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Interaction of methane and oxygen with the surface of Li–Mn–O catalyst

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Abstract

By thermo-programmed oxidation (TPO) and thermo-programmed reduction (TPR) methods the interaction of methane and oxygen with the Li-promoted and unpromoted surface of manganese oxide catalysts was investigated. The conclusions were made about the character of surface interaction. The promotion of manganese oxide led to the variation of Mn–O bond character and to the increase of the catalytic activity of the system in the oxidative condensation reaction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst; Oxidative condensation reaction; Thermo-programmed methods

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1. Introduction

Ethylene synthesis by means of methane oxidative dimerization is one of the perspective directions in the development of oxidative heterogenous catalysis [1]. Oxide systems modified by alkaline and alkaline-earth metals are effective catalysts for this process [2]. Amongst these oxides with alternating valency such oxides as manganese oxide are the most active [1,3]. In the present paper the purpose is to elucidate details of the surface mechanism by studying reduction and oxidation properties of the lithium promoted and unpromoted manganese oxide catalysts.

2. Experimental

In the present paper two samples have been used: Manganese oxide (S_{sp}=2.5 m^2/g) and Li–Mn–O catalyst (S_{sp}=1.6 m^2/g) synthesized by precipitation from $Mn(NO_3)_2$ aqueous solution with NH_4OH (LiOH) saturated solution at pH=12. Lithium content in the sample was 3.2% (mass). The deposits after drying (at T=400 K) were calcined for 10 h at 973 K.

Li content has been determined by a flame photometry method. Phase composition of the samples has been studied by means of X-ray diffractometer DRON-3 with Cu K_α-radiation. The catalytic properties of the samples have been investigated at the atmospheric pressure in a fixed bed catalytic microreactor with gas chromatographic analysis of the products. Methane–air mixture with the ratio of CH_4/O_2=3.5 has been used.

During TPR study the mixture of CH_4 in helium was used and during TPO a mixture of O_2 in He. Experiments on TPO were carried out at oxygen partial pressure P_{O_2}=6.8 kPa and linear rate of heating at 0.5 K/s. The samples' surfaces were calcined for 3 h in a flow of helium. A part of the samples was treated

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in a flow of methane with helium at 1000 K for an hour. TPR experiments were realized at methane partial pressure 6.8 kPa. The samples were previously calcined in a helium flow for 3 h or the additional treatment of the surface was carried out in regime of TPO at P_{O_2}=16.7 kPa and heating rate 0.5 K/s. The TPO and TPR experiments were started after cooling of the samples in a flow of helium up to 298 K.

3. Results and discussion

The phase composition and the catalytic properties of the samples are shown in Table 1. Introduction of 3.2% (mass) Li in the catalytic composition leads to considerable increase of the catalytic parameters of the process (selectivity of ethane and ethylene, conversion of methane).

In Fig. 1 TPO profiles of manganese oxide and Li–Mn–O catalysts are shown. After pretreatment of the catalysts in a flow of helium the oxygen impoverishment of the surface takes place. Following interaction by oxygen leads to the appearance of the peak (Fig. 1β-Mn_2O_3 (a)) corresponding to oxygen adsorption and transition to the initial state. The promotion of manganese oxide by alkaline addition resulted in the complication of the surface interaction character: On TPO profile the second maximum was observed at T=873 K (Fig. 1 Li–Mn–O (a)).

After reduction of the samples by methane at temperature of the oxidative condensation process, TPO peaks were observed to shift towards higher temperature and their area increases (Fig. 1, b(1)). In this case CO_x is not observed in the TPO products. It is evidently connected with the fact that while helium treatment of the samples of oxygen occur the impoverishment of the surface layer and the reduction of Mn^{3+} occur in Li-promoted samples as in the unpromoted samples. Further oxidation of these partially reduced structures demanded a higher energy of activation (Table 1). Increase of oxygen pressure resulted in a rise of the surface reoxidation and oxygen adsorption in several forms (Fig. 1 Li–Mn–O b(1)–(3)).

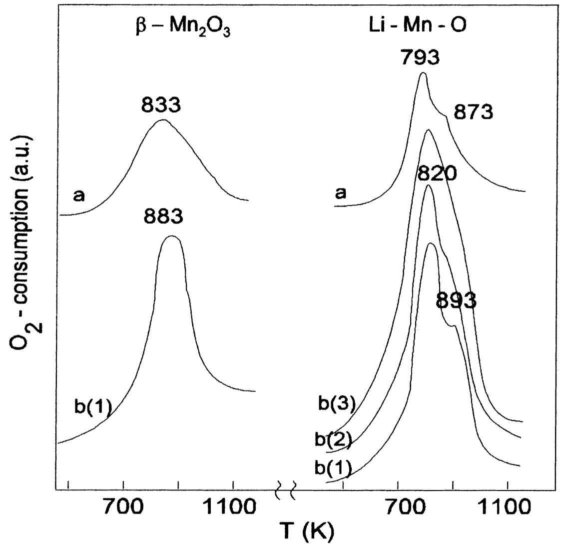

Fig. 1. TPO profiles: (a) after treatment in a helium flow at T=298–1073 K for 3 h; (b) after treatment in a flow of methane and helium at 1000 K for 1 h; at partial pressure of oxygen P_{O_2}, kPa: (1) 6.8; (2) 10.1; (3) 16.7.

