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MCM-41-supported mercapto platinum complex as a highly efficient catalyst for the hydrosilylation of olefins with triethoxysilane

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ABSTRACT

A novel MCM-41-supported mercapto platinum complex was conveniently synthesized from commercially available and cheap γ-mercaptopropyltriethoxysilane via immobilization on MCM-41, followed by reacting with potassium chloroplatinite. The powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to characterize the title platinum complex. It was found that the title complex is an efficient catalyst for hydrosilylation of olefins with triethoxysilane and can be reused several times without noticeable loss of activity.

1. Introduction

The hydrosilylation of alkenes is an important industrial process, but is also extremely valuable in laboratory scale synthesis as well and a variety of silicon monomers containing functional groups have been synthesized via this reaction [1]. Many metal complexes are known to be catalysts for the reaction [2], but the discovery by Speier et al. that hexachloroplatinic acid is a highly efficient catalyst, even under ambient conditions [3], has led to Pt complexes becoming the catalysts of choice for these reactions. Generally, hydrosilylation is performed in the liquid phase using a homogeneous catalyst. However, separation of the catalyst from the reaction mixture may be troublesome. Over the past few decades major research efforts have been devoted to the development of a new generation of heterogenized transition metal complex catalysts. This type of catalyst can combine the advantages of easy catalyst recovery, characteristic for a heterogeneous catalyst, with the high activity and selectivity of soluble complexes [4,5]. These ‘third generation’ catalysts [4,6] have received much attention [7–14]. In the preparation of supported catalysts a wide variety of support materials have been used including cross-linked polymers [12,14–16], silica [13,17–20], high surface area glasses [21] and dendrimers [22–25]. Functionalized polysiloxane grafted on fumed silica is a better support because they have large surface area, high mechanical strength, heat and chemical stability. Polysiloxane grafted on fumed silica-supported phosphine platinum complex has been proved to be efficient catalyst for hydrosilylation of olefins with triethoxysilane [26]. It is known that catalysts containing phosphine ligands are unstable at high temperatures [27–29]. Furthermore, the procedure for preparing the polymer-bound phosphine platinum complex is rather complicated since the synthesis of the phosphine ligands requires multi-step sequences. Therefore, the development of phosphine-free heterogeneous platinum catalysts having a high activity and stability 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 immobilization of homogeneous catalysts [30]. MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area >700 m^2/g. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [31,32]. Shyu et al. reported 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

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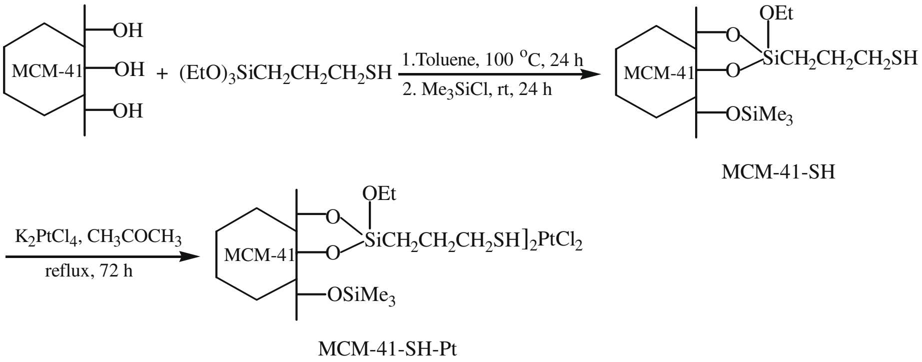

Scheme 1. Preparation of the MCM-41-SH-Pt complex.

of cyclohexene [33]. However, to the best of our knowledge, no hydrosilylation reaction of olefins with triethoxysilane catalyzed by MCM-41-supported transition metal complexes has been reported until now. In this paper, we wish to report the synthesis of MCM-41-supported mercapto platinum complex (abbreviation: MCM-41-SH-Pt) and its catalytic properties in the hydrosilylation of olefins with triethoxysilane.

2. Experimental

The mesoporous material MCM-41 was prepared according to literature procedure [34]. Acetone, triethoxysilane and olefins were distilled before use, other reagents were used as received without further purification.

