Supported organometallic complexes. Part XIII [1]. Catalytic studies on sol–gel processed (ether phosphine)ruthenium(II) complexes with different spacer lengths and different polysiloxane matrices [2]

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Abstract

The monomeric (ether–phosphine) ruthenium complexes cis-(H)ClRu(CO)(P $\sim$ O)$_3$ ($\mathbf{1a}$(T^0)$_3$), ($\mathbf{1b}$(T^0)$_3$), and ($\mathbf{1c}$(T^0)$_3$) (P $\sim$ O: P-coordinated PhP(CH$_2$CH$_2$OCH$_3$)(CH$_2$)$_x$Si(OMe)$_3$; $x = 3$ (a), 6 (b), 8 (c)) were immobilized by the sol–gel process under the employment of the cocondensates Si(OEt)$_4$ (Q^0), MeSi(OMe)$_3$ (T^0), and Me$_2$Si(OEt)$_2$ (D^0) to give the nine different polymer-bound (ether–phosphine) ruthenium complexes $\mathbf{1}$(a,b,c)(T^n)$_3$(Q^k,T^m,D^i)$_y$ (y = number co-condensed Q, T or D type; Q = Q type silicon atom (four oxygen neighbors), T = T type silicon atom (three oxygen neighbors), D = D type silicon atom (two oxygen neighbors); i, k, n, m = number of Si–O–Si bonds; $i = 0$–2; n, $m = 0$–3; $k = 0$–4) with three different polysiloxane matrices and three different spacers. The immobilized complexes were studied in their catalytic behavior with respect to the hydrogenation of n-butenal. The results demonstrate that the catalytic activity is dependent upon the type of matrix and the type of spacer of the polymer anchored catalysts. © 1998 Elsevier Science B.V.

Keywords: Immobilized catalysts; Hydrogenation; Ruthenium; Sol–gel

1. Introduction

The immobilization of transition metal complexes, acting as catalysts, is a field of growing interest [2,3]. Such systems are able to combine the adjustable selectivities and activities of homogeneous catalysts with the re-usability of heterogeneous catalysts. To achieve activities and selectivities of the immobilized catalysts being as high as in solution the immobilized complexes should be anchored as flexible as possible to the matrix and highly accessible for the substrates. On the other hand leaching of the catalysts must be reduced by high degrees of cross-linking of the active centers on the matrix.

These problems can be overcome if the stationary phase consisting of the matrix, the
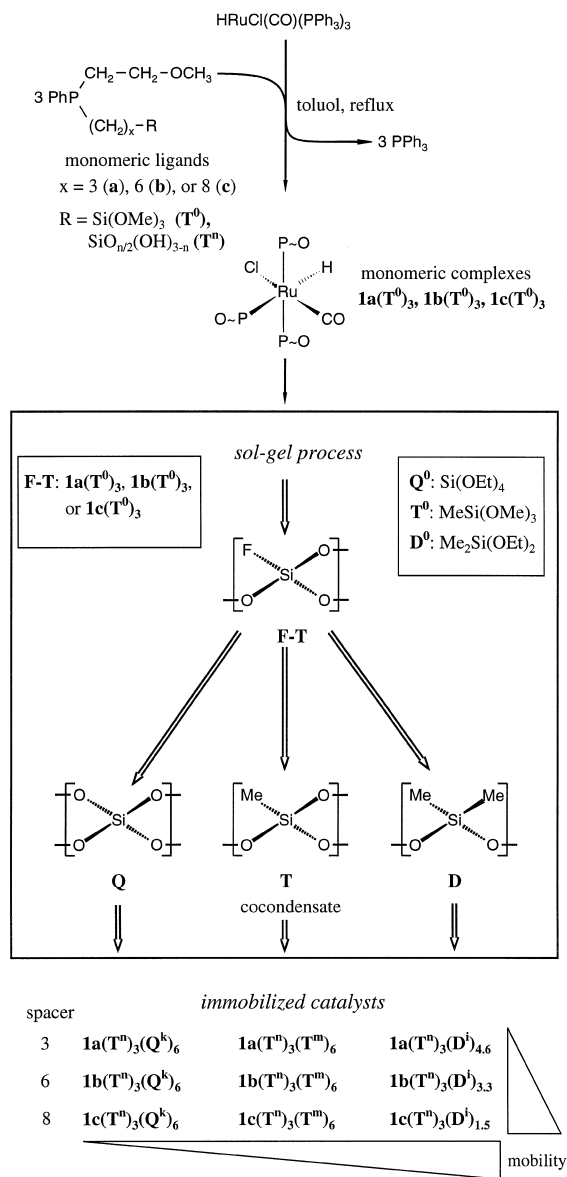
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spacer, and the reactive center is able to swell under the presence of an adequate solvent or substrate (mobile phase). The resulting penetration of the mobile and the stationary phase on a molecular scale is called 'interphase', since no homogeneous mixture is formed [4,5].

