A role of surface nitrite and nitrate complexes in NO_x selective catalytic reduction by hydrocarbons under oxygen excess

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NO adsorption over three types of catalytic systems, such as cation-exchanged zeolites, transition metal oxides supported on γ-Al_2O_3, and partially stabilised tetragonal ZrO_2 (PSZ) was studied by using the TPD method. NO forms several surface complexes having different desorption temperatures. TPD results compared with catalytic properties of these systems in the selective reduction of NO_x by propane under oxygen excess showed that strongly bound nitrites and nitrates appeared to be true intermediates in this reaction.

Keywords: TPD; cation-exchanged zeolites; modified zirconias; nitrite; nitrate; catalytic activity; NO selective reduction by hydrocarbons

1. Introduction

In 1990 Iwamoto et al. [1] and Held et al. [2] independently discovered a selective catalytic reduction of NO_x by hydrocarbons in oxygen excess, which appeared to be very promising for practice. Yet the reaction mechanism is still not clear, thus hindering the search for efficient catalysts for this process. Several reaction schemes are now considered as probable:

(1) NO is oxidized to NO_2 or adsorbed nitrite / nitrate complexes (NO_x), which then interact with hydrocarbons [3–8];

(2) hydrocarbons are converted to some intermediates interacting then with NO_x [9–12];

(3) a red-ox mechanism of the catalyst surface oxidation by NO_x and reduction by hydrocarbons operates [13,14].

In general, the reaction mechanism can vary from one catalyst to another depending also on the type of hydrocarbon and reaction conditions. The simplest way to check hypotheses about participation of adsorbed NO_x in the reaction scheme is to compare steady-state catalytic activities of a number of catalysts with the relative strength of various NO_x forms bonding with the surface. For the systems studied here: cation-exchanged zeolites, CuO/γ-Al_2O_3 and partially stabilized tetragonal ZrO_2 (PSZ), such surface NO_x complexes as nitrosyls (M–NO), nitrites (M–NO_2 or M–ONO) and nitrates (M–NO_3 or M–ONO_2) were revealed by IR-spectroscopy [3,15–18]. While weakly bound nitrosyls are known to easily desorb at room temperature, nitrites and nitrates are more stable decomposing in the range of 200–600°C. For various nitrite/nitrate complexes a mode of their decomposition as well as reactivity may crucially depend upon their bonding strength determined by the structure and nature of the adsorption center. To elucidate this question, we have studied temperature-programmed desorption (TPD) of NO_x combined with activity measurements for various types of oxide catalysts. Such method as ESR of TEMPO nitroxide radical was used to probe the surface centers of diamagnetic systems (PSZ), while the state of the transition metal cations in our zeolite systems was earlier studied by IR-spectroscopy of adsorbed CO [19].

2. Experimental

2.1. Catalyst preparation

To prepare γ-Al_2O_3 catalyst/support, a reprecipitated pseudoboehmite (AlOOH) was used. To obtain CuO/γ-Al_2O_3 (1 wt% of CuO), this support was impregnated with a copper nitrate solution (0.1 M) for 2 h, then dried at room temperature for 5–6 h and calcined at 550°C for 2 h. MO–ZrO_2 (M = Sr, Ca, Ba) systems were prepared via coprecipitation by adding NH_4OH (25%) to a mixed solution of zirconium oxynitrate and corresponding nitrates of alkaline-earth metals. Precipitates thus formed were washed, moulded, dried and calcined at 700°C. MO concentration in the samples was equal to 5 wt%.

A powdered zeolite H/ZSM-5 (Si/Al = 50) and H-mordenite (Si/Al = 12) were used to prepare Cu/ZSM-5, Sr–Cu/ZSM-5, Sr–Co/mordenite.

Cu/ZSM-5 was prepared via ion exchange between HZSM-5 and copper nitrate solution (0.15 M). The solution was stirred for 2 h at 80°C, then the zeolite was filtered, dried and calcined at 500°C. Copper content was equal to 3 wt%.

For Sr–Cu/ZSM-5, both metals were introduced simultaneously using mixed nitrate solutions and the same procedure. The catalyst contained 2 wt% of Cu and 0.8 wt% of Sr.

Sr–Co/mordenite was prepared similarly. The content of Co and Sr in the catalyst was 2 and 0.8 wt%, respectively.

