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Chemoselective reduction of α,β-unsaturated carbonyl compounds with UiO-66 materials

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ABSTRACT

Allylic alcohols, important intermediates in fine chemical industry, are typically obtained through chemoselective hydrogenation of α,β-unsaturated aldehydes. Here we show that UiO-66, a zirconium-based metal–organic framework can be used in the chemoselective hydrogenation of cinnamaldehyde, both under high hydrogen pressure as silver nanoparticle support, and as transfer hydrogenation catalyst in the Meerwein–Ponndorf–Verley (MPV) reduction. A recyclable 10 wt% Ag/UiO-66 catalyst reached complete conversion after 6 h and 50 bar of H_2 with 66% selectivity for cinnamyl alcohol in the inert solvent *N,N*-dimethylacetamide (DMA). Pure UiO-66 as MPV catalyst with isopropanol reached complete conversion with >90% selectivity after 24 h at 120 °C. The substrate scope was extended to citral and carvone, two α,β-unsaturated carbonyl compounds that are harder to reduce selectively. Introduction of a NO_2-functional group into the UiO-66 linker to increase the Lewis acidity was clearly beneficial for the conversion of carvone.

1. Introduction

Allylic alcohols, important intermediates in the pharmaceutical, fragrance and agrochemical industry, are typically obtained through chemoselective reduction of α,β-unsaturated aldehydes. Hydrogenation of the olefinic group yields saturated aldehydes whereas hydrogenation of the carbonyl group produces allylic alcohols. Cinnamaldehyde, citral and crotonaldehyde are widely used as reference α,β-unsaturated aldehydes [1]. The former two are attractive since the unsaturated alcohol products are used as raw material in e.g. the pharmaceutical and fragrance industry; the cardiovascular drug cinnarizine is derived from cinnamyl alcohol [2] and nerol and geraniol derived from citral are useful for the production of perfumes, food flavours and insecticides [3–5]. The chemoselective reduction of carbonyl bonds in enones or enals is however challenging. Typically, this reduction is performed either under high hydrogen pressure conditions with supported metal nanoparticle catalysts or via transfer hydrogenation with an alcohol as hydride donor and a Lewis acid catalyst. The former process is not straightforward since olefins are often preferentially reduced, due to thermodynamic and kinetic reasons [6–9], the latter on the contrary is selective in carbonyl-hydrogenation but also produces by-products [10–13] and has minor atom efficiency since besides the desired product also a ketone is formed [14].

The chemoselectivity in the metal nanoparticle catalysed hydrogenation of unsaturated carbonyl compounds to the unsaturated alcohol product depends on various factors such as the metal used as catalyst as well as the chemical nature of the aldehyde and reaction conditions. Various supported metal nanoparticles have been reported so far aiming for the selective hydrogenation of α,β-unsaturated aldehydes [2,5,15–22]. In these catalysts the use of small metal nanoparticles maximises the catalyst surface area; however, it also demands proper stabilisation by an appropriate catalyst support [23]. A well-considered choice of support is a key parameter in superior catalyst development as pore size, specific surface area and acidity can differ largely. These supports could also influence the selectivity towards carbonyl bond hydrogenation through metal–support interaction [24]. Typical supports are metal oxides, such as acidic Al_2O_3, SiO_2, TiO_2 and basic MgO, as well as active carbon [2,18,25–30]. Less studied support materials are metal–organic frameworks (MOFs). MOFs are crystalline, porous materials composed of metal (oxide) nodes interlinked by polytactic organic ligands, thus forming three dimensional zeolite-like structures with well-defined micropores and pore channels. These solids have attracted researchers' interest mainly due to their versatility, high surface area and acid-base properties. To the best of our knowledge there are only three reports on the use of a MOF-support in the chemoselective hydrogenation of α,β-unsaturated aldehydes. Pt nanoclusters were confined in the cavities of amino-functionalised UiO-66 and displayed high selectivity (92%) to cinnamyl alcohol [31]; MIL-101 supported Pt

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nanoparticles on the contrary were >99.9% selective in the hydrogenation of the C=C bond to form hydrocinnamaldehyde [15]. The results when using Pd/MIL-53(Cr) and Ru/MIL-53(Cr) in the hydrogenation of cinnamaldehyde and crotonaldehyde were somewhat mixed. In the case of cinnamaldehyde the Pd-catalyst preferentially hydrogenated the C=C bond while the Ru-catalyst preferentially hydrogenated the C=O bond. In the case of crotonaldehyde however, the selectivity trend was totally different: the C=C double bond was preferentially hydrogenated on Ru/MIL-53(Cr) whereas C=C and C=O hydrogenation occurred at a similar reaction rates on Pd/MIL-53(Cr) [19].