Polysiloxane matrices in which the active metal centers are covalently bound through bifunctional phosphine ligands can be prepared by the sol–gel process [5–8]. The physical and chemical properties of these stationary phases can be varied in a wide range by the employment of different co-condensates, e.g., $Si(OEt)_4$ (Q^0), $MeSi(OMe)_3$ (T^0), and $Me_2Si(OEt)_2$ (D^0) and with the use of ligands which contain different spacer lengths. Thereby the loading of the metal within the matrix can be adjusted and the leaching of the reactive centers is negligible.

In this study the catalytic behavior of the various polysiloxane-bound ruthenium(II) complexes cis-(H)ClRu(CO)(P ∼ O)$_3$ is investigated. The catalysts differ in their type of matrix, e.g., $F − T/Q$ (with Q^0 as co-condensate), $F − T/T$ (T^0), and $F − T/D$ (D^0) as well as in their lengths of the alkyl spacer, e.g., n-propyl (C3, (a)), n-hexyl (C6, (b)), and n-octyl (C8, (c)) so that a total number of nine samples result ($\mathbf{1}(a,b,c)(T^n)_3(Q^k,T^m,D^i)_y$) (see Scheme 1) [3].

In all experiments we employed 'hemilabile' ligands like ether–phosphines, which are strongly coordinated to the metal center via the phosphorus atom while the weaker donor in form of an ether moiety takes over the function of an intramolecular solvent in a catalytic cycle (Scheme 1) [9].

As a model reaction the hydrogenation of n-butenal was selected, because α,β-unsaturated aldehydes constitute important inter-

Scheme 1.

mediates in the field of flavor and flagrance chemistry [10,11].

The aim of this study is to correlate structural and dynamic properties of the various catalysts with their catalytic behavior. The synthesis and detailed solid-state NMR spectroscopic characterization of the catalysts is published elsewhere and will be summarized briefly here [8].

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[3] Nomenclature of the compounds. Integer: type of reactive center (1 = cis-(H)ClRu(CO)(P ∼ O)$_3$); small letter: type of spacer (a = n-propyl, b = n-hexyl, c = n-octyl); capital letter: type of silicon species (Q = four oxygen bonds, T = three oxygen bonds, D = two oxygen bonds); subscript: stoichiometry of the silicon species; superscript: number of Si–O–Si bonds.

2. Results and discussion

2.1. Synthesis and characterization

The sol–gel derived ruthenium catalysts have been synthesized by simultaneous cocondensation of the monomeric complexes *cis*-(H)ClRu(CO)(P ∼ O)$_3$ (**1**a(T^0)$_3$, **1**b(T^0)$_3$, and **1**c(T^0)$_3$) with specific amounts of the co-condensates Si(OEt)$_4$ (Q^0), MeSi(OMe)$_3$ (T^0), and Me$_2$Si(OEt)$_2$ (D^0) in the presence of water, ethanol, and (*n*-Bu)$_2$Sn(OAc)$_2$ acting as a mild sol–gel catalyst (see Scheme 1) [8]. The monomeric ruthenium complexes **1**a(T^0)$_3$, **1**b(T^0)$_3$, and **1**c(T^0)$_3$ are prepared by replacement of triphenylphosphine with the corresponding bifunctional ether–phosphine ligands in the starting complex *cis*-(H)ClRu(CO)(PPh$_3$)$_3$ (Scheme 1) [5,8].

From ^{13}C and ^{31}P solid-state NMR spectroscopy it is known that the polymer-bound complexes have the same structure as their soluble precursors. The investigation of the matrices by ^{29}Si solid-state NMR spectroscopy results in the quantitative determination of the various silyl species, e.g., T^n, Q^k, T^m, and D^i (i, k, n, m, = number of Si–O–Si bonds; $i = 0$–2; n, $m = 0$–3; $k = 0$–4). From this data it is possible to evaluate the complex to co-condensate ratios (see Scheme 2) and the degrees of cross-linkage for each matrix, which are in the range of 85–100% for all copolymers. From these data structure models of the matrices can be proposed: functionalized matrices with Q^k groups (F − T/Q) consist of three dimensional networks, F − T/T copolymers can be assigned as partially cross-linked two dimensional sheet structures and F − T/D matrices consist of branched chains [4,5,8].

