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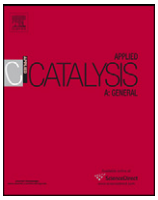

Effect of catalyst and solvent on the furan ring rearrangement to cyclopentanone

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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.

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 cyclopentenone. As shown in Scheme 1 cyclopentenones can be prepared from the corresponding furfuryl alcohols through intermediates, where R^1 and R^2 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-cyclopentenones is catalyzed by acids. Similar products can be obtained from substituted furfuryl alcohols in acetone/water mixture in the presence of $ZnCl_2$ 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

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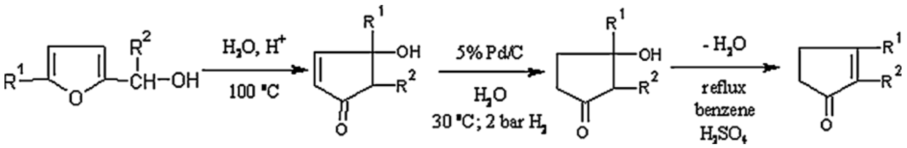

Scheme 1. Multi-step process of furfuryl alcohols conversion [15].

(99%), tetrahydrofurfuryl alcohol (99%), cyclopentanone (99%), cyclopentanol (99%), D_2O (99.9 atom% D), all from Sigma–Aldrich, 2-propanol (99%), n-butanol (98%) and n-decanol (97%), acetic acid (99.5%), H_3PO_4 (85%), $Ba(OH)_2{\cdot}8H_2O$, chemical purity from Microchem Slovakia, palladium (II) chloride, solution, Pd 9.0–11.0 wt.%, dihydrogen hexachloroplatinate (IV) hexahydrate (99.9%), ruthenium (III) chloride hydrate from Alfa Aesar. Furfural (Sigma–Aldrich, 99% assay) was purified by distillation and stored at −15 °C.

2.2. Commercial catalysts

5% Pt/C, 5% Pd/C, 5% Ru/C, all on activated carbon powder, standard reduced, nominally 50% water wet, were purchased from Johnson Matthey Co. The nickel catalyst Actimet C was purchased from BASF, NiSAT®320 RS and G-134 A from Süd Chemie. The catalyst G-134 A was ground to fine powder and in this form was used for experiments. Prior to the reaction catalysts were reduced in hydrogen (30 bar) for 2 h.

2.3. Preparation of supported catalysts

Catalysts supported on activated carbon (Norit), alumina (Eurosupport Czechia s.r.o., Czech Republic) and magnesium oxide were synthesized with the incipient wetness impregnation. Aqueous solutions of H_2PtCl_6, $PdCl_2$ or ruthenium (III) chloride were used as metal precursors in concentrations to obtain the given loading of metal on the catalyst. The bimetallic Pt–Ru catalyst was prepared by co-impregnation. The catalysts were dried at 120 °C for 5 h and then calcined at 300 °C for 5 h and hydrogen reduced at 390 °C for 5 h. Magnesium oxide was prepared by calcination of magnesium hydroxide (Duslo Šal'a Slovakia) at 500 °C for 3 h. Alumina prior to impregnation was calcined at 1050 °C for 5 h.

2.4. Catalyst characterization

The surface areas and pore diameters were determined from BET nitrogen adsorption measurements (Micromeritics ASAP 2020). The samples were degassed at 400 °C for 2 h. The dispersion of metals on the supports was estimated by H_2 and CO chemisorption measurements using helium as a carrier gas. The acidity of catalysts was determined from ammonia TPD measurements in the temperature range 100–500 °C in a nitrogen atmosphere. Measurements were carried out in a conventional flow-type apparatus at a heating rate of 20 °C min^{-1}.

2.5. Catalytic reaction and analysis of reaction products

Catalytic experiments were performed using procedure and analytical methods described in our previous paper [14]. For a typical reaction, 20 ml of water, 1.0 g of reactant and given amount of metal catalyst was added to the reactor vessel. After sealing the reactor was several times flushed with low pressure hydrogen and then pressurized with hydrogen usually to 30–80 bar (ambient temperature). The reactor was then heated to the desired temperature and the stirring speed fixed to 1500 rpm to eliminate the diffusion effects. After an appropriate reaction time the reactor was quickly cooled down, the reactor contents pour out to vial and the catalyst separated from aqueous phase by centrifugation. The quantitative determination of the liquid products concentration was done using gas chromatography by the external standard method using response factors of the corresponding standard compounds. A gas chromatograph–mass spectrometer combination was used to identify the organic compounds. The yields of all reaction products were calculated on the amount of reactant charged into the reactor.

The reactions in nitrogen atmosphere were carried out in a 100 ml Teflon lined stainless steel autoclave mixed with a Teflon bar. The autoclave was heated in an oil bath. The composition of reaction mixtures was determined by GC, GC/MS and NMR analysis (Supplementary information).

3. Results

The main physicochemical properties of the prepared catalysts are in Table 1. The chemisorption data show high dispersion of the metallic phase of carbon supported platinum and bimetallic Pt–Ru catalysts. A significantly lower dispersion of platinum is observed on the 5%Pt/MgO catalyst, probably related to the lower surface area of the MgO support. Acidity of the Pt/Al_2O_3 catalyst, measured by TPD of ammonia is low.

As shown in Table 2 all tested commercial catalysts are active, exhibiting nearly complete conversion of furfural derivatives in various solvents, except in n-decanol. However, significantly different is the distribution of reaction products. In water as solvent the 5% Pt/C catalyst and the nickel catalysts NiSAT®320RS and G-134 A are highly active for the rearrangement of furfuryl alcohol to cyclopentanone and cyclopentanol (C_{POL}). Using 5% Pt/C catalyst the comprehensive yield of cyclopentanone and cyclopentanol is even higher than in the experiment with furfural as reactant (Table 2, exps. 1 and 3). This difference might be caused by different reactivity of both reactants, but also by the partial decomposition of furfural. It was observed that in the absence of catalyst about 3–5% of furfural is decomposed during heating of its aqueous solution to the reaction temperature. In the absence of metal catalyst furfural and furfuryl alcohol under reaction conditions is not converted to cyclopentanone or cyclopentanol."

Products distribution is significantly different in the presence of 5% Pd/C catalyst. In this case the preferred reaction products are derived from the hydrogenation of the hydroxymethyl group and the furan ring. As was mentioned in our previous study, a key role in determining the selectivity of furfural transformation to cyclopentanone plays water used as solvent. The same is valid for the reaction of furfuryl alcohol in water, which in the presence of platinum and nickel catalysts is converted to cyclopentanone and cyclopentanol with very high selectivity. In contrast to the results in water, in 2-propanol as solvent, the dominant product is tetrahydrofurfuryl alcohol (Table 2, exps. 3 and 5). Similar results were obtained in 2-propanol using the 5%Ru/TiO_2 catalyst [18]. Furfural in 2-propanol is hydrogenated to furfuryl alcohol [19] or to products of the carbonyl group and the furan ring hydrogenation [14]. In water as solvent, the main product of furfural conversion is cyclopentanone (Table 2, exp. 1).

Furfuryl alcohol in n-decanol is hydrogenated to products of the furan ring and the hydroxymethyl group hydrogenation,