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Palladium supported on filamentous active carbon as effective catalyst for liquid-phase hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol

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Dedicated to Prof. J. C. Charpentier

Abstract

Structured palladium catalysts suitable for three-phase reactions have been developed based on woven fabrics of active carbon fibres (ACF) as the catalytic supports. The Pd/ACF were tested in liquid-phase hydrogenation of 2-butyne-1,4-diol showing a selectivity towards 2-butene-1,4-diol up to 97% at conversions up to 80%. The catalyst multiple reuse with stable activity/selectivity in a batch reactor was also demonstrated. The reaction kinetics was studied and the main kinetic parameters were obtained. Assuming a Langmuir–Hinshelwood kinetics and a weak hydrogen adsorption a suitable kinetic model was developed consistent with the experimental data. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Filamentous active carbon; Catalyst reuse; Pd dispersion; Multiphase reactor; Intrinsic kinetics; 2-butyne-1,4-diol hydrogenation; 2-butene-1,4-diol

1. Introduction

2-butene-1,4-diol is an important industrial product. It is used in the preparation of pharmaceuticals, like endosulfan and pyridoxine (vitamin B6) and several insecticides (Winterbottom, Marwan, Viladevall, Sharma, & Raymahasay, 1997; Gräffe et al., 2001). Industrially 2-butene-1,4-diol is synthesized by selective hydrogenation of 2-butyne-1,4-diol. The reaction is usually carried out in an aqueous solution at elevated pressures (Hort & Graham, 1962; Hoffmann et al., 1974). The reaction network (Winterbottom et al., 1997) is schematically presented in Fig. 1, showing that the target product, *cis*-2-butene-1,4-diol, is an intermediate and can undergo further hydrogenation. When supported, palladium is used as a catalyst (Gouge, 1951; Hort & Graham, 1962; Hoffmann et al., 1974), mainly *cis*-2-butene-1,4-diol is formed, but its selectivity is a function of temperature, catalyst loading, solvent, addition of base, metal additives and catalyst support. In general, the variation in selectivity is due to a change of the rate of hydrogenation relative to the rate of mass transfer, or the

rate of triple bond hydrogenation (of acetylene alcohol) relative to that of a double bond (olefin alcohol).

In order to avoid mass transfer limitations and control the selectivity towards 2-butene-1,4-diol catalytic particles of small diameter are required. In a technical application the minimal size of these particles is, however, limited by the filtration of catalyst powder from water after the reaction. Moreover, reuse of powdered catalysts is quite difficult. Therefore, new catalytic materials for performing liquid-phase hydrogenations are required.

Recently, we reported a new concept of the reactor with structured catalytic bed for performing of multiphase reactions (Kiwi-Minsker, Yuranov, Höller, & Renken, 1999; Höller, Wegracht, Kiwi-Minsker, & Renken, 2000; Höller, Radevik, Kiwi-Minsker, & Renken, 2001a; Höller, Radevik, Yuranov, Kiwi-Minsker, & Renken, 2001b; Höller, Yuranov, Kiwi-Minsker, & Renken, 2001c). The reactor is designed as a bubble column staged with trays of filamentous catalytic materials. Filamentous woven cloths, made of different types of glass and composite mixed oxides (Kiwi-Minsker et al., 1999), were used as supports for the deposition of active components: Pt, Pd, oxides of transition metals, etc. This type of catalysts should be classified as arranged catalysts (Cybulski & Moulijn, 1998). They were

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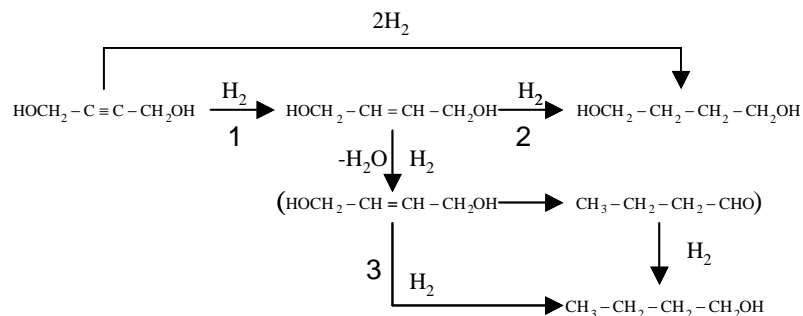


