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Potassium Effects on Kinetics of Propane Oxydehydrogenation on Vanadia-Titania Catalyst

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Oxidative dehydrogenation of propane (ODH) over V_2O_5/TiO_2 and V_2O_5/TiO_2 doped with K was carried out by measuring conversions and selectivities for various feed compositions, contact times and temperatures. The results obtained for both catalysts were interpreted on the basis of the mechanism, in which propene is formed through Eley-Rideal sequence of steps, *i.e.* without participation of the adsorbed propane species. Kinetic constants (activation energies, pre-exponential factors) for the model of ODH reaction of propane on these catalysts, obtained on the basis of steady-state results, are given. Addition of K to vanadia-titania catalysts leads to the decrease of total combustion of propane and consecutive combustion of propene. It has been found that the direct propane total oxidation is $5 \div 9$ times lower than that of the consecutive propene oxidation and is almost temperature independent for potassium doped catalyst, whereas it quickly decreases with temperature for a non-doped catalyst. Secondly, the addition of K to a vanadia-titania catalyst decreases the activation energies for propene formation (k_1), parallel formation of CO_x (k_3) and reoxidation of the catalyst (k_{OS}). Potassium exhibits a stronger inhibitory effect on the secondary propene combustion, what reflects the lower acidity of V^{+5} cations modified by the strongly basic alkali oxide species.

Key words: oxidative dehydrogenation of propane, kinetics model, potassium promotion

The oxidative dehydrogenation (ODH) of light alkanes provides a potential low temperature route for the synthesis of light alkenes [1–4], but its current practice is limited by the loss of alkene selectivity, particularly of propene, with increasing conversion [2,3,7–9], which leads to a propene yield lower than 30% [3]. Most oxidative dehydrogenation catalysts contain V or Mo oxides as the active component [3,7–9]. Many reports have suggested that the addition of alkalis increases the selectivity to propene on these catalysts [5–9], but the concurrent decrease in ODH rates leads to a lower conversion.

Kinetic information can give some insight into the reaction mechanism and the role of dopant on particular paths in propane ODH reaction. Papers, which have appeared recently on kinetics of the propane ODH, have been concerned with VMgO catalyst [10], unpromoted VTiO system [7,9,11], and vanadia supported on amorphous $AlPO_4$ [12]. Simple kinetic models were used in the studying the effect of promotion by alkali oxides (Cs, K, Li) of the MoO_3/ZrO_2 catalyst [13] and by K and Rb VTiO ca-

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talyst [17]. In the present work kinetics based on more complex model of the propane-oxygen interactions [9] for pure and K-doped vanadia-titania catalyst has been studied to check how potassium promotion affects the rates and energetics of the formation of different selective and non selective products and to explain in this way the effect of promotion on the activity and selectivity.

EXPERIMENTAL

The studied catalyst contained 1 monolayer (mnl) of vanadia phase deposited on TiO_2-anatase (22.5 m^2/g). Commercial TiO_2 (anatase) prior to preparation was calcined at 1023 K in order to remove sulfur from the surface of the support. A 1 mnl of V_2O_5 phase calculated from crystallographic data of V_2O_5 is equivalent to 10 V/nm^2. For given specific surface area of TiO_2 1 mnl catalyst contains 3.1% V_2O_5. The catalyst was prepared by impregnation from aqueous solution of ammonium metavanadate at pH = 6, followed by solvent evaporation, drying for 18 h at 393 K and calcination in a stream of air at 723 K for 5 h. 1 mnl VKTiO contained additionally a K promoter, the K /V ratio being equal to 0.1. The promoted VKTiO catalyst was obtained by adding the appropriate amount of potassium nitrate to the metavanadate solution.

