A comparative study of an MCM-41 anchored quaternary ammonium chloride/SnCl$_4$ catalyst and its silica gel analogue

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A novel reusable Lewis acid catalyst has been prepared by the heterogenization of a Lewis acid/tetrapropylammonium adduct; anchoring of tin chloride on quaternary ammonium chloride functionalized MCM-41 yielded a catalyst with higher activity compared to the corresponding silica analogue in terms of turnover rates and product yield in the Prins condensation of isobutene and formaldehyde to isoprenol.
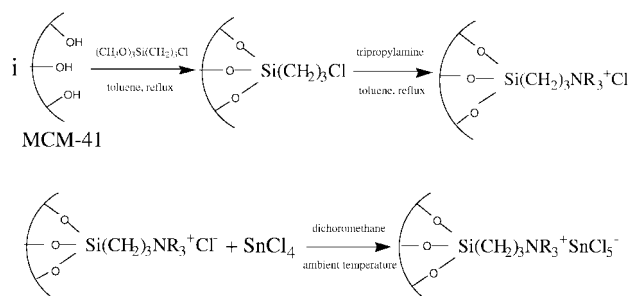
The heterogenization of common Lewis acid catalysts is a subject of immense importance in view of achieving clean technology, based on the fact that heterogeneous catalysts are, in principle, best suited for industrial applications, as ideally they can be recycled and reused easily.[1] A direct immobilization of such catalysts on an inorganic support is not often advantageous due to the possible leaching of the supported species during the reaction and also in many cases the activity is considerably less than for the unsupported Lewis acid.[2] To enhance the activity it may be preferable to anchor the metal catalyst to the support through a chemical chain rather than directly bond it to the support surface.

MCM-41 materials which are characterized by highly ordered pore systems with tunable pore sizes, large specific surface area and pore volume, and high density of surface silanols, provide excellent opportunities in inclusion chemistry and catalysis. A large number of functionalized entities including both organic and inorganic ligands has been introduced in the channels to generate novel catalyst materials.[3] Here we report the preparation of a novel Lewis acid catalyst comprising SnCl$_4$ as the active component anchored on a tetraalkylammonium chloride functionalised MCM-41 material. A comparison is made with the corresponding silica gel analogue in the model reaction of isobutene–formaldehyde condensation to 3-methylbut-3-en-1-ol (isoprenol), which is an important synthesis block for industrially valuable terpenes.[4] Lewis acid catalysts such as SnCl$_4$ and ZnCl$_2$ have been employed in the synthesis of isoprenol from isobutene and formaldehyde under mild conditions, however, the yield was low due to the formation of many side products (Scheme 1).[5]

So called ionic liquids or molten salts which can be prepared by the reaction of a tetraalkylammonium halide (NR$_4$$^+X^-$) and a Lewis acid (MX) are reported to be effective catalysts in Friedel–Crafts reactions and the utility of such catalysts directly

Scheme 1 Prins condensation of isobutene and formaldehyde; IP = 3-methylbut-3-en-1-ol (isoprenol), DMD = 4,4-dimethyl-1,3-dioxane.

Scheme 2 Preparation of SnCl$_4$ anchored on tetraalkylammonium chloride functionalized MCM-41; TPA = tetrapropylammonium chloride; R = propyl group.

immobilized on inorganic supports has been recently demonstrated by Holderich and coworkers among others.[6] Similarly, we adopted the nucleophilic addition of tetraalkylammonium chloride to tin chloride to obtain penta-coordinated tin anionic species, [NR$_4$$^+$][SnCl$_5$$^-$].[7] These types of complexes were immobilized on silica gel and MCM-41 supports by a three-step procedure (Scheme 2). Pure silica MCM-41 (pore diameter = 3.7 nm, surface area = 1100 m^2 g^{-1}) was synthesized following a modified procedure involving pH adjustment and salt addition during crystallization to improve the wetting stability.[8] Silica gel (pore diameter r = 6 nm, surface area = 500 m^2 g^{-1}) was purchased from Aldrich. To a suspension of 10 g of dehydrated silica/MCM-41 support in 50 g anhydrous toluene was added 6 g of a toluene solution of trimethoxysilylpropyl chloride. The suspension was refluxed for 6–7 h in an oil bath followed by filtering and washing with excess toluene to remove the excess of reagent. 5 g of chloropropylated silica and 7 g of tripropylamine were further suspended in 30 g of anhydrous toluene and refluxed for 24 h. After the reaction the material was filtered off, washed fully with excess toluene and dried *in vacuo*. Elemental analysis revealed a loading of 0.98 and 2.5 mmol of chloropropyl groups per gram of silica gel and MCM-41 supports, respectively. The amount of chloride ions present on the silica gel and MCM-41 support after the reaction with tripropylamine as determined by titration with standard AgNO$_3$ solution and potassium chromate indicator were found to be 0.50 and 1.20 mmol g^{-1} of support, respectively.

