Catalytic behaviour of metal ions located at different sites of heteropolycompounds

Yue Wu [1], Shu-Huo Qu, Hui-Min Ma and Sing-Kei Ye

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin 130022, PR China

Received 24 February 1993; accepted 11 August 1993

It was discovered experimentally that heteropolymolybdophosphoric acids (HPA) with Keggin and Dawson structure are inactive for H_2O_2-decomposition, while their salts (Fe^{3+}, Cu^{2+}, Co^{2+} and Mn^{2+}) all possess more activity. It could be concluded that the active species is the countercation of these kinds of heteropolymolybdates. The molybdenum ions in the polyanions are not active. If the molybdenum ions in the polyanions of these acids are substituted partly by vanadium ion (HPA-*n*), then not only does the catalytic activity increase regularly with the number of vanadium ions substituted (*n*) but the kinetic curve is also different from that of the salt, characterized by an S-shape, indicating the formation of an active intermediate as a result of the reaction between the polyanion of HPA-*n* and the substrate.

Keywords: H_2O_2-decomposition; heteropolycompounds; Keggin structure; Dawson structure

1. Introduction

In recent years, it has been brought to universal attention that heteropolyacid (HPA) and its salt function as catalysts because they act as both acid and redox catalyst [1]. In order to investigate the catalytic behaviour of HPA (salt) we selected the H_2O_2-decomposition as a diagnostic reaction because the catalytic behaviour of HPA (salt) toward this reaction is distinctive, i.e. the different catalytic behaviour depends on the nature of the countercations as well as on the metallic ion in the heteropolyanion. The kinetic curves of H_2O_2-decomposition catalyzed by the countercation of heteropolymolybdate show a conventional hyperbolic shape, while those of H_2O_2-decomposition catalyzed by the polyanion containing vanadium ion show an S-shape, indicating that the effect of the cations in different parts of HPA (salt) on its function as a catalyst is various.

---

[1] To whom correspondence should be addressed.

2. Experimental

2.1. MATERIALS AND REAGENTS

(1) 30% H_2O_2: A.R. grade.

(2) HPA: $H_3(PMo_{12}O_{40})$, $H_6(P_2Mo_{18}O_{62})$.

(3) HPA-n: $H_{3+n}[PMo_{12-n}V_nO_{40}]$ ($n = 1,2,3,4,6$), $H_{6+n}[P_2Mo_{18-n}V_nO_{62}]$ ($n = 2,3,4$).

(4) Salts of HPA: $Fe(PMo_{12}O_{40})$, $M_3(PMo_{12}O_{40})_2$ (M = Co, Cu, Mn), $Fe_2[P_2Mo_{18}O_{62}]$, $M_3[P_2Mo_{18}O_{62}]$ (M = Cu).

All HPA (salt) were prepared in our laboratory, according to ref. [2]; HPA containing vanadium ion $n > 4$ by using the method described in ref. [3]. The structure of HPA (salt) was confirmed by its IR and X-ray powder diffraction pattern. As shown in fig. 1 and table 1, the infrared spectra of some representative samples in the P–O, Mo–O stretching region are shown with those of Keggin and Dawson structure [4] (abbreviated as KS and DS).

2.2. KINETIC STUDY OF THE H_2O_2-DECOMPOSITION

The kinetics were followed on a manometer as reported elsewhere [5]. During the experiment a certain amount of aqueous solution of the catalyst was first added to the reaction bottle. Then the magnetic stirrer was started and the reaction temperature was controlled by circulating thermostatic water (±0.5°C). After the temperature became constant, H_2O_2 was injected into the bottle. The time the reaction started was recorded and the volume of oxygen released was measured with a gas burette.

