

Optimized palladium catalyst systems for the selective liquid-phase hydrogenation of functionalized alkynes

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Abstract

Silica-supported palladium catalysts for the selective liquid-phase hydrogenation of alkynes to alkenes were prepared. As a model reaction the hydrogenation of 3-methyl-1-pentyn-3-ol was chosen. The kinetics of this reaction were investigated. Different approaches were used to obtain an optimal catalyst system. The selectivity of the palladium catalysts was successfully improved by modifying the catalyst with copper and the effect of this modification on the reaction mechanism was studied. The addition of quinoline as a reaction modifier to the system was investigated as a manner to improve selectivity. Monolith supported catalysts were prepared to obtain a more convenient reactor configuration.

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1. Introduction

In this paper the selective hydrogenation of 3-methyl-1-pentyn-3-ol to 3-methyl-1-penten-3-ol (Scheme 1) is discussed as a model reaction for the selective hydrogenation of functionalized alkynes to alkenes. This model reaction was chosen since this propargylic alcohol resembles the structure of many synthetic intermediates used in fine-chemical industry. Palladium catalysts are commonly used in selective hydrogenation. This paper discusses the preparation of palladium on silica catalysts and different manners to optimize the catalysts system: by preparing bimetallic copper-palladium catalysts, by

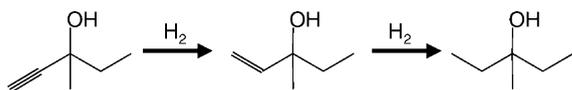
adding reaction modifiers to the system, and by using a structured support for the catalyst.

Bimetallic palladium-copper catalysts have been developed as an improvement for the commonly used palladium catalysts, which by itself already has a good performance in the selective partial hydrogenation of alkynes and diolefins. Recent articles on the use of these bimetallic catalysts for the selective hydrogenation of alkynes to alkenes have been published by Venezia et al. [1], Guzzi et al. [2], and Spee et al. [3]. Alkynes are versatile building blocks in fine chemistry for the creation of new carbon-carbon bonds. For the subsequent hydrogenation of the triple bond, the addition of copper to a palladium on silica catalyst proved to drastically reduce the overhydrogenation of the desired alkene to the alkane. The performance of this type of catalyst is competitive with that of the Lindlar catalyst [4], a lead-doped palladium on

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Scheme 1. Hydrogenation of 3-methyl-1-pentyn-3-ol to 3-methyl-1-penten-3-ol with unwanted consecutive hydrogenation to 3-methyl-3-pentanol.

calcium carbonate catalyst which is commonly used in fine-chemical industry for selective hydrogenation reactions.

An optimized procedure for preparing the bimetallic palladium-copper catalysts published by Spee [3] was used and the influence of the silica support and of some key preparational aspects were studied. The kinetics of the alkyne hydrogenation reaction catalyzed by an unmodified palladium on silica catalyst was investigated as well as the influence of mass-transfer on the reaction rate and selectivity. Subsequently, the effect of adding different amounts of copper to the catalyst is discussed.

Quinoline has been used as a reaction modifier [5]. The mode of operation of this commonly used modifier is still a matter of discussion in literature [6]. One assumption is that it adsorbs on the catalysts stronger than the desired product and less strongly than the reactant, thereby significantly decreasing the rate of the undesired consecutive reaction. The more recent view, however, is that electronic effects are dominating [7,8]. In this paper the benefits of using quinoline are compared to those of using a bimetallic catalyst.

Monolithic catalysts are an attractive replacement for conventional multiphase reactors [9]. When comparing a monolithic catalytic reactor to a slurry reactor, especially the separation of the catalyst from the liquid reactants is much easier since a (costly)

filtration is not necessary. Moreover, contamination of the product with catalyst can be prevented more easily. Another advantage of the monolithic catalysts over conventional packed bed reactors is that the selectivity of the monolithic catalysts is higher for a semi-hydrogenation reaction because of a shorter diffusion distance inside the catalyst and a narrow residence time distribution of the liquid flowing through the reactor. This has been demonstrated for e.g. the selective hydrogenation of benzaldehyde to benzyl alcohol [10]. Therefore, an attempt was made to prepare a Pd catalyst on a silica monolithic body to obtain an optimal reactor configuration. The overall aim of this research project is to combine an optimal reactor technology (i.e. a monolithic reactor) with an optimal catalyst system (i.e. a bimetallic catalyst).

2. Experimental

2.1. Catalyst preparation

Unless mentioned otherwise, all steps in the catalyst preparation were carried out in a nitrogen atmosphere using dried, freshly distilled solvents.

Catalysts were prepared on different silica supports of which the main characteristics are listed in Table 1. The silica was calcined in air in an oven at 523 K for 4 h after which it was transferred (hot) into a glass flask used for the metal deposition and evacuated for 15 min, after which it was kept in a nitrogen atmosphere. Some silica was given a pretreatment by boiling it 20 h in demineralized water to provide for additional silanol groups.

Palladium was deposited on the silica by means of an ion-exchange procedure. For this purpose 5 g

Table 1
Characteristics of silica supports for catalyst preparation

Support	Shape	Surface area (m ² /g)	Pore volume (ml/g)	Morphology
Davisil 643	Powder 35–74 μm	290	1.1	Mesoporous (15 nm)
Davisil 645	Powder 149–250 μm	300	1.1	Mesoporous (15 nm)
Davisil 710	Powder 4–20 μm	480	0.75	Mesoporous (6 nm)
Degussa OX-50	Aerosil powder, 10 μm agglomerates	50	1.2	Non-porous agglomerated microspheres of 10–200 nm
Corning all-silica monolith	Monolith 400 cpsi, 25 mm length and diameter	90	0.22	Macroporous (2 μm)

of silica was suspended in 100 ml of toluene by stirring (400 rpm), after which 225 mg palladiumacetate (corresponding to a palladium target loading on silica of 2 wt.%) (Degussa Pd(OAc)₂, 47.4 wt.% metal content, dried in vacuum for 15 min) dissolved in 50 ml of toluene was slowly added (30 min). This orange solution was stirred for 24 h, during which the solution slowly discolored and the silica particles gained a brown color.

