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Selective hydrogenation of citral with transition metal complexes in supercritical carbon dioxide

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Abstract

The activity and selectivity of the transition metal complexes formed from Ru, Rh, Pd and Ni with triphenylphosphine (TPP) have been investigated for hydrogenation of citral in supercritical carbon dioxide ($scCO_2$). High activities are obtained with Ru/TPP and Pd/TPP catalysts, and the overall activity is in the order of Pd≈Ru > Rh > Ni. The Ru/TPP complex is highly selective to the formation of unsaturated alcohols of geraniol and nerol. In contrast, the Pd/TPP catalyst is more selective to partially saturated aldehydes of citronellal. Furthermore, the influence of several parameters such as CO_2 and H_2 pressures, N_2 pressure and reaction time has been discussed. CO_2 pressure has a significant impact on the product distribution, and the selectivity for geraniol and nerol can be enhanced from 27% to 75% with increasing CO_2 pressure from 6 to 16 MPa, while the selectivity for citronellol decreases from 70% to 20%. Striking changes in the conversion and product distribution in $scCO_2$ could be interpreted with variations in the phase behavior and the molecular interaction between CO_2 and the substrate in the gas phase and in the liquid phase.

Keywords: Selective hydrogenation; Citral; Transition metal complexes; Supercritical carbon dioxide; Phase behavior

1. Introduction

Selective hydrogenation of α,β-unsaturated aldehydes is an important step in producing unsaturated alcohols, which are important intermediates in organic synthesis in fine chemical industries, such as the flavor, fragrance and pharmaceutical industries. Studies on hydrogenation of acrolein [1,2], crotonaldehyde [3–6], citral [7,8] and cinnamaldehyde [9–12] over transition metal catalysts are reported in the literature. Among these α,β-unsaturated carbonyl compounds, citral is a particularly attractive molecule, as it possesses an isolated C=C bond in addition to the conjugated C=C and C=O bonds. Scheme 1 displays the reaction network of citral hydrogenation reactions. Hydrogenation of the conjugated C=C and C=O bonds of citral yields citronellal and two isomers of unsaturated alcohols, geraniol and nerol, respectively. Further hydrogenation of the C=O bond of citronellal and the C=C bond of geraniol or nerol gives citronellol, which then changes to 3,7-dimethyl-1-octanol through hydrogenation of the remaining C=C bond.

The liquid phase hydrogenation of citral with transition metal catalysts have been well investigated in various organic solvents [13,14]. In general, Ru and Pt favor C=O bond hydrogenation, while Ni and Pd are more selective to C=C bond hydrogenation [15–18]. It is important to point out that the total activity and product selectivity are the chief criteria in the choice of catalysts and reaction conditions [13,14,17,19] (temperature, pressure, solvent, additive, etc.). It was reported [13] that solvents have a significant effect on the product distribution; when alcohol was used as solvent, an undesired side product of acetal was produced from citral and solvent. Recently, the product selectivity of citral hydrogenation catalyzed over supported Pd catalysts in $scCO_2$ has been compared with that in organic solvents [14,20]. Almost 100% selectivity for 3,7-dimethyl-1-octanal (complete hydrogenation of C=C bonds) was obtained in $scCO_2$, whereas 90% selectivity

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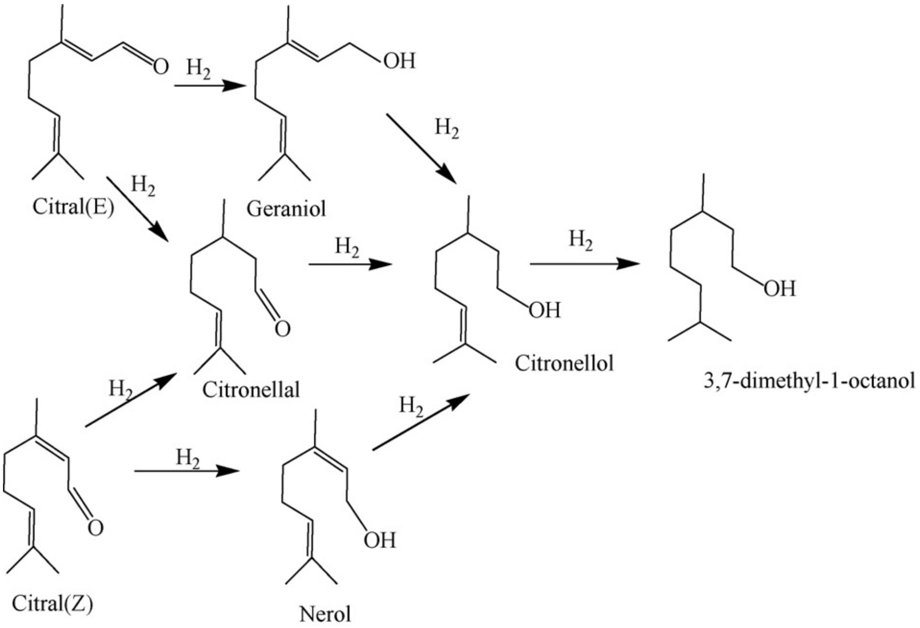

