



ELSEVIER

Journal of Molecular Catalysis A: Chemical 112 (1996) 311–316

 JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Unprecedented effects of solvent and temperature of preparation on hydrosilylating properties of alumina-supported platinum catalyst

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Received 16 January 1996; accepted 8 April 1996

Abstract

It is shown that the solvent and the temperature used during the coordination step in the preparation of an alumina-supported platinum catalyst have large effects on their observed hydrosilylating properties. These unprecedented observations lead to the preparation of a highly active and reusable catalyst.

Keywords: Hydrosilylating properties; Platinum/alumina; Solvent effects; Temperature effects

1. Introduction

The good prospects for the use of heterogenized metal complexes as catalysts are well known (see for example Ref. [1]). Especial importance is found when it is desired to associate high catalytic selectivity and activity with easy and thorough removal of the catalyst from the reagents. This requirement is needed for hydrosilylation catalysis, perhaps the most efficient and economical route to organosilanes [2,3], in which expensive platinum metal compounds are very efficient [3]. On the other hand, in homogeneous catalysis, it is also well known that the solvent of solubilization of H_2PtCl_6

plays an important part in the formation of the catalytic species [4]. It is now well agreed that these catalytic species are low oxidation state Pt species which have colloidal character [5].

In connection with our interest on the preparation of industrial silylated monomers, we needed an efficient, easily removed and reusable catalyst. Moreover, this catalyst must be convenient at ambient temperature and as neutral as possible in order to prevent monomers polymerization. Among numerous catalysts described in the literature, one alumina-supported platinum catalyst appeared to be a good candidate. Such a catalyst was previously described by Capka and Hetflejš [6] but unfortunately it offered low reactivity and a high cost of preparation. We describe in this paper improvements in the preparation of such a catalyst and conse-

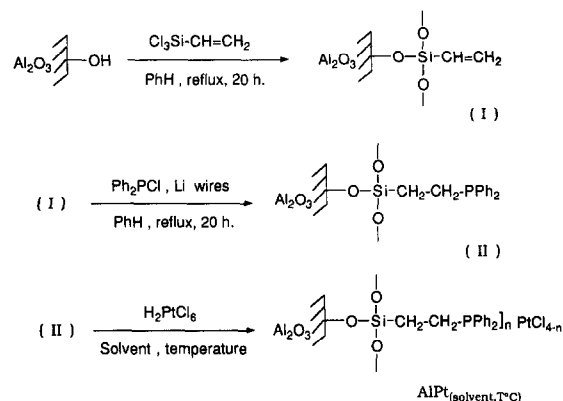
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quently enhancements of its hydrosilylating properties. These properties were found to be related to the temperature and the solvent used during the coordination step of the platinum species on the support.

2. Experimental

2.1. Materials and procedure

Alumina (aluminium oxide 60 active, basic activity I, 63–200 μ , Merck) was pre-treated under vacuum (20 mm Hg) at 100°C during 24 h. Trichloro-vinylsilane, chlorodiphenylphosphine, 1-octene and dimethylphenylsilane were purchased from Aldrich and used as such. H_2PtCl_6 (ca. 40% Pt) was purchased from Janssen and used as such. All the solvents were purified by reported literature procedures. Elemental analyses were performed by CNRS laboratory (Vernaison). The platinum contents were verified using colorimetric titrations according to Ref. [7] on a UV-vis Secoman spectrometer at $\lambda_{max} = 403$ nm. Gas chromatographic analyses were performed on a Shimadzu GC-8A instrument equipped with a Merck D2500 integrator. The analyses were accomplished with the internal standard method using a HP1 12 m capillary column and temperature programming. After isolation by flash chromatography, identifications of the reactions products were performed by IR, NMR and GC-MS techniques



Scheme 1. Route of preparation of platinum supported on alumina catalyst.

and were consistent with those of authentic samples [8].