1.04 g of a solution of anhydrous SnCl$_4$ in 10 ml dichloromethane was added dropwise to a suspension of the functionalized silica in 40 ml dichloromethane followed by stirring overnight at ambient temperature. After reaction, the material was exhaustively washed with dichloromethane and dried *in vacuo*. The starting silica gel and MCM-41 before use were dehydrated *in vacuo* at 450 °C. All operations including preparation of the unsupported SnCl$_4$–TPACl complex and its direct reaction with unfunctionalized silica were conducted inside the glove box under dry nitrogen atmosphere in order to prevent any hydrolysis of Sn compounds.

The tin chloride loadings of silica and MCM-41 hybrid catalysts as determined by energy dispersive X-ray analysis (EDAX-JEM-35, JEOL Co., link system AN-1000, Si–Li

Table 1 Condensation of isobutene and formaldehyde to 3-methylbut-3-en-1-ol (MBOH) over silica based catalysts and catalyst recycling[a]

Entry	Catalyst	$SnCl_4$ loading/mmol (g support)$^{-1}$	Conversion of formaldehyde[b] (%)	MBOH selectivity[c] (%)	MBOH yield[d] (%)
1	$SnCl_4$	—	97.4	54.6	53.0
2	$SnCl_4$–TPACl[e]	—	77.1 (2.68)	89.0	68.7
3	SIL–TPA$^+$SnCl$_5^{-}$[f]	0.46	64.1 (2.22)	88.1	56.4
4	MCM–TPA$^+$SnCl$_5^{-}$[g]	1.11	76.0 (2.63)	94.0	71.4
5	Recycling 1[h]	1.10	74.3	94.1	69.9
6	Recycling 2	—	74.9	93.5	70.0
7	MCM–TPA$^+$SnCl$_5^{-}$[i]	1.11	100	90.1	90.1
8	SIL–TPA–SnCl$_4$[j]	0.32	57.0	79.8	45.5
9	SIL/SnCl$_4$	0.95	77.9	63.2	49.2

[a] 56 g isobutene, 3 g paraformaldehyde, catalyst containing 4 mmol of SnCl$_4$ and 40 g of chloroform solvent were introduced in the reactor and stirred for 2 h at 60 °C. [b] The turnover number (TON) based on the no. of mol of formaldehyde converted per mol of catalyst per s ($\times 10^{-3}$) shown in parentheses. [c] Other products included 4,4-dimethyl-1,3-dioxane and traces of poly-condensation products. [d] Yield was determined by using butan-2-ol as an internal standard. [e] TPACl–SnCl$_4$ complex. [f] TPACl-functionalised silica–SnCl$_4$ complex. [g] TPACl-functionalised MCM-41–SnCl$_4$ complex. [h] Recycling of MCM–TPA$^+$SnCl$_5^{-}$ after exhaustive washing with dichloromethane. [i] Reaction continued for 3.5 h. [j] Direct immobilization of complex on silica.

detector, sensitivity > 0.1 wt%) were found to be 0.46 and 1.11 mmol g^{-1}, respectively. The MCM-41 structure remained intact after the catalyst anchoring. The retention of organic groups on the functionalized support after anchoring the SnCl$_4$ was proved by IR spectroscopy. The formation of a complex between tin chloride and tetrapropylammonium chloride in dichloromethane solution was confirmed by ^{119}Sn NMR (external standard). A shift in the NMR signal from -665.0 to -725.2 ppm after the reaction with tetrapropylammonium chloride reflects a change in the coordination number at tin.[7] The tin/chlorine atomic ratio in the anchored catalysts determined by elemental analysis (EDAX): 0.195 for SIL–TPA$^+$SnCl$_5^{-}$ and 0.204 for MCM–TPA$^+$SnCl$_5^{-}$, was in accordance with such complex formation. The solid state ^{119}Sn MAS NMR study of the SnCl$_4$–tetraalkylammonium adduct anchored on MCM-41 is now in progress in order to obtain more precise definition of the environment around the Sn.

