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Mechanistic study of aniline methylation over acidic and basic zeolites Y

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^{13}C MAS NMR has been performed *in situ* under batch conditions to investigate the mechanism of aniline alkylation with methanol on acidic zeolite H-Y and basic zeolite CsNa-Y impregnated with cesium hydroxide. The results suggest that on the acidic zeolite H-Y, methanol first reacts with zeolitic hydroxyl groups to give surface methoxy groups, which further play a role as alkylating species in aniline methylation. By contrast, on the basic zeolite, methanol is converted into formaldehyde, which is responsible for N-alkylation. Both on acidic and basic zeolites, N-methylaniline is the primary alkylation product. Toluidines and N-methyltoluidines are formed only on acidic zeolites at elevated temperatures after complete conversion of methanol into N-methylaniline. A mechanistic pathway involving isomerization and disproportionation of N-methylaniline on acid sites is proposed to account for the formation of toluidines.

1. INTRODUCTION

Mono- and di-N-methylation of aniline are important reactions for the synthesis of intermediates in fine chemistry. Up till now, the industrial processes leading to these products are based on the application of corrosive liquid acids as catalysts [1, 2] and should be replaced by environmentally safer processes using solid catalysts such as oxides, clays and zeolites [3-8]. It is known that alkylation of aniline can be performed on acidic [3-6] and basic [7, 8] zeolites. However, little is known about the reaction mechanisms involved on these solids. A detailed understanding of the mechanisms of the main and side reactions occurring during alkylation on various types of zeolites and an elucidation of the active sites and of their role in each elementary step may give a key to the design of novel tailored catalysts.

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This study aims to clarify the mechanism of aniline methylation on acidic and basic zeolites Y by means of *controlled atmosphere* ^{13}C MAS NMR spectroscopic experiments performed *in situ* under batch conditions.

2. EXPERIMENTAL SECTION

The study was performed on zeolite H-Y and cesium-exchanged zeolite Y after subsequent impregnation with cesium hydroxide (CsNa-Y/14CsOH). The degree of ion exchange for Cs was 70 %. The content of CsOH in the sample was 14 molecules per u.c. The sample preparation and characterization is given elsewhere [9, 10].

^{13}C MAS NMR measurements were carried out on an MSL-300 Bruker spectrometer operating at 75.15 MHz. Controlled atmosphere *in situ* experiments were performed in sealed glass NMR cells containing the catalyst and an adsorbate, and fitting precisely into MAS rotors. Methanol-^{13}C was the labeled reactant. The amount of methanol adsorbed was 1.5 molecules/u.c. (low loadings) and 7 molecules/u.c. (high loadings), and the molar aniline/methanol ratio amounted to 2 and 3, respectively. In a typical NMR experiment, the sealed NMR cell was rapidly heated to a selected reaction temperature outside the spectrometer and maintained at this temperature for a given period of time. MAS NMR spectra were recorded at 293 K after quenching the sample cell in liquid nitrogen. After recording the NMR spectrum, the NMR cell was returned to reaction conditions and heated for progressively longer periods of time. A more detailed description of controlled atmosphere *in situ* experiments is given in Reference [11].

3. RESULTS AND DISCUSSION

3.1. Aniline methylation on acidic zeolite H-Y

^{13}C MAS NMR spectra observed after adsorption and reaction of aniline and methanol on zeolite H-Y are presented in Figure 1. Adsorption of aniline leads to strongly adsorbed aniline species evidenced by observation of two very broad NMR lines at ca. 129 and 122 ppm, amenable to cross polarization. The line at ca. 122 ppm, attributed to C-atoms in ortho- and para-positions of the aniline molecule is shifted significantly to lower field with respect to solution data (114.4 and 116.3, respectively, [12]). This could be due to an interaction of the NH_2 groups of aniline molecules with zeolitic OH groups via H-bonding which causes a significant disturbance of the carbon atoms in ortho- and para-positions of the aromatic ring. Adsorption of methanol leads to three types of methanol species with different mobility: i) mobile "intracrystalline" methanol (48.5 ppm), ii) species with limited mobility due to an interaction with strongly adsorbed aniline molecules (50.7 ppm) and iii) small amounts of strongly bound surface methoxy groups (55.5 ppm). The results suggest that, upon adsorption at ambient temperature, aniline occupies most part of the Brønsted sites in zeolite H-Y. A small part of methanol molecules reacts with free Brønsted sites to form surface methoxy groups. Another part gives adsorption complexes with aniline molecules, and the remainder is present as methanol molecules with high mobility.

