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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Furfural Hemiacetals Germinal diols Tetrahydrofurfuryl hemiacetal Palladium catalyst	An entirely new and highly selective method for preparation of novel tetrahydrofurfuryl hemiacetals is de- scribed. The process is based on the catalytic hydrogenation of furfural in an alcohol under mild reaction conditions and at very short reaction times. As a highly active and selective catalyst palladium supported on calcium carbonate is used. Basic sites of the catalyst support enhance the formation of furfuryl hemiacetal as the intermediate which is instantaneously hydrogenated into stable tetrahydrofurfuryl hemiacetal. About 85–90 % yields of tetrahydrofurfuryl hemialkylacetals can be achieved within 20 min by reaction of furfural in alcoholic solutions at 60 °C and 0.3 MPa of hydrogen. The mechanism of reductive acetalization of furfural into tetra-

hydrofurfuryl hemialkylacetals is proposed.

1. Introduction

Furfural and 5-hydroxymethyl furfural (HMF) are the key chemicals produced from renewable agricultural sources. These platform chemicals are widely applied in the production of plastics, pharmaceuticals, agrochemicals, and its derivatives have the potential as fuel additives and lubricants [1–6]. Despite a large number of chemicals and materials prepared presently from furfural, further development of new upgrading processes of furfural is still a very attractive area of research. Depending on the process conditions, the type of catalyst and the solvent, furfural hydrogenation leads to the formation of a large number of products.

Using organic solvents, the main products of furfural hydrogenation are furfuryl alcohol, tetrahydrofurfuryl alcohol and 2-methyl furan, whereas, using aqueous solvent the products are cyclopentanone and cyclopentanol [7,8]. In alcoholic solvents, beside the reduction of the C=O group as well as the furan ring, the acetalization of furfural and other reactions can proceed, mainly in the presence of catalysts with acid properties [9–13]. The direct and reductive etherification of furans with alcohols was described for the preparation of furanyl ethers, which can be used as biofuels and specialty chemicals [6]. Over palladium supported on active carbon, alumina, SiO₂ and TiO₂, the reductive etherification of furfural with ethanol through the acetalization/hydrogenolysis pathways gives furfuryl ethyl ether (FEE) in yields up to 81 % [14]. The authors suggest that the intermediate is 2-(diethoxymethyl)furan, the formation of which is catalyzed by the palladium

hydride formed in situ. The consecutive hydrogenolysis of 2-(diethoxymethyl)furan leads to the formation of furfuryl ethyl ether. The hydrogenation of the furan ring was not observed. Under similar conditions in the presence of Pt/CeO2 catalyst the furfuryl diethyl acetal and furfuryl alcohol were obtained with 70 % and 27 % selectivity, respectively [15]. However, the furfuryl ethyl ether as a product was not detected. In contrast, during hydrogenation of furfural to tetrahydrofurfuryl alcohol, palladium supported on hydroxyapatite promotes the formation of furfuryl isopropyl ether as an intermediate [16]. On the other hand, in the reductive etherification of HMF in methanol to 2,5-bis(methoxymethyl)furan, catalyzed by Co₃O₄, it is considered [17] that the intermediate is the corresponding furfuryl alcohol, which undergo an acid-catalyzed attack by aliphatic alcohol to form the desired ether. At 140 °C and 2 MPa of hydrogen 98.5 % yield of the desired product was obtained.

We have found that in the presence of palladium catalyst supported on calcium carbonate the hydrogenation of furfural in ethanolic solution leads to the tetrahydrofurfuryl hemiethylacetal (THFHA) as the main stable product. The key intermediate of this reaction is furfuryl hemiethylacetal (FHEA) which over palladium catalyst is instantaneously hydrogenated to the tetrahydrofurfuryl hemiethylacetal (THFHA). To the best of our knowledge there is a lack of information in the literature about the preparation of stable hemiacetals from furfural.

