

PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF SPINELS FORMED BY SOLID-SOLID INTERACTION BETWEEN Fe_2O_3 AND V_2O_5

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Vanadium oxide catalysts doped or mixed with 1–50 mole % Fe^{3+} ions were prepared. The structure of the original samples and those calcined from 200 up to 500 °C were characterized by TG, DTA, IR and X-ray diffraction. The S_{BET} values and texture of the solid catalysts were investigated. The catalytic dehydration–dehydrogenation of isopropanol was carried out at 200 °C using a flow system. The results obtained showed an observable decrease in the activity of V_2O_5 on the addition of Fe^{3+} ions. Moreover, $\text{Fe}_2\text{V}_4\text{O}_{13}$ is the more active and selective catalyst than FeVO_4 spinels. The results were correlated with the active sites created on the catalyst surface.

Key word: Fe_2O_3 – V_2O_5 spinels, properties.

Vanadium pentoxide, both pure and mixed with foreign cations received a considerable work in the field of oxidation catalysis^{1–4}. A literature survey has shown that the phases resulting from interactions between Fe_2O_3 and V_2O_5 exhibit interesting catalytic properties^{5–8}. Recently, Clark et al.⁹ have studied interactions in alumina-based iron oxide–vanadium oxide catalysts under high calcination temperature and SO_2 oxidation conditions using low iron to vanadium oxide ratios in the mixtures. However, a little work has been done on the catalytic activity and selectivity of Fe_2O_3 – V_2O_5 at low and high Fe_2O_3 contents. Moreover, the structures accompanying solid–solid interaction between both oxides and their physicochemical properties need more studies.

The present work was undertaken to relate the structure of the catalyst produced by interaction of Fe_2O_3 with V_2O_5 to its catalytic properties in isopropanol conversion.

EXPERIMENTAL**Materials**

The starting materials were Analar grade chemicals. The doped and mixed samples were prepared by mixing together calculated amounts of ammonium metavanadate (AMV) and the corresponding volume of ferric nitrate solution. Then, calculated amount of (1 : 1) ammonia solution was added dropwise with stirring at room temperature till the formation of homogeneous mixture. The mixtures so prepared were dried on water bath until complete dryness and then heated in an oven at 110 °C to a

constant weight before being calcined in air from 200 up to 500 °C. The contents of Fe₂O₃ were 1, 10, 20, 25, 30 and 50 mole %.

Analytical grade isopropanol (BDH Ltd) was refluxed with sodium and distilled before use in catalytic runs. Its purity was checked by GC.

Apparatus and Techniques

Differential thermal analysis (DTA) and thermogravimetry (TG) of AMV and that mixed with Fe³⁺ ions were carried out using a Shimadzu Thermal Analysis System (DT-50). The heating rate was kept at 10 °C min⁻¹ in a Pt crucible using a static air atmosphere. α-Alumina powder was applied as a DTA reference.

X-Ray diffraction (XRD) analysis of the thermal products of prepared samples was performed with a Philips diffractometer (Model PW 2103, 35 kV and 20 mA) with a source of CuKα radiation and a Ni filter. The diffraction lines of the samples were matched with ASTM cards¹⁰.

IR spectra of the solid oxide catalysts were recorded in 1 600–400 cm⁻¹ region with a Shimadzu spectrophotometer model 740 using KBr disc technique.

Specific surface areas (S_{BET}) of the Fe₂O₃–V₂O₅ system calcined at 500 °C were determined from nitrogen adsorption isotherms at –196 °C using a conventional volumetric apparatus. The S_{BET} value was calculated using the BET equation in its normal applicability ($P/P_0 = 0.05\text{--}0.3$) and by adopting¹ a value of 16.2 Å² as the molecular area of adsorbed nitrogen.

The surface excess oxygen was determined by a gasometric technique¹¹ using N₂H₄ solution, to measure the amount of N₂ gas evolved.

The catalytic conversion of isopropanol was carried out in a conventional fixed-bed flow type reactor. The system comprised two reactors, one of them was used without any catalyst (control reactor), in which the blank conversion was measured and then subtracted from that obtained in the flow reactor. The outlet was analyzed by direct sampling of the gaseous products into a Pye Unicam gas chromatograph, determining isopropanol and its decomposition products. All the measurements were made after steady-state conditions had been reached.

