

# Synthesis and catalytic properties of large ligand stabilized palladium clusters

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## Abstract

Ligand stabilized palladium clusters in the size range of 3–4 nm on various supports are used as catalysts in gas phase and liquid phase hydrogenation reactions. 1,10-Phenanthroline and O<sub>2</sub> form the ligand shell for a mixture of seven- and eight-shell clusters, (Pd<sub>7</sub>/8(phen)), on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaCO<sub>3</sub>. The gas phase hydrogenation of 1,3-butadiene under various conditions gives results like established metal catalysts, i.e. low selectivities. In contrast with these observations liquid phase reactions show high selectivities which can additionally be influenced by variation of the ligand shell. Semihydrogenation of 2-hexyne with Pd<sub>7</sub>/8(phen) on TiO<sub>2</sub> in n-octane results in 93% of *cis*-2-hexene. If 3-*n*-butyl or 3-*n*-heptyl-phenanthroline is used instead of the unsubstituted ligand the selectivity is about the same, however, the formation of daughter products such as isomers or n-hexane is almost completely suppressed. The hydrogenation of a series of unsaturated carbonic acids again shows the influence of the nature of the ligands on the products. Here, phenanthroline and (–)-cinchonidine are compared. Finally, the hydrogenation of acetophenone is studied using di-2,9-(2-methyl-butyl)-1,10-phenanthroline and (–)-cinchonidine for comparison. The isopentyl substituted phenanthroline enforces high activities, whilst cinchonidine prevents the same reaction almost quantitatively. TEM and STM studies of the clusters have been performed and will be described.

**Keywords:** Cinchonidine; Hydrogenation; Palladium; Phenanthroline; Supported catalysts

## 1. Introduction

Activity and selectivity of a metal catalyst usually depend characteristically on the particle size and shape as well as on the environment such as the support and the reaction medium. Established methods for the generation of metal particles on supports [1–14] in general result in more or less broad size distributions. For reactions which are independent of the structure of the catalyst the particle size distribution does not play any role. However, others, especially stereoselective reac-

tions, can be dominated by the structural characteristics of the catalyst [15].

Metal clusters are defined to consist of a distinct number of structurally ordered atoms and represent ideally monodispersed metal particles. Preparative available metal clusters must be protected by a shell of appropriate ligands to prevent coalescence processes and so to save the individual properties of the single particles. These ligand molecules, however, may have considerable consequences with respect to the properties of the clusters. Compared with unligated naked clusters the electronic interactions between ligand molecules and cluster surface atoms change the electronic characteristics of the metal atoms. In

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addition, metal atoms which are coordinated to a ligand molecule cannot participate in the catalytic process as an unligated metal atom does. On the one hand, a cluster with a ligand shell can be regarded as a partially poisoned catalyst, on the other hand, the presence of ligand molecules on a cluster surface can influence the selectivity of a reaction in a favorable sense.

Due to their ligand shell clusters are soluble in solvents related to the nature of the ligand molecules. We know clusters with a high solubility in organic solvents if the ligands consist of organic molecules. The same cluster can be dissolved in water, however, if ionic substituents or at least polar moieties are present.

Ligand stabilized metal clusters have advantages compared with established metal catalysts, if high selectivities are demanded. Even homogeneous reactions should in principle be possible. However, as it turned out, numerous homogeneous catalytic reactions showed that the original cluster molecules could never be gained back after the reaction because of decomposition processes. For that reason all investigations described in the following have been carried out with supported clusters. Metal clusters on supports show greater stabilities, their frequent use is possible, coalescence processes are reduced up to a critical temperature and finally, the support material itself may cooperate with the clusters during the catalytic process. A further decisive advantage of ligand stabilized clusters in catalysis is the fact that they can be prepared and investigated in detail before their use in a supported form. Therefore, we know exactly what we start with. Of course one cannot exclude some change during catalysis, especially with respect to the ligand shell. The fact however, that activity and selectivity of supported clusters do not change over many cycles clearly indicates that significant degradation processes do not occur.

In the following we describe some studies of heterogeneous reactions using mainly seven- and eight-shell palladium clusters on different supports in gas phase and in liquid phase reactions, respectively.