TPR profiles of the samples are shown in Fig. 2. The results of thermal analysis indicated that at the

Table 1
Catalytic properties and kinetic features of TPO profiles for Mn-containing samples at T=1033 K, τ=1 s

Sample	Phase composition	Selectivity (%)			CH$_4$ conversion (mol %)	P_{O_2} (kPa)	E_a (kJ/mol)
		C_2H_6	C_2H_4	CO_2			
Mn_2O_3	β-Mn_2O_3	14.3	18.1	67.6	16.1	6.8[a]	62±3
						6.8[b]	90±5
						6.8[a]	119±6
Li–Mn–O	β-Mn_2O_3	16.8	43.3	39.9	20.6	6.8[b]	121±6
	$LiMn_2O_4$					10.1[b]	134±7
						16.7[b]	138±7

[a] Without methane pretreatment.
[b] After methane treatment (for 1 h at 1000 K).

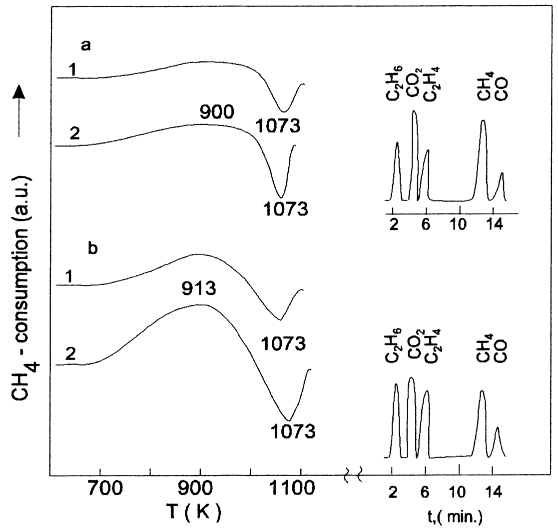

Fig. 2. TPR profiles of (a) β-Mn_2O_3 and (b) Li–Mn–O catalysts: (1) after treatment in a flow of helium (T=298–1073 K for 3 h); (2) after treatment in TPO regime (P_O2=16.7 kPa, heating rate=0.5 K/s). Chromatographic analysis in the temperature interval of 1000–1100 K.

lower temperatures (700 K) some surface adsorption of methane was observed. The inverse peak within 1000–1100 K was connected with the desorption of the reaction products by the samples surface: ethane, ethylene, CO_2 and CO. Methane interacted very weakly with the oxygen impoverished surface of the catalysts (Fig. 2 (a) and (b)(1)). Oxygen saturation of the samples in the regime of TPO resulted in the stronger adsorption of methane, while with the main reaction products were determined by the chromatographic method (Fig. 2 (a) and (b)(2)). As indicated in Fig. 2 (b)(2), the methane interaction was more intensive in the case of the Li–Mn–O sample.

Chromatographic analysis has shown that for the Li–Mn–O sample ethane and ethylene prevailed in the reaction products. At the alternate admitting of methane and oxygen the following reactions took place [3]:

$$2\mathrm{Mn}^{(2n+)}\mathrm{O}_n^{2-} + 2\mathrm{CH_4(g)} \rightarrow 2\mathrm{Mn}^{(2n-2)} + \mathrm{O}_{n-1}^{2-} + 2\mathrm{OH(a)} + 2\mathrm{CH_3(a)}$$

$$2\mathrm{CH_3(a)} \rightarrow \mathrm{CH_3CH_3(a)}$$

$$\mathrm{CH_3CH_3(a)} + \mathrm{Mn}^{(2n)+}\mathrm{O}_n^{2-} \rightarrow \mathrm{CH_2} = \mathrm{CH_2(g)} + \mathrm{Mn}^{(2n-2)+}\mathrm{O}_{n-1}^{2-} + \mathrm{H_2O}$$

$$2\mathrm{Mn}^{(2n-2)+}\mathrm{O}_{n-1}^{2-} + \mathrm{O_2(g)} \rightarrow 2\mathrm{Mn}^{(2n)+}\mathrm{O}_n^{2-}$$

$$\mathrm{CH_3CH_3(a)} \rightarrow \mathrm{CH_3CH_3(g)}$$

It can be suggested that on the surface of the Li–Mn–O sample the stronger connected oxygen was formed, which was responsible for the formation of ethane and ethylene. The promotion of manganese oxide led to the variation of Mn–O bond character and to the increase of the catalytic activity of the system in the oxidative condensation reaction.

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