Catalysis Letters Vol. 88, Nos. 3–4, June 2003 (© 2003)

Direct evidence for a catalytically active role of the hydrocarbon pool formed on zeolite H-ZSM-5 during the methanol-to-olefin conversion

Michael Seiler, Wei Wang, Andreas Buchholz, and Michael Hunger*

Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany

Received 7 January 2003; accepted 1 April 2003

The catalytic role of the hydrocarbon pool formed during the conversion of methanol on zeolite H-ZSM-5 was investigated by *in situ* MAS NMR spectroscopy under continuous-flow (CF) conditions and by changing of the methanol feed from $^{13}CH_3OH$ to $^{12}CH_3OH$ under steady state conditions. Utilizing this experimental approach, a decrease of the ^{13}C CF MAS NMR signals of alkyl groups bound at the olefinic and aromatic skeleton atoms of the hydrocarbon pool by 40% was observed. Simultaneously performed ^1H CF MAS NMR measurements ensured that the total amount of carboneous compounds on the zeolite catalyst was constant during the experiments. The decrease of the number of ^{13}C-isotopes of alkyl groups, observed after changing the ^{13}C-enrichment of the methanol feed, is the first direct evidence for the side-chain methylation of olefinic and aromatic skeleton carbon atoms as an important pathway of the hydrocarbon pool mechanism for the methanol-to-olefin conversion on acidic zeolites.

KEY WORDS: zeolite H-ZSM-5; methanol-to-olefin conversion; reaction mechanism; hydrocarbon pool; *in situ* NMR spectroscopy.

1. Introduction

Because of the increasing demands on light olefins in the chemical industry, the "methanol-to-olefin" (MTO) conversion on acidic zeolites find an increasing interest as a modern alternative way to the cracking of heavier hydrocarbons [1]. During the last decade, increasing efforts were made to clarify the mechanism of the conversion of methanol to olefins on acidic solids. Often discussed mechanisms for the formation of C–C bonds via conversion of methanol on acidic zeolites are the oxonium ylide mechanism [2,3], the carbene mechanism [4,5], the carbocationic mechanism [6,7], and the hydrocarbon pool mechanism [8,9]. More recent investigations of the methanol-to-olefin conversion on acidic zeolites by modern GC/MS and solid-state NMR approaches indicated that the hydrocarbon pool mechanism is the most favored reaction mechanism for the MTO process [10–17]. According to this mechanism, large carboneous compounds are formed on acidic catalysts, which add methanol and split off light olefins, such as ethene, propene and butenes (see reference [1]). By application of a pulse-quench reaction technique and studying the organic compounds formed on the catalyst material by solid-state ^{13}C MAS NMR spectroscopy, Haw and coworkers found that polymethylbenzenes are active compounds occurring in the hydrocarbon pool formed on acidic zeolites [17,18]. This finding agrees with the results of earlier catalytic investigations that showed that toluene can act as "cocatalyst" for the conversion of methanol to hydrocarbons on acidic zeolite H-ZSM-5 [19,20]. The experimentally obtained results were supported by quantum-chemical investigations, which indicated that polymethyl aromatics are very reactive compounds for methylation reactions [21]. *In situ* ^{13}C MAS NMR investigations of the methanol conversion on zeolite H-ZSM-5 and silicoaluminophosphates H-SAPO-18 and H-SAPO-34 under CF conditions showed that the hydrocarbon pool formed under steady state conditions consists of a mixture of aliphatic and cyclic olefins and alkylated aromatics with carbon numbers of C_6 to C_{12} [15,16]. Recently, Arstad and Kolboe [22] and Sassi *et al.* [23] found that the methanol-to-olefin conversion on the silicoaluminophosphate H-SAPO-34 and on the zeolite H-Beta, respectively, mainly proceeds via pentamethylbenzene and hexamethyl benzene.

In the present work, *in situ* MAS NMR spectroscopy was applied to study the catalytic role of the methyl groups of the hydrocarbon pool during the conversion of methanol on zeolite H-ZSM-5. These experiments were performed under CF conditions and by changing the methanol feed from $^{13}CH_3OH$ (^{13}C-enriched) to $^{12}CH_3OH$ (natural abundance of ^{13}C-isotopes). Using this experimental approach, the portion of the alkyl groups of the hydrocarbon pool contributing to the MTO process could be estimated by the decrease of their ^{13}C MAS NMR signals under steady-state conditions.

