Stabilisation of cationic iridium hydrogenation catalysts via intercalation in montmorillonite clay

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Received 30 September 1992; accepted 13 January 1993

The olefin hydrogenation catalysts $[Ir(COD)(PPh_3)_2]^+$ and $[Ir(COD)(NCMe)(PCy_3)]^+$ have been intercalated in montmorillonite clay via an ion-exchange procedure. While the initial activity of the intercalated catalysts for the hydrogenation of cyclohexene is generally 50–80% of that of their homogeneous analogues, the intercalated catalysts remain active for longer periods, indicating that dimer- and trimer-forming reactions, responsible for deactivation of the homogeneous catalysts, are partially suppressed upon intercalation. In the hydrogenation of 1-hexene the activity of $[Ir(COD)(NCMe)(PCy_3)][BPh_4]$ for the competing process of double bond isomerisation is found to increase with the catalyst concentration.

Keywords: Montmorillonite; clay; hydrogenation; iridium; catalyst; intercalation

1. Introduction

Smectite clays are increasingly attracting interest as supports for metal and metal complex catalysts [1–5]. An important property of clays in this respect is their high surface area, with the consequence that ion-exchange sites on the surface of the clay are well dispersed. For montmorillonite the average distance between exchange sites, calculated on the basis of the cation exchange capacity (CEC) and total layer area of the clay [6], is typically in the order of 12 Å.

These considerations suggest that clays might be suitably employed as supports for those homogeneous metal complex catalysts which are prone to undergo deactivation as a result of oligomerisation reactions. An example of a group of homogeneous catalysts which fall into this category are the iridium complexes $[Ir(COD)(L)(L')][X]$ (COD = 1,5-cyclooctadiene, L = PR_3, L′ = PR_3 or N-donor ligand, X = anion), known catalysts for the hydrogenation of olefins [7–10]. Although the activity displayed by these complexes in dichloromethane solution is initially very high, it has been shown by Crabtree that they are subject to deactivation as a consequence of dimer- and trimer-forming reactions [8],

$$2[\mathrm{Ir(COD)L_2}][\mathrm{PF_6}]+7\mathrm{H_2}\rightarrow[\{\mathrm{IrHL_2}\}_2(\mu\text{-}\mathrm{H})_3][\mathrm{PF_6}]+\mathrm{HPF_6}+2\mathrm{C_8H_{16}}, \qquad (1)$$

$$3[\mathrm{Ir(COD)(L)(L')}][\mathrm{PF}]_6+10\mathrm{H_2}$$
$$\rightarrow[\{\mathrm{IrH_2(L)(L')}\}_3(\mu_3\text{-}\mathrm{H})][\mathrm{PF_6}]_2+\mathrm{HPF_6}+3\mathrm{C_8H_{16}}. \qquad (2)$$

Immobilisation of the active catalyst on a rigid support would appear to offer a means of preventing the formation of such catalytically inactive species. Furthermore, these complexes appear particularly suitable for immobilisation on a clay since they are reported to be stable to the presence of water (invariably present, even after vacuum-drying of the clay), while their hydrogenation activity is not significantly inhibited by the presence of water [11,12]. In this communication we report on the synthesis of a number of cationic Ir(I) complexes intercalated in montmorillonite, and the preliminary results of a study aimed at assessing their catalytic properties in the hydrogenation of olefins relative to their homogeneous congeners.

2. Experimental

2.1. MATERIALS

Sodium montmorillonite (MM–Na$^+$) was obtained via purification of bentonite (BDH) according to the method of van Olphen [13]. The approximate anhydrous unit cell formula determined on the basis of elemental analysis and ^{27}Al NMR MAS spectroscopy was $\mathrm{Na_{0.62}[Al_{3.16}Fe^{III}_{0.36}Fe^{II}_{0.08}Mg_{0.40}](Si_{7.86}Al_{0.14})O_{20}(OH)_4}$; the measured CEC of the clay was 82 meq/100 g. Olefins were of the highest purity available and were degassed before use. Solvents were dried and degassed before use according to standard methods. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk and high vacuum line techniques. Satisfactory elemental analyses were obtained on all iridium complexes.