RESULTS AND DISCUSSION

Thermal Analysis

The TG and DTA curves of pure AMV and AMV mixed with Fe³⁺ ions are shown in Fig. 1. The pure AMV (curve a) exhibits two endothermic peaks located at 205 and 460 °C and two exothermic peaks with maxima at 256 and 304 °C. The TG curve shows that AMV loses weight on heating in three steps (total weight loss was 22%). The first three peaks correspond^{12–15} to the decomposition of AMV via intermediates to V₂O₅. The endothermic peak observed at 460 °C which was not accompanied by weight loss may be due to the phase transition¹⁶ of V₂O₅. It is reasonable to mention here that the decomposition of the second and third intermediates was accompanied by exothermic peaks which differed from our previous work^{12,13}. This difference may be due to the type of the crucible used. The decomposition of AMV was carried out in an alumina crucible in our previous work, whereas a Pt crucible was used in this work. Curves b–f represent the TG and DTA of AMV mixed with 10, 20, 25, 30 and 50 mole % Fe³⁺ ions,

respectively. The analysis of the resulting data for different solids indicates some trends. The following conclusions may be drawn:

1. The peak which corresponds to the decomposition of the third intermediate transformed into an endothermic one in the case of 10 and 20 mole % Fe^{3+} ions.
2. On increasing the Fe content up to 50 mole %, the decomposition takes place in one strong exothermic peak. This peak corresponds likely to the decomposition of AMV together with Fe^{3+} hydroxide to $\alpha\text{-Fe}_2\text{O}_3$ (ref.¹⁷).
3. The endothermic peak centered at 62 °C corresponds to the water physically adsorbed while three endothermic peaks with maxima at 96, 132 and 172 °C were attributed to the decomposition of the ammonium nitrate¹⁸ formed during preparation of the starting materials.
4. A small endothermic peak corresponds to the crystallization of V_2O_5 , exists in all mixed samples, which indicates that the solids produced after decomposition contain the excess V_2O_5 .

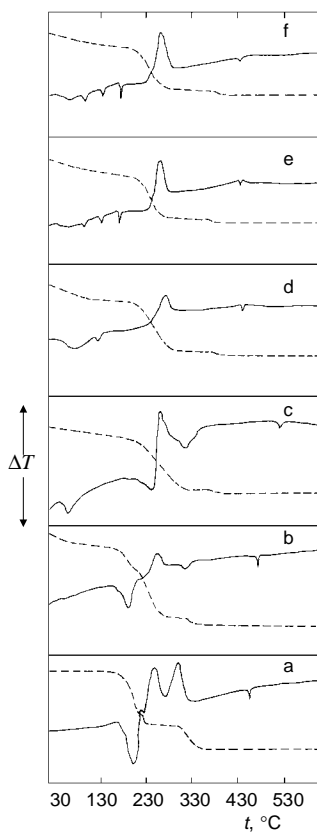


FIG. 1
TG-DTA curves of thermal decomposition of AMV (a), and mixed with 10 (b), 20 (c), 25 (d), 30 (e), and 50 (f) mole % Fe^{3+} ions

5. The samples containing 20, 25, 30, and 50 mole % Fe^{3+} ions exhibit small weight loss without exo- or endothermic peaks on the DTA curves on heating above the decomposition. This observation may result from a solid–solid reaction between Fe_2O_3 and V_2O_5 or from the decomposition of the compound to another one. This suggestion can be supported by the following X-ray and IR analysis.

XRD of Thermal Products of AMV Mixed with Fe^{3+} Ions

Figures 2 and 3 show XRD lines for AMV and AMV mixed with Fe^{3+} ions calcined at 400 and 500 °C for 5 h. The analysis of data for different solids leads to the following conclusions: (i) On the addition of 10 and 20 mole % Fe^{3+} ions and calcination at 400 °C, the main lines detected are d (Å) = 4.4, 3.6, 2.9, 5.8, and 4.1. They correspond to the characteristic structure⁵ of V_2O_5 , while new lines appear at d (Å) = 3.4 and 3.25. (ii) On increasing the Fe^{3+} content up to 30 mole %, the lines detected at d (Å) = 3.4, 3.25, 3.9, and 3.05 (which reach maximum at 30 mole % Fe^{3+}) correspond to the formation of a

