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Basic sites on the oxide surfaces: their effect on the catalytic methane coupling

A.A. Davydov [a], M.L. Shepotko [b], A.A. Budneva [a]

[a] *Boreskov Institute of Catalysis, Novosibirsk, Russia*
[b] *Institute of Solid State Chemistry, Novosibirsk, Russia*

Abstract

Basic sites of various oxide catalysts for oxidative methane coupling have been studied with the IR spectra of CO_2 probe molecules. It is possible to determine the concentration and strength of surface basic sites, by studying carbonate compounds, which form on surface oxygen sites. Since the surface structure is non-uniform, its oxygen ions carry different negative effective charges and thus produce carbonates, exhibiting different IR spectra. A correlation between the site strengths and carbonates' spectral behavior, found earlier, allows us to distinguish the sites rather well. The catalytic activity of oxide catalysts was found to depend on the presence and concentration of the strongest basic sites on the oxide surface.

1. Introduction

It is not possible to design good oxide catalysts for oxidative methane coupling (OCM) and for methane oxidation to formaldehyde without detailed information on reaction mechanism and on the character of paraffins activation on the catalysts surface. Therefore, we tried to elucidate by different spectral methods, which surface sites produce certain adsorbed species, which then convert to definite reaction products. The present work is aimed to study the properties of various active sites on the oxide catalysts surfaces and to understand how the surface sites' properties affect the catalyst activity.

Numerous studies concerning the mechanisms of catalytic paraffins conversion still do not answer precisely which active sites are responsible for certain reactions. For OCM, for example, some studies convince that basic sites are of importance for methane activation [1–6], while other studies give evidence for the radical nature of methane activation sites [7–10].

The recent studies, showing saturated and unsaturated hydrocarbon conversion on oxides with rupture of C–H bonds, allow us to suggest a heterolytic mechanism for methane activation.

In fact, the oxides of alkaline earth elements are the most active and selective OCM catalysts. They are famous for their strong basic properties. This fact supports the hypothesis on heterolytic methane activation. Sokolovskii et al. [2] have already demonstrated a particular catalytic activity of alkali earth oxides and phosphates for OCM. They have found that the overall concentration of basic surface sites correlates well with the catalyst activity.

Methane was shown to adsorb dissociatively on magnesium oxide at 573 K, then producing hydroxyl and magnesium methyl groups [2,11]. These data prove directly heterolytic dissociative CH_4 adsorption. Taking into account the UV–IR

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data [12,13] on the nature of active sites on MgO (basic sites appear to be unsaturated ions of various coordination), we think that on MgO CH_4 adsorbs on the 3-coordinated (unsaturated) sites. Indeed, some energy gain is possible only if methane dissociates on coordinatively unsaturated sites [14].

Therefore, we also assume that only some strongest basic sites (BS) can provide dissociative CH_4 adsorption on OCM catalysts. So, it is of importance to specify all basic sites on the surface and to determine their concentration and strength. Such sites can differ by their origin or have the same origin, but exhibit different properties (e.g., O^{2-} sites of different coordination caused by the sample's polydispersity).

We have tried to compare several methods with regard to their fruitfulness for BS studies and thought IR spectroscopy with adsorbed CO_2 probe molecules to be the best [15,16].

In this paper we report on the study of BS sites over OCM catalysts by means of this method. We have also compared the data on BS concentration and catalytic activity exhibited.

2. Experimental

2.1. Catalyst preparation

Table 1 shows the preparation conditions and properties of the catalysts obtained. The samples were heated at 1123 K for 2 h in helium flow (for catalyst activity measurements) or in vacuum (for IR spectra registering).

2.2. IR spectroscopy of adsorbed CO_2

Samples, pressed to tablets, were placed in a quartz holder and introduced into a glass cell. Then they were heated to 1173 K in vacuum (10^{-5} Torr) for 2 h. IR spectra were recorded with a FTS-113V Fourier transform and IR-M-80 spectrometer. CO_2 was introduced into the cell at room temperature or 393 K, pressure ranged from 1 to 10 Torr.

Spectra were processed with "Band Separation/Spectra Simulation" software. The number of iterations was 250.

