

Letter

Palladium catalyzed hydroxycarbonylation of olefins in biphasic system: beneficial effect of alkali metal salt and protective-colloid agents on the stability of the catalytic system

Franck Bertoux^a, Eric Monflier^{b,*}, Yves Castanet^a, André Mortreux^a

^a *Laboratoire de Catalyse Homogène et Hétérogène associé au CNRS, B.P. 108, 59659 Villeneuve d'Ascq, France*

^b *Université d'Artois, Faculté des Sciences J. Perrin, Laboratoire de Physico-Chimie des Interfaces et Applications, Rue Jean Souvraz, SP 18-62307 Lens cedex, France*

Received 26 May 1998; accepted 28 September 1998

Abstract

The addition of an alkali metal halide or a protective-colloid agent like polyvinylalcohol to water-soluble hydroxycarbonylation catalyst derived from PdCl₂ and the sulfonated phosphine TPPTS prevents the catalyst decay and allows to maintain high activities. The role of these additives is discussed in relation with the reaction mechanism. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxycarbonylation; Olefin; Two-phase system; Palladium; Alkali metal halides; Colloids

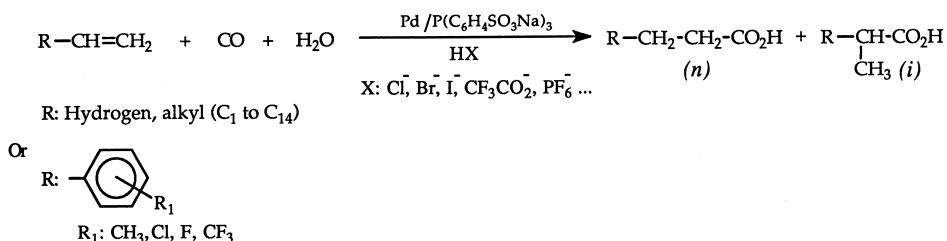
1. Introduction

The one step synthesis of carboxylic acids from alkenes, carbon monoxide and water appears as an economically and environmentally attractive process [1,2]. This reaction, called hydroxycarbonylation, is catalyzed by various transition metals such as nickel, cobalt, ruthenium, rhodium, platine or palladium. Among the catalysts mentioned, palladium is the catalyst of choice because the reaction occurs at low temperatures and pressures [3–7]. For instance,

the hydroxycarbonylation of 1-octene can be achieved at room temperature and atmospheric pressure with a mixture of PdCl₂, CuCl₂ and HCl [6,7]. However, although the chemo-, regio-, and atomselectivity are high and the reaction conditions are mild, no industrial application with palladium catalysts has been reported. This is mainly due to a tedious workup of the reaction crude and to the difficult separation of the homogeneous catalyst from products.

In this context, we have recently described a new catalytic system to carry out the hydroxycarbonylation of olefins in an aqueous–organic two-phase system [8–11]. This system consists of a water soluble palladium complex of trisulfonated triphenylphosphine as catalyst and a

* Corresponding author. Fax: +33-3-2179-1717; E-mail: monflier@univ-artois.fr



Scheme 1. Palladium catalyzed hydroxycarbonylation of olefins into carboxylic acids.

Bronsted acid as promoter dissolved in an aqueous solution. It allows to achieve in high yields and selectivities the hydroxycarbonylation of a wide range of substrates such as straight α -olefins [8,9] and styrene derivatives [10] (Scheme 1).

In the case of higher α -olefins, the presence of mass transfer promoters is nevertheless necessary due to their low water solubilities [11]. In the present paper, we wish to report that the addition of an alkali metal halide or a protective-colloid agent like polyvinylalcohol to the catalytic phase prevents the catalyst decay at high temperature ($> 100^\circ\text{C}$) and allows to maintain high activities.

