Kinetics of Heterogeneous and/or Homogeneous Catalytic Decomposition of Hydrogen Peroxide by Some Metal Vanadates and Their Primary Oxide Mixtures

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A study of the kinetics of catalytic decomposition of H_2O_2 by some metal (M) vanadates and their primary oxide mixtures, where M=Mg, Ca, Ni, Cu and $(Cu_{0.5}+Mg_{0.5})$ for catalysts (*I–V*), respectively, reveals that the decomposition reaction is homogeneous for catalysts (*I* and *II*), whereas for (*III—V*) the early stages of the reaction are mainly heterogeneous. However, whenever the vanadium, nickel or copper ions go into solution, in the form of the peroxo compounds of vanadium(V), they catalyze the reaction homogeneously at relatively low decomposition rates. Significance of the concept of bivalent catalytic centres towards enhancement of the catalyst activity has been established. It was found that the parameter which best characterizes the intrinsic order of catalytic activity is the activation entropy of the reaction and not the activation energy deduced. The activity order of catalysts (*I—V*) calcined in air at 500, 700 and 1000 °C for 5 hours was found to be *IV>V>III>II>I*.

INTRODUCTION

Drastic chemical and structural changes take place when mixtures of ammonium metavanadate and metal oxides are thermally treated under isothermal condition.[1,2] The result is the formation of the corresponding metal oxides and/or metal vanadates with structures depending on the calcination temperature.[2] These catalysts have found important applications in the field of selective oxidation reactions, for example, in the oxidation of methanol to formaldehyde,[3,4] *o*-xylene to phthalic anhydride[5,6] and benzene to maleic anhydride,[7] and other oxidation processes.[8,9] Interesting information might be gained from a study of these two-component catalysts, *i. e.* vanadium pentoxide with some metal oxides, as well as their calcination products, using the decomposition of hydrogen peroxide as a test reaction.

In order to specify the catalytic activity of the produced metal vanadates and their primary oxide mixtures towards the decomposition of H_2O_2 in aqueous media, the fol-

lowing questions must be answered. What is the contribution of the homogeneous catalytic part to the overall decomposition process?[10] Can the concept of bivalent catalytic centres be applied to these catalyst systems or not?[11] Which kinetic parameter can be taken as an intrinsic measure of catalytic activity?[12,13] The present paper reports an investigation of H_2O_2 decomposition catalyzed by some metal oxide-vanadium pentoxide mixtures (500 °C) and their calcination products (700 and 1000 °C) taking these points into account.

EXPERIMENTAL

Materials

All the reagents used in the present investigation were of analytical grade (BDH chemicals). Mixing of ammonium metavanadate with MgO, CaO, NiO and CuO was carried out in an agate mortar in a ratio of 2 : 1.[1,2] Twenty minutes were needed to obtain a homogeneous mixture. Parent mixtures were calcined in air for 5 hours at 500, 700 and 1000 °C. The catalyst samples applied in the present investigation are $Mg_{1.0}-V_{2.0}-O$ (I), $Ca_{1.0}-V_{2.0}-O$ (II), $Ni_{1.0}-V_{2.0}-O$ (III), $Cu_{1.0}-V_{2.0}-O$ (IV) and $Cu_{0.5}-Mg_{0.5}-V_{2.0}-O$ (V).

Apparatus and Technique,

The X-ray diffraction patterns were recorded using a Philips X-ray diffractometer, model PW 1710. A Philips generator operated at 40 kV and 30 mA provided the source of $CuK\alpha$ radiation (Ni filtered). Scanning speed was 2 deg. min^{-1}. The XRD patterns were matched with ASTM cards.[14]

The activity of the mixed oxide and/or vanadate catalysts towards H_2O_2 decomposition was determined in the liquid phase using the gasometric technique proposed by Deren et al.[15] A constant catalyst weight (10-50 mg, depending on the catalytic activity of the sample applied) was injected into a thermostated reaction vessel containing 5 cm^3 H_2O_2 (35.5 %). The oxygen evolution rate was monitored for a given temperature at atmospheric pressure, the oxygen displacing water from a Bunte gas burette. The time-dependent volume of evolved oxygen was monitored at 15-60 second intervals. The results were corrected for the self-decomposition of H_2O_2.[12,16] The oxygen evolution rate was found to be independent of the stirring speed[11] and directly proportional to the catalyst mass used in the reaction mixture.

