SLOVAK RESEARCH AND DEVELOPMENT AGENCY

ICCT INTERNATIONAL CONFERENCE ON CHEMICAL TECHNOLOGY

8. mezinárodní chemicko-technologická virtuální konference
3. – 5. 5. 2021

STU FCHPT

CATALYTIC OXIDATION OF FURFURAL TO MALEIC ACID IN THE PRESENCE OF IRON BASED CATALYSTS

Tomáš Soták, Blažej Horváth, Dana Gašparovičová, Milan Králik, Milan Hronec

(tomas.sotak@stuba.sk)

Department of Organic Technology, Catalysis and Petrochemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovakia

INTRODUCTION

Furfural (FUR) is a C_5 compound produced from hemicelluloses by dehydration in acidic media[1]. Selective oxidation of biomass-based furfural to maleic acid (MAc) or maleic anhydride, which are currently produced from benzene and/or butane, is an alternative route to the on-going fossil base processes. Oxidation of FUR in both vapor and liquid phases using various types of metal catalysts have been studied[2,3,4]. The recent developments in maleic acid synthesis from bio-derived chemicals over homogeneous or heterogeneous catalysts were summarized lately in a review paper[5].

OBJECTIVES

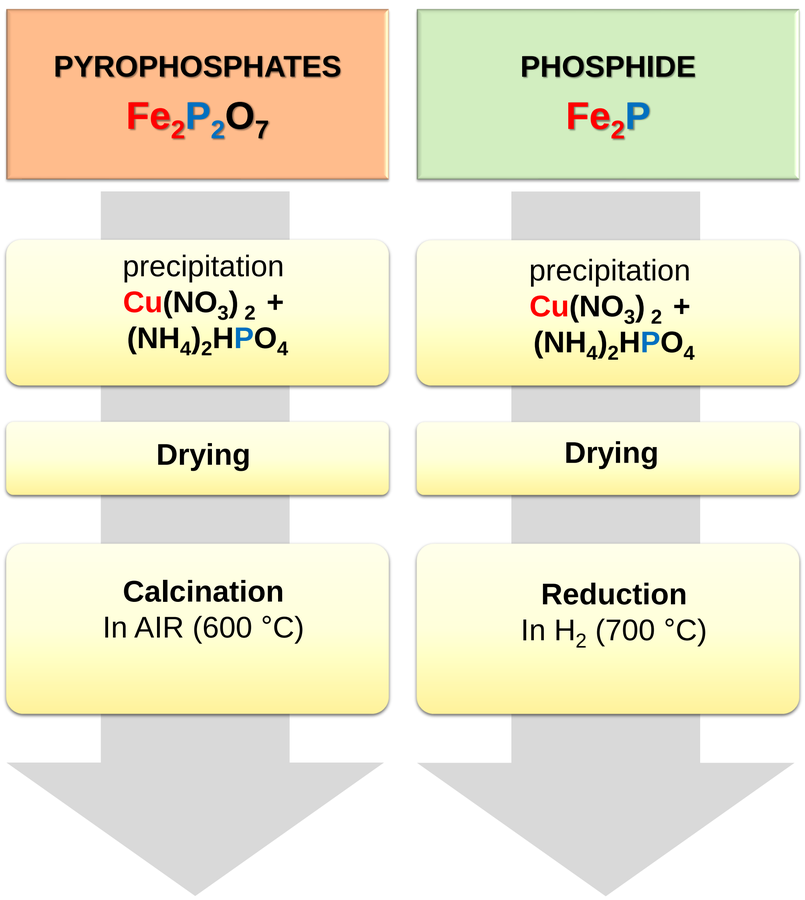
In the present study we show that furfural can be converted efficiently to maleic acid over some types of heterogeneous iron catalysts. The highest catalytic performance was observed in the presence of iron pyrophosphates.

EXPERIMENTAL

Catalysts preparation

The samples of pyrophosphate catalysts were prepared by calcination of precursors (Fe/P atomic ratios: 0.25-1.5) at various temperatures, mainly at 600 °C (Scheme 1).

