Full Papers

Synthesis, characterization and metal-uptake behaviour of pyrazole ligands immobilized on silica

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Abstract. The novel didentate ligand 2-(3,5-dimethyl-1-pyrazolyl)ethylamine (Naed) and the tridentate ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] amine (ddaH) were immobilized onto silica by two different methods. The first method involves the coupling of the ligand to silica, previously modified with (3-glycidyloxypropyl)trimethoxysilane (GLYMO). The second method involves the coupling of the ligand to the oxirane ring of GLYMO in a homogeneous reaction, followed by grafting onto silica, yielding the highest ligand concentrations on the silica (about 0.3 mmol/g silica). With the first method, only part of the epoxy group reacts with the ligand. With Naed, tertiary amines are also formed through reaction of the primary amine group of the ligand with two epoxy groups.

These new ion-exchange materials selectively adsorb Cu^{2+} (maximum capacity 0.11-0.26 mmol Cu^{2+} per gram of ion exchange) at pH > 2 from aqueous solutions containing a mixture of the bivalent metal ions, Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} . For products containing the didentate ligand Naed as the chelating group, the metal-ion capacity decreases rapidly with decreasing pH, while the Cu^{2+} -uptake capacity for the product containing the tridentate ligand ddaH is comparatively high at low pH.

Introduction

Our attempts to investigate the effect of the solid support on the metal-ion uptake characteristics of ion exchangers¹⁻³, together with the need for hydrophilic support materials, has led to the study of silica-bound ligands. Because of their versatility and superior selectivity, chemically modified silicas have been used as supports in a wide variety of chromatographic applications⁴⁻⁷.

The most convenient way to immobilize a ligand onto silica is by modification of the silica surface with a bifunctional spacer. The rather stable Si-O-Si-C linkage can be formed by reaction of the surface silanols with an alkoxysilane or chlorosilane reagent⁸. For the present work, the bifunctional spacer (3-glycidyloxypropyl)trimethoxysilane (GLYMO) was used. The epoxide group reacts with nucleophiles by ring opening, allowing the facile introduction of a variety of amines.

The ligands which have been used in the present investigation, *i.e.* 2-(3,5-dimethyl-1-pyrazolyl)ethylamine (Naed)* and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (ddaH)*, contain an aliphatic amine and one or two pyrazole rings. In a previous study attachment of these ligands to the copolymer glycidyl* methacrylate-co-ethylene dimethacrylate and their metal ion uptake characteristics was reported². In this paper, we present details of grafting of these ligands to silica⁹, either by first attaching the spacer GLYMO to silica and then attaching the ligand to the silica bound GLYMO, or by first coupling the spacer GLYMO to the ligand and then attaching the resulting molecule to silica¹⁰⁻¹³, and the characterization of the products obtained via both methods.

Experimental

Starting materials

All reagents and solvents were purchased from commercial sources and were used as received. Silica (SiS) was kindly provided by Shell Research, Amsterdam. Some structural information about SiS was provided by the manufacturer: batch Shell CLA-26404; mean diameter: 1.5 mm; average pore diameter: 15-20 nm: specific surface area: $253 \text{ m}^2/\text{g}$; pore volume: 0.76 ml/g. The beads were activated before use by heating them at 150°C in vacuo for 24 h.

Analyses

^{*} Naed is an acronym of *N*-*a*mino*e*thane-*d*imethylpyrazole ddaH is an acronym of *d*i-(*d*imethylpyrazolylethyl)*a*mine *H* Glycidyl = (oxiranylmethyl)

Elemental analysis (C, H, N, S) of the silica products was performed at the Mikroanalytisches Labor Pascher, Remagen-Bandorf (Germany).

Analysis of the adsorbent-bound metal ions was carried out on a Perkin-Elmer 460 atomic absorption (AAS) and flame emission spectrometer using the standard addition method.

Spectroscopic methods

¹H- and H¹³C-NMR spectra were recorded on a Jeol JNM-FX200 spectrometer using frequencies of 199.50 and 50.10 MHz for ¹H and ¹³C, respectively. Chemical shifts are quoted with respect to TMS as an internal reference. Solid-state CP MAS ¹³C- and ²⁹Si-NMR spectra were recorded on

Solid-state CP MAS ¹³C- and ²⁹Si-NMR spectra were recorded on a Bruker MSL 400 spectrometer, operating at 100.6, 79.5 and 400.1 MHz for ¹³C, ²⁹Si and ¹H, respectively. Sample-spinning frequencies were varied from 2800 to 5100 Hz. For ¹³C and ²⁹Si, the cross-polarization contact time was 1.0 ms, with 3–5 second recycle delays between successive scans. In general, about 17000 scans were used for ¹³C; for ²⁹Si, less than 1000 scans were used. TMS was used as the reference compound.

Infrared spectra were recorded using KBr pellets or thin films between KBr tablets on a Perkin-Elmer PE580 spectrophotometer equipped with a data station.

