

HYDRODEOXYGENATION OF FURAN ON H-ZSM-5 AND Pt-ZSM-5

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ABSTRACT

It is shown that the shape-selective hydrodeoxygenation of furan proceeds on the catalysts H-ZSM-5 and Pt-ZSM-5. The differences in the product spectra obtained on the two zeolite materials and the different coking rates are interpreted with the different hydrogenation capabilities of the two catalysts. The low H/C ratio of furan can be increased to the higher values of the products by activation of added molecular hydrogen or, in the case of Pt-ZSM-5, by hydrogen transfer from added molecules with high H/C ratios. Reaction mechanisms for the furan conversion are discussed, which comprise the observed oxygen eliminations by decarbonylation and dehydration as well as the 2,3-benzofuran formation.

INTRODUCTION

The elimination of the hetero atom from oxygen containing compounds on zeolite catalysts has been studied for a broad class of reactions [1], leading to the discovery of the methanol to gasoline process [2]. Moreover, shape-selective zeolite catalysts have been shown to convert a variety of oxygen containing biomass derived compounds to high-grade fuel [3]. Shape-selective catalysts exhibit the unique property to reconstruct large molecules of quite different type into very similar molecular weight-limited product mixtures. This capability of the pentasil type zeolites can be used to convert the pyrolysis products of the biomass containing municipal wastes and sewage sludges into gasoline. The main classes of organic compounds formed in the decomposition of cellulose, the main constituent of the biomass, i.e. methanol, acetic acid, phenols and furfurals, should undergo shape-selective conversions. For an exemplary clarification of this point, the deoxygenation of the furan, which is readily formed by the decarbonylation of the representative pyrolysis product furfural, is studied on the zeolites H-ZSM-5 and Pt-ZSM-5.

EXPERIMENTAL

Preparation of Catalysts. The sodium form of the ZSM-5 was synthesized according to the recipe example 24 of the patent of Argauer and Landolt [4]. The main variation concerns the manner to achieve the pH value of 11, which we did not adjust by addition of H_2SO_4 but by using colloidal solutions of silica gel (Kieselso1, Bayer, Leverkusen) instead of water glass, leading to lower NaOH portions in the reaction mixture. A teflon vessel equipped autoclave (Berghof, Tübingen) was used. The complete removal of the organic material from the template ion by the calcination procedure was controlled by infrared spectroscopy. No effect of stirring on the crystallinity of the products was observed.

The hydrogen form of the catalyst was obtained by repeated ion exchange in a 5% aqueous NH_4Cl solution (15 ml per g zeolite) at 353 K, subsequent washing, drying at 373 K and calcination at 623 K for 4 hours.

The platinum loaded catalyst was prepared by ion exchange in an aqueous solution of 0.5 % platinum tetrammine chloride at 353 K for 4 hours, using 7 ml solution per 1 g zeolite. After washing and drying the platinum complex was decomposed by temperature programmed heating ($5 K min^{-1}$) up to 673 K under argon ($5 l h^{-1}$) and subsequent reduction in hydrogen (1 bar, $5 l h^{-1}$) at 673 K. The platinum content of the catalyst was 2.2 wt%.

Characterization. The prepared ZSM-5 exhibited a silicon to aluminum atomic ratio of about 40. The infrared spectra and the X-ray diffraction patterns, typical for the ZSM-5 type zeolite were obtained. A small fraction of amorphous material of about 5% could be detected by X-ray diagrams. The nitrogen physisorption capacities at 77 K and $P/P_0 = 0.1$ were determined by a dynamic method [5] and gave 21 molecules per unit cell, confirming the good crystallinity of the zeolite [6]. From the scanning electron micrographs mean zeolite particle sizes around $1 \mu m$ were determined. No platinum lines were found in the X-ray diagram pointing to platinum particles located within the zeolite matrix. Since the amount of platinum corresponds to the aluminium content, a nearly complete ion exchange can be assumed.