2.2. PHYSICAL MEASUREMENTS

^{1}H and ^{31}P NMR spectra were recorded at room temperature on a Bruker AC 250 spectrometer using CD_2Cl_2 as solvent. Elemental analysis for Ir was performed using the ICP method. XPS spectra were recorded on a Kratos XSAM 800 spectrometer employing the C 1s line (284.6 eV) as a binding energy standard. X-ray diffraction measurements were performed with a Philips PW 1820 powder diffractometer using Cu Kα radiation.

2.3. PREPARATION OF IRIDIUM COMPLEXES

$[Ir(COD)(PPh_3)_2][ClO_4]$ ($1^+ClO_4^-$) was prepared according to a literature procedure [9,14].

$[Ir(COD)(NCMe)(PCy_3)][X]$ (2^+X^-, $X = ClO_4$ or BPh_4): $[Ir(COD)(py)_2][X]$ [15] was dissolved in CH_3CN and the solution stirred for 6 h at room temperature with 1.05 equivalents of PCy_3. Solvent was then removed under vacuum and the residue recrystallised from CH_2Cl_2/Et_2O to afford the product as an oily solid. Trituration of this material with Et_2O gave pure $[Ir(COD)(NCMe)(PCy_3)][X]$ as a deep orange microcrystalline solid. $2^+BPh_4^-$: ^1H NMR: δ 7.40–6.88 (m, 20H, C_6H_5), 4.59 (m, 2H, CH_2), 3.93 (m, 2H, CH_2), 1.94 (s, 3H, CH_3), 2.29–1.21 (m, 41H, Cy, CH_2). ^{31}P NMR: 18.1 (s, PCy_3).

2.4. INTERCALATION OF IRIDIUM COMPLEXES IN MONTMORILLONITE

Vacuum-dried MM–Na^+ was suspended in CH_3CN (≈ 20 ml/g clay) with stirring overnight. The requisite amount of iridium complex was then added to the swollen clay in the form of a concentrated dichloromethane solution and stirring continued for 3–4 h. The clay product was isolated by filtration, washed thoroughly with dichloromethane, followed by diethyl ether and dried under vacuum (10^{-5} mbar). The combined filtrate and washings from each experiment were analysed for iridium.

2.5. HYDROGENATION EXPERIMENTS

All hydrogenation experiments were conducted using a constant pressure apparatus operating at 1 atm. Catalyst samples were pre-swollen in the reaction solvent for 1 h under nitrogen before use. In a typical procedure, a solution of the olefin (12.5 mmol) in CH_2Cl_2 (10 ml) was injected into the reaction vessel, followed by a suspension of the catalyst (equivalent to 0.025 mmol iridium) in CH_2Cl_2 (40 ml). Stirring was commenced and the volume of hydrogen consumed measured as a function of time. At regular intervals 100 μl portions of the solution were taken for GLC analysis (HP-1 cross-linked dimethylsilicone column; heptane as internal standard).

3. Results and discussion

Experiments were conducted using the complexes $[Ir(COD)(PPh_3)_2][ClO_4]$ ($1^+ClO_4^-$) and $[Ir(COD)(NCMe)(PCy_3)][X]$ (2^+X^-, $X = ClO_4$ or BPh_4) and sodium montmorillonite (MM–Na^+) as the clay support. Intercalation of the complexes was conveniently performed by ion exchange in acetonitrile (eq. (3))

employing iridium loadings of 0.1–0.3 mmol/g clay, corresponding to replacement of about 12–35% of the Na^+ ions in the clay,

$$\mathrm{MM{-}Na^+ + [Ir(COD)(L)(L')][X] \rightarrow MM{-}[Ir(COD)(L)(L')]^+ + NaX}\,. \quad (3)$$

X-ray diffractograms of products confirmed that the complexes were intercalated between the clay sheets (vide infra), while XPS and elemental analysis data were consistent with a homogeneous dispersion of the iridium complexes throughout the clay support.

