Catalysis Letters 10 (1991) 325–334

Enantioselective hydrogenation of ethyl pyruvate on tin promoted Pt/Al_2O_3 catalysts

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Received 17 May 1991; accepted 6 August 1991

The enantioselective hydrogenation of ethyl pyruvate has been studied on a Pt/Al_2O_3-dihydrocinchonidine catalyst promoted with different amount of tin. The surface reaction between hydrogen adsorbed on Pt and tin tetraalkyls is used for the tin introduction. This reaction leads to the formation of surface organometallic complexes (I), with $SnR_{(4-x)}$ moieties anchored to the platinum surface. The enantioselectivity of the Pt/Al_2O_3-dihydrocinchonidine catalyst is found to change only slightly upon promotion with tin, while the rate of ethyl pyruvate hydrogenation depends strongly on the amount and the form of tin introduced. The hydrogenation activity is suppressed completely at relatively low tin coverage ($Sn/Pt_s < 0.06$) . The highest hydrogenation rate is measured over catalysts containing complex (I) ($Sn/Pt_s = 0.025$) on the platinum surface. On Sn-Pt alloy type active sites, which are formed after decomposition of (I) in hydrogen, the rate of hydrogenation is considerably lower than on the unpromoted reference Pt/Al_2O_3 catalyst.

Keywords: Pt/Al_2O_3; promotion by tin; modification by tin tetraalkyls; surface organometallic complexes; enantioselective hydrogenation; ethyl pyruvate; dihydrocinchonidine

1. Introduction

There is a great demand for tailored catalysts in organic synthesis and consequently understanding of the processes involved in catalyst tailoring is one of the most challenging areas in catalysis. The use of anchoring type "Controlled Surface Reactions" (CSRs) either in the preparation or the modification of

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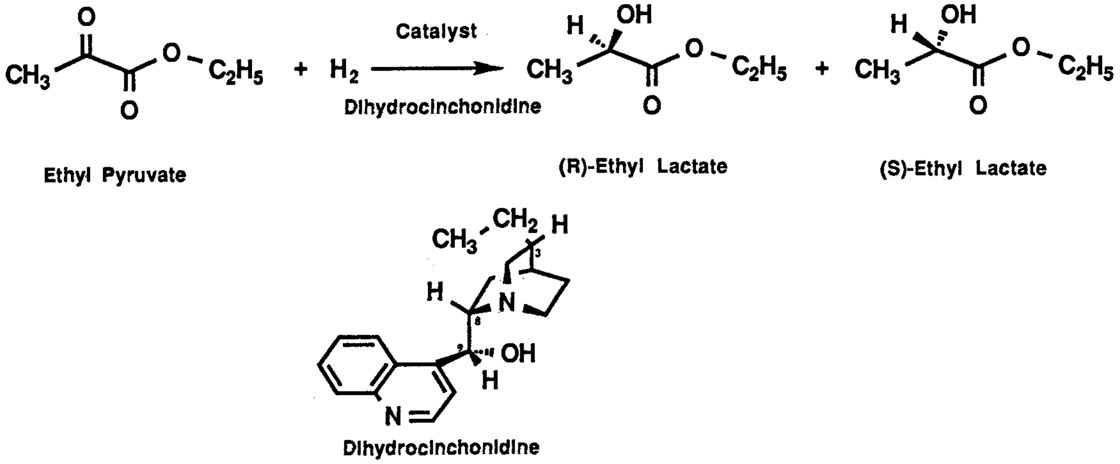


Scheme 1.

supported metal or metal oxide catalysts opens new possibilities for catalyst tailoring [1,2]. In this way the stabilized final form of the active site of a given catalyst can be controlled.

In this study we have investigated how the modification of an industrial alumina supported platinum catalyst with surface organometallic species influences its catalytic behaviour in enantioselective hydrogenation of ethyl pyruvate (scheme 1).

