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Aqueous phase hydrogenation of furfural to furfuryl alcohol over Pd–Cu catalysts

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ABSTRACT

A series of Pd, Cu and bimetallic Pd–Cu catalysts with different metals loadings on various supports were prepared for the selective hydrogenation of furfural to furfuryl alcohol in water as a solvent. In the literature are almost missing the data about the selective hydrogenation of furfural in water. Among the catalysts screened, bimetallic Pd–Cu catalysts supported on MgO and $Mg(OH)_2$ prepared by electroless plating method showed the highest conversion and selectivity to furfuryl alcohol. The catalysts 5% Pd–5% Cu supported on MgO or $Mg(OH)_2$ exhibited at 110 °C and 0.6 MPa of hydrogen complete conversion of furfural and higher than 98% selectivity toward furfuryl alcohol after 80 min of reaction. The complete conversion of furfural and the same selectivity could be achieved after five catalytic cycles without extra catalyst treatment or reactivation. Based on physico-chemical characterization the role of Cu loading on the performance of bimetallic Pd–Cu catalysts was discussed. We assume that over Pd–Cu catalyst prepared by electroless plating method on the surface are present monometallic Pd^0 sites and closely interacting bimetallic Pd^0–Cu_2O catalytic sites. The Cu^+ sites participate on activation of C=O group in furfural. The interaction between active metal species and the support also influence the performance of catalyst.

1. Introduction

Furfural, a compound derived from hemicellulose is a key intermediate for a variety of chemicals and components for biofuels. Catalytic hydrogenation of furfural is an important reaction since it allows obtaining products such as furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, cyclopentanone [1,2]. Furfuryl alcohol is widely used in the production of resins, liquid resins for strengthening ceramics, fine chemicals, lysine, vitamin C, lubricants, dispersing agents, plasticizers and in the synthesis of fibers [3,4].

A variety of catalysts including both noble and non-noble metals have been reported for selective vapor as well as liquid phase hydrogenation of furfural. The liquid phase hydrogenation has been studied with different chrome and non-chrome catalysts [5]. Usually Cu based catalysts exhibit a remarkable selectivity toward hydrogenation of the carbonyl group leaving the C=C double bonds in the furyl ring unreacted. Copper containing catalysts, such as Cu–Zn mixed oxides with Al, Mn and Fe, Cu/MgO, Cu–Ca/SiO_2 and Pt on different supports are most frequently employed for furfural hydrogenation [6–8]. Excellent activity and selectivity to furfuryl alcohol in liquid phase hydrogenation exhibit Raney nickel catalyst modified by heteropolyacids salts [9] and amorphous alloy catalysts, such as Fe or Mo promoted Ni-B and Co-B catalysts [10–12]. A second metal or promoter is added sometimes for improving the activity or/and the selectivity, by increasing the surface area or acting as Lewis acid site to polarize the C=O bond. Nevertheless, the main drawback is that most of them cannot be reused [9]. Methanol, ethanol or isopropyl alcohol was used as the solvent. Recently, Villaverde et al. [13] described the liquid-phase transfer hydrogenation of furfural into furfuryl alcohol employing Cu–Mg–Al catalysts with 2-propanol as hydrogen donor.

Despite the number of investigations in this field, there are almost missing data about the selective hydrogenation of furfural in water as a solvent. Very recently Lesiak et al. [14] described liquid phase hydrogenation of furfural in water at 90 °C and 2.0 MPa of hydrogen pressure over Pd–Cu/Al_2O_3 catalysts. After 2 h of reaction and using huge loading of monometallic 5% Cu/Al_2O_3 catalyst

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(about twice as the amount of furfural) 100% selectivity to furfuryl alcohol at 81% conversion was obtained. Monometallic Pd and bimetallic Pd–Cu/Al_2O_3 catalysts were unselective for this reaction.

Furfural is the product of acid catalyzed dehydration of pentoses proceeding in water. Very strong impact on its price has process of furfural separation from the formed aqueous solutions. Therefore, for preparation of some chemicals and fuels from furfural it is highly beneficial to use as a source of furfural diluted furfural-water streams (e.g., azeotropes) obtained in traditional distillation [15], stream stripping [16] or developing membrane [17] and reactive distillation [18] processes. This will significantly reduce the energy needed for production of furfural feedstock. For example, diluted aqueous solutions of furfural can be highly selectively converted to cyclopentanone [2] or C_{15} and C_{17} fuel precursors [19]. In a recent publication [20] we have demonstrated highly selective catalytic conversion of furfuryl alcohol to cyclopentanone (more than 90 mol% yield) in water as the solvent at mild reaction conditions. The conversion of furfuryl alcohol to cyclopentanone is important step toward cyclopentanone starting from aqueous solutions of furfural. Very important is also conversion of furfuryl alcohol to 4-hydroxy-2-cyclopentenone [21], an intermediate for the preparation of various specialty chemicals.

In the present contribution we have investigated the hydrogenation of furfural in water as a solvent. The main objective was to study the influence of supported Pd–Cu catalysts on the activity and the selectivity of furfuryl alcohol formation. In addition, various methods of catalyst preparation on catalyst performance and the effect of reaction parameters such as, reaction temperature, hydrogen pressure and catalyst loading and recycling were studied to optimize the furfural conversion to furfuryl alcohol.

