

ACTIVATION OF HYDROCARBONS IN THE OXIDATIVE DIMERIZATION OF
METHANE OVER ALKALINE EARTH METALS

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Oxidative dimerization of methane over alkaline earth metal oxides and phosphates has been studied. The rate-determining step is heterolytic C-H bond dissociation of methane on surface basic sites of the catalysts.

Изучена окислительная димеризация метана на оксидах и фосфатах щелочно-земельных металлов. Показано, что лимитирующей стадией реакции является гетеролитический разрыв C-H связи метана на основных центрах поверхности контакта.

It has been suggested previously [1] that the first step of selective oxidative conversions of hydrocarbons is the heterolytic C-H bond activation in methyl groups with displacement of a proton to a nucleophilic oxygen atom.

The aim of the present study is to examine the activation character of methane in oxidative dimerization over alkaline earth metal oxides and phosphates.

EXPERIMENTAL

Oxides of analytical grade alkaline earth metals (Mg, Ca, Sr, Ba) and their phosphates obtained from equimolar amounts of double-substituted ammonium phosphate and the respective metal nitrate, with subsequent drying at 423 K and 4 h calcination at 1073 K, were used as catalysts.

Catalytic activity was measured in a gradientless reactor under flow conditions at 1153 K and $\tau = 0.2$ s by using 20 vol.% O_2 + 80 vol.% CH_4 reaction mixture.

Kinetic isotope effect measurements were carried out in a gradientless reactor under pulse conditions over MgO and CaO at 1123 K by using 10 vol.% O_2 + 90 vol.% CH_4 (or CD_4). Several pulses of a CH_4 -containing mixture were admitted to the catalyst. Upon attaining a steady reaction rate, a pulse of a CD_4 -containing mixture was supplied.

Compositions of the initial mixture and reaction products were analyzed gas-chromatographically [2].

Concentration of surface base sites on the catalyst was determined like in Ref. [3].

RESULTS AND DISCUSSION

As is known, in deep oxidation and selective oxidative conversions of saturated hydrocarbons the rate-determining step involves heterolytic C-H bond dissociation in the paraffin molecule [1]. It ensures a considerable kinetic isotope effect when protium is substituted by deuterium [4-5].

To elucidate the character of the rate-determining step in oxidative dimerization of methane, we have compared dimerization rates of ordinary and deuterated methane on MgO and CaO. Experimental results are listed in Table 1. Reaction products are ethylene, ethane, CO and CO_2 with small amounts of C_3 - C_4 hydrocarbons.

As is seen from Table 1, the observed kinetic isotope effect is close to the theoretical value at the given temperature [6]. This suggests that the rate-determining step in oxidative dimerization of methane is C-H bond dissociation, which requires high activation energies. This suggestion agrees with the data [7] implying that the selectivity towards dimerization products rises with increasing temperature.

According to Ref. [1], the effective C-H bond activation for low-polar bond compounds like methane is possible in the presence of strong basic sites on the catalyst surface.

Table 1
 Kinetic isotope effect in oxidative dimerization of methane ($T = 1123 \text{ K}$, 0.5 cm^3
 catalyst samples, 10 vol.% O_2 + 90 vol.% CH_4 (or CD_4)

Catalyst	Hydrocarbon	CH ₄ conver- sion (%)	Reaction rate (10^{-13} molec. CH_4 / $\text{cm}^2 \text{ s}$)	C ₂ -C ₄	
				$\frac{W_{\text{total}}(\text{CH}_4)}{W_{\text{total}}(\text{CD}_4)}$	$\frac{W_{\text{C}_2\text{-C}_4}(\text{H})}{W_{\text{C}_2\text{-C}_4}(\text{D})}$
MgO	CH ₄	9.8	2.04	1.1	1.1
	CD ₄	8.9	1.85	1.0	1.1
CaO	CH ₄	11.9	33.7	21.25	1.12
	CD ₄	10.6	30.0	18.6	1.14

Reaction rates for oxidative dimerization of methane and concentrations of basic sites on alkaline earth metal oxides and phosphates are listed in Table 2.

Table 2
Dependence of oxidative dimerization rates of methane on the concentration of surface basic sites of catalysts
($T = 1153 \text{ K}$, $\tau = 0.2 \text{ s}$, 20 vol.% O_2 +80 vol.% CH_4)

Catalysts	Basicity ($10^{-6} \text{ mol C}_6\text{H}_5\text{COOH/m}^2$)	Reaction rate ($10^{-14} \text{ molec.CH}_4/\text{cm}^2 \text{ s}$)	
		total	$\text{C}_2\text{-H}_4$
<u>Phosphates</u>			
Mg	4.67	1.14	0.56
Ca	5.93	6.45	2.85
Sr	6.08	11.4	5.13
Ba	13.1	26.8	12.2
<u>Oxides</u>			
Mg	2.14	2.9	1.65
Ca	7.94	31.2	15.5
Sr	46.7	56.3	33.7
Ba	82.9	60.8	42.6

According to X-ray phase analysis data, Mg, Ca and Sr phosphates are orthophosphates and barium phosphate is a mixture of ortho- and pyrophosphates.

Studies of the dependence of the reaction rate on the catalyst basicity have revealed that the catalyst activity depends on its surface basicity. With increasing basicity, both the total reaction rate and the formation rate of dimerization products rise.

Thus, the results suggest that the rate-determining step

of oxidative dimerization of methane involves heterolytic C-H bond activation due to the presence of nucleophilic surface sites on the catalyst.

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