

CoX ZEOLITES AND THEIR EXCHANGE WITH DEUTERIUM

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Analysis of the gaseous phase by means of a mass spectrometer and analysis of the solid phase by means of an infrared spectrophotometer was used to investigate the deuterium exchange with hydrogen bound mostly in hydroxyl groups of zeolites CoX (21 and 47%) and NaX. It was found that with the increasing amount of cobalt ions the number of exchangeable hydrogens of the zeolite increases; the respective types of the hydrogen are discussed with respect to the particular dehydration temperatures. The rate of the exchange $D_2 + OH$ is substantially faster with the CoX than with the NaX zeolite, and exhibits a decrease with the increasing dehydration. On the other hand, the rate of exchange $D_2 + H_2$ without the zeolite hydrogen incorporation, catalyzed by the CoX zeolites, increases with the increasing dehydration. The increased activation of gaseous hydrogen molecules hangs together with the presence in the zeolite of cobalt ions whose properties change during dehydration with the change of their environment. Hydroxyl groups of the CoX zeolites are not equivalent during the exchange; the hydroxyl hydrogens of the 3740 cm^{-1} band are exchanged more slowly than the other hydrogens.

Simultaneous investigation of the exchange of deuterium with hydrogen bound in zeolites by analyzing both the gaseous (mass spectrometry) and the solid (infrared spectrometry) phase is of interest because of two reasons. First, the mechanism of the exchange itself can be studied, and — second — hydroxyl groups of zeolites can be characterized. This is of interest, because they presumably play an important role in some catalytic reactions. The zeolite-catalyzed $D_2 + H_2$ exchange in the gaseous phase provides information on the activation of hydrogen molecules (D_2 , HD, and H_2); this activation may be the process which determines the rate of the $D_2 + OH$ exchange.

The exchange $D_2 + OH$ in either the gaseous or the solid phase and the exchange $D_2 + H_2$ in the gaseous phase with cationic forms of zeolites was investigated by several authors. The main results of their work can be summarized as follows: 1) The amount of hydrogens in a zeolite increases with the exchange of a monovalent for a polyvalent cation (CaX (ref.^{1,2}), CaY (ref.^{1,2}), NaY, CeY (ref.³); 2) According to the authors studying the exchange $D_2 + OH$ in the gaseous phase, hydrogens of cationic forms of zeolites are equivalent (CaX, CaY (ref.²), NdY, CeY (ref.³); on the other hand, studies investigating the exchange in the solid phase by means of infrared spectroscopy conclude the opposite (CaX (ref.⁴), LaY (ref.⁵); 3) The exchange $D_2 + H_2$ occurs with a rate by as much as two orders of magnitude higher than the exchange $D_2 + OH$ (CaX, CaY (ref.²), CeY, NdY (ref.³). According to ref.⁶, a fast $D_2 + H_2$ exchange was found only with NiX; in the series Zn, Co, Mn, Ca of X-zeolites the rate was found to decrease substantially. A comparison with the rate of the $D_2 + OH$ exchange was not made in this study, but the temperatures at which the $D_2 + H_2$ exchange was carried out were lower than usual for the $D_2 + OH$ exchange. Both groups of authors found an increase of the $D_2 + H_2$ exchange rate with the zeolite dehydration.

As different conclusions of several papers may be caused by different methods used (analysis of the gaseous or the solid phase), we employed in our study both ways of analysis. The zeolites used were NaX and CoX zeolites, the latter with 21 and 47% Na⁺ exchanged for Co²⁺ ions.

EXPERIMENTAL

The studied zeolites had the following composition: NaX: (Na₂O)_{0.95}(CaO)_{0.03}Al₂O₃(SiO₂)_{2.66} (Research Institute of Oil and Hydrocarbon Gases — VÚRUP, ČSSR); CoX(21): (CoO)_{0.21} · (Na₂O)_{0.86}(CaO)_{0.01}Al₂O₃(SiO₂)_{2.76}; CoX(47): (CoO)_{0.47}(Na₂O)_{0.50}(CaO)_{0.01}Al₂O₃ · (SiO₂)_{2.53}.

The cobalt forms were prepared by the exchange of Na⁺ of the NaX zeolite in CoCl₂ solution at 50°C under such conditions that no hydrolysis occurred. The particle size distribution of NaX is given in Fig. 1 (obtained by Dr J. Blažek, Research Institute of Aerotechnology, using an optical microscope).

