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Catalytic Activity of Dealuminated Y and HZSM-5 Zeolites Measured by the Temperature-programmed Desorption of Small Amounts of Preadsorbed Methanol and by the Low-pressure Flow Reaction of Methanol

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The activity of HZSM-5, NH_4Y and Y zeolites, dealuminated using $SiCl_4$, in methanol transformation has been compared and correlated with the acid properties and the Si:Al ratio of the respective zeolites. The temperature-programmed desorption of small amounts of methanol preadsorbed at ambient temperature together with measurements in a flow reactor under low pressure allowed the primary reaction steps to be observed. HZSM-5 and Y zeolites which had been moderately dealuminated showed the highest activity; however, the product distribution was different above 630 K: HZSM-5 gave predominantly methane and formaldehyde (aromatics appearing at higher temperatures), while C_{3-5} olefins and aromatics were formed above the Y zeolite. HY and highly dealuminated Y zeolite with $Si/Al \geqslant 20$ were less active than moderately dealuminated Y and HZSM-5 zeolites. The high activity of the latter zeolites is caused by the action of strong proton-donor sites and electron-acceptor centres (extralattice aluminium in dealuminated zeolites). The difference between HZSM-5 and dealuminated Y zeolites is caused by their different structures, which lead to different reaction mechanisms.

For comparison, the temperature-programmed desorption of preadsorbed ethanol was also studied. This resulted predominantly in ethene formation *via* intramolecular dehydration of ethanol.

The unusual catalytic properties of HZSM-5 zeolites have been widely discussed over the last decade: their high Si:Al ratio, the strong acid sites and a structure which includes a special channel pore system have been assumed to be the main causes of their selectivity and catalytic stability.[1] Comparative studies of ZSM, mordenites, faujasites and other types of zeolites have been published, the differences in their behaviour being explained by some of the features mentioned above.[2–6] In the present paper, we have tried to compare the methanol interaction with HZSM-5 and with dealuminated Y zeolites. Y zeolites with Si:Al ranging from 2.5 to 43 were prepared by Beyer's method using $SiCl_4$. It was shown in a previous paper[7] that this thermochemical treatment not only changes the Si:Al ratio in the lattice but also results in the appearance of extralattice Al species, both of which influence the acidity of the zeolite. Thus it was possible to study the catalytic behaviour of HY zeolites covering a certain range of Si:Al ratio and acidity together with the behaviour of HZSM-5 whose Si:Al ratio and acidity lay within the same range. Comparison was also made between hydrothermally treated Y zeolites containing oxidic extralattice Al species in cavities and AlHY containing cationic Al.

In some cases, the interaction of ethanol was also investigated in order to study the behaviour of ethene, which is its main product.[9] Ethene is often assumed to be the first intermediate with a C—C bond in methanol conversion [see ref. (10) and references therein].

Temperature-programmed desorption (t.p.d.) of small amounts of methanol or ethanol, preadsorbed at room temperature (the number of alcohol molecules being one order of magnitude lower than the number of acid sites) was investigated mass spectrometrically. The catalytic conversion of methanol on our zeolites was performed in a flow reactor at low pressures (1 Pa) with mass-spectrometric analysis of the products.

EXPERIMENTAL

The parent NaY zeolite (Vúrup, Bratislava, Czechoslovakia) was dealuminated by Beyer's method using $SiCl_4$ [for details see ref. (7)]; after the reaction and careful washing it was exchanged with NH_4NO_3 in the same way as the parent zeolite, further referred to as HY. Dealuminated zeolites were denoted Y-A, Y-B, Y-C and Y-E in order of decreasing Si : Al ratio. Sample Y-A, with the highest level of dealumination, was kindly provided by Dr H. K. Beyer. The zeolite $Al_{25}H_{25}Y$ (denoted AlHY) was prepared from NH_4Y by ion exchange with 0.1 mol dm^{-3} $Al(NO_3)_3$ at pH 4. The hydrothermally stabilized Y (denoted SY) was obtained from NH_4Y by steaming at 1030 K for 3 h [details of both preparations are given in ref. (11)]. All the zeolites exhibited good crystallinity, as is evident from the infrared spectra, X-ray diffraction patterns and sorption capacities. ZSM-5 zeolite was synthesized according to ref. (12) and converted into the acid form using 0.5 mol dm^{-3} HNO_3. Prior to the measurements, the zeolites were dehydrated and deammonized at 670 K for 18 h *in vacuo* (10^{-4} Pa). Dealuminated Y zeolites were heated before this treatment in an oxygen flow at 800 K for 5 h and then rehydrated.