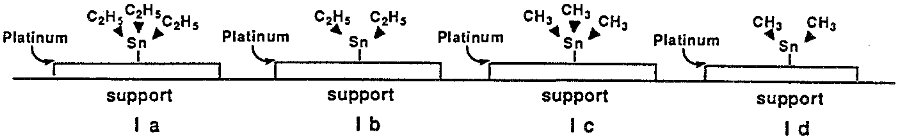
To our knowledge the modification of the catalytic properties of supported platinum catalyst by a surface organometallic moiety has not been reported before. It will be shown that the introduction of tin, in the form of surface organometallic entities anchored to the platinum, results in an increased rate of hydrogenation without loss of the high enantioselectivity.

2. Surface chemistry of the tin introduction

CSR (1) was used to anchor tin directly onto the platinum. In this surface reaction hydrogen adsorbed on platinum reacts selectively with tin tetraalkyls.

$$Pt(H)_a + SnR_4 \rightarrow \underset{[I]}{Pt - SnR_{(4-x)}} + x\ RH. \qquad (1)$$

Under properly chosen experimental conditions the formation of surface organometallic entities (I) is exclusive, i.e. no tin is introduced onto the alumina. Details of this type of surface reactions and catalyst modification have been given elsewhere [6–9]. After the tin anchoring step the platinum surface is covered by the surface organometallic complexes [6–9] shown in the subsequent scheme 2.



Scheme 2.

Surface organometallic complexes [Ia]–[Id] are stable at room temperature. Upon heating in a hydrogen atmosphere [I] decomposes with the formation of bimetallic surface entities and ethane [6–8] It has been shown recently that after complete decomposition of [I] followed by treatment in hydrogen at 400°C the alloy formation is complete and no other form of tin can be detected [9].

3. Experimental part

A commercial Pt/Al_2O_3 catalyst (Engelhard E 4759 with 5 wt% of Pt) was promoted with tin and was used in the hydrogenation of ethyl pyruvate. The dispersion of the catalyst measured by CO chemisorption after hydrogen treatment at 400°C was 0.23–0.28 [3–5].

PREPARATION OF TIN PROMOTED CATALYSTS

Prior to the promotion by tin the catalyst was treated in hydrogen at 400°C for 90 minutes. Reaction (1) was carried out in benzene solution (10 cm^3/g_{cat}) under an oxygen free argon atmosphere at 50°C. After reaction (1) the catalyst was washed three times with n-hexane. An unpromoted reference Pt/Al_2O_3 was prepared in the same way as the tin promoted catalysts, i.e. treated and cooled in hydrogen, slurried in benzene and washed with n-hexane, but without introduction of the tin precursor compounds. The tin content of the promoted catalysts was determined by atomic adsorption spectroscopy.

Prior to the hydrogenation experiments a further thermal treatment in a hydrogen atmosphere for 2 hours was carried out with both the promoted and the unpromoted reference catalysts. The temperature of this hydrogen treatment was found to be crucial for the activity control. Special care was taken to avoid contamination of the catalysts with air after promotion and after thermal treatment procedures.

CATALYTIC REACTIONS

The hydrogenation of ethyl pyruvate was carried out in a 50 ml stirred autoclave in the presence of dihydrocinchonidine added directly to the reaction mixture as described in earlier reports [4,5]. The reaction conditions were:

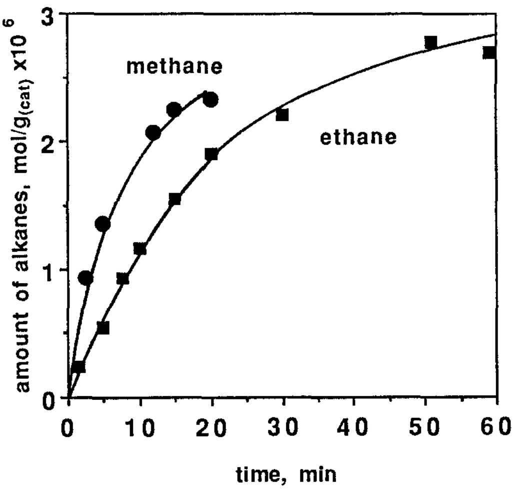


Fig. 1. Time dependence of the formation of alkanes in reaction (1) ■ - formation of ethane during the preparation of catalyst SnPt1; ● - formation of methane during the preparation of catalyst SnPt2. Amount of tin introduced into the reaction mixture: 7.6×10^{-6} mol/g_{cat}. Reaction temperature: 50°C.