Infrared spectra were measured with the help of an infrared spectrophotometer Perkin-Elmer 621. Details concerning sample preparation, cells used *etc.* were reported in earlier communications similarly as the conditions for the gas-phase exchange kinetics investigation by means of a mass spectrometer MCH 1302 (USSR) (ref.^{7,8}).

The pressure of the gas over the sample did not change during the experiment.

RESULTS AND DISCUSSION

Table I shows the dependence of the overall number of hydrogen atoms in hydroxyl groups (or adsorbed water) on the dehydration conditions, calculated after the equilibrium of the deuterium exchange with the zeolites NaX, CoX (21), and CoX (47) was reached. The samples dehydrated at temperatures lower than the temperature of exchange (300°C) release water during the exchange; the water hydrogen can then enable an exchange with the hydroxyl groups of the apparatus walls. Therefore, the

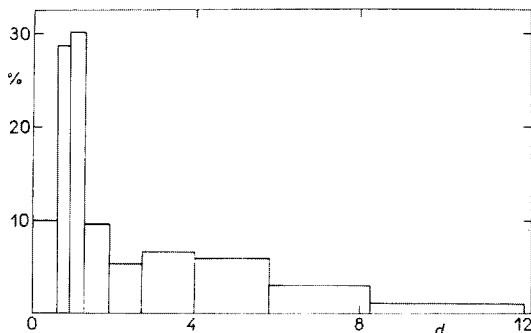


FIG. 1

NaX Zeolite Particle Size Distribution According to their Diameter, *d* (μm)

values obtained are probably somewhat distorted. As it follows from our earlier studies^{7,9}, this error cannot influence the conclusions which can be extracted from Table I: the number of exchangeable hydrogens increases with the content of cobalt ions in the zeolite and decreases with the dehydration temperature. Hydrogen is bound in the zeolites in the form of hydroxyl groups and adsorbed water, as can be seen from the infrared spectra in Figs 2, 3, and 4, in the wavenumber region 3800 to 3000 cm^{-1} . In this interval there are bands which were ascribed to the valence vibrations of OH-groups and of adsorbed water. In determining the presence of water in zeolites the band 1640 cm^{-1} (bending vibration of water) is of importance, too. This band is not shown in the figures, but its behaviour is described in detail in the following text.

After evacuation at the laboratory temperature (curve 1, Figs 2–4) all three zeolites contained water (a strong band at 1640 cm^{-1} was observed). Water is at least partly adsorbed on Na^+ ions, as evidenced by the bands at 3690, 3400, and 3230 cm^{-1} whose height decreases with the Na^+ content in the zeolites. The interpretation of these bands was treated by several authors, the above mentioned assignment was first introduced for NaX by Bertsch and Habgood⁹.

In CoX there appears — in comparison with NaX — in the spectrum a new band at 3650 cm^{-1} . The intensity of this band increases with the increasing content of cobalt ions. A similar band was found in CoY by Ward¹⁰, who assigned it — after

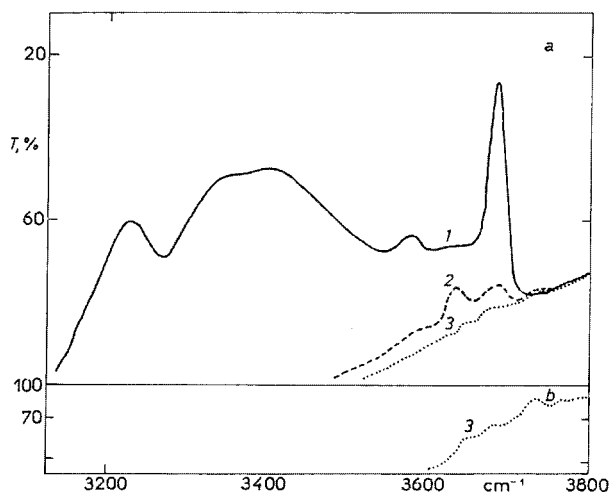
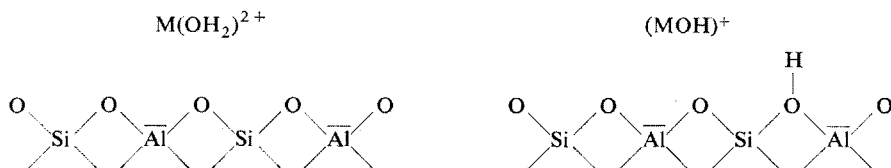


