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The influence of the reaction medium of oxidative methane coupling on the nature of bulk defects of the Li/CaO system

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The relationship of the catalytic activity of Li/CaO ($0 \leqslant \text{Li} \leqslant 1.7$ at%) in CH_4 oxidative coupling with the defectness of the matrix has been studied. It was shown that the activity of undoped CaO increases with the rise of concentration of anion and cation vacancies. The concentration and nature of defects in the pure CaO are independent of the composition of the gas (O_2, N_2O, CH_4 or reaction mixture). The incorporation of Li ions into the CaO lattice and also the treatment of Li/CaO with the reaction mixture lead to a change of the character of bulk defects and catalytic properties of the oxide. The signals from O_3^-, CO_2^- and $LiCO_3^-$ centers are detected in the EPR spectra of γ-irradiated Li/CaO catalysts after the contact with the CH_4–O_2 mixture. Such defects are not observed when a CH_4–N_2O mixture is used. Simultaneously, the replacement of O_2 by N_2O in the reaction mixture is accompanied by the decrease of the CO formation rate and the increase of activity in the C_2-product formation.

Keywords: Oxidative coupling of methane; calcium oxide; bulk defect; oxidant nature; the effect of reaction medium

1. Introduction

The formation of active oxygen forms for the oxidative coupling of CH_4 may occur with the participation of intrinsic and extrinsic defects of oxide catalysts [1,2]. The concentration of defects increases when alkaline ions are incorporated into the lattice of alkali-earth metal oxides [2–4]. Hereby, the major rises of activity of Li/MgO and Li/CaO are observed using a low amount of alkaline promoter ($\leqslant 1.5$ at%) [5,6]. We have previously noted that the replacement of O_2 by N_2O in the reaction mixture results in a change of catalytic properties of Li/CaO together with a change of the character of defects in the bulk of oxide [7,8]. It was suggested that the defect structure of these catalysts plays an important role in the formation of active centers for oxidative coupling of methane.

This paper reports the study of the character of defects in the catalytic system Li/CaO ($0 \leqslant \mathrm{Li} \leqslant 1.7$ at%) and the influence of the reaction medium of the methane oxidation on the defect nature.

2. Experimental

Reagents of high purity grade CaO ($\mathrm{Fe} \leqslant 0.01$, $\mathrm{Zn} \leqslant 0.005$, Mn, $\mathrm{Cu} \leqslant 0.001$ at%) and LiOH (impurities content: 0.0001–0.001 at%) were used to prepare the catalysts. Undoped calcium oxide was prepared by calcination of CaO: CaO(A) at 1273 K for 3 h; CaO(B) at 1273 K for 9 h, then at 1223 K for 2 h one year later after the storage. The Li/CaO catalysts were prepared by the impregnation method as described in ref. [2]. The Li content was determined by atomic absorption analysis on an AAS-1 apparatus. The surface areas of the catalysts measured by the BET method were 3.2 m^2/g for CaO(A); 1.9 m^2/g for CaO(B); 0.9 m^2/g for Li/CaO (0.4 at%); 0.7 m^2/g for Li/CaO (0.9 at%); 0.5 m^2/g for Li/CaO (1.7 at%).

Catalytic activity was examined at 1023 K in a flow microcatalytic set-up with quartz reactor using reaction mixtures of $CH_4:O_2:He = 30:15:55$ (vol%) and $CH_4:N_2O:He = 30:30:40$ (vol%). A typical flow rate of the reaction mixture was 0.83 cm^3/s. The volume of the fixed catalyst bed was usually 0.05 cm^3 (sample weight of 10–40 mg, particle size of 0.25–0.50 mm). The reaction products were analyzed on columns with Porapak Q (at 373 K) and NaX (at 293 K) using a "Biochrom-1" gas chromatograph with direct-connected detectors of thermal conductivity and flame ionization.

To study the defect nature of the oxide, the catalysts were pretreated at the reaction temperature (1023 K) in a He flow for 0.5 h, then in O_2, N_2O, CH_4 or the reaction mixture for 1 h. After removal of reactive gases by He and rapid cooling down to 77 K, the catalysts were γ-irradiated (3 Mrad). After quenching and γ-irradiation of samples at 77 K the point defects present in CaO produce paramagnetic centers which may be tested by EPR. At the same time, the generation of new defects under the irradiation is known to be not typical for CaO [9]. Therefore, the identification of defects was carried out by recording the EPR spectra of catalysts after irradiation. All spectra were obtained at 77 K on a RE 1307 Radiospectrometer. Spin concentrations were determined in reference to a standard of $Cr_2(SO_4)_3$ and $Cr/\gamma\text{-}Al_2O_3$. The values of absolute concentrations are accurate within ±30%. The identification of the EPR signals was done on the basis of g-values according to ref. [10]. The g-values were measured against DPPH ($g = 2.0036$): for F^+ (anion vacancy with electron trapped) $g = 1.998$; V^- (O^- near the cation vacancy) $g_\perp = 2.071$; O_3^- $g_x = 2.018$, $g_y = 2.013$, $g_z = 2.001$; CO_2^- $g_\perp = 2.0029$, $g_\parallel = 2.0009$; $LiCO_3^-$ $g_\perp = 2.0133$ with four components of a superfine structure (fig. 1).

