Chem. Rev. **2002,** *102,* 3543–3578

Applications of Sol–Gel-Processed Interphase Catalysts

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I. Introduction

Mankind's ever-growing demand for energy and raw materials is gradually pushing natural resources to their limits, giving rise to more environmental problems. In this regard, chemistry has played a contradictory role, although it represents one of the most successful and diverse sectors of manufacturing industries in many regions of the world. The range of chemical products is enormous, and they make invaluable contributions to our quality of life. However, these manufacturing processes also lead to millions of tons of waste. As a consequence, the role of chemistry is not generally accepted by governments or the public; chemistry is actually considered by many as the cause of the problems. Hence, the so-called "green chemistry" becomes increasingly important, with the objective to create new products, processes, and services that achieve societal, economic, and environmental benefits.[1−5]

The challenge for chemists include the discovery and evaluation of new synthetic pathways using alternative feedstocks, the elaboration and employment of more favorable reaction conditions and solvents for improved selectivity as well as energy minimization, and the design of less toxic and inherently safer chemicals.[6] In chemical synthesis, the ideal will be the combination of a number of environmental, health, safety, and economic targets. Catalysts are able to meet this lofty goal because they have widely recognized benefits — thermodynamically favorable reactions that have no low-energy pathways can be rendered possible under mild conditions. Moreover, catalysts are mandatory in the manufacture of a vast array of chemicals and fuels and as such significantly contribute to our economy and high living standards.[7−10] In addition, catalysts provide important environmental advantages, for example, in catalytic converters for automobiles.[5,11] Moreover, improved catalytic processes could lead to more efficient consumption of energy and natural resources as well as sequestration of the greenhouse gas CO_2.

Homogeneous catalysts have uniform and well-defined reactive centers, which lead to high and reproducible selectivities.[12−17] The activity and efficiency of these catalysts are generally high. However, one of the major problems is the separation of the catalyst from the reaction mixture. This procedure often generates large volumes of waste eluent and devours a lot of energy. Also, the process of extracting an expensive catalyst may lead to decomposition. Thus, elimination of this step would be favorable and is one of the major goals in modern catalyst research.

To solve this problem, several concepts have been tested to combine the advantages of homogeneous and heterogeneous catalysis. These include supported liquid-phase catalysts,[18,19] biphasic catalysts,[20−23] ionic liquids as solvents in catalysis,[24−27] the application of supercritical fluids,[28−31] dendrimer catalysts,[32,33] nanofiltration-coupled catalysis,[34] and supported catalysts.[35−52] A drawback of supported catalysts is the loss of homogeneity due to minor changes in the structure, which many reactive centers suffer from. This leads to a reduced activity and selectivity of the immobilized catalysts.[53] In several cases the influence of the matrix on the final outcome of the reactivity and selectivity is not known. This is due to the lack of structural knowledge about both the reactive centers and the polymer matrix.

The application of surface-modified inorganic and organic materials has been less successful because

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10.1021/cr010358t CCC: $39.75

Zhong-lin Lu, born in 1968 in Gansu Province (China), studied chemistry at Lanzhou University and earned his M.S. degree in 1993. He received his Ph.D. degree in 1997 at Nanjing University with Prof. Xiao-zeng You. In 1996, he worked 8 months at the University of Hong Kong in the group of Prof. Andreas Mayr. After two years of postdoctoral work with Prof. Bei-sheng Kang at Zhongshan University, he joined the group of Prof. Rudi van Eldik at the University of Erlangen-Nürnberg as a Humboldt Fellow. At present he works as a Humboldt Fellow with longer-cooperation fellowship in the group of Prof. Ekkehard Lindner at the University of Tübingen. His main research interests include coordination chemistry (transition metal and lanthanide complexes with tripodal ligands, aroylhydrazones, isocyanide, ether-phosphines), kinetics and mechanisms of metal complexes, and homogeneous and heterogeneous catalysis with ruthenium complexes.

Ekkehard Lindner, born in 1934 in Rottweil/Neckar (Germany), studied chemistry at the then Technische Hochschule in München and completed his Ph.D. thesis in 1962 with Walter Hieber on perfluorinated organocobaltcarbonyls. After his dissertation, he joined the group of H. Behrens at the University of Erlangen-Nürnberg and completed his Habilitation in 1967 with work on reactions of acid halides with Lewis acids and Lewis bases. In 1966 he was appointed Oberassistent and in 1970 Wissenschaftlicher Rat. In the same year he was awarded the Dozentenstipendium of the Fonds der Chemischen Industrie. In 1971 he accepted a position in the inorganic chemistry department (Anorganische Chemie II) at the Universität Tübingen. His main research interest is organometallic chemistry (transition metal mediated organic syntheses, macrocycles with reactive transition metal centers and their host/guest chemistry) and its application in homogeneous and heterogeneous catalysis (complexes with hemilabile ligands, chemistry in interphases). He is the author of about 450 publications.

of (i) the short lifetimes of these catalysts caused by the leaching of the reactive centers (poor anchoring), (ii) reduced accessibility of the catalysts, (iii) steric effects of the matrix, (iv) inhomogeneity of the reactive centers, and (v) difficulties in controlling the density of the reactive centers on the surface.[53,54]

Hermann A. Mayer was born in Heidelberg (Germany) in 1954 and received his Ph.D. degree in 1986 at the University of Tübingen with Prof. Dr. E. Lindner. After two years of postdoctoral work with Prof. Dr. W. C. Kaska at the University of California, Santa Barbara, he returned to the University of Tübingen. In 1994 he finished his Habilitation and was appointed Professor of Inorganic Chemistry in 2000. His research interests include the design of polyphosphine ligands, transition organometallic chemistry, concepts for catalyst immobilization, and the application of multinuclear NMR spectroscopy to organometallic chemistry in solution and in solid state.

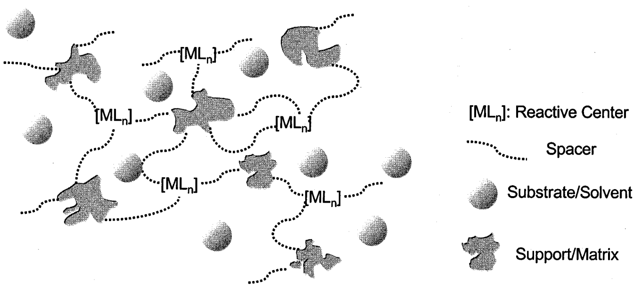


Figure 1. Schematic representation of an interphase.

With the aim to develop high-performance heterogenized homogeneous catalysts, the concept of *chemistry in interphases* has recently been introduced.[55] This term was imported from chromatography into the area of supported transition metal complexes in 1995.[56] An interphase is defined as a region within a material in which a stationary and mobile component penetrate each other on a molecular level (see Figure 1). The stationary phase is composed of an inert matrix, a flexible spacer, and an active center, whereas the mobile phase consists of a solvent or a gaseous, liquid, or dissolved reactant. In the case of chromatography, the active center fulfills the function of an interaction center, whereas in catalysis, the active site is a reactive center, for example, an organometallic complex. In an ideal interphase, the reactive center is uniform, well-defined, and highly mobile. Therefore, an interphase is able to simulate homogeneous reaction conditions, and at the same time it has the advantage of a heterogeneous catalyst. Rigid but highly porous materials can as well serve as supporting matrix provided that sufficiently long spacers lead to a satisfactory mobility of the reactive centers. Major drawbacks of conventional supported catalysts such as leaching, poor selectivity, and restricted accessibility of the reactive centers can be overcome. These systems combine many advantages of homogeneous (high activity, high selectivity, high reproducibility) and heterogeneous (easy separation and recovery of the catalysts from the reaction mixture) catalysis. In this review, the term "interphase catalysts" is introduced. The matrix is that part of the interphase catalyst which affects the cross-linking and therefore the insolubility of the support. Mainly, element−oxygen−element and carbon−carbon bonds form the polymer backbone. The spacer provides the linkage between the matrix and the reactive center. It usually consists of a chemically inert chain of variable length like hydrocarbons without or with heteroatoms ensuring sufficient mobility of the reactive center. The reaction centers are catalytically active groups, including organic moieties, metal complexes, or enzymes. Most of the typical homogeneous catalysts can be embedded into stationary phases by suitable T-silyl-functionalized ligands.

For the preparation of interphase catalysts, the sol−gel process is a powerful tool.[55,57−60] Suitable polysiloxane networks (hybrid polymers) are obtained under smooth and low-temperature conditions. Simultaneous co-condensation of T-silyl-functionalized metal complexes or ligands with various alkoxysilanes provide materials in which, in the case of an ideal interphase, the reactive centers are nearly homogeneously distributed across a chemically and thermally inert carrier matrix. Depending on the kind of application, sol−gel materials utilized in catalysis are either microporous or mesoporous. It should be stressed that the term "interphase catalysts" may be different in the literature. Encapsulation of catalytic groups into sol−gel materials, sol−gel-entrapped catalytic materials, immobilized catalysts, supported metal or organometallic complexes, etc., have many things in common with interphase catalysts. Furthermore, in many cases it is difficult to distinguish a complex that is just immobilized on a support from an interphase catalyst as described above. The main criterion should be the mobility of the reactive centers, which also depends on the flexibility of the spacer in the solvent used. Very often it is laborious to judge whether supported complexes reported in the literature meet the requirement of high mobility under reaction conditions. For these reasons in this review are discussed only those materials that have been prepared by polycondensation or poly-co-condensation of monomeric functionalized ligands, metal complexes, or other catalytically active groups by the sol−gel process. It will be demonstrated that the way a material was synthesized has a high impact on the performance of the catalyst. Therefore, in this review, emphasis is put on the preparation of catalytic systems related to chemistry in interphases, their catalytic activities, and in particular their recycling ability.

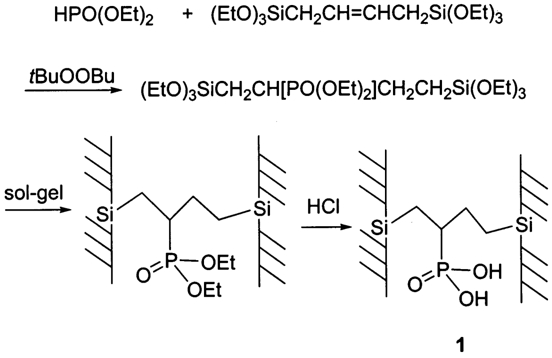
II. Organic Groups as Reactive Centers

Acids, bases, and oxidants are fundamental and important catalysts applied in a wide spectrum of organic conversions, for example, in addition, condensation, and redox reactions. However, the production of large amounts of waste and the costly separation and catalyst recovery have always caused problems. An additional intricacy is that some organic acids, such as peroxoacids, are not stable and therefore are unsafe for use on a large scale. Clearly, the immobilization of acids, bases, and oxidants within a solid support is a major advantage in the prolonged quest for heterogeneous catalysts for organic reactions, which results in an improvement with respect to workup, recycling, and stability.[61−67]

A. Solid Acids

A typical example is the preparation of uniformly modified polysilsesquioxanes from 1,4-bis(triethoxysilyl)but-2-ene and $HPO(OEt)_2$ to get 1,4-bis(triethoxysilyl)-2-(diethylphosphonato)butane via a radical addition reaction, which was then transferred to an insoluble product by an acid-catalyzed sol−gel process (Scheme 1).[68] The corresponding phosphonic acid modified polysilsesquioxane **1** was isolated after treatment of the phosphonate with concentrated hydrochloric acid and characterized by multinuclear solid-state nuclear magnetic resonance (NMR) spectroscopy.

Scheme 1



Polymer **1** offers a new class of solid acids, which has been considered as a catalyst in the pinacol−pinacolone rearrangement. Treatment of pinacol with **1** at 140 °C resulted in a high conversion to pinacolone after 12 h (eq 1a). The same catalyst was also successful in the dehydration of cyclohexanol at 120 °C, but with low activity (eq 1b; Table 1). Control experiments with mesoporous or microporous silica

Table 1. Performance of Catalysts 1−4

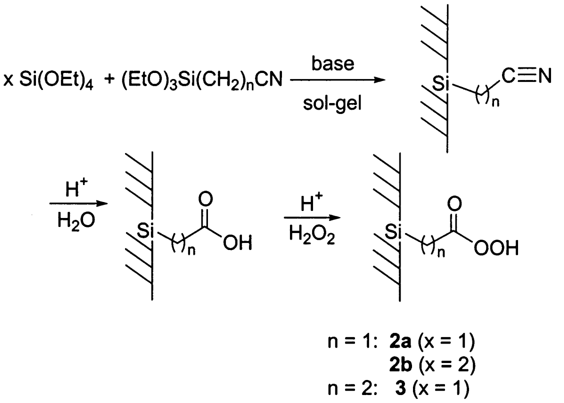
catalyst	type of catalysis	eq	yield (%)	selectivity(%)[a]	ref	comments
1	rearrangement[b]	1a	80		68	no recycling test
	dehydration[c]	1b	15			
2a	epoxidation[d]	2a	55	100	69	**2b** was used for
2b		2a	57	88		second run
		2b	57[e]	77[e]		
			56[f]	77[f]		
3		2a	62	96		
4	dehydrobromination[g]	3a	30		75	no recycling test
		3b	34			

[a] Selectivity to the oxide. [b] Reaction conditions: 0.2 g of catalyst, 6.0 g of pinacol, $T = 140$ °C, $t = 12$ h. [c] Reaction conditions: 0.25 g of catalyst, 25 mL of cyclohexanol, $T = 120$ °C, $t = 12$ h. [d] Reaction conditions: 4 mmol of alkene, 50 mL of chloroform, 0.75 g of catalyst, $T = 30$ °C, $t = 24$ h. [e] First run. [f] Second run. [g] Reaction conditions: 9×10^{-3} mol of substrate, catalyst prepared from 13.2×10^{-3} mol of TMOS and 6.8×10^{-3} mol of 3-(diethoxysilyl)propylamine, 5 mL of benzene, reflux, $t = 8$ h.

under the same conditions afforded no products for the above-mentioned two reactions. It should be pointed out that industrial processes for the access to cyclohexene require high temperatures and pressures where cyclohexanol is fed to activated catalysts such as silica, alumina, or zinc aluminate at 380–450 °C. Neat phosphoric acid in large excess is also active between 160 and 170 °C.

Peroxoacids function as active straightforward epoxidation reagents with wide applications. They are often employed for the epoxidation of unfunctionalized alkenes and do not require further catalysts. To immobilize peroxoacid, in a first step polysiloxane-supported nitriles are prepared by sol–gel processing of (2-cyanoethyl)triethoxysilane (CETS) in the presence of tetraethyl orthosilicate (TEOS) (Scheme 2).[69]

Scheme 2

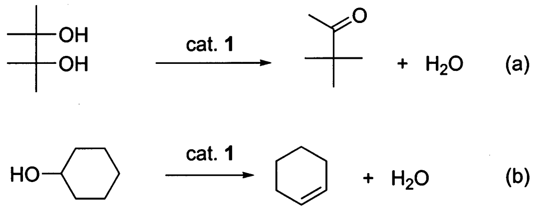


Subsequent hydrolysis by aqueous sulfuric acid afforded the polysiloxane-anchored carboxylic acids. Treatment of these materials with methanesulfonic acid and hydrogen peroxide gave the supported peroxocarboxylic acids **2a**,**b**. Both **2a** and **2b** were synthesized in CETS/TEOS ratios of 1:1 and 1:2, respectively. In the case of (3-cyanopropyl)triethoxysilane (CPTS), the supported peroxocarboxylic acid **3** was generated in a ratio of CPTS/TEOS = 1:1. The number of peroxoacid groups was determined by reductive titration with 0.1 M aqueous $Na_2S_2O_3$ in the presence of iodide.

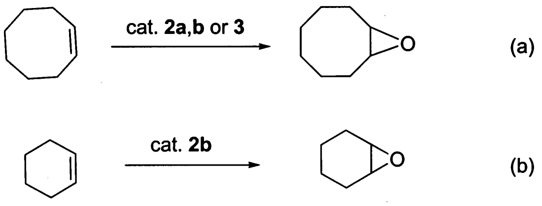
All three acids **2a**,**b** and **3** were successfully applied in the epoxidation of alkenes (eq 2). In particular, *cis*-cyclooctene and cyclohexene were converted with high to excellent selectivities (see Table 1). Although **2b** affords a lower selectivity than **2a**, after recycling and treatment with hydrogen peroxide/methanesulfonic acid, **2b** was still capable of epoxidizing cyclohexene. Compared to polymer-supported systems,[70] oxygen transfer efficiencies of silica materials were much higher (48 vs 76–91% for **2a**,**b** and **3**, respectively). At the same time **2a**,**b** have loadings and activities that are close to those found for conventional homogeneous peroxoacids, and they are stable under anhydrous conditions at room temperature.

B. Solid Bases

The preparation of organically modified silica-bearing amine groups via the sol–gel method has been known for some time, but their application as simple catalysts and reagents for organic synthesis is much less developed.[71–74] In particular, the group of Avnir was interested in the preparation of propylamine-anchored silica **4** obtained by the sol–gel process of tetramethoxysilane (TMOS) and 3-(diethoxymethylsilyl)propylamine (Scheme 3).[75]



(1)



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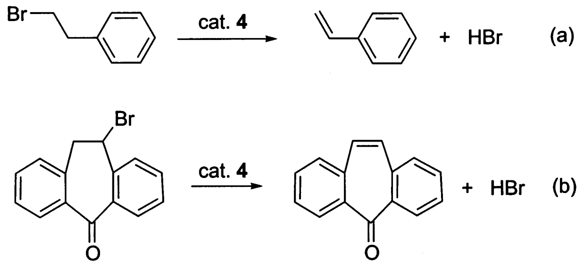
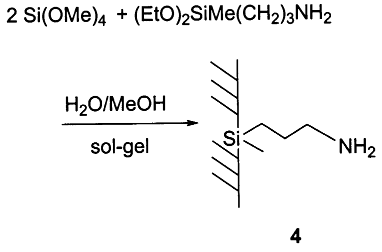


(3)

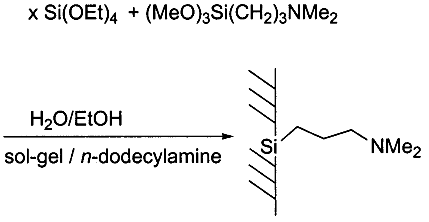
Scheme 3



The activity of supported amine **4** was determined by dehydrobromination of 2-phenylethyl bromide or 10-bromo-10,11-dihydro-5*H*-dibenzo[a,d]-cycloheptan-5-one (eq 3; Table 1). Considering that the substrate has been added in excess and that some of the amines are inaccessible due to microporosity and the known interaction of such amines with the silanols, the conversion of the actual catalytic active site is higher than the overall yield. This study unequivocally demonstrated the feasibility of organoamine modified sol–gel materials as recoverable catalysts and reagents.

Michael additions are essential carbon–carbon bond formation processes. A base is always required as catalyst to form the intermediate carbanion by abstracting a proton from an activated methylene precursor. Frequently this reaction serves as a test to study the catalytic activity of solid bases. Two novel catalysts based on hexagonal mesoporous silica (HMS) and *N*,*N*-dimethyl-(3-aminopropyl)trimeth-

Scheme 4



5a (x = 9)
5b (x = 4)

oxysilane were prepared using a templated sol−gel method and varying the amine-to-silane ratio.[76] In this way catalysts **5a**,**b** (Scheme 4) with TEOS/*N*,*N*-dimethyl-3-aminopropyltrimethoxysilane ratios of 9:1 and 4:1, respectively, are accessible. Their characterization by thermogravimetric analysis revealed a good thermal stability. Surface areas and loadings of the functional groups resulted from Brunauer, Emmett, and Teller (BET) methods and acid titrations. They were further characterized by diffuse reflectance Fourier transform infrared (FT-IR) spectroscopy (DRIFT).

Both catalysts **5a**,**b** were evaluated in the reaction of nitroalkanes with α,β-unsaturated carbonyl compounds (eq 4) and showed high selectivities and even higher activities than those prepared with amorphous silica (see Table 2). Rates are approximately 3 times faster compared to catalysts with similar loadings. No enantioselectivity was observed in the reaction between 2-cyclohexen-1-one and nitroethane/nitropropane. Altogether there is almost no difference in performance between **5a** and **5b**. After recovery, **5a**,**b** continued to catalyze the reactions three to five times. High yields were achieved even in a second or third repeated use.

Table 2. Michael Addition Reactions Catalyzed by 5a,b (Equation 4) (Data from Reference 76)[a]

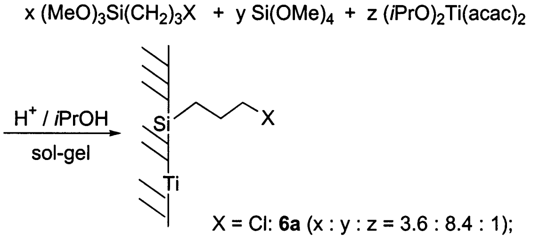
	eq 4a			eq 4b			
catalyst	R	time (h)	yield[b] (%)	R	time (h)	yield (%)	comments
c	H	7	58	H	13	58	
	CH_3	7.5	72	CH_3	5	65	
	CH_3CH_2	6.5	76	CH_3CH_2	8	82	**5a** was reused 3−5 times; no specific data are presented
5a	H	3	70	H	6	62	
	CH_3	2	92	CH_3	4.5	72	
	CH_3CH_2	2	90	CH_3CH_2	5	86	
5b	H	4	80	H	4	90	
	CH_3	1.2	94	CH_3	1.5	88	
	CH_3CH_2	1.5	95	CH_3CH_2	2.5	93	

[a] Typical reaction conditions: 0.5 g of catalyst **5a**, 25 mL of nitroethane, 20 mmol of but-3-en-2-one, reflux. [b] Yields of products by GC analysis. [c] *N*,*N*-Dimethyl-3-aminopropyl-silica prepared by postmodification.

Mesoporous mixed titania−silica materials dried by semicontinuous extraction with supercritical CO_2 turned out to be excellent catalysts for the epoxidation of alkenes, alkenols, and alkenones with alkyl hydroperoxides.[77−79] The structure and activity of these aerogels were controlled by adjustment of the sol−gel preparation and drying procedure. The acidity of the mixed oxide is crucial to activate the peroxide but can also result in acid-catalyzed side reactions of reactants and products.[80] Tuning the acidity with weakly basic organic and inorganic additives considerably improved the performance of the mixed titania−silica systems. Especially, amine addition enhanced epoxide formation. Thus, selectivities of up to 98% in the demanding epoxidation of 3-methylcyclohex-2-en-1-ol were achieved with high reaction rates.[81] The positive influence was explained by the neutralization of some acid sites that are present in the aerogels.

Baiker's group reported on the synthesis of novel organically modified mesoporous mixed titania−silica polymers with a target structure as illustrated in Scheme 5.[80] The functional groups were introduced via Si−C bonds during the sol−gel process and not only change the surface properties with respect to polarity and acidity but also are supposed to interact directly with the titanium active site as electron-donating ligands. The mentioned polymers were investigated by thermal analysis and BET methods as well as by FT-IR, DRIFT, and NMR spectroscopy.