2. Experimental

Zeolite Na-ZSM-5 with the chemical composition $Na_{4.2}Al_{4.2}Si_{91.8}O_{192}$ was synthesized as described else-

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* To whom correspondence should be addressed.
E-mail: michael.hunger@po.uni-stuttgart

1011-372X/03/0600–0187/0

where [24]. The ammonium form was prepared by fourfold ion exchange at 353 K in a 0.4 M aqueous solution of NH_4NO_3. After reaching an ion exchange degree of 98%, the zeolite powder was washed in demineralized water and dried at room temperature. Zeolite H-ZSM-5 was obtained after heating the ammonium-form zeolite in synthetic air (20 vol.% oxygen) with a rate of $20\,K\,h^{-1}$ up to the final temperature of 723 K and calcination at this temperature for 12 h. This material was characterized by AES-ICP, XRD, ^{27}Al and ^{29}Si MAS NMR spectroscopy to ensure that no dealumination and damage of the zeolite framework occurred as a result of cation exchange and calcination.

CF MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 MHz for ^1H and 100.6 MHz for ^{13}C nuclei. For each ^1H and ^{13}C MAS NMR spectrum, 100 and 240 free induction decays, respectively, were accumulated after a single-pulse $\pi/2$ excitation, and with a repetition time of 20 s. The sample spinning frequency was ca. 2.5 kHz. The ^{13}C MAS NMR spectra were obtained after direct excitation and proton decoupling. The ^1H and ^{13}C MAS NMR shifts were referred to TMS .

Prior to the NMR investigations, the zeolite material was dehydrated in vacuum ($p < 10^{-2}$ Pa) at 723 K for 12 h. Before the *in situ* MAS NMR experiments under flow conditions (CF), about 100 mg of the calcined zeolite were filled into the MAS NMR rotor reactor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed (see reference [25]). After transferring the rotor into the MAS NMR probe, a second dehydration of the catalyst was performed at 673 K for 1 h under flowing nitrogen ($30\,ml\,min^{-1}$). During the *in situ* MAS NMR experiments under continuous-flow conditions, nitrogen loaded with ^{13}C-enriched methanol ($^{13}CH_3OH$) or methanol with ^{13}C-isotopes in a natural abundance ($^{12}CH_3OH$) was injected into the MAS NMR rotor of a DSI-740 7 mm STD MAS NB NMR probe, Doty Scientific Instruments, Columbia, USA, equipped with an injection system as described elsewhere [25]. Via an exhaust tube on top of the MAS NMR rotor reactor, the CF MAS NMR probe was connected with the sampling loop of a gas chromatograph (see reference [25]). The reaction products were analyzed using an on-line gas chromatograph HP 5890 (Hewlett-Packard) equipped with a Coating Poraplot Q capillary column (Chrompack Plot fused silica, length 50 m, inner diameter 0.32 mm). The exhaust flow was sampled and analyzed in steps of 30 min. A constant flow of methane ($10\,ml\,min^{-1}$), added to the methanol feed, was used as an internal GC standard and allowed a quantification of the reaction products.

The *in situ* CF NMR investigations of the methanol conversion on zeolite H-ZSM-5 were performed with a modified residence time of $W/F = 25\,gh\,mol^{-1}$. The protocol applied for these experiments is described in figure 1. After transferring the dehydrated catalysts into the MAS NMR rotor reactor, the material was purged by dry nitrogen. At reaction temperatures of 548 and 573 K, at first a feed of $^{13}CH_3OH$ was injected into the MAS NMR rotor reactor. After a reaction time of 2.5 h during period (i), the feed was changed to $^{12}CH_3OH$ (period (ii)), while the methanol conversion was continued under the same reaction conditions as in period (i).

