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Kinetics, catalyst deactivation and modeling in the hydrogenation of β-sitosterol to β-sitostanol over microporous and mesoporous carbon supported Pd catalysts

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ABSTRACT

Kinetics of the hydrogenation of β-sitosterol to β-sitostanol is of industrial interest, since the desired product is used for suppressing cholesterol absorption in human body. The main drawback when using microporous Pd/C catalyst in this reaction is catalyst deactivation. In the current work the performance of microporous and mesoporous Pd catalysts in the hydrogenation of β-sitosterol was compared. The catalytic hydrogenations were performed in a shaking batch reactor in 1-propanol as a solvent. With larger amounts of catalyst less catalyst deactivation occurred due to the fact that the catalyst support acted also as an adsorbent. The mesoporous 4 wt.% Pd/C (Sibunit) catalyst showed higher sitosterol conversions and less catalyst deactivation compared to a microporous 5 wt.% Pd/C catalyst. The kinetics of the hydrogenation of β-sitosterol to β-sitostanol was studied over 4 wt.% Pd/C (Sibunit) catalyst at different temperatures between 60 °C and 80 °C and by reusing the catalyst. The origin for catalyst deactivation was poisoning by phosphorus and sulphur, as well as coking. In situ catalyst potential measurements showed that there is a correlation between catalyst deactivation and decreasing catalyst potential with increasing sitosterol conversion. A mechanistic kinetic model including a deactivation factor was successfully applied to this reaction and the kinetic parameters were determined.

1. Introduction

Nowadays, one of the most important problems for human health is high concentration of fats in food. Therefore, a lot of attention was devoted to β-sitostanol, which was proved to suppress cholesterol absorption in human body [1], and it is thus used as a constituent of some margarines available on the consumer market since 1995 [2]. The cholesterol lowering ability of sitostanol is superior to sitosterol, which is available from woody biomass. Furthermore, in margarine the sitostanols are used as esters. The raw material in the hydrogenation step of sitostanol esters production technology is β-sitosterol, a phytosterol being extracted mainly from tall oil pitch [3], which is the tall oil distillation residue. Sitosterol purification before hydrogenation is an essential production step [4]. The main reaction scheme is presented in Fig. 1. There exist more than 40 different phytosterols and typically the raw material from pulp waste streams contains besides β-sitosterol also β-sitostanol, a hydrogenated product of β-sitosterol as well as campesterol and its hydrogenation product campestanol. The difference in β-sitosterol and campesterol is in their side chain structures (Fig. 2).

Hydrogenation of β-sitosterol has been previously investigated over microporous Pd/C [5], Pd supported on polymer fiber [6] and some other Pd supported catalysts [7]. The challenge in industrial hydrogenation of sitosterol has been the catalyst deactivation. The origin for catalyst deactivation has been reported to be e.g. poisoning and sintering of Pd as well as pore blockage and coke formation [7]. Additionally it should be kept in mind, that sitosterol molecule is relatively large compared with the pore sizes in typical supported catalysts and thus when Pd is locating inside the microporous structure it can be partially inaccessible for sitosterol. The aim of the present work was to evaluate catalytic activity of a microporous Pd/C catalyst and compare its performance to that of a mesoporous Pd/C (Sibunit) in hydrogenation of β-sitosterol.

2. Materials and methods

2.1. Catalyst synthesis and characterization

4 wt.% Pd/C catalyst was synthesized by using Sibunit as the support material. The catalyst was prepared by hydrolysis of H_2PdCl_4 at pH 5–6 to yield so-called polynuclear hydroxocomplexes of palladium followed by their adsorption on carbon and increasing of

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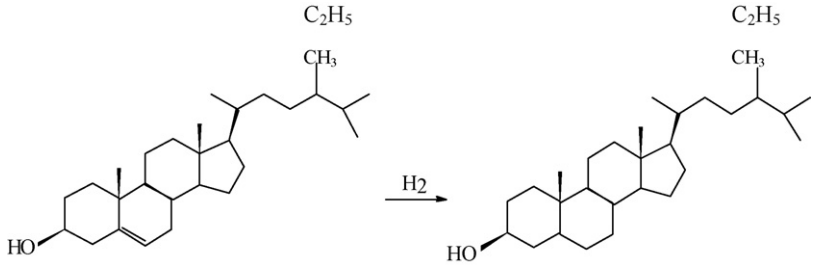

Fig. 1. Reaction scheme for β-sitosterol hydrogenation.

pH slurry up to Na/Pd ratio 1:2 [8]. Prior to the catalyst preparation, carbon was pre-oxidized by treating it by 5 wt% HNO_3 during 17 h, then washed by distilled water and dried. As a reference catalyst 5 wt.% Pd/C (Aldrich) was used.

The specific surface area of the catalysts was studied by nitrogen adsorption using Carlo Erba Instruments. The metal dispersion was measured by pulse CO-chemisorption (Micromeritics Autochem 2901). The catalyst was prereduced at 100 °C for 30 min with flowing hydrogen (AGA, 99.9995) and flushed with helium for 45 min. Thereafter the catalyst was cooled to ambient temperature and the CO-pulse chemisorption measurement was started by using 10 vol% CO in helium (AGA). The stoichiometric relationship between Pd and CO is assumed to be unity [9].

