

## Synthesis of Alkylpyrroles via O/N Transformation of 2-Methylfuran over HZSM-5 Zeolite

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The heterogeneous catalytic synthesis of alkylpyrroles from 2-methylfuran and ammonia, methyl-, ethyl- and *n*-propyl-amine by O/N transformation over HZSM-5 zeolite is reported.

Zeolites and zeolite-like materials as selective catalysts for the heterogeneous catalytic synthesis of fine chemicals and intermediates are steadily gaining in importance.<sup>1</sup> Such catalysts offer an interesting route for ring transformation reactions. These reactions are to be understood as the exchange of oxygen in heterocyclic compounds for nitrogen or sulfur,<sup>2-6</sup> offering an appreciable scope for the production of interesting compounds.<sup>7</sup> Thus, the reaction of saturated ring systems such as tetrahydrofuran with NH<sub>3</sub> leading to pyrrolidine can be carried out on HL or HY zeolites with high selectivity and high conversion.<sup>3</sup> The transformation of unsaturated ring systems requires the more moderate acidity of alkali cation-containing zeolites such as NaX<sup>2</sup> or BaY.<sup>8</sup> Furthermore, the ring size, the type of ring (saturated or unsaturated) and other structural parameters of the educts and products may influence the reaction significantly as well as the structural properties of the catalysts applied (pore opening, channel/cavity geometry, dimension of the framework).

This communication reports the conversion of 2-methylfuran (MF) and NH<sub>3</sub> or monoalkylamines to the corresponding alkylpyrroles, applying a ZSM-5 zeolite in the acid H-form as catalyst. The study looks for correlations between the spatial properties of the applied zeolite and structural properties of educts and products.

The HZSM-5 type zeolite (Si/Al = 18, crystallite size = 5–7 μm) was prepared without organic templating agents, treated with silica (10% by mass), shaped and activated stepwise up to 723 K. All catalytic runs were carried out in a bench-scale quartz glass reactor under atmospheric pressure.

MF (Merck) was fed by a micropump, vaporized and mixed in a preheated vessel with NH<sub>3</sub>, methylamine (MA) or ethylamine (EA) (all from Merck) after having passed flow controllers. *n*-Propylamine (PA, Merck) was introduced by another micropump and, after vaporization, passed to the preheated vessel. The gas mixture was then passed directly into the reactor. The outlet stream was analysed by on-line gas chromatography, using a stainless-steel column packed with Chromosorb W/AW (0.2–0.25 mm) (Serva) coated with 5% KOH and 20% Carbowax 20 M (Serva), at 423 K with flame ionization detector and argon as carrier gas.

Besides the desired alkylpyrroles [2-methylpyrrole (MP), 1,2-dimethylpyrrole (DMP), 1-ethyl-2-methylpyrrole (EMP) and 1-propyl-2-methylpyrrole (PMP)], some byproducts such as pyrrole or substituted methylpyrroles and, especially at higher reaction temperatures (> 583 K) and with increased length of the alkyl chain, a red-brown catalyst-colouring rapidly appeared indicating the formation of higher condensed N-containing heterocyclic systems and a fast activity decay. All catalytic runs were carried out on fresh catalyst samples. Used catalysts could be regenerated by air at elevated temperatures and reached almost the same activity and selectivity as they had prior to regeneration.

When NH<sub>3</sub> or alkylamines and MF are passed over the HZSM-5 catalyst, ammonium or alkylammonium ions are formed as proton carriers on the acid sites. MF should coordinatively adsorb on ammonium or alkylammonium ions as proved for the coadsorption of NH<sub>3</sub> and methanol on H-erionites.<sup>9</sup> Next, protonation of a double bond of the furanic ring should result in an HMF cation taking up an amine molecule. Then O/N transformation could be realized by a Dimroth rearrangement<sup>10</sup> (intermediate furanic ring opening on a C–O bond, ring closure forming a N-heterocyclic intermediate). This N-heterocyclic intermediate releases water and pyrrole is formed.

