Novel polymer-supported platinum catalyst for selective hydrogenation of crotonaldehyde

Z.M. Michalska [a,*], B. Ostaszewski [a], J. Zientarska [a], J.M. Rynkowski [b]

[a] *Institute of Polymers, Technical University of Łódź, Zwirki 36, 90-924 Łódź, Poland*
[b] *Institute of General and Ecological Chemistry, Technical University of Łódź, 90-924 Łódź, Poland*

Abstract

Platinum catalyst was prepared by immobilizing the metal precursor on polyamide support containing a pyridine moiety, $-[-CO-C_5H_3N-CONH(CH_2)_6NH-]-_n$, PA-py, and by reducing it with sodium borohydride solution at room temperature. The activity and selectivity of the catalyst were examined for liquid phase hydrogenation of crotonaldehyde (CAL) under 40 bar hydrogen pressure at 75 °C. Tin chloride was added to improve the reaction selectivity towards formation of unsaturated alcohol (UOL). The catalyst was characterized by X-ray diffraction (XRD). The repeated use of the Pt–Sn catalysts showed the increase of activity and selectivity of the catalyst. The maximum yield of crotyl alcohol achieved in the hydrogenation of CAL was about 55.1%, which was equivalent to 834 catalytic cycles per Pt atom. The effect of the polymer support on the reaction selectivity has been discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polyamide-supported catalyst; Selective hydrogenation; Crotonaldehyde; Crotyl alcohol; Pt–Sn catalyst; Effect of polymer support

1. Introduction

Unsaturated alcohols (UOLs) form a very important group of compounds for the synthesis of fine chemicals, especially for pharmacology, perfume and food processing industry. The catalytic hydrogenation of α,β-unsaturated aldehydes to produce UOLs is a difficult challenge because the hydrogenation of an alkene double bond catalyzed by noble metals is thermodynamically and kinetically more favored over the hydrogenation of a carbonyl group [1–4]. Therefore, the research efforts have been carried out in order to enhance reactivity of the C=O group of an unsaturated aldehyde towards hydrogen and simultaneously to suppress the hydrogenation activity of the C=C double bond. Interest in the selective hydrogenations of α,β-unsaturated aldehydes has been well documented in the literature. The different authors have studied the various factors that are able to influence the selectivity of this process: the effect of the nature of the precious metal used [4–10] or the mixture of metals [7–12], the addition of metallic salts [14–17] and particularly tin compounds [4,10–12,14,18,19]. The presence and the nature of solvent and the reaction conditions such as the temperature, and liquid or vapor phase may also have an influence [4,9,12,19]. Selective hydrogenation of α,β-unsaturated aldehydes has been carried out with catalysts supported on different matrices such as Al_2O_3 [9,10,23–25], SiO_2 [4,11,19], carbon [10,20–22], and on polymers such as polystyrene [13] and polyamide-6,6 [14–17]. An important enhancement of selectivity to UOLs has been found by using supports with strong metal support interaction (SMSI) properties [4,9,25–28].

* Corresponding author. Tel.: +48-42-6313204;
fax: +48-42-6362543.
E-mail address: zmich@ck-sg.p.lodz.pl (Z.M. Michalska).

Recently, we have also reported on the effect of metal–support interaction during selective hydrogenation of dienes and alkynes catalyzed by palladium supported on polyamides having a pyridine moiety, PA-py [29]. The donor effect of the Npy sites in the PA-py support increases electron density on the metal species and as a consequence decreases the ability of the metal to hydrogenate the C=C double bond. Therefore, we thought that this type of matrix might be suitable for the preparation of the Pt catalyst for selective hydrogenation of α,β-unsaturated aldehydes.

In this paper, we report our preliminary study on the hydrogenation of crotonaldehyde (CAL) over polyamide PA-py-supported platinum catalyst.

2. Experimental

2.1. Materials

All solvents and reagents were of analytical or chemical grades. Toluene was purified by a standard method and 1,6-hexamethylene diamine was distilled in the presence of KOH. 2,6-Pyridinedicarboxylic acid dichloride (2,6-pyH, Aldrich) was used as obtained. The hydrogen was applied from the cylinder (H_2 content 99.999%).

