

Oxidation of Terminal Olefins by Dioxygen in the Presence of $\text{Pd}^{\text{II}}(\text{NH}_3)_x/\text{Cu}^{\text{II}}/\text{Li}^{\text{I}}/\text{Cl}^-$ or Pd^{II} (or Pd^0)/Zeolites/ $\text{Cu}^{\text{II}}/\text{Li}^{\text{I}}/\text{Cl}^-$ Systems and a Coreducer (Ethanol)

Ourida Mohammedi^a, Farid Chemat^b, and Jean-Marie Brégeault^c

Institut de Chimie Industrielle, Université des Sciences et Techniques de Blida^a,
Boulevard El-Aich, BP 270, Blida, Algeria

Agrotechnological Research Institute, ATO-DLO^b,
Bornsesteeg 59, P. O. Box 17, NL-6700 AA Wageningen, The Netherlands

Département de Chimie, Systèmes Interfaciaux à l'Echelle Nanométrique, CNRS ESA 7069, Université Pierre et Marie Curie^c,
Tour 54, Case 196, 4 Place Jussieu, F-75252 Paris Cedex 05, France

Received March 6, 1998

Keywords: Alkenes / Ketones / O–O activation / Palladium / Zeolites

Simple ammonia complexes $\{cis\text{-}[\text{PdCl}_2(\text{NH}_3)_2], [\text{Pd}(\text{NH}_3)_4]\text{-Cl}_2$ or $[\text{Pd}(\text{NO}_2)_2(\text{NH}_3)_2]\}$ with copper(II) chloride and LiCl or Pd^{II} (or Pd^0) inserted into zeolite (faujasite Y or mordenite Z)/ $\text{Cu}^{\text{II}}/\text{Li}^{\text{I}}/\text{Cl}^-$ precursors in anhydrous ethanol catalyse the oxidation of terminal olefins to methyl ketones by dioxygen. One oxygen atom is incorporated into the olefinic substrate, while the other is involved in a cooxidation process of the solvent leading to the formation of water. With 1-octene and ethanol, octan-2-one can be obtained selectively (up to 99 %), acetaldehyde and diethyl acetal being the main

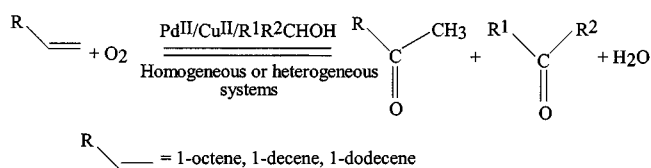
cooxidation products. Chlorohydridopalladium species are key intermediates in the isomerization of 1-alkenes; it appears that the introduction of NH_3 , NO_2^- or zeolite ligands reduces the extent of isomerization and subsequently the formation of isomeric ketones (octan-3-one and octan-4-one). Although homogeneous catalysis cannot be ruled out, the improved selectivities and variations of selectivity and conversion with different zeolites suggest that a "ship-in-a-bottle" catalysis may be important.

Introduction

Several studies have been undertaken with the goal of improving processes similar to the Wacker reaction. Some have been focused on modifying the reactive medium (phase transfer catalysis^[1] or introduction of cyclodextrins^[2] to adjust the reaction), while others have been aimed at immobilizing catalytic components^[3] in order to develop new and more selective routes for the oxidation of higher olefins. So far, no completely satisfactory solution for the catalytic oxidation of terminal olefins has been found.

Within the framework of research on the oxidation of simple or functionalized olefins^[4], we considered it of interest to modify the palladium environment in order to modulate the efficiency of catalytic systems involving a primary or secondary alcohol as cosubstrate. The results are given in Scheme 1.

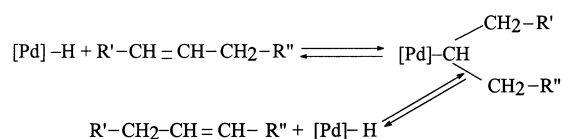
Scheme 1



One of the main problems is the isomerization of olefinic substrates, most probably by chlorohydrido complexes

which lead to alkyl complexes responsible for the formation of the starting olefinic isomers (Scheme 2)^{[5][6]}.

Scheme 2



To avoid this competing process, which is 300 times faster than that desired and responsible for the subsequent formation of isomeric ketones, we decided either to keep the σ -donor ligands within the coordination sphere of palladium or to create an environment which would prevent these transformations, by introducing a macro-anion controlling the palladium center.

