Liquid phase hydrogenation of 2-butyne-1,4-diol and 2-butene-1,4-diol isomers over Pd catalysts: roles of solvent, support and proton on activity and products distribution

M.G. Musolino [a], C.M.S. Cutrupi [a], A. Donato [a], D. Pietropaolo [b], R. Pietropaolo [a],*

[a] *Department of Mechanics and Materials, Faculty of Engineering, University of Reggio Calabria,
Loc. Feo di Vito, I-89060 Reggio Calabria, Italy*
[b] *ICOCEA, CNR, Bologna, Italy*

Abstract

Hydrogenation of 2-butyne-1,4-diol has been investigated over palladium supported catalysts. It was found that, besides butane-1,4-diol, side products such as *cis*- and *trans*-2-butene-1,4-diol, 2-hydroxytetrahydrofuran, *cis*- and *trans*-crotyl alcohol and *n*-butanol were also formed. The hydrogenation of the intermediates *cis*- and *trans*-2-butene-1,4-diol has been investigated too. On the basis of the results reported, a reaction scheme for the hydrogenation of 2-butyne-1,4-diol is proposed.

The influence of proton, nature of solvent and carbon support on activity and products distribution has been studied in the hydrogenation of *cis*-2-butene-1,4-diol. The use of water as solvent shows a better activity and selectivity to butane-1,4-diol and suppresses the hydrogenolysis reaction more than other solvents used. Addition of proton leads to a major formation of hydrogenolysis and isomerisation products. A higher activity and selectivity to isomerisation products were obtained on the palladium catalysts supported on acid modified carbon.
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1. Introduction

The catalytic hydrogenation of 2-butyne-1,4-diol is a process widely applied in the production of butane-1,4-diol, raw material used in the polymers industry and in the manufacture of tetrahydrofuran [1].

The hydrogenation of 2-butyne-1,4-diol has long been carried out over Ni or Ni-Cu catalysts at high pressures (150–300 atm) and temperatures (140–160 °C). Recently, the use of supported noble metals as catalysts has allowed to perform the reaction under mild operating conditions [2–6]. Literature data highlighted that, of all the metals studied for alkyne hydrogenation, supported palladium is the most active and selective [7]. However, the hydrogenation of 2-butyne-1,4-diol shows a complex reaction mechanism, due to the presence of several side reactions. The main intermediate of this reaction is *cis*-2-butene-1,4-diol, which is also a valuable product used in the synthesis of several insecticides, as endosulfan, and pharmaceuticals, as Vitamin B_6.

* Corresponding author. Tel.: +39-965-875256;
fax: +39-965-875248.
E-mail address: pietropaolo@ing.unirc.it (R. Pietropaolo).

Previous papers concerning this hydrogenation over Pd/C have been reported and show that the reaction proceeds through two steps: in the first one the hydrogenation leads to formation of *cis*-2-butene-1,4-diol that is subsequently reduced to 1,4-butanediol in the second step. Furthermore, the formation of side products from *cis*-2-butene-1,4-diol, such as *cis*- and *trans*-crotyl alcohol, *n*-butyraldehyde, *n*-butanol, γ-hydroxybutyraldehyde and an acetal, formed by condensation of γ-hydroxybutyraldehyde and butane-1,4-diol, was observed at the complete reduction stage [4,8]. The extent of formation of these products depends on the reaction conditions and therefore the study of side reactions becomes important.

In this work, a study on the hydrogenation of 2-butyne-1,4-diol over 0.5% Pd/C in a batch slurry reactor is reported with the aim to provide additional experimental evidence towards the possible mechanism of the reaction. A deeper knowledge of the reaction mechanism and the effect of reaction conditions, in particular on the second step of the hydrogenation of 2-butyne-1,4-diol, should be considered in order to address the reaction versus the desired product. So our attention was focused also in the hydrogenation of *cis*- and *trans*-2-butene-1,4-diol over 0.5% Pd/C, carried out independently. Furthermore, the influence of various reaction parameters, such as acidity of reaction medium, nature of the solvent and carbon supports properties on the activity and products distribution was evaluated in the hydrogenation of *cis*-2-butene-1,4-diol. The experimental results obtained have shown that the selectivity to butane-1,4-diol strongly depends on the acidity of the reaction medium, on the nature of the solvent and on the carbon support used.