Optionally copper was subsequently added to the catalyst. This was done by adding 50 ml of a solution of an organocopper compound. Mesityl copper, prepared according to Meyer et al. [11], and *p*-tolyl copper, prepared according to Spee et al. [3], were used, kindly provided by A.M. Arink of the Metal-Mediated Synthesis group of Utrecht University. Different amounts of copper were added, up to an amount corresponding to a 1:1 Cu:Pd molar ratio (1.2 wt.% Cu with 2 wt.% Pd). After addition the solution was stirred for an additional 72 h.

The nitrogen atmosphere in the catalyst preparation vessel was replaced by hydrogen and the catalyst was reduced (at room temperature) by stirring at 1200 rpm using a gas-inducing stirrer during 10 h. During this time the color of the catalyst particles changed from brown to black.

The toluene solvent was separated from the catalyst by decanting the toluene after the catalyst had settled when the stirrer was switched off. For the Degussa OX-50 supported catalyst centrifugation was necessary to separate the liquid. The catalyst was cleaned by washing it three times. This was carried out by stirring the catalyst with 200 ml of pentane followed by decantation. The catalyst was dried in vacuum for 3 h and stored under nitrogen.

2.2. Catalyst analysis

The prepared catalysts were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM)—coupled with energy dispersive X-ray (EDX) analysis, and elemental analysis by inductive coupled plasma (ICP) atomic adsorption spectroscopy (AAS).

CO chemisorption was performed using a Quantachrome Autosorb-1C at 308 K after evacuation and an additional reduction at 473 K (the catalyst was exposed to air prior to the analysis). Dispersions were

calculated using a shape factor of 6 and a Pd:CO stoichiometry of 1:1.

2.3. Catalyst testing

The catalysts were tested in the hydrogenation of 3-methyl-1-pentyn-3-ol. The reaction was carried out in ethanol as a solvent in a glass vessel containing three baffles and a double jacketed wall connected to a thermostat bath. The catalyst was transferred under nitrogen to a nitrogen atmosphere in the reaction vessel, which was subsequently replaced by hydrogen and the liquid was added. The catalyst concentration was typically 0.75 g/l, reactant concentrations of usually 0.3 or 0.03 mol/l were used. The pressure was 1100 mbar(a) and a temperature of 298 K was used. A gas-inducing stirrer (1200 rpm) was used to suspend the catalyst and dissolve hydrogen in the liquid. Liquid samples were taken and analyzed on GC to follow the course of the reaction. The 2 wt.% palladium on Davisil 643 supported catalyst was



Fig. 1. Monolithic stirred reactor.

used as the standard catalysts for the catalytic testing experiments.

2.4. Monolithic catalyst

The monolithic catalysts were prepared and tested in a well-defined monolithic stirred reactor configuration [12]. The configuration tested contained 300–700 ml of liquid and two all-silica monoliths, 2.5 cm diameter and 2.5 cm length. The monoliths had a cell-density of 400 cpsi (cells per square inch), with a channel diameter of 1.2 mm and a wall thickness of 0.16 mm. The monolith tips were 10 cm apart. The stirring rate was 300 rpm. Gas was induced into the liquid by the turbulence of the monolithic stirrer. Palladium-only monoliths were prepared similarly to the slurry catalysts. The monolith tests were also carried out at identical conditions. The monolithic test reactor is shown in Fig. 1.

3. Results

3.1. Standard palladium catalyst

3.1.1. Catalyst analysis

Elemental analysis of the prepared catalysts showed palladium loading of 1.7–2 wt.%, which corresponds nicely to the target (2 wt.%). TEM analysis of the catalysts showed all catalysts had a similar appearance. Palladium particles with a relatively broad distribution of 1–15 nm were visible. Some areas of the silica contained clusters of metal particles, while in other areas no particles could be found. A possible explanation for this is that the silica particles had the palladium distributed in an egg-shell type manner. Fig. 2 shows a TEM micrograph from a palladium-only on Davisil 643 catalyst. CO chemisorption of this catalyst showed an average metal particle size of 18 nm, which is in reasonable agreement with the TEM observations.

3.1.2. Kinetics

Experiments using different stirring rates and different catalyst amounts showed similar activities. Therefore, it can be concluded that external mass-transfer limitations on the catalyst activity are unlikely. The results of two typical experiments using a palladium on Davisil 643 catalyst are given in Fig. 3. In this figure,

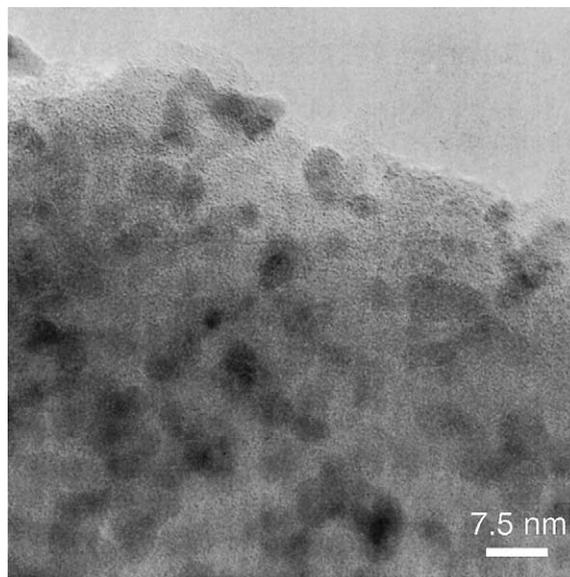


Fig. 2. TEM micrograph of Pd on silica catalyst.

the serial kinetics are clearly visible. It can also be seen that the initial concentration of the alkyne reactant has a strong influence on the maximum yield (%) of the desired alkene. The reproducibility of the catalyst performance was good. Both retesting the same catalyst and preparing a catalyst in duplicate proved to produce identical results within the experimental error.

