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Mechanistic insights on the hydroconversion of cinnamaldehyde using mechanochemically-synthesized Pd/Al-SBA-15 catalysts

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Abstract

The hydroconversion of cinnamaldehyde as α,β-unsaturated compound was studied using a simple and efficient hydrogen-donating protocol catalyzed by mechanochemically synthesized bifunctional Pd/Al-SBA-15 catalysts. Materials were characterized using TGA-TDA, nitrogen physisorption, TEM and EDX analyses. Catalytic results pointed to the presence of competitive pathways able to provide a selectivity switch from expected fully hydrogenated aromatic ring (e.g. cyclohexane) and hydrogenated products (e.g. hydrocinnamaldehyde, cinnamyl alcohol and 3-phenylpropan-1-ol) to unexpected ethylbenzene and oxalic acid products from hydrodeformylation and hydrocarboxylation reactions of cinnamaldehyde and formic acid, respectively.

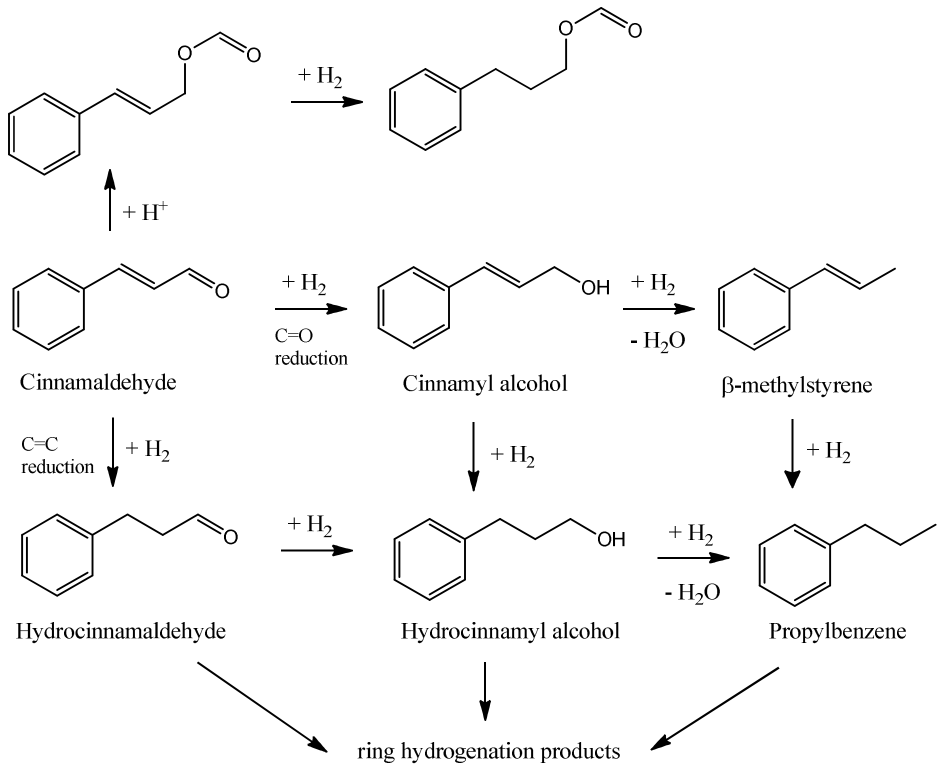
Keywords: Pd/AlSBA-15, cinnamaldehyde conversion, microwave irradiation

Introduction

The selective hydrogenation of α,β-unsaturated aldehydes has attracted significant interest in the production of fine chemicals especially for the fragrances and flavoring industries.[1] In particular, the hydroconversion of cinnamaldehyde to various important derivatives including cinnamyl alcohol and hydrocinnamaldehyde has been the subject of mechanistic studies with different types of catalytic systems to investigated C=C vs C=O hydrogenation selectivities and the potential existence of structure sensitive processes.[2-4] In any case, the process has also relevance from the industrial point of view as typically obtained products (e.g. cinnamyl alcohol, hydrocinnamaldehyde) can find applications as additives in the food and pharmaceutical industries.[5]

Reaction pathways and mechanism in cinnamaldehyde hydroconversion have been proposed under a rather general consensus that hydrogenations, hydrogenolysis and dehydrations are key processes leading to most compounds illustrated in Scheme 1.[2-7] A wide range of conditions and several heterogeneous catalysts have been utilized in the reaction, mostly supported noble metal catalysts (e.g. Pd, Pt, Ru) on porous materials including zeolites, silicates (SBA and MCM-type materials), alumina, etc. at moderate temperatures and high pressures of hydrogen.[5, 8-12] Interestingly, no literature reports could be found on the use of hydrogen-donating solvents for cinnamaldehyde hydroconversion.

