EFFECT OF DEFECT STRUCTURE ON THE CATALYTIC ACTIVITY OF MAGNESIUM OXIDE IN THE OXIDATIVE DIMERIZATION OF METHANE

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The increase in the activity and selectivity of magnesium oxide in the dimerization of methane upon the addition of lithium oxide is attributed to the generation of active sites containing Li^+-O^- defects and transition metal ions are considered not to be present in these catalysts [1]. In contrast, we have shown that going from pure MgO to samples with added oxides leads to an increase in the total defectivity of the structure, which is manifest in an increase in the concentration of impurity paramagnetic ions. There is also an increase in the activity and selectivity of the formation of C_2 -hydrocarbons. It was also established that the concentration of the impurity ions is sensitive to change in the oxygen content in the gas phase. The replacement of the reaction mixture by helium upon cooling of the catalysts leads to a different nature of the change in the concentration of a different type of defects. The lower content of impurities in MgO/Li upon cooling in the reaction mixture is in accord with the data of Boldu et al. [2], who showed that there is a rapid drop in the concentrations of Cr^{3+} and Fe^{3+} ions upon the formation of lithium defects in the MgO monocrystal in an oxygen atmosphere.

TABLE 1. Content of Impurity Ions and Catalytic Activity for MgO in Methane Conversion (CH₄:O₂:He = 30:15:55 vol. %), 1023 K

Catalyst	T _{con} ,K	Impurity ion content, '10 ⁻¹⁸ spins/g*				W-10-16, molecules/m ² ·			
		Mn ⁺²	Mn+4	CL+3	Fe+3	co	CO2	C_2H_4	C_2H_6
	1050				_				
MgO/Li 2,5%	$1273 \\ 1273$	-	1 †	3	$\begin{vmatrix} 7\\66 \end{vmatrix}$	6.3 16.9	1,4 1,5	$0,2 \\ 0,8$	$1,4 \\ 29,4$
MgO (analytical-grade)	1473	5 †	1† -	4	100 355	27,2	15,0	6,9	16,7
MgO/Li 3,5%	1473	4 T -	2	4 1,5	387	1,3	2,2	1,6	23,6

*Cooling of the stationary catalyst to 293 K in the reaction mixture.

[†]Cooling in a helium stream.

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