After heating the sample loaded with methanol and aniline at 373 K for 1 h, the concentration of methoxy groups increases, the lines at 48.5 and 50.7 ppm merge into one broad resonance signal centered at ca. 49 ppm, and a small signal appears at 38.5 ppm (Fig. 1). The latter signal was attributed to methyl groups of N-methylaniline molecules. This

assignment was confirmed by adsorption of pure N-methylaniline on zeolite H-Y. The significant shift of the line corresponding to N-methylaniline with respect to solution data (29.9 ppm [12]) is probably due to a strong interaction between the basic -NH- groups of

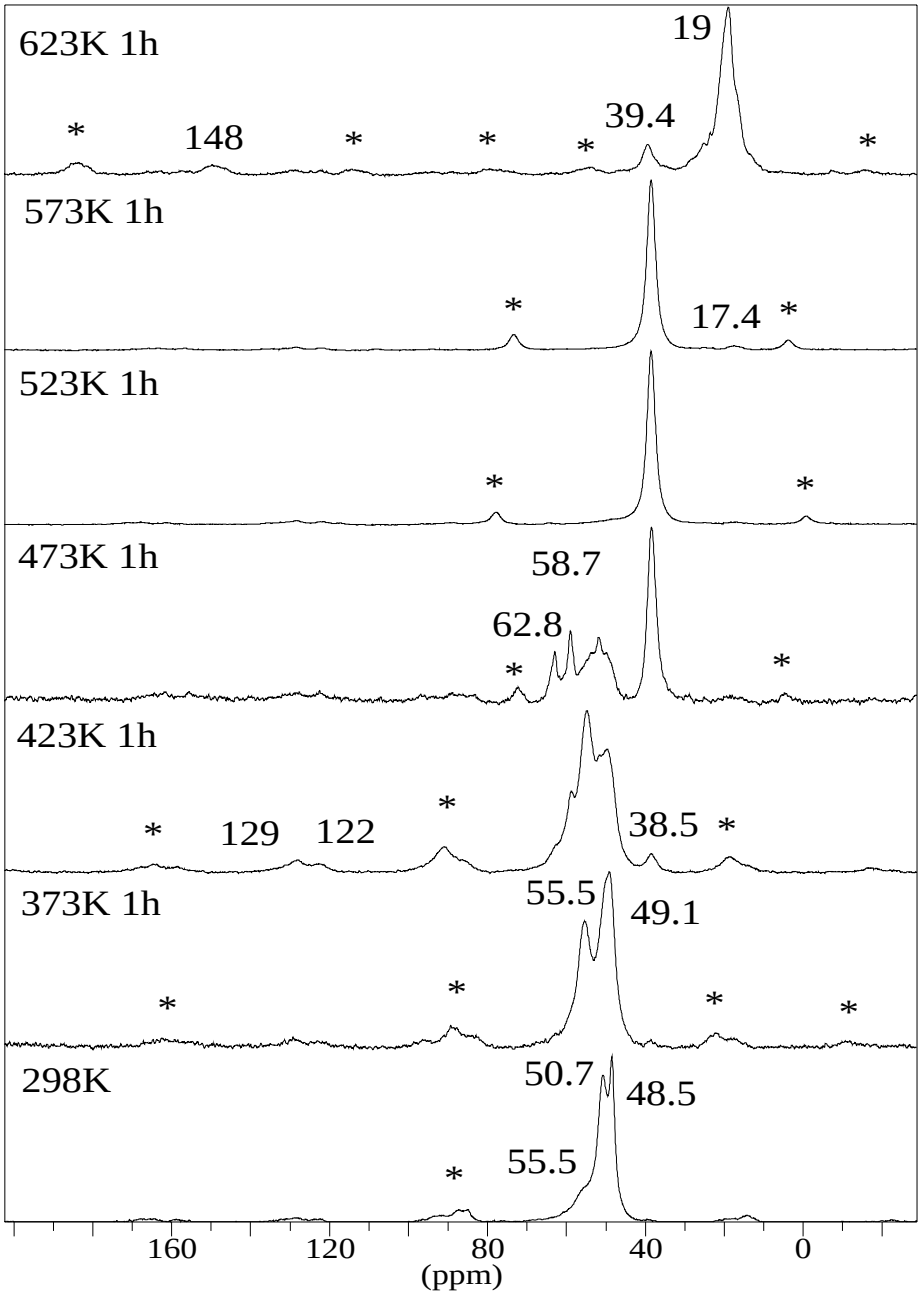


Fig. 1. ^{13}C MAS NMR spectra observed in the course of reaction of aniline (21 molecules/u.c.) and methanol-^{13}C (7 molecules/u.c.) on zeolite H-Y. Asterisks indicate spinning side bands.

N-methylaniline molecules and zeolitic OH groups leading to a significant disturbance of the methyl groups. At 423 K, the line at 55.5 ppm corresponding to methoxy groups yields the highest contribution to the NMR spectrum. The concentration of N-methylaniline also increases. In addition, two lines appear at 58.7 and 62.8 ppm caused by different conformations of adsorbed dimethyl ether. Further heating to 473 K leads to a disappearance of the signal due to methoxy groups followed by a rapid formation of N-methylaniline. This observation suggests that methoxy groups may play a role as intermediates in N-alkylation. Finally, at 523 K, all ^{13}C-labeled species were converted into methyl groups of N-methylaniline molecules. Consequently, N-methylaniline was found to be the only primary alkylation product on zeolite H-Y, and methoxy groups are suggested to be an intermediate species in this reaction.

The role of methoxy groups as intermediates in N-alkylation was further confirmed by the experiments on aniline interaction with methoxylated zeolite H-Y. In the latter case, the reaction took place already at ambient temperature [11]. It was thus demonstrated that formation of methoxy groups is the rate limiting step of the overall reaction on zeolite H-Y.