The first part of this work analyses the results obtained with amminepalladium complexes: $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$, or $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]$ were combined with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol in the presence of dioxygen for the oxidation of 1-octene. This study was necessary in order to understand what was observed in the following step of our work aimed at developing systems involving macrocyclic ligands and zeolites exchanged with amminepalladium(II) complexes thermally treated under well-defined conditions.

Other catalytic systems involve Pd^{II} or Pd^0 initially imprisoned in various zeolites (faujasite Y or mordenite Z) in

Table 1. Oxidation of 1-octene by the $[\text{Pd}^{\text{II}}(\text{NH}_3)_n]/\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}/\text{LiCl}/\text{O}_2$ systems in ethanol at $60^\circ\text{C}^{[\text{a}]}$

Entry	Precursor	[%] GC	Ketone yield mol/mol Pd	mol/mol O_2	2-one selectivity [%]	1-octene ^[b] [%]
1	1/4/LiCl	50	60	1.2	99	84
2	2/4/LiCl	52	68	0.9	96	52
3	3/4/LiCl	42	50	0.9	97	35
4	$\text{PdCl}_2/4/\text{LiCl}$	70	83	1.0	60	18

^[a] Conditions: $T = 60^\circ\text{C}$; reaction time = 24 h; **1** $[\text{Pd}(\text{NH}_3)_4\text{Cl}_2] = 0.02 \text{ mol} \cdot \text{l}^{-1}$; **2** $[\text{PdCl}_2(\text{NH}_3)_2] = 0.02 \text{ mol} \cdot \text{l}^{-1}$; **3** $[\text{Pd}(\text{NO}_3)_2(\text{NH}_3)_2] = 0.02 \text{ mol} \cdot \text{l}^{-1}$; $[\text{PdCl}_2] = 0.02 \text{ mol} \cdot \text{l}^{-1}$; **4** $[\text{CuCl}_2, 2\text{H}_2\text{O}] = 0.2 \text{ mol} \cdot \text{l}^{-1}$; $[\text{LiCl}] = 0.4 \text{ mol} \cdot \text{l}^{-1}$; solvent: ethanol (2.5 ml); olefin: 1-octene = 9.55 mmol (1.5 ml). – ^[b] % 1-octene in the residual octenes.

EtOH in the presence of $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$. These two catalysts which lead to modifications in activity and selectivity of the oxidation of terminal olefins will be presented below. The reaction test for both systems involves a terminal olefin (usually 1-octene) and a cosubstrate: ethanol was used in both series of experiments, but other primary or secondary alcohols could also be used.

Results and Discussion

Amminepalladium(II) Complexes

The introduction of the NH_3 ligand into the coordination sphere of the palladium complex used as a precursor obviously improved the selectivity for methyl ketone (ca. 97–99%) (entries 1–3, Table 1), with yields around 50%. All conditions being otherwise equal, the classical $\text{PdCl}_2/\text{Cu}^{\text{II}}/\text{Li}^{\text{I}}$ system leads to the formation of isomeric ketones in a yield close to 70% (60% selectivity in favour of methyl ketone), 3-octanone and 4-octanone also being formed.

Although this procedure has not yet been optimized, it appears that the introduction of new precursors of the $[\text{Pd}^{\text{II}}(\text{NH}_3)_{4-n}\text{X}_n]$ type with ammine ligands, provides better a selectivity for methyl ketone and reduces the isomerization (see Table 1). This may be used to advantage in modulating other Pd^{II} -based systems, notably in the Heck reaction.

The ketone/ O_2 molar ratio is always less than 2 (Table 1), which suggests that the mechanism in the presence of EtOH is very different from that of the Wacker process. The reaction yields acetaldehyde, ethyl acetate, diethyl acetal in a fashion similar to that observed with the Pd or Rh/Bi^[4], Pd/Cu^[7a], and Pd/Bi^[7b] systems under the same conditions. The cooxidation process is shown in Scheme 3.

Our results, and particularly those for the tetraammine/ $\text{Cu}^{\text{II}}/\text{Li}^{\text{I}}$ palladium system (entry 1, Table 1) are very similar

to published data^{[1][2]} on the use of phase transfer catalysis or β -cyclodextrin (β -CDS) to improve the selectivity. However, the ammine complexes give a turnover three to four times higher (Table 2).

This analysis involving ammine precursors was also necessary to understand the results of the following step. For this part we used $[\text{Pd}(\text{NH}_3)_4]^{2+}$ cationic complexes to insert palladium(II) into zeolites in order to develop new catalytic systems.