Diffuse-reflectance Fourier-transform IR spectra (DRIFT) were recorded on a Bruker IFS-113V instrument. The spectra were obtained by the diffuse-reflectance technique¹⁴ in the range $4000-800 \text{ cm}^{-1}$, using a liquid-nitrogen-cooled mercury-cadmiumtelluride detector. For elimination of the specular reflectance, a blocker was used¹⁵. The silica compounds were ground and mixed with KBr in a 1/20 w/w ratio in an automatic mulling device (Perkin-Elmer). The homogeneous powders were oven-dried for 24 h at 80°C *in vacuo*. Usually, 1024 scans were taken, with KBr as reference. After base-line linearization, the spectrum was converted to Kubelka-Munk units¹⁶.

For detection of secondary and tertiary amines, functional group test reactions were used. The dithiocarbamate reaction¹⁷ was used to detect secondary amines. Reagents were prepared as described by Siggia¹⁷. The carbon disulfide-containing reagent (5 ml) and the copper chloride solution (15 ml) were added to 0.3 g of the modified silica. After 2 h the beads were filtered off, washed three times with ethanol and dried with ether. The beads were dried for 24 h *in vacuo*. The *cis*-aconitic anhydride * reaction¹⁷ was used to determine tertiary amines. *cis*-Aconitic anhydride solution (5 ml) was added to 0.3 g of the modified silica. The mixture was heated for 20 s on a boiling water bath and allowed to cool to room temperature. The beads were filtered off after 30 min, washed with toluene and three times with ether and dried for 2 h *in vacuo*.

Electronic spectra in the visible- and near-infrared region were recorded in the diffuse-reflectance mode on a Perkin-Elmer 330 spectrophotometer equipped with a data station.

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-3 spectrometer at X-band frequencies at room temperature.

Batch metal-uptake experiments

Metal-uptake experiments were performed using 0.16 M standard metal chloride solutions prepared from analytical grade reagents. The buffer solutions (I 0.6 M) NaOAc/HOAc (pH 2.5-6) and NaCl/HCl (pH 0.9-2.3) were prepared from analytical reagents. All metal-uptake experiments were performed in polyethylene bottles mounted on a shaker at room temperature.

bottles mounted on a shaker at room temperature. The capacities for Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} and Ca^{2+} were determined as a function of pH. Batches of 0.2 g of the adsorbents were used, together with a mixture of 25 ml of buffer or water and 25 ml of metal stock solution (0.16 M M²⁺). The shaking time was taken as 24 h. The samples were filtered, thoroughly washed with water, ethanol and ether, successively, and dried *in vacuo* at 50°C. For determination of the Cu^{2+} capacity at pH > 5, a lower Cu^{2+} concentration (12.5 ml of the standard Cu^{2+} solution, 12.5 ml of water and 25 ml of the buffer) was used to prevent precipitation of $Cu(OH)_{2}$.

Samples for metal analyses were prepared by heating 0.1 g of the loaded samples with concentrated H_2SO_4 and, subsequently, with concentrated HNO₃ until colorless mixtures were obtained. After filtration of the mixture, the metal contents of the resulting solutions were measured by AAS spectroscopy using the standard addition method.

In order to study metal uptake under competitive conditions as a function of pH, 0.2 g of resin was added to an aqueous solution

containing 5.00 ml each of the standard metal chloride solutions of Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} and 25 ml of buffer.

 H_2SO_4 (0.1-0.5 M) was tested for its stripping potential. Batches of ion-exchange materials (each 1.0 g) were loaded with CuCl₂ (25 ml of the metal standard solution, 25 ml of water and 50 ml of NaOAc/HAc buffer) at pH 5.5 (shaking time 24 h). The loaded samples were stripped with H_2SO_4 (0.1-0.5 M) (50 ml, shaking time 2-24 h). This procedure was repeated several times with fresh solutions.

Synthesis of Naed (Scheme 3)

2-(3,5-Dimethyl-1-pyrazolyl)ethyl-*p*-toluenesulfonate¹⁸ (16.0 g, 55 mmol) was dissolved in 100 ml of DMF. Potassium phthalimide (10.1 g, 55 mmol) was added to the stirred yellow solution. The turbid solution was heated to 100°C for 1 h. The resulting clear red-brown solution was poured into water (400 ml) and extracted three times with 100 ml chloroform. The collected chloroform layers were extracted twice with 100 ml of water. After drying on anhydrous calcium sulfate, the chloroform layer was evaporated to dryness. The resulting oil was crystallized from hot water/ethanol 2/1 v/v and dried for 24 h at 50°C *in vacuo*. The product *N*-[2-(3,5-dimethyl-1-pyrazolyl)ethyl]phthalimide consisted of fine white needles. Yield 10.3 g (70%); m.p. 94–100°C. ¹H-NMR (CDCl₃) δ : 2.07 (3H, s, pyrazole-CH₃); 2.21 (3H, s, pyrazole-CH₃); 4.02 (2H, t, CH₂-pyrazole); 4.25 (2H, t, CH₂-phthalimide); 5.75 (1H, s, pyrazole C(4)H); 7.72 (2H, m, phthalimide); 7.82 (2H, m, phthalimide) pm.