Spectrophotometric measurements were made on a Shimadzu UV-200 S double beam spectrophotometer, using a rectangular cell of 1 cm pathlenght against hydrogen peroxide as blank. The pH changes in the H_2O_2 solution were monitored on Accumet pH-meter Model 810 (Fisher Scientific company).

RESULTS

Characterization

To detect any chemical or structural change, all the catalyst samples were subjected to X-ray analysis. The values obtained for the d-plane spacing and their relative intensities of reflection were compared with relevant ASTM cards[14] in order to determine the major phases present. The X-ray analysis data for different catalyst samples (I–V) calcined at 500–1000 °C for 5 hours are presented in Table I.

Catalytic Activity

Analysis of experimental data was carried out on the assumption[15,17] that the decomposition of H_2O_2 is a first order process. As the maximal conversion observed after 30 minutes never exceeded 0.05, it may be assumed in the first approximation that the reaction runs at a constant concentration of H_2O_2. In such conditions, integration of

TABLE I

The characteristic phases present in the catalysts (I—V) calcined at different temperatures for 5 hours.

Calcination temp. (°C)	Catalyst				
	I	II	III	IV	V
500	V_2O_5 + MgO	V_2O_5 + $Ca(OH)_2$ + $Ca_3V_2O_8$	V_2O_5 + NiO	β-$Cu_2V_2O_7$ + α-CuV_2O_6 + V_2O_5 + CuO	V_2O_5 + α-CuV_2O_6 + CuO + MgO
700	MgV_2O_6 + V_2O_5	Q + $Ca_3V_2O_8$	$Ni_2V_2O_7$ + V_2O_5 + NiV_3O_8	α-$Cu_2V_2O_7$ + α-CuV_2O_6	MgV_2O_6 + $Cu_2V_4O_{11}$ + Q
1000	$Mg(VO_3)_2$ + MgV_2O_6	Q + CaV_2O_6 + $Ca_2V_6O_{17}$	NiV_3O_8	$Cu_3V_2O_8$ + α-$Cu_2V_2O_7$	Q + α-CuV_2O_6 + α-$Cu_2V_2O_7$ + $Cu_2V_4O_{11}$ + MgV_2O_6 + $Mg(VO_3)_2$

Q = non-characterized phase.

TABLE II

Rate constants (k), activation energies ($\Delta E^{\neq}$), pre-exponential factors (A) and thermodynamic parameters of activation for H_2O_2 decomposition on catalysts (I—V) calcined at different temperatures for 5 hours

Catalyst	Calcination temperature (Tc/°C)	k (s^{-1} g^{-1})					$\Delta E^{\neq}$* kJ.mol^{-1}	ln A* (sec^{-1})	$\Delta H^{\neq}$** kJmol^{-1} (303 °K)	$\Delta G^{\neq}$** kJmol^{-1} (303 °K)	$\Delta S^{\neq}$** J K^{-1} mol^{-1} (303 °K)
		20 °C	25 °C	30 °C	35 °C	40 °C					
I	500	0.413	0.552	0.739	0.970	1.271	42.804	16.704	40.285	75.026	−114.66
	700	0.375	0.522	0.723	0.975	1.310	47.574	18.578	45.055	75.081	−99.10
	1000	0.186	0.273	0.399	0.571	0.815	56.125	21.381	53.606	76.578	−75.82
II	500	0.141	0.209	0.308	0.445	0.642	57.552	21.689	55.033	77.230	−73.26
	700	0.160	0.241	0.361	0.527	0.767	59.807	22.743	57.288	76.830	−64.50
	1000	0.056	0.088	0.137	0.210	0.317	66.452	24.415	63.933	79.271	−50.62
III	500	0.420	0.700	1.162	1.883	3.004	74.939	29.925	72.420	73.885	−4.83
	700	0.142	0.231	0.373	0.589	0.923	71.785	27.535	69.266	76.748	−24.69
	1000	0.070	0.120	0.202	0.332	0.536	77.270	29.101	74.751	78.293	−11.69
IV	500	1.756	3.050	5.259	8.758	14.732	81.039	33.858	78.520	70.082	+27.85
	700	1.889	3.004	4.807	7.389	11.508	69.427	29.155	66.908	70.308	−11.22
	1000	0.122	0.546	0.898	1.439	2.293	73.962	29.279	71.443	74.535	−10.20
V	500	1.556	2.560	4.221	8.248	10.773	73.836	30.776	71.317	70.636	+2.25
	700	1.323	2.090	3.320	5.155	7.870	69.221	28.703	66.702	71.241	−14.98
	1000	0.292	0.475	0.779	1.234	1.964	73.937	29.127	71.418	74.893	−11.47

