View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1993. Downloaded by University of Western Ontario on 30/10/2014 12:23:27.

Sol–Gel Encapsulated Transition Metal Quaternary Ammonium Ion Pairs as Highly Efficient Recyclable Catalysts

Ayelet Rosenfeld, David Avnir* and Jochanan Blum*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Sol-gel entrapped Rh–, Pt– and Co–ammonium ion pairs formed by polymerization of $(MeO)_4Si$ in the presence of the appropriate metal halides and quaternary ammonium salts, are highly stable, efficient and recyclable hydrogen transfer catalysts.

Organically doped sol–gel glasses have emerged as a new class of versatile ceramic materials with an exceedingly wide array of applications[1] to optics,[2] chemical sensing,[3] photochemistry[4] and biochemistry.[5] The chemical inertness of the matrix combined with the observed enhanced stability of the trapped molecules make these materials attractive for the preparation of catalysts. We have already demonstrated[4,5] that biocatalysts and photocatalysts prepared by the sol–gel method are superior in many respects to those immobilized by other techniques. Here we extend this approach of heterogenizing to metal–onium salt catalysts, $[R_4N]^+[MX_n]^-$ (where M represents a transition metal atom, X, a halide and $[R_4N]^+$ a tetraalkylammonium ion).[6] Under homogeneous conditions, these ion pairs proved to be highly active and versatile catalysts[7] but often failed to be recyclable.[8–10] In spite of intensive studies on sol–gel metal catalysts,[11–13] including those on polymerization of metal anchored functionalized monomers,[14] and in spite of the simplicity by which organic molecules can be entrapped, no encapsulations of metal–onium ion pairs have been reported.

We now report the formation of glass encapsulated metal–onium ion catalysts by polymerization of $(MeO)_4Si$ in the presence of $CoCl_2$, $RhCl_3$ and $PtCl_4$, together with quaternary ammonium salts, and demonstrate the utilization of the resulting glasses as recyclable catalysts for organic processes. In a typical preparation, a mixture of the silicon compound (2.5 ml), MeOH (3.5 ml), deionized water (2.5 ml), 0.05 mmol of the appropriate metal halide and cetyltrimethylammonium bromide (CTAB) (0.05 mmol) was stirred at 25 °C (30 min), left to stand in a desired mould until initial gelation was completed (1–6 days), heated at 40 °C to obtain constant mass and washed with boiling CH_2Cl_2. By this procedure, the metal halides and onium salts are assumed to exist as encapsulated ion pairs.

The rhodium containing glass has been used as a recyclable catalyst for the isomerization of both oct-1-en-3-ol and allylbenzene, as well as for disproportionation of cyclohexa-1,3-diene to give benzene and cyclohexene. The entrapped platinum compound was found to catalyse hydrogenation of olefins (*e.g.* dodec-1-ene) at 90 °C under atmospheric pressure, and the cobalt catalyst promoted hydroformylation of cyclohexene (40 atm H_2, 40 atm CO at 120 °C). While some of these catalyses (*e.g.* double bond migration in allylic compounds) could also be carried out by ammonium salt-deficient sol–gel catalysts, others (*e.g.* disproportionation of cyclodienes) did not take place when the onium salt was absent.

The stability, efficiency and recyclability of the sol–gel catlysts were shown to depend on the nature of the matrix, the reaction conditions and on the treatment of the glasses between sucessive runs. The effects of these factors are best demonstrated by some of the results of isomerization experiments by the entrapped $RhCl_3$–CTAB ion pair. When *e.g.* oct-1-en-3-ol (2.3 mmol) was heated in boiling toluene (3 ml) in the presence of a glass disc [prepared from $(MeO)_4Si$]

View Article Online

Published on 01 January 1993. Downloaded by University of Western Ontario on 30/10/2014 12:23:27.

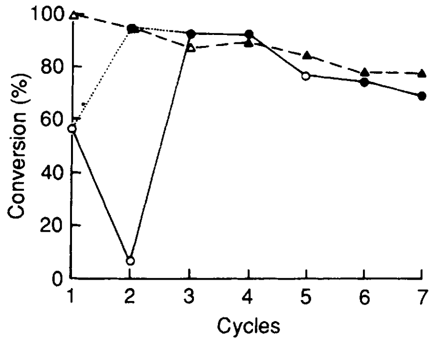

Fig. 1 Isomerization of oct-1-en-3-ol (- - - - -) and allylbenzene (—— and ·········), with (▲, ●) and without (△, ○) water treatment of the catalyst

containing 8.2 × 10^{-3} mmol Rh, a quantitative yield of octan-3-one was obtained after 110 min. (Under homogenous conditions, $RhCl_3 \cdot 3H_2O$ gave 95% of the ketone only after 60 h.) Substitution of the $(MeO)_4Si$- by a $(EtO)_4Si$-derived rhodium catalyst lead to only 62% of the ketone being formed within the 110 min period. The pH of the polymerization proved to have an even greater effect on the properties of the catalyst. Thus, by reducing the pH from 7 to 2.5 or increasing it to 11, the rate of isomerization of oct-1-en-3-ol decreased by a factor of 71 and 27, respectively. The dependence of the catalytic activity on the morphological changes of the matrix is currently under investigation.

