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PHASE DIAGRAM OF V_2O_5—MoO_3—Ag_2O

I. Phase diagram of V_2O_5—Ag_2O system

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Phase equilibria in the V_2O_5—Ag_2O system were investigated at a constant pressure of oxygen (0.2 atm) and the phase diagram found under these conditions was compared with the results of the authors who investigated the same system in vacuum and at an oxygen pressure of 1 atm. On the basis of all these results, an attempt was made to construct the hypothetical diagram of V_2O_5—Ag_2O—O_2.

Mixed oxides V_2O_5 and MoO_3 in appropriate proportions are basic components of catalysts for the oxidation of benzene to maleic anhydride. Small amount of other added oxides in the V_2O_5—MoO_3 system can improve the selectivity of this process. As a third oxide, small amounts of P_2O_5 [1], Ag_2O, Na_2O [2], Cr_2O_3 and Co_3O_4 [3] have been used. In particular, it was found that a low content of Ag_2O (about 1 mole %) considerably improved the selectivity of the V_2O_5—MoO_3 catalyst, but at higher concentration (about 10 mole %) it deactivated the catalyst completely [2]. Other authors [4–6], however, did not observe any distinct effect of Ag_2O on the selectivity of the V_2O_5—MoO_3 catalyst. It may be assumed that the mode of incorporation of Ag_2O into the V_2O_5—MoO_3 matrix influences the selectivity and activity of the catalyst in some way.

This may also be connected with the formation of various phases in the V_2O_5—MoO_3—Ag_2O system and that is why we undertook a systematic study of the phase diagram of this system.

The aim of the present investigation was to study the phase diagram of the V_2O_5—Ag_2O system. This system was earlier investigated by Wolkov et al. [8]. In their work the samples were obtained by heating mixtures of V_2O_5 and silver powder in vacuum at 600° for 100 hr. The thermal analysis was made in an argon stream. The concentration of silver was varied in the range 0–50 mole % Ag. Three bronze phases, α, β and σ—$Ag_xV_2O_5$, formed eutectic systems.

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In Fleury's work [9], V_2O_5—Ag_2O was heated in oxygen at various temperatures. The thermal analysis was made in an oxygen stream. Depending on the conditions, the following phases were observed: AgV_7O_{18}, $Ag_2V_4O_{11}$, $AgVO_3$ and Ag_3VO_4.

The samples in the present investigation were obtained in air in order to approximate to the conditions under which industrial catalysts are prepared.

Experimental

Samples were obtained by mixing V_2O_5 and Ag_2O powders in appropriate proportions and then heating in air in a quartz tube. The first series of samples covered the range 0–50 mole % Ag_2O (Table 1) and were obtained by heating at 640° for 24 hr and cooling during 4 hr to room temperature. These samples were used for the introductory thermal analysis. Knowledge of the melting points of these samples permitted choice of the proper compositions of the samples in the second series. These covered the whole range of V_2O_5—Ag_2O composition and were obtained by heating oxide mixtures in air at temperatures below the melting point for 24 hr and then rapidly cooling to liquid nitrogen temperature. In particular, the samples containing 1–55 mole % Ag_2O were heated for 24 hr at 400° and then rapidly cooled. The samples containing 1–33 mole% Ag_2O were again heated at 500° and then rapidly cooled. The samples with 1–15 mole % Ag_2O were heated a third time at 600° and cooled. The samples with 60–90 mole % Ag_2O were heated at 380° and similarly cooled.

Table 1 Samples heated at 640 °C and slowly cooled

No. Excepted mole % Ag_2O	Mole % Ag_2O from analysis	Temperatures of endothermic effects, °C				
		rate of heating 10 deg/min			"step by step" method	
0	—	671			662	666
1	1.04	672			652	665
2	2.07	670			649	667
5	4.89	665			648	689
10	10.13	680		710	664	696
15	14.74	600	665	710	—	
20	20.03	540		710	538	690
25	24.59	550		695	—	
33.3	32.49	465	540	560	—	
40	39.18	470	530		463	531
50	50.12	470			—	