* Calculated using Arrhenius equation.
** Calculated using Eyring equation.

the first order equation gives $v = v_0 + kt$, where v is the volume of oxygen evolved at time t and v_0 the volume of oxygen evolved up to the moment at which the time measurement started. The rate constant k was computed from the slope of v–t plots and was found to be directly proportional to the catalyst mass and to increase with temperature in accordance with the Arrhenius equation. Figure 1 (a–e) shows volume v of oxygen evolved as a function of time t at 36.5 °C for the catalyst samples (I–V) cal-
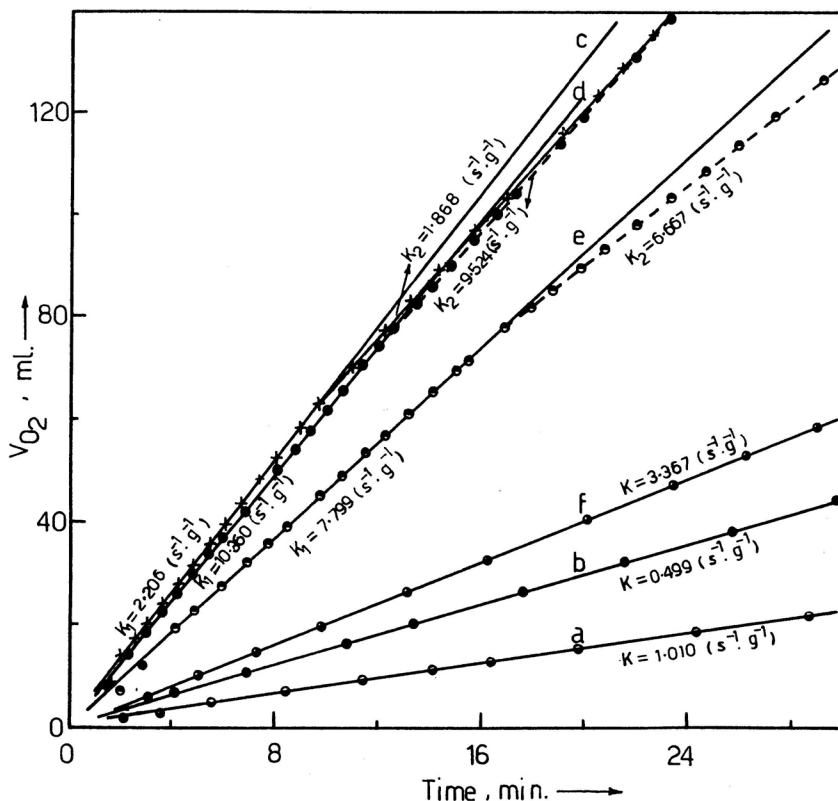
Figure 1. *V–t* plots for H$_2$O$_2$ decomposition at 36.5 °C by the catalysts (*I-V*) calcined at 500 °C for 5 hours. Plots (a–e) for 10, 50,50; 10 and 10 mg of catalysts (*I–V*), respectively. Plot (f) for the homogeneous decomposition of H$_2$O$_2$ by the solution leached by H$_2$O$_2$ (24 hours) from catalyst (*IV*).

