Completely selective hydrogenation of *trans*-cinnamaldehyde to cinnamyl alcohol promoted by a Ru–Pt bimetallic catalyst supported on MCM-48 in supercritical carbon dioxide

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Supercritical carbon dioxide ($scCO_2$) is a unique reaction medium for the selective hydrogenation of cinnamaldehyde using a well-defined Ru–Pt bimetallic catalyst supported on MCM-48. The reaction is completely selective to the unsaturated alcohol in supercritical carbon dioxide. The selectivity to the desired unsaturated alcohol shows a significant pressure dependence. By varying the pressure at the constant reaction temperature of 323 K, we are able to optimize the selectivity of cinnamyl alcohol to 100%. This is a particularly dramatic enhancement compared to that in organic solvents and under solventless conditions, where Ru–Pt bimetallic catalyst produces cinnamyl alcohol along with hydrocinnamaldehyde and 3-phenylpropanol. More importantly, the excellent physicochemical properties of the $scCO_2$ medium provide a significant influence on the selectivity, which goes beyond that of simple solvent replacement only.

Introduction

Supercritical carbon dioxide ($T_c = 31\,°C$, $P_c = 7.375$ MPa, $d_c = 0.468$ g mL^{-1}) has received significant attention during the past decades as a prospective solvent for organic synthetic reactions.[1–6] It is considered to be an environmentally benign reaction medium that can be easily tuned by changing the pressure and temperature. From a fundamental point of view it represents a new class of solvents with some properties between those of the gas and liquid phases. It can dissolve easily many reactant gases such as H_2, N_2, and O_2, *etc*. The $scCO_2$ medium not only enhances the miscibility of reactant gases, but it also reduces the viscosity and increases the diffusion rate, so that mass transfer is no longer the limiting factor.[7] The particular advantage of this medium is the ability to control conditions with great precision, to manipulate the selectivity of the reaction.

Selective hydrogenation of α-β unsaturated aldehydes to unsaturated alcohols is a stepping-stone for the production of fine chemicals, particularly used in the fragrance and flavor industry. It is well known that selective hydrogenation of the C=O double bond is much more difficult because reaction kinetics and thermodynamics both favor hydrogenation of the C=C double bond. This is due to the fact that the difference in negative free reaction enthalpy of ~35 kJ mol^{-1} favors the hydrogenation of C=C rather than C=O. Cinnamaldehyde (R), an example of a α-β unsaturated aldehyde, is of great practical importance; both the hydrogenated and semi-hydrogenated products find wide application in theperfume industry. Besides this, the unsaturated alcohol, cinnamyl alcohol (P1), is an important building block in organic synthesis.[8] Traditionally, the hydrogenation of R to P1 has been carried out in organic solvents using homogeneous catalysts.[9] The main drawbacks of this method lie in: (i) difficulty in separating the catalyst from the product and (ii) the use of organic solvents as reaction medium, which are not compatible with the use of green and clean technology. Hence, it is of practical importance to develop an environmentally friendly process based on heterogeneous catalysis. Although the hydrogenation of α-β unsaturated aldehydes using heterogeneous catalysts has been reviewed by several authors,[10] the design of catalysts to adapt the selectivity to C=O remains a challenging task. Several studies have searched for highly active and selective catalysts and it has been found that noble metal catalysts are active and selective to P1.[10*a*,11] In order to further improve the activity and selectivity, several suitable catalytic systems have been reported;[12] these often contain a second metal along with the noble metal. These bimetallic systems, like Pt–Sn,[12*a*] Pt–Fe,[13] Ru–Sn,[14] *etc*., are supported on conventional silica, alumina, zeolites or active carbon. Among these, Pt-containing bimetallic catalysts have attracted the most attention because of their activity and chemoselectivity. Several attempts were made to identify the factors that control the selectivity in hydrogenation of unsaturated carbonyl compounds. The most studied factors are the nature of the support,[15] shape selectivity,[16] electronic effects,[17] reaction conditions such as hydrogen pressure,[11] and solvent.[18] For instance, noble metal encapsulated zeolites have been considered as shape-selective catalysts in selective hydrogenation reactions. High selectivity to unsaturated alcohol at 50% conversion was observed on a platinum cluster supported zeolite Y (96%)[17] and zeolite beta (87%).[16] However, these catalysts suffer from quick inactivation, which slows down the reaction rate. It is well established that, compared to the zeolites, mesoporous materials can act as good supports[19] because of their incredible surface properties such as large surface area and tuneable pore size. The selective hydrogenation of α-β unsaturated carbonyl compounds on mesoporous supports has hardly been studied. Parvulesue *et al.*[20] compared the selective hydrogenation of R utilizing Ru supported on Beta zeolite MCM-41 and MCM-48 supported Ru catalyst in iso-propanol medium with Ru is the active species. The result showed lower selectivity (50% selectivity to P1