Formic acid is a biomass-derived chemical that readily decomposes under certain metal-catalysed and temperature conditions (e.g. microwave-irradiation) into H_2 and a mixture of CO + CO_2, providing a potentially useful alternative to conventional hydrogen-donors (e.g. isopropanol) in hydrogen-transfer reactions[13-15] as well as in nanomaterials synthesis.[16, 17] Due to its acid properties, formic acid has additionally been proven to be highly effective in promoting acidolytic cleavage of C-C and C-O bonds in starting materials as recalcitrant as lignin.[18]



Scheme 1. Reaction scheme of the cinnamaldehyde hydrogenation. Adapted from reference 3.

In light of the excelling features of formic acid as hydrogen-donor and (co-)catalyst as well as current possibilities to be derived from biomass (concomitantly produced with levulinic acid from cellulose hydrolysis/dehydration[19, 20]), we were prompted to explore a novel cinnamaldehyde hydroconversion strategy using formic acid as both hydrogen-donating solvent and co-catalyst under both conventional heating and microwave irradiation. Microwave protocols have been extensively reported to accelerate rates of reaction as compared to conventionally heated protocols, often changing selectivities to products, due to the rapid a homogeneous heating achieved in the bulk solution as compared to conventional heating.[21] Previous work from the group also pointed out a synergetic effect between the use of microwave irradiation and formic acid decomposition catalyzed by supported metal nanoparticles.[17, 18]

Herein, we report the mechanochemical preparation of various Pd-containing Al-SBA-15 with different Pd contents as bifunctional catalysts for the hydroconversion of cinnamaldehyde using formic acid. Results of the activity of supported Pd aluminosilicates were compared to that of a commercial 5%Pd/C.

Experimental

All chemicals and reagents used in this study (at least 99% purity) were purchased from Sigma Aldrich (unless otherwise stated) and were not further purified.

Synthesis of supports

Al-SBA-15 materials (Si/Al=20 ratio) were synthesized according to a previously reported protocol. A solution (300 mL) of hydrochloric acid at pH = 1.5 was prepared, then 8.07 g of surfactant (Poly (ethylene-glycol)-block (P123 Aldrich) was added to this solution. The mixture was stirred until having one final transparent solution. 0.82 g of Aluminum isopropoxide 98 wt. % (Aldrich) was then added to the mix followed by 18 mL TEOS (tetraethylortosilicate) dropwise (time 5-10 min). The final gel was stirred during 24 h and introduced in a furnace at 100 °C, t = 24 h. The products obtained were filtered and calcined in air at 600 °C during 8 h (2 h in nitrogen atmosphere and 6 h in air).

Mechanochemical synthesis of Pd/Al-SBA-15

Pd/Al-SBA-15 materials were synthesized following a previously reported mechanochemical protocol.[17, 22] Different quantities of solid Pd precursor [palladium (II) acetate] to reach theoretical Pd contents of 0.5, 1, 2 and 4 wt.% Pd in the materials were milled together with the pre-formed Al-SBA-15 in the solid phase in a Retsch PM 100 bioMETA planetary ball mill (optimum conditions: 350 rpm, 10 minutes milling[17]). Upon milling, the final mechanochemical material obtained was calcined at 450°C in air (10 °C/min) for 2 hours. For simplicity, supported Pd nanoparticle Al-SBA-15 materials have been denoted as PdX-Al where X stands for the Pd content in the materials and Al refers to Al-SBA-15. A commercial 5%Pd/C catalyst (Sigma-Aldrich) has been also employed as reference catalyst for comparative purposes.

Catalyst characterisation

Thermal analysis was performed by simultaneous TG-DTA measurement using a System Setaram Setsys 12 TGA instrument. Samples were heated at a heating rate of 10ºC min^{-1}, in air (40 mL min^{-1}) at the temperature range 50-1000 ºC. The compound α-Al_2O_3 was used as a reference material.

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 2 h at 373 K under vacuum ($p < 10^{-2}$ Pa) and subsequently analyzed. The linear part of the BET equation (relative pressure between 0.05 and 0.30) was used for the determination of the specific surface area. The pore size distribution was calculated from the adsorption branch of the N_2 physisorption isotherms and the Barret-Joyner-Halenda (BJH) formula. The cumulative mesopore volume V_{BJH} was obtained from the PSD curve.

Energy-dispersive X-ray spectroscopy (EDX) measurements were performed using a Scanning Electron Microscope (SEM) JEOL JSM 6300 provided with a microanalysis system

Inca Energy 250, with a SiLi detector. Detection interval: from boron to uranium, resolution: 137 eV to 5.9 keV.