FIG. 2

Infrared Spectrum of NaX Zeolite after 18 h Dehydration at the Laboratory Temperature (1), at 200°C (2), at 400°C (3)

Sample *a* 4.4 mg/cm^2 , *b* 17.7 mg/cm^2 .

a comparison with the bands of decationized forms — to hydroxyls containing oxygen of the Si—O—Al lattice. In this sense CoX exhibits a similar behaviour as CoY and even at the laboratory temperature the dissociation of water probably occurs with the formation of “lattice” hydroxyls. The dissociation is caused by the presence of Co ions. For cationic forms the following mechanism was suggested for this process, based on the infrared data¹¹:



The band at 3615 cm^{-1} was ascribed in CoY to the structure CoOH^+ . We cannot exclude that the band at 3600 cm^{-1} in CoX after the dehydration at the laboratory temperature corresponds to the same structure.

The spectra of all samples after the evacuation at the laboratory temperature are so complex (overlapping bands) that they do not justify any more detailed statement either about further water adsorption sites or other possible types of OH-groups. Therefore, in this case the reason of the increase of the total amount of the zeolite hydrogen with the content of Co^{2+} cannot be reliably determined.

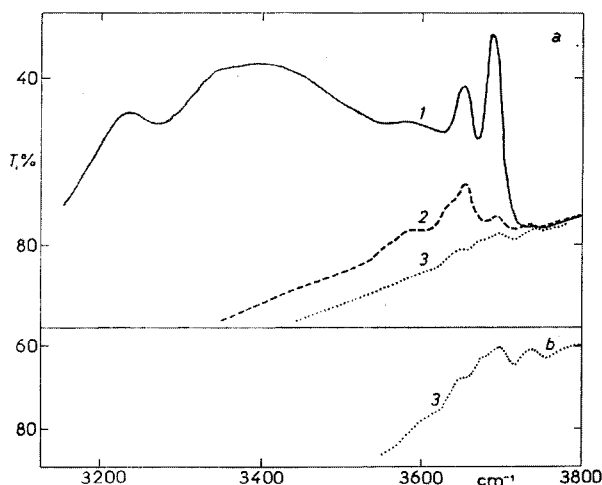


FIG. 3

Infrared Spectrum of CoX(21) after 18 h; Dehydration at the Laboratory Temperature 1, at 200°C 2, at 400°C 3

Sample a 5.1 mg/cm^2 , b 16.3 mg/cm^2 .

After evacuation at 200°C (curve 2, Figs 2–4) water is mostly desorbed from the zeolites, as indicated by the decrease of intensities of the bands at 3500–3000 cm⁻¹, 3690 cm⁻¹, and 1640 cm⁻¹; the height of the latter band decreased by an order of magnitude. The CoX zeolites differ significantly from the NaX zeolite in the occurrence of the bands at 3650 cm⁻¹ and 3580 cm⁻¹. Of those the latter belongs probably also to the hydroxyl groups containing the oxygen of the Si—O—Al lattice (Ward: CoY (ref.¹⁰), in HX we found⁸ a band of analogous hydroxyls at 3565 cm⁻¹). The intensity of the two above mentioned bands increases with the Co²⁺ content in the sample. Thus, in this case we may explain the increase of the total amount of hydrogen (Table I) by the “lattice” hydroxyls of the bands at 3650 and 3580 cm⁻¹. Analytical data in the experimental part show that in the exchange Na⁺—Co²⁺ the cationic deficit does not increase so that the differences observed cannot be ascribed to the decationization of the CoY zeolite.

After dehydration at 400°C (curve 3, Figs 2a, b; 3a, b; 4a, b) no bands of adsorbed water were found in the spectra of any of the three zeolites. The samples contained hydroxyl whose bands could not be always unambiguously interpreted with the use of the published data. With respect to the behaviour during the exchange with deuterium, the band at 3740 cm⁻¹ is of importance. This band is usually ascribed¹¹ to the terminal hydroxyls of the zeolite particles, to hydroxyls resulting from structural changes, and to hydroxyls of silica impurities.