Alternatively, unsaturated aldehydes and ketones can be selectively reduced to the corresponding allylic alcohols with high chemoselectivity in the absence of hydrogen gas via the Meer wein–Ponndorf–Verley (MPV) reduction [10]. The earliest reported MPV-catalysts were aluminium alkoxides [32], but in the last 15 years zirconium-based catalysts are attracting more and more attention [12,13,33–39]. With Zr-grafted siliceous MCM-41 and SBA-15 yields up to 95% were obtained within reasonable reaction times with relatively small amounts of catalyst (5–8.4 mol%) [12,33,34]. Catalytic performance was increased by incorporation of Zr in zeolite beta [35,36,40]. This heterogeneous catalyst was reusable, stable in water and only 1.3 mol% Zr was used. Recently a mesoporous zirconium–phytic acid hybrid material was tested as a MPV-catalyst for the conversion of levulinic acid into γ-valerolactone and other carbonyl compounds [39]; high yield and selectivity were obtained, however with 65 mol% Zr. In these MPV catalysts the presence of Lewis acid zirconium sites is essential. Recently, Cirujano and co-workers [41] successfully showed the presence of Lewis acid centres in UiO-66 and used these Zr-based MOFs for the esterification of levulinic acid with various alcohols. The catalytically active sites are coordination vacancies of the Zr-metal, arising from crystalline defects associated with linker deficiencies or from thermal dehydroxylation of the Zr-cluster [41,42]. Preliminary experiments with Zr-containing MOFs, UiO-66 and UiO-66-NO_2, as MPV reduction catalysts with *tert*-butylcyclohexanone as the reactant, already showed the potential of these materials for application in more challenging selective reductions such as those of unsaturated aldehydes and ketones used in this work [38]. Literature suggests that the use of HCl and trifluoroacetic acid can be used in the modulated UiO-66 synthesis to yield a more open framework structure with a large number of coordinative vacancies [38].

In this work we explored the use of UiO-66 as support for silver nanoparticles for the chemoselective high pressure hydrogenation of α,β-unsaturated aldehydes. From the literature it is known that the hydrogenation of C=O bonds over C=C bonds in α,β-unsaturated aldehydes decreases, roughly, in the order Ag > Au > Pd > Pt > Ru [2]. Alternatively, we explored the potential of bare UiO-66 materials without supported noble-metal particles as catalysts in the chemoselective formation of allylic alcohols in the MPV-reduction using isopropanol.

2. Materials and methods

2.1. Synthesis

All chemicals and solvents used in the syntheses were of reagent grade and used without further purification.

2.1.1. UiO-66 materials

All UiO-66 MOFs were made in a closed Schott DURAN® pressure plus bottle with a volume of 1 L under static conditions. UiO-66 and UiO-66-NO_2 were synthesised in the presence of a modulator, starting from an equimolar solution of $ZrCl_4$ (3.5 g, 15 mmol) and terephthalic acid (2.5 g, 15 mmol) or 2-nitroterephthalic acid (3.2 g, 15 mmol), dissolved in *N*,*N*-dimethylformamide (DMF) (155 mL, 2 mol). 1.5 mL of a 36 wt% solution of HCl (17 mmol) and 20 equivalents (23 mL) of the modulator CF_3COOH were also added to the mixture. UiO-66-NH_2 was synthesised without the modulator [31], also starting from an equimolar mixture of $ZrCl_4$ (0.48 g, 2.1 mmol) and 2-aminoterephthalic acid (0.372 g, 2.1 mmol) dissolved in DMF (120 mL), to which 0.15 mL of H_2O was added. All synthesis mixtures were placed in a preheated oven at 120 °C for 21 h (modulated) or 24 h (non-modulated synthesis). The powders were collected via centrifugation (10 min, 11 000 rpm) and thoroughly washed with DMF (3 times) and methanol (3 times). The powders were then dried at 60 °C over night and at 200 °C for 24 h to yield 3.48 g (UiO-66), 3.70 g (UiO-66-NO_2) and 0.727 g (UiO-66-NH_2) of activated sample, which correspond to respectively 84%, 80% and 98% molar Zr yield.

2.1.2. Supported Ag nanoparticles

Before impregnation, the MOF-supports are activated at 150 °C for 16 h. Silver nitrate (512 mg $AgNO_3$, 3 mmol) is dissolved in 6 mL of a H_2O:EtOH 1:5 solution. This aqueous–ethanolic $AgNO_3$ solution is added to a vial containing 200 mg MOF; the vial is sealed with a crimp cap and flushed with nitrogen to remove all O_2. Interaction of Ag^+ ions with light is prevented by a protective layer of aluminium foil around the vial. The MOF–$AgNO_3$ mixture is sonicated for 2 min and stirred continuously for 16 h at 500 rpm. The sample is thoroughly washed (5 times) with ethanol to remove remaining $AgNO_3$; centrifugation (8 min, 3000 rpm), removal of the supernatant and addition of fresh EtOH are performed under an inert atmosphere. Drops of a NaCl-solution are added to the supernatant solution to check whether there is still some Ag^+ present. After washing, the sample is dried in a vacuum oven at room temperature for 16 h.

2.1.3. Reference catalysts

γ-Al_2O_3 (Product No. 199974), silica gel (Product No. 60752) and ZrO_2 (Product No. 230693) were obtained from Sigma Aldrich. 13 wt% Ag/SiO_2 and Ag/Al_2O_3 were synthesised according to literature procedures [18,43].

2.2. Characterisation

Powder X-ray diffractograms were routinely collected on a STOE STADI COMBI P diffractometer in High-Throughput mode, equipped with an image plate detector using Cu Kα radiation (λ = 1.54056 Å). Scanning Electron Microscopy (SEM) images were obtained using a JEOL SEM (JSM-6010LV). Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics 3Flex 3500 physisorption instrument. The sample was degassed before measurement at 423 K for 6 h under vacuum (10^{-2} mbar). The pore size distribution was calculated using the BJH method (Harkins and Jura thickness curve and Faas correction, 3Flex 3.00 software). Diffuse Reflectance spectra (DRS) were measured on a Perkin Elmer UV/VIS spectrophotometer (Lambda 950) equipped with a integrating sphere. ICP-AES measurements (Varian 720-ES) were used to determine the Ag-loading. Thermal Gravimetric Analysis (TGA) was performed under a stream of N_2-gas using a Universal V4.5A TA Instrument running from room temperature to 800 °C with a scan rate of 3.5 °C/min.