The aim of this research is the study of the reductive acetalization of furfural in lower alcohols over palladium catalyst supported on calcium carbonate. The main products of the reaction are tetrahydrofurfuryl

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Fig. 1. XRD pattern of the 3%Pd/CaCO3 catalyst. (I) diffraction peaks of CaCO3 calcite, PDF-01-072-1651; (I) diffraction peaks of palladium.

hemialkylacetals formed in high yields. The identification, characterization and stability of these novel compounds was done using standard NMR and GC–MS analysis. The mechanism of acetalization reaction over palladium catalyst supported on calcium carbonate leading to tetrahydrofurfuryl hemialkylacetals is proposed.

2. Experimental

2.1. Materials

Furfural (FUR), furfuryl alcohol (FAL), tetrahydrofurfuryl alcohol (THFA), ethanol (96 % azeotrope with water), water-free ethanol, methanol, CD₃OD, n-propanol, cyclopentyl methyl ether, formaldehyde (37 %), furfuryl ethyl ether, palladium (II) chloride (99.9 %), and other reagents and solvents were purchased from Sigma Aldrich. Tetrahydrofurfuryl ethyl ether was purchased from FluoroChem. Calcium hydroxide was purchased from Centralchem (Slovakia).

2.2. Preparation of catalyst

Palladium catalyst supported on calcium carbonate (Pd/CaCO₃) was prepared by impregnation method. A suspension of 5 g of calcium hydroxide and an amount of Na₂CO₃ in 50 ml of distilled water was mixed at 40 °C for 4 h. Then a solution of palladium chloride in 10 ml of water was slowly added to the suspension and stirring was continued for 6 h. After raising the temperature to 80 °C 37 % formaldehyde solution (1 ml) was slowly added and the suspension was mixed 1 h in addition. The catalyst was collected on a filter and washed several times with distilled water. The Pd loading on the catalyst was 3 wt%.

2.3. Catalyst characterization

Surface area measurements were performed on a Micromeritics ASAP 2020 at -196 °C by adsorption and desorption of nitrogen. Before measurement, the samples were degassed at 250 °C in vacuum for 3 h. Isotherms were processed by the Brunauer–Emmett–Teller method (BET). Powder X-ray diffraction (XRD) patterns were acquired on a Bruker AX S D8 diffractometer using CuK_{α} radiation. Crystalline phases were identified by comparison with the JCPDS file. The metal particle size of the supported catalyst was determined by the Scherrer equation. The loading of palladium on the support was determined using Microwave Plasma-Atomic Emission Spectrometry (Agilent MP-AES).

The total basicity was determined by titration of the catalyst support as a suspension in toluene. Ca.150 mg of the catalyst was titrated using 0.01 mol L^{-1} solution of benzoic acid and bromthymol blue (pK_{HB} = 7.2) as an indicator. The measurements were made in triplicate.

2.4. Catalytic tests

The reaction of furfural in alcoholic solutions was conducted in a 50 ml pressure reactor connected with a flexible metal capillary to a hydrogen supply system at constant operating pressure and the consumption of hydrogen was recorded in defined reaction times. In a typical experiment the reactor was charged with an alcohol, furfural and the catalyst. The closed reactor was flushed with hydrogen 3 times and then immersed in a silicone oil bath with temperature control. After reaching the desired reaction temperature (5 min) the reactor was vigorously shaken using a vibrator. The reaction was stopped when during 3 min no consumption of hydrogen was observed. After the experiment the reactor was quickly cooled down, and small samples of the liquid phase were withdrawn and filtered through a $0.45\,\mu m$ syringe filter to obtain clear solutions. The quantitative determination of the liquid products concentration was done using gas chromatography (Agilent 8890, column 10 % SP2300, 70 cm x3 mm) and for the identification of organic compounds a gas chromatography-mass spectrometry (Shimadzu OP 2010, column HP-1, 50 m x0.2 mm) was used. The external standard method and response factors of the corresponding standard compounds were used. The samples of reaction products and samples prepared in deuterated solvent were analyzed by NMR. All NMR spectra were measured on Agilent/Varian VNMRS 600 MHz spectrometer using Nalorac 5 mm dual broadband gradient probe with the working frequencies of 599.7 MHz for ¹H and 150.8 MHz for ¹³C nuclei. Two to three duplicate runs were conducted for each experimental condition. The yields of the reaction products (in wt%) were calculated based on a measurement of standard, except THFHA where the yield was calculated using the response factor of tetrahydrofurfuryl ethyl ether. The error of determination of conversion and yield of products was \pm 3.6 %.

