MCM-41-immobilised bidentate nitrogen platinum complex: a highly efficient and recyclable phosphine-free catalytic system for the hydrosilylation of olefins

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An MCM-41-immobilised bidentate nitrogen platinum complex (MCM-41-2N-Pt) was very conveniently synthesised from commercially available and cheap 3-(2-aminoethylamino)propyltrimethoxysilane by immobilisation on the mesoporous silica nanoparticles, MCM-41, followed by reaction with potassium chloroplatinite. It was found that the MCM-41-2N-Pt complex is a highly efficient catalyst for the hydrosilylation of olefins with triethoxysilane and can be easily recovered and reused several times without significant loss of activity.

Keywords: supported catalyst, hydrosilylation, platinum, functionalised MCM-41, heterogeneous catalysis

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The hydrosilylation of alkenes is one of the most important Si-C bond formation reactions in organosilicon chemistry and a variety of silicon monomers containing functional groups have been synthesised by this reaction.[1] It is a homogeneous reaction, generally using soluble platinum or rhodium complexes such as $Pt(PPh_3)_4$, H_2PtCl_6, $RhCl(PPh_3)_3$ as catalysts.[2,3] However, industrial applications of these homogeneous platinum or rhodium complexes remain a challenge because the complexes are expensive and cannot be recycled. They are also difficult to separate from the product mixture, which is a particularly significant drawback for their applications in the pharmaceutical industry. From the standpoint of environmentally benign organic synthesis, development of immobilised transition-metal catalysts is challenging and important. In an ideal system, they can be recovered from the reaction mixture by simple filtration, re-used indefinitely and contamination of products by metals is prevented. Polymer-supported transition metal complexes catalysts are currently attracting great interest since they have the advantages of both homogeneous and heterogeneous catalysed processes.[4–6] So far, a number of supported platinum[7–12] or rhodium[13–16] complexes have proved to be efficient catalysts for the hydrosilylation of olefins. However, these catalysts have generally suffered from limited mass transfer and the leaching of the catalytic species from the surface of the support. Most of them are polystyrene or silica-supported phosphine platinum or rhodium complexes. It is known that catalysts containing phosphine ligands are unstable at high temperatures.[17–19] Furthermore, the procedure for preparing the polymer-bound phosphine platinum or rhodium complexes is rather complicated; the non-crosslinked poly(chloromethylstyrene) is not commercially available, and the chloromethylation requires the use of carcinogenic chloromethyl methyl ether. Therefore, the development of phosphine-free heterogeneous platinum or rhodium catalysts having a high activity and excellent recyclability is a topic of enormous importance.

Study of new types of supported platinum complexes catalysts which might be suitable for hydrosilylation of olefins with triethoxysilane has practical significance. Our approach was guided by three imperatives: the polymeric ligand should be easily accessible (1), starting from readily available and cheap reagents (2). The polymeric platinum catalyst should be air-stable at room temperature, which should allow its storage in normal bottles with unlimited shelf life (3). Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilisation of homogeneous catalysts.[20] MCM-41 has a regular pore diameter of *ca* 5 nm and a specific surface area > 700 $m^2\ g^{-1}$. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach the surface of the channel.[21,22] Shyu *et al.* reported a phosphinated MCM-41-supported rhodium complex for catalytic hydrogenation of olefins and found that the turnover frequency (TOF) of this MCM-41-supported phosphine rhodium complex is three times higher than that of $[RhCl(PPh_3)_3]$ in the hydrogenation of cyclohexene.[23] Recently, we have reported the synthesis of MCM-41-immobilised bidentate nitrogen palladium complex and found that it was a highly efficient and recyclable catalyst for the Suzuki reaction[24] and the carbonylative Suzuki coupling reaction.[25] In continuing our efforts to develop greener synthetic pathways for organic transformation, our new approach, described in this paper, was to design and synthesise a novel MCM-41-supported bidentate nitrogen platinum complex (MCM-41-2N-Pt), which was used as an effective catalyst for the hydrosilylation of olefins with triethoxysilane.

