



Tartaric acid–Ni supported catalysts obtained from hydrotalcite-like compounds: Effects of catalyst preparation variables on enantioselectivity

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ABSTRACT

The catalytic properties of tartaric acid–nickel supported catalysts obtained from hydrotalcite-like compounds have been assessed in the enantioselective hydrogenation of methyl acetoacetate. Ni particle size above a minimum threshold of ca. 20 nm was found to influence enantioselectivity. For materials with similar Ni crystallite size, e.e. progressively lowers as Mg is incorporated to Ni/Al, whereas incorporation of Zn improves e.e. for all Ni/Zn ratios. In general, activity is higher on Ni/Mg/Al than on Ni/Zn/Al series. Moreover, the synthetic method to obtain hydrotalcite-like compounds affects the catalytic properties of the resultant catalysts. For a series of materials of the same composition, the urea hydrolysis method leads to catalysts with enantiodifferentiation ability, whereas the coprecipitation method does not. Variables of reaction during chiral modification, such as pH and tartaric acid concentration, proved not to have a major effect on enantioselectivity. Furthermore, no direct correlation between the amount of tartaric acid adsorbed onto, or Ni leached from the surface, and the enantiodifferentiation ability of the catalysts was found.

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1. Introduction

A successful approach for the creation of heterogeneous enantioselective catalysts is by adsorbing a chiral molecule into an achiral metal surface from solution [1–5]. Not every single chiral molecule is suitable to a given metal and vice versa and the resulting system is substrate specific. One of the most successful catalysts is tartaric acid–nickel (TA–Ni) which leads to the highest enantiodifferentiation in the enantioselective hydrogenation of the simplest β -ketoesters: methyl acetoacetate (MAA) [6].

Even though the mechanism by which the hydrogenation reaction takes place is not fully understood, it is amply accepted that variables of reaction during chiral modification (e.g. pH and TA concentration) have an effect on the enantioselective ability of the catalyst [7–9]. In addition, Ni crystallite size and the nature of the material used as a support have proved to be important parameters in the performance of the catalyst [10–19]. For instance, the catalytic properties of a series of Ni/SiO₂ catalysts improved rapidly with increase in Ni loading up to 50% Ni wt. (Ni crystallite size was larger at higher Ni loadings) and then remained almost constant [18]. Preparation conditions such as temperature, stirring,

Na₂CO₃/Ni ratio and ageing time have an effect in Ni crystallite size for that particular system and the authors argue that narrow crystallite size distribution containing crystallites of size around 10 nm seems to be suitable for obtaining catalysts with high enantioselective ability in the hydrogenation of MAA. For a series of Ni/ α -Al₂O₃ catalysts (40% Ni wt.), Osawa et al. [9,19] found that the optical yield in the asymmetric hydrogenation of MAA was linked to the mean Ni crystallite size as this increased proportionally to the temperature of reduction, attaining the maximum optical yield at 500–600 °C. The researchers concluded that a Ni crystallite size of about 50 nm would provide a suitable surface for the effective enantiodifferentiation with the aid of TA.

These discrepancies make difficult to accurately compare between catalysts in order to delineate whether it is the Ni particle size or the nature of the material used as a support the responsible for the enantioselective function observed on the catalyst. Therefore, the development of a method of catalyst preparation that allows control over Ni particle size and at the same time flexibility in the choice of the nature of the material used as a support is highly desirable.

Hydrotalcite-like compounds (HLCs) is the term used to refer to a family of materials possessing a similar structure to the occurring naturally mixed hydroxycarbonate of Mg and Al: Mg₆Al₂(OH)₁₆CO₃·4H₂O (hydrotalcite). One particular feature of this family of materials is their characteristic structure which consists of sheets of octahedral metal hydroxides containing two

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