Hybrid Materials for Catalysis? Design of New Phosphonate-Based Supported Catalysts for the Hydrogenation of Ketones under Hydrogen Pressure

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Supported rhodium and iridium 2,2′-bipyridine complexes were prepared for the hydrogenation of aromatic ketones under hydrogen pressure. The key feature of the immobilization process is the functionalization of the 2,2′-bipyridine unit with two phosphonic acid moieties, thus allowing the covalent grafting of the catalytic complex onto in situ generated titanium oxide particles. A very good catalytic activity is observed with the resulting materials that compares well with the homogeneous parent system and gives evidence that the major part of the catalytic sites are readily accessible. Moreover, the catalyst can be reused, and no significant rhodium leaching is observed.

Introduction

Covalently supported metal complexes (on organic or inorganic polymers) having high catalytic activity and selectivity are currently attracting great interest, because they offer several advantages such as easy recovery of the supported ligand and possible shape selectivity induced by the topology of the heterogenized catalyst. For the preparation of such supported catalysts, various methodologies have been reported: (i) grafting of the active ligand−metal complex on functionalized organic polymers[1] (such as Merrifield resins) or inorganic matrixes (zeolites, MCM-41, silica, clays, metal oxides, etc.);[2] (ii) stepwise intrazeolite assembly of the catalyst ("ship in a bottle" approach);[3] (iii) functionalization of the desired metal−ligand complex with polymerizable groups Z, for their subsequent incorporation into polymeric networks of either purely organic (polyureas, polyamides, polystyrenes, etc.)[4] or inorganic [Z = $Si(OR)_3$ (silsesquioxanes)[5] or PO_3H_2 (metal phosphonates)[6]] content. The advantage of inorganic backbones over organic polymers as catalyst carriers stems from higher mechanical and thermal stability. In the case of phosphonates, the covalent immobilization of catalytic complexes as organic−inorganic hybrid polymers prepared by self-assembly techniques from molecular precursors in solution is very attractive; thus, when modification of the nature of the spacer separating the catalytic center from the polymerizable moieties, a tunability of the three-dimensional

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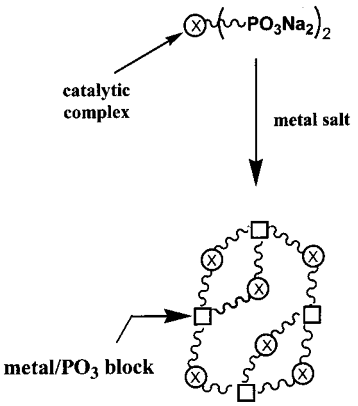

Figure 1. Schematic representation of the preparation of catalysts incorporated as part of the pure metal phosphonate networks.

network can be achieved. Our first attempts in that field were focused on the preparation of phosphonate-based supported manganese porphyrins for alkene epoxidation and alkane hydroxylation.[6a,c] The key feature of this approach is to functionalize the catalytic complex by phosphonic acid moieties that are then “polymerized” by reaction with a metal [M] salt in solution to build up MPO_3 blocks (Figure 1). However, the resulting materials have a homogeneous composition, and because they are usually nonporous, only the catalytic sites present on the surface of the solid particles participate in the catalytic reaction, making the bulk of each particle catalytically inactive.

To solve this problem, we propose a new heterogenization protocol based on the reaction of the PO_3H_2 groups with in situ generated TiO_2 particles with the aim of segregating most of the catalytic complexes on the surface of the oxide; in that way it should be possible to promote good access to the active sites. Our choice was motivated by the good chemical stability of the Ti−O−P link that should, in principle, prevent the immobilized catalytic complex from being washed out during the reaction. The binding properties of phosphonic acids to titanium molecular precursors or titanium oxide surfaces have already been studied, either for structural studies[7] or for direct applications,[8] such as the preparation of photovoltaic devices pioneered by Grätzel et al.[9] When molecular titanium derivatives such as alkoxides are used, organic-soluble titanium phosphonate cages can be obtained using nonhydrolytic synthetic procedures,[10] while oxide−phosphonate hybrids result from hydrolytic routes.[11] The use of this type of strategy for the design of immobilized catalysts is new and was tested for the preparation of supported iridium and rhodium/2,2′-bipyridine complexes from molecular precursors that we have previously used for the hydrogenation of a variety of aromatic ketones in water.[12]