3.1.3. Preparational aspects

The copper complexes used for the preparation of the bimetallic catalysts are very sensitive towards oxygen and water. Therefore, all catalysts were made using dry solvents and working under a nitrogen atmosphere. For the palladium-only catalysts, these precautions might not be necessary. Preparing a palladium-only catalyst in air using not-dried technical grade toluene as solvent, resulted in a catalyst with the similar activity and selectivity as those prepared oxygen/water free. The average crystal size, as determined by CO chemisorption, however, for this catalyst was 39 nm, i.e. much larger than the 18 nm found for the standard preparation procedure. The similar activity of the catalysts, is at least partly attributed to internal mass-transfer limitations.

Exposing a palladium on silica catalyst to air after reduction did not influence the catalyst performance.

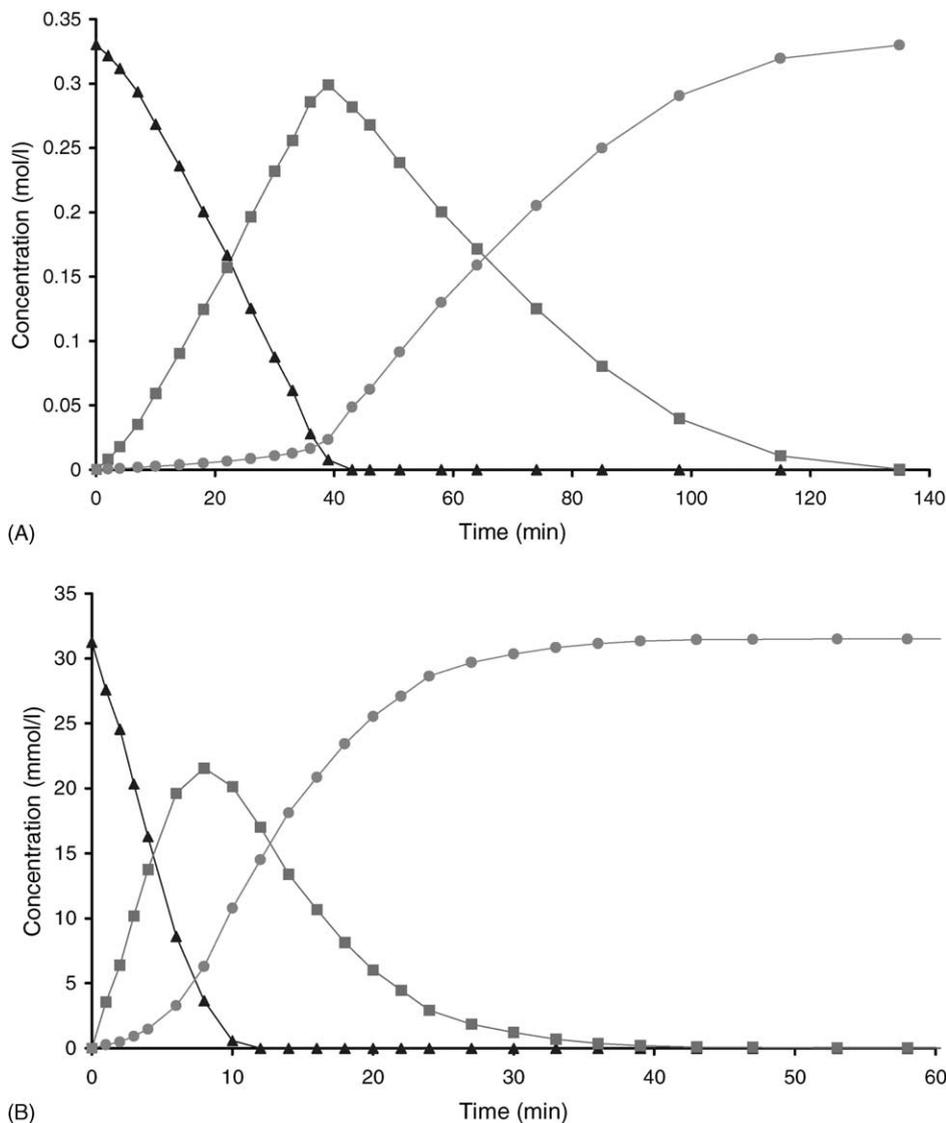


Fig. 3. Hydrogenation of 3-methyl-1-pentyn-3-ol over 'standard' 2 wt.% Pd on Davisil 643 catalyst (298 K): (▲) alkyne concentration; (■) alkene concentration; (●) alkane concentration. (A) High reactant concentration, catalyst 0.79 g/l; (B) low reactant concentration, catalyst 0.53 g/l.

3.2. Silica support

Catalysts were prepared on different types of silica. Three Davisils, Degussa OX-50, and a milled all-silica monoliths from Corning. TEM microscopy revealed that the metal particle size was similar on all catalysts. In Table 2 the initial activities for the catalysts are given. A comparison with the data in Table 1

shows that for the three catalysts supported on Davisil, both the activity and selectivity increase with a decreasing particle size, indicating internal mass-transfer limitations.