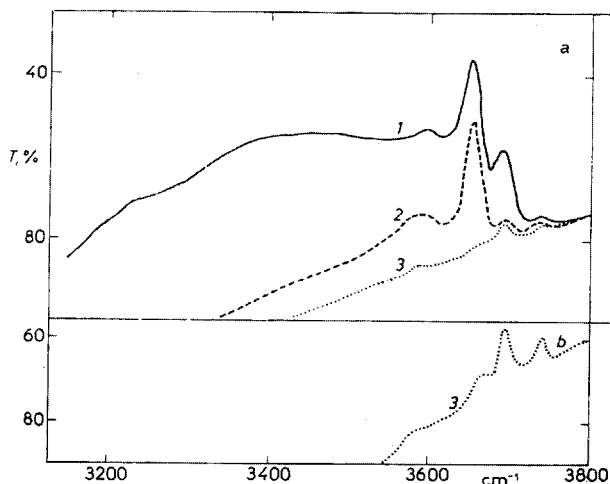


FIG. 4

Infrared Spectrum of CoX(47) after 18 h Dehydration at the Laboratory Temperature (1), at 200°C (2), at 400°C (3)

Sample *a* 4.4 mg/cm², *b* 14.5 mg/cm².

The presence of hydroxyl groups in the NaX zeolite can be explained by the low decationization within the limits of the experimental errors of the analytical methods used in determining the total composition (2% decationization: $0.56 \cdot 10^{20}$ OH/g; experimental value shown in Table I: $0.63 \cdot 10^{20}$ OH/g), and by structural defects; another possible source may be silica impurities. Terminal hydroxyls of the zeolite particles do not represent a substantial portion in the total amount of hydroxyl groups; their number was calculated from the particle size distribution (Fig. 1) using the relation derived by Uytterhoeven¹ as $0.02 \cdot 10^{20}$ OH/g.

The increase of the number of hydroxyl groups in the CoX zeolite in comparison with NaX is probably also connected with the presence of the lattice oxygen containing hydroxyls (bands at 3650, 3580 cm^{-1}). In comparison with the samples dehydrated at 200°C the number of these hydroxyls substantially decreased. A large difference in the spectra of the CoX zeolites in comparison with those of NaX, after dehydration at 400°C, represents the band 3695 cm^{-1} . The same band was found in the HX zeolite, too⁸. The occurrence of the corresponding hydroxyl groups probably hangs together with the hydrolytical changes of the Si—O—Al arrangement⁵.

The hydroxyls Co(OH) are more labile during dehydration than the "lattice" ones. In analogy with the published data¹¹ we could assume that during the removal of

hydroxyl groups the species CoO or $\text{Co}-\text{O}-\text{Co}$ are formed. The former would require the presence of two hydrogens on one Co, the latter one hydrogen on one Co ion. According to ultraviolet data^{12,13}, after dehydration at 400°C Co ions have the tetrahedral environment; therefore, the presence of Co^{2+} ions only is rather improbable. If only Co^{2+} ions were present, no lattice hydrogen would be necessary. After dehydration at 400°C the result is 0.9 H/Co (both for the CoX (21) and the CoX (47)

TABLE I

Dependence of Number of Hydrogens Bound in Zeolites NaX, CoX(21), and CoX(47) on the Dehydration Temperature (18 h in vacuum)

°C	H/g. $\cdot 10^{-20}$		
	NaX	CoX(21)	CoX(47)
20	6.4	98	122
100	1.2	56	41
200	0.92	13	29
300	—	4.3	8.7
400	0.63	2.5	5.5
600 ^a	—	1.6	4.8

^a There are no unambiguous published data^{6,12} concerning the lattice collaps at this temperature.

zeolite); the ratio is the experimental value from Table I divided by the number of Co: in CoX (21) $2.8 \cdot 10^{20}$, in CoX (47) $6.4 \cdot 10^{20}$. This would indicate the existence of the $\text{Co}-\text{O}-\text{Co}$ structure.

All the zeolites studied contained, in particular at lower dehydration temperatures, bands of carboxylate structures; during the dehydration the released CO and CO₂, including water, was registered even in the gaseous phase by means of mass spectrometry.

