

## SCREENING OF ZEOLITES FOR THE GAS-PHASE ACETALIZATION OF FORMALDEHYDE TO METHYLAL (DMM)

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### INTRODUCTION

Methylal can either be used as direct diesel fuel additive, or it can be blended with diesel fuel in form of the higher polymerized polyoxymethylene dimethyl-ether.[1,2] The present contribution deals with the continuous gas-phase acetalization of formaldehyde with methanol to form methylal. Although this route offers several advantages, it is nearly unexplored according to the current literature. The acetalization requires catalysts with suitable acid sites. Therefore, the catalytic activities of different zeolites were screened and compared with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

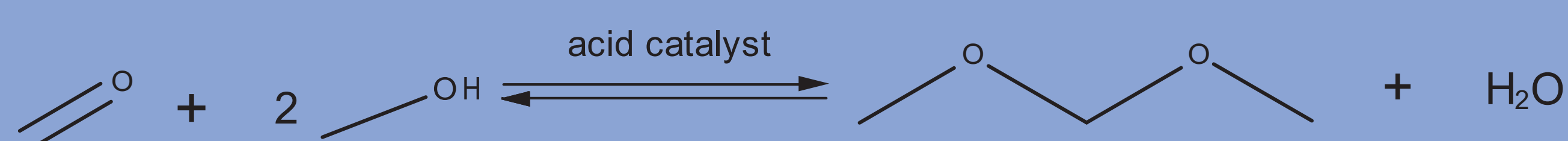


Figure 1: Acetalization of formaldehyde and methanol to methylal

### EXPERIMENTAL

A solution composed of formalin and methanol (2:1) was evaporated and mixed with Ar (internal standard) and N<sub>2</sub> leading to an inlet gas stream containing 5 % of the reactants. This gas stream was passed through the reactor filled with 3 g catalyst (diluted 1:2 with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>). Tests were performed at ambient pressure, while the temperature was varied between 120 and 220°C. Product analysis was performed by online GC-MS.

### RESULTS

Zeolite H-MFI-90 (H-ZSM-5; Si/Al = 45),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and three  $\beta$ -zeolites (H-BEA-35, Si/Al = 17.5; H-BEA-60, Si/Al = 30; H-BEA-150, Si/Al = 75) were chosen as catalysts and screened at different temperatures under atmospheric pressure.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed no activity up to 250°C. Above 250°C, only DME was produced. The H-MFI-90 catalyst initially showed the formation of methyl formate and DME in the range from 180°C up to 220°C at a methanol conversion of 9.9%. The  $\beta$ -zeolites selectively formed methylal right from the beginning in the temperature range from 120 to 180°C. At 140°C, methylal was the only product observed for H-BEA-35, with a MeOH conversion of 5.5 % and a productivity of  $6.5 \cdot 10^{-6}$  mol/(min $\cdot$ g<sub>Kat</sub>). H-BEA-60 also formed methylal as main product at 140°C ( $X_{\text{MeOH}} = 13\%$ ;  $S_{\text{Methylal}} = 89.2\%$ ;  $P = 1.6 \cdot 10^{-5}$  mol/(min $\cdot$ g<sub>Kat</sub>)), but undergoes severe deactivation. H-BEA-150 formed methylal with almost 100% selectivity over the whole temperature range of 120 °C up to 180 °C, at degrees of MeOH conversion between 2.8% (180°C) and 21.5% (120°C) and seems to be the best catalyst ( $P_{140^\circ\text{C}} = 1.2 \cdot 10^{-5}$  mol/(min $\cdot$ g<sub>Kat</sub>)).

In general, methylal-selectivity and productivity increased with decreasing temperatures, because less side products (DME and methyl formate) and more Methylal were formed.