2.3. Catalytic experiments

2.3.1. High H_2 pressure hydrogenation

For the high pressure hydrogenation reaction, 25 mg of catalyst, 1.15 mmol (145 µL) of cinnamaldehyde, 0.95 mmol *n*-tetradecane

(245 μL, internal standard) and 3.3 mL of *N,N*-dimethylacetamide (DMA, solvent) were introduced into a 15 mL autoclave. After flushing with N_2, the autoclave was pressurised with H_2 to 20–50 bar of H_2 and stirred with a magnetic stirring bar at 500 rpm. The hydrogenation reaction was performed at 140 °C for 6 h, unless stated otherwise. For analysis of the liquid products, the catalyst was removed by centrifugation (3000 rpm, 8 min) and analysis of the reaction products was carried out using a gas chromatograph (Shimadzu 2010 GC, CP-Sil 8, FID detector). *n*-Tetradecane was added as internal standard for quantitative GC analysis. Identification of the compounds was carried out using GC–MS.

For the recycling test, the used catalyst was isolated from the reaction mixture by centrifugation (3000 rpm, 10 min) and thoroughly washed with DMA (at least three times) until the supernatant was purely solvent, as confirmed by GC. The recovered catalyst was reactivated overnight (16 h) at room temperature in a vacuum oven (10 mbar) and reused under the same reaction conditions.

2.3.2. MPV-reduction

Before reaction, each catalyst was dried at 200 °C to remove residual solvent molecules; catalytic reactions were carried out in 10 ml glass crimp cap vials loaded with 20–30 mg catalyst and a magnetic stirring bar. A solution of the substrate in 3.3 mL isopropanol (IPA) was added; *n*-tetradecane was added as internal standard. For each catalyst, a substrate to Zr ratio of 7.8 was used as to compare the activity of each catalyst. After introduction of the reaction mixture, the vials were placed in an aluminium heating block (at 120 °C) and stirred. Reaction samples were filtered through a 0.2 μm filter and analysed with gas chromatography (Shimadzu 2010 GC, CP-Sil 8, FID detector). Reaction products were identified using GC–MS. Reactions were performed in duplo, and the results shown are averaged.

For the recycling test, the used catalyst was isolated from the reaction mixture by centrifugation (3000 rpm, 10 min) and thoroughly washed with isopropanol (at least three times) until the supernatant was purely solvent, as confirmed by GC. The recovered catalyst was reactivated at 60 °C (2–4 h) and 150 °C (overnight, 16 h) and reused under the same reaction conditions.

3. Results and discussion

3.1. Chemoselective reduction of cinnamaldehyde under high H_2 pressure

UiO-66 is a zirconium-terephthalate based metal–organic framework (MOF) which is best known for its high chemical and thermal stability and easy functionalisation. When HCl and trifluoroacetic acid are added to the MOF synthesis mixture, terephthalate linkers are partially replaced by trifluoroacetate, resulting in a more open framework with a large number of open sites [38]. Trifluoroacetate acts as a modulator in this case since it has a similar chemical functionality as the terephthalate linker, but has only one functional group. Since modulated synthesis also increases physical stability [44], we followed this approach to synthesise our catalyst support. Characterisation was performed with powder X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), N_2-physisorption and Fourier Transform Infrared (FTIR) spectroscopy (see supplementary information, Figs. S1–4). Ag nanoparticles were introduced into the porous MOFs via impregnation with an aqueous-ethanolic silver nitrate solution. Further, addition of a reductant or inclusion of an additional reduction step was not necessary since Ag(I) is effectively reduced in the presence of EtOH to Ag(0) [45]. The formation of Ag nanoparticles was evidenced by diffuse reflectance spectroscopy of the yellow Ag/UiO-66 powder (DRS) (Fig. 1); the extra absorption maximum around 400 nm can be assigned to surface plasmon resonance (SPR) of small Ag nanoparticles (<10 nm) [46]. The absence of larger silver particles was further supported by powder XRD of the Ag/UiO-66 which would give rise to 38.1° reflection of Ag [1 1 1], and further no significant framework decomposition was observed (Fig. S1). ICP-AES measurements show a Ag-loading of 10–14 wt%.