Experimental Section

Materials and Methods. All starting materials were purchased from Aldrich Chemical Co. and were used as received. The chemical analyses were performed by the CNRS Analysis Laboratory (Vernaison, France). Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 20SX FTIR spectrometer with the usual KBr pellet technique. A Perkin-Elmer TGS2 thermogravimetric analyzer (TGA) was used to obtain TGA thermograms that were run in an air atmosphere from room temperature to 500 °C at a scan rate of 5 °C/min. The ^1H and ^{31}P NMR spectra recorded in solution were taken on a Bruker AC 200 spectrometer, with trimethylsilane (TMS; respectively 85% H_3PO_4) as the reference. The solid-state ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DSX 300 spectrometer. The scanning electron microscopy (SEM) experiments were carried out on a JEOL 6400F microscope. The Brunauer−Emmett−Teller (BET) surface areas and pore volume distribution were obtained from nitrogen adsorption isotherms measured with a Micromeritics ASAP 2010C sorptometer. Samples were pretreated by heating to 150 °C and evacuated for 2 h under reduced pressure. Energy-dispersive X-ray fluorescence (EDXRF) measurements were performed with an Oxford ED 2000 apparatus; the concentration of iridium and rhodium in solution (see below) was determined with a standard curve in the concentration range 20−1200 ppm (for Ir) and 30−620 ppm (for Rh). The determination of the phosphorus content in solution[13] was performed using a Shimadzu UV-160A UV−visible spectrometer. For the catalytic tests, yields were determined by gas chromatography (GC) using an internal standard method (nonane); GC analyses were performed using a Hewlett-Packard HP 6890 GC with a J&W Scientific DB-1701 column ($l = 30$ m and i.d. $= 0.25$ mm). Energy-dispersive X-ray spectroscopy (EDXS) measurements were carried out on a JEOL JM-35C SEM with a Tracor TN5500 micro Z attachment. Rhodium leaching was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis on decanted samples that were filtered, furnaced at 550 °C, and extracted into a 2% (v/v) HNO_3 solution. The samples were analyzed on a VG elemental PQ ExCell ICP-MS instrument with a series of rhodium standards.

Typical Procedure for the Preparation of the Supported 2,2′-Bipyridines and the Evaluation of the Catalytic Activity. Ligand **1** (Figure 2) was prepared as previously described.[12] A total of 0.06 mmol of ligand **1** was suspended into 5 mL of a distilled water/2-propanol mixture (1:1), and 0.25 mL of 1 M sodium hydroxide was added. After complete dissolution, 0.015 mmol of $[M(COD)Cl]_2$ (M = Ir, Rh) were then added and the mixture was stirred for 48 h at room temperature. The titanium precursor [$Ti(O\text{-}i\text{-}Pr)_4$, 200 μL] was then added in one portion and stirred for 2 days. The reaction medium was centrifugated, and the solution was separated and analyzed to determine the amount of complex incorporated in the supported catalyst. The solid was washed four times with distilled water in the centrifugation tubes and then three

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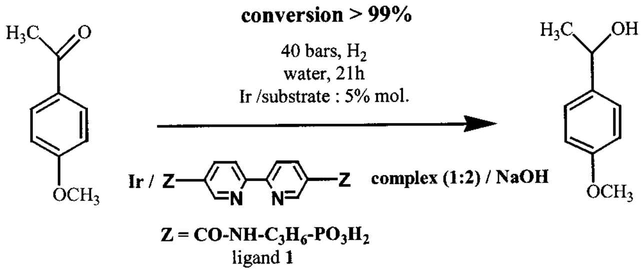

Figure 2. Water-soluble iridium–2,2′-bipyridine complex usable for the reduction of aromatic ketones under hydrogen pressure in water (according to ref 12).