3. Results and discussion

3.1. Catalytic investigation of methanol conversion on zeolite H-ZSM-5 in a spinning MAS NMR rotor reactor

Coupling of the *in situ* CF MAS NMR technique with an on-line gas chromatograph (CF MAS NMR/GC technique) allows a simultaneous spectroscopic investigation of reactants and intermediates adsorbed on the solid catalyst under steady state conditions and an analysis of the reaction products leaving the catalyst filled into the spinning MAS NMR rotor reactor [25]. The latter is useful to assess and to optimize the reaction conditions inside the spinning MAS NMR rotor reactor. Because of the partial loss of reaction products at the outlet of the spinning MAS NMR rotor reactor, quantitative investigations require the cofeeding of an internal gas standard. For this reason, a constant flow of methane, which is inert under the present reaction conditions, was added to the methanol feed.

Applying the CF MAS NMR/GC technique described in reference [25], at first the conversion of methanol with a natural abundance of ^{13}C-isotopes on zeolite H-ZSM-5 was investigated in a spinning MAS NMR rotor reactor and in a temperature range of 373 to 598 K. To ensure that the reaction conditions are equal in comparison with those of the later *in situ* CF NMR experiments, the reaction products were analyzed by on-line GC after a time-on-stream of 2.5 h at each temperature step. The reaction time of 2.5 h was chosen since the steady state could be reached after ca. 2 h at each reaction temperature step. The catalytic activities of zeolite H-ZSM-5 at the different temperature steps were investigated subsequently with the same catalyst material.

Figure 2 shows the conversion X_{me} of methanol and the yields Y_i of light olefins, such as ethene, propene, and butenes, plotted as a function of the reaction temperature. As found in previous studies (see reference [1]), the conversion of methanol at low reaction temperatures, such as at 373 to 498 K, is dominated by the formation of dimethyl ether. First, after raising the reaction temperature to 523 K and higher, significant amounts of light olefins occur in the product stream. Assuming that the hydrocarbon pool mechanism is the dominating route leading to the formation of light

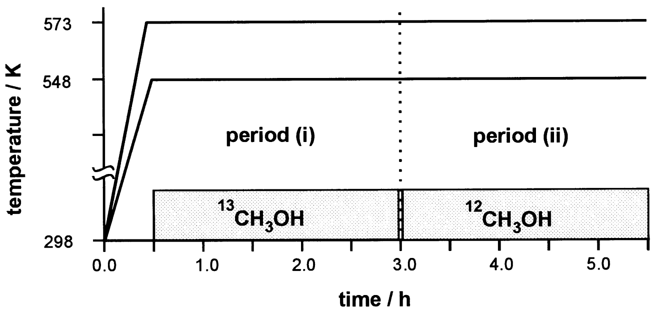

Figure 1. Protocol of the *in situ* continuous-flow (CF) MAS NMR experiments applied to obtain the spectra in figure 3.

olefins, the corresponding carboneous compounds must be present on zeolite H-ZSM-5 at reaction temperatures of 523 K and higher. Because of the significant yields of ethene and propene observed at reaction temperatures of 548 and 573 K, these reaction conditions were chosen for the *in situ* CF MAS NMR experiments. As shown in figure 2, the further increase of the reaction temperature T leads to a further increase of the yields of light olefins. However, due to Curie's law (magnetization $M_0 \propto 1/T$ [26]), the signal-to-noise ratio of the CF MAS NMR spectra would be strongly decreased, which makes a quantitative evaluation of the spectra recorded at higher temperatures more complicated.

3.2. In situ *CF MAS NMR investigations of methanol conversion on zeolite H-ZSM-5 using reactants with different ^{13}C-isotope abundances*