3. Results and discussion

3.1. Catalyst characterization

The physical properties of supported Pd catalyst are in Table S1. Xray diffraction study confirmed (Fig. 1) the formation of calcium carbonate by the reaction of calcium hydroxide with Na₂CO₃, which was then used as the palladium support. XRD revealed that the crystal structure of the CaCO₃ is calcite (PDF-01-072-1651). In the XRD pattern of the Pd/CaCO₃ catalyst, there are diffraction peaks indicating the presence of palladium particles with mean diameter 5.93 ± 0.15 nm. The peaks at 20 values of 40.1°, 46.6° and 68.1° are characteristic (111), (200) and (220) planes of isolated palladium crystalline particles. The surface area of the supported palladium catalyst was $11 \text{ m}^2 \text{ g}^{-1}$. The amount of basic sites measured through the titration using bromthymol blue as the indicator was 0.039 mmol.g⁻¹.

3.2. Reductive acetalization and identification of products

The selectivity of furfural hydrogenation in excess of ethanol was studied using 3%Pd/CaCO3 catalyst. The choice for the palladium catalyst was due to the efficiency of this metal to reduce the carbonyl group and the furan ring. The partial and total hydrogenation of furfural arising from the reduction of the C=O group and the furan ring, and the products of acetalization usually correlate with surface acidbase properties of the catalyst support, and lead to different distribution of reaction products of furfural hydrogenation in alcoholic solutions. The choice for 3%Pd/CaCO₃ as the catalyst was due to its basic properties and as is seen below for the low efficiency of this metal for the reduction of the C=O group and the furan ring at very mild reaction conditions, which eliminate undesired side reactions. As is evident from the results in Table 1 (Entry 1) under these conditions Pd/CaCO₃ catalyst in cyclopentyl methyl ether as a solvent and in the absence of an alcohol is almost inactive for hydrogenation of carbonyl group and furan ring. However, at the same condition furfural hydrogenation in ethanol (96 %) as the solvent is very rapid and within 15 min 94.8 % conversion of furfural is achieved. The gas chromatographic analysis of the reaction mixture has shown that with very high selectivity and the yield of 89.3 % an "unknown" product is formed (Table 1, Entry 2). Surprisingly, very high yields and selectivities were achieved in similar hydrogenation experiments performed in methanol and deuterated methanol (CD₃OD) but also in n-propanol 55.6 % yield of hemiacetal was obtained (Table 1, Entry 3,4 and 5). The identification of these products by GC-MS analysis has shown that despite different solvents used for the hydrogenation, the most abundant fragmentation ion observed in the spectra was always m/z = 71, which is consistent with the molecular formula C₄H₇O⁺, corresponding to fragment of a charged tetrahydrofurfuryl ring (Figs. S2 and S3). In the spectra the ion typical

Table 1

Furfural hydrogenation in the presence of 3 % Pd/CaCO₃ catalyst.

