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Journal of Molecular Catalysis A: Chemical 204–205 (2003) 737–745

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Leaching of anchored Rh and Pd species from thiourea-functionalized monolithic silica xerogel catalysts

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Received 8 October 2002; received in revised form 24 March 2003; accepted 27 March 2003

Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Hybrid monoliths able to bind metal species were prepared by sol–gel method using different catalysts and solvents. Starting materials were the “double” thioureas 1,4-$[(EtO)_3Si(CH_2)_3NHC(S)NH]_2(C_6H_4)$ (Siphen) and 1,12-$[(EtO)_3Si(CH_2)_3NHC(S)NH]_2(C_{12}H_{24})$ (SiC12). Rh(I) and Pd(II) species were anchored through sulphur co-ordination on the surface of the monoliths obtained from Siphen. In the case of Rh(I), anchored metal complexes were spectroscopically identified by FTIR microspectrometry. The metal leaching was determined in the hydroformylation (Rh) and hydrogenation (Pd) of styrene. The metal species present in reaction solutions were quantified using plasma atomic emission spectrometry.

Keywords: Hybrid catalysis; Metal leaching; FTIR microspectroscopy; Sol–gel; Monoliths

1. Introduction

The preparation of solid catalysts requires various synthetic procedures sometimes terminating either in drastic thermal treatments of oxide blends (after impregnation or co-precipitation steps), or in soft immobilization reactions of delicate organometallic species to porous supports [1–4]. The performance of the final product often appears strongly dependent on rather subtle changes in the process conditions.

In this regard, the sol–gel route [5,6] has intrinsic advantages compared with the other methods, because it allows a precise control of the synthetic conditions and hence of the factors relevant to catalytic activity, such as purity, stoichiometry, homogeneity (or controlled heterogeneity) and microstructural properties of the catalyst or catalyst support. Sol–gel synthesis of catalytic materials is a mature, rapid expanding research area, as documented by hundreds of papers published in the last 5 years and by authoritative reviews appeared in the last decade [7–11].

As most heterogeneous catalysts contain metals in the active centres or in the supporting medium, an important characteristic of the catalytic material is the amount of metal leaching during exposition to fluid substrates. This undesirable effect can occur in three different ways, as already pointed out [12]: (i) very low metal leaching (under the limit of detection (LOD) of an adequately sensible analytical technique),

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doi:10.1016/S1381-1169(03)00359-5

practically negligible; (ii) significant leaching of catalytically active metal species; (iii) significant leaching of inactive metal species. The last two cases can include total or partial readsorption of the metal species on the solid surface at the end of the process, mostly if the reaction medium is cooled before the catalyst recovery. If total readsorption occurs, troubles regarding effective catalyst recovery and metal pollution are avoided, but it is to remark that in this case the real catalyst is homogeneous, the solid material being a simple reservoir of catalytic species.

Four classes of sol–gel catalytic materials can be envisaged: (a) uni- and multiphasic oxides and mixed oxides; (b) metal particles dispersed on oxide matrices; (c) molecular species (mainly metal complexes) covalently bound to oxide matrices; (d) molecular species adsorbed or entrapped in oxide matrices.

The first class appears often leaching-free even in case of exposition to liquid phases. Nevertheless, release of metals can occur for some catalytic systems during oxidation processes, as was established for chromium-substituted molecular sieves [13].

Also, the second class of catalyst is generally leaching-free, particularly for numerous hydrogenation processes at room temperature. Release of metal species could occasionally become significant by exposure to CO at high temperature and pressure.

Classes (c) and (d) are the most delicate ones as the active metal species are anchored (or entrapped) co-ordination compounds which can easily undergo ligand substitution processes leading to the formation of unbound, soluble species. They are solid catalysts obtained by anchoring metal species (active as homogeneous catalysts in solution) onto insoluble solid matrices, without modifying the structural features of the metal catalytic centre. Such systems, called hybrid catalysts, should exhibit advantages typical of homogeneous (high activity, selectivity) and of heterogeneous catalysts (recoverability). Many hybrid metal catalysts have been produced by the sol–gel process via silicon alkoxides $R_nSi(OR')_{4-n}$ where R is a ligand function able to bind catalytic metal species [14].