Catalytic experiments

Conventional heating reactions

Reactions under conventional heating were conducted in a Carousel Radleys multi-reaction system (12 reaction vials) with controllable temperature using a thermocouple. In a typical experiments, 0.5 mL cinamaldehyde (4 mmol), 1.5 mL formic acid (40 mmol), 10 mL acetonitrile, 1 g catalyst were stirred together at 82 ºC (reaction temperature) for the desired time of reaction. The reaction was conducted at atmospheric pressure. Samples were then withdrawn from the reaction mixture and analyzed by GC using an Agilent 6890N fitted with a capillary column HP-5 (30 m × 0.32 mm × 0.25 m) and a flame ionisation detector (FID). The identity of the products was confirmed by GC–MS.

Microwave-assisted reactions

Microwave experiments were carried out in a CEM-DISCOVER model with PC control. Experiments were performed on a closed vessel mode (pressure controlled) under continuous stirring. The microwave method was generally power-controlled where reaction mixtures were irradiated with a power output of 200 W (180ºC maximum temperature reached, average temperature = 150ºC) under autogenously generated pressures for 15 min (maximum 250 PSI, 17.25 bar). In a typical reaction, 0.1 mL cinnamaldehyde (0.8 mmol) and 0.3 mL formic acid (8 mmol) in 2 mL acetonitrile were microwaved in the presence of the catalyst (0.5 g) for 15 min at 200 W. Products were identified and quantified in a similar way as reported above.

Results and discussion

TGA-DTA analyses were carried out to study the desorption-calcination of the parent materials (filtered material during the synthesis, previous to calcination at 600 °C to obtain the SBA-15 solids without added Pd). The first weight loss at 100 °C (endothermic – TDA signal) of 2-5 wt.% was due to the presence of water over the catalyst. The next weight loss (exothermic signals; T = 200 – 500 °C; 35 wt.% mass loss, Figure 1) can be assigned to the combustion-desorption of carbonaceous species used for the catalyst synthesis (mainly surfactants). From 500 °C only a small amount of weight loss was detected (dehydroxylation of –OH species over the surface of the support). DTA experiments showed an endothermic signal at ca. 100 °C and then two clear exothermic signals (230 and 270 °C) from the desorption - combustion of the surfactant species (Figure 2).

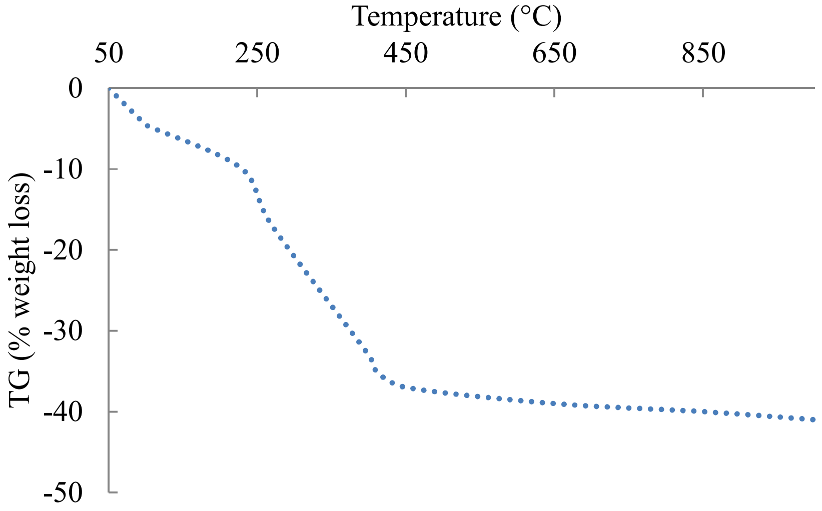


Figure 1. TGA of Al-SBA-15 prior to calcination.

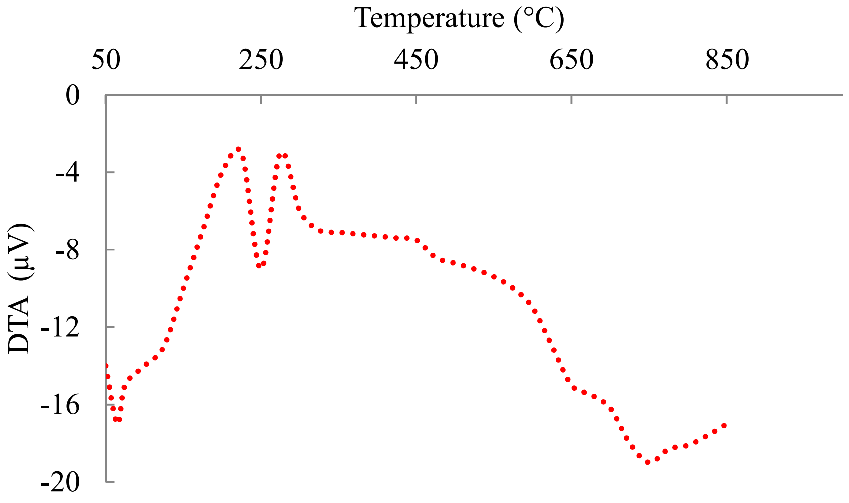


Figure 2. DTA of parent Al-SBA-15 before calcination.