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at 60% conversion) and the products were not restricted to P1 or the saturated aldehyde but also gave a number of side products depending on the solvent used.

To avoid the disadvantage of using conventional organic solvent√ as a reaction medium, we have chosen supercritical carbon dioxide as the solvent. Recently, we have reported the successful use of MCM-48 supported Pt as a suitable catalyst for the highly selective hydrogenation of R to P1 in $scCO_2$.[21] Herein we report the successful application of a Ru–Pt bimetallic catalyst supported on MCM-48 in $scCO_2$ as a reaction medium for the hydrogenation of R. In particular, we elucidate the behavior of the Ru–Pt catalyst in $scCO_2$ and the results are also compared with those in organic solvents to assist in the development of an environmentally friendly process.

Experimental

Materials and methods

The bimetallic catalyst was prepared by an *in situ* addition of a 1 wt % solution of Ru and Pt salts in a mixture of surfactant and silica precursor. The sources of silicon, Pt and Ru were tetraethylorthosilicate (TEOS; Nacalai Tesque, Japan), chloroplatinic acid (Aldrich) and ruthenium acetylacetonate (Aldrich), respectively. Cetyltrimethylammonium bromide (Merck) was used as a template in order to obtain the mesoporous structure. A 1:1 ratio of Ru and Pt solutions has been added to the starting gel containing template, sodium hydroxide and TEOS with constant stirring at room temperature. Finally, the resultant gel was autoclaved at 413 K for 48 h. The molar composition of the gel was 1 TEOS:0.27 CTABr:0.34 Na_2O:62.5 H_2O. The resultant material was filtered, dried and then calcined at 823 K for 10 h in air. The catalyst was primarily characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

Hydrogenation reaction

The hydrogenation of cinnamaldehyde (R) was carried out in a 50 ml stainless steel, high pressure, temperature-controlled, stirred batch reactor. Catalyst (0.1 g) and 7.5 mmol of the reactant was loaded into the reactor. Then the reactor was sealed and flushed with CO_2 to remove air. After flushing the reactor was heated to the reaction temperature of 323 K. A prescribed amount of hydrogen was first loaded into the reactor. Liquid CO_2 was charged into the reactor using a high- pressure liquid pump and then compressed to the chosen pressure. Pressure was kept constant by a back-pressure regulator in the system. The hydrogen and the reaction mixture were stirred continuously with a Teflon coated magnetic bar throughout the reaction. After the reaction was complete, the reactor was cooled by ice water and depressurized carefully using the back-pressure regulator. The liquid mixture was identified by GC/MS and analyzed quantitatively by GC (HP 5890) equipped with a flame ionization detector. Quantification of the products was obtained by a multipoint calibration curve for each product. For the recycling studies the catalyst was separated from the reactant and product and then mixed with fresh reactant.