Conditions: 0.25 g furfural; 10 ml solvent; 0.07 g catalyst; reaction temperature 60 °C; 0.3 MPa hydrogen

Entry	Solvent	React. Conversio		Yield ^a , %			
		min	%	FAL	THFA	THFHA b,c	
1	CPME	30	8.1	2.8	3.8	0	
2	Ethanol, 96 %	15	97.8	1.5	2.6	89.3	
3	Methanol	30	95.1	1.3	2.7	88.9 ^d	
4	CD_3OD	30	94.7	1.7	2.2	90.8 ^d	
5 ^e	Ethanol, 96 %	30	42.5 ^f	-	-	-	
6	n-Propanol	30	100	5.2	6.7	55.6 ⁸	

FUR = Furfural; FAL = Furfuryl alcohol; THFA = Tetrahydrofurfuryl alcohol; THFHA = Tetrahydrofurfuryl hemiethylacetal; FEE = Furfuryl ethyl ether; THFEE = tetrahydrofurfuryl ethyl ether.

^a Determined by GC analysis.

- ^b Determined using response factor of THFEE.
- ^c The yield check by NMR spectroscopy.
- ^d THFHA.
- ^e FEE instead of FUR was used.
- ^f Conversion of FEE.
- ^g Tetrahydrofurfuryl hemipropylacetal.

for the furfural ring fragment, was absent (Fig. S4). Surprisingly, despite very mild reaction conditions and short reaction times the furan ring is completely hydrogenated. Therefore, during hydrogenation of furfural in lower alcohols, using $3\%Pd/CaCO_3$ catalyst, the possibility of the formation of the furfuryl type compounds (acetals, ethers) as the main products is excluded. On the other hand, under identical reaction conditions and using the same palladium catalyst, only 42.5 % of furfuryl ethyl ether (FEE) was converted into tetrahydrofurfuryl ethyl ether in ethanolic solution (Table 1, Entry 5, Figs. S5 and S6b-e).

3.2.1. Nuclear magnetic resonance analysis

For the identification of the unknown products NMR analysis was used. All measurements were done at 25 °C with approx. 500 µl of sample was dissolved in deuterated DMSO. The usage of DMSO allowed the direct observation of OH groups of hemiacetals and geminal diols. Besides basic ¹H and ¹³C spectra, 1D selective TOCSY also 2D various correlation NMR experiments (1H-1H COSY, 1H-13C (one-bond correlation) HSQC and ¹H-¹³C (multiple-bond correlation) HMBC were used. All pulse sequences were provided by the spectrometer vendor. NMR allowed unambiguous identification of all products. Complete assignment of ¹H and ¹³C resonances as well as correlation signals in 2D experiments is shown directly in the spectra. The hemiacetal poses 2 chiral centres (carbons C2 and C6) therefore they occur in 2 different stereoisomers. This is reflected in NMR spectra as doubling of all signals, which is well visible on signals of OH groups in ¹H spectra and signals of all carbons in ¹³C spectra. The ¹H and ¹³C NMR spectra of tetrahydrofurfuryl hemimethylacetal and hemiethylacetals are shown in Fig. 2 while their 2D correlation spectra can be found in the ESI, Figs. S6a, S7a-c and S8a-c. According to the NMR results it can be unambiguously confirmed that the main products of furfural hydrogenation in methanol and ethanol in the presence of 3%Pd/CaCO₃ catalyst are corresponding tetrahydrofurfuryl hemialkylacetals.

3.3. Effect of reaction conditions

The investigation of the effect of hydrogen pressure on the product distribution has shown (Fig. 3) that using the 3% Pd/CaCO₃ catalyst furfural hydrogenation could be carried out even at very low pressure (0.15 MPa). Under this pressure, during 20 min of reaction, about 90 % furfural conversion and 80.2 % yield of desired product THFHA is achieved. At higher hydrogen pressures the conversion of furfural and THFHA yield increases. The maximal yield of the product is achieved at 0.3 MPa of hydrogen, and at higher pressure the yield is slightly decreasing, probably as a result of undesired competitive hydrogenation of furfural into tetrahydrofurfuryl alcohol, which is accelerated by higher pressures.