Scheme 5



X = Cl: **6a** (x : y : z = 3.6 : 8.4 : 1);
OAc: **6b** (x : y : z = 1.2 : 10.8 : 1);
NMe_2: **6c** (x : y : z = 1.2 : 10.8 : 1)
acac: acetylacetonate

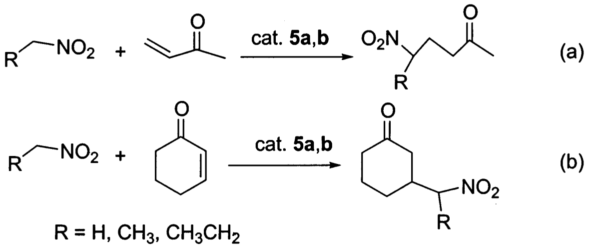
tert-Butyl hydroperoxide (TBHP) served as a probe for the catalytic potential of the organically modified titania−silica aerogels **6a**−**c** in the epoxidation of cyclohexene and cyclohexenol (eq 5). Differences among **6a**−**c** refer to initial rates in the epoxidation of cyclohexene/cyclohexenol, which decrease in the series **6b** > **6c** > **6a** (see Table 3). With regard to the epoxidation of cyclohexene, all catalysts were active. However, due to the rapid consecutive reactions, which can be traced back to residual HCl retained in the solid, no yield and selectivities were found for **6a**. For the epoxidation of cyclohexenol, experiments with **6a**−**c** were conducted under exactly the same conditions to ensure a direct comparison with the unmodified aerogel. Thus, the epoxide productivity of **6a**−**c** is similar to or even better than that of the unmodified aerogel and correlates well with the high initial activities. By organic modification a remarkable enhancement has been achieved in the epoxide selectivity of olefins, reaching 94% for **6c** with 91% peroxide conversion. Only a methyl-modified titania−silica aerogel afforded a higher olefin selectivity (98% after 10 min) and also a higher average rate. Compared to former studies the reactant-to-peroxide ratio in this work was improved.[82,83] Several advantages thus are realized by introducing organic functional groups to titania−silica catalysts. The materials combine the high activity of mesoporous titania−silica aerogels with high epoxide selec-

Table 3. Performance of Catalysts 6−8

catalyst	type of catalysis	eq	time (h)	initial rate[a]	yield (%)	selectivity (%) S_{olefin}[b]	$S_{peroxide}$[c]	ref	comments
6a	epoxidation[d]	5a	2	1.8				80	no recycling tests were reported
		5b	2	1.8	67	81	83		
			1		60	80	82		
6b		5a	2	8.1	90	97	90		
		5b	2	8.2	75	74	75		
			1		97	82	76		
6c		5a	2	3.1	75	96	86		
		5b	2	3.3	70	93	70		
			1		91	94	70		
7	epoxidation[e]	6a	2		65	89	56	84	reuse of catalysts indicated a poorer performance
			12		85	65	7		
			2[f]		34	93	52		
			2[g]		20	81	19		
			8[g]		51	78	6		
		6b	2		60	87	54		
8	oxidation[h]	7	4		95			87	**8** retained its activity and selectivity within four runs, no specific data are presented

[a] mmol g^{-1} min^{-1}. [b] $S_{olefin} = 100\%$ [epoxide]/([olefin]$_0$ − [olefin]). [c] $S_{peroxide} = 100\%$ [epoxide]/([peroxide]$_0$ − [peroxide]). [d] Reaction conditions: 70 mg of catalyst, 20 mmol of olefin, decane or pentane as internal standard, 2 mL of toluene, 5 mmol of TBHP, $T = 90$ °C. [e] Typical reaction conditions: 10 mmol of 2-cyclohexenone, 10 mL of methanol, 0.1 g of catalyst, $T = 20$ °C, hydrogen peroxide was added dropwise. [f] Using 2-propanol as solvent. [g] 0.2 g of silica was added. [h] Reaction conditions: 2.15 g of catalyst (0.5 mmol of radical), 10 mmol of MGP, 60 mL of H_2O containing KBr (1.4 mmol), 10% excess of 1.19 M NaOCl, pH 9.3, $t = 4$ h.

tivities. Furthermore, a reduction of the TiO_2 content below 10 wt % is possible without loss of activity when compared to the unmodified aerogel possessing 20 wt % of TiO_2.



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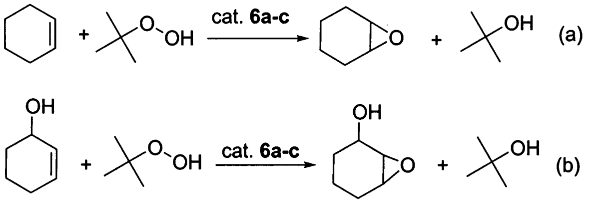

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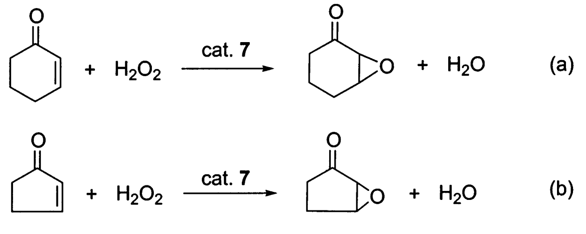

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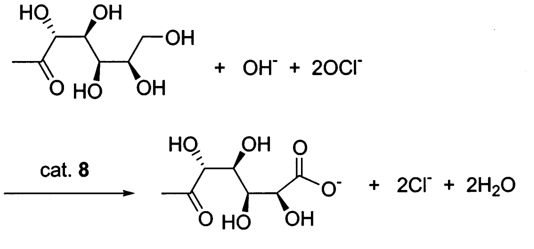
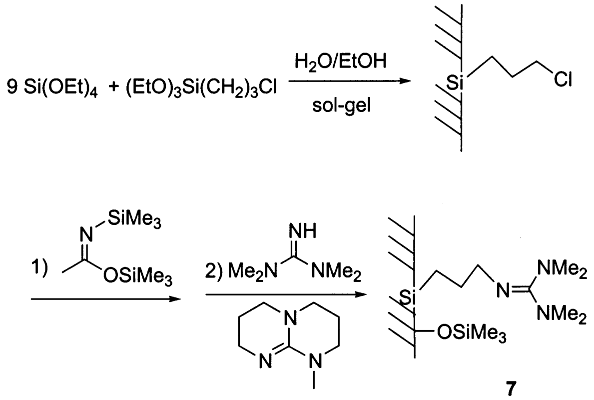


(7)

Guanidines are versatile strong bases and also candidates for supported catalysts. Previous work has demonstrated that guanidines can be supported, but their successful application in organic synthesis is limited. Novel guanidine bases supported on silica or micelle-templated silica (MTS) are typical examples (Scheme 6).[84]

Scheme 6



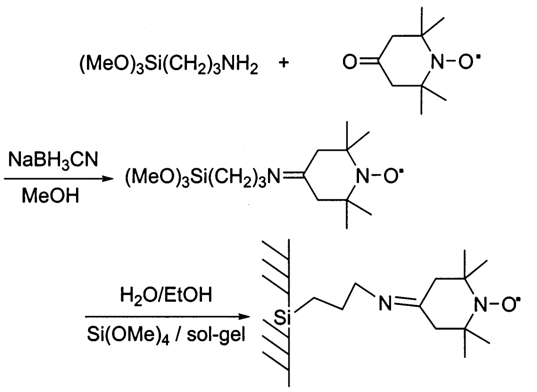
To prepare such systems, (chloropropyl)trimethoxysilane was sol−gel processed with TEOS in ethanol. Subsequent trimethylsilylation of the surfaces was achieved with *N*,*O*-bis(trimethylsilyl)acetamide. Treatment of this material with 1,1,3,3-tetramethylguanidine (TMG) and 1-methyl-1,5,9-triazabicyclo[4.4.0]-decane gave the final product **7**, which has been characterized by BET methods and ^{13}C magic-angle spinning (MAS) NMR spectroscopy.

Cyclohexenone was reacted with hydrogen peroxide in methanol at 20 °C to probe the catalytic activity (eq 6; Table 3). Excellent conversions and selectivities (89%) toward epoxides were achieved, whereas previously supported guanidines led to a conversion of only 42%.[85] Similar results were obtained with cyclopentenone. Repeated use of the recovered catalyst indicates a significantly poorer performance, possibly due to the adsorption of small quantities of byproducts such as diols at the active site.

C. TEMPO-Modified Sol–Gel Materials

Stable organic nitroxyl radicals belonging to the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) family are outstanding catalysts for selective oxidations.[86] The radicals are soluble in water (~1% w/w) where, in the presence of alkaline (pH 9−10) NaOCl as primary oxidant along with a catalytic amount of bromide, they mediate the conversion of $-CH_2OH$ groups into carboxylic functions with complete selectivity for the primary alcohols. Blum's group has recently disclosed that sol−gel-processed TEMPO is an effective catalyst for the oxidation of sugars with NaOBr into uronates (Scheme 7).[87] The TEMPO moiety was tethered to $(MeO)_3Si(CH_2)_3NH_2$ by reductive amination of 4-oxo-TEMPO (TEMPON). Then the radical monomer was homogeneously entrapped within a silica matrix by the sol−gel process with TMOS as a co-polycondensation agent to produce **8**.

Scheme 7



8

Catalyst **8** promoted the oxidation of methyl α-D-glucopyranoside to the corresponding uronic acid (eq 7). In each run no other products apart from the uronate (the content of which was also measured with the colorimetric test for uronic acids) were detected in the reaction mixture. In four consecutive reaction cycles the catalyst retained its activity, as well as its shape and appearance. Interestingly, after each run a higher degree of oxidation (~95%) was found (Table 3). Furthermore, no leaching of entrapped radicals into the solution was detected (with a spectroscopic limit of 10 ppm). This is important because many heterogeneous oxidations can actually be promoted by catalysts leached into the solution. By separating the catalyst from the reaction mixture shortly (30 min) after the beginning of the oxidation, the mother liquor has been investigated, which indicated no extra formation of uronate. The reuse activity of **8** was also confirmed by electron spin resonance (ESR) spectroscopy prior to and after consecutive reaction runs. Detailed aspects affecting the catalytic properties of **8** (including the ratio of metal to water, amount of alcohol, pH value, temperature, drying time, and other important parameters) have been patented.[88]

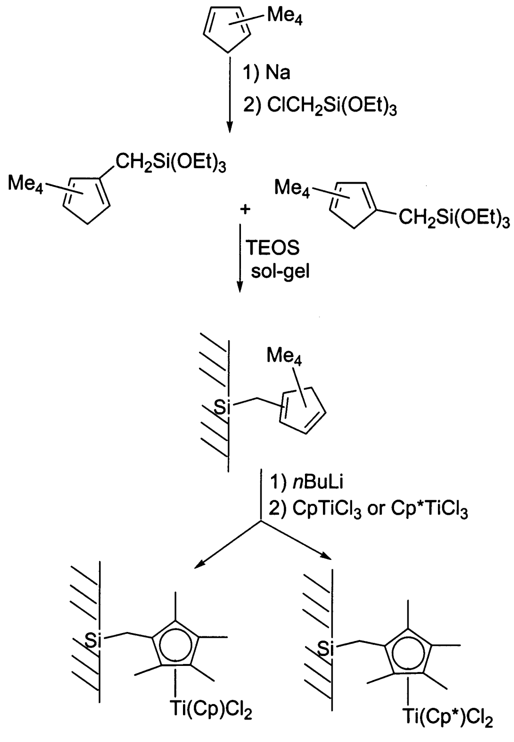
III. Metal Complexes as Reactive Centers

A. Titanium Complexes

Group 6 metallocences were discovered by Kaminsky and Sinn and viewed as the next generation of catalysts for olefin polymerization.[89−91] It was soon realized that the originally homogeneous metallocenes had to be heterogenized to avoid reactor fouling and to provide products with large, uniform particle sizes and higher bulk densities. Moreover, the facile control of the polymer particle morphology is achieved by using established technologies known from common Ziegler−Natta catalysts.[92−94] However, these systems will not be discussed here in detail because the actual active catalysts remain in the polymer and are not recovered.

Polymer-anchored cyclopentadienyl- and pentamethylcyclopentadienyltitanium catalysts were described by Cermak et al.[95] Polysiloxane-bound pentamethylcyclopentadiene was prepared by polycondensation of $C_5HMe_4CH_2Si(OEt)_3$ with TEOS. Subsequently, the obtained microparticulate polysiloxane was reacted with $CpTiCl_3$ and Cp^*TiCl_3 (Cp* = pentamethylcyclopentadienyl) in the presence of a large excess of *n*-butyllithium, respectively, to afford **9a**,**b** (Scheme 8). The hydrogenation potential of **9a** in the case of 1-octene [turnover frequency (TOF) = 14.5 min^{-1}] was 6.5 times lower than that of the homogeneous system $Cp^*CpTiCl_2$ but could be maintained even after a prolonged period of time (eq 8). Recycling was possible four times with gradual loss of activity (TOF changed from 14.5 min^{-1} in the first run to 5.1 min^{-1} in the second run and to 1.0 min^{-1} in the fourth run) without leaching of titanium. For

Scheme 8



9a **9b**

Table 4. Performance of Catalyst 10 in Hydrogenation Reactions (Data from Reference 99)[a]

eq	substrate (mol L^{-1})	solvent	[catalytst]/[substrate]	run no.	time (h)	yield (%)	selectivity (%) Z isomer	E isomer	comments
b	0.2	cyclohexane	1:20		2	96	100		**10** showed good recycling ability
9a	0.10		1:20[c]	1	6	74	96	4	
				4	5	47	95	4	
	0.16		1:20[d]	1	8	97.5	96	4	
				4	8	38	64	36	
	0.2		1:20	1	5	95	97	3	
				4	5	96	98	2	
	0.2	THF	1:20	1	3	100	95	1	
				4	3	21	90		
b	0.11	cyclohexane	1:10		24	92			
9b	0.11		1:10	1	16	95			
				5	17	80			
b	0.11	cyclohexane	1:10		38	94	100[e]		
9c	0.11		1:10	1	41	63	82[e]	18[f]	
				5	44	96	82[e]	18[f]	

[a] Reaction conditions: 0.1−0.2 mol L^{-1} of substrate, 200−250 mL of solvent, p[H$_2$] = 430 psi. [b] Homogeneous reaction with complex $(EtO)_3SiPhCr(CO)_3$. [c] Using catalyst prepared from commercial silica. [d] Using uncured catalyst **10**. [e] Product is 1-octene. [f] Product is 1-octane.

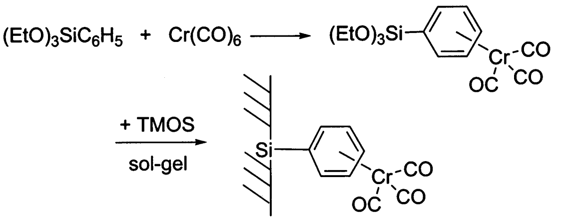
9b, the hydrogenation activity (TOF = 28.8 min^{-1}) was slightly higher than that of the homogeneous system $Cp_2^*TiCl_2$. It was still active in the absence of butyllithium and could be reused. The authors suggested that the variance in catalytic activity is attributed to variable methods of anchoring of the titanium complexes using different qualities of TEOS, which lead to altered morphologies of the polysiloxanes and hence different availabilities for the catalytically active centers.[95] Because in dependence on synthetic procedures the active sites are inside the matrix and not on the surface of the materials, the reaction conditions need to be selected carefully so that the accessibility of the reactive centers is maintained.

B. Chromium Complexes

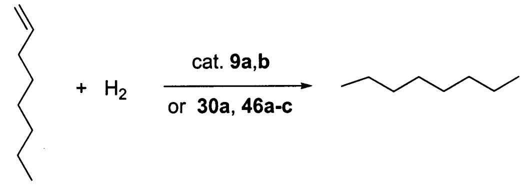
A well-known heterogeneous chromium system is the Phillips catalyst (CrO_3/SiO_2), which has played an important role in the production of polyolefins since it was discovered by Hogan and Banks more than 40 years ago.[96] Considering the concept of interphase, this process is not discussed in more detail.

Organometallic chromium complexes are effective in the regio- and stereoselective hydrogenation of various unsaturated systems.[97,98] Polysiloxane-bound chromium complexes were applied in the hydrogenation of methyl sorbate, 3-nonene-2-one, and 1-octyne. As a catalyst served **10**, which was obtained by co-condensation of η^6-$C_6H_5Si(OEt)_3Cr(CO)_3$ with TMOS and subsequent curing (Scheme 9; eq 9).[99] As methods for its characterization served X-ray photoelectron spectroscopy (XPS), BET analysis, and infrared spectroscopy. Detailed hydrogenation data for the above-mentioned three substrates are listed in Table 4. The activity of **10** was retained through several cycles and showed good regio- and stereoselectivities. Cyclohexane as a solvent is superior to THF in recovering the catalytic activity upon recycling of **10**. Experimental results indicate that the reaction has taken place within the polymer pores.

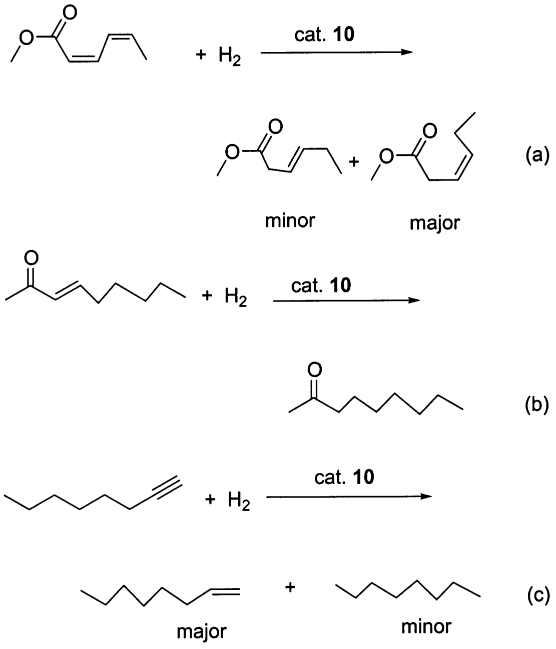
Scheme 9



10



(8)

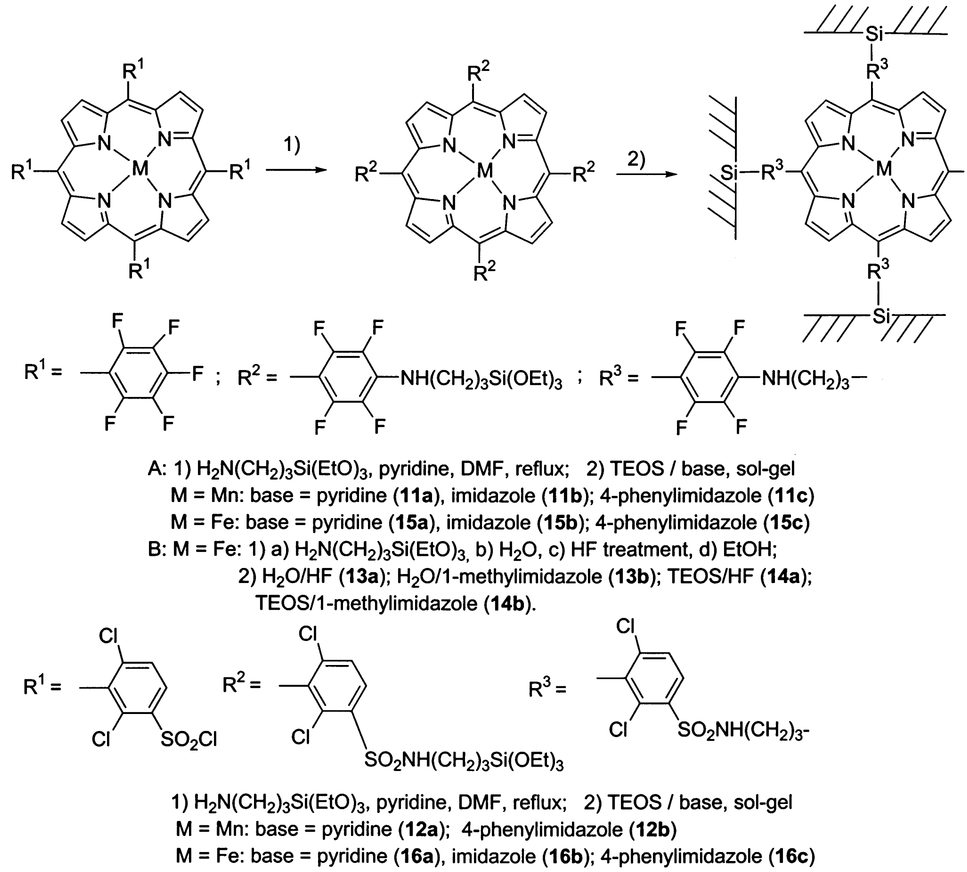


(9)

C. Manganese Complexes

Metalloporphyrins, mainly of iron(III) and manganese(III), represent versatile oxidation catalysts and

Scheme 10



A: 1) $H_2N(CH_2)_3Si(EtO)_3$, pyridine, DMF, reflux; 2) TEOS / base, sol-gel
M = Mn: base = pyridine (**11a**), imidazole (**11b**); 4-phenylimidazole (**11c**)
M = Fe: base = pyridine (**15a**), imidazole (**15b**); 4-phenylimidazole (**15c**)
B: M = Fe: 1) a) $H_2N(CH_2)_3Si(EtO)_3$, b) H_2O, c) HF treatment, d) EtOH;
2) H_2O/HF (**13a**); H_2O/1-methylimidazole (**13b**); TEOS/HF (**14a**);
TEOS/1-methylimidazole (**14b**).

1) $H_2N(CH_2)_3Si(EtO)_3$, pyridine, DMF, reflux; 2) TEOS / base, sol-gel
M = Mn: base = pyridine (**12a**); 4-phenylimidazole (**12b**)
M = Fe: base = pyridine (**16a**), imidazole (**16b**); 4-phenylimidazole (**16c**)

have been designed as models for monooxygenases based on cytochrome P-450.[100–109] Hybrid polymers containing manganese porphyrins as reactive centers were introduced by Iamamoto et al.[110] A tetrakis(pentafluorophenyl)porphyrinmanganese(III) complex served as starting material and was reacted with (3-aminopropyl)triethoxysilane (APTES) to afford a T-silyl-functionalized manganese porphyrin precursor. Subsequent poly-co-condensation with TEOS in the presence of nitrogen bases gave catalysts **11a**–**c** (Scheme 10), which were characterized by ultraviolet-visible (UV–vis) absorption spectroscopy, thermogravimetric analysis (TGA), electron paramagnetic resonane (EPR), and electron spectroscopy imaging (ESI). Polymers **11a**–**c** were active in the epoxidation of (*Z*)-cyclooctene using PhIO as oxidant (eq 10). The catalytic activities of **11a**–**c** were less than those of the corresponding homogeneous system, and the rate of conversion was also lower (Table 5).

Another modified tetrakis(2,6-dichlorophenyl)porphyrinmanganese species was heterogenized in the presence of TEOS to give **12a**,**b** (Scheme 10).[111] These immobilized complexes catalyzed the epoxidation of cyclooctene, using PhIO as oxidant (eq 10). In general, the reactions were complete after 24 h with yields of cyclooctene oxide between 69 and 96% (Table 5). It is obvious that the catalytic activity of **12a**,**b** is better than that of **11a**–**c**. No leaching of the metalloporphyrin from the stationary phase was observed during the reaction. Hydrogen peroxide as oxygen donor was also probed, but the yield was very low.

Table 5. Performance of Catalysts 11a–c, 12a,b, 15a–c, and 16a–c in the Epoxidation of (*Z*)-Cyclooctene (Equation 10a)[a]

catalyst	solvent	yield[b] (%) 1 h	yield[b] (%) 24 h	ref	comments
c	CH_2ClCH_2Cl	84	84	110	no recycling tests for catalysts **11a**–**c**, **12a**,**b**, **15a**–**c**, and **16a**–**c**
11a		0	34		
11b		7	27		
11c		7	30		
c	CH_2Cl_2	70	70	111	
12a		35	96		
12b		20	69		
c	CH_2ClCH_2Cl	89	89	110	
15a		43	85		
15b		7	31		
15c		14	50		
16a	CH_2Cl_2	97	100	111	
16b		10	47		
16c		13	100		

[a] Reaction conditions: 1 mL of solvent, 150 μL of (*Z*)-cyclooctene, 5 μL of cyclohexanone as internal standard, 5.0 mg of PhIO, 10 mg of catalyst, 25 °C. [b] Yield is based on PhIO. [c] Homogeneous reaction with the corresponding metal complexes without T-silyl groups.