Visual observation of the phase behavior in $scCO_2$

As the reactor used in this reaction was closed observation of the number of phase present during the reaction was not possible. A viewing cell was used to observe the phase behavior of R and $scCO_2$. The cell (internal volume 10 ml) was equipped with windows and connected to a temperature-controlled bath. A magnetic bar was used to mix the contents of the cell from the bottom. The phase behavior experiment of R in $scCO_2$ was conducted at 323 K, with 7.5 mmol of reactant in the presence of a constant hydrogen pressure of 4 MPa and with varying CO_2 pressure in the range of 7.0 to 17.0 MPa. From naked eye observations R is immiscible at 7.0–10.0 MPa of pressure. But the solubility increases with pressure to form a clearly visible uniform single phase at 12 MPa of CO_2.

Results and discussion

The XRD (Fig. 1) pattern of the bimetallic catalyst clearly implied the cubic crystallographic space group *Ia*3*d*, indicating that the mesoporosity of the material remain unaltered after the *in situ* addition of Ru and Pt solutions. The TEM (Fig. 2) also directly reveals the intact mesoporosity of the support after the encapsulation of Ru and Pt. Massive agglomerations of smaller particles are observed on the surface of the mesoporous support. These agglomerates consist of many small crystallites clustered together [Fig. 2(a)] to form larger aggregates that are distributed randomly on the support surface. The larger particles are manily located at the surface and the smaller particles reside inside the pores. In addition to this, the XPS study (results not shown) suggested the presence of Ru and Pt as the +3 and metallic states, respectively, in the calcined material.

Scheme 1 shows the general pathway and the products detected during the hydrogenation of R in $scCO_2$ under the studied reaction conditions using supported noble metal catalysts. Detailed results are summarized in Table 1. To keep the H_2 pressure and temperature of the reaction medium constant the CO_2 pressure has been changed from 7.0–17 MPa. Quantitative formation of P1 was observed over the Ru–Pt bimetallic catalyst in $scCO_2$ medium, depending on the CO_2 pressure. Table 1 exemplifies the interesting CO_2 pressure dependence on P1 selectivity. At a constant temperature of 323 K the selectivity to P1 rises to a maxima at around 7–7.5 MPa pressure of CO_2, which then falls off as the pressure is increased further. Clifford *et al.*[22] found a similar maximum for the ratio of endo to exo products in Diels–Alder reactions. From a theoretical calculation they suggested that this maximum can be associated with tuning of the average distance between the solute molecules and the transition state as the pressure density

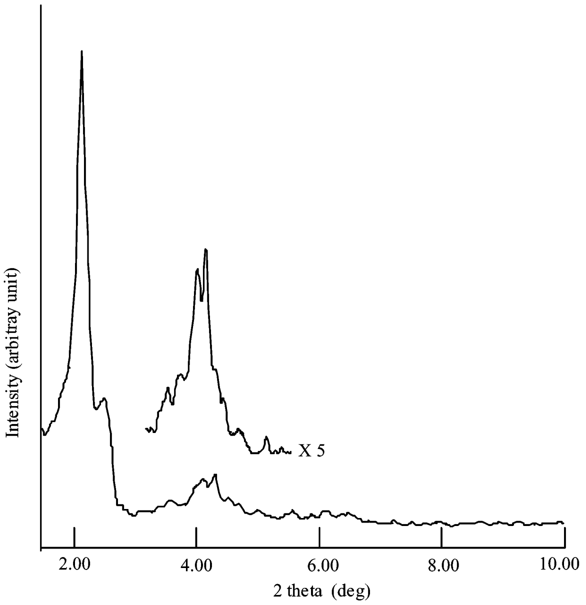


Fig. 1 X-Ray diffraction patterns of calcined Ru–Pt-MCM-48 representing the structural order of cubic space group *Ia*3*d* ($d_{211} = 3.84$ nm, $d_{220} = 3.32$ nm, $d_{321} = 2.79$ nm, $d_{400} = 2.29$ nm, $d_{420} = 2.40$ nm, $d_{421} = 2.05$ nm, $d_{332} = 1.96$ nm, $d_{422} = 1.87$ nm.

