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PREPARATION AND CHARACTERISATION OF SUPPORTED PALLADIUM, PLATINUM AND RUTHENIUM CATALYSTS FOR CINNAMALDEHYDE HYDROGENATION

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Mohamed Lashdaf

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PREFACE

The practical work for this thesis was carried out in the Laboratory of Volatec Oy. Funding from the Research Foundation of the Neste Corporation and from the Academy of Finland is gratefully acknowledged.

I am most grateful to Professor Outi Krause, my supervisor, for providing guidance and valuable advice throughout the study. Warm thanks are owed to my co-authors: to Mr. Timo Hatanpää at the University of Helsinki, Professor Jouko Lahtinen at the Helsinki University of Technology, Dr. Tapani Venäläinen at the University of Joensuu, Dr. Ville-Veikko Nieminen at Åbo Akademi University and Ms. Heidi Österholm, Dr. Marina Lindblad and Dr. Marja Tiitta at Fortum Oil Oy. Dr. Kathleen Ahonen is thanked for revising the language of this thesis and the appended publications.

Warmest thanks go to my family for their support.

Porvoo, September 2004

Mohamed Lashdaf

ABSTRACT

Hydrocinnamaldehyde and cinnamyl alcohol are produced in cinnamaldehyde hydrogenation. Both are of great practical importance with wide application in the fine chemicals, pharmaceuticals and perfume industries. In addition, cinnamyl alcohol is an important building block in organic synthesis. In view of the importance of these products, work was undertaken to prepare selective hydrogenation catalysts.

Palladium, platinum and ruthenium catalysts supported on alumina and silica were prepared by gas phase deposition in an atomic layer epitaxy (ALE) reactor and by impregnation techniques. For study of the effect of the acidity of the support, Ru/β zeolite and Pt/β zeolite catalysts were prepared solely by impregnation. The materials were characterised by a variety of techniques. The catalytic properties of the catalysts were studied in cinnamaldehyde hydrogenation.

Particle sizes were smaller for the ALE-deposited palladium than the corresponding impregnated samples. For the platinum and ruthenium samples, they were essentially the same for the two methods of preparation. Metal particles were small if a ligand exchange reaction occurred between metal precursor and support. In the ALE deposition, ligand exchange reaction and metal formation occurred for $Pd(thd)_2$ and $(CH_3)_3(CH_3C_5H_4)Pt$ both on alumina and on silica. Ligand exchange and metal formation also took place for impregnated Pt catalysts with

$(CH_3)_3(CH_3C_5H_4)Pt$ on both supports. In impregnation the interaction of $Pd(thd)_2$ and $Ru(thd)_3$ with the supports was associative adsorption.

Palladium catalysts were more active than ruthenium and platinum catalysts, and the palladium catalysts prepared by ALE showed the highest initial activity in cinnamaldehyde hydrogenation because of the small particle size of metals obtained by ALE. Ruthenium on β zeolites were more active than platinum on β zeolites. The acidity of β zeolites affected the reduction behaviour of ruthenium and the particle size, which subsequently influenced the activity. As acidity increased, particle size decreased and the activity increased.

The adsorption of cinnamaldehyde was preferably via the C=C bond on palladium catalysts, via the C=C and C=O bonds on ruthenium and via the C=O bond on platinum catalysts. Hydrocinnamaldehyde was the main product with all Pd catalysts. Ruthenium catalysts differ in selectivity. Only hydrocinnamaldehyde and 3-phenyl-1-propanol were produced with Ru/SiO_2 prepared by ALE. Ruthenium on β zeolites were selective to hydrocinnamaldehyde. The other ruthenium catalysts formed a variety of hydrogenated products.

The best choice of catalysts for cinnamyl alcohol formation is the impregnated 1.2 wt-% Pt/SiO_2 catalyst with particle size of 4 nm. With use of this catalyst the selectivity toward cinnamyl alcohol was as much as 90% at conversion of 15%. For the formation of hydrocinnamaldehyde, 4.9 wt-% Pd/SiO_2 is the best catalyst that was selective only to hydrocinnamaldehyde at conversion below 10%.

LIST OF PUBLICATIONS

This thesis is based on the following six appended publications, which are referred to in the text by the corresponding Roman numerals:

I. Lashdaf, M., Hatanpää, T., and Tiitta, M., Volatile ß-Diketonato Complexes of Ruthenium, Palladium and Platinum: Preparation and Thermal Characterisation, *J. Therm. Anal. Cal.* **64** (2001) 1171-1182.

II. Lashdaf, M., Hatanpää, T., Krause, A.O.I., Lahtinen, J., Lindblad, M. and Tiitta, M., Deposition of Palladium and Ruthenium ß-Diketonates on Alumina and Silica Supports in Gas and Liquid Phase, *Appl. Catal. A: General* **241** (2003) 51-63.

III. Lashdaf, M., Krause, A.O.I., Lindblad, M. and Tiitta, M., Behaviour of Palladium and Ruthenium Catalysts on Alumina and Silica Prepared by Gas and Liquid Phase Deposition in Cinnamaldehyde Hydrogenation, *Appl. Catal. A: General* **241** (2003) 65-75.

IV. Lashdaf, M., Tiitta, M., Venäläinen, T., Österholm, H. and Krause, A. O. I., Ruthenium on Beta Zeolite in Cinnamaldehyde Hydrogenation, *Catal.Lett.* **94** (2004) 7-14.

V. Lashdaf, M., Nieminen, V., Tiitta, M., Venäläinen, T., Österholm, H. and Krause, A. O. I., Role of Acidity in Hydogenation of Cinnamaldehyde on Platinum Beta Zeolite, *Micropor. Mesopor. Mater*. (2004), in press.

VI. Lashdaf, M., Lahtinen, J., Lindblad, M., Venäläinen, T. and Krause, A.O.I., Platinum Catalysts on Alumina and Silica Prepared by Gas and Liquid Phase Deposition in Cinnamaldehyde Hydrogenation, *Appl. Catal. A: General* (2004), in press.

The author's contributions to the appended publications:

I. Mohamed Lashdaf drew up the research plan, prepared the complexes and participated in the interpretation of the results and preparation of the manuscript.

II. Mohamed Lashdaf drew up the research plan together with the co-authors, prepared the impregnated catalysts and participated in the interpretation of the results and preparation of the manuscript.

III-V. Mohamed Lashdaf drew up the research plan, carried out the cinnamaldehyde hydrogenation experiments, interpreted the results and wrote the manuscripts together with the co-authors.

VI. Mohamed Lashdaf drew up the research plan, prepared the impregnated catalysts, carried out the cinnamaldehyde hydrogenation experiments, interpreted the results and wrote the manuscript together with the co-authors.

CONTENTS

1. INTRODUCTION

Catalytic hydrogenation is employed in large scale in the oil refining industry, where hydroprocessing involves several simultaneous reactions such as hydrodesulfurisation, hydrodenitrogenation, hydrodeoxygenation, hydrodemetallisation, and hydrogenation of aromatics and alkenes [1]. It is also used in small scale in organic chemistry [2] and in the fine chemicals and pharmaceuticals industries [3] where selective hydrogenation of unsaturated carbonyl intermediates is a critical step. An important hydrogenation reaction in the fine chemical industry is e.g. the hydrogenation of cinnamaldehyde to generate hydrocinnamaldehyde and cinnamyl alcohol.

Hydrocinnamaldehyde is an essential raw material in the production of cinnamic acid, which is important in the preparation of pharmaceuticals, including protease inhibitors used in the treatment of HIV [4]. Hydrocinnamaldehyde and its derivatives are also used as light penetration inhibitors in sunscreen formulations, in the preparation of herbicidal compositions, as substrates in the formation of photopolymers, as raw materials in the synthesis of heterocyclic colour complexes and in the electroplating process for zinc [5]. Cinnamyl alcohol is used in the production of photosensitive polymers, the manufacture of inks for multicolour printing, the formulation of animal repellent compositions, and the development of effective insect attractants [5]. Cinnamyl alcohol is also widely used for the preparation of cheap flavours for perfumery and as a precursor of esters valued in perfumery for their excellent sensory and fixative properties [6].

In general, products generated in the hydrogenation of α,ß-unsaturated aldehydes depend on the structure of the catalyst and also on molecular factors of the reactants, such as the steric and electronic effects produced by the substituents of aldehydes [7,8]. Most of the catalysts used in hydrogenation produce a mixture of hydrogenated compounds requiring an expensive separation. The preparation of a selective catalyst system for the hydrogenation of α,ß-unsaturated aldehydes that would avoid this step has been widely investigated [9-12].

The selective hydrogenation of cinnamaldehyde is affected by many factors, such as the type of catalyst [13-27], the reaction conditions [13,16,28], the solvents [14] and the addition of promotors [15]. The metal and the type of face exposed [8], morphological aspects of metal particles [17-22], the local structure and texture of the support [23,24] and the electronic effects of the support [25,26] all play a role in the selectivity in cinnamaldehyde hydrogenation. In addition, a second metal [27], metal ions [29] and metal complex additives [30,31] will affect the selectivity. Finally, the precursor and the method used in the catalyst preparation strongly influence the properties of the catalysts.

Despite the many studies on cinnamaldehyde hydrogenation, the development of a selective heterogeneous catalyst continues to be a challenge. The task of this work was to develop a selective catalyst for cinnamaldehyde hydrogenation to produce hydrocinnamaldehyde or cinnamyl alcohol. A further objective was to use cinnamaldehyde hydrogenation as a model reaction for study of the relations between activity, selectivity and catalyst properties. Noble metals (Pd, Pt and Ru) were selected for the catalyst because they have characteristics that make them useful in the manufacture of organic compounds. Among these characteristics is their ability for hydrogen adsorption [32,33], and they are rugged and inert [34]. They can be used without disintegration or attack by the reactants [34].

The precursors, supports and the techniques used in catalyst preparation, such as ion exchange [35, 36], grafting [37,38], impregnation [39-41] and gas phase deposition [42], influence the catalyst properties. In view of this, two different techniques, gas phase deposition and liquid phase impregnation, were employed and compared. The supports were alumina, β zeolites, and silica.

The requirement for precursors for ALE deposition made volatile Pd, Pt and Ru ß-diketonate metal complexes of interest, and these were prepared and characterised [I]. Comparative study was made of their application as precursors in catalyst preparations by ALE and impregnation and of their influence on the properties of the catalysts [II]. Another important volatile precursor, (trimethyl)methylcyclopentadienylplatinum (IV), was characterised [VI] and used for the preparation of platinum catalysts. For comparison, ruthenium chloride, ruthenium acetylacetonate and tetraammineplatinum(II)nitrate were applied as precursors for ruthenium and platinum catalysts. Finally, the activity and selectivity of the catalysts in cinnamaldehyde hydrogenation were evaluated [III – VI].