Ca–Fe/ZSM-5 was obtained via hydrothermal synthesis of Na–Fe/ZSM-5 with a subsequent Na removal by HNO_3 (5–15%) followed by cation exchange with a saturated solution of calcium hydroxide [20].

BET surface values were ca. 200 m^2/g for Cu- and Co-containing zeolites; 400 m^2/g for Ca–Fe/ZSM-5; $\sim$ 300 m^2/g for γ-Al_2O_3 and CuO/γ-Al_2O_3; and $\sim$ 100 m^2/g for MO–ZrO_2 systems (±10%).

2.2. *Activity measurements*

The catalysts were tested in a quartz flow reactor with the catalysts' amounts in the range of 1–4 g. Reaction mixture contained propane (1300 ppm), nitric oxide (1000 ppm), oxygen (1%) diluted in helium. Gas hourly space velocity (GHSV) was varied from 4000 to 16000 h^{-1}. Inlet and outlet gases were analyzed by gas chromatography and FTIR spectroscopy. Catalytic activity was estimated from the values of NO_x conversion into N_2.

2.3. *TPD*

The catalysts (0.5 g; 0.5 mm particle size) were loaded into a quartz microreactor. To ensure an oxidized state of the catalyst, it was treated in a flow of 10% oxygen in He for 1 h at 550°C and then cooled to room temperature in the same mixture. Before NO adsorption, He–O_2 flow was switched to pure helium. For a weak reduction, the catalysts were heated to 550°C and kept in helium for 1 h to desorb a part of the oxygen bound with the surface [21]. The isothermal NO adsorption (partial pressure 1 kPa) was performed in a He–NO mixture at 298 K. A chemiluminescence NO_x Beckman analyzer was used for monitoring the dynamics of the NO adsorption. To remove physisorbed forms, after adsorption the reactor was purged by a He stream at room temperature for 30 min. Standard TPD measurements were performed in the temperature range of 25–550°C at a 10°C/min heating rate while the flow rate was kept at 40 cm^3/min (STP). Desorption products were analyzed with a chemiluminescence NO_x analyzer and/or a tritium detector.

2.4. *ESR of adsorbed TEMPO nitroxide radical*

The indicator-2,2,6,6-tetramethylpiperidin-1-oxil (tanan) was adsorbed from the gas phase. The ESR spectra were recorded by using a RE-1306 spectrometer with a subsequent analysis according to ref. [22].

3. Results and discussion

3.1. *NO_x adspecies and adsorption centers*

3.1.1. *Assignment of TPD peaks*

All TPD data are summarized in table 1. As a typical example, the spectrum of NO_x desorption from CuO/γ-Al_2O_3 is shown in fig. 1. According to the data of Hierl et al. [18], three desorption peaks at 60, 180 and 480°C are assigned to decomposition of nitrosyls, nitrite and nitrate surface complexes, respectively. The observed trend in the relative stability of these surface species is rather predictable and agrees well with the data of refs. [15,16,23]. Unlike nitrite/nitrate complexes, nitrosyl complexes are very unstable. They partially decompose even in the course of the reactor purging by He at room

Table 1
Thermodesorption data

Catalysts	Low-temperature peak			Middle-temperature peak			High-temperature peak		
	T (°C)	θ[a]	E_a[b]	T (°C)	θ[a]	E_a[b]	T (°C)	θ[a]	E_a[b]
Ca–Fe/ZSM-5	60	0.8	14	300	0.2	71.3	–	–	–
Sr–Cu/ZSM-5	60	0.2	14	410	2.0	100.5	–	–	–
Cu/ZSM-5	65	0.8	15.2	390	0.5	91.1	–	–	–
Sr–Co/mordenite	90	0.8	24.4	430	8.0	105.1	–	–	–
CuO/γ-Al_2O_3	55	0.6	11.7	220	1.3	50.6	480	0.5	110
γ-Al_2O_3	–	–	–	220	2.7	50.6	510	0.7	119
SrO–ZrO_2	–	–	–	250	4.0	63.1	540	2.1	127
CaO–ZrO_2	–	–	–	180	6.5	43.2	550	3.0	129
BaO–ZrO_2	–	–	–	350	2.4	80.6	590	2.1	137

[a] Coverage as percent of monolayer.
[b] kJ/mol.