Fig. 5 shows the course of the D₂ + OH exchange for CoX(47) at 300°C in the gaseous phase. If all hydrogens of the zeolite exchange with the same rate, the first-order plot related to the isotopic composition must be linear (the deuterium diffusion towards the sample does not influence the exchange rate under our experimental conditions). The linear dependence was found with the samples dehydrated below or at 300°C. For higher dehydration temperatures the dependence shows a deviation from linearity.

Infrared spectra of the zeolites dehydrated at 400°C showed that — similarly as with the HY (ref.⁷) and HX (ref.⁸) zeolites — the hydroxyl groups of the band 3740 cm⁻¹ exchange with deuterium at a substantially lower rate than the hydroxyl groups of the other bands: *e.g.*, at 60% exchange of the latter only 20% of the hydroxyl groups of the 3740 cm⁻¹ band exchange. It follows from Figs 2—4 that with the increasing dehydration temperature the fraction of the 3740 cm⁻¹ band hydroxyl groups increases, and thus their influence on the course of the gas-phase exchange increases, too.

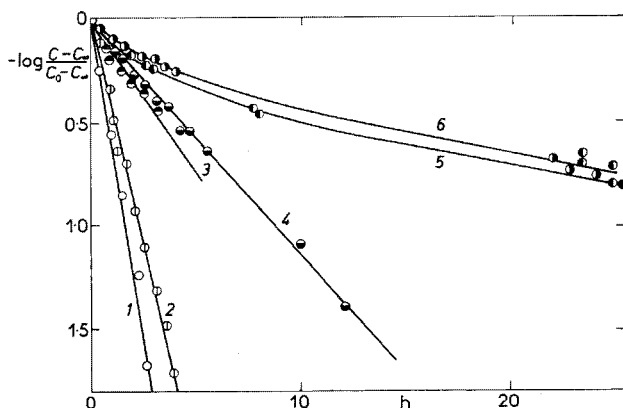


FIG. 5

Time Dependence of the D₂ + OH Exchange for CoX(47) at 300°C

c , c_0 , c_∞ are deuterium atom numbers at time t , t_0 , t_∞ , respectively. Sample: 0.13 k Nm⁻² of deuterium; dehydration at 1 20, 2 100, 3 200, 4 300, 5 400, 6 600 °C.

In the samples dehydrated at lower temperatures than 300°C the $D_2 + OH$ exchange could be influenced by the presence of water vapour: levelling off of different exchange rates of the various types of hydroxyl groups can occur⁸. To check this possibility, the exchange of the CoX(47) zeolite dehydrated at 400°C (*i.e.* containing a large fraction of the 3740 cm^{-1} band hydroxyl groups) was investigated with water vapour added to the gaseous phase. The partial pressure of water was chosen to be equal to the amount of water released during the exchange of the samples dehydrated at 100°C. It follows from Fig. 6 that the presence of water vapour does not compensate the deviation from the first-order kinetics. A detailed study of this effect of water vapour on the kinetics of exchange will be discussed in our next paper.

The rate of the $D_2 + OH$ exchange measured in the gaseous phase is substantially higher with the cobalt-containing species than with the original NaX zeolite (Table II). An increasing rate of the exchange $D_2 + H_2$ with the increasing amount of cobalt was found by Kemball and McCosh⁶; however, the difference in the exchange rates did not exceed one order of magnitude.

The dependence of the rates of both types of exchange on the dehydration temperature has the opposite character: it can be seen from Table II that the $D_2 + OH$ exchange rate decreases with the decreasing dehydration temperature, while the data from ref.⁶ (reproduced by us in several cases with our CoX zeolites) show that the $D_2 + H_2$ exchange rate increases with the sample dehydration. With the dehydration the symmetry of the environment changes^{12,13} as well as the ligands of the Co^{2+} ion, and this presumably influences the activation of gaseous molecules D_2 , HD, and H_2 . The sites active with respect to the exchange are thus probably connected with the presence of cobalt ions; the authors of ref.⁶ are of the same opinion.

