Zeolite Encapsulated Pd(salen),† a Selective Hydrogenation Catalyst

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Pd(salen) encapsulated in zeolites X and Y is shown to be a catalyst for the selective hydrogenation of hex-1-ene in the presence of cyclohexene at 25 °C and 400 Torr H_2.

The palladium(II) complex of salen was reported to be an effective homogeneous and heterogeneous catalyst for the hydrogenation of alkenes.[1] However, the substrate selectivity for this system was quite poor. We report here that encapsulation of Pd(salen) in zeolites X or Y greatly enhances the selectivity of this catalyst.

The intrazeolite Pd(salen) is not bound to the surface but simply trapped within the zeolite supercage and free to move within the confines of the 12 Å cavity. This ship-in-a-bottle complex was prepared using the flexible ligand method reported for other zeolite encapsulated M(salen) complexes.[2–4] A Pd^{2+} exchanged NaX (8.3% Pd wt) and NaY (5.0% Pd wt) zeolite was stirred in excess of molten salen at 140 °C for 24 h. During this period the flexible salen ligand diffuses into the zeolite where upon complexation with a Pd^{2+} it becomes too large to exit the 7.4 Å apertures to the supercage. The complex-containing zeolites were carefully extracted with methylene chloride to remove surface species, and then stirred with NaCl to reexchange uncomplexed palladium. The resulting Pd(salen)X and Pd(salen)Y zeolites contained 3.2 and 3.1% Pd respectively.

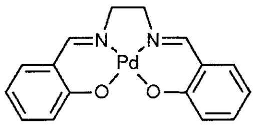
The zeolite-encapsulated Pd(salen) complexes were screened as catalysts for the hydrogenation of hex-1-ene and cyclohexene separately, then competitively. A glass batch reactor containing 25 mg of catalyst, 2 ml of substrate and 0.2 ml of heptane internal standard was charged with 400 torr of 99.99% hydrogen then stirred at 25 °C for 24 h. Products were analysed by GC. There was no detectable colour in the product solutions indicating that the leaching of complexes did not occur.

The results for the hydrogenation of hex-1-ene are shown in Fig. 1. The isomerization of hex-1-ene to the internal alkenes was noted previously for Pd(salen) in neat substrate.[1] The palladium-exchanged zeolites exhibited the highest degree of isomerization to *trans*-hex-2-ene with trace amounts of *trans*-hex-3-ene. The lowest degree of isomerization was observed for Pd(salen)Y. The activity towards the hydrogenation of hex-1-ene to n-hexane is comparable for the zeolite catalysts.

The hydrogenation of *trans*-hex-2-ene with the palladium-exchanged zeolites or Pd(salen) zeolites produced only trace amounts of n-hexane. A small amount of hex-2-ene was also isomerized to hex-1-ene, which may be the source of the n-hexane. The isomerization reactions clearly complicate this system such that we cannot evaluate shape selectivity based solely on a comparison of hydrogenation rates.

For the case of cyclohexene the results are shown in Fig. 2. Both the palladium-exchanged zeolites produced a substantial amount of benzene. This reactivity can be associated with palladium metal that must be formed under the partial pressure of hydrogen at 25 °C. This is not the case for Pd(salen) or the zeolite-encapsulated Pd(salen). The most active catalyst for the formation of cyclohexane was PdX which contains the highest loading of Pd (8.3%). It is surprising that the activity of Pd(salen)X and Pd(salen)Y is not substantially less than that of the exchanged zeolites, in particular because it was expected that occupation of the zeolite cages by the complexes might present diffusional problems in addition to the fact that there is less palladium in the complex-containing zeolites.

We have already noted that the rate of neat cyclohexene hydrogenation cannot be compared directly with the rate of hex-1-ene hydrogenation because of the competition with the isomerization reactions. Additionally, the activity of the intrazeolite complexes relative to the free complex is difficult to evaluate because of the difference in surface area. However, we can compare the selectivity in a competitive reaction. Fig. 3 shows the results for the catalytic hydrogenation of a 1 : 1 (v/v) mixture of hex-1-ene and cyclohexene. Pd(salen) exhibits essentially no preference for the terminal alkene over the cyclic alkene which is consistent with earlier



Pd(salen)