Catalytic activity measurements: The activity of the catalyst in oxidative dehydrogenation of propane was measured in a fixed bed flow apparatus. A stainless steel reactor (120 mm long, id. 13 mm) was coupled directly to a series of gas chromatographs. Propane, propene, CO and CO_2 were found to be the main reaction products. The amounts of the degradation, C_2 products and oxygenates, were below 1% of the total amount of products. The details of experimental set-up can be found in [7]. The 0.4–0.5 g (0.5 ml) samples of a catalyst of the grain size 0.6–1 mm diluted with glass beads were used. Kinetic data are presented in the form of selectivities to different products ($Sel_p = c_p/\Sigma c_j$) (p = propene, CO and CO_2) and conversion ($Conv = (c_i - c_f)/c_i$) propane as a function of contact time (τ), composition of the reaction mixture and temperature, where c_i and c_f are the concentrations of propane at the entrance and the exit of the reactor, respectively and c_p is the concentration of product p in the exit gas. The experimental data and the results of modeling of the propane ODH reaction are collected in Table 1 and 2.

Table 1. Kinetic data for VTiO catalyst.

Contact time [s]	Temp [K]	propane/O_2 ratio	Experimental conversion of propane	Calculated conversion of propane	Experimental selectivity to propene	Calculated selectivity to propene	Experimental selectivity to CO_x	Calculated selectivity to CO_x
0.5	250	1/2.6	0.032	0.032	0.501	0.501	0.500	0.500
1.0			0.041	0.041	0.421	0.366	0.579	0.635
1.5			0.060	0.060	0.308	0.297	0.691	0.704
0.5		1/1.2	0.024	0.024	0.595	0.595	0.406	0.406
1.0			0.034	0.037	0.501	0.447	0.509	0.553
1.5			0.045	0.050	0.404	0.373	0.597	0.627
0.5		2/1	0.018	0.018	0.698	0.698	0.302	0.302
1.0			0.027	0.027	0.581	0.541	0.420	0.459
1.5			0.033	0.033	0.511	0.463	0.490	0.537

Table 1 (continuation)

0.5	270	1/2.6	0.057	0.057	0.381	0.381	0.620	0.620
1.0			0.079	0.087	0.287	0.262	0.713	0.738
1.5			0.109	0.116	0.204	0.202	0.796	0.798
0.5		1/1.2	0.040	0.040	0.503	0.503	0.497	0.497
1.0			0.062	0.062	0.364	0.353	0.636	0.647
1.5			0.088	0.084	0.262	0.280	0.738	0.720
0.5		2/1	0.033	0.033	0.589	0.589	0.412	0.412
1.0			0.048	0.049	0.459	0.442	0.542	0.559
1.5			0.060	0.064	0.379	0.367	0.622	0.634
0.25	300	1/2.6	0.070	0.070	0.387	0.387	0.614	0.614
0.5			0.121	0.103	0.246	0.256	0.755	0.744
1.0			0.177	0.166	0.156	0.150	0.843	0.850
1.5			0.229	0.225	0.107	0.104	0.903	0.896
0.25		1/1.2	0.057	0.057	0.451	0.451	0.550	0.550
0.5			0.102	0.082	0.295	0.318	0.706	0.682
1.0			0.152	0.129	0.189	0.205	0.812	0.796
1.5			0.194	0.173	0.138	0.153	0.863	0.848
0.5		2.1	0.081	0.081	0.371	0.371	0.629	0.629
1.0			0.119	0.112	0.260	0.276	0.740	0.724
1.5			0.137	0.139	0.218	0.228	0.782	0.772
0.25	320	1/2.6	0.116	0.116	0.285	0.285	0.716	0.716
0.5			0.186	0.167	0.180	0.178	0.821	0.882
1.0			0.276	0.262	0.103	0.094	0.898	0.906
1.5			0.353	0.347	0.068	0.060	0.782	0.940
0.25		1/1.2	0.108	0.108	0.313	0.313	0.688	0.688
0.5			0.172	0.146	0.199	0.220	0.801	0.781
1.0			0.250	0.215	0.121	0.136	0.880	0.864
1.5			0.293	0.275	0.094	0.099	0.907	0.901
0.5		2/1	0.150	0.150	0.249	0.249	0.752	0.752
1.0			0.173	0.184	0.204	0.202	0.796	0.798
1.5			0.169	0.199	0.203	0.193	0.798	0.808

Table 2. Kinetic data for VKTiO catalyst.

