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Hydrodeoxygenation of Furfural Over Supported Metal Catalysts: A Comparative Study of Cu, Pd and Ni

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Abstract The hydrodeoxygenation of furfural has been investigated over three different metal catalysts, Cu, Pd and Ni supported on SiO_2, on a continuous-flow reactor under atmospheric pressure of hydrogen in the 210–290 °C temperature range. The distribution of products is a strong function of the metal catalyst used. High selectivity to furfuryl alcohol is obtained over Cu/SiO_2, with the formation of only small amounts of 2-methyl furan at the highest reaction temperature studied. In contrast to Cu catalyst, the conversion of furfural over Pd/SiO_2 mainly produces furan by decarbonylation. Furan can further react with hydrogen to form tetrahydrofuran (THF). Finally, on Ni/SiO_2 catalysts ring opening products (butanal, butanol and butane) can be obtained in significant amounts. The different product distributions are explained in terms of the strength of interaction of the furan ring with the metal surface and the type of surface intermediates that each metal is able to stabilize.

Keywords Furfural · Hydrogenation · Decarbonylation · Ring opening · Bio-oil upgrading

1 Introduction

Furfural is typically used as a precursor in the production of tetrahydrofuran (THF), an important industrial solvent, and sometimes used as a solvent itself for selective extractions [1]. However, recent studies have considered using it as a building block for transportation fuels [2]. Furfural is obtained from the dehydration of pentoses, five-carbon sugars, such as xylose and arabinose, commonly obtained by acid-catalyzed digestion of hemicellulose-rich agricultural wastes. Furfural is also obtained from the fast pyrolysis of biomass at moderate temperatures, high heating rates, and short residence times [3–8]. Bio-oil has a good potential as a second-generation bio-fuel, because it can be produced in high volumes without threatening food supplies and biodiversity, but due to its high oxygen and water content it requires a significant post-treatment before it can be used as transportation fuel [9, 10].

Furfural is one of the numerous oxygenated compounds commonly found in bio-oil [3, 11–22]. Due to their high reactivity, these compounds need to be catalytically hydrodeoxygenated to improve bio-oil storage stability, boiling point range, and water solubility [23].

Dumesic et al. [24, 25] have proposed that aldol condensation of furfural with small ketones is a promising approach to produce higher alkanes (C_8–C_{15}) for diesel fuel production. They have obtained high yields of condensation products by direct condensation of furfural with acetone in the presence of basic catalysts [25]. Selective hydrodeoxygenation may be an alternative route to increase the stability of furfural and convert it to compounds which may have value as gasoline components. For instance 2-methyl furan, could be a suitable option to be used as an octane booster (RON = 131). Hydrodeoxygenation under relatively mild conditions can be performed over metal catalysts [26, 27].

Within this context, the goal of this contribution is to compare the conversion of furfural over different silica-supported metals. Copper, palladium and nickel catalysts have been selected to study their activity, selectivity, and possible reaction pathways for the hydrodeoxygenation of

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furfural. The study of the behavior of different metals may be useful in designing catalytic strategies towards the production of fuel components with specific characteristics (e.g. vapor pressure, octane number, etc.)

2 Experimental Procedure

2.1 Catalyst Synthesis and Characterization

Three different catalysts were prepared by incipient wetness impregnation (IWI) of the support (SiO_2, Hisil 210) with an aqueous solution of the respective metal precursor ($Cu(NO_3)_2$, $Pd(NO_3)_2$ or $Ni(NO_3)_2$), obtained from Fluka (>99% purity). The choice of metal loading for each catalyst was made based on the intrinsic activity of each metal to compensate for the amount of catalyst needed to be loaded in the reactor. For example, the intrinsic activity of Cu<<Ni<Pd. So, the metals loading chosen for the preparations were 10, 5, and 1%wt, respectively. The three catalysts, 10% wt Cu/SiO_2, 5% wt Ni/SiO_2, and 1% wt. Pd/SiO_2 were prepared by adding metal salt aqueous solutions with the appropriate concentrations onto the silica support, keeping a liquid/solid ratio of 1 cc/g. After impregnation, the catalysts were dried overnight at room temperature and placed in an oven at 120 °C for 12 h. The oven-dried catalysts were finally calcined for 4 h at 400 °C, following a linear heating ramp of 10 °C/min, under a flow of pure air at 100 ml/min.