The characteristics of the zeolites used are listed in table 1. $Si:Al_{total}$ was determined using classical chemical analysis and $Si:Al_{lattice}$ from mid-infrared spectra.[7, 13] The Ar sorption capacities were measured in the usual way.[11] The number of strong Brönsted and Lewis acid sites was calculated from the heights of infrared bands of pyridinium ions (1545 cm^{-1}) and pyridine complexes with aluminium electron-acceptor centres (1455 cm^{-1}), both these complexes being retained in the zeolites after pyridine desorption at 530 K.[7] The acid strength was compared using t.p.d. of ammonia (see fig. 1): 3×10^{18} molecules of NH_3 were adsorbed at room temperature on 0.01 g of the zeolite for 30 min; then NH_3 was pumped off through the vacuum system of a mass spectrometer (modified MI 1305, U.S.S.R.). The temperature dependence of the NH_3 peaks was recorded, the heating rate being 6 K min^{-1}. From fig. 1 it follows that the maximum amount of ammonia evolved with HY occurs at a much lower temperature than the second maximum observed with HZSM-5 and dealuminated Y.

The interaction of zeolites with methanol (or ethanol) was studied by t.p.d. The alcohols were of A.R. grade and purified by repeating freezing and pumping. Alcohol vapour (10 μmol) was adsorbed at room temperature on 0.1 g of zeolite; after 1 h of adsorption the desorbate was analysed in the same way as for ammonia. The maximum pressure of released gases did not exceed 10^{-1} Pa.

The catalytic reaction of methanol under low pressure (1 Pa) was investigated with HZSM-5, HY, Y-C and Y-B at 293, 510, 630 and 670 K. The flow rate was 3×10^{-4} dm^3 h^{-1}. In these measurements, 0.05 g of zeolite was placed directly inside the mass spectrometer in the reactor previously used for the study of radical reactions.[14]

RESULTS

T.P.D. MEASUREMENTS

Typical t.p.d. curves for the products of the methanol–zeolite interaction are shown in fig. 2. The products appear in the following order: methanol at 300–600 K, dimethyl ether (and a small amount of methyl chloride at slightly higher temperatures, not shown in fig. 2) at 400–600 K, aromatics (up to C_{10}) and C_{3-5} olefins from Y zeolites and aromatics (especially xylenes) from HZSM-5 at 600–700 K. The release of aromatics from HZSM-5 is preceeded by the evolution of methane and formaldehyde

Table 1. Characteristics of zeolites used[a]

zeolite	Si : Al$_{\text{total}}$	Si : Al$_{\text{lattice}}$	C_{Ar}/ mmol g^{-1}	B/10^{20} g^{-1}	L/10^{20} g^{-1}
HY	2.5	2.5	10.9	7.9	0.15
Y-E	3.4	5.2	9.2	4.2	2.2
Y-C	5.7	10.8	9.2	3.8	2.0
Y-B	19.9	—	9.4	0.9	0.75
Y-A	43.5	—	9.4	0.2	0.25
HZSM-5	17.5	—	5.0	2.4	0.6
AlHY	2.0	2.9	9.0	3.3	2.6
SY	2.9	9.4	8.6	0.6	1.4

[a] C_{Ar} = Ar sorption capacity; B = number of Brönsted sites; L = number of Lewis sites.