2. GENERAL BACKGROUND

2.1 Impregnation and gas phase deposition

The methods to introduce a catalytically active species onto a porous material can be classified into the following groups: precipitation, deposition, encapsulation, and selective removal [43]. Both impregnation and atomic layer epitaxy (ALE) are deposition methods, along with ion exchange, grafting and chemical vapour deposition (CVD) [43].

In impregnation [43], the deposition is carried out from liquid phase and adsorption, ion exchange and selective reaction may take place on or with the surface of the support. During the removal of the liquid, crystallites rather than monolayers are formed on the surfaces [44].

In CVD, the material to be deposited is a volatile precursor of the catalytically active species. In CVD catalyst preparation, the primary focus of the synthesis is the nature of the chemical reaction between the adsorbent and adsorbate. For clarity's sake, it is important to distinguish between two kinds of CVD methods: (i) the two-step process that consists of gas phase adsorption of the precursor on the support followed by the thermal treatment required to obtain the active catalyst, and (ii) the one-step process in which the sublimed precursor is simultaneously adsorbed and decomposed on the heated support. ALE can be classified as a special mode of CVD. Recently, the ALE technique has been extended with good success to the preparation of catalysts for alkane dehydrogenation [45-49], ethene hydroformylation [50], toluene hydrogenation [51-55], alkene metathesis [56], methane oxidation [57], methanol oxidation [58], alkene polymerisation [59,60] and alcohol dehydration [61].

2.2 Precursors for catalyst preparation in the gas phase

An important step in catalyst preparation is selection of a suitable precursor. The nature and chemical reactivity of the precursor will determine its reaction with the support, the suitable reduction conditions of the catalyst materials and the state of metal dispersion [62]. The characteristics of activated catalysts and their selectivity may therefore differ with the precursor.

Special characteristics must be sought in choosing a metal precursor for catalyst preparation in the gas phase. These include good volatility, thermal stability under transport conditions, easy of preparation, high purity, simple and clean decomposition, low toxicity, and stability under storage conditions over a long period. In ALE depositions, precursors should also exhibit thermal stability in the reaction conditions, and they must not decompose before the surface reaction has taken place. At the same time, precursors useful in ALE depositions should be reactive enough to react with the support surface.

Typical precursors for catalyst preparation in the gas phase are volatile metal halides [63], oxyhalides [64], carbonyls [65-67] and alkoxides [58]. Recently, volatile ß-diketonate and cyclopentadiene compounds have become important [50-55,68-71].

Various noble metal compounds have been used as precursors for the preparation of catalysts in the gas phase, as summarised in Table 1. Carbonyl compounds have been used as the precursors for ruthenium and ß-diketonate and cyclopentadienyl complexes for palladium and platinum. Zero-valent carbonyl compounds of Pd and Pt are not stable enough for gas phase deposition.

Table 1. Noble metal, precursor and support used in the preparation of catalysts in the gas phase for use in different reactions.

Metal	Precursor	Support	Method	Subl. T, K	Decomp. T, K	Particle size, nm	Reaction	Ref.
Ru	$Ru_3(CO)_{12}$	NaY zeolite	Dry-mix, vacuum		403	2.4	CO_2 hydrogenation	65-67
Pd	$Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$	NaY, NaHY, zeolite	GPI-D*	298	473	1.3-2.5	MCP** reforming	68,69, 71
Pd	$Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$	MCM-41	GPI-D*	358-393	573-623	30% dispersion	Heck carbon-carbon coupling reaction	72,73
Pd	$Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$	SiO_2	One-step CVD	303-323	533	2-4	Octene hydrogenation	74,75
	$Pd(\eta^3\text{-}C_3H_5)$ (hfa)				683			
Pd	$Pd(acac)_2$	MgO	Dry mix	473	523	4-5	Methane combustion	76,77
			CVD	373	423			
Pt	$Pt(acac)_2$ $Pt(hfa)_2$	HL, KL zeolite	GPI-D*	343	523	0.7-0.8	MCP** to benzene	69,70 78-80
Pt	$Pt(hfa)_2$	SiO_2	One-step CVD	328	348-673		Octene hydrogenation	75 81,82
	$Pt(CH_3)_2$ (COD)			343	353-513	2-6		
	$Pt(CH_3)_2$ (COD)	Carbon				4-5		
Pt	$Pt(CH_3)_2$ (COD)	Carbon	One-step CVD	348	393	5-10	Benzene hydrogenation	83

*GPI-D means gas phase impregnation-decomposition (or two-step CVD)

**Methylcyclopentane

The next sections present a short overview of the properties of the precursors used in this work:

2.2.1 Metal ß-diketonate complexes

Metal ß-diketonates are complexes where the central atom is bonded coordinatively with the oxygen atoms of the ß-diketonate. A special feature of metal ß-diketonates is thermal stability, which is mainly due to steric coverage of the reactive central cation. The volatility is high because the reactive central element is protected, thermal movement is hindered and the interaction between the individual complexes is low.

In general, metal ß-diketonates can be prepared by allowing the dissolved ß-diketonate to react with a metal carbonate or hydroxide [84,85]. A comprehensive review of metal ß-diketonates was published by Niinistö and Tiitta [86].

In this work, the ß-diketonate precursors were tris(2,2,6,6-tetramethyl-3,5-heptane dionato)ruthenium for Ru catalysts and bis(2,2,6,6-tetramethyl-3,5-heptanedionato)palladium for Pd catalysts.

2.2.2 Metal cyclopentadienyl compounds

The cyclopentadienyl ligand (Cp) is one of the most common ligands in metal complex chemistry after the carbonyl group. The symmetrical five-carbon ring coordinates to one face of transition metal octahedra to define a pentahapto (η^5) coordination complex. This coordination is characterised as a π-bonding interaction, with the ligand treated as a 6-electron donating anion (C_5H_5-), or a 5-electron donating neutral substituent. Cyclopentadiene can also considered as a one-electron donor in a bonding situation known as monohapto (η^1) or σ-type structure.

Metal derivatives of cyclopentadiene can be classified as ionic cyclopentadienide or covalent cyclopentadienyl subgroups. The countless metal derivatives of cyclopentadiene that have been characterised have been placed in one or other of these subgroups.

In this work the cyclopentadienyl precursor used for catalyst preparation in the gas phase was $(CH_3)_3(CH_3C_5H_4)Pt$ complex [VI]. In the comparison of the ruthenium precursors the thermal behaviour of the ruthenocene was also studied [I]. A short description of platinum, palladium and ruthenium cyclopentadienyl compounds is given below.

Platinum cyclopentadiene

Cyclopentadiene forms both η^1- and η^5-bonded complexes with platinum (II) and platinum (IV) and the preparations are essentially identical [87]. There are no η^5-C_5H_5 complexes of platinum (0). The Pt(II)η^5-cyclopentadienyl complexes are prepared by treating halide complexes such as

$[Pt(PR_3)_2X_2]$ with either sodium or thallium(I) cyclopentadienide [88-92]. The treatment of $[Me_3PtI]_4$ with sodium cyclopentadienide in THF solution for the preparation of Pt(IV)η^5-cyclopentadienyl complexes yields highly volatile, air-stable, white prisms of $[Me_3Pt(\eta^5\text{-}C_5H_5)]$ [93,94]. Single-crystal X-ray diffraction studies have shown that the cyclopentadienyl ring is symmetrically bound to the platinum atom with Pt-C distances of about 2.2 Å [95]. The mass spectrum of $[Me_3Pt(\eta^5\text{-}C_5H_5)]$ has been reported [96]. On heating to 165 °C, the compound decomposes, apparently homogeneously, to form methane and platinum as main products.

Palladium cyclopentadiene

The most common η^5-cyclopentadienyl complexes of palladium (II) are those containing η^3-allylic, η^4-butadiene or η^4-1,5-cyclooctadiene [88, 97-100]. Minasyants and Struchkov [101] have determined the structure of (η^5-cyclopentadienyl)(η^3-allyl) palladium (II). Both organic groups were π-bonded to the metal and all the cyclopentadienyl and all the allylic carbons were equidistant from the metal (2.25 and 2.05 Å, respectively); the two ligands were not parallel. The cyclopentadienyl group is readily cleaved, and the $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ loses the cyclopentadienyl group with a variety of reagents, or exchanges with other ligands [102,103]. The thermal decomposition of $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ has been described by Shalnova et al. [104].

Ruthenium cyclopentadiene

The structure of ruthenocence is the "sandwich" arrangement typical for most $M(C_5H_5)_2$ complexes, in which the metal atom lies between two planar, parallel C_5H_5 rings [105]. The simplest route by which to prepare dicyclopentadienylruthenium is direct reaction between $RuCl_3$ and cyclopentadiene in ethanol [106], in the presence of zinc [107]. The properties and reactions of ruthenocence can be found in the literature [108-110].

2.3 Support materials

One important target in using a support is to achieve an optimal dispersion of the catalytically active components and to stabilise them against sintering. A support should also be stable under reaction and regeneration conditions and should not adversely interact with solvent, reactants or reaction products. Alumina, silica and β zeolite supports were used in this work.

Porous silica gel is an amorphous material which can be prepared with surface areas up to 1000 m^2/g [111]. The surface area is typically constant up to temperatures of 600-700 °C at least. The porosity is lost at temperatures higher than 1200°C [111]. γ-Alumina, in contrast, is a microcrystalline material typically having a surface area between 50 and 300 m^2/g [112]. The surface area of β zeolites is between 500 and 700 m^2/g [113].

Since silica is a neutral oxide, there are no strong Brönsted or Lewis acid or base sites on the surface. Untreated silica is totally hydroxylated and the hydroxyl layer is covered with physically adsorbed water [114]. The physically adsorbed water can be removed to 200 °C [115]. Alumina is a more ionic material than silica. The acidity and basicity of the hydroxyl groups depend on the number and coordination of the nearest aluminium atoms [111,116]. Coordinated water is still present on the surface at 200 °C and it can be removed at about 400 °C [117]. On β zeolite the active surface sites are Brönsted acid sites and Lewis acid sites [118].

Thermal treatment of the supports leads first to removal of water (dehydration) and then to combination of adjacent hydroxyl groups to form water (dehydroxylation). On silica, the dehydroxylation leads to the formation of surface siloxane bridges, which are less reactive than the coordinatively unsaturated (c.u.s.) surface aluminium and oxygen sites formed by dehydroxlation of alumina [119]. In thermal treatment of β zeolite above 500 °C, the Brönsted acid sites are partly dehydroxylated to form Lewis acid sites [120] as described in Fig. 1.