At this point, we decided to see if it was possible to modify the selectivity in the oxidation of terminal olefins employing zeolites comparable to those used for hydrogenation^[8].

Study of Pd^{II} or Pd^0 /Zeolites/ $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}/\text{O}_2/\text{EtOH}$

Two zeolites were used: mordenite Z which has a one-dimensional tubular structure^[9], and faujasite Y whose very open structure is associated with a large porous volume^[10].

The introduction of palladium(II) (around 5%) into the zeolite was carried out by exchange with tetraammine palladium(II) dichloride, and in certain samples by the palladium complex $[\text{Pd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ (see Experimental Section). Three types of samples were synthesized using different treatments for the preparation of the catalytic systems:

- Pd^{II} -amine/zeolite or $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ /zeolite
- Pd^{II} without an ammine/zeolite ligand
- Pd^0 without an ammine/zeolite ligand.

These different precursors, which define the Pd^{II} (or Pd^0)/zeolite/ $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}/\text{LiCl}/\text{EtOH}/\text{O}_2$ catalytic systems, were tested with 1-octene.

With the first samples (i), it was not possible to differentiate systems involving mordenite Z from those involving faujasite Y, as yields and especially selectivities were similar (entries 5–8, Table 3); these results are certainly related to

Scheme 3

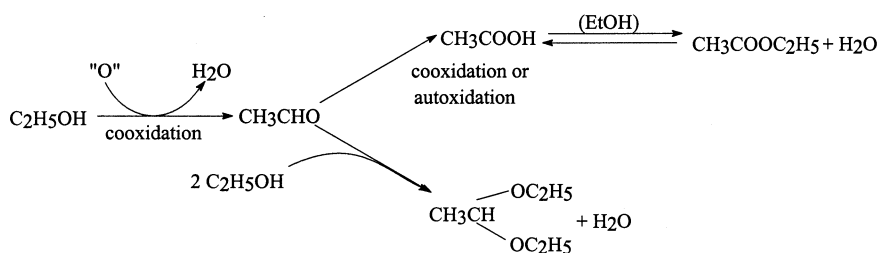


Table 2. Comparison of the $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2/\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}/\text{LiCl}$ precursor and recently described systems^{[1][2]} for the oxidation of terminal olefins by dioxygen

Entry	T [°C] t [h]	Precursor	Olefin	Oxidation products	Yield [%]	mol/mol Pd	mol/mol O_2
a	60°C 24 h	1/4 /LiCl	1-decene 1-dodecene	2-decanone 2-dodecanone	62 58	61 49	1.4 1.0
b	80°C 48 h	PdCl_2 / 4	1-decene 1-dodecene	2-decanone 2-dodecanone	73 62	18 15	? ?
c	65°C 24 + 48 h	PdCl_2 / 4	1-decene 1-dodecene	2-decanone 2-dodecanone	61 11	15 1.4	? ?

a: (this work) **1** $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 = 0.02 \text{ mol} \cdot \text{l}^{-1}$; **4** $[\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}] = 0.2 \text{ mol} \cdot \text{l}^{-1}$; $[\text{LiCl}] = 0.04 \text{ mol} \cdot \text{l}^{-1}$; solvent: ethanol (2.5 ml); olefin (1.5 ml). – b: (ref.^[1]) $[\text{PdCl}_2] = 0.034 \text{ mol} \cdot \text{l}^{-1}$; **4** $[\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}] = 0.34 \text{ mol} \cdot \text{l}^{-1}$; water 10 ml; solvent: benzene 1.5 ml; olefin 25 mmol; cetyltrimethylammonium bromide (CTAB) = 2 mmol. – c: (ref.^[2]) $[\text{PdCl}_2] = 0.04 \text{ mol} \cdot \text{l}^{-1}$; **4** $[\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}] = 0.4 \text{ mol} \cdot \text{l}^{-1}$; water 10 ml; hydrated β -cyclodextrin 0.4 g; olefin 12.5 mmol.