## 2. Experimental

### 2.1. Catalyst preparation

The cluster Pd<sub>7/8</sub>(phen) is prepared as described in Ref. [16]. The clusters Pd<sub>7</sub>(phen-butyl), Pd<sub>7</sub>(phen-heptyl), Pd<sub>8</sub>(phen-methyl-butyl), and Pd<sub>8</sub>(cinchon) are prepared analogously to Pd<sub>7/8</sub>(phen) using the appropriate ligands instead of phenanthroline. The yields are between 80 and 90%. The ligands 3-*n*-butyl- and 3-*n*-heptyl-1,10-phenanthroline were prepared by the procedure described in Ref. [17]. 2,9-Di(2-methyl-butyl)-1,10-phenanthroline was synthesised by the procedure described in Ref. [18]. The adsorption of the clusters on the supports succeeds if 50 mg of the cluster is dissolved in 250 ml of a 10:1 water pyridine mixture and if this solution is added slowly to a suspension of the corresponding support in 200 ml of the water-pyridine mixture. The adsorption is quantitative if the solvent has become colorless. After filtration and washing with acetone the catalyst is dried under vacuum.

### 2.2. Cluster characterisation

Besides elementary analyses the clusters were characterized by transmission electron microscopy with a Philips CM 200 FEG. The STM investigations have been performed with a Burleigh ARIS-4400 instrument at room temperature under air conditions. For these measurements the cluster powders were pressed into small pellets the surface of which was used for the imaging.

### 2.3. Catalytic reactions

The 1,3-butadiene gas phase hydrogenation was carried out in a conventional flow system, equipped with a glass frit and 200 mg of the catalyst. The flow stream was 14 l/h (measured at 25°C and atmospheric pressure) containing 1,3-butadiene, hydrogen and nitrogen ( $P_{\text{butadiene}} = 1670 \text{ Pa}$ ). As the reactions were exothermic a temporary increase of temperature of ca. 40° was

observed. The products were analyzed using a Shimadzu GC-8A gas chromatograph with Sebaconitrile ( $3\text{ m} \times 0.2\text{ cm}$ ) and  $\beta, \beta'$ -oxidipropionitrile ( $1.5\text{ m} \times 0.2\text{ cm}$ ) on a Chromosorb P column.

The liquid phase reactions were carried out in 25 ml flasks containing the solvent and 100 mg of the catalyst. The flasks were connected with a gas burette filled with hydrogen. When the gas absorption stopped a solution of the educt was dropped into the suspension. The products were analysed by a Dani 8520 gas chromatograph, equipped with a Hewlett Packard PONA column ( $50\text{ m} \times 0.2\text{ mm}$ ).

### 3. The nature of the catalysts

Seven- and eight-shell palladium clusters Pd7/8(phen) are formed together with a five-shell fraction Pd5(phen) if palladium(II) acetate is reduced by gaseous hydrogen in the presence of phenanthroline molecules, followed by a careful oxidation of non-ligated surface atoms by oxygen [16,19,20]. The oxygen, which is probably coordinated as  $\text{O}_2^{2-}$  units, protects the cluster particles from uncontrolled oxidation at air contact. During hydrogenation the oxygen is removed to generate catalytically very active free surface sites. In an

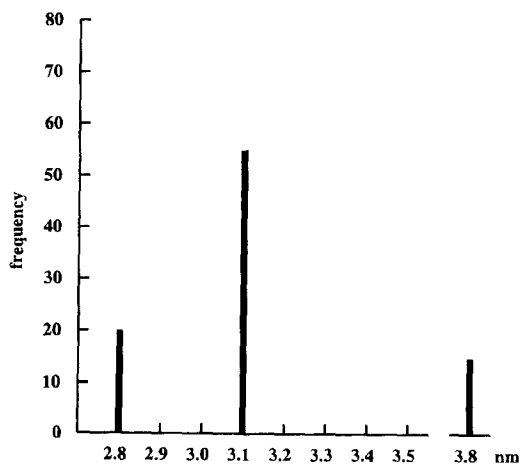
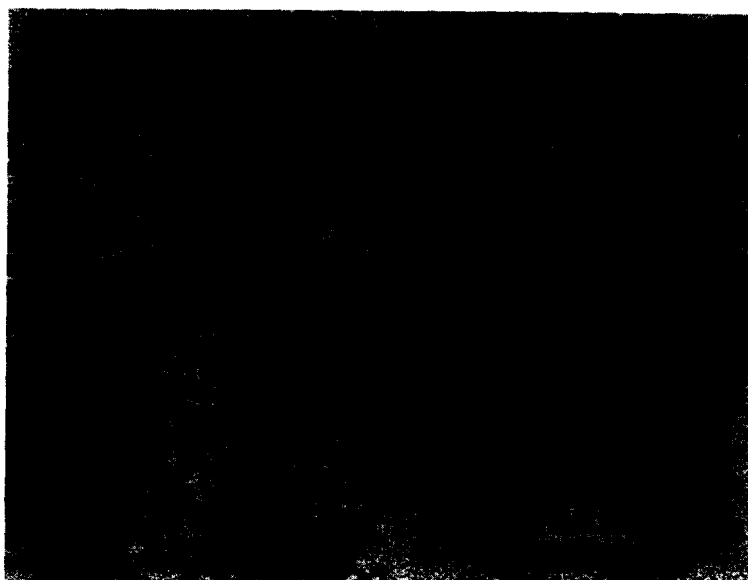


