Synthesis of SBA-15 mesoporous silica

A hexagonal (space group p6*mm*) material (SBA-15) was prepared using a poly (alkaline oxide) triblock copolymer surfactant in an acidic medium, according to the method of Zhao et al.[55]. Poly(ethylene glycol)-block-poly(propylene glycol)-block-polyethylene glycol) (4.00 g) was dissolved in water (30.00 g) and 2 M HCl (80.00 g) with stirring at 35 ºC. TEOS (8.80 g) was added to the homogeneous solution with stirring at room temperature for 20 h. The resulting solid product was filtered off, washed and air-dried at room temperature. The solid was calcinated in an atmosphere of air from room temperature to 500 ºC over 8 hours and heated at this temperature for 6 h.

55 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc*., 1998, **120**(24), 6024.

Preparation of functionalized mesoporous silica

MPY was covalently bonded to SBA-15 to give the mercaptopyrimidine-modified mesoporous silica (MPY-SBA-15) using the homogeneous method.

MPY (5.00 g, 44 mmol) was immersed in dimethylformamide (DMF) (50 mL). CPTS and triethylamine (TEA) were then added in a 1:2:1 stoichiometry (MPY:CPTS:TEA). The mixture was heated for 48 h at 115 ºC with magnetic stirring under a nitrogen atmosphere using standard Schlenk-tube techniques. The mixture was allowed to cool, the solvent was evaporated and the resulting product was extracted with hexane (2 × 30 mL). The hexane was evaporated and the excess CPTS was distilled under vacuum (150 ºC and 0.75 mm Hg). The resulting viscous oil (dark-orange colour, yield 96%) was characterized by ^{1}H NMR, ^{13}C NMR and IR

spectroscopy. The ^{1}H NMR spectra of the MPY derivative (See Fig. 1) contained signals corresponding to methylene 5 (a triplet centred at 3.16 ppm) and methylenes 3 and 4 (multiplets at 0.80 and 1.85 ppm, respectively). The signals due to the ethoxy groups were observed at 1.21 and 3.77 ppm. The sets of peaks found for protons of the MPY group appeared as triplets at 6.90 and as a doublet at 8.46 ppm, which can be attributed to the pendant alkyl chain, the ethoxy groups and the heterocycle. The ^{13}C NMR spectra of the MPY derivative (See Fig. 2) contained signals at 10.13, 22.93 and 33.91 ppm, which were assigned to the methylene groups 3, 4 and 5, respectively. The signal due to methylene 2 of the ethoxy group appeared at 58.42 ppm and the signal of the methyl group at 18.39 ppm. The carbon atoms of the heterocycle resonate at lower field: 116.17, 156.96 and 172.49 ppm. Infrared spectra (See Fig. 3) contained bands at ca. 2850 cm^{-1}, assigned to ν(C-H) stretching vibrations, and bands at ca. 1475 and 1600 cm^{-1}, which correspond, respectively, to ν(C=C) and ν(C=N) in the heterocycle.

The MPY derivative (5.00 g) was reacted with activated SBA-15 (5.00 g) (5 hours at 160 ºC under high vacuum) in dry toluene (50 mL) with mechanical stirring (48 hours under reflux conditions under a nitrogen atmosphere). The resulting modified mesoporous silica (MPY-SBA-15) was filtered off and washed with toluene (2 × 30 mL), ethanol (2 × 30 mL) and diethyl ether (2 × 30 mL). Finally, the product was heated for 4 hours at 110 ºC under vacuum.