The reducibility of the calcined samples was determined by temperature-programmed reduction (TPR). In these measurements, 50 mg of a sample was placed in a quartz reactor and heated at 10 °C/min up to 550 °C under a He flow of 20 mL/min, and held at this temperature for 1 h. The reactor was then cooled down to 0 °C and the sample exposed to a stream of 5% H_2/Ar at a flow rate of 20 ml/min. Subsequently, the sample was heated up to 600 °C at a heating rate of 10 °C/min. The amount of hydrogen consumed as a function of temperature was monitored on-line on a TCD detector. The maximum rate of H_2 consumption was used to choose the reduction temperature for each catalyst to be conducted in situ before reaction. The fraction of metals reduced was estimated from the H_2 uptakes in the TPR experiment, using a known amount of CuO for calibration. The BET surface area (Sg) was measured by N_2 physisorption in a Micromeritics ASAP 2010 unit. The samples were evacuated at 350 °C for 3 h prior to the measurements.

2.2 Catalytic Activity Testing

The vapor-phase reaction of furfural over the silica supported metal catalysts was conducted in a 1/4″ tubular quartz reactor. The pelletized catalyst (size range: 250–425 μm) was placed at the center of the reactor tube between two layers of glass beads and quartz wool. The amount of catalysts loaded in the reactor ranged between 15 and 120 mg, depending on the specific W/F. These amounts resulted in corresponding lengths of the catalyst bed that ranged between 0.5 and 2 cm. The catalyst was pre-reduced in H_2 flow (60 mL/min, Airgas, 99.99%) for 1 h at the temperature selected according to the TPR experiments (i.e., 250, 350, and 450 °C for $1\%Pd/SiO_2$, $10\%Cu/SiO_2$ and $5\%Ni/SiO_2$, respectively). After reduction, the catalyst was cooled down to the selected reaction temperature (230–250 °C) under the same H_2 flow. A 0.5 mL/h or 0.006 mol/h flow of liquid furfural (provided by Sigma-Aldrich, 99.5%) was fed continuously from a syringe pump (Cole Palmer) and vaporized into a gas stream of 60 mL/min H_2. The reaction products were analyzed online on a gas chromatograph (Agilent model 6890) using a HP-5 capillary column and a FID detector. The carbon balance was checked in every run and it was found to be higher than 95% in every case. The product yield and selectivity were calculated and defined as follows:

$$\text{Yield}(\%) = \frac{\text{mol of the product produced}}{\text{mol of furfural fed}} \times 100$$

$$\text{Selectivity}(\%) = \frac{\text{mol of the product produced}}{\text{mol of fufural consumed}} \times 100.$$

3 Results and Discussion

3.1 Catalyst Characterization

The BET surface areas from N_2 physisorption measurement are 129, 115, and 126 m^2/g for $1\%Pd/SiO_2$, $10\%Cu/SiO_2$ and $5\%Ni/SiO_2$, respectively. The metals loading after synthesis was estimated from the H_2 consumption experiment and found to be 1.2 wt%, 10.3 wt% and 5.9 wt% for $1\%Pd/SiO_2$, $10\%Cu/SiO_2$ and $5\%Ni/SiO_2$, respectively. The TPR profiles of the $1\%Pd/SiO_2$, $10\%Cu/SiO_2$ and $5\%Ni/SiO_2$ catalysts are shown in Fig. 1. For Pd/SiO_2, the TPR profile mainly exhibits one peak centered on 94 °C, which has been previously ascribed to the reduction of Pd(II) to Pd(0) [28, 29]. The reduction profile of Cu/SiO_2 was previously reported [30] and showed two overlapping peaks at 335 and 246 °C. According to previous studies, these peaks originate from the reduction of respectively more highly and more poorly dispersed Cu oxide species on silica [31]. Finally, the Ni catalyst shows the main reduction peak at 354 °C with smaller peaks at lower and higher temperature (330