Hydrazine hydrate 98% (1.9 g, 37 mmol) was added to a solution of *N*-[2-(3,5-dimethyl-1-pyrazolyl)ethyl]phthalimide (10.0 g, 37 mmol) in 80 ml of ethanol. The solution was refluxed for 1 h. After 15 min, a white precipitate formed. Concentrated hydrochloric acid (15 ml) was carefully added and the solution was refluxed for another hour. The phthalhydrazide was filtered and washed with water. The filtrate was partially evaporated to yield more phthalhydrazide. After drying for 24 h at 80°C in vacuo, the total yield was 4.89 g (81%). Sodium hydroxide was added to the filtrate to pH 13. The filtrate was extracted three times with 50 ml of chloroform. The collected chloroform layers were dried over anhydrous calcium sulfate. After evaporation of the solvent, a light yellow oil resulted (Naed). Yield 4.20 g (81%). ¹H-NMR (CDCl₃) δ: 1.68 (b, NH₂); 2.16 (3H, s, pyrazole-CH₃); 2.20 (3H, s, pyrazole-CH₃); 3.08 (2H, t, CH₂-N), 3.99 (2H, t, CH₂-pyrazole), 5.78 (1H, s, pyrazole C(4)H) ppm.

Synthesis of ddaH (Scheme 4)

The synthesis of ddaH was carried out according to Sorrell and Malachowski¹⁹. The ¹H-NMR spectrum of the product was in agreement with the spectrum reported earlier¹⁹. However, the melting point of the product was found to be considerably higher (*i.e.*, 73-76°C) than reported earlier (50-54°C).

Synthesis of SiSEp (Scheme 1)

SiS (silica, 50 g) was added to a solution of GLYMO (96%, 25 ml, 108 mmol) in dry toluene (100 ml). The mixture was refluxed under a nitrogen atmosphere for 5 h. After cooling, the beads were filtered off and washed with toluene. In all cases, the beads were directly used for further synthesis. To characterize the product, the beads were extracted with THF using a Soxhlet apparatus. The white product SiSEp was dried for 24 h at 50°C *in vacuo*.

Synthesis of SiSN1 (Scheme 1)

A solution of Naed (5.9 g, 42 mmol) in 100 ml of dry dioxane was added to SiSEp. After refluxing the mixture for 40 h under an insert nitrogen atmosphere, the beads (SiSN1) were filtered off and washed with dioxane. The product was purified by extraction with ethanol using a Soxhlet apparatus, after which the beads were dried for 24 h at 80°C *in vacuo*. The product was isolated as pale yellow beads.

Synthesis of SiSD1 (Scheme 1)

SiSD1 was synthesized as described for SiSN1, except that ddaH (13.6 g, 52 mmol) in 120 ml of dry dioxane was used. The mixture was refluxed for 114 h. The product was isolated as pale yellow beads.

^{*} IUPAC name: cis-1-propene-1,2,3-tricarboxylic acid.



SISN1, SISD1

Scheme 1. Immobilization of amines (Naed or ddaH) on silica according to method 1. Synthesis of SiSEp, SiSN1 $(R_1 = -H, R_2 = 2-(3,5-dimethylpyrazolyl)ethyl$ and SiSD1 $(R_1 = R_2 = 2-(3,5-dimethylpyrazolyl)ethyl$.





Scheme 2. Immobilization of amines (Naed or ddaH) on silica according to method 2. Synthesis of GLYMO-Naed, GLYMO-ddaH, SiSN2 ($R_1 = -H$, $R_2 = 2$ -(3,5-dimethyl-pyrazolyl)ethyl and SiSD2 ($R_1 = R_2 = 2$ -(3,5-dimethylpyrazolyl)ethyl.



Scheme 3. Synthesis of Naed.







Scheme 5. Numbering scheme of compounds used for ¹³C NMR.

Synthesis of SiSN2 (Scheme 2)

Naed (1.0 g; 7.2 mmol) and GLYMO (96%, 1.18 g, 4.8 mmol) were dissolved in 40 ml of methanol and refluxed for 65 h under an inert nitrogen atmosphere. The solution was evaporated to dryness. The oily product GLYMO-Naed was dissolved in 50 ml of toluene and silica beads (6 g) were added. After refluxing for 5 h under an inert nitrogen atmosphere, the product was filtered and extracted with ethanol using a Soxhlet apparatus. The product was dried at 80° C *in vacuo* for 24 h, resulting in off-white colored beads (SiSN2).

Synthesis of SiSD2 (Scheme 2)

The synthesis of SiSD2 was carried out according to the method for synthesis of SiSN2. However, in this case, a solution of ddaH (1.0 g; 3.8 mmol) and GLYMO (96%, 0.94 g, 3.8 mmol) in 40 ml of methanol was used. The solution was refluxed for 96 h, yielding GLYMO-ddaH. For reaction with silica, 5 g of silica beads were used. The color of the dried product (SiSD2) was off-white.

Results and discussion

Synthetic aspects

The synthetic routes to SiSEp, SiSN1, SiSD1, GLYMO-Naed, GLYMO-ddaH, SiSN2 and SiSD2 are shown in Schemes 1 and 2. In the second step of the preparation of compounds SiSN1 and SiSD1 (Scheme 1), either dioxane or ethanol were used as solvent. This appeared to have no effect on Cu^{2+} capacity of the resulting products, suggesting that the ligand concentrations of these products are similar.

