High efficiency and reusability of iridium complexes adsorbed in montmorillonite clay on catalytic hydrogenation of imines

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Heterogenised homogeneous catalytic hydrogenation of aldimines by removable and reusable immobilised iridium complexes on montmorillonite clay.

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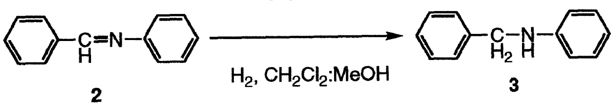
Although metal transition complexes are well known as homogeneous catalytic systems in the hydrogenation of imines to secondary amines [1], only little attention has been devoted to separating them from the products of the reaction. Efficient catalytic hydrogenation of imines has been achieved with a two-phase system using a water-soluble catalyst [2], reverse micelles [3] and zwitterionic complexes [4], but to our knowledge there have been no further studies into the recovery and reusability of the removable catalytic systems. Indeed, these properties might be ignored in small-scale hydrogenation reactions in the laboratory, but they are very significant for the economic and technological viability of the large-scale production of amines.

Immobilising complex catalysts in clay structures makes it possible to conduct solution-like reactions in the solid state and minimize many of the barriers associated with the unremovable homogeneous solution catalysts. Smectite clays such as montmorillonite have recently attracted interest as supports for heterogenised homogeneous catalysts, because they combine cation exchange, intercalation and swelling properties which makes them unique [5].

Thus, taking all these considerations into account, we report now the hydrogenation of imines with transition metal complexes heterogenised into montmorillonite in order to study the activity of the supported catalysts and compare them with their homogeneous counterparts. We have already reported that cationic iridium complexes can be efficiently used in the homogeneous hydrogenation of the aldimine N-benzylidene aniline [6]. We now describe the adsorption of $[Ir(COD)(PPh_3)_2]X$ (**1**) ($X = PF_6$, BF_4) into montmorillonite and its recovery and reusability for a number of recycles in the hydrogenation of N-benzylidene aniline with a consistently high rate of activity, depending on the previous treatment of the clay and the counterion of the cationic iridium complex (scheme 1).

The cationic iridium complex was immobilised into the clay under N_2 at room temperature by stirring **1** ($X = PF_6$, BF_4) and commercial montmorillonite K-10 in dichloromethane for 24 h. The amount of metal complex adsorbed by the clay was determined by gravimetric analysis in which the difference between the weights of the complex before and after immobilisation was measured (table 1). These data suggest that the percentage of iridium complex adsorbed into the clay (93%, table 1, entry 5), is highest when the counterion is BF_4 and the montmorillonite is previously dried at 90 °C for 24 h to eliminate the small amount of interlamellar water that the clay may contain. The reddish iridium-adsorbed montmorillonite was filtered off and washed with dichloromethane. Conductometric analysis of the filtrate and repeated washing indicated that M^{n+} from montmorillonite was not replaced by $[Ir(COD)(PR_3)_2]^+$ and, therefore, the metal complex was not intercalated, rather it was adsorbed (scheme 2). The powder X-ray diffraction of the product showed the characteristic structure of lamellar montmorillonite. The iridium complex was mainly adsorbed in the external surface in basis to the insignificant shift of the (001) diffraction line. Earlier however, it has been reported the immobilisation of the same cationic iridium complex into montmorillonite clay via intercalation, although in these cases the sodium montmorillonite was obtained by purifying bentonite according to the method of van Olphen [7], and before immobilisation the solid was swelled in acetonitrile [8] or water [9]. However, Crocker and Herold [10] noticed that Pd(II) complexes could also be immobilised in sodium montmorillonite via an ion-exchange procedure, but in the case of montmorillonite K-10 the palladium concentration



Scheme 1.

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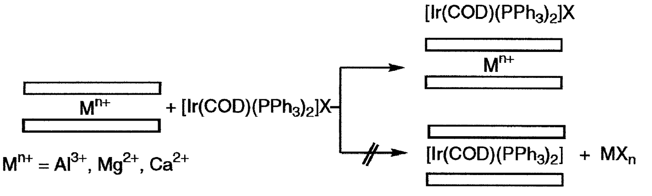
Table 1
Adsorbed $[Ir(COD)(PPh_3)_2]X$ (**1**) ($X = PF_6$, BF_4) in montmorillonite.

Entry	Clay[a]	Grams	Complex	Initial mg	Adsorbed mg	mmol complex/ g clay	Adsorbed %
1	K-10[b]	1.099	**1**, $X = PF_6$	98.7	12.0	0.075	88
2	K-10[c]	1.098	**1**, $X = PF_6$	98.6	33.3	0.058	66
3	K-10[d]	1.099	**1**, $X = PF_6$	99.3	28.8	0.062	71
4	K-10[e]	1.099	**1**, $X = PF_6$	99.2	13.9	0.074	86
5	K-10[b]	1.099	**1**, $X = BF_4$	94.0	6.7	0.081	93

[a] Clay: commercial montmorillonite Fluka K-10.
[b] Predried at 90 °C for 24 h.
[c] No predried at 90 °C for 24 h.
[d] Previously calcined at 500 °C for 30 min.
[e] Previously acidified with HNO_3.



