



Solvent effect in the liquid-phase hydrogenation of acetophenone over Ni/SiO₂: A comprehensive study of the phenomenon

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ABSTRACT

The solvent effect on catalyst activity and selectivity for the liquid-phase hydrogenation of acetophenone (AP) to 1-phenylethanol was thoroughly investigated over Ni/SiO₂. Solvents of different nature were used: protic (C₁–C₃ primary and secondary alcohols), aprotic polar (tetrahydrofuran, γ -butyrolactone, and acetonitrile) and apolar solvents (cyclohexane, toluene, and benzene). The solvent had a strong influence on the AP hydrogenation rate but did not modify significantly the selectivity to 1-phenylethanol that was always higher than 92%. The AP hydrogenation activity followed the order: C₂–C₃ alcohols > cyclohexane > toluene > tetrahydrofuran > γ -butyrolactone > methanol \gg benzene \cong acetonitrile. In order to explain this activity pattern, the solvent–AP, solvent–H₂ and solvent–catalyst interactions were analyzed. For the analysis of the solvent–AP interactions in liquid phase, both classical measures of polarity and others based on different solvatochromic scales were considered. The H₂ availability in the liquid phase was estimated from the H₂ solubility at reaction conditions. Solvent–catalyst interactions were characterized by means of the adsorption enthalpies measured calorimetrically. A reasonable correlation between the catalyst activity and some solvatochromic parameters was found only when solvents of similar nature were compared. For protic solvents, the AP hydrogenation rate decreased with the solvent polarity and its ability for H-bond formation with AP. Instead, the solvent–AP interactions were weak when using apolar solvents and thereby the activity pattern was essentially determined by the strength of solvent–catalyst interactions. In the case of aprotic polar solvents, both the solvent–AP interactions in the liquid phase and the solvent adsorption strength on the catalyst surface influenced the hydrogenation activity. The highest catalytic activities were obtained when using C₂–C₃ alcohol solvents. These protic solvents adsorbed dissociatively on metal nickel surface increasing the number of active H available for the hydrogenation reaction; this effect was much more important in the case of 2-propanol.

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1. Introduction

The synthesis of fine chemicals over solid catalysts often involves the use of solvents that may strongly influence the catalyst activity and selectivity. Thus, an inappropriate solvent selection can seriously hamper the development of potentially efficient catalytic processes. Although the presence of solvents in the reaction mixture increases the waste generation, the use of solvents in liquid-phase reactions is required to accomplish at least one of the following functions: (1) to dissolve solid reactants and products; (2) to control the reactant conversion rate in the case of very rapid chemical reactions; (3) to dissipate the heat generated in highly exothermic reactions. The choice of suitable solvents is frequently critical to obtain high catalytic activity and selectivity. However, the

optimal solvent selection needs a more detailed knowledge on the relationship between the chemical nature of the solvents and the interactions taking place in the gas–liquid–solid catalytic systems in fine chemical synthesis.

One of the most common types of catalytic reactions carried out in the presence of solvents is the hydrogenation of organic compounds. In particular, the selective hydrogenation of aromatic ketones into the corresponding alcohols on metal-based catalysts in the presence of different solvents has been widely studied for the synthesis of flavors, fragrances, additives and pharmaceuticals [1,2]. For example, the hydrogenation of acetophenone (AP) to 1-phenylethanol (PhE), is of industrial relevance because PhE is used in food, pharmaceutical, cosmetic and polymer industries [3]. The general reaction scheme for AP hydrogenation is shown in Fig. 1. The most important product is PhE, which is obtained by the hydrogenation of the AP carbonyl group. The hydrogenation of the AP aromatic ring leads to cyclohexylmethylketone (CHMK). Consecutively, both primary products, PhE and CHMK, can

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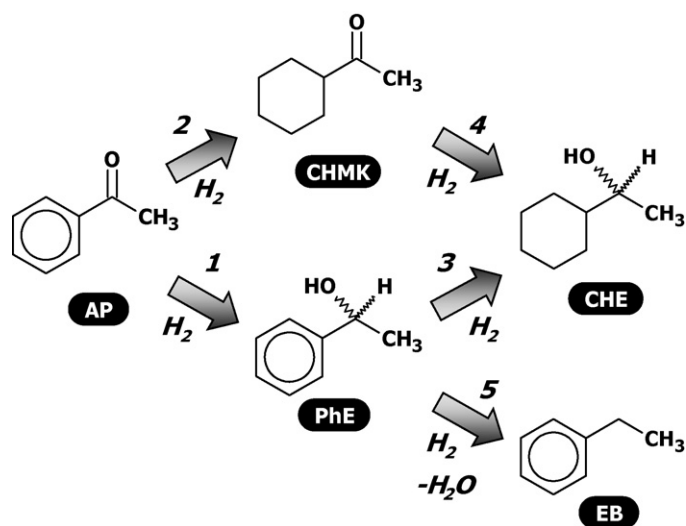


Fig. 1. Reaction network for acetophenone hydrogenation over metal catalysts.

