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The study of composition of novel high temperature catalysts for oxidative conversion of methane

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Abstract

The products of lignite and coal combustion were tested as the catalysts in two reactions of the oxidative conversion of methane: deep oxidation and oxidative coupling of methane (OCM). It has been observed that these products may display a good performance in either deep oxidation and OCM depending on reaction conditions – temperature and oxygen partial pressure. The detailed study of the composition of products obtained was carried out. It was established that the products are the glass-crystal microspheres with the content of crystal phase of 86–90 wt% and glass phase of 10–14%. The crystal phase consists of the complex solid solution with spinel structure based on magnetite ($FeFe_2O_4$) with Mg and Mn spinels ($MgFe_2O_4$, $MnFe_2O_4$) and small concentration of hematite Fe_2O_3. The basis of glass phase is calcium aluminosilicates. The active components which are responsible for the reaction proceeding over both routes are considered. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Oxidative coupling; Deep oxidation; Microspheres; Spinel structure; Oxygen defects

1. Introduction

It is well known that oxidative conversion of methane proceeds followed by three passways with the formation of different chemicals:

- products of deep oxidation (CO_2 and H_2O);
- oxygen containing products of partial oxidation (methanol, formaldehyde, syngas);
- products of the oxidative coupling of methane (ethane and ethylene).

The proceeding of processes on each passway mentioned above depends on temperature, kind of catalysts and composition of reaction mixture.

The mechanisms of the deep oxidation of low alkanes (C_1–C_3) are studied most of all over oxides of transition metals with the low (<100 kJ/mol) energy of bond Me–O [1]. It was established for reaction to proceed in two temperature intervals for such kind of the catalysts. Therefore, oxidative conversion of low alkanes may occur according to two mechanisms. Deep oxidation at low temperatures (473–723 K) proceeds according to concerted mechanism. Here, the limiting step is the oxidation of surface carbonate-carboxylated species by molecular oxygen with the formation of deep oxidation products. At temperatures above 673 K a stepwise (or redox) mechanism is observed. In this case almost the same values for the catalysis rate and the rate of the reduction of steady-state catalysts are obtained. Here, the rates

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of deep oxidation for homologous series of *n*-paraffins are determined by the energy of homolytic rupture of C–H bond [2].

Efficient catalysts for partial oxidation of methane are aluminosilicates, silicates modified by Mo and W, aluminium phosphate and phosphates of transition metals (Fe, Co, Ni), complex oxides of Bi–Mo–O, Sn–Sb–O, Fe–Sb–O, etc. For such type of catalysts the value of $E_{\mathrm{Me-O}}$ is limited by 200–350 kJ/mol. The reaction of partial oxidation proceeds according to the stepwise mechanisms at temperatures of 673–873 K.

OCM takes place at high temperatures (>973 K) and may be performed by two modes: cyclic mode with the alternate feeding of reactants (methane and oxidant) and cofeed mode with the simultaneous feeding of reactants. Reducible metal oxides such as NiO, Mn_2O_3, Bi_2O_3, PbO, doped by alkali metals are more efficient for the cyclic mode. Irreducible metal oxides, for example, the oxides of rare earth (excluding Ce, Pr, Tb) and alkaline earth metals, doped by alkali metals show the best results for cofeed mode. The last OCM catalysts belong to oxides with $E_{\mathrm{Me-O}}>400$ kJ/mol. It has been proposed that OCM reaction may occur according to stepwise mechanism.

The paper presents new results on choosing catalysts for two processes of oxidative conversion of methane (deep oxidation and OCM) based on consideration of the reaction mechanisms and defect structures of the catalysts.

2. Experimental

New type of catalysts based on ferriferrous oxides were produced in result of coal and lignite combustion followed by hydrodynamic classification of fly ash and magnetic separation.

The catalysts obtained were studied by different methods: XRD, SEM and electron probe microanalysis, chemical analysis, Mossbauer spectroscopy, and then were tested in the reactions of deep oxidation and oxidative coupling of methane.

The studies by scanning electron microscopy (SEM) and electron probe microanalysis were carried out using microanalyzers of type "Cameca" and "Camebax" with the size of electron beam ~2 μm at 600–1000-fold magnification. At least, five measurements in the different points were made for each sample.

