**Electronic supplementary materials** *Mendeleev Commun.*, 2022, **32**, 478–481

# Copper-containing polymethylsilsesquioxane nanocomposites in catalytic olefination reaction

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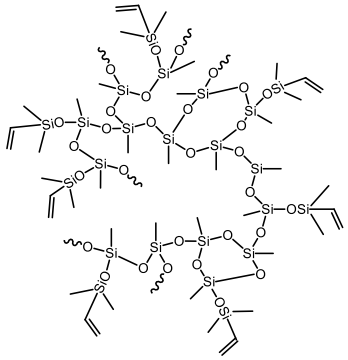

**Figure S1** 'Core-shell' structured polymethylsilsesquioxane with coordinately active vinyl-groups forming the surface of the polymer's molecular structure (PMSSO-VDMS) .

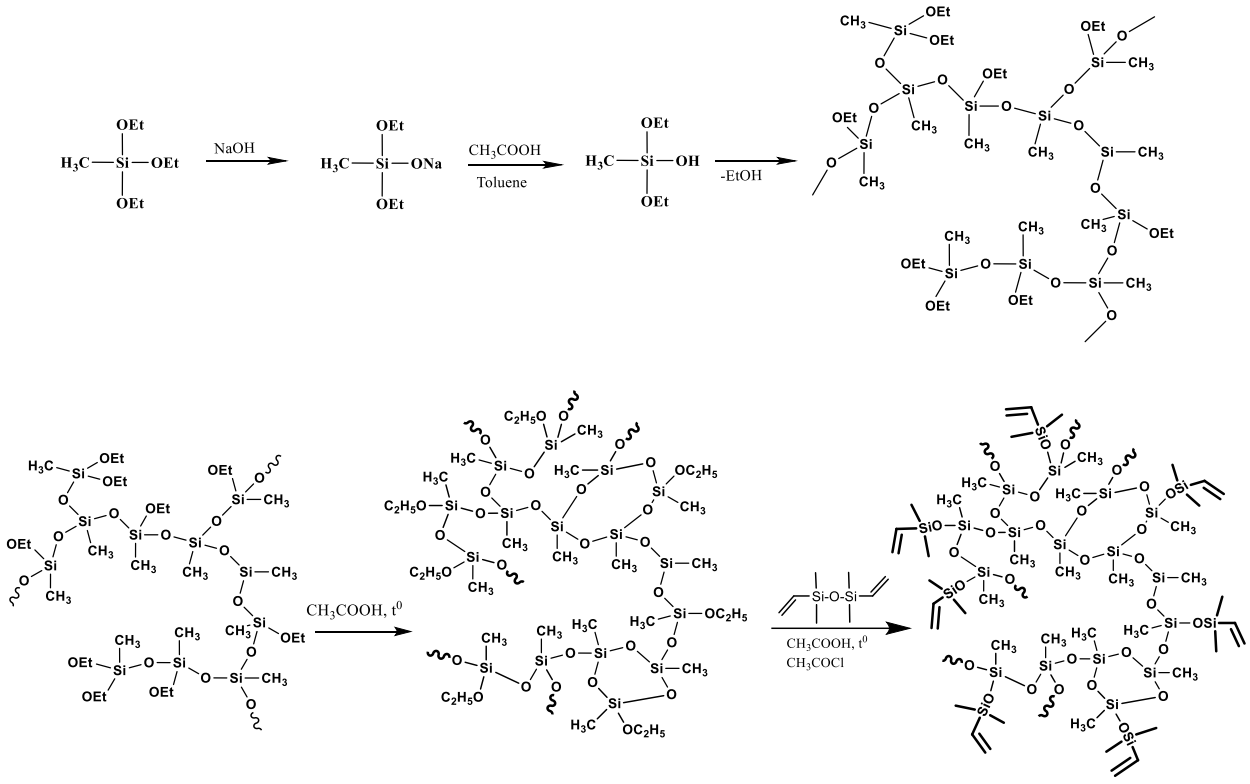


**Figure S2** Two stage synthetic scheme for polymethylsilsesquioxane nanogel blocked with vinyl-dimethylsiloxy groups (PMSSO-VDMS).