2. Experimental

2.1. Materials

2-Butyne-1,4-diol (Aldrich, purity 99%), 2-butene-1,4-diol (Aldrich, predominantly *cis*, purity 95%), ethanol (Fluka, 99.8% analytical grade), tetrahydrofuran (Fluka, 99.8% analytical grade), ethyl acetate (Riedel de Haën, 99.7% analytical grade), were employed without further purification. Water was doubly distilled. Ultra-high purity hydrogen (Multigas,

Table 1
Support materials used for the preparation of the Pd catalysts

Support code	SA (m^2/g)	pH_{slurry}
SCXII	1100	10.26
Graphite	3	7.06
C–HNO$_3$	825	5.73
C–HCl	931	5.83

>99.9%) was used directly from cylinder for the catalytic experiments. *trans*-2-Butene-1,4-diol was synthesised by reduction of 2-butyne-1,4-diol with lithium aluminium hydride in tetrahydrofuran, following the experimental procedure reported in the literature [9].

The supports used for the catalysts preparation were: commercial activated carbon (Chemviron SC XII) and low surface area graphite (#4444, Asbury Graphite Mills Inc.). The C–HNO$_3$ and C–HCl supports were obtained by pretreatment of activated carbon with aqueous solutions of 14.4 M HNO$_3$ and 12.1 M HCl under reflux for 6 h, respectively. After treatment the samples were washed with hot distilled water several times, filtrated and dried overnight at 110 °C. Surface area measurements were made by BET nitrogen adsorption method at 77 K using a Micromeritics ASAP 2010. The pH of the aqueous carbon slurry (pH$_{slurry}$) was measured with a 691 Metrohm pHmeter, according to the procedure reported in [10]. Table 1 lists the main properties of the carbon used as supports. PdCl$_2$, supplied by Fluka, was used as precursor (Pd content 60%).

2.2. Catalysts preparation

All 0.5% palladium catalysts were prepared by incipient wetness impregnation method. The preparation was performed by addition of an acidic aqueous solution of PdCl$_2$ in HCl 0.1N to supports. After impregnation, the catalyst was dried at 120 °C for 2 h and reduced at 150 °C for 1 h under flowing hydrogen.

The CO/Pd ratio was measured by CO chemisorption at room temperature using a pulse flow technique. Prior to measurement each sample was pretreated by exposure to hydrogen at room temperature for 30 min followed by helium purge at 120 °C for 1 h. The metal dispersion was calculated assuming a stoichiometry CO/Pd = 1.

The main physico-chemical characteristics of the supported catalysts used are reported in Table 2.

Table 2
Main characteristics of the palladium supported catalysts

| Catalyst code	Pd loading (wt%)	Support	CO/Pd
PdA	0.5	SCXII	0.10
PdB	0.5	Graphite	0.01
PdC	0.5	C–HNO$_3$	0.06
PdD	0.5	C–HCl	0.08

2.3. Reaction procedure

The hydrogenation of 2-butyne-1,4-diol, *cis*-2-but-ene-1,4-diol and *trans*-2-butene-1,4-diol was carried out at 30 °C and at atmospheric pressure under H$_2$ flow in a five-necked flask of 100 ml, equipped with a reflux condenser and a thermocouple. The reaction temperature was maintained at the constant value (± 0.5 °C) by circulation of silicone oil in an external jacket connected with a thermostat. The catalyst (150–300 mg) was added to the solvent used (25 ml) and reduced in "situ" at 50 °C for 1 h under H$_2$ flow. After cooling at the desired reaction temperature, 15 ml of a 0.6 M solution of 2-butyne-1,4-diol or of *cis*-2-butene-1,4-diol or of *trans*-2-butene-1,4-diol in the appropriate solvent, containing tetradecane as internal standard, was added through one arm of the flask. The reaction mixture was stirred with a stirrer head having a permanent magnetic coupling at a stirring rate of 500 rpm. The progress of the reaction was followed by analysing a sufficient number of samples withdrawn from the reaction mixture. Products analysis was performed with a gas chromatograph (HP model 5890) equipped with a flame ionisation detector. The products separation was obtained by a wide-bore capillary column (CP Wax 52 CB, 30 m, i.d. = 0.53 mm). Quantitative analyses were carried out by calculating the area of the chromatographic peaks with an electronic integrator (HP 3395).

Preliminary runs, performed with different amounts of catalyst and different stirring conditions, have shown the absence of external diffusional limitations.