X-ray diffraction study was carried out applying diffractometer "DRON-3" using Cu K_α irradiation, Ni filter.

Detailed description of the other techniques is given in [3,4].

3. Results and discussion

3.1. Criteria for choosing catalysts

Earlier [5,6] it has been shown that the OCM catalyst performance is determined by availability of oxygen defects and the catalyst ability to activate oxidants (both O_2 and N_2O) to form peroxide or atomic electrophilic oxygen species. The types of the structural defects and catalytic performance in OCM reaction for the most efficient catalysts are presented in Table 1. The kind of such oxygen defects depends on partial oxygen pressure: at $P_{O_2}<0.1$ kPa oxygen vacancies are available for the efficient OCM catalysts and at $P_{O_2}>0.1$ kPa interstitial oxygens serve as structural defects and active centres for OCM reaction. When interstitial oxygen becomes the dominant defect, these oxides exhibit p-type of conductivity [7]. The most efficient OCM catalysts, such as La_2O_3, Sm_2O_3, Nd_2O_3, are p-type semiconductors. As one can see from Table 1, doping oxides by alkali metals leads to the increase in the catalyst activity and selectivity. Doping by low valence additives (alkali metals) causes the rise of the concentration of oxygen vacancies [5]. Such sharp increase of the concentration of oxygen defects results in the rise of activity and selectivity of the catalysts.

Besides the requirements to the catalyst structure, high temperature catalysts for oxidation have to display the high thermal and mechanical stability.

The search of new catalysts which would satisfy above-mentioned conditions was carried out among the products of coal and lignite combustion. Based on an analysis of mineral part of different kinds of coal the mixed oxide systems MgO–FeO–Fe_2O_3 were chosen as the possible catalysts. During high temperature synthesis (1400°C) three main phases have formed in the system (Fig. 1). There are magnesiawustite, spinel and hematite. In the field of MgO concentration less

Table 1
The types of the structural defects and catalytic performance in the oxidative coupling of methane for the most active catalysts

Catalyst composition	Type of the structural defects		Methane conversion (%)	C_2-selectivity (%)
	$P_{O_2}<0.1$ kPa	$P_{O_2}>0.1$ kPa		
Sm_2O_3	Oxygen vacancies, V_O	Interstitial oxygen, O_i	5.8	93
Li/Sm_2O_3	$[V_O]$ increases	O_i	41.2	54
Nd_2O_3	V_O	O_i	1.5×10^{19a}	62
La_2O_3	V_O	O_i	0.8×10^{19a}	50
Sr/La_2O_3	$[V_O]$ increases	O_i	13.4×10^{19a}	72
CaO	$V_{Me}+V_O$	$V_{Me}+O_i$	3.0×10^{17a}	14
Li/CaO	$[V_O]$ increases	O_i	62.6×10^{17a}	46
Mn_2O_3/SiO_2	V_O	O_i	16.4	48
$Na/Mn_2O_3/SiO_2$	$[V_O]$ increases	O_i	24	70
$Mg_{1-x}Mn_xFe_2O_4/Fe_2O_3$	V_O+V_{Fe} for wustite	V_O+V_{Fe} for solid solution based on Fe_3O_4	15	61

[a] Specific rate of C_2-hydrocarbon formation, molecules $CH_4/(m^2\ s)$.

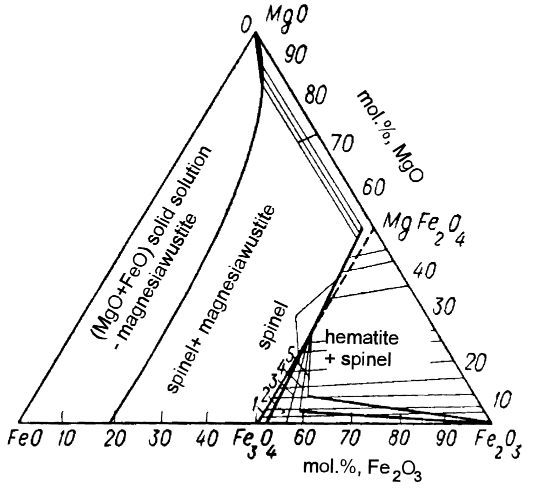


Fig. 1. Isothermal equilibrium diagram for the system of MgO–FeO–Fe_2O_3 at 1400°C [7]; Isobars of oxygen at P_{O_2} (kPa): (1) 0.1; (2) 2.0; (3) 21; (4) 66; (5) 101.