cined at 500 °C. The linear *v–t* plot is indicative of reaction kinetics which is zero order with respect to H$_2$O$_2$ as indicated above. Deviations from linearity, which increase with increasing reaction temperature, can be seen for samples (*III–V*). In Figure 2 the initial rate constants (k) per second per unit mass of catalyst at 35 °C are plotted as a function of the calcination temperature (T_c) of the catalyst, and the corresponding activation energies (calculated by the mean square root method) are plotted in Figure 3. The maximum error check of k values is ± 1.5 % and reproducibility was good. The error in activation energy is $\pm$ 3.6 kJ mol^{-1}. The decomposition activation parameters $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ were evaluated using the Eyring equation[13,18] and are given in Table II. The variation of entropy of activation with the calcination temperature for the different catalyst samples (*I–V*) is shown in Figure 4. The changes in activation enthalpy and entropy evaluated in this study were subject to an experimental error of $\pm$ 1.5 kJ mol^{-1} and $\pm$ 1.3 J K^{-1} mol^{-1}, respectively.

The following experiment was carried out to check the role of the homogeneous process in the most catalytically active sample (*i. e.* copper-vanadium-oxygen catalyst sample calcined at 500 °C).Where 50 mg of sample (*IV*) (*i. e.* five times that used in

the analysis of the catalyst (*IV*) activity) was added to 5 ml of 35.5 % H_2O_2 solution. The reaction mixture was allowed to stand for 24 hours to ensure complete decomposition of hydrogen peroxide. The catalyst was then filtered off; 1 ml of the filtrate was added to 5 ml of fresh 35.5 % H_2O_2 solution and the kinetics of the homogeneous decomposition was followed at 36.5 °C, Figure 1 f.
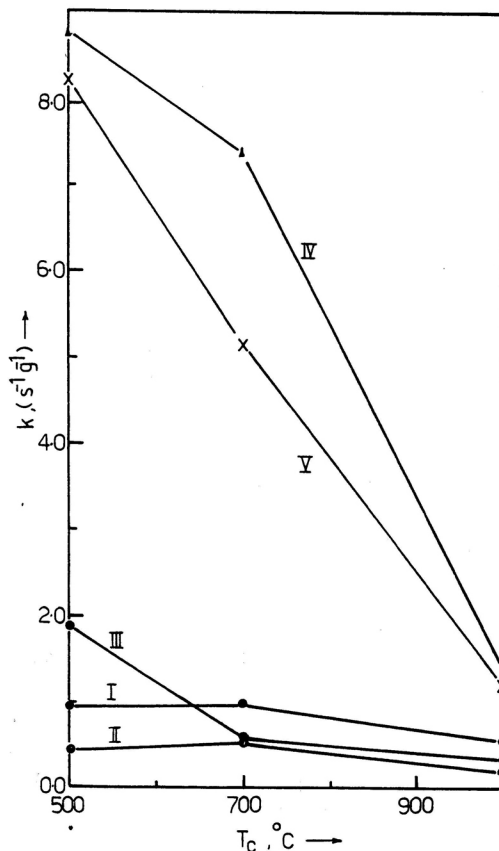

Figure 2. Plots of the rate constant (*k*) for the decomposition of H_2O_2 at 35 °C by the calcination products of the catalysts (*I—V*) as a function of the calcination temperature (T_c).

DISCUSSION

The X-ray analyses data summarized in Table I reveal that the major phases present in the catalyst (*I-V*) samples calcined at 500 °C are the primary metal oxides. Raising the calcination temperature up to 1000 °C, the metal vanadates represent the major constituents.

The activities of the catalysts investigated are checked using the decomposition of hydrogen peroxide in aqueous solution as a model catalytic process.[19] It has been stated[11,20] that the pentavalent vanadium containing structures exhibit a dissolution ten-
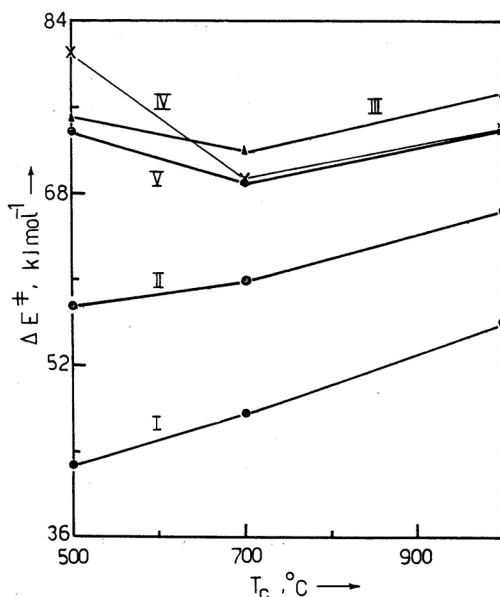
Figure 3. Plots of the activation energy ($\Delta E^{\neq}$) for the H_2O_2 decomposition vs. T_c for the catalysts (I—V).