2. Experimental

2.1. Materials and apparatus

Palladium chloride, alkali metal halides and polyvinylalcohol were purchased from Strem Chemicals, Aldrich Chemical and Acros Organics in their highest purity and used without further purification. Trisodium tris(*m*-sulfonylphenyl)phosphine (TPPTS) was synthesized as reported by Gärtner et al. [12]. The purity of TPPTS was carefully controlled. In particular, ^{31}P NMR indicated that the product was a mixture of TPPTS (ca. 98%) and its oxide (ca. 2%). Carbon monoxide and propene were used directly from cylinders ($> 99.9\%$ pure; Air Liquide). Distilled deionized water was used in all the experiments. All catalytic reactions were

performed under nitrogen using standard Schlenk techniques. All solvents and liquid reagents were degassed by bubbling nitrogen for 15 min before each use or by two freeze–pump–thaw cycles before use.

All the hydroxycarbonylation experiments were carried out in a 100 ml stainless steel autoclave. The autoclave supplied by Autoclave Engineer was equipped with arrangements for automatic temperature control, pressure regulation, and variable stirred speed. A safety rupture disk was also fitted to the reactor. Gas liquid chromatography analyses were carried out on a Chrompack 9001 apparatus equipped with a CP Sil 5-CB column (25 m \times 0.32 mm).

The transmission electron microscopy (TEM) observations were performed on an analytical microscope (Philips CM 30) at 300 kV. For the observations, the palladium colloidal suspension was deposited on a copper grid covered with a thin carbon film.

Voltammetry experiments were performed on a POL 150 Radiometer Copenhagen device. The working electrode was a rotating disk platinum electrode (1 mm²). The counter electrode was a platinum wire and the SCE reference electrode was separated from the electrolyte by a glass frit. All experiments were carried out under nitrogen atmosphere by using an acetic acid buffer.

2.2. Preparation of colloidal palladium dispersion

The colloidal palladium dispersion was prepared from a modified literature method [13–

15]. 1.1 g of polyvinylalcohol (M_w : 15 000–25 000; DP: 500; Aldrich) and 0.0438 g (0.25 mmol) of palladium chloride were dissolved in a methanol (190 ml) and water (190 ml) mixture. Refluxing the resulting solution under nitrogen for 4 h gave a homogeneous solution of colloidal palladium which was characterized by TEM experiments. The volume of the above colloidal solution was then reduced to 35 ml and used in catalysis as it is. Voltammetry experiments indicate that the amount of palladium(II) in the colloidal solution is inferior to 0.5%.

2.3. Catalytic runs

In a typical experiment, PdCl₂ 0.0438 g (0.25 mmol), TPPTS 0.85 g (1.5 mmol) and HCl (about 1 mmol; pH: 1.8) were dissolved in 35 ml of water. The resulting aqueous solution and an organic phase composed of toluene (35 ml) and cumene (1.2 mmol—GC internal standard) were charged under N₂ into a 100 ml stainless steel autoclave. Propene (100 mmol) was introduced by using a flow meter/totalizer (Aalborg instrument). The autoclave was then heated at 100°C and pressurized with 40 atm of CO. The pressure was kept constant throughout the whole reaction by using a gas reservoir along with a pressure regulator. The reaction was monitored by quantitative gas chromatographic analysis.

3. Results and discussion

In order to avoid mass transfer limitation and isomeric by-products, the effect of alkali metal halides or a protective-colloid agent like polyvinylalcohol on the stability of the catalytic system has been studied with propene as substrate (Table 1).

At 100°C, no decrease in activity occurred during the first hour and the catalytic system can then be recovered at least five times without significant loss of activity (entry 1) [8,11]. At

higher temperature, i.e., 120°C, the deactivation of the catalyst obviously occurred. Indeed, a total loss of catalytic activity and the formation of large amounts of black precipitates are observed after 1 h of reaction (entry 5). At this temperature, all attempts to recycle the aqueous layer were unsuccessful.