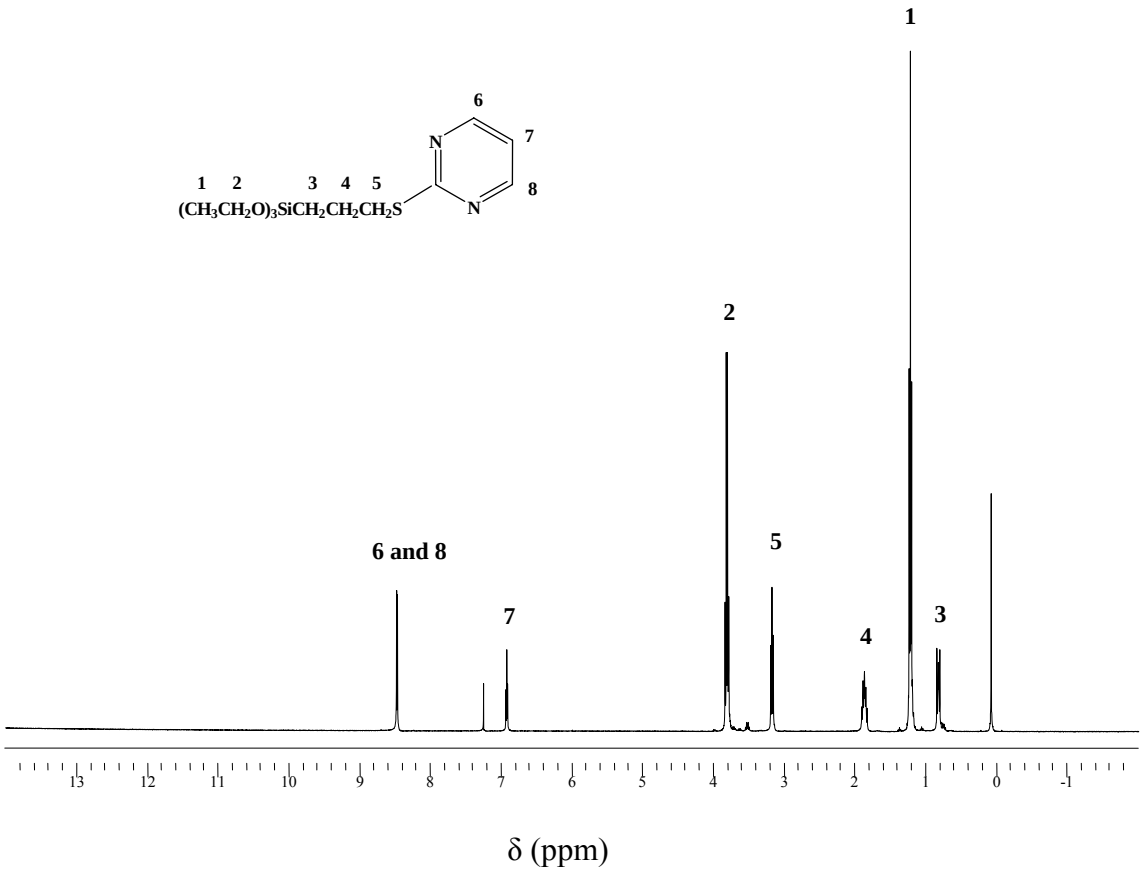

Fig. 1 ^{1}H NMR spectrum of mercaptopyrimidine derivative in deuterate chloroform.

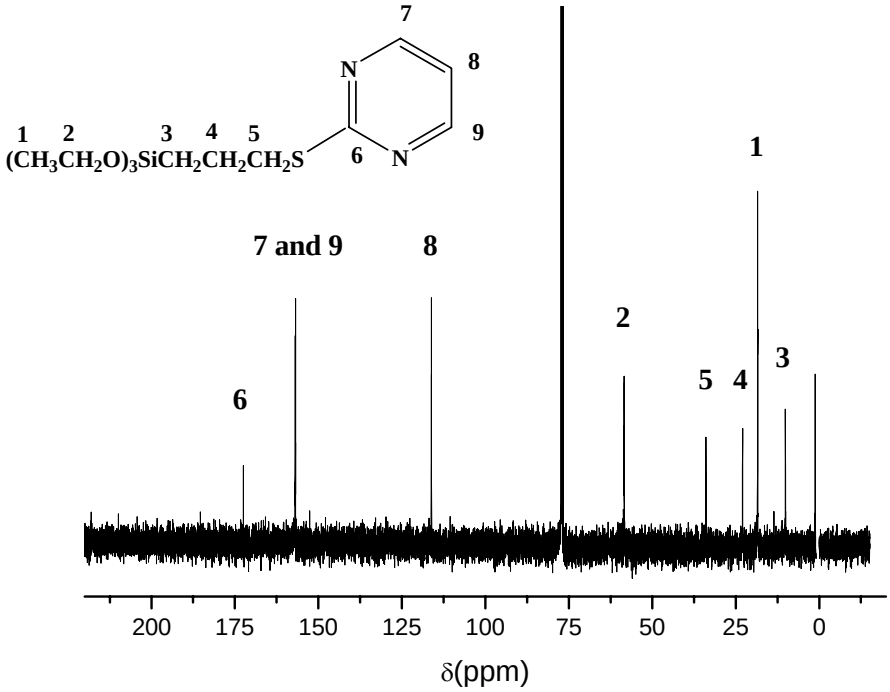

Fig. 2 ^{13}C NMR spectrum of mercaptopyrimidine derivative in deuterate chloroform.

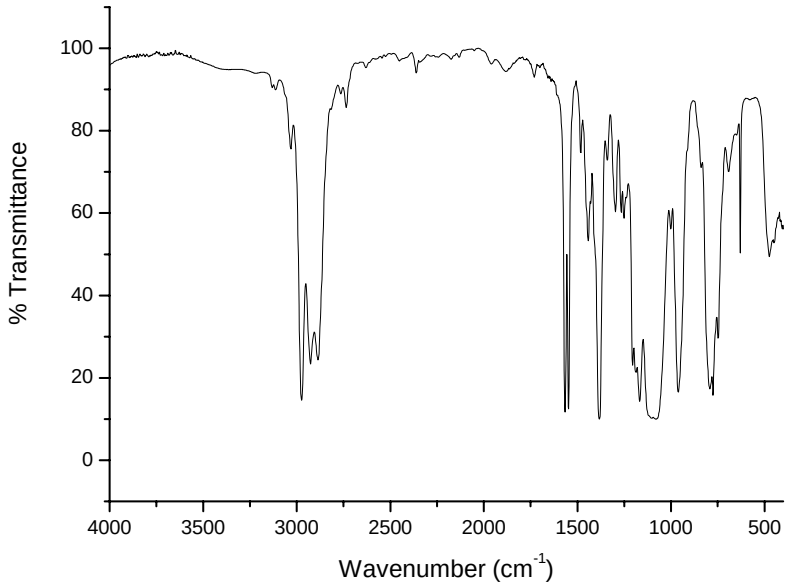

Fig. 3 FTIR spectrum of mercaptopyrimidine derivative.