2.4. Products identification

Scheme 1, discussed in details later, shows the reaction intermediates and products of the hydrogenation of 2-butyne-1,4-diol. The reactant, 2-butyne-1,4-diol, and the reaction products *cis*- and *trans*-2-butene-1,4-diol, *cis*- and *trans*-crotyl alcohol, *n*-butyraldehyde, *n*-butanol, were identified by comparison with standard samples in GC and confirmed using the GC–MS technique. 2-Hydroxytetrahydrofuran was identified by comparing the mass spectrum with literature data. Carrying out the hydrogenation in alcoholic medium, another compound was revealed: a condensation product of 2-hydroxytetrahydrofuran and ethanol (an ac-
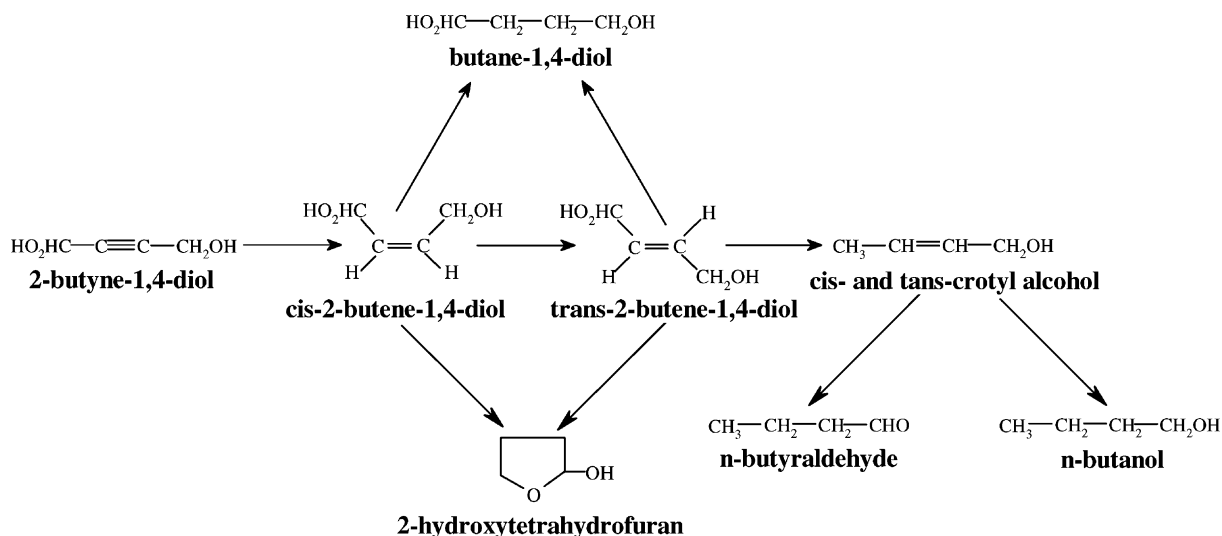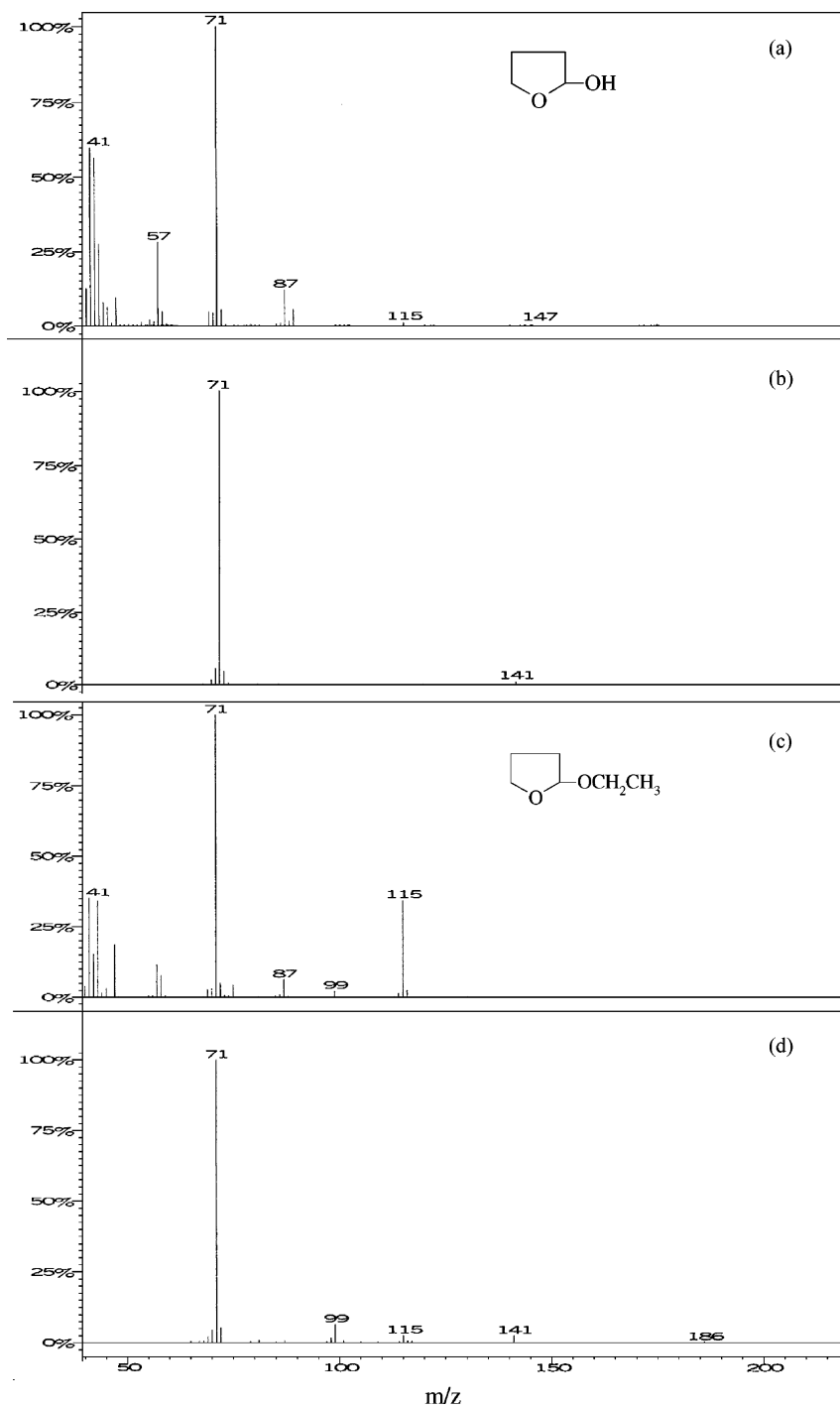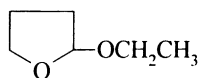