Contact time [s]	Temp [K]	propane/O_2 ratio	Experimental conversion of propane	Calculated conversion of propane	Experimental selectivity to propene	Calculated selectivity to propene	Experimental selectivity to CO_x	Calculated selectivity to CO_x
0.5	300	2/1	0.016	0.016	0.507	0.507	0.493	0.493
1.0			0.036	0.033	0.407	0.394	0.594	0.606
2.0			0.079	0.065	0.361	0.334	0.640	0.666
3.0			0.088	0.094	0.290	0.308	0.710	0.692
0.5		1/1	0.015	0.015	0.429	0.429	0.572	0.572
1.0			0.041	0.037	0.337	0.327	0.662	0.673
2.0			0.079	0.079	0.289	0.277	0.711	0.731
3.0			0.098	0.118	0.271	0.253	0.729	0.761
0.5		1/2	0.019	0.019	0.444	0.444	0.556	0.556
1.0			0.047	0.043	0.361	0.329	0.639	0.671
2.0			0.082	0.089	0.249	0.269	0.751	0.731
3.0			0.120	0.133	0.273	0.239	0.727	0.761
0.5	320	2/1	0.025	0.025	0.515	0.515	0.485	0.485
1.0			0.053	0.049	0.388	0.371	0.612	0.629
2.0			0.107	0.092	0.313	0.291	0.686	0.709
3.0			0.120	0.130	0.233	0.260	0.767	0.740
0.5		1/1	0.028	0.028	0.463	0.463	0.564	0.564
1.0			0.069	0.049	0.277	0.318	0.723	0.695
2.0			0.118	0.092	0.233	0.239	0.766	0.767
3.0			0.138	0.130	0.268	0.205	0.732	0.800
0.5		1/2	0.035	0.035	0.468	0.468	0.532	0.532
1.0			0.073	0.069	0.291	0.318	0.709	0.682
2.0			0.129	0.133	0.194	0.230	0.806	0.770
3.0			0.166	0.192	0.205	0.190	0.795	0.810
0.5	340	2/1	0.049	0.049	0.457	0.457	0.543	0.543
1.0			0.089	0.080	0.304	0.335	0.695	0.665
2.0			0.146	0.134	0.277	0.254	0.723	0.746
2.0		1/1	0.017	0.017	0.181	0.181	0.819	0.819
3.0			0.203	0.103	0.172	0.166	0.828	0.834

Table 2 (continuation)

0.5		1/2	0.197	0.197	0.156	0.156	0.843	0.843
1.0			0.255	0.274	0.163	0.126	0.837	0.873
0.5		2/1	0.082	0.082	0.394	0.394	0.605	0.605
1.0			0.137	0.121	0.260	0.292	0.740	0.707
0.5		1/1 1/1	0.086	0.086	0.331	0.331	0.668	0.668
1.0	360		0.139	0.141	0.230	0.224	0.770	0.776
2.0			0.222	0.236	0.138	0.149	0.861	0.851
0.5	360	1/2	0.096	0.096	0.328	0.328	0.672	0.672
1.0			0.190	0.157	0.185	0.213	0.815	0.787
2.0			0.279	0.268	0.108	0.131	0.892	0.869
3.0			0.338	0.363	0.117	0.094	0.883	0.906
0.5	400	1/1	0.234	0.234	0.186	0.186	0.813	0.813
1.0			0.266	0.302	0.167	0.131	0.833	0.868
0.5		1/2	0.278	0.278	0.149	0.149	0.850	0.850
1.0			0.402	0.366	0.095	0.095	0.905	0.904
2.0			0.418	0.507	0.111	0.051	0.888	0.949

