# Enhanced catalytic activity of MCM-41-grafted aluminium isopropoxide in MPV reductions

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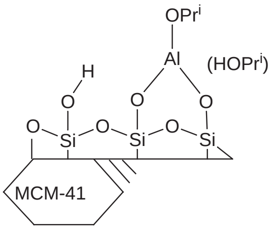
**Aluminium alkoxide moieties are grafted onto purely siliceous mesoporous MCM-41 *via* siloxide linkages, producing materials which reveal enhanced catalytic activity in the MPV reduction of cyclic ketones; nitrogen physisorption and $^{27}$Al MAS NMR spectroscopy are applied to characterise the catalytically active hybrid systems.**

The potential of aluminium reagents, in particular ‘Al(OPr$^i$)$_3$’, in Meerwein–Ponndorf–Verley (MPV) reductions and Oppenauer oxidations is well documented.[1,2] Although these transformations formally proceed catalytically, an excess of the aluminium compound is commonly required.[3] Heterogeneously performed MPVO reactions utilising, for example, oxidic or zeolitic materials have also been reported to cope better with catalyst separation.[4,5] Recently, we and others envisaged the mesoporous silicate MCM-41 as a versatile support material for metalorganic moieties.[6,7] As part of this program, we present our preliminary findings on the catalytic MPV reduction of 4-*tert*-butylcyclohexanone mediated by grafted aluminium alkoxide species, including a detailed $^{27}$Al MAS NMR study.

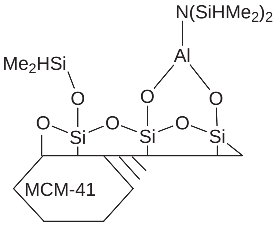
MCM-41-supported aluminium isopropoxide **2** was initially prepared according to a one-step solution impregnation by contacting Al(OPr$^i$)$_3$ and MCM-41 **1** in *n*-hexane.‡,§[8,9]

Assuming a monofunctional surface reaction, a ligand/metal ratio of *ca.* 2.0 can be derived for material **2** from elemental analysis (Table 1). Furthermore, an aluminium surface coverage of *ca.* 1.3 Al nm$^{-2}$ can be calculated from the metal content and the BET surface area of material **1** (1059 m$^2$ g$^{-1}$). A considerable amount of unreacted isolated silanol groups is still present after the grafting procedure as indicated by the $\nu$(OH) vibration mode at 3695 cm$^{-1}$ in the IR spectrum. Al(OPr$^i$)$_3$ immobilisation in the mesopores of material **1** drastically decreases the pore volume and pore diameter as revealed by nitrogen physisorption (Table 1). However, the obtained adsorption/desorption isotherm is still of type IV.

We found that careful drying of the solvent isopropanol ( = reductant) significantly increased the catalytic activity of Al(OPr$^i$)$_3$ in this MPV reduction (Table 2, run 1 *vs.* 2). In contrast, material **2** exhibits dramatically enhanced catalytic activity, producing 86% of the 4-*tert*-butyl cyclohexanol isomers after 5 h even at ambient temperature (run 5). At 80 °C material **2** afforded almost quantitative conversion after 30 min (run 6).¶[10] Hybrid material **2** could easily be separated from the reaction mixture of run 5 by centrifugation. After washing with HOPr$^i$ the catalytic activity of the recovered solid material (**2b**) remained unchanged (run 7). The combined HOPr$^i$ fractions showed no further activity upon addition of new substrate. We also found no catalytic activity for parent material **1** (run 3).



**2**



**3**

For comparison, recent studies by others revealed that H-MCM-41 and Na-MCM-41 (Si/Al = 15, activation temperature 450 °C) gave only 10% conversion of 4-*tert*-butylcyclohexanone after 6 h at 80 °C.[4] A zirconium hybrid system obtained according to the synthesis sequence: silica + Zr(CH$_2$Bu$^t$)$_4$ + HOPr$^i$, showed 75% conversion of cyclohexanone after 20 h at 80 °C.[5]

The efficiency of the MPV reduction is known to depend on the Lewis acidity of the metal center and the ligand exchange ability.[1,2] These factors are markedly affected by the type of (co-)ligand and co-ordination geometry at the metal center. In order to gain further insight into the co-ordination geometry of the catalytically active species, a detailed $^{27}$Al MAS NMR study was performed. The $^{27}$Al MAS NMR spectrum of Al(OPr$^i$)$_3$ shows a sharp resonance at 0 ppm typical of octahedral aluminium, accompanied by weak and broad signals