2.3. UV–VIS INVESTIGATION

The intermediates formed during reactions were confirmed by means of UV–

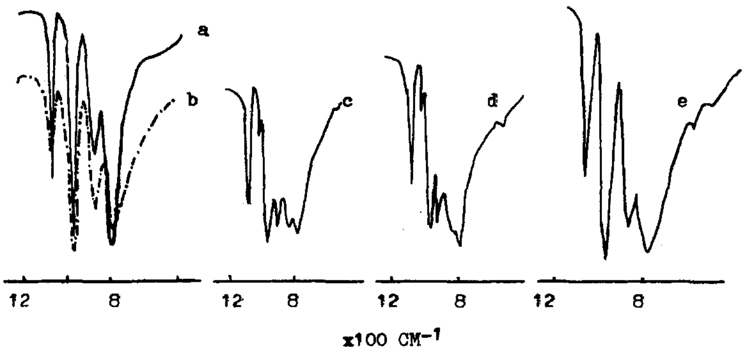

Fig. 1. Infrared spectra of some representative samples in KBr pellets. (a) $H_3PMo_{12}O_{40}$, (b) $H_5PMo_{10}V_2O_{40}$, (c) $H_6P_2Mo_{18}O_{62}$, (d) $Fe_2P_2Mo_{18}O_{62}$, (e) $H_8P_2Mo_{16}V_2O_{62}$.

Table 1
IR spectra of HPA (salt)

Structure	Compound[a]	ν (cm^{-1})		
		P–O$_p$	M=O$_t$	M–O–M
Keggin	H_3PMo_{12} (a)	1065	960	870 790
	$FePMo_{12}$	1060	955	860 770
	$H_5PMo_{10}V_2$ (b)	1060	955	860 780
	$H_7PMo_8V_4$	1055	955	855 780
Dawson	$H_6P_2Mo_{18}$ (c)	1080 1008	950 906	835 780
	$Fe_2P_2Mo_{18}$ (d)	1078 1000	945 905	830 775
	$H_8P_2Mo_{16}V_2$ (e)	1062	965	870 785
	$H_{10}P_2Mo_{14}V_4$	1060	960	865 780

[a] (a), (b), (c), (d), (e) correspond to the curves in fig. 1.

Vis study, using a Specord UV–VIS spectrophotometer (Carl Zeiss, Jena) at room temperature.

3. Results and discussion

3.1. CATALYTIC ACTIVITY OF HETEROPOLYMOLYBDOPHOSPHORIC ACID (HPA) WITH KS AS WELL AS DS FOR THE DECOMPOSITION OF H_2O_2

12-molybdophosphoric acid with KS is one the most noticeable HPA-catalysts, but few papers deal with the DS. It was found that varying of the reaction temperature, the concentration of catalysts, $[H_3(PMo_{12}O_{40})]$ and $[H_6P_2Mo_{18}O_{62}]$, as well as of $[H_2O_2]_{\text{initial}}$ has only a negligible effect on the rate of H_2O_2-decomposition. These results indicate that $H_3(PMo_{12}O_{40})$ and $H_6(P_2Mo_{18}O_{62})$, independent of their structure, do not possess catalytic activity towards the H_2O_2-decomposition. It also means that neither proton (H^+) nor heterpolyanion $(PMo_{12}O_{40})^{3+}$ and $(P_2Mo_{18}O_{62})^{6+}$ are active species.

3.2. CATALYTIC ACTIVITY OF HETEROPOLYMOLYBDOPHOSPHATES WITH DIFFERENT STRUCTURES IN THE H_2O_2-DECOMPOSITION

The salts of HPA with KS such as $Fe(PMo_{12}O_{40}), Co_3(PMo_{12}O_{40})_2$, $Cu_3(PMo_{12}O_{40})_2, Mn_3(PMo_{12}O_{40})_2$ made by substitution of H^+ in HPA with corresponding metallic ions all have higher activity in the decomposition of H_2O_2. Taking $Fe(PMo_{12}O_{40})$ as an example, when both the concentrations of $Fe(PMo_{12}O_{40})$ (0.01–0.08 mol/ℓ) and $[H_2O_2]_{\text{initial}}$ (0.56–1.87 mol/ℓ) were changed, a series of hyperbolic shape kinetic curves were obtained just as with Fenton's reagent [6]. Furthermore, there is a good linear relation if $\log(V_\infty - V_m)$ was plotted against time, as shown in fig. 2, where V_m and V_∞ are volumes [NTP] of O_2 evolved at reaction time m and total decomposition of H_2O_2. The rate equation of the H_2O_2-decomposition could be thus described for $PMo_{12}(KS)$ as