Table 3. Oxidation of 1-octene by the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ or $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}/\text{zeolite}/\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}/\text{LiCl}/\text{O}_2$ systems in ethanol^[a]

Entry	Precursor	[%] GC	Ketone yield mol/mol Pd	mol/mol O_2	2-one selectivity [%]	1-octene ^[b] [%]
5	$\text{Pd}^{\text{II}}\text{HZ}/\mathbf{4}/\text{LiCl}$	41	49	1	98	25
6	$\text{Pd}^{\text{II}}\text{NaZ}/\mathbf{4}/\text{LiCl}$	50	60	1.2	99	27
7	$\text{Pd}^{\text{II}}\text{LZY82}/\mathbf{4}/\text{LiCl}$	58	69	1.2	99	39
8	$\text{Pd}^{\text{II}}\text{LZY82}/\mathbf{4}/\text{LiCl}$	43	52	1.2	98.5	37
9*	$\text{Pd}^{\text{II}}\text{HZ}/\mathbf{4}/\text{LiCl}$	44	53	0.9	94	43
10*	$\text{Pd}^{\text{II}}\text{LZY82}/\mathbf{4}/\text{LiCl}$	51	61	0.97	57	7

^[a] Conditions: $T = 60^\circ\text{C}$; reaction time = 24 h; $[\text{Pd}^{\text{II}}] \approx 0.02 \text{ mol} \cdot \text{l}^{-1}$; **4** $[\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}] \approx 0.2 \text{ mol} \cdot \text{l}^{-1}$; $[\text{LiCl}] \approx 0.04 \text{ mol} \cdot \text{l}^{-1}$; 1-octene = 4.77 mmol (0.75 ml); solvent: ethanol (1.25 ml); impregnation solution: $[\text{Pd}(\text{NH}_3)_4]^{2+}(\text{OH}^-)_2$. – * Zeolite exchanged with the $[\text{Pd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ complex. – ^[b] % 1-octene in the residual octenes.

the NH_3 ligand effect (see Table 1 and below). We nevertheless noted that it was more difficult to limit the isomerization of olefins.

However, the results obtained with the zeolites exchanged with the $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}(\text{NO}_3^-)_2$ complex, show that the two types of zeolite behave differently (entries 9 and 10, Table 3). *The selectivity for 2-octanone obtained with the HZ zeolite (mordenite) is much higher than that for faujasite.*

Let us now look at the use of precursors involving Pd^{II} with an ammine/zeolite ligand (ii) obtained by a dynamic linear increase in temperature under oxygen (see Experimental Section). Following thermal treatment, most of the palladium remained entrapped in the zeolite, mainly in the form of “ $\text{Pd}(\text{O})_3(\text{H}_2\text{O})$ ” species, but in the case of the exchanged faujasite Y, there was also $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ after the same thermal treatment in the presence of dioxygen^[11].

The activity and selectivity of the system depend on the nature of the zeolite with all other conditions being equal (entries 11, 12, and 15, Table 4). With the HZ zeolite, the conversion to ketones was low (34%) with very good selectivity (ca. 98%) (entry 11, Table 4). In the presence of faujasite, results were comparable to those of entries 9 and 10 in that yields were much higher (61–69%) than those obtained in the presence of mordenite, but the selectivity was not as good (only ca. 76% for methyl ketone, entry 12) which could be related to the coexistence of two palladium(II) species, “ $\text{Pd}(\text{O})_3(\text{H}_2\text{O})$ ” and $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$. The

study of these multiparameter systems is complex, among other things, the selectivity also depends on the pH of impregnation (compare entries 12 and 13), with all other conditions being otherwise the same (an experimental fact that we are unable to interpret).

After standard treatment involving reduction in hydrogen carried out by a very slow linear increase in temperature ($13^\circ\text{C}/\text{h}$) to $300\text{--}350^\circ\text{C}$, it appears that with precursors involving reduced palladium dispersed in the zeolite support (iii), activity and selectivity also depend on the support (entries 16 and 20, Table 5), on the pH of the impregnation solution (entries 20 and 21) as well as on the initial distribution of the particles in the sample (HZ, entries 16 and 18). In the case of entry 18, the calcination preceding the reduction was taken to 600°C with an increase in temperature ($22^\circ\text{C}/\text{h}$) which led to a poorer dispersion of palladium (see Experimental Section).

From this study we found also that the two systems involving different zeolites, one with faujasite Y and the other with mordenite Z, behaved in two distinct ways during the oxidation of 1-octene.