The *in situ* CF MAS NMR spectra shown in figure 3 were recorded under reaction conditions equal to those used for the catalytic investigations described above. The only difference consists of the ^{13}C-enrichment of the methanol converted on zeolite H-ZSM-5. According to the protocol shown in figure 1, the conversion of methanol on zeolite H-ZSM-5 was started at reaction temperatures of 548 and 573 K with a feed consisting of $^{13}CH_3OH$ (99% ^{13}C-enriched). After a reaction time of 2 h, a ^{1}H and a ^{13}C CF MAS NMR spectrum was recorded at each temperature step (first set). By an analysis of the reaction products via the on-line coupled gas chromatograph, it could be ensured that the product distribution was comparable to that in figure 2. After a conversion of $^{13}CH_3OH$ on zeolite H-ZSM-5 for 2.5 h, the feed was changed to $^{12}CH_3OH$ (natural abundance of ^{13}C-isotopes). The second set of ^{1}H and ^{13}C CF MAS NMR spectra was recorded 1 h after changing the feed. Since the first and the second set of ^{1}H and ^{13}C CF MAS NMR spectra were recorded with the same parameters and at the same reaction temperatures, the integrals of the signal intensities could be quatitatively compared, and they indicate significant changes of the relative numbers of ^{1}H- and ^{13}C-isotopes on the working catalysts.

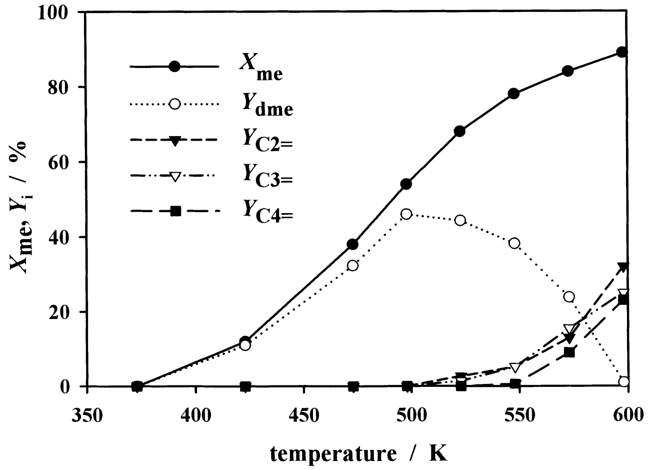

Figure 2. Conversion, X_{me}, of methanol (me) and yields, Y_i, of dimethyl ether (dme), ethene (C2=), propene (C3=), and butenes (C4=), plotted as a function of the reaction temperature. The catalytic investigations were performed with a modified residence time of $W/F = 25\,\mathrm{g\,h\,mol^{-1}}$ and in a spinning ($\nu_{rot} = 2$ kHz) MAS NMR rotor reactor (CF MAS NMR equipment).

The ^{13}C CF MAS NMR spectrum shown in figure 3, left, correspond to those observed in earlier *in situ* studies of methanol conversion on zeolite H-ZSM-5 [15] and silicoaluminophosphates H-SAPO-18 and H-SAPO-34 [16]. The weak low-field signals in the range (i) at 125 to 135 ppm are due to olefinic and aromatic carbon atoms, such as in polymethylated hexenes, hexadiens, cyclopentenes, and benzenes [27–29]. The strong high-field signals in the range (ii) at 10 to 40 ppm are caused by alkyl groups [27–29]. The ^{1}H CF MAS NMR spectra shown on the right-hand side of figure 3 are dominated by signals at 0 to 3 ppm due to protons of alkyl groups and broad signals at 5 to 8 ppm caused by protons of olefinic and aromatic compounds and of hydroxyl groups [30]. The strong dipolar interactions between neighboring protons and the limited sample spinning rate (ν_{rot} ca. 2.5 kHz) cause a strong broadening of the ^{1}H MAS NMR signals. The high mobility of the compounds at elevated temperatures, on the other hand, narrows the ^{1}H MAS NMR signals and make their quantitative evaluation possible. The comparison of the total integrals of the ^{1}H MAS NMR spectra, recorded at same reaction temperatures before and after changing the methanol feed from $^{13}CH_3OH$ to $^{12}CH_3OH$, indicates that the total number of protons is constant (accurracy of ±5%). Hence, the above-mentioned change of the methanol feed has no effect on the total amount of alkylated olefins and aromatics contributing to the hydrocarbon pool on the working zeolite catalyst. Comparison of the ^{13}C CF MAS NMR spectra recorded at reaction temperatures of 548 and 573 K before and after changing the methanol feed shows a decrease of the alkyl signals by 40% (accurracy of ±5%). The strong broadening of the weak low-field ^{13}C MAS NMR signals at 125 to 135 ppm made their