$$-\frac{d[H_2O_2]}{dt} = k[H_2O_2][\text{Cat-KS}]. \tag{1}$$

This relationship held also its validity for temperature variation. The activation energy calculated from Arrhenius plot is ~ 95 kJ/mol.

From these results it could be concluded that the active species in this reaction system is the countercation Fe^{3+} in the heteropolymolybdate, which acts just as that of Fe^{3+} in the Fenton reagent. The results obtained from other heteropolymolybdates were almost the same.

Heteropolymolybdates with DS are much more active than those with KS, although their apparent kinetic behaviour is the same as that with KS (hyperbolic shape curve) but it does not obey first order kinetics with respect to H_2O_2. A plot of $1/[H_2O_2]$ i.e. $1/(V_\infty - V_m) = 1/\Delta V$ versus t is linear, which means that a second order relationship would be obtained. The second order rate law is also applicable to data obtained by varying the reaction temperature as shown in fig. 3. Activation energy calculated from Arrhenius plot is 210 kJ/mol.

The effect of catalyst concentration upon the kinetics of the H_2O_2-decomposition is different from that of the concentration of reactant $[H_2O_2]$. Plotting the logarithmic value of the initial rate of reaction (log W_0) against the logarithmic value of catalyst concentration, as shown in fig. 4, a straight line could be obtained the slope of which is about 1.0. This means that the H_2O_2-decomposition reaction is first order with respect to catalyst concentration.

Based upon the kinetic studies the rate equation for this reaction system could be described as

$$-\frac{d[H_2O_2]}{dt} = k[H_2O_2]^2[\text{Cat-DS}]. \tag{2}$$

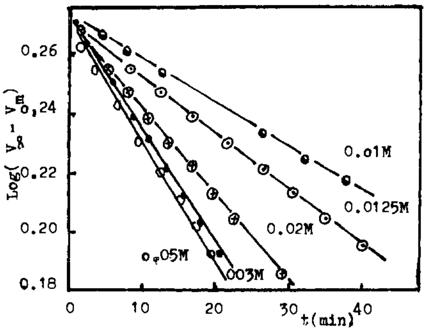

Fig. 2. Relation of $\log(V_\infty - V_m)$ with time (t) for H_2O_2-decomposition under different concentrations of catalyst. $[H_2O_2]_{\text{initial}} = 1.87\,\text{mol}/\ell$, $T = 35°C$.

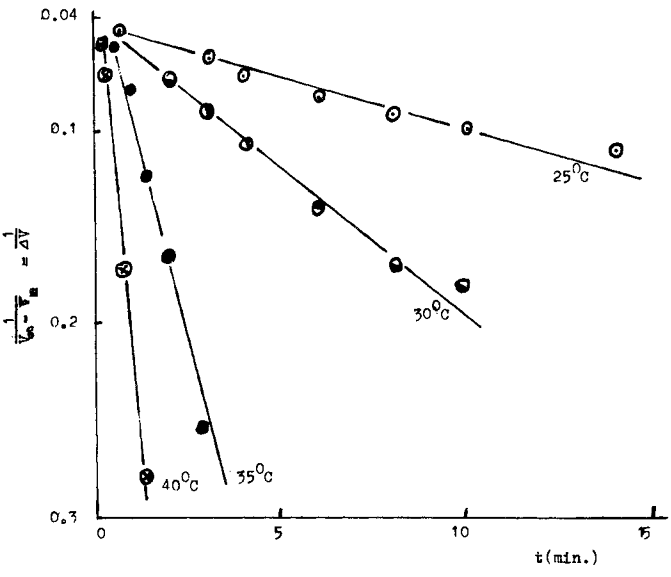

Fig. 3. Plot of second order kinetic data for H_2O_2 decomposition by $Fe_2(P_2Mo_{18}O_{62})$.

