METHANOL CARBONYLATION CATALYZED BY RHODIUM COMPLEXES IMMOBILIZED TO SILICA via PYRIDINE GROUP

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Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

2-(2-Trimethoxysilylethyl)pyridine (*I*) was used to prepare a series of rhodium carbonyl complexes bound to silica via pyridine group. The rhodium complex $Rh_2(CO)_4Cl_2$ (Rh_2) was used as a starting compound, and the immobilized complexes were prepared by the following routes: (i) by the reaction of untreated silica with a Rh complex formed from Rh_2 and *I*, (ii) by reaction of Rh_2 with a silica functionalized with *I*, (iii) by treatment of Rh_2 with a polycondensate prepared by hydrolysis and condensation of a mixture of *I* and tetraethoxysilane, and (iv) by sol–gel processing of tetraethoxysilane with a Rh complex formed from Rh_2 and *I*. These complexes were found to be efficient catalysts for the liquid phase methanol carbonylation. Their activity and stability in relation to their synthesis and structure is discussed, along with Rh leaching process.

Immobilization of homogeneous catalysts has long been the subject of intensive study, both due to the expected contribution to the better understanding of mechanism of homogeneously catalyzed reactions and due to the hope for the improvement of process economy[1,2]. Surprisingly, only scarce data exist, however, on other than phospohorus-containing ligands used to immobilize transition metal complexes to solid components. This holds also for the choice of method of immobilization. It seemed thus useful to extend such studies. In the present work we report on the efficiency and stability of rhodium complexes immobilized via pyridine-containing ligand to silica and prepared by untraditional procedures. For this purpose we used 2-(2-trimethoxysilylethyl)pyridine as N-ligand. The hydrolytic stability of the rhodium–pyridine bond allowed to prepare anchored complexes also by sol–gel processing[3]. In addition to the more common immobilization procedures[4], the latter method affords catalysts in which anchoring ligand or the whole complex are incorporated into support matrix.

The catalytic behaviour of this new class of immobilized catalysts was examined for methanol carbonylation. We have recently shown[5] that in this case the reaction rate in batch arrangement is the result of occurrence of both homogeneous and heterogeneous processes, as any rhodium species released from the support to the solution can still be catalytically active. Therefore, operation of immobilized catalysts was followed now for continuous process, attention being paid to Rh leaching.

EXPERIMENTAL

Materials and Methods

Silica (Kieselgel 100, Merck), 1-octene, triethoxysilane, 2-(2-trimethoxysilylethyl)pyridine (Petrach), the solvents and gases were commercial products. Tetracarbonyl(μ,μ-dichloro)-dirhodium(I) was prepared[6] as indicated. Reflection IR spectra (ν in cm^{-1}) of the solids were recorded on a Perkin–Elmer spectrophotometer 283 in toluene solutions or in nujol mull. UV spectra were taken on a Perkin–Elmer UV-VIS spectrometer Lambda 15 in hexane solution, or from solids in reflection. Rh-contents were determined spectrophotometricaly. Reaction rates of a continuous liquid phase carbonylation of methanol were determined as recently described[7].

Synthesis of Catalysts

Soluble catalysts were prepared by addition of 2-(2-trimethoxysilylethyl)pyridine dissolved in toluene to tetracarbonyl(μ,μ-dichloro)dirhodium(I).

Catalyst A (Method (i)). A total of 2 g of silica (Kieselgel 100) was dried by heating to 200 °C and added to 0.1 mmol of $Rh_2(CO)_4Cl_2$ (0.2 mmol Rh) and 0.4 mmol of the ligand *I* dissolved in 10 ml of toluene. The reaction mixture was stirred for 4 h. Then the immobilized catalyst was washed successively with two 20 ml portions of toluene and tetrahydrofuran and then dried in vacuo. The product contained 2.3% C, 0.4% N, and 0.5% Rh. IR spectrum: 2 082, 2 005 (CO). UV spectrum: two broad bands with maxima at 294 and 251 nm.