dency in hydrogen peroxide solution accompanied by a rapid drop in the pH value of the solution.[11] The dissolution process results in creation of diperoxoorthovanadate(V) ions,[20] $[VO_2(O_2)_2]^{3-}$, which, in turn, are transformed to peroxovanadate(V) ions,[11, 20] $[V(O_2)]^{3+}$.

UV-visible spectrophotometric studies at 25 °C on the filtrates extracted from (catalysts (I–V) + H_2O_2) as well as (V_2O_5 + H_2O_2) system, in which all solid samples were calcined at 500, 700 and 1000 °C, indicate the presence of two absorption bands, for all solutions, at 225 and 327 nm. This can be taken as good evidence for formation of the yellow coloured[20] diperoxoorthovanadate(V) ions (eq. 1):

$$V^{5+} + 4\,H_2O_2 = [VO_2(O_2)_2]^{3-} + 8\,H^+ + O_2 \qquad (1)$$
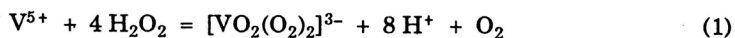
which transformed in time, due to the low pH value produced (≤ 1.12), to the red-brown peroxo compound of vanadium(V) (eq. 2):

$$[VO_2(O_2)_2]^{3-} + 6\,H^+ = [V(O_2)]^{3+} + H_2O_2 + 2\,H_2O \qquad (2)$$
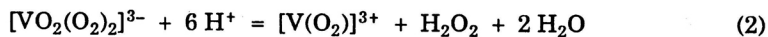
Examining the plots of O_2 volume (v) against the time of evolution for catalysts (I–V), Figure 1 (a–e), reveals the following:

(i)   Complete linear v–t plots are observed for the Mg– and Ca– catalysts (I and II);
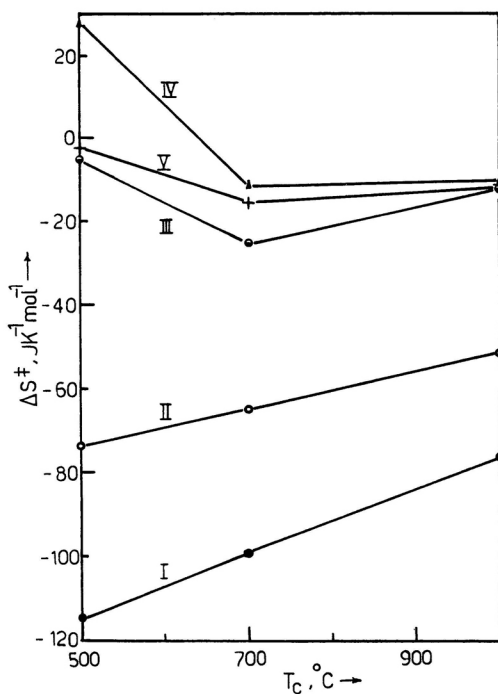(ii) Deviation from linearity can be seen for the other three Ni– and Cu– catalysts (III–V);

Figure 4. Plots of the activation entropy ($\Delta S^{\neq}$) for the H_2O_2 decomposition *vs.* T_c for the catalysts (*I—V*).

(iii) The activity order (k), considering the calcination products at 500 °C under similar experimental conditions is:

IV > V >> III > I > II. Figure 2 shows that the catalysts calcined at 700 and 1000 °C have the activity order:

IV > V >> I > III ≈ II.