## Experimental + Support

### Materials

Microgranulated sodium hydroxide (CHEMMED [chemically pure]), acetyl chloride (98%, Acros), hexane (CHEMMED [chemically pure]), toluene (KHIMMED [chemically pure]), and pyridine (KHIMMED [chemically pure]) were dried by distillation over $CaH_2$. Methyltriethoxysilane (MTEOS), tetramethyldivinyl-disiloxane (TMDVDS) (Sigma-Aldrich) were distilled prior to use. Acetic acid (Sigma-Aldrich) prior to use was dried by distillation over $P_2O_5$.

### Methods

$^1$H NMR spectra were taken with the Bruker AC -250 (250.13 MHz) (Germany). Chemical shifts are reported in ppm and referenced to residual nondeuterated solvent frequencies ($\delta$ = 7.25 ppm). Spectra were processed on a computer using the program ACDLABS. $^{29}$Si-NMR spectra were taken with the Bruker Avance II - 300 (59.6 MHz) (Germany), with the addition of accelerating the paramagnetic relaxation agent, chromium(III) acetylacetonate. Chemical shifts are reported in ppm and referenced to the internal standard, tetramethylsilane ($\delta$ = 0.00 ppm). Spectra were processed on a computer using the program "ACDLABS".

IR spectra were obtained with the Bruker Equinox 55 / S. Potassium bromide permanently-sealed liquid cells were used for measurements, and the solvent was $CCl_4$.

GPC analysis was conducted on a chromatographic system, consisting of a high-pressure pump of STAYER series II (Aquilon, Russia), a refractive index detector of RIDK 102 (Czech Republic), and a column oven of JETSTREAM 2 PLUS (KNAUER, Germany). Thermostating temperature was 40 °C (+ / -0.1 °C). The eluent was toluene, and the flow rate was 1.0 ml/min. A column of 300 × 7.8 mm was filled with sorbent Phenogel (Phenomenex, USA), with a particle size of 5, and a pore size of $10^3$ Å (passport range separation of up to 75,000 D). Registration and data-counting were performed using the Multichrom 1.6 GPC (Ampesand, Russia) program. The calibrant of the GPC data was conducted by the Polysterene Standard Calibration Kit for Liphophilic GPC (E. Merck, Darmstadt, F.R. Germany).

The X-ray photoelectron spectra were recorded using a Theta Probe spectrometer (ThermoFisher Scientific, UK) with monochromatic Al $K_\alpha$ radiation. Survey and high-resolution spectra of appropriate core levels were recorded at pass energies of 160 and 40 eV and with step sizes of 1 and 0.1 eV, respectively. The base pressure in the analytical UHV chamber of the spectrometer during measurements did not exceed $10^{-8}$ Torr. The energy scale of the spectrometer was calibrated to provide the following values for reference samples (i.e., metal

surfaces freshly cleaned by ion bombardment): Au $4f_{7/2}$–83.96 eV, Cu $2p_{3/2}$–932.62 eV, Ag $3d_{5/2}$–368.21 eV. The samples were mounted on a sample holder with a two-sided adhesive tape, and the spectra were collected at room temperature. The electrostatic charging effects were compensated by using an electron neutralizer. The surface charge was taken into account according to the Cu-O state identified in the O 1s spectrum, to which a binding energy of 530.3 eV was assigned, and the corresponding binding energy of the C 1s peak was 284.6 eV. After charge referencing, a Shirley-type background with inelastic losses was subtracted from the high-resolution spectra, and the spectra were fitted with some Gaussian profiles. The surface elemental composition was calculated using atomic sensitivity factors included in the software of the spectrometer corrected for the transfer function of the instrument.

