

**GELS BY POLYCONDENSATION OF TETRAETHOXYSILANE
AND $[\text{Co}(\text{CO})_3\text{L}]_2$ OR $\text{Rh}(\text{CO})\text{ClL}_2$ ($\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3$)
Interrelation between metal complex concentration and specific surface area**

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Co-condensation of tetraethoxysilane (TEOS) and $[\text{Co}(\text{CO})_3\text{L}]_2$ or $\text{Rh}(\text{CO})\text{ClL}_2$ ($\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3$) in different molar ratios has been studied in order to elucidate the influence of the metal complex concentration on the specific surface area of the obtained gels. Because the metal complex moieties are not decomposed and maximum surface areas are obtained, H_3PO_4 is superior to other acids as a catalyst for the condensation reaction. Elemental analyses show that no metal is lost during condensation. With increasing metal concentration the specific surface area of the polycondensates decreases rapidly: it drops to half its original value, if about 5 mol% metal complex is co-condensed with TEOS.

1. Introduction

Immobilization of homogeneous transition-metal catalysts by linkage to organic or inorganic solids yields systems that combine the advantages of both homogeneous and heterogeneous catalysts [1]. Whereas surface hydroxyl groups of inorganic oxides like silica or alumina are used to anchor the catalyst, the environment of the catalytic site on organic supports can be tailor-made: the support is easily functionalized, a higher catalyst-to-support ratio can be achieved and by variation in the degree of crosslinking its physical properties can be altered. Furthermore, the functional ligands are homogeneously distributed through the body of the organic polymer; bonding of the metal centers is therefore not restricted to the surface of the particles.

On the other hand, inorganic supports are superior with respect to thermal and mechanical stability. Due to the higher rigidity of the inorganic polymer matrix the environmental conditions (solvent, temperature, pressure) have no de-

cisive influence on the structure or microstructure of the support and hence on the support-dependent characteristics of the catalyst.

The advantages of organic and inorganic systems could be combined, if inorganic supports were prepared in a similar way as their organic counterparts, i.e. if the nature and concentration of the metal-binding sites and the physical properties of the support could be varied to a similar degree. Only a few efforts towards the realization of this goal have been reported [2]. The basic idea is to use metal complexes, $\text{L}_n\text{M}-\text{X}(\text{CH}_2)_n\text{Si}(\text{OR})_3$, which contain a multifunctional silane of the type $\text{X}(\text{CH}_2)_n\text{Si}(\text{OR})_3$ as a ligand, X being the ligating functional group. Co-condensation of such metal complexes with $\text{Si}(\text{OR})_4$ (fourfold cross-linking) should give silica gel-like metal-containing materials, the properties of which can be varied by the concentration and the nature of the reactants and by the reaction conditions.

The various parameters that influence hydrolysis and condensation reactions of (organo-)alkoxysilanes and introduce structural variations

into derived polymeric materials, have been investigated [3–5]. It is reasonable to assume that hydrolysis and condensation of alkoxy-substituted metal complexes, $L_nM-X(CH_2)_n-Si(OR)_3$ is governed by the same basic principles, but one has to be aware of the fact, that changes in composition and reaction conditions can change the material properties (e.g. microstructure of porous supports) remarkably. In the present work we restrict ourselves to the question, how the chemical composition and the surface area of the polycondensates are interrelated. Both parameters are important in respect to catalyst performance. For this purpose, co-condensation between tetraethoxysilane (TEOS) and two model complexes, $[Co(CO)_3L]_2$ and $Rh(CO)ClL_2$, $L = Ph_2PCH_2CH_2Si(OEt)_3$, were carried out for different TEOS:complex molar ratios.

2. Experimental

Preparation of trans- $Rh(CO)ClL_2$ (m.p. 109 °C, yield 83%) has already been described by Allum et al. [6].

2.1. Preparation of $Co_2(CO)_6[PPh_2CH_2CH_2Si(OEt)_3]_2$

The complex is prepared in an atmosphere of dry nitrogen. All solvents were dried by standard methods and saturated with nitrogen.