2.2. Synthesis of polymer supports

The polyamide with a pyridine moiety substituted in the 2,6-position in the main-chain was synthesized by a low temperature interfacial polycondensation between 2,6-pyH and 1,6-hexamethylene diamine. The preparation and characterization of the support (2,6-pyH) has previously been reported [30]. It had a BET surface area of $4.4\,m^2/g$, micropore ($<20\,Å$) volume of 29.2% and the degree of crystallinity of 26%.

2.3. Catalysts preparation

The polymer bound platinum catalyst was prepared under nitrogen from a known amount of polyamide (1 g) suspended in 15 ml of 96% ethanol to which a solution of 0.0410 g of chloroplatinic acid in 4 ml of 96% ethanol was added dropwise. The mixture was then stirred at room temperature for 2–3 days when all chloroplatinic acid had reacted with the polymer.

The supported platinum catalyst precursor was then filtered off, washed thoroughly with ethanol, dried under vacuum, and ground. The catalyst was suspended in ethanol under nitrogen, and a large excess of ethanolic solution of 1.53 g (40 mmol) of the sodium borohydride was added dropwise at 35 °C. The suspension was stirred for 5 h and then left at room temperature overnight. The reduced catalyst was filtered off and thoroughly washed with distilled water and ethanol. It was dried under reduced pressure at 75 °C to a constant weight. The amount of platinum loaded in the support was analyzed by a routine procedure. A sample of a polymer catalyst was heated up to 600 °C and then dissolved in aqua regia. The resulting solution was diluted and assayed by AAS. The platinum content was 2 wt.%.

2.4. X-ray diffraction (XRD) analysis

XRD experiments were carried out in a Siemens D5000 polycrystallic diffractometer using Cu Kα radiation (0.15418 nm). High quality scanning (long time if counting: 10 s per step, step scan mode with a small step size: $0.02°$, θ range: 24–60) was employed. The mean crystalline size was related to the pure X-ray broadening by the Scherer formula $D = K\lambda/\beta\cos\theta$. The measured line broadening B was corrected for instrumental broadening b, using an equation $\beta = (B^2 - R^2)^{1/2}$. The particle shape factor K was taken to be 0.9. The positions of the appropriate reflections of platinum were identified basing on JCPDS index (4-0802 Pt).

XRD analysis was performed for a sample of reused catalyst. It shows that platinum is dispersed on the polymer matrix in a form of crystallites of the mean size in the range 4–5 nm.

2.5. Catalytic tests

The reactions were carried out in 100 ml Parr microreactor model 4593 with glass liner. The typical hydrogenation run was as follows. The reactor was charged with 0.5 g of supported catalyst (0.05 mmol Pt), 4.1 ml of 96% ethanol, 0.5 ml (0.0214 mmol) of ethanolic solution of tin(IV) chloride and 0.41 ml (5 mmol) of CAL. The reactor was flushed several times with pure hydrogen and then the hydrogen

pressure and temperature were adjusted to the required level.

The composition of the samples was analyzed by means of a Hewlett-Packard gas chromatograph model 5890 II equipped with a thermal conductivity detector and 3396 series II integrator using $12\,ft \times 1/8''$ column with 10% FFAP on 100–120 mesh Chromosorb WHP operating at $90\,°C$ with helium as a carrier gas.

The reaction products were identified by GC–MS and were consistent with those of authentic samples.

3. Results and discussion

The hydrogenation of CAL has been carried out over Pt–Sn catalysts supported on the polyamide containing a pyridine moiety (PA-py) under different reaction variables. The reaction gives the mixture of saturated aldehyde (SAL, butyraldehyde), saturated alcohol (SOL, butanol), and UOL (crotyl alcohol). Besides, the diacetal (DA, 1,1-diethoxybutane) is also produced in the side reaction between CAL and ethanol used as a solvent.

