

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

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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 applications¹ to optics,² chemical sensing,³ photochemistry⁴ 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, [R₄N]⁺[MX_n]⁻ (where M represents a transition metal atom, X, a halide and [R₄N]⁺ a tetraalkylammonium ion).⁶ Under homogeneous conditions, these ion pairs proved to be highly active and versatile catalysts⁷ 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 CoCl₂, RhCl₃ and PtCl₄, 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 CH₂Cl₂. 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 H₂, 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 cyclo-dienes) did not take place when the onium salt was absent.

The stability, efficiency and recyclability of the sol-gel catalysts were shown to depend on the nature of the matrix, the reaction conditions and on the treatment of the glasses between successive runs. The effects of these factors are best demonstrated by some of the results of isomerization experiments by the entrapped RhCl₃-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]

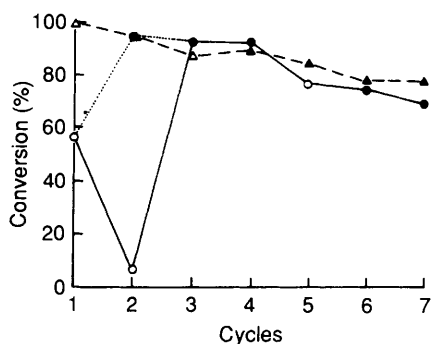


Fig. 1 Isomerization of oct-1-en-3-ol (---) and allylbenzene (— and ·····), with (▲, ●) and without (Δ, ○) water treatment of the catalyst

containing 8.2×10^{-3} mmol Rh, a quantitative yield of octan-3-one was obtained after 110 min. (Under homogenous conditions, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ gave 95% of the ketone only after 60 h.) Substitution of the $(\text{MeO})_4\text{Si}$ - by a $(\text{EtO})_4\text{Si}$ -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 $\text{RuCl}_2(\text{PPh}_3)_3$ during isomerization of the same substrate¹⁶].

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