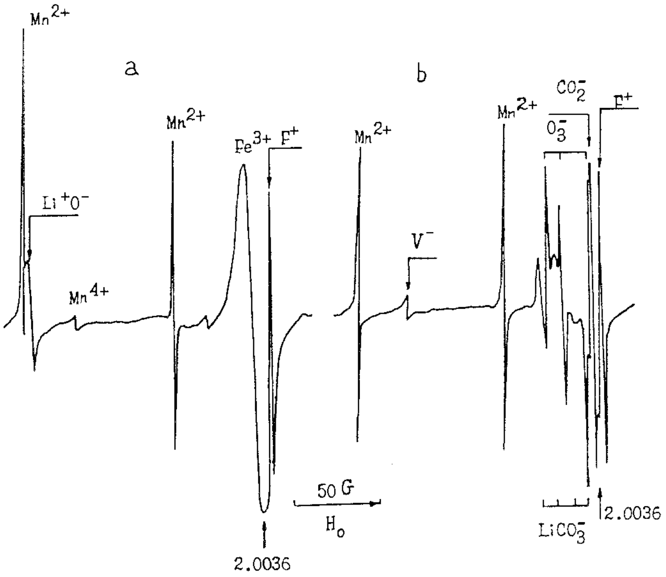

Fig. 1. EPR spectra of the γ-irradiated Li/CaO (0.4 at% Li) after the treatment at 1023 K in the flow of: (a) O_2; (b) $CH_4:O_2:He = 30:15:55$ (vol%).

It is necessary to note that all EPR signals belong to the bulk paramagnetic centers. Unfortunately, the low surface areas of the catalysts do not permit the evaluation of the concentration of the surface defects.

3. Results and discussion

The study of the catalytic properties of the Li/CaO system in the oxidative coupling of CH_4 has shown that the catalyst activity depends on the conditions of sample preparation, the concentration of the Li promoter and the nature of the oxidant (table 1). As it can be seen from the data in table 1, the characters of the bulk defects of undoped CaO and CaO doped by Li are also different.

It should be noted that the nature of defects in undoped CaO is the same after the treatment of catalyst both with the individual components of the reaction mixture and reaction mixtures of various compositions. The signals of F^+ and V^- centers in the EPR spectrum of CaO testify to the presence of anion and cation vacancies in the oxide structure. The more active catalyst among undoped calcium oxide (CaO(B)) has the higher concentration of these defects (table 1). Probably, at the storage of CaO catalysts, CO_2 and H_2O molecules are incorporated into the oxide lattice. The calcination of these catalysts leads to the formation of defects in the oxide structure [8,11]. It is known that defects of the type of anion vacancies may be the sites for oxidant activation [1]. Earlier we have suggested the conception of O_2 activation on the structural defects of

Table 1
Bulk paramagnetic centers (pc) and catalytic activity of Li/CaO system ($T = 1023$ K, CH_4 conversion $\leqslant 5\%$)

Catalyst (Li, at%)	Gas phase	Concentration (10^{-16} pc/g)							W (10^{-17} molec. CH_4/m^2 s)		
		F^+	V^-	Fe^{3+}	Li^+O^-	O_3^-	$LiCO_3^-$	CO_2^-	C_2	CO	CO_2
CaO(A) (0.0)	CH_4 or O_2	2	–	–	–	–	–	–			
	CH_4+O_2+He	1	–	–	–	–	–	–	8.5	8	22
CaO(B) (0.0)	CH_4, O_2, N_2O	10	2	–	–	–	–	–			
	CH_4+O_2+He	12	1	–	–	–	–	–	18	24	30
	CH_4+N_2O+He	13	1	–	–	–	–	–	43	7	44
Li/CaO (0.4)	CH_4, O_2, N_2O	2	–	70	30	–	–	–			
	CH_4+O_2+He	2	1	–	–	33	14	17	59	75	81
	CH_4+NO_2+He	3	12	68	22	–	–	–	153	22	65
Li/CaO (0.9)	CH_4 or O_2	1	0.5	60	30	–	–	–			
	CH_4+O_2+He	–	3	–	–	33	39	5	45	58	10
Li/CaO (1.7)	CH_4, O_2, N_2O	2	–	140	80	–	–	–			
	CH_4+O_2+He	–	15	–	–	13	84	68	45	21	11
	CH_4+N_2O+He	0.3	–	22	12	–	–	–	51	2.5	5