Table 1. Catalyst preparation conditions and properties (treatment at 1123 K)

Sample	Preparetion procedure	S_s, m^2/g
γ-Al_2O_3	Commercial	220
MgO	Precipitation from $Mg(NO_3)_2$ solutions and calcination at 773 K	150
CaO	Precipitation from $Ca(NO_3)_2$ solutions and calcination at 1073 K	40
La_2O_3	$La(NO_3)_3$ calcination at 1123 K	11
Sm_2O_3	$Sm(NO_3)_3$ calcination at 1123 K	9.5
PbO/MgO 5 mol.% PbO	Mixing of nitrates solutions, evaporation, 8 h drying at 393 K,	10
Sm_2O_3/MgO 10 mol.% Sm_2O_3	Calcination at 1123 K	15

2.3. Mechanochemical activation

Catalyst samples were activated using a centrifuge planetary mill of EI 2 × 150 with corundum drums and balls at an acceleration of 40 *g* per 30–60 s.

2.4. Catalytic measurements

Catalysts were tested in a fixed-bed microcatalytic reactor under dynamic conditions (CH_4:O_2 = 80:20) in a helium flow under atmospheric pressure. Samples were placed in a U-shaped quartz reactor (inner diameter 4 mm) heated by an electric furnace.

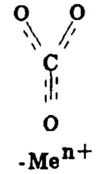
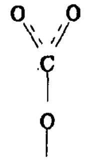
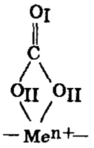
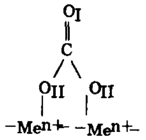
3. Results and discussion

IR data on CO_2 complexes with the oxide surface show that CO_2 reacts predominantly with O^{2-} and OH^- sites (BS), producing various carbonates and bicarbonates, respectively.

As we have found earlier, at least four types of carbonate species (see Table 2) form on MgO surface: bicarbonate (I) involving hydroxyls and carbonates (II–IV) involving basic surface oxygen species. The latter exhibit different properties and thus provide carbonates with different spectra.

IR spectra of CO_2 adsorbed on Sm_2O_3, La_2O_3, CaO, γ-Al_2O_3 (Fig. 1) are less complex. So, the BS on the surface of these oxides exhibit more uniform properties than BS on MgO.

Table 2. Types of surface carbonate species, forming at CO_2 adsorption on oxides, and their IR spectra parameters

Type of carbonate	Structure of carbonate	ν, cm^{-1}			
		MgO	CaO	La_2O_3	Sm_2O_3
(IV) Symmetrical		1450-1440	-	-	-
(III) Monodentate		1530-1520 1405-1395	1490 1410	1500 1400	1540 1410
(II) Bidentate		1585 1385- 1370	-	1585 1350	-
		1630-1620 1315-1310	-		1630 1330-1310
		1680-1670 1280	-	-	-
(I) Bicarbonate		1690-1680	-	-	-

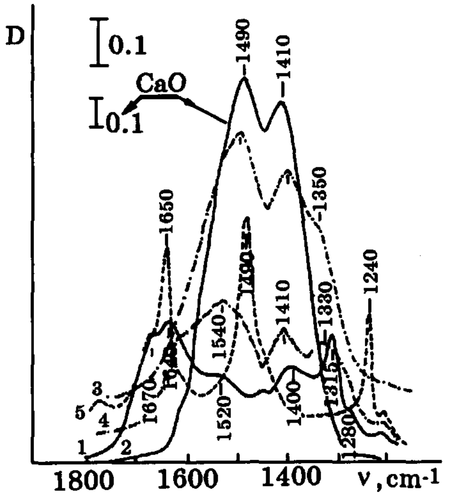


Fig. 1. IR spectra of CO_2 adsorbed at 573 K on MgO (1), CaO (2), La_2O_3 (3), Sm_2O_3 (4) and γ-Al_2O_3 (5) samples dehydrated at 1073 K.

Apparently, the non-uniform structure of the oxide surface provides surface oxygen ions with different effective negative charges (i.e., different basicity).

The basicity of surface oxygen ions, producing bidentate carbonates (II), is known to be less than that of ions, producing monodentate carbonates (III) [17]. Thus we can specify these BS with regard to their strength. Moreover, the split value $\Delta\nu = \nu(C\text{–}C_I) - \nu(C\text{–}O_{II})$ appears to be 300 cm^{-1} [17,18] for bidentate carbonates and increases with increasing covalent degree of the Me–O bond (i.e., with decreasing oxygen basicity). The data on various bidentate carbonates show that oxygen basicity produces a determining effect on the split value [17].

