Cyclopropanation of olefins with heterogeneous catalysts

(Comment to the paper "Cyclopropanation of olefins using a silica gel anchored palladium phosphine complex" by M. Lakshmi Kantam, Y. Haritha, N. Mahender Reddy, B.M. Choudary, and F. Figueras)

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In the paper of Kantam *et al.* [1] the preparation of a phosphine–palladium complex anchored onto silica is described. This catalyst is used in the cyclopropanation of styrene and other alkenes with ethyl diazoacetate and the results are compared with some of the first results published by our group with heterogeneous copper catalysts [2].

However, there are in our opinion at least two important mistakes in that paper. The first comes from the assertion that "there are few reports on the cyclopropanation reaction catalyzed by heterogeneous catalysts, copper bronze, Cu-exchanged clays and zeolites" included in the introduction. If only non-chiral heterogeneous catalysts are taken into account, this claim might be correct, given that in our hands only five papers on Cu catalysts have been published [2–6] together with two others on Rh and Ru catalysts [7,8].

However, when asymmetric heterogeneous catalysts are also taken into account, the number of papers devoted to cyclopropanation increases considerably. Most of these papers deal with chiral copper complexes immobilized by different strategies. Cationic exchange is a simple and efficient strategy, already used in the case of non-chiral catalysts [2–4]. For this purpose, clays [9–14] and nafion-type solids [14,15] have been used as supports. The covalent anchoring to insoluble supports has also been used as an immobilization strategy. In that case both organic polymers [11,16–19] and inorganic solids [19–24] have shown their efficiency. Even the natural polymer chitosan has been used as a chiral support to form copper complexes active in cyclopropanation reactions [25]. The anchoring of a chiral complex to an organic polymer has been also used to immobilize chiral dirhodium(II) carboxamidates [26–28] and pybox–Ru complexes [29].

Although the lack of a thorough bibliographical search is clearly detrimental for a high-quality paper, it is even worse, from our point of view, for a tendentious comparison of their own results with those of other colleagues. In the paper commented on here [1], the authors use in table 3 a parameter called "specific activity", whose units are "moles of product obtained per mole of catalyst", measured at different reaction times. In our opinion this parameter is not a true activity, given that the concept of activity in catalysis is always related to reaction rate and, in this case, the time is not taken into account. Moreover, it is very difficult (even impossible) measuring the reaction rate in the case of the slow addition of one of the reagents. Thus it would be more reliable to name this parameter as "productivity".

With this concept in mind, the authors try to demonstrate the high efficiency of the palladium catalyst in comparison with copper ones. However, from previous results [2] the picture is completely opposite to that shown in the paper of Kantam *et al.* In the experimental part of our paper [2] it is clearly stated that 300 mg of catalyst and 10 mmol of styrene are used. In the case of K10-Cu, the copper content of the catalyst is 0.09 mmol/g, that is 0.027 mmol Cu per run. Ethyl diazoacetate was added portion-wise up to a diazoacetate/styrene ratio of 2:1 as stated in table 1 of our paper [2]. With an initial styrene/Cu ratio of 370 and 40% yield, the productivity of K10-Cu is 148 mol of products per mol of copper (table 1), more than three times the productivity of the palladium catalyst (46 mol/mol Pd). The efficiency is much higher from an economical point of view, given the price of the copper precursor ($CuCl_2 \cdot 2H_2O$ 5.23 euro/mol in Aldrich) and the palladium one ($PdCl_2(PhCN)_2$ 11 656 euro/mol).

This is but one example. In table 1 there are several more that demonstrate the high productivity of copper catalysts in this reaction, usually under non-optimized reaction conditions. We find it remarkable that the result with the homopolymer of box(Ph) [16] reaches a

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Table 1
Comparison of the productivities of different heterogeneous catalysts in the cyclopropanation reaction of styrene with ethyl diazoacetate

Catalyst	Runs	Productivity [a]	Ref.
Non-enantioselective catalysts			
SiO_2-Pd	1	46	[1]
K10-Cu	1	148	[2]
$BpCu/SiO_2$	11	338	[5]
Enantioselective catalysts			
Lap-Cu(box-^{t}Bu)	2	169	[10]
SAC13-Cu(box-Ph)	2	180	[15]
Poly-box(Ph)-$Cu(OTf)_2$	2	3795	[16]
USY-prolinamide-Cu	1	150	[23]

[a] Moles of products per mole of catalyst. In the case of several runs, overall productivity is considered.

productivity of 3795 mol of cyclopropane per mol of copper.

In conclusion, it is simply not the case that the palladium catalyst described by Kantam *et al.* [1] is one of the "few examples" of heterogeneous catalysts for cyclopropanation reactions nor that the "productivity" (better than "activity") of this catalyst is 5–46 times that over other solid catalysts.

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