In method 2 (Scheme 2), ring opening of the epoxide occurs in the homogeneous phase. A possible complication in the reaction of GLYMO with Naed could have been the reaction of Naed with the trimethoxysilyl group. However, a possible Si-N (ligand) bond would have been readily converted to an Si-OCH₃ bond²⁰, as dry methanol was used as the solvent. An excess of Naed was used for synthesis of GLYMO-Naed to prevent the reaction of the primary amine of Naed with two epoxy groups, which would result in the formation of a tertiary amine. After the reaction, the excess was not removed from the product, as Naed is unlikely to interfere with the reaction of GLYMO-Naed with silica. The GLYMO-Naed and GLYMO-ddaH products, which were obtained as oils, solidified within a week upon standing in the air, probably due to polymerization. Purification of these compounds is difficult due to the reactivity of the trimethoxysilane substituent. Nevertheless, this reaction sequence has several advantages over method 1, as the soluble products obtained in the homogeneous reaction are easier to characterize and to purify than the silica-bound species.

Characterization of low-molecular-weight compounds

¹³C NMR was used to characterize the soluble products and the results are listed in Table I. The numbering of the carbon atoms is shown in Scheme 5. In the spectrum of GLYMO, the peak at 43.9 ppm can be assigned to one of the C atoms of the epoxide ring. For GLYMO-Naed, obtained with GLYMO/Naed = 1/1.5 in dilute methanol solution, no peak is observed at 43.9 ppm, which implies that most of the epoxy groups have been converted. Comparison of the spectra of Naed and GLYMO-Naed shows that the signal from C(8) has shifted from 41.5 ppm (primary amine) in the spectrum of Naed to 47.9 ppm (secondary amine) in the spectrum of GLYMO-Naed. In the spectrum of GLYMO-daH, the C(8) peak is found at 54.5 ppm, which is typical for a methylene group next to a tertiary amine. Small peaks at 46.5 and 58.0 ppm in the

Carbon	¹³ C-NMR (solutions in CDCl ₃)					¹³ C CP MAS NMR		
	Naed	GLYMO- Naed	ddaH	GLYMO- ddaH	GLYMO	SiSEp	SiSN1 SiSN2	SiSD1 SiSD2
C(1)		50.1		49.5	50.2		10	10
C(2)		5.1		5.0	5.0	8	23	23
C(3)		22.5		22.8	22.6	23	72	73
C(4)		73.3		73.8	73.2	73	72	73
C(5)		73.3		71.4	71.2	73	72	73
C(6)		68.7		68.8	50.6	49	49	58
C(7)		51.7		58.0	43.9	43	49	58
C(8)	41.5	47.9	48.1	54.5			49	49
C(9)	51.0	48.9	49.0	46.4			10	10
C(10)	10.7	10.8	10.9	10.5			10	10
C(11)	13.0	13.2	13.3	12.9			139	140
C(12)	138.7	139.1	139.0	138.9			146	147
C(13)	147.0	147.2	147.4	147.0			103	104
C(14)	104.6	104.9	104.7	104.7				

Table I Tentative ¹³C-NMR chemical shift assignment. Chemical shifts are reported relative to TMS. The numbering of the carbon atoms is shown in Scheme 5.

spectrum of GLYMO-Naed were assigned to small amounts of tertiary amine. The spectrum of GLYMO-ddaH shows small peaks at δ 59.4 and 77.0 ppm, which may result from CH or CH₃ groups of a by-product. Using a ratio GLYMO/ddaH different from 1/1 had no effect on the intensity of these peaks. No unreacted GLYMO could be detected in the NMR spectrum, while free ddaH is clearly present in the product. The results suggest that the byproduct is a reaction product of GLYMO and methanol (denoted as GLYMO-MeOH). Apparently, the reaction of the epoxy groups with ddaH is not fast enough to prevent the incorporation of a considerable amount of methanol into the product.

The presence of GLYMO-MeOH in GLYMO-ddaH implies that the silica product derived from this compound, *i.e.*, SiSD2, is a poorly defined product. This was confirmed by elemental analysis of SiSD2 (see below). Therefore, it was decided not to use this compound for metal-uptake experiments.

Characterization of silica compounds

Elemental analysis. Results of elemental analysis of the modified silicas are listed in Table II. Method 2 leads to a lower concentration of the spacer group on silica, but to a higher ligand concentration on silica than method 1. The bulkier GLYMO-Naed and GLYMO-ddaH molecules apparently cannot reach all the reaction sites on silica which can be reached by the GLYMO molecule itself. Still, method 2 must be preferred over method 1, because of the low conversion of attached epoxy groups in method 1. This low conversion is probably a consequence of inhomogeneous ligand-immobilisation reaction, while the size of the

