



Simplified preparation of chirally modified nickel catalyst for enantioselective hydrogenation: A step forward to industrial use

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ABSTRACT

A chirally modified nickel catalyst for the enantio-differentiating hydrogenation of β -ketoesters is conventionally prepared by immersing the pre-activated metallic nickel into an aqueous solution of enantiopure tartaric acid (so called “modification step”). During the pre-activation step, nickel precursor is commonly treated with hydrogen gas at elevated temperatures of up to 473 K. The X-ray photoelectron spectral examinations of chirally modified nickel catalysts obtained under the different modification conditions revealed that the chiral modification process itself plays a major role in activating the nickel surface whilst the pre-activation procedure is a less important factor. The corresponding enantio-differentiating hydrogenations of methyl acetoacetate in the liquid phase using the prepared chiral catalysts unambiguously confirmed this conclusion, providing quantitative conversions and high enantioselectivities of up to 90%.

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1. Introduction

Developing a facile method for preparing optically pure compounds is one of the most important yet challenging tasks of current synthetic chemistry. Amongst various chemical and biochemical procedures for manufacturing optically active compounds, the use of heterogeneous chiral catalysts is a very promising approach in particular for the large-scale industrial production [1]. This type of catalysts can be readily prepared, recovered, and reused, yet is less expensive and ecologically benign. Furthermore, the desired products prepared by such catalytic processes are easily separable from the reaction mixture. In the case of enantio-differentiating heterogeneous hydrogenations, two catalytic systems, i.e., cinchon alkaloid-modified precious metals [2–4] and tartaric acid (TA)-modified nickels [5–8], are known to be the most efficient types of catalysts giving high enantioselectivities for specific prochiral substrates. Thus, the alkaloid based platinum catalysts are commonly used for the hydrogenation of α -ketoesters and other activated ketones (95–98% ee) [9–17], whilst the modified

palladium catalysts are applied for the hydrogenation of alkene derivatives (90–94% ee) [18–21]. On the other hand, the nickel catalysts co-modified with TA and NaBr are known to be effective in hydrogenating various prochiral ketones, such as β -ketoesters and 2-alkanones, yielding the corresponding chiral alcohols with the enantiomeric excess of up to 85% for 2-alkanones [22] and 98% for β -ketoesters [23].

Whilst the types of prochiral substrates are different for the above-mentioned catalytic systems, the procedures used for preparing these catalysts are also distinguishable. For example, the alkaloid modified precious metal catalysts are generally prepared in situ by adding a chiral modifier directly into the reaction medium. Although the in situ modification can also be applied for the preparation of tartaric acid-modified nickel catalyst [24], the chiral catalyst obtained by this method shows a rather modest performance. Therefore, the modification procedure is usually carried out prior to the hydrogenation reaction typically by immersing the activated nickel precursor into a solution of TA [25–27] or TA and NaBr (so-called a conventional modification) [27–31]. By employing the conventional modification method, we aim to expand the range of nickel sources suitable for the heterogeneous hydrogenation.

It has been postulated that the modification of nickel with TA and NaBr plays two major roles, i.e., (i) the adsorption of TA and NaBr on the surface of Ni and (ii) the formation of appropriate

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