stirring rate, 1000 rpm; solvent, toluene (20 ml); ethyl pyruvate (Fluka), 0.04 mol (freshly distilled); amount of catalyst, 0.050 g; dihydrocinchonidine, 0.010 g; reaction temperature, 25 ± 3°C; initial hydrogen pressure, 100 bar. Gas chromatography was used for product analysis and for the determination of the optical yield [3–5]. The latter was calculated as the enantiomeric excess (ee (%) = (R – S)/(R + S) × 100).

4. Results

A. PREPARATION OF TIN PROMOTED CATALYSTS

$Sn(CH_3)_4$, $Sn(C_2H_5)_4$ and $Sn(C_2H_5)_2Cl_2$ were used as the precursor of tin. The formation of the corresponding alkanes in reaction (1) is shown in fig. 1. No other hydrocarbons were detected in the above reaction. In agreement with our earlier findings [8] $Sn(CH_3)_4$ reacted faster than $Sn(C_2H_5)_4$. No surface reaction was observed when $Sn(C_2H_5)_2Cl_2$ was used as tin precursor. However, in the latter case strong adsorption of the tin precursor compound onto the support occurred resulting in a relatively high tin loading (0.09%). Consequently by using $Sn(C_2H_5)_2Cl_2$ the surface reaction (1) could not be controlled. The amount of tin anchored was controlled by the concentration of the tin presursor compounds and by the duration of reaction (1). The tin content of the promoted catalysts and conditions of the preparation are given in table 1. No indication was found for any loss of tin of the promoted catalysts during reaction.

B. HYDROGENATION OF ETHYL PYRUVATE ON UNPROMOTED AND TIN PROMOTED Pt/Al_2O_3 CATALYSTS

Reaction rates and optical yields measured for the hydrogenation of ethyl pyruvate are listed in table 1. The three-dimensional graph shown in fig. 2 illustrates the dependence of the rate on the modification parameters: amount of tin anchored and the temperature of hydrogen pretreatment prior to the hydrogenation. Note that already a relatively small amount of anchored tin strongly changes the overall activity of the catalysts.

Table 1
Hydrogenation of ethyl pyruvate in the presence of tin promoted Pt/Al_2O_3 catalysts

Exp. N°	Catalyst				
	Code No	Temperature of H_2 treatment, °C	Sn/Pt_s[g]	Rate of hydrogenation mol $(kg_{cat}\ sec)^{-1}$	Optical yield, %
1.	Pt [a]	no	0.000	0.83	64
2.	Pt [a]	150	0.000	1.70	82
3.	Pt [a]	200	0.000	1.66	87
4.	Pt [a]	400	0.000	2.00	88
5.	PtSn-1 [b]	no	0.025	3.00	89
6.	PtSn-1 [b]	100	0.025	2.60	84
7.	PtSn-1 [b]	200	0.025	2.12	80
8.	PtSn-1 [b]	200	0.025	2.17	86
9.	PtSn-1 [b]	400	0.025	1.15	85
10.	PtSn-2 [c]	200	0.036	1.06	72
11.	PtSn-2 [c]	400	0.036	1.08	81
10.	PtSn-3 [d]	200	0.056	0.02	72
11.	PtSn-3 [d]	400	0.056	0.74	81
13.	PtSn-4 [e]	no	0.030	1.77	86
14.	PtSn-4 [e]	no	0.030	1.55	86
15.	PtSn-5 [f]	no	0.008	2.00	89
16.	PtSn-5 [f]	no	0.008	1.77	88

[a] the unpromoted reference catalyst prepared without introduction of tin tetra alkyl compounds but treated in the same way as the tin promoted catalysts

[b] modified with $Sn(C_2H_5)_4$, the duration of surface reaction (1) was 60 minutes, $[Sn(C_2H_5)_4]_0 = 7.6 \times 10^{-4}$ mol/dm^3