RESULTS AND DISCUSSION

Our previous experiments [8,17] have shown that the total activity in ODH of propane is lower for K promoted than for non-promoted catalysts. However, the propene yields and selectivities at equal conversion are higher for a K doped catalyst. The data for both catalysts under study, presented in Table 1 and 2, show, that the increase in conversion of propane with the increase in contact time and/or temperature is accompanied by a considerable decrease in selectivity to propene and at the same time by an increase in the selectivity to CO_x ($S_{CO_x} = S_{CO} + S_{CO_2}$). Some amounts of carbon oxides are also observed at low conversions. Such a course of changes of the selectivities with the conversion implies a parallel-consecutive mechanism of formation of carbon oxides from propane. As it was shown in [9], the most appropriate model is based on the assumption that the alkane is not adsorbed at the catalyst surface and reacts directly from the gas phase (Eley-Rideal type mechanism). The reaction products desorb immediately from the catalyst surface to the gas phase, leaving oxygen vacancies. At the catalyst surface, stationary oxygen coverage is established [14,15]. The surface oxygen is responsible both for the selective ODH of propane and for the total oxidation reactions. Equations (1)–(4) represent the sequence of the reaction steps of the propane ODH.

$$C_3H_{8(g)} + O_S \xrightarrow{k_1} C_3H_{6(g)} + H_2O_{(g)} + V \qquad (1)$$

(R) (Π)

$$C_3H_{6(g)} + 3(1+x)\,O_S \xrightarrow{k_2} 3CO_{x(g)} + 3H_2O_{(g)} + 3(1+x)V \qquad (2)$$

$$C_3H_{8(g)} + (4+3x)\,O_S \xrightarrow[k_{OS}]{k_3} 3CO_{x(g)} + 4H_2O_{(g)} + (4+3x)V \qquad (3)$$

$$O_2 + 2V \longrightarrow 2O_S \qquad (4)$$

in which V – denotes a surface oxygen vacancy and O_S – surface oxygen. It is obvious that none of the above reactions is an elementary reaction. As it was showed in a transient experiments [9], hydrocarbon reacts directly from the gas phase with the surface oxygen of the catalyst, the reaction products desorb quickly and the surface is not blocked. However, the curves for $CO_x(CO+CO_2)$ obtained in transient experiments have a different shape than that for propene (fast initial increase is followed by an equally fast decrease, more steeper than that for propene), what suggests different orders with respect to oxygen coverage in propene and CO_x formation. These orders are taken as 1 and 2 respectively. At the same time, reactions (1)–(3) should be of the first order with the respect to propane and propene concentrations respectively.

The analysis of the evolution of the selectivities to propene and to CO_x and of the conversion of propane was performed using the method proposed by M. Ai *et al.* [16]. This leads to an ordinary differential equation, which can be written as

$$\frac{d\theta}{dt} = 2\cdot k_{OS}\cdot\sqrt{c_O}\cdot(1-\theta) - k_1 c_R\cdot\theta - k_2\cdot c_\Pi\cdot\theta^2 - k_3\cdot c_R\cdot\theta^2 = 0 \qquad (5)$$

where θ is the surface coverage by oxygen, and c_R, c_Π, c_O are concentrations of propane, propene and oxygen in the gas phase. In the case of reaction (4) two possibilities were considered: a) the adsorption of gaseous oxygen on the vacancies is slow compared to its dissociation and therefore the reaction rate is proportional to the oxygen concentration c_O; b) the oxygen dissociation is slow, thus the rate is proportional to $c_O^{0.5}$. As it was showed in [9], oxygen is replenished by the dissociative adsorption and the rate of this process is proportional to $c_O^{0.5}$. At steady-state conditions $d\theta/dt$ should vanish, leading to an algebraic equation, which should be solved in relation to θ.

The set of differential equations describing propane, propene and CO_x concentrations in the gas phase can be written as:

Concentration of propane in reaction mixture $\dfrac{dc_R}{d\tau} = -c_R\cdot(k_1\cdot\theta + k_3\cdot\theta^2)$ (6)

Concentration of propene $$\frac{dc_{\Pi}}{d\tau} = k_1 \cdot c_R \cdot \theta - k_2 \cdot c_{\Pi} \cdot \theta^2 \tag{7}$$

Concentration of Co_x $$\frac{dc_{CO_x}}{d\tau} = 3 \cdot (k_2 \cdot c_{\Pi} + k_3 \cdot c_R) \cdot \theta^2 \tag{8}$$

where: τ – contact time.