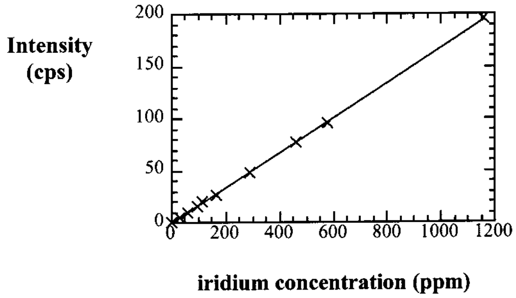

Figure 3. Calibration curve for the measurement of the iridium content by X-ray fluorescence, in solution in the 20–1200 ppm range.

times with acetone and was finally collected by filtration on a Millipore apparatus. The light-brown (Ir) or yellow (Rh, noted compound **A**) powder was dried at room temperature in air and then transferred into a 30 mL stainless steel glass-coated autoclave. A total of 5 mL of methanol, a 1 M sodium hydroxide aqueous solution (NaOH/Ir or Rh = 5), and the substrate (the desired acetophenone with a 2.5 mol % iridium or rhodium/substrate ratio) were then added. The autoclave was purged three times with argon, followed by three times with hydrogen, and the final H_2 pressure was adjusted to 40 bar. The mixture was stirred at room temperature for 21 h and then centrifugated. The liquid phase was then separated and analyzed by GC to determine the conversions and reaction yields. For the recycling experiments, after testing the solid was washed three times with methanol and three times with acetone, air-dried for 2 h, and used immediately.

Results and Discussion

In a previous study, we have demonstrated that the introduction of phosphonic acid moieties into 2,2′-bipyridine[12] opened the way to prepare rhodium or iridium complexes soluble in water. In that context ligand **1** showed very good activity in the reduction of various substituted acetophenones under hydrogen pressure in basic aqueous media (Figure 2), thus facilitating catalyst–product separation.

Besides this liquid–liquid biphasic approach, our purpose was to graft these latter ligand **1** based complexes onto titanium oxide surfaces to produce supported catalysts in which problems of accessibility to the catalytic sites could be minimized. At the outset, arbitrary conditions were used for the immobilization protocol and consisted of contacting an aqueous solution of a Ir/ligand **1** complex [1:2, thus corresponding to an Ir/P ratio of 1:4; pH 12.5 adjusted by the addition of 1 M NaOH (6.5 equiv of OH^-/ligand **1**)] with a TiO_2 source [Ti(O-*i*-Pr)$_4$; Ti/P molar ratio = 4.2] for 2 days. The solid was separated by centrifugation, and the filtrate was analyzed using X-ray fluorescence to determine the residual amount of iridium still present in solution (Figure 3). On the other hand, the residual amount of phosphorus in the supernatant was also quantified as described by Ames,[13] using ascorbic acid and ammonium molybdate to determine inorganic phosphate, after preliminary ashing of the solution; the phosphorus concentration was obtained from the absorbance measured at 820 nm (Figure 4). In all cases the amount of residual phosphorus in the filtrate was exactly 4 times higher than the amount of residual iridium. This clearly shows that the anchoring of the Ir/ligand **1** (1:2) complex on the titanium oxide proceeds efficiently, with no degradation of the catalyst. It was then possible to determine by difference the exact amount of catalytic complex incorporated into the solid and to test its catalytic activity for the hydrogenation of acetophenone with a fixed iridium-to-substrate ratio (2.5 mol %). Finally, the experimental conditions used for the heterogenization procedure were optimized on the basis of the catalytic results. The fixation of the phosphonate-based complex on the solid appears to be nearly completed after 1 h of reaction time, but the catalytic activity was slightly improved after 48 h (Table 1). Moreover, a significant effect of the initial pH is observed: for a high pH value (12.9, 14 equiv of OH^- added/ligand **1**), only a small amount of catalyst is incorporated into the solid. At this pH value, the Ti–phosphonate bonds are not stable and no surface-anchored complex is present. In this case, the incorporated catalyst (24%) is likely entrapped within the bulk of the titanium oxide particles and no catalytic activity is observed. At lower pH (9.4, corresponding to the exact titration of the two PO_3H_2 groups), the amount of catalyst on the solid is the same as that observed for a pH of 12.5 (6.5 equiv of OH^- added/ligand **1**), but the conversion of acetophenone is now improved (55%; Table 1), probably as a result of a better repartition of the catalytic sites on the surface of the oxide particles. Then, a solution of the complex in water [pH 9.4] was divided into equal parts that were treated with various amounts of Ti(O-*i*-Pr)$_4$ in order to investigate the influence of the Ti/P ratio on the catalytic performances of the resulting supported catalysts. A value of 5.6 was found to be optimal, because it corresponds to the best compromise to get the highest amount of anchored complex while