Fig. 1. Reaction scheme in hydrogenation of 2-butyne-1,4-diol over Pd/C catalyst (Winterbottom et al., 1997).

tested for intrinsic activity/selectivity in liquid phase hydrogenation of benzaldehyde to toluene (Kiwi-Minsker et al., 1999), nitrobenzene to aniline (Perez, Martinez de Lecea & Solano, 1997; Höller et al., 2000) and nitrite ions in water to nitrogen (Höller et al., 2001b). The palladium-based catalysts demonstrated high efficiency in these model reactions. The hydrodynamics in the bubble column staged with filamentous glass fabrics (cold model of the structured multiphase reactor), was also studied (Höller et al., 2000). The reactor was shown to have a low pressure drop during a fluid passage through the catalytic bed, redistribution of gas and liquid phases on each layer and narrow residence time distribution. Thus, this reactor design has shown an improved performance in multiphase reactions.

The results obtained motivated the application of filamentous catalysts in selective hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol. Pd supported on active carbon filaments (ACF) in the form of woven fabrics was tested for activity/selectivity in this reaction. Metallic palladium is known to selectively reduce triple bonds (Tedeschi & Clark, 1962) and Pd/C catalysts are known to hydrogenate 2-butyne-1,4-diol to 2-butene-1,4-diol with selectivity up to $\geq 99\%$ (Chaudhari, Gholap, Emig, & Hofmann 1987a; Chaudhari, Jaganathan, Kohle, Emig, & Hofmann, 1987b; Winterbottom et al., 1997). The use of activated carbon in the form of filamentous woven materials as catalytic supports have been already reported in the scientific literature (Jin, Park, Lee, & Ryu, 1996; Mochida et al., 1997; Mochida et al., 1997a,b; Perez et al., 1997; Yoshikawa, Yasutake, & Mochida, 1998; Moon, Park, Kim, & Seo, 1999; Ryu, Kim, Li, & Jaroniec, 1999; Mochida et al., 2000). These supports have advantageous characteristics as compared to traditional activated carbons, like: (a) high specific surface area (SSA) of 600–3000 m²/g; (b) morphological network formed by short micro-pores with narrow size distribution, ensuring fast adsorption/desorption; (c) easy reuse due to simple handling (could be bent and rolled); (d) low resistance to the passage of fluid; (e) high fluid permeability. ACF materials have been proven to have a great potential as catalytic supports, especially for expensive noble metals, since a high metal dispersion can be achieved via impregnation. Pd and Pt supported on ACF were highly active

in catalysing liquid-phase hydrogenations of nitrobenzene to aniline (Perez et al., 1997), C₆ olefins to corresponding saturated hydrocarbons (Okhlopkova, Lisitsyn, Likhobolov, Gurrath, & Boehm, 2000), and in the reduction of the oxygen dissolved in water (Moon et al., 1999).

The present paper reports on the activity/stability of Pd supported on ACF cloth catalysts in liquid-phase hydrogenation of 2-butyne-1,4-diol selectively to 2-butene-1,4-diol. The reaction kinetics was studied and kinetic model was proposed allowing a determination of the kinetic parameters. The catalyst reactivation for multiple reuse in a batch reactor module is also discussed.

2. Experimental

2.1. Preparation of Pd/ACF catalysts

Fabrics of activated carbon fibres (Taiwan Carbon Technology CO) were used as supports for catalyst preparation. The ACF supports were pre-treated in boiling aqueous solution (6.5 wt%) of HNO₃ and then rinsed in distilled water. The PdCl₂ (purum, Fluka, Switzerland) was used as a precursor for palladium deposition via ion-exchange from aqueous solution of Na₂PdCl₄. After drying, the catalysts were heated at 150°C for 1 h in hydrogen flow (100 ml/min, STP). The loading amount of palladium was determined by atomic absorption spectroscopy at 247.6 nm via Perkin Elmer "Atomic Absorption Spectrometer 1100A" instrument, supplied with a Pd hollow cathode lamp as a radiation source. The palladium catalysts are denoted as Pd(x)/ACF. The number in the parentheses is the loading amount in mass percentage.

2.2. Characterization of Pd/ACF catalysts

The fibrous active carbon catalyst is woven from long threads of ca. 0.5 mm in diameter (Fig. 2a). These threads consist of a bundle of elementary filaments of 3–5 μm in diameter as shown in Fig. 2b.