Chemical analysis at the end of the reaction gave the same palladium content (0.3%) and similar ratios of copper(II) and Cl^- in solutions from catalytic systems with mordenite Z or faujasite LZY82, whether the catalysts were used before or after reduction by dihydrogen. Catalysis can only be carried out in solution and a part of the pal-

Table 4. Oxidation of 1-octene by the Pd^{II}-zeolite/CuCl₂·2 H₂O/LiCl/O₂ system in ethanol (calcination 300–350°C)^[a]

Entry	Precursor	[%] GC	Ketone yield mol/mol Pd	mol/mol O ₂	2-one selectivity [%]	1-octene [%] ^[e]
11 ^[b]	Pd ^{II} HZ/4/LiCl	34	40	1	98	69
12 ^[b]	Pd ^{II} LZY82/4/LiCl	69	82	1.1	76	12
13 ^[c]	Pd ^{II} LZY82/4/LiCl	61	73	0.9	95	27
14 ^[d]	Pd ^{II} HZ/4/LiCl	25	29	0.9	98	68
15 ^[b]	Pd ^{II} NaZ/4/LiCl	13	16	1.0	98	86

^[a] Conditions: $T = 60^\circ\text{C}$; reaction time = 24 h; $[\text{Pd}^{\text{II}}] \approx 0.02 \text{ mol}\cdot\text{l}^{-1}$; $4 [\text{CuCl}_2\cdot 2 \text{H}_2\text{O}] = 0.2 \text{ mol}\cdot\text{l}^{-1}$; $[\text{LiCl}] = 0.04 \text{ mol}\cdot\text{l}^{-1}$; 1-octene = 4.77 mmol (0.75 ml); solvent: ethanol (1.25 ml). – ^[b] Very basic impregnation solution (pH = 11.8). – ^[c] Impregnation solution (pH = 7.5), $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ precursor. – ^[d] HZ exchanged with the $[\text{Pd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ complex. – ^[e] % 1-octene in the residual octenes.

Table 5. Oxidation of 1-octene by the Pd⁰-zeolite/CuCl₂·2 H₂O/LiCl/O₂ system (reduction 300–350°C)^[a]

Entry	Precursor	% GC	Ketone yield mol/mol Pd	mol/mol O ₂	2-one selectivity [%]	1-octene [%] ^[e]
16 ^[b]	Pd ⁰ HZ/4/LiCl	44	52	1.4	98	68
17 ^[b,d]	Pd ⁰ HZ/4/LiCl	50.5	60	1.7	98	83
18 ^{[b]*}	Pd ⁰ HZ/4/LiCl	52	62	0.9	84	22
19 ^[b]	Pd ⁰ LZY52/4/LiCl	72	86	1.1	62	24
20 ^[b]	Pd ⁰ LZY82/4/LiCl	68	81	0.9	52	15
21 ^[c]	Pd ⁰ LZY82/4/LiCl	91	108	1.4	71	26

^[a] Conditions: $T = 60^\circ\text{C}$; reaction time = 24 h; $[\text{Pd}^{\text{II}}] \approx 0.02 \text{ mol}\cdot\text{l}^{-1}$; $4 [\text{CuCl}_2\cdot 2 \text{H}_2\text{O}] = 0.2 \text{ mol}\cdot\text{l}^{-1}$; $[\text{LiCl}] = 0.04 \text{ mol}\cdot\text{l}^{-1}$; 1-octene = 4.77 mmol (0.75 ml); solvent: anhydrous ethanol (1.25 ml). – ^[b] Very basic exchange solution (pH = 11.8) – ^[c] pH = 7.5 $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ precursor. – ^[d] $[\text{Pd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ precursor. – ^[e] % 1-octene in the residual octenes. – *Calcination at 600°C with an increase of $22^\circ\text{C}/\text{h}$.

ladium(0) is reoxidized by CuCl₂/O₂ in the presence of ethanol. *These analyses show the role of the HZ zeolite structure in the induction of selectivity in contrast to zeolite LZ.*

Nevertheless, taking our observations as a whole, it is difficult to establish the respective roles of cavity size or that of the acid-base properties of the zeolite structure, since the two zeolite supports differ in their SiO₂/Al₂O₃ ratios. Work is now in progress to determine the roles played by the electric field created in the zeolite cavities and the porous supports considered as macrocyclic ligand.

Conclusion

The oxidation reaction of terminal olefins by dioxygen can be achieved under very mild conditions with conversion close to 50–60% without optimization. Modification of the coordination sphere of palladium by introducing the NH₃ ligand leads to very good selectivity in methyl ketone (98–99%) in ethanol, a solvent which usually facilitates isomerization of the olefin and formation of isomeric ketones in the presence of chloro complexes of palladium(II).