The rate equations (1) and (2) might account for the difference of reaction order with respect to $[H_2O_2]$ in both systems (1 : 2), in that there exist in one DS-molecule twice as much Fe^{3+} ions as in one KS-molecule.

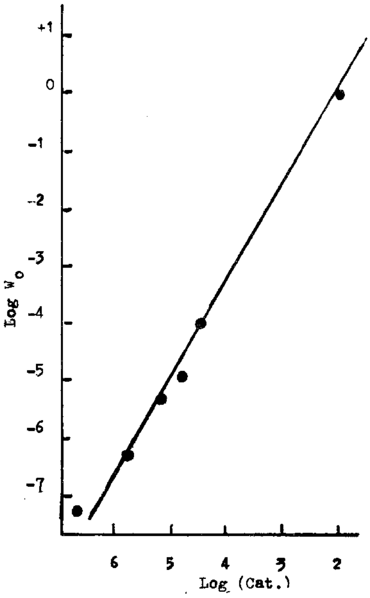

Fig. 4. Plot of log W_0 versus log[Cat-DS]. Reaction conditions: $[H_2O_2]_{\text{initial}} = 0.96\,\text{mol}/\ell$, $T = 35°\text{C}$.

3.3. CATALYTIC ACTION OF HETEROPOLYMOLYBDOPHOSPHORIC ACID CONTAINING VANADIUM ION (HPA-*n*) IN H_2O_2-DECOMPOSITION

If part of the molybdenum ions in the heteropolyanion with different structure were substituted by vanadium ions a highly active catalyst toward the H_2O_2-decomposition could be obtained. This phenomenon is evidently connected with the substituted vanadium ion. The catalytic activity of these two kinds of heteropolymolybdophosphoric acids containing different numbers of vanadium ions toward H_2O_2-decomposition are shown in figs. 5 and 6.

Experimental results showed that the reaction rate increases with increasing V/Mo ratio. Moreover, the kinetic behaviour of these kinds of catalysts is, entirely different from that of Fenton's reagent as well as of heteropolymolybdophosphate, independent of variations in the concentration of catalyst, $[H_2O_2]_{\text{initial}}$ and temperature. In all cases only S-shape curves were obtained. According to chain reaction theory [7], this kind of reaction belongs to the degenerated branching one, involving the formation of an active intermediate between the catalyst and the substrate, which can initiate the formulation of free radicals more easily than the reaction molecules, or, according to general kinetic theory to autocatalytic reaction [8], involving the formation of some product which can accelerate the reaction itself.

Treating the S-shape curves with H_2O_2 conversion less than 50% following the degenerated branching reaction mechanism, i.e. plotting $\log \Delta V$ versus time (t), a straight line should be obtained. This is just what we have obtained in our experiments, one example is given in fig. 7. It means that the decomposition kinetics of H_2O_2 now obeys Semenoff's equation:

$$\Delta V = Ae^{kt} . \tag{3}$$

From the kinetic curves (figs. 5 and 6) it could be seen that the reaction occurs in two stages. In the initial stage, there is no relation between the reaction rate and the consumption of H_2O_2 – since the concentration of H_2O_2 is far more than that of the catalyst, it makes the reaction to proceed according to zero order – but as soon as some active intermediates are formed due to the action between catalyst

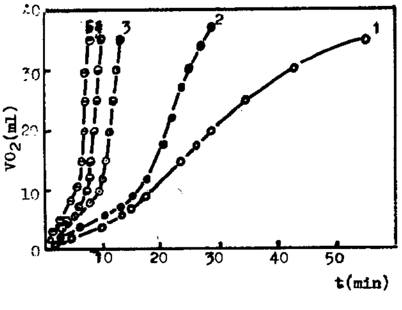

Fig. 5. Kinetic curves of H_2O_2 decomposition catalyzed by $H_{3+n}PMo_{12-n}V_nO_{40}$ ($n = 1,2,3,4,6$). [Cat-KS] = 0.14 mol/ℓ; $T = 35°C$, $[H_2O_2]_{\text{initial}} = 2.77$ mol/ℓ.