Catalysts were prepared on Davisil 643 silica, boiled in demineralized water for 20 h. This procedure was also carried out in earlier work [3] as a standard pre-treatment for the silica support to create additional

Table 2

Activities (in initial zero order region) and maximum yield for 2 wt.% Pd catalysts supported on different silica's in slurry experiments

Support	Activity (mol/g _{Pd} /min)	Maximum yield (%)
Davisil 643	0.46	79.7
Davisil 645	0.13	90.2
Davisil 710	0.55	90.4
Degussa OX-50	0.53	90.7
Milled Corning silica monolith ^a	0.21	87.4

298 K, 1 bar(a) H₂, 0.3 mol/l 3-methyl-1-pentyn-3-ol, 0.75 g/l catalyst.

^a Monolith milled before Pd deposition.

silanol groups on the support, and thereby prepare a more disperse catalyst. TEM analysis of this catalyst showed similar metal particles compared to the standard catalyst. CO chemisorption showed a slightly smaller average crystal size of 13 nm, from which it can be calculated the number of metal particles has doubled. No influence on either the catalyst activity or selectivity was found.

3.3. Addition of copper

3.3.1. Catalyst analysis

Elemental analysis showed that for the bimetallic catalysts based on mesityl copper, the measured loading were close to the target copper loading (typically 5–10 wt.% lower). For the catalyst prepared using *p*-tolyl copper the analyzed copper loading was about 40% of the target loading (0.58 wt.% versus 1.38 wt.%). This difference can be explained by the instability of the complex. During handling of this complex already some deposition of metallic copper was observed.

TEM microscopy of the bimetallic catalysts revealed that the metal particles visible did not differ much in size from those of the catalysts with only palladium. The particles were only slightly larger in size, ranging from 3 to 15 nm. A TEM micrograph is given in Fig. 4. For pumice supported catalysts the absence of a significant effect on the metal particle size by the addition of copper was also observed by Guzzi et al. [2] for Pd and Pd Cu catalysts. Benedetti et al. [13] on the other hand did observe a change in particle size for silica supported catalysts, which does not fully correspond to the minor influence found in

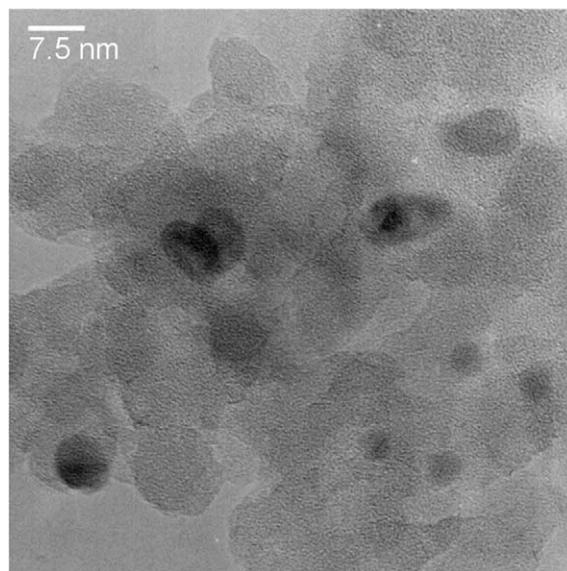


Fig. 4. TEM micrograph of bimetallic PdCu on silica catalyst.

this paper. Similar to the palladium-only catalysts, the particles were present in clusters on the silica. EDX analysis of the metal particles revealed that all particles were bimetallic and more or less uniform in composition. No particles of either only palladium or only copper could be found. EDX analysis of silica areas where no particles were visible showed no significant EDX signal of either palladium or copper.

In an earlier stage of the research project [3] the bimetallic catalysts were also examined using extended X-ray absorption fine structure spectroscopy (EXAFS). These analyses showed a good agreement between the metal particle size that could be calculated from the Pd coordination and the particle size observed with TEM. The analyses also showed that this preparational method produces well-mixed bimetallic palladium-copper particles. No conclusions could be drawn regarding a possible surface enrichment for one of the metals.

3.3.2. Activity/kinetics

Catalysts with different copper to palladium ratios supported on Davisil 643 silica were prepared using mesityl copper as precursor. The activities and maximum yields of the desired alkene for this series of catalysts are given in Table 3. It can be seen that adding copper to the catalyst decreases the overall activity, but

Table 3

Influence of copper on catalyst (Davisil 643 supported catalysts, prepared using mesityl-Cu)

Catalyst	Pd (wt.%)	Cu (wt.%)	Maximum yield alkene (%)	Activity (mol/g _{Pd} min)
Pd-only	2.0	–	90.2	0.49
PdCu-low	2.1	0.16	91.7	0.44
PdCu-med	2.0	0.51	92.3	0.40
PdCu-high	1.9	1.1	95.3	0.07

298 K, 1 bar(a) H₂, 0.3 mol/l 3-methyl-1-pentyn-3-ol, 0.75 g/l catalyst.

clearly increases the yield of the desired alkene. The effect of the addition of small amounts of copper to the palladium catalyst is clearly visible in Fig. 5. When a small amount (8:1 Pd:Cu atomic ratio (0.16 wt.% Cu:2 wt.% of Pd)) of copper is added to the palladium catalyst, the hydrogenation rate of the alkyne remains almost constant, whereas the alkene is hydrogenated at a significantly lower rate, resulting in a higher maximum yield of the desired product.

The catalyst prepared with *p*-tolyl copper had no significant activity at all (<0.001 mol/g_{Pd} min).