We have obtained, with the $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ precursors, a methyl ketone/Pd^{II} ratio higher than for more sophisticated systems involving phase transfer catalysis or β -cyclodextrins^{[1][2]}. It is noteworthy that olefin isomerization is very limited. From these results, we can propose other modifications leading to more efficient processes.

By employing different zeolites (mordenite Z, faujasite Y) in the catalytic system in an ethanol medium in the presence of CuCl₂·2 H₂O, we have shown that it is possible to

modify the activity and selectivity of the oxidation of terminal olefins. Our results show the difference between two types of zeolites and the importance of further research to exploit *the macrocyclic ligand effect which can modulate the equilibrium between the active species and the σ -donor ligands in solution*. In all these systems ethanol serves as co-substrate; overall one atom of dioxygen is used for the oxidation of the olefinic substrate, while the other oxidizes the solvent which plays the role of the “sacrificial substrate”. This mechanism is comparable to that proposed for the Rh^{III}/Bi^{III}/Li^I/Cl[−]/R¹R²CHOH/O₂ or Pd^{II}/Bi^{III}/Li^I/Cl[−]/R¹R²CHOH/O₂ systems with the hydroperoxo [Rh]-OOH or [Pd]-OOH complex^{[4][5]}.

The authors are grateful to Dr. P. Baumier and Professor G. Djega-Mariadassou for electron microscopy analyses, as well as to Professor M. Delamar for photoelectron spectrometry analyses.

Experimental Section

Reagents: Precursors: PdCl₂, CuCl₂·2 H₂O, LiCl, olefins and anhydrous ethanol were commercial products. The following complexes were prepared by reported procedures: $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]$, $[\text{Pd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$.

Characteristics of Zeolites: Two commercial samples (Grande Paroisse) of mordenite Z, a quasi-one-dimensional structure, were examined.

– The NaZ sodium form, “small pore” species (SiO₂/Al₂O₃ ratio = 5.7:6.75)

– The HZ acid form, “large pore” species (SiO₂/Al₂O₃ ratio = 8)

– The HZ zeolite used in our experiments was obtained by controlled thermal decomposition of the NH_4Z ammonium form (calcination with oxidation in the presence of dioxygen). This is a two-step method: preparation of the NH_4Z form from the NaZ form by exchange, then calcination from NH_4Z to HZ (500–600°C). This decomposition is accompanied by aluminum extraction of the zeolite structure ($\text{Al}_{\text{IV}} \rightarrow \text{Al}_{\text{VI}}$) and deblocks the pores: adsorption of benzene goes from 1% (NaZ form) to around 6% (HZ form).

Faujasite Y has a very open structure associated with a very large volume; two Y zeolites were used:

– The LZY82 zeolite (Union Carbide) ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 5.6–6.5)

– The LZY52 zeolite (Linde) ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 4.75).

Preparation of Zeolite Samples. – Exchange of the Zeolite (Mordenite or Faujasite): The conventional method for introducing palladium(II) into zeolites was used^[12]. For all samples, about 5% (w/w) of the palladium complex was added. A solution (pH = 11.8) of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ was passed three times through an Amberlite anion exchanger; the absence of Cl^- ions from the resulting solution was checked by silver nitrate. The Cl^- ions are exchanged by OH^- giving $[\text{Pd}(\text{NH}_3)_4]^{2+}(\text{OH}^-)_2$ dissolved in water. Following the third exchange, the base was added dropwise onto the zeolite suspended in water and maintained for 20 h at ambient temperature with slight stirring. After filtration, the product was carefully washed with distilled water and dried for 12 h at 110°C.

The catalysts prepared by ion exchange from the $[\text{Pd}(\text{NH}_3)_4](\text{OH})_2$ complex contain a large amount of ammonia which must be eliminated under conditions that avoid palladium(II) ion reduction which would result in the migration and clustering of the metallic atoms thus formed.

Thermal Treatment in Dioxygen: Following the work of Bergeret et al.^[13], we adopted a calcination procedure in which the temperature was very slowly increased (13°C/h) with a continuous flow of dioxygen (ca. 5 l/h) through the zeolite (ca. 1 g), spread on a thin layer of a glass frit in a vertical tubular reactor of transparent silica. The final calcination temperature (300–350°C) was maintained for 15 h.

Thermal Treatment in Dihydrogen: Fast reduction was carried out by placing around 1 g per sample, already treated with dioxygen, on a thin layer of a glass frit in the same double-walled reactor after purging the tube under hydrogen (ca. 5 l/h); the precursor was reheated (13°C/h) to 300–450°C; this temperature was maintained for 15 h making it possible to obtain similar samples for the products treated under comparable conditions.