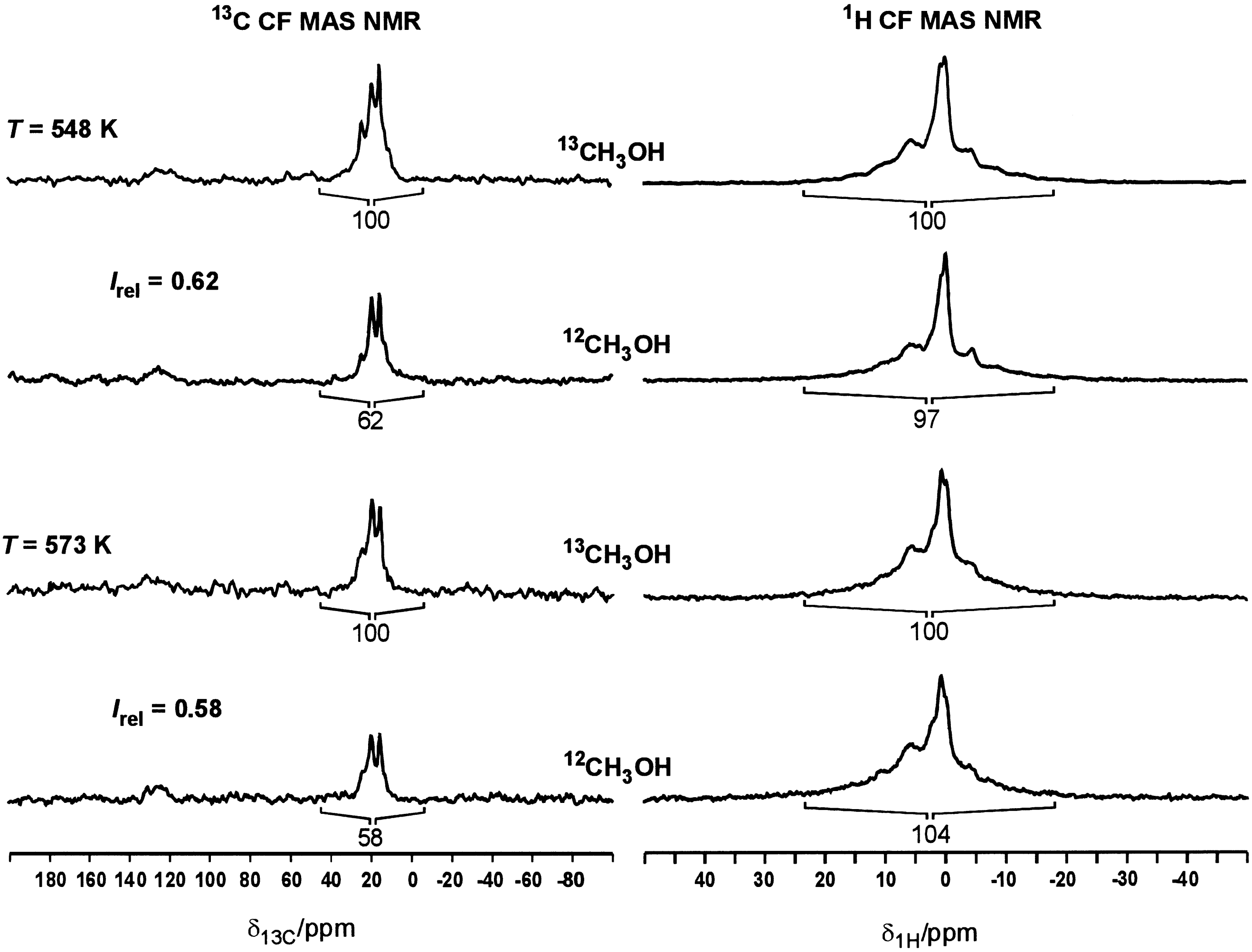

Figure 3. *In situ* ^{13}C CF MAS NMR (left) and ^{1}H CF MAS NMR spectra of zeolite H-ZSM-5 recorded during conversion of methanol ($W/F = 25$ gh mol^{-1}) at reaction temperatures of (a) 548 K and (b) 573 K. After a reaction time of 2.5 h, the feed was changed from ^{13}C-enriched methanol ($^{13}CH_3OH$) to methanol with ^{13}C-isotopes in a natural abundance ($^{12}CH_3OH$).

quantitative evaluation difficult. A rough estimation indicates that there is no significant change in the intensity of the low-field signals before and after changing the methanol feed.