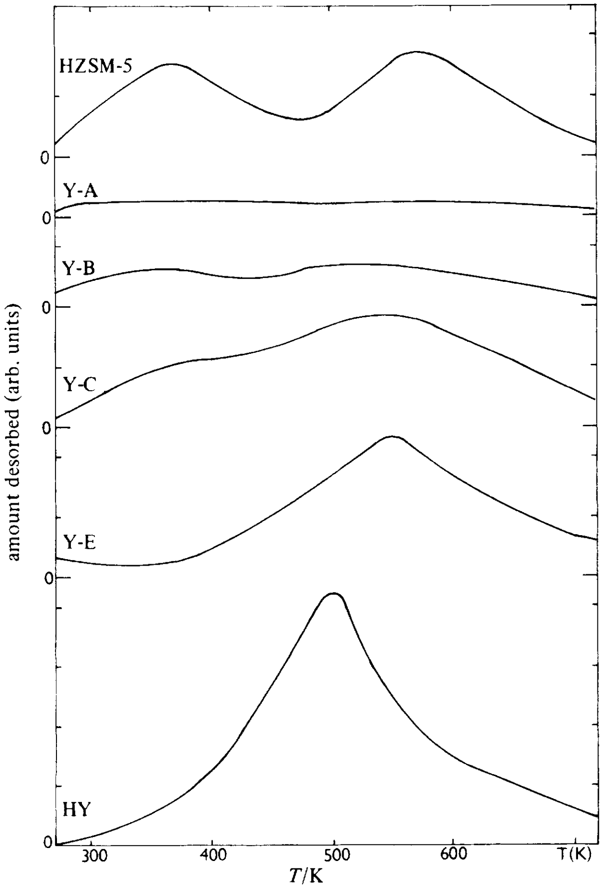

Fig. 1. T.p.d. of ammonia, preadsorbed on HY, dealuminated Y and HZSM-5.

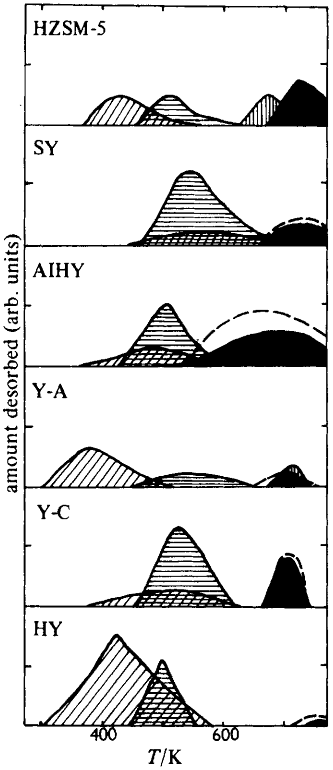

Fig. 2. T.p.d. of methanol and its interaction products with HY, Y-C, Y-A, AlHY, SY and HZSM-5. ▨, CH_3OH; ▤, $(CH_3)_2O$; ▥, $CH_4 + HCHO$; ☐, C=C; ■, aromatics.

in the approximate ratio 1 : 1. The latter two compounds are observed at the same temperature as the aromatics over highly dealuminated Y-A and HZSM-11 (the latter not being dealt with in this paper). Note that the most active zeolites are HZSM-5 and moderately dealuminated Y zeolite Y-C as well as AlHY and SY. HY and highly dealuminated Y-A are less active.

In fig. 3, the maxima of released products are plotted against the molar fraction of aluminium. Fig. 3 includes all the dealuminated Y zeolites, HY and HZSM-5. Desorbates of both methanol and ethanol are shown. The moderately dealuminated zeolites Y-E and Y-C are the most active as far as the formation of aromatics and C_{3-5} olefins from methanol and ethene from ethanol is concerned. With increasing dealumination and for HY the amount of these products is decreased; HY gives the largest amount of diethyl ether from ethanol; Y-A has a yield of ether similar to that of Y-B and Y-C while the amount of other products formed from ethanol is very low. The formation of dimethyl ether from methanol does not depend strongly on the Al content. HZSM-5 differs from Y-B in spite of possessing almost the same molar fraction of aluminium and has a total activity [fig. 3(*a*)] comparable to that of moderately dealuminated zeolites. Fig. 3 also shows the formation of methyl and ethyl chloride from methanol and ethanol, respectively, from traces of chlorine left in the dealuminated zeolites. This amount of chlorine is so small that it cannot be detected by any other method; only in Y-E was a very small amount of Cl observed, by X.p.s.,