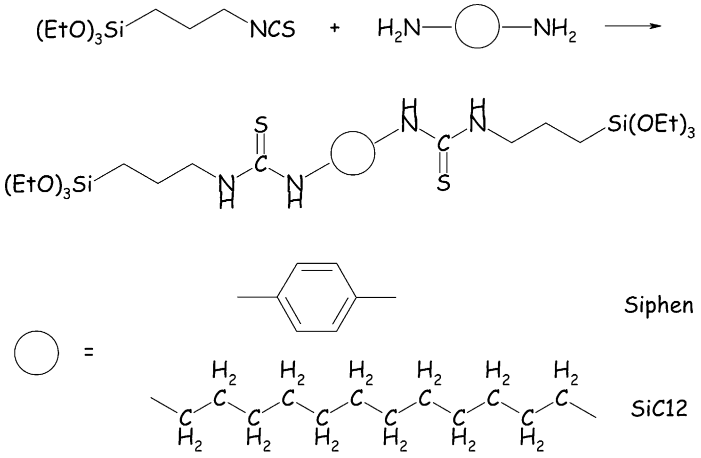
This paper deals with the study of metal leaching from hybrid catalysts containing thiourea functions during reactions as olefin hydroformylation (Rh) and hydrogenation (Pd). In previous studies done by us on these systems [15–20], metal leaching was evidenced by spectrometric techniques like EDX and XPS [15–17]. As the catalyst was used as powder, it was difficult to separate it from the viscous solution after the catalytic runs. A non-negligible amount of powder was lost during filtration and some other was dispersed as colloidal suspension in the recovered liquid. This loss of catalyst can be referred as "mechanical" leaching besides "chemical" leaching, due solely to chemical bonds cleavage. It is evident that metal determinations carried out on these recovered solutions are affected by both contributions. For this purpose, large monoliths were prepared, by the same sol–gel procedure previously used to produce powder catalysts. Rh(I) and Pd(II) species were covalently anchored on their surface. As sol–gel processable ligating molecules the thioureas Siphen and SiC12, depicted in Scheme 1, were used. They possess two C=S groups, able to bind catalytically active transition metals, and two $(EtO)_3Si$– groups able to build up the inorganic network when sol–gel processed. Siphen has been previously used [18,19], while SiC12 is a new compound.

By using these molecules alone or mixed with $(EtO)_4Si$ (TEOS) in different ratios, cylindrical monoliths (ca. diameter 2 cm; thickness 0.2–0.5 cm) could be prepared; they were designed to be very robust when used in catalysis but they have very low specific surface area, which seriously limits their activity. Nevertheless, we found them useful for the set-up of an analytical procedure for the recovering and determination of the metal species released in the solution.

2. Experimental

2.1. Methods and reagents

The solvents were reagent grade and were dried and distilled under nitrogen using standard techniques. All manipulations, except sol–gel processing, were performed under nitrogen using Schlenk glassware and a standard vacuum line. FTIR spectra were registered using a Nicolet Nexus spectrometer; single reflection horizontal ATR (HATR) spectra of hybrid monoliths were collected directly on the samples surface without any treatment using a Pike Smart MIRacle HATR accessory equipped with a flat, polished ZnSe crystal of 2 mm. FTIR microspectroscopic measurements were performed using a Nicolet Continuμm Microscope



Scheme 1.