The BET SSA and pores size distribution (PSD) of the supports and catalysts were measured using N₂ adsorption–

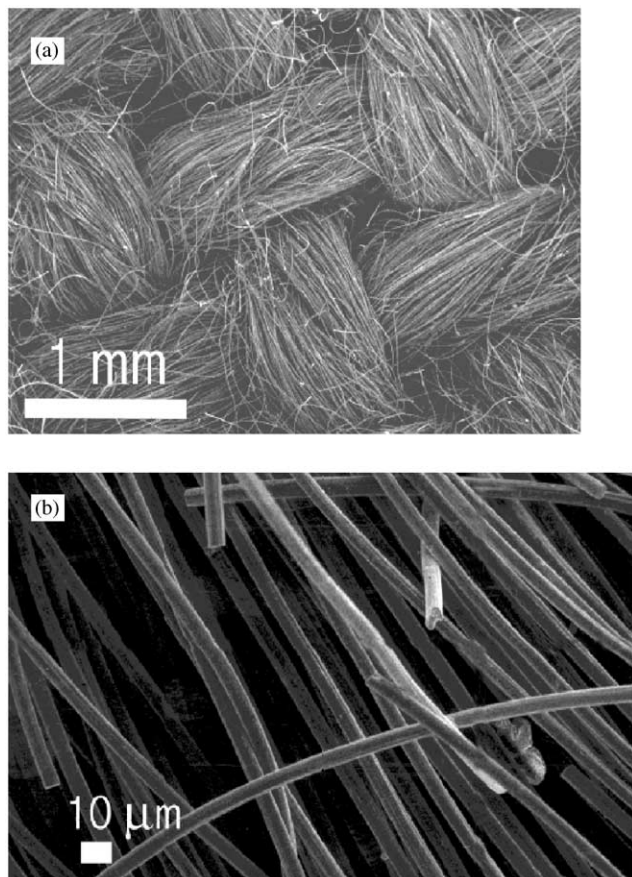


Fig. 2. Structure of woven active carbon fiber support (SEM), (b) SEM of active carbon filaments in a thread.

desorption at 77 K via a Sorptomatic 1990 (Carlo Erba) instrument. The samples were set in the ampoule in woven form. The SSA of the samples was calculated employing the BET method, while the Dollimore/Heal method was applied for the calculation of PSD.

The dispersion of palladium particles on ACF was determined by pulse chemisorption of carbon monoxide via “AutoChem 2910” instrument (Micromeritics S.A., Belgium). The catalyst with a charge corresponding to 25 μmol of Pd was placed in a quartz reactor. Before the measurements, the samples were pre-treated in the flow of He (10 ml/min (STP)) at 150°C and reduced in a flow of H₂ (20 ml/min (STP)) at 150°C.

2.3. Experimental set-up

The reaction was carried out in a batch reactor (150 ml autoclave, Buechiglas, Uster, CH), at isothermal conditions kept by a heating jacket. The autoclave is provided with a quantitative gas supply system and the experimental set-up is schematically shown in Fig. 3. The fibrous catalysts were placed between two metal gauzes (20 × 40 mm) fixed on the stirrer (Fig. 4). The amount of catalyst placed in the reactor was varied between 150 and 35 mg. The agitation speed

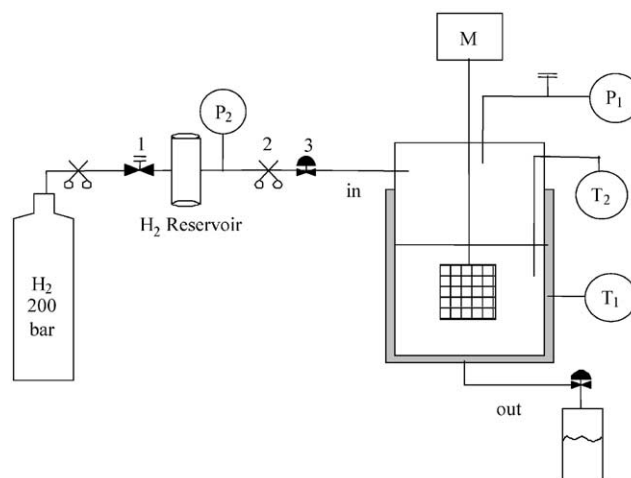


Fig. 3. Scheme of the experimental set-up.