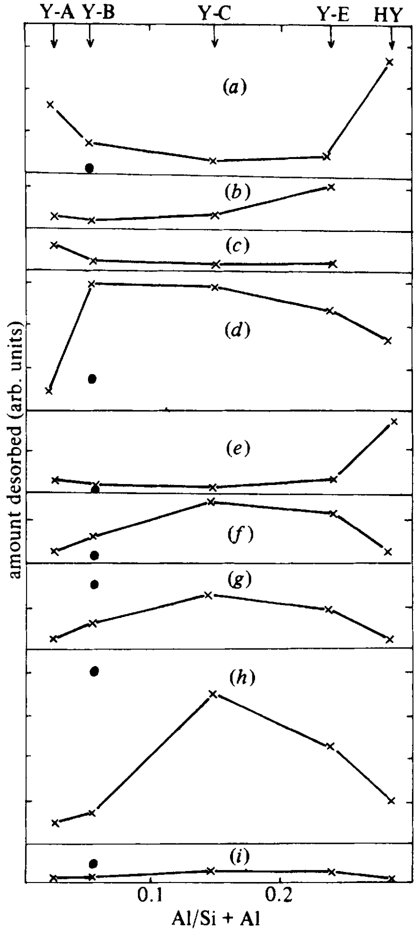

Fig. 3. Dependence of amount of methanol, ethanol and their interaction products on the aluminium mole fraction (Al:Si+Al): ×, HY and dealuminated Y; ●, HZSM-5. (*a*) Methanol and ethanol, (*b*) methyl chloride from methanol, (*c*) ethyl chloride × 10 from methanol, (*d*) dimethyl ether from methanol, (*e*) diethyl ether × 10 from ethanol, (*f*) C_{3-5} olefins from methanol, (*g*) aromatics from methanol, (*h*) ethylene from ethanol and (*i*) aromatics from ethanol.

in the surface layers of the zeolite. HY and HZSM-5 also give negligible methyl and ethyl chloride formation, probably because of the chlorine impurities introduced into these zeolites during their preparation. From methanol, the maximum amount of methyl chloride is found with Y-E, which has, relatively, highest chlorine content. The release of ethyl chloride shows the same dependence as the formation of ethyl ether.

LOW-PRESSURE FLOW MEASUREMENTS

The time dependence of the amount of the individual components in the reactor output for the HY, Y-C, Y-B and HZSM-5 zeolites at various reaction temperatures is shown in fig. 4. No selective reaction products were found under these conditions with HY: it exhibits minimum absorption of methanol at room temperature, at higher

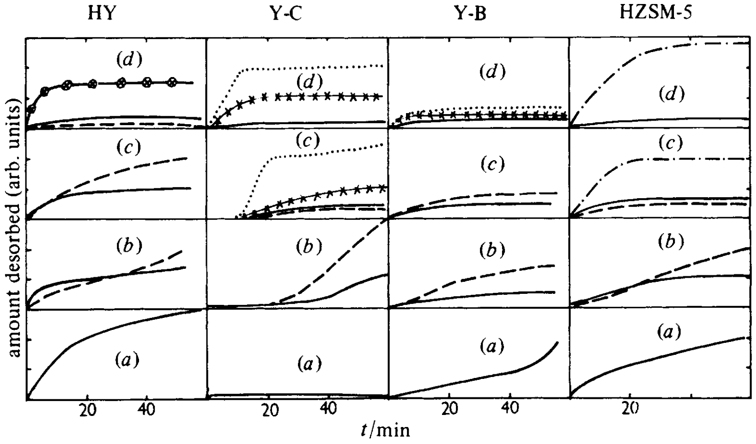

Fig. 4. Time and temperature dependence of methanol conversion in a low-pressure flow reactor over HY, Y-C, Y-B and HZSM-5. (——) Ethanol, (----) dimethyl ether, (× - × - × -) aromatics, (. . . .) olefins, (–·–·) methane and formaldehyde and (⊗–⊗–⊗–) carbon dioxide; (*a*) 295, (*b*) 510, (*c*) 630 and (*d*) 670 K.

temperatures only dimethyl ether is formed and at 670 K an appreciable amount of carbon dioxide appears. Moderately dealuminated Y-C absorbs all the methanol input within the studied time interval at room temperature and the composition of the reaction products at higher temperatures is the same as in the t.p.d. experiments. Y-B, dealuminated to a greater extent, behaves as for the t.p.d. experiments, exhibiting lower activity than Y-C. HZSM-5 also gives the same products at the relevant temperatures as for the t.p.d. experiments, except that the formation of formaldehyde was greater than that of methane. After increasing the temperature to 770 K (not shown in fig. 4) aromatics appear as the reaction products.