D. Iron and Ruthenium Complexes

1. Iron Complexes

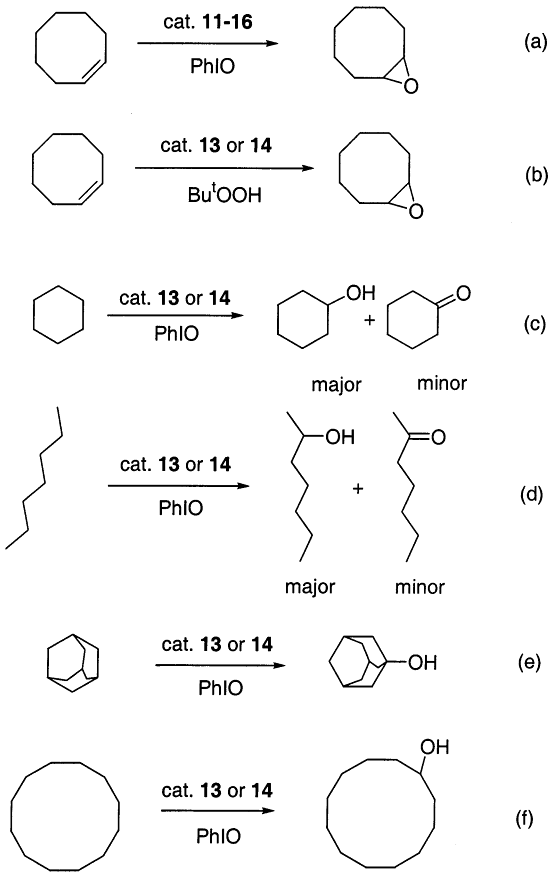
As models for cytochrome P-450, iron porphyrins have received much attention. Heterogenized catalysts based on iron phorphyrins adsorbed or covalently bound to inorganic polymers have also been reported.[100,103–107,112–119] In several cases they were

Table 6. Performance of Catalysts 13a,b and 14a,b (Data from Reference 121)

	yield (%)					
catalyst	eq 10b[a] (epoxidation)	eq 10c[b] (epoxidation)	eq 10d[c] (hydroxylation)	eq 10c + 10e (ratio)[d] (hydroxylation)	eq 10c + 10f (ratio)[e] (hydroxylation)	comments
13a	48	64	41	54 (5.6)	30 (1.1)	catalysts showed shape selectivity
13b	47	45	49	64 (9.9)	52 (1.1)	
14a	41	54	45	50 (12)	38 (1.7)	
14b	44	50	47	57 (17)	45 (2.0)	

[a] Reaction conditions: molar ratio of hydrocarbon/*t*-BuOOH/catalyst = 600:200:1, 1 mL of CH_2Cl_2/CH_3OH (1:3), yield based on *t*-BuOOH. [b] Reaction conditions: molar ratio of hydrocarbon/PhIO/catalyst = 800:20:1, 1 mL of CH_2Cl_2, [catalyst] = 1 mmol L^{-1}, $T = 20$ °C, $t = 2$ h; yields were based on PhIO and referred to cyclohexanol and cyclohexanone. [c] Reaction conditions: molar ratio of hydrocarbon/PhIO/catalyst = 2100:20:1, 1 mL of CH_2Cl_2/CH_3CN (1:1), yields referred to heptanols and heptanones. [d] Molar ratio of adamantane/cyclohexane/PhIO/catalyst = 200:200:20:1, 1 mL of CH_2Cl_2, total yields (adamantanols/cyclohexanol in molar ratio). [e] Molar ratio of cyclododecane/cyclohexane/PhIO/catalyst = 400:400:20:1, 1 mL of CH_2Cl_2, total yields (cyclododecanol/cyclohexanol in molar ratio).

obtained from surface-supported or entrapment methods.[100,103,117,120] Earlier work to incorporate iron porphyrins into interphases originates from Battioni et al., and they designated their system as metalloporphyrinosilica.[121] Respective catalysts **13a**,**b** and **14a**,**b** were obtained as outlined in Scheme 10. From (3-aminopropyl)triethyoxysilane and *meso*-tetrakis(pentafluorophenyl)porphyrin the monomer was formed. Subsequent hydrolysis and polycondensation in a biphasic CH_2Cl_2/H_2O system in the presence of a catalyst (HF or 1-methylimidazole) afforded **13a**,**b**, whereas **14a** and **14b** were produced by hydrolysis and co-condensation of modified porphyrin with TEOS in EtOH. The content of porphyrin in **13a**,**b** was higher than in **14a**,**b**. However, **13a**,**b** exhibited lower specific surface areas (30−105 $m^2\ g^{-1}$) than **14a**,**b** (>690 $m^2\ g^{-1}$). All of them catalyzed the epoxidation of cyclooctene in high yields (>90%) as well as the hydroxylation of cyclohexane and heptane with PhIO with yields of ~50% (eq 10; Table 6). The hybrid polymers **14a**,**b** promoted also the epoxidation of cyclooctene with *t*-BuOOH in a yield between 45 and 64%. Interestingly, the corresponding homogeneous catalyst was deactivated under the same reaction condition. Some preliminary results were also described in the oxidation of an adamantane/cyclohexane mixture (1:1) with PhIO. It was found that the adamantane/cyclohexane oxidation product ratio was much higher for **14a**,**b** than for **13a**,**b**, which is traced back to the difference in the specific surface area. Hydroxylation of cyclohexane, which is less reactive and bulky, was thus favored in the case of **13a**,**b**, where the metal center is less accessible. Similar results were achieved for the oxidation of a cyclododecane/cyclohexane mixture (1:1). Catalysts **14a**,**b** led to cyclododecanol/cyclohexanol ratios of ~2, whereas **13a**,**b** gave a ratio of 1.



(10)

Iamamoto et al. prepared the ironporphyrinosilica **15a**−**c**[110] and **16a**−**c**[111] according to Scheme 10 and compared their properties with those of the corresponding manganese porphyrins (vide supra, Scheme 10). The porphyrins **15a**−**c** proved to be more active than **11a**−**c** in the epoxidation of (*Z*)-cyclooctene with PhIO as oxidant (eq 10; Table 5). The best performance was obtained by **15a** in which pyridine was used as a template and the yield was similar to that of the homogeneous iron porphyrin. In particular, **15b**,**c** led to a lower product yield, caused by the reduction of iron(III) to iron(II) during the catalyst preparation. The properties of **16a**−**c** were similar to those of **12a**,**b**, and the catalytic epoxidation of cyclooctene was possible using PhIO as oxidant (eq 10). After a reaction time of 24 h, **16a**,**c** gave yields of 100% (Table 5). In contrast to surface-supported iron porphyrins,[115] no leaching in **15a**−**c** and **16a**−**c** was observed during the reaction, which was confirmed by UV−vis spectroscopy and further epoxidation tests of the filtered reaction mixture. Unfortunately, no recycling of the catalysts was mentioned.

2. Ruthenium Complexes

Ruthenium complexes incorporated into interphase systems are discussed in the sequence of ether−phosphine-, phosphorus-, and nitrogen-containing ligands.

a. Ether−Phosphine Ligands. Hemilabile ether−phosphines have been extensively investigated in

Table 7. Performance of Catalysts 17, 19a,b, 20a–i, and 21a–i in the Hydrogenation of 2-Butenal (Equation 11)[a]

					selectivity (%)					
						2-butenol				
catalyst	*T* (°C)	time (h)	run no.	yield (%)	butanal	*trans* isomer	*cis* isomer	*n*-butanol	ref	comments
17	120	3.3	1	51.3	37.2	32.2	4.6	25.9	130	**17** was reused in four cycles
			4	50.1	37.1	44.4	4.1	14.3		
19a	80	4	1	20	19	73	4	4	131	catalysts **19a**,**b** and **20a**–**i** were recovered, but details were given only for **19a**, **20a**, and **20c**
	150	1	1	65	23	51	5	21		
			2	63	22	55	5	18		
19b	80	4	1	20	19	72	4	5		
	150	1	1	81	18	46	4	32		
20a[b]	120	1	1	35	28	60		12	132	
20b			1	52	17	62		21		
20c[c]			1	71	11	65		24		
20d			1	37	23	63		14		
20e			1	48	18	63		19		
20f			1	69	12	64		22		
20g			1	38	23	60		17		
20h			1	47	18	59		22		
20i			1	60	15	64		21		
21a	80	4	1	5	38	58		4	133	catalysts **21a**–**i** were recovered, but details were given only for **21g** and **21i**
21b			1	21	28	63		9		
21c			1	44	20	65		15		
21d			1	15	28	62		10		
21e			1	27	20	64		16		
21f			1	45	12	64		22		
21g			1	21	27	64		9		
21h			2	20	26	65		9		
			3	20	26	64		10		
			1	26	24	66		10		
21i			1	51	19	64		17		
			2	35	22	67		11		
d			3	34	23	66		11		
			1	34	29	41		30		

[a] Reaction conditions: $p[H_2] = 50$ bar, Ru/*n*-butenal = 1:250 for catalyst **17**, 1:1000 for catalysts **19**–**21**. [b] Second run with 33% yield, third run with 34% yield. [c] Second run with 65% yield, third run with 64% yield. [d] Homogeneous reaction with monomeric complex.

organometallic chemistry as a tool to stabilize empty coordination sites at reactive centers.[122] Ligands of this type form a close contact to the metal center via the phosphorus atom so that the ligand cannot dissociate completely from the metal center. At the same time the oxygen atom in the ether moiety coordinates to the metal in a labile manner and is involved in an opening and closing mechanism taking over the function of an intramolecular solvent. It is important for catalysis that the hemilabile character of ether–phosphines is present not only in homogeneous but also in interphase systems.[123–127] With the aim to correlate structural and dynamic properties of various interphase catalysts with their catalytic activity, many polysiloxane matrices in which ruthenium complexes were covalently bound via silyl-modified ether–phosphines have been synthesized and characterized.[56,128,129] Physical properties of these stationary phases can be varied in a wide range by employment of different co-condensation agents, for example, TEOS, $MeSi(OMe)_3$ (MTMS), $Me_2Si(OMe)_2$ (DMOS), $(MeO)_2SiMe(CH_2)_6MeSi(OMe)_2$, and $Al(O\textit{i}Pr)_3$, as well as with ether–phosphine ligands that contain different spacer lengths. The loading of the matrix with metal centers within the matrix can be adjusted by an appropriate amount of the co-condensation agent. Multinuclear CP/MAS solid-state NMR spectroscopy gave insight into the stereochemistry of the metal complexes, the integrity of the spacer, the polymer backbone, and the mobility of the reactive centers. In addition, extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD), etc. were also applied to characterize these interphase systems.

Approximately 10 years ago, the first polysiloxane-supported ether–phosphine ruthenium(II) complexes of the type **17** were introduced (Scheme 11).[130] $(MeO)_3Si(CH_2)_6PPh(CH_2CH_2OMe)$ was treated with $[RuCl_2(CO)_2]_n$, and the resulting complex was poly-co-condensed with TEOS to afford **17**. Catalyst **17** was active in the heterogeneous hydrogenation of crotonaldehyde with comparatively high selectivities (eq 11; Table 7). Moreover, no loss of metal or ligand

Scheme 11

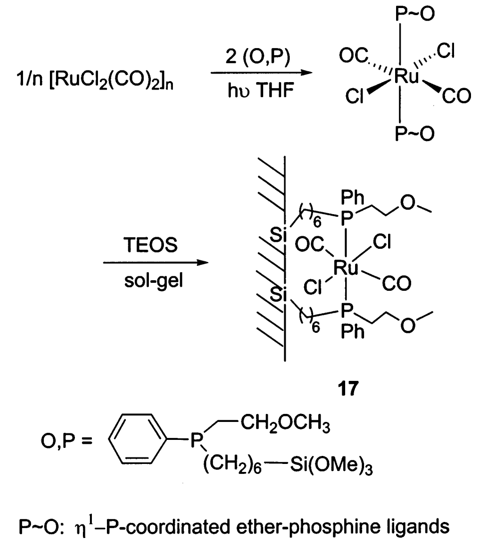


Table 8. Performance of Catalysts 18a−c in the Hydrogenation of *n*-Butyraldehyde (Equation 12) (Data from Reference 125)[a]

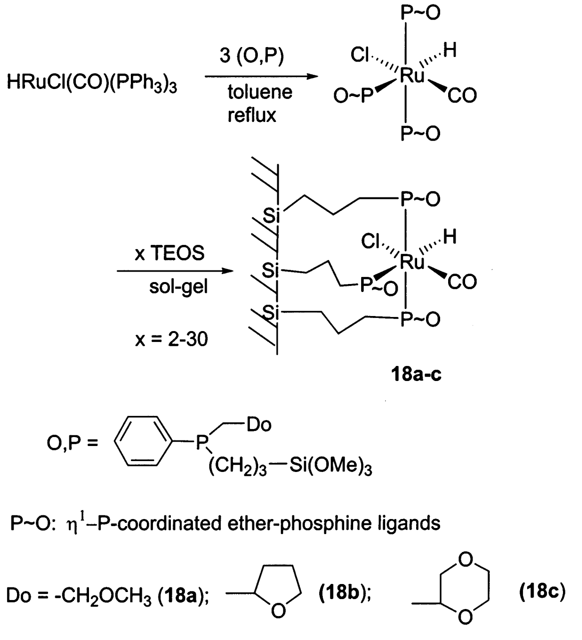
catalyst	*T* (°C)	time (min)	run no.	yield (%)	TOF (min^{-1})	comments
18a[b]	80	60	1	62.2	10.4	**18a**−**c** showed good recycling abilities in the second and third runs
			2		10.0	
	150	60	1	99.5	22.1	
18b[b]	50	60	1	2.4	0.04	
	150	60	1	98.5	18.0	
			2		16.9	
			3		17.0	
18c[b]	100	60	1	32.5	3.9	
	150	45	1	100	22.2	
18c[c]	150	60	1	91.8	15.2	
18c[d]	150	60	1	74.9	12.5	
18c[e]	150	15	1	100	66.6	
			2		65.9	

[a] Reaction conditions: 0.1 mmol of catalyst with respect to Ru, 7.2 g (100 mmol) of *n*-butyraldehyde, starting H_2 pressure = 50 bar. [b] Ru/TEOS = 1:6. [c] Ru/TEOS = 1:10. [d] [Ru]/TEOS = 1:30. [e] [Ru]/TEOS = 1:6, and the matrix was doped with Mg^{2+}.

from the support occurred, which was confirmed by atomic absorption spectroscopy (AAS).

Via exchange reactions between $HRuCl(CO)(PPh_3)_3$ and ether−phosphine ligands such as $(MeO)_3Si(CH_2)_3(Ph)PCH_2Do$ (Do = methoxymethyl, tetrahydrofuryl, and 1,4-dioxanyl), three different *P*-coordinated trimethoxysilyl-functionalized ruthenium complexes of the type $HRuCl(CO)(P{\sim}O)_3$ were prepared.[125] Poly-co-condensation of the monomeric species with variable amounts of TEOS under various sol−gel conditions gave the polymeric (ether−phosphine)ruthenium(II) complexes **18a**−**c** (Scheme 12).

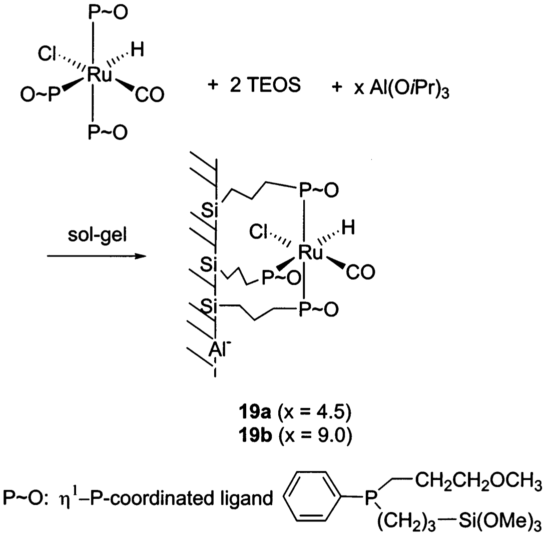
Scheme 12



Small amounts of magnesium salts were introduced into the matrix to increase the polarity of the network, which led to an improved product/catalyst separability. These materials were used in the hydrogenation of *n*-butyraldehyde (eq 12; Table 8). Catalysts with a higher amount of Q-silyl species could be well separated from the reaction medium but suffered from a lower activity due to the nonflexibility of the matrices and occlusion of the complexes. Those with lower Q-type silicons and a small particle size were highly active, but separation was possible only by the addition of nonpolar solvents. Mg^{2+}-doped catalysts were featured by a higher activity and were completely recovered by centrifugation after the hydrogenation. No leaching of ruthenium took place in these interphase systems as was determined by AAS measurement. Constant analytic values of the materials after several catalytic runs have been found, and no loss of activity was established for Mg^{2+}-doped catalysts.

To transfer distinct properties of polysiloxanes to poly(alumosiloxane) matrices and to incorporate ion charges into network builders, poly(alumosiloxane)-bound ether−phosphine ruthenium complexes have been prepared in a simultaneous sol−gel process (Scheme 13).[131] Two different amounts of $Al(OiPr)_3$ acting as an aluminum-containing precursor were hydrolyzed in methanol. The resulting sols were co-condensed with mixtures of the monomeric complex *cis*-$Cl(H)Ru(CO)(P{\sim}O)_3$ [P∼O = $PhP(CH_2CH_2OCH_3)(CH_2)_3Si(OMe)_3$)] and TEOS to afford catalysts **19a**,**b**. Both systems were applied to the hydrogenation of *trans*-crotonaldehyde (eq 11). At 80 °C conversions of 20% were observed with chemoselectivities being higher than 3:1 with regard to the formation of

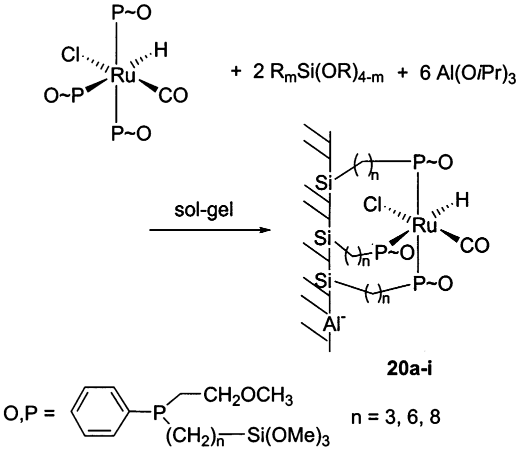
Scheme 13



unsaturated alcohols. Increasing the temperature from 120 to 150 °C resulted in conversions of up to 81% (see Table 7). However, the chemoselectivities decreased and considerable amounts of the hydrogenation product *n*-butyl alcohol was formed. The better activities of **19b** compared to **19a** at elevated temperatures are traced back to the stronger polarity of **19b**. Both materials **19a**,**b** could be recovered from the reaction mixture by simple centrifugation, and after being washed with acetone and *n*-hexane, they revealed the same catalytic activities in the second run.

Further poly(alumosiloxane)-bound ruthenium(II) complexes were made accessible by sol–gel processing of the trimethoxysilyl-functionalized ruthenium(II) complexes *cis*-Cl(H)Ru(CO)(P~O)$_3$ [P~O = PhP(CH$_2$CH$_2$OCH$_3$)(CH$_2$)$_n$Si(OMe)$_3$, n = 3, 6, 8] with the different co-condensation agents TEOS, MTMS, DMOS, and aluminum-2-propanolate [Al(O*i*Pr)$_3$] (Scheme 14).[132] All materials **20a–i** proved to be successful as hydrogenation catalysts for 2-butenal (eq 11; Table 7). Catalysts **20a**, **20d**, and **20g** displayed conversions in the range of 35–38%, and the selectivities in the formation of unsaturated alcohols compared to saturated aldehydes were approximately 2.5:1. Variation of the matrices led to higher conversions (~70% for catalysts **20c**, **20f**, and **20i**) and chemoselectivities toward the hydrogenation of carbonyl double bonds (**20c**: 2-butenol/*n*-butanol = 6:1). Dynamic solid-state NMR investigations indicated that the mobility of the reactive centers is determined by the length of the spacers and not by the type of the co-condensation agent. Complete recycling of the catalysts from the reaction mixture by simple centrifugation after a catalytic run and a re-employment with constant activity after washing with acetone and *n*-hexane was demonstrated.