As evidenced by Fig. 4, the reaction temperature has a significant effect on the product distribution. In the narrow temperature range from 40 to 60 °C the yield of THFHA increases from 78.5 % to 89.3 %, while the yields of both competitive undesired products, FAL and THFA decrease. It suggests that higher temperature accelerates more the rate of acetalization and promotes the equilibrium of furfural acetalization to the reaction intermediates, rather than the rates of competitive undesired hydrogenation reactions of furfural. However, increase of reaction temperature to 75 °C influences negatively the selectivity to THFHA, and the by-products comprise mainly hydrogenated compounds.

The effect of catalyst loading is presented in Fig. 5. The experiments were performed using ca. 5 wt% solution of furfural in ethanol (96 %). The data showed that increasing the catalyst loading only from 12.5 to 8.6 (expressed as weight ratio of furfural to catalyst) led to a significant increase in furfural conversion (from 27.0 to 85.3 %) and the yield of THFHA, from 22.1 to 73.7 %. The maximal furfural conversion and the yield of THFHA is achieved at the catalyst loading 6.6. Further increase of catalyst loading to 3.1 led to a slight decrease of conversion and the yield of desired product.







3.4. Effect of water

It is known from literature that hemiacetals are usually unstable compounds and in the presence of an acid, but not base, can undergo an elimination reaction that leads to acetals. The presence of water in an alcohol can lead to the formation of geminal diol, therefore, water might have a negative influence on the yield of hemiacetals. As is seen in the results in Table 2, when the concentration of water in ethanol is higher than 4 wt%, the conversion of furfural and the yield of THFHA determined by GC analysis decreases. As it was found by NMR analysis, the reaction mixtures prepared in ethanolic solutions containing water, beside the main reaction product, THFHA, also contain tetrahydrofurfuryl geminal diol (THFD). Under basic conditions in alcoholwater mixtures, water adds rapidly to the carbonyl group of the hemiacetals of furfural or tetrahydrofurfural. Thus, the concentration of water in alcohol determines the ratio of the formation of tetrahydrofurfuryl diols/hemiacetals. Both these compounds are stable enough to be detected by GC and NMR spectroscopy. The identification of geminal diol by GC–MS analysis has shown that the most abundant fragmentation ion observed in the spectra was m/z = 71, which is consistent with the fragment of a charged tetrahydrofurfuryl ring. The structure of the tetrahydrofurfuryl diol, being a relatively stable compound, was confirmed by detailed NMR analysis (Figs. 6 and S9). Probably the steric hindrance due to bulky tetrahydrofurfuryl substituent, the ring strain and formation of hydrogen bond between –OH group and oxygen in nonplanar tetrahydrofurfuryl moiety are important factors which contribute to the stability of this compound.

aldehyde establishing a reversible equilibrium with geminal diols and

Fig. 2. (a) ¹H NMR spectrum of tetrahydrofurfuryl hemiethylacetal in DMSO with signal assignment. "*" assigns OH groups belonging to geminal diol derivate and # marks signals belonging to other furfuryl derivatives. The two signals of OH hydrogens belong to 2 diastereoisomers of tetrahydrofurfuryl hemiethylacetal while the 2 OH signals in geminal diol are from the same molecule. After addition of D₂O signals of OH groups are attenuated as shown in the inset. (b) $^{13}\mathrm{C}$ NMR spectrum of tetrahydrofurfuryl hemiethylacetal in DMSO with signal assignment. "*" assigns signals of free ethanol. As evident from peak picking all signals are doubled because of the presence of the 2 diastereoisomers



Fig. 3. Effect of hydrogen pressure. Conditions: 0.25 g furfural; 10 ml ethanol (96 %); 0.07 g catalyst; reaction temperature 60 $^\circ$ C; reaction time 20 min.



Fig. 4. Effect of reaction temperature. Conditions: see Fig. 3; 0.3 MPa hydrogen.