DISCUSSION

Amongst the numerous mechanisms for methanol conversion on zeolites which have been suggested in the literature is the assumption of the principal action of strong Brönsted acid sites [*e.g.* ref. (2), (5) and (15)] supported by the presence of Lewis acid sites.[16, 17]

Though the amount of information on methanol conversion keeps growing, the mechanism of this reaction, especially formation of the first C—C bond, has still not been elucidated. It is also not clear whether the basic steps are the same for all zeolites or whether the properties of the relevant zeolite affect the interaction from its very beginning. It is difficult to establish the reaction mechanism because of a number of sequential and parallel reactions which are more or less pronounced under various experimental conditions and which give rise to a broad range of products.

The experimental conditions used in our investigation allowed us to study the reactions at very low concentrations of both surface species and gas molecules. The path of the latter between the catalyst and the analyser is so short that interaction between the molecules themselves is almost eliminated. Using this technique we can approach the primary steps of the reaction.

The first interesting result is the coincidence of the product composition for the t.p.d.

experiments and the low-pressure flow experiments at the relevant temperatures. This might be explained by the participation of the same surface species, the reactivity and composition of which are strongly temperature dependent. Similarly, this temperature dependence also holds for the function of the active sites. Thus, it follows that dimethyl ether need not be an intermediate in the reaction of methanol to hydrocarbons: (i) it does not appear in the gas phase above 600 K and (ii) its formation at lower temperatures does not follow the activity of zeolites under study as far as the conversion to higher hydrocarbons is concerned. The formation of dimethyl ether is a well known property of acid catalysts[18] and it seems that neither strong acidity of the Brönsted type nor a large number of these centres is needed for this reaction.

HY, releasing almost no selective products during the t.p.d. of methanol, exhibits at 670 K in the flow experiments increased consumption of methanol. However, only the products of deep oxidation appear in the gas phase. Carbon dioxide was found at higher temperatures in the reaction with methanol for all the zeolites, but the amount was much lower compared with HY. Recently, the use of silica–alumina as a catalyst in methanol oxidation has been described.[19] In our case only methanol (without added oxygen) interacts with the zeolites and this carbon dioxide formation might take place *via* the incorporation of oxygen from the zeolite or by the decomposition of methanol molecules. Experiments to ascertain the stoichiometry of this reaction (hydrogen and water release) are in progress.

Both t.p.d. and flow experiments showed the maximum consumption of methanol with moderately dealuminated Y zeolites. In the flow experiments, the appearance of not only methanol at room temperature but also other products at higher temperatures is connected with an induction period which is especially pronounced for Y-C. In this case olefins and aromatics are apparently secondary reaction products formed *via* oligomerization, cyclization, hydrogen transfer *etc.*; no assumptions about the primary steps of the methanol–zeolite interaction can be made on the basis of these experiments.

A not very pronounced induction period is found with HZSM-5, which is the only zeolite studied here which releases simple C_1 products (methane and formaldehyde) at a relatively low temperature. Methane is assumed to be a primary product from methanol and not a compound accompanying coking as supposed previously.[5] Methane was mentioned as a product in the very low conversion of methanol over HZSM-5 in ref. (20). Note that the absence of methane from the products was considered to be evidence against the participation of methyl cations in the first C—C bond formation [ref. (20) and (21)]. In our opinion, methane formation might also support the assumption of Zatorski and Krzyzanowski[22] on the radical mechanism: some papers have recently appeared concerning the formation of radical species on the surface of HZSM-5 during the interaction with hydrocarbons.[23] Formaldehyde was assumed to be an intermediate in methanol conversion in ref. (5). The equimolecular desorption of methane and formaldehyde during the experiments indicates random attack of acid sites on the different bonds of the methanol molecule (or its fragments) or the simultaneous action of different zeolite sites (Brönsted or Lewis). Note that the methane:formaldehyde ratio changes towards higher formaldehyde yield in the low-pressure flow experiments. A more detailed study of the surface species under such low coverages will be needed to explain these findings. In the t.p.d. of methanol, aromatics are released from HZSM-5 at a slightly higher temperature than with dealuminated Y, so it is not surprising that in the flow experiments at 670 K almost no aromatics appeared. It seems therefore that aromatics are more strongly bound in HZSM-5 and that diffusion limitations may play an important role. Although HZSM-5 has a similar Si:Al ratio as dealuminated Y-B zeolite, its activity is considerably higher; it reaches the activity of moderately dealuminated Y zeolites. Nevertheless, from the different composition of the products from methanol conversion the pathway of the reaction is different. The properties of HZSM-5, including the acidity, Si:Al ratio and structure, are responsible for its high activity as well as for the reaction mechanism, which is probably different from that on Y zeolites.