Characterization of Pd^{II} /Zeolite Samples by UV/Vis Spectrometry: The coordination of Pd^{2+} ions was followed by UV/Vis spectrometry in diffuse reflexion with a Beckmann 5270 spectrometer equipped with a double monochromator. Barium sulfate was used as reference.

A UV/Vis spectroscopic study of the exchanged zeolite, non-calcined (dried at 110°C for 20 h), showed that the tetraammine complex was introduced into the zeolite without any modification. This is shown by the absorption at 1540 nm characteristic of the $\text{Pd}-\text{NH}_3$ system^[11].

Following thermal treatment in the presence of dioxygen, the catalyst took on an orange-rose colour which, upon contact with air, progressively changed to rose-beige due to absorbed water. This colour change probably indicates the formation of two species. One could be the tetrahedral “ $\text{Pd}(\text{O})_3(\text{H}_2\text{O})$ ” with C_{3v} symmetry of the $\text{Pd}(\text{O})_3$ group^[11]. The other, the planar species $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$, which

could correspond to the appearance of the maximum around 375 nm, was only observed with the LZY82 zeolite (vide supra).

Characterization of Pd^0 /Zeolite Samples by Electron Microscopy: The exchanged zeolite samples, calcined and reduced, were examined by electron microscopy at high resolution using a J.E.M. 120 apparatus (JEOL) allowing the palladium particles on the zeolite support to be observed by transmission.

The histograms of the calcined and reduced samples using a linear increase in temperature (13°C/h) to 300–450°C showed a relatively homogeneous particle size distribution (ca. 20–30 Å). On the other hand, all the Pd^0/HZ samples resulting from calcination at 600°C with a slightly higher temperature gradient (22°C/h), then reduction at 13°C/h to 350°C had a heterogeneous particle dispersion. The majority of particles showed a diameter close to 30 Å; however, a few very large clusters were observed in the 10^3 – 10^4 Å range, proving that partial coalescence occurred with certain particles.

Analysis of Pd /Zeolite Samples by X-ray Photoelectron Spectroscopy: Palladium is characterized by the $3d_{3/2}$ and $3d_{5/2}$ peaks, which correspond to the 3d electron emission having a J spin-orbit coupling of either 3/2 or 5/2 ($J = L + S$ with $L = 2$). The kinetic energy of this electron can be obtained from the spectra and the energy of the bond is calculated by using, as internal reference, the C_{1s} line of carbon whose bond energy is 285 eV.

$$E_1(\text{Pd } 3d_{3/2} \text{ or } 5/2) = 285 + E_c(\text{C}_{1s}) - E_c(\text{Pd } 3d_{3/2} \text{ or } 5/2)$$

To estimate the palladium, a sensitivity factor of 10 was used for the $3d_{5/2}$ line with respect to C_{1s} . This value was taken from literature data. For the spectrometer used, a correction factor had to be determined from a defined compound. The Pd/Si ratios measured by X-ray Photoelectron Spectroscopy or by chemical analysis were very similar for the two types of zeolites. Moreover, XPS allowed the characterization of the nitrogen remaining after thermal treatment. The bond energies for N_{1s} (401.5–403 eV) showed that it was not NH_3 but perhaps a form of oxidized nitrogen^[14]. These species cannot be held responsible for the difference in the selectivity found at different stages of thermal treatment for both zeolites.

Catalyst Tests: In a routine experiment, the palladium-based precursor was introduced into a Schlenk tube at a concentration equivalent to $0.02 \text{ mol} \cdot \text{l}^{-1}$ if all the palladium were in solution with the cocatalysts, followed by addition of the solvent (absolute ethanol) and the olefin. After cold degassing, dioxygen was introduced at atmospheric pressure and the reaction tube was plunged into a thermostated bath. Adsorption of oxygen was measured during the reaction time (from 1 to 24 h). The systems were analysed by gas chromatography.

At the end of the reaction, an internal reference (*ortho*-dichlorobenzene, for example) was added to estimate the ketones formed.