Since the split $\Delta\nu$ is a function of the Me–O bond ionic degree and thus oxygen charge (i.e., basicity) [17,19], we can use this spectral param-

Table 3. Results of spectral and catalytic investigations

Oxide		CaO	La_2O_3	Sm_2O_3	MgO	MgO(MA)
IRS	Number of the Strong Basic Sites 10^{-18}, sites/m^2	6,9	3,8	3,3	0,3	1,5
	$\Delta\nu$, cm^{-1}	80	100	130	125	110
Catalysis	Selectivity (C_2), %	49,3	42,9	45,6	7,0	15,0
	Conversion, %	22,1	19,6	23,2	6,8	10,1

Table 4. OCM rates (T=1023 K, CH_4:O_2=80:20) and BS numbers for various oxide catalysts.

Catalysts	Rate 10^{-14}, molec/(cm^2/s)		Number of strong basic sites 10^{-18}, sites/m^2
	Overall	Dimerisation	
MgO	0,7	0,02	0,3
5 mol.% PbO/MgO	3,8	1,60	0,6
10 mol.% Sm_2O_3/MgO	44,0	20,00	1,2

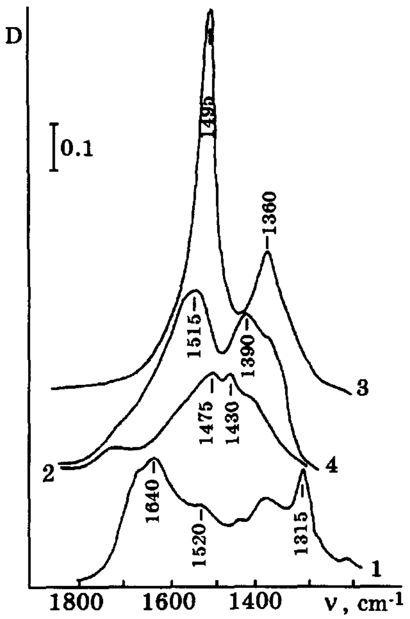


Fig. 2. IR spectra of CO_2 adsorbed at 573 K on MgO (1), 5% Na_2O/MgO (2), 5% PbO/MgO (3), Sm_2O_3/MgO (4) samples dehydrated at 1073 K.

eter to estimate the relative strength of BS: the smaller $\Delta\nu$, the more basic is the site which interacts with CO_2. Therefore, we believe that the surfaces of CaO, La_2O_3 and Sm_2O_3 possess strong and uniform BS.

If we choose $\Delta\nu$ as a criterion for BS strength, we obtain the following strength series for BS responsible for the monodentate carbonates formation:

$$MgO < Sm_2O_3 < La_2O_3 < CaO$$

This series, which we have determined in accordance with the spectral data, coincides with the series of oxide basicity based on the general fundamental assumptions reported elsewhere [20,21].

Besides BS specification with respect to their type and strength, our approach allows to estimate the absolute number of particular BS, if the corresponding extinction coefficients ε are known. For the sites producing monodentate carbonates, ε is 4.2×10^{-19} cm^2/molecule [16]. The absolute number of such BS differs greatly for various oxides (Table 3).

If we compare the spectral data on oxide systems with their catalytic performance for OCM (Table 3), we see that oxides, possessing similar amounts of strong BS (CaO, La_2O_3, Sm_2O_3) are quite good catalysts. MgO, which has far less and weaker sites, exhibits a low catalytic activity.

Taking into account our spectral and catalytic data, we suppose that the strongest BS, responsible for the monodentate carbonates formation, provide a main contribution to methane activation along the C–H bond (see Tables 2 and 3). The content of such sites is the highest in the systems like Sm_2O_3/MgO. They appear to be the most active and selective OCM catalysts (see Table 4).

The introduction of Sm_2O_3, PbO and Na_2O admixtures (Fig. 2) affects greatly the content and strength of BS on MgO surface (Table 4). We have found that mechanical activation (MA) also changes the BS number. Hence, for MgO ($\tau_{MA} = 60$ s), the BS number increases considerably after MA (Table 3) providing a higher MgO activity in OCM.

According to our data, strong basic sites, forming on the surface of active and selective OCM catalysts, indeed participate in methane activation. We have proved this by direct experiments on methane interaction with MgO surface by means of IR and UV spectroscopy. This fact is also supported by quantum-chemical calculations [14]. All these data show that heterolytic methane activation is possible only on sites like $Mg^{2+}O^{2-}$, involving 3-coordinate oxygen ions, which are less coordinated and thus the most active basic sites.

Therefore, we can explain the reasons for a high catalytic activity of Sm_2O_3/MgO systems (Table 4) and design catalysts by varying BS strength and number. We can do this (i) by doping catalysts with various admixtures and (ii) by increasing the number of coordinatively unsaturated states on the surface via, e.g., mechanical activation. The latter serves for structure disordering and increases the coordinatively unsaturated sites number.

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