Fig. 1. Top: Transmission electron micrograph of Pd7(phen-heptyl) clusters. Bottom: Histogram of the Pd7(phen-heptyl) clusters. The mean diameter is 3.1 nm, corresponding with seven shell clusters.

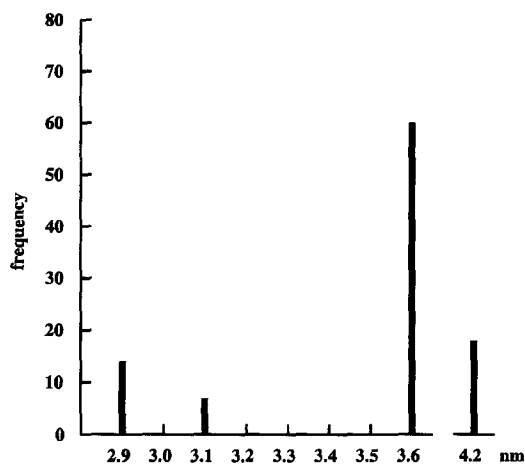
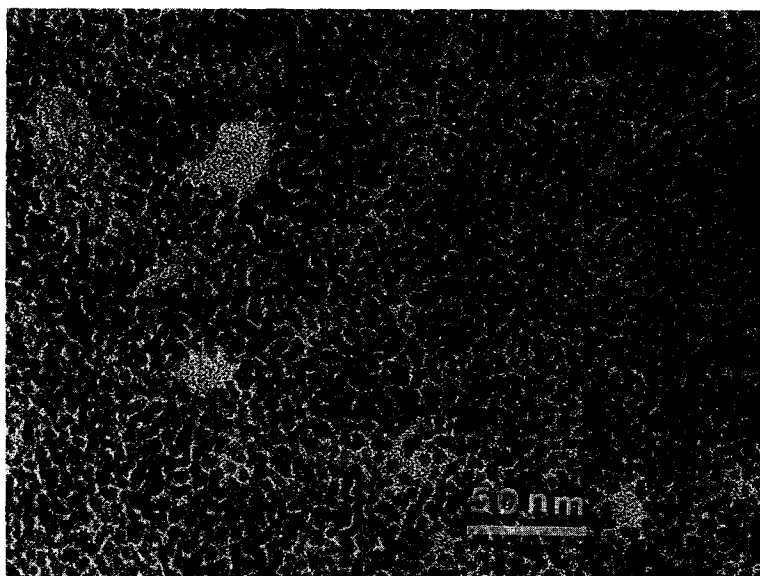


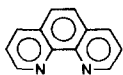
Fig. 2. Top: Transmission electron micrograph of Pd8(cinchon) clusters. Bottom: Histogram of the Pd8(cinchon) clusters. The mean diameter of 3.6 nm corresponds with eight-shell clusters.

idealized description these clusters consist of cubic close-packed arrangements of Pd atoms with  $10n^2 + 2$  atoms in the  $n$ th shell. This does not mean, however, that the calculated number of atoms, namely 561 (five-shell), 1415 (seven-shell), and 2057 (eight-shell) are quantitatively reached, but from high resolution transmission electron microscopy (HRTEM) we know that the number of atomic rows in single particles agrees with the definition of a full-shell cluster [16]. Scanning tunnelling microscopy (STM) is the best tool to characterize the clusters together with

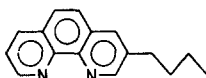
their ligand shell. Usually the Pd5 fraction can easily be separated from Pd7/8 due to the different solubilities in benzene. The Pd7/8 fraction, which is about 90% of the total yield, could not yet be separated into the Pd7 and Pd8 compounds. As the difference in the metal core diameters is only 3.1 (Pd7) versus 3.6 nm (Pd8) it can be supposed that the Pd7/8 mixture will not deviate significantly in its catalytic behavior from that of the pure Pd7 or Pd8 fractions. Deviations in the particle size distribution are observed if the phenanthroline ligand molecules are substituted by

phenanthroline derivatives or completely different compounds. The following ligands were used:

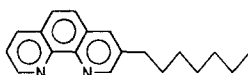
1. 1,10-phenanthroline (phen)



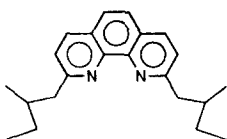
2. 3-n-butyl-phenanthroline (phen-butyl)



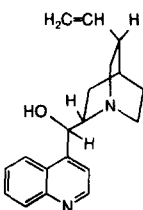
3. 3-n-heptyl-phenanthroline (phen-heptyl)



4. di-2,9-(2-methyl-butyl) phenanthroline (phen-methyl-butyl)



5. (–)-cinchonidine (cinchon)



The microscopy of Pd7/8(phen) has already been described in Ref. [16]. Substitutionally transmission electron micrographs of the 3-n-heptyl-phenanthroline and of the (–)-cinchonidine ligated clusters are shown (Fig. 1 and Fig. 2).

As can be seen from Fig. 1 the particles with 3-n-heptyl-phenanthroline ligands mainly consist of 3.1 nm Pd7 clusters, whereas the (–)-cinchonidine stabilized clusters predominantly show diameters of 3.6 nm, corresponding with a Pd8 fraction. The particle size distributions of the 3-n-butyl-phenanthroline and the di-2,9-(2-methyl-butyl)-

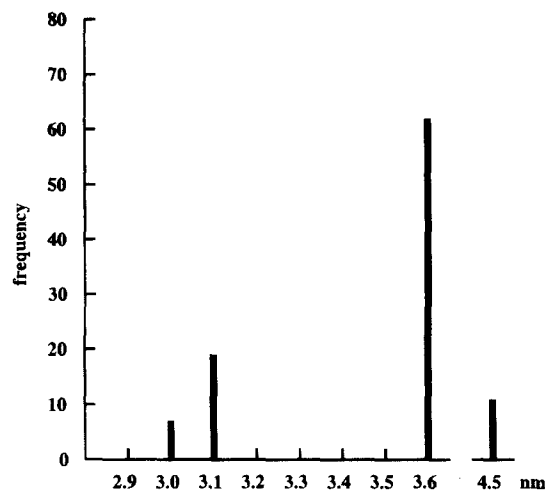
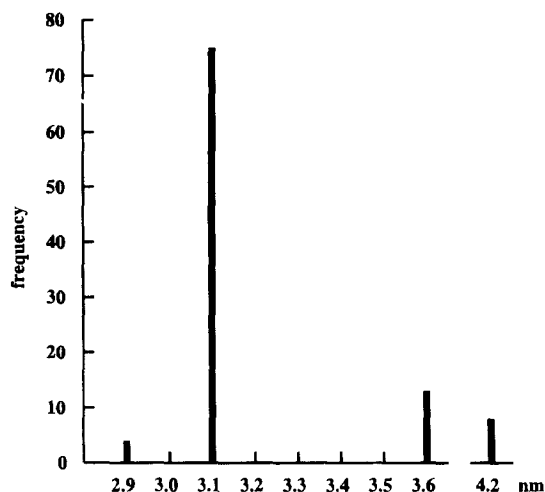


Fig. 3. Histograms of Pd7(phen-butyl) (top) and Pd8(phen-methyl-butyl) (bottom). The phen-butyl ligated particles mainly consist of seven-shell clusters, whereas the particle size distribution of phen-methyl-butyl derivative mainly consist of Pd8 clusters.

phenanthroline protected clusters are shown in Fig. 3.

In the following the catalysts are abbreviated as Pd7/8(phen), Pd7(phen-butyl), Pd7(phen-heptyl), Pd8(phen-methyl-butyl), and Pd8(cinchon). Fig. 4 shows an STM image of a Pd7/8(phen) sample. In contrast to this cluster mixture the very uniform particle size of a Pd5(phen) fraction can be seen in Fig. 5.