Gas Chromatography and Tandem Gas Chromatography–Mass Spectrometry (GC-MS)

Gas Chromatography: The reaction mixtures were analysed by chromatography: column length 3 m, diameter 2.16 mm of Chromosorb WAW-DMCS treated by FFAP (10 or 20%); injected volume: 0.3 µl. Analytical conditions: chromatography with flame ionization detector: Girdel model 330; Delsi Enica 10 integrator; vector gas: N_2 ($40 \text{ ml} \cdot \text{min}^{-1}$); hydrogen ($20 \text{ ml} \cdot \text{min}^{-1}$); air ($300 \text{ ml} \cdot \text{min}^{-1}$). Column temperature: 65 or 100°C; injector temperature: 180°C; detector temperature: 190°C.

Capillary Columns: Capillary columns allow more efficient separations with similar compounds such as olefin isomers. Analyses were carried out with a silica capillary column (length: 50 m; diam-

eter 0.25 mm; OV 1701). The operating conditions were as follows: Girdel 30 gas chromatography equipped with a flame ionization detector; Delsi Enica 10 integrator; helium vector gas: 40 ml·min⁻¹; hydrogen: 20 ml·min⁻¹; air: 300 ml·min⁻¹; initial column temperature: 40°C followed by a linear temperature program (5°C/min, to a final 150°C); injector: 140°C; detector: 200°C.

GC-MS: The mass spectral data were obtained at 70 eV using a Kratos MS 50 mass spectrometer coupled with a DS 55 data system and a GC apparatus (Philips-Pye Unicam 104).

- [1] K. Januszkiewicz, H. Alper, *Tetrahedron Lett.* **1983**, 24, 5159–5162.
- [2] H. A. Zahalka, K. Januszkiewicz, H. Alper, *J. Mol. Catal.* **1986**, 35, 249–253.
- [3] [3a] K. Fujimoto, Y. Negami, T. Takahashi, T. Kunigi, *Ind. Eng. Chem., Prod. Res. Develop.* **1972**, 11, 303–308. — [3b] K. Fujimoto, O. Kuchi-Ishi, T. Kunigi, *Ind. Eng. Chem., Prod. Res. Develop.* **1976**, 15, 259–264. — [3c] K. Fujimoto, H. Takeda, T. Kunigi, *Ind. Eng. Chem., Prod. Res. Develop.* **1974**, 13, 237–242.
- [4] [4a] M. Faraj, J. Martin, C. Martin, J.-M. Brégeault, J. Mercier, *J. Mol. Catal.* **1985**, 31, 57–71. — [4b] C. Martin, M. Faraj, J. Martin, J.-M. Brégeault, J. Mercier, J. Fillaux, P. Dizabo, *J. Mol. Catal.* **1986**, 37, 201–212. — [4c] B. El Ali, J.-M. Brégeault, J. Martin, *J. Organomet. Chem.* **1987**, 327, C9–C14. — [4d] F. Dardar, J. Martin, C. Martin, J.-M. Brégeault, J. Mercier, *J. Organomet. Chem.* **1988**, 338, C21–C26.
- [5] J.-M. Brégeault, *Catalyse Homogène par les Complexes des Métaux de Transition*, Masson, Paris, **1992**.
- [6] M. L. Kirova, D. B. Dhal, W. G. Lloyd, *J. Mol. Catal.* **1994**, 88, 301–310.
- [7] [7a] K. Takehira, T. Hayakawa, H. Orita, M. Shimizu, *J. Mol. Catal.* **1989**, 53, 15–21. — [7b] J.-M. Brégeault, M. Faraj, J. Martin, C. Martin, *New J. Chem.* **1987**, 11, 337–343.
- [8] C. A. Tolman, *Chem. Rev.* **1977**, 77, 313–348.
- [9] F. Raatz, Thesis, Univ. Pierre et Marie Curie, Paris, France, **1982**.
- [10] [10a] P. Gallezot, *Catal. Sci. Technol.* **1984**, 5, 221–273. — [10b] G. Spector, Thesis, Univ. Pierre et Marie Curie, Paris, France, **1984**.
- [11] E. Garbowski, M. Vital, M. Mathieu, *J. Chim. Phys.* **1975**, 72, 1249–1252.
- [12] F. Ribeiro, C. Marcilly, *Rev. Inst. Fr. Pétrole* **1979**, 34, 405–428.
- [13] G. Bergeret, P. Gallezot, B. Imelik, *J. Phys. Chem.* **1981**, 84, 411–416.
- [14] R. Nordberg, R. G. Albridge, T. Bergmark, V. Ericson, J. Hedman, C. Nordling, K. Siegbahn, B. J. Lindberg, *Ark. Kemi.* **1967**, 28, 257–278 (*Chem. Abstr.* **1968**, 68, 82717e)
- [98134]