The results are summarized in Table 1. Preliminary tests performed under atmospheric pressure showed a very low reaction rate and preferential hydrogenation of C=C double bond leading to SAL as the only product. The optimal product distribution seems to be reached under 40 bar of hydrogen pressure at $75\,°C$ with the Sn/Pt atomic ratio of 0.84. The results in Table 1 also indicate that at higher hydrogen pressure (60 bar, run 7) the hydrogenation process was accelerated but the selectivity towards UOL was lowered. When hydrogenation of CAL was carried out at lower temperature (runs 11 and 12) DA and saturated compounds: SAL + SOL were main products with yields over 40 and 50%, respectively. Comparison of runs 6–9 show that when the Sn/Pt atomic ratio increased to 1.66 the catalyst became less active leaving 55.1% of CAL unreacted, whereas lower values of the Sn/Pt ratio between 0.41 and 0.84 proved to attain catalyst with satisfactory activity and selectivity.

An important observation was made during the repeated use of the 2,6-pyH/Pt–Sn catalyst. The catalyst was recycled by two ways. The first way involves decanting off the reaction mixture, washing a catalyst with a solvent and reusing it in a subsequent cycle (runs 4 and 4.1). In the second way the catalyst was left in the reacting mixture to which a fresh portion of CAL was added after each run (runs 5, 5.1 and 5.2). The data

Table 1
The hydrogenation of CAL over the polyamide PA-py/Pt–Sn catalyst[a]

Run	Pressure (bar)	Sn/Pt atomic ratio	Reaction temperature (°C)	Reaction time (h)	Product distribution (%)				
					CAL	SAL	SOL	UOL	DA
1	1	0.84	40	24	18.1	81.1	–	–	–
2	5	0.84	75	4	42.0	13.2	6.8	14.5	21.5
3	10	0.84	75	4	32.6	14.1	8.7	19.8	25.0
4	20	0.84	75	4	23.3	11.0	12.7	29.5	23.5
4.1[b]	20	0.84	75	4	13.0	4.0	22.0	36.0	25.0
5	40	0.84	75	4	3.3	11.5	31.9	35.7	17.6
5.1[c]	40	0.84	75	4	5.0	6.0	28.7	50.3	10.0
5.2[c]	40	0.84	75	4	3.6	3.4	29.6	55.7	7.7
6	40	0.84	75	8	–	1.3	98.7	–	–
7	60	0.84	75	4	–	15.4	38.7	19.8	23.4
8	40	0.41	75	4	13.7	18.5	25.1	34.2	5.7
9	40	1.66	75	4	55.1	8.1	8.2	10.1	23.0
10	40	1.66	75	8	20.5	10.5	11.6	13.7	37.7
11	40	0.84	25	4	–	6.7	44.4	3.2	45.8
12	40	0.84	50	4	–	15.3	33.5	9.1	42.1

[a] Conditions: [CAL]:[Pt] = 100; solvent: 96% ethanol; the overall volume: $5\,cm^3$; unidentified reaction products are not shown.

[b] The catalyst used in this run was recycled from run 4 by decanting off the reaction mixture and washing it with a solvent being the reaction medium.

[c] The catalyst used in run 5 was left in the reaction mixture to which a new portion of CAL was added after each catalytic cycle (both these runs).

in Table 1 show that in both cases the catalyst selectivity towards crotyl alcohol was increased after each catalytic cycle. This increase was more pronounced in the second case. The 55.7% yield of UOL achieved in run 5.2 is equivalent to 834 catalytic cycles per Pt atom. The yields in the range 50–55% of crotyl alcohol are similar to those reported by other authors for liquid phase hydrogenation of CAL. The higher selectivity to UOL is likely the result of a large increase in the rate of the hydrogenation of the C=O group. Consequently, a high selectivity to UOL means a low selectivity for the hydrogenation of the olefinic C=C bond yielding only 3.4 and 6% of SAL (butyraldehyde) for runs 5.1 and 5.2, respectively. Fast conversion of CAL to UOL also means a low yield of the DA (7.7 and 10% for runs 5.1 and 5.2, respectively).

The improvement in selectivity might be the effect of several factors of different character. It can be explained as a reactant induced catalyst activation that takes place during the aging period. It has been suggested by Ponec and coworkers [4,11] and Margitfalvi et al. [19] that the surface of the Pt–Sn particles is mildly oxidized by the reaction mixture itself and the formed SnO_x species activate the aldehyde group.