Table 1. Optimization of the Immobilization Protocol (Iridium Catalyst): Effect of the pH and the Reaction Time

	reaction time[a]				pH of the complex solution[b] (final pH value at the end of the reaction)		
	1/4 h	1 h	24 h	48 h	9.4 [4 equiv of OH^-/ligand **1**] (8.5)	12.5 [6.5 equiv of OH^-/ligand **1**] (9.5)	12.9 [14 equiv of OH^-/ligand **1**] (12.8)
amount of complex incorporated in the solid (%)	54	60	64	**65**	**65**	65	24
acetophenone conversion (%)	19	29	33	**35**	**55**	36	2

[a] pH of the complex solution: 12.5 [6.5 equiv of OH^-/ligand **1**]. Initial Ti/P: 4.2. [b] Reaction time: 48 h. Initial Ti/P: 4.2. Test conditions: CH_3OH, 40 bar of H_2, ambient temperature, 21 h, Ir/substrate 2.5%, NaOH/Ir 5 equiv.

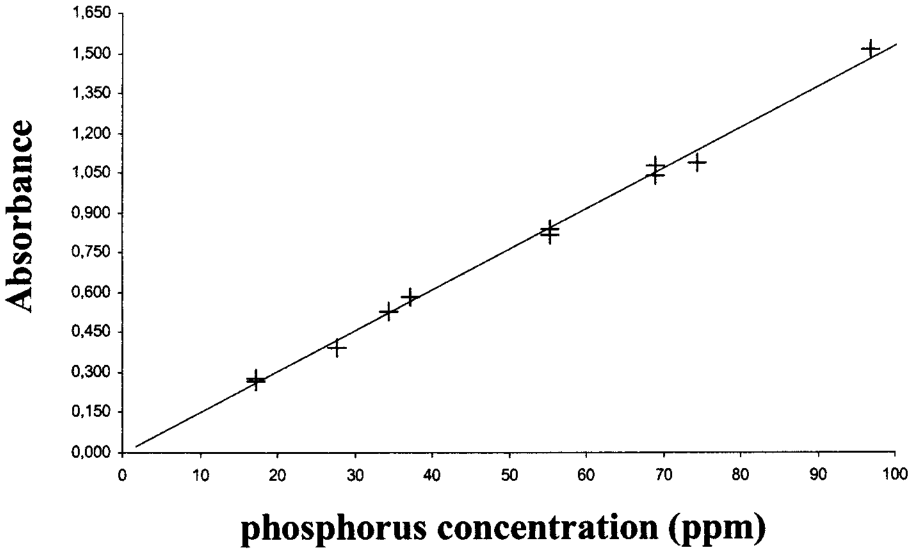

Figure 4. Calibration curve for the measurement of the phosphorus content by UV–visible according to ref 13, in the 20–100 ppm range.