[c] modified with $Sn(CH_3)_4$, the duration of surface reaction (1) was 20 minutes, $[Sn(CH_3)_4]_0 = 7.6 \times 10^{-4}$ mol/dm^3

[d] modified with $Sn(CH_3)_3$, duration of surface reaction (1) was 60 minutes, $[Sn(CH_3)_4]_0 = 7.6 \times 10^{-4}$ mol/dm^3

[e] modified with $(C_2H_5)_4$, the duration of surface reaction (1) was 90 minutes, $[Sn(C_2H_5)_4]_0 = 7.6 \times 10^{-4}$ mol/dm^3

[f] modified with $Sn(C_2H_5)_4$, the duration of surface reaction (1) was 90 minutes, $[Sn(C_2H_5)_4]_0 = 1.9 \times 10^{-4}$ mol/dm^3

[g] the Sn/Pt_s ratio was calculated based on CO/Pt = 0.22 – 0.28 measured earlier [3–5].

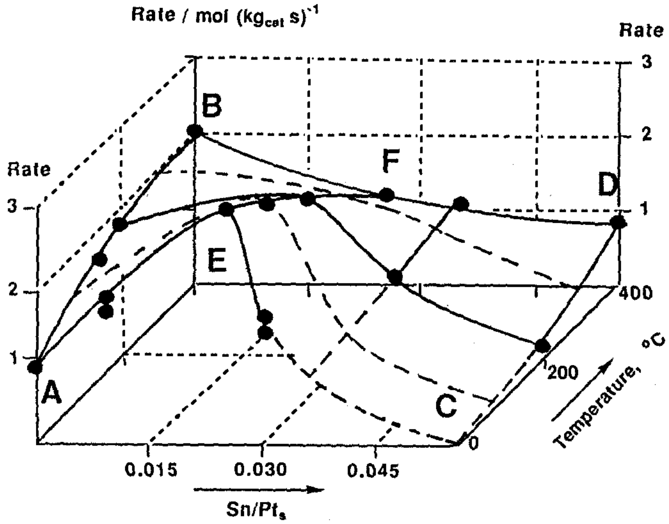


Fig. 2. Dependence of the rate of hydrogenation of ethyl pyruvate on the amount of tin anchored (Sn/Pt_s) and the temperature of hydrogen treatment carried out prior to the hydrogenation experiment (t_{H_2}).

On unpromoted Pt/Al_2O_3 catalyst the rate of hydrogenation of ethyl pyruvate and the optical yield increase (exp. No 1–4) when the temperature of hydrogen pretreatment is raised. Similar behaviour has been observed earlier [4,10,11]. It should be mentioned that in our case the thermal treatment in hydrogen prior to the hydrogenation cannot be considered as a re-reduction due to the fact that the unpromoted reference Pt/Al_2O_3 catalyst has already been reduced before its pretreatment, according to the procedure given in the experimental part.

As emerges from our results the hydrogenation activity is almost completely lost at a relatively low tin coverage ($Sn/Pt_s = 0.056$) (exp. N° 12). This indicates that the number of active sites involved in the hydrogenation is relatively small. Upon increasing the temperature of hydrogen treatment the activity of this catalyst slightly increases (exp. N° 13), however it is still much lower than that of the unpromoted reference platinum catalyst. Similar behaviour, i.e. a decrease of activity, was observed for all Sn-Pt catalysts treated at 400°C.

The behaviour of catalysts with low tin loading ($Sn/Pt_s = 0.008–0.025$) is particularly interesting. Catalysts containing surface organometallic complex (I), are more active than the unmodified one (experiments N° 5–9 and 14–17). The activity of catalysts containing (I) shows a well defined maximum. It seems that by anchoring surface complexes $SnR_{(4-x)}$ on the platinum, new type of active sites are formed. At optimum coverage of the $SnR_{(4-x)}$ moieties, the rate of hydrogenation has the highest value and then it decreases with higher $SnR_{(4-x)}$ coverage (exp. N° 14, 15) and with decomposition of (I) induced by higher pretreatment temperature (exp. N° 6–9).