**Table 1** Analytical data, pore volume and pore diameter

| Sample[a] | Elemental analysis[b] wt.% C | wt.% Al | $V_p{}^c$/cm$^3$ g$^{-1}$ | $d_{p,max}{}^d$/nm |
|---|---|---|---|---|
| **1** | — | — | 0.89 | 2.8 |
| **2** | 15.61 | 6.2 | 0.33 | 1.75 |
| **2a** | 8.61 | 6.6 | 0.46 | 2.0 |
| **2b**[e] | 10.39 | 6.9 | 0.45 | 2.0 |
| **3** | 9.97 | 2.5 | 0.35 | 1.7 |
| **4** | 9.89 | 2.5 | 0.40 | 1.85 |

[a] Pretreatment temperature: 250 °C, 3 h, 10$^{-3}$ Torr for **1**; 100° C, 3 h, 10$^{-3}$ Torr for **2a**, **2b** and **4**; 25 °C, 3 h, 10$^{-3}$ Torr for **2** and **3**. [b] Al by ICP analysis. [c] BJH desorption cumulative pore volume of pores between 1.5 and 4.5 nm diameter. [d] Pore diameter according to the maximum of the BJH pore size distribution calculated form the desorption branch. [e] Recovered material from run 5 (Table 2).

**Table 2** Catalytic activities of aluminium isopropoxide species in the MPV reduction of 4 *tert*-butylcyclohexanone[a]

| Run | Precatalyst | Conversion (%) (*trans*:*cis*) 5 h | 24 h |
|---|---|---|---|
| 1[b] | [Al(OPr$^i$)$_3$] | < 1 | 7 (4.0) |
| 2 | [Al(OPr$^i$)$_3$] | 16 (2.1) | 59 (2.1) |
| 3[c] | **1** | — | < 1 |
| 4[d] | **1** (silylated) | — | < 1 |
| 5 | **2** | 86 (2.3) | > 99 (2.2) |
| 6[e] | **2** | > 99 (2.1) | > 99 (2.2) |
| 7 | **2b** | 85 (2.3) | > 99 (2.3) |
| 8 | **4** | 88 (2.6) | > 99 (2.6) |

[a] Conditions: 25 g HOPr$^i$, 0.1 g *n*-nonane, 0.78 g ketone, *ca.* 5 mol% of precatalyst, 25 °C (mol% = 100 $n_{aluminium}/n_{substrate}$). [b] HOPr$^i$ not predried. [c] 0.20 g mesoporous material. [d] 0.20 g SiMe$_3$-silylated material. [e] 80 °C.

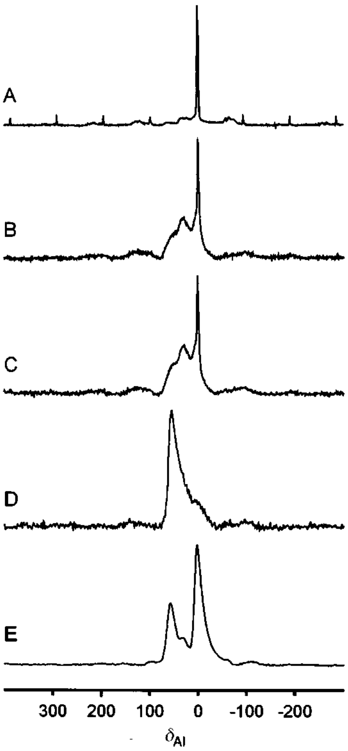


**Fig. 1** $^{27}$Al NMR spectra: (A) Al(OPr$^i$)$_3$ as received from Aldrich; (B) material **2**; (C) recovered material **2a**; (D) material **4**; (E) material **2** exposed to air for several days (completely hydrolysed); all hybrid materials were evacuated for 5 h at 25 °C, $10^{-2}$ Torr prior to measurement