Fig. 5. Effect of catalyst loading. Conditions: 0.25 g furfural; 5 ml ethanol (96 %); reaction temperature 60 °C; 0.3 MPa hydrogen; reaction time 25 min.

As it was found out, on the column used for the GC analysis both compounds eluted in the same peak, therefore, for determination of the contents of these reaction products in the samples containing water in ethanol NMR analysis was carried out. As illustrated in Table 2, Entry 1 and 2, in the experiments performed in water-free ethanol and ethanol (96 % azeotrope with water), the contents of THFD in these reaction products varies from almost zero to about 6%. However, when furfural hydrogenation was performed in ethanol containing 11.8 % and 15.7 % of water, the decrease of furfural conversion (to 91.4 % and 92.8 %), and the yield of the mixture of THFHA with THFD determined by the GC analysis (to 79.0 % and 76.7 %), was observed. The NMR analysis of these reaction mixtures has shown (Table 2, Entry 3 and Entry 4) that at higher concentration of water the formation of THFD further increases, i.e. the molar ratio of THFHA to THFD is changing to about 91:9 and 90:10, respectively. When in the experiment D₂O was used instead of water (Table 2, Entry 5), about 1/3 of THFHA and all THFD was

Ef	fec	t of	water	on	furfural	hvdre	ogenation	in	ethanolic solutions.	

Conditions: 0.25 g FUR; 5 ml ethanol + water; 0.038 g catalyst; reaction temperature 60 °C; 0.3 MPa hydrogen, reaction time 30 min.

Entry	Water in Conversion		Yield	Yield ^a , %		
	wt. %	%	FAL	THFA	THFHA	IHFD
1	0	98.7	1.4	2.8	90.1	~ 99: 1
2	4	97.8	1.5	2.6	89.3	94: 6
3	11.8	91.4	1.2	1.9	79.0	91: 9
4	15.7	92.8	0.9	1.9	76.7	90: 10
5	15.7 ^d	93.4	1.1	2.2	71.3	92 ^e : 8
6	36.5	68.3	1.3	2.2	42.0	_ c

^a Determined by GC analysis.

^b Determined by NMR analysis.

Not analysed.

^d Instead of water D₂O was used.

e 1/3 of THFHA was in deuterated form.

transformed into the deuterated form. At very high concentration of water in ethanol (36.5 wt%), the furfural conversion significantly decreases, and various reaction by-products, difficult to identify, are formed.

3.5. Stability of tetrahydrofurfuryl hemiethylacetal

A hemiacetal comprises an alcohol and ether group attached to the same carbon. Hemiacetals are stable under neutral or basic conditions but in acidic conditions are unstable and are converted to acetals [18]. The tetrahydrofurfuryl hemiethylacetal dissolved in ethanol is a stable compound. In order to verify whether the tetrahydrofurfuryl hemiethylacetal can be converted into the tetrahydrofurfuryl geminal diol in the presence of water, a part of the ethanolic solution of THFHA prepared by hydrogenation of furfural in ethanol (96 %), after separation of the catalyst, was diluted with water and heated at 60 °C under nitrogen for 60 min (Table 3, Entry1 and 2). The NMR analysis has shown that at the temperature of 60 °C about 10 % of THFHA during 1 h is hydrolyzed to THFD in ethanolic solution containing 28.7 wt % of water. Under identical conditions, but in the presence of Pd/CaCO₃ catalyst, similar conversion to THFD was also achieved (Table 3, Entry 3). Since the basic catalyst increases only the rate of hydrolysis, but does not affect the equilibrium itself, it indicates that the conversion of tetrahydrofurfuryl hemiethylacetal into the tetrahydrofurfuryl geminal diol is a reversible reaction, and under given conditions the equilibrium composition of both compounds was probably achieved. As indicated the data in Table 4, Entry 4 and 5, after removing of water from the reaction mixture (by treating with molecular sieves) the tetrahydrofurfuryl geminal diol is almost completely converted back into tetrahydrofurfuryl hemiethylacetal. These data unambiguously confirm that conversion of THFHA to THFD is a reversible reaction depending on the concentration of water in an alcohol. Thus, the geminal diol species should occur in the mechanism of furfural hydrogenation reactions in ethanolic solutions containing water.