Table 2 Phase analysis of samples obtained at different temperatures

No.	Excepted mole % Ag_2O	400 °C	500 °C	600 °C	640 °C
1	2	3	4	5	6
	1	V_2O_5, β[1] (traces)	V_2O_5, β	V_2O_5, β	V_2O_5
	2	V_2O_5, β	V_2O_5, β	V_2O_5, β	V_2O_5, traces of β
	5	V_2O_5, β	V_2O_5, β	V_2O_5, β	V_2O_5, β
	7.5	V_2O_5, β	V_2O_5, β	V_2O_5, β	—
	10.0	V_2O_5, β	V_2O_5, β	V_2O_5, β	β, V_2O_5
	12.0	—	—	V_2O_5, β	—
	14.0	—	—	β, V_2O_5	—
	15.0	β, V_2O_5, Ag (traces)	β, V_2O_5, Ag (traces)	β, V_2O_5 (traces), Ag	β, V_2O_5 (traces), Ag (traces)
	16.0	—	β, V_2O_5, Ag (traces)	β, V_2O_5 (traces), Ag	—
	17.0	—	β, $Ag_2V_4O_{11}$, V_2O_5 (traces), Ag	β, $Ag_2V_4O_{11}$, V_2O_5 (traces), Ag	—
	18.0	—	β, $Ag_2V_4O_{11}$, V_2O_5 (traces), Ag	β, $Ag_2V_4O_{11}$, V_2O_5 (traces), Ag	—
	19.0	—	β, $Ag_2V_4O_{11}$	—	—
	20.0	β, $Ag_2V_4O_{11}$, V_2O_5 (traces)	β, $Ag_2V_4O_{11}$	—	β, $Ag_2V_4O_{11}$
	22.0	—	—	β, $Ag_2V_4O_{11}$	—
	25.0	β, $Ag_2V_4O_{11}$	β, $Ag_2V_4O_{11}$	—	$Ag_2V_4O_{11}$, β
	30.0	$Ag_2V_4O_{11}$, β	$Ag_2V_4O_{11}$, β	—	—
	33.3	$Ag_2V_4O_{11}$	—	—	$Ag_2V_4O_{11}$, $Ag_2V_4O_{11-y}$ (trac)
	35.0	$Ag_2V_4O_{11}$, $AgVO_3$-β	—	ú	—
	40.0	$Ag_2V_4O_{11}$, $AgVO_3$-β	—	—	$Ag_2V_4O_{11}$, $AgVO_3$-β
	50.0	$AgVO_3$-β	—	—	$AgVO_3$-β
	55.0	$AgVO_3$-β, Ag_3VO_4	—	—	—
		380 °C			
	60.0	Ag_3VO_4, $AgVO_3$-β	—	—	—
	70.0	Ag_3VO_4, $AgVO_3$-β	—	—	—
	80.0	Ag_3VO_4, Ag	—	—	—
	90.0	Ag_3VO_4, Ag	—	—	—

[1] β — $Ag_{0.3}V_{1.7}O_{4.25}$

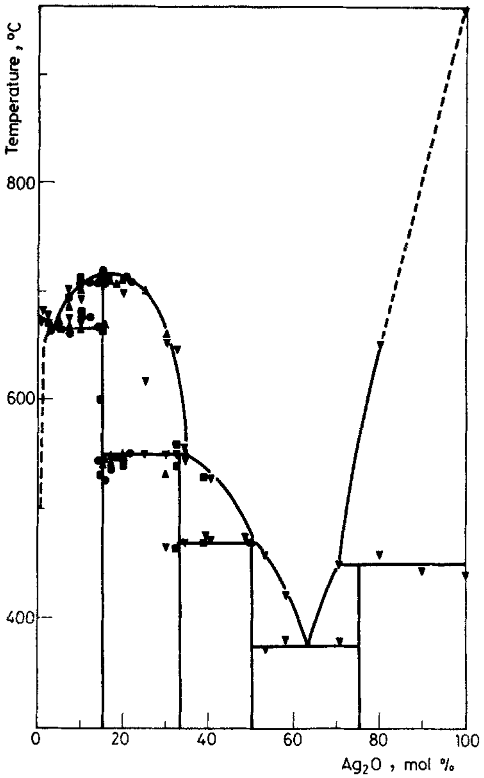

Fig. 1 Phase diagram of V_2O_5—MoO_3 system: ▼ 400°; ▲ 500°; ○ 600°' □640°

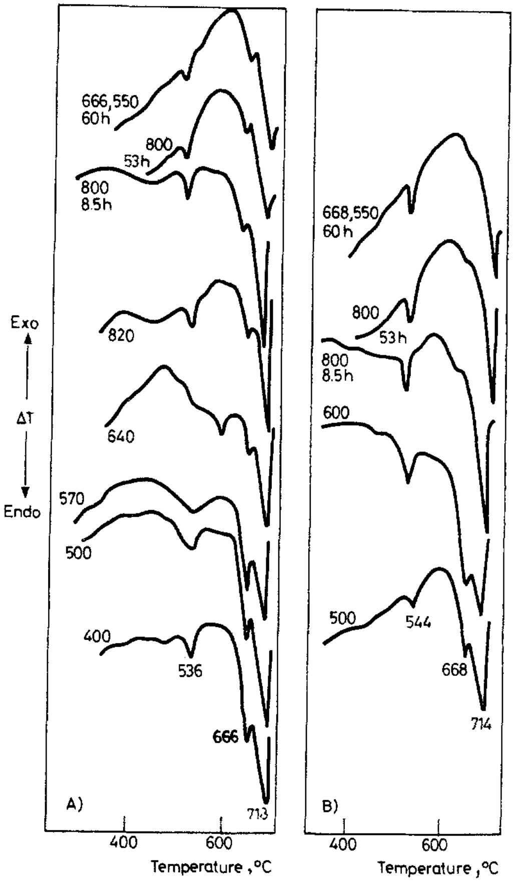

Fig. 2 DTA curves of samples 15 mol % Ag_2O (A) and 16 mole % Ag_2O (B) heated at various temperatures. The endothermic effect at 666 °C gradually diminishes for sample with 15 mole % Ag_2O The endothermic effect at 668 °C diminishes completely for the sample with 16 mole % Ag_2O