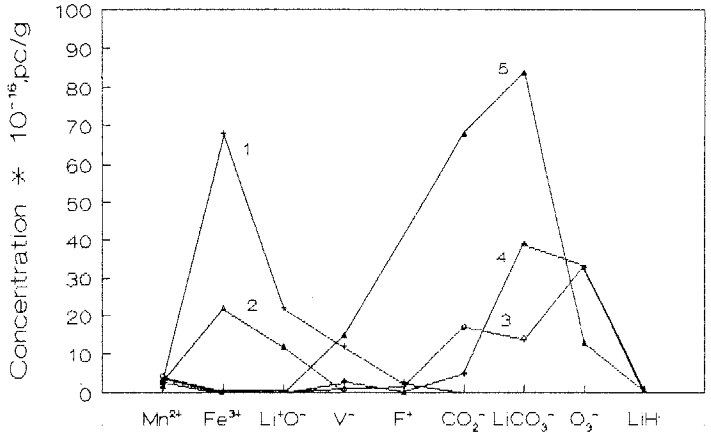

Fig. 2. The concentration of paramagnetic centers (pc) in γ-irradiated Li/CaO after the treatment by the reaction mixture: (1) 0.4 at% Li, (2) 1.7 at% Li (mixture of $CH_4:N_2O:He = 30:30:40$ vol%); (3) 0.4 at% Li, (4) 0.9 at% Li, (5) 1.7 at% Li (mixture of $CH_4:O_2:He = 30:15:55$ vol%).

oxides which has included the stage of O_2^{2-} ion formation and their transformation into two oxygen forms, O and O_{cus}^{2-} (cus: coordination-unsaturated site) [2]. These oxygen species participate in the production of C_2H_6 and CO, respectively. As compared with O_2, using N_2O in the CH_4 oxidation over CaO results in a higher activity in the C_2-hydrocarbon production and the decrease of the rate of CO formation (table 1). This may be due to the generation of one oxygen form (O or O^-) when N_2O is activated on the anion vacancy [12,13].

In comparison with undoped CaO, the introduction of Li ions ($\geqslant 0.4$ at%) into the CaO lattice causes the rise of the total defect concentration in an order of magnitude. At the same time, the rate of methane conversion over CaO doped by Li increases essentially and has a maximum value for the catalyst with low Li content (0.4 at%) (table 1). Based on the results reported in ref. [14], we propose that the point defects which are isolated from each other when formed at low Li concentration are favorable to activate the oxidant with generation of active oxygen species.

In contrast to undoped CaO, in Li/CaO catalysts the character of bulk defectness is changed under the influence of the reaction medium of the oxidative methane coupling (fig. 2). Thus, the signals from O_3^-, CO_2^- and $LiCO_3^-$ centers are detected in the EPR spectrum of γ-irradiated Li/CaO only after treatment with the CH_4–O_2 mixture (fig. 1b). Hereby, the signals of Fe^{3+} disappear because the impure ions of transition metals are the acceptors for radiation-induced electrons:

$$Fe^{3+} + O_3^{2-} \overset{\gamma}{\rightleftarrows} Fe^{2+} + O_3^- . \tag{1}$$

Then, under the catalysis conditions (without γ-irradiation) these defects may be stabilized as O_3^{2-}, CO_2^{2-} and $LiCO_3^{2-}$ centers.

In this case, one of the reasons of the change of the product formation rate over Li/CaO with various promoter contents may be the different concentration of defects which are formed under the influence of the reaction medium.

The decomposition of O_3^{2-} type defects at high reaction temperature may result in the formation of oxygen particles such as O and O_{cus}^{2-}. On the other hand, O_3^{2-}, CO_2^{2-}, $LiCO_3^{2-}$ defects can also be involved in the stages of electron transfer. For example, the ratio of CO/H_2 has been found to be 0.6–0.7 when O_2 is used as oxidant. According to ref. [15], it testifies to the CO production by the reaction

$$CH_3^{\cdot} + O^{2-} \longrightarrow CH_3O^- + e^- \longrightarrow CO + \tfrac{3}{2}H_2 + 2\,e^- . \tag{2}$$

The signals from O_3^-, CO_3^-, and $LiCO_3^-$ centers are not detected in the EPR spectrum of Li/CaO after the reaction using the CH_4–N_2O mixture. In this case, the EPR spectrum is similar to the spectrum presented in fig. 1a with the exception of the concentration of centers (table 1). At the same time, the ratio of CO/H_2 is lowered to 0.3–0.4 and the rate of CO formation is also decreased.