In order to compare the activity and stability of the intercalated catalysts with their homogeneous counterparts, hydrogenation reactions were carried out under standard conditions (CH_2Cl_2 as solvent, 1 atm hydrogen pressure, 17°C) using cyclohexene as substrate. Considering first complex $\mathbf{1}^+$, it is found that the homogeneous system, in the form of the ClO_4^- salt, initially shows high activity (765 turnovers h^{-1}, see table 1), after which deactivation occurs (at about 55% olefin conversion). In comparison, $\mathbf{1}^+$ intercalated in MM–Na^+ shows about 50% of the initial activity of the homogeneous system, but is more stable, so that quantitative yields of cyclohexane can be obtained. Similar results are obtained with $\mathbf{2}^+$ (fig. 1), the intercalated cation showing $\approx$ 85% of the initial activity of $\mathbf{2}^+ClO_4^-$.

A marked difference is also observed in the hydrogenation activity of the ClO_4^- and BPh_4^- salts of $\mathbf{2}^+$ (fig. 1), the BPh_4^- salt undergoing deactivation more rapidly, so that an olefin conversion of only 2% is obtained. Similar findings have been previously reported by Schrock and Osborn [16] for hydrogenation reactions catalysed by cationic rhodium complexes, deactivation of the BPh_4^--containing catalysts occurring as a result of coordination of the anion to the metal via a π-bonded interaction of one of the phenyl rings. This would also appear to be the case for $\mathbf{2}^+BPh_4^-$.

The possibility that the catalysis observed in the above intercalated systems actually originates from the presence of the leached complex (in the liquid phase), or

Table 1
Cyclohexene hydrogenation catalysed by homogeneous and intercalated iridium complexes[a]

Complex[b]	Support	Cyclohexane yield (%)	Reaction time (min)	Turnover rate (mol alkane/ mol Ir · h)[e]
$1^+ClO_4^-$	–	55[c]	165	765
1^+ (1.9%)	MM–Na^+	37[d]	150	385
$2^+ClO_4^-$	–	53[c]	180	990
$2^+BPh_4^-$	–	2[c]	60	>250
2^+ (6.5%)	MM–Na^+	83[d]	221	865

[a] Conditions: [Ir] = 0.5 mM, [alkene] = 0.5 M, T = 290 K, $P(H_2)$ = 1 bar, solvent = CH_2Cl_2 (50 ml).
[b] Figures in parentheses represent Ir loading (wt%) on support.
[c] Final yield (measured after deactivation of catalyst).
[d] Yield at termination of experiment (catalyst still active).
[e] Measured initial rate (calculated from linear portion of hydrogenation curve).

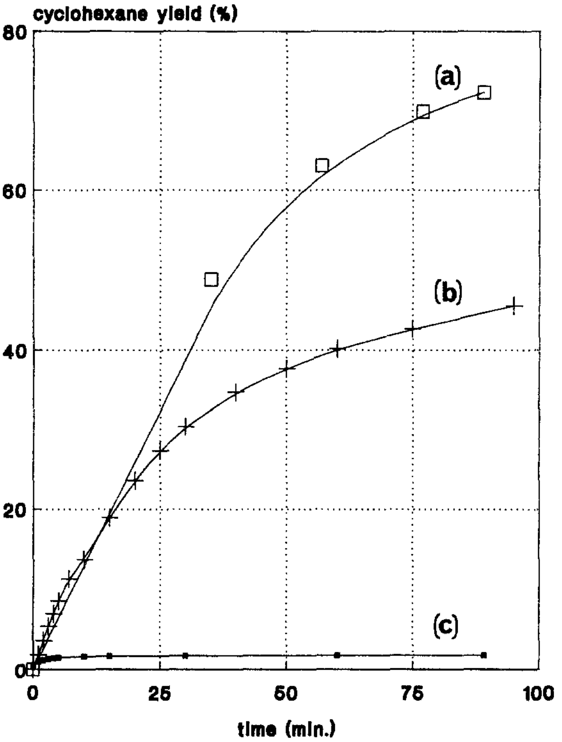

Fig. 1. Reaction profiles for cyclohexene hydrogenation catalysed by (a) MM–$Na^+/2^+$, (b) $2^+ClO_4^-$ and (c) $2^+BPh_4^-$.