connected to the Nexus spectrometer; 0° specular reflection spectra were converted using the Omnic 6 software Kramers–Kroenig equation. ^{1}H NMR were recorded on a AC300 Bruker instrument. CHNS elemental analyses were performed with a Carlo Erba EA 1108 automated analyzer. Gas chromatographic analyses were carried out using a DANI 3900 fitted with a methyl-silicone OV101 coated capillary column. The hydroformylation reactions were performed in a 50 ml stainless steel autoclave (Parr) equipped with a magnetic stirrer and thermostatted in a silicone–oil bath (Heidolph). Hydrogenation reactions were performed in Schlenk glassware connected to a Bunte burette. Regarding metal leaching determination, three analytical techniques have been considered, i.e. atomic absorption spectrometry with electrothermal atomization (GF-AAS Philips model PU9200) or flame atomization (F-AAS Perkin-Elmer model 303). The parameters for quantitative measurements were determined by a plasma emission spectrophotometer with optical detection (ICP-AES Philips Analyticals model 7450). The limit of detection, the limit of quantitation (LOQ) and the metal recovery range on suitable prepared matrices were determined according to Eurachem Guide [21]. BET specific surface areas were measured using a Micromeritics Pulse ChemiSorb 2705 instrument. A cross-section of the XGSiphenRh monolith (vide infra) was prepared by embedding a fragment of Rh containing monolith in moulded polystyrene resin and the section was exposed by polishing the hardened polymer with abrasive paper. All reagents were pure commercial products except $(EtO)_3Si(CH_2)_3NCS$, which was prepared as previously reported [22] with minor modifications [18].

2.2. Preparations

2.2.1. Preparation of 1,4-[$(EtO)_3Si(CH_2)_3NHC(S)NH]_2(C_6H_4)$ (Siphen) and 1,12-[$(EtO)_3Si(CH_2)_3NHC(S)NH]_2(C_{12}H_{24})$ (SiC12)

7.03 g (26.68 mmol) of $(EtO)_3Si(CH_2)_3NCS$, dissolved in 50 ml of dry ethanol, were slowly added to 50 ml of a ethanol solution of 1.44 g (13.34 mmol) of 1,4-phenylenediamine (or 2.67 g of 1,12-diaminododecane). The resulting solution was gently refluxed for 2 h and then dried. The white precipitate was washed with hexane and filtered. Yield: Siphen 97%; SiC12 93%.

2.2.1.1. Siphen. IR (Solid, KBr, cm^{-1}): 3240s (sh) 3189s (br) (νNH); 2974s 2927 m 2884 m (νCH); 1550s 1538s 1522s, (ν_{as}NCN); 1505s (νC=C aromatic);1103vs 1082vs (νSiO).

^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 8.6 (s br, 2 H, C_6H_4NH); 7.22 (s, 4 H, C_6H_4); 6.42 (s br, 2 H, CH_2NH); 3.75 (q, 12 H, CH_2O); 3.61 (m, 4 H, CH_2NH); 1.66 (q, 4 H, CH_2); 1.13 (t, 18 H, CH_3CH_2O); 0.56 (m, 6 H, CH_2Si).

Elemental analysis (%): Calcd. for $C_{26}H_{50}N_4O_6S_2Si_2$: C 49.18; H 7.94; N 8.82; S 10.10. Found: C 48.87; H, 8.15; N 8.95; S 10.45.

2.2.1.2. SiC12. IR (KBr cm^{-1}): 3248s 3074s (νNH); 2966m 2917s 2848s (νCH) 1572vs (ν_{as}NCN) 1104vs 1090vs (νSiO).

^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 6.18 (s br, 2 H, $CH_2N\mathit{H}$); 6.03 (s br, 2 H, $CH_2N\mathit{H}$); 3.74 (q, 12 H, $C\mathit{H_2}O$); 3.35 (s br, 8 H, $C\mathit{H_2}NH$); 1.65 (q, 4 H, $C\mathit{H_2}CH_2NH$); 1.51 (q, 4 H, $C\mathit{H_2}CH_2NH$); 1.23 and 1.19 (s br, 16H $C\mathit{H_2}$); 1.15 (t, 18 H, $C\mathit{H_3}CH_2O$); 0.58 (t, 6 H, $C\mathit{H_2}Si$).

Elemental analysis (%): Calcd. for $C_{32}H_{70}N_4O_6S_2Si_2$: C 52.85; H 9.70; N 7.70; S 8.82; Found: C 53.10; H 9.65; N, 7.81; S 8.9.

2.2.2. Preparation of hybrid monoliths by sol–gel method

2.2.2.1. XGSiphen. The reported preparation regards the monoliths is used in catalysis. Others were successfully prepared using different conditions (summarized in Scheme 2) but were not used as catalyst supports and their preparative details are not reported here.