The results obtained point to the following mechanism of alkylation on an acidic zeolite Y under batch conditions:

$$CH_3OH + ZO\text{-}H \rightarrow ZO\text{-}CH_3 + H_2O \quad (1)$$

$$ZO\text{-}CH_3 + C_6H_5NH_2 \rightarrow C_6H_5NHCH_3 + ZO\text{-}H \quad (2)$$

During the first step of the reaction, methanol reacts with the zeolite surface to give methoxy groups. As a result of this step, part of the aniline molecules is removed from the Brønsted sites to the gas phase by the more stable surface methoxy groups. In the second step of the reaction, gaseous aniline molecules react with the methoxy groups to give N-methylaniline adsorbed on a Brønsted site. The data suggest that the second reaction step is much faster than the first one and that the formation of surface methoxy groups is the rate limiting step of the overall reaction.

Formation of the secondary reaction products - toluidines or N-methyltoluidines, evidenced by the appearance of ^{13}C MAS NMR signals at 17 to 24 ppm (Fig. 1) - was observed only at reaction temperatures of 523 to 623 K after complete conversion of methanol species into N-methylaniline. Therefore, it is concluded that toluidines are formed via isomerization or disproportionation of N-methylaniline:

$$C_6H_5NHCH_3 \rightarrow CH_3C_6H_4NH_2 \quad (3)$$

$$2\ C_6H_5NHCH_3 \rightarrow CH_3C_6H_4NHCH_3 + C_6H_5NH_2 \quad (4)$$

3.1. Aniline methylation on basic zeolite CsNa-Y/14CsOH

Figure 2 shows the spectra obtained for aniline alkylation with methanol on zeolite CsNa-Y/14CsOH. In contrast to acidic zeolite H-Y, no strongly adsorbed aniline species were detected on zeolite CsNa-Y/14CsOH. All aniline signals were narrow, and their chemical shifts were close to the solution data. In addition, they were not amenable to cross polarization. On the contrary, methanol was strongly adsorbed which was evidenced by its line broadening, the appearance of side bands and the enhancement of the signal intensity in experiments with cross-polarization. However, no indications of the formation of methoxy groups or adsorbate complexes with aniline were observed after adsorption of methanol.