Textural properties of mechanochemically synthesized supported nanomaterials have been included in Table 1. As expected, a significant decrease on surface area of all catalysts could be observed upon metal incorporation. Pore sizes were also observed to decrease particularly for samples with higher metal loading (e.g. Pd4-Al = 4%Pd/Al-SBA-15). Interestingly, no significant pore blocking could be observed at low incorporated metal loadings (nanoparticles are distributed within the external surface and the pores of the material as previously demonstrated[17, 22]). Pd4-Al experienced a remarkable reduction in pore size as compared to parent Al-SBA-15 (from 8.9 to 6.8) which may be due to a partial pore blocking upon Pd incorporation within the pores of the material. Pore volumes also followed a similar trend, being significantly reduced upon metal incorporation in Al-SBA-15. Representative TEM images of the metal-containing SBA-15 materials as compared to the parent Al-SBA-15 have been included in Figure 3. A well structurally ordered Al-SBA-15 material can be observed in Figure 3A, with clearly visible mesopore sizes in good agreement with porosity data (< 10 nm, Figure 3A).

Table 1. Nitrogen physisorption and EDX elemental analysis.

Catalyst	Si/M Molar ratio[a] (M= Zr, Al)	Metal Loading[a] (wt. %)	S_{BET} (m^2g^{-1})	D_{BJH} (Å)	V_{BJH} (mL g^{-1})
Al-SBA-15	-	-	756	8.9	0.72
Pd0.5-Al	29.5	0.4	625	8.6	0.50
Pd-1-Al	30.2	1.2	533	8.5	0.32
Pd-2-Al	28.2	1.9	363	8.1	0.24
Pd-4-Al	33.5	2.9	527	6.8	0.51
5%Pd/C	-	5	1220	-[b]	1.5

[a]Measured by EDX; [b]Pd/C is a microporous material

Upon Pd incorporation via ball milling, TEM images clearly depict a fairly good dispersion of tiny Pd nanoparticles in the materials, with <10 nm as average NP size (ca. 7-9 nm). No observable sintering could be found for low loaded materials (e.g. 0.5 to 2%Pd, Figure 3B and C) although the presence of significantly larger aggregates could be observed at higher loadings (Figure 3C-bottom of image-and 3D). The structural order in SBA-15 was largely preserved upon milling although the presence of some amorphous silica domains was also evidenced in TEM images (Figures 3B and C).[17]

The catalytic activity of mechanochemically synthesized Pd/Al-SBA-15 was subsequently investigated in the hydroconversion of cinnamaldehyde with formic acid under conventional heating using acetonitrile as solvent under reflux conditions. Formic acid has been previously reported to readily decompose into CO + CO_2, hydrogen and water under heating conditions in the presence of noble metals, providing an *in-situ* source of hydrogen for hydrogen-transfer reactions.[12]