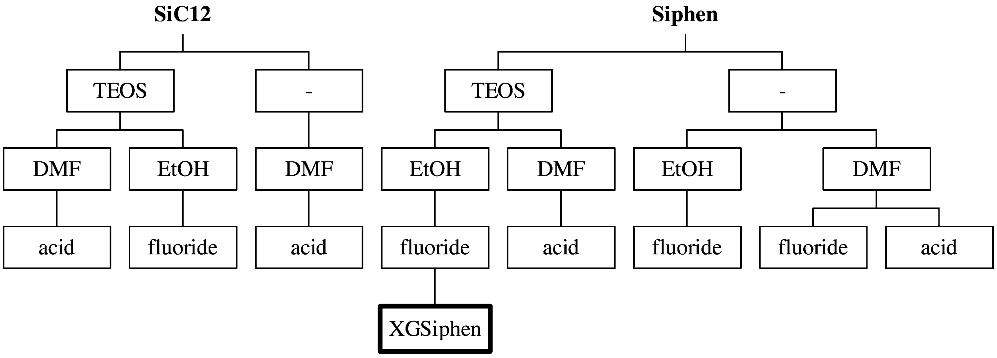
One gram (1.575 mmol) of Siphenditu in 7 ml of dry ethanol were introduced into a plastic container with screw cap of internal diameter of 5 cm and gently heated in a water bath to complete dissolution. Under continuous stirring, 0.7 ml (3.15 mmol) of TEOS and then 0.39 ml of a NH_4F solution (obtained dissolving 60 mg of NH_4F in 10 ml of water) were added. After 1 min, stirring was stopped, the magnetic bar taken out and the container sealed with the cap. After 2 days, gelation occurred and the elastic gel was washed with ethanol in order to eliminate the syneresis liquid. The gel was allowed to dry by covering the container with filtering paper. Reagents ratios: TEOS/Siphenditu 2:1; concentration of silicon about 1 M; Si/F 100:1; EtO/H_2O 1:1.

FTIR (HATR, neat, cm^{-1}): 3226w (νNH, OH); 2972w, 2925w, 2885w (νCH) 1535m (ν_{as}NCN) 1508m (νC=C aromatic) 1044vs (νSiO).

Specific surface area (BET): $<1\ m^2/g$.

2.2.3. Anchoring of Rh(I) and Pd(II) on XGSiphen

A XGSiphen monolith was prepared, washed with ethanol and left immersed in ethanol for 2 days or 1 month. After this period, the monolith was washed with CH_2Cl_2 just before anchoring of the metal species. The catalyst precursor, $[Rh(cod)Cl]_2$ (cod: 1,5-cyclooctadiene) for XGSiphenRh or $Pd(PhCN)_2Cl_2$ for XGSiphenPd, was dissolved in a volume of CH_2Cl_2 sufficient to completely cover the XGSiphen monolith, with an approximate total (CS groups)/metal ratio equal to 100:1. The ratio was calculated from the total mmol of Siphen used to prepare the monolith, considering that all the precursor is transformed in gel and nothing is lost in the syneresis liquid. (This fact was confirmed by FTIR analysis of the dried syneresis liquid that did not contain any band of the Siphen reagent.) The solution was left in contact with the monolith for 1 day. The monolith was then washed with CH_2Cl_2 and dried in the air. The yield of anchoring was approximately calculated



Scheme 2.

by weighing the residual metal precursor after evaporation of the mother and washing solutions. Evidence of the presence of co-ordinated metals species came from the colour of the monoliths and from the shifts of the thiourea bands in the FTIR-HATR spectra. For 1 g (1.575 mmol) of Siphen precursor, 0.03 mmol of Rh and Pd were used, that is about 7.4 mg of $[Rh(cod)Cl]_2$ and 11.44 mg of $Pd(PhCN)_2Cl_2$. Average anchoring yields, calculated on three different anchoring tests, were: 80% in the case of Rh and 89% in the case of Pd.

2.2.3.1. XGSiphenRh. FTIR (HATR, neat, cm^{-1}): 3267w (νNH, OH); 2921w, 2852w (νCH) 1637m (δOH); 1547m (ν_{as}NCN) 1507m (νC=C aromatic) 1033vs (νSiO).