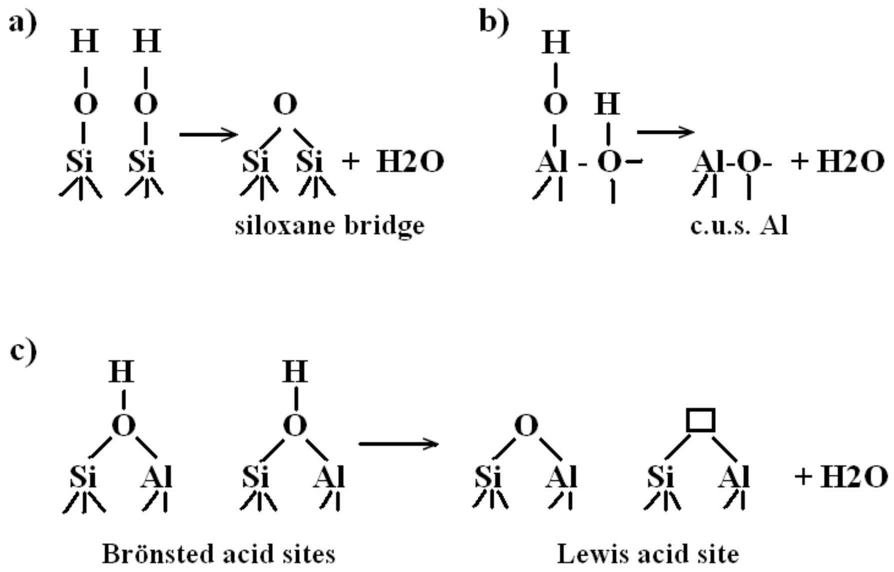

Figure 1. Surface groups and dehydroxylation of a) silica, b) alumina and c) zeolite.

2.4 Surface reactions of metal precursors with oxide supports

The interactions of the "molecular" species in gas phase or in organic solution with oxide supports can be classified in terms of three main mechanisms: associative adsorption, dissociative adsorption and ligand exchange reaction [111, 121-128].

In associative adsorption, the metal precursor interacts with support surfaces while retaining its ligands (1). The interaction occurs mainly at low reaction temperature. In dissociative adsorption, one or more ligands are directly bonded to the support (via the aluminium ion when the support is alumina) and the metal is coordinated to surface oxygen ions (2). In ligand exchange reaction, the metal precursor reacts with one or more OH groups on the surface with the release of ligands and formation of covalent oxygen─ metal bonds (3):

$$\|\mathrm{Al{-}OH} + \mathrm{M(L)}_n \rightarrow \|\mathrm{Al{-}OH} \ldots\ldots (\mathrm{L})_n \mathrm{M} \qquad n=2\text{-}4 \tag{1}$$

$$\|\mathrm{Al{-}O}\| + \mathrm{M(L)}_n \rightarrow \|\mathrm{Al{-}L} + \|\mathrm{O{-}M(L)}_{n-1} \qquad n=2\text{-}4 \tag{2}$$

$$\|\mathrm{Al{-}OH} + \mathrm{M(L)}_n \rightarrow \|\mathrm{Al{-}O{-}M(L)}_{n-1} + \mathrm{H\text{-}L} \qquad n=2\text{-}4 \tag{3}$$

In the equations (1, 2 and 3), the $\|$ denotes the surface, M the metal and (L) the ligand; in this work the ligands are 2,2,6,6-tetramethyl-3,5-heptanedionato with Pd and Ru and cyclopentadienyl and methyl groups with Pt.

2.5 Hydrogenation of cinnamaldehyde and adsorption states of α, ß-unsaturated aldehydes

The reaction scheme of cinnamaldehyde hydrogenation is illustrated in Fig. 2 and discussed in detail in publications III-VI. Depending on the position of the initial hydrogen addition to the cinnamaldehyde molecule, the carbonyl group and the double bonds will be hydrogenated in different series of reactions. Cinnamaldehyde hydrogenation may lead to hydrocinnamaldehyde (reaction 1), cinnamyl alcohol (reaction 2), 3-phenyl-1-propanol (reactions 3, 4) and phenyl propane (reaction 8). In addition, acid-site reactions may occur as a result of reaction of solvent with either cinnamaldehyde or hydrocinnamaldehyde to form acetals (reactions 5,9), solvent may react with 3-phenyl-1-propanol to form an ether (reaction 6), dehydration reaction may occur with formation of ß-methyl styrene (reaction 7) and hydrocinnamaldehyde may isomerise to cinnamyl alcohol (reaction 10).

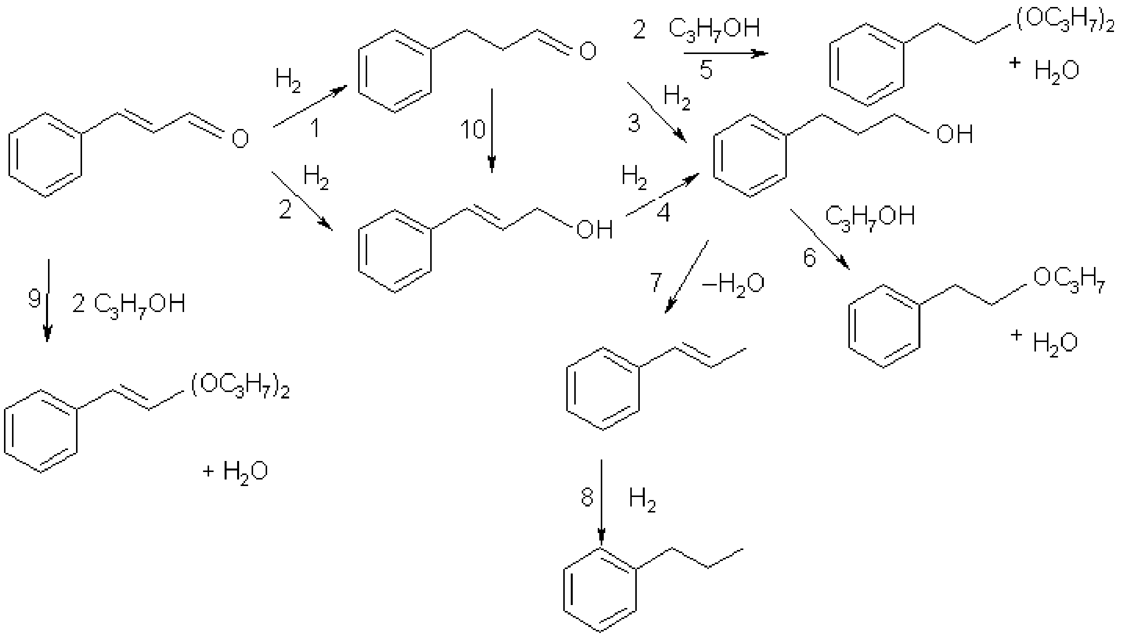

Figure 2. Reaction scheme of cinnamaldehyde hydrogenation.

According to Sautet et al. [8], and as shown in Fig. 3, the following adsorption states of an α,ß-unsaturated aldehydes are possible on a metal surface. For adsorption through the C=O double bond, resulting in the formation of cinnamyl alcohol, the geometries are on-top, di-σ_{CO} and π_{CO} (adsorption states 1, 2 and 3 in Fig. 3). For adsorption through the C=C double bond, resulting in the formation of hydrocinnamaldehyde, the geometries are di-σ_{CC} and π_{CC} (adsorption states 4 and 5). With the quasi-planar (η_4) geometry the adsorption involves both the C=C and C=O double bonds (adsorption state 6) and results in either the formation of the enol as intermediate product [III] or the formation of the unsaturated alcohol 3-phenyl-1-propanol as primary product. The enol isomerises to the hydrocinnamaldehyde.

The adsorption mode of an α,ß-unsaturated aldehyde on a metal surface also depends on the nature of the metal and the type of the exposed crystal face [8]. When the C=C bond is unsubstituted or monosubstituted, the adsorption of α,ß-unsaturated aldehyde on Pd (111) [8] occurs through both double bonds in a tetrahepto di-π geometry (adsorption state 6 in Fig. 3). Cinnamaldehyde is a monosubstituted molecule with a phenyl ring. When the C=C bond is disubstituted, the di-σ_{CO} geometry (adsorption state 2 in Fig. 3) is the most stable.