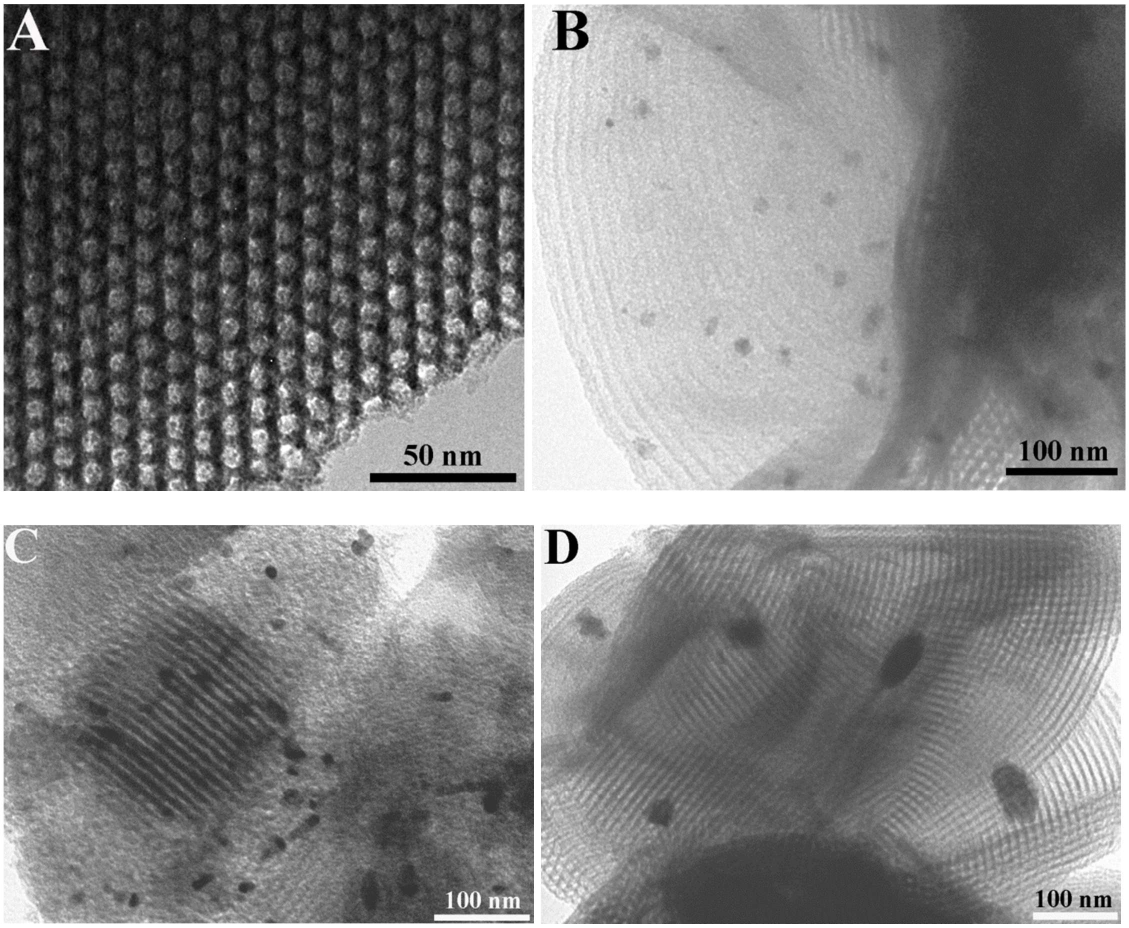


Figure 3. TEM images of A) Al-SBA-15 support; B) Pd1-Al; C) Pd2-Al; D) Pd4-Al

Results of catalytic activity were compared to those of a commercial 5%Pd/C. Most Pd/Al-SBA-15 catalysts exhibited an almost negligible conversion to products (< 10 %) even after 24 h reaction with the exception of Pd-4-Al for which a 50% conversion was obtained after 24 h (Table 2, Figure 4). The commercial 5%Pd/C system provided almost quantitative conversion after 24 h, with a remarkably different selectivity to that of Pd/Al-SBA-15 catalysts (Figures 4 and 5). Taking into account the Pd loadings in the catalysts (2.9 wt.% in Pd4-Al and 5 wt.% in Pd/C) and the reaction profiles depicted in Figure 4, it can be clearly visualized that Pd/C possessed almost comparable rates of reaction with respect to Pd4-Al with very slow initial reaction rates, after which Pd/C provided improved reaction rates after prolonged reaction times (>4 h). These results may indicate some diffusional/mass transfer limitations in Pd/C as compared to the lower active Pd/Al-SBA-15 materials (with significantly reduced Pd content) as expected from the inherent microporous nature of Pd/C.

Table 2. Comparison of catalytic activity between Pd/Al-SBA-15 materials and commercial 5%Pd/C in the hydroconversion of cinnamaldehyde under conventional heating.

Catalyst	Time of reaction (h)	Conversion (mol%)
Blank	24	<1
Pd0.5-Al	1	-
	4	<5
	24	<5
Pd1-Al	1	-
	4	<5
	24	<5
Pd2-Al	1	-
	4	5
	24	10
Pd4-Al	1	10
	4	17
	24	50
5%Pd/C	1	12
	4	36
	24	96

Reaction conditions: 0.5 mL cinamaldehyde, 1.5 mL formic acid, 10 mL acetonitrile, 1 g cat, 83ºC reaction temperature.

Selectivities were significantly different between both systems as illustrated in Figure 5. The three main competitive and most plausible pathways identified for the products obtained in the hydroconversion of cinnamaldehyde with formic acid have been summarized in Scheme 2. In pathway I, cinammaldehyde undergoes C=O hydrogenation to cinnamyl alcohol (Pd sites) followed by dehydration to β-methylstyrene (promoted by acid sites, Scheme 2-**I**). C=C reduction to hydrocinnamaldehyde can further lead to hydrocinnamyl alcohol (Scheme 2-**II**) which can be followed by subsequent dehydration to β-methylstyrene.. Ethylbenzene can also be produced through pathway III via hydrogenation of styrene) produced via cinnamaldehyde hydrodeformylation (Scheme 2-**III)** or by direct hydrodeformylation of hydrocinnamaldehyde generared in pathway II upon C=C bond reduction of cinnamaldehyde.

