Immobilization of Rh(PPh$_3$)$_3$Cl on phosphinated MCM-41 for catalytic hydrogenation of olefins

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The complex Rh(PPh$_3$)$_3$Cl immobilized on MCM-41 modified with (OEt)$_3$Si(CH$_2$)$_3$PPh$_2$ results in a stable hydrogenation catalyst with turnover frequency (TOF) three times higher than that of Rh(PPh$_3$)$_3$Cl in the hydrogenation of cyclohexene.

Immobilization of homogeneous catalysis by anchoring the catalyst (usually a metal complex) on a solid support has been studied extensively in the past two decades.[1,2] Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[3] MCM-41 has a regular pore diameter of *ca.* 50 Å and a specific surface area > 700 m^2 g^{-1}.[4] 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.[5] In addition, the regular pore size of MCM-41 can provide shape selectivity not provided by silica gel.

Homogeneous catalysts RhR$_3$Cl (R = Ph, C$_8$H$_{12}$) have been successfully immobilized on solid supports through anchoring ligands [*e.g.* –(CH$_2$)$_n$PPh$_2$] (n = 1, 2) which are chemically bonded to the surface of the support.[6] For Rh(III) complexes, enhancement of reactivity after immobilization was also reported.[7] By using the same method, Rh(PPh$_3$)$_3$Cl was chemically attached on the surface of MCM-41. The resultant catalyst was characterised by various spectroscopic methods, and its catalytic activity evaluated. Herein, we report the preparation, characterisation and catalytic reactivity of this heterogeneous catalyst.

MCM-41 was prepared by hydrothermal reaction of SiO$_2$ and Me$_3$(CH$_2$)$_{15}$NMe$_3$Br.[8] A powder X-ray pattern indicates that the resultant mesoporous material has a pore diameter of *ca.* 43 Å. MCM-41 was contacted with water for 10 h in order to convert the surface to Si–OH which was further reacted with (OEt)$_3$Si(CH$_2$)$_3$PPh$_2$ to produce a phosphinated MCM-41(MCM-41-P) (Scheme 1).[9] Energy dispersive spectroscopy (EDS) of MCM-41-P clearly indicates that the mesoporous material contains phosphorus.† Solid state ^{31}P NMR of MCM-41-P showed a signal at δ −23.2. This further indicates the ligand has been successfully anchored to the material. The complex Rh(PPh$_3$)$_3$Cl was reacted with MCM-41-P in benzene at room temperature overnight (Scheme 2). After filtration, the resultant yellow particles were washed with benzene until the filtrate was colourless. EDS showed that the sample contained Rh.‡ Solid state ^{31}P NMR of the sample showed three signals [Fig. 1(b)]. One of these corresponds to the unreacted anchoring
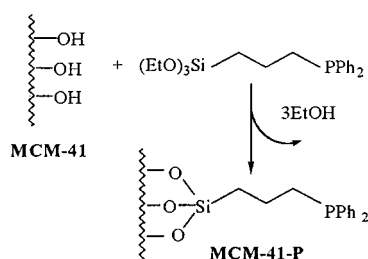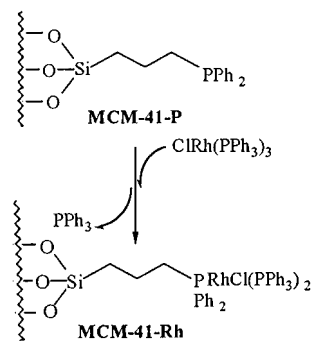
Scheme 2

ligand while the other two are assigned to the anchoring ligand and triphenylphosphine ligand coordinated to the Rh complex since they are shifted relative to the ^{31}P signal of Rh(PPh$_3$)$_3$Cl. However, exact assignments cannot be concluded. These observations indicate that Rh has been successfully immobilized on the mesoporous material.