3.4. Reaction modifiers

To increase the selectivity of a catalyst in a liquid-phase hydrogenation reaction, sometimes reaction modifiers are used [5]. One such modifier for semi-hydrogenations is quinoline. The effect of adding quinoline to a 'bare' palladium on silica catalyst is shown in Fig. 6. Comparing Figs. 3A–6 shows that the addition of a small amount (0.02 mol/l) of quinoline drastically decreases the rate of alkene hydrogenation (0.42 → 0.021 mol/g_{Pd} min). The alkyne

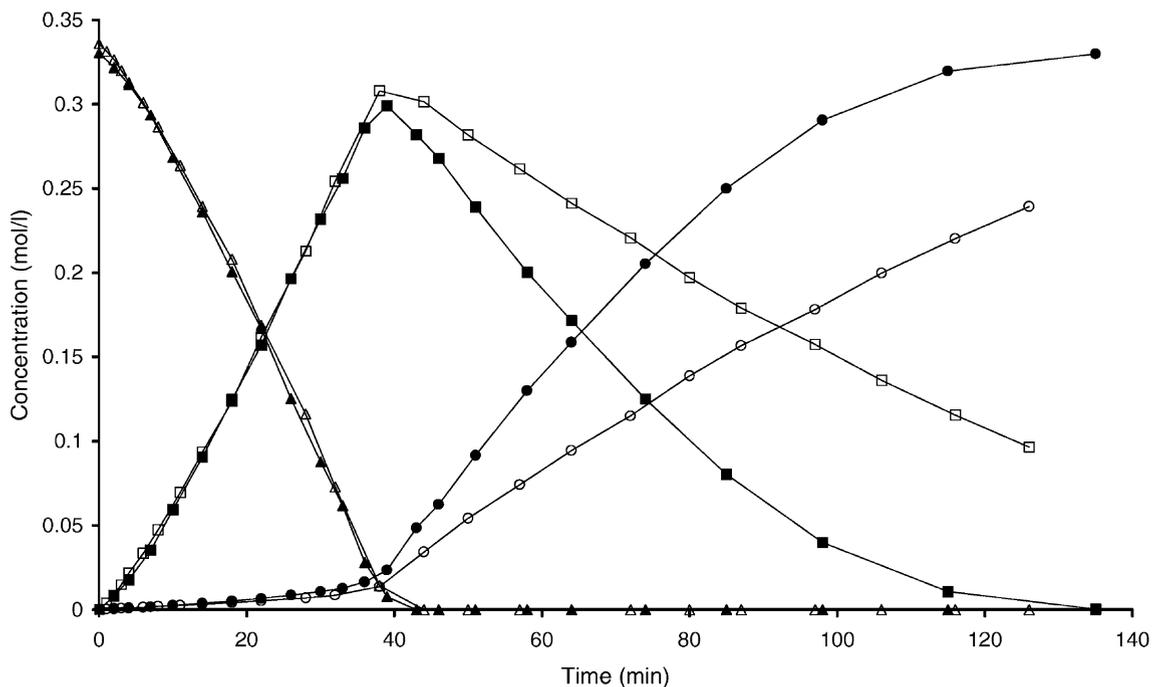


Fig. 5. Effect of Cu addition to Pd catalyst for hydrogenation of 3-methyl-1-pentyn-3-ol (298 K): (▲) alkyne concentration; (■) alkene concentration; (●) alkane concentration. Closed symbols: 2 wt.% Pd on Davisil 643 catalyst, 0.79 g/l; open symbols: 2 wt.% Pd with 0.16 wt.% Cu on Davisil 643 catalyst, 0.86 g/l.

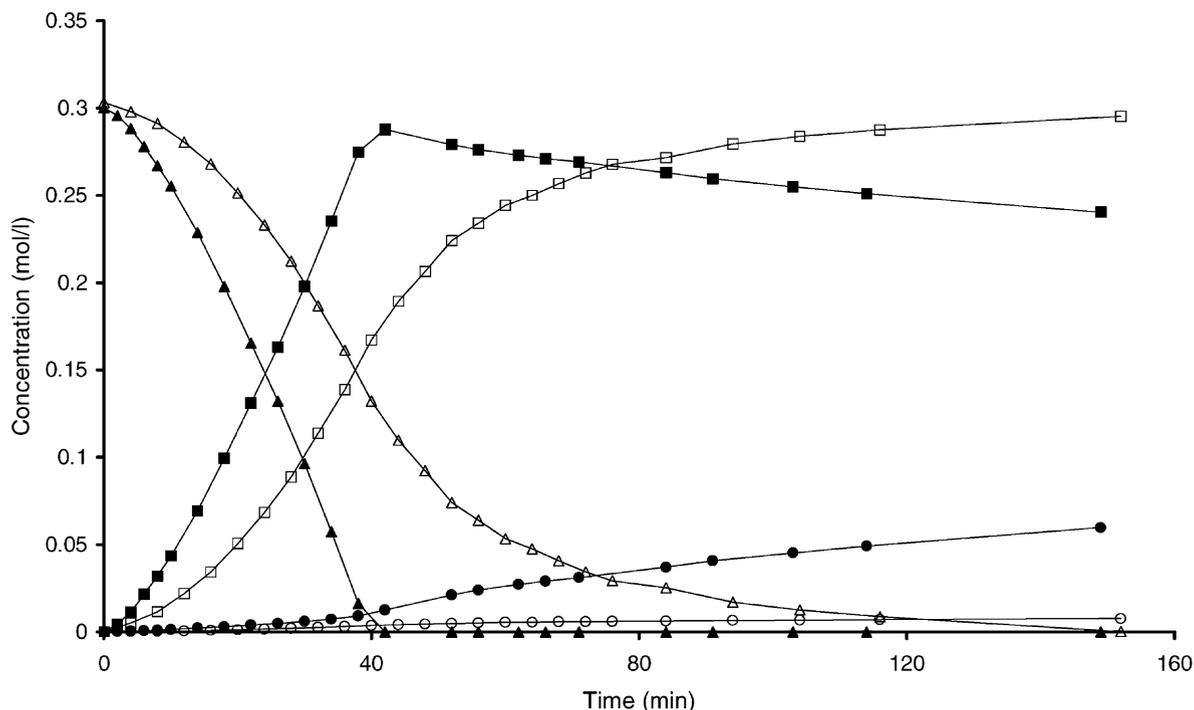


Fig. 6. Effect of quinoline addition to reaction mixture for hydrogenation of 3-methyl-1-pentyn-3-ol (298 K): (▲) alkyne concentration; (■) alkene concentration; (●) alkane concentration. Closed symbols: 2 wt.% Pd on Davisil 643 catalyst 1.03 g/l, quinoline 0.02 mol/l; open symbols: 2 wt.% Pd on Davisil 643 catalyst 1.28 g/l, quinoline 0.2 mol/l.

hydrogenation rate, on the other hand, is hardly influenced (drops from 0.44 to 0.39 mol/g_{Pd} min). As is also visible in Fig. 6, the overhydrogenation is almost completely blocked at a quinoline concentration of 0.2 mol/l, however, in this case also the alkyne hydrogenation is significantly slower.