Chemoselective hydrogenation of cinnamaldehyde (CALD) was carried out at 140 °C and 30 bar of H_2 in *N,N*-dimethylacetamide (DMA) as the solvent. Catalytic activity of UiO-66 supported silver is clearly visible; in contrast to the thermodynamically favoured C=C hydrogenation, cinnamyl alcohol (CALH) is the preferentially formed product with a selectivity of 66 ± 3% (Table 1, entry 1). As expected, the hydrogenation rate increases with higher hydrogen pressures, increasing pressure from 30 to 40 and 50 bar of H_2 increases the turn-over frequency to respectively 3.5 ± 0.1 and 5.5 ± 0.1 mol cinnamyl alcohol per mol Ag per hour (Table 1, entry 1–3). Interestingly this pressure increase has no significant effect on the selectivity towards cinnamyl alcohol, which remains 65–70%. Reference Ag/SiO_2 and Ag/Al_2O_3 catalysts with similar Ag-loadings were used under the same reaction conditions (Table 1, entry 5–6). The Ag/SiO_2 powder shows a comparable reaction selectivity (71 ± 3%), however with a slightly higher hydrogenation rate (TOF of 6.1 ± 0.1 mol CALH/mol Ag/h). On the other hand, strongly reduced CALH selectivity of 47 ± 5% was obtained with Ag/Al_2O_3. This is most probably related to the formation of larger Ag nanoparticles as seen on powder XRD of this black powder (Fig. S1). The choice of the support has thus an important influence on the formation and stabilisation of the Ag nanoparticles and the resulting catalytic properties. The chemoselective formation of CALH has been reported before for PVP-stabilized Ag nanocolloids, with up to 93% selectivity after 48 h [17]. Although these stabilized nanoparticles were successfully recycled, heterogenisation of nanoparticles on solid supports typically facilitates synthesis and removal of the reaction medium, and improves thermal and chemical stability [47]. In contrast, the use of silica supported copper catalysts resulted exclusively in the undesired HCAL during the initial stages of the reaction [27].

As can be seen in Table 1 the main products are cinnamyl alcohol (CALH, 66–69% selectivity) and hydrocinnamaldehyde (HCAL, 27–30% selectivity). The consecutive hydrogenation product of both compounds, hydrocinnamyl alcohol (HCALH), is only formed in small amounts, even at high conversions. One other by-product was detected in small amounts, typically 1–2%, and identified by GC–MS as *N,N*-dimethylcinnamylamine (DMC). As shown in Scheme 1, in the presence of an acid catalyst cinnamaldehyde

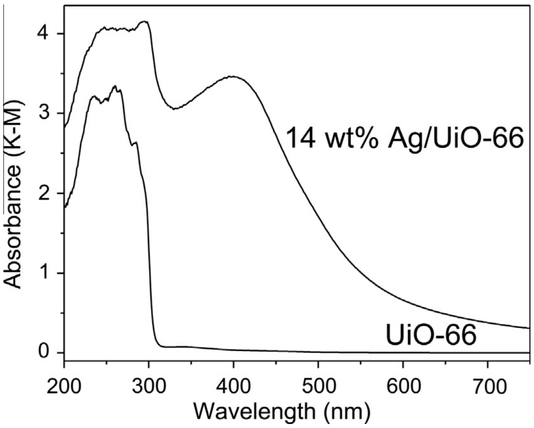


Fig. 1. Diffuse reflectance UV/visible spectra of UiO-66 and 14 wt% Ag-loaded UiO-66 after Kubelka–Munk (K–M) correction.

Table 1
Conversion and selectivity in the reduction of cinnamaldehyde (CALD) in *N,N*-dimethylacetamide, catalysed by UiO-66, Ag/UiO-66 and a Ag/SiO$_2$ reference catalyst.

Entry	Catalyst	H$_2$ (bar)	Wt% Ag[a]	X (%)	TOF[b]	S_{CALH} (%)	S_{HCAL} (%)	S_{HCALH} (%)
1	Ag/UiO-66	30	14	82	3.3	66	30	2
2	Ag/UiO-66	40	10	64	3.5	69	29	1
3	Ag/UiO-66	50	10	>99	5.5	66	27	6
4	UiO-66	30	0	<1	/	/	/	/
5[c]	Ag/SiO$_2$	30	13	90	6.1	71	28	1
6	Ag/Al$_2$O$_3$	50	13	96	2.9	47	36	18

CALD = cinnamaldehyde, CALH = cinnamyl alcohol, HCAL = hydrocinnamaldehyde, HCALH = hydrocinnamyl alcohol; reaction conditions: CALD (1.15 mmol), *n*-tetradecane (0.95 mmol), solvent *N,N*-DMA (3.3 mL), 25 mg catalyst, 140 °C, 6 h, 500 rpm.

[a] Determined via ICP-AES.

[b] mol CALH per mol Ag per h.

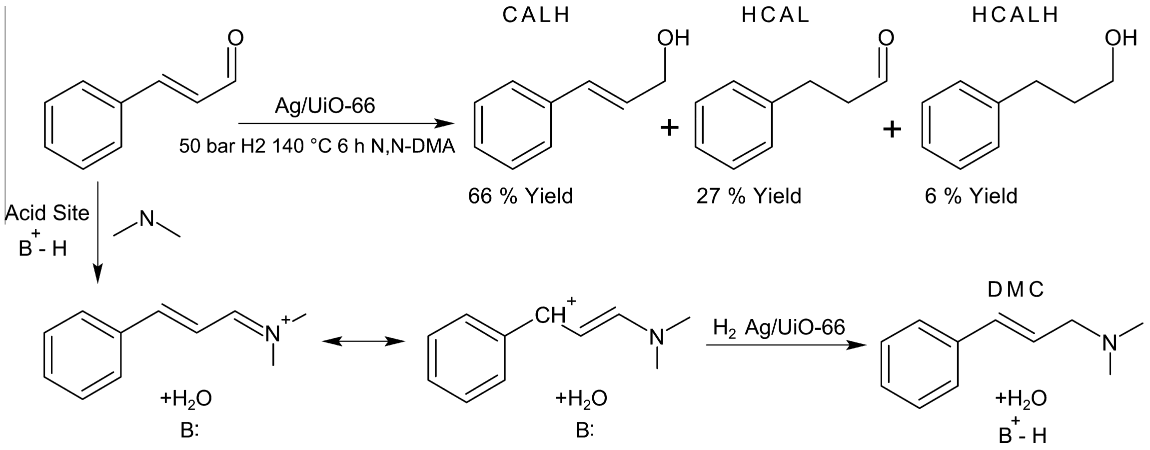
[c] 4 h.