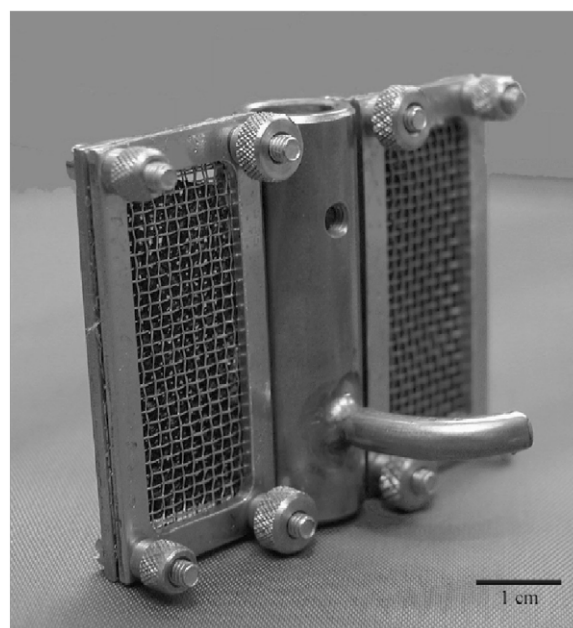


Fig. 4. Self-gassing hollow shaft stirrer with fibrous structured catalyst.

was kept at 1500 rpm to avoid mass transfer limitations. To achieve an efficient gas–liquid contact a self-gassing hollow shaft stirrer was used. The autoclave was fed with hydrogen (> 99.99%, Carbagas, Switzerland) under isobaric reaction conditions.

After the required temperature was attained, the reactor was flushed with hydrogen and pressurized to the desired level. During the course of the reaction, the pressure of H₂ in the reactor was maintained constant by supplying hydrogen from the reservoir at the rate of consumption. The pressure in the H₂ reservoir was monitored continuously allowing in situ measurement of the instantaneous hydrogen consumption.

The reaction temperature was varied from 20°C to 68°C, at H₂-pressures between 0.5 < P < 2.0 MPa. Butynediol

Table 1
Characteristics of the ACF catalysts

Sample	Catalyst	Content of Pd (wt%)	Dispersion of Pd (%)	Average particle diameter (nm)	BET (m ² /g)
1	2% Pd/ACF	2	42.9	2.6	780
2	3% Pd/ACF	2.95	33.2	3.4	780
3	4% Pd/ACF	3.98	28.6	3.9	780
4	5% Pd/ACF	4.82	19.6	5.7	780

(puriss. $\geq 99\%$, Fluka, Switzerland) was purified by recrystallization to obtain complete solubility in water, and its concentration was varied between 1.2 and 0.3 M.

Samples of liquids were withdrawn from the autoclave via a sampling tube and analysed by gas chromatography (Auto System XL, PERKIN ELMER) with He as a carrier gas and a FID-detector. Product separation was performed on a 30 m Perkin Elmer Elite Series 0.25 mm capillary column with a 0.25 μm coating, at temperature ramp of 20°C/min from 100–220°C.

The initial reaction rate, used as a characteristic of catalytic activity, was determined from the hydrogen consumption, r_0 (mol g_{Pd}⁻¹ h⁻¹). The selectivity towards 2-butene-1,4-diol was calculated as $S_i = c_i / \sum c_i$; with i = reaction products.

3. Results and discussion

3.1. Characterization of ACF supports and Pd/ACF catalysts

The SSA of the ACF cloths was 880 m²/g with an average pore diameter of 2.0 nm. After treatment in boiling HNO₃ and rinsing by water, the SSA was increased up to 950 m²/g with the same average pore diameter. The average pore diameter and SSA of ACF was almost not affected by palladium deposition, as seen from the Table 1. These results indicate no significant blocking of the ACF by supporting metallic Pd.

The dispersion of supported Pd and the ease of its reduction (characterized by a minimal temperature of reduction) are two important characteristics of a catalyst, related to metal interaction with the support. Palladium supported on granulated carbons, can attain a wide range of metal dispersion. The values of the dispersion depend on different factors, like the method of preparation, the precursor used, the type of support and the method of catalyst reduction to obtain palladium in its metallic form. Usually, palladium reduction is performed by heating a catalyst in hydrogen flow. In the present work palladium reduction was studied by TPR in hydrogen. The results indicated that the minimal temperature necessary for the reduction is in the range 130–170°C. After the treatment at 150°C for one hour in the flow of hydrogen, 100% of supported Pd was in its metallic form, as shown by XPS study. Therefore, all catalysts were reduced at 150°C for 1 h before the reaction.

