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Catalytic oxidative conversion of methane

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Abstract

The role of acid–base properties of the surface in the oxidative dimerisation of methane to C_2-hydrocarbons has been shown on the species of SnO_2 modified by Li_2O.

1. Introduction

In our previous paper [1] the effect of the process parameters and catalysts' modification on the oxidative conversion of methane to C_2-hydrocarbons and formaldehyde was shown. The present paper provides information on the role of acid–base properties of oxide catalysts' surface modified by Li_2O in oxidative conversion of methane.

2. Experimental

Tin–lithium oxide catalysts were prepared by mixing of tin hydroxide with lithium nitrate followed by drying at 473 K and annealing at 1073 K for 10 h. $Sn(OH)_2$ was obtained from $SnCl_2$ by ammonia precipitation at pH 12; the precipitate being washed many times and the Cl^- in filtrate water was controlled. According to [2], the Cl^- content in an unannealed $Sn(OH)_2$ gel is less than 0.3% m/m when prepared the same way. After annealing the Cl^- content is sure to be even less and such a minor concentration of Cl^- would in our opinion not effect the catalytic properties in question [3,4].

The catalytic properties of the samples were studied in a flow reactor. The temperature of reaction was 1013 K, the composition of the reactant gases: CH_4:O_2:N_2 = 3.5:1:5; τ = 0.5 s. The composition of the reaction mixture was determined by gas chromatography.

Acid–base properties of the catalysts were investigated by a temperature-programmed desorption of CO_2 and NH_3 in a flow installation with temperature raised linearly from 293 up to 873 K and a constant flow rate of 16.6 K/min.

3. Results and discussion

The experimental results are presented in Table 1. The increase in concentration of Li promoting additive from 5 to 15% leads to methane conversion decrease, and at the same time to increase of the ethane selectivity. The change in selectivity towards ethylene is more complicated. The ethylene yield at 1013 K reaches 20–22% over the samples which contain 10 and 5% of Li_2O.

According to the thermal desorption data a number of basic sites, differing in their strength, were found on sample surfaces (Table 1). The

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Table 1
Catalytic activity and surface characterization of catalysts

Catalysts	Surface area (BET), m^2/g	CH_4 conversion, %mol	Selectivity, %		CO_2 Adsoprtion (323K)	
			C_2H_4	C_2H_6	Tmax, K	Basic centres concentration x 10^{-7} mol/m^2
5% Li_2O/SnO_2	7.9	51	41	8	393	2.2±0.2
					433	2.5±0.2
					703	6.8±0.7
10% Li_2O/SnO_2	10.5	35	66	14	493	7.9±0.8
15% Li_2O/SnO_2	0.8	23	22	20	473	4.0±1.0
					533	8.0±2.0

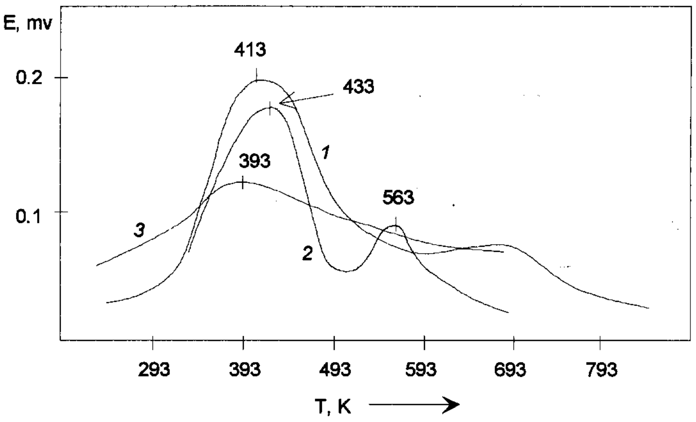

Fig. 1. TDP curves of NH_3. $T_{ads}=323K$, *1* = 5%, *2* = 10%, *3* = 15% Li_2O/SnO_2.

sample containing 5% of Li_2O has the most active sites. This sample showed a high methane conversion at a significant ethylene yield. It proves the hypothesis of heterolytic activation of C–H bond in a methane molecule on the nucleophilic surface sites, where O^{2-} ions can be used as these sites [5,6]. According to [7] strong-basic sites existing on the catalyst surfaces are responsible for initial conversion of methane to ethane. The surfaces of all samples contain also basic sites of mean strength, on which the activation of a methane molecule can proceed.

Basic sites existing on a SnO_2 surface and on that modified with Li_2O have been studied by IR spectroscopy in diffused light. As it is seen from Table 2 during CO_2 adsorption on the SnO_2 surface at 298 K the appearance of adsorption bands at 1500 cm^{-1} and 1720 cm^{-1} was observed in IR-spectrum, characterizing vibrations in a surface monodentate carbonate and in bicarbonate, respectively [8]. During heating the sample in CO_2 at 423 K an adsorption band at 1610 cm^{-1} was observed characterizing vibrations of weakly coupled surface forms of CO_2 with surface basic sites. Bicarbonates characterize site's basicity, surface OH-groups included; mono- and bidentate carbonates are referred to the basicity of oxygen surface ions [9]. On the surface of Li-containing catalyst one can observe carbonate compounds of

Table 2
Characteristics of carbonates

Catalysts	Bands, sm^{-1}	Carbonates
SnO_2	1500 ν as (COO^-)	monodentate
	1610 ν (C=O)	bidentate
	1720 ν (C=O)	bicarbonate
Li/SnO_2	1450 ν as (CO_3^{2-})	non-co-ordinate carbonate
	1500 ν as (COO^-)	monodentate
	1600 ν (C=O)	bidentate
	1645 ν (C=O)	bidentate
	1690 ν (C=O)	bicarbonate

five types. It enables to define five types of basic sites: surface hydroxyl groups, where CO_2 adsorption leads to bicarbonates formation, and surface basic oxygen in various states, which takes part in the formation of carbonates of four types. A decrease in vibration frequency v (C=O) in a bidentate carbonate (1600 cm^{-1}), as compared to the same structure on the SnO_2 surface, indicates a covalence decrease in M–O bond, i.e. an increase in oxygen basicity for a lithium-containing catalyst.

Thus, the use of CO_2 molecule as a probe for basic sites has demonstrated that a number of various basic sites, differing in their strength, exists on the surface of Li-containing catalysts.

As it is seen from the Figure, sample surfaces contain also acid sites weakly coupled with the surface. The role of acid sites in oxidative dimerization of methane has not been determined. It is presumed that they are responsible for complete oxidation of methane as well as of the products obtained.

Thus, the present study has elaborated the role of acid–base properties exhibited by the surfaces of tin-containing oxide catalysts during oxidative dimerization of methane.

4. References

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