The integration of (6–8) for the above described model, using the values of surface coverages obtained by solution of (5) and the minimization of the object function defined as a sum of squared differences of experimental and calculated selectivities and conversions, were performed using coupled Runge-Kutta and Marquardt methods in a program written in BASIC. Table 4 gives the activation energies and pre-exponential factors for the different reaction steps, obtained by fitting the above-described model to the experimental data for both catalysts. As can be seen from the calculated results, the fit obtained with the model is better for non-doped than for potassium doped catalyst (matching error is 7 and 8.6%, respectively). In Table 3 the results of approximate lack of fit test are also given. Comparison of the results with the appropriate tabulated F value revealed no lack of fit. Figures 1 and 2 show the parity plots for both studied catalysts obtained from the fitted multiresponse model for conversion of propane, selectivity to propene and CO_x.

Table 3. Approximate lack of fit test (SS_{lf}/SS_{pe})*.

Response	VTiO catalyst SS^2_{lf}/SS^2_{pe}	VKTiO catalyst SS^2_{lf}/SS^2_{pe}
Conversion of propane	1.76	0.73
Selectivity to propene	1.26	0.76
Selectivity to CO_x	1.18	0.74
Deegres of freedom for each response	F(21, 11, 0.95) = 2.28 $\nu_{lf} = 40$, $\nu_{pe} = 12$	F(28, 9, 0.95) = 2.24 $\nu_{1f} = 45$, $\nu_{pe} = 10$

*SS_{lf}, sum of squares for lack of fit, SS_{pe}, sum of squares for pure error.

Table 4. Rate constants for VO_x/TiO_2 catalyst undoped and doped by K in ODH reaction of propane.

Catalyst	Rate constants				Fit error [%]
	k_1	k_2	k_3	k_{OS}	
VTiO	77* (37.7)**	13950 (43.9)	672900 (71.7)	12715000 (82.4)	7.0
573 K	0.028	1.388	0.195	0.391	
VKTiO	2 (22.1)	20520 (54.4)	7400 (56.8)	51600 (60.3)	8.6
573 K	0.012	0.278	0.050	0.159	

* pre-exponential factor
** activation energy [kJ/mol] in parentheses
***k_i values at 573 K

