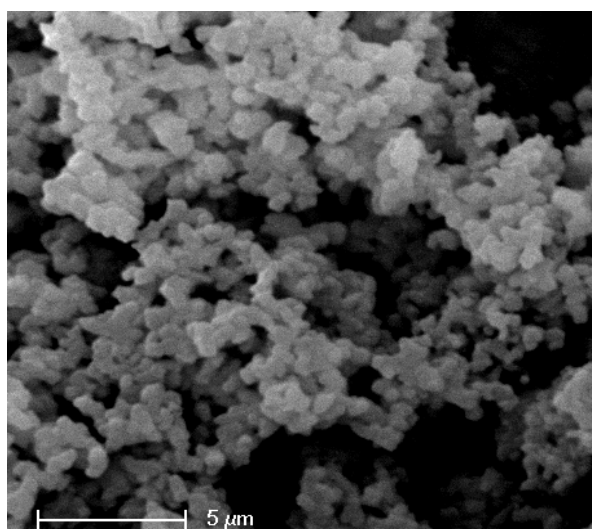

Fig. 2 – SEM image of MS sample.

The amounts of the functional groups grafted on the MS surface have been calculated on the basis of elemental analysis and DTG measurements as shown in Table 1.

Nitrogen adsorption-desorption isotherms for the studied samples are shown in Figure 3 and the main textural properties of solids are listed in Table 2.

The functional groups contained in the organic-inorganic hybrid materials were identified by FTIR.

Figure 4 shows FTIR spectra of pure MS, NH$_2$-MS, SA-MS and AcAc-MS samples.

The metal loading capacities of silica supports, obtained by atomic absorption spectrometry are listed in Table 3.

Contribution of the function groups to adsorption of metal cations are presented in Table 4.

The catalytic activity of metal-organic hybrids in oxidation of cyclohexene with hydrogen peroxide is evidenced in Fig. 5.

Table 1

Chemical composition of the functionalized organic entities grafted on SBA-16 and Silica-gel

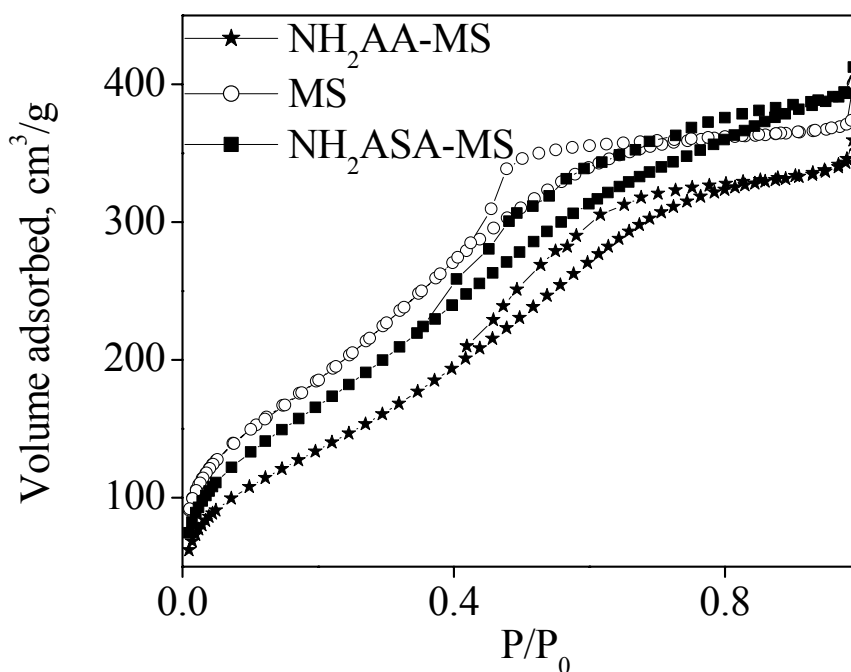| Solid	Aminopropyl group mmol g^{-1} SiO$_2$/ molecules nm^{-2}	Salycilaldehyde mmol g^{-1} SiO$_2$ / molecules nm^{-2}	Acetylacetone mmol g^{-1} SiO$_2$ / molecules nm^{-2}
MS (SBA-16)	1.38 / 1.6	1.36 / 1.58	1.32/1.53
silica	1.78 / 2.02	0.88 / 1.58	0.80 / 1.43

Fig. 3 – N$_2$ adsorption-desorption isotherms for MS materials.