Surprisingly, the addition of lithium chloride to the aqueous catalytic solution allows to preserve the catalytic activity at 120°C. Indeed, the initial activity and the TOF(1) reached 500 h⁻¹ and 290 h⁻¹, respectively, against 460 h⁻¹ and 0 h⁻¹ without salt (entries 5 and 6). Moreover, the precipitation of palladium black and the colour change of the aqueous solution (yellow to dark-brown) have not been observed in this experiment. The lithium chloride molar ratio has also a significant influence on the reaction rate as shown in Fig. 1.

The maximum activity was obtained for a lithium chloride/palladium molar ratio of 10–20; deviations from these values led to decreased activities. As addition of a water soluble salt to an aqueous solution increases solution ionic strength and diminishes the solubility of propene in water, a drop in the activity is then expected when a salt is added to the aqueous catalytic solution. Fig. 1 shows that this effect is only observed at high molar ratio (> 20) and emphasizes once again the peculiar role played by lithium chloride which increases the activity at low ratio (< 20). The beneficial effect of lithium chloride on the activity and the catalyst stability led us to test other alkali metal halides at a salt to palladium molar ratio of 20. The results are presented in Fig. 2.

In all cases, the catalytic activities after 1 h of reaction were higher than those obtained without salt addition. However, it must be pointed out that some differences between the halides and the alkali metal emerged from the data presented in Fig. 2. So, whatever the alkali metal, the initial catalytic activity decreases with the coordinating ability of the anion, i.e., Cl⁻ > Br⁻ > I⁻. The loss of catalytic activity during the first hour of reaction is less marked with

Table 1
Biphasic hydroxycarbonylation of propene in the presence of various catalytic systems^a

Run	Catalytic system	Temperature (°C)	TOF(0) (h ⁻¹) ^b	TOF(1) (h ⁻¹) ^c	Acids yield after 1 h (mol. %) ^d	Acids yield after 3 h (mol. %) ^e	<i>i/n</i> ^f ratio	Black precipitate
1	PdCl ₂ /TPPTS/HCl	100	280	270	66	96	0.75	+
2	PdCl ₂ /TPPTS/HCl/PVA ^g	100	280	260	64	96	0.75	–
3	Pd-colloids ^h	100	0	0	0	0	(–)	–
4	Pd-colloids/TPPTS ⁱ	100	20	5	6	12	0.73	–
5	PdCl ₂ /TPPTS/HCl	120	460	0	80	80	0.76	++++
6	PdCl ₂ /TPPTS/HCl/LiCl ^j	120	500	290	100	100	0.76	–
7	PdCl ₂ /TPPTS/HCl/PVA ^g	120	460	280	100	100	0.76	–
8	PdCl ₂ /TPPTS/HCl/PVA ^k	120	475	110	78	100	0.77	–
9	PdCl ₂ /TPPTS/HCl/PVA ^l	120	480	170	84	100	0.77	–
10	Pd-colloids ^h	120	0	0	0	0	(–)	–
11	Pd-colloids/TPPTS ⁱ	120	90	85	19	51	0.77	–

^aExperimental conditions: PdCl₂: 0.0146 g (0.08 mmol); TPPTS: 0.283 g (0.5 mmol); pH was adjusted to 1.8 with HCl; water: 11.5 ml; toluene: 11.5 ml; propene: 33 mmol; cumene (internal standard: 0.13 mmol); P_{CO}: 40 bar. ^bTOF(0) number defined as mol of initially converted propene per mol of palladium per hour. ^cTOF(1) number defined as activity after 1 h of reaction. ^dAcids yield after 1 h of reaction determined by GLC. The carboxylic acids selectivity was 100%. ^eAcids yield after 3 h of reaction determined by GLC. ^f2-Methylpropanoic acid to butanoic acid ratio. ^g0.375 g of polyvinylalcohol (*M_w*: 13 000–23 000; Aldrich[®]) was added. ^hThe aqueous suspensions of Pd(0) particles was stabilized by polyvinylalcohol (*M_w*: 13 000–23 000, Aldrich[®]) and was prepared in according to Ref. [13–15]. ⁱ0.283 g (0.5 mmol) of TPPTS was added to the aqueous suspensions of Pd(0) particles defined in footnote h. ^j0.0356 g (0.84 mmol) of LiCl was added. ^k0.125 g of polyvinylalcohol (*M_w*: 13 000–23 000; Aldrich[®]) was added. ^l0.375 g of polyvinylalcohol (*M_w*: 31 000–50 000; Aldrich[®]) was added.