2.2. Phosphinated support preparation

The support was prepared according to Ref. [6] by a modified procedure using chlorodiphenylphosphine and lithium wires in order to avoid the use of expensive diphenylphosphine (Scheme 1). In a typical experiment, a mixture of 15 g of alumina, 10 g of trichlorovinylsilane and 50 ml of benzene was kept under mild reflux during 20 h. The support, separated by filtration, was then washed successively with 30 ml of benzene, a mixture of 30 ml of ethanol and 1.5 ml of pyridine, 30 ml of a 10% sodium carbonate solution and finally 30 ml of dry ethanol. It was then dried under vacuum (20 mm Hg) at 75°C during 16 h. To a

Table 1
Hydrosilylation of 1-octene with dimethylphenylsilane catalyzed by platinum on alumina supported catalysts^a

Run	Catalyst ^b			Hydrosilylation yields (%) ^c after					
	solvent of preparation	temperature of preparation (°C)	preparation time (h)	0.25 h	0.5 h	1.5 h	4 h	8 h	24 h
1	EtOH-C ₆ H ₆	RT	24	nd	nd	nd	nd	nd	< 5
2	ethanol	RT	24	5	7	12	16	21	29
3	EtOH-C ₆ H ₆	reflux	2	< 5	5	7.5	10	13	15.5
4	ethanol	reflux	2	16.5	37	55	59.5	65	72
5	<i>n</i> -butanol	reflux	2	48	89	90	95	95	95

^a All experiments were performed on a 10 mmol equimolar scale of 1-octene and dimethylphenyl silane at 25°C without solvent.

^b Catalyst ratio used: 100 mg.

^c Yields in silylated adducts determined by GC analyses using internal standard method.

suspension of the support in 50 ml of benzene was then added dropwise a red solution of lithium diphenylphosphine, prepared from 6.75 g of chlorodiphenylphosphine and 0.4 g of lithium wires in 25 ml of dry THF according to Ref. [9]. The mixture was heated at 70°C during 16 h. After cooling, the so treated support was filtered, washed thrice successively with 100 ml of benzene and 100 ml of ethanol, and dried under vacuum at 80°C during 16 h (C: 3.68%; H: 1.04%; Si: 2.03%; P: 0.39%).

2.3. Pt/Al₂O₃ catalyst preparation (general procedure)

0.3 g (or 1 g for catalysts described in Table 1) of hexachloroplatinic acid (ca. 40% Pt) was reacted with 15 g of the phosphinated support in an appropriate solvent under the temperature conditions recorded in tables. Note that preparations at 100°C in ethanol, isopropanol or ethanol–benzene solution were conducted in sealed tubes (internal pressure near to 1.25 atm). After 2 h (or 24 h at room temperature), the so prepared catalyst was separated by filtration with suction and washed thrice with dry ethanol. The catalyst was then dried at 75°C during 16 h (C: 3.48%; H: 1.01%; Si: 2.00%; P: 0.38%, for the catalyst prepared in *n*-butanol at 90°C).

2.4. Procedure for test hydrosilylation runs

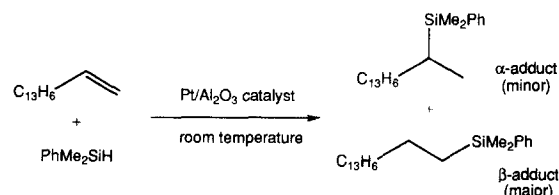
The reaction was carried out under normal atmosphere in a 50 ml Schlenk tube equipped with a reflux condenser and a magnetic stirrer. The reactor was charged with 100 mg of catalyst and a solution of 1-octene (10 mmol), triethylsilane or dimethylphenylsilane (10 mmol) and decane as internal standard (2 mmol) was dropwise added over a period of 2 min. The mixture was stirred at 25°C. It must be noted that many reactions were exothermic. In order to correctly compare our results, all hydrosilylation runs were conducted in thermostated conditions. The course of the reaction was monitored by removing samples of the reaction mixture at

fixed intervals. After filtration through glass wool, the reaction yields were determined by gas chromatography analyses. The turnover numbers (expressed in s⁻¹) were calculated from the yields after 5 min. The catalysts used in repeated runs were removed from the reaction mixture by centrifugation. It was reused after washing with ethanol (5 ml) and drying under vacuum (20 mm Hg) during 16 h at room temperature.