from dispersed metal particles formed via decomposition of the immobilised complex, can be discounted on the basis of the observations that:

(1) the filtrate from an active catalyst suspension is completely inactive - thus leaching of the Ir complex is not responsible for the observed activity; furthermore, X-ray diffraction data on used catalyst samples are consistent with the continued presence of Ir complexes between the clay sheets (fig. 2);

(2) XPS data on the immobilised complexes before and after hydrogenation show no change in the surface iridium concentration; furthermore, after hydrogenation no Ir(0) is detected, the observed binding energies for the Ir $4f_{7/2}$ level being consistent with the presence of iridium in the 3+ oxidation state (fig. 3; note that the increased oxidation state of the Ir as compared with the starting Ir(I) complexes is consistent with their conversion to dihydride or alkyl–hydride complexes);

(3) addition of Hg to the catalyst suspension does not result in any lowering of the catalytic activity, implying that iridium metal is not responsible for the observed hydrogenation activity [17].

On the basis of these observations we conclude that the catalytically active species is an immobilised iridium complex. It appears that the formation of catalyti-

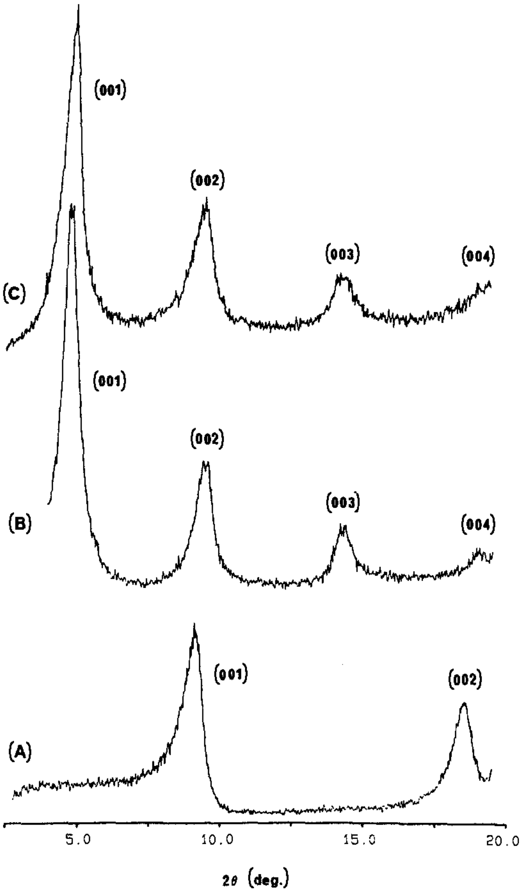

Fig. 2. X-ray diffractograms of (A) MM–Na$^+$, (B) MM–Na$^+$/2$^+$ before cyclohexene hydrogenation and (C) MM–Na$^+$/2$^+$ after cyclohexene hydrogenation.

cally inactive hydrogen-bridged dimeric and trimeric iridium species cannot be completely suppressed by intercalation of the precursors, however, since the intercalated systems tend towards deactivation when the olefin has been consumed, although this phenomenon is less marked than for their homogeneous analogues.

Intercalation of the cations 1^+ and 2^+ in montmorillonite also proves beneficial in the hydrogenation of 1-hexene. For both the homogeneous and intercalated catalysts isomerisation of the olefin to cis- and trans-2-hexene is found to be a competing reaction (table 2). Interestingly, the isomerisation activity of the homogeneous catalysts is found to increase with the catalyst concentration, as illustrated by the results obtained with $2^+BPh_4^-$ (see fig. 4 and table 2). This suggests that at high catalyst concentrations a second, possibly polynuclear iridium species is formed which contributes significantly to the isomerisation activity of the system. These putative iridium species do not correspond to catalyst deactivation products (such as the dimers and trimers discussed in section 1), since cessation of hydroge-

