# Catalytic hydrogenation of condensation product of furfural with cyclopentanone using molecular hydrogen and formic acid as hydrogen donor

Katarína Fulajtárová[a], Milan Hronec[a,*], Tibor Liptaj[b], Naďa Prónayová[b], Tomáš Soták[a]

[a] Department of Organic Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia
[b] Central Laboratories, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

## A B S T R A C T

In this study we report the catalytic hydrogenation of biomass-derived condensation product of furfural and cyclopentanone ($F_2C$) with molecular hydrogen and formic acid as a source of hydrogen. Supported palladium catalysts have been used for hydrogenation and decomposition of formic acid. Complete conversion of $F_2C$ and higher than 90% yield of $C_{15}$ bis-cyclic ether were achieved over 5% Pd/C catalyst at mild reaction conditions and short reaction time by catalytic hydrogenation with molecular hydrogen. Despite high activity of palladium catalysts in $F_2C$ hydrogenation with molecular hydrogen and also decomposition of formic acid to hydrogen these catalysts exhibited significantly lower activity in transfer hydrogenation. A dramatic activity loss in transfer hydrogenation may be caused by a strong adsorption of formic acid on Pd sites which hinders the competitive adsorption of $F_2C$ molecules solvated with formic acid.

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## 1. Introduction

Lignocellulosic materials as feedstocks for biofuels and chemicals are oxygen-rich derivatives, mainly components of five- and six-carbon sugars. Several reaction pathways have been suggested to remove oxygen from the structure of biomass [1–5]. The conversion of cellulose and hemicellulose fractions through hydrolysis and dehydration to 5-hydroxymethylfurfural and furfural, respectively, decreases simultaneously the oxygen content in the formed chemicals. Upgrading of these two platforms and products from their subsequent processes (*e.g. via* aldol condensation) is therefore focused on removing of the remaining oxygen and converting intermediates into liquid fuels and fuel additives. Most specifications for diesel can meet cyclic ethers produced by converting the furan rings into aldol condensation products [6–10]. These compounds do not need complete oxygen removal from the molecule of a fuel precursor, hence, can be produced more economically.

Currently the main challenge is being made to reduce external hydrogen consumption during hydrogenation of biomass platform molecules by utilization of a renewable source of hydrogen. An alternative to hydrogenation with molecular hydrogen is the hydrogen transfer reaction [11]. Typical hydrogen donors are alcohols, such as ethanol and 2-propanol, and formic acid derivatives; and as catalysts homogenous or heterogeneous complexes of transition metals. The catalytic transfer hydrogenation can be a vial route to upgrade also biomass-derived molecules. Recently, several authors studied catalytic transfer hydrogenation of furfural and 5-hydroxymethylfurfural in the presence of alcohols as hydrogen donors [12–14]. Much interest in green chemistry has attracted formic acid, a co-product formed during hydrolysis/dehydration of biomass [15], because of its potential as a hydrogen-carrier and also as a mean of $CO_2$ utilization [16]. As a hydrogen source it has been used in conversion of various compounds [17–19].

In the previous study we have demonstrated a three-step process starting from the biomass-derived furfural, for the selective preparation of bis-cyclic ether having 15 carbon atoms in the molecule (Scheme 1) [20–23]. Using commercial 5% Pd/C catalyst and hydrocarbons as solvents the aldol condensation product $F_2C$ is hydrogenated to bis-cyclic ether at 130 °C and 0.7 MPa of hydrogen pressure with more than 90% selectivity and about 96 mol% cumulative yield of the mixture of mono- and bis-cyclic ethers [21].

The present work describes the study of catalytic hydrogenation of the biomass-derived aldol condensation product of furfural and cyclopentanone, 2,5-bis(2-furylmethylidene)cyclopentan-1-one, with molecular hydrogen and the hydrogen transfer hydrogenation using formic acid as a source of hydrogen. The target

* Corresponding author. Tel.: +421 2 59325328.
 *E-mail address:* milan.hronec@stuba.sk (M. Hronec).

**Scheme 1.**
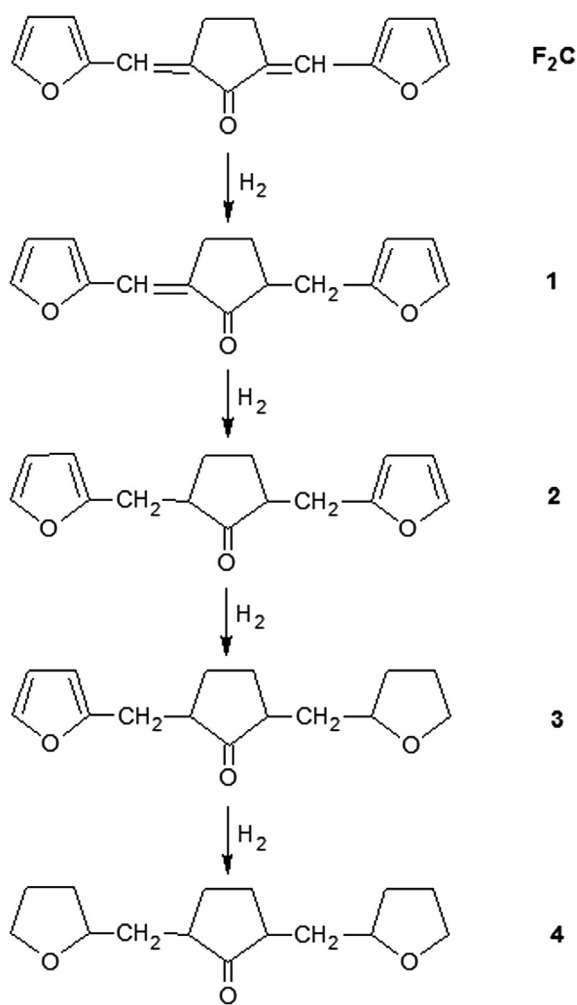
products, $C_{15}$ cyclic ethers, can be used as renewable bio-fuel additives.