2. Experimental

2.1. Chemicals

Furfural (98% purity), furfuryl alcohol (98%), tetrahydrofurfuryl alcohol (98%), tetrahydrofuran (98%), 2-propanol (98%), dioxane (97%), methyl–isobutyl ketone (97%), palladium chloride, $CuSO_4{\cdot}5H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, formaldehyde (37%) and $NaBH_4$ were purchased from Sigma–Aldrich. Activated charcoal Norit (1030 $m^2\,g^{-1}$) was from Fluka and MgO (55 $m^2\,g^{-1}$) was obtained by calcination of hydroxide at 450 °C for 5 h. The supports were ground to a particle size between 0.075 and 0.125 mm. Furfural was purified by vacuum distillation and stored at −15 °C.

2.2. Catalysts preparation

Supported monometallic palladium catalysts with different Pd loadings were prepared by impregnation method using H_2PdCl_4 (dihydrogen tetrachloropalladate(II)) from aqueous solutions of $PdCl_2$ in hydrochloric acid. After impregnation a part of prepared catalyst precursors was reduced with formaldehyde or sodium borohydride and then was washed to remove chloride ions. Final concentration of chloride ions in waters was detected using $AgNO_3/HNO_3$. Other part of the precursors was dried at 120 °C for 2 h. After drying, the samples were calcined at 250 °C for 5 h in flowing air and then reduced at 300 or 450 °C for 2 h under flowing hydrogen. Bimetallic Pd–Cu catalysts with different metal loadings supported on activated carbon, MgO and $Mg(OH)_2$ were prepared by the following methods. Method A: a given amount of a monometallic Pd catalyst prepared by reduction with formaldehyde was placed into aqueous solution containing mixture of $CuSO_4.5H_2O$, NaOH, sodium–potassium tartrate and 37% aqueous solution of formaldehyde in the weight ratio 1:1:4.5:2.2. This solution was used in the amount to obtain the required loading of copper on the bimetallic catalyst. The mixture was heated at 40 °C and stirred 8 h, while the solution was regularly checked for the presence of copper ions in solution. Method B: the procedure was similar as in Method A, while the mixture heated at 40 °C was reduced with formaldehyde which was added separately during 1 h. The catalyst was designed 5% Pd–5% Cu/MgO (sep). Method C: 3% Pd–Cu/C catalysts with 5% and 10% loading of copper supported on activated carbon were prepared using co-impregnation method. The samples were dried at 120 °C for 2 h, calcined at 250 °C for 5 h in flowing air and then reduced at 300 °C or 450 °C for 2 h under flowing hydrogen. The catalysts are designed 3% Pd–5% Cu/C(CM) and 3% Pd–10% Cu/C(CM), respectively. Pd-hydrotalcite (Pd/HT) catalyst was prepared by a standard method described earlier [22]. Aqueous solutions of $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (Mg:Al = 2:1) were added dropwise to a NaOH solution under nitrogen atmosphere during stirring, which was maintained at 50 °C for 5 h. The pH of the reaction system was adjusted to between 9 and 10. When the reaction was completed, the formed white precipitate was aged in an aqueous solution at 70 °C for 2 days. The precipitate was filtered and washed repeatedly till the filtrate was neutral, then was dried at 110 °C for 24 h. Onto HT was impregnated H_2PdCl_4 solution to get 5 wt% of Pd. XRD spectra indicated that the sample has a typical structure of hydrotalcite.

2.3. Catalysts characterization

The BET surface area of the samples was determined by nitrogen adsorption at 77 K after activation of the sample in vacuum at 300 °C for 2 h. Powder X-ray diffraction (XRD) patterns were acquired on a Bruker AX S D8 diffractometer using CuKα radiation. Crystalline phases were identified by a comparison with the JCPDS file. The metal particle size distributions of the supported catalysts were determined by transmission electron microscopy: JEOL 1200EX microscope at accelerating voltage of 120 kV. The XPS signals were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a microfocused, monochromatic Al KαX-ray source (1486.6 eV). An X-ray beam of 400 μm size was used at 6 mA × 12 kV. Temperature programmed reduction (TPR) profiles of the catalysts were obtained with ChemiSorb 2720 (Micrometrics, USA) equipped with a TCD detector. The fraction of Pd exposed (CO/Pd) was estimated from dynamic CO chemisorptions, measured in a pulse system equipped with TCD detector. The chemisorption analysis was performed by passing pulses of CO until a constant CO peak area was observed. The exposed metal fraction was calculated from the moles of adsorbed CO per total moles of Pd impregnated onto the catalyst.

2.4. Experimental set up and reaction procedure

Furfural hydrogenation reactions were performed in a 50 ml stainless steel reactor connected with a flexible metal capillary to a hydrogen supply system recording at constant pressure the consumption of hydrogen in defined reaction times. The reactor was loaded with the liquid reaction mixture (usually 5 ml) and the catalyst. The air was purged out from the reactor by flushing with nitrogen and then four times with hydrogen. The reactor pressurized to the desired pressure with hydrogen was placed into thermostatic oil bath, and after 5–7 min of heating, the reactants were mixed by shaking the reactor using a vibrator. This moment was the start of reaction. A constant hydrogen pressure was maintained throughout the reaction. The vigorous agitation ensured that the measured rate of hydrogen consumption was not influenced by mass-transfer effects. Hydrogenation was stopped when during 3–5 min hydrogen consumption was practically zero. The samples were analyzed using a gas chromatography (Shimadzu GC-17A) equipped with flame ionization detector by the formerly described