Using N_2O the major activity in the production of C_2-hydrocarbons is observed over Li/CaO with 0.4 at% Li. According to ref. [16], the isolated point defects (ions of transition metals in a low concentration) are the sites for N_2O decomposition with generation of atomic oxygen. Side by side with this, the appearance of V^- centers (O^- near the cation vacancy) at the simultaneous decrease of Li^+O^- concentration after the γ-irradiation in the CH_4–N_2O reaction mixture (table 1) may arise from the Li^+ migration from cation sites in the oxide bulk towards the catalyst surface. Then, under the catalysis conditions O_{cus}^{2-} centers will be able to electron detachment. It is believed that a charge transfer between the bulk and the surface occurs through the levels of impurity ions of transition metals [17]. In this case the formation of O^- is possible when N_2O is activated on the catalyst surface. Thus, the high activity of Li/CaO with 0.4 at% Li for C_2-hydrocarbon production may be the result of the formation of active atomic oxygen species (both O and O^-).

The reasons of Fe^{3+} and Li^+O^- concentration decrease and absence of other paramagnetic centers (V^- type) for Li/CaO with high Li content (1.7 at%) after the treatment by the CH_4–N_2O mixture (table 1) are not clear. This experimental fact may be explained by profound changes in the catalyst structure with the formation of defects undetected by EPR.

4. Conclusion

The activity of undoped CaO in the oxidative coupling of CH_4 has been found to increase when anion and cation vacancies are present in the oxide structure. The character of the defectness in pure calcium oxide is not changed under the effect of O_2, N_2O, CH_4 or a reaction mixture with various oxidants.

However, the incorporation of Li ions into the CaO lattice and also the treatment of Li/CaO by the reaction mixture result in a change of the nature of defects in the oxide bulk. The formation of point defects isolated from each other causes the rise of catalytic activity of Li/CaO with low promoter concentration in the presence of both O_2 and N_2O. But, the rates of product formation are distinguished using various oxidants. One of the reasons of this fact may be the formation of different defects under the catalyst conditions. Under the influence of the CH_4–O_2 mixture the defects of O_3^{2-}, CO_2^{2-} and $LiCO_3^{2-}$ may be formed in the bulk of Li/CaO. Both the transformation of these defects into different oxygen species and their participation in the electron transfer are possible. The formation of the defects mentioned is not observed using the CH_4–N_2O mixture and the CO formation rate is lowered.

References

[1] A.G. Anshits, E.N. Voskresenskaya and L.I. Kurteeva, Catal. Lett. 6 (1990) 67.

[2] A.G. Anshits, N.P. Kirik, V.G. Roguleva, A.N. Shigapov and G.E. Selyutin, Catal. Today 4 (1989) 399.

[3] C.-H. Lin, T. Ito, J.-X. Wang and J.H. Lunsford, J. Am. Chem. Soc. 109 (1987) 4808.

[4] M. Anpo, M. Sunamoto, T. Doi and I. Matsuura, Chem. Lett. (1988) 701.

[5] N.P. Kirik, V.G. Roguleva, G.E. Selyutin, N.G. Maksimov and A.G. Anshits, *Proc. II Int. Symp. Techn. Catal. and Catal. Processes*, Szczecin 1989, p. 153.

[6] F.P. Larkins and M.R. Nordin, *Proc. Symp. Prod. Fuels and Chem. Natur. Gas*, Amsterdam 1988, p. 409.

[7] V.G. Roguleva, M.A. Nikiphorova, N.G. Maksimov and A.G. Anshits, Catal. Today 13 (1992) 219.

[8] V.G. Roguleva, M.A. Nikiphorova, G.E. Selyutin, V.P. Selina, A.I. Rubaylo and A.G. Anshits, Catal. Today 13 (1992) 581.

[9] L.I. Barsova, T.K. Yurik and V.I. Spitsyn, Izv. Akad. Nauk SSSR Ser. Khim. 6 (1985) 1223 (in Russian).

[10] P.W. Atkins and M.C.R. Symons, *The Structure of Inorganic Radicals. An Application of Electron Spin Resonance to the Study of Molecular Structure* (Elsevier, Amsterdam, 1967).

[11] F. Freund, Phys. Chem. Miner. 15 (1987) 1.

[12] E.R.S. Winter, J. Catal. 15 (1969) 144.

[13] E.R.S. Winter, J. Catal. 19 (1970) 32.

[14] A. Cimino and F. Pepe, J. Catal. 25 (1972) 362.

[15] K.-i. Aika and J.H. Lunsford, J. Catal. 81 (1977) 1393.

[16] K.-i. Aika, M. Isobe, K. Kido, T. Moriyama and T. Onishi, J. Chem. Soc. Faraday Trans. I 83 (1987) 3139.

[17] E.G. Derouane and V. Indovina, Bull. Soc. Chim. Belg. 82 (1973) 645.