Catalyst B (Method (ii)). Toluene (20 ml) was added to 2.5 g of silica dried as described for catalyst A. After addition of 0.5 mmol of ligand *I* under stirring, the latter was continued for 3 h. The mixture was allowed to stand overnight and then 0.125 mmol of Rh_2 were added. The mixture was shaken for 5 h and allowed to stand for 2 days. Then, the catalyst was filtered off, washed with toluene and acetone, and dried in vacuo. It contained 2.3% C, 0.4% N, and 0.5% Rh. IR spectrum: 2 082, 2 011 (CO). UV spectrum: broad bands with maxima at 287 and 201 nm.

Catalyst C (Method (iii)). A total of 3 mmol of ligand *I*, 70 mmol of tetraethoxysilane and 39 ml of 0.2M ammonia were added to 300 ml of ethanol. The mixture was stirred at 70 °C for 70 h and then transferred into an open beaker. During 7 days the solvent was allowed to evaporate in a hood. Then, the residual solvent was removed at 100 °C. The mixture was ground, washed with water and acetone, dried in vacuo, twice treated with an excess of trimethylethoxysilane in toluene, filtered, washed with acetone and dried again in vacuo (yield 4.6 g). A total 20 ml of toluene were added to 2 g of thus prepared support, followed by solution of 39 mg Rh_2 in 10 ml of toluene while stirring the mixture. Stirring was continued for another 2 h, the catalyst was filtered off, washed with acetone and dried in vacuo. It contained 7.6% C, 0.9% N, and 0.6% Rh. IR spectrum: 2 081, 2 012 (CO). UV spectrum: two broad bands with maxima at 284 and 214 nm.

Catalyst D (Method (iv)). A solution of 165 mg Rh_2 and 1.7 mmol of ligand *I* was added under stirring to 300 ml of ethanol. Then, 8 ml of tetraethoxysilane and 20 ml of 0.2M ammonia were added. The mixture

was stirred for 14 days and then transferred into an open beaker. The solvent was allowed to evaporate in a hood. The residual solvent was removed in vacuo, and the mixture was ground, washed with acetone and dried in vacuo. The product contained 4.6% C, 0.8% N, and 1.2% Rh. IR spectrum: 2 086, 2 012 (CO). UV spectrum: bands with maxima at 281 and 214 nm.

RESULTS AND DISCUSSION

Synthesis of Immobilized Complexes

Except poly(vinylpyridine), solid supports containing pyridine groups were not frequently used. Only few examples of inorganic supports modified in this way were reported. Thus, for example, a silica functionalized with butylpyridine groups was used for immobilization of rhodium complexes[8]. Later tests showed that these catalysts were not effective in hydroformylation[9]. On the other hand, rhodium complexes bound to vinylpyridine–methyl methacrylate copolymers seemed to be perspective methanol carbonylation catalysts[7,10,11].
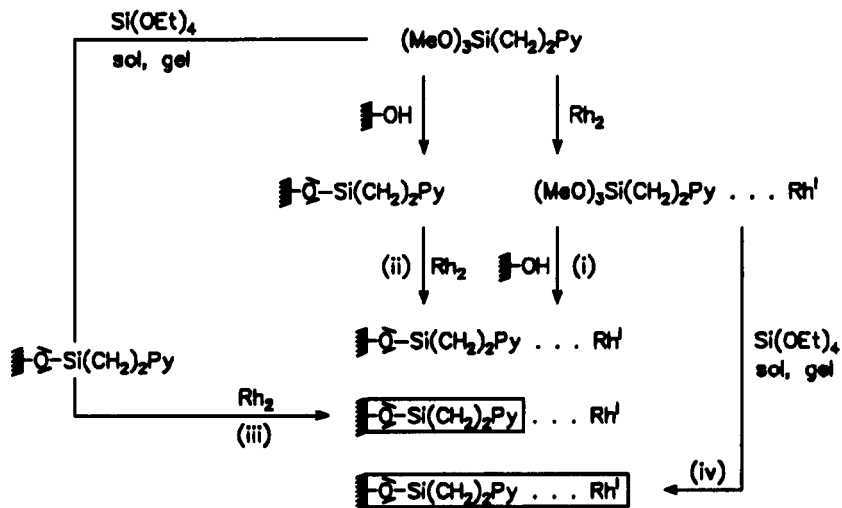
Interestingly, it was proposed[7,10,11] that the transition metal is in these complexes bound by two anchoring ligands. Therefore the question arises whether the catalytic efficiency is a consequence of this mode of metal binding. Such a conclusion is somewhat surprising as the bridge of dimeric tetracarbonyldichlorodirhodium(I) is known to be cleaved by amines and N-heterocycles (L) to form $Rh(CO)_2ClL$ complexes[12]. These products were found to be non-ionic, monomeric, square planar complexes[13], having their two carbonyls in mutual *cis* position[14].