2.2.3.2. XGSiphenPd. FTIR (HATR, neat, cm^{-1}): 3281w (νNH, OH); 2923w, 2853w (νCH) 1637m (sh) 1565 (ν_{as}NCN) 1508m (νC=C aromatic) 1042vs (νSiO).

2.3. Catalytic reactions

2.3.1. Hydroformylation of styrene with XGSiphenRh

One millilitre (8.73 mmol) of styrene and 10 ml of toluene were put in a 50 ml Parr autoclave. The Rh(I) containing monolith (about 0.03 mmol of Rh, styrene/Rh = 290) was suspended in solution using a filter paper support, in order to allow magnetic stirring without breaking it. The autoclave was then charged with a 1:1 CO/H_2 mixture up to 60 atm. The reactor was then heated at 80 °C for 7 h. The solution was analyzed by gas chromatography.

2.3.2. Hydrogenation of styrene with XGSiphenPd

One millilitre (8.73 mmol) of styrene was put in a glass balloon, containing the XGSiphenPd (about 0.03 mmol of Pd, styrene/Pd = 290) monolith suspended in ethanol using a filter paper support, in order to allow magnetic stirring without breaking the monolith. The balloon was then connected to a Bunte burette and was heated to 40 °C. After 72 h, the solution was analyzed by gas chromatography.

2.3.3. Mineralization of the samples

The solution derived from the catalytic hydroformylation and hydrogenation processes (eventually containing leached metals) were mineralized following a procedure which enabled analyte recoveries greater than 90% [23]. After catalytic runs, all the volatile liquids present in the quantitatively recovered solutions were evaporated with a vacuum pump. Aqua regia (3 ml) was added and then the mixtures were vigorously stirred while heating at 70 °C for 15 min. After complete dissolution, the cooled solutions were transferred to a 50 ml volumetric flask.

In order to verify accuracy of the mineralization method by means of an evaluation of the recovery range, standard samples were prepared with a known amount of precursor metal complexes ($[Rh(cod)Cl]_2$ and $Pd(PhCN)_2Cl_2$) into an "artificial" matrix similar to that of the reaction mixtures. The matrix was prepared with 9 ml of toluene, 0.2 ml of styrene, 470 mg of 2-phenylpropionaldehyde and 470 mg hydrocinnamaldehyde. The recovery range resulted $94 \pm 4\%$ for Rh and $97 \pm 2\%$ for Pd.

2.3.4. Metal determination

As mentioned before three spectrometric techniques were used for this purpose, namely GF-AAS, F-AAS and ICP-AES.

The best performance in terms of repeatability and sensitivity were obtained with the last technique. The limit of detection and the limit of quantitation were, respectively, 0.5 and 1.4 mg/l for Rh, 37.5 and 63.5 μg/l for Pd.

These values were calculated with calibration curves obtained with six points; relevant variance homogeneity and linear approximation significance were verified. In particular, homogeneity persists along all concentration ranges, considering also the blank values. The "lack of fit" and Mandel test values, performed to verify the goodness of the linear model approximation, resulted significant for both metals, owing to the calibration strategy used.

3. Results and discussion

By direct reaction of $(EtO)_3Si(CH_2)_3NCS$ and diamines 1,4-phenylenediamine or 1,12-diaminododecane, two sol–gel processable "double" thioureas were prepared, as reported in Scheme 1.

Siphen and SiC12 were sol gel processed in different conditions, with or without TEOS (thiourea/TEOS

Fig. 1. View of (a) an aged hybrid monolith containing Siphen and TEOS in 1:2 ratio (fluoride catalysis) and (b) a flexible Siphen TEOS 1:2 monolith obtained in DMF with acid catalysis. The diameter of monoliths is about 2 cm.

ratio 1:2) as cross-linking and diluting agent, with different sol–gel catalysts (ammonium fluoride or hydrochloric acid) and solvents (EtOH or DMF) as reported in Scheme 2.