Table 1 shows the dispersion and the average Pd particle diameter for different amounts of supported Pd. The dispersion decreases with increasing Pd loading from 0.43 to 0.19. These values are in agreement with those reported for ACF supports (Okhlopkova et al., 2000). The results of Table 1 confirm that ACF are suitable supports for metallic palladium, since particles of few nanometers can be obtained for the Pd loading of 2–5%. This concentrations are in the range of industrial Pd catalysts based on granulated active carbons.

3.2. Catalytic activity/selectivity of Pd/ACF

Hydrogenation of 2-butyne-1,4-diol was carried out in the batch-wise operated stirred tank reactor under isobaric conditions. In preliminary runs the agitator speed was varied in the range 1200–2000 rpm (conditions: 8 g butynediol in 100 ml H₂O; 70 mg Pd(4)/ACF; 0.6 MPa H₂; temperature 30°C). As the initial hydrogenation rate was not influenced by the stirrer speed, gas–liquid mass transfer limitation could be excluded.

The catalytic activities for catalysts with different Pd-loading are compared on Fig. 5. The initial hydrogenation rate, calculated as the rate of hydrogen consumption referred to the amount of palladium supported, r_0 (mol h⁻¹ g_{Pd}⁻¹) was observed to decrease with increasing Pd loading. This can be explained by the lower Pd dispersion. In fact, the calculated turnover frequencies (TOF) based on the measured specific surfaces of active Pd (Table 1), give the same values for all catalysts of TOF = 1.2 \pm 0.1 s⁻¹. The deposition of a smaller amount of palladium results in a higher dispersion, leading to a more efficient use of the expensive noble metal. The fact that the TOF is independent of the number of active sizes indicates that an influence of liquid–solid mass transfer can be neglected and the intrinsic reaction kinetics can be studied.

3.3. Reaction kinetics over Pd/ACF

The kinetics of the catalytic hydrogenation of butynediol was studied over Pd(4)/ACF catalyst varying the hydrogen pressure, butynediol concentration and the reaction temperature. Experimental results of the H₂ consumption as a function of time are presented on Fig. 6. For all runs constant hydrogen consumption was observed confirming a zero order towards butynediol up to approximately 80%

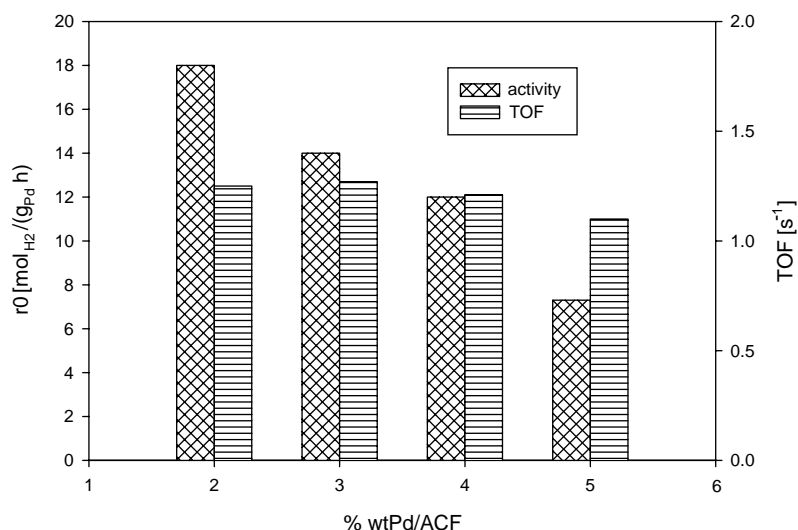


Fig. 5. Activity and turnover frequency (TOF) of ACF catalyst of different Pd loading.

