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The influence of defect nature on catalytic performance of Li, Na-doped MgO, CaO and SrO in the oxidative coupling of methane

N.G. Maksimov*, G.E. Selyutin, A.G. Anshits, E.V. Kondratenko, V.G. Roguleva

Institute of Chemistry of Natural Organic Materials, 42 K. Marx, Krasnoyarsk 660049, Russian Federation

Abstract

The study of the defects in MgO, CaO doped by alkali metals and SrO has been carried out by ESR-method using γ-irradiation at 77 K. It established the influence of reaction medium on formation of the active centers in oxidative coupling of methane. It has been shown that selectivity of C_2 products over CaO is dependent on the quantity of $M^+CO_3^-$ centers while for SrO catalyst the high activity and C_2-selectivity may be caused by oxyfluoride species. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In early studies the question of the bulk defects in the reaction of oxidative coupling of methane (OCM) on the doped oxides of MgO and CaO has been considered [1]. When SrO oxide was used as a catalyst instead of CaO, it leads to the new catalytic properties [2]. The detailed ESR study was undertaken to elucidate the defect composition and associated properties for the whole series of MgO, CaO and SrO catalysts.

2. Experimental

The samples studied were exposed to the reaction medium at 1000 K. The ESR spectra of these samples were measured at the temperature of liquid nitrogen. The untreated and exposed samples were γ-irradiated to activate the initially non-paramagnetic defects.

3. Results and discussion

The ESR data of the transition metals incorporated as the impurities in the alkaline earth oxides are reported in Table 1. From the difference observed in the relative percentage of high and low valence ions we can conclude that the redox potential increased when the oxides were doped with alkali ions but decreased after the exposition in methane containing reaction medium.

The typical defect composition of the catalysts studied after γ-irradiation is shown in Table 2. For MgO and CaO such defects as M^+O^- and HM^+ are formed by partial substitution of the host lattice ions by $M^+{=}Li^+$ or Na^+ [3,4]. These defects were found to be predominant. HM^+ defects are assumed to form as a mobile proton located in the interstitial positions.

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*Corresponding author.

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Table 1
The effect of Li, Na doping and reaction medium on ESR signal of transition metals

Catalyst	Fe^{3+}	Mn^{2+}	Mn^{4+}	Cu^{2+}	Cu^{3+}
Mgo	+	+	+	+	−
MgO/Li	Incr.	Decr.	Incr.	Decr.	+
MgO/Li+react. medium	Decr.	Incr.	Decr.	Incr.	−
CaO	+	+	−	+	−
CaO/Na, Li	Incr.	Decr.	+	+	−
CaO/Na, Li+react. medium	Decr.	Incr.	Decr.	+	−
SrO	−	+	−	−	−
SrO/Li	−	+	−	−	−

+: detected by ESR; −: not detected by ESR.

For the samples exposed in the OCM reaction medium the defects of carbonate type $M^+CO_3^-$ were detected (see Fig. 1). These centres are dominant if N_2O is used as oxidant.

For SrO the oxyfluoride species were observed as the predominant point defects. The SrO sample tested had some amount of F^- ions as impurity. In addition the ESR signal assigned to the formation of $H_2CO_2^-$ radicals were measured (Fig. 2). That assignment was confirmed by IR spectroscopy of C–H absorption bands. The $H_2CO_2^-$ and CO_2^- centres are predominant if reaction medium contains O_2 as oxidant.

The rates of product formation in the OCM reaction are given in Table 3. It was established that the selectivity of C_2 products over CaO is dependent on the quantity of $M^+CO_3^-$ centres while CO_2-selectivity correlates with number of O_3^- and CO_2^- centres. For SrO catalyst the highest activity was found when N_2O was used as oxidant in contrary with that when O_2 was used as oxidant. This effect is a clear evidence that the activation of oxidant is a limiting factor of the total rate of reaction. The two possible schemes of the activation process in OCM reaction may be suggested:

Table 2
The types of paramagnetic centres observed on active oxides after γ-irradiation[a]

Catalyst, medium	O_v^-	Hole centres	Electron centres	Carbon containing centres
MgO/Li	+	O^-Li^+	HLi^+	
MgO/Li+react. medium	+	Decr.		
CaO/Na, Li	+	O^-Li^+, O^-Na^+	HNa^+, HLi^+	
CaO/Na, Li+react. medium	+	O^-Li^+, O^-Na^+, O_3^-	Decr.	CO_2^-, $LiCO_3$
SrO	+	$O_v^- \ldots FO^-$	FO^{2-}	
SrO+react. medium	Decr.	Decr.	Decr.	CO_2^-, $NaCO_3$, $H_2CO_2^-$

[a]We observed the signal of F^+ centres for all samples studied.