Catalytic hydrogenation of cyclohexene to cyclohexane was used to test the catalytic activity of the hybrid complex MCM-41-Rh under 150 psi of hydrogen at 75 °C in a Parr reactor. After one cycle, the mixture was filtered and the catalyst was recovered on a filter paper. The filter paper was then cut into small pieces and used as a catalyst in the next cycle of hydrogenation. After fifteen cycles, the catalyst was still active (Fig. 2). The TOF for the first cycle was lower than that of the second cycle. This indicates that it takes some time to activate
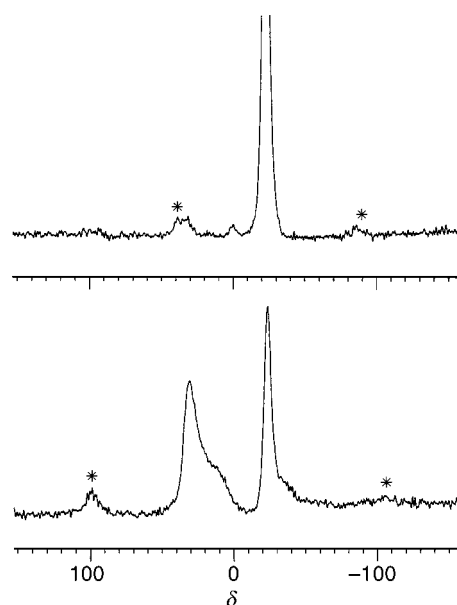
Fig. 1 Solid state ^{31}P NMR spectra of (a) MCM-41-P and (b) MCM-41-Rh. ^{31}P one-pulse experiments were performed on a Bruker AMX 400 spectrometer at a ^{31}P frequency of 161.98 MHz at room temperature. Chemical shifts were referenced to Na$_2$HPO$_4$ at 0 ppm. Signals arising from side bands are marked with asterisks.
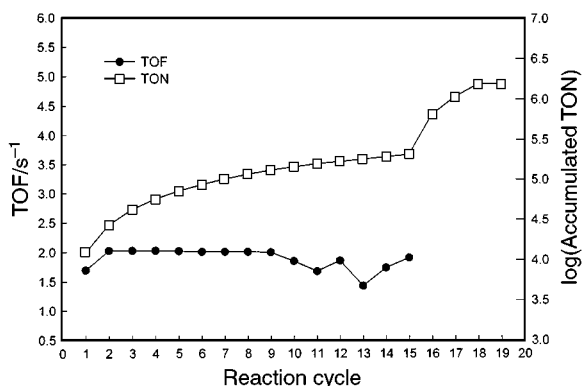
Scheme 1

Fig. 2 Turnover frequecy (TOF) and accumulated turnover number (TON) for hydrogenation of cyclohexene by MCM-41-Rh under 150 psi of hydrogen at 75 °C. Product yields were determined by GC. For cycles 1–14, each cycle took 2 h and the solution concentration (cyclohexene in benzene) was 1.6 M. For cycles 15–18, pure cyclohexene was used. The catalyst was prepared by immobilization of 5.01 mg (5.41×10^{-3} mmol) of $Rh(PPh_3)_3Cl$ on 17.1 mg of MCM-41-P.

the catalyst to its best performance level. After the first cycle, the TOF reached *ca.* 2.0 s^{-1} and remained steady up to ten cycles.§ In order to estimate the TON, the hydrogenation of cyclohexene was carried out in pure cyclohexene. The total turnover number was $>10^6$.¶

In order to evaluate the possibility of leaching,[10] solvent was removed from the reaction solution and benzene (3.0 ml) was added to the reactor to dissolve any possible remaining Rh complex. The UV spectrum of the solution was then recorded. The solution was then filtered through silica gel which can remove any Rh complex and the UV spectrum of the filtrate was run. The difference in absorbance between these two measurements should correspond to absorbance of leached Rh complex. The concentration of leached Rh complex was calculated according to the reported ε value (≈ 6000) at 360 nm of $Rh(PPh_3)_3Cl$.[11] The calculated amount of leached Rh complex is 1.4×10^{-9} mol *i.e. ca.* 0.3% of the Rh complex in the original catalyst.‖

The hydrogenation reaction was also carried out at ambient temperature under 1 atm of hydrogen. The catalyst was prepared by immobilization of 15.5 mg (1.68×10^{-2} mmol) of $Rh(PPh_3)_3Cl$ on 51.0 mg of MCM-41-P. For the first few hours, the catalyst was inactive. This indicates again that some time is required to activate the catalyst. The TOF is *ca.* 150 h^{-1} after subtracting the activation period from the total reaction time.

In order to evaluate the relative activity of MCM-41-Rh, hydrogenation of cyclohexene to cyclohexane with an equivalent amount of $Rh(PPh_3)_3Cl$ was carried out under the same reaction condition (150 psi hydrogen, 75 °C) and theTOF of the

reaction was 0.7 s^{-1}. Hence, the TOF of MCM-41-Rh is *ca.* three times that of $Rh(PPh_3)_3Cl$.

The reason for the higher TOF for the hybride catalyst relative to the homogeneous catalyst is not clear. Similar observations were reported when a solid support such as SiO_2 was used for the immobilization of homogeneous catalysts.[7]

Notes and references

† P/Si ratio analysis by EDS: 18(1). The ZAF (Z: atomic number effect, A: absorption of X-rays within the specimen, F: fluorescence effect) method was used in the analysis. 30 data points were randomly obtained from each sample.
‡ Rh/Si ratio analysis by EDS: 6.0(7). The ZAF method was used in the analysis. 10 data points were randomly obtained from each sample.
§ Mol substrate reduced (mol catalyst)$^{-1}$ s^{-1}.
¶ Mol substrate reduced (mol catalyst)$^{-1}$.
‖ For the fifth reaction cycle, the absorbance of the solution is 7.32×10^{-3} ($\sigma = 0.84 \times 10^{-3}$). The absorbance of the filtrate is 4.62×10^{-3} ($\sigma = 0.58 \times 10^{-3}$).

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