3.6. Reaction mechanism

In order to explain and confirm the pathways of the reductive acetalization of furfural into hemiacetals, several tests were performed. To eliminate consecutive reaction of hemiacetals to acetals in an alcohol, the hydrogenation was performed under basic conditions. Therefore, the use of $Pd/CaCO_3$ catalyst, having the basic properties, can enhance the formation of hemiacetals and eliminate the subsequent conversion of hemiacetals into acetals. A proposed mechanism is shown in Scheme 1. The mechanism of reductive acetalization involves the base catalyzed activation of the hydroxyl group in the first step, which



Fig. 6. (a) ¹H NMR spectrum of tetrahydrofurfuryl geminal diol in DMSO after partial ethanol removal. Geminal protons of all CH2 groups as well as two OH groups are non equivalent because of the chirality of C2 carbon. As shown in inset signals of H2 and H5b protons are overlapping, which is reflected as second order effects in HMBC correlation spectra (see Fig. S9). "*" marks residual signals of other furfuryl derivatives. (b) ¹³C NMR spectrum of tetrahydrofurfuryl geminal diol after partial ethanol removal in DMSO with signal assignment." *" marks residual signals of other furfuryl derivatives.

is followed by addition of furfural to form the furfuryl hemiacetal intermediates. The rate of this reaction is increased by the presence of a base. The absence of furfuryl hemiacetal in all the reaction mixtures suggests that this intermediate is unstable and undergoes instantaneous hydrogenation of the furan ring in furfuryl hemiacetal to the corresponding stable tetrahydrofurfuryl hemialkylacetal.

As illustrated in Table 4, under comparable reaction conditions, in the absence of hydrogen, the Pd/CaCO₃ catalyst or Ca(OH)₂ alone do not exhibit activity for the conversion of furfural in ethanol (96 %) into furfuryl hemiacetal (Table 4, Entry 2 and 3). Other tests were carried out under identical conditions in the presence of 3%Pd/CaCO₃ catalyst but employing furfuryl alcohol and tetrahydrofurfuryl alcohol as the substrates instead of furfural. The aim was to rule out the THFHA formation via these furfural hydrogenation products. Therefore, it seems the most probable that the stable tetrahydrofurfuryl hemiethylacetals can be prepared from furfural in ethanolic solution only when both, basic palladium catalyst and hydrogen are employed (Table 4, Entry 1). Under these conditions, by the cooperative effect between basic support

The conversion	of THFHA	and THFD	at 60 °C	under nitroger	for 1 h.
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Entry	Hydrolysis of THFHA	Acetalization of THFD	THFHA: THFD ^a
1	RM-1; products composition	-	94: 6
2	$1.22 \text{ g RM-1} + 0.42 \text{ g H}_2\text{O};$	-	87: 13
3	$1.42 \text{ g RM-1} + 0.49 \text{ g H}_2\text{O};$	-	85: 15
	0.021 g 3 % Pd/CaCO ₃ ;		
4	-	RM-2; products composition	90: 10
5	-	3.0 g RM-2 treated with 3 + 2.2 g molecular sieves 5A	~ 99: 1

RM-1 and RM-2 are the reaction mixtures from experiments no.2 and 4 in Table 2, respectively.

^a Molar ratio determined by NMR analysis.

Table	4
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The conversion of reactants.