Apparatus. The furan conversion was studied in a continuous flow stainless steel microreactor (6 mm inner diameter) with a fixed bed (0.2 g) of the undiluted, pressed (14 MPa) and pelletized (0.35 - 0.5 mm diameter) zeolite catalyst. The reaction was studied at 673 K and at $WHSV = 0.5 h^{-1}$. Argon and hydrogen were used as carrier gases and were flowing through the catalyst bed until constant reaction temperatures were reached. They were then loaded with furan by streaming through a thermostated saturator. The reaction products were analyzed by gas chromatography (F 22, Perkin Elmer) using a thin film quartz capillary (25 m, OV 101, Perkin Elmer) and temperature programs. Product identifications were made using internal standards.

RESULTS

H-ZSM-5. The catalyst exhibited strong fluctuations in the product distribution during the first minutes, which disappeared after 10 minutes. The distribution of the hydrocarbon mixture, i.e. without water and carbon monoxide, in dependence on the time on stream of the educt furan is shown in Figure 1. The high fraction of BTX (benzene, toluene and xylenes) aromatics formed in the very beginning decreases rapidly in favour of C_{9+} aromatics, e.g. methylethylbenzenes, mesitylenes, durenes and naphthalenes and especially high fractions of the compound 2,3-benzofuran. The catalyst is deactivated to more than 90% after 1 hour. Its nitrogen physisorption capacity decreases sharply, i.e. by 25%, within the first 10 minutes and then more slightly but continuously.

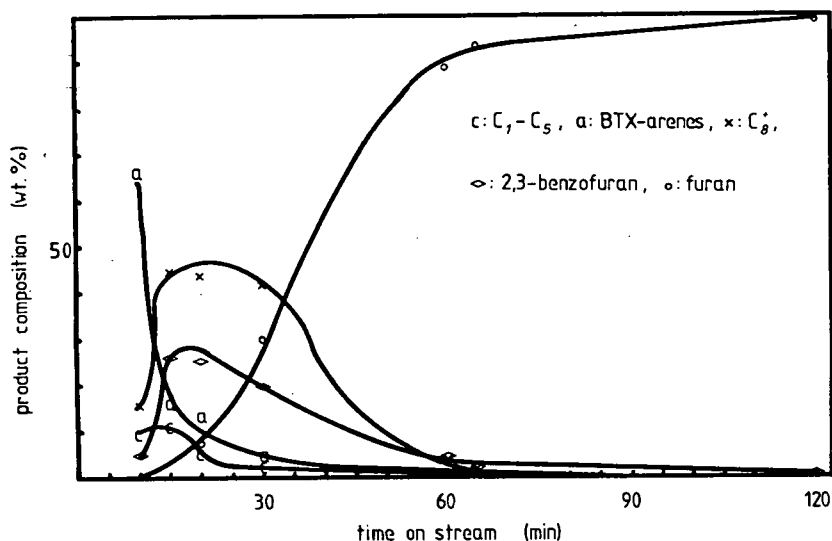


Fig. 1. Product composition (without water and CO) of furan conversion on H-ZSM-5 in hydrogen (673 K, WHSV = 0.5 h^{-1} , 11 kPa furan)

Pt-ZSM-5. Furan was converted to $C_1 - C_4$ paraffins and BTX aromatics, mainly, without any fluctuations of the product concentrations during the first minutes (Fig. 2). The BTX fraction decreases more slightly as compared to the H-ZSM-5. The fractions of 2,3-benzofuran, the educt furan and the higher aromatics rise slowly