Upon completion of the catalytic process the immobilized catalyst could be removed from the reaction mixture, and reused in further runs. However, to do so we had to overcome the observation that the efficiency of the recovered catalyst diminished substantially, especially in the absence of a quaternary ammonium salt. (Typical conversions after 120 min in the first, second, third and fourth runs were 100, 57, 27 and 13%). Since metal leaching was found to be negligible after the first run (0–5 ppm) we attribute the loss in activity to the blocking of pores through which the substrate penetrates the sol–gel. Reopening of these pores by ultra-sound treatment (in boiling CH_2Cl_2), followed by breaking of some Si–O bonds by boiling water[14,15] (or better by dilute base) regenerated most of the original activity. The catalyst deactivation and reactivation proved to be even more pronounced when allylbenzene rather than oct-1-en-3-ol was isomerized. Representative conversions of oct-1-en-3-ol and of allylbenzene by water treated and non-treated catalysts are shown in Fig. 1, which also indicates that in the allylbenzene isomerization the catalyst does not reach full activity in the first run. Only in the second or third cycle is the reaction completed within 2 h, yielding the equilibrium mixture of 2.6% of the starting compound, 8.1% of *cis*, and 89.3% of *trans*-3-propenylbenzene. [*Cf.*, also the gradual activation of polystyrene-bound $RuCl_2(PPh_3)_3$ during isomerization of the same substrate[16]].

We thank the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities, and the US-Israel Binational Science Foundation for financial support of this study.

Received, 15th January 1993; Com. 3/00256J

References

1 For a recent review, see, D. Avnir, S. Braun and M. Ottolenghi, *Am. Chem. Soc. Symp. Ser.*, 1992, **499**, 384.
2 *Sol-Gel Optics II*, ed. J. D. Mackenzie, *SPIE Proc. Ser.*, 1992, **1758**, the entire volume.
3 C. Rottman, M. Ottolenghi, R. Zusman, O. Lev, M. Smith, G. Gong, M. L. Kagan and D. Avnir, *Mater. Lett.*, 1992, **13**, 293.
4 A. Slama-Schwock, M. Ottolenghi and D. Avnir, *Nature*, 1992, **355**, 240.
5 S. Braun, S. Shtelzer, S. Rappoport, D. Avnir and M. Ottolenghi, *J. Non-Cryst. Solids*, 1992, **147/148**, 739.
6 A. Zoran, Y. Sasson and J. Blum, *J. Org. Chem.*, 1981, **46**, 255.
7 See, J. Blum, H. Huminer and H. Alper, *J. Mol. Catal.*, 1992, **75**, 153 and references cited therein.
8 J. Blum, I. Amer, K. P. C. Vollhardt, H. Schwarz and G. Höhne, *J. Org. Chem.*, 1992, **52**, 2804.
9 I. Amer, T. Bernstein, M. Eisen, J. Blum and K. P. C. Vollhardt, *J. Mol. Catal.*, 1992, **60**, 313.
10 Y. Badrieh, A. Greenwald, H. Schumann and J. Blum, *Chem. Ber.*, 1992, **125**, 667.
11 For a recent review, see, M. A. Caugni and J. M. Rodriguez-Izquierdo, *J. Non-Cryst. Solids*, 1992, **147/148**, 724.
12 T. López, J. Mendez-Vivar and R. Juarez, *J. Non-Cryst. Solids*, 1992, **147/148**, 778 and references cited therein.
13 C. J. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press, Boston, 1990.
14 E. J. M. Schubert, C. Egger, K. Rose and C. Alt, *J. Mol. Catal.*, 1989, **55**, 330.
15 K. K. Unger, *Porous Silica*, Elsevier, Amsterdam, 1979.
16 A. Zoran, Y. Sasson and J. Blum, *J. Org. Chem.*, 1981, **46**, 255.

Typeset and printed by Black Bear Press Limited, Cambridge, England