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Effect of carbon support properties on enantioselective hydrogenation of isophorone over palladium catalysts modified with (−)-dihydroapovincaminic acid ethyl ester

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Abstract

The support-effect was investigated in the enantioselective hydrogenation of isophorone over Pd catalysts prepared on different carbon supports. Carbon supports with different specific surface area and activated carbons with different surface chemistry were used. The Pd catalysts, obtained by different reduction methods of the catalyst precursor, had different dispersion. The low dispersion was advantageous for the high enantioselectivity and the different supports had influence on the ee due to their different specific surface area and surface chemistry. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The enantioselective hydrogenation of α-keto esters over Pt catalyst modified with cinchona alkaloids and the hydrogenation of β-keto esters over Ni catalyst modified with tartaric acid are widely studied and published in the literature [1–13]. In both systems, high enantioselectivities were achieved (95%), although they were effective only in the hydrogenation of C=O bond. In our prochiral substrate, isophorone, a C=C double bond was reduced over Pd catalysts modified with (−)-dihydroapovincaminic acid ethyl ester. Previously, the effect of different catalyst supports (C, TiO$_2$, SiO$_2$, Al$_2$O$_3$, BaSO$_4$) on the enantiomeric excess was investigated and it turned out that the enantioselectivity strongly depended on the type of the support, and that a low surface area was advantageous for the higher optical yield [14,15]. Hydrogenations with Pd black catalyst afforded the best enantioselectivities (up to 55%).

In order to find out the role of the support in these enantioselective reactions we have

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screened different types of carbon support. We used carbons with different BET surface area, and we prepared activated carbons with different surface chemistry. In this paper, the characterization of the support and the influence of catalyst dispersion on ee is described.

2. Experimental

2.1. Materials

Pd/C catalysts were prepared according to the following procedures. The calculated amount of catalyst precursor (K_2PdCl_4) was added to the aqueous suspension of the support. The pH value of the solution was adjusted to 10–11 by addition of KOH. The suspension was boiled for an hour then HCOONa was added to the boiling mixture. After half an hour the suspension was cooled, the catalyst was filtered and washed with distilled water. The other method comprised, after similar preparation steps, the reduction of $Pd(OH)_2$ precursor with H_2 in water on 5 bar in a stainless steel autoclave with magnetic stirrer.

As support different carbon types were used: activated carbons, graphite and carbon black. The starting material for support preparation was a commercial activated carbon ROX (NORIT NV) which was washed for 18 h with 0.2 N HCl solution (type A). Type A was heated in nitrogen–oxygen (5%) mixture at 425°C for 10 h (type B). Type A was oxidized in 5 M HNO_3 for 10 h in a Sohxlet apparatus (type C).

Graphite (Aldrich) and carbon black (Printex G) were commercial products.

2.2. Hydrogenations

Hydrogenations were carried out in methanol, in a conventional apparatus, at room temperature, under atmospheric pressure or at 30 bar in an stainless steel autoclave with magnetic stirrer, at room temperature.

The reaction mixtures were analyzed by GC according to the procedure described in Ref. [1].

2.3. Characterization of the supports

The amount and the types of surface oxygen complexes on the carbons were determined by temperature-programmed desorption (TPD) under helium. Samples (around 100 mg) were placed in a U-shaped quartz cell and treated at room temperature for 1 h in helium flow (50 ml/min). Then, the temperature was raised at 5 K min^{-1} up to 1373 K. The decomposition products (carbon monoxide, carbon dioxide and water) were measured by on-line mass spectrometry.

The dispersion of the catalysts was measured in the TPD apparatus, the method was based on H_2 chemisorption.

The BET surface areas were determined by N_2 adsorption at 77 K with an equipment Coulter Omnisorp 1000 CX by continuous flow techniques.

3. Results and discussion

3.1. Characterization of carbons

The behaviour of carbon surfaces strongly depends on the oxygen containing surface complexes. The wettability and adsorptive be-
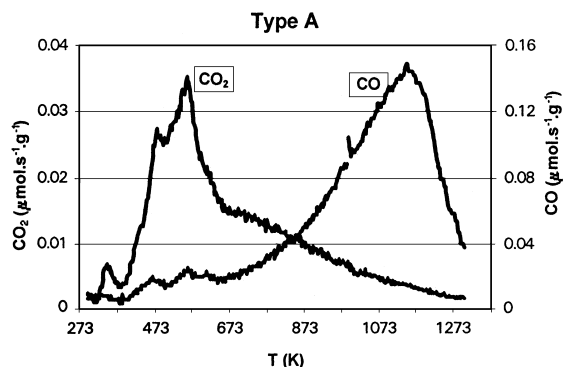

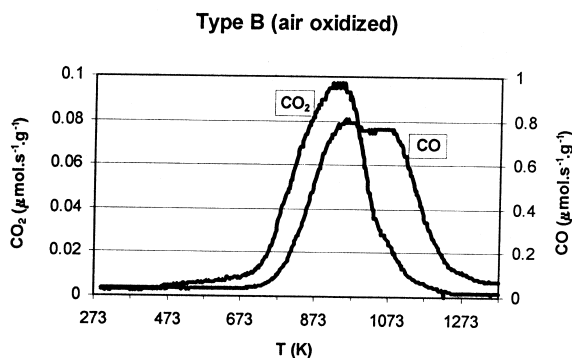Fig. 1. Gas evolution profiles (CO and CO_2) of support Type A, 5 K/min, He.