### ACKNOWLEDGEMENT

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### IN COORPARATION WITH

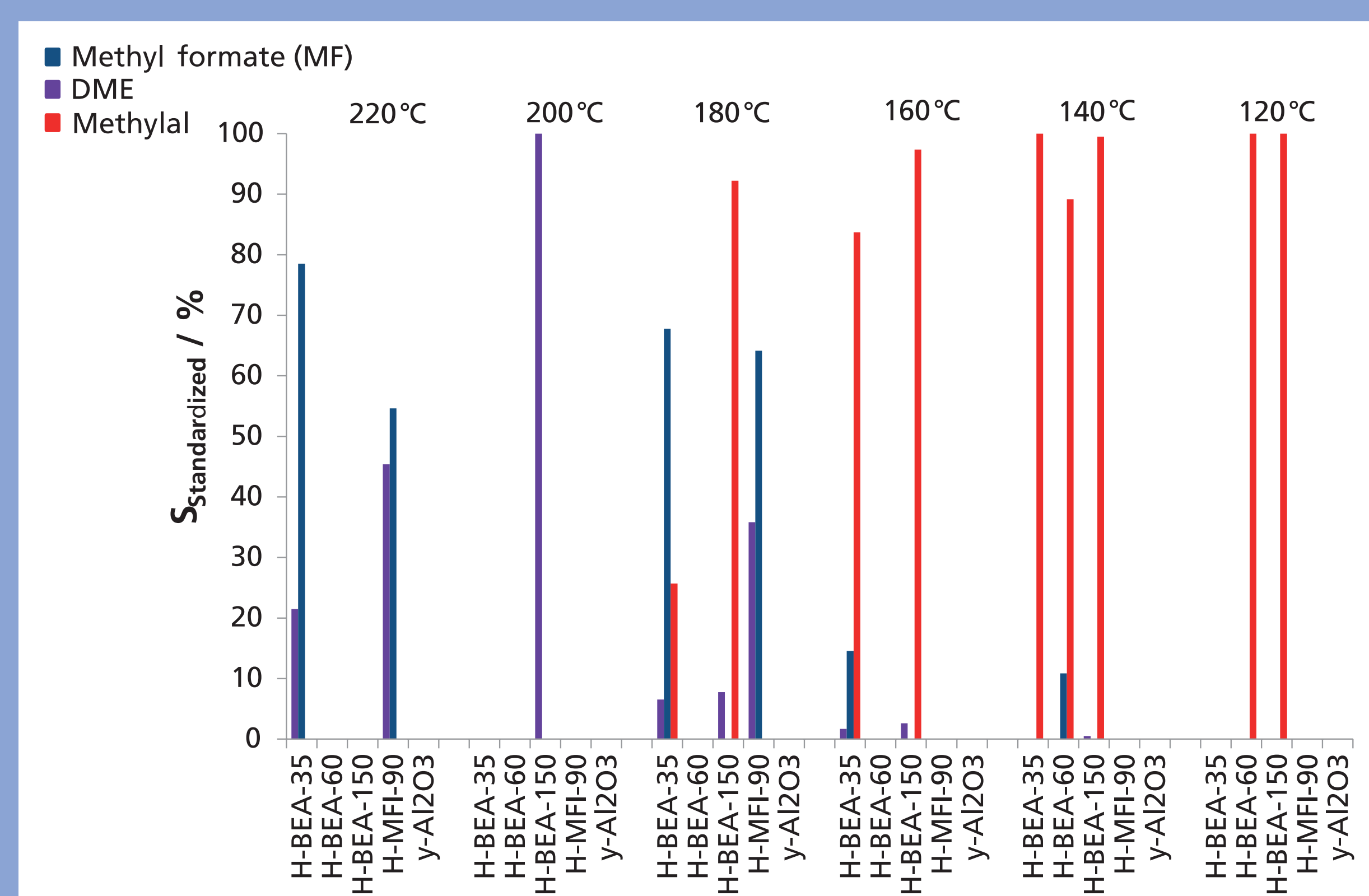


Figure 2: Comparison of standardized selectivities for methylal-synthesis

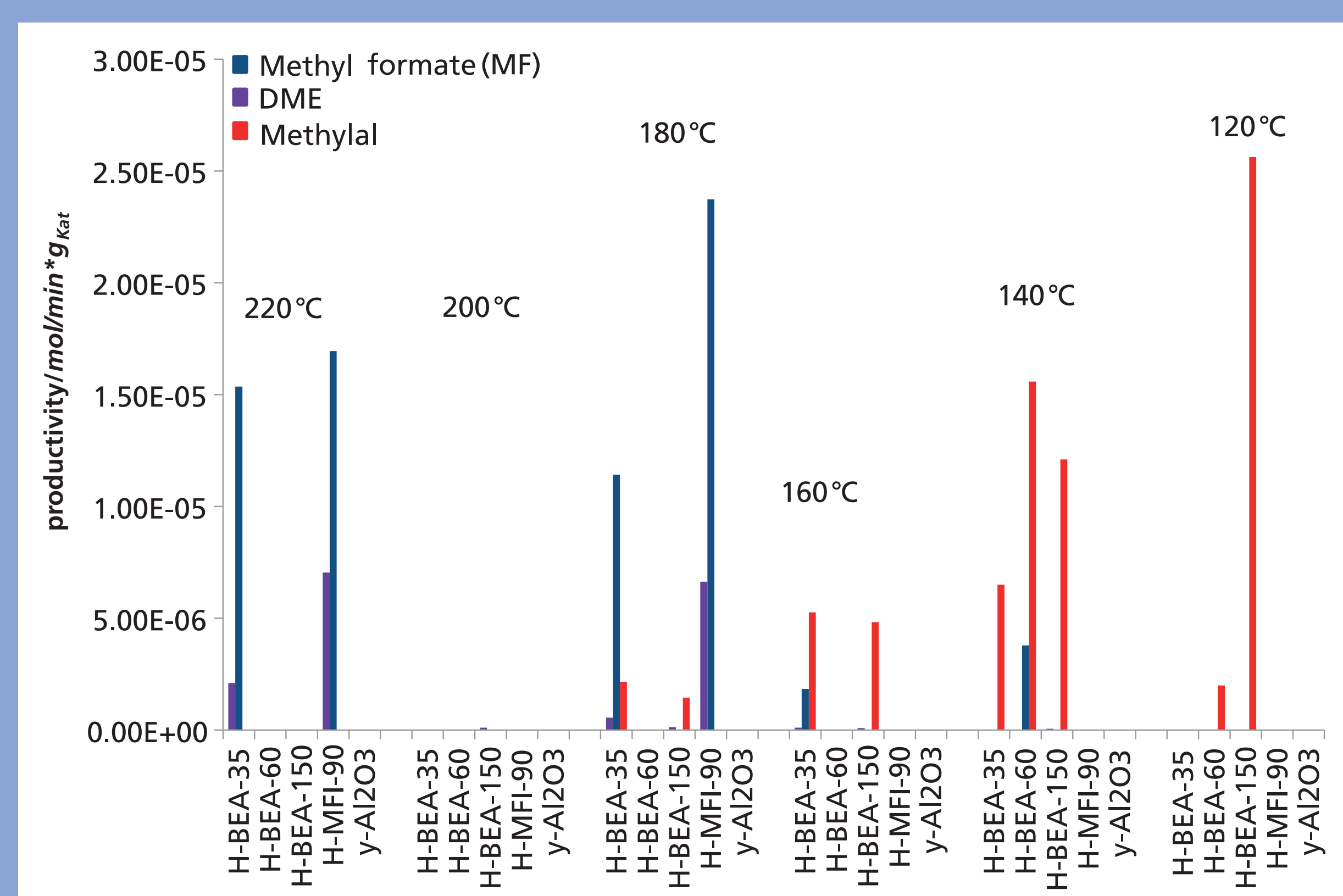


Figure 3: Comparison of productivities for methylal-synthesis

### CONCLUSION

$\beta$ -zeolites were found as suitable and promising catalyst systems for the acid-catalyzed formation of methylal by gas-phase acetalization of formaldehyde and methanol. The suitable catalytic performance is assumed to be caused by the specific acid properties of the catalysts. NH<sub>3</sub>-TPD experiments revealed two different kinds of acid sites. The stronger sites are expected to be favored for the selective formation of methylal.[3] Based on the preliminary results, the  $\beta$ -zeolite catalysts were chosen for more detailed investigations including catalyst optimization by tuning the acid properties and testing at elevated pressure, which is known to further increase the degree of conversion due to thermodynamic considerations.

### LITERATURE

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