The photoelectron spectra of the copper-containing nanogel were recorded for a film prepared by pouring palladium foil with a solution of the MVS product and dried from toluene in a vacuum.

The XANES/EXAFS X-ray absorption spectra at the Cu K-edge for the composite Cu/PMSSO sample were measured at the 'Structural Materials Science' beamline of the Kurchatov synchrotron radiation source (NRC 'Kurchatov Institute', Moscow).[S1] To monochromatize the incident X-ray beam, a channel-cut Si(111) monochromator was used, providing an energy resolution $\Delta E/E \sim 2 \cdot 10^{-4}$. The spectra were recorded in the X-ray fluorescence yield mode using an avalanche-amplified Si diode (APD, FMB Oxford, UK). To calibrate the energy scale, a copper foil spectrum was used. The quantitative analysis of X-ray spectral data was carried out using the Athena and Artemis programs from the IFEFFIT package.[S2]

Best-fit results are shown in Table S1.

**Table S1** Parameters of the local environment of copper atoms in the catalyst **1** according to EXAFS data

| Coordination sphere | N | R, Å |
|---|---|---|
| Cu-O | 1.4 | 1.94 |
| $Cu\text{-}Cu_1$ | 1.6 | 2.58 |
| $Cu\text{-}Cu_2$ | 0.6 | 2.71 |

**Synthesis of sodium diethoxy(methyl)silanolate**

Sodium hydroxide (40 g, 1.0 mol) of was added to methyltriethoxysilane (534.9 g, 3.0 mol). Stirring was carried out at room temperature until complete dissolution of the sodium hydroxide. Volatiles were removed in vacuum (1 mbar, 60 °C). The thus obtained sodium diethoxy(methyl)silanolate (172 g [99 % yield, calculated relative to NaOH]) was dissolved in dry toluene (1 $dm^{-3}$).

**Synthesis of hyperbranched polymethylethoxysiloxane**

To a toluene solution of sodium diethoxy(methyl)silanolate (1.0 mol) was added anhydrous acetic acid (60 g, 1.0 mol). After 24 h, the solution was filtered and dried. The volatiles were removed in vacuum (1 mbar). Hyberbranched polymethylethoxysiloxane was obtained at a yield of 87% (calculated for the theoretical structure $[CH_3SiO(OC_2H_5)]_n$); GPC: $M_w$ = 800 g $mol^{-1}$, $M_w/M_n$= 1.5; $^1$H NMR (250 MHz, $CDCl_3$, δ): 0.02-0.22 (m, 3H, Si-$CH_3$), 1.16-1.29 (m, 3H, Si-O-$CH_2$-$CH_3$), and 3.74-3.94 (m, 2H, Si-O-$CH_2$-$CH_3$).

**Synthesis of polymethylsilsesquioxane nanogel capped with TMDVDS (PMSSO-VDMS)**

Hyperbranched polymethylethoxysiloxane (2.5 g, 0.0205 mol of EtO groups) was boiled for 2 h in acetic acid (30% solution, 8.35 g, 0.139 mol). Disiloxane TMDVDS (5.72 g, 0.0308 mol) was added followed by acetyl chloride (0.08 ml, 0.001 mol), and the refluxing was continued for additional 14 h. The product was extracted with toluene, and the organic layer was left overnight over anhydrous $Na_2SO_4$. The volatiles were removed in vacuum (1 mbar) to leave 2.62 g of the product. Gel permeation chromatography (GPC): $M_w$ = 4520 g $mol^{-1}$, $M_w/M_n$ = 2.1.

Some essential characteristics of the starting polymethylethoxysiloxane and PMSSO-VDMS are shown in Figures S3-S7.

