

Letter to the Editor

The enantioselective hydrogenation of 1-phenyl ethanol and of ketones using Pt and Pd supported on natural polymers

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In [1], the group of Jiang described the asymmetric hydrogenation of alpha 1-phenyl ethanol on a heterogeneous Pt-Chitin-silica catalysts. The paper is related to work published earlier, where the enantioselective hydrogenation of ketones with similar chiral heterogeneous catalysts (Pt and Pd supported on chitosan and wool) is described [2–4]. In all papers, the reported enantioselectivities are very high and in some cases up to 100%, even for very simple aliphatic ketones. If these results were genuine this would be absolutely unprecedented and a true sensation, since up to now, metals deposited on chiral supports were not very effective enantioselective catalysts (for a review see [5]). Even more importantly, only very few catalysts give e.e.'s > 85% for the hydrogenation of simple ketones like methyl isobutyl ketone [6,7]. However, when we noticed how the e.e.'s were determined we came to the conclusion that this might be a case of experimental artifacts. Our main concern is that in all the four papers, optical rotation using the reaction solution is the only method for the determination of the enantioselectivity. We think that this is not a suitable method under these circumstances. On the one hand, it is only applicable if there is one single chiral product and when the conversion is known very accurately. Especially for 1-phenyl ethanol this is not the case. The

unreacted 1-phenyl ethanol is also chiral (this is really a kinetic resolution) and will certainly influence the net optical rotation; in addition (chiral) partially hydrogenated intermediates can also be formed. On the other hand, the chiral polymers or supports used in all papers could partially dissolve and thereby influence the comparably small optical rotations very strongly. In order to make these results meaningful, it is mandatory that at least one other method like NMR with a shift reagent or even better, chiral GLC or HPLC is used to confirm the high e.e.'s.

Another concern is the rather cursory description of how the catalysts were prepared and the lack of characterization of both the starting polymer support as well as the final catalysts. For example, in the case of wool [2,4], what kind of animal was it? How was the wool washed and chemically treated before spinning, etc.? Or, what kind of Chitin was used in [1] and what was the molecular weight of the chitosan used in [3]? If the catalysts should ever be applied on a preparative scale—and if these results are reproducible, these would be extremely attractive catalytic systems—such details would be of utmost importance for the reproducible preparation of such extraordinary materials. Terms like 'commercial white wool' or 'chitin' is not sufficient. When we tried to reproduce the Pt on wool catalyst described in [4], we got a material that showed only low activity for the

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hydrogenation of methyl isobutyl ketone, and the product was racemic.

We are looking forward to more details about these fascinating catalysts, that could enlarge the scope of heterogeneous enantioselective catalysts considerably.

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