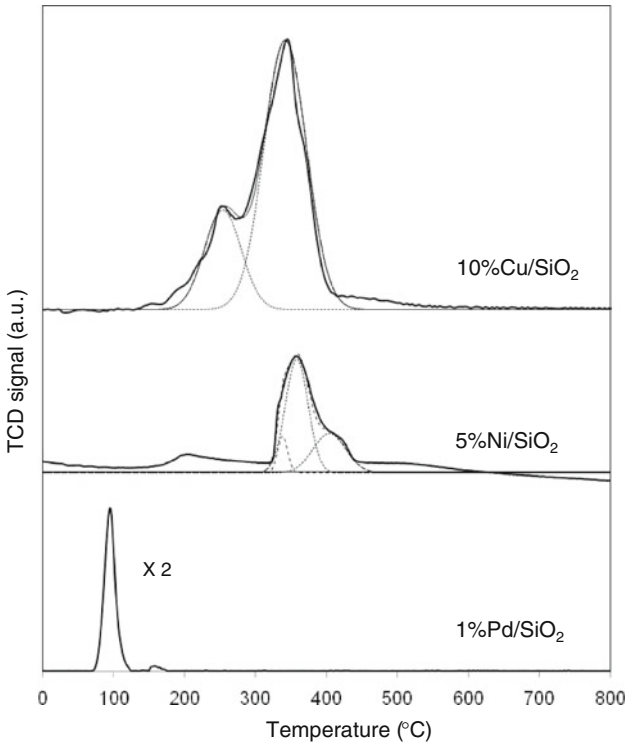


Fig. 1 Temperature programmed reduction profiles (TPR) of 1%PD/Sio_2, 5%Ni/Sio_2 and 10% Cu/Sio_2 [30] Catalysts

and 393 °C, respectively), as previously seen [32, 33]. The main peak has been attributed to the reduction of NiO to Ni metal [34]. The small peak at higher temperatures could be due to the reduction of small NiO particles or possibly nickel hydrosilicate species, resulting from strong metal-support interactions [35].

3.2 Conversion of Furfural Over Cu/SiO_2

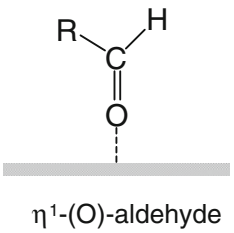
Table 1 summarizes the conversion and product distribution from the reaction of furfural over the Cu/SiO_2 catalyst [30]. These results clearly show that the reaction of furfural mainly produces its corresponding alcohol, with only small amounts of 2-methyl furan (MF), formed as a by-product via C–O hydrogenolysis. A relatively higher yield of 2-methyl furan can be obtained at the highest reaction temperature studied (290 °C). These results are in agreement with previous reports of furfural conversion over Cu-based catalysts, which show that furfuryl alcohol is the main product [36–39]. As we have recently shown [30], the conversion of furfural on Cu catalyst involves the interaction of the surface preferentially with the carbonyl group, rather than the furanic

Table 1 Conversion and yield of products from the reaction of furfural over 10%Cu/SiO_2 catalyst (adapted from [30])

Temp. (°C)	W/F g_{cat}/(mol/h)	Conv. (%)	Yield (%)	
			FOL	MF
230	10.4	24	24	0.2
	20.7	53	53	0.5
	41.3	69	68	1.5
270	3.5	15	14	0.2
	10.4	46	45	1.2
	20.7	66	63	2.9
	41.3	77	71	6.0
290	3.5	20	19	0.3
	10.4	48	46	1.7
	20.7	64	60	4.3
	41.3	71	63	8.2

Reaction conditions: H_2/Feed ratio = 25, H_2 pressure = 1 atm, TOS = 15 min. *FOL* furfuryl alcohol, *MF* 2-methyl furan

ring. Furfural tends to adsorb through carbonyl O in a η^1(O)-aldehyde configuration, as previously proposed for all Group IB metals, according to HREELS and DFT evidence [40].