Scheme 1
Constituent steps for the preparation of catalysts.



Catalytic tests

- ***REACTION CONDITIONS:***
  - ***Temperature: 120 ˚C***
  - ***O_2 pressure: 0.8 MPa***
  - ***Time: 18 h***
- ***REACTOR:***
  - ***10 ml stainless steel tubes***
- ***RAW MATERIAL:***
  - ***furfural + water + catalyst***

Analysis

The yields of reaction products (oxalic acid – OAc, maleic acid – MAc and formic acid – FAc) and furfural conversion were analyzed using HPLC equipped with DAD and RI detectors.

RESULTS AND DISCUSSION

Different iron-based catalysts

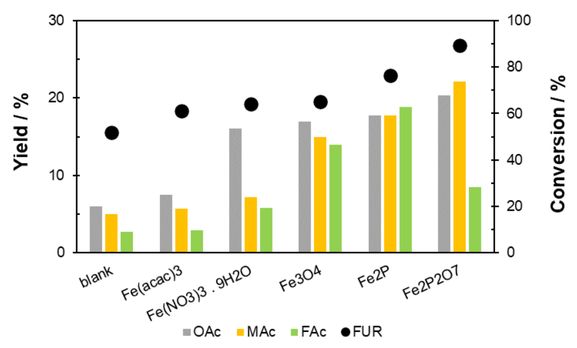


Fig. 1 Comparison of different Fe-based catalysts in furfural oxidation.

The results of a preliminary study of the furfural oxidation (Fig. 1) showed a significant effect of different types of iron-based catalysts on the distribution of oxidation products. When the reaction was in progress without a catalyst (blank), the yield of desired MAc and other products were very low (<10%). In the presence of Fe nitrate as a catalyst a significant increase in the yield of OAc and only slight increase in the yield of MAc were observed. However, using of heterogeneous Fe_3O_4 and Fe_2P catalysts the yield of desired MAc increased rapidly. A further increase in the yield of MAc in the presence of $Fe_2P_2O_7$ catalyst was achieved.

Effect of Fe/P molar ratio

A significant increase in both FUR conversion and yield of MAc was observed using heterogeneous Fe-type phosphate catalysts (Fig. 2). An increase in the Fe/P molar ratio in the catalyst enabled a gradual increase in the conversion of FUR and yields of the desired products. Among the given series of tested catalysts, the best results were achieved using the $Fe_2P_2O_7$ catalyst with an atomic ratio of Fe/P = 1.

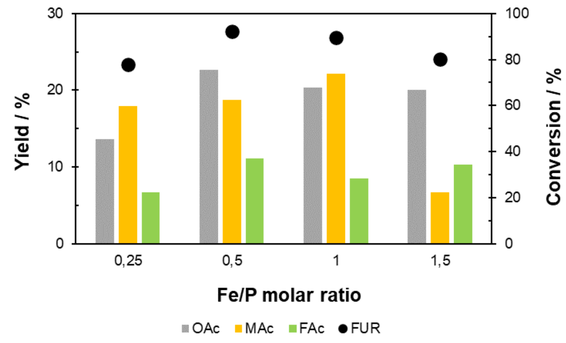


Fig. 2 Effect of the Fe/P molar ratio in Fe-P-O catalysts calcined at 600 °C.

Effect of calcination temperature

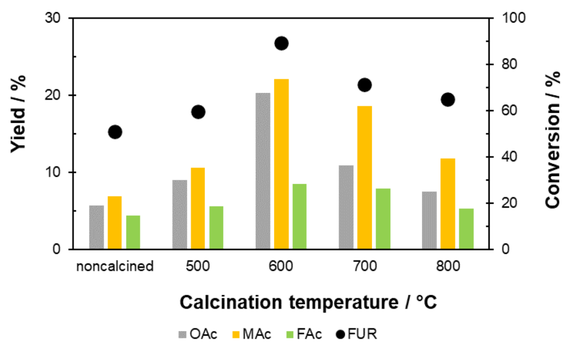


Fig. 3 Effect of calcination temperature in Fe-P-O (Fe/P=1) catalysts.

