THE INFLUENCE OF METALLIC PROMOTERS ON ACTIVITY AND SELECTIVITY OF PALLADIUM CATALYST IN FURFURAL REDUCTION

UTICAJ METALA NA AKTIVNOST I SELEKTIVNOST PALLADIUMOVIH KATALIZATORA PRILIKOM SMANJENJA FURFURALA

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ABSTRACT

The studies presented in this paper concern the choice of an effective bimetallic catalyst for the reduction of furfural to furyl alcohol (FA) and tetrahydrofuranyl alcohol (THFA) in the liquid phase. The way of furfural reduction greatly depends on the catalyst system used. In the study the effect of the addition of metallic promoter (Au, Bi, Fe, In, Te, Tl) into 5 % Pd/SiO₂ on the activity and selectivity in furfural reduction was investigated. Depending on the bimetallic catalysts used in the process, furyl alcohol, tetrahydrofuranyl alcohol or condensation products were mainly obtained.

Key words: furfural, fine chemicals, biofuels, catalytic hydrogenation, bimetallic catalysts.

INTRODUCTION

Furfural can be prepared from any material containing pentoses (Modelska, 2015). The annual world production of this compound is about 280,000 tons. The greatest amount of furfural is produced in China (200,000 tons), Dominican Republic (32,000 tons) and South Africa (20,000 tons) (Win, 2005). Furfural may be widely used in the industry as a versatile building material because its molecule contains two reactive functional groups (a carbonyl group and furan ring). The aldehyde group (C=O) of furfural may undergo typical reactions such as acylation, acetylation, reduction to alcohols, aldolisation and Knoevenagel condensation, decarboxylation, oxidation to carboxylic acids, and Grignard reactions. The double bonds of the furan ring (C=C-C=C) can undergo hydrogenation, oxidation, alkylation, halogenation, ring opening and nitrination reaction (Yan, 2014).

The most popular product of the furfural hydrogenation is furyl alcohol (FA). Above 60 % of the annual production of furfural is converted to this alcohol. FA is used, for example, for the production of cross-linked polymers, characterized by unique chemical, thermal and mechanical properties. Moreover, FA, due to high corrosion resistance, is used in the production of furan fiber-reinforced plastics for the construction of pipelines (Yan, 2014). This compound is also used in the production of fragrances, paints, non-reactive diluents for epoxy resins, phenolic and urea resins modifier, in the production of tetrahydrofuranyl alcohol and other chemicals, coatings, selective solvents, adhesives, corrosion-resistant mortar for acid-resistant bricks, binders carbon compounds, impregnating compounds, for laminating corrosion-resistant fiberglass equipment, resins for polymer, furan concrete, resins for bonding sand used for the preparation of cores and molds for metal casting. Furthermore, furyl alcohol is an intermediate used in the production of lysine, vitamin C, lubricants, dispersants, and plasticizers. Furfuryl alcohol is formed by hydrogenation of the furfural aldehyde group (Yan, 2014; Rao, 1999; Bankmann, 1997; Nagaraja, 2005).

The second important product of furfural hydrogenation is tetrahydrofuranyl alcohol (THFA). It is considered a green solvent used in agriculture, industrial printing inks as well as cleaning agents in electronics. It may be obtained by hydrogenation of furfural or furfuryl alcohol. However, on an industrial scale, THFA is produced by a two-step method: hydrogenation of furfural to FA and further reduction to THFA (Yan, 2014).

Other products that may be obtained from furfural and are considered interesting for the industry are 2-methylfuran, 2-methyltetrahydrofuran, tetrahydrofuran, furan, cyclopentanone, cyclopentanol and many others. These compounds may be used as fuel biocomponents or important chemical intermediates (Yan, 2014).

Furfural can be reduced into both furyl and tetrahydrofuranyl alcohol in a gas phase over the following catalysts: copper-chromites (Rao, 1997; Seo, 1981), Raney Ni (Wojcik, 1948), Raney Co (Bankmann, 1997), Raney Cu (Bankmann, 1997), nickel amorphous alloy (Lee, 1999; Luo, 2001), Al, Fe or Mn-doped mixed copper-zinc oxides (Nowicki, 1997) or homogeneous complexes of Ru, Rh or Pt (Burk, 1994; Karakhanov, 1985). The systems mentioned are sometimes promoted by Na, Ca, Co, La and Ni (Hao, 2005; Reddy, 2007; Wu, 2005).
In the literature data, there is some information about the use of copper catalysts in the reduction of furfural to FA in the gas phase (Rao, 1999; Bankmann, 1997; Nagaraja, 2003; Nagaraja, 2007; Sitthisa et al., 2011). Sitthisa and Resasco (2011) compared the activity of copper, palladium and nickel catalysts in that reaction. Only in the case of the use of copper catalyst the main product of the reaction was FA, in other cases furan was mainly obtained. However, when copper was introduced into palladium catalysts, selectivity to furan decreased, while an increase in selectivity to FA was observed (Sitthisa, et al., 2011).

It is well known that carrying out chemical processes in the liquid phase is more favorable in terms of energy and ecology. In this context, a method for the selective reduction of furfural in the liquid phase is being developed in our research team. The first part of our studies is reported in the Journal of Molecular Catalysis A: Chemical (Lesiak, 2014). In that paper, the catalytic reduction of furfural in the liquid phase over Pd/Al2O3 and Pd-Cu/Al2O3 catalysts was described. It can be observed that the addition of copper influences significantly the selectivity of palladium catalyst. As the amount of copper introduced to the palladium system rises, the selectivity towards furfuryl alcohol increases. On the basis of experimental results one can say that the influence of co-metal on the catalytic performance of Pd will be affected by the degree of intimate interaction between the two components and by the chemical state of both the Pd and co-metal.