Scheme 1. Hydrogenation reactions of citral.

was found for citronellal in hexane under the same reaction conditions [20].

Attention has been particularly paid to the use of $scCO_2$ as a new clean reaction medium to replace conventional organic solvents [21–23], because it is nontoxic, inexpensive, nonflammable and readily separable from products through depressurization. In most cases, it is also chemically inert toward the substrates. All of these considerations make $scCO_2$ a particular promising solvent for catalytic processes. $scCO_2$ has been demonstrated to be an effective and green medium for organic synthesis [24] and nano-materials preparation [25]. It has been reported in the literature [17,26–28] that the hydrogenation of α,β-unsaturated aldehydes could be performed successfully in $scCO_2$ with a significant improvement in activity and product selectivity.

In the present work, we have studied the activity and selectivity of complexes formed from transition metals with a phosphine ligand, triphenylphosphine (TPP) in hydrogenation of citral in $scCO_2$. The influence of several parameters including CO_2 and H_2 pressure, reaction time, and phase behavior has been investigated in detail. Striking changes in the conversion and product distribution in $scCO_2$ have been discussed with variations in the phase behavior and interactions between the reacting species and CO_2 molecules.

2. Experimental

All the chemicals such as citral (*trans* and *cis*), $RuCl_3{\cdot}3H_2O$, $Pd(OAc)_2$, $Ni(OAc)_2{\cdot}4H_2O$, $RhCl_3$ and triphenylphosphine (TPP) were purchased from Aldrich, and used without further purification. Gases of CO_2 (99.9%), N_2 (99.9%) and H_2 (99.999%) (Changchun Xinxing Gas Company) were used as delivered.

2.1. Catalyst synthesis

The metal complexes were prepared under hydrogen atmosphere as described in the literature [17]. A 50 ml stainless steel reactor was charged with a metal precursor (0.05 mmol), ethanol (5 ml) and TPP, the ratio of TPP/metal being 3 in most cases. Then the reactor was sealed and flushed with 2 MPa CO_2 twice to remove the air. After flushing, 1.0 MPa H_2 was introduced into the reactor; it was heated up to 338 K using a water bath, and then stirring was started using a magnetic stirrer. The mixture was kept at 338 K for 40 min while stirring. Then, the reactor was cooled in water, carefully depressurized by a backpressure regulator, and the solvent, ethanol, was evaporated. The solid metal complex that formed was collected and vacuum dried at 353 K overnight.

2.2. Hydrogenation of citral in supercritical carbon dioxide

The hydrogenation of citral was carried out in a stainless steel batch reactor (50 ml). Certain amounts of catalyst (0.05 mmol) and the reactant citral (5 mmol) were loaded into the reactor and then the reactor was sealed and flushed with 2 MPa CO_2 twice. After the reactor was heated up to a reaction temperature of 338 K, first H_2 and then CO_2 were introduced into the reactor to a certain pressure using a high-pressure liquid pump. The reaction mixture was stirred continuously with a Teflon-coated magnetic bar during the reaction. Then the reactor was cooled to room temperature and depressurized carefully by a backpressure regulator. The liquid mixture was diluted with acetone and then analyzed by gas chromatography (GC-Shimadza-8A, FID, Capillary column, Rtx-Wax 30 m × 0.53 mm × 0.25 μm) and gas chromatography/mass spectrometry (GC/MS, Agilent 5890). The conversion was calculated