The high activity and selectivity of moderately dealuminated zeolites is caused by the presence of an appreciable number of strong proton-donor sites together with electron-accepting sites originating from extralattice aluminium species, whose formation in Y zeolites treated by $SiCl_4$ was proved in ref. (7) and explained by the hydrolysis of aluminium chloride complexes remaining in the zeolite cavities after substitution of lattice Al with silicon from $SiCl_4$:

$$Na_x(AlO_2)_x(SiO_2)_y + SiCl_4 \rightarrow Na_{x-1}(AlO_2)_{x-1}(SiO_2)_{y+1} + AlCl_3 + NaCl.$$

This aluminium helps to compensate the lattice charge as cationic or oxidic species and it exhibits strong electron-accepting properties. The influence of the Lewis acid sites on the catalytic activity was confirmed by the behaviour of AlHY and SY zeolites. In the former case, aluminium was introduced into the zeolite cavities by cation exchange while in the latter case the extralattice aluminium species were formed by delocalization of lattice aluminium during the hydrothermal process.

The reaction of methanol with traces of chlorine left in the zeolite proceeds regardless of all the properties of the studied zeolites and is most pronounced with Y-E, which contains a relative maximum of chlorine. The low temperature of the methyl chloride release shows that abstraction of the methyl group from methanol can proceed, in these cases, quite readily. The presence of traces of chlorine has no influence on the type and relative amounts of the products. In the flow experiments chlorine in the form of methyl chloride was removed in a very short time while the course of formation of the remaining products with temperature and time was unchanged.

The t.p.d. of ethanol with all the dealuminated Y zeolites, as well as with HY and HZSM-5, was investigated for comparison. The amount of unreacted ethanol was almost the same as that of methanol, the main product of the reaction being ethene, with the highest yield over moderately dealuminated Y and HZSM-5. With less active zeolites the formation of diethyl ether was also observed. The formation of ethyl chloride showed the same dependence on the molar fraction of Al in the zeolites as the release of diethyl ether. The yields of aromatics were appreciably lower than from methanol, the highest amount being formed on HZSM-5. From the reaction studies at lower pumping speed (*i.e.* with a longer contact time of the ethene with the zeolite) and from the interaction of ethene alone it seems that the formation of aromatics from ethanol proceeds *via* ethylene oligomarization and cyclization.

As almost no ethene was found under our conditions in the transformation of methanol, we assume in accordance with ref. (15) that ethylene need not be a primary product in methanol conversion.

CONCLUSIONS

The t.p.d. of small amounts of alcohols and the catalytic flow experiments at low pressure are evidently controlled by the most active sites, so a deeper insight into the first steps of the interaction of zeolites with these reactants may be obtained. The correlation between the acid properties, the Si:Al ratio and the activity for methanol transformation over zeolites of different structural types reveals the importance of these features for the reaction in question. The most active Y zeolites are those moderately dealuminated ($Si:Al_{lattice} = 5$) containing an appreciable amount of extra-lattice aluminium with electron-acceptor properties and a high number of strong proton-donor sites. HZSM-5 ($Si:Al = 17.5$) with a similar number of strong proton-donor sites and a lesser amount of Lewis sites exhibits comparable activity, although with a different product distribution. This difference is most pronounced at lower interaction temperatures, where simple C_1 compounds (methane and formaldehyde) appear over HZSM-5 as the primary products. Dealuminated Y zeolites yield C_{3-5} olefins and aromatics directly, apparently as secondary reaction products. Their release is accompanied by a long induction period.

From the temperature dependence of the formation of dimethyl ether during the conversion of methanol it may be assumed that dimethyl ether is not an intermediate in this process. Similarly, the same assumption concerning ethene may be made when the interactions of methanol and ethanol with zeolites are compared.

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