can react with a secondary amine, like dimethylamine, the thermal decomposition product of *N,N*-dimethylacetamide, to form an enamine [48,49]. After selective hydrogenation catalysed by the Ag/UiO-66 catalyst, *N,N*-dimethylcinnamylamine (DMC) is formed, which proves that the Ag catalyst typically also prefers C═N over C═C hydrogenation. *N,N*-DMA was chosen as solvent since the amide group will coordinate with free Zr-sites of the MOF framework, avoiding the influence hereof (vide infra) and thus only the catalytic selectivity of the Ag nanoparticles is observed.

To confirm that the observed catalytic activity can solely be attributed to the Ag nanoparticles, the reaction was also performed with pure UiO-66. As can be seen in Table 1 (entry 4) no significant conversion of CALD was detected in this blank reaction after 6 h. A known problem with supported silver catalysts is the facile silver aggregation during the catalytic experiment resulting in a rapidly decreasing catalytic performance. The aggregation of silver in larger clusters typically induces a colour change in the material. Upon visual inspection no significant colour changes occurred with the yellow Ag/UiO-66 powder during the catalytic test which shows that the UiO-66 support strongly suppresses Ag nanoparticle aggregation. This is further supported by powder XRD of the Ag-loaded materials before and after CALD hydrogenation (Fig. S5). Powder XRD of the Ag-loaded UiO-66 after catalytic reaction indicates that the crystallinity of the UiO-66-framework remained intact and no additional diffraction peaks were observed. In the case of Ag-loaded silica on the contrary, an additional diffraction at 38.3° can be attributed to Ag [1 1 1] reflections from larger aggregated Ag particles. Ag leaching from the UiO-66 support to the reaction mixture during the course of the reaction was furthermore not detected by ICP-AES on the product mixture (<0.05 ppm, detection limit). To further test the stability of the Ag/UiO-66 catalyst, a recycle study was conducted. The used catalyst was isolated from the reaction mixture by centrifugation (3000 rpm, 10 min) and thoroughly washed with DMA until the supernatant was purely solvent, as evidenced by GC. The recovered catalyst was reactivated overnight at room temperature in a vacuum oven (10 mbar) and reused under the same reaction conditions. Powder XRD and SEM showed that the crystallinity was retained after the washing and reactivation (see supplementary information, Fig. S5). In reactions with the recycled catalysts, the original catalytic activity was retained at >99% up to 5 times recycling with only minor loss in chemoselectivity which in the last reaction was still 60 ± 3% to cinnamyl alcohol (see supplementary information, Fig. S6). These recycling experiments evidence the durability and reusability of the catalyst. The conversion and selectivity obtained with these recyclable UiO-66 supported silver catalysts are however still lower than the results for the reference silver on silica catalyst. Under these high pressure and temperature conditions with an inert solvent such as DMA, higher selectivity can probably only be achieved by the use of multi-component metal nanoparticles [6,25].

3.2. Transfer hydrogenation with UiO-66 and analogues

High conversions in the cinnamaldehyde (CALD) chemoselective hydrogenation are often reported when using isopropanol (IPA) as a solvent. Under such conditions, using IPA instead of DMA as solvent and with 30 bar of H$_2$, the Ag/UiO-66 catalyst shows a remarkably higher hydrogenation selectivity of 83 ± 2% and a conversion of 81 ± 3% after 6 h at 140 °C (Table 2, entry 1). Even higher reaction selectivity is obtained in the absence of the



Scheme 1. Reaction products of the hydrogenation of cinnamaldehyde with UiO-66 supported Ag nanoparticles, determined via GC–MS (CALD = cinnamaldehyde, CALH = cinnamyl alcohol, HCAL = hydrocinnamaldehyde, HCALH = hydrocinnamyl alcohol).

Table 2
Conversion and selectivity in the reduction of cinnamaldehyde in isopropanol, catalysed by Ag-loaded UiO-66 or by UiO-66 as such.

Entry	Catalyst	H_2 (bar)	X (%)	S_{CALH} (%)	S_{HCAL} (%)	S_{HCALH} (%)	S_{Ether}[a] (%)	S_{Acetal}[b] (%)
1	Ag/UiO-66	30	81	83	5	11	<1	1
2	UiO-66	30	>99	93	0	6	1	<1
3	UiO-66	0	>99	92	0	6	1	<1

CALD = cinnamaldehyde, CALH = cinnamyl alcohol, HCAL = hydrocinnamaldehyde, HCALH = hydrocinnamyl alcohol; reaction conditions: CALD (1.15 mmol), *n*-tetradecane (0.95 mmol), solvent IPA (3.3 mL), 25 mg catalyst, 500 rpm, 140 °C, 6 h, 30 bar of H_2.

[a] 1-Cinnamyl-2-propyl ether.

[b] Cinnamaldehyde diisopropyl acetal side products (Scheme 2).

Table 3
Conversion and selectivity in the CALD transfer hydrogenation catalysed by UiO-66, NO_2- and NH_2-functionalised UiO-66 and a reference ZrO_2 catalyst in isopropanol.