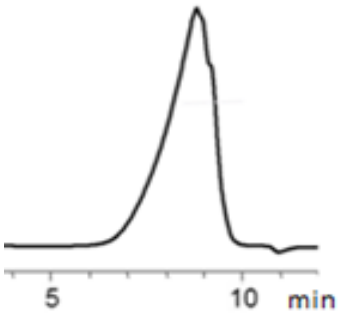


**Figure S3** GPC curve of hyperbranched polymethylethoxysiloxane.

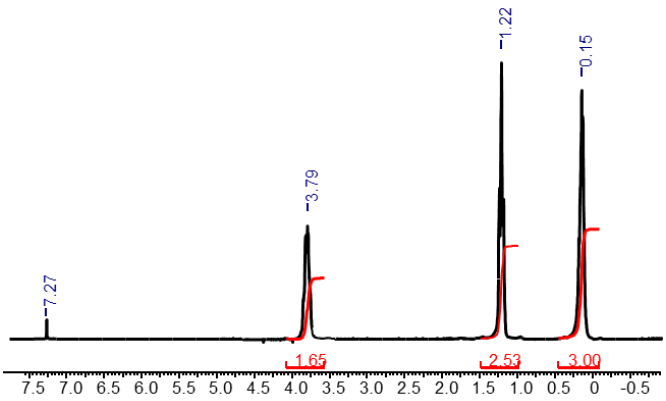


**Figure S4** [1]H-NMR spectrum of hyperbranched polymethylethoxysiloxane.

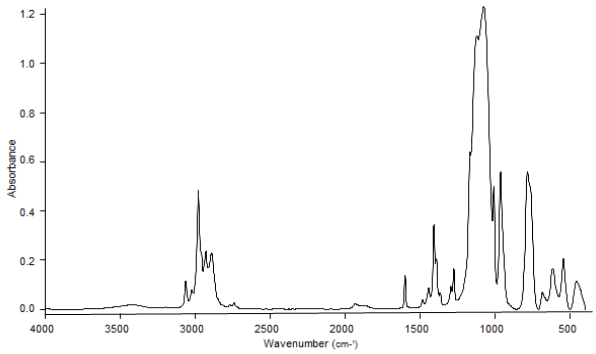


**Figure S5** The IR spectrum of hyperbranched polymethylethoxysiloxane (HBPMES).

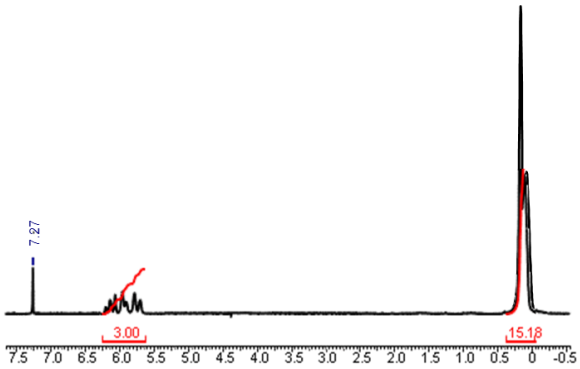


**Figure S6** [1]H-NMR spectrum of PMSSO-VDMS**.**

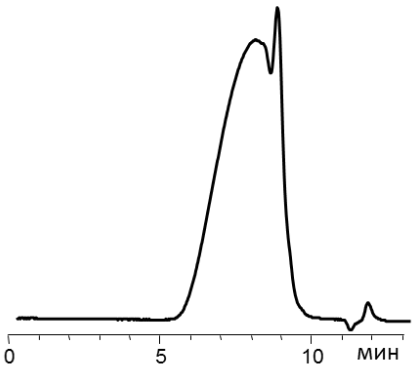


**Figure S7** GPC curve of PMSSO-VDMS**.**

**Modification of PMSSO-VDMS with Cu-based nanoparticles.** Toluene (99%, Aldrich) was dried over Na and distilled in an Ar atmosphere, and before the synthesis it was degassed in a vacuum at 0.1 Pa by alternating freeze-thaw cycles. Before the introduction of metal nanoparticles, the organosilicon gel was degassed for 6 h at 90 °C in a vacuum of 0.1 Pa.