Table 2. Optimization of the Immobilization Protocol (Iridium Catalyst): Effect of the Titanium/Phosphorus Molar Ratio

	Ti/P molar ratio[a] (final pH value at the end of the reaction)						
	2.8 (8.7)	4.2 (8.5)	5.6 (8.5)	7.0 (8.3)	8.4 (8.0)	9.7 (7.7)	11.1 (7.5)
amount of complex incorporated in the solid (%)	50	65	**76**	84	90	96	97
acetophenone conversion (%)	53	55	**55**	41	30	25	24

[a] pH of the complex solution: 9.4 [4 equiv of OH^-/ligand **1**]. Reaction time: 48 h. Test conditions: see Table 1.

Table 3. Optimization of the Immobilization Protocol (Iridium Catalyst):[a] Effect of the Titanium Precursor

	titanium precursor (Ti/P)[a]						
	$Ti(O\text{-}i\text{-}Pr)_4$	$Ti(O\text{-}n\text{-}Bu)_4$		$Ti(OEt)_4$		TiO_2 BET surface area: 429 m^2 g^{-1}	$Ti(acac)_2(O\text{-}i\text{-}Pr)_2$
	(**5.6**)	5.6	11.1	5.6	11.1	(4 < Ti/P < 12)	(5.6)
amount of complex incorporated in the solid (%)	**76**	37	69	25	63	12–43	no solid
acetophenone conversion (%)	**55**	25	35	18	27	<5	

[a] pH of the complex solution: 9.4 [4 equiv of OH^-/ligand **1**]. Reaction time: 48 h. Test conditions: see Table 1.

keeping the conversion at a maximum (Table 2). For high Ti/P ratios, the main portion of the Ir/ligand **1** complex is incorporated in the solid, a significant part of which being encapsulated and consequently non-accessible to the reagents, thus explaining the poor conversions observed for the reduction. At this stage, the influence of the solvent used for the catalytic tests was examined and confirmed that methanol was the best choice (55% conversion) compared to ethanol (17% conversion), 2-propanol (13% conversion), THF (6% conversion), or toluene (5% conversion). In addition, various titanium sources were used (Table 3), such as other titanium alkoxides (butoxide and ethoxide), a modified alkoxide [$Ti(acac)_2(O\text{-}i\text{-}Pr)_2$],[14] or commercial TiO_2 (429 m^2 g^{-1}), with no improvement of the catalytic performances compared to titanium isopropoxide that appeared to be the best titanium precursor. Surprisingly, direct grafting of preformed TiO_2 led to very poor activities with low complex incorporation. This observation suggests that, to a certain extent, the PO_3^{2-} groups present on ligand **1** control the hydrolysis–condensation process of the titanium alkoxide precursor, probably by capping the nucleating and growing oxotitanium particles. The hydrolysis rate of the titanium precursor appears to influence this phenomenon significantly, and the best results were observed for $Ti(O\text{-}i\text{-}Pr)_4$ that has a monomeric nature compared to titanium ethoxide or *n*-butoxide that are oligomeric.[15] Furthermore, in $Ti(acac)_2(O\text{-}i\text{-}Pr)_2$, the interaction of the acac ligand with titanium is too strong and prevents the condensation process from occurring, so that no solid is isolated.