be hydrogenated to 1-cyclohexylethanol (CHE). Ethylbenzene (EB), which is not a valuable product in this reaction, can be produced by a hydrogenolytic splitting of the C–OH bond in PhE. Earlier studies on the hydrogenation of AP were performed on Pt [4,5], Ru [6–8], Pd [9–11], Ni [12–19] and Cu [20] based catalysts, at various temperatures and pressures and using different solvents. Results showed that the solvent nature strongly influences the catalyst activity and selectivity. In general, authors tried to explain the observed catalyst activity differences by correlating the reaction rates with classical solvent polarity parameters, i.e. dipolar moment (μ) and dielectric constant (ϵ) [9–11,19]. However, most of these studies used either solvents belonging to the same chemical family (e.g. alcohols) or a reduced group of solvents of different chemical nature. Masson et al. [19] studied the selective hydrogenation of AP in liquid phase over Ni-Raney catalysts, using alcohols and cyclohexane as solvents. They found that the AP hydrogenation rate decreases linearly with the increase of the dielectric constant of C₁–C₃ alcohols. Besides, the reaction rate was higher in cyclohexane (apolar) than in 1-propanol (polar) but lower than in 2-propanol (polar) showing no direct correlation between catalyst activity and solvent polarity. Aramendía et al. [9], in agreement with Masson et al. [19], found that the AP hydrogenation rate over Pd/AlPO₄ diminishes linearly with the increase of the dielectric constant of protic C₁–C₅ alcohols. Drelinkiewicz et al. [10] studied the AP hydrogenation over polymer-supported Pd catalysts using three different alcohols and cyclohexane as solvents. They pointed out that the AP hydrogenation rate was higher in alcohol solvents than in cyclohexane; they also observed that catalyst activity was more influenced by the solvent polarity than H₂ solubility. These authors mentioned that alcohol solvation could hinder the AP adsorption on Pd. Bejblova et al. [11] hydrogenated AP over different supported Pd catalysts in *n*-hexane and methanol. Remarkable differences in activity and product distribution were observed in both solvents. They briefly explained these results based on the acidity of the supports and catalyst deactivation. Malyala et al. [17] reported that the hydrogenation of AP over Ni/Y zeolite was faster in protic solvents (C₁–C₃ alcohols) than in aprotic ones such as *n*-hexane and suggested that differences in hydrogen bonding would explain this solvent effect on catalyst activity. Cheng et al. [8] studied the enantioselective hydrogenation of AP on chiral Ru-based catalysts using different solvents. They found that the hydrogenation activity was higher in C₁–C₄ alcohols than in aprotic polar and apolar solvents. There are few papers on the hydrogenation of other carbonyl compounds using a wider group of solvents. For example, Mukherjee

and Vannice [21] studied the citral hydrogenation on Pt/SiO₂ in eight solvents belonging to different chemical families and tried to correlate the activity pattern with the solvent dielectric constant and dipole moment. On the other hand, Hájek et al. [22] used 12 solvents of different chemical nature for the hydrogenation of cinnamaldehyde over Ru/Y zeolite. They found a satisfactory correlation between solvent polarity and hydrogenation rate only in the case of protic solvents.

In summary, the analysis of the literature dealing with the solvent effect on catalyst activity and selectivity for AP hydrogenation shows that all the studies have been performed using either a small number of solvents or solvents belonging to a single chemical family (e.g. alcohols). Although in several cases a good correlation between hydrogenation rates and classical parameters of solvent polarity was reported, the interpretation of catalytic results when using solvents of different nature was in general not satisfactory or incomplete. A more detailed analysis supported on basic scientific principles is therefore required to better predict the solvent effect on catalyst activity. To accomplish this analysis, a bigger group of solvents should be tested in order to reach valid conclusions for a wider range of solvent properties. Furthermore, other scales, more appropriated than μ and ϵ , should be considered to describe the solvent solvation properties and to interpret the solvent influence on the catalytic activity. In addition, all the possible interactions occurring in the three-phase catalytic system have to be taken into account.

In this paper, we have thoroughly investigated the solvent effect on catalyst activity and selectivity for the liquid-phase hydrogenation of AP over Ni/SiO₂. The kinetic aspects were carefully examined using 10 different solvents. The solvents were chosen to provide a wide range of different properties and polarities: (1) protic (C₁–C₃ alcohols); (2) aprotic polar (tetrahydrofuran, γ -butyrolactone, and acetonitrile); (3) non-polar aromatic (toluene and benzene) and naphthenic (cyclohexane) compounds. The relative interactions solvent–catalyst, solvent–reactant and reactant–catalyst and their influence on the activity pattern were considered in the analysis. Concerning the influence of the solvent–reactant interaction, classical polarity parameters (e.g. dipole moment μ and dielectric constant ϵ) and other solvatochromic scales (e.g. hydrogen-bond donor (α) and hydrogen-bond acceptor (β) parameters, π^* polarity/polarizability index, Kosower's *Z* and *E*_T(30) scales) were taken into account. The influence of H₂ solubility in each solvent was also considered. For the solvent–catalyst and reactant–catalyst interactions, the corresponding molar adsorption enthalpies were estimated and compared. From the whole analysis, an explanation for the solvent influence on the catalytic activity is given on the basis of the solvent properties and the different types of interactions existing in the three-phase reaction system studied in this work.

2. Experimental

2.1. Catalyst preparation

A supported Ni/SiO₂ catalyst with a 7.6 wt.% nickel load, prepared by the incipient wetness impregnation method, was used for the hydrogenation of AP. Nickel was deposited on commercial silica (Grace G62, 99.7%, *S*_g = 230 m²/g, *V*_p = 0.49 cm³/g) adding dropwise a 0.57 M aqueous solution of Ni(NO₃)₂. The solid was subsequently dried in an oven at 373 K for 12 h and afterwards calcined in air flow at 673 K for 3 h. Previously to the catalytic test, the oxide precursor was activated *ex situ* in a 60 cm³/min H₂ flow at 673 K for 2 h. Then, it was charged into the reactor while keeping an inert atmosphere of N₂ in order to avoid metal reoxidation.

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