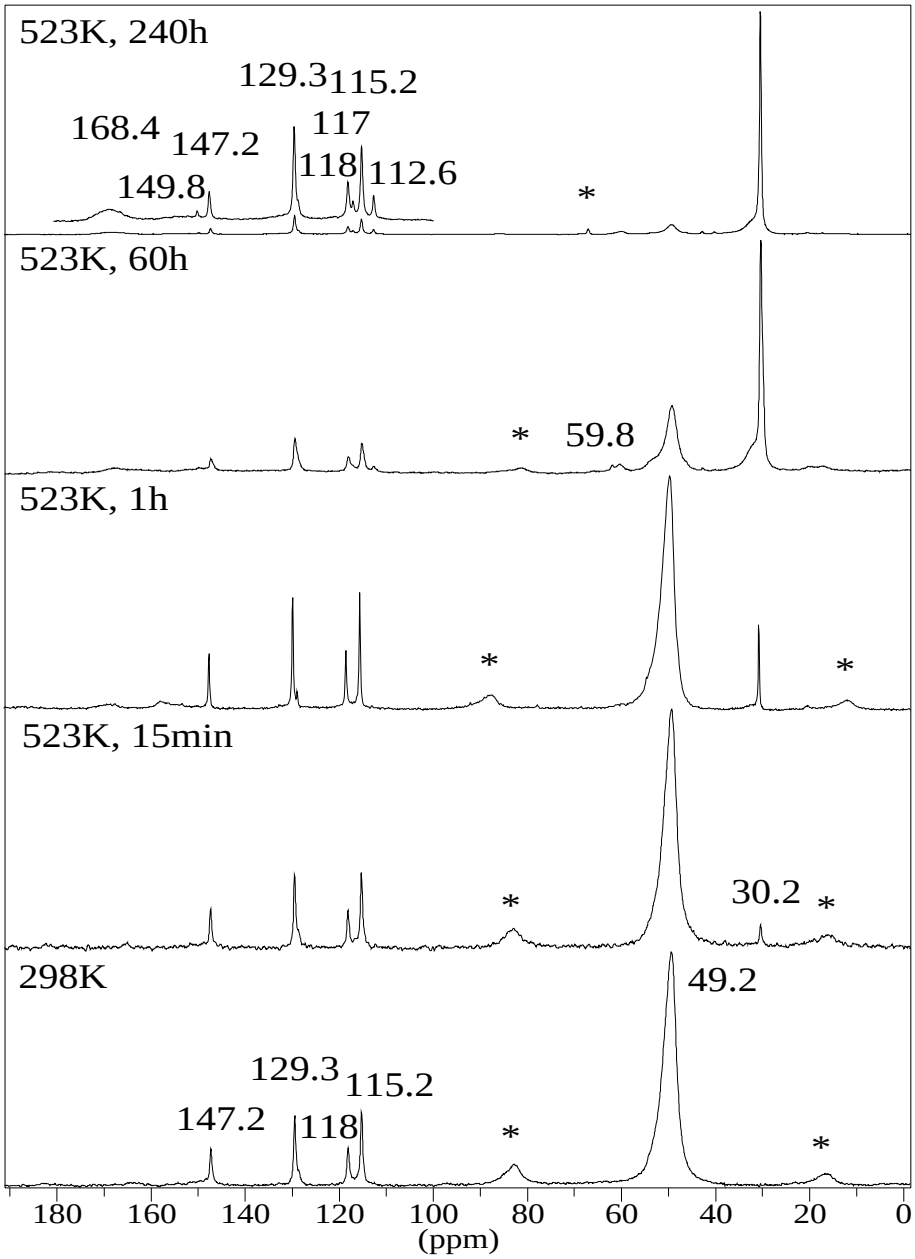


Fig. 2. ^{13}C MAS NMR spectra observed in the course of the reaction of aniline (21 molecules/u.c.) and methanol-^{13}C (7 molecules/u.c.) on zeolite CsNa-Y/14CsOH. Asterisks indicate spinning side bands.

