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Selectivity shifts in hydrogenation of cinnamaldehyde on electron-deficient ruthenium nanoparticles

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ABSTRACT

Ruthenium fulleride nanospheres were produced and decorated with small (<1.5 nm) ruthenium nanoparticles. These materials, which present a significant charge transfer from ruthenium to the electron acceptor C_{60} fullerene, were tested in the hydrogenation of cinnamaldehyde. In alcoholic solvents, very large amounts (≈90%) of acetals were formed, pointing out the high acidity of the Ru sites. The addition of a weak base and the use of methanol as a solvent allow to reach high activity and selectivity toward cinnamyl alcohol, whereas the use of an aprotic and apolar solvent decreases the activity and yields mainly hydrocinnamaldehyde. Density functional theory calculations show that this selectivity shift is not correlated to a specific precoordination of cinnamaldehyde on the ruthenium nanoparticles.

1. Introduction

Selective hydrogenation lies at the heart of several industrial processes. Concepts and frontiers developed in the last decade to improve catalyst chemoselectivity have been recently reviewed [1]. These include (1) the nanostructuration of less conventional metals to improve their ability to activate H_2, (2) the use of oxides as active phases, (3) alloying, (4) the ensemble control in hybrid materials, and (5) site isolation approaches in single-site heterogeneous catalysts. Catalytic hydrogenation of organic compounds possessing multiple unsaturated bonds, such as α,β-unsaturated aldehydes, is particularly challenging, requiring active sites able to (1) discriminate closely related moieties, and in some cases, (2) achieve preferential activation of a more thermodynamically stable function [2]. The selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) is of both fundamental and industrial interest. COL is one of the important perfumery chemicals, which is commercially manufactured from CAL by a well-known process called Meerwein–Ponndorf–Verley reduction, where aluminum triisopropoxide is used as a reagent. Although COL is obtained in high yields by this process, disposal of aluminum salts is a major drawback of this method [3]. Hence, it is necessary to develop a process based on catalytic hydrogenation, which will avoid the use of stoichiometric reagents.

The hydrogenation of CAL can produce COL, hydrocinnamaldehyde (HCAL), and/or hydrocinnamyl alcohol (HCOL; Scheme 1). The selective production of COL is difficult because the hydrogenation of the C=C bond is thermodynamically favored over that of the C=O one.

Moreover, acetals and other unidentified high molecular weight compounds can also be produced in significant quantities. Although much research has already been focused on this issue, the selective hydrogenation of

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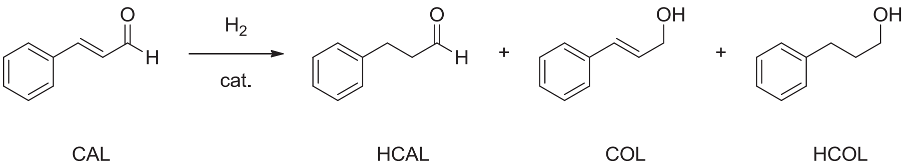

Scheme 1. *trans*-CAL hydrogenation reaction.

α,β-unsaturated aldehydes remains a challenge. High selectivity toward COL has been regularly reported on supported ruthenium catalysts [4–18]. In particular, ruthenium catalysts have been supported on a wide variety of carbon supports, including activated carbon (AC), fullerene C_{60}, multiwalled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), graphite (G), organized mesoporous carbon (OMC), few-layer graphene (FLG), and carbon nanofibers (CNFs). Turn-over frequencies (TOF) ranging between 6 and 450 h^{-1} and selectivity values ranging between 0% and 90% have been reported for these systems (Table 1). Although a particle size effect has been shown for this reaction [8,14,19], the lower Ru dispersions usually lead to the higher COL selectivity. The results presented in Table 1 clearly point out a possible role of the metal support interaction on catalytic performances. Charge transfer between the support and the metallic phase has been analyzed as a possible lever to increase COL selectivity [6]. Thus, electron-rich active sites created on the catalyst surface normally allow to reach high selectivity toward COL. Such an increase in the surface electron density could not only enhance the repulsion between the active site and C=C bond, but also favor the C=O bond activation through favored back-bonding interactions between the catalyst and the π*CO of CAL orbitals, thus favoring the production of COL [20].

Nevertheless, electron-deficient gold nanoparticles (NPs) have shown remarkably high activity and selectivity for this reaction [23]. Furthermore, it is known that Lewis acids or metallic promoters can be used in this reaction to increase COL selectivity [24]. In that case, the electropositive metals or oxidized metal species on the surface act as electrophilic or Lewis sites for the adsorption and activation of the C=O bond via the lone electron pair of the oxygen atom. For example, in bimetallic PtRu NPs, it has been proposed that electropositive Ru atoms act in this way. This second mechanism, referred to as the “electrophilic C=O activation”, was the most frequently invoked to account for the promoting effect of electropositive species [25,26].

We recently reported the synthesis and complete physicochemical characterization of ruthenium fullerides and ruthenium fullerides decorated with ruthenium NPs [27]. The aim of the present study was to evaluate the reactivity of these materials in the selective hydrogenation of CAL. We have investigated the role of several parameters such as the choice of the solvent, the addition of a base, and the Ru/C_{60} ratio on the course of the reaction.

2. Materials and methods

All operations were carried out under argon atmosphere using standard Schlenk techniques or in an MBraun glovebox. Solvents were purified by standard methods or with an MBraun SPS-800 solvent purification system. [Ru(COD)(COT)] (COD = 1,5-cyclooctadiene, COT = 1,3,5-cyclooctatriene) was purchased from Nanomeps Toulouse, fullerene C_{60} (99.5%), CAL (>99.0%), and nonane (>99%) from Sigma–Aldrich, and H_2 from Air Liquide. All these reactants were used as received. The ruthenium content was measured by inductively coupled plasma optical emission spectroscopy on a Thermo Scientific ICAP 6300 instrument.

2.1. Synthesis of Ru@C_{60} nanostructures

In a typical experiment, the [Ru(COD)(COT)] complex was introduced in a Fisher–Porter bottle, and a solution of fullerene C_{60} in CH_2Cl_2 was then introduced in the bottle. The resulting purple solution was stirred for 30 min at

Table 1
Catalytic systems based on carbon-supported ruthenium catalysts for CAL hydrogenation and their performances.

Catalyst	Ru NP size (nm)	*T* (°C)	P_{H_2} (bar)	TOF (h^{-1})	Conversion	COL selectivity	Ref.
Ru@MWCNT	1–2	100	20	450	88	30	[11]
Ru@MWCNT	1.6	70	10	49	40	32	[18]
Ru/MWCNT	2–4	80	30	15	70	25	[7]
Ru/MWCNT	2–3.5	70	10	45	40	39	[17]
Ru/MWCNT	1.6–2.8	70	10	41–52	40	32–43	[18]
Ru/MWCNT	1.7	100	20	50	66	35	[21]
Ru/AC	1.8	100	20	19	22	51	[21]
Ru/AC	10	60	1	–	–	61	[8]
Ru/AC	<1	60	40	180	25	5	[6]
Ru/C_{60}	Not given	60	40	6	7	60	[12]
Ru/OMC	<2	100	30	432	92	54	[10]
Ru/SWCNT	3.5	110	45	–	80	92	[4]
Ru/CNF	1–2	110	45	108	60	43	[22]
Ru/G	Not given	110	45	31	50	76	[14]
Ru/G	<1	60	40	324	50	53	[6]
Ru/FLG	2.3	70	10	120	40	30	[17]

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