As shown in Table 1, only furfuryl alcohol and 2-methyl furan were observed in the reaction of furfural over Cu/SiO_2. No products from hydrogenation of the furanyl ring were obtained at any temperature or at any W/F. This result is in good agreement with the conclusion that the adsorption of the furan ring is not favored on the Cu surface. In fact, the DFT calculations in our recent study give evidence for a strong repulsion of the Cu(111) surface to the furan ring, presumably due to the overlap of the 3d band of the surface Cu atoms and the anti-bonding orbital of the aromatic furan ring [30].

A molecule that has shown similar behavior on Cu(111) is crotonaldehyde, which contains a carbonyl group and a C=C bond. As demonstrated by Boronat et al. [41] crotonaldehyde is bonded to the surface through the O of the carbonyl group, while the C=C bond remains undistorted and far from the surface. Likewise, several studies have shown that Cu catalysts are always more selective in the

hydrogenation of the C=O bond in conversion of aldehydes containing C=O and C=C bonds than other metal catalysts [42, 43]. We conclude that the Cu surface exerts a selective attraction to the O end of the carbonyl, but repulsion on the rest of the molecule.

3.3 Conversion of Furfural Over Pd/SiO_2

A very different behavior from that of Cu is observed for Pd. As shown in Table 2, the product distribution from the reaction of furfural over Pd/SiO_2 at different W/F and temperatures is clearly different from that on Cu. The main product is furan, which derives from the decarbonylation of furfural [44]. In contrast to Cu, Pd only produces small amounts of furfuryl alcohol, which indicates that on Pd decarbonylation is more favorable than hydrogenation. Another significant difference is the appearance of terahydrofuran (THF) and tetrahydro-furfuryl alcohol (HFOL) at high W/F. These hydrogenated ring products were not observed in the case of Cu catalyst and clearly indicate that the interaction with the furan ring is favored on Pd.

To interpret the observed results we need to elucidate which intermediate leading to decarbonylation is favored on the Pd surface. One can refer to the work of Barteau et al. [45, 46], who made extensive studies of the interaction of aldehydes on metal single crystals. They showed that on Pd surfaces, aldehydes tend to form η^2 (C, O) surface intermediates, in which both C and O atoms of the carbonyl group interact with the metal. In the presence of hydrogen, this intermediate can be hydrogenated to alcohol. However, when the temperature is high enough, the η^2 (C, O) aldehyde may further convert into a more stable acyl surface species, in which the C atom of the carbonyl is strongly attached to the surface. This acyl species may in fact be a precursor for the decarbonylation reaction, producing hydrocarbon fragments and CO. In the case of furfural conversion, this path results in furan, which is the main product. Interestingly, as shown in Fig. 2, the selectivity to decarbonylation significantly increases as a function of temperature, which is consistent with an enhanced conversion of η^2 (C, O) into acyl species on the surface as temperature increases.

η^2-(C-O)-aldehyde Acyl species

Table 2 Conversion and yield of products from the reaction of furfural over $1\%Pd/SiO_2$ catalyst

Temp. (°C)	W/F g_{cat}/(mol/h)	Conv. (%)	Yield (%)			
			Furan	THF	FOL	HFOL
210	2.4	15	10	2	3	0.0
	4.8	27	17	5	5	1.1
	9.6	40	22	8	8	3.0
230	2.4	27	20	3	4	0.0
	4.8	46	30	7	7	2.0
	9.6	69	42	14	10	3.5
250	2.4	40	33	3	4	0.0
	4.8	63	46	8	7	1.5
	9.6	85	59	14	9	2.7