As evidenced by the observation of a line at 30.2 ppm due to labeled methyl group of N-methylaniline (Fig. 2), the alkylation reaction starts at 523 K. It is noteworthy that in the case of zeolite CsNa-Y/14CsOH, the interpretation of this line was straightforward since the chemical shift is close to the solution data (29.9 ppm [12]). Further heating for longer periods resulted in a gradual conversion of the reactants into N-methylaniline and, after 10 days of

heating at 523 K, all methanol molecules were converted into N-methylaniline. The small lines at 112.6, 117.0 and 149.8 ppm were due to unlabeled aromatic carbon atoms of N-methylaniline. Small amounts of dimethyl ether (δ = 59.8 ppm) and surface formate species (δ = 168.4 ppm) were also observed at the end of the reaction. It should be noted, however, that no intermediates were detected in the course of the reaction on zeolite CsNa-Y/14CsOH, probably due to their high reactivity on this catalyst.

For very low loadings of reactants, the situation was quite different (Fig. 3). No N-methylaniline was observed, and methanol was converted into surface formate species while aniline remained unreacted. This result indicates that, at low loadings, the reactants are adsorbed on different sites and the distance between them is too long for a reaction.

A study of the reactivity of pure methanol under the same reaction conditions has demonstrated that the main reaction products of the methanol conversion are dimethyl ether and surface formate species. The reaction pathways which may account for these products include methanol dehydration and dehydrogenation, respectively:

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (5)$$

and

$$CH_3OH \rightarrow CH_2O + H_2$$

$$2\ CH_2O + OH^- \rightarrow CH_3OH + HCOO^- \quad (6)$$

It appears that the first route is completely inhibited in the presence of aniline since no dimethyl ether was observed, neither at high loadings nor at low loadings of methanol. The explanation for this phenomenon is a blocking by aniline the active sites responsible for dehydration.

The second route leading to surface formate species is also inhibited at high aniline coverages. However, it is the main reaction pathway at low coverages. These observations indicate that in the presence of aniline, formate formation and aniline alkylation are competing reactions and that they most probably occur on the same type of active sites and involve the same intermediates. Consequently, formaldehyde may play the role of an intermediate in the alkylation reactions. This conclusion is consistent with previous findings [10,13,14], suggesting formaldehyde to be an alkylating agent in the side-chain methylation of toluene on basic zeolites.

The results obtained allow to propose the following mechanism of aniline alkylation over basic zeolites. Upon adsorption, aniline is associated with Lewis sites of the catalyst while methanol is strongly adsorbed on basic sites. Heating of the reaction system to 523 K leads to dehydrogenation of methanol on basic sites and to the formation of very reactive formaldehyde which can alkylate aniline leading to $C_6H_5N{=}CH_2$. The latter molecule can further be hydrogenated to N-methylaniline with H_2 generated in the first step:

$$CH_3OH \rightarrow CH_2O + H_2$$

and

$$CH_2O + C_6H_5NH_2 \rightarrow C_6H_5N{=}CH_2 + H_2O \quad (7)$$

$$C_6H_5N{=}CH_2 + H_2 \rightarrow C_6H_5NHCH_3 \quad (8)$$

At low surface coverages with aniline, alkylation is competing with the side reaction (6) leading to surface formate species.