3.5. Lindlar catalyst

Since the bimetallic catalysts should be seen as an attractive replacement for a commonly used selective

hydrogenation catalyst like a Lindlar catalyst, the performance of this catalyst was compared to that of the PdCu catalysts. Testing the Lindlar catalyst (at a reactant concentration of 0.3 mol/l), showed an alkyne hydrogenation rate of 0.43 mol/g_{Pd} min and a maximum alkene yield of 91.9%.

3.6. Monoliths

Monolithic palladium catalysts were prepared successfully. An example of an experiment using a

Table 4

Activities (in initial zero order region) and maximum yield for 2 wt.% Pd catalysts supported on Corning monolithic silica support

Support	Catalyst (g/l)	Activity (mmol/g _{Pd} min)	Activity (mmol/m ² min)	Maximum yield (%)
Monolith	28.9	13	36	89.4
Milled monolith, Pd deposited after milling	1.34	212	53	87.4
Milled monolith, Pd deposited on monolith (before milling)	1.53	182	45	85.0

298 K, 1 bar(a) H₂, 0.3 mol/l 3-methyl-1-pentyn-3-ol.

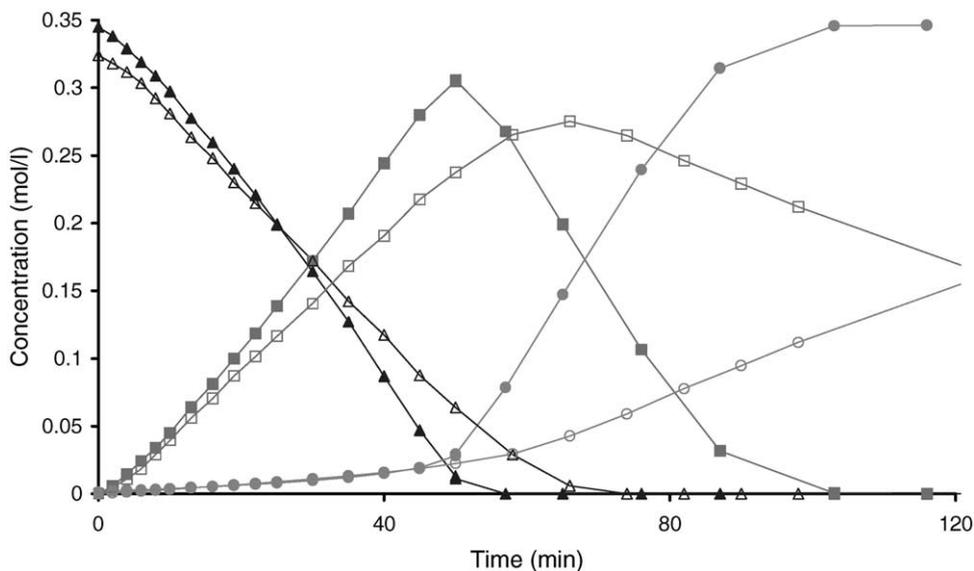


Fig. 7. Experiment using monolithic catalyst (closed symbols) and milled monolithic catalyst (open symbols). Hydrogenation of 3-methyl-1-pentyn-3-ol over 'standard' 2 wt.% Pd on all-silica monolithic catalyst. Monolithic experiment: two 400 cpsi monoliths, 2.5 cm length and diameter, 325 ml liquid; slurry: catalyst 1.5 g/l (both 298 K): (▲) alkyne concentration; (■) alkene concentration; (●) alkane concentration.

monolithic catalyst is shown in Fig. 7, together with an experiment of the same catalyst after it was milled and tested as a slurry catalyst. The performance of the catalysts on monolithic silica are summarized in Table 4. The selectivity of the monolithic catalysts was similar to that of the slurry catalysts with the small particle size. If one compares the monolithic selectivity to that of the same catalyst after it had been milled to fine particles, it can be seen that the selectivity of the monolith is higher. The activity of the monolithic catalysts, however, was much lower than that of the slurry catalysts (13 instead of 490 mmol/g_{Pd} min).

The easy reusability of the monolithic catalysts was utilized by performing repeated tests with the monoliths. In these experiments no significant changes in either activity or selectivity were observed.

4. Discussion

4.1. Standard palladium catalyst

Fig. 3 gives typical performance profiles for two different reactant concentrations. In both cases the se-

rial character of the kinetics is clear: first the alkyne is hydrogenated up to nearly full conversions following zero order kinetics. When the concentration of the alkyne is sufficiently low, the hydrogenation to the alkane is observed. It should be noted that right from the start (when no significant amount of alkene is present) some alkane is formed, though at a relatively low rate. This seems to indicate a slower parallel reaction pathway for the direct hydrogenation of the alkyne to the alkane. The maximum yield of alkene depends on the concentration regime.