Entry	Catalyst	*T* (°C)	*t* (h)	X (%)	S_{CALH} (%)	S_{Ether}[a] (%)	S_{Acetal}[b] (%)
1	UiO-66	82	24	17	68	2	29
2	UiO-66-NO_2	82	24	18	78	4	17
3	UiO-66-NH_2	82	24	7	28	2	66
4a	UiO-66	120	8	82	95	1	<1
4b			24	>99	94	2	0
5a	UiO-66-NO_2	120	8	52	94	1	1
5b			24	84	93	1	<1
6a	UiO-66-NH_2	120	8	10	87	1	7
6b			24	17	90	1	5
7	ZrO_2	120	24	2	0	0	100

CALD (1.15 mmol), *n*-tetradecane (0.95 mmol), solvent IPA (3.3 mL), 7.8 mol% Zr, 500 rpm.

[a] 1-cinnamyl-2-propyl ether.

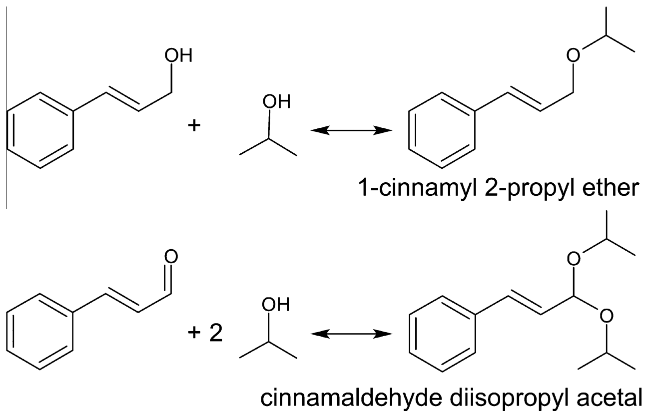
[b] Cinnamaldehyde diisopropyl acetal side products (Scheme 2).

supported silver nanoparticles; pure UiO-66 displays over 90 ± 2% selectivity towards cinnamyl alcohol (CALH) at complete conversion (Table 2, entry 2). This can be explained by the fact that zirconium is known to be a transfer hydrogenation catalyst, often in combination with IPA as hydride donor, a mechanism called the Meerwein–Ponndorf–Verley (MPV) reduction [50]. MPV-reduction with modulated UiO-66 and UiO-66-NO_2 as catalysts and with *tert*-butylcyclohexanone as the reactant obtained 93 ± 2% yield with 10 mol% Zr within 24 h [38]. The excellent catalytic performance of UiO-66, even in the absence of H_2 (Table 2, entry 3), can thus be explained by the MPV-reduction mechanism [10,51].

As mentioned above MPV-reduction of unsaturated aldehydes and ketones to the corresponding alcohols is an alternative route to obtain allylic alcoholic intermediates with high chemoselectivity and without the use of hydrogen gas. MPV-reductions in isopropanol (IPA) are typically performed at reflux conditions, more specifically at 82 °C with IPA in large excess, to force the equilibrium reaction towards the allylic alcohol product. With Zr-grafted siliceous SBA-15 cinnamyl alcohol yield of 56% was obtained at 82 °C within 5 h with 8.4 mol% Zr [34]. Catalytic performance was increased by incorporation of Zr in zeolite beta, after 3 h at 82 °C, and 96% yield was obtained with 1.3 mol% Zr [36]. When UiO-66 is used in these conditions, conversion is relatively low (17 ± 2%) and the selectivity for the desired CALH drops back to 68 ± 3% after 24 h (Table 3, entry 1). The reported selectivity in this case however does not reflect the intrinsic hydrogenation selectivity towards the carbonyl group as the unwanted hydrocinnamaldehyde (HCAL) is not formed, but rather reflects the formation of other side products. Based on GC–MS these compounds were identified as 1-cinnamyl-2-propyl ether and cinnamaldehyde diisopropyl acetal (Scheme 2) which form as a result of etherification with an excess of isopropanol. These side products are also reported in the literature when hydrous zirconia is used in the MPV-reduction of cinnamaldehyde [11]. After 24 h of reaction at 80 °C, the selectivity to 1-cinnamyl 2-propyl was 7.8% with this hydrous Zr catalyst.

Electron withdrawing groups (NO_2) on the organic UiO-66 linker are known to enhance the Lewis acid strength of coordination vacancies of the Zr atoms in the adjacent node [52], while introducing a basic amino site creates an acid-base catalyst [53]. When UiO-66-NO_2 is used (Table 3, entry 2) conversions only slightly increase from 17% to 18%, but the selectivity clearly increases to 78 ± 3% due to decreased side product formation. As expected amine-functionalisation of the linker has the opposite effect; it slows down the reaction with a conversion of only 7% after 24 h and has a dramatic impact on selectivity, that decreases to 28 ± 5% (Table 3, entry 3). However, the decreased performance can also partly be explained by the fact that the UiO-66-NH_2 sample was prepared without modulation. As mentioned before, when HCl and trifluoroacetic acid are used in the modulated UiO-66 synthesis, terephthalate linkers are partially replaced by trifluoroacetate, resulting in a more open framework with a large number of coordinative vacancies.

Recently a mesoporous zirconium–phytic acid hybrid material was tested as a MPV-catalyst for the conversion of carbonyl



Scheme 2. Side products during transfer hydrogenation of cinnamaldehyde in isopropanol: 1-cinnamyl 2-propyl ether and cinnamaldehyde diisopropyl acetal.