2.1. Preparation of the catalyst

2.1.1. Preparation of MCM-41-SH

A solution of γ-mercaptopropyltriethoxysilane (1.70 g, 7.1 mmol) in dry $CHCl_3$ (12 ml) was added to a suspension of the mesoporous support MCM-41 (2.20 g) in dry toluene (120 ml). The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2×20 ml), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me_3SiCl (3.05 g, 28 mmol) in dry toluene (100 ml) at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3×20 ml) and diethyl ether (3×20 ml), and dried in vacuum at 160 °C for 5 h to obtain 2.82 g of hybrid material MCM-41-SH. The sulfur content was found to be 0.95 mmol/g by elemental analysis.

2.1.2. Preparation of MCM-41-SH-Pt

To a solution of K_2PtCl_4 (0.205 g) in acetone (50 ml) was added MCM-41-SH (1.51 g). The mixture was heated at reflux under nitrogen for 72 h. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under nitrogen for 3 h to give 1.438 g of the light yellow platinum complex (MCM-41-SH-Pt). The sulfur and platinum content was 0.78 mmol/g and 0.22 mmol/g, respectively.

2.2. Characterization techniques of the catalyst

Microanalyses were obtained using a Perkin–Elmer 240 elemental analyzer. 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 (Rigaku). The BET surface area and pore analysis were performed on ASAP2010 (micromeritics) by N_2 physical adsorption–desorption at 77.4 K.

2.3. Hydrosilylation of olefins with triethoxysilane

Hydrosilylation was carried out in a 5 ml plane-bottomed flask equipped with a magnetic stirrer and a reflux condenser to the upper of which a drying system was attached. Olefin and 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 5.0 mmol, platinum complex 5.0×10^{-3} mmol Pt. The catalyst can be recovered by simple filtration and reused in the next run without any treatment.

All hydrosilylation products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were obtained using a Perkin–Elmer 683 instrument. ^1H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent.

3. Results and discussion

The novel MCM-41-supported mercapto platinum complex [MCM-41-SH-Pt] was conveniently synthesized from commercially available and cheap γ-mercaptopropyltriethoxysilane via immobilization on MCM-41, followed by reacting with potassium chloroplatinite (Scheme 1). The XRD analysis of the MCM-41-SH-Pt indicated that, in addition to an intense diffraction peak (1 0 0), two higher order peaks with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41. The nitrogen adsorption studies demonstrated that significant decreases in surface area and pore size by virtue of modification of the MCM-41 were observed. The MCM-41 had surface area of 904.6 m^2/g and diameter of 2.7 nm, however, MCM-41-SH-Pt had surface area of 653.5 m^2/g and diameter of 2.2 nm. Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize this polymeric platinum complex. The S:Pt mole ratio of the MCM-41-SH-Pt was determined to be 3.54. The XPS data for MCM-41-SH-Pt, MCM-

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

Sample	$Pt_{4f7/2}$	S_{2p}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-SH-Pt	72.2	163.9	103.4	532.9	198.8
MCM-41-SH		163.4	103.4	532.8	
K_2PtCl_4	73.1				198.9
Pt foil	71.2				

[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.

41-SH, 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-SH-Pt are similar to those of MCM-41-SH, and the binding energy of Cl_{2p} of MCM-41-SH-Pt is similar to that of K_2PtCl_4. However the difference of S_{2p} binding energies between MCM-41-SH-Pt and MCM-41-SH is 0.5 eV. The binding energy of $Pt_{4f7/2}$ in MCM-41-SH-Pt is 0.9 eV less than that in K_2PtCl_4, but 1.0 eV larger than that in Pt foil. These results show that a coordination bond between S and Pt is formed. Considering the fact that the S:Pt mole ratio of the MCM-41-SH-Pt is 3.54 and platinum usually forms four coordinate complexes, we supposed that two SH groups are coordinated to one platinum center in MCM-41-SH-Pt.