The results of the Prins condensation of isobutene and formaldehyde to isoprenol over different catalysts are summarized in Table 1.†‡ It is clear that complexation of tin chloride with tetrapropylammonium chloride improves the selectivity towards the unsaturated alcohol. Tin chloride alone under anhydrous conditions displayed high activity but the selectivity to MBOH was poor. The tin chloride catalysts immobilized on organic quaternary ammonium functionalized silica/MCM-41 showed highest selectivity towards the unsaturated alcohol, MBOH (88–95%). More interestingly, the MCM-41 based catalyst is far more active than its silica counterpart and outperforms the latter both in terms of isoprenol yield and catalyst turnover. An X-ray fluorescence spectroscopic analysis of the filtrate after the reaction (X-ray spectrometer Phillips PW-1410; sensitivity > 0.5 ppm Sn) revealed that the new catalysts are resistant to leaching under the reaction conditions. Furthermore, when a subsequent reaction was performed with the filtrate after separating the catalyst by adding fresh formaldehyde and isobutene, no formaldehyde conversion was observed. Recycling of the catalyst leads to no appreciable loss in activity. Increasing the reaction time to 3.5 h, increased the MBOH yield to a maximum of 90%. The performance of an SnCl$_4$/silica catalyst, prepared by treating a chloroform solution of tin chloride and silica, in the selective synthesis of MBOH is poor compared to immobilized complexes. Also, a direct immobilization of the complex on silica (Silica/TPA–SnCl$_4$) was not advantageous in terms of MBOH yield.

The present MCM-41 based Lewis acid catalyst system satisfactorily meets the ultimate aims of heterogenization of metal complexes. In short, we have demonstrated the preparation and application of a novel stable, reusable, heterogeneous Lewis acid catalyst, which shows almost the same turnover rate

(TON = 2.63×10^{-3} s^{-1}) as that obtained in solution with the homogeneous catalyst (TON = 2.68×10^{-3} s^{-1}). We believe that the accessibility of the active sites for the reactants will be highest in the present case as it is anchored to the support through a organic chain rather than being directly bonded to the support surface. In addition, the regular and well ordered hexagonal array of pores present in the MCM-41 support provides nanosized micro-reactors for the reaction. The better catalytic activity obtained with the MCM-41 supported catalyst compared to the silica supported counterpart indicates a favorable reaction environment inside the well ordered pores of the former where the active sites are grafted through an organic spacer. Another important feature of this catalyst is the higher concentration of active sites per gram of the support compared to the silica support.

Notes and references

1 *Chemistry of Waste Minimisation*, ed. J. H. Clark, Chapman and Hall, London, 1995, p. 141.
2 R. S. Drago, S. C. Petrosius and P. B. Kaufman, *J. Mol. Catal.*, 1994, **89**, 317; A. A. Krzywicki and M. Marczewski, *J. Chem. Soc., Faraday Trans. 1*, 1980, 1311; S. J. Barlow, T. W. Bastock, J. H. Clark and S. R. Cullen, *Tetrahedron Lett.*, 1993, **34**, 3339; A. Cornelis, A. Gerstmans, P. Laszlo, A. Mathy and I. Zreba, *Catal. Lett.*, 1990, **6**, 103.
3 D. Brunel, *Microporous Mesoporous Mater.*, 1999, **27**, 329.
4 A. P. Courtot, *J. Chem. Soc.*, 1906, **90**, 788.
5 E. Arundale and L. A. Mikelska, *Chem. Rev.*, 1952, **52**, 505.
6 G. A. Parshall, *J. Am. Chem. Soc.*, 1972, **94**, 8716; P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; C. DeCastro, E. Sauvage, M. H. Valkenberg and W. F. Holderich, *J. Catal.*, 2000, **196**, 86.
7 S. E. Johnson and C. B. Knobler, *Organometallics*, 1992, **11**, 3684; Kuraray Co. Ltd., *Jpn. Pat.*, H09-262478, 1997.
8 M. V. Landau, S. P. Varkey, M. Herskowitz, O. Regev, S. Pevzner, T. Sen and Z. Luz, *Microporous Mesoporous Mater.*, 1999, **33**, 149.