then 50 mol% the phase mixture of magnesiawustite and spinel with the significant disorder in oxygen sublattice exists at $P_{O_2}<0.1$ kPa. In other words, there is the phase of spinel with the high concentration of oxygen vacancies. At $P_{O_2}>0.1$ kPa the mixture of spinel and hematite Fe_2O_3 becomes more stable [7]. One can see from Fig. 1 that the field of spinel existence is expanded with the increase of partial oxygen pressure. In the interval of partial oxygen pressures from 0.1 to 101 kPa, there is a wide field of solid solutions based on spinel phase with various concentrations of oxygen defects which are desirable for OCM reaction.

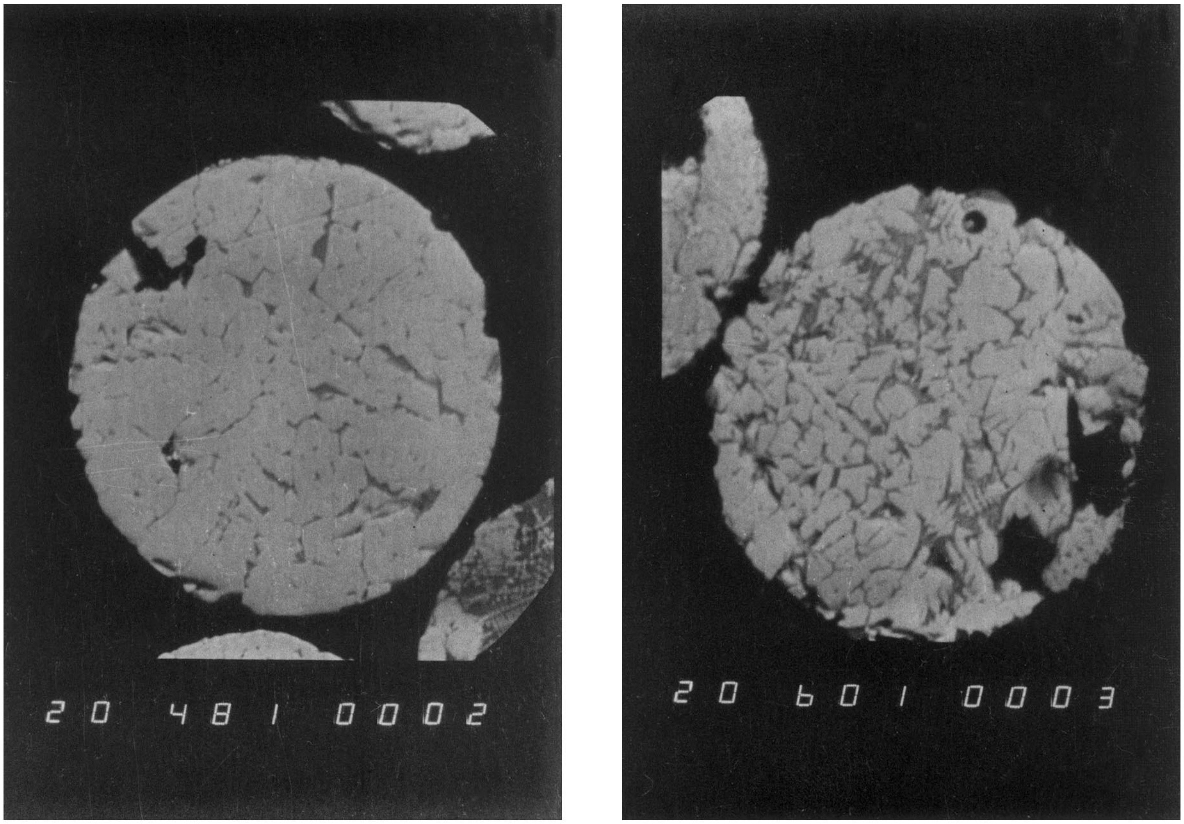
It is known [1] that α-Fe_2O_3 is the catalyst for deep oxidation with $E_{Me-O}=142$ kJ/mol.