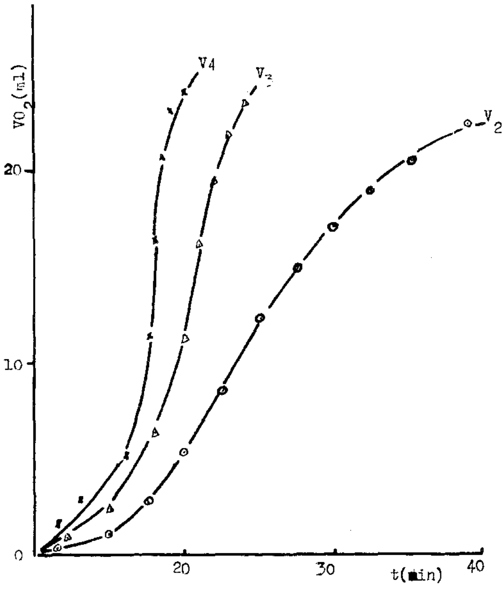

Fig. 6. Kinetic curves of H_2O_2 decomposition catalyzed by $H_{6+n}P_2Mo_{18-n}V_nO_{62}$ ($n = 2, 3, 4$). [Cat-DS] = 0.08 mol/ℓ, $T = 35$°C, $[H_2O_2]_{\text{initial}} = 0.96$ mol/ℓ.

and H_2O_2, a chain (or autocatalytic) reaction could take place at once and the reaction steps into the second stage. The activation energies obtained by treating the kinetic curves of the initial stage according to zero order rate law and that of the second stage following the degenerated branching kinetic equation, are given in table 2. It could be seen that the values of initial stage (E_1) are very close to the acti-

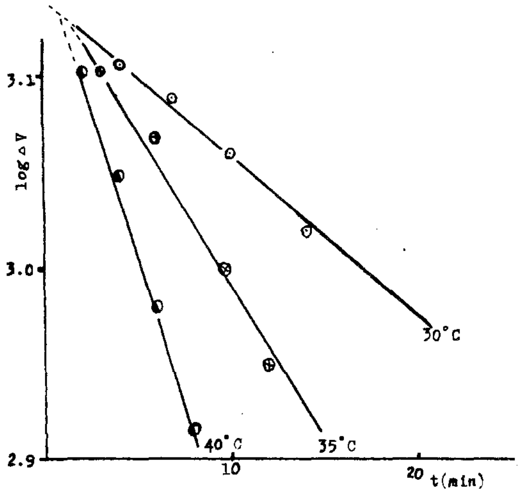

Fig. 7. Relationship between log ΔV and H_2O_2 decomposition time with $H_{6+n}P_2Mo_{18-n}V_nO_{62}$ as catalyst. $[H_{10}P_2Mo_{14}V_4O_{62}] = 0.08$ mol/ℓ, $[H_2O_2]_{\text{initial}} = 0.96$ mol/ℓ, $T = 30, 35, 40$°C.