Conditions: (Conditions: 0.25 g reactant; 10 ml ethanol (96 %); reaction temperature 60 °C; 0.3 MPa hydrogen, reaction time 30 min								
Entry	Reactant	Catalyst	Atmosphere	Conversion,	Yield ^a , %				
				20	FAL	THFA	THFHA		
1	FUR	3 % Pd/CaCO ₃	hydrogen	97.8	1.5	2.6	89.3		
2	FUR	3 % Pd/CaCO ₃	nitrogen	0	0	0	0		
3	FUR	Ca(OH) ₂	hydrogen	88.9	0	0	0		
4	FAL	3 % Pd/CaCO ₃	hydrogen	28.7	< 1	21.7	0		
5	THFA	3 % Pd/CaCO ₃	hydrogen	0	0	0	0		

^a Determined by GC analysis.

and the hydrogenation capacity of metallic palladium, the unstable furfuryl hemiethylacetal primary formed by reversible reaction is instantaneously hydrogenated into the stable tetrahydrofurfuryl hemiethylacetal. To achieve the equilibrium of the reaction, the converted furfuryl hemiethylacetal must be continuously generated by acetalization of furfural. A basic catalyst increases the rate of furfuryl hemiacetal formation but has no effect on the equilibrium itself (Scheme 1). Both required catalytic properties are well achieved using a base-supported metal catalyst having low activity to reduce the carbonyl group in the raw material, i.e. in furfural, but having high efficiency to hydrogenate the furan ring to furfuryl hemiethylacetal intermediate at mild reaction conditions. Therefore, the presence of basic sites and hydrogen, and the activity of metallic palladium to hydrogenate the furan ring to furfuryl hemiethylacetal intermediate at very mild reaction conditions, appears



Scheme 1. Proposed mechanism of tetrahydrofurfuryl hemiacetal synthesis using Pd/CaCO₃ catalyst.

to be critical for achieving high yields of tetrahydrofurfuryl hemiethylacetal. It is important to emphasize that the used metal catalysts should be almost inactive for the competitive reduction of the carbonyl group and the furan ring in the starting furfural into the corresponding alcohols. These requirements are fulfilled by the $Pd/CaCO_3$ catalyst, which at very low hydrogen pressure and reaction temperature is almost inactive in the hydrogenation of furfural alone but facilitates almost exclusively the hydrogenation of furfural ring in the furfuryl hemiacetal into desired tetrahydrofurfuryl hemiacetal. However, when hydrogenation of furfural is performed in aqueous alcoholic solutions, the carbonyl compounds can exist in equilibrium with their hydrated forms (gem-diols). Therefore, the competitive pathway leading to THFHA through the hydrogenation of furfuryl geminal diol intermediate cannot be excluded.

4. Conclusions

Herein, we describe for the first time a facile and very selective synthesis of novel tetrahydrofurfuryl hemiacetals. The direct synthesis of these compounds is based on the reductive acetalization of furfural in alcoholic solutions using palladium catalyst supported on $CaCO_3$. The yields of the desired products, about 85–90 %, can be achieved within 15-30 min under very mild reaction conditions (40-60 °C and 0.15-0.3 MPa hydrogen). In the proposed mechanism the basic sites on the catalyst support enhance the formation of unstable furfuryl hemiacetals as the intermediates, which are instantaneously hydrogenated into the stable tetrahydrofurfuryl hemialkylacetals. Experimental data supported by GC–MS and NMR analysis show that in alcohol-water solutions furfural can be converted also to the tetrahydrofurfuryl geminal diol. The pathway to THFD proceeds through hydrolysis of tetrahydrofurfuryl hemiacetals. The hydrolysis is reversible reaction depending on the concentration of water in an alcohol.

The described method of synthesis of stable tetrahydrofurfuryl hemialkylacetals and the reasonably stable tetrahydrofurfuryl geminal diol is opening a new route for further utilization of furfural. The tetrahydrofurfuryl hemiethylacetal with the smell of freshly sliced apples can be applied, e. g. for the preparation of fragrances.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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