Scheme 2.

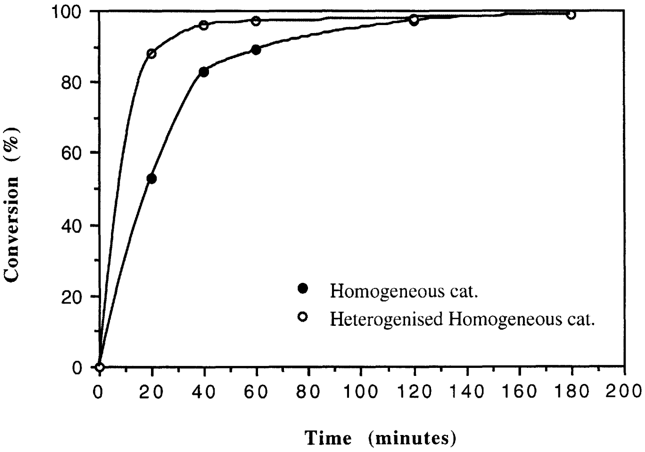


Figure 1. Evolution of the hydrogenation of N-benzylidene aniline with heterogenised homogeneous and homogeneous catalysts.

tended to be higher on the surface than in the bulk. This is problably due to acid treatment in the commercial production of K-10, which destroys the octahedral layer of the clay resulting in a partial suppression of the lattice negative charge and a reduction of the crystallinity of the solid.

To compare the activity and stability of the supported catalyst K-10/**1**, $X = PF_6$, with its homogeneous counterpart, the hydrogenation of N-benzylidene aniline was carried out under standard conditions (CH_2Cl_2/MeOH (1 : 1) as the solvent, 5 atm hydrogen pressure, 40 °C, 3 h). The initial activity of the heterogenised catalyst was found to be higher than that of the homogeneous system (figure 1). It appears that immobilising the active catalyst on a rigid support could prevent catalytically inactive species from forming as a result of oligomerisation reactions of $[Ir(COD)(PPh_3)_2]PF_6$ [11]. Leaching the iridium complex is not responsible for the observed activity, because the amount of Ir found by adsorption analysis of the filtrate in the heterogenised hydrogenation reaction is neglible.

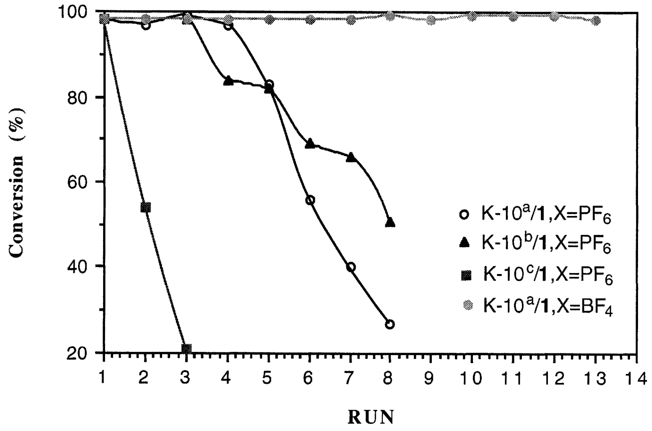


Figure 2. Catalytic activity of the heterogenised precursor of catalyst in the hydrogenation of N-benzylidene aniline. Standard conditions: N-benzylidene aniline, 4 mmol; catalyst precursor, 0.08 mmol Ir; solvent: CH_2Cl_2/MeOH (1 : 1), 8 ml; $P(H_2)$: 5 atm; temperature: 40 °C; reaction time: 3 h. [a]Commercial montmorillonite K-10. [b]Commercial montmorillonite K-10, previously calcined at 500 °C for 30 min. [c]Commercial montmorillonite K-10, previously acidified with HNO_3.

The recovered supported catalyst, K-10/**1**, $X = PF_6$, can be reused in consecutive hydrogenations and consistently shows a high activity (>97% conversion), for at least four runs (figure 2). The catalytic system was less able to be recycled than the commercial montmorillonite when the latter was previously calcined at 500 °C or acidified with HNO_3 to increase the Lewis and Brønsted centres [12] (figure 2). There was also a marked difference in the hydrogenation activity of K-10/**1**, $X = BF_4$ (figure 2), since the catalytic system could be reused in all the consecutive reactions performed, at least thirteen, with a surprisingly high activity (>98% conversion). This also shows that the counterion of the cationic iridium complex is also adsorbed into the montmorillonite, because the BF_4 seems to make the heterogenised catalytic system much more stable.

Further work related to the recycling capacity of heterogenised iridium catalyst systems in asymmetric hydrogenation of imines is in progress.

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