Reaction conditions: H_2/Feed ratio = 25, H_2 pressure = 1 atm, TOS = 15 min

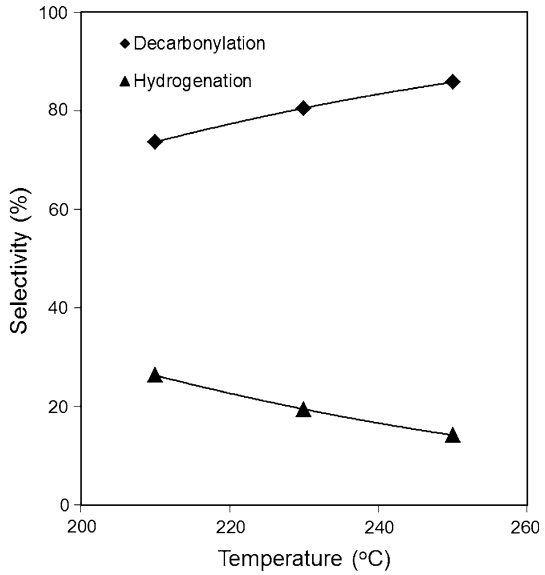


Fig. 2 Selectivity of products from decarbonylation (Furan + THF) and hydrogentaion (FOL + HFOL) reactions at difference temperatures. W/F = 9.6 g_{cat} mol^{-1} H_2/Feed ratio = 25 H_2 pressure = 1 atm, TOS = 15 min

The formation of hydrogenated furan ring compounds, THF and HFOL, on Pd as opposed to Cu is also an important aspect to discuss. As opposed to Cu, Pd can readily adsorb the furan ring due to a strong interaction between the metal and the π bonds in the molecule. A rehybridization of the carbon bonds from sp^2-to-sp^3 has been proposed to occur on Pd, which may account for the strong interaction [47].

Table 3 Conversion and yield of products from the reaction of furfural over 5% Ni/SiO_2 catalyst

Temp. (°C)	W/F g_{cat}/(mol/h)	Conv. (%)	Yield (%)					
			Furan	FOL	HFOL	BAL	BOL	Butane
210	2.4	26	11	10	1	3	0	1
	4.8	41	16	16	2	3	1	2
	9.6	84	32	31	5	5	3	5
230	2.4	37	16	10	1	5	1	3
	4.8	72	31	18	3	9	2	7
	9.6	100	45	19	5	6	9	12
250	2.4	51	23	7	1	9	1	8
	4.8	100	50	3	3	7	11	22
	9.6	100	50	0	3	4	14	24

Reaction conditions: H_2/Feed ratio = 25, H_2 pressure = 1 atm, TOS = 15 min. *FOL* furfuryl alcohol, *HFOL* tetra hydrofurfuryl alcohol, *BAL* butanal, *BOL* butanol

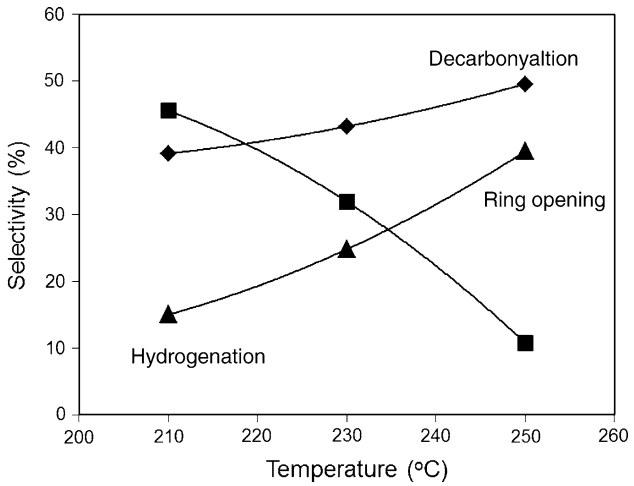
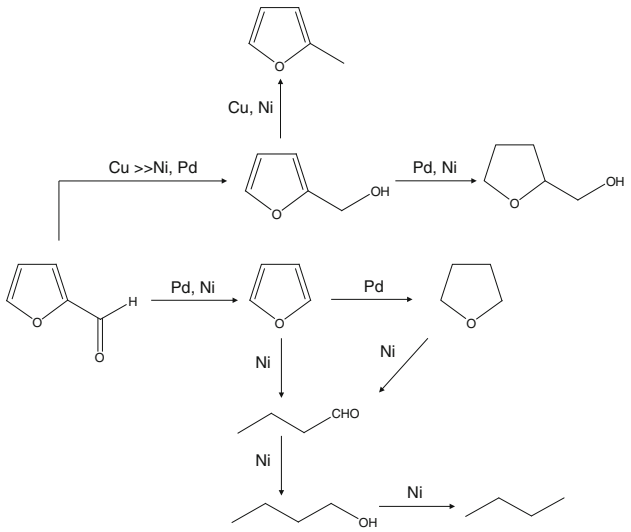