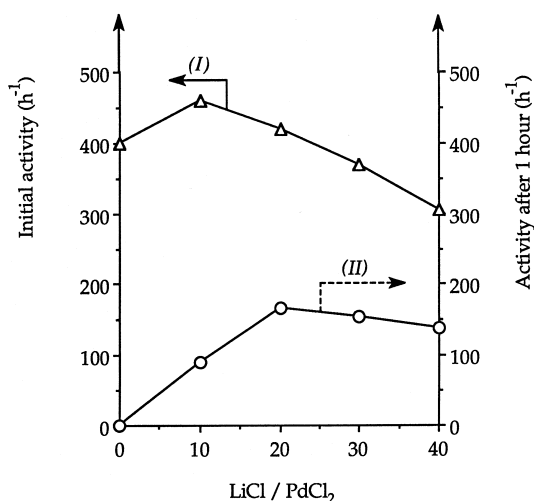


Fig. 1. Initial activity (I) and activity after 1 h of reaction (II) as a function of the LiCl/PdCl₂ molar ratio. Experimental conditions: PdCl₂ 0.0438 g (0.25 mmol); TPPTS: 0.85 g (1.5 mmol); pH was adjusted to 1.8 with HCl; water: 35 ml; toluene: 35 ml; propene: 100 mmol; P_{CO}: 40 bar; T: 120°C.

strongly coordinating anions. For instance, the hydroxycarbonylation rates decrease by a factor about 2–3 with chlorides and by only a factor 1.5 with iodides during the first hour of reaction. Although the differences are not very marked, it seems that the nature of the cation influences also the catalytic activity. Best activities are obtained with Na⁺ and K⁺.

Interestingly, the catalytic activity can also be maintained by adding polyvinylalcohol (PVA) to the aqueous medium. For instance, after addition of 0.25 equivalent of PVA (*M_w*: 13 000–23 000), the results are the same as those obtained with 10 equivalent of LiCl (compare entries 6 and 7). A lower amount of PVA or a higher molecular weight of this compound led to decreased activities (entries 8 and 9).

Effect of alkali metal halides and polyvinylalcohol on the catalyst stability can be interpreted by considering the different species involved in the hydroxycarbonylation mechanism (Scheme 2) [8,16]. In the catalytic cycle, the key intermediate is a palladium hydride complex rapidly generated from the zero valent palladium complex Pd(TPPTS)₃. The insertion of the olefin into the palladium–hydride bond, followed successively by carbon monoxide insertion and nucleophilic attack of water leads then to carboxylic acids as described in Scheme 2.

We assume that the main pathway of catalyst deactivation results in the formation of colloidal Pd(0) particles from the species Pd(0)(TPPTS)₃. These colloidal Pd(0) particles which can be stabilized by the TPPTS ligand [17–23] lead to black palladium agglomerates which precipitate when their sizes are too important (see deactiva-