Irrespective of the cluster size and the type of ligand molecules all clusters are soluble in a

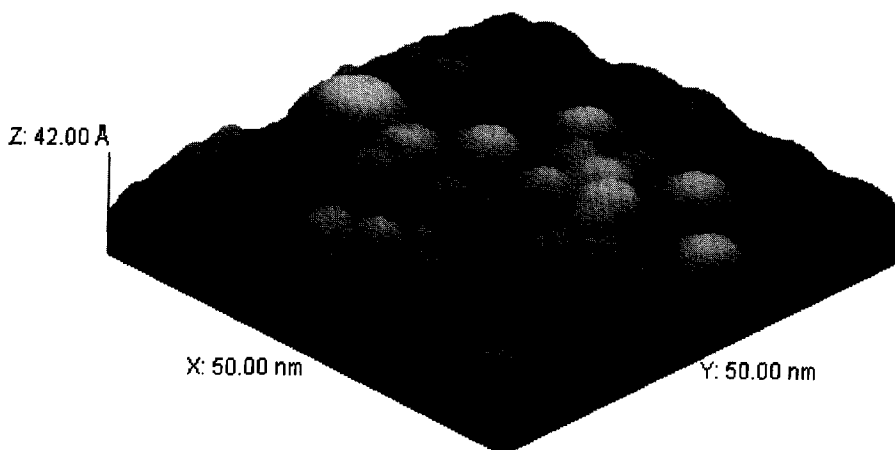


Fig. 4. Scanning tunneling microscopic image of Pd7/8(phen) clusters on the surface of a cluster pellet.

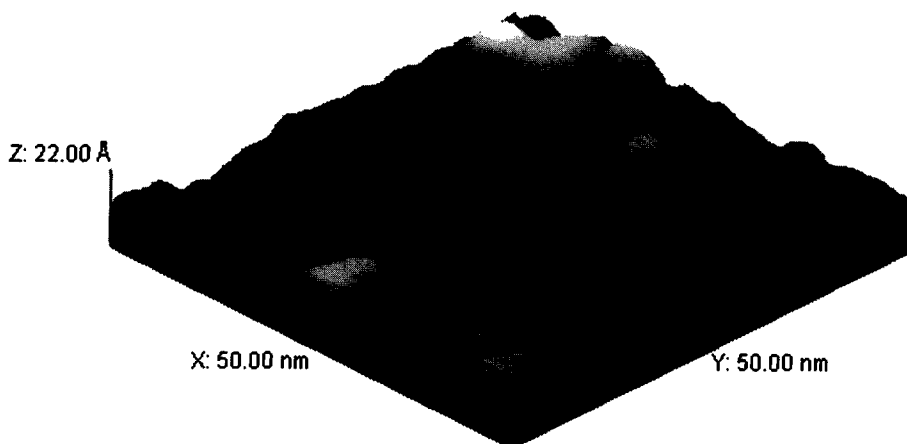


Fig. 5. Scanning tunneling microscopic image of Pd5(phen) clusters on the surface of a cluster pellet. In contrast to the Pd7/8(phen) sample the Pd5(phen) clusters are monodisperse, as can be seen from this image.

water–pyridine 10:1 mixture. From such solutions they can be adsorbed on different supports such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub> or active carbon spontaneously. In this way catalysts containing 1–5 wt% clusters can easily be prepared.

## 4. Gas phase reactions

### 4.1. Hydrogenation of 1,3-butadiene

If gaseous 1,3-butadiene is hydrogenated in the presence of 1% Pd7/8(phen) on TiO<sub>2</sub> in an integrated reactor system (see Experimental Part) at room temperature using a diene:H<sub>2</sub> ratio of 1.2 in a stream of nitrogen of 14 l/h the simultaneous

formation of 1-butene, *trans*-2-butene, n-butane, and *cis*-2-butene is observed (Fig. 6).

The main product is 1-butene, the *trans*:*cis*-2-butene ratio is remarkably greater than 1, indicating a  $\pi$ -allylic coordination of the semihydrogenated species in agreement with different literature data [21,22]. All products are directly formed from 1,3-butadiene. If the diene:H<sub>2</sub> ratio is <0.8 the main product is n-butane. A diene:H<sub>2</sub> ratio of  $\approx$ 0.9 gives a significantly different result, as the formation of 1-butene dominates the reaction up to an olefin concentration of about 25%. After that point isomerization to *cis*- and *trans*-2-butene is observed, as can be seen from Fig. 7.