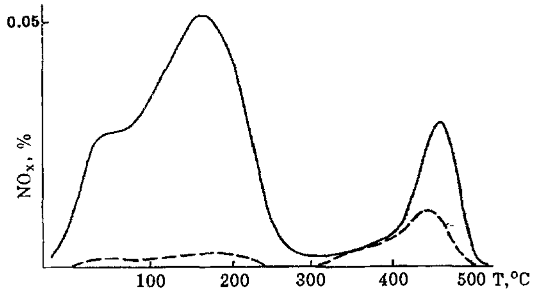

Fig. 1. TPD of NO_x from $CuO/\gamma\text{-}Al_2O_3$. (——) NO_x; (– – –) NO_2.

temperature. Recent work [25] has demonstrated that in the low-temperature region not only nitrosyls, but "N_2O_3" adspecies can decompose as well, and simultaneous evolution of NO and NO_2 in the low-temperature peak can be a result of this reaction.

For $\gamma\text{-}Al_2O_3$ and PSZ, TPD data indicate the absence of the nitrosyl complexes (table 1) which agrees well with the IR-spectroscopy data of Lunina et al. [24].

3.1.2. Routes of nitrites and nitrates formation

Generally, nitrites and nitrates can be formed either via NO disproportionation during adsorption [18] or through NO oxidation by the surface oxygen. To elucidate the routes of nitrites and nitrates formation, we have varied the catalysts pretreatment for all systems studied. For cation-exchanged zeolites and $CuO/\gamma\text{-}Al_2O_3$, weak reduction by high-temperature treatment in He decreases the intensity of the peaks assigned to nitrites/nitrates decomposition; an example is shown in fig. 2 for Ca–Fe/ZSM-5. In addition, the NO_2 relative content in the low-temperature desorption peak decreases. These results imply that for these systems nitrites and nitrates are formed via interaction of NO with a weakly bound surface oxygen either during adsorption or in the course of TPD. Hence, for catalysts containing transition metal cations, nitrites and nitrates formation most likely follows the second route.

For partially stabilized zirconias, pretreatment in He has not changed appreciably the TPD spectra, which can be explained by the absence of easily reducible cations in these systems. Hence, for PSZ, nitrites and nitrates appear to be formed via NO disproportionation in the course of adsorption. Indeed, for these systems after room-temperature adsorption of NO, the IR band at 2240 cm^{-1} assigned to N_2O was detected [24] evidencing such disproportionation.

3.1.3. Routes of nitrites and nitrates decomposition

Thermal destruction of these surface species may be a rather complex process. Thus, according to Hierl et al. [18], for $CuO/\gamma\text{-}Al_2O_3$ the mechanism of nitrites decomposition can be described by the following equation:

$$2Cu^+\text{–}ONO \rightarrow Cu^+\text{–}ONO_2 + Cu^0 + NOgas$$

At the same time, direct nitrite decomposition yielding NO_2 is quite possible. As our data show (fig. 3), a fraction of NO_2 in the desorption peaks changes markedly depending on the catalyst composition. Thus, NO_2 desorbs in large amounts from Ca–Fe/ZSM-5 and Cu/ZSM-5 catalysts, while only a minor quantity of nitrogen dioxide was detected for Zr catalysts. It implies that the bonding strength of oxygen with the surface cations determines the nitrite decomposition route yielding either NO_2 or NO. To check this hypothesis, we have studied the oxygen thermodesorption from these catalysts. Fig. 4 shows that weakly bound oxygen desorbs well from the Sr–Cu/ZSM-5 catalyst (T_{des} = 60°C). Its amount is somewhat lower for the Sr–Co/mordenite sample (T_{des} = 50°C). As for Ca–Fe/ZSM-5, only minor oxygen desorption was observed in this temperature range. According to ref. [26], for Fe/ZSM-5 weakly bound oxygen has heat of adsorption of ca. 1–6 kcal/mol. Hence, in our experiments this oxygen has been probably completely removed from the surface by He purging at room temperature before TPD run. Our TPD and TPR results (not shown here for the sake of brevity) revealed that for PSZ any weakly bound oxygen species are absent. Usually these forms of oxygen are assigned to clusters of transition metal ions located within the zeolite matrix or on the alumina support surface. Such