Fig. 3 Selectivity of products from decarbonylation (Furan), and hrdrogenation (FOL + HFOL) and ring opening (BAL + BOL + Butane) reactions at difference temperatures. W/F = 4.8 g_{cat} mol^{-1} H_2/Feed ratio = 25 H_2 pressure = 1 atm, TOS = 15 min



Scheme 1 Possible reaction pathways for furfural conversion over Cu, Pd and Ni catalysts

3.4 Conversion of Furfural Over Ni/SiO_2

A third different pattern of furfural conversion is observed on Ni, which exhibits unique characteristics with respect to Cu and Pd. Table 3 summarizes the product distribution over Ni/SiO_2 at different temperatures and W/F. While furan is the main product, and similar to Pd, Ni is active for decarbonylation, various other products are observed. At high W/F, in addition to furfuryl alcohol, tetrahydro furfuryl alcohol and 2-methyl furan are observed, but most interestingly, butanal (BAL), butanol (BOL), and butane were observed in significant amounts.

These products were not observed on Cu or Pd and can derive from the ring opening of furan. The C–O bond cleavage results in butanal, which can be further hydrogenated to butanol. At elevated temperature, butanol can be dehydrated to butene, which is rapidly hydrogenated to butane.

The reaction selectivity as a function of temperature at constant W/F is shown in Fig. 3, in which we have lumped the products arising from each principal reaction path. That is, decarbonylation includes furan, hydrogenation includes FOL and HFOL, and ring opening includes butanal, butanol, and butane. It is clear that while hydrogenation dominates at low temperatures, decarbonylation and ring opening become dominant at high temperatures.

One can speculate about the intermediates that lead to the furan ring opening and why this reaction is only observed on Ni. We note that, in principle, it is possible that the ring opening products can derive either from furan or THF, or both (see Scheme 1). However, THF was not

observed among the products on Ni catalyst, which might be due to either a very fast ring opening of THF, or that THF is not formed on Ni.

In order to decide which of the two possibilities is correct, a reaction study was conducted at 250 °C, using either furan or THF at the same W/F (9.6 g_{cat} mol^{-1} h). This comparative study showed that the highest yield of ring opening products was obtained with furan (32% and 8% yield for feeding furan and THF, respectively). That is, while THF resulted in some ring opening, it was much lower than that obtained with furan. Therefore, it is unlikely that the first possibility is correct. We can then conclude that on Ni, THF is not significantly formed and the ring opening path occurs preferentially via furan.

It is interesting to note that while the aromaticity of furan makes it more stable than THF, the activity for ring opening is much higher with furan than with THF. That is, one expects that the delocalization of the π electrons makes the C–O bonds in furan stronger than in THF. Therefore, the reason for the higher reactivity of furan compared to THF should be ascribed to the stronger interaction of the ring with the metal surface. In fact, Bradley et al. [47] have shown that the relatively strong adsorption of furan on Group VIII metals is due to the interaction of the π bonds with the d orbitals of the metal, which in turn weakens the C–O bond. In contrast, this type of interaction with the metal does not happen with THF. Thus, the difference in the reactivity for ring opening observed between the two molecules can be ascribed to the role played by the presence of the aromatic ring.