Scheme 14

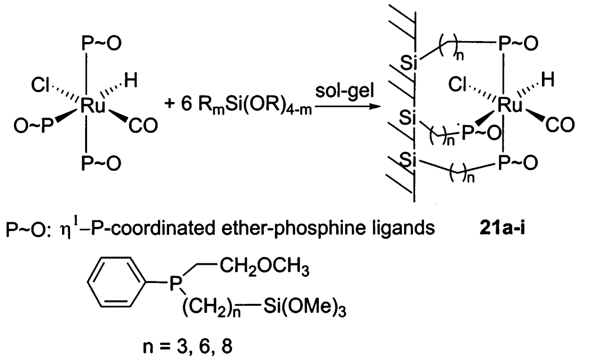


P~O: η^1–P-coordinated ether-phosphine ligands

n = 3: R= Et, m = 0, **20a**; R = Me, m = 1, **20b**; R = Me, m = 2, **20c**
n = 6: R= Et, m = 0, **20d**; R = Me, m = 1, **20e**; R = Me, m = 2, **20f**
n = 8: R= Et, m = 0, **20g**; R = Me, m = 1, **20h**; R = Me, m = 2, **20i**

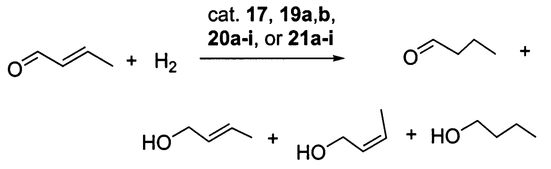
Several (ether–phosphine)ruthenium(II) complexes of the type *cis*-Cl(H)Ru(CO)(P~O)$_3$ [P~O = PhP(CH$_2$CH$_2$OCH$_3$)(CH$_2$)$_n$Si(OMe)$_3$, n = 3, 6, 8] were co-condensed with TEOS, MTMS, and DMOS, respectively, to afford nine polysiloxane-bound ruthenium species **21a–i** (Scheme 15).[133] Further studies were oriented with respect to the hydrogenation of *n*-butenal (eq 11). The most rigid material **21a** showed hardly any catalytic activity at the applied reaction conditions. Increasing the spacer length from *n*-propyl to *n*-hexyl or *n*-octyl afforded conversions from 15 to 21% (see Table 7). The more flexible catalysts **21g–i** displayed even a higher activity and selectivity with conversions between 44 and 51%. In the case of corresponding homogeneous catalysts, the overall conversion was less and the selectivities were poorer. An important point is the fact that the activities of sol–gel-immobilized ruthenium complexes can be adjusted by the properties of the carrier matrix and the spacer. Enhanced mobility increased the activity and selectivity of **21g–i**. It was also concluded that the diffusion of the substrate into the matrix is not the rate-determining step. Moreover, these catalysts could be easily recovered from the reaction mixture by precipitation of the highly swollen gels with *n*-hexane followed by simple filtration. The same catalytic activity was found after three consecutive

Scheme 15

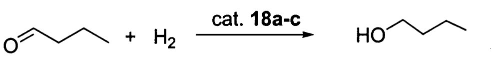


P~O: η^1–P-coordinated ether-phosphine ligands

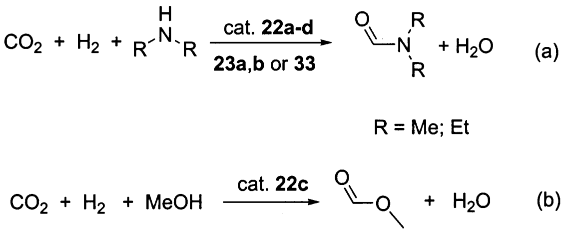
n = 3: R= Et, m = 0, **21a**; R = Me, m = 1, **21b**; R = Me, m = 2, **21c**
n = 6: R= Et, m = 0, **21d**; R = Me, m = 1, **21e**; R = Me, m = 2, **21f**
n = 8: R= Et, m = 0, **21g**; R = Me, m = 1, **21h**; R = Me, m = 2, **21i**



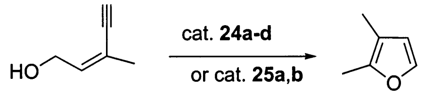
(11)



(12)



(13)



(14)

Table 9. Performance of Catalysts 22a,b and 23a,b

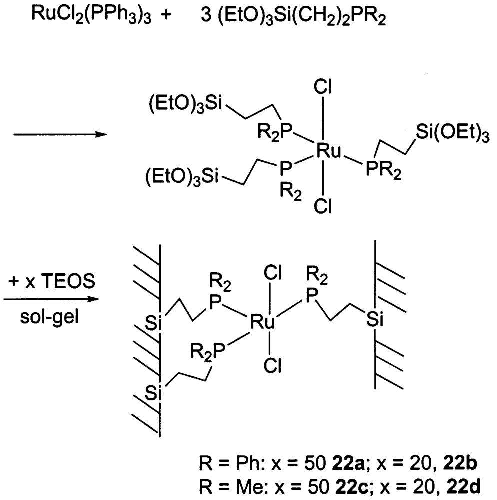
catalyst	type of catalysis	eq	yield (%)	selectivity (%)	TON[a]	TOF (h^{-1})	ref	comments
22a[b]	synthesis of DMF	13a	25	100	3230	220	134	reused in three cycles, no detailed data were presented
22b[b]			35	100	4420	290		
22c[b]			94	100	13670	900		
22c[c]			82	100	110800	1860		
22d[b]			84	100	11800	790		
22c[d]	synthesis of methyl formate	13b			1740	115		TOFs for **22c**[d] and **23a**[e] are higher than those in homogeneous phase
23a[e]	synthesis of *N*,*N*-diethylformamide	13a				18400	137	
23b[e]						2210		

[a] Turnover number [mol(DMF)/mol(catalyst)] for eq 13a, and [mol(methyl formate)/mol (catalyst)] for eq 13b. [b] Reaction conditions for reaction eq 13a with **22a**−**d**: 500 mL stainless steel autoclave; $n[\mathrm{Me_2NH}] = 0.71$ mol; $p[\mathrm{H_2}] = 8.5$ MPa; $p[\mathrm{CO_2}] = 13.0$ MPa; $T = 373$ K; $t = 15$ h; stirring rate = 300 $\mathrm{min^{-1}}$; $n[\mathrm{catalyst}] = 5 \times 10^{-5}$ mol (Ru). [c] $n[\mathrm{Me_2NH}] = 6.4$ mol; $T = 406$ K; $t = 60$ h; stirring rate = 500 $\mathrm{min^{-1}}$; $n[\mathrm{catalyst}] = 1.8 \times 10^{-5}$ mol (Ru). H_2 and CO_2 were recharged regularly to keep constant pressure. [d] Reaction conditions for eq 13b with **22c**: 500 mL stainless steel autoclave; n[MeOH] = 0.75 mol; $p[\mathrm{H_2}] = 8.5$ MPa; $p[\mathrm{CO_2}] = 13.0$ MPa; $T = 373$ K; $t = 15$ h; stirring rate = 300 $\mathrm{min^{-1}}$; $n[\mathrm{catalyst}] = 1.77 \times 10^{-5}$ mol (Ru). [e] Reaction conditions: $T = 110$ °C; total pressure = 18 MPa; $n[\mathrm{catalyst}] = 7.5 \times 10^{-7}$ mol.

runs for **21g**, whereas **21i** loses some of its activity in the first reuse. However, after the second run the activity remains constant.

b. Phosphorus Ligands. Sol−gel-derived ruthenium catalysts for the synthesis of *N*,*N*-dimethylformamide (DMF) from supercritical carbon dioxide were reported by the group of Baiker.[134,135] As ligands, T-silyl-functionalized phosphines of the type $Ph_2P(CH_2)_2Si(OEt)_3$ and $Me_2P(CH_2)_2Si(OMe)_3$ were applied (Scheme 16).[134] Co-condensation with TEOS produced the ruthenium(II) catalysts **22a**−**d**. Under the required reaction conditions both candidates were stable and able to produce DMF with 100% selectivity (eq 13a). Independent of the preparation conditions, the employment of methylphosphine **22c**,**d** resulted in higher activities, as compared to the phenylphosphine congeners **22a**,**b** (Table 9). For **22c**,**d** a maximum turnover number (TON) of 110800 corresponding to a TOF of 1860 h^{-1} at 100% selectivity was attained under specific conditions (see Table 9). Leaching of active species from the catalysts could be neglected, because the filtrate exhibited no catalytic activity in subsequent activity tests. Moreover, using the same catalyst for three consecutive experiments resulted in a marked increase of activity for the second run, and it remained stable in the third experiment. The stabilizing effect of sol−gel-processed homogeneous complexes was supported by the long-lasting activity of **22a**−**d**. However, no data for turnover numbers were presented in the literature.[134] Fresh and used hydridometal catalysts, which were reinstalled for catalytic testing after storage under air for one year, showed no loss of activity. This is in contrast to the findings with homogeneous analogues, with which the reaction mixtures rapidly changed their color or precipitated, indicating decomposition.

Scheme 16



Interestingly the above-mentioned catalyst **22c** was also active in the generation of methyl formate in 100% selectivity (eq 13b; Table 9). The TOF maximum of 115 h^{-1} was >2 times higher than for the best reported homogeneous systems.

In addition, the effects of reaction variables on the reactivity and selectivity of **22a** by varying the initial concentration of the catalyst and dimethylamine, the partial pressures of hydrogen and carbon dioxide, the temperature, and the stirring frequency were studied.[136] With regard to the influence of reaction time, it was found that there is a nearly constant reaction rate as long as enough dimethylamine is available. Below 100 $\mathrm{min^{-1}}$, the turnover frequency of the reaction increased with the stirring frequency. Between 100 and 300 $\mathrm{min^{-1}}$, the kind of stirring does not influence the turnover frequency, indicating a negligible influence of external mass transport on the reaction rate under standard reaction conditions. With respect to the effect of dimethylamine, the reaction rate appeared to be of first order at lower concentration and of zero order at higher concentration. The carbon dioxide partial pressure seemed to be negligible in the range investigated. Kinetic data indicated an approximately 0.6th order with regard to the dependence of the rate on the hydrogen partial pressure. An activation energy of 69.8 ± 2.4 kJ $\mathrm{mol^{-1}}$ was calculated for the synthesis of DMF in the temperature range between 333 and 413 K. Above 413 K, the formation of byproducts and the decomposition of the catalyst were observed.

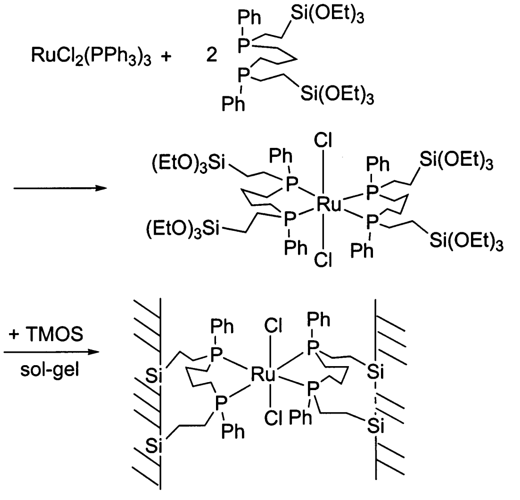
Recently Baiker synthesized the mesoporous hybrid aerogels **23a**,**b** (Scheme 17).[137] A functionalized bidentate ruthenium(II) phosphine complex was used

Table 10. Performance of Catalysts 24a–d and 25a,b in the Cyclization of (*Z*)-3-Methylpent-2-en-4-yn-1-ol (Equation 14)[a]

catalyst	time (h)	yield (%)	time (h)	yield (%)	TOF (h^{-1})	ref	comments
b	1.5	77	6	80		141	catalysts **24a**–**d** were reused, but no specific data were presented
24a	15	63	72	88			
24b	15	27	72	85			
24c	15	20	70	65			
24d	15	66	70	80			
25a				45–89	10–96	142	catalysts **25a**,**b** were reused 5 times, but no specific data were presented
25b				76–92	64–230		

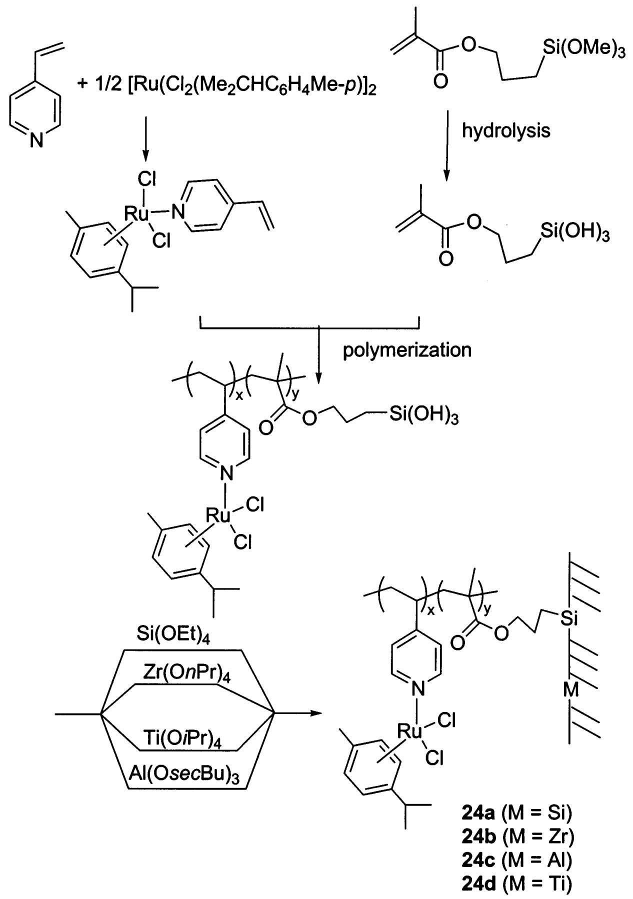
[a] Reaction conditions: 0.1 g of catalyst, 100 mg of (*Z*)-3-methylpent-2-en-4-yn-1-ol, $T = 80$ °C. [b] Homogeneous reaction with [Ru(η^6-$Me_2CHC_6H_4Me$-*p*)(4-ethenylpyridine)Cl_2].

Scheme 17



23a (aerogel)
23b (xerogel)

Scheme 18



as precursor to react with TMOS via a sol–gel process. Aerogel **23a** was isolated by extraction of the solvent with supercritical CO_2 from the produced gel, and xerogel **23b** was obtained by slow evaporation of the solvent. Polymers **23a**,**b** were used to prepare *N*,*N*-diethylformamide from CO_2, H_2, and diethylamine (eq 13a; Table 9). Depending on the conditions, turnover frequencies up to 18400 h^{-1} were achieved with aerogel **23a**. Under the same conditions the microporous xerogel **23b** afforded only 2210 h^{-1}. The difference was attributed to the favorable texture properties of the aerogel, eliminating intraparticle diffusion limitations. The measured turnover frequency for **23a** was even significantly higher than that for the monomeric congener under the same conditions (3130 h^{-1}).

c. Nitrogen Ligands. Preparative and catalytic studies on nitrogen-bound ruthenium complexes are of considerable relevance, because of their potential applications in catalysis as well as in functional materials.[138,139] Typical examples are sol–gel-processed η^6-arene ruthenium(II) complexes coordinated with functionalized pyridine. 4-Vinylpyridine and [$RuCl_2$(*p*-$Me_2CHC_6H_4Me$)]$_2$ served as starting materials for the access to the catalyst precursor.[140,141] A mixture of hybrid polymers was prepared by free radical polymerization of the precursor species and the hydrolysis product of (3-methacryloxypropyl)trimethoxysilane (MEMOS). The polymers were then co-condensed with TEOS, Ti(O*i*Pr)$_4$, Zr(O*n*Pr)$_4$, and Al(O*sec*Bu)$_3$ in the presence of an acid to afford **24a**–**d** (Scheme 18),[141] which were characterized by FT-IR spectroscopy. The different metals incorporated in the polymer function as network builders. When catalysts **24a**–**d** were checked for the cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol (eq 14; Table 10), they showed a reduced activity compared to the homogeneous congener, but they offered the advantage of a heterogeneous catalyst. Further details are summarized in Table 10.

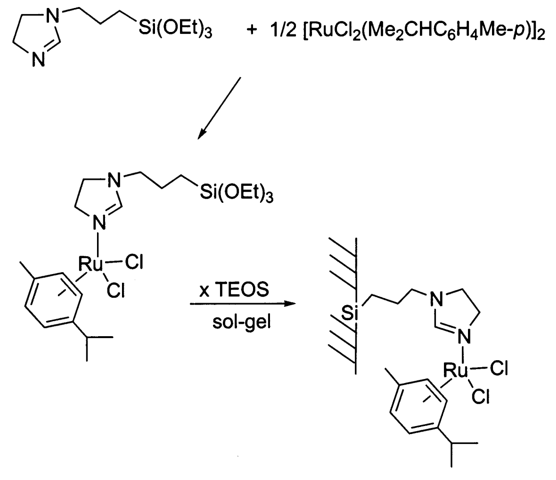
Another important contribution is the sol–gel synthesis of the ruthenium(II) complexes **25a**,**b** containing a polysiloxane-bound imidazole ligand (Scheme 19).[142] 3-(4,5-Dihydroimidazol)-1-yl-propyltriethoxysilane was employed as a coordinating agent with (η^6-arene)ruthenium(II) complexes to synthesize the catalyst precursor, which was polycondensed or poly-co-condensed with TEOS to afford **25a**,**b**. Methods for characterization were FT-IR spectroscopy,

Table 11. Performance of Catalysts 26 and 27 in the Oxidation of Alkylbenzenes

					selectivity (%)			
catalyst	eq	time (h)	yield[a] (%)	rate[b]	-one[c]	-ol[d]	ref	comments
26[e]	15a	1.5	6.4	0.35	71.9	28.1	143	no recycling tests were reported
		24	70.4	0.24	75.2	8.0		
		48	89.9	0.15	77.0	4.2		
		72	99.9	0.11	78.7	2.3		
27[f]	15a	22	76	na[g]	94		144	catalyst was reused by adding a small amount of pyridine, but no detailed data were presented
	15b	22	25		100[h]			
	15c	22	6					

[a] Total yields of products. [b] Rate conversion (mol L^{-1} h^{-1}). [c] Acetophenone. [d] Methylphenylmethanol. [e] Reaction conditions: 0.6 g of catalyst, 40 g of ethylbenzene, $T = 130$ °C. [f] Reaction conditions: 0.8 g of catalyst, 400 mL of substrate, stirring rate at 700 rpm, air stream rate 400 mL min^{-1}, $T = 130$ °C for eq 15a,b, $T = 100$ °C for eq 15c. [g] Not available. [h] The product is 4-chlorobenzoic acid.

Scheme 19



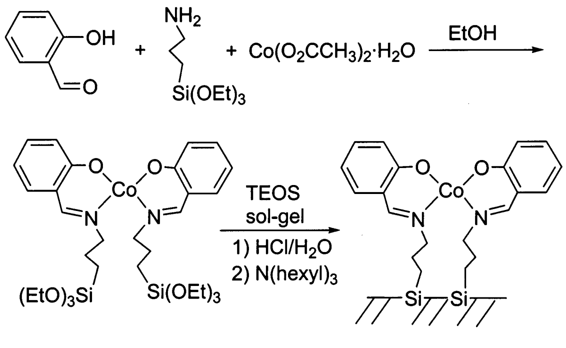
25a (x = 0)
25b (x = 1-10)

differential thermal analysis (DTA), TGA analysis, NMR, Raman spectroscopy, and BET measurements. Their catalytic activity was tested for the cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran (eq 14). At room temperature it was low but raised when the temperature was increased to 80 °C. The catalysts were recovered by microporous filtration and reused five times without significant loss of activity or selectivity. The kind of preparation and the amount of employed TEOS also affected the catalytic property. In most cases the performance of **25b** is superior to that of **25a**, leading to higher product yields and turnover numbers (see Table 10). This effect is traced back to the higher surface area of **25b**.

E. Cobalt, Rhodium, and Iridium Complexes

1. Cobalt Complexes

Scheme 20

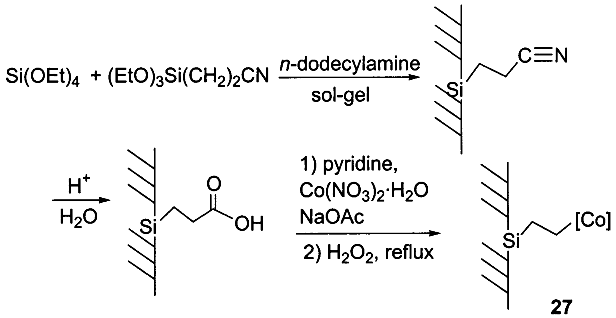


26

An attractive topic is the nondestructive immobilization of cobalt Schiff base complexes (Scheme 20).[143] As an example, in a first step a cobalt (salen) compound was obtained by reaction of cobalt acetate with a solution of aminopropyltriethoxysilane and salicylaldehyde. Then the silyl-modified salen complex was poly-co-condensed with TEOS to give **26**. Using cobalt (salen) as starting material in the sol–gel process not only avoided the reverse Schiff base reaction but also accelerated the gelation rate due to autocatalysis. The polysiloxane **26** was characterized by FT-IR, UV–vis, and XPS spectroscopy, laser ablation ICP-MS, EPR, BET, and TGA studies. Oxidation of ethylbenzene to acetophenone (eq 15a; Table 11) by **26** was carried out in DMSO or DMF at 130 °C under an oxygen atmosphere in the presence of pyridine and potassium *tert*-butoxide. After 72 h, the conversion achieved a value of 99.9%. During the catalytic reaction the rate of conversion decreased, which was attributed to a competitive adsorption of the reactants and products at the active sites. Ethylbenzene oxidation could be conducted without any solvent under oxygen. Removal of water produced during the reaction was necessary. Leaching of cobalt analyzed with ICP-AES in the filtrate amounted to <0.1 wt %.

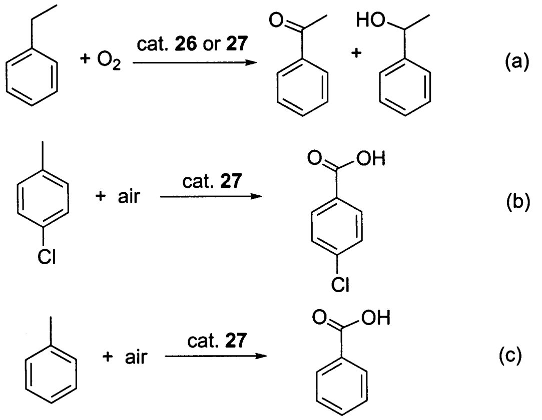
In another investigation it was highlighted that immobilized cobalt(III) complexes act as oxidation catalysts (Scheme 21).[144] Cyanoethylsilica was formed by a sol–gel reaction of TEOS and cyanoethyltri-

Scheme 21



27

[Co] = reactive center in the supported catalyst (see text) ethoxysilane in water in the presence of *N*-dodecylamine as template. Treatment of the polymeric material with aqueous sulfuric acid transformed the cyano group to a carboxylic acid function. Complexation of cobalt to the modified matrix proceeded via reaction of the polymer with $Co(NO_3)_2 \cdot 6H_2O$, sodium acetate, pyridine, and hydrogen peroxide in water under reflux. Atomic absorption analysis, optical and scanning electron microscopy, BET, powder X-ray diffraction, FT-IR, and UV−vis studies together with a comparison of the corresponding homogeneous complex allowed the characterization of the immobilized catalyst **27** containing a complicated cobalt species with two pyridine and two carboxylato ligands per cobalt atom. Immobilized **27** was applied in the aerial oxidation of neat ethylbenezene, chlorotoluene, and toluene (eq 15a−c). After 22 h, 76% of ethylbenzene was oxidized with a selectivity to acetophenone of 94% (Table 11). The rate of oxidation was almost linear up to 70% conversion. Under the same conditions 25% of pure 4-chlorobenzoic acid was isolated. Toluene was also oxidized to benzoic acid at 100 °C in the presence of 1% benzaldehyde as a promoter, but the yield was only 6% after 22 h. No leaching of cobalt took place in the above-mentioned reactions as detected by atomic absorption spectroscopy. However, pyridine was completely lost during the reaction, which resulted in a failure of repeated use. Upon treatment of the recovered catalyst with pyridine, the catalytic activity returned to close to its original value.



(15)

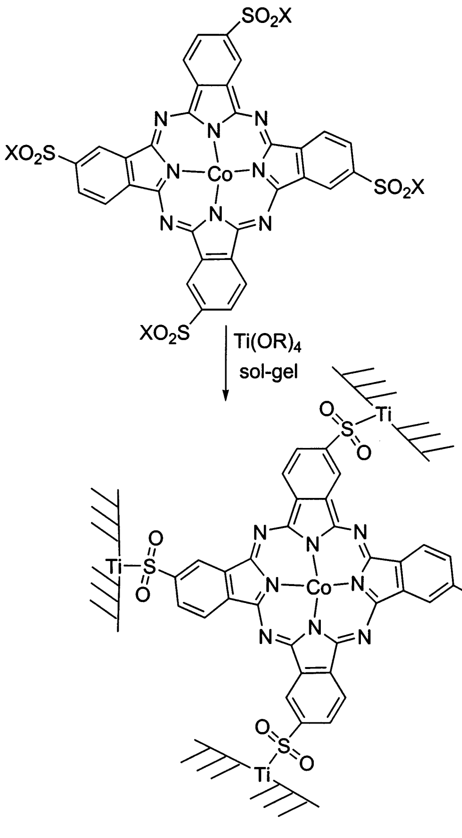
$$2Na_2S + O_2 + 2H_2O \xrightarrow{\text{cat. 28a-c/29a-d}} 2S + 4NaOH \quad \text{(a)}$$

$$4RSH + O_2 \xrightarrow[\text{or 29a-c}]{\text{cat. 28a}} 2RSSR + 2H_2O \quad \text{(b)}$$

(16)

Cobalt phthalocyanine complexes can also be anchored to titanium dioxide (Scheme 22).[145] Cobalt(II) tetrasulfonylphthalocyanine and cobalt(II) tetra(chlorosulfonyl)phthalocyanine were co-condensed with titanium alkoxides upon sol−gel procedures to form **28a**−**c** and **29a**−**d**. Sulfide and ethanethiol liquid-phase oxidations using the above-mentioned catalysts were investigated in the presence of oxygen (eq 16; Table 12). In the oxidation of Na_2S, the main product was elemental sulfur together with small quantities of thiosulfate. Remarkably, the catalytic activity did not change during repeated use. Catalyst **28a** was the most active for sodium sulfide oxidation, the rate of the conversion was 35.3 mol(S^{2-})/mol(catalyst)·min. In the oxidation of ethanethiol **28a** and **29d** showed the highest activities. They were all stable in the reaction media, and no leaching of the active component was established by checking the activity of the filtrate.