Table 2

Textural properties of calcined and modified SBA-16[a]

Material	S$_{BET}$/m^{2}g^{-1}	Vp/ml g^{-1}	d$_p$/ nm
MS (SBA-16)	702	0.94	4.5
NH$_2$-MS	659	0.77	4.0
SA- MS	486	0.58	3.5
AcAc-MS	534	0.68	3.8

[a]S$_{BET}$, specific surface area; V$_p$, pore volume; d$_p$, pore diameter
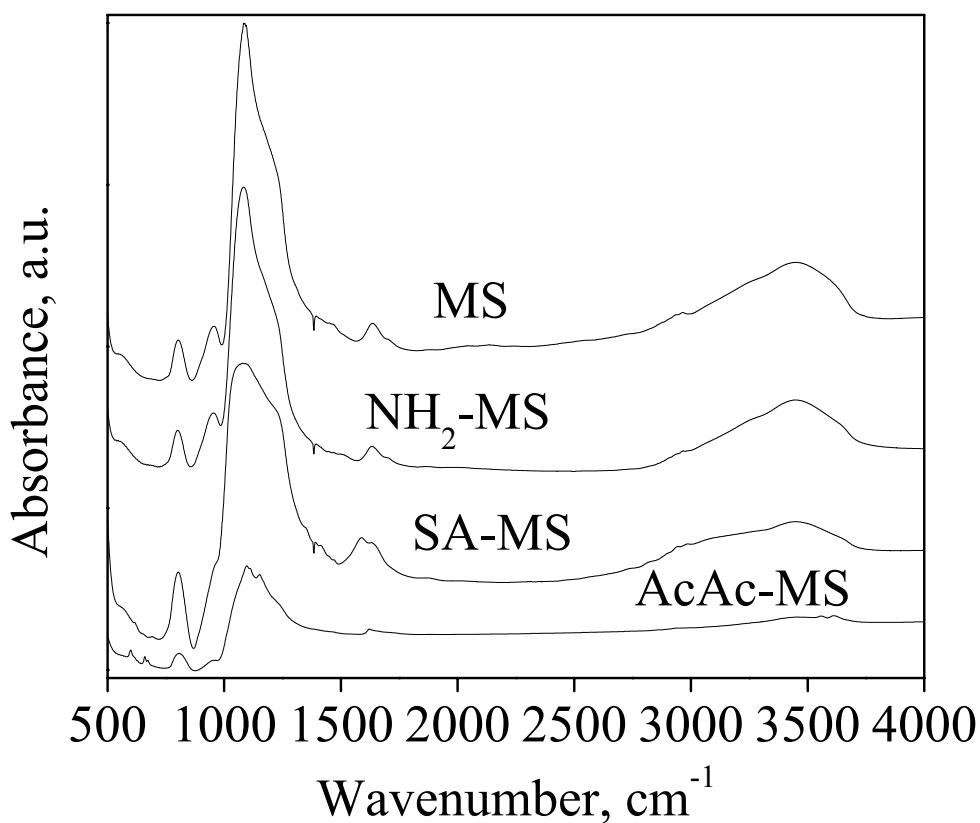
Fig. 4 – FTIR spectra of the mesoporous silica materials.

Table 3

Metal Ion-Loading Capacities of SBA-16 and silica type adsorbents

Solid	Cu (II), mg/g	Co (II), mg/g	Mn (II), mg/g
MS (SBA-16)	5.4	1.6	0.6
NH₂-MS	58.0	16.0	5.6
SA -MS	15.2	4.5	1.5
AcAc-MS	10.5	3.6	0.1
NH₂-SG	45.2	11.2	4.9
SA-SG	10.2	3.6	2.0
AcAc-SG	4.2	1.2	0.1