It was also found[15] that the Rh–Cl bridge cleavage is effected not only monomeric heterocycles but also by polymer-bound pyridine. Such a process would lead to a distinct shift of the CO stretching vibrations.

Table I shows that the magnitude of this shift does not depend on the rhodium to ligand ratio employed in the synthesis of the catalysts. Thus, in all soluble and also in all heterogenized complexes (Scheme 1), the same type of metal complex moiety should be present, independent of the immobilization procedure. One can thus assume that differences in catalytic activity of the immobilized complexes are mainly caused by differences in the mobility, accessibility and stability of anchoring ligands or whole complexes, which in turn are mainly affected by matrix and by texture of the support, i.e. by the method of synthesis.

Methanol Carbonylation

The reaction is industrially important as a low pressure process for the production of acetic acid[16], and was studied in detail kinetically[17]. Several attempts to heterogenize expensive rhodium catalysts were also reported (cf. ref.[7] and references therein). The use of a plug flow reactor and liquid phase continuous arrangement provides[7] very

$Si(OEt)_4$
sol, gel ——— $(MeO)_3Si(CH_2)_2Py$

$\blacksquare$–OH $\downarrow$ $\downarrow$ Rh_2

$\blacksquare$–Ō–$Si(CH_2)_2Py$ $(MeO)_3Si(CH_2)_2Py$ ... Rh^I

(ii) $\bigg|$ Rh_2 $\blacksquare$–OH $\bigg|$ (i)

$\blacksquare$–Ō–$Si(CH_2)_2Py$ ... Rh^I $Si(OEt)_4$ sol, gel

$\blacksquare$–Ō–$Si(CH_2)_2Py$

$\boxed{\blacksquare\text{–Ō–}Si(CH_2)_2Py}$ ... Rh^I

Rh_2
(iii) $\longrightarrow$

(iv)

$\boxed{\blacksquare\text{–Ō–}Si(CH_2)_2Py}$ ... Rh^I

Py 2–pyridyl; Rh_2 $Rh_2(CO)_4Cl_2$; $\blacksquare$–surface bonded to silica;
$\boxed{\blacksquare}$ incorporated in silica matrix

SCHEME 1

TABLE I
Carbonyl stretching frequencies $\nu(CO)$ (cm^{-1}) of N-donor adducts of $Rh_2(CO)_4Cl_2$

Donor	Rh : N ratio	$\nu(CO)$	Ref.
Ligand *I*	1 : 1	2 082, 2 004	this work
"	1 : 2	2 080, 2 003	"
"	1 : 3	2 080, 2 003	"
"	1 : 4	2 082, 2 004	"
Catalyst A	[a]	2 082, 2 004	"
Catalyst B	[a]	2 082, 2 005	"
Catalyst C	[a]	2 084, 2 012	"
Catalyst D	[a]	2 086, 2 012	"
Pyridine	1 : 1	2 075, 2 010	12
Pyridine	1 : 1	2 089, 2 005	15
2,6-Dimethylpyridine	1 : 1	2 080, 2 005	13
Poly(vinylpyridine)	[a]	2 085, 2 010	15
Silica-bonded pyridine	[a]	2 084, 2 008	8

[a] Not determined exactly.

favourable conditions for leaching of rhodium. As a consequence of methanolysis is not only the transition metal–ligand bond but also the complex as a whole (including the silyl substituted spacer) can be cleaved. Furthermore, in this continuous flow, the equilibrium is constantly disturbed by the supply of fresh reagents.