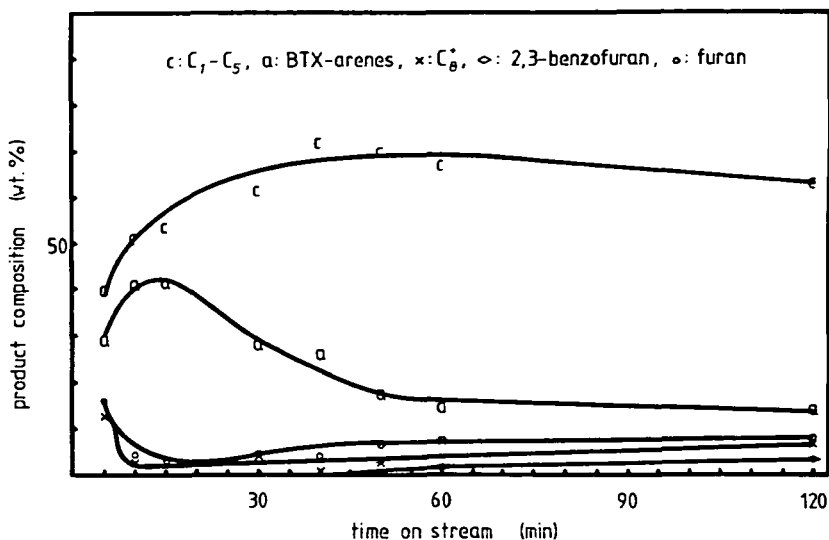


Fig. 2. Product composition (without water) of furan conversion on Pt-ZSM-5 in hydrogen (673 K, WHSV = 0.5 h^{-1} , 11 kPa furan)

in correspondence to the decrease of the nitrogen physisorption capacity (Fig. 3). No decarbonylation is observed, i.e. no CO is found among the gaseous products.

DISCUSSION

Rates of Deactivation. The nitrogen physisorption capacity of the H-ZSM-5 catalyst is decreased by 25% in a time where the catalyst is fed by a number of furan molecules, which is of the order of magnitude of the number of active centers calculated from the aluminum content. This indicates that the conversion proceeds in a relatively thin external shell of the zeolite crystals, leading to a sealing of a fraction of the channels by coke deposition and resulting in the observed strong decrease of the nitrogen physisorption capacity. Pore plugging by coke deposition, which is a general phenomenon in zeolite chemistry and which is found to proceed at reduced rates on the pentasils, is obviously enhanced in the conversion of molecules like furan, which have low hydrogen to carbon ratios.

The relatively low coking rate on the Pt-ZSM-5 catalyst can be referred to the hydrogen activation ability of the platinum metal resulting in an increased hydrogenation rate of potential coke precursors [7].

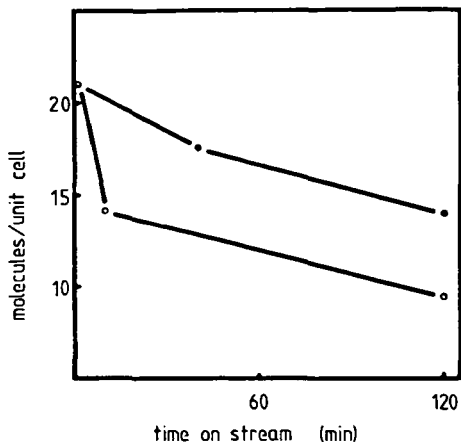
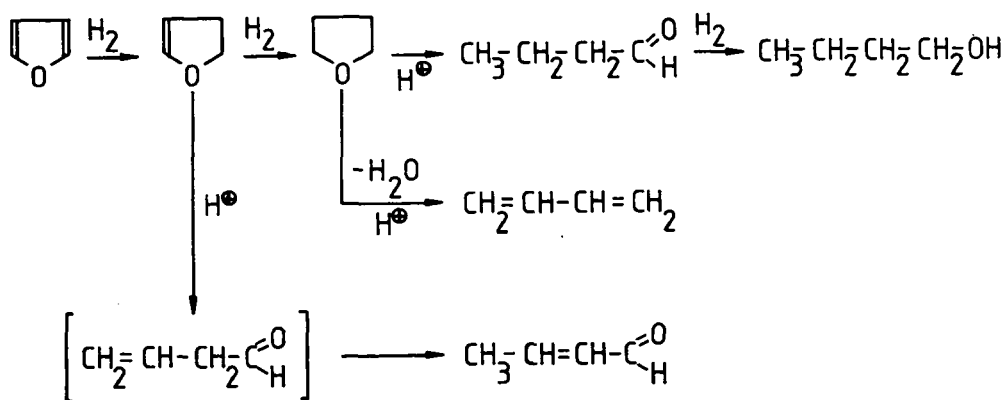