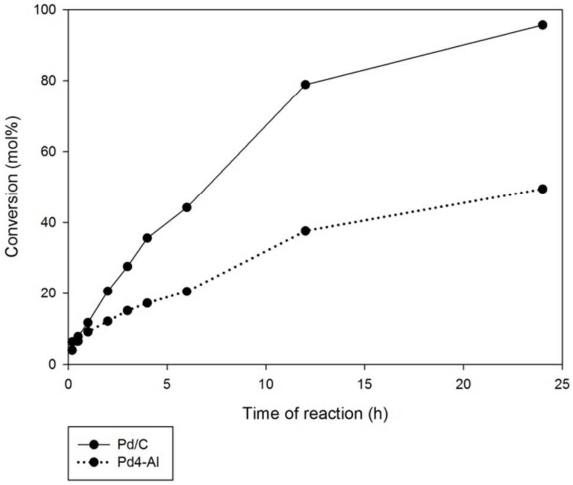
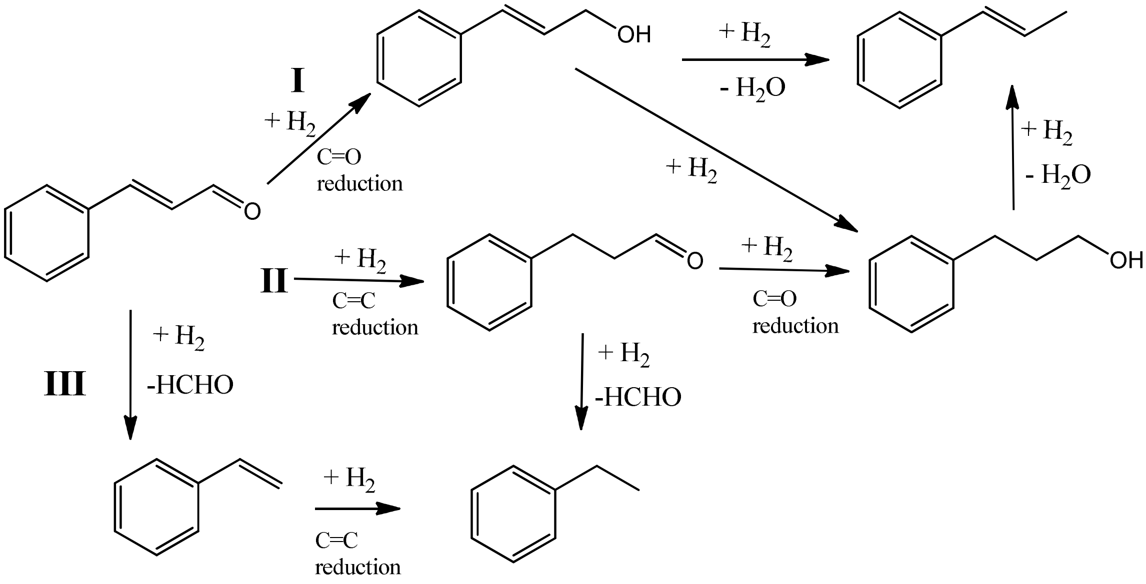


Figure 4. Reaction profiles for Pd4-Al (dotted line) and Pd/C (solid line) in the hydroconversion of cinnamaldehyde with formic acid under conventional heating. Reaction conditions: 0.5 mL cinamaldehyde, 1.5 mL formic acid, 10 mL acetonitrile, 1 g cat, 83ºC.

Results indicated that Pd/C favored typical hydrogenation reactions for the production of major quantities of hydrocinnamaldehyde (pathway II). Since no cinnamyl alcohol was detected as product for Pd/C and only low selectivities to β-methylstyrene were obtained at short times of reaction (<10 mol%, times of reaction under 4-6 h), it is clear that the C=C reduction to hydrocinnamaldehyde is the rate determining step in the Pd/C catalyzed hydroconversion of cinnamaldehyde. These results were in good agreement with previous literature reports. [4, 23] Interestingly, as the reaction progresses, C=O reduction leads to the formation of hydrocinnamyl alcohol which undergoes dehydration to β-methylstyrene as major product (ca. 60 mol% selectivity) observed after 24 h (Figure 4, Mestyrene for Pd/C). Due to the low acidity of Pd/C, dehydration may be promoted by formic acid present in excess in the reaction media.



Scheme 2. Possible competitive pathways (I to III) for the production of ethylbenzene, hydrocinnamaldehyde and β-methylstyrene, main products different from cyclohexane obtained in the hydroconversion of cinnamaldehyde with formic acid.