Another possible explanation comes from the report by Englisch et al. [27]. They found that an increase in selectivity to crotyl alcohol occurs as Pt crystallites become larger. The XRD analysis of the reused PA-py-supported Pt–Sn catalyst (Fig. 1) showed that the mean size of Pt particles on the polymer is in the range 4–5 nm. These may favor the adsorption of the carbonyl bond.

We also believe that the nature of the polyamide support containing a pyridine moiety in the repeat unit significantly contributes in the decrease of the catalyst activity toward hydrogenation of the C=C double
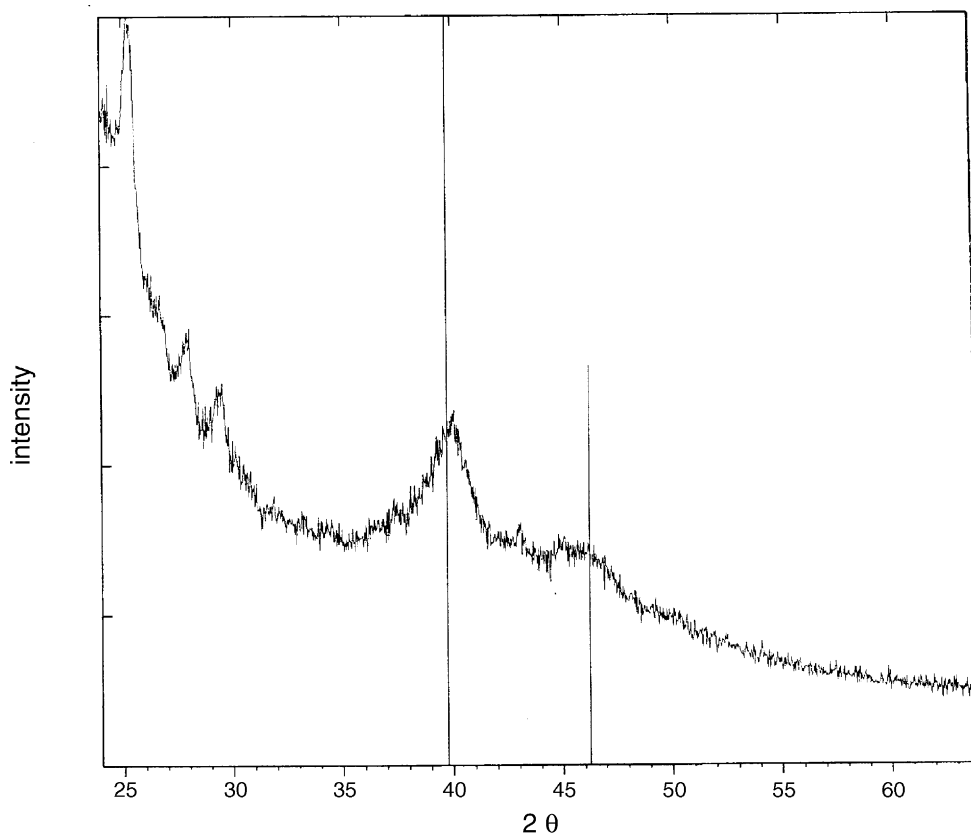

Fig. 1. XRD pattern of the reused PA-py-supported Pt–Sn catalyst.

bond. We have postulated before [29] that the metal active sites situated on the Npy donor centers possess a weak chemisorption ability for the olefinic C=C bond and suffer, therefore, a lower reactivity. This observation was in agreement with recent studies on hydrogenation of C=C double bonds over Pt catalyst supported on nylon [15].

In conclusion we have showed that the polyamides PA-py-supported Pt–Sn catalyst may serve as efficient catalyst for the hydrogenation of α,β-unsaturated aldehydes. Further efforts are in progress to improve catalyst selectivity towards hydrogenation of the C=O double bond and to elucidate the nature of the catalytic system.

Acknowledgements

References

[1] P.N. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, 1967.