Scheme 1.

Fig. 1. GC–MS analysis of 2-hydroxytetrahydrofuran and 2-ethoxytetrahydrofuran, carried out using both techniques of electron ionisation and chemical ionisation. 2-Hydroxytetrahydrofuran: (a) electron ionisation; (b) chemical ionisation. 2-Ethoxytetrahydrofuran: (c) electron ionisation; (d) chemical ionisation.

etal) with structure

2-ethoxytetrahydrofuran

This structure was assigned on the basis of the following observations:

(i) a like compound is observed only in the presence of alcoholic solvents, such as ethanol and methanol, and it is absent in other solvents, as tetrahydrofuran, ethyl acetate and water;

(ii) 2-hydroxytetrahydrofuran slowly transforms into 2-ethoxytetrahydrofuran in ethanol and this reaction becomes faster in acidic ethanol;

(iii) an accurate evaluation of the GC–MS analysis of 2-hydroxytetrahydrofuran and 2-ethoxytetrahydrofuran, carried out by both techniques of electron ionisation and of chemical ionisation and reported in Fig. 1, was made. The mass spectrometric analysis of both compounds performed by using chemical ionisation with isobutane has not displayed the ion molecular peak (very weak), as major peak, but an intense fragment ion at m/z of 71. This fragment corresponds to $(M–OH)^+$ for 2-hydroxytetrahydrofuran and $(M–OCH_2CH_3)^+$ for 2-ethoxytetrahydrofuran. Since the fragmentation pathways of the molecular ion depend on the structure of the molecule, the results obtained suggest that both compounds present similar structures. Furthermore, the fragmentation patterns of 2-ethoxytetrahydrofuran, obtained by electron ionisation, show significant peaks at m/z of $115(M–H)^+$, $87(M–CH_2–CH_3)^+$, $71(M–OCH_2CH_3)^+$ which are consistent with the structure of the acetal assigned. All these observations confirm the formation of 2-ethoxytetrahydrofuran for which no spectral data are reported in the literature.

