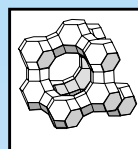


CONVERSION OF METHANOL TO HYDROCARBONS ON ACIDIC HZSM-5, HMOR, SAPO-34 AND SAPO-18 INVESTIGATED BY *IN SITU* MAS NMR SPECTROSCOPY UNDER FLOW CONDITIONS AND ON-LINE GAS CHROMATOGRAPHY



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Summary

In situ MAS NMR spectroscopy and *on-line* gas chromatography have been applied to study the steady state of the conversion of methanol on HZSM-5, HMOR, SAPO-34 and SAPO-18 under continuous-flow conditions. The first step of the catalytic reaction is the condensation of methanol to dimethyl ether (dme) at 373 to 473 K. At reaction temperatures of $T > 500$ K broad ^{13}C MAS NMR signals at 12 to 39 ppm and 125 to 137 ppm indicate the presence of adsorbed C_2 to C_6 olefins. This finding supports the 'hydrocarbon pool' mechanism previously proposed by Dahl and Kolboe [1].

Experimental Section

The MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequency of 100.6 MHz for ^{13}C nuclei and with sample spinning rate of 1.8 kHz. The *in situ* MAS NMR flow probe is based on a modified DSI-740 7 mm STD

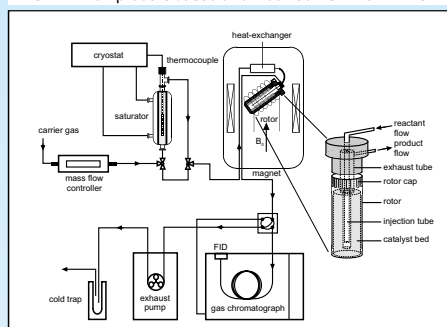


Fig. 1: Scheme of the equipment applied for simultaneous *in situ* MAS NMR spectroscopy and *on-line* gas chromatography and the design of the modified MAS NMR rotor with axially placed tubes for the injection of reactant molecules and the exhaust of reaction products.

Introduction

Since the first reports on the conversion of methanol on acidic catalysts, a number of experimental and theoretical works have established various mechanisms for this reaction [2-3]. Generally, three reaction steps are distinguished: (i) the dehydration of methanol to dimethyl ether, (ii) the conversion of a mixture of methanol and dimethyl ether to olefins and (iii) a bond chain polymerization and isomerization of the olefins. According to the 'hydrocarbon pool' mechanism, the formation of olefins is explained by 'big' carbonaceous species existing inside the zeolite pores adding and splitting off reactants and products, respectively. In the last decade a growing number of groups applied *in situ* MAS NMR spectroscopy to study methanol conversion on various aluminosilicates and silicoaluminophosphates under batch conditions [4]. In our group, a new technique was introduced allowing a continuous injection of reactant molecules into the spinning rotor [5]. Recently, this method was coupled with *on-line* gas chromatography to investigate simultaneously surface complexes formed on the catalyst by *in situ* MAS NMR spectroscopy and reaction products leaving the rotor by a gas chromatographical analysis [6].

MAS NB NMR probe delivered by Doty Scientific Instruments (Columbia, Texas) allowing measurements at temperatures up to 873 K with sample spinning rates up to 3.5 kHz. During the *in situ* MAS NMR experiments under flow conditions, nitrogen

loaded with $^{13}\text{CH}_3\text{OH}$ was injected into the MAS NMR rotor (Fig. 1). Comparing yields of products obtained in a fixed bed reactor with those obtained in the MAS rotor reactor, maximum differences in the values of 10 % were found (Fig. 2).

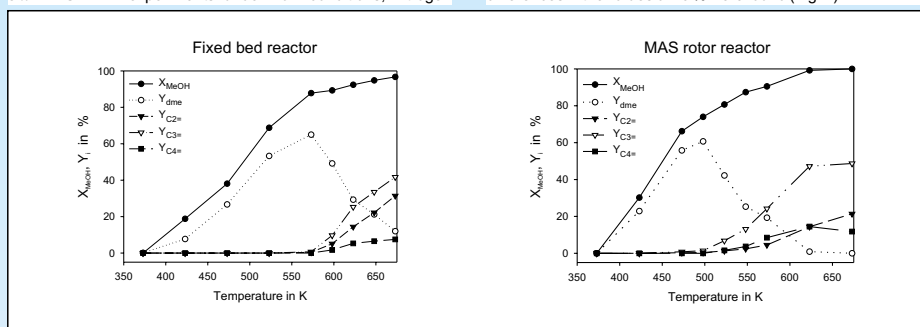


Fig. 2: The conversion of methanol (X_{MeOH}) and the yields of dimethyl ether, ethene, propene and butenes (Y_i) determined for the reaction of methanol on SAPO-18 at temperatures between $T = 373$ K and 673 K using a) a fixed bed reactor and b) an MAS rotor reactor.