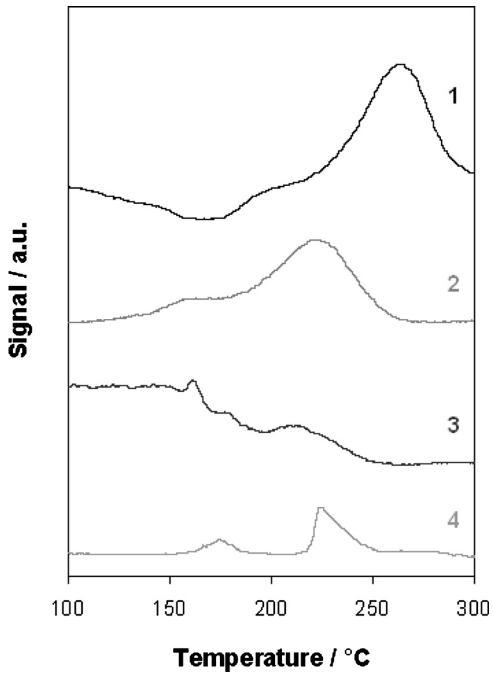

Fig. 1. TPR profiles of reduced catalysts: (1) 5% Pd–5% Cu/MgO; (2) 5% Pd–10% Cu/C; (3) 3% Pd–10% Cu/C (CM) reduced at 450 °C with hydrogen; (4) CuO

procedure [2]. The qualitative determination of products was done by the external standard method using aqueous solutions of each product with known concentration and response factors. Performance of catalysts was evaluated in terms of (%) conversion of furfural and (%) selectivity to furfuryl alcohol calculated on the amount of converted furfural.

3. Results and discussion

3.1. Catalyst characterization studies

From the large number of prepared catalysts the highest conversion and selectivity to furfuryl alcohol was achieved over 5% Pd–5% Cu catalysts supported on MgO, $Mg(OH)_2$ and activated carbon; hence, characterization of these catalysts is discussed in detail. The catalysts were characterized by X-ray diffraction, transmission electron microscopy, XPS, CO chemisorption and temperature-programmed reduction with H_2.

H_2-TPR was used to determine the reducibility of prepared supported catalysts. TPR profiles of supported bimetallic Pd-Cu catalysts prepared and reduced by different methods are displayed in Fig. 1. The TPR profiles of the reduced monometallic Pd/C and Pd/MgO catalysts did not show any peak at 80–300 °C (not shown) which confirms the presence of only metallic Pd in the catalysts. However, TPR profiles of the bimetallic catalysts supported on active carbon and MgO show main peaks at the temperatures of about 225 °C and 260 °C, respectively. These peaks should be assigned to the reduction of Cu_2O which remains present in these catalysts after reduction of the copper precursor with formaldehyde. As is seen from the figure the reduction of pure CuO normally takes place in two stages, Cu(II) to Cu(I) at about 175 °C and at about 225 °C to metallic copper. Compared with the catalyst supported on active carbon the reduction of Cu_2O takes place at similar temperature, however, the both peaks observed for catalyst supported on MgO are shift to higher temperatures (to about 195 and 260 °C, respectively). The most probable explanation for their reduction at higher temperature is that interaction with MgO stabilize both, Cu(II) and Cu(I) phases, which using the XRD technique were observed on the catalyst and thus decreases their reducibility [23,24]. Different TPR profile was recorded for the bimetallic Pd–Cu catalyst prepared by reduction with hydrogen. As is evident from Fig. 1 the TCD signal profile show three small peaks, indicating that copper oxide species with different redox behavior are present. In accordance with the foregoing TPR data the peaks appeared at higher temperatures belong to the reduction of Cu(II) and Cu(I) phases. The peak at about 160 °C can be attributed to the formation of alloys in bimetallic Cu–Pd catalyst that are easily reduced, what is in agreement with previous TPR studies [25].

CO chemisorption measurements were carried out in order to measure the number of accessible Pd sites. The results obtained with the reduced catalysts are reported in Table 1. The bimetallic Pd–Cu samples show only slightly lower CO/Pd ratios compared to the monometallic samples. For the monometallic 5% Pd/MgO and 5% Pd/C samples CO/Pd ratios of 0.16 and 0.19 were measured, respectively. The number of accessible Pd sites on the samples doped with 5% Cu loading decreases only slightly. This indicates that the formed Cu species inhibits the capability of palladium to chemisorb carbon monoxide only a little. Since the same samples of palladium catalysts were used for the loading of copper it indicates that accessible Pd sites are only partly decorated with the copper species formed by reduction of copper precursors.

The XRD patterns of the most active bimetallic Pd–Cu-catalysts obtained using different methods of preparation and reduction are shown in Fig. 2. The XRD pattern of catalyst 5% Pd–5% Cu supported on MgO revealed that the difraction peaks corresponding to MgO phases at 2θ values 42.9^0 and 62.3^0 are in this catalyst almost missing and in the pattern are plenty of peaks characteristic for the presence of $Mg(OH)_2$. It means that aqueous impregnation with palladium salt resulted in an almost complete transformation of MgO to $Mg(OH)_2$. Moreover, this catalyst displayed many diffraction peaks barely discernible suggesting the presence of highly dispersed phases with small particle sizes and/or not ordered structures. The peaks located at 2θ values of ca. 39.1°, 45.6° and 67.1° should be characteristic of isolated palladium crystallite, and two peaks at about 35.8° and 42.2° to Cu_2O phase. The diffraction peaks characteristic to isolated metallic Cu are not present. The same composition of Pd–Cu catalyst, but supported on activated carbon displayed the XRD pattern with well separated diffraction peaks assigned to metallic Pd and Cu_2O, with crystallite sizes 6.8 and 28.8 nm, respectively. The different copper species were detected for carbon supported 3%Pd–10%Cu catalyst prepared by co-impregnation method and reduced with molecular hydrogen at 450 °C. This catalyst displayed diffraction peaks suggesting the presence of metallic particles which can be attributed to the existence of different copper species, preferably CuO and Cu and Pd–Cu alloys. The absence of metallic Pd phase indicates that Pd–Cu alloys with different composition are present in this catalyst. The peaks appearing between 39.5 and 43.5° are usually associated with the formation of Pd–Cu alloys [26].