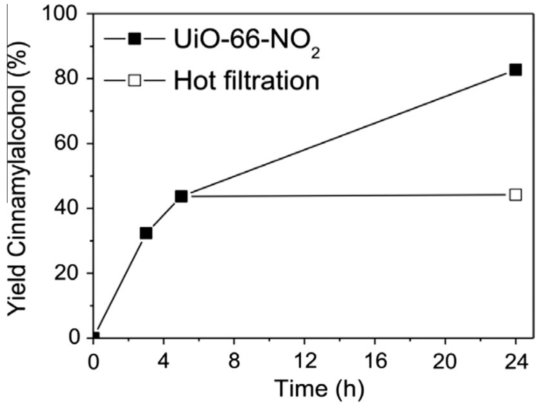


Fig. 2. MPV reduction of CALD with UiO-66-NO_2 (■) and hot filtration of the catalyst (□).

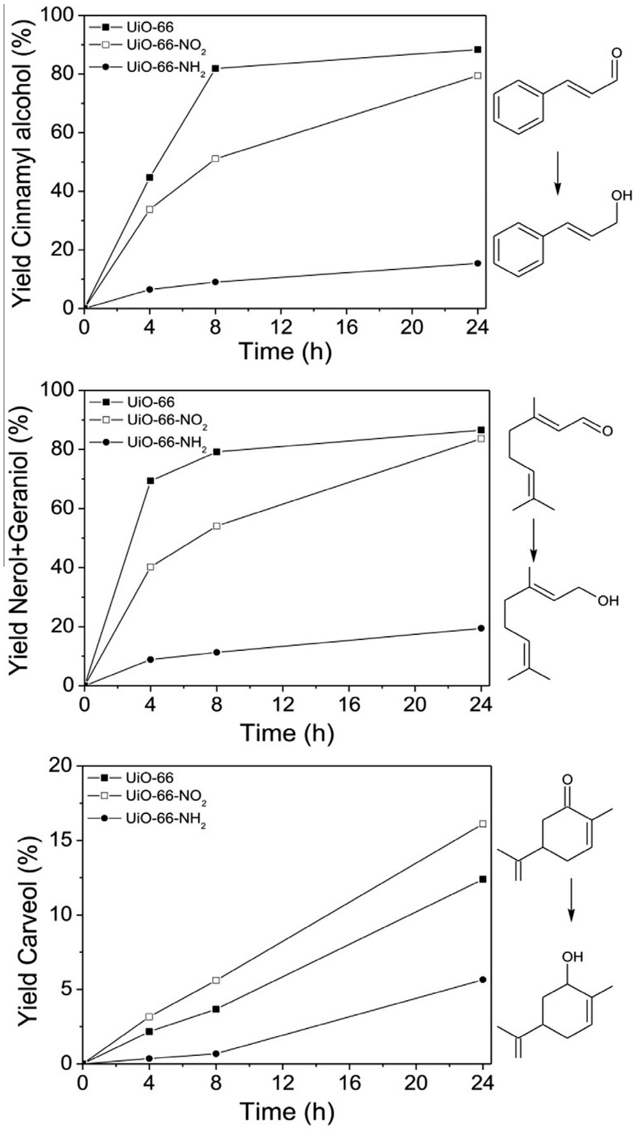


Fig. 3. MPV reduction of 3 different α,β-unsaturated carbonyl compounds: cinnamaldehyde (A), *cis,trans*-citral (B) and carvone (C) catalysed by UiO-66 (■), UiO-66-NO_2 (□) and UiO-66-NH_2 (●) (120 °C, 3.3 mL IPA, substrate:Zr = 7.8).

compounds in isopropanol [39]; high yield and selectivity were obtained, however with 65 mol% Zr and at 100 °C instead of 82 °C. When increasing reaction temperature to 120 °C for all three UiO-66 materials, conversion and selectivity are considerably improved and side product formation markedly decreases, especially for UiO-66 and UiO-66-NO_2. After 24 h respectively 94 ± 4% and 93 ± 1% selectivity to cinnamyl alcohol is reached at complete conversion for UiO-66 and 84 ± 2% conversion for UiO-66-NO_2. At low conversion cinnamaldehyde diisopropyl acetal was the major side product, when conversion increased also the formation of 1-cinnamyl-2-propyl ether increased. However the side products only account for maximum 2 mol% of the product mixture after 24 h in the case of UiO-66 and UiO-66-NO_2. In the MPV-reduction with UiO-66-NH_2 at 120 °C, the selectivity to cinnamaldehyde diisopropyl acetal and 1-cinnamyl-2-propyl ether is respectively 7% and 1%, considerably less than the reduction at 82 °C where selectivity was respectively 66% and 2%. All reactions were carried out in duplo and after hot filtration of the reaction mixture after 5 h to remove the catalyst, conversion did not increase after 24 h, indicating that there is no leaching of Zr into the solution and the catalyst is truly heterogeneous (Fig. 2). To test the recycling of the UiO-66 catalyst, the used catalyst was isolated from the reaction mixture by centrifugation and thoroughly washed with isopropanol until the supernatant was purely solvent, as evidenced by GC. The recovered catalyst was reactivated at 150 °C and reused under the same reaction conditions. Every recycling step causes a loss in activity of about 35%; however, selectivity to the alcohol is retained at >90%. After three recycling steps about 25% of the initial cinnamyl alcohol yield is preserved. Powder XRD confirms that recycling does not cause a measurable loss in crystallinity (see supplementary information, Fig. S5). Further, thermal gravimetric analysis (TGA) shows an increase of about 50 °C in the temperature at which the BDC linker is lost from the UiO-66 framework and decomposed (see supplementary information, Fig. S7). This indicates stronger bonding of the remaining linkers as the result of a decrease in linker molecules per Zr-cluster during reaction and washing [54]. In a UiO-66 metal–organic framework, the Zr-metal is theoretically 8-fold coordinated and possesses no free coordination sites. But as the result of thermal activation and linker deficiency, coordinatively unsaturated Zr-sites (cus Zr) arise turning the Zr-metal into Lewis-acid catalytically active site. The further BDC linker loss during recycling makes the Zr-sites more accessible and also more prone for poisoning, which is confirmed by a visual colour change to light yellow. Linker loss can also lead to leaching of zirconium and empty microdomains [55,56]. However, hot filtration of the catalyst (Fig. 2) indicates that leached species are not active as MPV catalyst. Clearly UiO-66 is a very active and selective cinnamaldehyde MPV catalyst, although there is still room for improvement in recyclability of the material.