Results and Discussion

- $T < 500$ K: formation of dme (Fig. 3a)
 - methanol (50 ppm) reacts with an acid site and forms a methoxy group causing a signal at 58 ppm.
 - methanol reacts with a methoxy group and forms dme (61 ppm).
- $T > 500$ K: formation of higher hydrocarbons (Fig. 3b to 3g). The chemical shift data indicate the formation of:

2-methylhexane (14.3, 22.9, 23.1, 29.8, 38.9 ppm)
 3-methylhexane (9.4, 14.2, 19.8, 29.7, 34.3, 39.0 ppm)
 2-methyl-3-hexene (13.9, 22.0, 25.9, 31.4, 129.2, 136.9 ppm)
 2,5-dimethyl-3-hexene (22.3, 31.0, 31.6, 134.5, 134.9 ppm)
 2,4-hexadiene (19.5, 132.3, 132.7 ppm)
 3-methyl-2,4-hexadiene (12.2, 20.2, 114.9, 126.8, 134.0, 135.0 ppm)

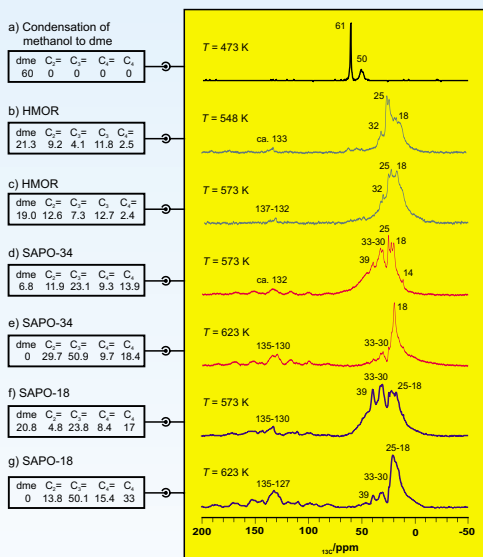


Fig. 3: ^{13}C MAS NMR spectra recorded during the conversion of $^{13}\text{CH}_3\text{OH}$ on HMOR, SAPO-34 and SAPO-18 under continuous-flow conditions with a modified residence time of $W/F_{\text{me}} = 25$ g/hol. On the left hand side, the yields (in %) of dimethyl ether (dme), ethene ($\text{C}_2=$), propene ($\text{C}_3=$), propane (C_3), butenes ($\text{C}_4=$) and butanes (C_4) determined by *on-line* gas chromatography are given.

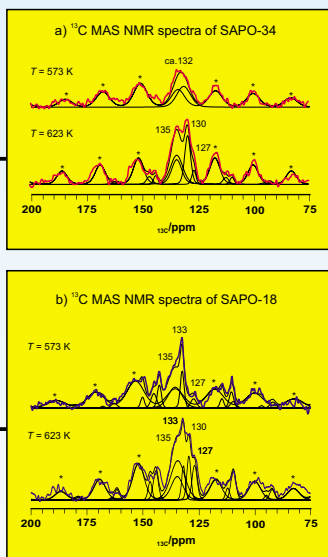
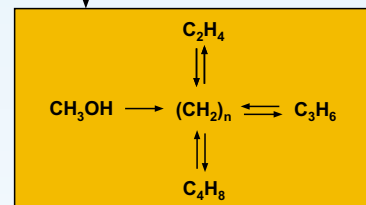


Fig. 4: Simulation of the olefinic and aromatic range of the ^{13}C MAS NMR spectra recorded during conversion of $^{13}\text{CH}_3\text{OH}$ on a) SAPO-18 and b) SAPO-34 (Fig. 3d to 3g).

Conclusions

- for the first time intermediates formed in the steady state of the methanol conversion on acidic zeolites were observed by *in situ* ^{13}C MAS NMR spectroscopy under continuous-flow conditions.
- these intermediates are C_6 to C_9 olefins formed at reaction temperatures of $T > 500$ K on HZSM-5, HMOR, SAPO-34 and SAPO-18.
- the observed higher olefins are retardates, but can be removed by purging the catalysts with dry carrier gas.
- the comparison of the occurrence of C_6 to C_9 olefins with the simultaneously determined yields of reaction products indicates that this olefin pool supports the formation of lower olefins, such as ethene and propene (see scheme).



- methoxy groups (58 ppm) could be only observed after conversion of methanol at reaction temperatures of $T < 500$ K.
- no hints were found for the formation of ethoxy, propoxy or butoxy species (77 to 87 ppm) and for the presence of alkyl oxonium ions (80 ppm) by *in situ* ^{13}C MAS NMR spectroscopy.

Acknowledgements

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- C_6 to C_9 hydrocarbons staying on the catalyst could be observed in the steady state by *in situ* MAS NMR spectroscopy while they couldn't be detected by gas chromatography.

- the degree of dehydrogenation of higher hydrocarbons grows with increasing reaction temperatures (compare spectra at $T = 573$ K and $T = 623$ K, Fig. 3d to 3g). The intensity of characteristic signals of saturated hydro-

while the signals of olefins ($^{13}\text{C} = 127$ to 137 ppm) increase.

- these higher hydrocarbons are not coke deposits.
- they leave the catalyst after purging with nitrogen at reaction temperature.
- the higher hydrocarbons are cracked to shorter products.
- *in situ* ^1H MAS NMR spectroscopy yields that all Brønsted acid sites (SiOHAl) are involved in the methanol to hydrocarbon conversion.