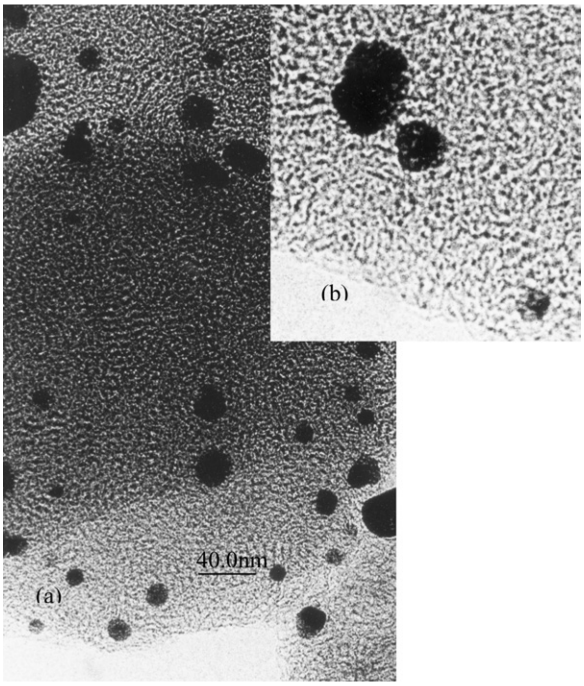
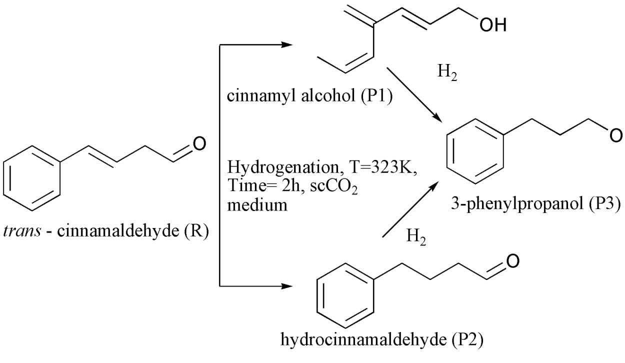


Fig. 2 Transmission electron micrograph of calcined Ru–Pt-MCM-48 (a); a closer view of the larger crystal is also shown (b).

varies; for a compressed liquid such as a supercritical fluid the variation of density causes a change in physical or chemical equilibrium and affects the activity and selectivity of a reaction. Oakes *et al.*[23] also observed a significant enhancement of distereoselectivity from ~35% to ~95% for sulfoxidation of a cysteine derivative upon varying pressure (~6–18 Mpa). Now, it is well established that the density of $scCO_2$ changes with pressure. For instance, for a change of pressure from 6 to 8 MPa the density changes from 160.0 to 520.8 kg m^{-3}.[24] Therefore, CO_2 pressure depending complete selectivity to the cinnamyl alcohol in $scCO_2$ can be appropriately related to the density of the medium. The actual reason for this effect may be debatable but there is no doubt that pressure effects have a strong influence on the selectivity.

The fact that marked decrease in activity and selectivity of the reaction was observed in organic solvent (Table 1, Run 10) strongly suggests that the reaction medium plays an important role in the activity and selectivity of the reaction. The effect of $scCO_2$ becomes more prominent when the reaction is carried out only in the presence of hydrogen, resulting in a much lower conversion as well as selectivity (Run 1).

The nature of the metal can also be an important factor to increase the selectivity of the reaction, since lower selectivity to P1 was observed with Ru alone (substrate conversion was slow and gave 56.5% selectivity). For the studied catalyst the physicochemical characterization gives firm evidence for the presence of metallic platinum. Chemisorbed hydrogen can be transferred from metallic Pt to a carbonyl group (as the surface exposed metallic Pt is more favorable for C=O adsorption), resulting in the hydrogenation of C=O, followed by formation of the unsaturated alcohol. Compared to previous data[21,25] the activity and selectivity to P1 increases upon the addition of Ru. Concerning the role of Ru, it can be suggested that the more electropositive Ru transfers an electron to Pt[26] to cause electrophilic activation to C=O, leading to selective hydrogenation of that bond. Further hydrogenation of the unsaturated alcohol to saturated alcohol (P3) remains very low under the applied reaction conditions. Above a CO_2 pressure of 10 MPa (runs 7 to 10) the increasing amount of CO_2 dilutes the R concentration.[22] It has already been said that the mode of adsorption on the catalyst surface can depend on the R concentration[27] At lower concentrations more space is available for adsorption. Hence, R preferably adsorbs through C=C on the catalyst surface and the selectivity is shifted to P2.