Type B (air oxidized)

Fig. 2. Gas evolution profiles (CO and CO_2) of support Type B, 5 K/min, He.

haviour of a carbon, as well as its catalytic and electrical properties, are influenced by the nature and concentration of these complexes [16].

Figs. 1–3 present duplicate TPD profiles for the supports type A (original), type B (air oxidized) and type C (HNO_3 oxidized).

It has been reported that the treatment of carbons with HNO_3 does not affect their physical morphology but alters their surface chemical properties, and HNO_3 treatment is effective to increase the surface acidity of the carbon [17,18].

The first CO peak is seen at ~ 900 K and the other at ~ 1100 K. The air oxidizing the surface of the carbon increases the CO-yielding complexes (e.g., phenol and carbonyl groups) more than the treatment with HNO_3. The nature of the CO_2-generating groups on these two oxidized samples is quite different. The CO_2 com-
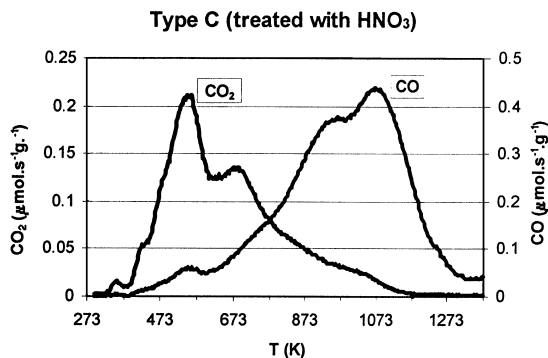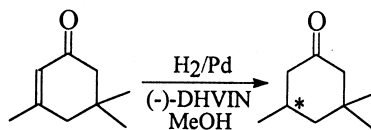
Type C (treated with HNO₃)

Fig. 3. Gas evolution profiles (CO and CO_2) of support Type C, 5 K/min, He.

Scheme 1. Hydrogenation of isophorone.

plex decomposed most rapidly on the HNO_3 char near 570 K, while for the air char it has a peak at ~ 900 K.

Free carboxyl groups decompose at relatively low temperatures with formation of CO_2, and that is the situation with the Type C support, the HNO_3 treatment increased the acidity of this carbon. In the case of Type B support, the evolution of CO_2 in TPD comes mainly from the decomposition of lactone and/or acidic anhydride type surface species. When carboxylic anhydrides are present, $CO_2 + CO$ are formed [19,20].

3.2. Catalytic tests

The catalysts prepared on the different carbon supports were tested in the enantioselective hydrogenation of isophorone (Scheme 1).

The enantioselectivities with different carbon supports and different preparation methods of the catalyst are summarized in Table 1.

Low catalyst dispersion was advantageous for the ee, this result is in agreement with our previous work [15]. This is the trend for each support and for each reduction method, occurring different dispersion of the catalyst (Table 2).

Table 1
Characteristics of the supports

Support	S_{BET}^a (m^2 g^{-1})	V_0 (N_2)[b] (cm^3 g^{-1})	CO^c (μmol g^{-1})	CO_2^c (μmol g^{-1})
Type A	1000	0.37	490	104
Type B	1130	0.46	2880	273
Type C	910	0.42	1995	740

[a] Calculated from the BET equation for N_2 at 77 K.
[b] Calculated from the Dubinin–Radushkevich (DR) equation for N_2 at 77 K.
[c] Amount of gas evolved in TPD experiments up to 1373 K.

Table 2
Effect of catalyst dispersion on ee
Conditions: 0.05 mol isophorone, 0.02 g (−)-DHVIN, 0.2 g AcOH, 30 ml methanol, 25°C.

Support	S_{BET} (m^2 g^{-1})	Dispersion of the catalyst		Pressure (bar)	Reaction time (h)	Conversion (%)	ee (%)
		a	b				
Type A	1000	0.48		1	2.5	100	9
			0.1	30	10	100	12
Type B	1130	0.41		1	2	100	3
			0.2	1	4	96	9
Type C	910	0.50		1	3.5	100	9
			0.2	1	7	97	15
Graphite	8.4	0.48		30	5.5	44	15
			0.2	30	8	64	18
C black	36	0.43		30	3	100	14
			0.1	30	6	100	20
Carbopal	1506	0.55		1	3.5	100	9

[a] The catalyst preparation method reduced with H$_2$.
[b] The catalyst preparation method reduced with HCOONa.

In the case of activated carbon supports, Pd catalyst on support type B (air oxidized) gave lower enantioselectivity compared to type A and C. On this support, carbonyl surface groups were in greater amount (Fig. 2), and it is possible, that the surface carbonyl groups compete with the substrate carbonyl group for bonding the modifier molecule. The HNO$_3$-treatment, i.e., the increasing of carboxylic groups on the carbon surface, had no influence on the enantioselectivity.

Supports with rather different surface area were examined: activated carbons, graphite and carbon black. The enantioselectivity depended not only on catalyst dispersion but also on specific surface area of the support. Where the surface area was lower, the enantioselectivity was somewhat higher.

4. Conclusions

The different carbon supports with different specific surface area and surface chemistry had influence on enantiomeric excess. The surface chemistry of the carbon did affect the enantioselectivity in the hydrogenation of isophorone, when the catalyst surface competes with the modifier in the solution bonding the substrate.

The reduction method, which influenced the catalyst dispersion, affected the optical yield also. On the same support, catalysts with low dispersion were more effective, this phenomenon was significant for each catalyst. The specific surface area of the carbon supports was quite different, those with much lower surface area were the best with respect to the optical yield.

Acknowledgements

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