Copper (shavings, 99%) was evaporated from a tantalum boat with resistive heating in a vacuum of $10^{-2}$ Pa. The copper vapours (0.32 g) and toluene (120 ml) were simultaneously condensed on the walls of a glass reactor cooled with liquid nitrogen. After the end of the synthesis, the cooling was stopped, the co-condensate matrix was heated to melting, and the resulting organosol Cu – toluene was introduced in a vacuum into a flask with the above organosilicon nanogel. The product is a gray-black oily substance, easily converted (dispersed) into a homogeneous suspension when stirred in traditional organic solvents. It was stirred for 1 hour; toluene was distilled off at 0.1 Pa.

**Catalytic olefination reaction of of *p*-chlorobenzaldehyde hydrazone with polyhaloalkanes using Cu-containing nanogel as catalyst (general procedure).** A 50 ml round-bottom flask was charged with *p*-chlorobenzaldehyde hydrazone (0.455 g, 3 mmol), DMSO (10 ml), $NH_3$(aq.) (1.2 ml, 15 mmol, 25% aqueous solution) and Cu-containing nanogel (10 mol %). The corresponding polyhaloalkane (6 mmol) was added, and the resulting solution was stirred at room temperature overnight. The reaction mixture was poured into aqueous HCl (50 ml, 0.5 M), and the water phase was extracted with $CH_2Cl_2$ (3x20 ml). The combined extracts were washed with water (2x20 ml), dried over $Na_2SO_4$ and the volatiles were evaporated *in vacuo*. The residue was purified by passing through a short silica pad using hexane as an eluent. Evaporation of the solvents afforded pure products. The characterization data of the reaction products are identical to those described in the literature.[S3]

***1-Chloro-4-(2,2-dichlorovinyl)benzene*** was obtained using $CCl_4$ (0.6 ml). Colourless oil, yield 0.534 g (86%); $^1$H NMR (400 MHz $CDC1_3$) 6.81 (s, 1H, C<u>H</u>=$CCl_2$), 7.30 (d, 2H, Ar, *J* = 8.3), 7.49 (d, 2H, Ar, *J* = 8.4).

***1-(2,2-Dibromovinyl)-4-chlorobenzene***. Was obtained using $CBr_4$ (1.99 g). Colourless crystals; mp 35-37 °C (lit.[4] 35-37 °C), yield 0.730 g (82%); $^1$H NMR (400 MHz $CDC1_3$) 7.26 (d, 2H, Ar, *J* = 8.7), 7.35 (s, 1H, C<u>H</u>=$CBr_2$), 7.39 (d, 2H, Ar, *J* = 8.7).

***1-(2-Bromo-3,3,3-trifluoroprop-1-enyl)-4-chlorobenzene*** was obtained using $CF_3CBr_3$ (1.93 g). Colourless oil; a 88:12 *Z/E* isomer mixture; yield 0.712 g (83%); $^1$H NMR (400 MHz $CDC1_3$) *Z*-isomer: 7.40 (d, 2H, Ar, *J* = 8.8), 7.55 (s, 1H, C<u>H</u>=$CBrCF_3$), 7.66 (d, 2H, Ar, *J* = 8.8). *E*-isomer: 7.20 (d, 2H, Ar, *J* = 8.5), 7.34 (d, 2H, Ar, *J* = 8.5), 7.45 (s, 1H, C<u>H</u>=$CBrCF_3$).

## References


S1. A. A. Chernyshov, A. A. Veligzhanin and Y. V. Zubavichus. Nucl. *Instrum. Methods Phys. Res. A.* 2009, **603**, 95, 498.

S2. M. Newville. *J. Synchrotron Radiat.,* 2001, **8**, 96.

S3. V. M. Muzalevskiy, A. V. Shastin, N. G. Shikhaliev, A. M. Magerramov, A. N. Teymurov, V. G. Nenajdenko. *Tetrahedron.* 2016, **72**, 7159.