Table 2
Energy of activation of H_2O_2-decomposition catalyzed by vanadium ion substituted heteropolymolybdophosphoric acids

Catalyst	E_1 (kJ/mol)	E_2 (kJ/mol)
Fenton reagent	90.4	–
$H_4PMo_{11}VO_{40}$	97.5	114.6
$H_5PMo_{10}V_2O_{40}$	91.6	71.1
$H_6PMo_9V_3O_{40}$	91.2	57.3
$H_7PMo_8V_4O_{40}$	102.9	41.3
$H_{10}P_2Mo_{14}V_4O_{62}$	89.1	57.7

vation energy of H_2O_2 decomposition catalyzed by Fenton's reagent and that, no matter what the number of substituted vanadium ions is, the values almost remain constant. In the second stage, the E_2's decrease proportionally with every increase of number of vanadium ions. These results fully state that the catalytic activity of the heteropolymolybdophosphoric acid substituted by vanadium ions (HPA-*n*) in this reaction is in close relationship with the number of vanadium ions.

The changes in absorption spectra of H_2O_2-decomposition catalyzed by HPA-*n* with different structures were traced during the reaction. Examples of the results obtained are shown in figs. 8 and 9. After H_2O_2 has been added into the system, a minus absorption appeared at 19.80×10^3 cm^{-1} with the reaction being in the first stage and indicating the formation of an associated complex of catalyst with H_2O_2, which was the same as that when reducing agent (e.g. ascorbic acid) was added into the system. It could be concluded that reduction of HPA-*n* by H_2O_2 occurs in the initial period (fig. 8 (1)). With the color of the solution gradually changing from orange into dark red, a plus absorption band developed at 18.52×10^3 cm^{-1} and the reaction began to accelerate while the minus absorption at 19.80×10^3 cm^{-1} decreased (fig. 8 (2)). With the rapid consumption of H_2O_2,

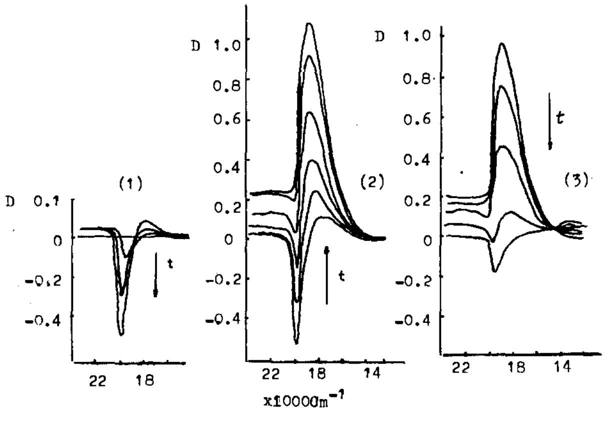

Fig. 8. Spectral evolution of H_2O_2 decomposition catalyzed by HPA-2 (KS).

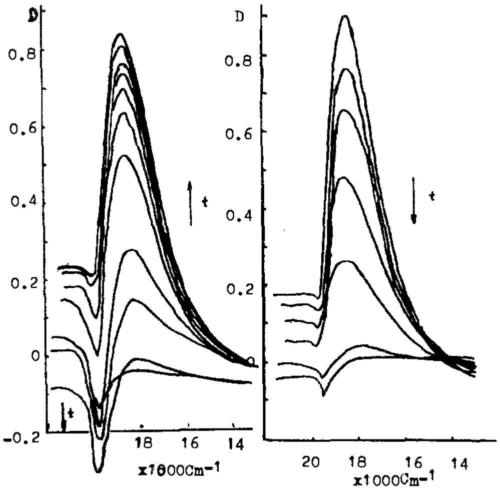

Fig. 9. Spectral evolution of H_2O_2 decomposition catalyzed by HPA-2 (DS).

the absorption peak at 18.52×10^3 cm^{-1} began to decline. Finally when the reaction ended, the minus absorption at 19.80×10^3 cm^{-1} appeared again as shown in fig. 8 (3). This indicated that the catalyst was not fully regenerated; a part still remained in reduced state. Drawing figures with the absorbance at 18.50×10^3 cm^{-1} versus time (t), we obtained from the value of optical density an S-shape curve (figs. 10 and 11), which completely coincides with the kinetic curves of H_2O_2-decomposition.