Xerogels prepared from Siphen in EtOH were robust, transparent and rigid materials, their surface area being very low. DMF was used as drying control chemical additive (DCCA) [5,6]. As expected, monoliths prepared in DMF with acid catalysis were found to be very elastic, but after 2 weeks of ageing they lost flexibility and became fragile. Moreover, the residual DMF was found to be cause the decomposition of the anchored metal species. On the other hand, xerogels from SiC12 were fragile. For our purpose, the materials prepared in EtOH with 2:1 TEOS and with fluoride catalysis were used. They were of better mechanical properties than those obtained without TEOS. The use of greater amounts of TEOS caused the monoliths to be very brittle without a significant raise of the specific surface area.

Pictures of a typical rigid monolith obtained with Siphen and TEOS in ethanol (fluoride catalysis) and of a flexible one obtained in DMF (acidic catalysis) are reported in Fig. 1a and b, respectively.

3.1. *Preparations of the catalysts*

Thiourea functionalized monolithic xerogels were exposed to dichloromethane solutions of Rh(I) and Pd(II) precursors. The xerogels were used after 2 days of ageing, in order to allow the metal species to diffuse better inside the matrix, the anchoring yield on fresh gel being higher [20].

Metal concentrations were defective with respect to anchored ligand functions; typically the metal/tiourea (M/tu) ratios were 1:100. By this way it was expected that metal anchoring occurred only on the surface; it seemed unuseful to anchor metal species also inside the solid as inner sites are inaccessible for reagents. Moreover, from previous works [18] it was known that, using this method, the maximum surface metal/ligand ratio is achieved.

The single reflection HATR FTIR spectrum showed significant blue shifts, due to co-ordination, of the thiourea NCN anti-symmetrical stretching band at 1535 cm^{-1}: 1565 cm^{-1} in the xerogel with Pd and 1547 cm^{-1} with Rh [15–20]. A comparison of the spectra in the NCN stretching region is depicted in Fig. 2.

In the case of XGSiphenRh, a section of the monolith, perpendicular to its surface, was made and 0° specular reflection FTIR spectra were measured using a FTIR microspectrometer on the metal-containing surface layer and on the monolith bulk. Fig. 3 shows the visible fluorescence photograph of the section taken under UV light irradiation corresponding to the layers analysed by MicroFTIR.

The Rh containing layer (thickness 20–25 μm) is well evidenced and homogeneous. The thickness resulted homogeneous all around the monolith surface. MicroFTIR spectra were measured in specular reflection on the Rh containing layer and on the bulk of the monolith; they are reported in Fig. 4 (the dimension of the microscope aperture was about 20 μm × 100 μm, resolution 4 cm^{-1}) The ν_{as}(NCN) band of the thioureic groups was found at 1586 cm^{-1} for the Rh layer and 1545 cm^{-1} in the monolith bulk. These values are shifted to higher wavenumbers respect to those found in the HATR spectra of the external surface of the monolith (1547 and 1535 cm^{-1} for the XGSiphenRh and XGSiphen monoliths, respectively) but the expected blue shift on the frequency band suggests that also inside the material all the CS groups are co-ordinated by the metal. MicroFTIR

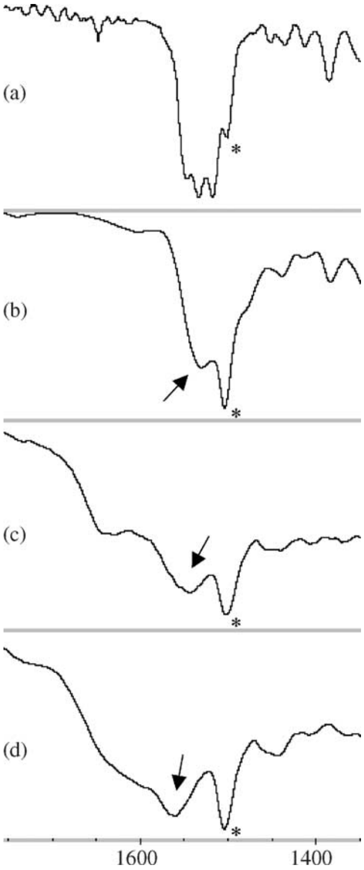


Fig. 2. Comparison of FTIR spectra of (a) Siphen; (b) XGSiphen; (c) XGSiphenRh; (d) XGSiphenPd. Spectrum (a) was registered in KBr pellet, spectra (b), (c) and (d) are HATR spectra taken directly on the monoliths surface. The asterisk evidences the aromatic ring absorption. The arrows point the ν_{as}NCN band typical of the thioureic group. The large bands at about 1650 cm^{-1} were attributed to the water present in the xerogels surface.