Cyclohexane from hydrogenation of the aromatic ring as well as ethylbenzene and methylstyrene as minor products together with traces of propylbenzene and short amides (e.g. formamide) were also observed in Pd/C catalyzed reactions under conventional heating (Figure 5). Findings seemed to point out a favored competitive reaction for the production of ethylbenzene to the typical C=C and C=O reductions steps observed in most reports as proposed in Scheme 2. Ethylbenzene can be most plausibly obtained via hydrodeformylation of hydrocinnamaldehyde in a similar way to previous reports using Ni/Al_2O_3.[23] The catalytic decarbonylation of cinnamaldehyde was also reported many years back using Pd and Pt/C,[24] Ni raney catalysts[25] and Ru and Rh homogeneous complexes.[26, 27] Alternatively, hydrodeformylation of cinnamaldehyde could generate styrene and ethylbenzene upon subsequent hydrogenation on the metal sites. This route, however, is not likely to generare ethylbenzene as no traces of styrene could be detected in the reaction under the investigated conditions.

Pd4-Al comparatively exhibited a major hydrogenation selectivity to hydrocinnamaldehyde (C=C bond reduction, pathway II) and cyclohexane (aromatic ring hydrogenation). Interestingly, a high selectivity to oxalic acid (15-20 mol%) was observed even after 24 h reaction (Figure 5). Minor quantities of β-methylstyrene and traces of ethylbenzene were also detected in the catalytic system under conventional heating.

The formation of ethers or acetals from cinnamaldehyde and/or hydrocinnamaldehyde via acid-catalysed reactions (Scheme 1) was not observed in any Pd-containing system even in the presence of Al-SBA-15 as solid acid support and formic acid under the investigated reaction conditions in conventional heating.

Based on these findings, particularly related to oxalic acid production for Pd/Al-SBA-15 materials, we were prompted to investigate the proposed hydroconversion reaction at shorter times of reaction under microwave-irradiation pushing the reaction conditions to maximize product yields.

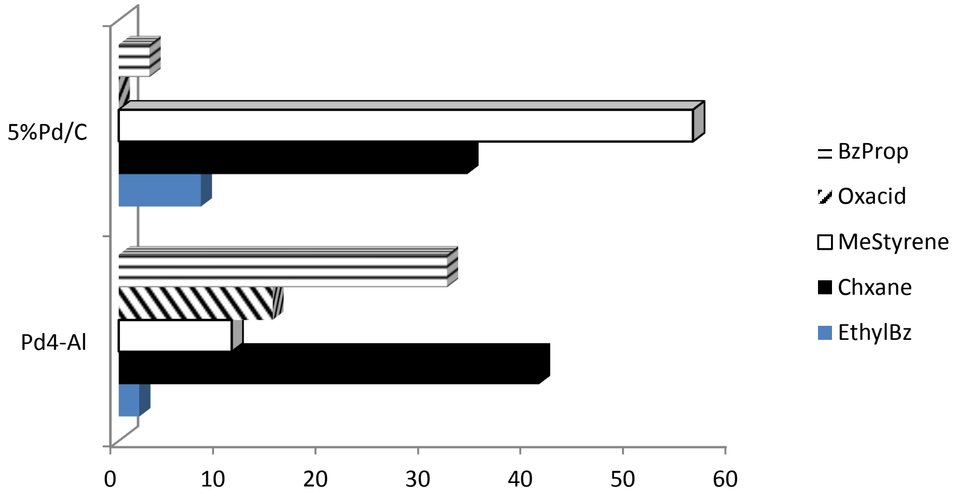
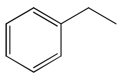
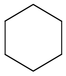
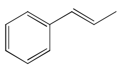
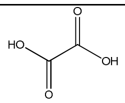
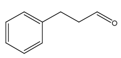
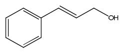


Figure 5. Selectivity comparison (X axis, mol%) between Pd4-Al containing ca. 2.9 wt.% Pd and a commercial 5%Pd/C in the hydroconversion of cinnamaldehyde in formic acid. Reaction conditions: 0.5 mL cinamaldehyde, 1.5 mL formic acid, 10 mL acetonitrile, 1 g cat, 83ºC reaction temperature, 24 h reaction. Products legend: BzProp= hydrocinnamyl alcohol; Oxacid= oxalic acid; MeStyrene= β-methylstyrene; Chxane= cyclohexane; EthylBz= ethylbenzene

