

Review

# Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts

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## Abstract

Chemoselective hydrogenation of unsaturated aldehydes and ketones over heterogeneous catalysts is a demanding task. The achieved selectivity levels depend both on the electronic and geometric structures of reactants and metal surfaces. Recent development in catalyst preparation, selection of new solvents, catalyst and reactor structures have been reviewed in this work. Additionally, catalyst characterization technique, especially alloy formation and in situ characterizations have been discussed in detail. The deep understanding of the catalyst structure is necessary for development of tailor-made catalysts for chemoselective hydrogenations. The state of art in both kinetic and molecular modelling used in chemoselective hydrogenations was presented. Some special features, like conversion–selectivity relationship and the performance in gas and liquid phase hydrogenations were discussed.

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*Keywords:* Chemoselective hydrogenation; Unsaturated aldehyde; Heterogeneous catalyst

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## 1. Introduction

The chemoselective hydrogenation of a carbonyl bond in multi-unsaturated aldehydes and ketones is a difficult task [1–4], since thermodynamics favors C=C hydrogenation over C=O by ca. 35 kJ/mol [5]. These unsaturated alcohols are used as fragrances and drugs and thus this field has an industrial interest. In principle these compounds can be selectively hydrogenated by using homogeneous catalysts, but the heterogeneous catalysts are environmentally more friendly and easier to separate and re-use than their homogeneous counterparts. The rational design of active and selective heterogeneous metal supported catalyst is not however very easy task. There are several factors, which can affect the activity and selectivity of a catalyst. These are metal and support selection, metal precursor, catalyst preparation and activation methods, selection of reaction conditions and operation mode (e.g. gas or liquid phase system).

It is thus important to understand the catalyst structure and relate performance of the catalyst (e.g. activity and selectivity) to its structure. This task is quite demanding, because hydrogenation over heterogeneous catalysts proceeds via several surface reaction steps, like adsorption, reaction and desorption. Additionally, the reaction mechanism is rather complicated including competitive/non-competitive and dissociative/non-dissociative adsorption as well as adsorption of solvents, formation of coke etc. In order to rationalize the catalyst preparation and to be able to achieve higher production capacities in intermediate products with high selectivities, it is important to get a whole picture of all these phenomena on the catalyst surface.

The selectivity to an intermediate product is defined as a ratio between the yield of the desired product and the

conversion. High selectivity to an intermediate product (in this case an unsaturated alcohol) at high conversion level is from synthetic point of view a very important topic. It should, however be pointed out that the selectivity can be strongly dependent on the conversion level. This issue is summarized in more detail in Section 4.5. Regarding the effect of other parameters, like substrate structure, catalyst type and structure as well as solvent etc., on product selectivity, these parameters are interdependent. These effects will be treated separately in the review with the aim to show the influence of each parameter on selectivity.

Kinetic modelling is important for optimization of the reactor performances. Such models are usually based primarily on kinetic data, but recently physical methods of in situ catalyst characterization have given additional information for proposing, for example reaction intermediates, which can be used in kinetic models. Moreover, kinetic data can be interpreted by means of molecular modelling, which gives the most stable adsorption modes. These results can be combined with spectroscopic adsorption measurements. The adsorption mode of the reactant can, for example vary with increasing initial concentration of the reactant.

There exist several reviews from chemoselective hydrogenations of carbonyl compounds. One very recent review on kinetics of liquid phase hydrogenation reactions is published by Singh and Vannice [1]. Other reviews found in the literature are from Gallezot [2], where the following items, like metals, metal particle sizes, supports, catalyst modifiers, graphite, solvents and side reactions were presented. Additionally, Ponc [3] considered effect of promoters, alloys, poisons, structure sensitivity, zeolite,

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