Table 4

Contribution of the function groups to adsorption of metal cations

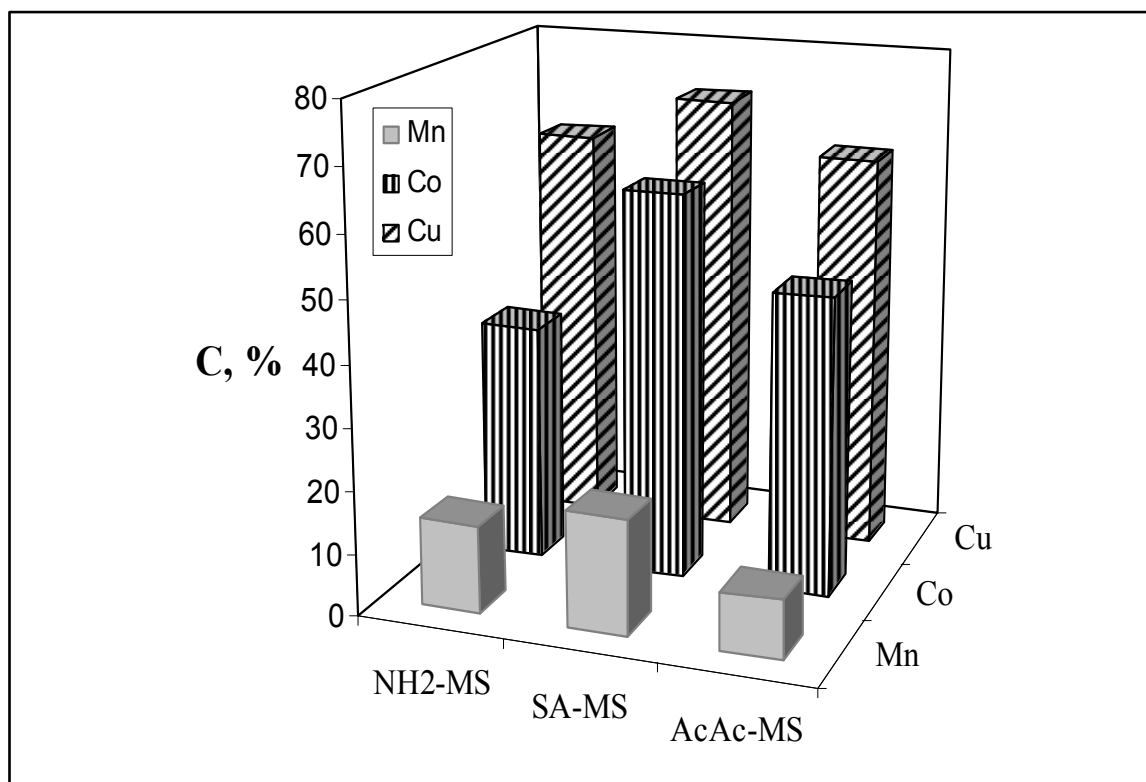| Solid	Cu(II)	Co(II)	Mn(II)
NH₂-SBA-16	100	44.1	12.2
SiO2-NH₂	100	31.8	8.6

Fig. 5 – Results of catalytic tests obtained for Cu and Co catalysts in oxidation of cyclohexene with hydrogen peroxide.

DISCUSSION

The (100) diffraction peaks are characteristic for mesoporous SBA-16 silica with cubic symmetry of structure. These results (Fig.1) also indicate the maintenance of the structural orderness of the solids throughout the treatment of functionalization. The cell parameter calculated from the d_{100} spacing value of SBA-16 was 12 nm. The morphology of these materials, illustrated by SEM images, is the characteristic of mesoporous molecular sieves like SBA-16 (Fig.2). For all obtained samples SEM images show small globular particles of around 1 μm in diameter.

The silanol groups of the SBA-16 mesoporous silica were functionalized by two-step post-synthesis modification with 3-aminopropyltriethoxysilane and salicylaldehyde, or 3-bromo-2,4-pentanedione, respectively (Scheme 1).

MS and modified MS materials featured the irreversible type IV isotherms with a H1 hysteresis loop with a desorption step at P/P_0=0.5, as the characteristic of materials with 3.5-4.5 nm pore diameter (Fig.3). For the functionalized SBA-16 materials the surface and the volume have been standardized versus pure silica weights. We can observe that the surface area and the mesopore volume as well as the pore size decreased with the extent of functional groups attached. For example, for the aminopropyl functionalized mesoporous silica (NH$_2$-MS), the surface area and the mesopore volume were diminished with 45 % and 5.4 %, respectively, comparatively with the SBA-16 support. This is consistent with the location of the grafted species inside the mesopores.