The activity of copper catalyst (*IV, V*) superseded that of nickel (*III*). This can be accounted for by the concept of bivalent catalytic centres,[13,21] according to which the activity of nickel catalyst (*III*) is governed by the Ni^{3+} ions present.[11,22] The concentration of these ions is low due to the presence of a large amount of V^{5+} ions. A charge interaction is assumed to occur, where the concentration of Ni^{3+} ions drops largely in the presence of large concentration of V^{5+} ions.[11] Thus, the minor catalytic centres are the Ni^{3+} ions in equilibrium with the major Ni^{2+} centres and the redox-couple mechanism postulated is hindered.[13]

Catalysts of types (*I–V*) exhibit an EPR signal belonging to the V^{4+} ion.[11] In the case of samples (*I*) and (*II*) calcined at 500 °C, the solid catalysts dissolved rapidly and completely in the hydrogen peroxide solution forming the peroxovanadate(V) ions $[V(O_2)]^{3+}$, where the produced homogeneous solutions have pH's equals to 0.53 and 0.67, respectively. Thus, their activity reflects the activity of the dissolved peroxo-compounds of vanadium(V), giving linear v–t plots with low (k) values. Mucka[11] found that

the dissolution of vanadium(V) containing catalysts is partially hindered in the presence of some metal oxides. As the content of these oxides is increased, the relative amount of dissolved species decreased. For catalysts (*III–V*), the first decomposition periods, which mainly represent heterogeneous catalytic stages, involve the contribution of Cu^+/V^{5+}, Cu^{2+}/V^{4+} and Ni^{2+}/V^{5+}, Ni^{3+}/V^{4+} mixed catalytic centres[11] in addition to the main redox-couple centres Cu^{2+}/Cu^+ and Ni^{3+}/Ni^{2+}.[13,19] Due to the relatively slow[11] dissolution of vanadium(V) ions in the hydrogen peroxide solution, in the course of the reaction, a pronounced decrease in the catalytic activity follows. Thus, the activity (k_1) of the first reaction stages is greater than that (k_2) of the last ones and thus broken $v–t$ plots for the last three catalysts (*III–V*) are obtained.

Careful examination of plots d, f and a (Figure 1) may answer the question of the extent of contribution of homogeneous catalysis to the overall decomposition process. For the most catalytically active sample (*IV*), it was found experimentally that i) the rate (k_1 = 10.36 s^{-1}g^{-1}) of the first reaction steps, which are mainly heterogeneous in nature (Figure 1 d), is about three times the rate (k = 3.37 s^{-1}g^{-1}) of the homogeneous catalytic reaction displayed in the bulk of the solution (Figure 1 f); ii) the rate of the homogeneous reaction (k = 3.37 s^{-1}g^{-1}) for the Cu-catalyst (*IV*) is more than six times that for the Mg-catalyst (*I*). This can be attributed to the dissolution of the Cu^{2+} ions, in addition to the V^{5+} ones, of the copper meta- and pyrovanadates in the solution, which thus participate and play a great part in the homogeneous catalytic decomposition reaction of H_2O_2, *i. e.* the potent redox couple centres Cu^{2+}/Cu^+ are established in the bulk of solution, which normally are absent in the case of the Mg-catalyst (*I*).

Since the catalyst samples (*I–V*) dissolve completely (*I*) or partially (*II–V*) in the course of hydrogen peroxide decomposition reaction, the suggestion of Cota *et al.*[23] that the reaction rate should be normalized to unit surface area, thus offering an intrinsic catalytic activity, is invalid in the present investigation. At the same time, the internal surface (pores) of the undissolved solid residue of the catalysts make no contribution to H_2O_2 decomposition in aqueous media.[12] Therefore, the rate constants in the present investigation are expressed per unit mass of catalyst, *i. e.* s^{-1}g^{-1}.

The final goal in the present study is to arrive at an intrinsic order of catalyst activities which is much more dependent on the chemical and eletronical structure than on the microstructural features, *i. e.* surface nonstoichiometry and area. One possible approach to ascertaining the intrinsic activity is to make use of a kinetic parameter which is effectively independent of the catalyst microstructure for each of the catalyst samples (*I-V*). A suitable choice of such a parameter would be the activation energy or entropy for the peroxide decomposition reaction. These kinetic parameters depend on catalyst composition rather than on surface morphology.[24] Thus, the values of activation energy (Figure 3) and entropy (Figure 4) were evaluated at different calcination temperatures (T_c).