5. Discussion

The enantioselectivity of the catalysts studied is relatively high, it is in the range of 64–88% for the unpromoted reference Pt/Al_2O_3 catalyst and 72–89% for tin promoted catalysts. Note that the rate of hydrogenation is more strongly influenced by the tin promotion than the enantioselectivity. Under the conditions of our experiments no direct relationship could be found between the rate of hydrogenation and the enantioselectivity.

We propose that the modification procedure used in this study leads to the formation of different types of active sites with different intrinsic catalytic activity. The monometallic platinum is first decorated by organometallic moieties and by heating in hydrogen the latter is transformed to an alloy type Sn-Pt species. Between the two relatively well defined active sites, i.e. monometallic platinum and bimetallic Sn-Pt alloy, possibly, new types of active sites are formed. The activity of the catalysts strongly depends on both the coverage and the form of the tin containing surface species.

When moving in the two-parameter field $X = Sn/Pt_s$ and $Y =$ temperature of hydrogen treatment as shown in fig 2, we are moving from one form of active site to another. In the coordinate (0, 0), i.e. in state A we propose an alumina supported platinum catalyst which contains "organic moities" or "carbonaceous overlayer" formed during the contact with organic solvents (benzene and n-hexane used in surface reaction (1) and in the subsequent washing procedure). The formation of this type of "carbonaceous overlayer" has been suggested both in gas and liquid phase reactions [12,13]. By increasing the temperature of hydrogen treatment, part of the "organic moities" are removed resulting in a "relatively clean" platinum surface, which exhibits an increased catalytic activity and high enantioselectivity (state B).

Particularly interesting is the increase of the rate of hydrogenation and the appearance of the maximum when moving along the X axis from state A to state C. When moving from state A along the X axis the surface coverage of $Sn(C_2H_5)_{(4-x)}$ moieties is increased. It seems likely that by decorating the platinum surface with organometallic surface complexes, (Ia–Id), the formation of "carbonaceous overlayer" is strongly suppressed and that the most reactive platinum sites are covered by $Sn(C_2H_5)_{(4-x)}$ moieties. It seems feasible that the presence of the above surface complexes can (i) change the surface coverage of hydrogen and substrate, (ii) alternate the mode of adsorption of the reactants, and (iii) change the mechanism of hydrogenation with involvement of the surface alkyl groups in transfer hydrogenation reactions.

It is also remarkable that at relatively low Sn/Pt_s ratios ($Sn/Pt_s < 0.06$) the rate of hydrogenation is almost completely lost (state C) . It has recently been shown by STO technique that in Pt/CPG hydrogenation catalysts with a Pt particle size above 3 nm the number of sites responsible for hydrogenation is only 5–10% of the total surface platinum atoms [14]. Our findings are in line with this observation. It appears that by anchoring $Sn(C_2H_5)_{(4-x)}$ moieties to the platinum surface complete poisoning of sites responsible for hydrogenation is accomplished at $Sn/Pt_s = 0.056$.

When moving from state C to state D along the Y axis the activity increases only slightly. This increase may be considered as indirect evidence for (i) the decomposition of the primary formed surface organometallic complex (I) and (ii) the formation of alloy type Sn-Pt surface entities. State D can also be reached starting from state B, i.e. by moving along the X axis, corresponding to an increase of the amount of tin introduced. The continuous decrease of the rate of hydrogenation indicates that the intrinsic catalytic activity of alloy type Sn-Pt surface species formed after high temperature hydrogen treatment is lower than that of the monometallic platinum.

The decrease of the rate of hydrogenation observed when moving from state E to state F can also be attributed to the decomposition of the surface organometallic complex (I) with formation of alloy type Sn-Pt surface entities.