ligands also plays a role, as this effect is more pronounced for the ligand ddaH, than for the less bulky ligands Naed and histamine^{3,21}. In the case of Naed and histamine, the reaction of their primary amine substituents with two epoxy groups may also be responsible for the low conversion. With method 2, the ligand concentrations of Naed and ddaH on silica are comparable. Apparently, the effect of ligand size is less important in this case, as it will have a relatively little influence on the size of the whole "GLYMO + ligand" molecule. For SiSD2; the large difference between the concentration of the ligand (0.28 mmol/g) and that of the spacer (0.53 mmol/g) implies that a considerable amount of GLYMO-MeOH is bound to the silica. ¹³C solid state NMR. The peaks in the ¹³C-CP-MAS-NMR spectrum of SiSEp (Figure 1A) can all be assigned to carbon atoms of GLYMO (Table I). Spectra of both compounds have already been published^{22,23}. The strong peaks at 18 (CH₃) and 58 ppm (CH₂-O) in the spectrum of SiSEp suggest the presence of adsorbed ethanol, which was probably introduced during the washing procedure. The spectra of SiSN1 and SiSD1 are very similar (Figure 1, Table I) and show pyrazole peaks at ca. 104 ppm [pyrazole C(4)] and in the region 139-147 ppm [pyrazole C(3) and C(5)]. In the spectrum of SiSN1, the peak at 49 ppm is more intense than that in the spectrum of SiSD1, which agrees with the presence of secondary amines in the former product. The peak at 58 ppm in the spectra of SiSN1 and SiSD1 was assigned to methylene carbon atoms next to tertiary amines. Apparently, SiSN1 contains a small but significant amount of tertiary amine. The CH₂-O group of adsorbed ethanol, which is clearly present in the starting compound SiSEp (Figure 1A), may also contribute to the intensity of this peak. However, the low intensity of the

Table II Elemental analysis of silica products.

Compound	C (°,)	N (%)	ligand (mmol/g)	spacer (mmol/g)
SiSEp SiSN1 SiSN2 SiSD1 SiSD2	4.7 6.6 5.6 7.5 8.9	1.1 1.3 0.9 2.0	0.26 0.32 0.12 0.28	0.65 0.61 0.39" 0.74 0.53"

^a In the calculation of the spacer concentration, it is assumed that the epoxy groups that do not react with the ligand, are converted with methanol. Furthermore, it is assumed that the silicon-bound methoxy groups are all hydrolyzed during the immobilization procedure.

peak at 18 ppm [CH₃ (ethanol)] in the spectra of SiSN1 and SiSD1 suggests that most of the adsorbed ethanol is removed during ligand attachment. The spectra of SiSN2 and SiSD2 are not given here, as they resemble qualitatively the spectra of SiSN1 and SiSD1, respectively: The ligand peaks are relatively stronger due to the higher ligand concentrations of the products obtained by method 2.



Figure 1. CP/MAS ¹³C-NMR spectra of A, SiSEp (1029 FIDs collected at 3-s intervals; 100-Hz LB; SSR 3063 Hz); B, SiSN1 (14,029 FIDs collected at 3-s intervals; 40-Hz LB; SSR 5000 Hz); C, SiSD1 (3102 FIDs collected at 3-s intervals; 40-Hz LB; SSR 5014 Hz). p = pyrazole peak, s = spinning sideband.

²⁹Si solid-state. ²⁹Si solid-state CP/MAS NMR is a powerful technique to study silica surfaces, as the signals of the surface species are strongly enhanced by cross-polarization. The spectrum of activated silica (not shown) shows a single asymmetric broad peak at δ – 101 ppm, indicating the presence of mainly (\equiv Si-O)₃Si-OH on the silica surface²⁴. After reaction with GLYMO, additional peaks appear at $\delta - 49$, - 57 and - 66 ppm in the spectrum of SiSEp (Figure 2A), which are assigned to $(\equiv Si-O)(OR)_2SiR'$, $(\equiv Si-O)_2(OR)SiR'$ and $(\equiv Si-O)_3SiR'$, respectively. The peak at $\delta - 109$ ppm, due to (\equiv Si-O)₄Si, becomes more pronounced, due to reaction of the surface hydroxyl groups with the silane compound. In the ²⁹Si-NMR spectra of SiSN1 and SiSD1, the intensity of the peak at -49 ppm has decreased, while the intensities of the peaks at -57 and - 66 ppm have increased compared to those found in the spectrum of SiSEp. This suggests that the reaction between Si-OCH, and surface Si-OH groups proceeds during coupling of the ligand, yielding more Si-O-Si links. The spectra of SiSN2 and SiSD21 show no peak at -49 ppm, indicating that no (\equiv Si-O)SiR'(OR)₂ is present in this case. As demonstrated by the spectra of SiSN1 and SiSN2 (Figures 2B and 2C, respectively), the final surface structures of the products prepared by methods 1 and 2 are qualitatively similar.



Figure 2. CP/MAS ²⁹Si-NMR spectra of A, SiSEp (1000 FIDs collected at 2-s intervals; 100-Hz LB; SSR 4139 Hz); B, SiSN1 (500 FIDs collected at 2-s intervals; 100-Hz LB; SSR 4530 Hz); C, SiSN2 (801 FIDs collected at 2-s intervals; 100-Hz LB; SSR 4173 Hz).