Table 4 Selectivity of products from the reaction of furfural over 10%Cu/SiO_2, 1%Pd/SiO_2 and 5%Ni/SiO_2 catalysts

Catalysts	10%Cu/SiO_2	1%Pd/SiO_2	5%Ni/SiO_2
Temp. (°C)	230	230	230
TOF (s^{-1})	1.3	265.8	76.5
W/F (g_{cat} mol^{-1} h)	41.3	9.6	4.8
Conversion (%)	69	69	72
Hydrogenation (%)			
FOL	98	14	25
MF	2	–	3
HFOL	–	5	4
Decarbonylation (%)			
Furan	–	60	43
THF	–	20	–
Ring opening (%)			
BAL	–	–	12
BOL	–	–	3
Butane	–	–	10

Reaction conditions, Temp = 230 °C, H_2/Feed ratio = 25, H_2 pressure = 1 atm, TOS = 5 min

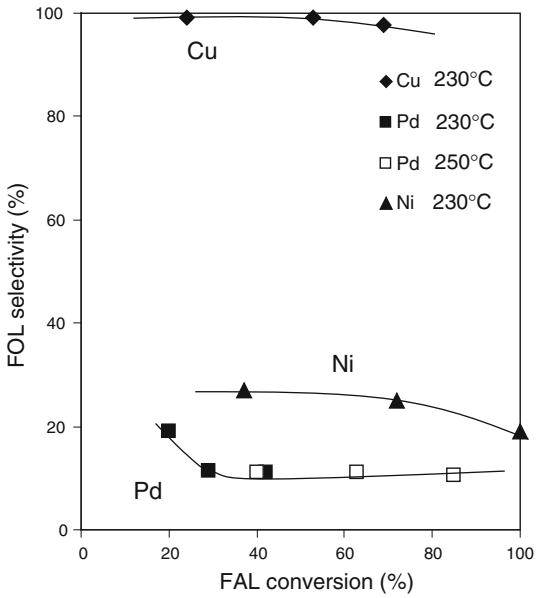


Fig. 4 Selectivity of products from hydrogenation (FOL) over 1%Pd/SiO_2 and 10% Cu/SiO_2 at difference conversions. H_2/Feed ratio = 25 H_2 pressure = 1 atm, TOS = 15 min

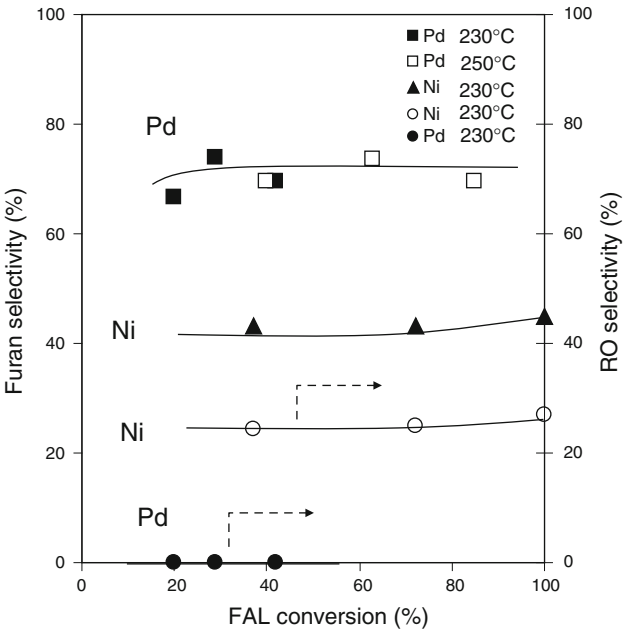


Fig. 5 Selectivity of products from decarbonylation (Furan), and ring (opening BAL + BOL + Butane) reactions (RO) over 1%Pd/SiO_2 and 5%Ni/SiO_2 at different conversions. H_2/Feed ratio = 25, H_2 pressure = 1 atm, TOS = 15 min

3.5 Comparative Analysis of the Furfural Conversion on Cu, Pd and Ni Catalysts

A comparison of the overall furfural conversion at 230 °C over the three different metal catalysts is made in Table 4. Large changes in turnover frequencies (TOF) were observed. The TOF were calculated from initial rates of

reaction, measured at low conversions (<3%) at 230 °C, and the average metal particle size, as determined from TEM (Cu = 3.2 nm, Ni = 15.0 nm, Pd = 10.14 nm). The resulting TOFs at 230 °C were Cu (1.3 s^{-1}), Ni (76.5 s^{-1}), and Pd (265.8 s^{-1}), which is the typical trend observed in hydrogenation catalysts, and usually explained in terms of the degree of d-orbital filling. That is, Cu is always much less active than Pd and Ni, with partially filled d-orbitals. However, the most interesting variations are in the distribution of products obtained over the three different metals. An interesting comparison is made in Table 4 for the three metals at the same temperature (230 °C) and about the same total conversion (~70%). It must be noted that the changes in selectivity due to changes in conversion or in temperature are minor compared to the drastic changes in selectivity observed from one metal to another. This comparison is clearly shown in Figs. 4 and 5.