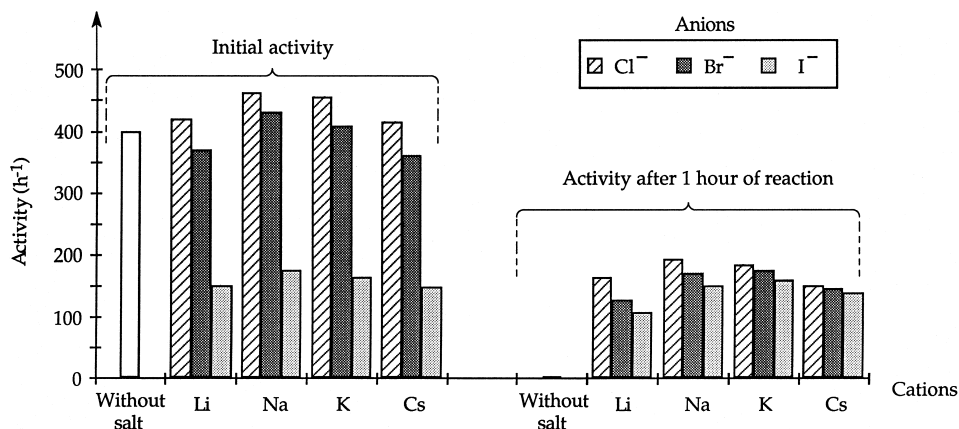
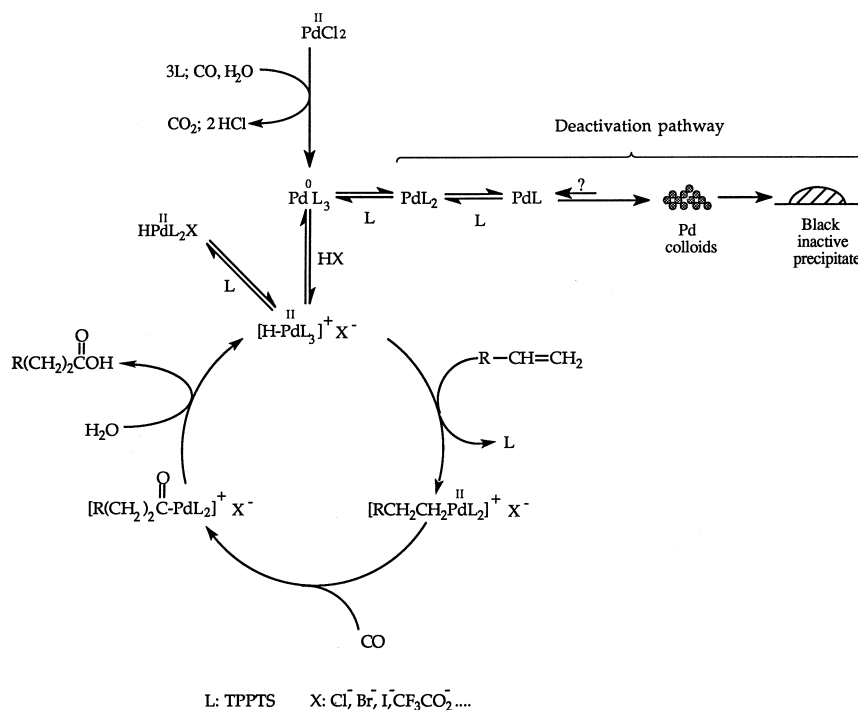


Fig. 2. Influence of various alkali metal halides on the initial activity and on the activity after 1 h of reaction. Experimental conditions: PdCl₂: 0.0438 g (0.25 mmol); TPPTS: 0.85 g (1.5 mmol); pH was adjusted to 1.8 with HCl; alkali metal halide: 5 mmol; water: 35 ml; toluene: 35 ml; propene: 100 mmol; P_{CO}: 40 bar; T: 120°C.



Scheme 2. Proposed catalytic cycle and deactivation pathways for the palladium catalyzed hydroxycarbonylation of olefins in two-phase system.

tion pathway in Scheme 2). Such a deactivation process has already been reported in the literature for the palladium catalyzed carbonylation of benzyl chloride [24].

With this hypothesis based on the observation of large amount of black precipitates at the end of several reactions, the probable role of polyvinylalcohol is to protect palladium colloidal suspensions in water against aggregation. Indeed, it is well known that polyvinylalcohol is an efficient water soluble protective-colloid agents [13–15] and this property has already been used by Larpent et al. [25] to carry out the hydrogenation of olefins in a two-phase system.