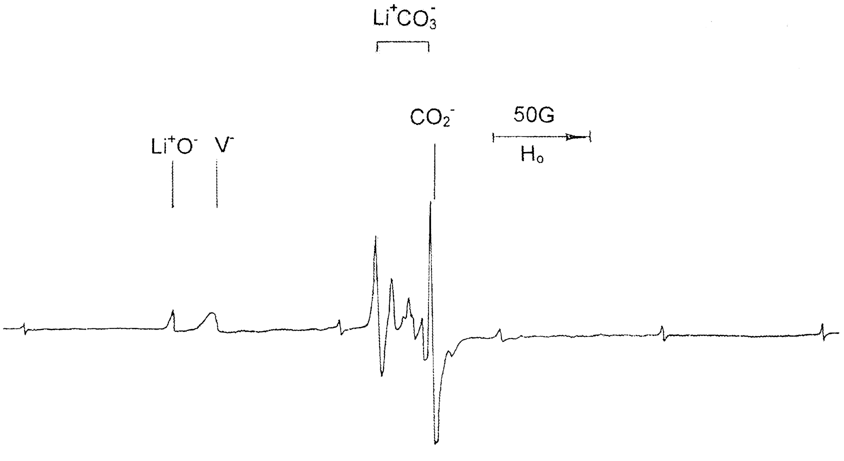

Fig. 1. The ESR spectrum of CaO doped by Li treated in the reaction mixture (CH_4:O_2:He) after γ-irradiation at 77 K.

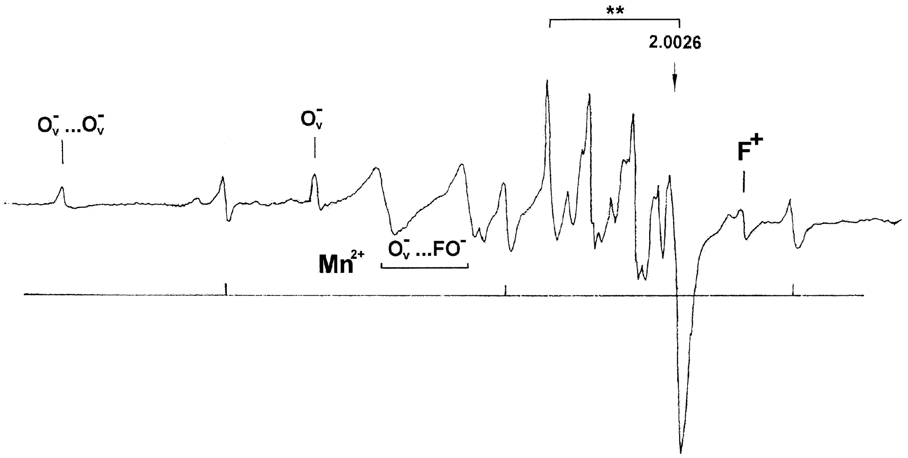

Fig. 2. The ESR spectrum of SrO treated in the reaction mixture (CH_4:O_2:He) after γ-irradiation at 77 K. (**) The group of lines belong to $[H_2CO_2]^-$ and $NaCO_3$ paramagnetic centres.

Table 3
The rates in OCM reaction for Na/CaO, Li/CaO, SrO catalysts at T=1023 K and reaction mixture (CH_4:O_2:He=30:15:55), (H_4:N_2O:He=30:30:40) (methane conversion <5%)

Catalyst	Oxidant	W ($\times 10^{18}$ molecules CH_4 s^{-1} m^{-2})		
		C_2	CO	CO_2
Na/CaO (0.1 at%)	O_2	0.8	0.7	0.8
	N_2O	5.2	2.5	0.75
Li/CaO (0.1 at%)	O_2	5.3	7.5	8.1
	N_2O	14	2.2	6.5
SrO	O_2	9.8	3.0	2.3
	N_2O	74.1	3.2	2.4

1. The activation is caused by an electron transfer from the low valence transition metal ions with formation of the reaction centre located near a low co-ordinated alkaline earth cation. This scheme may explain the correlation found between the rates of OCM reaction and the transition metal impurity concentration.
2. The activation may be associated with formation of some active surface complex and does not include a direct participation of the transition metal cations. In the case of SrO oxide the substituted F^- anions are likely to react with an oxidant. This interaction causes the stabilisation of the lattice FO^- species. Unusual high activity of SrO may be explained by this fact and it is confirmed by high concentration of FO^{2-} centres observed after γ-irradiation.

4. Conclusion

A number of the bulk point defects, including the transition cations, are formed in the lattice of the alkaline earth oxide catalysts. The defect structure of the samples strongly depends on the composition of the reaction medium. The major difference found for the reaction rates in the OCM reaction of MgO, CaO and SrO correlates with the difference of defect structure of catalysts studied. The high activity of SrO catalyst may be caused by the formation of lattice oxyfluoride species.

References

[1] A.G. Anshits, N.P. Kirik, V.G. Roguleva, A.N. Shigapov, G.E. Selyutin, Catal. Today 4 (1989) 399.
[2] A.G. Anshits, E.N. Voskresenskaya, E.V. Kondratenko, N.G. Maksimov, Catal. Today 24 (1995) 217.
[3] M.M. Abraham, W.P. Unruh, Y. Chen, Phys. Rev. B 10(8) (1974) 3540.
[4] M.M. Abraham, Y. Chen, Phys. Rev. B 5(12) (1972) 4945.