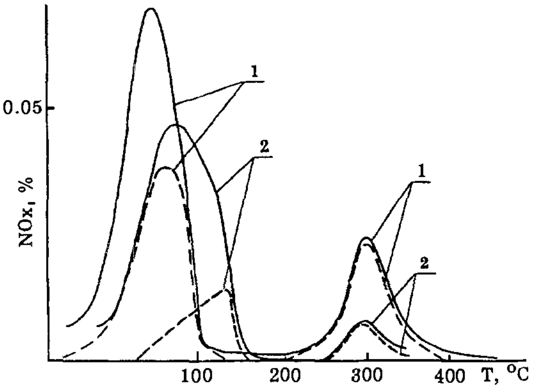

Fig. 2. TPD of NO_x from Ca–Fe/ZSM-5. (——) NO_x; (– – –) NO_2. (1) Oxidative pretreatment, (2) high-temperature pretreatment in He.

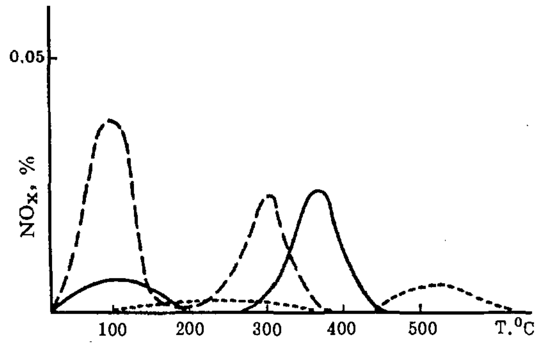

Fig. 3. NO_2 evolution from Ca–Fe/ZSM-5, Cu/ZSM-5 and $SrO\text{–}ZrO_2$ catalysts. (——) Cu/ZSM-5; (– – –) Ca–Fe/ZSM-5; (. . .) $SrO\text{–}ZrO_2$.

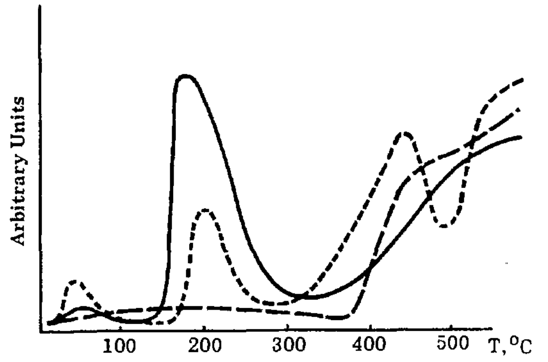

Fig. 4. TPD of O_2 from Sr–Cu/ZSM-5, Sr–Co/ZSM-5 and Ca–Fe/ZSM-5. (——) Sr–Cu/ZSM-5; (– – –) Sr–Co/mordenite; (. . .) Ca–Fe/ZSM-5; tritium ionization detector.

clusters were earlier observed for the Cu- and Fe-containing catalysts [26–28]. For Sr–Co/ZSM-5, easily reduced clustered cobalt ions were recently found using IR-spectroscopy of adsorbed CO [19].

Hence, evolution of NO_2 in the course of surface nitrites and nitrates thermal decomposition is mainly observed for catalysts where a part of surface oxygen is weakly bound. Therefore, the mechanism suggested in ref. [18] appears not to be unique or at least predominant for the systems studied.