Although phosphine ligands stabilise platinum and influence its reactivity, the simplest and cheapest platinum catalysts are of course phosphine-free systems, specifically when used in low loading. A novel MCM-41-immobilised bidentate nitrogen platinum complex (MCM-41-2N-Pt) was very conveniently synthesised from commercially available and cheap 3-(2-aminoethylamino)propyltrimethoxysilane by immobilisation on MCM-41, followed by reaction with potassium chloroplatinite (Scheme 1). The X-ray powder diffraction (XRD) analysis of the MCM-41-2N-Pt indicated that, in addition to an intense diffraction peak (100), two higher order peaks (110) and (200) with lower intensities were also present, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterise this heterogeneous platinum complex. The N:Pt mole ratio of the MCM-41-2N-Pt was determined to be 5.15. The XPS data for MCM-41-2N-Pt, MCM-41-2N, K_2PtCl_4 and Pt foil are listed in Table 1. It can be seen that the binding energies of Si_{2p} and O_{1s} of MCM-41-2N-Pt are similar to those of MCM-41-2N and the binding energy of Cl_{2p} of MCM-41-2N-Pt is similar to that of K_2PtCl_4. However, the difference of N_{1s} binding energies between MCM-41-2N-Pt and MCM-41-2N is 0.9 eV. The binding energy of $Pt_{4f7/2}$ in MCM-41-2N-Pt is 1.1 eV less than that in K_2PtCl_4, but 0.8 eV larger than that in Pt foil. These results show that a coordination bond between N and Pt is formed.

In order to evaluate the catalytic activity of the MCM-41-immobilised bidentate nitrogen platinum complex (MCM-41-2N-Pt), the hydrosilylation reactions of olefins with triethoxysilane were studied. At first, the catalytic activity of the platinum

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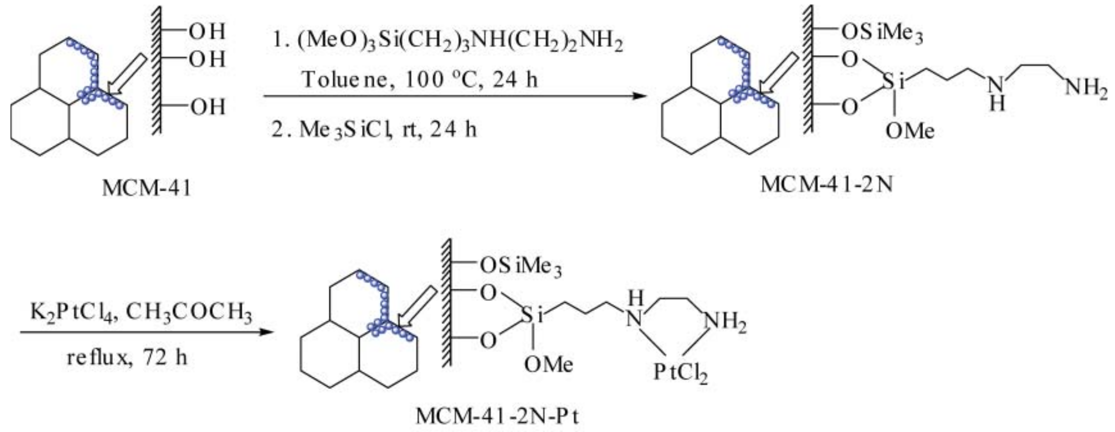


Scheme 1

Table 1 XPS data for MCM-41-2N-Pt, MCM-41-2N, K_2PtCl_4 and Pt foil (in eV)[a]

Sample	$Pt_{4f7/2}$	N_{1s}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-2N-Pt	72.1	400.6	103.4	532.9	198.8
MCM-41-2N		399.7	103.4	532.8	
K_2PtCl_4	73.2				198.9
Pt foil	71.3				

[a] The binding energies are referenced to C_{1s}(284.6 eV), and the energy differences were determined with an accuracy of ± 0.2 eV.