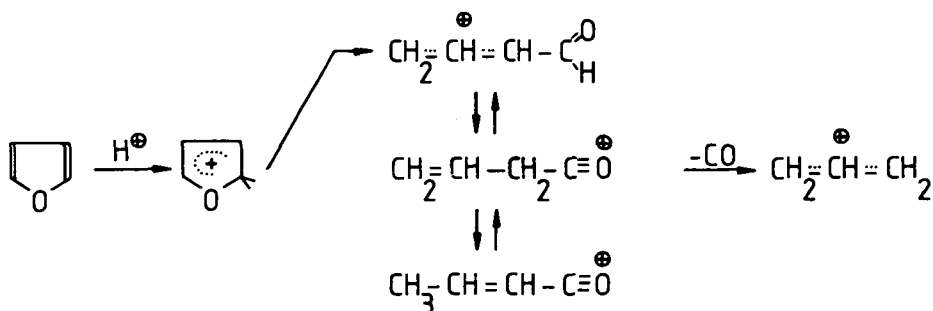
Fig.3 Nitrogen adsorption (77 K, $p/p_0=0,1$) on H-ZSM-5 (○) and Pt-H-ZSM-5 (●) versus time on stream in furan conversion

Hydrodeoxygenation of furan. The hydrodeoxygenating conversion of furan in acidic media can follow different routes depending on the hydrogenation activity and the strength of the Brönsted acidity. At high hydrogenation rates, which might be realized on the Pt-ZSM-5, the hydrogenation will precede the protonation of the molecule. In this case the reaction routes depicted in the following scheme should be favoured for the formation of primary compounds [8], which can undergo oxygen



elimination as well as shape-selective cyclization and aromatization reactions via carbenium and carbonium ion intermediates. The high fractions of paraffins and BTX aromatics found on Pt-ZSM-5 support such assumption.

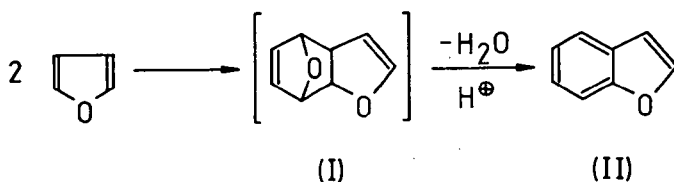
On H-ZSM-5, however, a protonation of the furan followed by ring opening might be an initial step as depicted in the following scheme.



This assumption may find support by the fact that the acylium ion, or crotonylium ion respectively, is stable in super acid media [9]. A subsequent decarbonylation leads to the stable allyl cation, which can be suspected to be a coke precursor due to its low hydrogen to carbon ratio.

With increasing deactivation by coke deposition large fractions of C_{9+} aromatics and of 2,3-benzofuran are found. Since these molecules cannot be formed in the pores of the pentasil zeolites they might originate from alkylation and oligomerization reactions on the external surface of the zeolite crystals. The formation of highly alkylated aromatics might be favoured by an enhanced intermolecular alkyl shift from coke precursors to xylenes.

The 2,3-benzofuran might be formed by a Diels-Alder reaction between two furan molecules, where one furan molecule is activated by the acidic catalyst becoming a dienophile. The bridge oxygen of the dimer ((I)) will be readily eliminated in an acidic medium [10] as is shown in the following scheme.



Using argon as a carrier gas resulted in an increased rate of deactivation of the conversion of furan on H-ZSM-5 and Pt-ZSM-5. The prolonged stability in hydrogen indicates that H-ZSM-5 has considerable hydrogenation activity. The hydrogen molecules are presumably activated via hydronium ions [11]. Addition of propane gave

rapid deactivation for the reaction on H-ZSM-5, but resulted in a prolonged shape-selective conversion of furan on Pt-ZSM-5.

CONCLUSION

Biomass compounds with low H/C ratios, like furan, can undergo shape-selective conversions on pentasil type zeolites better if a hydrogen source is provided to the reaction mixture. The H-ZSM-5 has only a limited hydrogen activation ability, whereas Pt-ZSM-5 can readily transfer hydrogen, even from paraffins, to educts and intermediates, which are deficient in hydrogen.

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