In order to evaluate the catalytic activity of the novel MCM-41-supported mercapto platinum complex catalyst, the hydrosilylation reaction of olefins with triethoxysilane was studied. At first, the catalytic activity of this supported platinum complex at different temperatures was investigated using the hydrosilylation of 1-decene with triethoxysilane as the model reaction. The results are presented in Fig. 1. The experimental results show that there was an induction period of about 15 min at 90 °C, however, no remarkable induction period was observed at 100 °C and the reaction rate increased with increase in the reaction temperature. When the hydrosilylation reaction was carried out at 110 °C, decyltriethoxysilane was obtained in 94% yield after 80 min. So, for the temperatures evaluated [90, 100, 110, 120 °C], 110 °C gave the best result, which has good reproducibility of the experiments.

The effect of the amount of the MCM-41-SH-Pt complex on the hydrosilylation reaction was also investigated using 5.0 mmol of 1-decene as substrate at 110 °C and the results are shown in Fig. 2. It was found that the reaction rate increased with increase of the amount of the catalyst, for the amount evaluated [1.0×10^{-3}, 5.0×10^{-3}, 2.0×10^{-2} mmol Pt], 5.0×10^{-3} mmol Pt gave the best result, decyltriethoxysilane was obtained in 94% yield. When 2.0×10^{-2} mmol of MCM-41-SH-Pt was used, the reaction rate was the fastest, but the final yield of decyltriethoxysilane was only 89% and tetraethoxysilane was formed in 4% yield.

Hydrosilylation reactions of a variety of olefins with triethoxysilane were studied at 110 °C using 1 mol‰ of MCM-41-SH-Pt as catalyst, the typical results are listed in Table 2. As shown in Table 2, in the presence of catalytic amount of MCM-41-SH-Pt catalyst, hydrosilylation reactions of 1-decene, 1-dodecene and ω-chloro-1-undecene with $HSi(OEt)_3$ proceeded smoothly, the corresponding hydrosilylation products were obtained in 90–94% yields. Speier's catalyst was not so effective when $HSi(OEt)_3$ was used. It was reported that the yield of decyltriethoxysilane was only 40% in the case of using H_2PtCl_6 as catalyst [35]. Under the same conditions, hydrosilylation reactions of allyl phenyl ether, allylbenzene and allyl glycidyl ether with $HSi(OEt)_3$ could also proceed smoothly to give the corresponding addition products in good yields. Hydrosilylation of styrene with $HSi(OEt)_3$ afforded α-adduct in 18% yield in addition to the β-adduct as a major product. In order to show the effect of mesoporous structure on activity of MCM-41-SH-Pt, we prepared the silica-supported mercapto platinum complex ("Si"-SH-Pt) from γ-mercaptopropyltriethoxysilane via immobilization on silica, followed by reacting with potassium chloroplatinite. It was found that hydrosilylation reaction of 1-decene with $HSi(OEt)_3$ at 110 °C using 1 mol‰ of "Si"-SH-Pt as catalyst afforded decyltriethoxysilane in only 82% yield, which showed that the mesoporous structure of MCM-41 plays an important role in hydrosilylation reaction catalyzed by MCM-41-SH-Pt. We also measured the activity of MCM-41-SH (without Pt) in hydrosilylation of olefins with $HSi(OEt)_3$ and it was found that no reaction was observed.

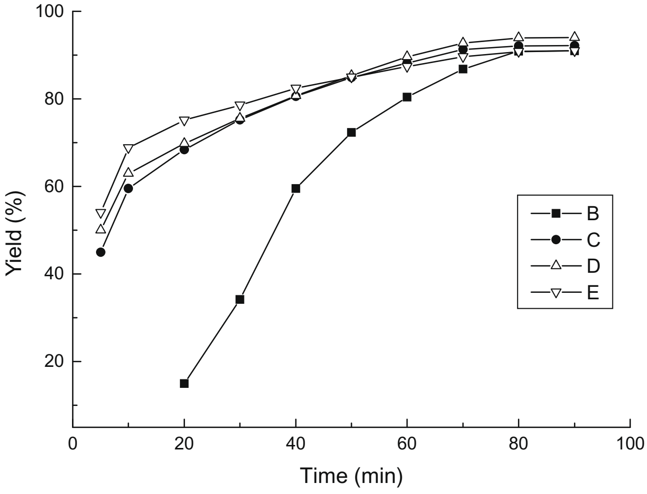

Fig. 1. Effect of reaction temperature on the yield of decyltriethoxysilane. *Conditions:* 1-decene 5.0 mmol, HSi(OEt)3 5.0 mmol, catalyst 5.0×10^{-3} mmol Pt. B: 90 °C, C: 100 °C, D: 110 °C, E: 120 °C.