FTIR spectrum of MS support shows typical bands around 3500 cm^{-1} due to the presence of silanol groups (Fig. 4). After the functionalization with aminopropyl groups, the intensity of silanol groups significantly decreases with the concomitant increase of bands characteristics for the immobilized aminopropyl groups (NH$_2$-SBA-16 spectrum). These bands were attributed to both the symmetric and asymmetric stretching of CH$_3$ and CH$_2$ groups ($\nu_{as}(CH_3) = 2975$ cm^{-1}, $\nu_{as}(CH_2) = 2928$ cm^{-1}, $\nu_s(CH_3) = 2886$ cm^{-1}, and $\nu_s(CH_2) = 2870$ cm^{-1}) and those of NH$_2$ ($\nu_{as}= 3450$ cm^{-1}, and $\nu_s= 3400$ cm^{-1}). The IR spectrum of SA-MS present the vibration bands characteristic to C=N (1650 cm^{-1}) and C-O (1250 cm^{-1}) groups, which confirm the covalent grafting of the Schiff base.
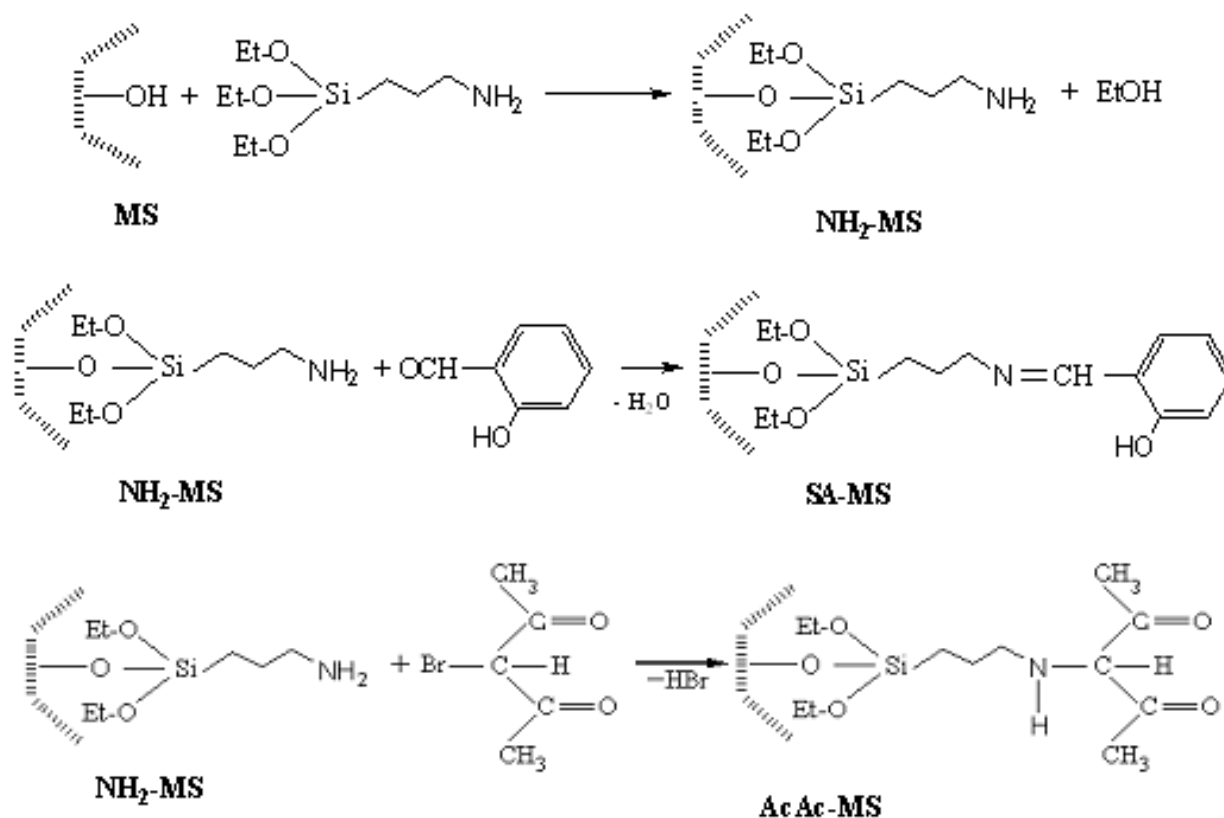
Scheme 1 – Schematic functionalizations of SBA-16 silanol groups.