TEM pictures of Pd–Cu catalysts supported on MgO and activated carbon are shown in Fig. 3. From the pictures it is evident that in both catalysts the distribution of metallic particles is homogeneous and particles are very small.

The chemical states of palladium and copper species were determined by XPS analysis of 5% Pd + 5% Cu/MgO catalyst, and the spectra of the reduced catalyst are recorded in Fig. 4. The observed binding energy for Pd $3d_{5/2}$ in the catalyst was 334.98 eV, what is in agreement with those reported in the literature [27]. In contrary to TPR data, a part of noble metal on the catalyst surface is found in the oxidized state Pd(II), (binding energy 336.96 eV). Copper has two different oxidation states. The sample displayed the peak (Cu $2p_{3/2}$) at 933.61 eV, which was attributed to the copper oxidation state +2. The peak at binding energy 933.53 eV is probably inferred to have two species Cu^+ and Cu^0. On the basis of binding energy analysis

Table 1
Catalysts screening for the hydrogenation of furfural.[a]

Run	Catalyst	React. time (min)	Conversion (%)	S_{FAL}, (%)	CO/Pd[c]
1	5% Pd/HT	80	83.5	33.5	
2	5% Pd/MgO	130	92.1	59.6	0.16
3	5% Cu/MgO	80	3.8	–	
4	5% Pd/C	100	96.8	87.1	0.19
5	1% Pd– 10% Cu/MgO	150	99.5	86.3	
6	1% Pd–20% Cu/MgO	90	98.5	93.0	
7	3% Pd–10% Cu/MgO	40	99.2	85.6	
8	5% Pd–5 % Cu/MgO	30	100	98.7	
9	5% Pd–5% Cu/MgO	55	100	99.0	0.15
10 [b]	5% Pd–5 % Cu/C	25	100	91.2	0.17

S_{FAL} – selectivity to furfuryl alcohol.

[a] Conditions: 0.60 g FA, 10 ml H_2O, 0.10 g catalyst prepared by reduction with formaldehyde at 40 °C for 8 h, 130 °C, 0.8 MPa H_2.

[b] At 120 °C and 0.6 MPa.

[c] Chemisorption of CO.

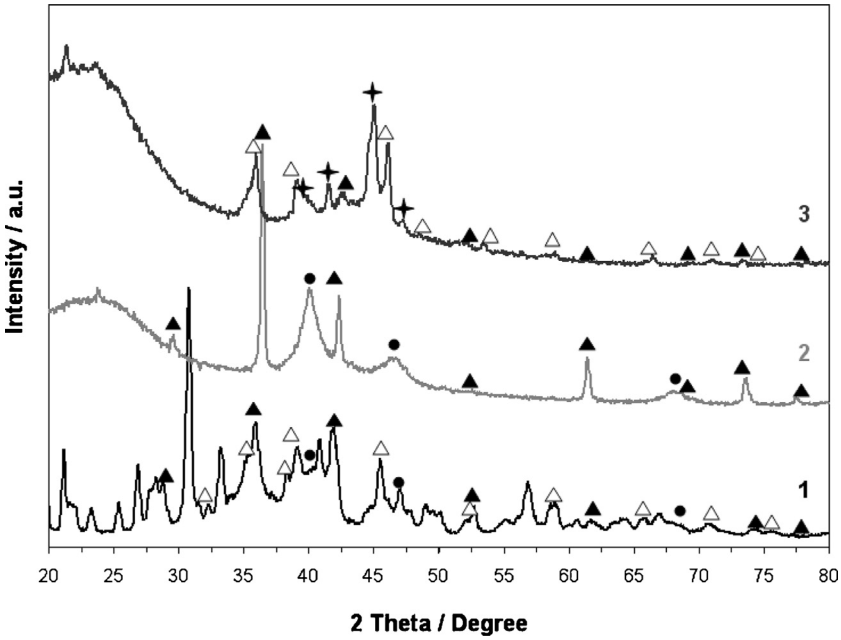

Fig. 2. XRD patterns of reduced catalysts: (1) 5% Pd–5% Cu/MgO; (2) 5% Pd–5% Cu/C; (3) 3% Pd–5% Cu/C (CM450); (●) Pd^0 phase; (▲) Cu_2O; (△) CuO; (✦) Pd–Cu alloys; (□) Cu^0.