complex at different temperatures was investigated by using hydrosilylation of 1-dec-1-ene with triethoxysilane as the model reaction. The results are summarised in Table 2. The experimental results show that no remarkable induction period was observed and the reaction rate increased with the increase in the reaction temperature. When hydrosilylation reaction was carried out at 120 °C, decyltriethoxysilane was obtained in 92% yield after 1.5 h (entry 3). So, for the temperatures evaluated [100, 110, 120, 130 °C], 120 °C gave the best result. The effect of the amount of the MCM-41-2N-Pt complex on the hydrosilylation reaction was also investigated using 5.0 mmol of dec-1-cene as substrate at 120 °C. The experimental results are shown in Table 2. The reaction rate became larger with the increase in the amount of the catalyst, for the amounts evaluated [2.5×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2} mmol Pt], 5.0×10^{-3} mmol Pt gave the best result when decyltriethoxysilane was obtained in 92% yield (entry 3). When 1.0×10^{-2} mmol of MCM-41-2N-Pt was used, the reaction rate was the largest, but the final yield of decyltriethoxysilane was only 84% and tetraethoxysilane was formed in 7% yield (entry 6).

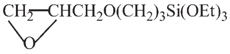
Hydrosilylation reactions of a variety of olefins with triethoxysilane were studied at 120 °C using 0.1 mol% of the MCM-41-2N-Pt as catalyst, the typical results are summarised in Table 3. As shown in Table 3, in the presence of 0.1 mol% of MCM-41-2N-Pt complex, hydrosilylation reactions of dec-1-ene, dodec-1-ene, allyl phenyl ether, and ω-chloroundec-1-ene with $HSi(OEt)_3$ proceeded smoothly and the corresponding hydrosilylation products were obtained in 91–95% yields (entries 1–3 and 5). Speier's catalyst (H_2PtCl_6) was not as effective when $HSi(OEt)_3$ was reacted; it was reported that the yield of decyltriethoxysilane was only 40%.[26] Under the new conditions, hydrosilylation reactions of allylbenzene and allyl glycidyl ether with $HSi(OEt)_3$ could also proceed smoothly to give the corresponding addition products in good yields (entries 4 and 7). Hydrosilylation of styrene with $HSi(OEt)_3$ afforded the α-adduct in 15% yield in addition to the β-adduct as a major product (entry 6).

Table 2 The effects of reaction temperature and amount of the catalyst on the catalytic activity of MCM-41-2N-Pt[a]

Entry	Temp. /°C	Amount of catalyst/mol%	Time/h	GC yield/%
1	100	0.1	2.0	81
2	110	0.1	1.7	87
3	120	0.1	1.5	92
4	130	0.1	1.2	88
5	120	0.05	2.2	89
6	120	0.2	1.1	84

[a] Reaction conditions: dec-1-ene (5.0 mmol); $HSi(OEt)_3$ (5.5 mmol).

Table 3 Catalytic activity of MCM-41-2N-Pt for the hydrosilylation reaction of olefins with triethoxysilane

Entry	Olefin	Product[a]	Time /h	GC yield[b] /%
1	$CH_3(CH_2)_7CH{=}CH_2$	$CH_3(CH_2)_9Si(OEt)_3$	1.5	92
2	$CH_3(CH_2)_9CH{=}CH_2$	$CH_3(CH_2)_{11}Si(OEt)_3$	1.6	91
3	$C_6H_5OCH_2CH{=}CH_2$	$C_6H_5O(CH_2)_3Si(OEt)_3$	1.4	95
4	$C_6H_5CH_2CH{=}CH_2$	$C_6H_5(CH_2)_3Si(OEt)_3$	1.6	86
5	$Cl(CH_2)_9CH{=}CH_2$	$Cl(CH_2)_{11}Si(OEt)_3$	1.7	91
6	$C_6H_5CH{=}CH_2$	$C_6H_5(CH_2)_2Si(OEt)_3$	1.3	73
7	 $CH_2{-}CHCH_2OCH_2CH{=}CH_2$	 $CH_2{-}CHCH_2O(CH_2)_3Si(OEt)_3$	1.3	82

[a] The structure of product was further identified by ^1H NMR.
[b] No increase in yield with increasing the reaction time.
Reaction conditions: olefin (5.0 mmol); triethoxysilane (5.5 mmol); MCM-41-2N-Pt (0.1 mol%); temperature (120 °C).