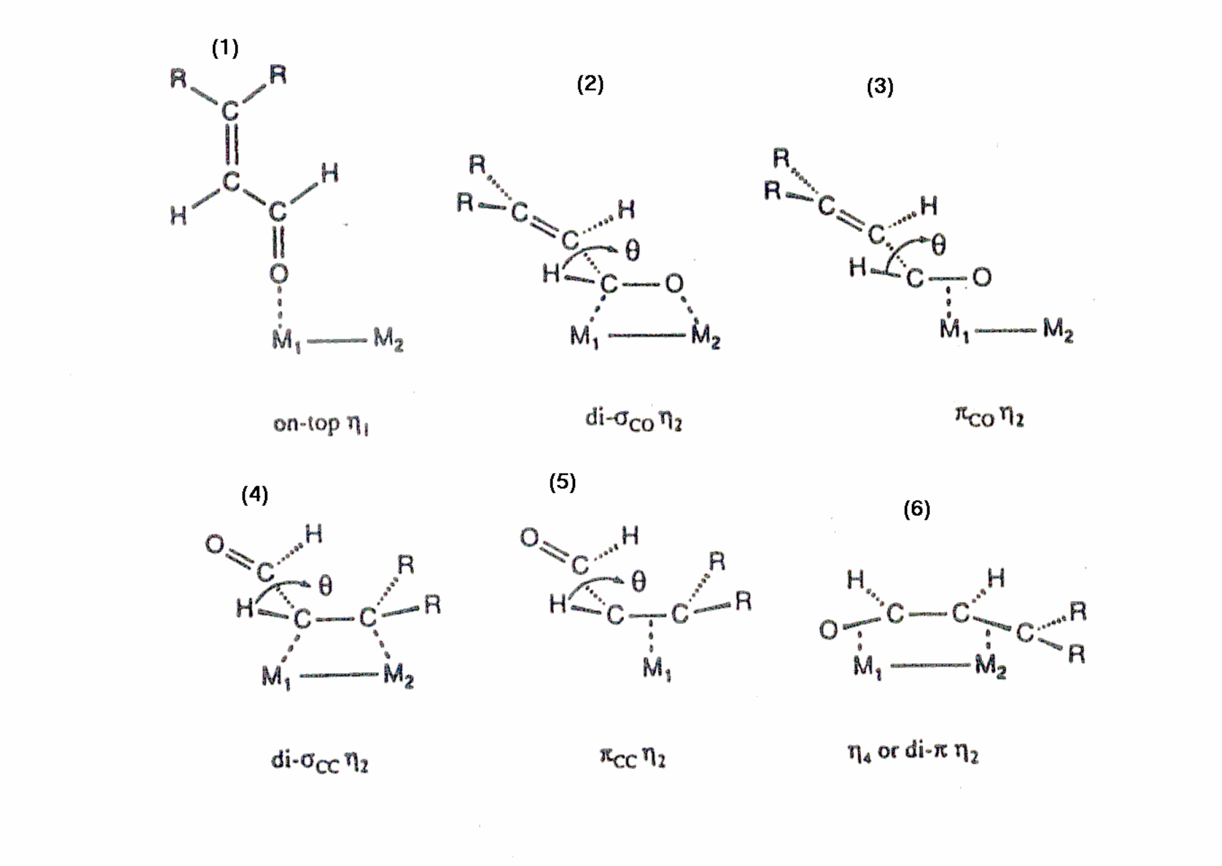

Figure 3. **Adsorption modes of α,β unsaturated aldehydes [8].**

3. EXPERIMENTAL

3.1 Preparation of precursors

ß-Diketonate complexes of palladium, platinum and ruthenium were synthesised by modifying the procedure described in the literature (see Publication I). The complexes were separated from the solvent by filtration and dried in vacuum. Final purification was carried out by vacuum sublimation [I]. Ruthenocene was purchased from Aldrich [I]. Trimethylmethylcyclopentadienyl platinum (IV), $(CH_3)_3(CH_3C_5H_4)Pt$, was obtained from Strem Chemicals [VI]. Ruthenium trichloride $RuCl_3$ (99%) and platinum tetraammine nitrate $[Pt(NH_3)_4](NO_3)_2$ (99.995%) were obtained from Aldrich and used as precursors for ruthenium and platinum catalysts [IV, V].

3.2 Characterisation of precursors

Thermogravimetric analysis (TGA), single differential thermal analysis (SDTA) and differential scanning calorimetry (DSC) were used to determine the thermal behaviour of the metal complexes. The molecular formulas of the volatilised species were determined by field ionisation/desorption technique with a mass spectrometer. ^{1}H and ^{13}C NMR methods were used for identification of the complexes. The characterisation of metal complexes is presented in detail in publications I and VI.

3.3 Catalyst supports

The supports used in the catalyst preparation were alumina from Crosfield with surface area 114 m^2/g, pore volume 0.5 cm^3/g and average pore diameter 18.1 nm; silica SG 340 from Grace with surface area 420 m^2/g, pore volume 1.9 cm^3/g and average pore diameter 17.9 nm [II, III, VI]; and β zeolites from TOSOH Corporation. Both alumina and silica were calcined at 200 °C and dried overnight at 90 °C. β zeolites were calcined at 500 °C and dried overnight at 115 °C. The properties of the β zeolite supports are described in detail in publications IV and V. The particle sizes (grain sizes) of the catalysts were 75-150 μm.

3.4 Preparation of catalysts

Pd/SiO_2, Pd/Al_2O_3, Ru/SiO_2, Ru/Al_2O_3, Pt/SiO_2 and Pt/Al_2O_3 catalysts were prepared by impregnation and ALE methods [II, VI]. Ru/β zeolite and Pt/β zeolite catalysts were prepared solely by impregnation [IV, V]. In impregnation, a calculated amount of $Pd(thd)_2$, $Ru(thd)_3$ or $(CH_3)_3(CH_3C_5H_4)Pt$ was introduced to alumina and silica and $RuCl_3$, $[Pt(NH_3)_4](NO_3)_2$ to the β zeolite supports. Toluene, distilled water or ammonia solution (25%) was used as solvent. In the ALE preparation the metal complexes $Pd(thd)_2$, $Ru(thd)_3$ and $(CH_3)_3(CH_3C_5H_4)Pt$ were vaporised and introduced in the vapour phase to alumina and silica supports [II, VI]. The prepared catalysts are listed in Table 2.

For comparison, Ru/Al_2O_3, Pd/Al_2O_3, Pt/Al_2O_3 and Pt/SiO_2 catalysts were obtained from Johnsson Matthey [III, VI].

Table 2. Catalyst materials and preparation methods.

Catalyst material	Precursor	Preparation method	Publications
Pd/SiO_2	Pd$(thd)_2$	Impregnation/ gas phase deposition	II,III
Pd/Al_2O_3	Pd$(thd)_2$	Impregnation/ gas phase deposition	II,III
Ru/SiO_2	Ru$(thd)_3$	Impregnation/ gas phase deposition	II,III
Ru/Al_2O_3	Ru$(thd)_3$	Impregnation/ gas phase deposition	II,III
Ru/β zeolites	$RuCl_3$	Impregnation	IV
Pt/SiO_2	$(CH_3)_3(CH_3C_5H_4)Pt$	Impregnation/ gas phase deposition	VI
Pt/Al_2O_3	$(CH_3)_3(CH_3C_5H_4)Pt$	Impregnation/ gas phase deposition	VI
Pt/β zeolites	$Pt[(NH_3)_4](NO_3)_2$	Impregnation	V

3.5 Calcination and reduction of catalyst materials

TGA, SDTA [I, II, VI] and TPR [IV, V] measurements were performed to determine suitable calcination and reduction temperatures for the catalysts. TGA and SDTA measurements were made in flowing air, nitrogen and reductive hydrogen/nitrogen (5% H_2) atmosphere. The TGA/SDTA studies were carried out with a Mettler-Toledo TA 8000 system equipped with a

TGA 850 thermobalance. The sample size was about 10 mg and the heating rate was 10 °C/min in all the measurements.

The instrument for the TPR measurements was an Altamira AMI-100 equipped with a TC detector. The amount of the sample used for the analysis was 100 mg. The TPR procedure consisted of initial drying with 5% O_2 in helium at 240 °C with a ramp rate of 2 °C/min, followed by an isothermal step at 240 °C for 30 min. The temperature was then decreased to 50 °C prior to the reduction. The TPR curve was collected between 50 °C and 500 °C at a rate of 10 °C/min; the reduction gas was 11% H_2 in argon.

Impregnated and ALE-prepared palladium and ruthenium on alumina and silica were reduced at 90 °C for palladium and 140 °C for ruthenium. Palladium and ruthenium catalysts prepared by ALE and the platinum catalysts were also reduced at 300 °C.

The ruthenium-containing zeolites were dried at 115 °C and calcined in a muffle oven. The heating rate was 1 °C/min to 500 °C, where it was held for two hours [IV]. The platinum zeolite catalysts were dried at 110 °C for 24 hours and then calcined at 350 °C for two hours in a muffle oven. The heating rate in calcination was 0.2 °C/min [V]. The deposited platinum samples were calcined for five hours in air at 350 °C in the ALE reactor (ALE samples) or in a muffle oven (impregnated samples) [VI].

The calcined ruthenium and platinum on zeolites were reduced with hydrogen in a flow reactor at 250 °C for three hours [IV, V]. Deposited and calcined platinum on alumina and silica were reduced at 300 °C for three hours under hydrogen [VI].

3.6 Characterisation of catalysts

Several techniques were used to characterise the precursors and the catalyst materials. These techniques and their application are listed in Table 3.

Table 3. Techniques used to characterise the samples.

Technique	Target	Publications
Mass spectrometry (MS)	Identification of synthesised Ru- Pt- and Pd- complexes Determination of the molecluar formulas of volatilised species of impregnated and ALE samples	I II, VI
Proton nuclear magnetic resonance spectroscopy (^{1}H NMR)	Identification of synthesised Ru- Pt- and Pd- complexes	I
Solid state magic-angle spinning proton nuclear magnetic resonance spectroscopy ^{1}H MAS-NMR	Determination of OH groups of alumina and silica supports Determination of Brönsted acid sites of β zeolites	II IV, V
Carbon nuclear magnetic resonance spectroscopy (^{13}C NMR)	Identification of synthesised Ru-,Pt-, and Pd- complexes	I
Differential scanning calorimetry (DSC)	Measurement of sublimation, melting and decomposition temperatures	I

Table 3 continues. Techniques used to characterise the samples.

Technique	Target	Publications
Thermogravimetry–single differential thermal analysis (TG-SDTA)	Identification of the reduction and thermal behaviour of metal complexes	I
	Identification of the reduction and thermal behaviour of metals complexes on supports	II
	Identification of the thermal behaviour of Pt precursor Determination of reduction temperatures	VI
N_2-Physisorption	Determination of specific surface area and pore volume	II, IV, V
Carbon analyser (LECO)	Determination of carbon contents of the metal complexes on supports before and after reduction	II, VI
Instrumental neutron activation analysis (INAA)	Measurement of Ru contents of the catalysts	II, IV
Atomic absorption spectroscopy (AAS)	Measurements of Pd contents of the catalysts and metal contents in some reaction products	II, IV
X-ray photoelectron spectroscopy (XPS)	Determination of the oxidation state of palladium and platinum before and after reduction	II, VI
X-ray diffraction (XRD)	Identification of crystal phases Determination of crystal size of the metals	II, IV, V
Scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS)	Determination of the particle size and support morphology	II
Temperature-programmed reduction (with hydrogen) TPR	Determination of reduction temperature	IV, V, VI
CO-Chemisorption	Determination of the metal dispersion and particle sizes of the metals	III- VI
Temperature programmed desorption of ammonia (NH_3-TPD)	Measurement of the support acidity	III, IV, V
X-ray fluorescence spectrometry (XRF)	Determination of silicon and aluminium contents of β zeolites	IV, V
	Determination of phosphorus contents on β zeolites (external acidity test)	IV
Solid state magic-angle spinning aluminum nuclear magnetic resonance spectroscopy (^{27}Al MAS-NMR)	Determination of aluminium contents and distribution of β zeolites	IV
Solid state magic-angle spinning phosphorus nuclear magnetic resonance spectroscopy (^{31}P MAS-NMR)	Determination of the bonding of phosphorus on β zeolites	IV
	Determination of the external acidity of zeolites via adsorption of triphenylphosphine (TPP)	V
Inductively coupled plasma emission spectroscopy (ICP)	Determination of platinum contents of catalysts	IV, VI

3.7 Activity and selectivity of catalysts

The activity and selectivity of the catalysts in cinnamaldehyde hydrogenation were measured in a batch reactor system. A series of tests were performed to determine suitable test conditions for the comparison of catalysts.

Before the hydrogenation, 200 mg of the pre-reduced catalyst was activated with H_2 in situ in the reactor at 60 °C for 20 hours. After activation, cinnamaldehyde and 2-propanol in ratio 1:1 were loaded into the reactor. The reaction was carried out at 60 °C under 10 bar hydrogen pressure and at stirring speed of 500 rpm [III-VI]. Platinum catalysts were additionally tested at 100 °C. Experiments were also made with the supports without metal loading in order to study the effect of the support on the cinnamaldehyde reaction. Blank tests were performed without catalyst. Further hydrogenation tests were made for hydrocinnamaldehyde under the same reaction conditions to identify the formation of cinnamyl alcohol from hydrocinnamaldehyde through isomerisation reaction.