The conversion of MF in the presence of the different amines and the selectivities of the desired O/N transformation products are shown in Table 1. The conversion data depend strongly on the amine fed, the pyrrole formed and possible side reactions causing deactivation (addition reactions of the pyrroles themselves). The MF conversion increases with rising

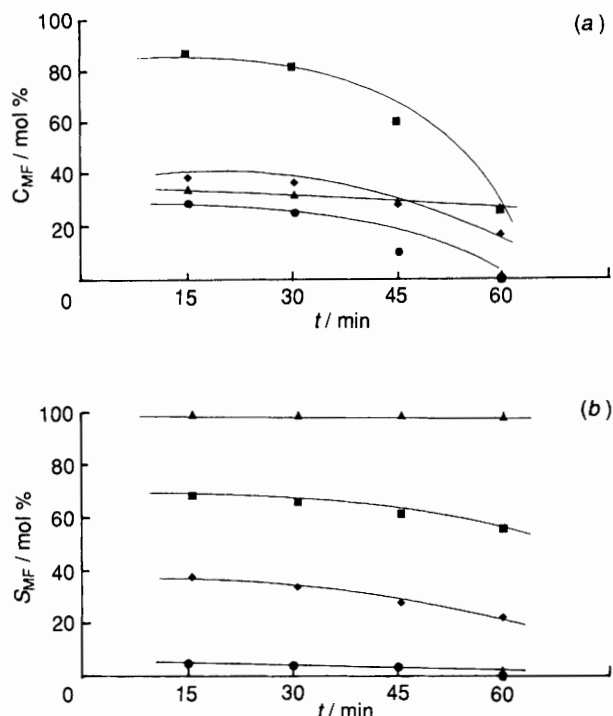


Fig. 1 MF conversion (a) cofeed: ▲ NH<sub>3</sub>, ■ MA, ◆ EA, ● PA, the selectivity of the desired pyrroles (b) ▲ MP, ■ DMP, ◆ EMP, ● PMP, dependence on time on-stream amine:MF, 2.5:1, 533 K, M/F = 39.6 g h mol<sup>-1</sup>, 1 atm

Table 1 Activity and selectivity of HZSM-5 in the O/N transformation reaction of 2-methylfuran with different amines as cofeed<sup>a</sup>

Reaction temperature/K	483	533	583	633
Conversion MF/mol%				
Cofeed: ammonia	22.1	33.4	48.9	84.9
methylamine (MA)	69.9	82.1	71.3	39.8
ethylamine (EA)	14.9	37.6	24.4	—
<i>n</i> -propylamine (PA)	7.9	26.5	—	—
Selectivity/mol%				
2-Methylpyrrole (MP)	91.3	99.1	99.4	99.6
1,2-Dimethylpyrrole (DMP)	99.8	66.4	39.6	38.3
1-Ethyl-2-methylpyrrole (EMP)	47.6	34.6	8.7	—
1- <i>n</i> -Propyl-2-methylpyrrole (PMP)	8.6	3.5	—	—

<sup>a</sup> Conditions used: feeding molar ratio of amine/MF 2.5, catalyst mass  $M$  6 g and space velocity of  $M/F$  39.6 g<sub>cat</sub> h mol<sup>-1</sup>. The results were obtained after 30 min on-stream and expressed in terms of conversion  $C_{MF}$  (mol% of the MF fed) and selectivity  $S_{MP}$  (mol% of the converted MF transformed into the particular pyrrole).

reaction temperature if  $\text{NH}_3$  is used as feed. Using MA as feed, the MF conversion is about three times higher than that with the  $\text{NH}_3$  feed at 483 and 533 K, though a further increase in the reaction temperature leads to a rapid decline in the MF conversion. The differences in the MF conversion when feeding  $\text{NH}_3$  or MA may be caused by the different basicity of the reaction products (pyrroles substituted in the 1-position by H or alkyl groups). Thus, on Brønsted-acid sites the MP formed should be adsorbed more strongly than  $\text{NH}_3$  blocking these acid sites, especially at lower temperatures, for further reaction cycles. Its desorption is favoured only at elevated temperatures as reflected in the increased MF conversion in contrast to the reaction with MA, which forms the less basic N-alkyl substituted pyrrole. Furthermore, with increasing chain length of the amine applied (EA, PA) and time on-stream, a rapid deactivation occurs by addition reactions of the pyrroles formed, causing a blockage of the active surface of the HZSM-5 zeolite as demonstrated in Fig. 1(a). The decreasing selectivity values for the desired pyrroles (Table 1) clearly mirror processing side reactions increasing with enhanced reaction temperature and chain length of the amine fed. Only MP and DMP can be synthesized in high selectivities as shown in Fig. 1(b).

Conversion and selectivity are also influenced by the transition state shape selectivity and product selectivity of the zeolite used, especially in the application of EA and PA. The formed transition complexes and products are too large to pass

through the HZSM-5 zeolite channels. Therefore, they cause additional deactivation.

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