A further objective of our studies was to determine whether the catalysis was due to the MCM-41-2N-Pt complex or to a homogeneous platinum complex that leaves the support during the reaction and then returns to the support at the end. To test this, we focused on the hydrosilylation reaction of dec-1-ene with triethoxysilane. We filtered off the MCM-41-2N-Pt complex after 30 min of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (120 °C) in order to avoid possible recoordination or precipitation of soluble platinum upon cooling. We found that, after this hot filtration, no further reaction was observed. This suggests that the platinum catalyst remains on the support at elevated temperatures during the reaction. The hydrosilylation of dec-1-ene with triethoxysilane was examined to evaluate the reusable property of MCM-41-2N-Pt. It was demonstrated that the novel supported bidentate nitrogen platinum complex could be recovered by simple filtration and reused several times. The hydrosilylation of dec-1-ene with triethoxysilane was repeated five times using the same batch of supported catalyst, the yields of decyltriethoxysilane from the first to the fifth run were 92%, 92%, 91%, 90% and 90% clearly illustrating good reusability of the catalyst. The high stability and good reusable property of MCM-41-2N-Pt should result from the strong coordination of bidentate nitrogen ligand on platinum and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view.

In conclusion, we have developed a novel, phosphine-free, practical and economic catalyst system for the hydrosilylation of olefins with triethoxysilane by using MCM-41-immobilised bidentate nitrogen platinum complex [MCM-41-2N-Pt] as catalyst. This novel heterogeneous platinum catalyst can be conveniently prepared by a simple two-step procedure from commercially available and cheap reagents and can be reused at least five times without significant loss of activity. This novel platinum complex has not only high activity for the heterogeneous hydrosilylation of olefins with triethoxysilane, but offers practical advantages such as easy handling, easy separation from the product and reuse.

Experimental

All hydrosilylation products were characterised by comparison of their spectra and physical data with authentic samples. IR spectra were obtained using a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyser. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a KRATOS XSAM 800 electron energy spectrometer. X-ray powder diffraction patterns were obtained on Damx-rA (Rigaka). Platinum content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). The mesoporous material MCM-41 was prepared according to a literature procedure.[27] Acetone, triethoxysilane and olefins were distilled before use, other reagents were used as received without further purification.

Preparation of MCM-41-2N

A solution of 3-(2-aminoethylamino)propyltrimethoxysilane (1.54 g) in dry chloroform (18 mL) was added to a suspension of the MCM-41 (2.2 g) in dry toluene (180 mL). The mixture was stirred for 24 h at 100 °C. Then the solid was filtered off and washed by $CHCl_3$ (2 × 20 mL), and dried under vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me_3SiCl (3.1 g) in dry toluene (100 mL) at room temperature under stirring for 24 h. Then the solid was filtered off, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried under vacuum at 120 °C for 5 h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol g^{-1} by elemental analysis.

Preparation of MCM-41-2N-Pt

In a small Schlenk tube, the above-functionalised MCM-41 (MCM-41-2N) (1.52 g) was mixed with K_2PtCl_4 (0.249 g, 0.6 mmol) in dry acetone (50 mL). The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5 h to give 1.61 g of a yellow platinum complex [MCM-41-2N-Pt]. The nitrogen and platinum content was found to be 1.65 mmol g^{-1} and 0.32 mmol g^{-1}, respectively.