A sample was taken every hour during the four-hour hydrogenation tests [III-V] and after 2, 4, 6, 26, 29 and 32 hours during the 32-hour hydrogenation tests [VI]. The samples were analysed with a gas chromatograph (Varian 3400) equipped with a temperature program and flame ionisation detector [III-VI]. Samples were analysed with a mass spectrometer (VG 7070E) to confirm the identification of the GC peaks. The conversion, turnover frequency (TOF) and selectivity in the hydrogenation were calculated on the basis of the GC results.

4. RESULTS AND DISCUSSION

4.1 Metal precursors

As seen in the TGA measurements, complexes Pd(thd)$_2$, Ru(thd)$_3$, Ru(C_5H_5)$_2$ and $(CH_3)_3CH_3C_5H_4Pt$ evaporated easily in the inert atmosphere, whereas Ru(acac)$_3$ decomposed [I, VI]. Ru(acac)$_3$ evaporates in vacuum at 210 °C. All these complexes were stable enough to serve as precursors in gas phase preparation of catalysts.

In reductive atmosphere [I] and when impregnated or ALE-deposited on alumina or silica surface [II], the Pd(thd)$_2$ complex was partly reduced to metallic palladium. Similarly, the $(CH_3)_3CH_3C_5H_4Pt$ compound was partially reduced to metallic platinum when impregnated or ALE-deposited on alumina or silica [VI].

Ru(thd)$_3$ complex sublimed in reductive atmosphere [I], but it did not sublime when impregnated or ALE-deposited on alumina or silica [II]. Ru(C_5H_5)$_2$ sublimed during reduction with hydrogen [I]. A detailed discussion of the properties of the metal precursors is presented in publications I, II and VI.

4.2 Surface reactions of metal precursors with oxide supports

The surface reaction mechanisms proposed for $Pd(thd)_2$, $Ru(thd)_3$ complexes and $(CH_3)_3CH_3C_5H_4Pt$ compound during deposition on alumina and silica are discussed in publications II and VI. In impregnation at room temperature, the $Pd(thd)_2$ was mainly associatively bonded on on the alumina and silica surfaces (Fig. 5a, II). In ALE depositions on these supports, ligand exchange reaction took place (Fig. 5c, II), and on alumina, a small amount of $Pd(thd)_2$ was dissociatively adsorbed in addition (Fig. 5b, II). Some other reactions occurred during the preparation as well:

a) Impregnation: the metal was formed during drying of the solvent under reduced pressure at 50 °C (Pd^0 was 13-17%, no Ru^0 was detected).

b) ALE deposition: the metal was formed through reduction with the decomposition products of the ligand at 180 °C (Pd^0 comprised 70% on silica and 51% on alumina, and Ru^0 could not be detected because of the small amount of ruthenium).

A ligand exchange reaction took place in both gas phase and impregnation in the deposition of $(CH_3)_3(CH_3C_5H_4)Pt$ complex on alumina and silica, releasing methane [VI]. Platinum (Pt^{4+}) was reduced to (Pt^{2+}) during the deposition. Further reduction of the platinum to metallic state also took place. The amount of metal formed during the deposition was, on silica, 21% Pt^0 by ALE and 31% Pt^0 by impregnation and, on alumina, 56% Pt^0 by ALE and 57% Pt^0 by impregnation.

Metal cyclopentadienyl complex $(CH_3)_3(CH_3C_5H_4)Pt$ was more reactive than the metal ß-diketonates: it reacted with the supports via ligand exchange at room temperature, while the metal ß-diketonates reacted only at high temperatures. Furthermore, the reactivity of the metal ß-diketonates was not high enough to open siloxane bridges on silica.

The models proposed for surface reactions of $Pd(thd)_2$ on the alumina support are illustrated in Figure 5 [II]. The surface reactions of $(CH_3)_3(CH_3C_5H_4)Pt$ complex on alumina and silica are discussed in publication VI. A comparison of the Ru, Pd and Pt catalysts prepared by impregnation and ALE is presented in Table 4.

Table 4. Comparison of the catalysts prepared by impregnation and ALE.

		Impregnation			**ALE**		
		Pd	Ru	Pt	Pd	Ru	Pt
Precursors		$Pd(thd)_2$	$Ru(thd)_3$	$(CH_3)_3(CH_3C_5H_4)Pt$	$Pd(thd)_2$	$Ru(thd)_3$	$(CH_3)_3(CH_3C_5H_4)Pt$
Deposition conditions	T (°C)	25	25	25	180	180	100
	P (bar)	1	1	1	0.05-0.1	0.05-0.1	0.05-0.1
Solvent		toluene	toluene	toluene	no	no	no
Surface reactions*	Al_2O_3	A , D	A	L	L	A	L
	SiO_2	A	A	L	L	A	L
Total amount of metal (wt-%)**	Al_2O_3	3.9	3.7	1.2	3.5	0.62	1.2
	SiO_2	4.1	3.4	1.2	5.4	0.76	1.5
Metal (M^0) formation, %	Al_2O_3	17	not detected	57	51	not detected	56
	SiO_2	13	not detected	31	70	not detected	21

*A: associative adsorption, D: dissociative adsorption and L: ligand exchange reaction.

**After the deposition

4.3 Reduction of catalysts

The reduction of catalysts was studied by TGA, SDTA and TPR [II-VI]. The reduction temperatures for Pd(thd)$_2$, Ru(thd)$_3$ and $(CH_3)_3(CH_3C_5H_4)Pt$ impregnated on alumina and silica were chosen on the basis of the results obtained in TGA measurements [II,VI]. The reduction temperatures selected were 90 °C for palladium, 140 °C for ruthenium and 300 °C for platinum. For comparison, the ALE-deposited materials were reduced at the same temperatures and in the case of palladium and ruthenium catalysts also at 300 °C. Again on the basis of the TPR results [IV,V], the ruthenium and platinum β zeolites were reduced at 250 °C. The reduction was for three hours under hydrogen flow.

The TGA diagram of Pd(thd)$_2$ impregnated on alumina measured in hydrogen describes the reduction of associatively adsorbed Pd(thd)$_2$ (Fig. 4). The first region of weight decrease, with maximum rate of weight loss at 115 °C, is related to the loss of one thd ligand and to the partial reduction of palladium. The second region of weight decrease, with maximum rate of weight loss at 220 °C, represents the removal of the second thd ligand and the reduction of the rest of the palladium. The third region of weight decrease, with maximum rate of weight loss at 550 °C, is related to the dehydroxylation of the alumina support.

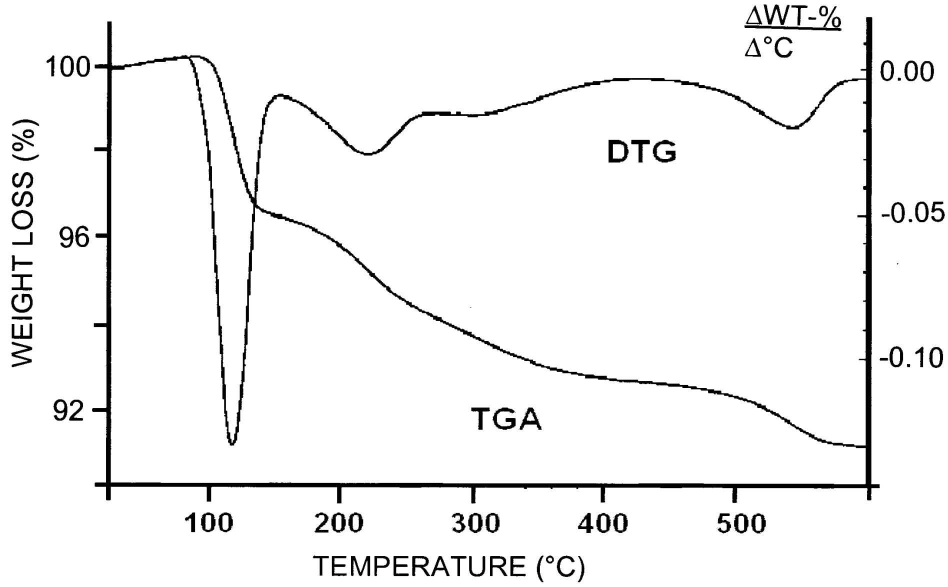

Figure 4. TGA and DTG diagrams of impregnated Pd(thd)$_2$ on alumina measured in hydrogen atmosphere.

Only a part of the surface–Pd(thd) complex formed in ligand exchange reaction in the ALE deposition was reduced in hydrogen at 90 °C. Increase in the reduction temperature up to 300 °C did not increase the amount of metallic palladium. However, the removal of ligands was observed during the reduction since the carbon content decreased from 1.2 wt-% to 0.4 wt-% (Pd/SiO_2) and from 2.6 wt-% to 0.8 wt-% (Pd/Al_2O_3).

On the basis of the TPR analysis, a reduction temperature of 300 °C was chosen for the Pt catalysts on alumina and silica prepared by ALE. The amount of metallic state clearly increased in the reduction of the calcined samples. However, in all the reduced samples, platinum was still present in oxidation state +2. The amount of Pt^0 was greater in the samples that were calcined before reduction than in the samples that were directly reduced. In the ALE samples the amount of metallic platinum was higher (87%) on alumina than on silica (57%). In the impregnated samples, the amount of metallic platinum was present at about the same level on alumina and silica (73% and 77%, respectively).

TPR analysis of the platinum on β zeolites calcined at 350 °C [V] showed no signal, which indicates that platinum is not further reduced up to 500 °C. The TPR analysis [IV] of ruthenium on β zeolites calcined at 500 °C suggested 250 °C as a suitable reduction temperature. The TPR profiles for ruthenium on β zeolites are displayed in Fig. 1 of publication [IV].

4.4 Properties of catalysts

The properties of all the catalysts prepared by impregnation and ALE on alumina and silica, after reduction, are summarised in Table 5.

Table 5. Properties of the catalysts prepared by impregnation and ALE on alumina and silica, after reduction.