New type of catalysts based on ferriferrous oxides were produced in result of coal and lignite combustion at 1400–1600°C followed by hydrodynamic classification of fly ash and magnetic separation. The high thermal and mechanical stability of catalysts were achieved by that the active phases are enclosed in glass-crystal microspheres with the grain sizes of 10–400 μm. The basis of glass component is calcium aluminosilicates of the different composition.

3.2. *Mineralogical study of the systems*

It was obtained that the magnetic products separated from various kinds of coals are of almost the same chemical and mineral compositions. Two series of magnetic microspheres – P and K were studied in detail. Microspheres of K-series were produced from lignite while the microspheres of P-series were obtained from coal.

It has been shown by mineralogical study that glass-crystal microspheres are of dendrite structure with the block surface and consist of the crystal phase (86–90 wt%) and glass phase (10–14 wt%). Approxi-



(a) (b)

Fig. 2. SEM photographs of the polished cross-sections of glass-crystal microspheres: (a) K-series, fraction 0.16–0.1 mm (×480); (b) P-series, fraction 0.16–0.1 mm (×600).

mately 85–90% of K-microspheres and 50% of P-microspheres are monolithic globules. The other part of microspheres are hollow globules. It was of interest to study the monolithic globules in detail. Monolithic globules consist of the dendrite crystals which connected with each other by silicate glass as a binding material (Fig. 2). The difference in composition between K- and P-series is due to the higher content of glass in the microspheres of P-series in comparison with K-series. For example, globules of K-series, fraction 0.16–0.1 mm, maintain 10.4% of glass phase (Fig. 2(a)) while the microspheres of P-series, fraction 0.16–0.1 mm, contain 13.5% of the glass (Fig. 2(b)).

It was established by XRD study that the crystal phase for both series consists of the complex solid solution with spinel structure based on magnetite ($FeFe_2O_4$) with Mg and Mn spinels ($MgFe_2O_4$, $MnFe_2O_4$) and small concentration of hematite Fe_2O_3 (not more than 10 wt% from content of crystal phase). Lattice parameter "*a*" of magnetite for K-series (0.16–0.1 mm) is 8.405 Å, the same parameter of magnetite for P-series (0.16–0.1 mm) is 8.398 Å. The presence of quartz (1–2 wt%) in crystal phases for both series should be noted.

Composition of monolithic globules of K-series on profile centre-edge according to data of electron probe microanalysis is present in Table 2 (points 1–14). All iron was determined as Fe^{2+}, and then calculation of true content of Fe^{3+} was made. Deficiency of total concentration may be explained by more high content of iron in state Fe^{3+}. Average composition of crystal phase in globules of K-series (0.16–0.1 mm) obtained in 19 points is determined as follows: CaO – 1.95; MgO – 1.88; MnO – 2.02; FeO – 22.4; Fe_2O_3 –

Table 2
Composition of monolithic globules of K-series (0.16–0.1 mm) on profile centre-edge according to data of electron probe microanalysis

Phase	Points	Concentration (wt%)							
		CaO	TiO_2	MgO	Al_2O_3	SiO_2	FeO	MnO	Total
Crystal phase	1	0.550	0.000	2.08	0.129	0.001	88.25	2.13	93.15
	2	17.69	0.000	0.880	0.110	3.32	69.36	1.82	93.17
	3	0.717	0.000	1.96	0.186	0.002	87.80	2.09	92.75
	4	1.09	0.000	1.60	0.244	0.075	87.30	2.04	92.36
	5	2.71	0.000	1.76	0.104	0.051	86.50	3.56	94.69
	6	0.738	0.000	4.25	0.710	0.158	83.49	2.17	91.52
	7	0.316	0.000	3.21	0.147	0.014	86.12	2.15	91.97
	8	0.657	0.000	1.87	0.288	0.134	86.31	2.17	91.43
	9	0.438	0.000	2.46	0.170	0.014	86.19	2.13	91.40
	10	6.50	0.000	0.935	0.253	1.20	80.75	1.94	91.57
	11	4.65	0.000	1.26	0.323	1.18	83.50	2.03	92.93
	12	2.95	0.000	1.92	0.059	0.105	86.88	2.88	94.80
	13	1.81	0.000	1.80	0.130	0.014	87.94	2.71	94.39
	14	3.01	0.000	1.69	0.165	0.411	86.23	2.60	94.10
Hematite	1	0.370	0.000	0.087	0.085	0.223	91.37	0.010	92.15
	2	0.284	0.000	0.088	0.073	0.153	91.52	0.008	92.12
Glass phase	1	18.24	0.343	2.28	5.74	31.70	36.07	1.03	95.48
	2	9.91	0.208	4.00	4.74	19.67	56.01	1.54	96.08
	3	3.58	0.059	2.84	1.28	5.27	76.68	2.29	92.09
	4	12.53	0.297	2.50	4.31	23.52	51.14	1.38	95.73