With the reference ZrO_2 catalyst no MPV-reduction activity is measured (Table 3, entry 7), indicating the successful development of catalytically active cus Zr-sites by incorporation in a metal–organic framework.

UiO-66 was thus successfully used as heterogeneous MPV reduction catalyst for the α,β-unsaturated aldehyde CALD. Even more challenging is the selective reduction of the α,β-unsaturated linear aldehyde citral and the α,β-unsaturated ketone carvone (Fig. 3B and C). The unsaturated alcohol product of the latter is also an important component in the flavour industry.

After 24 h more than 90% citral conversion is reached, with both UiO-66 and UiO-66-NO_2 and selectivities of respectively 93 ± 1% and 91 ± 2%. The negative impact of amine-functionalised linkers is also clearly observed in hydrogenation of both citral and carvone; in all reactions lower conversions and selectivities were reached. Unsaturated ketones are typically harder to selectively reduce than aldehydes, so it is no surprise carveol yields are lower.

In this more demanding reduction reaction higher the stronger acidic UiO-66-NO_2 outperforms UiO-66 (Fig. 3C), both catalysts display an excellent hydrogenation selectivity of 92 ± 3% towards the desired carveol. Infrared spectroscopy with CD_3CN as probe [27], confirmed that the NO_2-functionalisation enhances the Lewis acidity of coordination vacancies of the adjacent Zr-metal. Therefore, the catalytic performance in MPV reactions can be expected to decrease in the following order: UiO-66-NO_2 > UiO-66 > UiO-66-NH_2. This trend is not fully obeyed in the MPV-reduction of CALD (Fig. 3A) and citral (Fig. 3B). This can be due to several reasons: (1) the already high transfer hydrogenation activity of UiO-66 with these substrates might mask the enhancement by the NO_2-group, (2) NO_2-functionalisation not only induces the electronic effect of increased Lewis acidity, but may also increase steric hindrance, (3) UiO-66 and UiO-66-NO_2 do not necessarily have exactly the same amount of active sites. However, with more difficult substrates such as carvone the beneficial effect of NO_2-functionalisation on the conversion is clearly observed in the transfer hydrogenation.

4. Conclusion

Zr-based UiO-66 metal–organic frameworks were successfully used for the chemoselective hydrogenation of cinnamaldehyde, both in high pressure hydrogenation as supports for Ag nanoparticles, and as transfer hydrogenation catalyst in the Meerwein–Ponndorf–Verley reduction. A 10 wt% Ag/UiO-66 catalyst reached complete conversion after 24 h at 50 bar of H_2 with 66% selectivity for cinnamyl alcohol in the inert solvent *N,N*-dimethylacetamide (DMA). Recycling experiments evidenced the durability and reusability of the catalyst since the original catalytic activity was retained up to 5 times recycling with only minor loss in chemoselectivity. Compared to silver loaded alumina and silica, the UiO-66 framework offers a more efficient stabilisation of the Ag nanoparticles during catalytic reaction as evidenced by powder XRD. The conversion and selectivity obtained with these UiO-66 supported silver catalysts are however still lower than the reported results for other supported metal catalysts. If high pressure hydrogen driven reduction of α,β-unsaturated carbonyl compounds is compared to Meerwein–Ponndorf–Verley (MPV) reduction, MPV is much more selective in the hydrogenation of $C{=}O$ bonds when pure UiO-66 was used as transfer hydrogenation catalyst. Complete conversion was reached with >90% selectivity without the need of a precious metal. The substrate scope was further extended to citral and carvone, two other α,β-unsaturated carbonyl compounds that are harder to selectively reduce. Although there are side products, the higher selectivity obtained at milder conditions and excellent Lewis acid properties of the Zr-metal in the modulated UiO-66 framework make transfer hydrogenation with this material preferable over high H_2 pressure hydrogenation. The successful use of one material, such as UiO-66, for the same reaction both as support and as catalyst demands critical interpretation of experimental results when using a Lewis acid support material in the high pressure hydrogenation of carbonyl compounds. The catalytic performance of the supported metal nanoparticles in the H_2-driven hydrogenation could be strongly biased by the support-catalysed transfer hydrogenation. Advances in both H_2-driven hydrogenation and MPV-reduction are reported on a regular basis; however, reports investigating both mechanisms at the same time are rare.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.05.013. These data include MOL files and InChiKeys of the most important compounds described in this article.

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