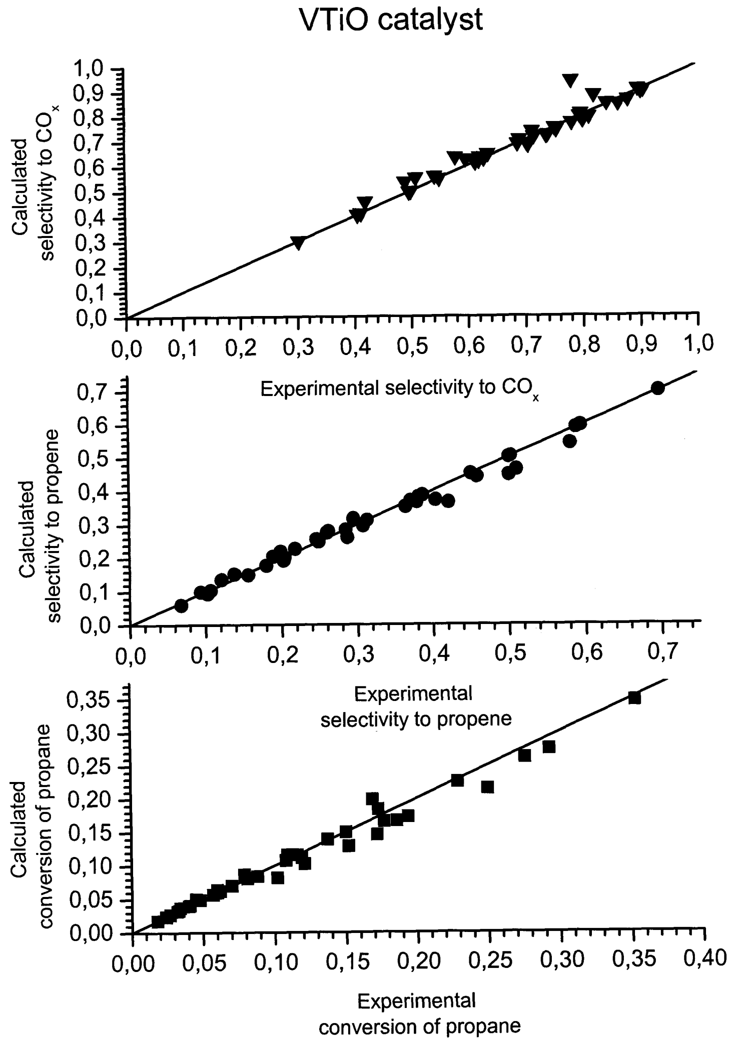

Figure 1. Parity plots for conversion of propane, selectivity to propene and CO$_x$ for VTiO catalyst.

As can be seen from Table 4, the activation energies obtained for doped and non-doped catalyst change in a different way for different stages of the reaction. Concurrently, the presence of potassium increases the activation energy for propene total oxidation (k_2) and decreases all remaining activation energies (k_1, k_3, k_{OS}). At the same time pre-exponential coefficients strongly decrease for rate constants (k_1, k_3, k_{OS}) and slightly increase for k_2, when potassium is added to VTiO catalyst in the studied temperature range. In Fig. 3 changes with the temperature of k_3/k_1, $k_1/(k_2+k_3)$ and k_2/k_1 for both catalysts are shown. The k_3/k_1 ratio reflects the contribution of the parallel combustion of propane. As can be seen from this figure, this ratio is smaller

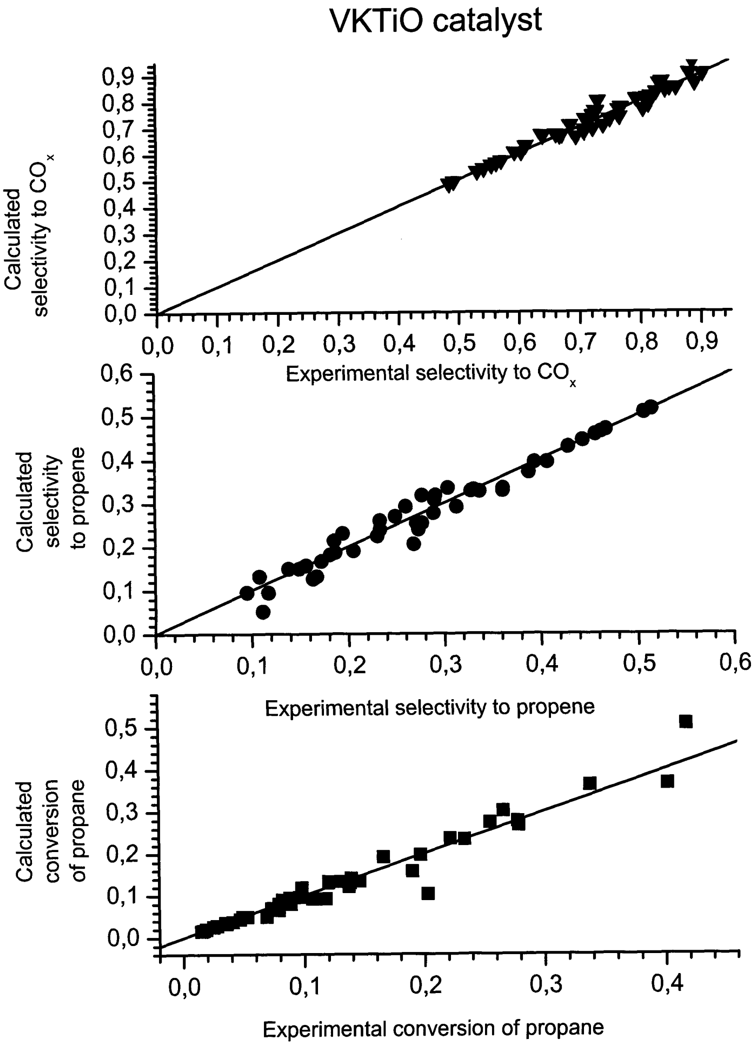

Figure 2. Parity plots for conversion of propane, selectivity to propene and CO$_x$ for VKTiO catalyst.