These results can again be compared with experiments using commercial Pd/Al<sub>2</sub>O<sub>3</sub> cata-

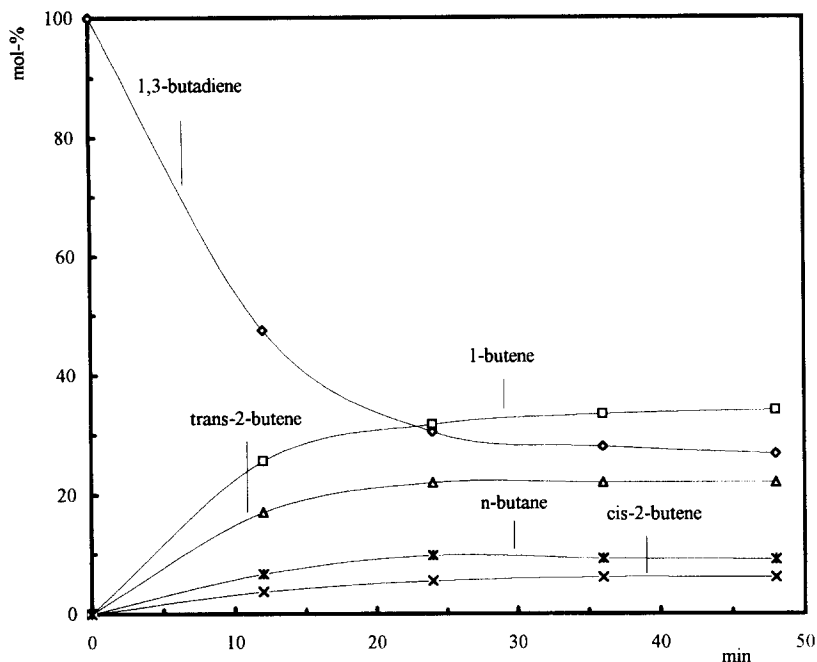


Fig. 6. Gas phase hydrogenation of 1,3-butadiene with 1 wt% Pd7/8(phen) on  $\text{TiO}_2$  as catalyst. The 1,3-butadiene: $\text{H}_2$  ratio is 1.2 in a stream of  $\text{N}_2$ .

lysts [23]. They indicate that hydrogenation of 1,3-butadiene in the gas phase obviously occurs independently of the particle size and the ligand shell, respectively. Change of the supports to  $\text{Al}_2\text{O}_3$  or  $\text{CaCO}_3$  does not influence the results.

$\text{TiO}_2$  effects a slightly higher activity with respect to 1-butene formation. The comparison of the Pd7/8(phen) catalyst with three commercially available Pd catalysts (HO-12 and HO-13 from BASF AG, Ludwigshafen, Lindlar from Degussa,

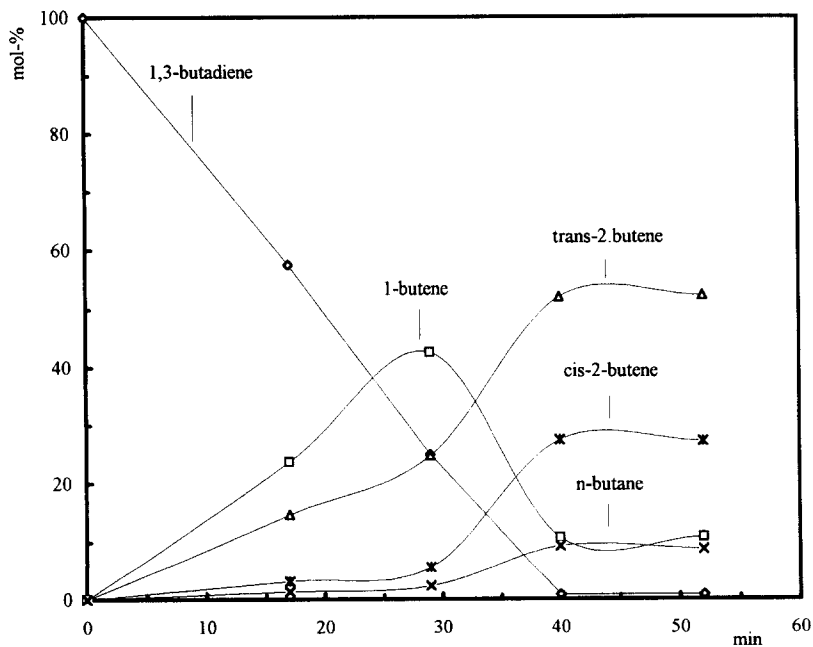


Fig. 7. Gas phase hydrogenation of 1,3-butadiene with 1 wt% Pd7/8(phen) on  $\text{TiO}_2$  and a butadiene: $\text{H}_2$  ratio of  $\approx 0.9$ .