Scheme 22



X = OH, R = *i*Pr: **28a**; X = OH, R = *n*Pr: **28b**; X = OH, R = Et: **28c**
X = Cl, R = *n*Pr: **29a**; X = Cl, R = Et: **29b**; X = Cl, R = *n*Bu: **29c**
X = Cl, R = *i*Pr: **29d**

2. Rhodium Complexes

Rhodium complexes incorporated into interphase systems can be arranged according to T-silyl-modified phosphorus, cyclopentadienyl, nitrogen, sulfur, and oxygen ligands.

a. Phosphorus Ligands. Brzezinska et al. described the application of polymeric siloxyphosphine rhodium complexes as catalysts for the hydrogenation of olefins, in particular, styrene. Hydrolysis of rhodium complexes with the phosphines $Cl_3Si(CH_2)_nPPh_2$ (n = 2, 8) either with trichloromethylsilane or in the presence of excess ligands afforded **30a**−**c** (Scheme 23).[146] The authors noticed that these materials were effective in the hydrogenation of olefins, but some activity got lost on recycling (eq 17; Table 13).[147] Polymer **30c** lost half of its activity after five cycles and was the best candidate. The authors noticed that the performance and the activity were always higher for catalysts containing a longer spacer, which is consistent with the interphase concept.

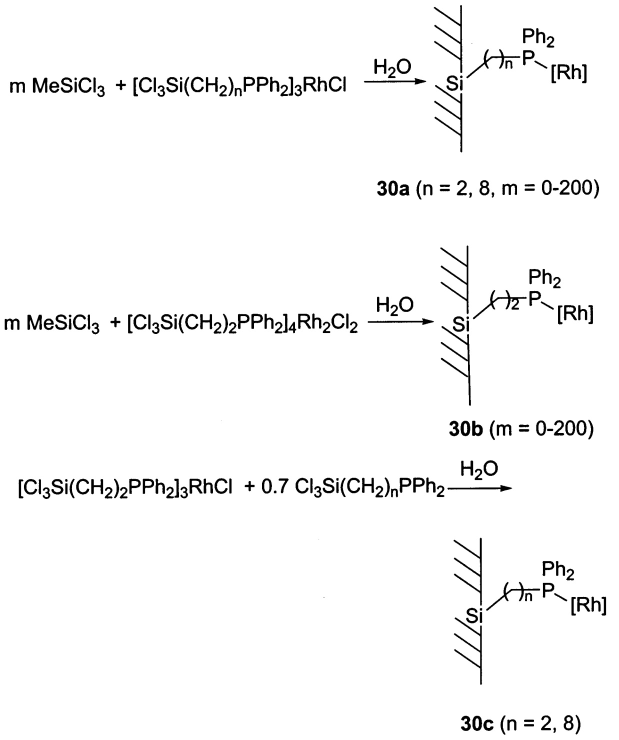
Compared to $Rh(CO)Cl[PPh_2CH_2CH_2Si(OEt)_3]_2$, the sol−gel-processed rhodium complexes **31a**,**b** exhibited higher stability and better catalytic properties

Table 12. Performance of Catalysts 28a–c and 29a–d in the Sulfide and Ethanethiol Oxidation (Data from Reference 145)[a]

catalyst	type of catalysis	eq	time[b] (min)	V_m[c] (mL/min)	$V(O_2)$[d] (mL)	TOF[e]	comments
28a	sulfide oxidation	16a	9		16.4	35.3	second run with fresh catalyst in 1:1 ratio showed no decrease in activity, but no further specific data were presented
28b			16.5		19.9	16.2	
28c			24		19.6	11.3	
29a			18.5		18.7	10.6	
29b			18		27.1	9.9	
29c			19		16.2	8.5	
29d			31		17.8	7.1	
28a	ethanethiol oxidation	16b		2.1		80.3	>3 runs for each catalyst, data represent average results
29a				1.1		15.4	
29b				2.2		31.4	
29d				2.2		84	
f				0.25		3.53	
g				0.25		3.52	
h				1.7		33.1	

[a] Reaction condition for eq 16a: 25 °C, pH 7.3, $[Na_2S] = 5 \times 10^{-2}$ M, molar ratio $[Na_2S]/[catalyst] = 110$. Reaction conditions for eq 16b: 25 °C, pH 11, $[ethanethiol] = 7.5 \times 10^{-2}$ M, molar ratio [ethanethiol]/[catalyst] = 110. [b] Time for complete oxidation. [c] Amount of oxygen consumed. [d] Maximum oxygen consumption per minute. [e] For eq 16a [mol(S^{2-})/mol(catalyst) min]; for eq 16b [mol(HS)/mol(catalyst) min]. [f] Without catalyst. [g] Filtrate after four runs of **28a**, molar ratio [ethanethiol]/[catalyst] = 300. [h] CoPc(4-$SO_2X)_4$ on activated charcoal.

Scheme 23

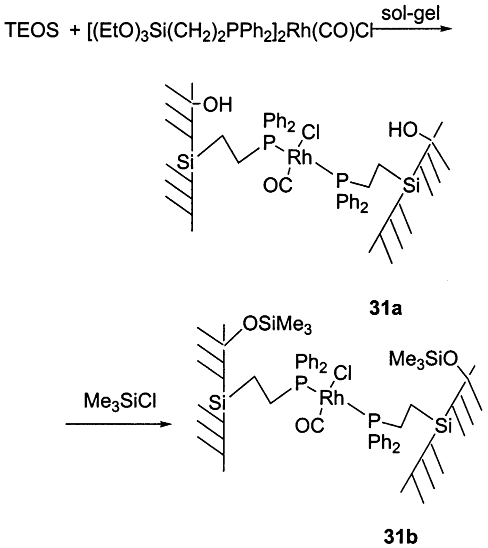


30a (n = 2, 8, m = 0-200)

30b (m = 0-200)

30c (n = 2, 8)

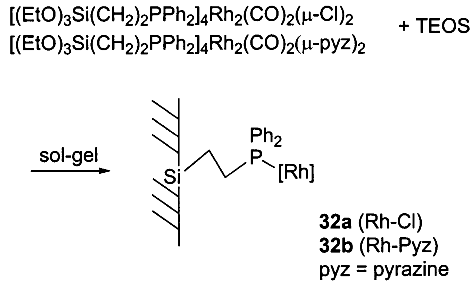
Scheme 24



31a

31b

Scheme 25

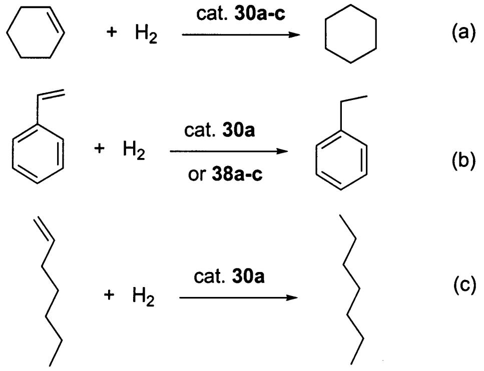


32a (Rh-Cl)
32b (Rh-Pyz)
pyz = pyrazine

in the hydrosilylation of 1-hexene (Scheme 24; eq 18).[148] There is no significant loss of rhodium in repeated uses. Poly- and oligosilanes from hydrosilanes were also formed by **31a**,**b**. Interestingly, **31a**,**b** catalyzed the CO oxidation and the water-gas shift reaction, whereas the homogeneous complex Rh(CO)-$Cl(PR_3)_2$ normally does not work under the selected reaction conditions.

It should be mentioned that Avnir, Blum, and Schumann have carried out several investigations in the heterogenization of soluble transition metal catalysts by employing the sol–gel process.[75,87,149–152] A remarkable part of their work is devoted to the entrapment of catalytically active complexes into plain SiO_2 sol–gel matrices. Catalysts **32a**,**b** were obtained by poly-co-condensation of TEOS with $[(EtO)_3SiCH_2CH_2PPh_2]_4Rh_2(CO)_2(\mu\text{-pz})_2$ and $[(EtO)_3SiCH_2CH_2PPh_2]_4Rh_2(CO)_2(\mu\text{-Cl})_2$, respectively, and showed higher thermal stability (Scheme 25).[153] However, the ability to isomerize allylbenzene was not satisfying compared to physically encapsulated complexes (eq 19; Table 13).

As already mentioned due to its broad availability, carbon dioxide was introduced as a starting material for the synthesis of valuable chemicals. Transferring it into DMF and methyl formate is an interesting route. To find an efficient and reusable catalyst for this transformation, Kroecher and Baiker et al. employed sol–gel-derived silica-anchored rhodium,



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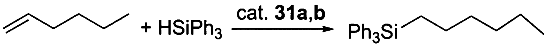

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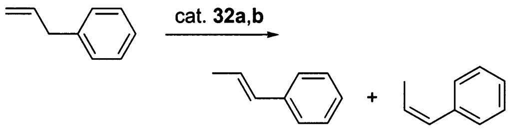
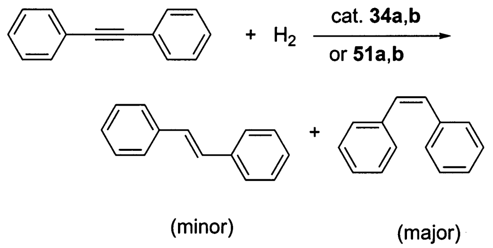


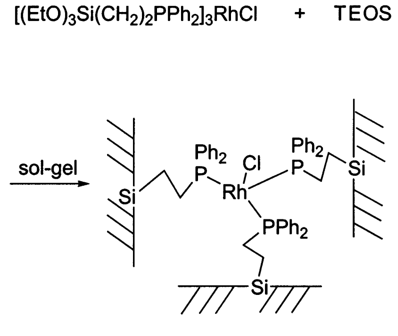
(19)



(20)

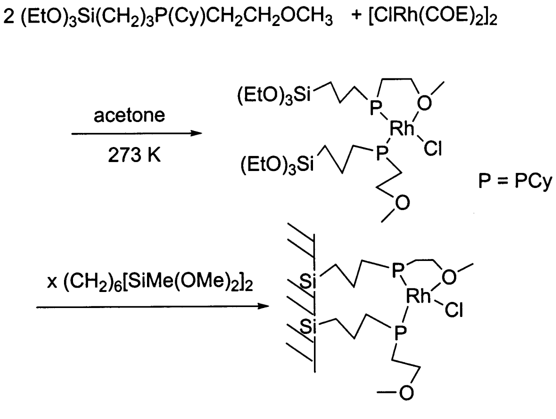
iridium, palladium, platinum, and ruthenium complexes for the solvent-free synthesis of DMF from carbon dioxide, hydrogen, and dimethylamine under supercritical conditions.[134,135] Textural and structural properties of the hybrid gels were characterized by means of NMR spectroscopy, EXAFS, XRD, TEM, and BET measurements. In the case of the rhodium species **33** only low activity was detected and the catalyst decomposed under the reaction conditions (Scheme 26; Table 13; eq 13a).[134]

Scheme 26



33

Scheme 27



34a (x = 2)
34b (x = 8)

To study the accessibility of reactive centers in interphase catalysts, organometallic model reactions and catalytic investigations of polysiloxane-bound (ether−phosphine)rhodium(I) complexes **34a**,**b** have been carried out (Scheme 27).[154,155] Treatment of the trimethoxysilyl-functionalized ether−phosphine ligand CyP(CH$_2$CH$_2$OCH$_3$)(CH$_2$)$_3$Si(OMe)$_3$ with [μ-ClRh(COE)$_2$]$_2$ afforded ClRh(P$^\cap$O)(P$\sim$O), which was further reacted with the co-condensation agent MeSi(OMe)$_2$(CH$_2$)$_6$(MeO)$_2$SiMe to give the desired materials **34a**,**b**. Complexes **34a**,**b** are efficient catalysts in the hydrogenation of diphenylacetylene in organic solvents under mild conditions, typically at 303 K and 5 bar of hydrogen pressure (eq 20; Table 14).[155]

Table 13. Performance of Catalysts 30a−c, 32a,b, and 33

				conversion (%)					
catalyst	type of catalysis	eq	rate[a]	total yields	saturated product	isomerized product	TON[b]	ref	comments
30a	hydrogenation[c]	17a		8.1	8.1			146	**30a**−**c** were recycled; **30c** lost half of its activity after 5 cycles and was the best candidate
		17b		88.5	88.5				
		17c		86.4	46.3	40.1			
		8		88.8	42.9	45.9			
30b		17a	na[d]						
30c		17a	na						
e	isomerization[f]	19	3.44	98			1079	153	no recycling tests were reported for **32a**,**b**
32a			0.55	28			187		
g			0.33	43			276		
32b			0.71	32			734		
33	*h*	13a		4			530	134	decomposed under the reaction conditions

[a] Initial rate in mmol min^{-1}. [b] Turnover number [mol (prod.)/mol(cat.)]. [c] Reaction conditions: 3 mmol of olefin, benzene as solvent, p[H$_2$] = 1 atm, 1.33 × 10^{-2} mmol of catalyst, T = 25 °C, t = 23h. [d] Not available. [e] Physical entrapment of the reactive metal complex in **32a**. [f] Reaction conditions: T = 120 °C, 0.05 mmol of catalyst, 2 mL of allylbenzene. [g] Physical entrapment of the reactive metal complex in **32b**. [h] Synthesis of N,N-dimethylformamide, reaction conditions: 500 mL stainless steel autoclave; n[Me$_2$NH] = 0.71 mol; p[H$_2$] = 8.5 MPa; p[CO$_2$] = 13.0 MPa; T = 373 K; t = 15 h; stirring rate = 300 min^{-1}; n[catalyst] = 5 × 10^{-5} mol (Rh).

Table 14. Performance of Catalysts 34a,b in the Hydrogenation of Tolan (Equation 20) (Data from Reference 155)

catalyst	reaction conditions	conversion (%)	*cis*-stilbene (%)	*trans*-stilbene (%)	bibenzyl (%)	TON[a]	TOF[b]	comments
34a	*c*	61.9	99.0	1.0		96	288	catalyst **34a** was reused in 4 cycles
	d	88.3	97.6	1.4	1.0	137	411	
	e	85	96.8	2.2	1.0	132	395	
	f	89.9	98.3	1.3	0.4	899	449	
	toluene[g]	19.9	95.4	4.6		31	93	
	THF[g]	34.2	98.6	1.1	0.3	53	159	
	ethanol[g]	75.8	99.3	0.7		117	352	
	methanol[g]	94.3	96.1	3.3	0.6	146	438	
	cycle 1[h]	92.1	97.8	1.8	0.4	143	190	
	cycle 4[h]	82.5	98.2	1.5	0.3	128	171	
34b	*c*	74.7	99.2	0.7	0.1	116	347	

[a] Turnover number [mol(substrate)/mol(catalyst)]. [b] Turnover frequency [mol(substrate)/mol(catalyst) h]. [c] Standard reaction conditions: $T = 303$ K, $t = 20$ min, 5 bar of H_2, 30 mL of methanol/toluene = 1:1, tolan/rhodium = 155:1. [d] See footnote *c* except $p[H_2] = 40$ bar. [e] See footnote *c* except $T = 333$ K. [f] See footnote *c* except tolan/rhodium = 1000:1, $t = 120$ min. [g] See footnote *c* except using different solvent. [h] See footnote *c* except $t = 45$ min.

Table 15. Performance of Catalysts 35a−c and 36a−d in the Hydroformylation of Alkenes

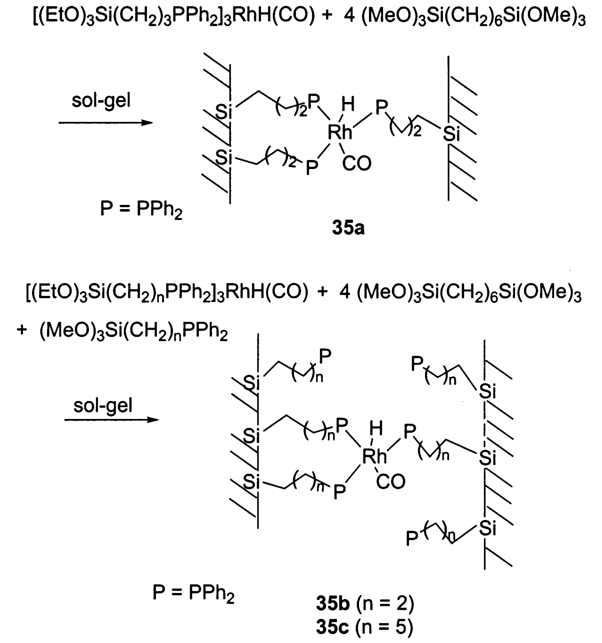
catalyst	eq	solvent	conversion (%)	isomerization (%)	hydroformylation (%)	$n/(n + iso)$	TON[a]	TOF[b]	ref	comments
35a	21a[c]	toluene	52.2	31.8	67.0	73.0	521		156	no recycling tests were reported
		THF	52.5	19.3	79.7	75.0	525			
		acetone	38.9	10.2	88.1	77.5	389			
		ethanol[d]	49.2	19.4	79.6	71.4	492			
		ethanol	58.6	12.7	85.0	84.7	586			
		ethanol[e]	77.2	67.3	12.1	96.9	772			
		methanol	85.5	19.5	80.5	76.7	854			
		water	50.2	20.6	77.1	69.7	52			
35b		ethanol	41.0	5.0	92.4	93.4	410			
35c		ethanol	29.6	6.2	90.9	86.4	296			
35c	21b[c]	ethanol	29.0	3.4	92.0	84	290			
35c	21c[c]	ethanol	20.6	2.7	96.1	84.9	206			
f	21a[g]	toluene	100	17.4	82.6	0.57	13216	777	157	no recycling tests were presented
36a			100	33.7	66.3	0.67	10608	624		
36b			100	20.9	79.1	0.58	12656	734		
36c			100	5.3	94.7	0.53	15152	891		
36d			100	7.5	92.5	0.53	14800	870		
f		dichloromethane	66.5	27.7	72.3	0.69	7496	451		
36a			88.9	49.5	50.5	0.72	7184	423		
36b			69.3	30.7	69.3	0.69	7680	451		
36c			100	13.0	87.0	0.58	13920	819		
36d			100	23.9	76.1	0.65	12176	716		

[a] Turnover numbers for catalysts **35a−c** [mol(substrate)/mol(catalyst)]; for catalysts **36a−d** [mol(ald.)/mol(catalyst)]. [b] Turnover frequencies [mol(ald.)/mol(catalyst) h]. [c] Reaction conditions except indicated: 10 bar of CO, 10 bar of H_2, 20 mmol of alkene, 20 μmol of catalyst, 20 mL of solvent, $T = 373$ K, $t = 150$ min. [d] $T = 353$ K. [e] $T = 393$ K. [f] Homogeneous reaction with monomeric metal complex. [g] Reaction conditions: 30 bar of CO, 30 bar of H_2, 10 mL (80 mmol) of 1-hexene, 5 μmol of catalyst, $T = 70$ °C, $t = 1020$ min.

Favorably the selectivity toward *cis*-stilbene was high (usually 98%), as long as the conversion of tolan did not exceed 95%. When the catalyst was recovered from the reaction mixture and used again, hydrogenation was observed with identical selectivity and only slightly smaller conversions. This finding depends markedly on the amount of the co-condensation agent and on the polarity of the solvent. Raising the ratio of the co-condensation agent $MeSi(OMe)_2(CH_2)_6(MeO)_2SiMe$ from 2:1 (catalyst **34a**) to 8:1 (catalyst **34b**) led to an increase of the turnover frequency (see Table 14). It can be seen that turnover numbers and frequencies rise with increasing solvent polarity. The lower concentration of reactive centers in **34a**,**b** prevented a dimerization of the catalysts, which resulted in a higher activity compared to their monomeric congener. To study leaching effects, the reaction solutions of four consecutive hydrogenation runs were separated from the polymer, concentrated, and subjected to catalysis. No hydrogenation of tolan took place. To further check the accessibility of the reactive centers, reactions of **34a** in solid/gaseous and solid/liquid interphases with small molecules such as CO, $CH_2{=}CH_2$, CS_2, and H_2/pyridine were also investigated. All reactions proceeded quantitatively, showing that the coordination centers were readily accessible for the mentioned substrates, which is a valuable precondition for catalysis.[155]

To achieve recyclable catalysts in the hydroformylation of olefins, the preparation of the sol−gel-processed rhodium complexes **35a−c** was described (Scheme 28).[156] The bifunctional co-condensation agent $(MeO)_3Si(CH_2)_6Si(OMe)_3$ and a carbonylhydrido(trisphosphine)rhodium complex with T-silyl-functionalized diphenyl phosphine ligands containing three- or six-membered hydrocarbon spacers were employed as starting materials. The polymer-bound complexes **35a−c** are excellent catalysts for the hydroformylation of 1-hexene in the presence of a wide variety of solvents (eq 21; Table 15). Polar

Scheme 28



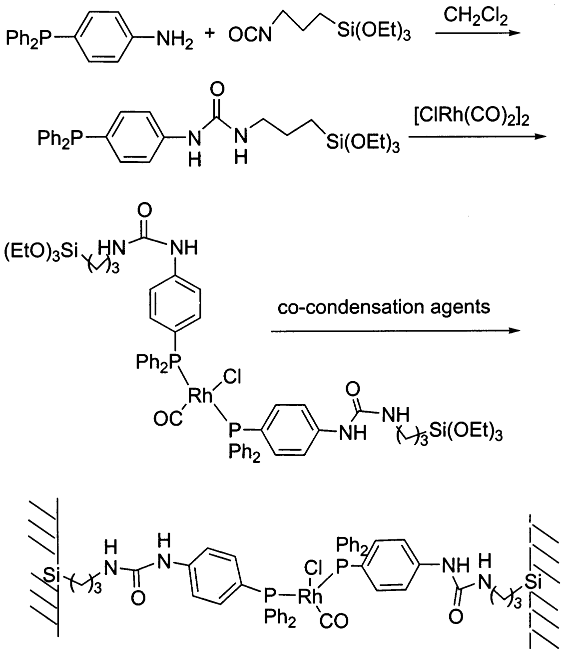
35a

35b (n = 2)
35c (n = 5)

solvents such as methanol afforded the highest activities, whereas the selectivity toward the formation of 1-heptanal was optimal in solvents of medium polarity such as ethanol or acetone. Application of materials with non-coordinated ligands raised the selectivity toward hydroformylation up to 92% and the *n*/*iso* ratio to 14:1 with an average turnover frequency of 164 mol(sub) mol(cat)$^{-1}$ h^{-1}. Due to longer spacers, **35c** was expected to exhibit a higher mobility and thus an improved selectivity. However, the *n*/*n* + *iso* ratio and turnover frequencies obtained with **35c** were inferior to those observed with **35b** (see Table 15). The behavior was attributed to the lower actual concentration (millimoles of P per volume unit of swollen catalyst bead) of phosphine functions in **35c** (constant P/Rh) in the swollen polymer. Olefins higher than 1-hexene were also hydroformylated with **35c**, and similar turnover frequencies and selectivities were obtained. ^{31}P CP/MAS and (^{1}H, ^{31}P) wide-line separation (WISE) NMR spectroscopic investigations gave an insight into the dynamic behavior and mobility of these materials.