for the catalyst doped by potassium than for a non-doped catalyst. Similar effect was observed for vanadia-titania catalyst promoted by Rb [17]. This effect could be explained by the involvement of chemisorbed oxygen in parallel reaction, as it was postulated for methane or ethane [18]. As shown in the measurements of surface potential, performed on potassium doped titania [19] and vanadia-titania and molybdena-titania catalysts [20], potassium located on oxide ions changes the sign of the surface dipole and indeed decreases the number of O$^-$ chemisorbed species. A little stronger (especially at low temperatures) effect of potassium addition is observed for

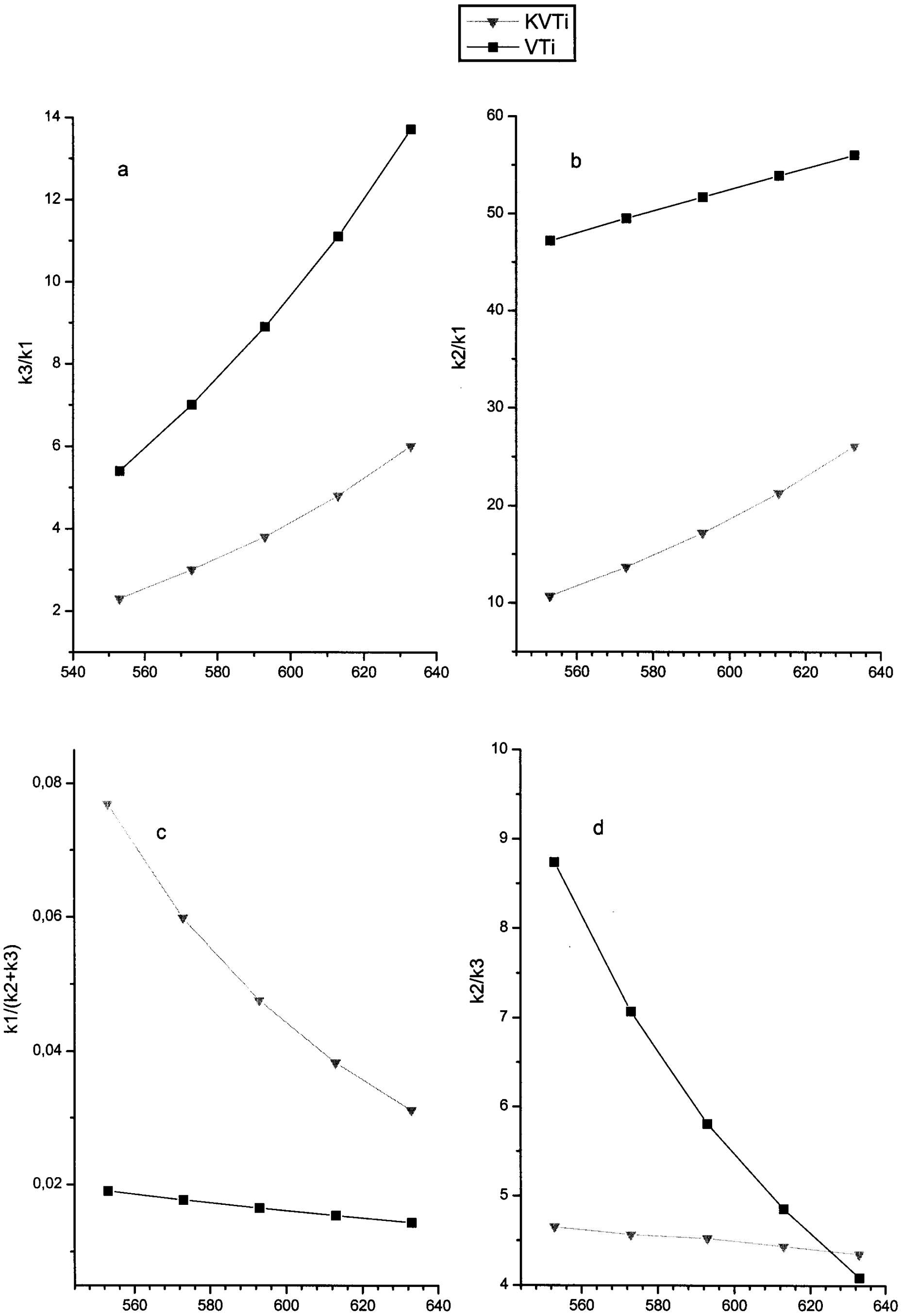

Figure 3. Temperature dependence of k_3/k_1, k_2/k_1, $(k_3 + k_2)/k_1$ and k_2/k_3 values for VTiO catalyst and VKTiO catalyst.

k_2/k_1 ratio (Fig. 3b). It seems that the decisive factor in the consecutive reaction is that propene molecules contain a π-bond, which makes them more basic than propane. Addition of strongly basic potassium leads to electron transfer from K, increasing the electron density on V^{+5} cation, which becomes more basic. Indeed, measurements of acid-base properties have shown the decrease in the acidity and the increase in basicity of V_2O_5-TiO_2 catalysts on doping with alkalis [21]. These results correspond to the decrease of the heat adsorption of propene, observed for the alkali promoted catalysts [21,13]. Concluding: the apparent activation energy for propene combustion (Table 4) containing heat of adsorption should be higher for the alkali promoted VTiO catalyst. From this fact it follows that the desorption of propene from the K-doped catalyst will be easier and hence k_2/k_1 ratio must be smaller. This decrease in k_2/k_1 ratio causes the observed higher propene selectivity on potassium-modified vanadium-titania catalyst. The influence of the potassium on selectivity to propene is better visible in Fig. 3c, where the ratio of selective reaction (k_1 – formation of propene) to total oxidation ($k_2 + k_3$ – combustion