69.6 wt%. So, spinel phase consists of the solid solution based on magnetite ($FeFe_2O_4$) with $MnFe_2O_4$ (7 mol%) and $MgFe_2O_4$ (11 mol%).

It should be noted that significant content of calcium oxide is included into the crystal phase. It is well known [8,9] that Ca^{2+} is not able to incorporate into spinel structure due to so large ion radius. The most likely form for calcium is calcium ferrite ($CaO{\cdot}Fe_2O_3$), but it distributes in such a way that it is not possible to observe the ferrite phase by XRD method.

It was observed that the smallest glass incorporations were captured in the crystal phase (Table 2, points 2, 10, 11, and 14 when silica concentration was more than 0.3%).

The composition of glass phase even for the single globule is not homogeneous. The content of silica is relatively small ($SiO_2<32\%$), but concentrations of CaO and iron oxides are significant. Such composition is likely to be caused by the smallest inclusions of crystal phase. Besides, iron is a component of glass. It should be noted that Al and Ti impurities incorporated only to the glass phase, but not to spinel. This fact may be an evidence that mineral phase of globules crystallized from silicate melt with high iron concentration at relatively high partial oxygen pressure. Morphology of the magnetite with Mg, Mn impurities which cause the formation of compounds of Fe^{3+} proves this conclusion. On the contrary the presence of isomorphic Al^{3+}, Ti^{4+} impurities due to which the spinel with Fe^{2+} is formed would be the proof that crystallization of mineral phase occurred in reducing atmosphere.

The rate of crystallization seems to be so high, in other words, it is quenching. The first phase which crystallizes directly from the melt is likely to be the magnetite. The glass is formed after that and located between dendrite crystals.

The composition of pure hematite phase is given in Table 2. It was proposed that hematite α-Fe_2O_3 is formed by oxidation of magnetite Fe_3O_4 (but not from silicate melt) because the hematite phase does not include any impurities such as Al, Ti which are usually intrinsic to hematite.

Chemical composition of globules of P-series is shown in Table 3. Microspheres of P-series differ

Table 3
Composition of monolithic globules of P-series (0.16–0.1 mm) according to data of electron probe microanalysis

Phase	Points	Concentration (wt%)							
		CaO	TiO_2	MgO	Al_2O_3	SiO_2	FeO	MnO	Total
Crystal phase	1	0.162	0.000	4.54	0.750	0.107	82.94	1.72	90.22
	2	0.163	0.000	4.78	0.789	0.131	82.28	1.86	90.00
	3	0.103	0.000	5.22	0.937	0.027	81.77	1.77	89.83
	4	9.02	0.001	3.65	0.956	0.982	71.79	3.14	89.54
	5	0.881	0.000	9.73	0.641	0.017	75.77	3.08	90.12
Glass phase	1	1.80	0.440	3.11	11.22	39.10	32.17	1.27	89.11
	2	1.54	0.524	2.74	12.01	41.50	31.65	1.38	91.36
	3	2.07	0.506	2.67	12.43	41.97	31.02	1.22	91.88
Glass glouble with a little crystal	1	2.02	0.137	7.43	8.15	9.57	63.76	1.62	92.68
	2	2.38	0.131	7.32	8.51	8.98	62.83	1.57	91.72
	3	12.91	0.401	6.36	11.12	38.09	16.25	1.63	86.77
	4	11.73	0.342	6.49	10.27	36.05	20.47	1.67	87.03
	5	10.83	0.437	6.00	11.61	35.14	23.32	1.53	88.87