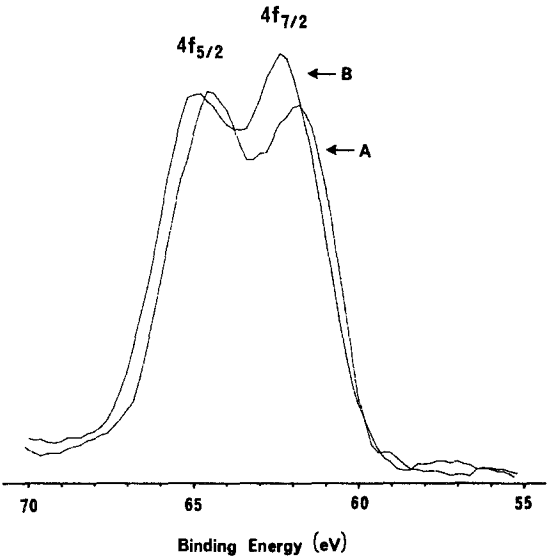

Fig. 3. XPS spectra (70–55 eV) of MM-$Na^+/2^+$ before (A) and after (B) cyclohexene hydrogenation.

nation activity is always accompanied by a concomitant cessation of olefin isomerisation. In contrast, increasing the quantity of intercalated clay catalyst employed for the hydrogenation reaction (at a given loading of the iridium complex) has no effect on the observed isomerisation activity.

We note that Evans and Morrissey [18] have previously postulated the existence of catalytically active oligomeric iridium species in hydroxyl-directed hydrogenation reactions of olefinic alcohols catalysed by $[Ir(COD)(py)(PCy_3)][PF_6]$. On the basis of their observation that the selectivity to the directed hydrogenation product was greater at lower catalyst–substrate stoichiometries for a given substrate concentration, they suggested that at high catalyst concentrations a second catalyti-

Table 2
1-hexene hydrogenation catalysed by homogeneous and intercalated 2^+ [a]

Complex	[Ir] (mmol/ℓ)	Yield (%)[b]			Reaction time (min)	Turnover rate (mol hexane/ mol Ir · h)
		hexane	t-2-hexene	c-2-hexene		
$2^+BPh_4^-$	0.5	11[c]	0.5 (0.6)	0.2 (0.5)	60	825
$2^+BPh_4^-$	2.3	34[c]	7.4 (7.6)	1.0 (1.4)	555	175
$2^+BPh_4^-$	6.7	62[c]	26 (27)	5.7 (6.3)	165	65
MM-$Na^+/2^+$	0.5	89[d]	4 (5)	0.7 (1.8)	60	835

[a] Conditions as for table 1, except [alkene] = 0.25 M.

[b] Maximum yields of 2-hexene attained during experiment given in parentheses.

[c] Final yield (measured after deactivation of catalyst).

[d] Yield at termination of experiment (catalyst still active).

