



Effect of catalyst and solvent on the furan ring rearrangement to cyclopentanone

Milan Hronec^{a,*}, Katarina Fulajtarová^a, Tibor Liptaj^b

^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

ARTICLE INFO

Article history:

Received 12 April 2012

Received in revised form 14 May 2012

Accepted 14 June 2012

Available online 23 June 2012

Keywords:

Cyclopentanone

Furfural

Furfuryl alcohol

Solvent effect

Hydroxy-cyclopentanone

Ring rearrangement

ABSTRACT

The effect of solvent and Ni, Pt, Pd, Pt–Ru and Ru catalysts on the products distribution has been investigated in the reaction of furfural, furfuryl alcohol and 2-methyl furan under hydrogen pressure of 30–80 bar and at the reaction temperatures of 160–175 °C. In water as solvent the main reaction pathway is the rearrangement of furfural and furfuryl alcohol to cyclopentanone. In alcohols, the reaction leading to the furan ring rearrangement does not proceed. The distribution of reaction products is influenced by the furfural concentration and acid–base properties of solvent and supported metal catalyst. The important factor influencing the selectivity of the furan ring rearrangement to cyclopentanone is proposed to be stabilization of carbocation by strong binding on the metal surface and by additional interaction with co-adsorbed water and furfural or furfuryl alcohol. In excess of hydrogen this species is created by the scission of the C–O bond in the alkoxide or hydroxyalkyl intermediates. A plausible reaction mechanism for the furan ring rearrangement was proposed.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The acid-catalyzed dehydration of pentoses and hexoses derived from renewable biomass resources can produce furan derivatives, such as furfural (FA) and 5-hydroxymethylfurfural [1–4]. Furfural is typically used as a precursor in the production of solvents, e.g. 2-methylfuran (2-MeF), furfuryl alcohol (FAL), tetrahydrofurfuryl alcohol (THFA) used in the chemical industry, and recently it is considered as a building block for transportation fuels [5–7]. Recently a number of studies have been published regarding the preparation of these compounds by hydrogenation of furfural on various metal catalysts [8–11].

The main products of furfural hydrogenation arise from the reduction of the C=O group and/or the furan ring. Depending on the application of metal catalysts for the hydrogenation of furfural or its primary products, decarbonylation [12] and hydrogenolysis of the etheric C–O bond [13] can also proceed. Due to the wide variety of available hydrogenation products of furfural, it is still attractive to design catalysts that are highly selective to the desired products.

Previously we have reported [14] that in water as solvent and under hydrogen pressure the catalytic reaction of furfural can lead to unexpected and highly selective transformation to cyclopentanone. This reaction pathway has not been reported so far in the literature dealing with the hydrogenation of furfural in the liquid phase.

In the US Patent [15] is described the multi-step process for the conversion of furfuryl alcohol to cyclopentanone. As shown in Scheme 1 cyclopentanones can be prepared from the corresponding furfuryl alcohols through intermediates, where R¹ and R² are hydrogen, lower alkyl or alkenyl substituents. As it is evident from examples described in the patent, the first step of rearrangement of furfuryl alcohol or its derivatives in an aqueous solution leading to the corresponding hydroxy-cyclopentanones is catalyzed by acids. Similar products can be obtained from substituted furfuryl alcohols in acetone/water mixture in the presence of ZnCl₂ catalyst [16]. However, this reaction is characterized by an extremely low rate and poor yields (16–18% after 72 h).

Cyclopentanone (C_{PON}) is a versatile compound used for the synthesis of fungicides, pharmaceuticals, rubber chemicals, flavor and fragrance chemicals. Potentially, it can be used for preparation of polyamides. Cyclopentanone can be prepared by the catalytic cyclization of 1,6-hexanediol or adipic esters [17].

In the present contribution, we have studied the effect of various solvents and Pt, Pd, Ru, Pt–Ru and Ni catalysts on the transformation of furfural, furfuryl alcohol and 2-methylfuran to cyclopentanone. Based on the composition of reaction products, the reaction mechanism of furfural conversion to cyclopentanone was proposed.

2. Experimental

2.1. Chemicals

All chemicals were obtained from commercial suppliers and used as provided: furfuryl alcohol (98%), 2-methylfuran

* Corresponding author. Tel.: +421 2 59325328.

E-mail address: milan.hronec@stuba.sk (M. Hronec).