To a solution of 2.22 g (6.5 mmol) $Co_2(CO)_8$ in 100 ml benzene, a solution of 4.9 g (13 mmol) $Ph_2PCH_2CH_2Si(OEt)_3$ in 35 ml benzene is added dropwise during 1 h. The mixture is then refluxed for 1 h. After cooling, the solvent is removed in vacuo. The dark red residue is dissolved in 80 ml hexane, refluxed for 30 min and then slowly cooled to -20 °C. The precipitate is filtered off, washed with three portions of 4 ml hexane and dried in vacuo. Yield 5.95 g (88%); m.p. 99 °C (dec.). Found: C, 52.98; H, 5.52; Co, 11.05. $C_{46}H_{58}Co_2O_{12}P_2Si_2$ (1038.93) calc.: C, 53.18; H, 5.63; Co, 11.35. I.r. (benzene) $\nu(CO)$ 1974 m, 1950 vs cm^{-1} . 1H -NMR ($CDCl_3$, rel. int. TMS) δ 7.50 (m, 10 H, Ph), 3.80 (q, 6 H, OCH_2), 2.49 (m, 2 H, PCH_2), 1.21 (t, 9 H, CH_3), 0.85 (m, 2H, $SiCH_2$) ppm.

2.2. Condensation reactions

To eliminate the influence of other parameters than the TEOS:complex ratio, standard conditions were used for all condensation reactions. This procedure implies that the condensation reactions were not optimized in respect to maximum BET surface areas or to complete condensation of the obtained gels.

5–10 mmol TEOS and $Rh(CO)ClL_2$ or $[Co(CO)_3L]_2$ in the desired molar ratio are dissolved in 20–30 ml acetone. To this mixture 2.8 n aqueous H_3PO_4 is added. The amount of acid, which serves as a catalyst and supplies the water

Table 1

Analytical data and specific surface areas for the gels obtained by co-condensation of $[Co(CO)_3L]_2$ and $Si(OEt)_4$ ($L = Ph_2PCH_2CH_2Si(OEt)_3$). Theoretical values (in brackets) were calculated assuming complete condensation of both $[Co(CO)_3L]_2$ and $Si(OEt)_4$ in the specified ratio

Molar ratio TEOS:[$Co(CO)_3L$] $_2$	Elemental analyses			Co:C ratio	BET surface area (m^2/g)
	Metal	C	H		
1:1	14.1 (13.5)	40.4 (46.6)	3.8 (3.2)	1:14	3
2:1	12.3 (12.6)	37.5 (43.6)	3.8 (3.0)	1:15	25
4:1	10.4 (11.2)	36.7 (38.6)	3.6 (2.7)	1:17	60
8:1	7.8 (9.1)	25.4 (31.5)	3.1 (2.2)	1:16	110
10:1	7.5 (8.3)	24.3 (28.8)	2.9 (2.0)	1:16	180
14:1	5.9 (7.1)	21.2 (24.6)	2.5 (1.7)	1:18	200
20:1	4.8 (5.9)	19.3 (20.2)	2.1 (1.4)	1:20	480
50:1	3.2 (3.1)	8.9 (10.7)	1.6 (0.7)	1:14	700
70:1	1.8 (2.4)	8.1 (8.1)	1.6 (0.6)	1:22	720
90:1	1.4 (1.9)	7.2 (6.6)	1.5 (0.5)	1:25	600
100:0					890

Table 2

Analytical data and specific surface areas for the gels obtained by co-condensation of $\text{Rh}(\text{CO})\text{ClL}_2$ and $\text{Si}(\text{OEt})_4$ ($\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3$). Theoretical values (in brackets) were calculated assuming complete condensation of both $\text{Rh}(\text{CO})\text{ClL}_2$ and $\text{Si}(\text{OEt})_4$ in the specified ratio

Molar ratio TEOS:Rh(CO)ClL ₂	Elemental analyses					Rh:C ratio	Rh:Si ratio	P:Si ratio	BET surface area (m ² /g)
	Metal	C	H	Si	P				
1:1	11.9 (13.6)	39.4 (46.0)	4.2 (3.7)			1:28			3
2:1	10.9 (12.6)	35.3 (42.6)	3.8 (3.5)			1:28			4
4:1	10.1 (11.0)	30.8 (37.2)	2.9 (3.0)	17.9 (18.0)	6.5 (6.6)	1:26	1:6.5	1:2.5	35
8:1	7.2 (8.7)	22.6 (29.6)	3.4 (2.4)			1:27			215
10:1	7.8 (7.9)	21.9 (26.8)	2.8 (2.2)			1:24			215
14:1	6.5 (6.7)	18.0 (22.7)	2.4 (1.8)	20.7 (29.2)	2.9 (4.0)	1:24	1:12	1:8	400
20:1	4.9 (5.4)	14.9 (18.4)	2.4 (1.5)			1:26			465
50:1	2.7 (2.8)	8.1 (9.4)	2.2 (0.8)			1:26			630
70:1	2.0 (2.1)	7.1 (7.1)	1.5 (0.6)	41.0 (41.2)	1.3 (1.3)	1:30	1:74	1:35	695
90:1	1.5 (1.7)	5.2 (5.7)	1.9 (0.5)			1:30			665
100:0									890

which is needed for hydrolysis, is determined as follows: from the sum of all ethoxy groups (both from TEOS and the metal complex) the stoichiometric amount of water is calculated. For the reaction a 7-fold excess is employed. However, instead of water, an equal amount of acid is used.