		Impregnation			ALE		
		Pd	Ru	Pt	Pd	Ru	Pt
Precursors		$Pd(thd)_2$	$Ru(thd)_3$	$(CH_3)_3(CH_3C_5H_4)Pt$	$Pd(thd)_2$	$Ru(thd)_3$	$(CH_3)_3(CH_3C_5H_4)Pt$
Reduction	T, °C	90	140/300	300	90/300	140/300	300
	Reduction degree, %	69-88	(91-90)*	73-77	70-78	(21-93)*	57-87
Total metal content, %	Al_2O_3	4.5	4.3	1.2	3.6/3.5	0.6/0.5	1.2
	SiO_2	4.9	5.4	1.2	5.0/5.2	0.7/0.8	1.5
Metal^0 content, %	Al_2O_3	3.1	3.9	0.8	2.5	0.1/0.5	1.0
	SiO_2	4.3	4.9/0.9	0.9	3.9/3.6	0.2/0.7	0.9
Dispersion, %		2-4	11-18	24-91**	30-40	10-83	36-90**
Particle size, nm		28-54	7-12	1-5	3-4	2-13	1-2
Crystallite size, nm		13-14	3-12	-	2	-	-

*calculated, not measured, because signals of ruthenium and carbon were overlapping in XPS analysis, **dispersion values for Pt are not corrected with reduction degree

Particle size of the metal was small when the reaction between the precursor and the support occurred via ligand exchange. Large metal particles were obtained when the interaction of the precursor with the support was associative adsorption.

The dispersions of platinum on β zeolites ranged between 20% and 68%. The average particle sizes for the reduced platinum on β zeolites were 2 - 6.8 nm. The dispersions of metallic ruthenium on β zeolites were between 0.4% and 2.7% with particle size between 52 nm and 360 nm. The correlation between the particle sizes and the acidity for Ru β zeolites (Fig. 2, IV) describes the effect of the acidity on the particle sizes of metallic ruthenium. Ruthenium particles were smallest on the β zeolite with high acidity, and largest when the acidity of β zeolite was low. Similar dependency was observed for Pt β zeolites [V].

4.5 Activity of catalysts

The factors influencing on the activity of the catalysts were the metal, the particle size of the metal and the support. The type of metal affected the activity more than did the support and particle size. The influences of support and particle size on the activity were of similar magnitude. The effect of particle size varied with the metal and support in a different way with each catalyst.

4.5.1 Effect of metal

The palladium catalysts were more active than the ruthenium and platinum catalysts in cinnamaldehyde hydrogenation. The effect of the metal on the activity was evident in a comparison of impregnated Pd/Al_2O_3 and Ru/Al_2O_3 catalysts and of impregnated Pd/SiO_2 and Ru/SiO_2 catalysts with similar metal content. The conversion of cinnamaldehyde on the Pd/Al_2O_3 catalyst after four hours hydrogenation was 94%, whereas with the Ru/Al_2O_3 catalyst it was only 40%. The conversion of cinnamaldehyde on the Pd/SiO_2 catalyst after four hours hydrogenation was 100%, whereas with the Ru/SiO_2 catalyst it was only 30% [III].

Conversions of cinnamaldehyde were lowest with platinum. All impregnated platinum catalysts and the platinum catalysts prepared by ALE on alumina and silica gave about 3% conversion, and the 5 wt-% Pt on β zeolite a conversion of only 11%, after four hours hydrogenation at reaction temperature of 60 °C [V,VI]. The conversions of impregnated platinum catalysts and the platinum catalysts prepared by ALE on alumina and silica were also between 9-17% at 100°C and after 26 hours hydrogenation [VI].

Effect of the metal on the activity in cinnamaldehyde hydrogenation was also clearly observed in a comparison of the ruthenium and platinum catalysts supported on β zeolite. The Ru-Beta2 (1.6 wt-% Ru) catalyst showed a conversion of 25% after four hours hydrogenation, whereas Pt-Beta2 (2.5 wt-% Pt) showed only 5% [IV,V]. Similary, comparison of the ALE-prepared Ru and Pt catalysts supported on silica showed the influence of the metal on activity in cinnamaldehyde hydrogenation. Although both catalysts had a particle size of 2 nm and the metal content of the Ru catalyst was lower than that of the Pt, the conversion of the Ru catalyst was 23% after four hours hydrogenation and that of the Pt catalyst only 2%.

Figure 5 shows the influence of the metal on the activity of Pd, Ru and Pt supported on silica in cinnamaldehyde hydrogenation. The impregnated 4.9 wt-% Pd catalyst is compared with the impregnated 5.4 wt-% Ru catalyst, and the ALE-prepared 0.8 wt-% Ru catalyst with the ALE-prepared 1.2 wt-% Pt catalyst.

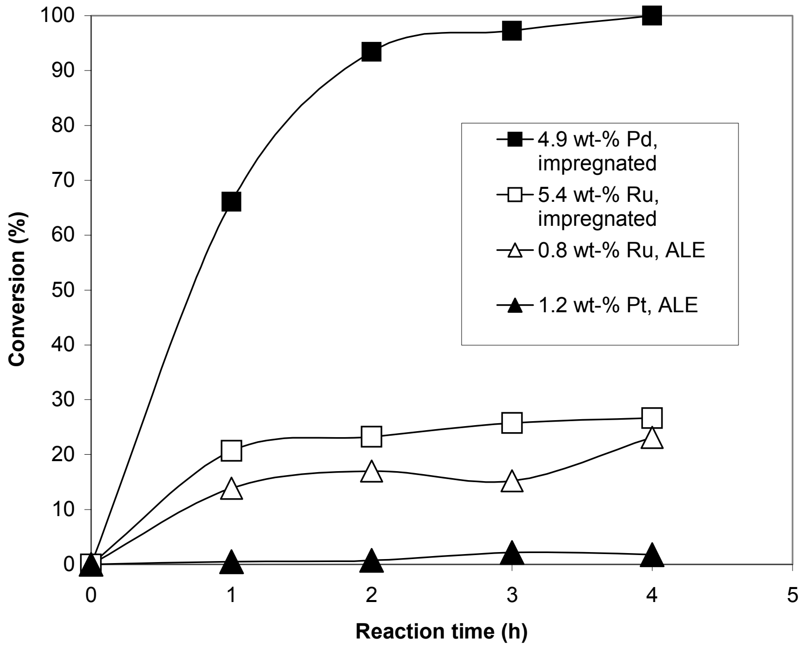

Figure 5. Comparison of the activities in cinnamaldehyde hydrogenation of silica-supported Pd, Ru and Pt catalysts with different metal loading. Catalysts were prepared by impregnation and ALE.

TOF values of different catalysts are summarised in Table 6 [III-VI]. The TOF values of platinum catalysts were essential lower than the TOF values of Pd and Ru catalysts, showing that platinum is the least reactive metal in this reaction.

Table 6. Comparison of TOF values of different metals and supports.

TOF (1/s)	Pd		Ru		Pt	
	Impreg.	ALE	Impreg.	ALE	Impreg.	ALE
SiO_2	3.4	0.3	0.2	2.5	0.1 (100 °C)	0.04 (100 °C)
Al_2O_3	1.9	0.3	0.6	0.7	0.01 (100 °C)	0.01 (100 °C)
β zeolites			0.1-1.7		0.02-0.04	

4.5.2 Effect of particle size

Another factor besides the metal that affects the activity in cinnamaldehyde hydrogenation is the particle size of the catalyst. The catalysts with smaller particle size were more active than those with large particle size because of the essential increase in the number of active sites [III, VI]. Although the metal content of ALE-prepared Pd/Al_2O_3 after reduction was less than that of impregnated Pd/Al_2O_3, the ALE-prepared Pd/Al_2O_3 catalyst with average particle size of 3 nm gave a conversion of 78% after one hour hydrogenation, whereas the impregnated Pd/Al_2O_3 catalyst with average particle size of 28 nm gave a conversion of only 42% (Fig. 6). Similarly, after one hour hydrogenation, the ALE-deposited (3.9 wt-%) Pd/SiO_2 catalyst with average particle size of 4 nm gave a conversion of 90% and the impregnated (4.3 wt-%) Pd/SiO_2 catalyst with average particle size of 54 nm a conversion of just 66% [III].

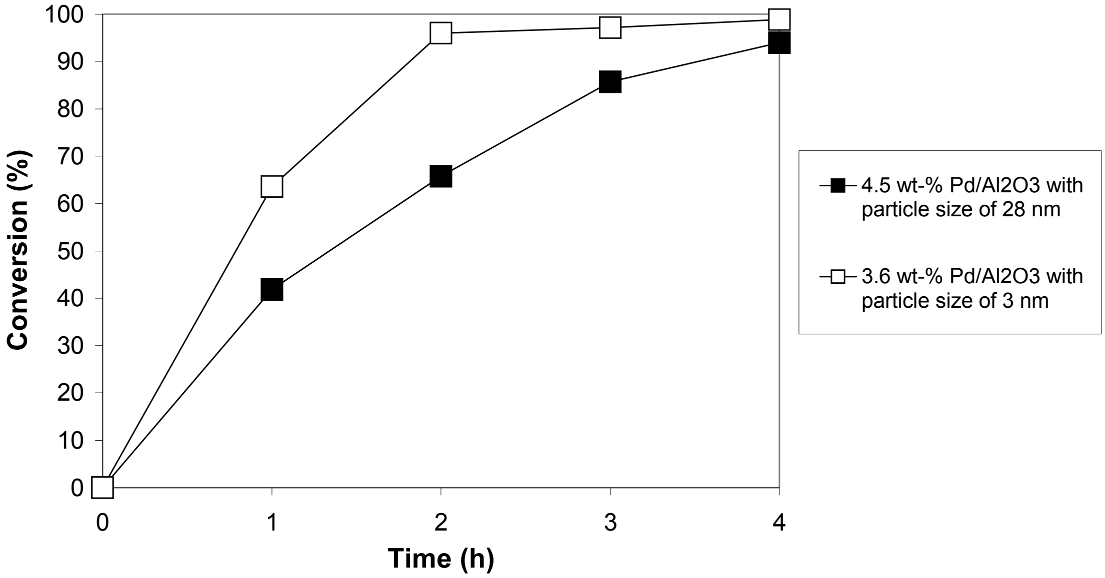

Figure 6. Comparison of the activities of Pd/Al_2O_3 catalysts with different particle sizes.

For platinum on silica, and on β zeolites too, the catalysts with smaller particle size were more active than those with larger particle size. After 26 hours hydrogenation, the Pt/SiO_2 catalysts with particle size of 4.8 nm gave a conversion of 14%, whereas for Pt/SiO_2 catalysts with particle size of 6.8 nm the conversion was 13%[VI]. After four hours hydrogenation, the platinum on β zeolite with particle size of 2 nm gave a conversion of 9%, whereas the platinum on β zeolite with particle of 6.8 nm gave a conversion of only 3%[V].

In a similar way to the Pd and Pt catalysts, the particle size of the ruthenium catalysts (ALE deposited Ru/SiO_2 with Ru content 0.8 wt-% and impregnated Ru/SiO_2 with Ru content 1.0 wt-%

both reduced at 300 °C) affected the activity. After four hours hydrogenation, ALE-deposited Ru/SiO_2 catalyst with particle size of 13 nm gave a conversion of 32%, whereas the impregnated Ru/SiO_2 catalyst with particle size of 42 nm gave a conversion of only 5% [III].