Immobilized catalysts A – D were active in this reaction (Fig. 1). The reaction promoted by methyl iodide was run by operating the reactor in differential mode using low conversion and practically constant methanol concentration, the main product being methyl acetate, in agreement with the homogeneously catalyzed reaction[16,17]. The highest rate observed with immobilized catalysts was $1.3 \cdot 10^{-4}$ mol s^{-1} g$_{Rh}^{-1}$, which is lower than with homogeneous analogues[17] or those bound to organic polymers[7].

The behaviour of the catalysts in relation to their structure is of interest. The poorest catalyst is the surface-bonded complex A that lost its activity within 2 h. The performance of another surface-bonded catalyst B shows maximum activity after 25 min, but then it is rapidly deactivated. It seems that the observed reaction rates agree with previous proposal[7] that the activity results from the combination of heterogeneous and homogeneous catalysis (because the species released from the support could behave as a homogeneous catalyst).

The stability of the rhodium catalysts prepared by the sol–gel process is much better. The lifetime of the catalyst C having pyridine groups caged in the matrix and rhodium complexes on the surface is better than that of catalyst A. The catalyst D in which the pyridine–rhodium complex is completely incorporated into the bulk of silica shows best catalytic performance. These findings and the fact that analogous Rh complexes bound to pyridine-containing organic polymer are more stable[7,10] support the assumption that in this reaction the Si–O–Si bond linking the spacer and anchoring ligand to the support is cleaved more easily than the metal–ligand coordination bond.
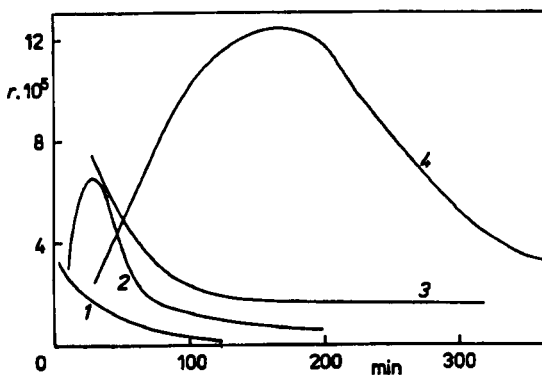

FIG. 1
Rates r (mol s^{-1} g$_{Rh}^{-1}$) of methanol carbonylation (at steady state) catalyzed by immobilized Rh complexes *1* A, *2* B, *3* C, *4* D. Reaction conditions: 140 °C, 2 MPa, [MeOH] 19.8 mol l^{-1}, [MeI] 3.1 mol l^{-1}, approximately 1 g of the catalyst

This conclusion is further supported by the results depicted in Fig. 2. It was found that rhodium is easily split off from the complexes in which silylated anchoring ligand is bound to the surface of the support. On the other hand, the location of transition metal (on the surface or in the matrix) is not so determining for its leaching. So, in contrary to the generally accepted explanation[1,2] in this case the Rh leaching is due to splitting off of the spacer rather than to the rupture of Rh-ligand coordination bond.
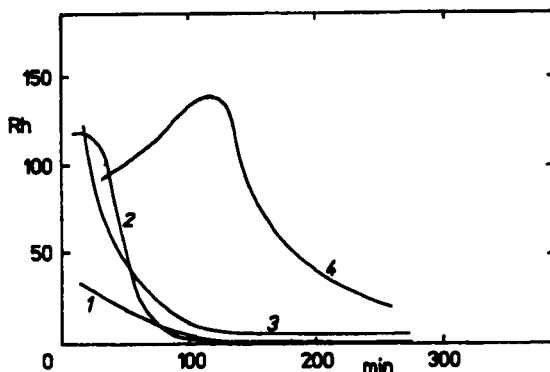
Fig. 2

Time dependence of Rh concentration $(mg\ kg^{-1})$ in the outlet of the plug reactor (for conditions and curves numbering see Fig. 1)

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