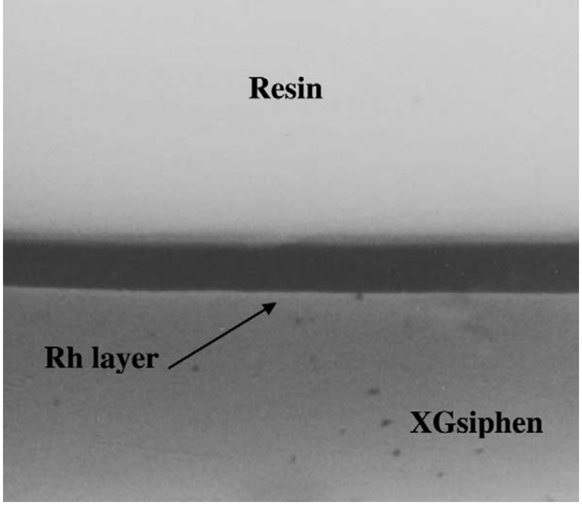


Fig. 3. Visible fluorescence photograph of a cross-section of XGSiphenRh. In this image, the layer containing Rh is dark grey. Its thickness is 20–25 μm.

spectra of the XGSiphenRh and XGSiphen monoliths surfaces were also measured, using a 200 × 200 aperture area. The ν_{as}(NCN) stretching frequencies were similar to those found on the section (1587 and 1550 cm^{-1}), suggesting that the difference from the HATR values is due to the different technique and that Rh complexes which are formed on the surface are the same found inside the layer.

3.2. Catalysis and metal leaching

Metal leaching appears undervalued in the literature. Sometimes it is reported that metal leaching was

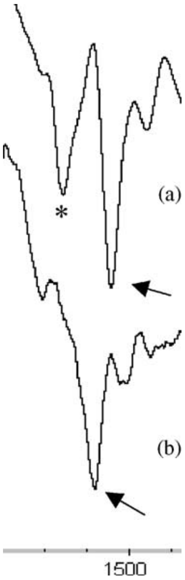


Fig. 4. MicroFTIR spectra of the XGSiphenRh cross-section (reported in Fig. 3). (a) Spectra of the monolith bulk; (b) spectra of the Rh containing layer. The asterisk indicates the OH stretching, the arrows the ν_{as}NCN stretching (every division on the *x*-axis corresponds to 50 cm^{-1}).

not observed without mentioning experimental evidence and details. It is obvious that also trace leaching of precious metals is fatal for the practical use of the catalysts. In our previous works, surface metal leaching was evidenced comparing EDX and XPS analysis; metal determination in solution was not performed. As assessed in the introduction, the use of powders obtained by sol–gel method often causes the production of very fine particles (sometime colloidal, that can be difficult to filter) which can change dramatically the results of the metal determination in the reaction mixture. Monoliths were just made to avoid the formation of unfilterable particles.

The solid–solution interphase at the surface of the monolith should behave as in small particles of the same material treated in the same way. In fact if the metal complex is anchored after the formation of the functionalized gel, and not previously prepared with a sol–gel processable ligand [20], both in monoliths and in powders metals are mainly located on the surface and scarcely inside the material, as evidenced by the comparison of XPS and EDX measurements [18].

The XGSiphenRh monolith was used to catalyse the styrene hydroformylation in toluene, at 80 °C and 60 atm (CO/H_2) for 7 h. At the end of the process, the presence of the relevant aldehydes was verified by gas chromatographic analysis. The catalysts were recovered, washed with dichloromethane and reused in a new catalytic run. A total of four catalytic runs were carried out. Only in the first two runs the presence of the aldehydes was found; in the subsequent runs the catalysts was practically inactive. The reaction solutions, added with washing solvent, were quantitatively transferred in Schlenk tubes to evaluate the metal leaching of the catalysts.