Detailed dynamic studies of the catalysts by various solid-state NMR methods, e.g., ^{31}P solid-state NMR relaxometrie and ^{13}C–^{1}H wideline-separation (WISE) proved that the flexibility of the active centers are dependent on the types of co-condensates and the spacers used. The mobilities of the catalytic reactive

Scheme 2.
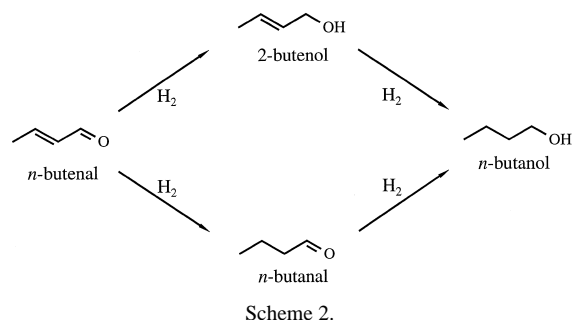
centers can be ranked in the following way: F − T/Q ≤ F − T/T < F − T/D with respect to the co-condensates and C8 ≥ C6 > C3 with respect to the spacer lengths [8].

2.2. Catalytic investigations

α, β-unsaturated aldehydes are valuable starting compounds for organic syntheses, since they are easy accessible by aldol condensations. For our catalytic studies we therefore select *n*-butenal (see Scheme 2) as a model substrate. Three different products are expected in the hydrogenation of *n*-butenal. Selective hydrogenation of the C=O double bond yields the unsaturated alcohol 2-butenol. This is the most desired product in terms of economic interest, because α, β-unsaturated alcohols are valuable intermediates in the synthesis of natural products [10,11]. Hydrogenation of the C=C double bond leads to the saturated aldehyde *n*-butanal which is of minor interest. Dihydrogenation of the substrate results in the formation of *n*-butanol. In the course of the catalytic reaction an increasing formation of side products (10%) is caused by condensation reactions of the educt.

Since the aim of this study is the comparative investigation of the different catalysts reaction conditions have been chosen in which the conversions are not quantitative within the reaction time.

The most rigid catalyst **1**a(T^n)$_3$(Q^k)$_6$ (run 1, see Table 1) shows hardly any catalytic activity at the applied reaction conditions. This is in agreement with earlier investigations on the hy-

Table 1
Hydrogenation of 2-butenal[a]

Run	Catalyst	Spacer (%)	Cocondensate	Surface area (m^2/g)	conversion (%)	Selectivity (%)		
						n-butanal	2-butenol	*n*-butanol
1	$1a(T^n)_3(Q^k)_6$	*n*-propyl	Q^0 ($Si(OEt)_4$)	15–20	5	38	58	4
2	$1b(T^n)_3(Q^k)_6$	*n*-hexyl	Q^0 ($Si(OEt)_4$)	15–20	15	34	60	6
3	$1c(T^n)_3(Q^k)_6$	*n*-octyl	Q^0 ($Si(OEt)_4$)	15–20	21	27	64	9
4	$1a(T^n)_3(T^m)_6$	*n*-propyl	T^0 ($MeSi(OMe)_3$)	3–8	21	28	63	9
5	$1b(T^n)_3(T^m)_6$	*n*-hexyl	T^0 ($MeSi(OMe)_3$)	3–8	27	28	62	10
6	$1c(T^n)_3(T^m)_6$	*n*-octyl	T^0 ($MeSi(OMe)_3$)	3–8	26	24	66	10
7	$1a(T^n)_3(D^i)_{4.6}$	*n*-propyl	D^0 ($Me_2Si(OEt)_2$)	1–3	44	20	65	15
8	$1b(T^n)_3(D^i)_{3.3}$	*n*-hexyl	D^0 ($Me_2Si(OEt)_2$)	1–3	45	20	64	16
9	$1c(T^n)_3(D^i)_{1.5}$	*n*-octyl	D^0 ($Me_2Si(OEt)_2$)	1–3	51	19	64	17
10	$HRuCl(CO)(P \sim O)_3^b$	—	—	—	34	29	41	30

[a] H_2 pressure = 50 bar, T = 80°C, reaction time = 4 h, Ru:*n*-butenal = 1:1000.
[b] Homogeneous analogous catalyst ($P \sim O = Ph_2PCH_2CH_2OCH_3$).