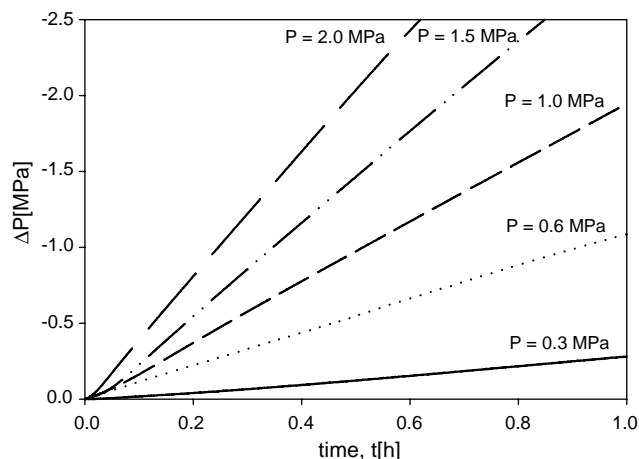


Fig. 6. Hydrogen consumption during hydrogenation of 2-butyne-1,4-diol over Pd(4)/ACF (change of the hydrogen pressure in the reservoir) conditions: 8 g butynediol in 100 ml of H₂O; 30°C; 65 mg of catalyst; 1500 rpm.

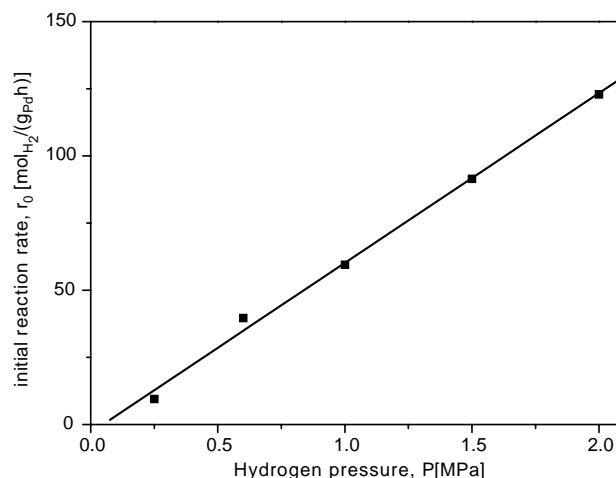


Fig. 7. Initial reaction rate as a function of hydrogen pressure (conditions: see Fig. 6).

conversion. A similar kinetic behaviour was reported in the literature (Gouge, 1951; Fukuda & Kusama, 1957; Chaudhari et al., 1987a,b). The initial hydrogenation rate as a function of hydrogen pressure is presented in Fig. 7. A first order towards hydrogen was found as already reported (Cerveny & Ruzicka, 1982).

With the same catalyst, Pd(4)/ACF, the initial hydrogenation rates were measured at different temperatures from 20°C to 68°C. The obtained apparent energy of activation ($E_A = 17.7$ kJ/mol) and the pre-exponential factor ($k_\infty = 0.54$ mol/h g_{Pd}) are close to the values reported (Gouge, 1951; Fukuda & Kusama, 1957; Chaudhari et al., 1987a,b). Nevertheless, the low apparent energy of activation may be due to an influence of mass transfer at temperatures higher than 30°C.

A typical plot of reactant and products concentrations as a function of time is shown in Fig. 8a. Within the first 2.5 h the butynediol concentration decreases linearly with time confirming the zero order towards butynediol. At the same time the concentration of butenediol increase and passes through the maximum at a reaction time of 3 h, corresponding to a butyne conversion of about 90%. The initial selectivity towards butenediol is close to 100% as can be seen from Fig. 8b, where the selectivity (S_{en}) and the product yields ($Y_i = C_i/C_{yn,0}$) are plotted against the butynediol conversion. Therefore, the direct formation of butanediol from butynediol, as suggested in Fig. 1, can be neglected. The supposed intermediates crotylalcohol and *n*-butyraldehyde were not found during the experiments, probably due to their small concentrations. Therefore,

