

METHYLAL SYNTHESIS BY GAS-PHASE ACETALIZATION OF FORMALDEHYDE AND METHANOL

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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 dimethylether [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. By preliminary screening experiments of various zeolites, β -zeolites were found to be promising catalysts and chosen for further detailed investigations.

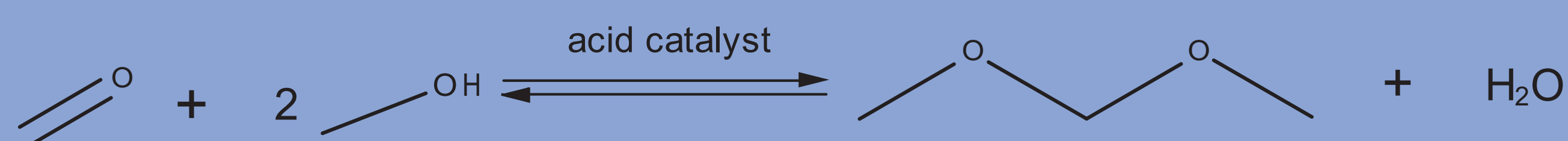


Figure 1: Acetalization of formaldehyde and methanol to methylal

EXPERIMENTAL

A solution composed of formalin and methanol (2:1) was evaporated and mixed with Ar (internal standard) and N₂ leading to an inlet gas stream containing 2 – 5 % of the reactants. This gas stream was passed through the reactor filled with 3 g catalyst (diluted 1:2 with α -Al₂O₃). Tests were performed at pressures from 1 bar to 20 bar, while the temperature was varied between 110°C and 160°C. Product analysis was performed by online GC-MS.

RESULTS

The zeolites H-BEA-35 (Si/Al = 17.5); H-BEA-60 (Si/Al = 30); H-BEA-150 (Si/Al = 75) and a completely K⁺ ion-exchanged H-BEA-35 (Si/Al = 17.5) (K-BEA-35) were chosen as catalysts for the acetalization reaction. NH₃-TPD experiments revealed two different kinds of acid sites for the pure zeolites, assigned to weak (NH₃ desorption: 120 – 250°C) and moderate (NH₃ desorption: 250 – 450°C) acid strength, respectively. By K⁺ ion-exchange the moderate acid sites were selectively neutralized leaving only weak acidity. All catalysts were tested applying the same temperature and pressure program. The tests revealed that with higher Si/Al ratio (lower amount of acid sites) less byproducts (methyl formate, DME) were formed. The productivities of methylal for the pure zeolites were nearly independent of the Si/Al-ratio and thus, independent from the amount of acid sites under the applied reaction conditions. The K-BEA-35 showed a significantly lower productivity at 110°C and 120°C, which might be caused by the reduced overall acidity.

After stepwise reduction of the reaction temperature, the temperature was raised to the initial value (160°C) again. While the methylal productivity is almost the same, a significant decrease in the productivities of the byproducts is observed indicating a selective deactivation. By increasing the pressure all catalyst show almost 100% selectivity to methylal. However, the increase of the productivities is not as significant as expected with respect to thermodynamic calculations. This might be caused by a gradual deactivation (coking).

ACKNOWLEDGEMENT

We would like to thank Süd-Chemie (now Clariant) for providing the zeolite samples and the Max Plank Society for the financial support.

