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Mechanisms of catalytic activation of methane and ethylene on magnesia surface elucidated by isotopic kinetics

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Abstract

Activation of C_nH_4 (n = 1,2) and H_2 on MgO, elucidated by new isotopic method, proceeds as a results of reversible adsorption with extraction of one atom H.

The use of the rigorous kinetic equations of redistribution of isotope molecules [1–3] allows to discriminate types of dissociation of molecules on the surface on the basis of kinetic parameters obtained from experimental data. It was shown that dissociation proceeds with formation of single atomic surface hydrogen:

I. $CH_4 + 2Z = ZCH_3 + ZH$

II. $C_2H_4 + 2Z = ZC_2H_3 + ZH$

III. $H_2 + 2Z = 2ZH$

The reversible performance of these reactions realizes the homoexchange (variants 1–3 in Table

Table 1
Rates of homoexchange (K) and heteroexchange (R) of methane, ethylene and dihydrogen on magnesium oxide ($P_A = P_B = 33.3$ Pa, T=295 and 688 K)

No	Isotopic variant		$K_A \cdot 10^{10}$ molecules / sec·sm^2		R_A/K_A	n_A	E_A, kj
	Exchanging gas	Exchange partner					
	A	B	295 K	688 K			
1	H_2+D_2	-	13	>100	-	1	-
2	CH_4+CD_4	-	<<0.1	1.8	-	1	85
3	$C_2H_4+C_2D_4$	-	1.5	>100	-	1	17
4	H_2+D_2	C_2H_4	9	>100	<<1	1	-
5	CH_4+CD_4	D_2	<<0.1	1.7	0.24	1	~90
6	$C_2H_4+C_2D_4$	D_2	0.5	>100	0.23	1	19
7	CH_4+CD_4	C_2D_4	<<0.1	1.4	0.27	-	-
8	$C_2H_4+C_2D_4$	CD_4	~1	>100	<<1	-	-

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1). Addition of hydrogen leads to decreasing homoexchange rates of methane and ethylene.

The surface forms ZH in these reactions are identical. This conclusion follows from the experimental results of investigation of the heteroexchange between different chemical partners (variants 4–8): CH_4–H_2 (the result of simultaneously performance of reactions I and III), C_2H_4–H_2 (reactions II and III) and CH_4–C_2H_6 (reactions I and II). The heteroexchange rate in each of these cases is nearly equal to a quarter of the homoexchange rate (R_A/K_A in Table 1) of the less active partner. It means that one of four atoms of the molecule C_nH_4 is involved in an heteroexchange act (in accordance to reactions I and II).

1. References

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