from K-series by more high contents of MgO in crystal phase and SiO_2, Al_2O_3 in glass phase. Average composition of crystal phase is determined as follows: CaO – 2.06; MgO – 5.58; MnO – 2.31, FeO – 12.98; Fe_2O_3 – 65.10 wt%. Solid solution with spinel structure contains 35.7 mol% $MgFe_2O_4$ and 8.5 mol% $MnFe_2O_4$. Due to the higher concentration of magnesiaferrite $MgFe_2O_4$ in spinel phase the magnetite shows smaller lattice parameter "a" in comparison with K-series as mentioned above. So, content of Fe^{2+} became smaller than that for K-series: relation Fe^{2+}/Fe^{3+} was equal 1/5 for magnetite of P-series instead of 1/3 for K-series.

The peculiarities of glass phase for P-series consist in rather high concentration of SiO_2 (up to 42%), Al_2O_3 (up to 12%) and smaller concentration of CaO (up to 2%). Iron oxide content is 31–32%, it is more likely that iron includes to the glass phase as component of glass and does not form a separate smallest crystal.

Hematite is formed from magnetite during quenching as in the previous case.

3.3. *Catalytic performance of the catalysts*

It has been shown that chosen multiphase catalysts may exhibit a good performance in deep oxidation and/or OCM reaction depending on reaction conditions. The active catalyst components are assumed to be the phase mixture of solid solution based on Mg–Mn–Fe spinel and α-Fe_2O_3. The ratio spinel/hematite may change depending on partial oxygen pressure. Under conditions of deep oxidation reaction (T=793 K) the concentration of molecular oxygen in gas phase was significant (15 vol% and oxygen conversion does not exceed 5%) [3]. Under such conditions magnetite partially converts to hematite Fe_2O_3 and such catalysts show high activity in deep oxidation of methane [3]. It was found by Mossbauer spectroscopy that the ratio of spinel/magnetite changed from 10/1 before reaction to 2/3 after reaction [4]. We believe that hematite phase is responsible for the reaction proceeding over route of deep oxidation.

Under experimental conditions of OCM reaction (at T=1123°C and at oxygen conversion of 90–95%, i.e. at low P_{O_2}) the part of available hematite reduces to magnetite. Moreover, a degree of disorder in oxygen sublattice of spinel increases. Such phenomenon is accompanied by the rise of Fe^{2+} concentration in spinel structure, as it has been observed by Mossbauer spectroscopy. In other words, some part of Fe^{3+} located in octahedral positions of spinel structure reduces to Fe^{2+} with formation of holes and growth of p-semiconductivity according to the equation:

$$Fe^{3+} + O^{2-} \Leftrightarrow Fe^{2+} + O^{-}$$

where $O^{-}=O^{2-}+p$; p is the hole.

Electrophilic oxygen species such as O^- are likely to be responsible for methane activation with formation of OCM products as it was mentioned above.

As it has been shown in [3], the rate of deep oxidation decreased and selectivity in C_2 hydrocarbon formation increased with the growth of Fe^{2+} concentration in spinel structure. One can see from Table 1 that the multiphase catalysts based on ferriferrous systems (K-series, fraction 0.16–0.1 mm) indicate good performance in the OCM reaction.

So, solid solutions based on spinel allow to create the needful concentration of the desirable defects depending on doping impurity and oxygen partial pressure. Imperfect spinel phase is assumed to be responsible for the proceeding reaction on the OCM route.

It has been indicated [4] that OCM reaction as well as reaction of deep oxidation over catalysts studied proceeds according to the stepwise mechanism. The rates of catalysis and reoxidation of catalyst surface are almost the same, but the total process rate is likely to determine by the stage of oxygen activation. This proposition proves by the fact that catalyst performance strongly depends on the kind of oxygen defects.

4. Conclusion

It has been suggested to choose the catalysts on the basis of consideration of the reaction mechanisms and defect structure of the catalysts. New type of multifunctional catalysts based on ferriferrous oxides with novel design has been produced for the reactions of deep oxidation and oxidative coupling of methane. It was suggested that imperfect Mg–Mn–Fe spinel phase is responsible for the proceeding reaction on the OCM route while the hematite phase is responsible for the reaction proceeding over route of deep oxidation.

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