Finally, the bipyridine complex was prepared in a water/organic solvent mixture (1:1) instead of water prior to adding $Ti(O\text{-}i\text{-}Pr)_4$, leading to a significant increase of the amount of complex incorporated on the solid (Table 4), while the acetophenone conversion was improved as well. The best results are observed for the *i*-PrOH/water mixture (acetophenone conversion 94% and amount of incorporated complex 90%). At this juncture these optimized conditions were used to immobilize the rhodium analogue [Rh/ligand **1** (1:2)] and led to compound **A**, which gave even better results

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Table 4. Optimization of the Immobilization Protocol (Iridium Catalyst): Effect of the Solvent Used for the Preparation of the Catalytic Complex[a]

	solvent					
	H_2O	$MeOH/H_2O$ (1:1)	$EtOH/H_2O$ (1:1)	*i*-$PrOH/H_2O$ (1:1)	THF/H_2O (1:1)	acetone/H_2O (1:1)
amount of complex incorporated in the solid (%)	76	57	80	**90**	86	94
acetophenone conversion (%)	55	57	65	**94**	87	61

[a] Amount of sodium hydroxide added: 4 equiv of OH^-/ligand **1**. Reaction time: 48 h. Titanium precursor: Ti(O-*i*-Pr)$_4$. Initial Ti/P: 5.6. Test conditions: see Table 1.

Table 5. Reduction of Para-Substituted Acetophenones Using Rhodium/2,2′-Bipyridine Complexes in Homogeneous and Supported Conditions

	catalyst							
	supported rhodium/ligand **1** (1:2) complex[a] (compound **A**)				rhodium/2,2′-bipyridine (1:2) complex in MeOH			
Rh/substrate (%)	2.5	2.5	2.5	1.5	2.5	2.5	2.5	1.5
para substituent of acetophenone	H	C_2H_5	OCH_3	OCH_3	H	C_2H_5	OCH_3	OCH_3
conversion (%)	>99	98	98	72	98	96	94	94

[a] Amount of NaOH added in the complex solution [4 equiv of OH^-/ligand **1**]. Solvent: water/*i*-PrOH (1:1). Reaction time: 48 h. Titanium precursor: Ti(O-*i*-Pr)$_4$. Initial Ti/P: 5.6. Test conditions: see Table 1.

Table 6. Results from the Hydrogenation of *p*-Methoxyacetophenone Using Rhodium Catalyst A and 40 bar H_2

catalyst [cycle][a]	conversion after 21 h	color before test	color after hydrogen release (after test)	entry
A [1]	72%	light yellow	green	1
A [2]	98%	light brown	green	2
A [3]	98%	light brown	green	3
A [4]	98.5%	light brown	green	4
test using supernatant of cycle 4	no conversion	colorless	colorless	5

[a] The rhodium-to-substrate ratio is 1.5%. Compound **A**: 360 mg, 15 mL of methanol, 5 equiv of NaOH/Rh, ambient temperature; the time between two successive runs was 3.5 h (used for isolation, washing, and drying of the catalyst).

(Table 5) with a 95% incorporation rate of the complex and excellent yields for the reduction of acetophenones even deactivated (>98% for acetophenone and *p*-ethyl- and *p*-methoxyacetophenones). The product−catalyst separation efficiency of compound **A** was examined on performance of recycling experiments with a 1.5% Rh/substrate molar ratio (Table 6). Importantly, a significant increase in conversion (from 72 to 98% yield) is observed for the second cycle and the other successive runs. This can be explained by a relatively long activation period of the catalyst during the first use. This is probably closely related to the observation that immediately after release of the hydrogen pressure at the end of the test the color of the supported rhodium catalyst **A** was deep green (probably indicative of the catalytically active species); moreover, by exposure to air during the recycling workup (duration: 3.5 h), the color of the solid faded slowly and turned light brown before the next run. Afterward, the color switching between deep green (under H_2 pressure) and light brown (in air) appeared to be reversible for the successive cycles. Moreover, the extent of rhodium leaching was determined by ICP-MS analyses of the upper phase after the first catalytic cycle, for two different batches of compound **A**. The rhodium loss was determined as (0.065 ± 0.001)% in one case (substrate: acetophenone) and (0.063 ± 0.001)% in the second case (substrate: *p*-methoxyacetophenone), thus demonstrating that the catalyst recycling is efficient. The filtrate was also tested for its content of leached rhodium complex by its ability to hydrogenate a fresh sample of *p*-methoxyacetophenone [Table 6, entry 5], and the result of this blank test was negative.