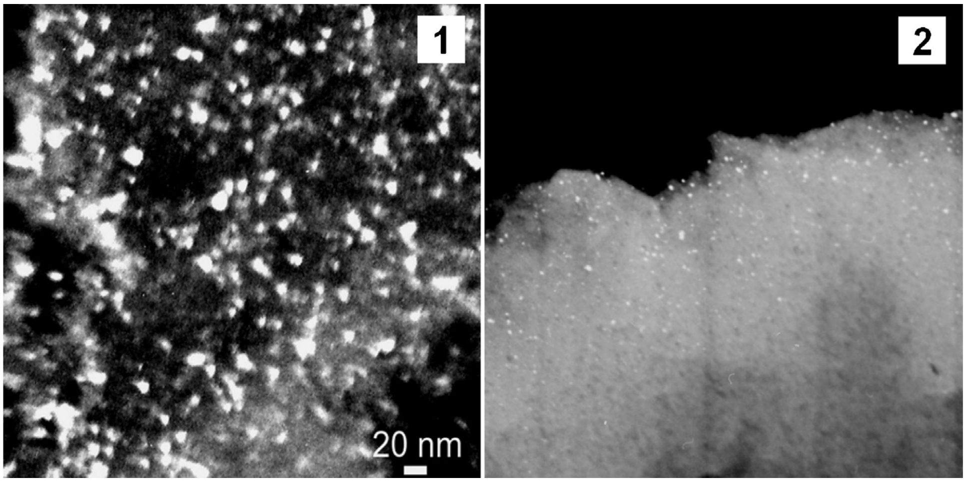

Fig. 3. TEM images of catalysts: (1) 5% Pd–5% Cu/MgO; (2) 5% Pd–5% Cu/C

alone it is impossible to make a distinction between them. Satellite peaks at 940.87 and 964.98 eV are evidence for CuO. Due to the differences in symmetry of CuO and Cu_2O nanoparticles, the percentage of Cu(II) state is probably much lower than was observed

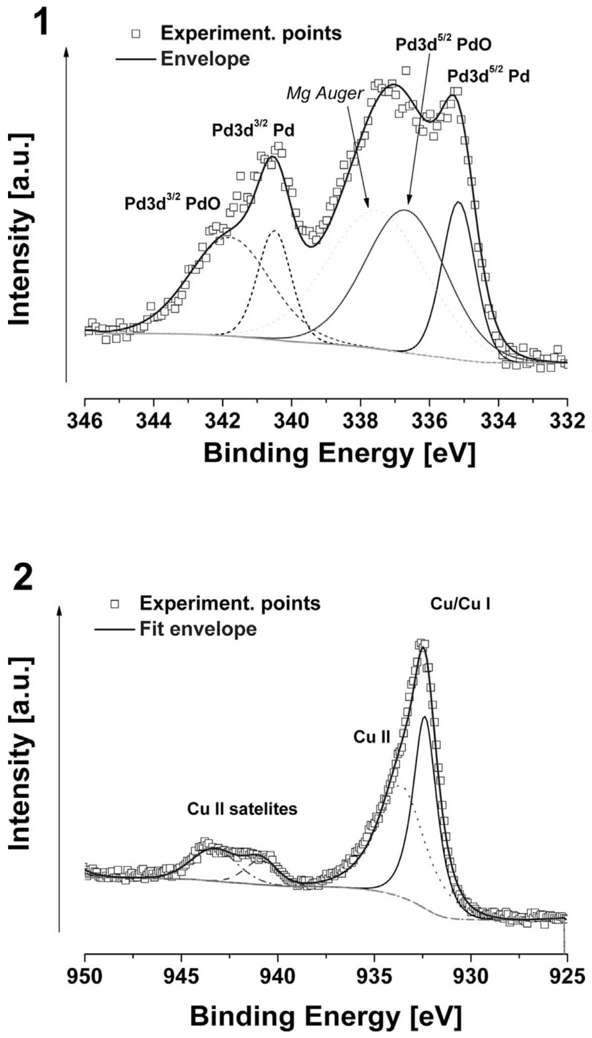

Fig. 4. XPS Pd3d (1) and Cu 2p (2) spectra of 5% Pd–5% Cu/MgO catalyst.

from the XPS technique and the intensities corresponding to the Cu2p and Cu1p do not precisely reflect the ratio of them in the sample [28].

3.2. Catalysts screening

Several supported metal catalysts were screened for the hydrogenation of furfural in a batch reactor at temperatures 80–130 °C under pressure of hydrogen 0.6–0.8 MPa. Preliminary study of ca. 6 wt% aqueous solution of furfural (the solubility of furfural in water at ambient temperature is about 8.3 wt%) at reaction temperature 130 °C have shown that monometallic copper catalysts supported on activated carbon or MgO are almost inactive for hydrogenation (Table 1). Enhanced furfural conversion but very low selectivity to FAL exhibited monometallic palladium catalysts supported on hydrotalcite and MgO. Palladium catalyst supported on activated carbon is at higher conversion much more selective. As shown in this table, the 5% Pd/HT gave at 83.5% conversion 33.5% selectivity to FAL and 5% Pd/C catalyst at 96.8% conversion 87.1% selectivity to FAL. The main side products were tetrahydrofurfuryl alcohol, 2-methylfuran and cyclopentanone. It confirms the important role of the support in enhancing the activity and FAL selectivity. As the XRD data revealed MgO support during preparation of catalyst is almost completely transformed into hydroxide.