3. Results and discussion

3.1. Exploratory experiments

In exploratory experiments, we found that a catalyst prepared according to Ref. [6] showed a low activity in hydrosilylation of 1-octene with dimethylphenylsilane at room temperature (Scheme 2). Indeed, less than 5% of silylated adducts were formed after 24 h of reaction. Using modified procedure for the preparation of the support (see Experimental) the results were quite similar (run 1, Table 1). GC analyses of the crude products showed that the reaction was largely limited by the classical isomerization of 1-octene into unreactive internal olefins [10]. Thus, we decided to modify the temperature used during the coordination step (Scheme 1). We found that a catalyst prepared using a refluxed ethanol–benzene (1/1) solution exhibited a threefold activity (compare runs 1 and 3, Table 1). The same beneficial effect was observed for the catalysts prepared in ethanol (runs 2 and 4). These latter catalysts exhibited higher activity than the previous ones. These significant solvent and temperature effects led us to



Scheme 2. Hydrosilylation of 1-octene with dimethylphenylsilane.

use *n*-butanol which allowed a higher reflux temperature. Moreover, this solvent has often been described in the preparation of functional polystyrene supported complexes [9]. In these conditions, the obtained catalyst, named Pt/Al₂O₃(*n*-butanol, reflux), contained 18 mg Pt per g and was found as more active than the previous ones (run 5, Table 1). The hydrosilylation yield reached up to 95% within 4 h at room temperature.

These interesting properties motivated us to examine the ability of Pt/Al₂O₃(*n*-butanol, reflux) to be recycled. Unfortunately, we found that the catalyst activity was strongly decreased after three repeated runs. This deactivation may be related to metal leaching during hydrosilylation. Indeed, the initial Pt content of the catalyst was 18 mg per g (9.2×10^{-2} mmol) while it was only 8 mg per g (4.1×10^{-2} mmol) after the second use. These results indicated that the platinum species were not irreversibly linked to the support [11,12]. The explanation may be that using the modified procedure described, the functionality of the prepared support was near to 0.125 mmol of phosphino group per g and did not ensure an efficient coordination of the platinum species. It is classically admitted that the optimal phosphine:metal ratio must be equal to 2:1 [12]. We then decided to engage only 8 mg Pt per g of support during the following catalyst preparations. It must be noted that we

have subsequently verified that using higher ratio platinum leaching was observed.

3.2. Effects of the solvent used during the coordination step

The above results prompted us to next examine the effects of various alcohols, used as solvent during the coordination step, on Pt/Al₂O₃ hydrosilylating activity. All catalysts were prepared at 100°C in various solvents. The hydrosilylating properties were tested in the hydrosilylation of 1-octene with dimethylphenylsilane at room temperature (Scheme 2) and the obtained results are reported in Table 2. We found that the platinum content and the hydrosilylating activity of a catalyst were dependent on the solvent used for its preparation. However, the catalytic activity must not be completely correlated to the platinum content. For example, the use of an ethanol–benzene mixture, ethanol or *n*-pentanol as solvent led to high platinum contents with strongly different activities (runs 1, 2 and 5, respectively). Finally, it appeared that *n*-pentanol was the most appropriated solvent of preparation. Indeed, Pt/Al₂O₃(*n*-pentanol, 100°C) allowed a rapid and complete reaction and the highest turnover number (run 5). In terms of rate, yields and selectivity (up to 95% of β -adduct), our catalyst gave comparable results as H₂PtCl₆. This led us to