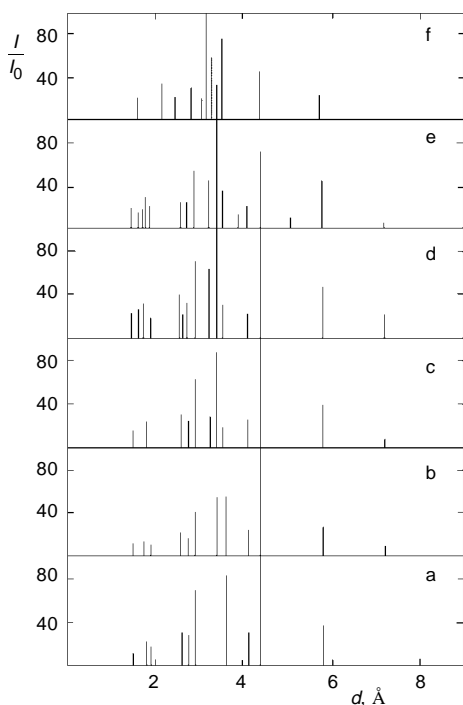


FIG. 2

XRD lines of AMV (a) and AMV mixed with 10 (b), 20 (c), 25 (d), 30 (e), and 50 (f) mole % Fe^{3+} ions calcined at 400 °C

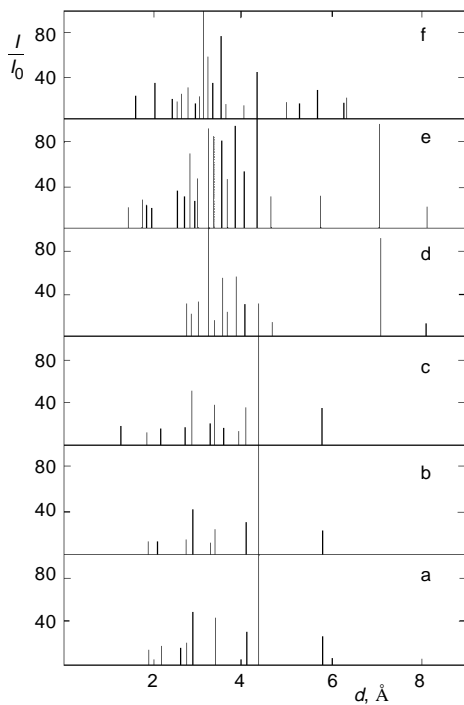
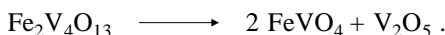


FIG. 3

XRD lines of AMV (a) and AMV mixed with 10 (b), 20 (c), 25 (d), 30 (e), and 50 (f) mole % Fe^{3+} ions calcined at 500 °C

$\text{Fe}_2\text{V}_4\text{O}_{13}$ spinel^{19,20}. (iii) Interesting results are obtained on increasing the content of Fe^{3+} ions to 50 mole %. New lines appear at d (Å) = 3.2, 3.55, and 3.3 together with the lines which correspond to the $\text{Fe}_2\text{V}_4\text{O}_{13}$ compound. The existence of these new lines relates to the formation of FeVO_4 spinel^{19,20}. (iv) On increasing the calcination temperature to 500 °C, all the samples gave the same diffraction lines as on calcination at 400 °C. From our X-ray results one can suggest that a solid–solid interaction between Fe_2O_3 and V_2O_5 can occur below 400 °C. However, the weight loss observed on the TG curves around 350 °C may be attributed to the formation of $\text{Fe}_2\text{V}_4\text{O}_{13}$ spinel. It is worth mentioning that the literature survey showed that no data have been reported on the formation of iron vanadate spinels below 400 °C. On the other hand, the presence of $\text{Fe}_2\text{V}_4\text{O}_{13}$ spinel and V_2O_5 with FeVO_4 spinel at 50 mole % Fe^{3+} ions can be explained by the following solid–solid reaction:



This indicates that the part of $\text{Fe}_2\text{V}_4\text{O}_{13}$ spinel decomposes to FeVO_4 and V_2O_5 .