First, regarding hydrogenation at the C=O bond, the three metals are all active in the conversion of furfural into the corresponding alcohol (FOL). However, extremely high selectivity (>98%) towards furfuryl alcohol can be obtained over the Cu catalyst. The formation of only the η^1-aldehyde intermediate of furfural on Cu surface [40] seems to be responsible for the high selectivity towards alcohol formation. In contrast, the most likely intermediate on Pd and Ni surfaces is the η^2-aldehyde [48], which can react further with hydrogen to form either the corresponding alcohol or decompose to the acyl intermediate that results in the formation of furan. Therefore, the selectivity towards alcohol gets reduced for the case of Ni and Pd catalysts.

Second, regarding the selectivity towards furan, one can see that this is much higher on Pd than on Ni (i.e., 60 vs. 43%). Here again, the lower selectivity on Ni can be ascribed to further reaction on this metal to subsequent products obtained from the ring opening reaction, which only occurs on Ni, most probably due to a strong interaction with the furan ring, which weakens the C–O bond enough to open the ring. In fact, recent studies have shown that ring opening of furfural can even be achieved at low temperatures by Ni-based catalysts in aqueous-phase [49].

Third, interesting differences are seen regarding the reaction of the furan ring. No hydrogenation of the ring happened on Cu but significant amounts were obtained on Pd. In addition, both hydrogenated and ring opening products were obtained from Ni. To explain this trend it would be interesting to compare the adsorption energies of the furan ring on the three difference metal surfaces. To our knowledge there is no published theoretical or experimental study that includes adsorption data for furan on Cu, Ni and Pd surfaces calculated or measured under the same conditions. However, it is possible to evaluate the trends observed with the closely related thiophene molecule, C_4H_4S to draw conclusions about our molecule of interest, furan, C_4H_4O. Coincidentally, Orita and Itoh [50] have conducted DFT calculations of the adsorption of thiophene on Ni(100), Cu(100) and Pd(100) surfaces. They report that the highest heat of adsorption of thiophene is on Ni, followed closely by Pd, and much farther by Cu (i.e., −2.8, −2.2, and −0.47 eV for Ni(100), Pd(100) and Cu(100) surfaces, respectively). From this trend, one could expect that the strength of interaction of the furan ring with the three metals would also follow the trend Ni>Pd>>Cu. Therefore, the differences in product distribution can then be interpreted as follows. The ring/metal interaction on Ni is so strong that it promotes the weakening of the C–O bond leading to ring opening. On Pd the interaction is weaker, but still significant as to allow for ring hydrogenation. Finally, on Cu the interaction with the ring is so weak that no ring-conversion products are observed. Scheme 1 summarizes the possible reaction pathways for conversion of furfural and indicates which paths are favored over Cu, Pd, or Ni.

4 Conclusion

In summary, the very different distributions of products observed on silica-supported Cu, Pd, and Ni catalysts can be explained in terms of the extent of molecular interactions with the metal surface as follows:

a) Cu mainly produces furfuryl alcohol via hydrogenation of the carbonyl group. This behavior is explained in terms of the preferred adsorption mode on Cu, η^1(O)-aldehyde, since the interaction of Cu with C=C bond is very weak. No products involving the activation of the furan ring are observed
b) Pd yields decarbonylation products due to the favorable formation of acyl surface species. It also generates products of ring hydrogenation and they are the result of a strong interaction of Pd with the ring.
c) While Ni has a product distribution similar to that of Pd, furan is not as abundant because it can further react with hydrogen, thus forming ring opening products, due to the interaction of the ring with the surface that is even stronger than on Pd.

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