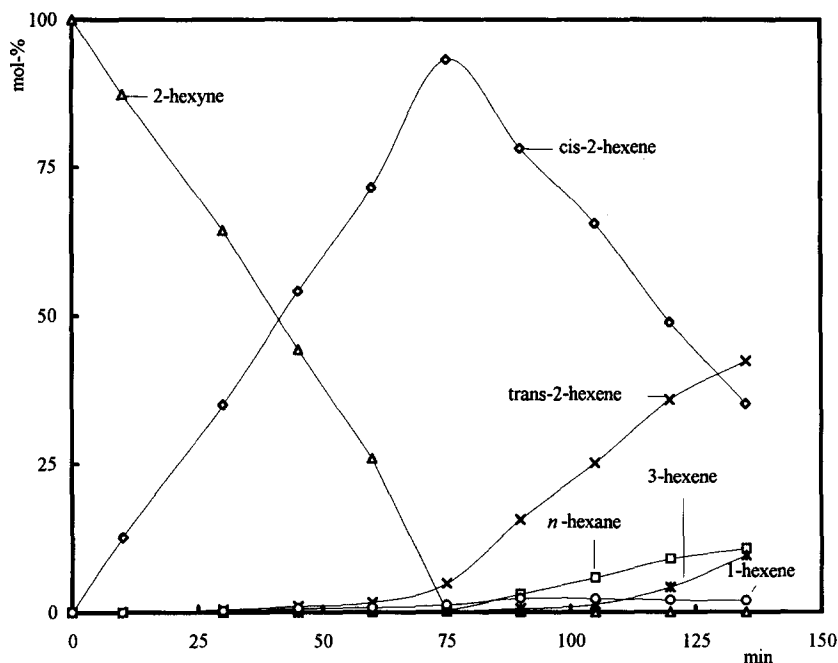


Fig. 8. Hydrogenation of 2-hexyne in n-octane with 1 wt% Pd7/8(phen) on TiO<sub>2</sub> and 1 bar of H<sub>2</sub> pressure.

Hanau) under identical conditions shows that the activity of Pd7/8(phen) on Al<sub>2</sub>O<sub>3</sub> is comparable with the most active commercial ones (HO-12,13), whereas the selectivity of all investigated systems is the same within the experimental error.

## 5. Liquid phase reactions

In the gas phase reactions described above we studied activities and selectivities using only one ligand type, namely 1,10-phenanthroline. In the following the influence of modified ligands enveloping palladium clusters of roughly the same size as in the gas phase studies are described. As will be shown, even minor changes at the ligand molecules can result in dramatic differences of the products, indicating the powerful tool given by the ligand shell of the clusters.

### 5.1. Hydrogenation of 2-hexyne

2-Hexyne can be used to study activity as well as selectivity of a hydrogenation catalyst. Pd7/8(phen) on TiO<sub>2</sub> in n-octane catalyses the semih-

ydrogenation of 2-hexyne to *cis*-2-hexene very selectively. Only after formation of 93% of *cis*-2-hexene are other isomers and n-hexane formed, as can be seen from Fig. 8. The TOF value is about 35 (min<sup>-1</sup>).

Substitution of phenanthroline by n-butyl and n-heptyl groups in 3 position results in a decreased activity with a TOF of only 3 (min<sup>-1</sup>) and a selectivity of 98 and 96%, respectively. However, as is shown in Fig. 9 for Pd7(phen-butyl), only a very small decrease of the *cis*-2-hexene concentration is observed over a period of 300 min. This is a remarkable result indicating that this catalyst exhibits almost no activity with respect to the hydrogenation of *cis*-2-hexene. In some experiments, however, we observed an initiation period before deactivation towards *cis*-2-hexene begins. At present we cannot explain this behavior.

### 5.2. Hydrogenation of unsaturated carbonic acids

Another example proving the decisive role of the ligand shell will be described by the hydrogenation of some unsaturated carbonic acids.



Table 1 summarizes the TOF values for various  $R^1$  and  $R^2$  substituents of two catalysts: Pd7/8(phen) and Pd8(cinchon). It should be stated that we do not know how cinchonidine coordinates on the cluster surface. A model describes the coordination of cinchonidine molecules on a platinum surface via the quinoline moiety [24]. Whatever the type of coordination on Pd8(cinchon) clusters may be, this ligand leads to astonishing results compared with phenanthroline ligated clusters. Table 1 lists the TOF values for the hydrogenation of different acids by Pd7/8(phen) and Pd8(cinchon) catalysts.

Cinchonidine reduces the speed of hydrogenation of cinnamic acid by a factor of ca. 0.33. With  $R^1 = \text{HNCCH}_3$ , the activity is considerably reduced for Pd7/8(phen), however for Pd8(cinchon) it is more or less lost. In the case of  $R^1 = \text{HNCCH}_3$ ,  $R^2 = \text{H}$  the activity for Pd7/8(phen) is comparable with the former example, the TOF for Pd8(cinchon) is now about half of the value.