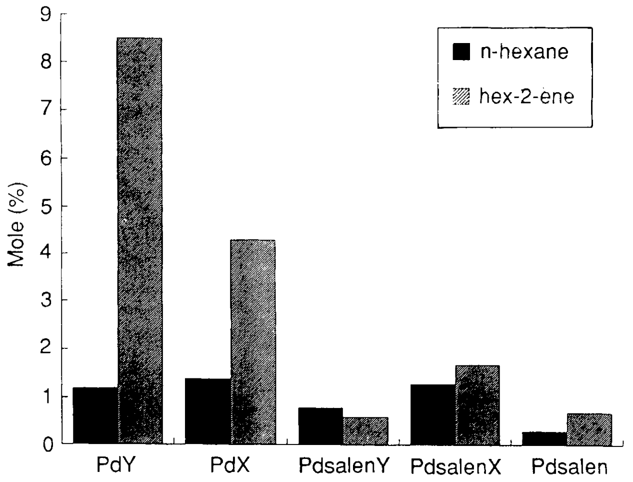


Fig. 1 Hydrogenation of hex-1-ene at 25 °C and 400 torr H_2

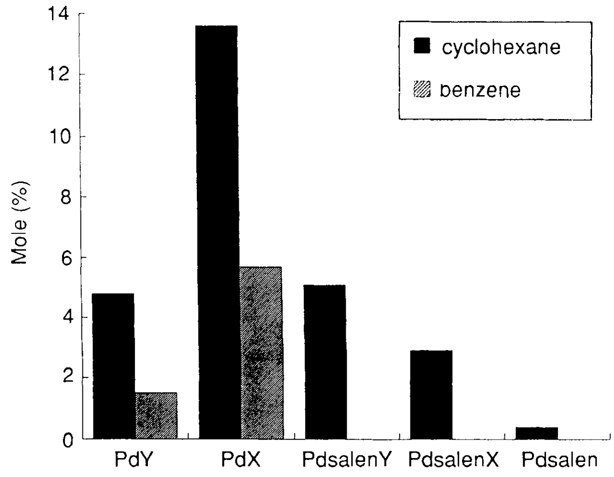


Fig. 2 Hydrogenation of cyclohexene at 25 °C and 400 torr H_2

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† H_2 salen = bis(salicylidene)ethylenediamine.

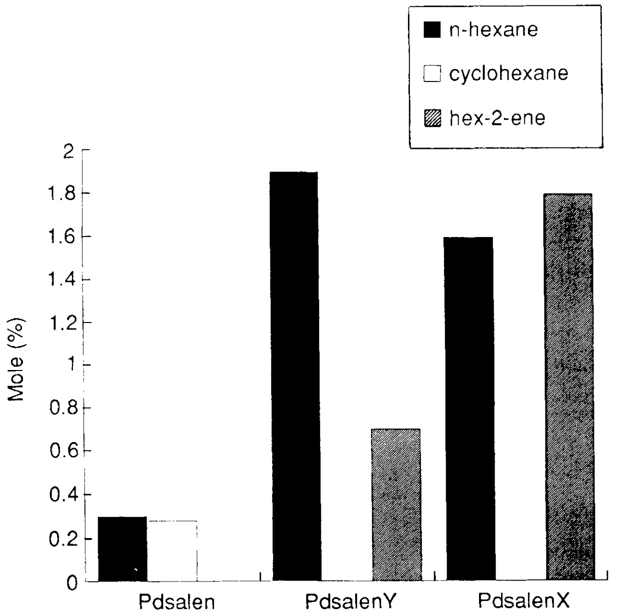

Fig. 3 Hydrogenation of a 1:1 (v/v) mixture of hex-1-ene and cyclohexene at 25 °C and 400 torr H_2

reports.[1] The zeolite-encapsulated Pd(salen) produces only n-hexane and *trans*-hex-2-ene with no observable cyclohexane after 24 h. These results are reproducible to within ± 0.05 mole%. Preliminary results with PdX and PdY reveal similar selectivities.

Coupling the shape selectivity of the zeolite with the activity of the metal chelate complex has produced a catalyst with reactivity not observed for either component separately. Experiments have shown that this selectivity does not arise from hex-1-ene hydrogenation by cyclohexane. In spite of the fact that these zeolites will catalyse the hydrogenation of neat cyclohexene, the presence of the terminal alkene which is less sterically demanding appears to prevent the cyclic alkene from accessing the supercage at an efficient rate. Even small amounts of hex-1-ene inhibit the hydrogenation of cyclohexene. In a competitive experiment 20:1 (v/v) cyclohexene and hex-1-ene there was no evidence of cyclohexene hydrogenation. This selectivity may be more complex than simply size exclusion but more experimentation will be required to define better the mechanism.

In conclusion we have demonstrated that encapsulation of Pd(salen) in zeolites X and Y greatly enhances selectivity in the catalytic hydrogenation of alkenes. Also, complexation of Pd^{2+} exchanged into the zeolites prevents leaching since the complexes are trapped and reactions associated with palladium reduction are not observed.

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