IR Spectra of Thermal Products of Ammonium Metavanadate Mixed with Fe^{3+} Ions

The IR spectra of the thermal products of AMV mixed with Fe^{3+} ions and calcined at 400 and 500 °C are shown in Figs 4 and 5, respectively. Figure 4, curve 1 shows that the absorption bands at 1 020 and 820 cm^{-1} can be attributed to $\nu(\text{V}=\text{O})$ and $\nu(\text{V}-\text{O}-\text{V})$, respectively^{21,22}. For mixed samples containing Fe^{3+} ions up to 50 mole % and calcined at 400 °C, the presence of 10 mole % Fe^{3+} has no effect on the two absorption bands characterizing V_2O_5 solid. On increasing the Fe^{3+} content to 20 mole %, new bands appear, reaching maximum at 30 mole % Fe^{3+} . These new bands at 990, 910, 880, 660, and 500 cm^{-1} indicate a strong interaction between $\text{Fe}-\text{O}$ and $\text{V}-\text{O}$ vibrations, along with the formation of a new compound. These bands may correspond to the formation of $\text{Fe}_2\text{V}_4\text{O}_{13}$ spinel. On increasing Fe^{3+} content to 50 mole %, a new band at 735 cm^{-1} has appeared. The band may be attributed to the formation of FeVO_4 spinel²². Figure 5 shows IR spectra of the thermal products of pure AMV and AMV mixed with Fe^{3+} ions calcined at 500 °C. A comparison between these spectra, that of the pure V_2O_5 (curve 1) and that obtained on calcination at 400 °C, shows that the absorption bands due to the formation of $\text{Fe}_2\text{V}_4\text{O}_{13}$ start to appear on the addition of 10 mole % Fe^{3+} . Furthermore, on increasing the Fe^{3+} loading to 50 mole %, a similar behaviour is observed. However, from IR spectra it follows that the band corresponding to the presence of $\text{V}=\text{O}$ at 1 020 cm^{-1} occurs in all spectra of the binary oxides, which confirms strong formation of $\text{Fe}-\text{O}-\text{V}$ bands, instead of $\text{V}-\text{O}-\text{V}$ ones²².

Texture Assessment

The adsorption of nitrogen on the investigated catalysts proved to be rapid and reversible, yielding type II or BDDT classification²³. The variations in the texture of the catalysts calcined at 500 °C for 5 h were monitored for both pure and mixed oxides (Table I).

From Table I it can be seen that the S_{BET} of V_2O_5 gradually increases on increasing Fe^{3+} ions up to 50 mole %. This increase can be interpreted in terms of either vanadium vacancies and holes in the low range of mixing or formation of vanadate compounds which have different surface properties compared to the pure oxide. On examination of the sample porosity using V_a-t plots, all samples were found to have an upward deviation indicating mesoporous nature. This is supported also by the pore volume distribution, where $S_{\text{cum}} < S_{\text{BET}}$. Moreover, all the S_v/S_{BET} are $\geq 95\%$, which speaks for the validity of the standard t -curve used.

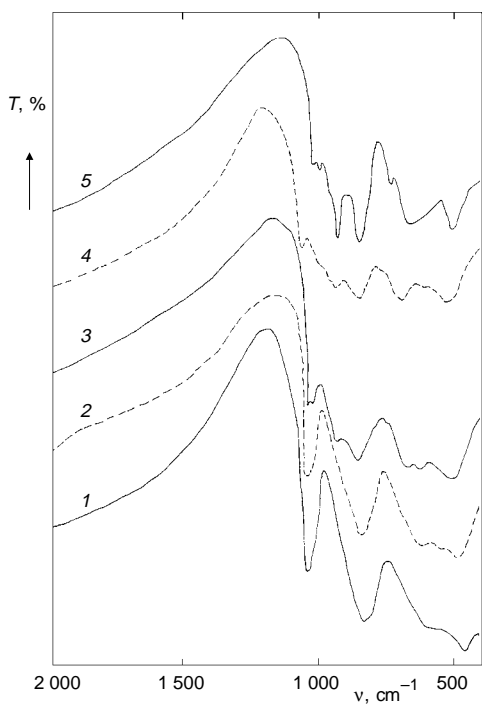


FIG. 4

IR spectra of thermal products of AMV (1) and AMV mixed with 10 (2), 20 (3), 30 (4), and 50 (5) mole % Fe^{3+} ions and calcined at 400 °C