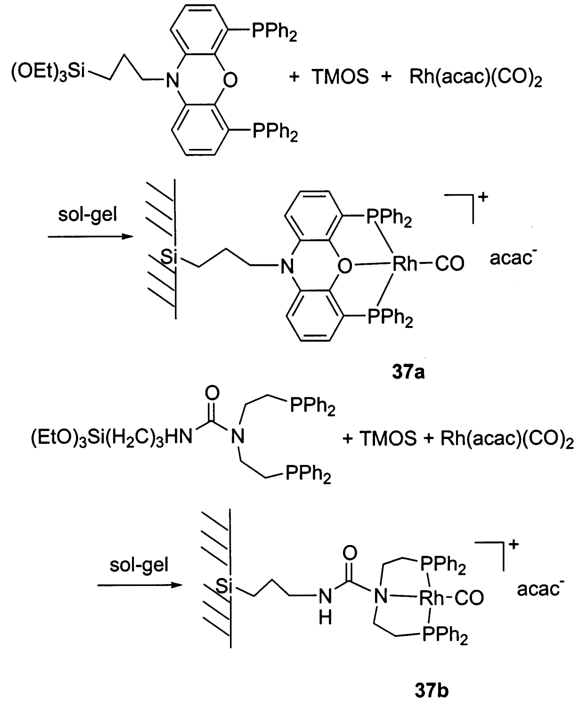
Other examples are the hybrid polymers **36a**–**d** (Scheme 29).[157] A novel T-silyl-functionalized triphenylphosphine ligand had to be prepared to introduce the spacer in the para-position of only one phenyl ring, which reacted with a rhodium precursor to give the catalytically active T-silyl-functionalized rhodium(I) compound $ClRh(CO)[PPh_2C_6H_4NHCONH(CH_2)_3Si(OEt)_3]_2$. The modified complex was then co-condensed with $(MeO)_2MeSi(CH_2)_6SiMe(OMe)_2$, $(MeO)_2MeSi(CH_2)_3(1,4\text{-}C_6H_4)(CH_2)_3SiMe(OMe)_2$, $(MeO)_3Si(CH_2)_6Si(OMe)_3$, and $(MeO)_3Si(CH_2)_3(1,4\text{-}C_6H_4)(CH_2)_3Si(OMe)_3$. Structural and mobility investigations of these novel stationary phases were carried out by multinuclear solid-state NMR spectroscopy (^{13}C, ^{29}Si, ^{31}P). Complexes **36a**–**d** were successfully employed in the hydroformylation of 1-hexene with good turnover numbers (eq 21; Table 15). The catalytic activity mainly depends on the mobility of the matrices and the reactive centers. No leaching of the transition metal complexes during the reactions was observed by atomic absorption spectroscopy.

Scheme 29



$(MeO)_2MeSi(CH_2)_6SiMe(OMe)_2$ (**36a**)
$(MeO)_2MeSi(CH_2)_3(1,4\text{-}C_6H_4)(CH_2)_3SiMe(OMe)_2$ (**36b**)
$(MeO)_3Si(CH_2)_6Si(OMe)_3$ (**36c**)
$(MeO)_3Si(CH_2)_3(1,4\text{-}C_6H_4)(CH_2)_3Si(OMe)_3$(**36d**)

Scheme 30

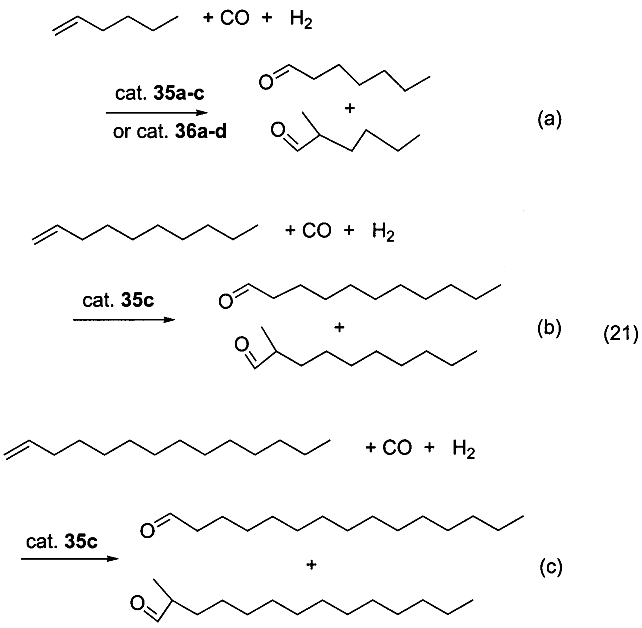


37a

37b

Of particular interest are the silica-supported, switchable, and recyclable hydroformylation/hydrogenation catalysts **37a**,**b** (Scheme 30).[158] They were obtained from [Rh(A)CO]$^{+}$ (A = the corresponding ligand system in Scheme 30) and TMOS and characterized by means of ^{31}P and ^{29}Si CP/MAS NMR, FT-

IR, and X-ray photoelectron spectroscopy. Independently, complexes **37a**,**b** and the same catalyst supported on commercial silica were applied in the hydroformylation of 1-octene (eq 22a). It was shown that the different preparation procedures led to different performances of the catalysts, which are summarized in Table 16. Supported **37a** showed an overall selectivity for linear aldehydes of 94.6% (linear to branched aldehyde ratio of 65, whereas that for **37b** is only 2.4). The authors attributed the high selectivity of **37a** to its larger P−Rh−P bite angel of 108° compared to 93° for **37b**. Recycling capabilities of **37a**,**b** were uncovered from a series of consecutive runs. Selectivities remained high, and no leaching was found by rhodium elemental analysis of the product. Also, **37a** was remarkably stable under catalytic conditions and worked for more than two weeks without any loss of activity. From detailed studies it was evaluated that 1-nonanol, obtained via the hydrogenation of the corresponding aldehyde, was formed as an unexpected byproduct (3.6% at 20% conversion). Under standard hydroformylation conditions, **37a** and its hydrido species $HRh(A)(CO)_2$ coexisted on the support. This dual system acted as a hydroformylation/hydrogenation sequence catalyst, giving selectively 1-nonanol from 1-octene; ultimately, 98% of 1-octene was converted to mainly 1-nonanal and 97% of the nonanal was hydrogenated to 1-nonanol (eq 22b). Addition of 1-propanol to the reaction mixture changed the system to a hydroformylation catalyst, which produces 1-nonanal with an overall selectivity of 93%, and completely suppressed the reduction reaction. If the atmosphere was changed from CO/H_2 to H_2, the system switched to the hydrogenation mode, which showed a clean and complete hydrogenation of 1-octene and 1-nonanal within 24 h. Active **37a** was recycled, and the system could be reversibly switched between the three “catalyst modes”, hydroformylation/hydrogenation, hydroformylation, and hydrogenation, completely retaining the excellent performance in each mode (see entries 14−18 in Table 16). With regard to the surface-supported catalysts with the same reactive center, **37a** showed a good recoverability and easy control in its catalytic performance.



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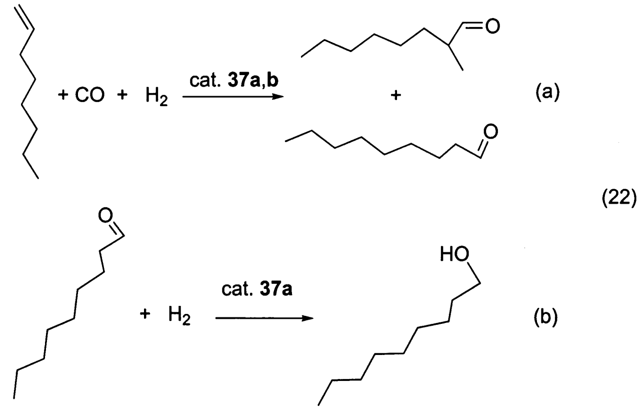

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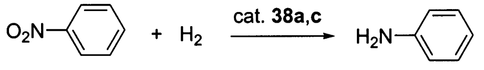
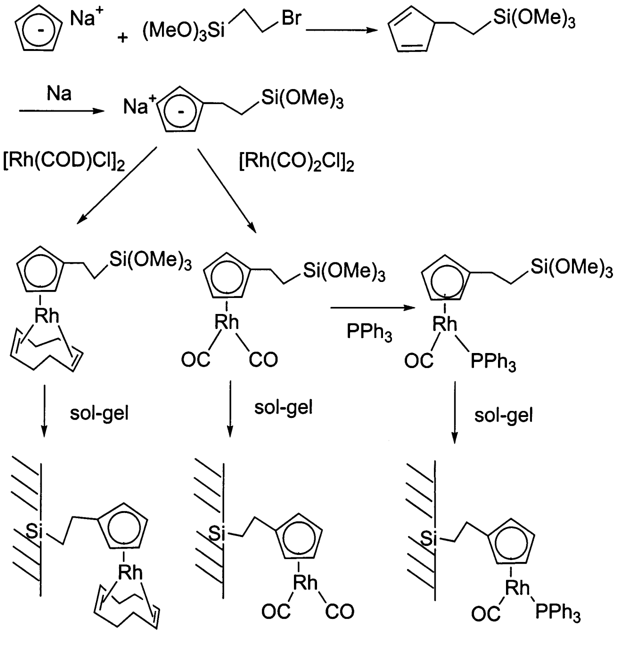


(23)

b. Cyclopentadienyl-Derived Ligands. Cyclopentadienylmetal complexes have experienced wide applications in homogeneous and heterogeneous catalysis;[93,159−162] however, polysiloxane-bound congeners were reported only recently.[8,163,164] Schumann et al. prepared three sol−gel-processed rhodium complexes **38a**−**c** (Scheme 31).[165] With $C_5H_4CH_2CH_2Si(OMe)_3$ as well as two different precursors $[Rh(CO)_2Cl]_2$ and $[Rh(COD)Cl]_2$ as starting materials, T-silyl-functionalized cyclopentadienyl rhodium(I) complexes were attained. The monomeric precursors were then poly-co-condensed with TEOS to give the desired hybrid polymers **38a**−**c**, which catalyzed the hydrogenation of alkenes, in aromatic as well as in aliphatic hydrocarbons (eq 17b; Table 17). It was established that the reaction rates with **38a**−**c** were either the same or somewhat lower than those of the

Scheme 31



38a **38b** **38c**

Table 16. Performance of Catalysts 37a,b in the Hydroformylation/Hydrogenation of 1-Octene (Equation 22) (Data from Reference 158)

no.	catalyst (cycle)	reaction conditions[a]	time (h)	conversion (%)	TOF[b]	*n*-aldehyde	*iso*-aldehyde	ratio (*n*/*iso*)	1-alcohol	octene isomers and octane (%)	comments
1	**37a** (1)	A	2	20	18	94.6	1.5	65	3.6	0.2	**37a** was recycled and the system could be reversibly switched between the three “catalyst modes” hydroformylation/hydrogenation, hydroformylation, and hydrogenation
2	**37a** (4)		2	12	12	89.6	1.6	62	8.8	0	
3	**37a** (1)		18	38	23	61.0	4.1	22	29.6	5.3	
4	**37a** (2)		18	30	17	77.9	3.7	25	15.1	3.43	
5	**37a** (1)	B	24	69	35[c]	92.8	3.0	32	2.5	1.7	
6	**37a** (8)		24	63	33[c]	95.0	2.6	37	0.5	2.0	
7	**37b**		24	72	119[c]	70.0	28.9	2.4	0.1	1.0	
8	HM[d]		24	19	283[c]	93.3	2.9	32	0	3.7	
9	PE[e]		24	64	175[c]	26.3	16.3	1.6	0	57.4	
10	SC1 (1)[f]	A	22	37	13	90.7	2.6	37	5.1	1.6	
11	SC1 (3)[f]		72	61	8	79.9	3.5	27	13.2	3.4	
12	SC2 (1)[g]		23	24	8	85.5	4.5	19	0	9.9	
13	SC2 (4)[g]		72	44	5	84.8	5.4	16	0	9.8	
14	**37a**	A	172	97	75[h]	18.5	3.6	23	66.7	11.2[i]	
15	**37a**	A[j]	24	100	100[h]	0	0		100	100[i]	
16	**37a**	A	68	60	16[h]	65.2	4.5	18	13.7	16.6[i]	
17	**37a**	A[j]	2	98	10[h]	0	0		9.7	98[i]	
18	**37a**	B	96	96	0[h]	90.7	5.1	18	0	4.3[i]	

[a] Reaction conditions: (A) $p(CO/H_2)$ (1:1) = 50 bar, $T = 80$ °C, ligand/Rh = 10, substrate/Rh = 637:1, Rh content = 1×10^{-5} mol, 1 mL of octene, 13 mL of toluene, 1 mL of decane as internal reference; (B) 1 mL of 1-propanol was added to the catalyst mixture of A. [b] Average turnover frequencies were calculated as [mol(product)/mol(catalyst)h]. [c] Initial turnover frequencies were calculated at 10–20% conversion. [d] Homogeneous reaction with monomeric complex in Scheme 30. [e] Physical entrapment of $[Rh(acac)(CO)_2]$ without T-silyl-functionalized diphosphine in polycondensed TMOS. [f] Silica-supported catalyst: the corresponding ligand in **37a** was covalently tethered to silica and then modified with dimethoxydimethylsilane, subsequently reacted with $[Rh(acac)(CO)_2]$. [g] Silica-supported catalyst: the corresponding ligand in **37a** was reacted with $[Rh(acac)(CO)_2]$, then covalently tethered to silica. [h] Conversion of aldehyde (%). [i] Yield of octane (%). [j] Addition of 1 mL of 1-nonanal and $p[H_2]$ = 50 bar instead of $p[CO/H_2]$ = 50 bar.

Table 17. Performance of Catalysts 38a,b and 39a,b in Hydrogenations

catalyst	eq	time (h)	yield (%)	catalyst	eq	time (h)	yield (%)	ref	comments
a	17b[b]	3	76	*a*	23[b]	40	46	165	**38a**–**c** were recycled, but no specific data were reported
38a		4	54	**38a**		40	10		
c		3	100	*d*		40	100		
38b		4	59	**38c**		40	100		
d		3	100						
38c		4	100						

catalyst	eq	*e*	TOF[f]	TON[g]	ref	comments
39a	24[h]	0.017	1.61	65	166	no recycling tests were carried out
39b		0.025	0.23	13		
		0.050	0.14	14		
		0.098	0.14	9		

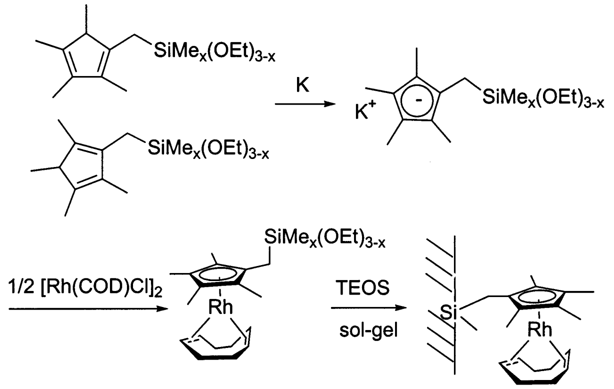
[a] Homogeneous reaction with T-silyl-functionalized rhodium complex in **38a**. [b] Reaction conditions: 2.5 mmol of substrate, 6.25×10^{-2} mmol of rhodium catalyst, 3 mL of benzene, 14 atm H_2, $T = 80$ °C for styrene and 90 °C for nitrobenzene. [c] Homogeneous reaction with T-silyl-functionalized rhodium complex in **38b**. [d] Homogeneous reaction with T-silyl-functionalized rhodium complex in **38c**. [e] Ratio of catalyst/substrate. [f] In [mol(H_2)/mol(Rh) min]. [g] In [mol(H_2)/mol(Rh)]. [h] Reaction conditions: substrate concentration 0.25 M, 60 °C, $p(H_2)$ = 127.7 kPa.

soluble catalysts. However, they were air stable and recyclable in numerous runs and were leaching-proof. On the contrary, the corresponding homogeneous catalysts could be handled only with exclusion of air and in a single catalytic run. The activities of **38a**–**c** were superior to those of physically entrapped rhodium complexes, which deactivated gradually in consecutive runs because either the pores containing the metal nuclei were blocked or the complexes were partially reduced to metallic rhodium. Catalysts **38a**,**c** also promoted the hydrogenation of nitro compounds (eq 23; Table 17).

Another example of a sol–gel-processed Cp-Rh complexes **39** was presented by Cermak et al. (Scheme 32).[166] The precursor complex was obtained from the corresponding alkoxysilyl-substituted tetramethylcyclopentadiene and chloro(1,5-cyclooctadiene)rhodium(I) dimers. The resulting complexes were then included as components in the sol–gel preparations of polysiloxanes. Catalysts **39a**,**b** were characterized by BET and ^{13}C CP/MAS NMR spectroscopy. The hydrogenation of crotonic acid in water by **39a**,**b** showed a moderate activity up to 1.6 mol (mol of Rh)$^{-1}$ min^{-1} (eq 24; Table 17). The TOFs did not change dramatically with the substrate/catalyst ratio, and turnover numbers were improved by increasing the substrate/catalyst ratio (Table 17). Analysis by reversed-phase HPLC revealed that the hydrogenation produced butyric acid as the only product.

c. Nitrogen Ligands. Other than interphase catalysts with phosphorus ligands, those with nitrogen-containing rhodium(I) complexes are relatively

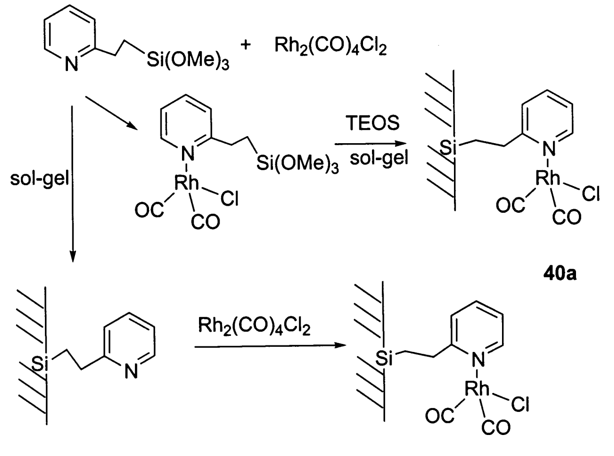
Scheme 32



39a (x = 0)
39b (x = 1)

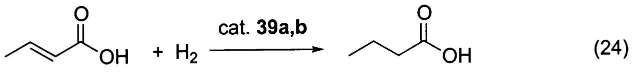
rare.[167,168] Capka and Schubert et al. reported on the application of sol–gel-processed rhodium(I) complexes with pyridine-containing ligands.[168] With 2-(2-trimethoxysilylethyl)pyridine (TMEP) as starting material, the hybrid catalysts **40a**,**b** were prepared by two routes: (i) treatment of $[Rh(CO)_2Cl]_2$ with a polycondensate prepared by hydrolysis and condensation of a mixture of TMEP and TEOS and (ii) sol–gel processing of TEOS with a rhodium(I) complex coordinated to TMEP (Scheme 33). With **40a**,**b** the methanol carbonylation was investigated (eq 25). Although the reaction rates (the highest rate was 1.3×10^{-4} mol s^{-1} g(Rh)$^{-1}$) were lower than those of the homogeneous analogues, **40b** displayed good catalytic performances. Compared to the surface-supported catalysts prepared from the same monomeric rhodium complex and commercial silica, the stability of **40a**,**b** was much better according to time-dependent measurements of the rhodium concentration in the outlet of the plug reactor.[168]

Scheme 33



40a

40b



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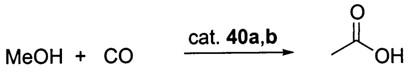

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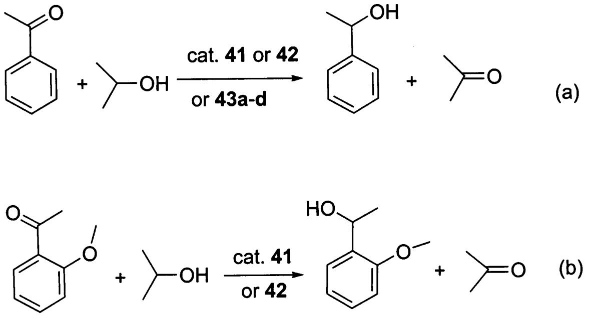

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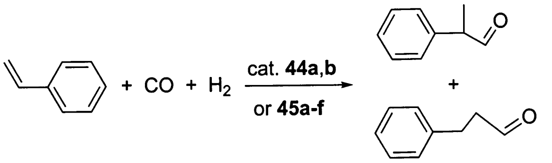
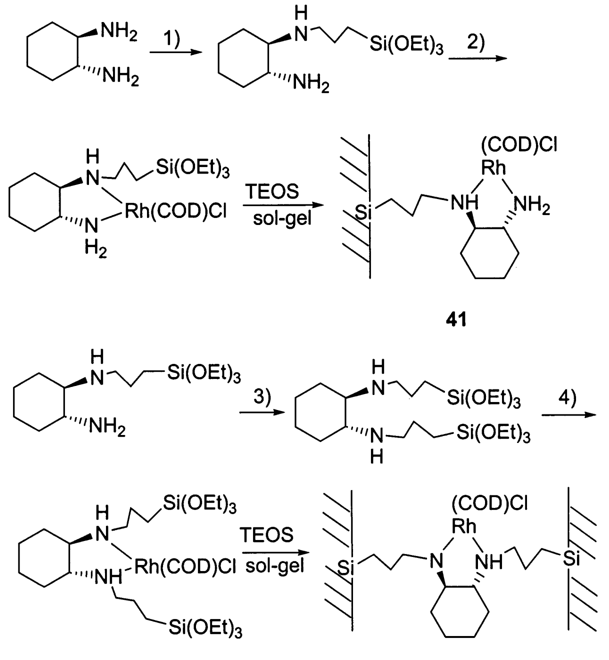


(27)

New and diverse selective catalytic materials arise from the sol–gel route to hybrid organic–inorganic solids. Examples are studies of materials containing chiral diamine ligands.[167] Catalysts **41** and **42** were prepared by reaction of silylated amines with [Rh(COD)Cl]$_2$ in ethanol, and the obtained precursor materials were poly-co-condensed with TEOS without any catalyst (Scheme 34). They were characterized by elemental analysis, UV–vis, multinuclear solid-state NMR spectra, and BET measurements. Subsequently, supported **41** and **42** were applied as catalysts in the asymmetric hydride transfer reduction of acetophenone and *o*-methoxyacetophenone (eq 26; Table 18). The ee values were higher compared to those found for the soluble catalytic species. A related material accessible by immobilization of diamine-

Scheme 34



41

42

1) Cl(CH$_2$)$_3$Si(OEt)$_3$, 2) [Rh(COD)Cl]$_2$
3) Cl(CH$_2$)$_3$Si(OEt)$_3$, 4) [Rh(COD)Cl]$_2$

Table 18. Performance of Catalysts 41–43

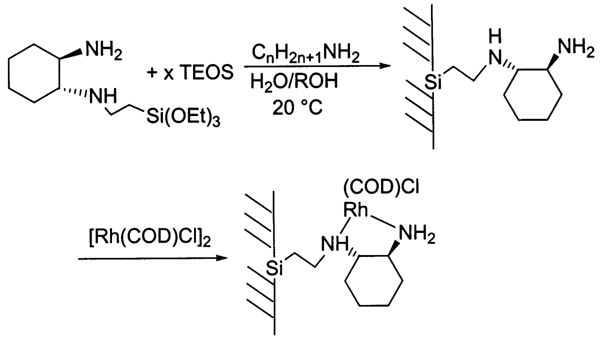
catalyst	type of catalysis	eq	time	conversion (%)	ee[a] (%)	ref	comments
b	reduction[c]	26a	5 days	95	14	167	no recycling tests were reported
41			5 days	80	25		
d			5 days	95	26		
42			5 days	75	58		
e			14 days	10	22		
42		26b	7 days	30	80		
43a	reduction[f]	26a	20 h	91	15	169	**43c** showed the same activity in 3 runs
43b			24 h	97	10		
43c			18 h	82	16		
43c[g]			24 h	90	13		
43d			20 h	87	12		
h			24 h	10			

[a] Determined using HPLC on a chiral colum, (*S*)-phenylethanol was obtained with (*R*,*R*)-diamine ligand. [b] Homogeneous reaction using [Rh(COD)Cl(L)], where L = silyldiamine ligand in **41**. [c] Reaction conditions: 8.3 mmol of acetophenone or *o*-methoxyacetophenone, 20 mL of 2-propanol, 2.5 mmol of KOH, $T = 25$ °C, catalyst containing 1 mol % of rhodium. [d] Homogeneous reaction using [Rh(COD)Cl(L)], where L = silyldiamine ligand in **42**. [e] Catalyst prepared by immobilization of diaminerhodium complex in **42** at the surface of silica gel. [f] Reaction conditions: 12 mL of 2-propanol, 2 mmol of acetophenone, 2 mol % (0.04 mmol) of the rhodium containing catalyst, 0.24 mmol of KOH, $T = 85$ °C. [g] Using twice-recycled catalyst **43c**. [h] Corresponding rhodium catalyst prepared from silyldiamine and TEOS in molar ratio 1:20.

rhodium complexes at the surface of silica showed a much lower activity (see Table 18).