It is very unexpected that the same results have been obtained from HPA-n with different structure, including the kinetic behaviour, spectral evolution and energy of activation in the first and second stages (E_1 and E_2). The unique reasonable explanation might consist in the similar environment of the vanadium ion in KS and DS.

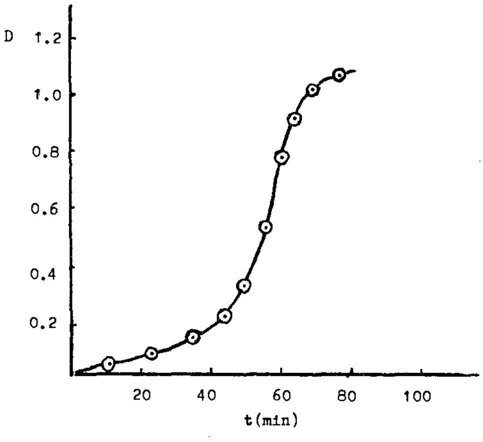

Fig. 10. Absorbance at 18.52×10^3 cm^{-1} as a function of time. Catalyst: HPA-2-KS.

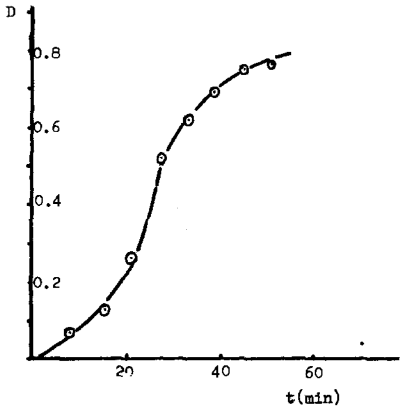

Fig. 11. Absorbance at 18.52×10^3 cm^{-1} as a function of time. Catalyst: HPA-2-DS.

4. Conclusion

Metallic ions in different parts of HPA (salt) possess different catalytic behaviour in H_2O_2-decomposition. In general, the countercation in the salt plays the role of a free cation as iron in Fenton's reagent. Nevertheless, vanadium ion in the heteropolyanion is characterized by the formation of an intermediate from the reaction with the reagent playing a major role in the activation of H_2O_2. The catalytic activity of HPA substituted by vanadium (HPA-*n*) is in close relationship with the nature of the active cation, i.e. the number of the vanadium ions independent of their structure (KS or DS).

Acknowledgement

We thank the National Natural Science Foundation of China for support of this work.

References

[1] M. Misono, Kagaku no Ryiki 35 (1981) 519, in Japanese;
I.B. Kozhevnikov and K.I. Matveeb, Usp. Khim. 51 (1982) 1875, in Russian;
B. Xu and Y. Wu, Chemistry (China) (4) (1985) 32, in Chinese.
[2] G.A. Tsigdinos, Ind. Eng. Chem. Prod. Res. Dev. 13 (1974) 267;
I.B. Kozhevnikov and K.I. Matveeb, Appl. Catal. 5 (1983) 135;
A. Aoshima and T. Yamaguchi, Chem. Soc. Japan (1985) 2237.
[3] Y.-G. Chen, E.-B. Wang, S.-L. Zhao, J.-F. Liu and R.-L. Zheng, Inorg. Chem. (China) 1 (1985) 21; C.A. 105 71418g (1986).
[4] S.P. Harmalker, M.A. Leparulo and M.T. Pope, J. Am. Chem. Soc. 105 (1983) 4286.

[5] S.K. Ye, F.R. Han, S.S. Chang, S.H. Qu and Y. Wu, Oxid. Commun. 3 (1983) 135.
[6] C. Walling, Accounts Chem. Res. 8 (1975) 125.
[7] N.N. Semenoff, *Chemical Kinetics and Chain Reaction* (Oxford University Press, Oxford, 1935).
[8] J.W. Moore and R.G. Pearson, *Kinetics and Mechanism, A Study of Homogeneous Chemical Reaction*, 3rd Ed. (Wiley, New York, 1981) ch. 2.