The reaction mixture is kept at room temperature in an open vessel for 24–48 h. During this time the solvent evaporates. The remaining water-insoluble, yellow to brown material is stirred with 20 ml water for 2–3 h, filtered off, washed with water and acetone and then dried at 60°C and 10⁻² Torr for 16 h. The washing solutions do not contain any metal compound. The products are characterized by IR spectroscopy and by elemental analyses (tables 1, 2). Phosphorus analyses of selected Rh-containing materials show no increased values (table 2), indicating that no or very few phosphate (from H₃PO₄) is built into the polymer.

2.3. Determination of the specific surface area

Determination was made on a Carlo Erba Sorptory 1750 instrument by the BET method using N₂ adsorption at 77 K.

3. Results and discussion

Co-condensation of $[\text{Co}(\text{CO})_3\text{L}]_2$ or $\text{Rh}(\text{CO})\text{ClL}_2$ with TEOS in the presence of an aqueous acid results in the formation of powdery to granular, water insoluble solids. The choice of the proper acid, which serves as a catalyst for the hydrolysis and condensation reaction is important with respect to the question whether the metal complex entity survives the condensation reaction. Only when H₃PO₄ is used as a catalyst, the infrared spectra of the polymeric material show about the same $\nu(\text{CO})$ bands as the starting complexes. We attribute the absorptions to $[\text{Co}(\text{CO})(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiO}_{3/2})_2]$ or $\text{Rh}(\text{CO})\text{Cl}[\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiO}_{3/2}]_2$ moieties within the polymeric network. Since these bands are observed even if the TEOS: complex molar ratio is high (up to 90:1) we assume that most of the metal complex is built into the polymer without major decomposition or reorganization of ligands (vide infra). With HCl or H₂SO₄ instead of H₃PO₄ the typical $\nu(\text{CO})$ bands are no longer observed in the product, if the TEOS: complex ratio exceeds 10:1. Total decomposition of the metal complex or incomplete condensation (at standard conditions) result from the

use of HBF_4 , HPF_6 , HClO_4 , CCl_3COOH or CF_3COOH .

Although co-condensation of $\text{Rh}(\text{CO})\text{CIL}_2$ and TEOS in various ratios in the presence of $2n$ HCl results in materials, which show no or only weak $\nu(\text{CO})$ absorptions, the material contains nearly the whole amount of the metal and the ligand L employed in the reaction. This is indicated by elemental analyses (Rh, C, H) and by the presence of $\nu(\text{PC})$ bands in the infrared spectra of the polycondensates. To find out which rhodium species are formed in the reaction with HCl, we treated the obtained gels with 1 atm of carbon monoxide at 100°C for 1 h. At these conditions the $\nu(\text{CO})$ band of $\text{Rh}(\text{CO})\text{CIL}_2$ reappears and a new $\nu(\text{CO})$ band appears in the infrared spectrum at 2090 cm^{-1} . The latter is typical of a compound of the type $\text{Rh}(\text{CO})\text{Cl}_3(\text{PR}_3)_2$ [7]. It is known that in solution $\text{RhCl}_3(\text{PR}_3)_3$ reacts with CO to yield a mixture of $\text{Rh}(\text{CO})\text{Cl}(\text{PR}_3)_2$ and $\text{Rh}(\text{CO})\text{Cl}_3(\text{PR}_3)_2$ [8]. We therefore conclude that on co-condensation of $\text{Rh}(\text{CO})\text{CIL}_2$ with TEOS in the presence of HCl a part or the total amount of the metal complex is transformed to $\text{RhCl}_3[\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiO}_{3/2}]_3$ moieties.

The kind of acid employed in the condensation reaction also exerts some influence on the physical properties of the products. The highest specific surface areas at any TEOS:complex ratio are obtained if H_3PO_4 is used. Use of HCl gives somewhat lower, use of H_2SO_4 only about half of the surface areas at the same reaction conditions (e.g. TEOS: $[\text{Co}(\text{CO})_3\text{L}]_2 = 20:1$, H_2SO_4 170, HCl 250, H_3PO_4 480 m^2/g ; 70:1, H_2SO_4 345, HCl 700, H_3PO_4 720 m^2/g).