3.3. Catalytic role of the hydrocarbon pool present on zeolite H-ZSM-5 during conversion of methanol

The decrease of the ^{13}C MAS NMR signals of alkyl groups in the *in situ* experiments after changing the methanol feed from $^{13}CH_3OH$ to $^{12}CH_3OH$ indicates that a significant portion (40%) of the ^{13}C-enriched alkyl groups bound at the olefinic and aromatic compounds, which contribute to the hydrocarbon pool, were replaced by alkyl groups with a natural abundance of the ^{13}C-isotopes. A splitting-off of the ^{13}C-enriched alkyl groups without a replacement by nonenriched alkyl groups can be excluded since the total ^{1}H CF MAS NMR intensities are equal, comparing the spectra before and after changing the methanol feed. Therefore, the decrease of the ^{13}C CF MAS NMR intensities of alkyl groups indicates the occurrence of reactions that are generally described in scheme 1.

According to scheme 1, the hydrocarbon pool formed during the conversion of ^{13}C-enriched methanol on zeolite H-ZSM-5 consists of olefinic and aromatic skeleton carbon atoms, denoted by $(^{13}CH_2)_n$, and ^{13}C-enriched alkyl groups. The splitting-off of the alkyl groups leads to the formation of light olefins that leave the catalyst as reaction products. Under steady-state conditions of the methanol conversion, a continuous alkylation of the olefinic and aromatic skeleton carbon atoms occurs. After changing the methanol feed from $^{13}CH_3OH$ to $^{12}CH_3OH$, however, the alkyl groups added to the skeleton carbon atoms, $(CH_2)_n$, have a natural abundance of ^{13}C-isotopes. Each splitting-off and addition of alkyl groups, therefore, decreases the total number of ^{13}C-isotopes of alkyl groups in the hydrocarbon pool on the zeolite catalyst. The experimentally observed decrease of the ^{13}C MAS NMR signals of alkyl groups of 40% after changing the methanol feed from $^{13}CH_3OH$ to $^{12}CH_3OH$ indicates that a corrresponding portion of alkly groups contributes to the hydrocarbon pool mechanism. The remaining 60% of alkyl groups are not accessible or are bound at nonreactive carboneous compounds. Hence, the results of the *in situ* CF MAS NMR experiments support the side-chain methylation of the olefinic and aromatic skeleton carbon atoms as an important pathway of the hydrocarbon pool mechanism for the methanol-to-olefin conversion on acidic zeolites.

4. Conclusions

Application of *in situ* CF MAS NMR spectroscopy and the change of the methanol feed under steady-state conditons from $^{13}CH_3OH$ to $^{12}CH_3OH$ allow a direct spectroscopic investigation of the catalytic role of the hydrocarbon pool formed on zeolite H-ZSM-5 during the conversion of methanol. Via this experimental approach, the reactivity of the hydrocarbon pool formed on zeolite H-ZSM-5 under steady-state conditions was directly studied for the first time. The decrease of the ^{13}C MAS NMR signals of the alkyl groups in the hydrocarbon pool after changing the methanol feed by 40% indicates that a corresponding number of alkyl groups bound at olefininc and aromatic skeleton atoms of the hydrocarbon pool contribute to the alkylation and splitting-off reactions on zeolite H-ZSM-5. This is a direct experimental evidence that the side-chain methylation of the olefinic and aromatic skeleton carbon atoms is an important pathway of the hydrocarbon pool mechanism. The remaining 60% of alkyl groups that were not influenced by the change of the methanol feed from $^{13}CH_3OH$ to $^{12}CH_3OH$ are unaccessible and are bound at nonreactive carboneous compounds on the zeolite catalyst.

Acknowledgments

Financial support by Deutsche Forschungsgemeinschaft, Max-Buchner-Forschungsstiftung and Volkswagen-Stiftung Hannover is greatfully acknowledged.

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