Highly selective rearrangement of furfuryl alcohol to cyclopentanone

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A B S T R A C T

The aqueous phase hydrogenation of furfuryl alcohol to cyclopentanone was carried out on a series of metal supported and bulk catalysts. The effect of catalyst concentration, temperature, hydrogen pressure and reaction time has also been investigated. By changing the partial hydrogen pressure and concentration of metal catalyst it is possible to transform furfuryl alcohol with a very high selectivity either to furfuryl alcohol or cyclopentanone. High hydrogen pressure and catalyst concentration favours the formation of tetrahydrofurfuryl alcohol. At very low concentration of metal catalyst (0.25–1.0 wt%) and 0.8–2.5 MPa of hydrogen pressure, the product is exclusively cyclopentanone formed in yields higher than 95 mol%. Very active and selective are nickel type catalysts. The differences in selectivities of products distribution are explained by the proposed reaction mechanism consisting of two parallel reactions. One reaction is catalyzed preferably by hydrogen ions produced by self-dissociation of water and other by metal catalyst.

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1. Introduction

In the past years the production of chemicals from biomass has received increased attention in view of the replacement of petroleum. Furfural is one of basic chemicals obtained from hemicellulose raw material via acid-catalyzed dehydration [1–7]. Gas or liquid-phase hydrogenation of multifunctional furfural (FA) over heterogeneous catalysts can produce various useful products described recently in overviews by Nakagawa et al. [8] and Gallezot [9].

Selective hydrogenation of the C=O bond of furfural leads to an industrially important chemical, furfuryl alcohol (FAL), which is applied mostly in polymer industry for the production of corrosion and acid-resistant materials. Subsequent hydrogenation of the C=C bonds of furfuryl alcohol gives tetrahydrofurfuryl alcohol (THFA), usually used as a green solvent. Nickel based catalysts [10,11] and noble metals [12,13] are generally applied for this reaction in a liquid phase. Recently, we have reported [14] that in water as a solvent furfural and furfuryl alcohol in the presence of heterogeneous Pt, Pd, Ru, Ni catalysts are at higher temperatures and hydrogen pressures selectively converted to cyclopentanone. Under these conditions and in the absence of metal catalysts the main products of furfuryl alcohol conversion in water are 4-hydroxy-2-cyclopentenone (4-HCP) and polymers of furfuryl alcohol [15]. These products are result of acid-catalyzed ring-rearrangement reaction of furfuryl

alcohol and its polymerization. Acid catalyst (H_3O^+) is formed by self-dissociation of water serving as the solvent.

Cyclopentanone is a versatile compound used for the synthesis of fungicides, pharmaceuticals, rubber chemicals, and flavour and fragrance chemicals [16]. Potentionally, it can be used for preparation of polyamides [17] and C_{15}–C_{17} diesel or jet fuels [18]. Cyclopentanone can be prepared by the catalytic vapour-phase cyclisation of 1,6-hexanediol [19] or adipic esters [20–22] or by the liquid phase oxidation of cyclopentene with nitrous oxide [23,24]. In all these processes petroleum-based products are used as feed stocks.

In this paper, we report how we can principally change the selectivity of furfuryl alcohol conversion in water either to tetrahydrofurfuryl alcohol or to cyclopentanone by varying the hydrogen pressure or concentration of metal catalyst. The knowledge of this dependence offers us the possibility to achieve very high yields of cyclopentanone directly from furfuryl alcohol at very low catalyst concentrations and hydrogen pressures. To the best of our knowledge, no available literature describes such highly selective conversion of furfuryl alcohol to cyclopentanone under comparable concentration and reaction conditions.

2. Materials and methods

2.1. Materials

Furfuryl alcohol (98%), tetrahydrofurfuryl alcohol (99%), cyclopentanone (99%) and cyclopentanol (99%) were purchased from Sigma–Aldrich, and were used without purification. Pt, Pd

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and Ru catalysts with 5 wt% of metal on activated carbon powder were purchased from Johnson Matthey Co. The nickel catalysts G-134, G-49 and NiSat® 320 RS were purchased from Sud Chemie and catalyst Actimet C from BASF. Supported nickel catalysts were prepared by incipient wetness impregnation of powdered (particle sizes < 110 μm) activated charcoal Norit (Fluka) and SiO_2 Sylobloc 46 (surface area 306 $m^2 g^{-1}$, Grace Davison) with aqueous solutions of nickel nitrate. The concentration of solutions was settled in order to obtain nominal metal loadings of 5 and 10 wt%, respectively. After drying at 100 °C for 6 h solids were reduced in hydrogen at 500 °C for 2 h. The prepared nickel catalysts had average metal particle size determined from XRD data 13.5 and 15.7 nm, respectively. The mixed oxide Ni–Mg–Al catalyst with molar ratio of metals 1:1:1 in fresh catalyst was prepared using the coprecipitation method [25]. As the precipitant was added dropwise 4% NH_4OH to an aqueous solution containing an appropriate amount of $Ni(NO_3)_2$, $Al(NO_3)_3$ and $Mg(NO_3)_2$. The solution was stirred at 40 °C until the pH reached 8.0. The precipitate was separated by a centrifuge, and then dried at 110 °C overnight and calcined at 650 °C for 5 h. Before reaction, the precursor was grinded and sieved to 75–110 μm, and reduced at 500 °C in hydrogen atmosphere for 3 h.