Combining these observations leads to the conclusion that a Langmuir–Hinshelwood kinetics is most likely to hold for this reaction system. The zero order reaction of the alkyne can be explained by an alkyne adsorption which is much stronger than the adsorption of alkene and alkane, resulting in a catalyst surface being essentially completely occupied by the alkyne and thereby reacting at a constant rate. The zero order conversion of the alkene once the alkyne has been depleted, can similarly be explained by a much stronger adsorption of the alkene compared to the alkane. An extensive discussion on kinetics of the reaction is given in a separate paper [14].

4.2. Silica support

In Table 2 an increasing activity with a decreasing support particle size is visible. From calculating the Thiele-modulus [15], it was estimated that internal mass-transfer limitations are absent for particles smaller than 10 μm . It can therefore be assumed the activity for the Davisil 710 supported catalyst is the intrinsic activity. For the silica supports with a larger particle size (Davisil 643 and 645) internal mass-transfer effects did have a significant influence on both the selectivity and the activity of the catalysts. The modeling work which demonstrates these effects by calculating concentration profiles in the catalyst particles can be found in Nijhuis et al. [14]. In Fig. 3 the presence of internal mass-transfer effects are also visible. In this figure it can be seen that the Davisil 643 (medium particle size) supported catalysts produces different selectivities for different initial reactant concentrations. With a high initial alkyne concentration (3A) the reaction is hydrogen limited in the catalyst particles and the alkyne and alkene react according to their kinetic preference. In Fig. 3B, on the other hand, inside the catalyst particles the reaction is more limited by the diffusion of the organic molecules and the overhydrogenation occurs more easily, explaining the lower selectivity.

The activity and selectivity was similar for the two silica's with small particles (Davisil 710, Degussa OX-50). Apparently the type of silica support is not important for the catalyst. If then the Davisil 710 and Degussa OX-50 based catalysts are compared, using the Davisil 710 based catalyst is preferred, since the particles are still relatively large and they can be separated relatively simple from the liquid by settling followed by decantation. The much smaller particles of the Degussa OX-50 based catalyst can only be separated by centrifugation or filtration, while the other silicas could be easily separated by settling.

4.3. Addition of copper

The addition of copper to the palladium on silica catalyst results in an increase of the selectivity towards the desired alkene, at the expense of some catalytic activity. This effect of the copper in the bimetallic particles is most likely a change in adsorption strength of the hydrocarbons on the metal surface. The

increasing selectivity towards the desired alkene points to a stronger decrease in adsorption strength for the alkene than for the alkyne. This can be explained by the Langmuir–Hinshelwood kinetics. Kinetic modeling of the experiments showed that in case copper is present on the catalyst the relative adsorption strength of the alkene is significantly less than that of alkyne in comparison with the catalyst containing palladium only.

The large drop in the activity of the catalyst when the copper content is increased from 0.5 to 1.1 wt.% can be explained by a necessity for an ensemble of palladium sites for the reaction to proceed. When palladium is 'diluted' with too much copper, these ensembles are no longer present. Also the increased selectivity by the addition of copper can be explained using an ensemble theory. In case the alkene hydrogenation requires a larger ensemble than the alkyne hydrogenation, an increase in copper in the catalyst would then cause a stronger decrease in available adsorption positions for the alkene than for the alkyne. This then is in agreement with the relatively weaker alkene adsorption observed in the modeling, since the adsorption constants determined in that way are not so much expressing an adsorption strength, but a measure for the coverage on the surface. A direct effect of the addition of copper on the adsorption strength of the different molecules by electronic effects can also be possible, although according to Skoda et al. [16] the electronic properties of palladium atoms are not modified strongly by copper addition.

In the review on multimetallic catalysts by Gucci [17] it is concluded that the ensemble size effect is often the most important factor when one 'dilutes' one metal with a second metal, but in most cases this is not the only factor. This is in agreement with the observations in this study.

The difference in stability between *p*-tolyl copper and mesityl copper is very large. This explains why the copper loading of the catalyst prepared using *p*-tolyl copper was significantly lower than planned. The catalyst prepared using this copper-precursor showed no significant activity, while catalysts prepared with a higher copper content using mesityl copper were still active. Possibly this can be explained by the preparation using *p*-tolyl copper resulting in palladium particles that were covered with copper, instead of the preparation resulting into true bimetallic particles. In

that case insufficient palladium ensembles will have been available for a significant catalytic activity of the catalysts prepared with *p*-tolyl copper.

4.4. Reaction modifiers

It can be concluded that adding quinoline or a similarly working component to the reaction system is beneficial for the reaction selectivity. However, one should note that the penalty one pays for using such a component is that an additional separation step is required. Using an intrinsically more selective catalyst, like the copper modified palladium catalyst is in that respect more attractive.

The manner in which a reaction modifier like quinoline operates is sometimes described as by adsorbing on the catalyst with a strength stronger than the desired product (alkene), but less strongly than the reactant (alkyne), thereby effectively blocking the adsorption of the alkene and thus the overhydrogenation [18]. If one, however, adds an additional intermediate adsorbing component to a Langmuir–Hinshelwood kinetic expression and tries to model this effect, this is not possible: although the overall rate changes as different amounts of a non-reacting component with different adsorption strengths are added, the maximum yield of the desired intermediate product is not affected. This phenomenon can be explained as follows:

The increase in selectivity might also be due to changes in mass-transfer limitations. The increase in maximum yield is the result of the lower catalyst activity, providing extra time for the mass-transfer processes in the catalyst particles. With a high catalytic activity the alkene is hydrogenated further before it desorbs and diffuses out of the catalyst particle. Modeling calculations [14] have shown that although the contribution of quinoline to a higher selectivity can be explained partly by a mass-transfer explanation, this is insufficient for the entire observed effect.

