INTRODUCTION

Furfural (FUR) is a C₅ compound produced from hemicelluloses by degradation in acidic media. 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. The recent developments in maleic acid synthesis from bio-derived chemicals over homogeneous or heterogeneous catalysts were summarized lately in a review paper.

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).

RESULTS AND DISCUSSION

Different iron-based catalysts

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 Fe₃P₂O₇ catalyst with an atomic ratio of Fe/P = 1.

Effect of calcination temperature

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 Fe₃P₂O₇ (Fe/P=1) catalyst were optimized. The highest yield of desired MAC was obtained at the temperature of 120 °C and the O₂ pressure of 0.8 MPa.

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REFERENCES


CONCLUSIONS

The highest yield of maleic acid (22.1 %) as the desired reaction product was achieved at 89.4 % conversion of furfural using Fe₃P₂O₇ 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.