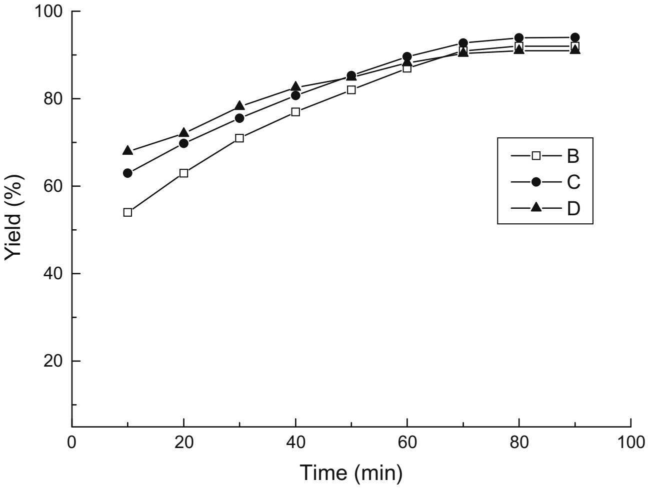

Fig. 2. Effect of the amount of the catalyst on the yield of decyltriethoxysilane. *Conditions:* 1-decene 5.0 mmol, HSi(OEt)3 5.0 mmol, reaction temperature 110 °C. B: 1.0×10^{-3} mmol Pt, C: 5.0×10^{-3} mmol Pt, D: 2.0×10^{-2} mmol Pt.

A further objective of our studies was to determine whether the catalysis was due to the MCM-41-SH-Pt complex or to a homogeneous platinum complex that comes off the support during the reaction and then returns to the support at the end. To test this, we focused on the hydrosilylation reaction of 1-decene with triethoxysilane. We filtered off the MCM-41-SH-Pt complex after 20 min of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (110 °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 1-decene with triethoxysilane was examined to evaluate the reusable property of MCM-41-SH-Pt. It was demonstrated that the novel supported mercapto platinum complex could be recovered by simple filtration and reused several times. The hydrosilylation of 1-decene with triethoxysilane was repeated five times using the same batch of supported catalyst, the yields of decyltriethoxysilane from the first to the 5th run were 94%, 92%, 91%, 90% and 87% clearly illustrating good reusability of the catalyst. The high stability and good reusable property of MCM-41-SH-Pt should result from the strong coordination

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

Olefin	Product[a]	Time (min)	Yield[b] (%)
$CH_3(CH_2)_7CH{=}CH_2$	$CH_3(CH_2)_9Si(OEt)_3$	80	94
$CH_3(CH_2)_9CH{=}CH_2$	$CH_3(CH_2)_{11}Si(OEt)_3$	90	90
$C_6H_5OCH_2CH{=}CH_2$	$C_6H_5O(CH_2)_3Si(OEt)_3$	70	86
$C_6H_5CH_2CH{=}CH_2$	$C_6H_5(CH_2)_3Si(OEt)_3$	110	74
$Cl(CH_2)_9CH{=}CH_2$	$Cl(CH_2)_{11}Si(OEt)_3$	80	92
$C_6H_5CH{=}CH_2$	$C_6H_5(CH_2)_2Si(OEt)_3$	130	63
 $\underset{O}{CH_2{-}CH}CH_2OCH_2CH{=}CH_2$	 $\underset{O}{CH_2{-}CH}CH_2O(CH_2)_3Si(OEt)_3$	100	85

Conditions: olefin, 5.0 mmol; triethoxysilane, 5.0 mmol; MCM-41-SH-Pt, 5.0×10^{-3} mmol; temperature, 110 °C.

[a] The structure of product was further identified by ^1H NMR.

[b] No increase in yield with increasing the reaction time.

of mercapto ligand on platinum and the mesoporous structure of the MCM-41-support.

4. Conclusion

We have described a novel MCM-41-supported mercapto platinum complex whose preparation is very simple and convenient. This complex has not only high activity for hydrosilylation of olefins with triethoxysilane, but offers practical advantages such as easy handling, separation from the product and reuse.

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