Although no conclusive evidence has been obtained, we assume that the role of alkali metal halides is to avoid the formation of $\text{Pd}(\text{CO})(\text{TPPTS})_2$ or $\text{Pd}(\text{CO})_2(\text{TPPTS})$ species which can more readily form agglomerates. This would proceed via the electrostatic stabilization of the phosphorus rich palladium complexes such as $[\text{HPd}(\text{O})(\text{TPPTS})_3]^+$ or $\text{Pd}(\text{O})(\text{TPPTS})_3$ and/or

via the formation of a neutral palladium hydride complex $\text{HPdX}(\text{TPPTS})_2$ from the cationic palladium hydride complex (Scheme 2) [26]. The stabilisation of $[\text{HPd}(\text{O})(\text{TPPTS})_3]^+$ or $\text{Pd}(\text{O})(\text{TPPTS})_3$ could be due to the increased ionic strength. Indeed, as reported for $\text{HRh}(\text{CO})(\text{TPPTS})_3$ in aqueous solution [27–29], a high ionic strength impedes the phosphines dissociation and thus the formation of carbon monoxide rich species such as $\text{Pd}(\text{CO})(\text{TPPTS})_2$ or $\text{Pd}(\text{CO})_2(\text{TPPTS})$ (see the equilibrium of deactivation pathway in Scheme 2). In line with this hypothesis, we have observed that an increase in the phosphine to palladium molar ratio increases the catalyst stability. However, it is worth mentioning that the hydroxycarbonylation rate dramatically dropped when this ratio exceeded 15, probably because the first step of the catalytic cycle requires dissociation of one phosphine. Owing to the high concentration of halides, equilibrium between $[\text{HPd}(\text{O})(\text{TPPTS})_3]^+$ and $\text{HPdX}(\text{TPPTS})_2$ lies in favour of

HPdX(TPPTS)₂ leading to a lower concentration of active cationic hydride species and zero valent palladium species. This is in agreement with the fact that the initial catalytic activity decreases with the coordinating ability of the anions. As no variation of the normal to branched acids ratio was observed with the various alkali metal salts, we think that the HPdX(TPPTS)₂ complex is catalytically inactive and that anions do not modify the coordination sphere of species involved in the catalytic cycle leading to the carboxylic acids.

In order to get a better insight into the catalytic properties of palladium colloids and black palladium precipitates, we have collected agglomerates at the end of some experiments and synthesized water-soluble palladium colloids [13–15]. The palladium colloids have been prepared by reduction of palladium chlorides in aqueous solution of polyvinylalcohol and characterized by transmission electron microscopy. These colloids are made of particles of about 50 Å with a narrow size distribution. Despite our numerous efforts, the recovered and synthesized colloids showed no activity in hydroxycarbonylation (see entries 3 and 10 for synthesized colloids). However, we have found that the synthesized colloidal Pd(0) particles showed a mid catalytic activity in the presence of TPPTS at 100°C and 120°C (entries 4 and 11). As we have carefully checked by voltammetry experiments that no trace of palladium(II) was still present in the prepared colloidal Pd(0) solution, this result raises the problem of nature of the catalytic species involved in this particular experiment. As no variation of the normal to branched acids ratio vs. standard experiments was observed, the catalytic activity of colloidal particles stabilized by the TPPTS appears not very likely. However, the dissociation of this colloidal particles to molecular palladium which would act as soluble homogeneous catalyst could account for the above results. Further investigations are currently underway in our laboratory to clarify these unusual results.