3. Results and discussion

3.1. Hydrogenation reactions

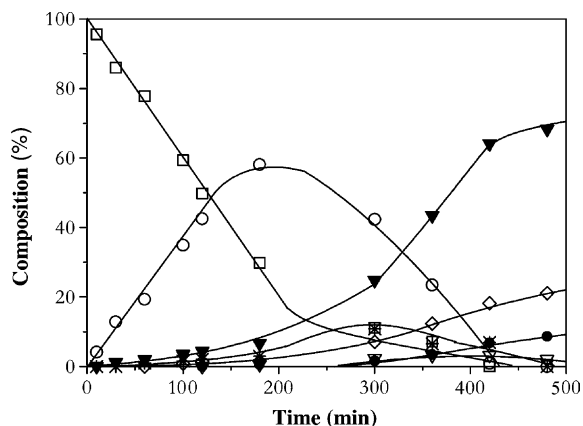Fig. 2 shows a typical plot products composition versus time for the hydrogenation reaction of

Fig. 2. Hydrogenation of 2-butyne-1,4-diol over PdA catalyst. Reaction conditions: $T_r = 30\,^\circ$C, $P = 1$ atm; solvent = ethanol; (□) 2-butyne-1,4-diol; (○) cis-2-butene-1,4-diol; (▼) butane-1,4-diol; (◇) 2-hydroxytetrahydrofuran; (✳) trans-2-butene-1,4-diol; (▽) cis- and trans-crotyl alcohol; (●) n-butanol.

2-butyne-1,4-diol over PdA catalyst carried out at 30 °C and using ethanol as solvent. Under the experimental conditions used, this reaction proceeds through two steps. In the first one the half-hydrogenation of alkyne occurs, resulting in the formation of cis- and trans-2-butene-1,4-diol with a large predominance of the cis isomer. However, the highest cis stereoselectivity was observed at the beginning of the reaction. The curve of disappearance of 2-butyne-1,4-diol with time is a straight line up to high conversions, indicating a zero order kinetic. This behaviour has been already observed in the catalytic hydrogenation of acetylenic compounds [4,11].

In the second step, besides the hydrogenation of cis- and trans-2-butene-1,4-diol to butane-1,4-diol, side reactions leading to double bond isomerisation and hydrogenolysis also occur. Such reactions are, in principle, not surprising due to the easier capability of palladium catalysts to promote hydrogenolysis and isomerisation reactions of alkenes [12]. The products observed are 2-hydroxytetrahydrofuran, cis- and trans-crotyl alcohol, n-butanol and 2-ethoxytetrahydrofuran. The formation of n-butyraldehyde by isomerisation of crotyl alcohol was found to be negligible. 2-Hydroxytetrahydrofuran is the cyclic hemiacetal of 4-hydroxybutyraldehyde. It is well known that the presence of alcoholic and carbonyl groups in the same molecule in 1,4 or 1,5 position leads easily to stable hemiacetals of five or six members ring [13]. Then formation

of 2-hydroxytetrahydrofuran takes place through the following sequence:

Cis- and trans-2-butene-1,4-diol   **1-butene-1,4-diol**   **γ-hydroxybutyraldehyde**   **2-hydroxy-tetrahydrofuran**
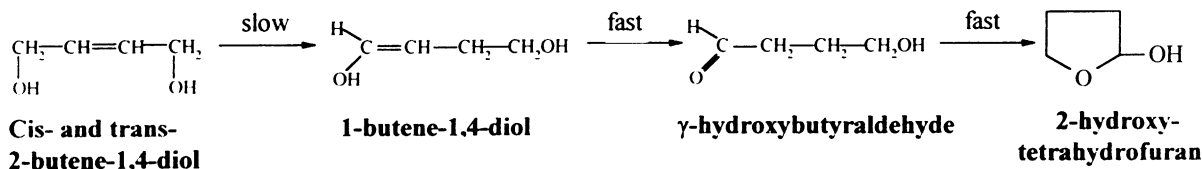
2-Ethoxytetrahydrofuran, formed by reaction between 2-hydroxytetrahydrofuran and the solvent, ethanol, is in equilibrium with 2-hydroxytetrahydrofuran. Therefore, for the sake of simplicity, data concerning their composition are reported together. The second step occurs after almost all 2-butyne-1,4-diol has been converted. This is a consequence of the strong adsorption of 2-butyne-1,4-diol on the active sites of the catalysts as compared to that of the olefin. Butane-1,4-diol was obtained with a yield more than 60% at 30 °C. In the literature it is reported that *trans* alkenes can be obtained in the hydrogenation of alkynes either as direct derivative or as a result of isomerisation of the *cis* stereoisomer [14]. Our experimental data show that only a small amount of *trans*-2-butene-1,4-diol was formed when the *cis* isomer is at the maximum composition (Fig. 2). This indicates that *cis*-2-butene-1,4-diol is the only direct product of the half-hydrogenation of the analogous alkyne, whereas the *trans* stereoisomer is formed from *cis* → *trans* isomerisation.