An alternative more complex explanation for the manner in which quinoline operates is given by Mallat and Baiker [6]. The nitrogen atom of the reaction modifier is supposed to donate electrons to the metal surface, thereby altering the electronic properties of the Pd–H bond (hydrogen becomes more negatively charged), making it more reactive towards alkynes and less reactive towards alkenes. Yu et al. [7,8] have provided experimental proof for this assumption by

performing H–D exchange experiments. The effect of lead in the Lindlar catalyst is supposed to similarly originate from alternating the electronic properties.

4.5. Monolithic catalysts

The difference in activity between a monolithic and a slurry catalyst can be explained by the much lower geometrical surface area of the monolithic catalyst ($2700 \text{ m}^2/\text{m}^3$), which is about 50 times lower than the geometrical surface area of the ‘standard’ Davisil 643 supported catalyst. The activity of the monolithic catalyst is most likely limited by external mass-transfer. If one assumes that the reaction is completely externally mass-transfer controlled, a *k*-value of $1.7 \times 10^{-4} \text{ m/s}$ can be calculated. Such a *k*-value is reasonable for mass-transfer in the laminar flow in the monolith channel, and supports the assumption of external mass-transfer control for the monolithic catalyst. From Table 4 it can also be seen the lower activity is caused by the geometry of the catalyst, since once milled the activity is similar to that of the slurry catalyst made on the same silica. The activity values given in Table 4 per external catalyst surface area are similar, which also confirms the assumption of external mass-transfer limitation for the monolithic catalyst. Therefore, it is recommended to prepare the catalyst on a silica-washcoated monolith. In that case the palladium is used much more effectively. Alternatively higher cell-density monoliths can be used (up to 1600 cpsi monoliths are available at this moment). These have a larger geometrical surface area and thinner walls, resulting in a more efficient catalyst utilization.

When a comparison is made in Fig. 7 for the rate of alkene hydrogenation, it is visible that this rate is relatively fast for the monolith compared to the slurry. This can also be explained by the external mass-transfer limitations. In the monolithic reactor far more catalyst is present. In the slurry reactor the intrinsically slower alkene hydrogenation is kinetically limited, while for the monolith the larger amount of catalyst makes it mass-transfer limited, explaining why the alkene and alkyne hydrogenations both occur at the same rate. Using a washcoated monolith will also prevent this relatively fast alkene hydrogenation since the amount of catalyst present is much less, while the alkyne hydrogenation activity in the reactor will remain the

same. Some extent of external mass-transfer limitation in hydrogen, however, does also have an advantage. In Fig. 7 it can be seen that the maximum yield is higher for the monolithic catalysts, which is caused by a shortage of hydrogen further inside the catalyst, caused by the external mass-transfer limitation. This prevents overhydrogenation of the alkene product at this location.

Although the activity of the monolith catalyst appeared to be relatively low, even for the present monolithic catalyst the usability is demonstrated. The lower catalyst activity will be compensated by an easier reusability of the catalyst (no losses when the catalyst is separated from the liquid). Furthermore, monolithic catalysts allow for a flow-through reactor with good mass-transfer properties and thus high selectivities. This type of reactor is often preferred over a slurry reactor in industry because of the cheaper and simpler continuous operation. The development of more active monolithic catalysts is in progress [19]. It can be easily calculated that for a commercially available 900 cpsi monolith, containing the catalyst on a typical 10 wt.% silica-washcoat on which the palladium is deposited, the activity will be just over 200 mmol/g_{Pd} min. This activity is about 40% the highest activities obtained using slurry catalysts without any mass-transfer effects. Such an activity value makes the monolithic reactor with its operational benefits [20] competitive to slurry reactors. With even higher cell-density monoliths becoming available the activity values will converge even further. Once these active monolithic catalysts are made with a bimetallic PdCu catalyst the most convenient reactor system becomes available, since than both a separation step for the catalyst and for the reaction modifier, necessary for the highest possible selectivity, can be avoided.

5. Conclusions

Bimetallic PdCu catalysts for the selective hydrogenation of alkynes to alkenes have been prepared successfully. It is shown that the addition of a small amount of copper to a palladium catalysts increases the catalyst selectivity while the activity is retained. Of the different silica's tested, Davisil has been found to be the best, because of superior handling properties. No influence of the silica support on either

activity or selectivity was found. The selectivity enhancing effect of copper can be explained by copper decreasing the relative adsorption strength of the alkene compared to that of the alkyne. Alternatively copper addition can increase the selectivity by reducing the size of the available ensembles of palladium sites, assuming for the alkene hydrogenation larger ensembles are required than for the alkyne hydrogenation. For the bimetallic PdCu catalysts, the increased yield of the alkene is achieved at the expense of a somewhat lower catalytic activity. Compared to the Lindlar-catalyst used conventionally for this type of reactions, the PdCu with 2 wt.% palladium and 0.16 wt.% copper has a comparable performance. The major advantage of the PdCu catalysts being to tailor the catalyst for either activity or selectivity by varying the palladium to copper ratio.

The hydrogenation of 3-methyl-1-pentyn-3-ol proceeds via a Langmuir–Hinshelwood mechanism, although this mechanism is not able to completely describe all observed phenomena (a.o. dependency of maximum yield of alkene on initial reactant concentration). The addition of a reaction modifier like quinoline can help to increase the yield of the desired product. The effect of quinoline seems to be partly by blocking the adsorption of adsorption sites on the catalyst resulting in a lower catalyst activity and changing mass-transfer influences. Secondly electronic effects of quinoline change the relative adsorption strength of the reactant and product molecules. Using a PdCu catalyst is preferable to using a reaction modifier, since adding a reaction modifier makes an additional separation step in the process necessary.

Monolithic catalysts have been prepared successfully. The selectivity of the monolith supported palladium catalysts was similar to that of the slurry catalysts. The activity was lower, which is explained by the lower geometrical surface area. Optimized monolithic catalysts will be able to compete with slurry catalysts.

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