Because the metal complex moieties are not decomposed and maximum surface areas are obtained, H_3PO_4 is superior to other acids as a catalyst in the condensation reactions described here. H_3PO_4 was therefore used exclusively for our investigation on the interrelation between complex concentration and specific surface area. For this purpose $[\text{Co}(\text{CO})_3\text{L}]_2$ and $\text{Rh}(\text{CO})\text{CIL}_2$ were co-condensed with TEOS in different ratios. We used standard conditions for all experiments in order to eliminate influences of other parameters than the TEOS:complex molar ratios and did not enforce complete condensation. Therefore, the obtained

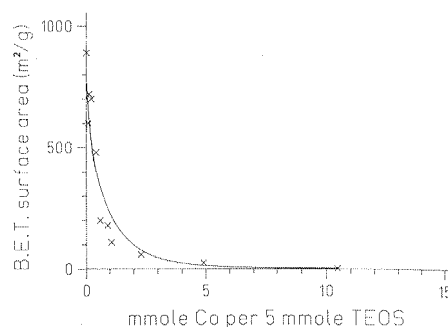


Fig. 1. Polycondensation of $[\text{Co}(\text{CO})_3\text{L}]_2$ with TEOS: surface area vs. mmol metal (from metal analysis) per 5 mmol TEOS.

products still contain undetermined amounts of water and/or uncondensed OH groups, and the absolute values of the elemental analyses (tables 1 and 2) deviate from theoretical values, which were calculated on the assumption of complete condensation. However, the analytical data clearly show that the products contain the metal compound in the original ratio. This means, that the metal content of the gels can simply be adjusted by co-condensing an appropriate mixture of TEOS and metal complex.

The relationship between the specific surface area of the polycondensates and their metal concentration is shown in figs. 1 and 2. There is a distinct dependence of the specific surface area on the analytically found metal concentration (which approximately corresponds to the molar concentration of the metal complex moieties): with increasing metal complex concentration the surface area decreases rapidly. If TEOS is polycondensed without an admixture of metal complex using our

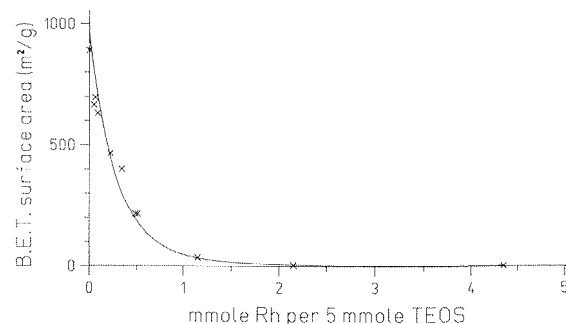


Fig. 2. Polycondensation of $\text{Rh}(\text{CO})\text{CIL}_2$ with TEOS: Surface area vs. mmol metal (from metal analysis) per 5 mmol TEOS.