3.1.4. Adsorption centers and stability of nitrites/nitrates

Another important question concerns the effect of the chemical nature and properties of adsorption centers on bonding strength and coverages of the NO_x adspecies. Table 1 lists saturation coverages of the catalysts' surfaces by various NO_x forms together with the values of the activation energy of desorption calculated by using the first-order desorption rate equation found to be appropriate for our systems (for the same catalysts T_{max} were independent of the coverage). These data demonstrate that both active component and promoter influence appreciably the relative stability of the high-temperature NO_x species. From the chemical point of view, more acidic nitrate anions are expected to be more tightly held by cations as compared with nitrites. If this is so, ad-species decomposing at high temperatures and prevailing for such systems as alumina, CuO/alumina and modified zirconias, could be termed as nitrates while nitrites seem to dominate on the cation-exchanged zeolites. Within each group of surface species, bonding strength (temperature of decomposition) obviously depends upon the effective charge of the coordinatively unsaturated (cus) cation. Thus, for cation-exchanged zeolites nitrites are the most strongly held by Co^{3+} cations. Among PSZ, T_{max} of the decomposition of nitrates stabilized on cus Zr^{4+} [24] increases in the order Sr–Zr < Ca–Zr < Ba–Zr (table 1). The same trend was observed for the anisotropic constant of the triplet ESR spectra splitting ($A_{\|}$) for TEMPO complexes with coordinatively unsaturated Zr^{4+} ions (table 2; full description of spectra will be given in ref. [24]). According to ref. [29], $A_{\|}$ is a measure of the acceptor properties of the cus center (here its effective charge). Hence, nitrates are also more strongly held by cations with higher effective charges. These data also demonstrate that even for the same cus cation (here Zr^{4+}), its strength of bonding with NO_x species depends upon the cation environment (its coordination and chemical nature of the promoting cations in the second coordination sphere).

The role of coordination was found to be especially important for the copper-containing systems. Thus, comparison of the TPD data for CuO/γ-Al_2O_3 and Cu/ZSM-5 shows that the peak at 480°C assigned to decomposition of nitrates is observed only for the former system, while peaks assigned to decomposition of nitrites differ by their position (~ 220 and ~ 390°C, respectively). Coincidence of the nitrites decomposition temperatures for CuO/γ-Al_2O_3 and γ-Al_2O_3 (table 1) implies that for the supported copper oxide system these species are mainly (if not exclusively) located on the support. Hence, the predominant type of NO_x species bound with the copper ions seems to be determined by the structures of the Cu–O species in these systems which differ substantially. Thus, according to Tikhov et al. [28], for CuO/γ-Al_2O_3 two-dimensional (2D) clusters of copper ions predominate while concentrations of isolated Cu^{2+} ions and highly reactive 3D clusters are rather low. Bridged oxygen atoms (Cu–O–Cu) in 2D clusters are more strongly bound ($q_{des} \approx 288$ kJ/mol O_2) than on-top oxygen forms located on the isolated copper ions ($q_{des} \approx 123$ kJ/mol O_2) or on 3D clusters ($q_{des} \approx 5$–10 kcal/mol O_2) [28]. This suggests that nitrates are mainly stabilized on rather large 2D clusters which are absent in zeolites.

As follows from this analysis, the thermal stability of nitrites and nitrates correlates rather well with the bonding strength of the surface oxygen. This is rather expected if we take into account the routes of these adspecies formation/decomposition (vide supra). However, for all systems studied here this correlation is not universal due, probably, to some variation of the nitrites and nitrates structure caused by change in the chemical composition. Thus, Sr addition to Cu/ZSM-5 does not change appreciably T_{max} of the nitrites decomposition though increasing the amount of these complexes (table 1). As revealed by IR data [16,19], for Sr-promoted Cu/ZSM a shift of the nitrite absorption band to

Table 2
Acceptor properties of modified zirconia catalysts ($A_{\|}$ = anisotropic constant of triplet splitting)

Catalysts	$A_{\|}$ (Oe)
SrO–ZrO_2	38.9
CaO–ZrO_2	43.3
BaO–ZrO_2	44.4

lower frequency occurs (from 1640 to 1632 cm^{-1}), evidencing some rearrangement of the structure of these adspecies. Moreover, our experiments showed that nitrites and nitrates can decompose in nearly the same temperature region (for Sr–Co/mordenite nitrites disintegrate at 430°C, whereas for CuO/alumina T_{des} of nitrates is in the range of 400–480°C). Therefore, if detailed IR data on the NO_x adspecies structure are not available, a rather broad "nitrite/nitrate" term appears to be more adequate for high-temperature TPD peaks.