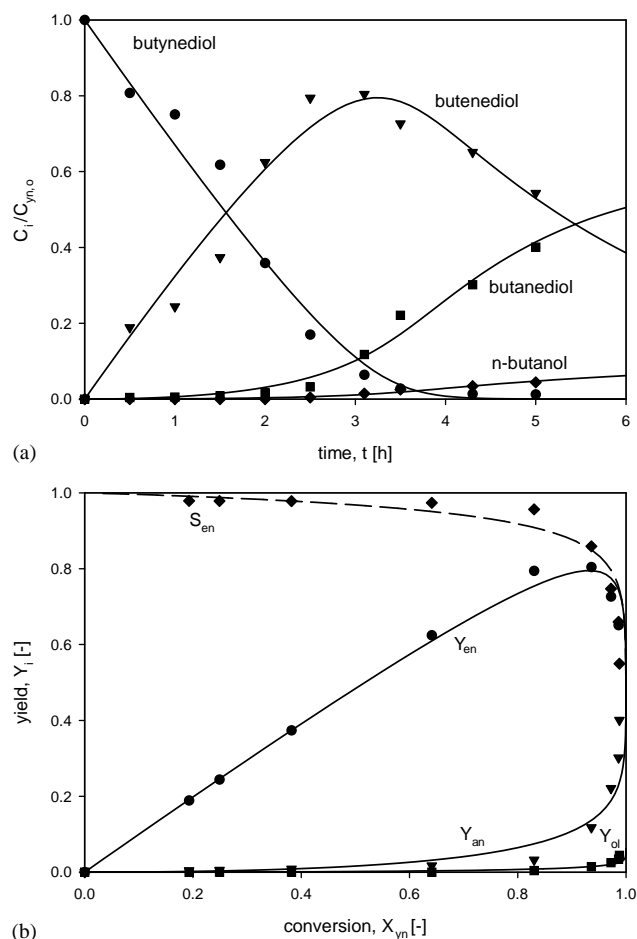


Fig. 8. (a) Measured and predicted reactant and product concentrations as function of time (conditions: see Fig. 6), (b) Measured and predicted selectivity of 2-butene-1,4-diol and product yields as function of conversion (conditions: see Fig. 6)

only a direct hydrogenation of butenediol to *n*-butanol (reaction 3) is suggested as a consecutive step in the reaction network.

The observed kinetics can be explained on the basis of a Langmuir–Hinshelwood relation assuming adsorption equilibrium of all components present in the mixture on the catalyst surface (Cervený & Ruzicka, 1982; Chaudhari et al., 1987a,b).

Based on the reaction scheme presented in Fig. 1 and assuming only a weak adsorption of hydrogen and neglecting the adsorption of water on the active sites, the transformation rate of butynediol can be expressed as follows:

$$r_1 = \frac{k'_1 K_{yn} C_{yn} K_{H_2} C_{H_2}}{1 + K_{yn} C_{yn} + K_{en} C_{en} + K_{an} C_{an} + K_{ol} C_{ol}} \quad (1a)$$

As the hydrogen pressure is held constant, the numerator in Eq. (1) can be simplified to

$$r_1 = \frac{k_1 C_{yn}}{1 + K_{yn} C_{yn} + K_{en} C_{en} + K_{an} C_{an} + K_{ol} C_{ol}} \quad (1b)$$

with $k_1 = k'_1 K_{yn} K_{H_2} C_{H_2}$. For the consecutive reactions leading to butanediol and *n*-butanol analogical expressions can be developed

$$r_2 = \frac{k_2 C_{en}}{1 + K_{yn} C_{yn} + K_{en} C_{en} + K_{an} C_{an} + K_{ol} C_{ol}} \quad (2)$$

with $k_2 = k'_2 K_{en} K_{H_2} C_{H_2}$,

$$r_3 = \frac{k_3 C_{en}}{1 + K_{yn} C_{yn} + K_{en} C_{en} + K_{an} C_{an} + K_{ol} C_{ol}} \quad (3)$$

with $k_3 = k'_3 K_{en} K_{H_2} C_{H_2}$.

The mass balances for butynediol and the reaction products is given by the following differential equation:

$$\frac{dC_{yn}}{dt} = -\frac{m_{cat}}{V_L} r_1, \quad (4)$$

$$\frac{dC_{en}}{dt} = \frac{m_{cat}}{V_L} (r_1 - r_2), \quad (5)$$

$$\frac{dC_{an}}{dt} = \frac{m_{cat}}{V_L} r_2, \quad (6)$$

$$\frac{dC_{ol}}{dt} = \frac{m_{cat}}{V_L} r_3. \quad (7)$$

In general, the adsorption equilibrium constant (K) for an acetylenic compound is known to be much higher than those of olefinic and aliphatic compounds (Cervený, Thanh, & Ruzicka, 1984). Therefore, at high concentrations of butynediol the adsorption of the products on the catalyst can be neglected resulting in a zero order towards the reactant, being in agreement with the experimental observations

$$\frac{dC_{yn}}{dt} = -\frac{m_{cat}}{V_L} r_1 \cong -\frac{m_{cat}}{V_L} (k_1/K_{yn}) \quad (8)$$

with $K_{yn} C_{yn} \gg (1 + K_{en} C_{en} + K_{an} C_{an} + K_{ol} C_{ol})$.