This optimized rhodium catalyst was then characterized using different experimental techniques. First of all, the chemical analyses of the immobilized rhodium/bipyridine showed the expected P/N (expected 0.5; found 0.54), C/P (expected 9; found 8.9), and Rh/P (expected 0.25; found 0.24) ratios, while the Ti/P value (6.0) agrees well with the amount of complex incorporated from the solution into the solid determined using X-ray fluorescence and colorimetry (95%, for a 5.6 initial Ti/P ratio). The TG−MS experiments gave evidence of two weight losses at 100 °C (endothermic) and 450 °C (exothermic), respectively. The first one (ca. 30%, $m/z = 18$ for water) corresponds to a water release, and the second mass loss (ca. 8.3%, $m/z = 44$ for propane) is due to the degradation of the bipyridine moiety. We have also checked that the expected signals corresponding to the incorporated

Table 7. Experimental Data for the Supported Rhodium/Ligand 1 Complex A

chemical analyses	% P 2.74, % C 9.48, % N 2.30, % H 3.34, % Na 3.24, % Rh 2.21, % Ti 25.40
FTIR (cm^{-1}) (data for ligand **1**)	amide linkage: 1641, 1554; 1322 (1646, 1557; 1323) PO_3: 1111, 990 (1075, 106, 961)
^{13}C CPMAS NMR (data for ligand **1**)	166, 156, 150, 138, 132, 124, 41, 23 ppm (CO, 164.2 ppm; bipyridine, 155.3, 148.1, 136.8, 130.6, 121 ppm; CH_2N, 48.6 ppm; CH_2CH_2P, 25.3 and 22.9 ppm)
^{31}P MAS NMR (data for ligand **1**)	27.9 (63%), 24.1 (25%), 21 (12%) ppm (26.5 ppm)
BET surface area	94 m^2 g^{-1}

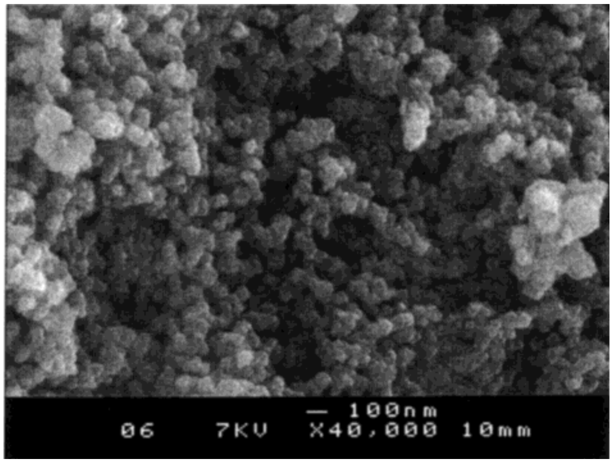

Figure 5. SEM (×40 000) of the optimized supported rhodium/ligand **1** complex **A**.

rhodium complex are present on the FTIR, ^{13}C CP MAS, and ^{31}P MAS spectra (Table 7). SEM investigations (Figure 5) showed that the sample is made of particles of small size in the range of ca. 20−100 nm; the measured surface area was 94 m^2 g^{-1}, and no microporosity or mesoporosity could be detected.

In conclusion, experimental conditions were successfully optimized so that high loading of the catalytic complex on the surface of the particles was achieved, along with excellent activity of the supported catalyst [compound **A**], that compares well with the parent homogeneous system (Tables 5 and 6). We have demonstrated in this paper that the Rh/ligand **1** complex, which was previously used in a water-soluble form, is efficient in its supported version as well. The resulting solid is stable in air before use and is easy to handle and recycle. The extension of these results to chiral series is showing promise, and this is ongoing.

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