FTIR spectra of AcAc-MS show, with respect to the parent materials, some changes in the region where vibration from APTES occur, i.e., in the 3500-3000 cm^{-1} region due to the N-H streching vibrations, and in the 1700-1300 cm^{-1} weak absorption region due to the H-N-H and H-C-H bending vibration, suggesting that some molecular changes in the spacer took place. On the other hand, after the acetylacetone grafting in the spectrum appear another band at about 1560 cm^{-1} assignable to the vibration of the acetylacetonate ring.[17]

The metal–organic hybrids were obtained by adsorption of the metal (Cu, Co, and Mn) cations on the modified MS supports. The adsorption capacities are very high for Cu and very lower for Mn cation (Table 3). For all cations a high adsorption was obtained for supports with NH$_2$ functions. The order of activities for the function groups is NH$_2$ >SA>AcAc. Contribution of the NH$_2$ groups is very high for Cu cations and higher for SBA-16 support (Table 4). These results evidence a different affinity of the metals on the NH$_2$, SA, AcAc ligands and formation of complexes.

All the tested solids present very weak manganese adsorption capacity. Only the silicas functionalised with 3-aminopropyltriethoxysilane possesses the grater adsorption capacity; for instance, for NH$_2$-MS, 6.52 % of the amino group participate to the Mn(II) complexation, comparatively with 2.04 % salycilaldimine groups for SA-MS. The silicas functionalised with 3-bromo-2,4-pentane dione practically has not adsorption for the manganese ions.

The catalytic tests (Fig. 5) evidence the influence of ligands on oxidation of cyclohexene with hydrogen peroxide. The best conversion was obtained with Cu-SA-MS catalyst. Though the adsorption capacity of Cu on SA-MS is lower than NH$_2$MS, effect of ligand is more favorable to catalytic activity. A similarly effect was evidence for materials with Co. The catalytic performance of hybrids with Mn is result of very low capacity of metal adsorption on all the supports. A significantly effect of ligands on selectivity was evidenced for Cu and Co catalysts. A very high percent of diol was obtained for Cu NH$_2$-MS. All the results sustain the favorable effect of the ordered mesoporous structure and functionalization of silica surface on adsorption capacity and catalytic activity. The lower catalytic performances were obtained with amorphous commercial silica. The adsorption capacity and catalytic performances are

results of the metal complexes formation on functionalized support. The electronic changes of the metal after formation of the complexes explain the catalytic activity and adsorption capacity.

EXPERIMENTAL

Preparation of the functionalized silica support

The mesoporous silica support (MS) was synthesized according to the procedure described in the literature.[1] Thus, 1.5 g of amphiphilic triblock copolymer (Pluronic P123, EO_{20}-PO_{70}-EO_{20}, average molecular weight 5800, BASF) was dispersed in 15 g of H_2O and 45 g of HCl 2 M with stirring at 313 K for 4 hours. 3.15 g of tetraethylorthosilicate (TEOS, 98 % Aldrich) was added in the obtained homogeneous solution. The molar gel composition was 1.0 TEOS/ 0.017 P123/5.8 HCl/210 H_2O. The gel was stirred at 313 K for 24 hours and then hydro thermally treated in a Teflon-lined autoclave at 373 K for 2 days. The resulting solid was centrifuged, filtered, washed with deionized water, and dried in air at room temperature. The calcination of the as-synthesized MS was performed at 823 K during 8 hours under air flow.

Grafting the silica surface by covalently attaching aminopropyl functional groups proceeds via a reaction between the silanol groups of the MS surface and 3-aminopropyltriethoxysilane (APTES). The reaction was carried out in dry toluene, according to the procedure proposed by Brunel et al.[7]. MS (1 g), freshly activated overnight at 453 K under vacuum, and 1 mL of APTES (99 % Aldrich) were added to 50 mL of dry toluene. After stirring the solution at reflux of toluene for 2 hours, the ethanol released was distilled off and the mixture was kept under reflux for 90 min. The NH_2-functionalized mesoporous silica (referred as NH_2-MS) was filtered and washed with toluene, ethylic alcohol and then diethyl ether. It was then submitted to the continuous extraction run overnight in the Soxhlet apparatus using diethylether/dichloromethane (v/v, 1/1) at 373 K and dried overnight at 403 K.