Eqs. (4)–(7) were solved numerically with a Rosenbrock method using Berkeley Madonna Software (Macey & Oster 1993–2001). The model parameters were estimated by fitting the simulated curves to the experimental data. As the adsorption equilibrium constants of the products are small compared to the adsorption constant of the reactant, a unique value was supposed, thus, reducing the fitted model parameters

$$K_{yn} \gg K \cong K_{en} \cong K_{an} \cong K_{ol}. \quad (9)$$

The proposed kinetic model describes the experimental data quite satisfactorily as can be seen from Fig. 8a and b. The error between the experimental and simulated data is in the range of 15%. The adsorption equilibrium constant of butynediol is found to be two orders of magnitude higher compared to those of the products: $K_{yn}/K = 105$.

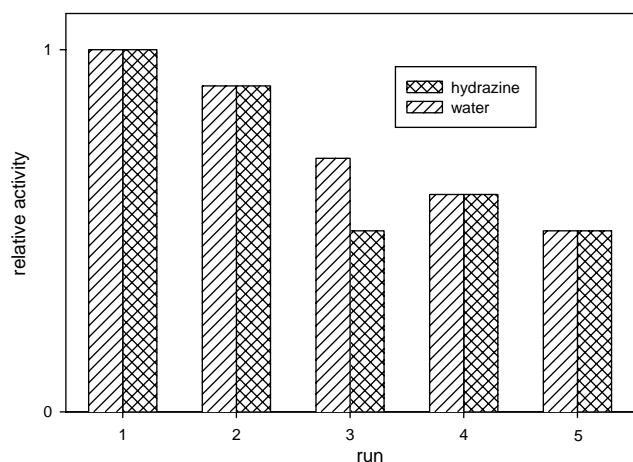


Fig. 9. Catalyst deactivation and regeneration for consecutive runs. (8 g butynediol in 100 ml H₂O; 70 mg Pd(4)/ACF; 0.6 MPa H₂; 1500 rpm; reaction time: 2 h).

3.4. Deactivation and reuse of Pd/ACF

The stability of the catalyst was tested by using the same sample, Pd(4)/ACF, in several reaction runs. Two different treatments were applied between each run: (1) cleaning of the catalyst surface by rinsing in water and (2) rinsing in water followed by reductive activation via boiling in hydrazine 10% aqueous solution for 2 h. The rinsing in H₂O followed by hydrazine treatment showed the best results (Fig. 9). After the first two runs, the catalytic activity stabilized at 50% of the initial value obtained with the fresh catalyst. No loss in the selectivity towards butenediol was observed. Thus, Pd supported on ACF in the form of woven fabrics can be reused in a batch reactor, avoiding a time-consuming step of catalyst separation via filtration after the reaction. This step is generally necessary for the catalysts based on granulated carbons. Moreover, these arranged catalysts are suitable materials for the reactors with structured catalytic beds for performing multiphase reactions.

4. Conclusions

- Activated carbon fibres (ACF) in the form of woven fabrics are shown to be suitable supports for the preparation of structured palladium based catalysts. Dispersion of metallic Pd up to 43% was obtained after Pd deposition via ion exchange from aqueous solutions and the catalyst reduction in hydrogen at 150 °C.
- Pd/ACF arranged catalysts were tested in the 2-butyne-1,4-diol hydrogenation in aqueous solutions with selectivity up to 97% towards 2-butene-1,4-diol at conversions up to 80%. Catalyst multiple reuse with stable activity/selectivity in a batch reactor was demonstrated.

- The reaction kinetics was studied, showing zero reaction order with regard to butynediol concentration and first order with regard to hydrogen pressure. The value found for an apparent activation energy was 17.7 kJ/mol.
- Assuming Langmuir–Hinshelwood kinetics and a weak hydrogen adsorption kinetic model was developed in agreement with the experimental data.

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