By employing primary amines as templates, the immobilized chiral rhodium complexes **43a**–**d** were accessible (Scheme 35).[169] The monosilylated derivative of (1*R*,2*R*)-diaminocyclohexane was cohydrolyzed with TEOS under different conditions. Treatment of the immobilized chiral ligands with $[Rh(COD)Cl]_2$ afforded **43a**–**d**. The enantioselective reduction of acetophenone served to screen the catalytic activity of **43a**–**d** (eq 26a). For **43a**–**d**, conversions between 82 and 97% were achieved after 20–24 h at 85 °C (Table 18). The alcohol was obtained with low ee values between 10 and 16%. Conversions and enantioselectivities were similar to those observed in homogeneous phase. The efficiency of **43a**–**d** is much higher than that of **41** and **42**, which is attributed to the higher porosity of the templated materials **43a**–**d**, having higher BET surface areas between 700 and 1100 $m^2\ g^{-1}$. Twice-recycled **43c** showed the same conversion and enantiomeric excess. EDX analyses of the catalysts collected after the reaction indicated that their chemical composition did not change. It was concluded that the templated materials have much higher activities and stabilities than the related non-templated species.

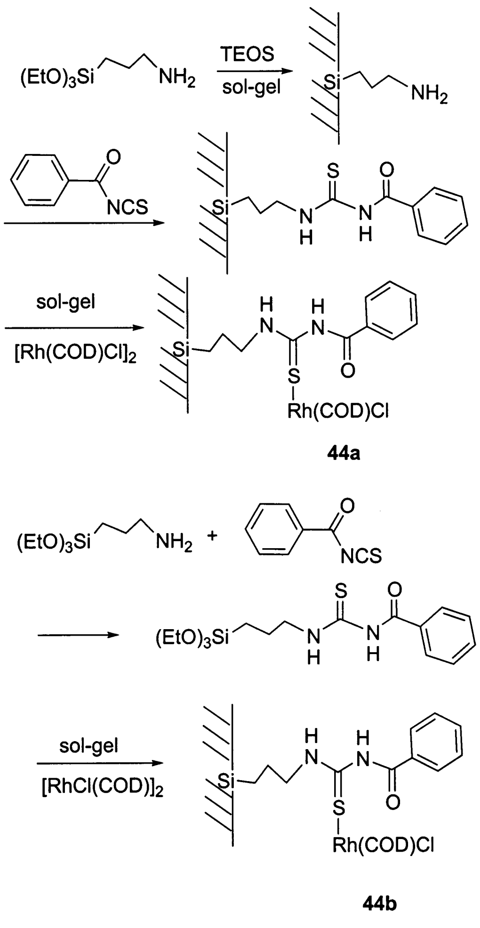
Scheme 35



43a (n = 12, x = 12)
43b (n = 12, x = 20)
43c (n = 16, x = 12)
43d (n = 16, x = 20)

d. Sulfur Ligands. In the quest for new ancillary ligands for catalytic processes, Tiripicchio et al. were interested in xerogels modified with sulfur ligands and their rhodium(I) complexes.[170] The potentially bidentate benzoylthiourea $(EtO)_3Si(CH_2)_3NHC(S)NHC(O)Ph$ was synthesized as a precursor of the functionalized xerogels and then sol–gel-processed either with TEOS or alone. Anchoring of $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ with the above-mentioned xerogels resulted in the hybrid catalysts **44a**,**b** (Scheme 36), which were active in the hydroformy-

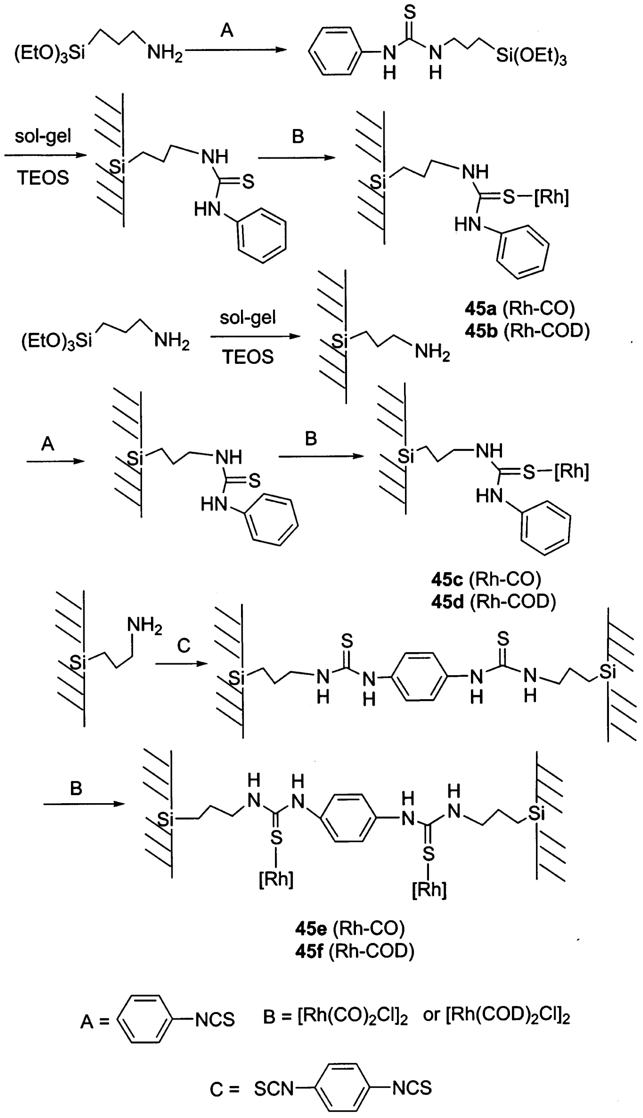
Scheme 36



lation of styrene (eq 27). Styrene was quantitatively converted into the corresponding linear and branched aldehydes under relatively mild conditions. After filtration, **44a**,**b** could be reused without any loss of activity. It was found that the anchored species underwent major changes during the catalytic cycles.[170] The thioureato complexes in **44b** appeared to be more stable than those in **44a**, and no degradation to oxidized rhodium species was detected by XPS after three cycles. However, some metal and sulfur leaching occurred in **44b** as indicated by EDX measurements, but no detailed data were reported.

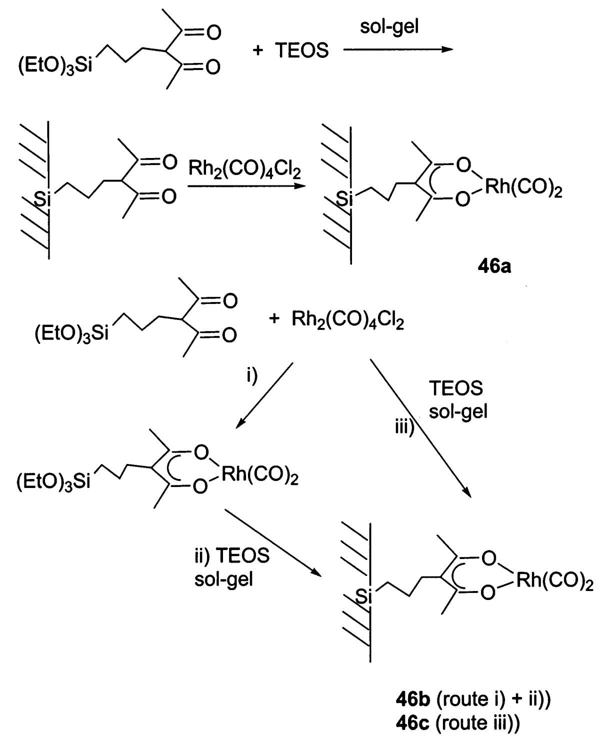
Recently, Tiripicchio anchored rhodium(I) complexes to thiourea-functionalized xerogels and silsesquioxanes and studied the matrix effects dependent on the selectivity in the hydroformylation of styrene.[171] Catalysts **45a**−**f** were prepared according to Scheme 37 and contain $(EtO)_3Si(CH_2)_3NCS$, $(EtO)_3Si(CH_2)_3NH_2$, $PhNH_2$, PhNCS, 1,4-diaminobenzene, 1,4-phenylenediisocyanate, $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, and TEOS as building blocks. As their above-mentioned relatives, **45a**−**f** were active in the hydroformylation of styrene at 80 °C and 60 atm with a 1:1 mixture of CO/H_2 (eq 27). Styrene was completely converted into the branched and linear aldehyde. Only traces of ethylbenzene were detected, and no alcohols were formed. However, no data for TOFs and TONs were presented. Some catalysts showed a variation in regioselectivity when applied in consecutive catalytic runs. Recovery of **45a**−**f** was possible, and prior to repeated use, they have been investigated by XPS and EDX. A change in regioselectivity was ascribed to matrix effects. It was elucidated that the surface leaching of rhodium complexes forced the catalytic process to move to the inside of the materials.

Scheme 37



e. Oxygen Ligands. With the intention to improve the stability of heterogenized catalysts to oxygen, Capka et al. designed a rhodium(I) complex bound to supports with oxygen-containing anchoring ligands.[172] To solve this problem alkoxysilyl-substituted 2,4-pentanediones of the type $(RO)_3Si(CH_2)_n$-$CH(COCH_3)_2$ were coordinated to rhodium(I) compounds and immobilized via a sol−gel process (Scheme 38). The catalytic activities of **46a**−**c** were probed for the hydrogenation and hydrosilylation of 1-octene (eqs 8 and 28; Table 19). Notably **46a**−**c** showed lower activities than the corresponding silica-supported catalysts, which is attributed to the low metal loading of **46a** and the imperfect accessibility of the reactive centers in **46b**,**c** due to the small pore size of the polymers.

Scheme 38



3. Iridium Complexes

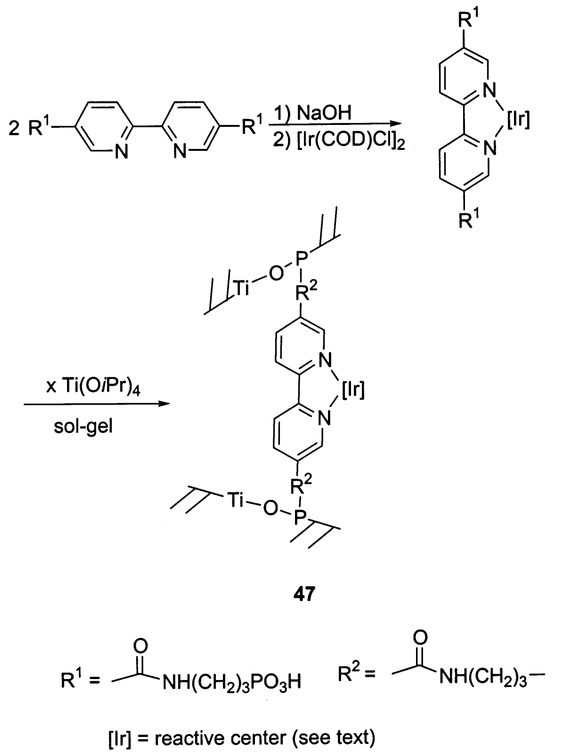
Because of the remarkable chemical stability of Ti−O−P bonds, Maillet et al. considered phosphonate-based supported iridium(I) complexes as catalysts (Scheme 39).[173] Functionalized 2,2′-bipyridine ligands containing two phosphonic acid moieties were reacted

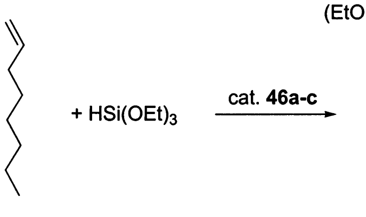
Table 19. Performance of Catalysts 46–48

catalyst	type of catalysis	eq	initial rate[a]	catalyst	type of catalysis	eq	TON[b] (s^{-1})	conversion (%) 10 min	conversion (%) 120 min	ref	comments
46a	hydrogenation[c]	8	2.9	**46a**	hydrosilylation[d]	28	0	0	0	172	no recycling tests
46b			4.9	**46b**			0	0	2		
46c			1.2	**46c**			0	0	8		
e			4.9	*e*			0	0	37		
f			12.5	*f*			2.5	45	72		
g			13.1	*g*			33	68	81		
47[h]	hydrogenation	29						94		173	no recycling tests
48a[i]		30	11							174	catalysts were reused, but no specific data were presented
48b[j]			31								

[a] [Mol(product)/mol(catalyst) min]. [b] Based on initial rates in the first 5 min. [c] Reaction conditions: 6.4 mmol of 1-octene, 10 μmol of catalyst (Rh), $p[H_2] = 110$ kPa, 3 mL of toluene, $T = 65$ °C. [d] Reaction conditions: 10 mmol of 1-octene, 10 mmol of triethoxysilane, 3×10^{-4} mmol of catalyst, $T = 100$ °C. [e] T-silyl-functionalized rhodium complex. [f] Silica-supported catalyst from T-silyl-functionalized rhodium complex. [g] Silica-supported catalyst from T-silyl-functionalized ligand and rhodium complex. [h] Reaction conditions: 5 mL of methanol, 40 bar of H_2, Ir/substrate 2.5%, NaOH/Ir = 5:1, room temperature, $t = 21$ h. [i] Reaction conditions: 150 mg of catalyst **48a** (16 μmol of Ir), 2 mmol of 1-hexene, 3.5 mL of ethanol. [j] Reaction conditions: 100 mg of catalyst **48b** (32 μmol of Ir), 4 mmol of 1-hexene, 18 mL of ethanol.

Scheme 39





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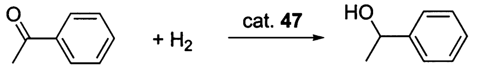

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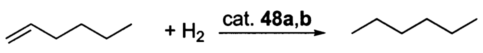

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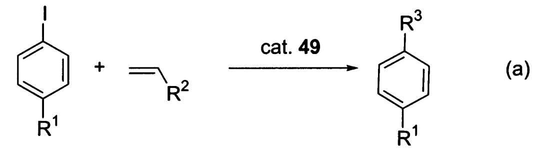
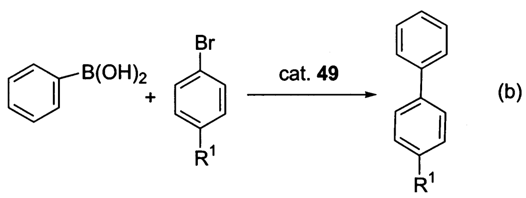


R^1 = H, OH; R^2 = CO_2CH_3, CH_2OH, $CH(OH)CH_3$;
R^3 = $CH{=}CHCO_2CH_3$, CH_2CH_2CHO, $CH_2CH_2COCH_3$

(31)

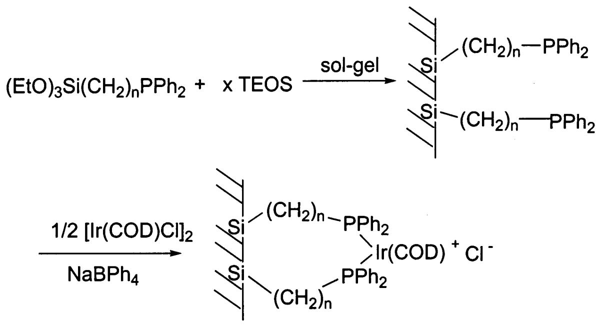


R^1 = H, CN, Cl, OCH_3, CH_2Br

with $[Ir(COD)Cl]_2$ in basic media. Co-condensation of the resulting iridium(I) precursor with $Ti(OiPr)_4$ afforded **47**, which was applied in the hydrogenation of acetophenone. Optimizations of reaction conditions for the access to **47** were based on pH effects, the molar ratio of titanium/phosphorus, titanium precursors, and solvents. The best experimental conditions were achieved by the following parameters: pH 9.4, Ti/P = 5.6, $Ti(OiPr)_4$ as titanium precursor, *i*PrOH/H_2O as solvent. These boundary conditions resulted in an acetophenone conversion of 94% (eq 29; Table 19). This work clearly indicates that reaction conditions in the preparation of interphase catalysts greatly influence their performance.

A further example of a polysiloxane-supported phosphine–iridium complex should be mentioned and was introduced by Parish et al.[174] The T-silyl-functionalized phosphine ligands $(EtO)_3Si(CH_2)_nPPh_2$ ($n = 2, 3$) were co-condensed with TEOS, and the resulting polymer was characterized by solid-state NMR spectroscopy. Treatment of these polymer-anchored ligands with $[Ir(COD)Cl]_2$ afforded the hybrid catalysts **48a**,**b** (Scheme 40), which showed a significant activity in the hydrogenation of 1-hexene (eq 30; Table 19). Although **48a**,**b** are subjected to some decomposition on repeated use, these systems were still active after 10 cycles.

Scheme 40



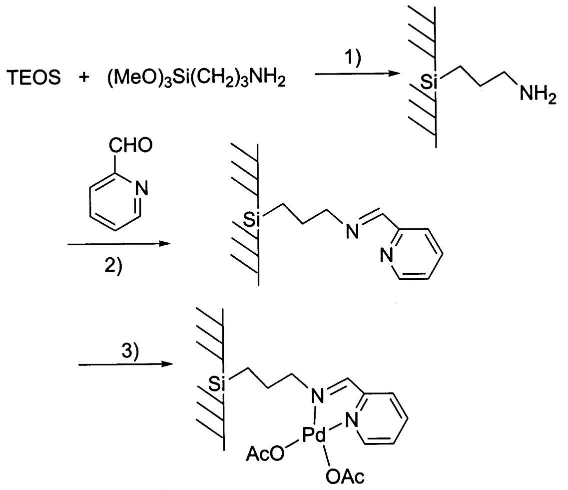
48a (n = 2, x = 2)
48b (n = 3, x = 4)

F. Palladium and Platinum Complexes

1. Palladium Complexes

An area of intense research has been oriented to supported palladium catalysts for cross-coupling reactions, which represent excellent methods for the synthesis of various organic molecules.[128,175−181] Clark et al. developed a range of heterogeneous palladium catalysts based on chemically modified mesoporous silica gel, which was either commercially available or prepared via sol−gel technology. The hybrid palladium catalyst **49** was prepared by reaction of sol−gel-processed aminopropyl-modified micelle-templated silica (3-aminopropyl-MTS) with pyridinecarbaldehyde, followed by complexation with palladium acetate (Scheme 41).[182] To ensure stability in subsequent reactions, **49** was heated in different solvents. The activity of **49** was investigated in the Heck reaction of aryl iodides with olefins in an acetonitrile suspension (eq 31a; Table 20). In the first 6 h the conversion rate was ~4% h^{-1} after an induction period of ~1 h. Supposedly the decrease of the activity after 6 h to 2% h^{-1} is due to the congestion of the gel pores by the products. By decanting the liquid from the reactor the active polymer **49** could be recycled and was further applied without any conditioning and regeneration. Only after five additional runs (corresponding to a turnover number of >2000) was a significant drop in activity observed. There was no induction period on repeated use. Analysis by atomic absorption spectroscopy corroborated that no detectable amounts of palladium leached during the reaction. No conversion was observed in the hot filtrate, which further implied that the transition metal species did not dissociate from the support during the reaction. The same polymer **49** was also successful in the Heck reaction of aryl iodides with allylic alcohols to give carbonyl compounds (see Table 20). Repeated use of **49** occurred without noticeable loss of activity.

Scheme 41



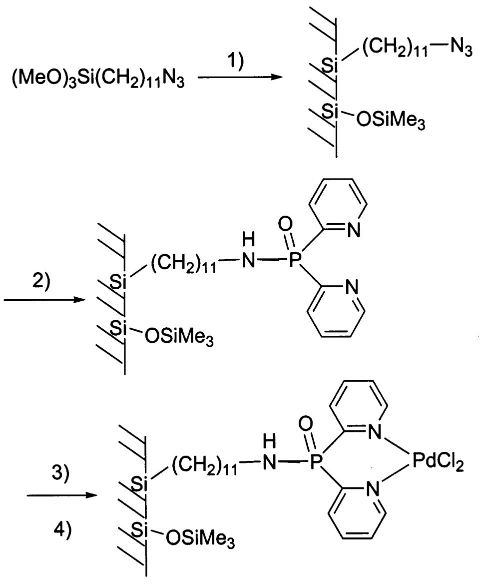
49

1) sol-gel/*n*-dodecylamine, EtOH/toluene, 18 h
2) EtOH, 18 h, 3) $Pd(OAc)_2$/acetone, 24 h

In the Suzuki C−C coupling between phenylboronic acid and bromobenzene in xylene in the presence of potassium carbonate as a base catalyst **49** was also reported to give excellent results concerning the activity and recycling ability (eq 31b; Table 20).[183] High yields of biaryls were obtained at 95 °C. Stable palladium complex **49** was also effective for substituted bromobenzenes (see Table 20).