drogenation of *n*-butanal in which was found that this type of catalysts with $F - T/Q$ matrixes and *n*-propyl spacers show only remarkable conversions if temperatures above 100°C are applied [5]. Increasing of the spacer length from *n*-propyl to *n*-hexyl or *n*-octyl lead to conversions of 15% and 21% (run 2 and 3, respectively). The catalyst $1a(T^n)_3(T^m)_6$ with a *n*-propyl spacer shows already 21% conversion (run 4). The increase in the spacer length from 3 to 6 or 8 raises again the conversions to 27% and 26% (run 5 and 6, respectively). The more flexible $F - T/D$ copolymers show even a higher catalytic activity with conversions of 44–51% (run 7, 8, and 9). The selectivities toward the formation of the desired product 2-butenol are also enhanced with increasing conversions. However remarkable amounts of the dihydrogenation product *n*-butanol are formed with the more active catalyst.

In run 10 the result of the analogous homogeneous catalyst is displayed. The overall conversion of the soluble catalyst is 34%. This is less conversion than in the case of the best immobilized complexes $(F - T/D)$. The selectivity with respect to the formation of 2-butenol is also quite poor under homogeneous reaction conditions, since 30% of *n*-butanol are formed (see Table 1).

From BET surface measurements (see Table

1) it can be excluded that diffusion of the substrate into the matrix is the rate determining step in these reactions, because the fastest catalysts $(F - T/D)$ have the smallest BET surface area. It is therefore concluded that diffusion of the reactants within the matrices or various reaction rates of the complexes itself are responsible for the different conversions.

The employed catalysts can be easily recovered from the reaction mixture by precipitation of the highly swollen gels with *n*-hexane followed by simple centrifugation. After washing with ethanol and *n*-hexane the catalysts have been dried under vacuum and can be re-used. Catalyst $1c(T^n)_3(Q^k)_6$ shows the same catalytic activity during three consecutive runs (run 3, 11, and 12; see Table 2), whereas catalyst $1c(T^n)_3(D^i)_{1.5}$ loses some of its initial activity

Table 2
Repeated use of the catalysts[a]

Run	Catalyst	Conversion (%)	Selectivity (%)		
			n-butanal	2-butenol	*n*-butanol
3	$1c(T^n)_3(Q^k)_6$	21	27	64	9
11	re-use of run 3	20	26	65	9
12	re-use of run 4	20	26	64	10
9	$1c(T^n)_3(D^i)_{1.5}$	51	19	64	17
13	re-use of run 9	35	22	67	11
14	re-use of run 13	34	23	66	11

[a] H_2 pressure = 50 bar, T = 80°C, reaction time 4 h, Ru:*n*-butenal = 1:1000.

in the first re-use (run 13). However after the second run the activity remains constant at 34% conversion (run 14).

In conclusion we have shown that the catalytic activities of sol–gel immobilized ruthenium complexes can be adjusted by the properties of the carrier matrix and the spacer. The more mobile catalysts according to previous solid-state NMR studies have proven to be the more active and selective catalysts.

3. Experimental

3.1. Catalysts

The synthesis and characterization of the polysiloxane-bound ruthenium complexes is described elsewhere in detail [5,8]. The surface areas were determined by nitrogen sorption and calculated with the BET equation on a Micromeritics Gemini 2375.

3.2. Hydrogenation procedure

A typical run was carried out in a 100 ml stainless steel autoclave, which was agitated by stirring with a magnetic bar. Catalyst (150 μmol catalyst with respect to ruthenium) and n-butenal (150 mmol; purchased from Merck–Schuchardt) were introduced into the autoclave under the exclusion of oxygen. The reactor was purged three times with hydrogen, before setting the required hydrogen pressure. During the reaction the hydrogen pressure was kept constant by feeding from a high pressure reservoir. At the end of the reaction the autoclave was cooled and vented carefully with argon. The catalyst was precipitated in the obtained suspension by addition of n-hexane (20 ml). The catalyst was then separated by centrifugation (5 min at 4000 rpm). The supernatant solution was analyzed by gas chromatography, whereas the catalyst was washed with ethanol (twice 20 ml) and n-hexane (twice 20 ml), and then dried under vacuum (0.1 hPa; 25°C, 4 h) before being recovered.

3.3. Product analysis

The products of the hydrogenation of n-butenal were identified by gas chromatography. The analyses were performed on a GC 6000 Vega Series 2 (Carlo Erba Instruments) with a FID and a capillary column SP 1000 (60 m; carrier gas, He (50 kPa); integrator, 3393 A (Hewlett Packard)). The peaks were identified by comparison with authentic samples. The gas chromatograph was calibrated to calculate concentrations of products on a mol percent basis.

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