In order to obtain more information on the reaction mechanism, the hydrogenation of the intermediates *cis*- and *trans*-2-butene-1,4-diol has been carried out over PdA catalyst. A typical composition–time plot for the hydrogenation of the *cis* isomer, carried out using the same reaction conditions of 2-butyne-1,4-diol, is reported in Fig. 3. Butane-1,4-diol is the main product of the hydrogenation with a yield of about 60% at 30 °C. The reaction also leads to the formation of the side products, 2-hydroxytetrahydrofuran and, through *cis*- and *trans*-crotyl alcohol (detectable in the course of the reaction), *n*-butanol and *n*-butyraldehyde. Furthermore, *trans*-2-butene-1,4-diol is formed with a selectivity of about 15% at 30 °C and 80% conversion (Table 3). However, we should consider that the reactant *cis*-2-butene-1,4-diol contains about 5% of the *trans* isomer as impurity. Then *trans*-2-butene-1,4-diol transforms giving the same products of the analogous *cis* isomer. This is confirmed by data obtained

from the direct hydrogenation reaction of *trans*-2-butene-1,4-diol carried out independently.

On the basis of all these observations a possible reaction mechanism for hydrogenation of 2-butyne-1,4-diol is proposed and reported in Scheme 1. In order to get more light on the rate of single paths of the proposed mechanism, detailed kinetic studies will be published in forthcoming papers.

3.2. Effect of the solvent

The nature of the solvent influences both products distribution and reaction rate in the hydrogenation of *cis*-2-butene-1,4-diol, carried out over PdA catalyst at 30 °C. The selectivity, calculated at 80% conversion, the maximum yield to main reaction products and the specific activity (expressed per atom of palladium on the surface) are reported in Table 3. The rate of reduction is mainly affected by the polarity of the
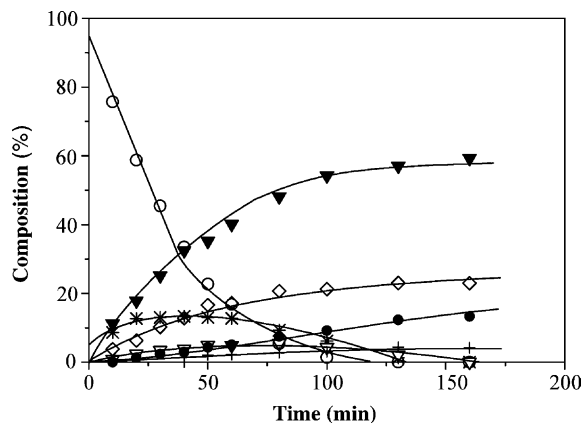

Fig. 3. Hydrogenation of *cis*-2-butene-1,4-diol over PdA catalyst. Reaction conditions: $T_r = 30$ °C, $P = 1$ atm; solvent = ethanol; (○) *cis*-2-butene-1,4-diol; (▼) butane-1,4-diol; (◇) 2-hydroxytetrahydrofuran; (✳) *trans*-2-butene-1,4-diol; (▽) *cis*- and *trans*-crotyl alcohol; (●) *n*-butanol; (+) *n*-butyraldehyde.