Main findings for the microwave-assisted hydroconversion of cinnamaldehyde have been summarized in Table 3. Blank runs provided almost negligible activity in the systems (<10%). Interesting catalytic trends were observed in the proposed microwave-assisted system for Pd-containing catalysts (Table 3). Quantitative conversion was achieved for all Pd/Al-SBA-15 materials as compared to a 71% conversion comparatively obtained for Pd/C. The activities of Pd-containing systems were remarkably superior to Pd/C as compared to reactions conducted under conventional heating. These findings are in good agreement with previously reported results from the group[28] and illustrate the advantages of microwave-activation in mechanochemically synthesized Pd systems as compared to commercial Pd catalysts (e.g. Pd/C). Most importantly, inherent mass transfer and diffusional limitations have already been demonstrated in the Pd/C system under conventional heating present at short times of reaction due to its microporous nature (Figure 4 reaction profiles) are. Hence, short times of reaction under microwave irradiation can justify the reduced activity of Pd/C under the investigated reaction conditions. Previously reported Pd-aluminosilicate interactions as well as the most important preferential external deposition of highly accessible, active and easier to activate nanoparticles in the proposed bifunctional Pd/Al-SBA-15 materials may also partially contribute to the improved activities under microwave irradiation.[28]

Table 3. Total conversion (mol %) and selectivities to products (mol %) of different supported Pd nanoparticles on Al-SBA-15 as compared to a commercial 5%Pd/C material in the microwave-assisted hydroconversion of cinnamaldehyde in formic acid.

Catalyst	Conversion (mol %)	Selectivity (mol %)					
							
Blank	<5	-	-	-	-	-	-
Pd0.5-Al	97	<5	52	26	16	<5	-
Pd1-Al	>99	<5	64	11	18	-	-
Pd2-Al	98	<5	66	18	13	-	-
Pd4-Al	85	13	44	41	<5	-	-
5%Pd/C	71	21	48	27	-	<5	-

Reaction conditions: 0.1 mL cinnamaldehyde (0.8 mmol), 0.3 mL formic acid (8 mmol), 2 mL acetonitrile, 0.5 g catalyst, microwave irradiation, 200 W (180ºC maximum temperature reached, averaged temperature 150ºC, 250 PSI maximum pressure), 15 min reaction.

Selectivities in the systems followed the similar trend observed under conventional heating, with expected high activities towards complete aromatic ring hydrogenation as well as hydrogenolysis of the side chain to generate cyclohexane as final product. The formation of β-methylstyrene, ethylbenzene and oxalic acid accounted for most remaining product selectivity. An increasing in Pd loading generally favored the formation of β-methylstyrene as major by-product, with the exception of Pd0.5-Al (Table 3).

The formation of relevant quantities of oxalic acid was repeatedly observed in microwave-assisted reactions for catalysts containing low Pd content (0.5-2 wt.%), generally decreasing with Pd content in the materials. Oxalic acid was not detected in blank runs, using similar Pt-based catalysts or in the Pd/C catalyzed hydroconversion of cinnamaldehyde (Table 3). With formic acid decomposing into CO + CO_2, hydrogen and water under the investigated microwave-assisted conditions[12], the most plausible mechanism for oxalic acid production is a Pd catalysed hydrocarboxylation. This is a type of reaction which has been previously reported to be catalyzed by various type of Pd catalysts[29] including analogous heterogeneous Pd complexes on MCM-41 and MCM-48 materials.[30]

A plausible explanation for the observed decrease in concentration of oxalic acid at increasing Pd loadings may relate to the presence of large Pd clusters in materials over 2 wt.% Pd which favor hydrogenation reactions as compared to hydrocarboxylations promoted in smaller size Pd nanoparticles. The proposed change in selectivity in size-sensitive reactions has been previously reported.[4, 31] Calculated TON values of the catalysts for microwave-assisted reactions were in the 5-10 range while a maximum catalyst TOF for cinnamaldehyde conversion to products of 42 h^{-1} (Pd1-Al) and minimum of 15 h^{-1} (Pd4-Al) were obtained.

Conclusions

Mechanochemically synthesized Pd/Al-SBA-15 materials with different Pd loadings (0.5, 1, 2 and 4 wt.%) have been synthesized and characterized using a range of analytical techniques including TG/DTA, N_2 physisorption and TEM and subsequently employed as heterogeneous catalysts in the hydroconversion of cinnamaldehyde with formic acid both under conventional heating and microwave irradiation. In contrast to potentially expected products, an interesting selectivity to products including ethylbenzene (via Pd-catalysed hydrodeformylation reactions) and oxalic acid (via Pd-catalysed hydrocarboxylation) were observed. Formic Acid was proved to be an effective hydrogen donor in the hydroconversion of cinnamaldehyde under heating (both conventional and microwave). The proposed Pd systems are envisaged to be of potential interest to the extension of the proposed chemistries to related hydro(de)formylation reactions which will be reported in due course.

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