DRIFT spectroscopy. DRIFT (diffuse-reflectance Fourier transform) spectroscopy is a relatively new method to study surface modification^{14,24}. The DRIFT spectra of modified silica show the organic modification, especially the strong C-H stretching vibrations near 3000 cm⁻¹. For detailed analysis of the organic modification, a frequency range is needed in which silica itself does not absorb. A useful range appears to be the 1600–1300-cm⁻¹ region. The DRIFT spectra of SiS, SiSEp, SiSD1, SiSD2, SiSN1 and SiSN2 are shown in Figure 3. In the spectra of the pyrazole-modified products, the peak at 1554 cm⁻¹ can be assigned to a vibration of the pyrazole ring. For SiSN2 and SiSD2, these peaks are stronger compared to those in the spectra of the products obtained by method 1, which confirms the



Figure 3. DRIFT spectra of SIS (A), SiSEp (B), SiSD1 (C), SiSD2 (D), SiSN1 (E) and SiSN2 (F).

higher degree of modification obtained by method 2. The IR spectrum of GLYMO shows intense bands at 1339 cm⁻ and 1413 cm⁻¹, which can be assigned as CH-bending vibrations of the epoxy group²⁵. In the DRIFT spectrum of SiSEp, these peaks appear at 1348 and 1413 cm⁻¹, respectively (Figure 3). The observed shift of the first peak may indicate hydrogen bonding between the epoxy group and the surface silanol groups. In the DRIFT spectra of SiSN1 and SiSD1, the peaks at 1413 cm⁻¹ and 1348 cm⁻¹ have not completely disappeared. This implies that part of the epoxy groups has not reacted, possibly due to steric hindrance on the surface. In the case of SiSN2, the peak at 1413 cm⁻¹ is missing, while a peak is observed at 1348 cm⁻¹, which may be due to a weak ligand vibration not originating from the epoxy group. Immobilized Naed and ddaH have very similar spectra in the frequency range used.

Functional-group tests. A number of functional-group tests was carried out to investigate the presence of secondary and/or tertiary amines in the silica products. Secondary amines are detected by adding the sample to carbon disulfide and a solution of $CuCl_2$ (resulting in the so-called secondary-amine test reagent)¹⁷. The dithiocarbamic acids formed on the silica surface react with Cu^{2+} to form a yellow-coloured salt, which can be detected spectrophotometrically. Tertiary amines do not react with carbon disulfide, but can be detected selectively with *cis*-aconitic acid (the so-called tertiary amine test reagent)¹⁷.

The reaction of the secondary amine test reagent with SiSN1 and SiSN2 results in a light yellow-brown colour $(\lambda_{max} 440 \text{ nm})$, indicating the presence of secondary amines. The reaction of the secondary amine test reagent with silica, SiSEp, SiSD1, and SiSD2 results in very little color change. The addition of the tertiary amine test reagent to the silica products SiSN1, SiSN2, SiSD1 and SiSD2 immediately results in a deep-purple color, qualitatively indicating the presence of tertiary amines in all these products, with a broad peak at λ_{max} 515 nm in their reflectance NIR-VIS spectra. As pyrazole also contains a tertiary amine and, therefore, could interfere in the analyses, spectra were recorded of reaction products of the tertiary amine test reagent with 2-(3,5-dimethyl-1-pyrazolyl)ethanol (Nhed) and with triethylamine. The Nhed test product absorbs at significantly higher energy (i.e., at 542 nm) than the triethylamine-test product (i.e., at 520 nm). Furthermore, the intensity of the peaks are different: $\varepsilon(\lambda 520 \text{ nm}) > \varepsilon(\lambda 542 \text{ nm})$. Thus, although the pyrazole ring itself reacts with the reagent, the presence of tertiary amines in the silica samples is evident. This implies that part of the NH₂ substituents of Naed reacts twice with epoxy groups to form tertiary amines.

Metal-uptake experiments

Elemental analysis of the Cu²⁺-loaded products. The data for Cu²⁺-loaded SiSN1 (pH 4.5), *i.e.* C 5.7%, N 0.8%, Cu 0.9%, correspond to a Cu²⁺-Naed ratio of 0.7/1. For Cu²⁺⁻loaded SiSN2 (pH 4.5), the Cu²⁺-to-ligand ratio is significantly higher, *i.e.*, 1.1/1, from C 4.3%, N 1.0%, Cu 1.7%. This may be ascribed to better accessibility of the ligand in SiSN2, due to the lower concentration of spacer molecules on the surface (see below). The data for SiSD1 (pH 4.5), *i.e.*, C 7.1%, N 0.9%, Cu 0.7%, correspond to a Cu²⁺-toddaH ratio of 0.9/1, which is higher than the Cu²⁺-to-ddaH ratios found for ddaH immobilized on glycidyl methacrylateco-ethylene glycol dimethacrylate². This may be ascribed to low ligand concentration on the silica, causing less steric hindrance. The Cu²⁺-to-ligand ratios suggest that 1/1 complexes are formed in all cases. Capacity measurements. The metal-ion capacities of SiSN1, SiSD1 and SiSN2 were measured under noncompetitive conditions as functions of pH for Cu²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Co²⁺ and Ca²⁺. The results are given in Figure 4. The capacities of SiSEp itself (*i.e.*, the control experiment) were found to be very low, *i.e.*, 0.001–0.004 mmol M²⁺/g. Therefore, it can be assumed that unreacted epoxy substituents do not affect the metal-uptake behaviour of SiSN1 and SiSD1.



Figure 4. Capacity of SiSN1 (a), SiSD1 (b) and SiSN2 (c) for divalent metal ions as function of pH.