Table 2
Influence of the solvent of preparation for a fixed temperature of 100°C

Run	Catalyst ^b		Turnover number ^c (s ⁻¹)	Hydrosilylation yields (%) ^d after					
	solvent of preparation	platinum content (mg/g)		0.25 h	0.5 h	1.5 h	4 h	8 h	24 h
1	EtOH–C ₆ H ₆ ^e	7.9	2.05	84.5	86	87	88	89	90
2	ethanol ^e	7.2	1.35	32	45	55	69	82	87.5
3	<i>i</i> -propanol ^e	4.6	1	16.5	25	41	52.5	59	63
4	<i>n</i> -butanol	4.5	1	19.5	42	63	77.5	82	89
5	<i>n</i> -pentanol	7.6	4.7	84	89	91	94	99.5	99.5
6	<i>n</i> -hexanol	5.1	0.95	17	34	57	72	86	90

^a All experiments were performed on a 10 mmol equimolar scale of 1-octene and dimethylphenyl silane at 25°C without solvent.

^b Catalyst ratio used: 100 mg.

^c Turnover calculated after 5 min of reaction.

^d Yields in silylated adducts determined by GC analyses using internal standard method.

^e Preparation performed in sealed tube.

conclude that the reaction mechanism is not fundamentally different than the Chalk and Harrod's one [13]. It must also be hypothesized that the used conditions allow the efficient reduction of Pt(IV) in active and stable low oxidation state platinum species as described for Speier's catalyst [14]. This assumption is consistent with the fact that no induction period is observed with Pt/Al₂O₃. However, at this time, these unprecedented solvent effects are difficult to understand. The dependence of the catalytic activity on the nature of the alcohol used during the preparation is probably due to some structural modifications of the support. If under our conditions, the alcohol reacts with the support, it may be assumed that steric interactions can suppress a possible dimerization of the reactive catalytic intermediates resulting in enhancement of activity as described for immobilized rhodium complexes [15]. The bulkiness of the lipophilic chain of the alcohol must then have a predominant role.

3.3. Effects of the temperature used during the coordination step

We then examined the influence of the temperature used during the coordination step conducted in *n*-pentanol. The results obtained with these catalysts are gathered in Table 3. It appeared that the catalytic activity was strongly dependent on the temperature used. We found that Pt/Al₂O_{3(n-pentanol,90°C)} exhibited the highest

catalytic activity during the hydrosilylation of 1-octene with dimethylphenylsilane. The reaction obtained was nearly instantaneous (run 2). In order to determine the maximum turnover number of this catalyst, we performed an hydrosilylation run by using only 50 mg of catalyst (run 3). In these conditions, the calculated turnover number (after 5 min) reached 8.13 s⁻¹ showing the exceptional activity of this new catalyst. It must also be underlined that the use of *n*-pentanol at 90°C during the coordination step allowed a complete deposit of the initial platinum species. Indeed, the platinum content of the catalyst Pt/Al₂O_{3(n-pentanol,90°C)} was equal to 8 mg/g. All other temperature conditions led to a lower platinum content and to less active catalysts. These results indicated that the active species was formed at an optimal temperature. The easy and irreversible reduction of Pt(IV) in inactive Pt(0) is probably favored by high temperatures [2]. If our hypotheses are valuable, lower temperature do not allow an efficient modification of the support resulting in a less active catalyst.

3.4. Determination of the Pt / Al₂O_{3(n-pentanol,90°C)} lifetime

In order to determine if the solvent and the temperature have an influence on platinum leaching, we finally tested Pt/Al₂O_{3(n-pentanol,90°C)}, our best catalyst, in re-

Table 3
Influence of the temperature of preparation in *n*-pentanol

Run	Catalyst			Turnover number ^b (s ⁻¹)	Hydrosilylation yields (%) ^c after				
	preparation temperature (°C)	platinum content (mg/g)	used ratio (g)		0.25 h	0.5 h	1.5 h	4 h	24 h
1	80	7.4	0.1	3.52	73	75	80	81	83
2	90	8	0.1	4.47	99	99.5	99.8	99.8	99.8
3	90	8	0.05	8.13	91.7	93	93.7	96.3	98
4	95	7.7	0.1	4.22	93	95	94	95	97
5	100	7.6	0.1	3.85	85	94	97	97	94
6	115	7.3	0.1	0.53	17	38	61	74	79
7	115	6.9	0.1	0.24	6	14	29	56	72

^a All experiments were performed on a 10 mmol equimolar scale of 1-octene and dimethylphenyl silane at 25°C without solvent.

