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Note to the Editor

The enantioselective hydrogenation of 1-phenyl ethanol and of ketones using Pt and Pd supported on natural polymers: work of the group of Ying-Yang Jiang, Institute of Chemistry, Chinese Academy of Science, China

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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 catalyst. 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. 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 homogeneous or heterogeneous catalysts give e.e.'s > 85% for the hydrogenation of simple ketones like methyl isobutyl ketone [6,7].

However, when we saw how the e.e.'s were determined we came to the conclusion that some results might be experimental artifacts. Our main concern is the following: in all the four papers, the only method used for the determination of the

enantioselectivity was the measurement of the optical rotation of the reaction solution. 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 chemical composition of the reaction mixture 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 independent method like NMR with a shift reagent or even better, chiral GLC or HPLC is used to confirm the high ee'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 of 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

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

We are looking forward to an independent confirmation of the analytical results and to more details on the preparation and properties of these novel

catalysts, which could significantly enlarge the scope of heterogeneous enantioselective catalysts.

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