at about 60 and 30 ppm attributable to distorted 4- and 5-co-ordinated aluminium (Fig. 1A).‖[11] In contrast, the spectrum of hybrid material **2** (Fig. 1B) exhibits, besides the sharp resonance at 0 ppm (15%), an intense broad signal pattern in the range of 75 to $-25$ ppm, clearly indicating the formation of additional aluminium sites. Deconvolution by computer simulation (Bruker WINFIT) yields a Gaussian line at 54 ppm (25%) of regular tetrahedral aluminium sites, and a quadrupolar line shape ($\delta_{iso}$ = 49, QCC = 7.5 MHz, 60%), typical of heavily distorted 4-co-ordinated aluminium.[12] Interestingly, this signal pattern did not change after the first catalytic run (material **2a**, Fig. 1C), proving the preservation of the lower-co-ordinated, surface constrained and hence stronger Lewis acidic aluminium centres which are proposed to contribute to the enhanced catalytic activity of material **2**. This is in accord with a previous kinetic study.[13] where the 'melt' form of Al(OPr$^i$)$_3$ which consists of the predominantly trimeric form with 4- and 5-co-ordinated aluminium centres was found to be $10^3$ times more reactive in MPV reductions than the tetrameric form containing 4- and 6-co-ordinated aluminium.

This finding could be corroborated by applying a synthetic approach which exclusively produces lower-co-ordinated aluminium surface species. Novel 4-co-ordinate Al[N(SiHMe$_2$)$_2$]$_3$·thf was reacted with material **1** to yield material **3** *via* a siloxide formation/silylation sequence (*ca.* 0.5 Al nm$^{-2}$).**[6] Subsequent treatment of hybrid material **3** with a slight excess of HOPr$^i$ afforded material **4** (Table 1). The pore texture of material **4** is roughly comparable to that of material **2**, supporting a disruption of the tetrameric form of Al(OPr$^i$)$_3$ upon grafting. The $^{27}$Al MAS NMR spectrum of material **3** revealed poor signal intensity (not shown in Fig. 1), probably due to the formation of surface-docked alumoxo-silylamide sites in highly distorted co-ordination environments.[14] Upon silylamide/HOPr$^i$ ligand exchange the co-ordination geometry at the aluminium center is markedly relaxed. The resulting $^{27}$Al MAS NMR spectrum now features a broad, asymmetric signal with a maximum at 55 ppm, indicating the presence of predominantly 4- and 5-co-ordinated aluminium species (Fig. 1D). Material **4** displayed catalytic activity comparable to that of material **2** (run 8). Although silylated **1** was shown to be catalytically inactive (run 4), the partly silylated surface of material **4** may affect its catalytic performance by hydrophobicity effects.[15] Spectrum E in Fig. 1 shows the $^{27}$Al resonances of a completely hydrolysed sample of material **2**. The three overlapping signals of tetrahedral (58 ppm), 5-co-ordinated (34 ppm) and octahedral (0 ppm) aluminium sites are now clearly visible.

We have shown that MCM-41-grafted aluminium isopropoxide is an efficient catalyst in the MPV reduction of 4-*tert*-butylcyclohexanone. A detailed $^{27}$Al MAS NMR study revealed that the enhanced catalytic activity can be ascribed to the formation of low-co-ordinated (4-, 5-), geometrically distorted aluminium species. Surface confinement prevents the aluminium alkoxide moieties from self-association, while the silicate material simultaneously acts as an electron-withdrawing matrix.

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## Notes and References

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‡ All manipulations were performed in a nitrogen-filled glovebox (MB Braun MB150B-G-II) as described elsewhere.[6] Purely siliceous MCM-41 was prepared according to the literature and dehydrated at 280 °C, $10^{-5}$ Torr prior to use. All of the resulting hybrid materials were synthesized in *n*-hexane at ambient temperature in 24 h and subsequently washed several times with *n*-hexane to remove unreacted educt compounds.

§ A similar post-synthetic aluminium incorporation was recently applied to produce mesoporous aluminosilicates.[9]

¶ Although it was shown earlier that addition of Al(OPr$^i$)$_3$ to alumina significantly enhanced its catalytic activity at 80 °C, this phenomenon was not further explained.[10]

‖ The solution spectrum of Al[(μ-OPr$^i$)$_2$Al(OPr$^i$]$_3$ in toluene at 25 °C gives a similar spectrum with the very broad signal of the 4-co-ordinated Al disappearing into the base line.[11]

** The formation of both surface bonded metal silylamide '[μSiO]$_x$–Al[N(SiHMe$_2$)$_2$]$_y$' [$\nu$(SiH) = 2102 cm$^{-1}$], silylated species '≡SiO–SiHMe$_2$' [$\nu$(SiH) = 2151 cm$^{-1}$] and the consumption of all surface silanol groups was revealed by FTIR spectroscopy.

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