Regarding the hydrogenation reactions of styrene, two monoliths containing Pd(II) were prepared: the first was aged for a month before anchoring, the second was used fresh. In this way, we wanted to see the effect of the ageing on the metal leaching. Although the reactions were performed in 3 days at atmospheric pressure of hydrogen at 40 °C, no catalytic activity was observed for both catalysts. Probably the low M/tu ratio favoured the formation onto the surface of anchored mononuclear metal species well protected by the matrix network and unable to transform into colloidal Pd particles, which are responsible for the hydrogenating catalytic activity, as shown in previous papers [15,17,20].

3.3. Metal leaching determination

In the case of the hydrogenation reactions (Pd), both the solutions deriving from aged and fresh monoliths showed analytical responses below the detection limits (LOD = 37.5 μg/l). By applying the “worst case” considering the total amount of Pd anchored on the monoliths, it can be stated that, if leaching occurred, it was less than 0.07%.

In the case of hydroformylation (Rh), analytical data showed the presence of rhodium in all four samples, but only in the first one (from the first catalytic run) it was possible to determine the amount of leaching (7%). In the other three samples the rhodium concentration was less than the quantitation limit of the instrument ICP-AES (LOD = 500, LOQ = 1400 μg/l).

3.4. Homogeneous catalysis tests

In the case of Pd-containing monoliths, no activity was found together with no detectable metal leaching. Anchored Pd(II) species are not active and their reduction to colloidal Pd was not possible.

In the case of rhodium, the first catalytic run showed formation of aldehydes together with sensible metal leaching. In the second run, the leaching was observed but was less than the LOQ and styrene conversion was observed. In the third and fourth runs, Rh was detectable but not quantifiable and no styrene conversion was observed.

In order to find a rationale for these results, we performed two tests of homogeneous hydroformylation of styrene using $[Rh(cod)Cl]_2$ as catalyst. In the first test, we used the quantity of Rh corresponding to the LOD concentration, in the second test we used the quantity of Rh leached in solution after the first catalytic run. After mineralization of the samples, the recovered solutions were diluted to 50 ml in a volumetric flask. For a concentration of 0.5 mg/l, corresponding to the LOD, the detectable quantity of Rh in 50 ml of solution is 0.025 mg. Analogously, in the second test, 0.44 mg of Rh were used. In the first test no styrene conversion was observed but in the second test complete conversion was found. It must be kept in mind that, for a given LOD, the detection of Rh is depending on the dilution made after mineralization. If the dilution is relatively too large the Rh is not detected, but this does not mean that Rh was not leached and active "homogeneously". Obviously, if we decided to use a final volume of 5 ml instead of 50 ml (that is more convenient for routine analysis), the Rh concentration would have been 10 times higher. It is very important when metal leaching determination are made, to keep in mind this fact, because quantities of leached metals close to the detection limit can still be active in homogenous catalysis.

4. Conclusions

The use of large monoliths as models for studying the metal leaching besides promising practical advantages revealed, in the examined cases, important drawbacks. While it is easy to separate the monoliths from the reaction solution avoiding contamination of the sample due to non−filterable colloidal particles, they do not show appreciable catalytic properties. In fact, it has been found that in the case of Pd(II), the monolith texture probably protects the metal from reduction to metal particles and metal leaching was not observed. In the case of Rh, after the first run, leached metal active in catalysis was determined. After the second run the presence of Rh was below quantitation limits but activity was observed. After the fourth run Rh was still detectable but no conversion was found.

It appears that the catalytic activity found in the first use is due to the surface metal leaching. From the third catalytic run, the monoliths are not active. In the second run it is not completely clear if the active species are those in solution or those anchored, since a homogeneous test with the same quantity of Rh present in solution did not show any conversion. In the previous works on powders, metal leaching was observed but a dramatic change in the selectivity suggested that the anchored species did contribute to the styrene conversion [16,18]. In the case of powders the BET area was about 200 m^2/g and this difference in activity is probably due to the difference in specific surface area. Finally, this research, nonetheless, allowed us to validate a method of metal recovery and analysis for this kind of systems.

Acknowledgements

Financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Roma, Cofin 2000) is gratefully acknowledged.

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