4. Conclusion

Our works demonstrate undoubtedly the beneficial effect of salts or polyvinylalcohol on the thermal stability of the Pd/TPPTS catalytic system. This effect can be turned to good account to achieve the hydroxycarbonylation at higher temperatures and, so, to obtain higher catalytic activities. The catalysts deactivation requires nevertheless other studies to be understood further. In particular, the role played by the colloidal particles stabilized by the TPPTS during the hydroxycarbonylation of olefins needs to be shed light.

Acknowledgements

Financial support of this research by the Elf-Atochem and by the Centre National de la Recherche Scientifique (CNRS) is gratefully acknowledged. We thank Dr. Carole Lamonier and Dr. Jean Hennion for their skilful assistance in the transmission electron microscopy experiments and cyclic voltammetry studies.

References

- [1] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. 104 (1995) 17.
- [2] B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996, pp 104–187.
- [3] J.Y. Yoon, E.J. Jang, K.H. Lee, J.S. Lee, J. Mol. Catal. 118 (1997) 181.
- [4] E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, G.N. Boiko, Russ. Chem. Bull. 43 (1994) 360.
- [5] D.M. Fenton, J. Org. Chem. 38 (1973) 3192.
- [6] H. Alper, J.B. Woel, B. Despeyroux, D.J.H. Smith, J. Chem. Soc., Chem. Comm. (1983) 1270.
- [7] H. Alper, B. Despeyroux, J.B. Woel, D.J.H. Smith, British Petroleum, PCT Int. Appl. WO 84/01376 (1984).
- [8] F. Bertoux, S. Tilloy, E. Monflier, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 529.
- [9] E. Monflier, A. Mortreux, Catal. Lett. 50 (1998) 115.
- [10] F. Bertoux, S. Tilloy, E. Monflier, Y. Castanet, A. Mortreux, J. Mol. Catal. (1998) in press.
- [11] S. Tilloy, E. Monflier, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 857.

- [12] R. Gärtner, B. Cornils, H. Springer, P. Lappe, (Ruhchemie, A.G.), DE-B 3235030 (1982).
- [13] H. Hirai, J. Macromol. Sci. Chem. A 13 (1979) 633.
- [14] H. Hirai, Y. Nakao, N. Toshima, J. Macromol. Sci. Chem. A 13 (1979) 727.
- [15] H. Hirai, Y. Nakao, N. Toshima, J. Macromol. Sci. Chem. A 13 (1979) 1117.
- [16] G. Papadogianakis, G. Verspui, L. Maat, R. Sheldon, Catal. Lett. 47 (1997) 43.
- [17] C. Larpent, H. Patin, J. Mol. Catal. 44 (1988) 191.
- [18] C. Larpent, R. Dabard, H. Patin, Tetrahedrons Lett. 28 (1987) 2507.
- [19] C. Larpent, F. Brisse-Le Menn, H. Patin, New J. Chem. 15 (1991) 361.
- [20] C. Larpent, F. Brisse-Le Menn, H. Patin, J. Mol. Catal. 65 (1991) L35.
- [21] C. Larpent, H. Patin, J. Mol. Catal. 61 (1990) 65.
- [22] G. Schmid, A. Lehnert, Angew. Chem. Int. Ed. Engl. 28 (1989) 780.
- [23] G. Schmid, A. Lehnert, U. Kreibig, Z. Adamczyk, P.Z. Belouschek, Naturforsch 45b (1990) 989.
- [24] C.W. Kohlpaintner, M. Beller, J. Mol. Catal. A: Chem. 116 (1997) 259.
- [25] C. Larpent, E. Bernard, F. Brisse-Le Menn, H. Patin, J. Mol. Catal. 116 (1997) 277.
- [26] V.V. Grushin, Chem. Rev. 96 (1996) 2011, and references therein.
- [27] H. Ding, B.E. Hanson, J. Mol. Catal. 99 (1995) 131.
- [28] H. Ding, B.E. Hanson, J. Chem. Soc., Chem. Commun. (1994) 2747.
- [29] H. Ding, B.E. Hanson, T.E. Glass Inorg. Chim. Acta 229 (1995) 329.