The surface metal atoms of palladium on alumina and silica prepared by impregnation were more reactive than those of catalysts prepared by ALE because of the larger particle size (see Table 6). For platinum catalysts, the reactivity was higher for the impregnated than the ALE-prepared catalysts when supported on silica, but similar when on alumina. All the TOF values for platinum catalysts were very small, however. No relation between particle size and TOF value was found for the ruthenium catalysts [III].

4.5.3 Effect of support

The support played an important role in the activity of all the catalyst. After four hours hydrogenation the conversions of cinnamaldehyde were 8–25% for Ru/β zeolite catalysts (impregnated) [IV], 24–40% for Ru/Al_2O_3 catalysts (impregnated and ALE)[III] and 5–32% for Ru/SiO_2 catalysts (impregnated and ALE). After the same time the conversions with the Pd/SiO_2 (impregnated and ALE) catalysts were 100% and for Pd/Al_2O_3 (impregnated and ALE) were 94% and 100%, respectively [III].

Platinum catalysts supported on silica were more active than those supported on alumina. After 26 hours hydrogenation, the conversions of the Pt/SiO_2 catalysts (impregnated and ALE) were

13–17%, whereas the conversions of the Pt/Al_2O_3 catalysts (impregnated and ALE) were 9–13%.

Figure 7 shows the effect of the support on the activity of the platinum catalysts with small particle size in cinnamaldehyde hydrogenation. The metal content and particle sizes after reduction of both catalysts were of similar magnitude.

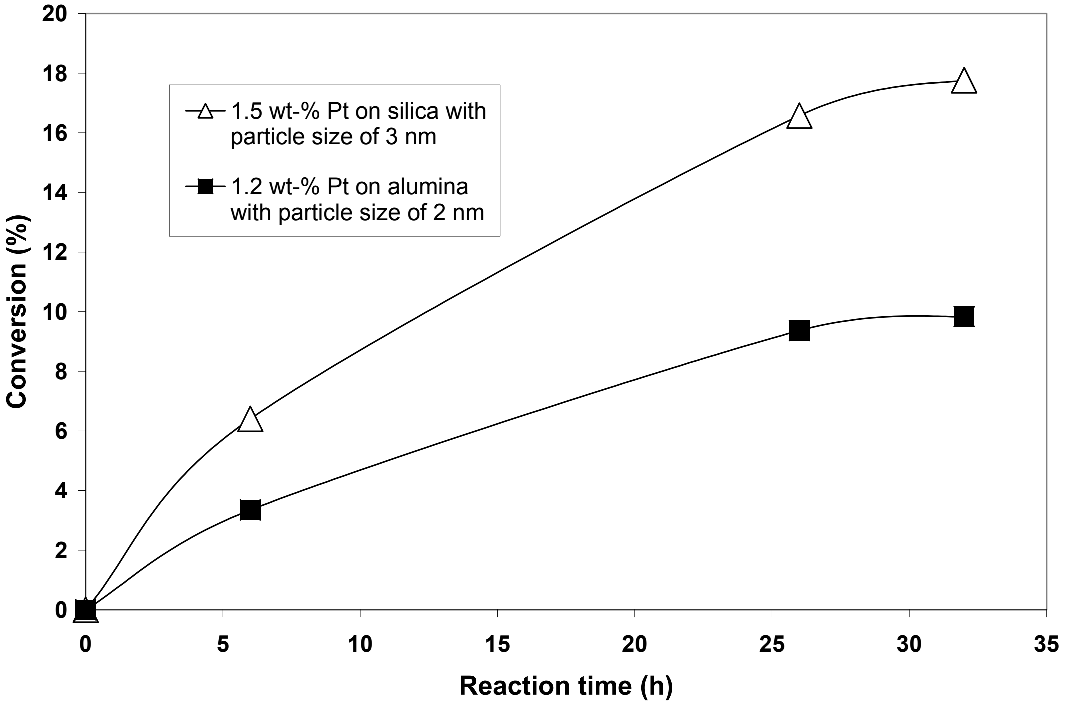

Figure 7. Influence of the support on the platinum activity in cinnamaldehyde hydrogenation.

The activity of ruthenium increases according to the support in the following order: β zeolite < SiO_2 < Al_2O_3. For platinum the order is: β zeolite < Al_2O_3 < SiO_2 and for palladium the activity increases according to the support in the following order: Al_2O_3 < SiO_2 .

4.5.4 Effect of metal content

The metal loading effect was studied for platinum catalysts supported on β zeolites with similar particle sizes [V]. Increase in the metal loading was found to increase the total conversion and the conversion to hydrogenated products, but the conversion to acid-site catalysed products was decreased.

4.6 Selectivity of catalysts

Comparison of the catalysts showed that the type of metal, type of support, the particle size of the metal and the precursor used in the preparation all affect the selectivity. The extent of the impact was dependent on the catalyst material.

4.6.1 Effect of metal

Selectivities of the ruthenium, palladium and platinum supported on alumina, silica and β zeolites in cinnamaldehyde hydrogenation and factors influencing the selectivity are discussed in detail in publications III – VI.

Palladium catalysts favoured the adsorption of cinnamaldehyde via the C=C bond, platinum catalysts via the C=O bond, and ruthenium catalysts via the C=C and C=O bonds [III-VI]. This difference in the adsorption can be explained in terms of the different radial expansion of the d band of the three metals [129]. The effect of the metal on the selectivity is illustrated in Fig. 8.

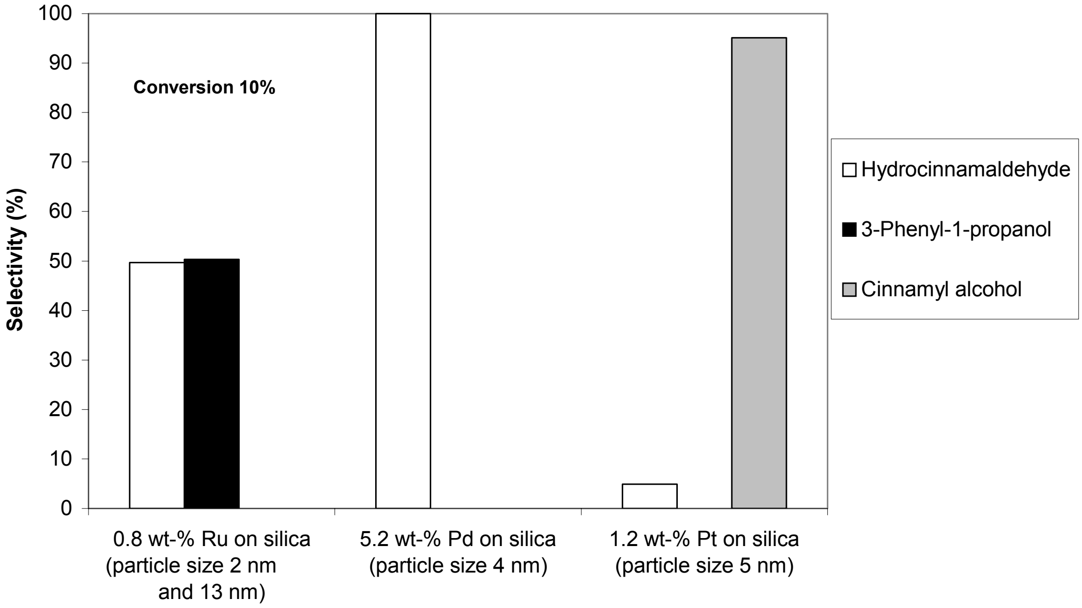

Figure 8. Influence of metal on the selectivity in cinnamaldehyde hydrogenation.

At low conversion (<15%), hydrocinnamaldehyde was the sole product in cinnamaldehyde hydrogenation with the Pd catalyst on silica. Both hydrocinnamaldehyde and 3-phenyl-1-propanol were formed with the Ru catalyst on silica even that these catalysts exhibited different

Ru particle sizes [III] and more than 90% cinnamyl alcohol and less than 10% hydrocinnamaldehyde with the Pt catalyst on silica. The selectivity to cinnamyl alcohol followed the series Pt > Ru > Pd, in agreement with the results reported by Giroir-Fendler et al. [25].

4.6.2 Effect of support

The marked effect of the support on selectivities is best illustrated with the ruthenium catalysts (Fig. 9). The Ru/SiO_2 catalysts prepared by ALE produced only hydrocinnamaldehyde and 3-phenyl-1-propanol, whereas the Ru/Al_2O_3 catalyst (η-Al_2O_3) prepared by ALE produced hydrocinnamaldehyde, cinnamyl alcohol and 3-phenyl-1-propanol and also phenyl propane. By comparison, the commercial Ru/Al_2O_3 catalyst (γ-Al_2O_3) formed cinnamyl alcohol, hydrocinnamaldehyde and 3-phenyl-1-propanol [III, IV].

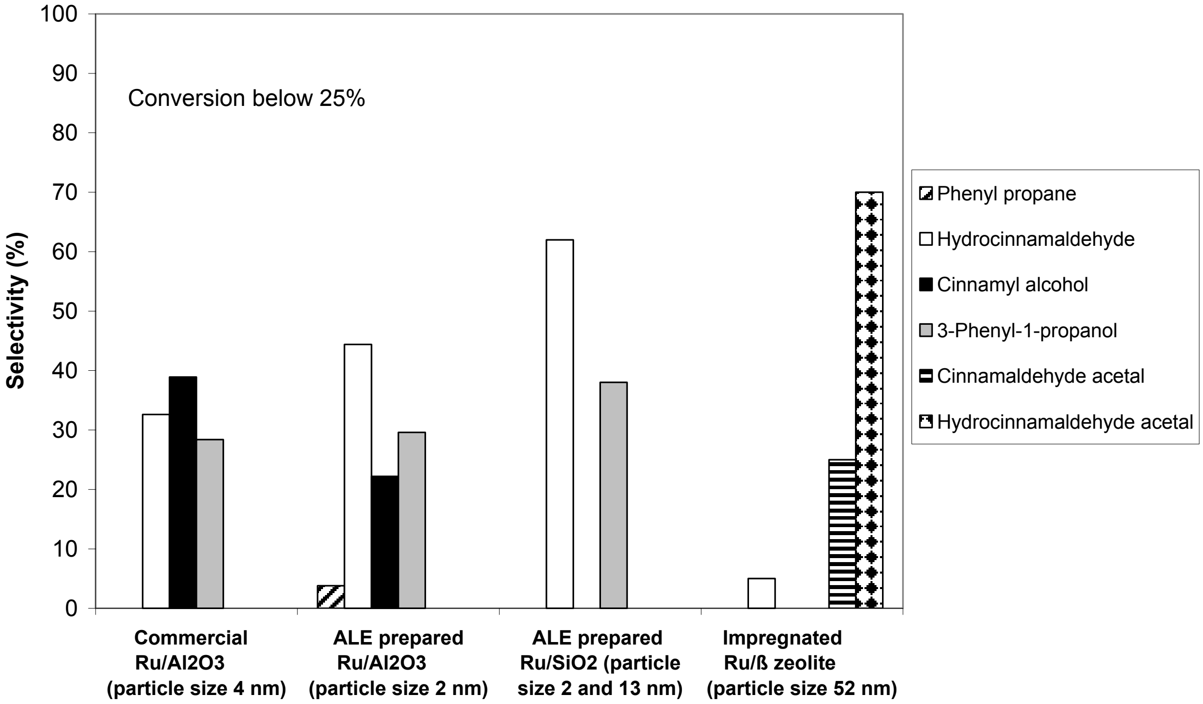

Figure 9. Selectivity of ruthenium on different supports in cinnamaldehyde hydrogenation. The β zeolite has the highest content of acid sites.