3.3. The effect of catalyst reduction

To study the influence of the method of reduction of palladium precursor on catalyst performance a series of monometallic palladium catalysts supported on activated carbon were prepared by impregnation method. As is described above the palladium precursor was reduced using formaldehyde, sodium borohydride or with hydrogen at two reduction temperatures, 300 °C and 450 °C. To better distinguish the differences between their catalytic activities, the catalytic tests were conducted at lower reaction temperature, hydrogen pressure, catalyst loading and at constant reaction time. It was shown that also at reaction temperature 80 °C the prepared catalysts are highly active and their performance is strongly dependent on the method of reduction of palladium precursor (Table 2). Palladium catalysts prepared using formaldehyde or sodium borohydride after 90 min of reaction exhibited lower furfural conversion but higher selectivity to FAL than the Pd catalysts reduced with hydrogen at temperatures 300 °C or 450 °C. Catalysts reduced at these temperatures converted 93.2 and 95.5% of furfural but only with 14.3 and 32.8% selectivity, respectively (Table 2 runs 1 and 2). In order to enhance conversion and mainly selectivity of furfural hydrogenation to furfuryl acohol, Cu was incorporated into the Pd catalysts. Copper-based catalysts [29] have been the most widely used to achieve selective hydrogenation of the C=O bond while leaving the C=C bonds in the furan nucleus intact. Among all bimetallic Pd–Cu catalysts supported on MgO and activated carbon screened for hydrogenation of furfural, the highest conversion and selectivity to furfuryl alcohol showed the catalysts prepared by electroless plating method. Electroless copper plating method is widely used in electronics for deposition of metallic copper layers on semiconductors or dielectrics. It is an alternative and promising way to deposit metal nanoparticles onto the surfaces of porous solid supports. As is seen from results in Table 1 the optimum catalyst performance was achieved by changing the support and the loading of Pd and Cu and mutual ratio of both metals. The bimetallic catalyst supported on MgO with quasi optimum combination of Cu with Pd resulted in complete furfural conversion and 98.7% FAL selectivity (Table 1 run 8). On the contrary, the bimetallic Pd–Cu catalysts supported on activated carbon but prepared by co-impregnation method and reduced with hydrogen are at slightly lower furfural conversion much less selective to FAL (Table 2 runs 5–7). Using catalyst containing 5 wt% loading of copper 96.4% conversion of furfural and 83.8% selectivity was achieved; and over catalysts containing 10 wt% loading of Cu and reduced at 450 and 300 °C in hydrogen 96.6 and 94.9% conversion and 89.1 and 84.1% selectivity, respectively. On the other hand, the runs 5 and 7 demonstrate that highly positive effect on selectivity has Cu also on catalysts supported on activated carbon having lower (3%) Pd loading. At comparable furfural conversion these catalysts are significantly more selective than monometallic Pd/C catalysts with higher (5%) palladium loading (runs 1 and 2), and prepared using the same procedure and reduction methods.

The better catalytic performance was achieved using bimetallic Pd–Cu catalysts supported on MgO. Addition of copper leads to enhancement in the conversion of furfural (from 92.1% to 100%) and significantly is increased furfuryl alcohol selectivity, from 59.6% up to 98.7% (Table 1 runs 2 and 5–8). In the presence of bimetallic catalysts was shorten the reaction time required for obtaining almost complete furfural conversion. From experiments performed with bimetallic catalysts supported on different carriers is clear that not only the interaction between active metal sites and support but also cooperative effect of metal sites play crucial role in determining catalytic performance. From the studied catalysts the best performance demonstrates bimetallic 5%Pd–5%Cu catalyst supported on MgO. Since MgO is during preparation of catalyst almost completely transformed into $Mg(OH)_2$, as the XRD data proved, it is anticipated

Table 2
Effect of copper and catalyst reduction on the performance of palladium catalyst supported on activated carbon.[a]

Run	Catalyst	Reduction	React. time (min)	Conversion (%)	S_{FAL}, (%)
1	5% Pd/C	H_2 at 300 °C	90	93.2	14.3
2	5% Pd/C	H_2 at 450 °C	90	95.5	32.8
3	5% Pd/C	$NaBH_4$	90	71.5	72.3
4	5% Pd/C	Formaldehyde	90	46.1	86.3
5	3% Pd–5% Cu/C	H_2 at 450 °C	90	96.4	83.8
6	3% Pd–10 % Cu/C	H_2 at 450 °C	90	96.6	89.1
7	3% Pd– 10% Cu/C	H_2 at 300 °C	90	94.9	84.1
8[b]	5% Pd–5 % Cu/C	Formaldehyde	60	96.8	91.0

[a] Conditions: 0.60 g FA, 10 ml H_2O, 0.05 g catalyst, 80 °C, 0.6 MPa H_2.
[b] At 110 °C and 0.10 g catalyst.

Table 3
Effect of copper on performance of Pd/MgO catalyst.[a]

Run	Catalyst	React. temp. (°C)	React. time(min)	Conversion (%)	S_{FAL}, (%)
1	5% Pd–5% Cu/MgO	80	110	79.1	95.7
2	5% Pd–5% Cu/MgO	80	140	97.5	94.4
3[b]	5% Pd–5% Cu/MgO	80	100	100	97.5
4	5% Pd–5% Cu/MgO	110	80	100	98.6
5	5% Pd–5% Cu/$Mg(OH)_2$	110	75	100	98.3
6	5% Pd–10% Cu/MgO(sep)	110	95	77.9	57.2

[a] Conditions: 0.60 g FA, 10 ml H_2O, 0.05 g catalyst prepared by reduction with formaldehyde at 40 °C for 8 h, 0.6 MPa H_2.
[b] 0.10 g catalyst.

that at the same reaction conditions the identical performance will have the Pd–Cu catalyst supported on $Mg(OH)_2$ (Table 3 runs 4 and 5). Complete conversion and more than 98% selectivity for the hydrogenation of furfural to furfuryl alcohol were obtained in the presence of very low concentrations of these catalysts under optimal reaction temperature and hydrogen pressure (110 °C and 0.6 MPa) and reaction times 75–80 min. As is evident from the table the catalytic performance of MgO supported Pd-Cu catalyst is very high also at reaction temperature 80 °C. At this temperature the increase of furfural conversion from 79.1 to 97.5% by prolongation of reaction time has only slight effect on selectivity to FAL. To obtain highly active and selective Pd–Cu catalyst important is not only the presence of tartrate ligands during deposition of copper but also the method of reduction of copper precursor. If the Cu precursor was reduced using different procedure (Method B) less active and selective catalyst of furfural hydrogenation was obtained (Table 3 run 6).