Significant effect was also observed using different calcination temperatures of the Fe-P-O (Fe/P=1) catalysts (Fig. 3). Using the uncalcined Fe-P-O catalyst, the lowest yields of the carboxylic acids (<10%) were obtained. As the calcination temperature increased during the preparation of the catalysts, there was a gradual increase in the product yields in furfural oxidation. The best results were obtained using a catalyst calcined at 600 °C. Catalysts with a higher calcination temperature (700 °C and 800 °C) revealed themselves with decreases in both the conversion of the reactant and the yields of the studied reaction products.

Optimization of reaction parameters

Based on previous results the reaction temperature (Fig. 4a) and pressure of oxygen (Fig. 4b) using the $Fe_2P_2O_7$ (Fe/P=1) catalyst were optimized. The highest yield of desired MAc was obtained at the temperature of 120 °C and the O_2 pressure of 0.8 MPa.

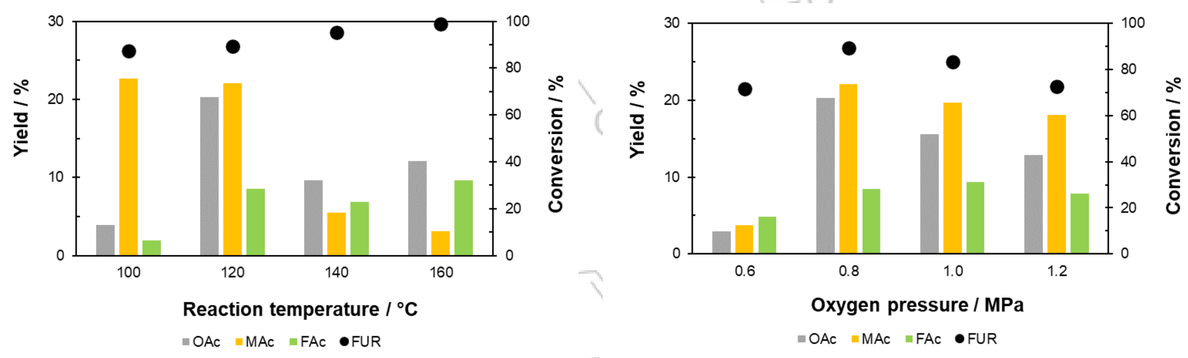


Fig. 4 Influence of reaction temperature and oxygen pressure in furfural oxidation.

ACKNOWLEDGEMENT

The authors gratefully thank to the Slovak Research and Development Agency under the Contract no. APVV-17-0302.

CONCLUSIONS

The highest yield of maleic acid (22.1 %) as the desired reaction product was achieved at 89.4 % conversion of furfural using $Fe_2P_2O_7$ catalyst prepared with ratio Fe/P=1 and calcined at 600 °C. This catalyst can be easily removed from the reaction mixture by filtration. The same selectivity to MAc was proven in 3 reaction runs in recycling studies.

REFERENCES

[1] Zeitsch, K. J. *The chemistry and technology of furfural and its many by-products*. Elsevier, Amsterdam, **2000**.
[2] Alonso-Fagúndez, N.; Granados, M. L.; Mariscal, R.; Ojeda, M. *ChemSusChem* **2012**, 5, 1984-1990.
[3] Lan, J.; Chen, Z.; Lin, J.; Yin, G. *Green Chem*. *2014*, 16, 4351-4358.
[4] Soták, T.; Hronec, M.; Gál, M.; Dobročka, E.; Škriniarová, J. *Catal. Lett*. **2017**, 147, 2714-2723..
[5] Wojcieszak, R.; Santarelli, F.; Paul, S.; Dumeignil, F.; Cavani, F.; Gonçalves, R. V. *Sustain. Chem. Process* **2015**, 3, 9.