IN COOPERATION WITH

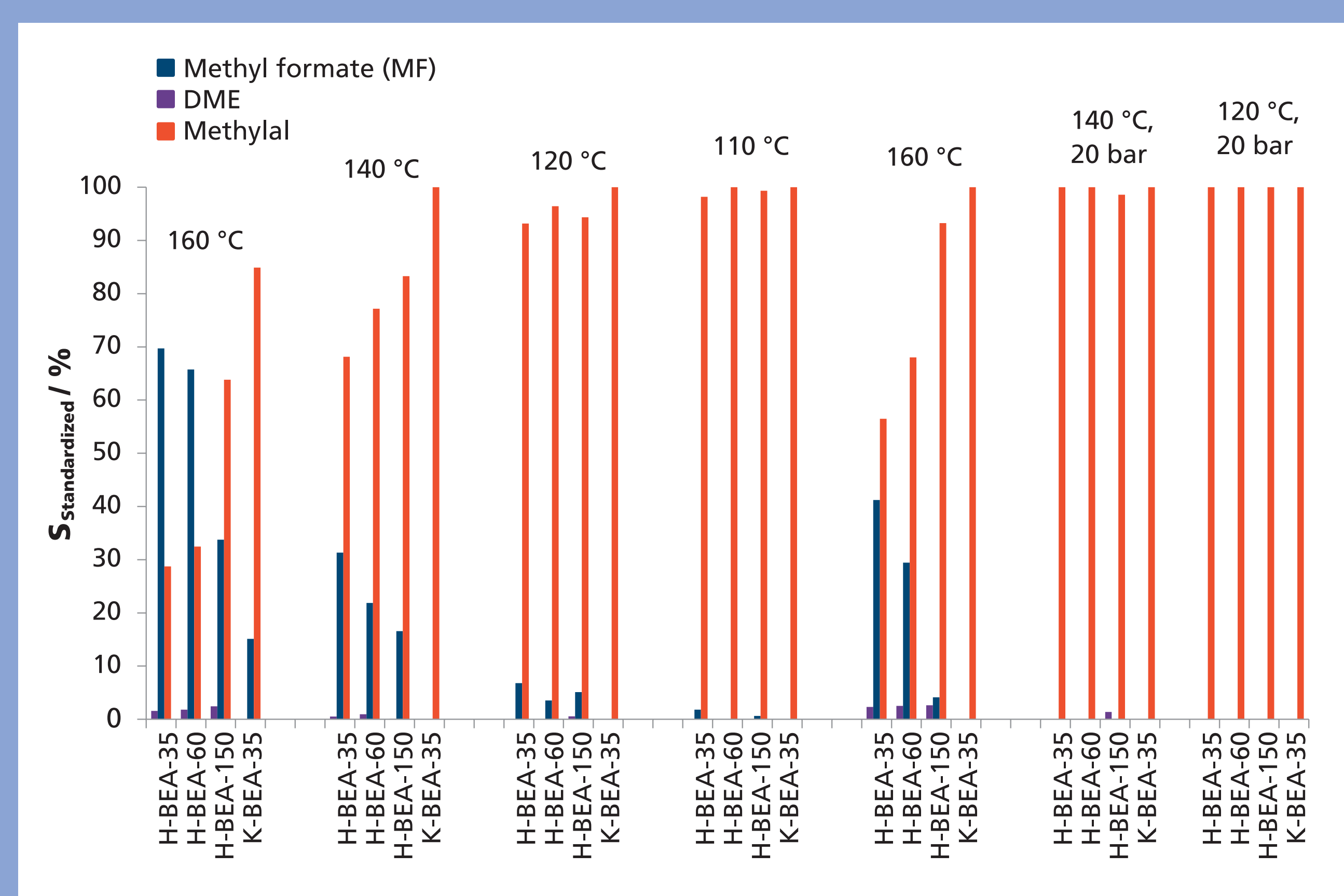


Figure 2: Comparison of standardized selectivities for methylal synthesis

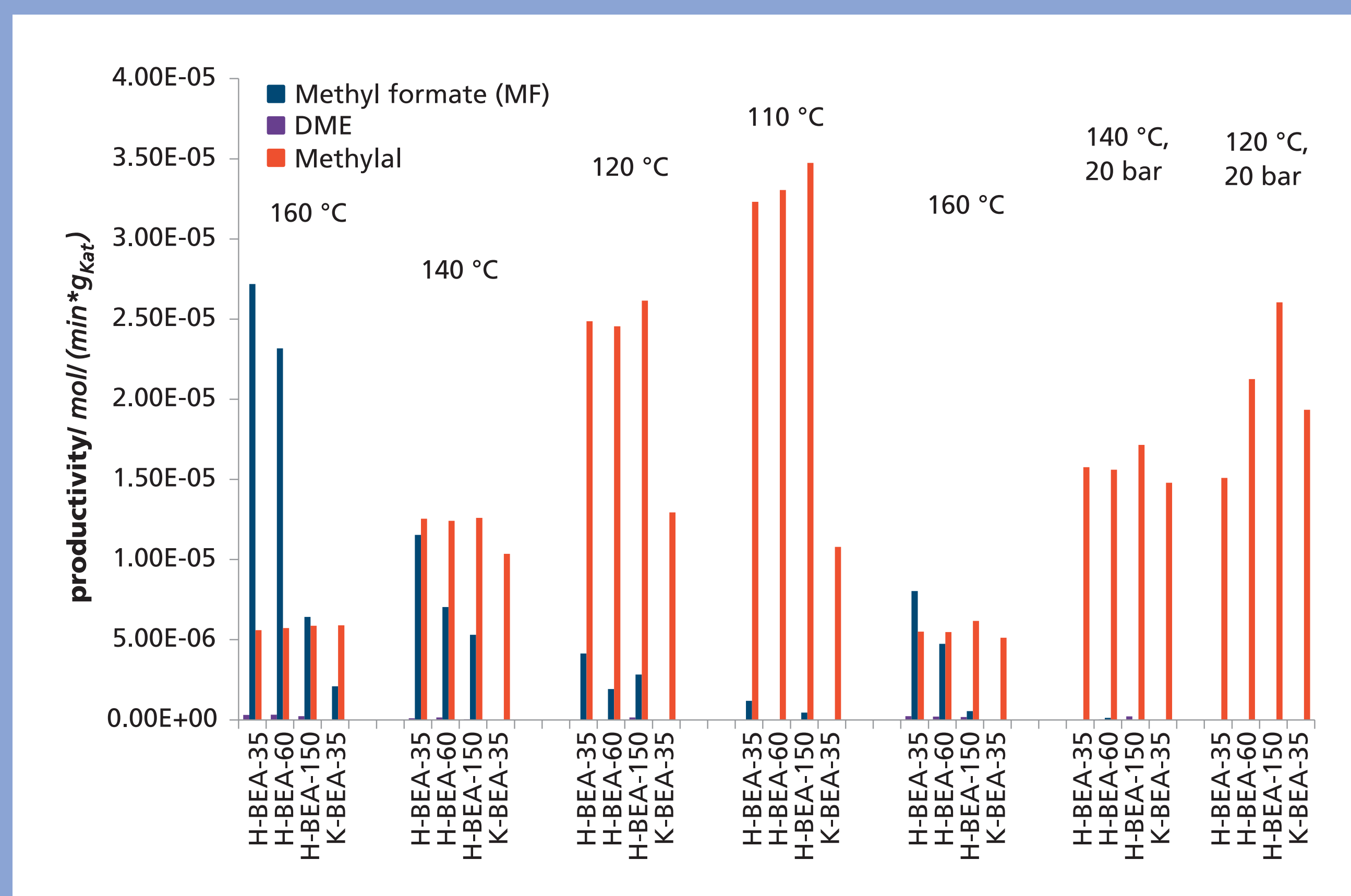


Figure 3: Comparison of productivities for methylal synthesis

CONCLUSION

β -zeolites were found as suitable catalysts for the synthesis of methylal by the direct gas-phase acetalization of methanol and formaldehyde. By tuning the acidic properties of the zeolites (Si/Al ratio, K⁺ ion-exchange) the formation of unwanted byproducts, such as DME or methyl formate, can be significantly reduced.

However, the overall activity still suffers from deactivation (coking). Further studies will focus on investigating of the nature of methylal formation sites and reducing coke formation.

LITERATURE

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- [2] Burger J., Siegert M., Ströfer E., Hasse H., Fuel, 3315-3319, 2010(89)