3.4. *The effect of Pd–Cu interaction*

The above mentioned results indicated that by the variation of support and the ratio of Pd–Cu metals in the bimetallic catalysts and the procedure of metals reduction can be tuned the surface composition and the structure of active sites and thus the chemical reactivity. It is known that furfural is strongly adsorbed on the palladium surface [29]. The addition of Cu to Pd catalyst decreases furfural adsorption on Pd sites with low coordinative unsaturation. Moreover, when some amounts of Cu are incorporated into the catalyst multi-bonding of furfural may be reduced due to the dilution of Pd ensembles. However, the way in which the additive Cu modifies the properties of the Pd–Cu catalysts is not yet fully elucidated [30].

The location of the Cu atoms on the Pd particles and the interaction between metal and support relate closely to the selectivity change, as is discussed above. In the catalysts with high loadings of Cu, most of the Pd atom should be isolated by the effect of Cu species. In order to explain the different catalytic behavior between Pd–Cu catalysts in the hydrogenation of furfural we can consider the results obtained by TPR, CO chemisorption, XRD and XPS. A comparison of the TPR and XRD patterns (Figs. 1 and 2) indicates that in the Pd–Cu/C catalyst prepared by co-impregnation after reduction at 450 °C the copper exists as a mixture of Cu^{2+} and Cu^{+} oxidation states and the absence of metallic Pd phase indicates that also Pd–Cu alloys with different composition are present. As the TEM spectra shown (Fig. 3) the distribution of metallic species in this catalyst is homogeneous. The formation of Pd–Cu alloys modify electronic density of Pd due to a partial positive charge transfer from Cu species and thus influence of activation of molecular H_2 which is more likely to occur on a metallic Pd surface. On the contrary, as indicated XRD and XPS spectra (Figs. 2 and 4) in the most active and selective 5%Pd–5%Cu catalysts supported on MgO, $Mg(OH)_2$ and activated carbon prepared by electroless plating method, Pd–Cu alloys are not present. Thus, depending on the Pd/Cu ratio and the method of catalyst preparation, on the catalyst surface may exist monometallic Pd^0 sites and probably closely interacting bimetallic Pd^0–Cu_2O catalytic sites. The main differences between samples with different Cu loadings are attributed to changes in these two metallic phases and they are reflected in the activity and selectivity of furfural hydrogenation. However, in the case of bimetallic Pd–Cu catalyst activation of molecular H_2 is more likely to occur on a metallic Pd surface. Therefore, the presence of both Cu+ and Pd° sites is required for optimal performance, although a surface consisting of only Cu° can display some activity because the aldehyde can also be adsorbed and activated on a Cu° surface [31]. This is supported by the fact that a sample of Cu/C reduced in H_2 which was used in a reaction displayed very low activity. In this regard, a surface consisting of only Cu° active sites is not optimal for the studied reaction.

We assume that aqueous phase hydrogenation of the $-C{=}O$ group in the presence of bimetallic Pd–Cu catalysts occurs preferably on sited associated with Cu^{+} ions. On these sites, which can act as an electrophile, the carbonyl group is polarized, facilitating hydrogen transfer from the adjacent Pd–H sites. Moreover, the interaction of Cu_2O surface with the solvent molecules, i.e., water, causes that water contribute for furfural interaction with Cu_2O surface. Providing that Pd^0 sites are present to dissociate hydrogen, hydrogenation of $-C{=}O$ group in adsorbed species created on Cu^{+} sites readily occurs. To produce selectively furfuryl alcohol during furfural hydrogenation, weaker interactions between the furyl ring and surface of active metal species would be desired.

Table 4
Effect of solvent.[a]

Run	Solvent, 10 ml	React. time (min)	Conversion (%)	S_{FAL}, (%)	r^{rel}
1	Water	80	100	98.6	1.00
2	Isopropyl alcohol	150	89.9	96.8	0.18
3	Methanol	120	64.9	98.1	0.09
4	Tetrahydrofuran	120	14.1	11.9	0.03
5	Cyclohexane	90	7.9	–	0.04
6	MIBK	60	11.7	–	0.14
7	Dioxane	90	9.5	–	0.03

r^{rel} relative rate of hydrogenation (mol H_2 g FA-1 min-1).

[a] Conditions: 0.60 g FA, 0.05 g catalyst 5% Pd–5% Cu/MgO, 110 °C, 0.6 MPa H_2.

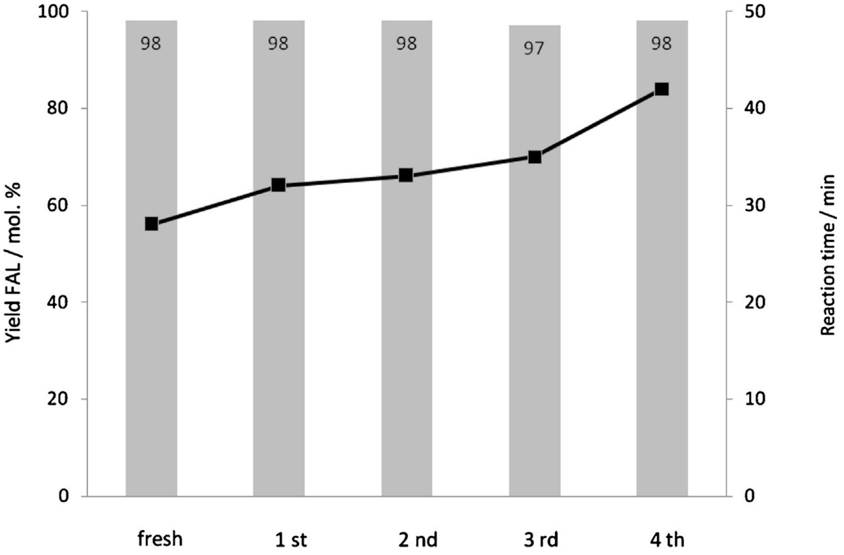

Fig. 5. Catalyst recycling study. Reaction conditions: temperature 110 °C; hydrogen pressure 0.60 MPa; 0.6 g furfural; 10 ml water, 0.05 g catalyst 5% Pd–5% Cu/MgO