## 2. Experimental

### 2.1. Materials

The 2,5-bis(2-furylmethylidene)cyclopentan-1-one was prepared according to the method described in [20]. Pd/C catalysts with 0.35, 1 and 5 wt % nominal metal loadings on active carbon Norit were prepared using the incipient wetness method and reduced by formaldehyde. Formic acid (98%) and the solvents used were of analytical grade purity and were purchased from Merck.

### 2.2. Catalyst characterization

The surface area was determined from BET nitrogen adsorption measurements (Micromeritics ASAP 2020). Before measurement the samples were degassed at 300 °C for 2 h. Powder X-ray diffraction (XRD) patterns were acquired on a SIEMENS D 5000 X-ray diffractometer using CuK radiation. Crystalline phases were identified by a comparison with the JCPDS file. The particles morphology was obtained using a JEOL JEM 2010 TEM operating at 200 kV. The fraction of Pd exposed (CO/Pd) was estimated from dynamic CO chemisorptions measured in a pulse system equipped with a TCD detector. The chemisorption analysis was performed bypassing pulses of CO until a constant CO peak area was observed.

**Table 1**
Physico-chemical characterization of the Pd/C catalysts.

| Catalyst | Particle size (nm[a]) | Pd dispersion[b](%) | BET (m$^2$g$^{-1}$) |
|---|---|---|---|
| 0.35% Pd/C | n.d. | 31 | 886 |
| 1% Pd/C | n.d. | 29 | 864 |
| 5% Pd/C | 6.8 | 26 | 875 |

[a] Determined from XRD data.
[b] Determined by CO chemisorption; n.d. not determined.

The metal dispersion was calculated from the moles of adsorbed CO per total moles of Pd impregnated onto the catalyst.

### 2.3. Catalytic tests

The hydrogenation with molecular hydrogen was conducted using the procedure described previously [21]. Transfer hydrogenation with formic acid as a hydrogen source was carried out in a 50 mL stainless steel reactor with a glass vessel placed inside. The reactor was loaded with the solvent (usually 5 mL), $F_2C$, formic acid and catalyst. After flushing with nitrogen, the reactor was placed into an oil bath and at desired temperature shaken using a vibrator. After cooling the reactor, the content was poured out on a glass filter and the catalyst separated. The reactor and the solid catalyst were washed twice with *n*-octane (ca. 5 mL) and the liquids mixed with the mother liquor. Then the catalyst was washed twice with THF (ca. 5 mL) and the solutions collected in a vial. Both liquids were heated at 30°C in vacuum to evaporate solvents. The resulting materials were weighed (sum of mass balance > 97%) and analyzed using the NMR technique (Varian VNMRS-600 spectrometer operating at 600 MHz for $^1$H and 150 MHz for $^{13}$C nuclei) described previously [20–22]. The content of cyclic ethers in the samples was also checked using gas chromatography (Hewlett Packard 5990 with FID detector, column $0.3 \times 60$ cm packed with 10% SE 30 on Chromaton N AW) with diphenylamine as the internal standard [23]. For identification of peaks GC/MS analysis (Shimadzu, HP-1 column) was used.

Decomposition of formic acid was carried out in a 50 mL stainless steel reactor with a glass vessel placed inside. The reactor was loaded with 5 mL of solvent, a given amount of formic acid and catalyst. After flushing with nitrogen it was quickly placed into an oil bath heated to desired temperature and shaken using a vibrator. The pressure increase with evolution of gases was monitored by the pressure measurement inside the reactor. The pressure calculation was corrected for the pressure resulting from thermal expansion of nitrogen and evaporation of solvent. Such control experiments were performed with a reactor loaded with the solvent in the absence of catalyst. The conversion profiles were used for estimation of the extent of the reaction [24].

## 3. Results and discussion

### 3.1. Catalyst characterization studies

Physico-chemical characterization of catalysts is given in Table 1 and Fig. 1. Palladium catalysts loaded on activated carbon have almost the same BET surface area. In the XRD pattern of 5% Pd /C catalyst characteristic peaks of isolated palladium crystalline were registered (not shown). The crystallite size estimated from line broadening according to Scherrer's equation was 6.8 nm. In contrast, the XRD patterns of 1% Pd/C and mainly 0.35% Pd/C catalyst displayed broad diffraction peaks with relatively low intensity. It suggests that crystallinity of these samples was not very good and/or the average crystallite size may be very small. The dispersity of palladium on the catalyst surface, determined by CO chemisorption, only slightly decreases with the palladium loading.