Scheme 1

Table 1 Hydrogenation of cinnamaldehyde at different CO_2 pressures using Ru–Pt supported on MCM-48[a]

Run	$P(CO_2)$/MPa	% Conversion	% Selectivity		
			P1	P2	P3
1	–	9.6	38.2	59.3	2.4
2	6.0	25.2	90.2	9.6	0.2
3	6.5	40.6	99.0	1.0	0.0
4	7.0	46.5	100.0	0.0	0.0
5	7.5	45.7	100.0	0.0	0.0
6	8.0	44.8	99.7	0.3	0.0
7	10.0	40.9	95.8	4.2	0.0
8	12.0	38.9	91.1	8.5	0.4
9	17.0	35.6	88.9	10.2	0.9
10[b]	–	20.2	54.7	34.6	10.7

[a] Reaction conditions: catalyst = 0.1 g (Ru = 0.18 wt %, Pt = 0.25 wt %), cinnamaldehyde = 7.5 mmol, pressure of H_2 = 4.0 MPa, time = 2 h, temperature = 323 K. [b] Isopropanol is used as reaction medium instead of $scCO_2$.

Supercritical carbon dioxide is completely miscible with hydrogen,[28] leading to an increase in hydrogen concentration at the catalyst. Thus, the influence of hydrogen pressure has been considered to be an important factor to direct the activity and selectivity of the reaction. At a constant pressure of CO_2 (7 MPa), an enhancement in the activity has been observed with increasing pressure of hydrogen (Fig. 3), increasing to 68.7% at 6 MPa of H_2. Moreover, considering the effect of temperature the catalyst is unimpaired at the studied reaction temperature, because higher selectivity and conversion are observed. Similar

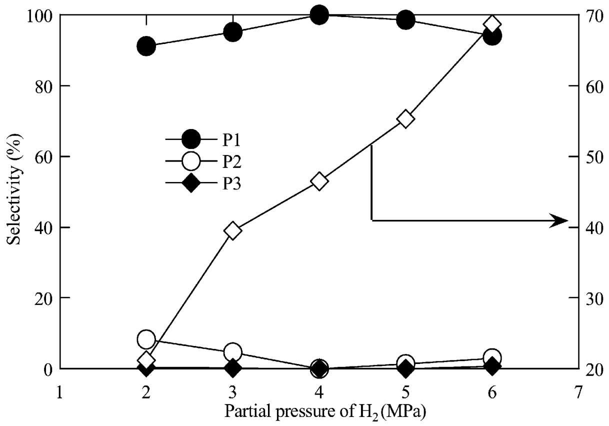


Fig. 3 Hydrogen pressure dependence of the activity and selectivity of cinnamaldehyde hydrogenation in $scCO_2$.

conversion and selectivity were obtained during the additional two cycles of recycling studies.

Conclusion

Supercritical carbon dioxide is shown to be a versatile reaction medium for the selective hydrogenation of R to P1 using a MCM-48 supported Ru–Pt bimetallic catalyst. Most significantly, the product distribution obtained in $scCO_2$ differs remarkably from that in organic solvents. To the best of our knowledge, compared to other heterogeneous catalysts in $scCO_2$ medium, this is the best selectivity to the P1 that has ever been achieved. Particular advantages can be obtained by exploiting the unique properties of the $scCO_2$ medium. This pertains to a simplified and convenient workup for selective hydrogenation reactions by simply tuning the density. Together with its environmentally and toxicologically benign character, these characteristics sum up to a very attractive solvent profile for CO_2. Therefore, the simple catalyst methodology presented here could be highly relevant for the further development of clean chemical process based on heterogeneous catalysts in $scCO_2$ medium.

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