The observed differences between Pd–Cu catalysts supported on MgO and active carbon with similar amounts of added Cu can be attributed to the action of the metal-support interaction between active metal species and their support [12,32]. A metal-support interaction probably affects the reducibility of Cu allowing its stabilization in the oxidised form (i.e., Cu^+). Creation of special defect sites at the Cu–MgO interface was reported to be responsible for the selective furfural hydrogenation [33]. The defect sites at the metal-support interfacial region are helpful to coordinate –C=O group and thus activate its hydrogenation to alcohol [34]. Some authors showed [35] that increasing the basicity of the catalyst gave rise to higher selectivities toward alcohol in the hydrogenation of 3-methylcrotonaldehyde over Ru, Pt and Rh supported on zeolites modified with alkali cation. In the present investigation MgO or $Mg(OH)_2$ supports are basic, i.e., helpful in getting high selectivity. All these factors are reflected in the activity and selectivity of furfural hydrogenation.

3.5. *The effect of solvent*

Catalytic properties of 5%Pd–5%Cu/MgO catalyst for hydrogenation of furfural to FAL were investigated also in other solvents than water (Table 4). Solvent properties, such as polarity, could affect solvent–reactant interactions and consequently, furfural hydrogenation. It means that with increasing polarity of the solvent, possibly due to increased furfural–solvent interaction should decrease FAL yield as a result of retardation of furfural adsorption on the catalyst. A similar trend was observed in acetophenone hydrogenation [36]. The retardation effect of water on the gas phase hydrogenation of furfural was observed by Sitthisa et al. [31], who explained that water competes with furfural for adsorption sites. However, as is seen from Table 4 the order of the reaction rates and in some solvents also selectivities follow the reverse trend. The highest rate was observed in the most polar solvent, water ($\epsilon = 80$), while in significantly less polar media (alcohols, $\epsilon \sim 20$–33) the rates were low, and in ethers ($\epsilon \sim 4.4$–7.5) or hydrocarbons ($\epsilon \sim 2$) hydrogenations proceeded with very low rates. A drastic decrease of activity of bimetallic PtSn catalyst during liquid phase hydrogenation of furfural in non-alcoholic and non-polar solvents observed also Merlo et al. [8]. Probably due to the strong adsorption of furfural in the non-polar media the catalyst is reversibly deactivated. This aspect needs to be further investigated.

3.6. *Catalyst reusability*

Catalyst recycling in heterogeneous reactions is very important from the cost point of view. Catalyst reusability was studied using 5%Pd–5%Cu/MgO catalyst exhibiting the highest catalytic performance, and the results are shown in Fig. 5. The catalyst recycle study was carried out as follows. After each reaction, the reactor with reaction mixture was centrifuged at 4500 rpm for 15 min. After centrifuging was removed very carefully about 95% of the supernatant liquid and to the settled down solid phase was added ca. 5 ml of deionised water. After mixing (ca. 5 min) and subsequent centrifugation the supernatant liquid was again removed. This procedure was repeated twice to ensure that all water soluble reaction products were recovered from the catalyst. Then the reactor was charged with the fresh furfural and water and after reaction the same procedure was repeated for four times. As is seen from the figure after these recycling runs almost the same performance as that of the fresh catalyst was observed. Small difference was only in the reaction time (increase from 30 to 43 min), required for obtaining almost complete furfural conversion. Analysis of the liquid reaction mixture did not show the presence of palladium, but in some experiments small amounts of dissolved Cu and Mg were measured. MgO was partly solubilized by water.

4. Conclusions

The novelty of this study is the use of water as a solvent for selective hydrogenation of furfural to furfuryl alcohol. For this study a series of Pd–Cu based catalysts supported on different carriers were prepared by various methods. The main objective was to investigate the influence of copper in bimetallic Pd–Cu catalysts on the activity and the selectivity of furfuryl alcohol formation. The best catalytic performance exhibited catalysts prepared by electroless plating method. Studies on catalyst screening revealed that both the metal function and the support were critical for directing the selectivity to furfuryl alcohol. The main differences among samples with different Cu loadings are attributed to changes between monometallic Pd^0 sites and probably closely interacting bimetallic Pd^0–Cu_2O catalytic sites over the surface.

We assume that hydrogenation of the –C=O group mainly occurs on sited associated with Cu^+ ions. On these sites, the carbonyl group is polarized, facilitating hydrogen transfer from the adjacent Pd-H sites. To produce selectively furfuryl alcohol, weaker interactions between the furyl ring and surface of active metal species would be desired. Among all bimetallic Pd–Cu catalysts screened, catalysts supported on MgO or $Mg(OH)_2$ prepared by modified electroless plating method showed the highest conversion and selectivity to furfuryl alcohol. In the furfural hydrogenation over 5%Pd–5%Cu/MgO catalyst almost complete conversion and higher than 98% selectivity to furfuryl alcohol were achieved at reaction temperatures 110–130 °C and hydrogen pressures 0.6–0.8 MPa. This catalyst, only washed with water after each run, exhibited after five catalytic cycles practically the same performance as that of the fresh catalyst.

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