Recently, it has been reported that the modification of supported rhodium catalyst with $Sn(C_4H_9)_4$ results in a catalyst containing $Sn(C_4H_9)_2$, an organometallic moiety on the rhodium surface [15–17]. This catalyst showed high activity and unique selectivity for the hydrogenation of unsaturated aldehydes. The activity and selectivity changes were attributed to the presence of a stable surface organometallic complex, $Sn(C_4H_9)_2$. Note that in the formation of $Sn(C_4H_9)_2$ moieties on rhodium another CSR is involved [15–17]. With this surface reaction relatively high Sn/Rh_s ratios were obtained. Despite these differences it seems likely that in both cases, i.e. for the modification of platinum with $Sn(CH_3)_{(4-x)}$ or $Sn(C_2H_5)_{(4-x)}$, and rhodium with $Sn(C_4H_9)_2$ moieties, the observed high activity is due to the presence of the given surface organometallic complex.

The present study indicates that the enantioselectivity of the Pt/Al_2O_3-dihydrocinchonidine system is relatively weakly influenced by the tin promotion, while a comparably strong effect on the reaction rate is observed.

The final answer for the origin of this behaviour cannot be given on the basis of the present results. Further work towards the elucidation of this phenomenon is presently under way in our laboratory.

Acknowledgement

The authors are grateful to Mrs. K. Hanko (Central Research Institute for Chemistry, Budapest) for the preparation of catalyst samples PtSn-4 and PtSn-5.

References

[1] Y.I. Yermakov, B.N. Kuznetsov and V.A. Zakharov, in: *Catalytic Hydrogenation*, ed. L. Cerveni (Elsevier, Amsterdam, 1986) pp. 459–485.

[2] J. Margitfalvi, S. Szabo and F. Nagy, in: *Catalytic Hydrogenation*, ed. L. Cerveni (Elsevier, Amsterdam, 1986) pp. 373–395.

[3] J.T. Wehrli, Ph.D. Thesis No 8833, Swiss Federal Institute of Technology, 1989.

[4] J.T. Wehrli, A. Baiker, D.M. Monti and H.U. Blaser, J. Mol. Catal. 61 (1990) 207.

[5] H.U. Blaser, H.P. Jalett, D.M. Monti, A. Baiker and J.T. Wehrli, Stud. Surf. Sci. Catal. 41 (1988) 153.

[6] J. Margitfalvi, M. Hegedüs, S. Göbölös, E. Kern-Tàlas, P. Szedlacsek, S. Szabo and F. Nagy, in: *Proc. 8th Int. Congr. Catal.*, Berlin, 1984, Vol. 4. (Verlag Chemie, Weinheim, 1984) pp. 903–913.

[7] E. Kern-Talas, M. Hegedüs, S. Göbölös, P. Szedlacsek and J. Margitfalvi, Stud. Surf. Sci. Catal. 31 (1987) 689.

[8] J. Margitfalvi, E. Tàlas, and S. Göbölös, Catal. Today 6 (1989) 73.

[9] Cs. Vèrtes, E. Tàlas, I. Czako-Nagy, J. Ryczkowski, S. Göbölös, A. Vèrtes and J. Margitfalvi, Appl. Catal. 28 (1991) 256.

[10] I.M. Sutherland, A. Ibbotson, R.B. Moyes and P.B. Wells, J. Catal. 125 (1990) 77.

[11] Y. Orito, S. Imai and S. Niwa, J. Chem. Soc. Jpn (1979) 1118.

[12] S.M. Davis, F. Zaera and G.A. Somorjai, J. Catal. 77 (1982) 439.

[13] S.J. Thomson and G. Webb, J. Chem. Soc., Chem. Comm. (1976) 526.

[14] R.L. Augustine, D.R. Baum, K.G. Heith, L.S. Szivos and S.T. O'Leary, J. Catal. 127 (1991) 675.

[15] M. Agnelli, P. Loussard, A. El Mansour, J.P. Candy, J.P. Bournonville and J.M. Basset, Catal. Today 6 (1989) 63.

[16] B. Didilon, A. El Mansour, J.P. Candy, J.P. Bournonville and J.M. Basset, Stud. Surf. Sci. Catal. 59 (1991) 137.

[17] B. Didilon, J.P. Candy, J.M. Basset, F. Pletier and J.P. Bournonville, Stud. Surf. Sci. Catal. 63 (1991) 717.