What can be concluded is that, without having a theoretical explanation, the change from phen ligands to cinchonidine enforces very selective reactions, obviously depending on the pathways the educt and product molecules can follow

Table 1

Comparison of TOF values for the hydrogenation of unsaturated carbonic acids by Pd7/8(phen) and Pd8(cinchon) catalysts

Ligand	$R^1$	$R^2$	TOF ( $\text{h}^{-1}$ )
phen	H	$\text{C}_6\text{H}_5$	536
cinchon	H	$\text{C}_6\text{H}_5$	173
phen	$\text{HNCCH}_3$	$\text{C}_6\text{H}_5$	13.3
cinchon	$\text{HNCCH}_3$	$\text{C}_6\text{H}_5$	0.1
phen	$\text{HNCCH}_3$	H	13.9
cinchon	$\text{HNCCH}_3$	H	5.8

through the ligand shell on the cluster surface. A very last example will underline this statement.

### 5.3. Hydrogenation of acetophenone

Acetophenone can be hydrogenated by established Pd catalysts to phenyl-ethanol. The phenyl group is not attacked. Di-2,9-(2-methyl-butyl)-1,10-phenanthroline, used in Pd8(phen-methyl-butyl) leads to a TOF of  $45.5 (\text{h}^{-1})$ . However, cinchonidine reduces the activity to almost zero. Even the increase of the  $\text{H}_2$  pressure up to 100 bar and the temperature up to  $60^\circ\text{C}$  gives no speeding-up of the reaction. Obviously there is no pathway for acetophenone to the Pd surface atoms if they are covered by cinchonidine.

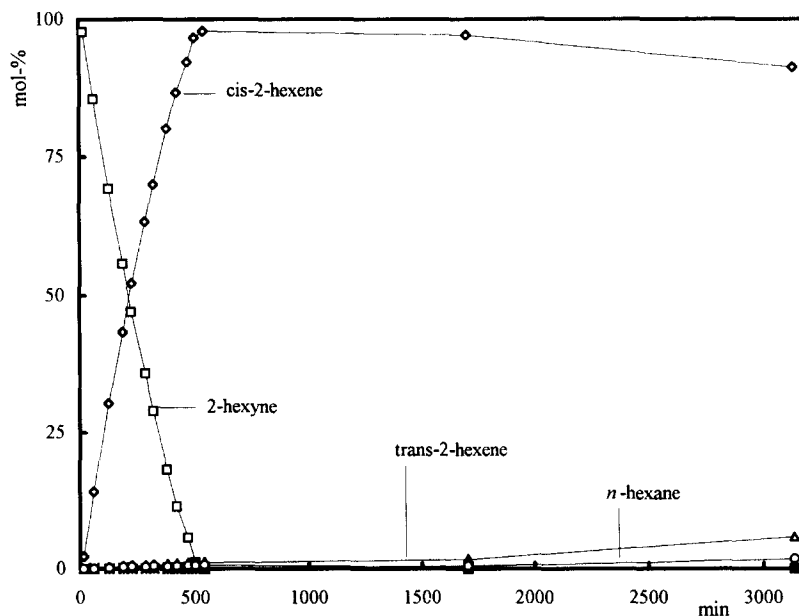


Fig. 9. Hydrogenation of 2-hexyne in ethanol with 1 wt% Pd7(phen-butyl) on active carbon and 1 bar of  $\text{H}_2$  pressure.

Another almost complete loss of catalytic activity has recently been observed by us for hydrogenation reactions with nickel colloids, enveloped by an unusually dense ligand shell of PC<sub>6</sub>H<sub>5</sub> moieties [25].

## 6. Conclusions

Supported ligand stabilized Pd clusters can be used for heterogeneous gas phase or liquid phase catalysis. In gas phase reactions selectivities are reduced compared with liquid phase reactions. In principle the catalytic behavior can be compared with that of established supported palladium catalysts.

Modification of the ligand molecules affects activity and selectivity considerably in liquid phase reactions. This is probably a breakthrough in the application of ligand stabilized clusters in catalysis. Their use in a supported state leads to a decisive stabilization. The possibility to synthesize them before adsorption on the support, to modify the ligand molecules and to study the chemical and the physical properties [26] of the pure compounds are big advantages for practical applications. Now it is necessary to study the special situations on the cluster surfaces by molecular modelling calculations for a better understanding of what we have observed experimentally.

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