of propane and propene) as a function of temperature is shown. On the basis of this information, changes of k_2/k_3 can be estimated (Fig. 3d) and it is evident that in the case of a potassium promoted catalyst, the ratio is equal about 5 and changes only little with the temperature. For an undoped catalyst, the ratio is changed quickly with the temperature (9÷5). From the kinetic calculations it is clear, that the difference between a doped and an undoped catalyst results from the fact that the most active centers are poisoned by K and on the surface remain only those with lower activation energies (decrease of the all pre-exponential factors and the activation energies but those of the consecutive combustion of propene).

CONCLUSIONS

1. The propane-oxygen reaction on vanadia-titania catalyst can be described adequately by a parallel consecutive kinetic network. According to the model based on this network, carbon oxides are formed in parallel oxidation of propane (k_3) and consecutive oxidation of propene (k_2).
2. Contribution of the direct propane total oxidation to formation of carbon oxides is 5÷9 times lower than that of the consecutive propene oxidation. It is almost independent of the temperature for a potassium doped catalyst and quickly decreases with temperature for a non-doped catalyst.
3. Addition of K to vanadia-titania catalyst decreases the activation energies for propene formation (k_1), parallel formation of CO_x (k_3) and reoxidation of the catalyst (k_{OS}) and increases for consecutive oxidation of propene (k_2). Lowering of the rate constants results mainly from the decrease of pre-exponential factors, due to the blocking of the active centers of the catalyst by potassium.
4. Addition of potassium leads to the increase in basicity and decrease in acidity of the catalyst. These changes in acid-base properties decrease the interaction between propene and the surface of the catalyst and in consequence contribute to the observed increase of the selectivity to propene.

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