2.2. Reactor setup and analysis

The kinetic experiments were performed in a shaking reactor using 1-propanol as a solvent. The volume of the liquid phase was 110 mL and the pressure was set to 4 bars. The raw material according to the mass spectrometer results contained: 82 wt.% β-sitosterol, about 7 wt.% campesterol, 9 wt.% β-sitostanol and 1 wt.% campesterol. The β-sitosterol hydrogenation was carried out in the presence of several supported Pd catalysts. The samples were withdrawn periodically from the reactor which operated in a temperature range of 60–80 °C at 3.7 bar hydrogen. After addition of an internal standard solution consisting of heneicosanoic acid and betulinol, the reaction mixture was evaporated under nitrogen and silylated at 60 °C for 45 min with BSTFA-TMCS-pyridine solution and analyzed by a GC equipped with a HP-1 column (length 25 m, internal diameter 0.20 mm, film thickness 0.11 μm) using hydrogen as carrier gas and FI detector. The split ratio was 24:1. The products were identified with GC–MS. The catalyst potential was measured in situ using an Ag, AgCl/2 M LiCl electrode.

Additionally, ICP-OES (Inductively coupled plasma optical emission spectrometry) and IC (ion chromatography) techniques were used to detect the presence of chlorine and another potential poisoning agents in the raw material. For this purpose, a sample of 0.1 g sitosterol was immersed in 5 ml of concentrated HNO_3 (65%) and 1 ml H_2O_2 (30%). Later on, this solution was digested in a microwave oven (Anton Paar, Multiwave 3000) and diluted to 100 ml with deionized water. The ICP-OES was performed in a PerkinElmer, Optima 5300 DV and the target was to see the presence of S and P. Moreover, IC was performed in Waters, HPLC 2690 with conductometric detector and suppressor, using a Dionex IonPac AS22 column and the target was to investigate the presence of Cl^-, SO_4^{2-} and PO_4^{3-}.

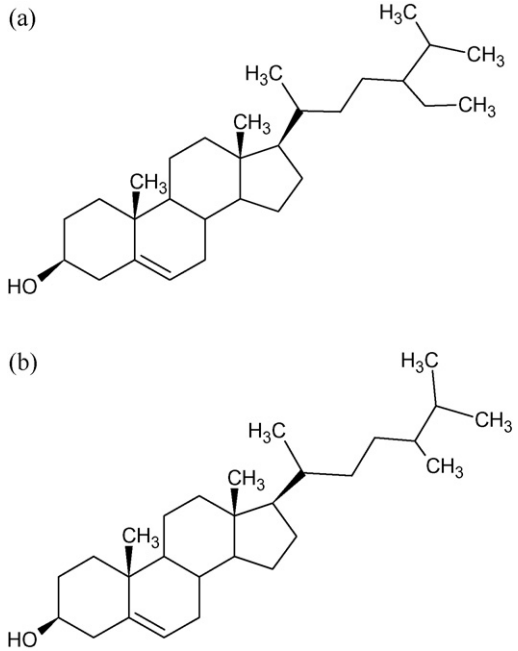

Fig. 2. Chemical structures of (a) sitosterol and (b) campesterol.

3. Results and discussion

3.1. Catalyst characterization results

The average Pd particle sizes determined by CO-chemisorption were for Pd/C (Sibunit) and for Pd/C (Aldrich) 3.1 nm and 5.4 nm, respectively. The specific surface areas for the former and the latter catalysts are given in Table 1, which shows that the specific surface area of the used Pd/C (Aldrich) decreased by 68% indicating that one reason for catalyst deactivation was coking (see Section 3.2). The pore size distribution of Pd/C (Aldrich) and Pd/C (Sibunit) is given in Table 2. The average pore sizes for Pd/C (Aldrich) and for Pd/C (Sibunit) were 2–3 nm and 7 nm, respectively. The microporous Pd/C (Aldrich) could thus be more easily prone to coking than Pd/C (Sibunit) when comparing the average pore size to the size of the reactant molecule.

Temperature programmed desorption of hydrogen showed the total amount of hydrogen desorbed from Pd/C (Aldrich) was 88% of the value for Pd/C (Sibunit) (Fig. 3, Table 3). The maximum temperature for hydrogen desorbed from Pd/C (Aldrich) was about 170 °C, whereas two maximum temperatures were obtained for Pd/C (Sibunit), i.e. 130 °C and 338 °C (Table 3). Although less hydrogen was desorbed at relatively low temperature over Pd/C (Sibunit)

Table 1
Specific surface areas for catalysts.

Catalyst	Specific surface area ($m^2/g_{cat.}$)	
	BET	Dubinin
5 wt% Pd/C (Aldrich)	974	1310
5 wt% Pd/C (Aldrich), used	313	439
4 wt% Pd/C (Sibunit)	243	286