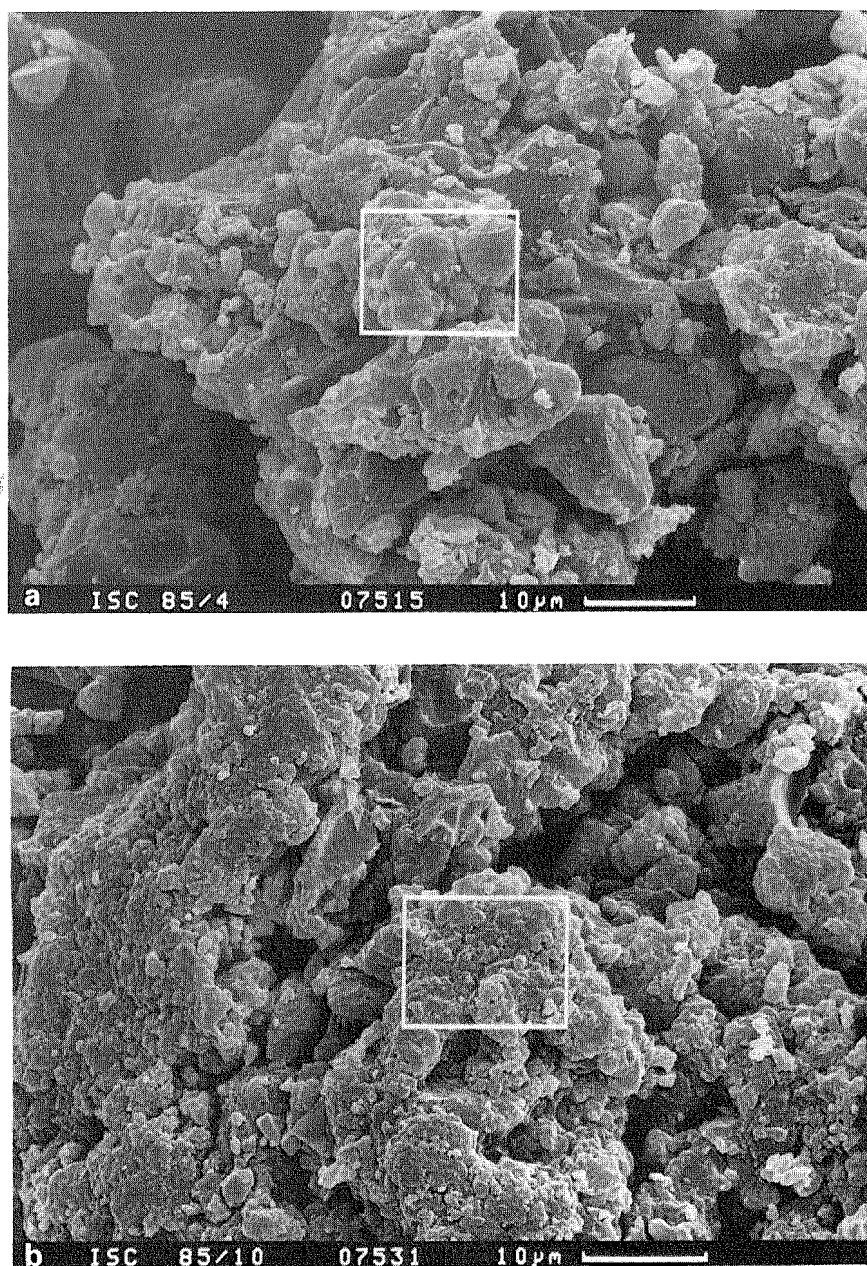


Fig. 3. Scanning electron micrographs of gels obtained by co-condensation of TEOS and $\text{Rh}(\text{CO})\text{ClL}_2$. (a) molar ratio 8:1 (BET surface area 215); (b) molar ratio 90:1 (BET surface area 665).

standard conditions, a value of $890 \text{ m}^2/\text{g}$ is obtained. The surface area drops to about half this value, if about 5 mol% metal complex (TEOS: complex molar ratio about 20:1) is co-condensed with TEOS.

The opposite result has been found on HCl-catalyzed cocondensation of $\text{Si}(\text{OMe})_4$ and $\text{MeSi}(\text{OMe})_3$ [9]. With an increasing percentage of $\text{MeSiO}_{3/2}$ in the polycondensates the BET surface area increases, due to an increasing hydrophobic-

ity of the pores, which tends to expel water from the capillaries. In our case, i.e. on co-condensation of TEOS with the metal complexes, this effect is overcompensated by network modification induced by the bulky moieties. An increasing amount of these groups enables the polymeric network to relax more easily. Another factor could be a different particle growth induced by either the steric bulk of the metal complex moieties or the electronic influence of the alkyl chain attached to the $\text{Si}(\text{OEt})_3$ groups of the ligand L. Organic groups R in organo-alkoxysilanes, $\text{R}_{4-n}\text{Si}(\text{OR}')_n$ ($n = 1-3$), have been shown to influence the polarity of the Si-O bond and therefore the reactivity of the alkoxides [4,10].

Gels obtained by co-condensation of TEOS with $[\text{Co}(\text{CO})_3\text{L}]_2$ or $\text{Rh}(\text{CO})\text{ClL}_2$ appear homogeneous macroscopically. Preliminary scanning electron micrographs from the Rh series are shown in fig. 3. The surface of the particles is smoother and globular particles are observed, if the metal content is high, i.e. if the BET surface is low (fig. 3(a)). In the Co series the same phenomenon is found. To get information on the dispersion of the metals, we analyzed samples with different metal contents by EDAX. In polycondensates from TEOS and $[\text{Co}(\text{CO})_3\text{L}]_2$ or $\text{Rh}(\text{CO})\text{ClL}_2$ in a 50 : 1 molar ratio, selected areas from the particles showed different metal concentrations. Contrary to this, the metal distribution appeared uniform in gels with higher metal concentrations (within the

resolution of EDAX of a few μm). Although this point needs further clarification by more detailed investigation, we conclude that the metal compounds are evenly distributed in the bulk of the gels and no unmixing of the two starting compounds occurs during condensation, although we cannot exclude that aggregates of metal-containing moieties are formed on a molecular level.

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