

Effect of Organic Impurities on the Hydrocarbon Formation *via* the Decomposition of Surface Methoxy Groups on H-SAPO-34

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Introduction

The process of converting methanol to olefins (MTO) on zeolite catalysts was developed as the second step of the route to produce light olefins from natural gas [1]. The mechanism of methanol conversion on zeolite catalysts has been intensively studied for several decades. Nowadays, it is well accepted that the steady state of the MTO process is dominated by the "hydrocarbon-pool" route [1]. Recent investigations by *in situ* MAS NMR spectroscopy further indicated that surface methoxy groups may contribute to the formation of first hydrocarbons during the induction period of the MTO process [2]. On the other hand, it has been suggested that the initiation of the MTO process is typically caused by organic impurities instead of any direct route from pure methanol and dimethyl ether [3]. In the present work, the recently introduced MAS NMR-UV/Vis spectroscopy is utilized to clarify, whether traces of organic impurities in the ¹³C-enriched methanol govern the formation of primary hydrocarbons by conversion of surface methoxy groups on zeolite catalysts.

Experimental Section

The preparation of surface methoxy groups was performed by adsorption of ¹³C-enriched methanol (¹³C-enrichment of 99%. with total organic impurities of ca. 1000 ppm) and highly purified nonenriched methanol (organic impurities < 30 ppm, denoted as ¹²CH₃OH) on H-SAPO-34. Thereafter, an evacuation for 6 hours at 393 K and additional evacuation for 6 hours at 473 K were performed. Subsequently, the methylated zeolite were fused for further thermal treatments at 473 to 673 K for 20 minutes. ¹³C-1-ethanol or ¹³C-2acetone, as model compounds of typical impurities in methanol, was loaded on dehydrated H-SAPO-34 and heated at a given temperature between 473 and 673 K for 20 minutes. The ¹³C MAS NMR investigations were performed on a Bruker MSL-400 spectrometer at a resonance frequency of 100.6 MHz. UV/Vis spectra were recorded with an AvaSpec-2048 Fiber Optic spectrometer, an AvaLight-DH-S deuterium light source, and a glass fiber reflection probe FCR-7UV20-3-SR-S1 by Avantes, as shown in Fig. 1.

Results and Discussion

¹³C MAS NMR (signal assignments as Scheme 1) and UV/Vis spectra recorded for ¹³CH₂-SAPO-34 and ¹²CH₂-SAPO-34 indicate that the formation of first aromatics and carbenium ions occured at same reaction temperatures for both ¹³C-enriched and highly purified non-enriched surface methoxy groups (Fig. 2). Hence, traces of organic impurities occurring in the ¹³C-enriched methanol (ca. 1000 ppm) have no influence on the formation of primary hydrocarbons on H-SAPO-34 as detected by UV/Vis spectroscopy. In Fig. 3, studies of the ethanol loaded H-SAPO-34 show that a coverage of at least 0.1 ethanol molecules per bridging OH group is necessary to obtain neutral aromatics and carbenium ions, similar to those formed by conversion of the methylated catalyst at the same reaction temperature. The ethanol coverage mentioned above is more than two orders of magnitude higher in comparison with the ethanol coverage attainable by impurities in the methanol feed. A similar result was obtained after thermal treatment of the acetone-loaded H-SAPO-34 catalysts (not shown).



Fig. 3 ¹³C HPDEC MAS NMR (left) and UV/Vis spectra (right) recorded after thermal treatment (673 K) of silicoaluminophosphate H-SAPO-34 loaded with 0.02 (a) to 0.25 molecules (d) ¹³C-1-ethanol per bridging OH group (SiOHAI).

Acknowledgements

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organic impurities.

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