With the aim to mimic the surface of silica but with properties that are more readily controlled than those of silica, heterogenized homogeneous palladium(II) complexes on polysiloxanes with controlled solubility have been prepared and characterized (Scheme 42).[184]

Scheme 42



50a,b

1) a) 3 M HCl/THF, room temperature, 12 h; b) Me_3SiCl, reflux, 3 h
2) $P(2\text{-py})_3$/acetone, microwave, 3 h
3) $PdCl_2/CH_3CN$, reflux, 24 h (**50a**)
4) HCl/THF, room temperature, 24 h (**50b**)

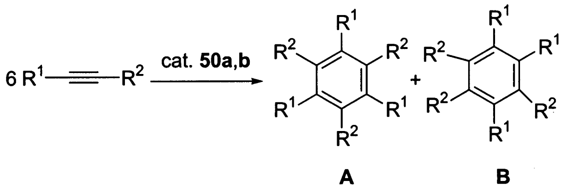
$(MeO)_3Si(CH_2)_{11}N_3$ as starting material produced silica fragments small enough to be soluble in conventional organic solvents by incomplete acid hydrolysis. Subsequent silylation with trimethylsilyl chloride and substitution with $P(2\text{-py})_3$ afforded a polysiloxane matrix with an $NHP(O)(2\text{-py})_2$ functionality. By coordination of both pyridyl groups to palladium acetate, the soluble, anchored palladium-

Table 20. Performance of Catalysts 49 and 50a,b

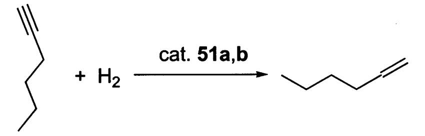
catalyst	type of catalysis	eq	R^1	R^2	time (h)	catalyst/ substrate	yield[a] (%)	ref	comments
49	Heck reaction[b]	31a	H	CO_2CH_3	24		82	182	catalyst **49** was reused, but no specific data were presented
			HO	CO_2CH_3	24		31		
			H	CH_2OH	24		21		
			HO	CH_2OH	24		15		
			H	$CHOHCH_3$	24		41		
			HO	$CHOHCH_3$	24		27		
	Suzuki reaction[c]	31b	H		1	83	75[d]	183	**49** showed good performance in 5 runs
			H		1	83	96[e]		
			H		1	83	45[f]		
			H		3	833	98		
			CN		2	167	98		
			Cl		3	167	98		
			OMe		6	167	82		
			CH_2Br		6	167	79		
50a	cyclotrimerization[g]	32	Me	Me	12		94	184	**50a** and **50b** exhibited stability with >99% 4-octyne conversion through 6 cycles
			*n*Pr	Me	16		96[h]		
			Et	Et	16		91		
			*n*Pr	*n*Pr	16		93[i]		
			Ph	H	16		94[j]		
			Ph	Ph	16		95		
50b			Me	Me	12		94		
			*n*Pr	Me	16		86[k]		
			Et	Et	16		94		
			*n*Pr	*n*Pr	16		95[i]		
			Ph	H	16		92[l]		
			Ph	Ph	16		90		

[a] For eq 31 yields were measured from GC, for eq 32 yields are based on the purified products by flash chromatography on SiO_2. [b] Reaction conditions: 30 mmol of substrate, 0.2 g of catalyst, 30 mmol of triethylamine, 30 mL of acetonitrile, $T = 82$ °C. [c] Reaction conditions: 13 mL of xylene, 5 mmol of bromobenzene, 7.3 mmol of phenylboric acid, 10 mmol of K_2CO_3, $T = 95$ °C. [d] First cycle. [e] Fifth cycle. [f] Sixth cycle. [g] Reaction conditions: 0.56 mmol of alkyne, 3 mL of $CHCl_3$, catalyst loading = 4 mol %, $T = 62$ °C. [h] Product ratio **A**/**B** = 91:9. [i] Yield > 99% in cycles 1−6 were determined by NMR spectroscopy at 62 °C. [j] Product ratio **A**/**B** = 81:19. [k] Product ratio **A**/**B** = 90:10. [l] Product ratio **A**/**B** = 79:21.

(II) catalyst **50a** was available. Progressive heterogenization was conducted by further treatment of **50a** with HCl to yield **50b**, which was insoluble in organic solvents. Both materials displayed excellent activities for various alkyne cyclotrimerizations (eq 32; Table 20). Monitoring experiments of the cyclotrimerizations by ^{1}H NMR spectroscopy corroborated that **50a** was stable against decomposition and palladium leaching. Neither color change nor precipitation occurred during the reaction under similar conditions. Lack of any palladium species detected by AAS in the filtrate of the reaction solution further verified that **50b** resisted leaching. Both species **50a**,**b** were regioselective in the case of asymmetric alkynes such as 2-hexyne and phenylacetylene. Regarding catalyst recycling, **50a** and **50b** were tested for the cyclotrimerization of 4-octyne. Both of them exhibited good stability with a 4-octyne conversion of 99% in six cycles.



(32)



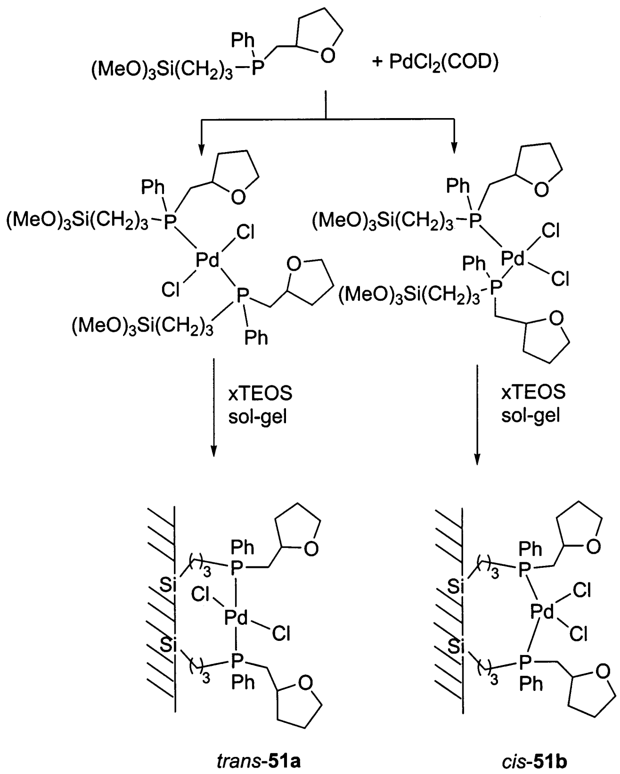
(33)

$$R_3Si{-}H \; + \; H{-}OR' \xrightarrow{\text{cat. } \mathbf{52a,b}} R_3Si{-}OR' \; + \; H_2 \qquad (34)$$

R = Et, EtO, Me_3SiO, etc.; R' = Et, *i*Pr, *t*Bu *n*Pr etc.

Various ether−phosphine palladium(II) complexes were transferred into the interphase.[170,178,185−187] Treatment of 2 equiv of T-silyl-functionalized ether−phosphines with $PdCl_2(COD)$ afforded monomeric complexes, which were sol−gel-processed with variable amounts of TEOS to give the hybrid materials **51a**,**b** (Scheme 43).[185] They revealed high activity and selectivity in the hydrogenation of tolan and 1-hexyne (eqs 20 and 33). The hydrogenation of 1-hexyne succeeded without any solvent. Within 10−20 min the H_2 uptake was finished with conversions of >99% between 65 and 70 °C. Turnover frequencies depend on the hydrogen pressure at the beginning of the reaction. Repeated use up to 10 times without noticeable loss of the activity was possible. Leaching of 0.2−1% of the original palladium quantity was established after each run. Because the recovered reaction solution is inactive in the hydrogenation of 1-hexyne, it was suggested that palladium still embedded in the polysiloxane matrix was the active catalyst rather than the palladium species in the reaction solution. Lower amounts of the co-condensation agent TEOS ($x = 4$, 12) influenced the selectivity with respect to 1-hexene, ranging from 96 to 98% during seven runs. However, the selectivity decreased to 62% with high amounts of TEOS ($x = 36$). The decomposition of the polymeric palladium complexes **51a**,**b** during the hydrogenation resulted in a reaction at the boundary phase solid−liquid, and the desired reaction in the

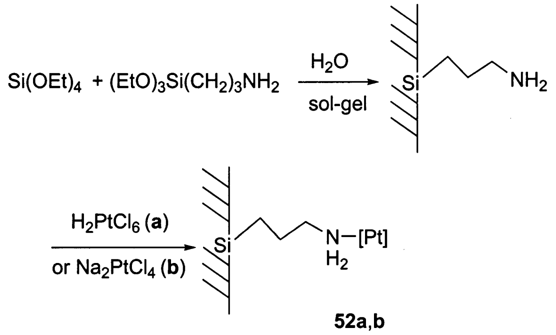
Scheme 43



trans-**51a** *cis*-**51b**

x = 4, 12, 36

Scheme 44



52a,**b**

[Pt] = reactive center (see text)

interphase failed. This was confirmed by high-resolution scanning electron microscopy, ^{31}P CP/MAS NMR spectra, and XPS studies. In the hydrogenation of tolan toluene served as a solvent (eq 20). Within a limited time (1 h) the conversion of diphenylacetylene was strongly dependent on the temperature, but selectivities were constant: 89% of *cis*-stilbene, 5% of *trans*-stilbene, and 6% of the fully hydrogenated products. It was found that a higher amount of ethanol in an ethanol/toluene solvent mixture accelerates the conversion.

2. Platinum Complexes

Due to economic considerations, the recovery of platinum catalysts is absolutely indispensable.[188−190] Hilal et al. synthesized supported **52a**,**b** (Scheme 44)[191] and evaluated the catalytic activity for O-silylations. In the first step a T-silyl-modified amine ligand and TEOS were sol−gel-processed to afford the solid polymer. Subsequent treatment with H_2PtCl_6 or Na_2PtCl_4 resulted in the formation of **52a** and **52b**. Effects of the substrates, solvents, concentrations, and temperature on the catalytic O-silylation of $R_3Si{-}H$ compounds were studied in detail (eq 34). Regarding the substrate, two factors affect the reactivity: (i) the steric factor in the sequence *n*PrOH > *i*PrOH > *t*BuOH and (ii) the electronic factor with regard to the nucleophilicity of alcohols; for example, ethanol is less reactive than propanol. The reaction rate is slowed when polar solvents are used and is faster at higher temperature. Furthermore, catalysts used at higher temperatures were less active on recovery than samples used at lower temperatures due to decomposition. **52a** showed a remarkable catalytic activity, whereas **52b** was inactive. With respect to recovery and repeated use, **52a** partially retained its activity after three different runs, and the catalytic activity was highly reproducible within the same batch.

IV. Enzymes as Reactive Centers

The immobilization of biological catalysts (e.g., enzymes, catalytic antibodies, and whole cells) in robust matrices to enhance their lifetime as well as their recovery and repeated use have been the focus of attention for several years.[192,193] From economical and ecological points of view, such catalysts are important if they can be separated from the reaction products and used again without significant loss of activity. A common approach is the encapsulation of catalytic species inside silica via the sol−gel process.[194−196] Although this is on the borderline of the concept of chemistry in interphases, some interesting examples are summarized in this section. In 1995, Reetz et al. demonstrated the entrapment of lipases into the hydrophobic sol−gel materials, which resulted in interphase catalysts with long-term stability as well as pronounced degrees of enhanced activity in esterifications and transesterifications in organic solvents.[197] The catalysts were prepared via a base-promoted hydrolysis of trialkoxysilanes $RSi(OMe)_3$ (R = alkyl) or mixtures of these or other silanes with TMOS in the presence of a lipase. Relative activities of 500−800% in esterification reactions with respect to the traditional use of corresponding enzyme powders in organic solvents were achieved. The authors found that incorporating hydrophobic alkyl groups in the silicon oxide matrix markedly improved the activity. Recently, they reported also on the entrapment of certain lipases such as SP 625 (*Candida antactia* B) or SP 523 (*Humicola lanuginosa*) in sol−gel materials.[194] The preparation methods are the same as those above-mentioned. Different alkoxysilanes such as TMOS, MTMS, n-$C_3H_7Si(OMe)_3$ (PTMS), $HO[Me_2SiO]_nSiMe_2OH$ (PDMS), or mixtures of them were chosen as sol−gel precursors. As a test reaction the hydrolysis of the propionic acid 4-nitrophenyl ester was selected. Relative enzyme activities of 93, 107, and 110% for the entrapped lipase in PDMS/TMOS (1:3), PDMS/(MTMS (1:3), and PTMS/TMOS (5:1), respectively, were found. This means that enzyme activities in homogeneous and heterogeneous systems are actually comparable. In optimal cases, it was possible to recycle the catalysts with little or no decrease in enzyme activity. The catalysts with hydrophobic alkyl groups also showed higher activities.

Several difficulties emerge in the synthesis of sol−gel-encapsulated biological catalysts. The resulting alcohol from the hydrolysis of SiOR functions often irreversibly decomposes the catalyst. Its activity is also reduced by a reaction between silica precursors and the active centers. In addition, shrinkage of the gel upon drying leads to localized pressure and a reduction in enzyme activity and poor diffusion characteristics. Investigations of Gill and Ballesteros have highlighted a general approach to this problem.[198] An important key to their success was to move away from standard silica precursors such as TMOS and TEOS, since both of them eliminate alcohols decomposing the catalysts. Glycerol, which was liberated during the preparation of the materials, is biocompatible and helps the gel to dry in a controlled fashion, leading to stable matrices for the enzyme. For a range of enzymes and whole cells (yeast, *R. miehei*, and *P. oleovorans* were all successfully encapsulated) the activity of the encapsulated catalysts is between 83 and 98% of the native material. The amounts of biomaterial (20−30 wt %) encapsulated is much higher than with traditional methods. A striking example of the importance of the glycerol-based route over the traditional method is given by the hydrolysis of the nerve agent diethyl 4-nitrophenyl phosphate by a phosphatase enzyme. A hydrolysis of >95% was achieved under continuous conditions over a period of 700 h, compared to 35−40% with conventional materials. Under the same conditions polyurethane-encapsulated materials, initially very active, had lost ∼30% of their original activity.

V. Summary and Outlook

Chemistry in interphases offers a versatile method to combine the advantages of homogeneous and heterogeneous catalysis. As such it has opened a wide area of heterogenized catalysts. By careful design homogeneous catalysts can be transferred to interphase systems. In the case of highly swellable or porous polymeric materials a solution-like state is imitated in which the reactive centers are nearly homogeneously distributed across the entire polymer and therefore are similarly accessible as in homogeneous phase.[55] The polymeric part of the stationary phase consists mainly of flexible polysiloxanes, but oxides of aluminum, as well as polyalumosiloxanes, titanium, and phosphorus, were also introduced into the framework.[55,131,132,141,145,173] As a consequence of these favorable circumstances the activity of such hybrid catalysts is markedly improved. Furthermore, they can be separated from the reaction products and reused with a considerable reduction of the common drawbacks. On the basis of these latest scientific findings this review presents a survey of the preparations and applications of new interphase catalysts, with an emphasis on their recyclability. It was highlighted that the reactive centers may range from functional organic groups to transition metal complexes and also enzymes. Hybrid polymers, which are provided with metal complexes as reactive centers, constitute the dominant part of this paper. Metals encompass titanium, chromium, manganese, and most of the group 8 metals. A special appeal of interphase catalysts is that they are able to promote several kinds of reactions, such as specific hydrogenations,[99,125,130−133,155,165−167,173] oxidations,[69,87,110,111,121,143−145] hydroformylations,[155−158,170,171] coupling reactions,[182,183] and O-silylations.[191] As has been demonstrated hybrid catalysts may be more efficient and display better performances than their homogeneous counterparts.[133,137,158] Furthermore, embedding a highly active center into a polymer network often improved its stability and resulted in better handling.[69,134,135] This not only enhances the safety but also offers better storage possibilities over a longer period of time, which makes them attractive for industrial applications.

An evaluation of Tables 1−20 reveals that the comparison of the performance of the catalysts is exceedingly difficult. The large variety of catalysts, the different preparation methods, and the diverse levels of characterization of the hybrid polymers complicate the extraction of common factors affecting the catalytic activity. Furthermore, the complexity of the reaction system is increased as the influence of the support is not well understood. As an example, the BET surface area and the pore size volume (Table 21) are generally accepted parameters to characterize the support of immobilized catalysts; for example, the catalytic activity is enhanced the higher the surface and the larger the pore size volume are. In contrast to this, if the amount of organic building blocks is increased in the so-gel-processed materials, in some cases the BET surface area is strongly reduced and hardly any pore size is generated as long as the material is dry. However, in an appropriate solvent the swelling ability of this organic/inorganic hybrid polymer is improved, which can lead to an extremely good performance of the catalyst.[155] Some rules are becoming obvious as to how the catalytic performance is related to chemistry in interphases. The length of the spacer, the density of the reactive centers, and the amount and kind of copolymer as well as the way the sol−gel process is performed have an impact on the activity and selectivity of the active site. Unfortunately, each parameter has to be optimized for a wanted catalytic system. In general, compared to the homogeneous congeners the fixed catalysts in stationary phases display lower reaction rates (TOF). This is more than compensated by much longer lifetimes of the active site (TON), as has been demonstrated in many cases. In part this is due to the reduced leaching of these materials, which is a result of the sol−gel process because this preparation method incorporates the active centers into the volume of a material.

Although some salient aspects of interphase catalysts have already been developed, it is apparent that a great number of opportunities, challenges, and applications are to be expected. Thus, the fact that there are examples of sol−gel-processed active centers which promote reactions while their homogeneous counterparts are inactive implies that there

Table 21. Physical Data of Catalysts 1−52

catalyst	$S_{\mathrm{BET}}{}^{a}$	V^b	d^c	l^d	ref	catalyst	$S_{\mathrm{BET}}{}^{a}$	V^b	d^c	l^d	ref
1	354	0.192	*e*	3.87	68	**22a**	460		2.8	1.7	134
2a	426^f			3.54	69	**22b**	200		3.4	2.8	
2b	1080^f			2.88		**22c**	510		2.3	1.9	
3	597^f			3.31		**22d**	<5			3.7	
4					75	**23a**	670	1.74			137
5a	925		≈5	1.2	76	**23b**	1000	0.44			
5b	370		>10	2.2		**24a−d**					141
6a	228	0.27	5.8		80	**25a**	148−222				142
6b	251	1.61	16.7			**25b**	105−550				
6c	312	1.01	11.6			**26**	620	1.35^j			143
7	1281		2.4	1.4	84	**27**	528	0.315		0.668	144
8	400		10−20	0.24	87	**28a−c**					145
9a				4.53	95	**29a−c**					145
9b				1.25		**30a−c**					146
10	321.5				99	**31a**	719	0.69	1.9	2.7	148
11a	132			3^g	110	**31b**	415	0.31	1.5	2.0	
11b	142			2^g		**32a,b**					153
11c	159			2^g		**33**	800		2.4	2.0	134
12a	66			18^g	111	**34a**	1.6				155
12b	674			5^g		**34b**	0.9				
13a	60			59^h	121	**35a**	0.6			4.02	156
13b	105			61^h		**35b**	2.06			2.82	
14a	690			15^h		**35c**	1.05			2.69	
14b	770			16^h		**36a−d**					157
15a	142			3^g		**37a,b**					158
15b	152			2^g		**38a−c**					165
15c	141			2^g		**39a**	360			1.0	166
16a	19			9^g		**39b**	305			1.8	
16b	37			8^g		**40a**				1.2	168
16c	85			9^g		**40b**				0.6	
17						**41**				10.8	167
18a	5−9		$5−15^i$	7.55		**42**				16.0	
18b	1−10		$10−20^i$	6.72		**43a**	676	0.31			169
18c	1−14		$0.5−30^i$	6.99−3.43		**43b**	808	0.36		13.8	
						43c	686	0.32		19	
19a	60		$0.1−0.5^i$	5.75		**43d**	869	0.45		12.2	
19b	70		$0.1−0.5^i$	5.10		**44a,b**				21.8	170
20a	60			5.90		**45a−f**					171
20b	120			6.39		**46a**	127	0.78	12.3	0.09	172
20c	75			6.93		**46b**	104	0.47	9.0	4.40	
20d	45			5.01		**46c**	205	1.16	15.8	0.11	
20e	60			5.32		**47**					173
20f	50			6.14		**48a,b**					174
20g	50			4.03		**49**					182
20h	70			4.90		**50a**	25				184
20i	75			5.12		**50b**	190				
21a	15−20				133	**51a**	2.8			9.31	185
21b	3−8					**51b**	3.5				
21c	1−3					**51c**	280				
21d	15−20			7.11		**52a**				3.4	191
21e	3−8			6.39		**52b**				1.6−6.4	
21f	1−3			8.15							
21g	15−20			6.91							
21h	3−8			5.95							
21i	1−3			8.11							

[a] In m^2/g. [b] Pore volume in cm^3/g. [c] Pore size in nm. [d] Loading of reaction centers in mmol/g for catalysts **1**−**8** and the percentage of metal in other catalysts except indicated. [e] Microporosity. [f] Determined for the parent COOH-silica. [g] Content of porphyrin in the catalysts in m/m. [h] Content of porphyrin in the catalysts in m/m(%). [i] In μm. [j] Average pore volume between 1.7 and 300 nm.

is a huge potential of synergism between supported catalyst and matrix.[55,57,59,60,192,199] Therefore, in future, more emphasis should be put on the preparation of the hybrid catalysts by carefully designing and modifying the reactive centers, the condensable groups, and the way the sol−gel process is performed. Along with this improved and new physical methods have to be developed and applied to study in more detail the structure of stationary phases and of the reactive centers as well as all of the interactions that take place between the hybrid material and the substrates. This will lead to the development of new materials that are capable of promoting more than one reaction or even allow sequences of catalytic conversions to be performed in one batch.[200,201] Hybrid polymers with more than one supported type of catalyst will be worked out. In this context new classes of nanostructured materials with well-defined porosities and shapes will have potential applications. As an example, the shape of the pores will determine the diffusion of the substrate to the embedded catalyst and will thus have an impact on the selectivity of the conversion. Due to the many factors affecting catalytic properties and the demands in accelerating the discovery of new catalysts, parallelization and high-throughput screening methods will have to be applied.[202−204] Tools from information sciences will be relevant to handling the multiparameter space.[205]

VI. Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (Forschergruppe FOR 184/3-1 and Graduiertenkolleg Chemie in Interphasen, Grant GRK 441/2-01), Bonn, Bad Godesberg, the Fonds der Chemischen Industrie, Frankfurt/Main, and the Alexander von Humboldt Foundation for generous financial support.

VII. List of Abbreviations

AAS	atomic absorption spectroscopy
AD	asymmetric dihydroxylation
APTES	3-(aminopropyl)triethoxysilane
BET	method according to Brunauer, Emmett, and Teller
CETS	(2-cyanoethyl)triethoxysilane
COD	1,5-cyclooctadiene
COE	cyclooctene
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
CP/MAS NMR	cross-polarization magic-angle spinning NMR
CPTS	(3-cyanopropyl)triethoxysilane
DMF	*N*,*N*-dimethylformamide
DMOS	dimethyldimethoxysilane
DMSO	dimethyl sulfoxide
DRIFT	diffuse reflectance infrared Fourier transform spectroscopy
D-silyl	difunctional-silyl
DTA	differential thermal analysis
EDX	energy-dispersive X-ray analysis
EPR	electron paramagnetic resonance
ESI	electron spectroscopy imaging
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
FT-IR	Fourier transform infrared spectroscopy
HMS	hexagonal mesoporous silica
ICP-AES	induced coupled plasma atomic emission spectroscopy
ICP-MS	induced coupled plasma mass spectroscopy
MEMOS	(3-methacryloxypropyl)trimethoxysilane
MTMS	methyltrimethoxysilane
MTS	micelle-templated silica
NMR	nuclear magnetic resonance
PDMS	HO[Me$_2$SiO]$_n$SiMe$_2$OH
P∼O	monodentate coordinated ether−phosphine ligand
P⌒O	bidentate coordinated ether−phosphine ligand
PTMS	*n*-propyltrimethoxysilane
py	pyridine
pyz	pyrazine
Q-silyl	quadrifunctional-silyl
salen	*N*,*N*′-ethylenebis(salicylideniminato)
TBHP	*tert*-butyl hydroperoxide
TEM	transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
TEMPON	4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl
TEOS	tetraethoxysilane
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEP	2-(2-trimethylsilylethyl)pyridine
TMG	1,1,3,3-tetramethylguanidine
TMOS	tetramethoxysilane
TOF	turnover frequency
TON	turnover number
T-silyl	trifunctional-silyl
UV−vis	ultraviolet−visible
WISE NMR	wide-line separation NMR
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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CR010358T