2.2. Catalytic tests

Catalytic experiments were performed using procedure and analytical methods described in our previous paper [26]. For a typical reaction 20 ml of water, 1.0 g of furfuryl alcohol and a given amount of metal catalyst were loaded into the reactor vessel. After sealing, the reactor was several times flushed with low pressure hydrogen and then pressurized with hydrogen usually to 0.8–2.5 MPa (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 poured out to vial and the catalyst separated from the aqueous phase by centrifugation. The aqueous phase was analyzed using gas chromatography (Hewlett Packard 5890 Series II, with FID detector). The quantitative determination of the reaction products was done by the external standard method using aqueous solutions of each product with known concentration and response factor. A gas chromatograph–mass spectrometer combination (GC/MS QP 5000 Shimadzu with HP-1, 50 mm × 0.2 mm capillary column) was used to identify the organic compounds. Prior to GC/MS analysis, the aqueous phase saturated with NaCl was several times extracted with dichloromethane. The composition of the gas phase was determined using gas chromatography (Shimadzu GC-17A equipped with TC and FID detectors). We found only trace amounts of carbon oxides, methanol and light hydrocarbons in the gas phase. FAL conversion (X_{FAL}), yield (Y_i) and selectivity of product i (S_i) were calculated as follows:

$$X_{FAL} = \frac{n_{FAL}^0 - n_{FAL}}{n_{FAL}^0} \times 100\%$$

$$Y_i = \frac{n_i}{n_{FAL}^0} \times 100\%$$

$$S_i = \frac{Y_i}{X_{FAL}} \times 100\%$$

where i represents mol of the corresponding product, and n_{FAL}^0 and n_{FAL} depict the mol of FAL in the reaction mixture before and after reaction, respectively.

3. Results and discussion

The study of the influence of reaction parameters on the hydrogenation of furfuryl alcohol in water as a solvent has shown, that crucial parameters affecting the selectivity to the main reaction products are concentration of the heterogeneous metal catalyst (Fig. 1) and partial pressure of hydrogen (Fig. 2). These data were obtained at an impeller speed of 1500 rpm, which ensured that in the given volume of reaction mixture the gas–liquid and liquid–solid mass-transfer resistance can be ignored. The catalyst particle size was varied to test the significance of intra-particle mass-transfer resistance. Two experiments were carried out at 160 °C and 2.5 MPa of hydrogen using catalyst particle sizes <75 μm and in the range between 75 and 110 μm, respectively. It was found that in these ranges the metal catalyst particle size had no effect on the yields of two main reaction products, cyclopentanone and tetrahydrofurfuryl alcohol. From these results it is seen that the mass-transfer resistances do not influence the distribution of the main reaction products.

The observed differences in selectivities depicted in Figs. 1 and 2 are apparently related to the mechanism of conversion of furfuryl alcohol in water as a solvent. As we have found ([15] and Table 1, Run 1) in nitrogen or hydrogen atmosphere at temperatures above 110 °C furfuryl alcohol dissolved in pure water is by the furan ring-rearrangement reaction rapidly converted to 4-hydroxy-2-cyclopentenone and by parallel reaction to condensation products and polymers (Scheme 1). These reactions are catalyzed by hydrogen ions formed by auto-dissociation of water. However, if in the similar reaction system is present also the hydrogenation catalyst
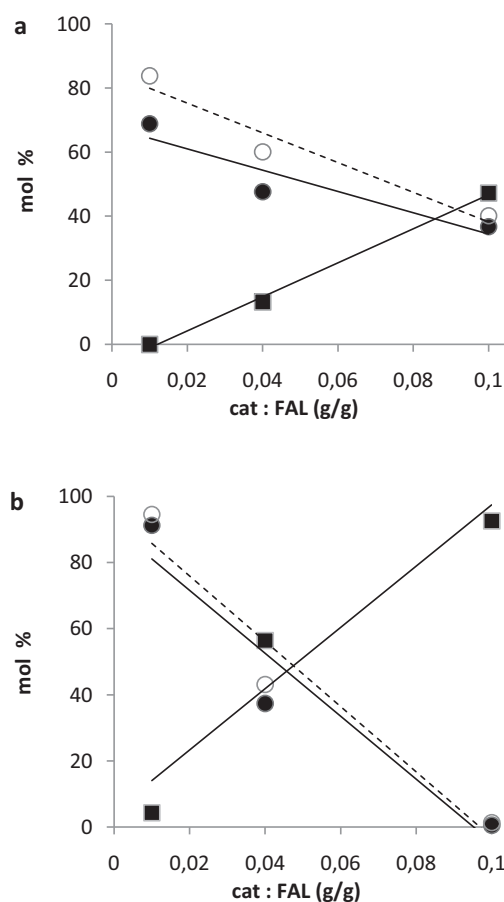
Fig. 1. Effect of catalyst concentration on the yield of THFA (■), C_{PON} (●) and the sum of $C_{PON} + C_{CEON}$ (○) at partial hydrogen pressure (a) 0.8 MPa and (b) 2.5 MPa. *Conditions:* 1.0 g FAL; 20 g H_2O; 160 °C; reaction time: 60 min; nickel catalyst G-134