The catalyst activities in the samples (*I–V*) may be compared on the basis that the most effective H_2O_2 decomposition catalyst possesses the lowest activation energy value. For the 500 °C catalysts, the activity order is *I > II > V > III > IV*, whereas for the 700 and 1000 °C catalysts, the activity order is *I > II > V > IV > III*, Figure 3. Accordingly, the order of the apparent activation energies deduced did not reflect the actual order[13, 25–27] of catalyst activities, *i. e.* this activity order is suspect. In an investigation for the decomposition of H_2O_2 with inorganic salts, Tumanova *et al.*[26] found that the most active inhibiting cation is Mg^{2+}. This cation blocks decomposition of H_2O_2 in bleaching processes.[27] The relatively low activation energies for catalysts (*I*)

and (II) compared with (III-V) may be attributed to their rapid and complete dissolution in H_2O_2 solution giving homogeneous solutions of relatively low reaction activation energies, i. e. the V^{5+} ions go into solution and catalyze the decomposition homogeneously. In the case of catalysts (III–V), it is plausible to suggest that the early stages of H_2O_2 decomposition are purely heterogeneous and the diffusion-control effects[12] in the heterogeneous peroxide decomposition reaction play a significant role. According to Goldstein et al.,[12] when reaction turbulence occurs near the surface of a solid dispersed in a liquid, a thin liquid layer adheres to the solid surface. Furthermore, they reported[12] that for peroxide decomposition characterized by a three phase (liquid-solid-gas (oxygen)) heterogeneous reaction, the ingress of fresh reactant (H_2O_2) through such a layer to the solid (catalyst) surface to sustain the reaction becomes restricted. The high values of the activation energy for catalysts (III–V) compared with those for (I and II), were consistent with this diffusion-control phenomenon. There is in each case (III–V) a pronounced minimum at 700 °C. The increase in $\Delta E^{\neq}$ beyond this value in samples (III–V) is consistent with a lower mean aggregate diameter,[13] which promotes the diffusion control effect on the catalysts activity, leading to an increase in activation energy, Figure 3. The restricted redox-couple mechanism (Ni^{2+}/Ni^{3+}) could account for the poor activity of the Ni-catalyst (III) calcined at 700 and 1000 °C relative to the Cu-catalysts (IV and V).[13] The relatively low activation energy recorded for the Ni-catalyst calcined at 500 °C is suspect, because steric hindrance accompanying the attainment of $\Delta E^{\neq}$ is not reflected in the activation entropy, as shown in Figure 4. This figure shows clearly that in the present work the parameter which best characterized the intrinsic order of activity is the activation entropy $\Delta S^{\neq}$ of the reaction. The values of the $\Delta S^{\neq}$ in the peroxide-catalysed decomposition could be related to the more easily available redox couple Cu^{2+}/Cu^+ or the entropy of adsorption of the peroxide on the catalyst.[13] This postulation is reflected in the less negative $\Delta S^{\neq}$ values recorded for the Cu-catalyst (IV) than for the Ni-sample (III). Thus, the variation of entropy with composition (Figure 4) is considered to be significant in the overall assessment of the five catalyst samples (I–V). Nevertheless, the activities of the five catalyst samples may be compared on the basis that the more effective catalyst for peroxide decomposition possessed a less negative entropy without a corresponding low activation energy. In this work, an attempt has been made to establish the activity order of the five catalysts considered using the composition factor. Thus, the activity order of the catalysts (I–V) calcinated at 500, 700 and 1000 °C is IV > V > III > II > I.

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SAŽETAK

Kinetika heterogene i homogene katalitičke razgradnje vodikova peroksida nekim metalnim vanadatima i njihovim smjesama s primarnim oksidima

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Studij kinetike katalitičke razgradnje H_2O_2 metalnim vanadatima i njihovim smjesama s primarnim oksidima upućuje na homogenu reakciju razgradnje za neke katalizatore, dok su za druge katalizatore početni koraci reakcije uglavnom heterogeni. Kada ioni vanadija, nikla i bakra prelaze u otopinu u obliku perokso-spojeva vanadija(V), oni homogeno kataliziraju reakciju uz relativno niske brzine razgradnje. Potvrđena je uloga dvovalentnih metalnih iona u poboljšanju katalitičke aktivnosti. Nađeno je da aktivacijska entropija kao parametar najbolje karakterizira slijed katalitičke aktivnosti.