Table 3
Effect of the solvent in the hydrogenation of *cis*-2-butene-1,4-diol over PdA catalyst at 30 °C

Solvent	Dielectric constant (ε)	Solubility of H_2 ((mol% H_2) $\times 10^2$)[a]	r_1 ($mol_{butend}\ s^{-1}\ Pd_s^{-1}$)	Selectivity (%) at 80% conversion		Maximum yield (%)		
				trans-2-Butene-1, 4-diol	*cis*- and *trans*-crotyl alcohol	Butane-1, 4-diol	2-Hydroxytetrahydrofuran	*n*-Butanol + *n*-butyraldehyde
Water	80.1	0.14	3.73	25.0	–	72.1	24.6	–
Ethanol	25.1	2.06	3.69	15.3	5.8	59.3	23.0	17.5
Tetrahydrofuran	7.5	2.89	2.49	24.2	2.0	62.4	32.2	5.4
Ethyl acetate	6.0	–	1.42	25.6	2.3	65.3	28.6	6.1

[a] At 25 °C, 1 atm [15].

solvents. In fact, it increases on raising the dielectric constant and it is in the order $H_2O \cong C_2H_5OH >$ THF > ethyl acetate. Conversely, the hydrogen solubility changes in the opposite sense. Similar results in hydrogen reduction processes were already reported and may be explained on the basis of an easier interaction of H_2 with the metal catalyst surface as the solvent changes from ethyl acetate to water [16]. Moreover, water is a better solvent as far as the yield to butane-1,4-diol (more than 70%) and the activity are concerned and gives no hydrogenolysis reaction. On the other hand, tetrahydrofuran and ethyl acetate enhance the yield to 2-hydroxytetrahydrofuran reducing, in the same time, that to hydrogenolysis deriving products, *n*-butanol and *n*-butyraldehyde. These results are in agreement with the literature data which report that the hydrogenolysis reaction is unfavoured by less polar solvents [17].

Generally speaking, the explanation of the solvent effect on the catalytic hydrogenations has always been a contradicting issue. However, it cannot be excluded that in our conditions the loss of hydrogenolysis in water may depend on a deeper solvolysis of the carbon bonded OH group.

3.3. Effect of the proton

Results related to the catalytic hydrogenation reaction of *cis*-2-butene-1,4-diol in ethanol over PdA at 30 °C and at different proton concentrations are reported in Table 4. It is clearly evident from data in this table that the activity of the catalyst decreases as the proton concentration increases.

The addition of H^+ leads also to significant changes in the products distribution. On adding, in fact molar concentrations 0.01 and 0.1 of HCl, the yield to butane-1,4-diol decreases about three and seven times, respectively, in comparison with those calculated in absence of acid. Inversely, yields to double bond isomerisation and hydrogenolysis products increase. Furthermore, the formation of a remarkable amount of isomerisation product of crotyl alcohols, *n*-butyraldehyde, was observed. The maximum yield of *n*-butyraldehyde is about 13% on using a 0.1 M concentration of HCl. On the other hand, it is reported in the literature that isomerisation and hydrogenolysis reactions are catalysed by acids [17]. In order to get more light on such important effect some ex-

periments using 0.01 M ethanolic solutions of LiCl, NaCl and KCl were performed in order to exclude any influence of chloride ion on the rate of the process. Indeed, in these cases, only a small decrease of the rate was observed. Therefore, the experimental results display a peculiar behaviour of the solvated H^+ in decreasing the reaction rate. In principle, such acidic effect can be due both to a proton interaction with the palladium bonded olefin and/or the palladium surface. Although this last possibility cannot be excluded a priori, it is likely that the interaction of solvated H^+ with the palladium bonded olefin makes more difficult the hydrogenation reaction. However, even though the overall rate decreases, the selectivity towards the isomerisation and hydrogenolysis products, 2-hydroxytetrahydrofuran and crotyl alcohols, increases. Therefore, we infer that isomerisation and hydrogenolysis reactions are less sensitive to the proton effect than the hydrogenation process.

3.4. Effect of carbon supports properties

In order to investigate the effect of the chemical nature of the carbon support on the hydrogenation reaction of *cis*-2-butene-1,4-diol, new palladium catalysts were prepared using different modified activated carbons and a low surface area graphite and tested in ethanol at 30 °C. On refluxing the commercial SCXII carbon in aqueous solutions containing HNO_3 and HCl, respectively, we performed oxidative and non-oxidative modifications on the support surface with the aim of studying such effect on the catalytic behaviour of supported palladium. Indeed, these treatments lead to a small reduction of the surface area and do not affect significantly the palladium dispersion (Tables 1 and 2). Furthermore, they generally remove all impurities (if present) and, in particular, nitric acid treatment increases the amount of surface oxygen groups, especially acidic functional groups [18,19]. Table 5 lists the initial rate of the reaction based on moles of *cis*-2-butene-1,4-diol reacted per second and per gram of catalyst and the products distribution. It appears that PdC and PdD samples, having similar dispersion, display an improvement of the catalytic activity with respect to PdA. It is reasonable to attribute the markedly high activity to a reduction of impurities which can act as poison. Moreover, in the case of PdC