Although various metallic promoters have been used for different oxidation and reduction reactions, their precise role in the catalytic reduction of furfural is still undetermined. In this paper, an impact of other metals on the activity and selectivity of palladium catalysts was studied. Monometallic 5 % Pd/SiO2 and bimetallic 5 % Pd-1 % M/SiO2 (M = Bi, Au, In, Te, Tl, Fe) catalysts were investigated in the reduction of furfural in the water phase. Hydrogenation of furfural was performed in an autoclave at a temperature of 90 °C, under 20 bar of H2 pressure. The reaction mixture was analyzed using HPLC method to determine the concentration of furfural. The products of furfural hydrogenation were screened using GC-FID analysis (Hewlett Packard 5890A; packed column 8 % Carbowax 1540 on Chromosorb W; injection port temperature: 170 °C, injection volume: 5 µl; FID detector temperature: 250 °C; column oven temperature: 190 °C; He (Linde, 99.999 %, 30 ml min−1). The liquid products were additionally analyzed using a Perkin Elmer GC–MS (model Clarus 580 with MS Clarus SQ 8 S) equipped with an Elite-5MS capillary column (30 m length, 0.25 mm i.d. and 0.5 m film thickness). The operating conditions of the GC–MS analysis were: Electron Impact at 70 eV; 35–350 m/z mass range; injection port temperature 250 °C; interface temperature 300 °C; column oven temperature programme: 35 °C for 7 min, ramped at 3 °C min−1 to 155 °C, ramped at 20 °C min−1 to 300 °C with 3 min hold; helium carrier gas (flow rate of 30 cm3/min); 1 µl injection volume; 1:200 split ratio.

Catalytic results are expressed as conversion (X, %) and selectivities (S, %). Those parameters were defined as:

\[ X = \left[ 1 - \frac{C}{C_0} \right] \times 100\% \]

\[ S = \left[ \frac{C_P}{C_0 - C} \right] \times 100\% \]

where C0 is a molar concentration of furfural at the beginning of the hydrogenation process, C is amolar concentration of furfural at the end of reaction, Cp is a molar concentration of products (furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofuran, 2-methyltetrahydrofuran and condensation products) at the end of the reaction. The tests of catalytic activity were conducted for each catalyst three times and the presented results constitute arithmetical mean of these three measurements.

**RESULTS AND DISCUSSION**

Monometallic palladium catalyst was not selective to any product of furfural hydrogenation. In the reaction mixture, the presence of furfuryl alcohol, tetrahydrofurfuryl alcohol and the condensation products in comparable amounts was stated. In the case of the catalysts promoted with gold and tellurium mainly condensation products were obtained. When the reaction was passed over the catalyst promoted by bismuth, a preferred way of reaction was the reduction of all double bonds in the furfural molecule and mainly tetrahydrofurfuryl alcohol was obtained. However, in the case of the bimetallic system a significant number of condensation products were observed too. In the case other bimetallic systems used as a catalyst of furfural reduction, furfuryl alcohol was detected as a main product. The
concentration of THF and MTHF did not exceed 4 % in any of the analyzed reaction mixtures (Tab. 1).

5 % Pd-1 % M/SiO₂ (M = Au, Bi, Fe, In, Te, Ti) systems after activation in H₂ at the temp. 300°C were characterized by good activity and varied selectivities to the desired products in the tested reaction. For this reason, the physico-chemical properties of the obtained bimetallic catalysts were studied. Activation of the bimetallic catalysts at 300 °C in a H₂ atmosphere led to the formation of alloys or intermetallic products was stated. For the supported palladium catalysts investigation, the improvement in selectivity towards one of the influence of the metallic interaction in the studied bimetallic catalysts plays a key role in the selectivity to various products of reduction products: furfuryl alcohol [S FA], tetrahydrofurfuryl [STHF+MTHF] and condensation products [SCP].

Table 1. Furfural conversion [X] and selectivity to furfural reduction products: furfuryl alcohol [S FA], tetrahydrofurfuryl alcohol [STHF], tetrahydrofuran and 2-methyltetrahydrofuran [STHF-MTHF] and condensation products [SCP].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>X [%]</th>
<th>S FA [%]</th>
<th>S TFA [%]</th>
<th>S THF-MTHF [%]</th>
<th>S CP [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Pd-1%Fe/SiO₂</td>
<td>100</td>
<td>90</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5%Pd-1%In/SiO₂</td>
<td>100</td>
<td>70</td>
<td>27</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>5%Pd-1%Te/SiO₂</td>
<td>100</td>
<td>68</td>
<td>26</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>5%Pd/SiO₂</td>
<td>100</td>
<td>42</td>
<td>32</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>5%Pd-1%Bi/SiO₂</td>
<td>100</td>
<td>4</td>
<td>51</td>
<td>4</td>
<td>41</td>
</tr>
<tr>
<td>5%Pd-1%Au/SiO₂</td>
<td>100</td>
<td>3</td>
<td>0</td>
<td>1</td>
<td>96</td>
</tr>
</tbody>
</table>

CONCLUSION

From the obtained results it can be concluded that the influence of the metallic interaction in the studied bimetallic catalysts plays a key role in the selectivity to various products of furfural reduction. For all bimetallic systems used in our investigation, the improvement in selectivity towards one of the products was stated. For the supported palladium catalysts promoted with Ti, Fe and In, the main product of reaction was FA. On the other hand, the use of Bi, Te and Au causes an increase in the selectivity to THFA or condensation products.

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