The capacity determinations gave promising results: above pH 2, all materials exhibited a substantially higher capacity for Cu^{2+} than for any of the other metal ions; at pH 4.5, the uptake capacities were 0.14, 0.11 and 0.26 mmol of Cu^{2+} per g of silica for SiSN1, SiSD1 and SiSN2, respectively. At low pH, the capacity was lower for all metals, due to protonation of the amine groups in the ligand. No detectable uptake of Ca^{2+} took place in the pH range studied. The high capacity for SiSN2, compared to that of SiSN1, is



Figure 5. Capacity of SiSN1 (a), SiSD1 (b) and SiSN2 (c) for divalent metal ions under competitive conditions as function of pH.

caused by both the higher ligand concentration of SiSN2 and the higher Cu^{2+} -to-Naed ratio in the final product (see above). The higher Cu^{2+} -to-Naed ratio for SiSN2 may be explained by better accessibility of the ligands in this product. The higher concentration of the spacer in the products obtained via method 1 causes more steric hindrance in SiSN1, which may result in a lower Cu²⁺-to-Naed ratio. Although the adsorption capacity of SiSN2 for all the metal ions tested was higher than that of SiSN1, the capacity patterns look similar (see Figure 4). This suggests that the method of immobilization does not influence the metal-ion selectivity of the immobilized species, resulting in equal M_1^{2+} -to- M_2^{2+} ratios for both resins. The origins of the relatively low Cu²⁺ uptake by SiSN2 at pH 5.6 is not clear. For SiSD1, the capacity for Cu²⁺ is comparatively high at low pH. This may be explained by the presence of two pyrazole groups per ligand. Pyrazole substituents are much less basic $[pK_a(pyrazole) 2.5]^{26}$ than tertiary amines and will be capable of binding metal ions even at low pH values.

Metal uptake under competitive conditions. Figure 5 presents the uptake of Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} under competitive conditions for SiSN1, SiSD1 and SiSN2. It is clear that all ion exchangers tested are selective for Cu^{2+} , SiSN1 and SiSN2 being more selective than SiSD1.

Regeneration of ion exchangers. H_2SO_4 was tested for its stripping potential and results for 0.5 M H_2SO_4 are given in Table III. Unfortunately, the Cu²⁺ capacities of SiSN1 and SiSD1 were found to have decreased considerably after four cycles of loading and stripping (24 h) with 0.5 M H_2SO_4 . Apparently, the silica-ligand bound was hydrolyzed by the acid. Therefore, both the acid concentration and the duration of the stripping procedure were varied. The stripping of SiSN1 with 0.1 M H_2SO_4 (24 h) did not result in a decrease of the Cu²⁺ capacity. For SiSN2, complete stripping of Cu²⁺ could be achieved within 2 h using 0.5 M H_2SO_4 . No decrease of the Cu²⁺ capacity was observed after 5 cycles of loading and stripping. These results show that H_2SO_4 solutions can be used as the stripping reagent.

Ligand-field and EPR-spectroscopic data of the loaded samples

The ligand-field (LF) spectra of the light blue Cu²⁺ complexes on SiSN1, prepared in the pH 2.2-5.8 range, show absorption bands at *ca*. 13.0-14.3 \cdot 10³ cm⁻¹ with tails on the low energy side. This shows that pH has a considerable effect on the position of the absorption band. Around pH 5, the coordination number is probably higher than that at low pH, due to coordinating acetate ions and/or water molecules. The LF spectra of SiSD1-bound Cu²⁺ complexes prepared in the pH 2.0-5.6 range show bands at *ca*. 13.9-14.3 \cdot 10³ cm⁻¹ with a tail on the low energy side. In this case, the pH effect is much less important, which is consistent with the relatively small pH dependence of the Cu²⁺ uptake (see above).

Table III Cu^{2+} capacities for SiSN1, SiSD1 and SiSN2 (mmol Cu^{2+} /g-resin) after several cycles of loading (24 h with 0.08M $CuCl_2$ solution containing acetate buffer) and stripping (24 or 2 h with 0.5M H_2SO_4 or 0.1M H_2SO_4).

cle		SiSN1 (0.5M, 24 h)	SiSD1 (0.5M, 24 h)	SiSN1 (0.1M, 24 h)	SiSN2 (0.5M, 2 h)
1	loaded	0.14	0.08	0.15	0.29
	stripped	0.00	0.00	0.00	0.00
2	loaded	0.14	0.07	0.16	0.28
	stripped	0.00	0.00	0.00	0.00
3	loaded	0.10	0.07	0.17	0.27
	stripped	0.00	0.00		0.00
4	loaded	0.10	0.07		0.27
	stripped	0.00	0.00		0.00
5	loaded	0.08	0.06		0.29
5	loaded	0.08	0.06		

The EPR spectra of Cu²⁺-loaded SiSN1 and SiSD1 are all axial with well-resolved hyperfine-splitting patterns and similar values for g_{\perp} (2.06–2.09), g_{\parallel} (2.26–2.28) and A_{\parallel} (138–150 G). The pH was found to have a negligible influence on these parameters. These spectral data are normal for Cu²⁺ in a ligand environment of nitrogen donors²⁷. The LF spectra of the green Ni²⁺-loaded beads of SiSN1 and SiSD1 prepared at pH 3.4–5.7 are consistent (spectra with bands at *ca.* 9.9, 16.2, and 25.3 cm⁻¹) with a distorted octahedral coordination geometry²⁷.