Impregnated ruthenium on silica produced several hydrogenated products. Impregnated Ru/Al_2O_3 catalyst produced ether as main product and no cinnamyl alcohol was detected. Impregnated ruthenium on β zeolites, in turn, was selective to hydrocinnamaldehyde and acetals. The ruthenium contents of catalysts were between 0.5 and 5.4 wt-% [III,IV].

In agreement with the results obtained by Szöllösi et al.[130], platinum catalysts supported on silica were more selective to cinnamyl alcohol than those supported on alumina [VI]. In contrast, palladium catalysts on silica were less selective to cinnamyl alcohol than palladium catalysts on alumina [III].

The acidity of the support affected the acetal formation. The molecular modeling together with acidity measurerments have proofed that acetalization occurred on the external catalyst surface on Brönsted acid sites [V]. In a comparison of ruthenium and platinum on β zeolites with different amounts of acid sites, acetals formation was greatest for the catalyst with the highest amount of Brönsted acid sites [IV,V].

4.6.3 Effect of particle size

The influence of particle size on the selectivity of the catalysts can be seen in a comparison of the Pd/Al_2O_3 catalysts. Relative to large particle size (28 nm), the small particle size (3 nm) of palladium favoured the formation of cinnamyl alcohol. The selectivity to cinnamyl alcohol at conversion of 90% was 26% for the catalyst with small particle size, but only 5% for the catalyst with large particle size [III]. Similarly, in a comparison of the Pd/SiO_2 catalysts, the selectivity to cinnamyl alcohol at conversion 90% was 32% for the small particle size (4 nm) catalyst, and only 17% for the catalyst with large particle size (54 nm) [III].

In contrast to the Pd catalysts, the Pt/SiO_2 catalysts with large particle size of 6.8 nm were more selective to cinnamyl alcohol than those with small particle size of 3.1 nm [VI]. At conversion of 15%, the selectivities were 90% and 70%, respectively [VI]. These results were in agreement with the results reported by Gallezot et al. [131]. No relation was found between the selectivity to cinnamyl alcohol and the particle size of the ruthenium catalysts [III].

4.6.4 Effect of precursor

The precursor used in the catalyst preparation affected the selectivity. The effect was observed with impregnated Pd, Pt and Ru catalysts on silica prepared from different precursors. Acetals were formed with Pd and Ru catalysts where ß-diketonate complexes were used as precursors, whereas no acetals were formed with Pt catalysts prepared from cyclopentadienyl compound as precursor. With proper choice of the precursor, the formation of the undesired products catalysed by acid sites could be avoided. The best selectivity to cinnamyl alcohol (over 90%) was obtained at conversion of 15% with the platinum catalyst supported on silica where (trimethyl)methylcyclopentadienyl platinum(IV) was used as precursor [VI].

5. CONCLUSIONS

Palladium and ruthenium ß-diketonate and platinum cyclopentadienyl complexes were suitable precursors for the preparation of ALE catalysts. They are thermally stable and evaporate easily in inert atmosphere. In ALE deposition of Pd(thd)$_2$, ligand exchange reaction and metal formation (51-70%) occurred on both alumina and silica. A small part of the Pd(thd)$_2$ on alumina was dissociatively adsorbed. In impregnation of Pd(thd)$_2$ and Ru(thd)$_3$, the interaction with the alumina and silica supports was associative adsorption and 13-17% of the palladium was reduced to metallic form. The particle sizes of palladium formed in ALE deposition and in the reduction after ALE deposition were smaller than the particle sizes of palladium formed in the reduction of impregnated samples.

In deposition of $(CH_3)_3(CH_3C_5H_4)Pt$ complex on alumina and silica by both ALE and impregnation, a ligand exchange reaction took place releasing methane. The amount of metal formed during the deposition by impregnation on alumina and silica was 57% and 21%, respectively, whereas for preparation by ALE on alumina and silica it was 56% and 31%. After reduction the particle size of platinum for both ALE and impregnated Pt/Al_2O_3 catalysts was 1 nm, for ALE-prepared and impregnated Pt/SiO_2 catalysts it was 2 nm and 4-5 nm, respectively.

On both alumina and silica, activity in cinnamaldehyde hydrogenation was higher for the Pd catalysts than for the Ru and Pt catalysts. After four hours hydrogenation, the conversions with palladium catalysts were 90-100% and those with ruthenium catalysts 5- 42 %. The conversions of Pt catalysts were only 13-18% after 32 hours hydrogenation, though the reaction temperature was 100°C.

Palladium catalysts prepared by ALE showed better initial activity than the impregnated catalysts because small metal particles were formed in the deposition. Although the metal content of the Ru catalysts prepared by ALE on alumina and silica was lower than that of the impregnated catalysts, the activities were of the same order of magnitude. The conversion was 35% after four hours hydrogenation.

The acidity of the β zeolites affected the reduction behaviour of ruthenium and the particle size of ruthenium, which further influenced the activity. The particle size increased with decrease in the acidity. Acetal formation was found to increase with the Brönsted acidity of zeolite supports; thus Ru and Pt on β zeolites with the highest Brönsted acidity also gave the highest conversions of cinnamaldehyde. Acetalization occurred on the external surface of Pt β zeolites based on results from molecular modeling and acidity measurements [V]. Ruthenium on β zeolites were more active than platinum on β zeolites. After four hours hydrogenation the conversions with Ru on β zeolites were between 8% and 25%, and with Pt on β zeolites 5% and 9%. The surface Ru atoms on β zeolites showed higher reactivity than those of platinum on β zeolites.

Palladium catalysts favoured adsorption of cinnamaldehyde via the C=C bond and ruthenium catalysts adsorption via C=C and C=O bonds. On platinum catalysts, adsorption on the C=O bond was favoured. With all the Pd catalysts supported on alumina and silica, hydrocinnamaldehyde was formed as the main product.

The ruthenium catalysts showed an essential difference in selectivity. With the Ru/Al_2O_3 catalyst prepared by ALE the main product was cinnamyl alcohol, whereas with Ru/SiO_2 prepared by ALE, only hydrocinnamaldehyde and 3-phenyl-1-propanol were produced. The impregnated Ru on β zeolites were selective to hydrocinnamaldehyde.

Impregnated and ALE-prepared platinum on alumina and silica formed as much as 90% cinnamyl alcohol as main product, and also some hydrocinnamaldehyde. The platinum on β zeolites catalysed the isomerisation of hydrocinnamaldehyde to cinnamyl alcohol. All other catalysts were selective to a variety of hydrogenated products.

Side-products (acetals and ether) were sometimes formed in reactions between the solvent and reactants. The Brönsted acidity and the protons formed by reduction of catalysts with hydrogen caused the formation of products catalysed by acid sites. These products can be avoided through proper choice of the precursor and preparation method; namely, no acetals or ethers were formed with the platinum on alumina and silica catalysts prepared from trimethyl(methylcyclopentadienyl)platinum or with the ruthenium on alumina and silica catalysts deposited by ALE.

According to the results obtained in this study, the best choice for a selective catalyst for the production of cinnamyl alcohol would be a platinum catalyst supported on silica. As has been shown, the best selectivity to cinnamyl alcohol, over 90% at conversion of 15%, was achieved with the impregnated 1.2 wt-% Pt/SiO_2 catalyst with particle size of 4 nm. If hydrocinnamaldehyde is the desired product, a palladium catalyst supported on silica is recommended. At conversion below 10%, only hydrocinnamaldehyde was formed when impregnated or ALE-prepared Pd/SiO_2 catalysts were used.

LIST OF ABBREVIATIONS

Catalyst precursors

$Pd(thd)_2$	Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)palladium
$(CH_3)_3(CH_3C_5H_4)Pt$	(trimethyl)methylcyclopentadienylplatinum (IV)
$Ru(acac)_3$	Tris(2,4-pentanedionato)ruthenium
$Ru(C_5H_5)_2$	Bis(cyclopentadienyl)ruthenium
$Ru(thd)_3$	Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium
$RuCl_3$	Ruthenium chloride
$Pt[(NH_3)_4](NO_3)_2$	Tetraammineplatinum(II)nitrate

Catalysts

Pd/Al_2O_3	Palladium on alumina
Pd/SiO_2	Palladium on silica
Pt/Al_2O_3	Platinum on alumina
Pt/SiO_2	Platinum on silica
Pt/ß zeolite	Platinum on beta zeolite
Ru/Al_2O_3	Ruthenium on alumina
Ru/SiO_2	Ruthenium on silica
Ru/ß zeolite	Ruthenium on beta zeolite

Analytical techniques

AAS	Atomic absorption spectroscopy
^{27}Al MAS-NMR	Solid state magic-angle spinning aluminum nuclear magnetic resonance spectroscopy
BET	Brunauer Emmett Teller method
^{13}C NMR	Carbon nuclear magnetic resonance spectroscopy
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EDS	Energy dispersive spectroscopy
GC	Gas chromatography
^{1}H NMR	Proton nuclear magnetic resonance spectroscopy
^{1}H MAS-NMR	Solid state magic-angle spinning proton nuclear magnetic resonance spectroscopy
INAA	Instrumental neutron activation analysis
ICP	Inductively coupled plasma emission spectroscopy
MS	Mass spectrometry
^{31}P MAS-NMR	Solid state magic-angle spinning phosphorus nuclear magnetic resonance spectroscopy
SDTA	Single differential thermal analysis
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TPR	Temperature–programmed reduction (with hydrogen)
XPS	X-ray photoelectron spectroscopy

XRD	X-ray diffraction
XRF	X-ray fluorescence spectrometry

Others

ALE	Atomic layer epitaxy
CVD	Chemical vapour deposition
HIV	Human immunodeficiency virus

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