[2] A. Giroir-Fendler, D. Richard, P. Gallezot, in: M. Guisnet, et al. (Eds.), Heterogeneous Catalysis and Fine Chemicals, Elsevier, Amsterdam, 1988, p. 171.

[3] G. Cordier, Y. Colleuille, P. Fouilloux, in: B. Imelik, et al. (Eds.), Catalyse par les Metaux, CNRS, Paris, 1984, p. 349.

[4] V. Ponec, Appl. Catal. A: Gen. 149 (1997) 27.

[5] A. Giroir-Fendler, D. Richard, P. Gallezot, Stud. Surf. Sci. Catal. 41 (1988) 171.

[6] C. Ando, H. Kurokawa, H. Miura, Appl. Catal. A: Gen. 185 (1999) L181.

[7] B. Coq, P.S. Kumbhar, C. Moreau, M. Warawdekar, J. Mol. Catal. 85 (1993) 215.

[8] H. Nishiyama, T. Kubota, K. Kimura, S. Tsuruya, M. Masai, J. Mol. Catal. A: Chem. 120 (1997) L17.

[9] P. Kluson, L. Cerveny, Appl. Catal. A: Gen. 128 (1995) 13.

[10] A.B. da Silva, E. Jordao, M.J. Mendes, P. Fouilloux, Appl. Catal. A: Gen. 148 (1997) 253.

[11] T.B.L.W. Marinelli, V. Ponec, J. Catal. 156 (1998) 51.

[12] T.B.L.W. Marinelli, S. Nabuurs, V. Ponec, J. Catal. 151 (1995) 431.

[13] T. Mizoroki, K. Seki, S. Neguro, A. Ozaki, Bull. Chem. Soc. Jpn. 50 (1977) 2148.

[14] S. Galvagno, Z. Poltarzewski, A. Donato, G. Neri, R. Pietropaolo, J. Chem. Soc., Chem. Commun. (1986) 1729.

[15] Z. Poltarzewski, S. Galvagno, R. Pietropaolo, P. Staiti, J. Catal. 102 (1986) 190.

[16] S. Galvagno, A. Donato, G. Neri, R. Pietropaolo, D. Pietropaolo, J. Mol. Catal. 49 (1989) 223.

[17] S. Galvagno, Z. Poltarzewski, A. Donato, G. Neri, R. Pietropaolo, J. Mol. Catal. 35 (1986) 373.

[18] S. Galvagno, A. Donato, G. Neri, R. Pietropaolo, Catal. Lett. 8 (1991) 9.

[19] J.L. Margitfalvi, A. Tompes, I. Kolosova, J. Valyon, J. Catal. 174 (1998) 246.

[20] P. Gallezot, A. Giroir-Fendler, D. Richard, Catal. Lett. 5 (1990) 175.

[21] F. Coloma, A. Sepulveda-Escribano, J.L.G. Fierro, F. Rodriguez-Reinoso, Appl. Catal. A: Gen. 150 (1997) 165.

[22] F. Coloma, A. Sepulveda-Escribano, J.L.G. Fierro, F. Rodriguez-Reinoso, Appl. Catal. A: Gen. 148 (1996) 63.

[23] M. Arai, A. Obata, K. Usui, M. Shirai, Y. Nishiyama, Appl. Catal. A: Gen. 146 (1996) 381.

[24] M. Arai, K. Usui, Y. Nishiyama, J. Chem. Soc., Chem. Commun. (1993) 1853.

[25] M.A. Vannice, B. Sen, J. Catal. 115 (1989) 65.

[26] M.A. Vannice, J. Mol. Catal. 59 (1990) 165.

[27] M. Englisch, A. Jentys, J.A. Lercher, J. Catal. 166 (1997) 25.

[28] A. Dandekar, M.A. Vannice, J. Catal. 183 (1999) 344.

[29] Z.M. Michalska, B. Ostaszewski, J. Zientarska, J.W. Sobczak, J. Mol. Catal. A: Chem. 129 (1998) 207.

[30] Z.M. Michalska, K. Strzelec, React. Funct. Polym. 44 (2000) 189.