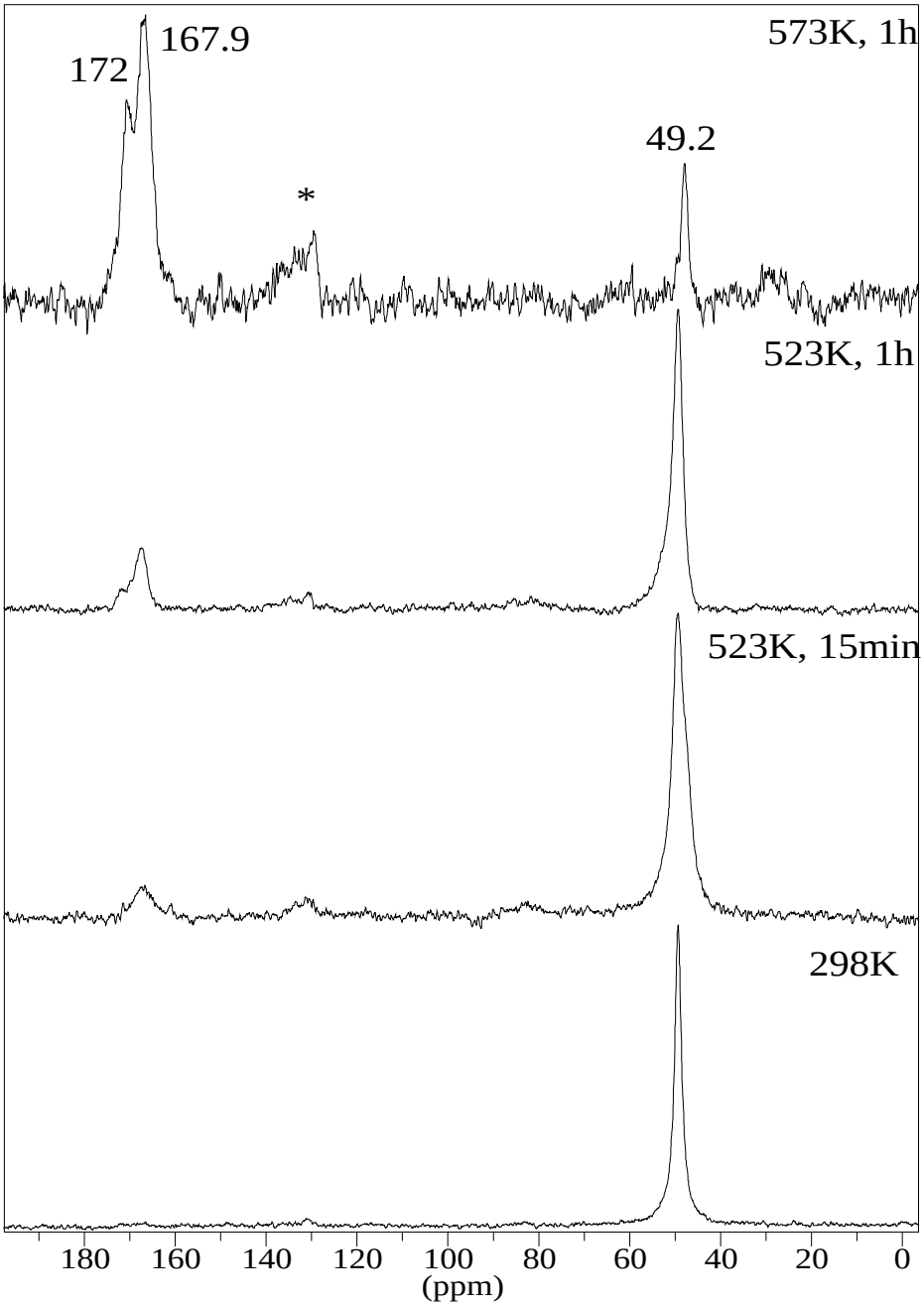


Fig. 3. ^{13}C MAS NMR spectra observed in the course of the reaction of aniline (2.4 molecules/u.c.) and methanol-^{13}C (1.5 molecules/u.c.) on CsNa-Y/14CsOH. Asterisks indicate spinning side bands.

It is noteworthy that the above-mentioned mechanism should be considered as a working hypothesis since it is based on the assumption of formaldehyde formation. Further experiments with formaldehyde are in progress to confirm this hypothesis.

4. CONCLUSIONS

N-methylaniline is the primary product of aniline alkylation both on acidic and basic zeolites. Surface methoxy groups may play the role of an intermediate in N-alkylation on zeolite H-Y, while on zeolite CsNaY/14CsOH formaldehyde is responsible for N-methylation. In this case, the rate limiting step of the reaction on acidic and basic zeolites is the formation of methoxy groups and formaldehyde, respectively.

Formation of N-methylaniline is accompanied by the formation of surface formate species on basic zeolites and toluidines on acidic zeolites. Formate species are formed on the basic zeolite from formaldehyde, i.e., the same reaction intermediate as N-methylaniline. Toluidines are obtained via isomerization or disproportionation of N-methylaniline on acidic zeolite. Surface formate species could be responsible for a fast deactivation of basic catalysts while toluidines lead to the decrease of the selectivity to N-methylaniline on acidic zeolites.

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