3.2. Catalytic activity versus TPD data

Typical temperature dependencies of NO conversion to N_2 over various catalysts are shown in fig. 5. According to these data, for selective reduction of NO by propane, temperatures of the efficient catalyst operation exceed 300°C. The TPD data (table 1) suggest that under such conditions nitrosyls are absent on the surface and, therefore, they can hardly take part in the reaction. On the contrary, strongly bound NO_x can provide a selective reduction route competing with molecular oxygen for activated hydrocarbons. This conclusion allows one to explain why different catalysts are efficient at different temperatures. Indeed, to become active, strongly bound species must be thermally activated. On the other hand, when temperature increases, surface coverages by these species decrease due to their desorption thus suppressing the route of selective reduction. Hence, activity in NO_x reduction passes through the maximum mainly due to decrease of the surface coverage by nitrite and nitrate complexes as the temperature increases. Concomitant increase in the rate of complete CH_x oxidation by oxygen seems to be a consequence (but not the cause) of this phenomenon. This conclusion is supported by a reasonable correlation between "operating temperatures" and relative stability of nitrites and nitrates (table 1). Thus, low-temperature catalysts such as cation-exchanged zeolites have also the lowest temperatures of strongly bound ad-NO_x decomposition. The most thermally stable nitrates are located on such high-temperature catalysts as modified zirconias and γ-Al_2O_3, while less stable nitrates are typical for middle-temperature catalyst CuO/γ-Al_2O_3. When the catalysts are of the same type (for example a series of partially stabilized ZrO_2 catalysts), catalytic activity changes rather monotonously as a function of nitrates "bonding strength" (table 3). However, for chemically different catalysts, such as SrO–ZrO_2 and γ-Al_2O_3, catalytic and TPD characteristics do not correlate. It implies that catalysts' operating temperatures are also dependent upon their ability to activate hydrocarbons. Indeed, coordinatively-unsaturated zirconium ions are known to activate hydrocarbons more efficiently than the surface sites of γ-Al_2O_3 [22]. Among cation-exchanged zeolites, Sr–Cu/ZSM-5 demonstrates the highest activity [19] while having also very strongly bound nitrites. In this case specific activation of propane on coordinatively unsaturated copper ions in a unique square–planar coordination seems to be of importance. The ZSM-5 structure also appears to affect substantially both structure and reactivity of Cu^{2+} ions, since these ions in the same square–planar coordination on the surface of γ-Al_2O_3 have rather moderate activities [28].

For all systems studied, positions of the high-temperature peaks were not affected by using a reaction mixture (NO + O_2 + C_3H_8) to form nitrites and nitrates on the surface, which strengthens our conclusions about the role of strongly bound species in the mechanism of NO selective reduction.

4. Conclusions

In this paper, we have estimated bonding strengths of adsorbed NO_x species for several catalytic systems by using the TPD method. Nitrites and nitrates were found to be the most stable surface species and their break-up temperatures are in reasonably good agreement with the catalysts' operating temperatures. The strength of these complexes bonding with the surface was shown to depend upon that of the surface oxygen as well as on the nature of adsorption center (cus cation) and its coordination.

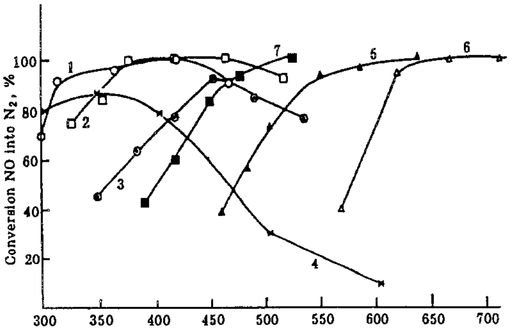

Fig. 5. HC-SCR NO_x activity "windows" for different catalyst types with propane as reducing agent. (1) Sr–Cu/ZSM-5, (2) Ca–Fe/ZSM-5, (3) Sr–Co/mordenite, (4) Cu/ZSM-5, (5) SrO–ZrO_2, (6) γ-Al_2O_3, (7) CuO/γ-Al_2O_3; GHSV = 4000 h^{-1}.

Table 3
TPD characteristics and catalytic properties

Catalysts	T_{des} (°C)	E_a (kJ/mol)	$T_{50\% conv}$ [a]
Ca–Fe/ZSM-5	300	71	280
Cu/ZSM-5	390	91	330
Sr–Cu/ZSM-5	410	105	293
Sr–Co/mordenite	430	80	360
CuO/γ-Al_2O_3	480	110	410
γ-Al_2O_3	510	119	580
SrO–ZrO_2	540	127	470
CaO–ZrO_2	550	129	505
BaO–ZrO_2	590	137	540

[a] Catalytic activity was defined as temperature of 50% conversion of NO_x to N_2 at GHSV = 4000 h^{-1}.

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