Table 4
Effect of the proton in the hydrogenation of *cis*-2-butene-1,4-diol over PdA catalyst, carried out at 30 °C and using ethanol as solvent

$[H_3O^+]_{add}$ (M)	r_1 (mol_{butend} s^{-1} Pd_s^{-1})	Selectivity (%) at 80% conversion		Maximum yield (%)		
		trans-2-Butene-1, 4-diol	*cis*- and *trans*-crotyl alcohol	Butane-1,4-diol	2-Hydroxytetrahydrofuran	*n*-Butanol + *n*-butyraldehyde
–	3.69	15.3	5.8	59.3	23.0	17.5
0.01	1.65	18.4	14.2	18.7	41.6	38.9
0.1	0.56	13.3	20.9	8.5	49.2	41.7

Table 5
Effect of the carbon support in the hydrogenation of *cis*-2-butene-1,4-diol, carried out at 30 °C and using ethanol as solvent

Catalysts	CO/Pd	r_1 (mol$_{\text{butend}}$ g$_{\text{Pd}}^{-1}$ s^{-1}) $\times 10^3$	Selectivity (%) at 80% conversion		Maximum yield (%)		
			trans-2-Butene-1, 4-diol	*cis*- and *trans*-crotyl alcohol	Butane-1,4-diol	2-Hydroxytetrahydrofuran	*n*-Butanol + *n*-butyraldehyde
PdA	0.10	3.50	15.3	5.8	59.3	23.0	17.5
PdB	0.01	2.62	32.5	0.4	41.4	56.5	1.2
PdC	0.06	6.54	26.3	3.0	23.1	66.1	10.7
PdD	0.08	5.33	20.5	3.8	20.8	66.9	12.3

catalyst, the increase of surface oxygen groups in the carbon can give an additional contribution to the activity [19]. However, no activity comparison is possible with PdB, since the catalyst used has a very low dispersion. Furthermore, the massive agglomeration of palladium particle in the last case, probably related to the very low surface area of the graphite support, precludes any reliable determination of the CO/Pd ratio.

As far as the products distribution is concerned, data in Table 5 show that the yield towards the isomerisation product, 2-hydroxytetrahydrofuran, is higher than that of the analogous palladium supported on untreated carbon. In this regard we recall that all supports used show different acidic characteristics, as assessed from measurement of pH_{slurry} (Table 1). C–HNO$_3$ and C–HCl supports are indeed more acidic than the commercial carbon and this contributes to explain the increase of isomerisation products ($\sim$66% in presence of PdC and PdD catalysts). On the other hand, the yield to hydrogenolysis deriving products, n-butanol and n-butyraldehyde, is poorly influenced by the pretreatment of the carbon support. A peculiar behaviour displays the palladium supported on the graphite. In this case a drastic decrease of the yields to hydrogenolysis products and a high yield to 2-hydroxytetrahydrofuran ($\sim$56%) were observed. Experimental data cannot be explained only accounting the pH_{slurry} value, slightly more acidic than that of the carbon. A parameter that can, in principle, influence the products distribution is the noble metal particle size. The PdB sample shows a poorer dispersion than other catalysts and a possible effect of the palladium particle size on the products distribution cannot be ruled out.

4. Conclusions

The results obtained in this work indicate that under the experimental conditions adopted, the hydrogenation reaction of 2-butyne-1,4-diol proceeds through a complex two-step mechanism involving cis-2-butene-1,4-diol as intermediate. The latter compound is further hydrogenated and undergoes isomerisation and hydrogenolysis reactions. The final products are butane-1,4-diol, 2-hydroxytetrahydrofuran, n-butanol and n-butyraldehyde. On the basis of the results obtained a scheme of reaction is proposed. The effect of the addition of proton, of the nature of solvent and carbon support was investigated in the hydrogenation reaction of cis-2-butene-1,4-diol. Water is a better solvent as far as the activity and the yield to butane-1,4-diol are concerned and precludes any hydrogenolysis reaction. The presence of proton decreases the reaction rate and enhances the yield towards the isomerisation and hydrogenolysis products. Properties of the carbon support play an important role on the products distribution.

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