^b Turnover calculated after 5 min of reaction.

^c Yields in silylated adducts determined by GC analyses using internal standard method.

peated hydrosilylation runs. We found that this catalyst can be used twelve times without significant decrease in activity. The yield obtained during the twelfth run reached up to 95% within 1 h of reaction. We also found that these repeated runs can be performed with a restricted platinum leaching in the reaction medium. A twelve fold used catalyst contained more than 7 mg Pt per g of catalyst.

4. Conclusion

In summary, we have shown the large influence of the solvent and of the temperature used in the coordination step of the preparation of a platinum supported on alumina catalyst. The use of *n*-pentanol as solvent at 90°C was found as the most appropriate conditions allowing the preparation of a highly active and reusable catalyst. Applications of this catalyst in the preparation of sensitive silylated monomers are currently under investigation.

Acknowledgements

We thank Professor P. Caubere for helpful discussions during this work and Dr. W. MacRae for correction of english. We also thank referees for interesting comments.

References

- [1] P. Laszlo, in: *Preparative Chemistry Using Supported Reagents* (Harcourt Broce Javonovich/Academic Press, Inc., San Diego, 1987).
- [2] F.R. Hartley and P.N. Vezey, *Adv. Organomet. Chem.* 15 (1977) 189; J.L. Speier, *Adv. Organomet. Chem.* 17 (1979) 407; I. Ojima, in: *The Chemistry of Organic Silicon Compounds*, S. Patai (Ed.) (John Wiley and Sons, Chichester, 1989).
- [3] B. Marciniec and J.J. Gulinski, *J. Organomet. Chem.* 446 (1993) 15, and references cited therein.
- [4] R.A. Benkeser, S. Donny, G.S. Li, P.G. Nerlakar and S.D. Work, *J. Am. Chem. Soc.* 90 (1968) 1872; V.O. Reikhfel'd and M.I. Astrakhanov, *Chem. Abstr.* 78 (1973) 16273n.
- [5] L.N. Lewis and R.J. Uriarte, *Organometallics* 9 (1990) 621; L.N. Lewis, R.J. Uriarte and N. Lewis, *J. Catal.* 127 (1991) 67.
- [6] M. Capka and J. Hetflejš, *Collect. Czech. Chem. Commun.* 39 (1974) 154.
- [7] T.D. Rees and S.R. Hill, *Talanta* 15 (1968) 1312.
- [8] J.E. Hill and T.A. Nile, *J. Organomet. Chem.* 137 (1977) 293; A.J. Cornish, M.F. Lappert, G.L. Filatovs and T.A. Nile, *J. Organomet. Chem.* 172 (1979) 153.
- [9] K.G. Allum, R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, *J. Organomet. Chem.* 87 (1975) 189; B. Loubinoux, J.J. Chanot and P. Caubere, *J. Organomet. Chem.* 88 (1975) C4.
- [10] J.F. Harrod and A.J. Chalk, *J. Am. Chem. Soc.* 86 (1964) 1776.
- [11] I. Dietzmann, D. Tomanova and J. Hetflejš, *Collect. Czech. Chem. Commun.* 39 (1974) 123.
- [12] M. Capka, *Collect. Czech. Chem. Commun.* 55 (1990) 2803.
- [13] A.J. Chalk and J.F. Harrod, *J. Am. Chem. Soc.* 87 (1965) 16.
- [14] R.A. Benkeser and J. Kang, *J. Organomet. Chem.* 185 (1980) C9.
- [15] M. Capka, M. Czakoova, W. Urbaniak and U. Schubert, *J. Mol. Catal.* 74 (1992) 335.