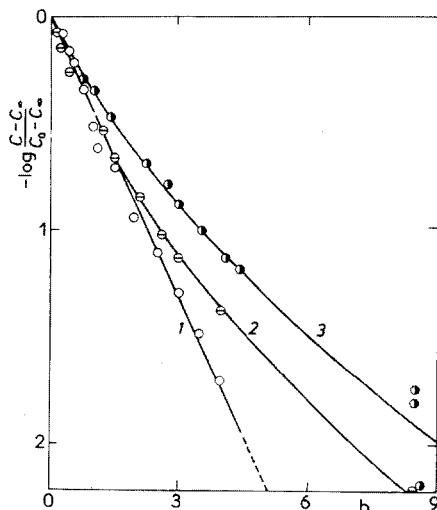


FIG. 6

Influence of Water Vapour on the Time Dependence of the $D_2 + OH$ Exchange for CoX(47) at 300°C

Sample: 0.1 g; deuterium pressure: 0.13 kNm^{-2} . Sample dehydrated at 100°C (1), at 400°C, exchange with 0.15 kNm^{-2} water vapour in the system (2), at 100°C, before the exchange kept 18 h in the closed apparatus at 400°C (3).

The different influence of the temperature on the two exchange processes was also observed by Minachev and coworkers³ for Ca-zeolites. He concludes, therefore, that the sites of deuterium activation are different in the $D_2 + H_2$ exchange and in the $D_2 + OH$ exchange. However, according to our opinion the different dependence of both exchange rates on the dehydration temperature does not necessarily prove the existence of different sites for deuterium activation; the $D_2 + H_2$ exchange occurs more easily on a dehydrated CoX than on its hydrated form, therefore, the dissociation and recombination of deuterium molecules is evidently easier and even the lifetime, of the dissociated particles on the zeolite surface is shorter (according to Kemball the dissociation of H_2 on the CoX zeolite is heterolytic). However, the concentration of hydroxyl groups decreases with dehydration, and thus the shorter lifetime of active particles may become insufficient for the $D_2 + OH$ exchange. Thus the activation of deuterium molecules is evidently not the rate determining step in the $D_2 + OH$ exchange. The rate determining step may be both the strength or the nature of the OH bond and the distance from the activation sites. One of these factors probably causes the lower exchange rate of the 3740 cm^{-1} band hydroxyl groups. Against the direct connection between the activation sites and the hydroxyl groups speaks the experimental fact that the exchange rate $D_2 + OH$ does not increase proportionally to the increase of the Co^{2+} content in the zeolites from 21% to 47%, despite the fact that the number of the hydroxyl groups containing the "lattice" oxygen increases considerably (Fig. 2, 3).

In our earlier studies concerning the deuterium exchange with hydrogen of hydroxyl groups in HX and HY zeolites^{7,8} we forwarded the hypothesis that the active sites of

TABLE II

Dependence of the $D_2 + OH$ Exchange Rate Constants at 300°C for NaX, CoX(21), and CoX(47) on the Dehydration Temperature (18 h in vacuum)

$R = -\ln [(c - c_\infty)/(c_0 - c_\infty)] \cdot 2am/(2a + m) \cdot t$; c_0, c, c_∞ are numbers of deuterium atoms at time t_0, t, t_∞ , respectively; $2a$ is the number of deuterium and hydrogen atoms in the gaseous phase; m is the number of hydrogen atoms bound in the zeolite¹⁵; the rate constants were determined from the initial parts of the kinetic curves.

$^\circ\text{C}$	$R \cdot 10^{-17}$ atom/min		
	CoX(47)	CoX(21)	NaX
20	5.5	3.2	0.92
100	3.7	4.8	0.09
200	1.2	—	—
300	0.83	3.5	0.01
400	0.62	—	—
600	0.45	1.4	—

the $D_2 + OH$ and $D_2 + H_2$ exchange in these zeolites hang together with the splitting off of the oxygen from the Si—O—Al lattice during dehydroxylation. In this step the formation of Lewis acid centers occurs, too. The activity of the CoX zeolites in the $D_2 + H_2$ exchange increases with dehydration. During the lowering of the number of the hydroxyl groups oxygen is removed, either from the Si—O—Al lattice or from that one bound to cobalt ions. According to the published data^{11,14} in the dehydration of the CoX zeolite the Lewis centra of the same type as in HX and HY zeolites (*i.e.* triple-coordinated Al) are not formed. This means that the lattice oxygen is not split off. Therefore, it is probable that the sites of deuterium activation in the CoX zeolites are different from those in decationized zeolites.

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