The hybrid NH_2-MS (1 g), activated under vacuum at 403 K for 1 hour, was dispersed in dry toluene (50 mL) before adding 1 mL of salicylaldehyde. The mixture was refluxed at 398 K overnight and the obtained yellow solid (referred as SA-MS) was collected by filtration and washed with toluene, ethylic alcohol and then diethyl ether. The excess of salicylaldehyde was removed by the Soxhlet extraction using diethyleter/dichloromethane (v/v, 1/1). The obtained SA-MS was dried overnight at 313 K.

The hybrid NH_2-MS (1 g), activated under vacuum at 403 K for 1 hour, was dispersed in the mixture of THF (15 mL) and dry toluene (15 mL) before adding 1 mL of 3-bromo-2,4-pentane dione. The mixture was refluxed at 398 K for 8 hours and the obtained product (referred as AcAc-MS) was collected by filtration and washed with toluene, ethylic alcohol and then with diethyl ether. The obtained AcAc-MS was dried under vacuum overnight at room temperature.

Silica gel 60 (0.015-0.040 mm particle size, Merck) was used as a reference material. It's functionalization with 3-aminopropyl-triethoxysilane, salicylaldehyde and 3-bromo-2, 4-pentane dione was effectuated using the same procedure as described for MS. The two obtained materials will be referred as NH_2-SG, SA-SG, and AcAc-SG, respectively.

Metals Adsorption

Metal standard solution (1000 mg L^{-1}) was obtained from Merck and intermediate standard solutions were prepared by appropriate dilution. Metal ion solutions were prepared in high purity water obtained from a Millipore Milli-Q water purification system. For the pH adjustment at 4.0, a phthalate buffer solution was prepared and was used to prevent the precipitation of metal ions during the adsorption experiment. Adsorption experiments were carried out in batch conditions, by suspending 50 mg of adsorbent (MS, NH_2-MS SA-MS, AcAc-MS and NH_2-SG, SA-SG and AcAc-SG) in 10 mL of 4 mg/L metal solution. After equilibration under constant stirring for 24 hours, solid particles were filtered off and the remaining metal concentrations in the supernatant were determined quantitatively by atomic absorption spectrometry, to allow calculation of the amounts of adsorbed species on the solid phases by difference with respect to the starting concentrations.

Characterization

The solids were characterized by X-ray diffraction (XRD) (Bruker diffractometer using Cu Kα radiation), adsorption-desorption isotherm (Micromeritics ASAP 2010 instrument), scanning electron microscopy (SEM-Phylips), FTIR spectroscopy (Bruker Vector 22). Atomic adsorption spectroscopy (FAAS) measurements were performed on a Spectra AA-220 Varian spectrometer equipped with Varian multi-element hollow cathode lamps and air-acetylene burner. Thermogravimetric-differential thermal analysis (TG-DTA) was carried out in a Netzsch TG 209C thermobalance. About 15 mg of catalyst was loaded, and the airflow used was 50 cm^3 min^{-1}. The heating rate was 20 °C min^{-1} and the final temperature was 850 °C.

Catalytic experiments

Oxidation reactions were carried out at 303 K in a quartz mini reactor (5 ml) under stirring conditions and acetonitrile as solvent. Time of reactions was 12 h and the molar ratio of hydrocarbon/hydrogen peroxide was 1/1.8/3. After separation of the catalyst with a Millipore filter, the analyses of the oxidation products were performed using a DANI 1000 gas chromatograph, with capillary columns, connected to a FID detector.

CONCLUSIONS

In this present study, SBA-16 mesoporous silica materials were modified with n-propyl-salicylaldimine and acetylacetone by the two-steps post-synthesis method. The results were compared with those of amorphous silica gel functionalized by the same procedure. Silica mesoporous sieves with SBA-15 structure with amina, salycilaldimine and acetylacetone groups presented the high adsorption capacity for Cu and Co cations and the very weak adsorption capacity for Mn cations. The obtained Cu and Co catalysts are active in catalytic oxidation of cyclohexene with hydrogen peroxide. Effect of ligands on selectivity of Cu catalysts was evidenced.

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