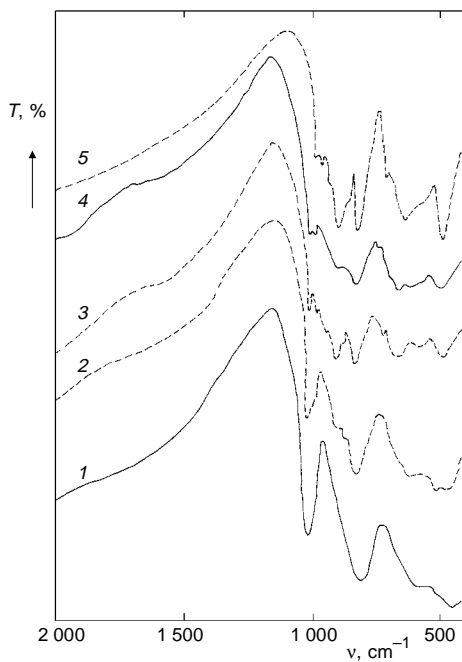
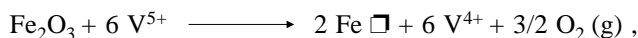


FIG. 5

IR spectra of thermal products of AMV (1) and AMV mixed with 10 (2), 20 (3), 30 (4), and 50 (5) mole % Fe^{3+} ions and calcined at 500 °C

Catalytic Activity

The catalytic decomposition of isopropanol was performed over V_2O_5 and the oxide mixed with Fe^{3+} ions calcined at 500 °C for 5 h. The isopropanol conversion and product yields were obtained after 1 h (the time to achieve steady-state conditions). The W/F ratio was 0.26 gcat mol⁻¹ h, where W refers to the mass of the catalyst and F is the total flow rate. The amount of isopropanol in the gas feed was 4.2 vol.%, and the reaction temperature was 200 °C. The analysis of the mixture after the reaction revealed that propylene and acetone were the major products. The percentage conversion of isopropanol, the yield and selectivity have been calculated, and the results are shown in Fig. 6. The figure shows that the activity of the pure V_2O_5 decreases sharply on the addition of 1 mole % Fe^{3+} ions (the conversion decreases from 85 to 32%), is followed by steady increase up to 30 mole % and then it decreases again on the addition of 50 mole % Fe^{3+} ions. These results can be divided into three regions. The first one is accompanied by a sharp decrease in the activity of V_2O_5 in the presence of small amounts of Fe^{3+} ions. This behaviour may be attributed to the doping effect, the mechanism²⁴ of which is as follows:



where $Fe \square$ represents Fe^{3+} ions located in an interstitial position or in a cationic vacancy present in the V_2O_5 lattice. Therefore, the oxygen deficiency may be responsible for such an observable decrease in the catalytic activity of V_2O_5 . The second region is accompanied by an increase in the catalyst activity on increasing the Fe^{3+} loading up to 30 mole %. The reason for such an increase is formation of $Fe_2V_4O_{13}$ spinel, as pre-

TABLE I
Texture data for V_2O_5 - Fe_2O_3 system calcined at 400 °C

Fe^{3+} mole %	S_{BET} m ² g ⁻¹	S_t m ² g ⁻¹	S_{cum} m ² g ⁻¹	V_p m ³ g ⁻¹	$V_{p(cum)}$ m ³ g ⁻¹	S_t/S_{BET}
0	5.4	5.3	5.9	0.0481	0.0409	0.98
1	6.5	6.3	6.5	0.0533	0.0308	0.97
10	7.7	7.5	7.9	0.0600	0.0442	0.97
20	10.6	10.2	10.6	0.0696	0.0540	0.96
25	11.5	11.2	11.9	0.0700	0.0560	0.97
30	13.0	12.4	15.2	0.0712	0.0600	0.95
50	14.0	13.3	16.4	0.0836	0.0630	0.95