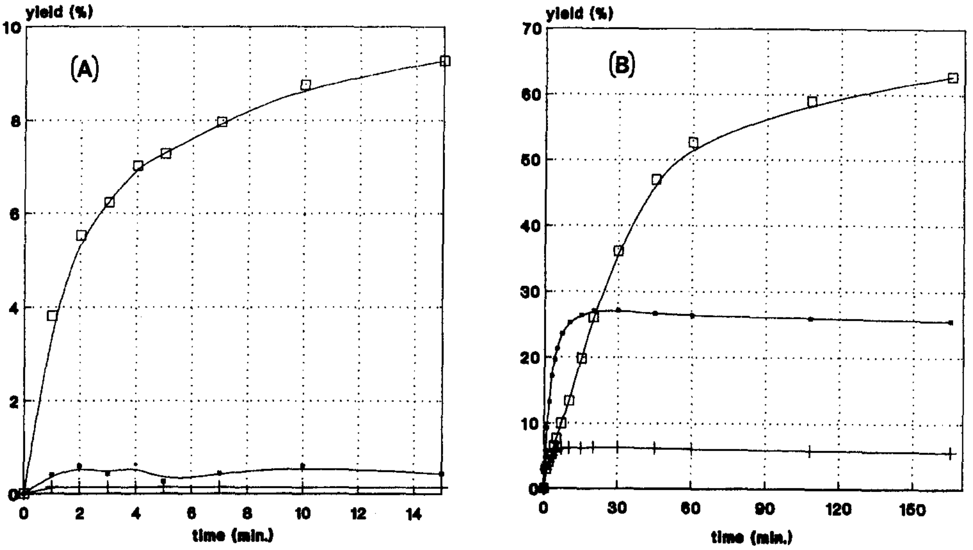

Fig. 4. Reaction profiles for homogeneous 1-hexene hydrogenation catalysed by $2^+BPh_4^-$ at concentrations of (A) 0.5 mM and (B) 6.7 mM. (■) t-2-hexene, (+) c-2-hexene, (□) hexane.

cally active species may be present (possibly a polynuclear iridium species), which is not constrained to the same hydroxyl directivity effects as the mononuclear complex. Our observations suggest that such species also possess considerable isomerisation activity.

4. Conclusion

In summary, it has been demonstrated that the stability of a number of cationic iridium hydrogenation catalysts can be improved by intercalation in montmorillonite clay. Observations made concerning the hydrogenation of 1-hexene suggest that at high (homogeneous) catalyst concentrations oligomeric iridium species can form which possess significant isomerisation activity, an effect which can be avoided by intercalation of the catalyst in montmorillonite. These results exemplify the benefits that can arise from "heterogenising" homogeneous catalysts when due regard is paid to the choice of catalyst and support.

Acknowledgement

The authors thank M. Krijger and G.M. Mulder for X-ray diffraction and XPS measurements, M. Oude-Wolbers for preliminary experiments and Dr. H.P.C.E. Kuipers for helpful discussions.

References

[1] T.J. Pinnavaia, in: *Preparative Chemistry Using Supported Reagents*, ed. P. Laszlo (Academic Press, London, 1987) pp. 483–501.

[2] B.M. Choudary, K. Ravi Kumar and L. Lakshmi Kantam, J. Catal. 130 (1991) 41.

[3] M.M. Taqui Khan, S.A. Samad, M.R.H. Siddiqui, H.C. Bajaj and G. Ramachandraiah, Polyhedron 10 (1991) 2729.

[4] S. Shimazu, T. Ishida and T. Uematsu, J. Mol. Catal. 55 (1989) 353.

[5] M. Crocker and R.H.M. Herold, J. Mol. Catal. 70 (1991) 209.

[6] H. van Olphen, *An Introduction to Clay Colloid Chemistry*, 2nd Ed. (Wiley–Interscience, New York, 1977) p. 254.

[7] J.R. Shapley, R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc. 91 (1969) 2816.

[8] R.H. Crabtree, Acc. Chem. Res. 12 (1979) 331.

[9] R. Uson, L.A. Oro and M.J. Fernandez, J. Organomet. Chem. 193 (1980) 127.

[10] C.S. Chin and B. Lee, J. Chem. Soc. Dalton Trans. (1991) 1323.

[11] R.H. Crabtree, P.C. Demou, D. Eden, J.M. Mihelcic, C.A. Parnell, J.M. Quirk and G.E. Morris, J. Am. Chem. Soc. 104 (1982) 6994.

[12] R.H. Crabtree, H. Felkin and G.E. Morris, J. Organomet. Chem. 141 (1977) 205.

[13] H. van Olphen, *An Introduction to Clay Colloid Chemistry*, 2nd Ed. (Wiley–Interscience, New York, 1977) pp. 249–251.

[14] L.M. Haines and E. Singleton, J. Chem. Soc. Dalton Trans. (1972) 1891.

[15] R.H. Crabtree and G.E. Morris, J. Organomet. Chem. 135 (1977) 395.

[16] R.R. Schrock and J.A. Osborn, Inorg. Chem. 9 (1970) 2339.

[17] D.R. Anton and R.H. Crabtree, Organometallics 2 (1983) 855, and references therein.

[18] D.A. Evans and M.M. Morrissey, Tetrahedron Lett. 25 (1984) 4637.