Hydrosilylation of olefins with triethoxysilane

Hydrosilylation was carried out in a 5 mL flat-bottomed flask equipped with a magnetic stirrer and a reflux condenser to the upper of which a drying system was attached. The olefin and the platinum complex were stirred at the reaction temperature for 30 min before triethoxysilane was added. The structure and yield of hydrosilylation products were determined based on a standard sample and a standard curve by GLC at regular intervals. Typical reaction conditions are as follows: olefin 5.0 mmol, triethoxysilane 5.5 mmol, platinum complex 0.1 mol%. The products were isolated by distillation under reduced pressure and characterised by IR and ^{1}H NMR.

Decyltriethoxysilane: Oil,[28] b.p. 149–150 °C/8 mmHg. IR (film): ν (cm^{-1}) 2974, 2927, 2855, 1469, 1391, 1295, 1158, 1106, 1083; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (q, J = 7.2 Hz, 6H), 1.41–1.38 (m, 2H), 1.31–1.22 (m, 23H), 0.88 (t, J = 7.2 Hz, 3H), 0.66–0.64 (m, 2H).

Dodecyltriethoxysilane: Oil,[28] b.p. 151–152 °C/3 mmHg. IR (film): ν (cm^{-1}) 2973, 2926, 2853, 1468, 1390, 1294, 1157, 1105, 1084; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (q, J = 7.2 Hz, 6H), 1.40–1.38 (m, 2H), 1.32–1.21 (m, 27H), 0.89 (t, J = 7.2 Hz, 3H), 0.67–0.64 (m, 2H).

3-Phenoxypropyltriethoxysilane: Oil,[29] b.p. 154–155 °C/6 mmHg. IR (film): ν (cm^{-1}) 3056, 2943, 2841, 1595, 1471, 1389, 1245, 1086, 753, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.13 (m, 2H), 6.91–6.78 (m, 3H), 3.94 (t, J = 7.6 Hz, 2H), 3.83 (q, J = 7.2 Hz, 6H), 1.83–1.78 (m, 2H), 1.23 (t, J = 7.2 Hz, 9H), 0.59–0.57 (m, 2H).

3-Phenylpropyltriethoxysilane: Oil,[30] b.p. 139–141 °C/6 mmHg. IR (film): ν (cm^{-1}) 3058, 2980, 1594, 1576, 1494, 1465, 1390, 1107, 1067, 750, 692; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.18 (m, 5H), 3.76 (q, J = 7.2 Hz, 6H), 2.64–2.61 (m, 2H), 1.75–1.72 (m, 2H), 1.19 (t, J = 7.2 Hz, 9H), 0.57–0.54 (m, 2H).

11-Chloroundecyltriethoxysilane: Oil,[30] b.p. 147–149 °C/2 mmHg. IR (film): ν (cm^{-1}) 2977, 2927, 2856, 1441, 1391, 1297, 1167, 1104, 1081, 957, 791; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (q, J = 7.2 Hz, 6H), 3.42 (t, J = 6.8 Hz, 2H), 1.83–1.76 (m, 2H), 1.42–1.39 (m, 2H), 1.35–1.21 (m, 23H), 0.68–0.64 (m, 2H).

Phenylethyltriethoxysilane: Oil,[31] b.p. 129–131 °C/6 mmHg. IR (film): ν (cm^{-1}) 3057, 2974, 1598, 1575, 1497, 1461, 1392, 1104, 1076, 752, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.18 (m, 5H), 3.82 (q, J = 7.2 Hz, 6H), 2.75–2.73 (m, 2H), 1.22 (t, J = 7.2 Hz, 9H), 1.01–0.97 (m, 2H).

3-(2,3-Epoxypropoxy)propyltriethoxysilane: Oil,[30] b.p. 134–135 °C/2 mmHg. IR (film): ν (cm^{-1}) 2944, 2841, 1468, 1264, 1194, 1160, 1088, 910, 821; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (q, J = 7.2 Hz, 6H), 3.52–3.49 (m, 2H), 3.42–3.33 (m, 2H), 2.91–2.80 (m, 1H), 2.61–2.49 (m, 2H), 1.55–1.46 (m, 2H), 1.23 (t, J = 7.2 Hz, 9H), 0.58–0.56 (m, 2H).

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