dicted by XRD. According to the electron donating nature²⁵ of the reaction of isopropanol, one can explain the increase in the activity and selectivity of this spinel catalyst in terms of the coordination and electronic state of the active sites exposed on the surface planes, which in turn is influenced by the electron availability at the surface. The third region shows a sharp decrease in the catalyst activity at 50 mole % Fe^{3+} ions. This behaviour may be attributed to the formation of FeVO_4 spinel. It is clear from the IR results that the formation of this spinel strongly decreases the intensity of the band corresponding to $\text{V}=\text{O}$. The decrease in the $\text{V}=\text{O}$ intensity observed in the IR spectrum of FeVO_4 is due to the disorder in the structure and to the overlap of the bonds. This indicates the presence of VO_5 groups with a short nonbridging $\text{V}=\text{O}$ bond in the structure²². The strong shift of the frequency to 930 cm^{-1} proves the interaction of the $\text{V}=\text{O}$ bonds with the Fe^{3+} ions with the formation of $\text{Fe}-\text{O}-\text{V}$ bridges and the transformation of VO_5 groups into VO_4 ones. Moreover, there are no $\text{V}-\text{O}-\text{V}$ chains in the structure²⁶ of FeVO_4 but there exist FeO polyhedron and VO polyhedra bonded along the tops,

TABLE II

Surface excess oxygen of the pure V_2O_5 and V_2O_5 mixed with Fe^{3+} ions (mole %) calcined at $500\text{ }^\circ\text{C}$ for 5 h

Fe^{3+} , mole %	0	1	10	20	25	30	50
Surface oxygen, 10^2 mg g^{-1}	30	20	22	23	24	24.5	19

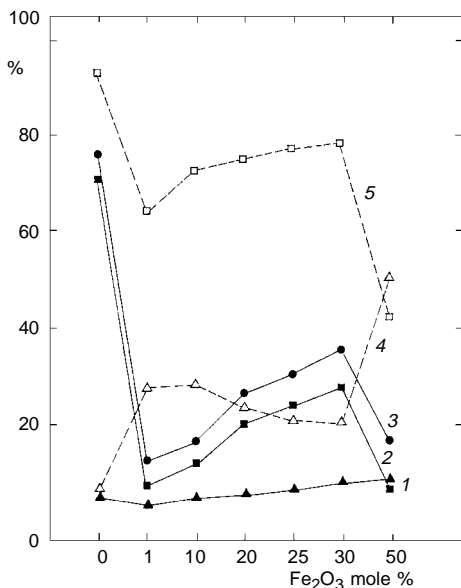


FIG. 6

Dependence of the yield of acetone (1) and propylene (2), isopropanol conversion (3), and the selectivity to acetone (4) and propene (5) on Fe_2O_3 content in the samples calcined at $500\text{ }^\circ\text{C}$

which indicates the formation of Fe–O–V bonds instead of V–O–V ones. Furthermore, we concluded earlier²⁷ that the sample containing 50 mole % Fe³⁺ (formation of FeVO₄) led to the decrease in E_a value. This was attributed to the oxygen deficiency associated with the solid state formation of FeVO₄ at elevated temperature. The oxygen non-stoichiometry will give rise to some V⁴⁺ ions.

In addition, the correlation between the concentration of V=O species on the surface of V₂O₅ mixed with Fe³⁺ ions, the catalytic activity and surface excess oxygen has been carried out, and the results are shown in Table II.

The results indicate that the amount of excess oxygen decreases on the addition of 1 mole % Fe³⁺, then it increases up to 30 mole %, and decreases again on the addition of 50 mole % Fe³⁺ ions. This behaviour parallels the results obtained in the catalytic decomposition of isopropanol.

According to the above results and the model proposed by other authors²⁸, the dehydration of isopropanol can occur on a pair of adjacent sites, viz. V⁵⁺ and O²⁻ as the acidic and basic sites, respectively. Thus, the decrease in the activity of the catalysts found in this work may be also related to the decrease in O²⁻ as an active surface site.

CONCLUSIONS

The main conclusions are as follows:

1. Fe₂O₃ readily reacts with V₂O₅ below 400 °C, yielding Fe₂V₄O₁₃ and FeVO₄ spinels.
2. The formation of Fe₂V₄O₁₃ spinel occurs on the addition of 10 to 30 mole % Fe³⁺ ions, while FeVO₄ is formed in the presence of 50 mole % Fe³⁺ ions.
3. In general, the addition of Fe³⁺ ions into V₂O₅ decreases its activity. In addition, the Fe₂V₄O₁₃ spinel is more active and more selective towards propylene formation than the FeVO₄ spinel.
4. The oxygen deficiency accompanying the low and high additions of Fe³⁺ ions is responsible for a decrease in the catalytic activity of V₂O₅.

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