The LF absorption bands of the purple Co^{2+} -loaded beads of SiSD1 are weak, broad and, therefore, difficult to interpret, which is due to low Co^{2+} concentration on the modified silica. The purple color of the sample suggests that Co^{2+} in the complexes is five-coordinated. When water is added to the Co^{2+} -loaded beads, their color changes to pink, suggesting that octahedral complexes are formed^{27,28}. No spectra could be obtained of Co^{2+} -loaded SiSN1, due to low Co^{2+} concentration on the silica surface.

Conclusions

Immobilization of the pyrazole ligands Naed and ddaH via method 2 (spacer and ligand assembled in the homogeneous phase followed by grafting on silica) leads to higher degrees of modification than immobilization via method 1 (grafting of the spacer on silica followed by reaction of the ligand with the immobilized spacer). The higher modification degree results in considerably larger metal-uptake capacities.

As described elsewhere², both Naed and ddaH have also been immobilized onto the organic polymer glycidyl methacrylate-co-ethylene dimethacrylate (GMA-EDMA). Their metal-uptake characteristics, both capacities and selectivity for Cu^{2+} over Zn^{2+} , Cd^{2+} and Co^{2+} , are somewhat better than for the analogous silica modifications.

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References

- ¹ P. D. Verweij, T. Dugué, W. L. Driessen, J. Reedijk, B. Rowatt and D. C. Sherrington, Reactive Polym. 14, 213 (1991).
- ² P. M. van Berkel, P. D. Verweij, W. L. Driessen and J. Reedijk, Eur. Polym. J. 28, 747 (1992).
- ³ P. D. Verweij, S. Sital, M. J. Haanepen, W. L. Driessen and J. Reedijk, in preparation.
- ⁴ D. E. Leyden and G. H. Luttrell, Anal. Chem. 47, 1612 (1975).
- ⁵ D. E. Leyden and W. Collins (Eds.), Silylated Surfaces, Gordon and Breach, New York (1980).
- ⁶ V. I. Fadeeva, T. I. Tikhomorova, I. B. Yuferova and G. V. Kudryavtsev, Anal. Chim. Acta **219**, 201 (1989).
- ⁷ V. Dudler, L. F. Lindoy, D. Sallin and C. W. Schlaepfer, Aust. J. Chem. **40**, 1557 (1987).
- ⁸ K. K. Unger, "Porous Silica: Its Properties and use as Support in Colomn Liquid Chromatography", Journal of Chromatography Library Vol. 16, Elsevier Scientific Co., New York (1979).
- ⁹ U. Descher, P. Kleinschmit and P. Panster, Angew. Chem. Int. Ed. Engl. 25, 236 (1986).
- ¹⁰ R. Däppen, V. R. Meyer and H. Arm, J. Chromatogr. 361, 93 (1986).
- ¹¹ H. G. Kicinski and A. A. Kettrup, Reactive Polym. 6, 229 (1987).
- ¹² J. S. Bradshaw, K. E. Krakowiak, B. J. Tarbet, R. L. Bruening, J. F. Biernat, M. Bochenska, R. M. Izatt and J. J. Christensen, Pure Appl. Chem. 61, 1619 (1989).
- ¹³ *M. R. Weaver* and *J. M. Harris*, Anal. Chem. **61**, 1001 (1989).
- ¹⁴ R. S. Shreedhara Murthy and D. E. Leyden, Anal. Chem. 58, 1228 (1986).
- ¹⁵ R. G. Messerschmidt, Applied Spectroscopy 39, 737 (1985).
- ¹⁶ P. Kubelka and F. Munk, Z. Tech. Phys. 12, 593 (1931).
- ¹⁷ S. Siggia, Instrumental Methods of Organic Functional Group Analysis, p. 251. Wiley Interscience, New York (1972).
- ¹⁸ W. G. Haanstra, W. L. Driessen, J. Reedijk, U. Turpeinen and R. Hämäläinen, J. Chem. Soc. Dalton Trans, 2309 (1989).
- ¹⁹ T. N. Sorrell and M. R. Malachowski, Inorg. Chem. 22, 1883 (1983).
- ²⁰ J. L. Speier, C. A. Roth and J. W. Ryan, J. Org. Chem. **36**, 3120 (1971).
- ²¹ P. D. Verweij, "New selective chelating ion exchangers, based on glycidyl methacrylate polymers and silica", Ph.D. Thesis, Leiden (1991).
- ²² A. M. Zaper and J. L. Koenig, Polym. Compos. 6, 156 (1985); Chem. Abs. 104, 110736t (1986).
- ²³ J. E. Sandoval and J. J. Pesek, Anal. Chem. 61, 2067 (1989).
- ²⁴ T. L. Weeding, W. S. Veeman, I. W. Jennekens, H. Angad Gaur, H. E. C. T. Bein and W. G. B. Huysmans, Macromolecules 22, 706 (1989).
- ²⁵ E. Mertzel and J. L. Koenig, Adv. Polym. Sci. 75, 73 (1986).
- ²⁶ L. C. Behr, R. Fusco and C. H. Jarboe, Pyrrazoles, pyrrazolines, pyrrazolidines, indazoles and condensed rings, Interscience, New York (1967).
- ²⁷ A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam (1984).
- ²⁸ F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Interscience, New York (1988), p. 607.