A few samples (15–18 mole %, 33 mole %, 70–90 mole % Ag_2O) were repeatedly heated and slowly cooled in order to obtain the best possible equilibration. The samples were characterized by X-ray powder diffractometry (Table 2) using a DRON–2 X-ray diffractometer (CuK_α radiation). The interplanar distances for the samples were compared with the data from [9, 10] and the Powder Diffraction File. DTA and TG analyses were carried out using a Mettler TA–2 Thermoanalyser. Al_2O_3 was used as reference material. The flow of air over the sample was 4 l/h and

Table 3

No.	Excepted mole % Ag_2O	Mole % Ag_2O from analysis	Heating temperatures of samples		
			400 °C	500 °C	600 °C
			Temperatures of endothermic effects, °C	Temperatures of endothermic effects, °C	Temperatures of endothermic effects, °C
1	2	3	4	5	6
1	0	0			672
2	1	1.0	682	—	—
3	2	2.08	676	668	672
4	5	5.07	670	670	672
5	7.5	7.16	672 700	665 686	663 694
6	10	9.94	669 694	664 702	675 708
7	12	12.00	—	—	676 708
8	14	13.96	—	—	665 708
9	15	14.95	536 666 713	540 667 713	544 662 717
10	16	15.48	—	544 668 714	528 664 710
11	17	16.93	—	543 658 710	535 655 714
12	18	17.23	—	547 656 714	536 546 650 710
13	19	18.39	—	548 708	—
14	20	19.87	546 700	550 710	—
15	22	21.63	—	—	550 708
16	25	24.95	550 618 700	550 700	—
17	30	29.68	463 550 655	532 554 660	—
18	33.3	32.38	550 646	—	—
19	35	34.48	469 545 556	—	—
20	40	39.69	472 528	—	—
21	50	48.44	475	—	—
22	55	53.43	372 458	—	—
			380 °C		
23	60	58.04	380 422	—	—
24	70	70.58	380 450	—	—
25	80	—	458 650	—	—
26	90	—	443 ...		

the heating rate was 10 deg/min. The samples were heated from room temperature to 800°. In particular cases they were heated to 1000°. In the course of cooling, the material of the fused samples crept out from the crucible, destroying the thermocouple. The points of fusion of the samples with 1–10 mole % Ag_2O were determined using the "step-by-step" method [11]. This yielded the melting points with an accuracy of ~ 1°. The results of thermal analysis are given in Tables 1 and 3 and Figs 1–3. The results of chemical analysis are given in Tables 1 and 3.

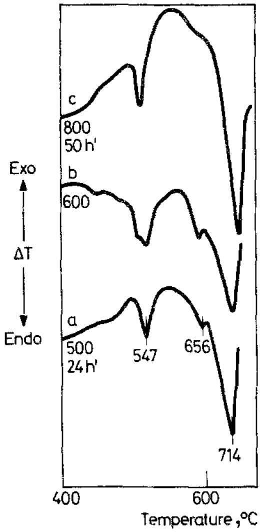

Fig. 3 DTA curves of sample 18 mole % Ag_2O heated at various temperatures. The endothermic effect at 656 °C disappeares completely in the course of heating

Results and discussion

In Fig. 1 the phase diagram of the V_2O_5—Ag_2O system, obtained by heating samples in air, is shown. There are seven phases: V_2O_5, a solid solution of Ag or Ag_2O in V_2O_5, β-$Ag_{0.30}V_{1.7}O_{4.25}$, $Ag_2V_4O_{11}$, β-$AgVO_3$, Ag_3VO_4 and Ag (above 440°). In the samples containing about 1 and 2 mole % Ag_2O, the solid solution of Ag or Ag_2O in V_2O_5 is present at about 670°. The range of solid solution is still narrower at 600° and below this temperature; in the sample with about 1 mole % Ag_2O traces of β-$Ag_{0.30}V_{1.7}O_{4.25}$ are present when it is heated at 400°, 500° and 600°. There is no evidence of the presence of β-$Ag_{0.3}V_{1.7}O_{4.25}$ traces in the sample with 1 mole % Ag_2O heated at 640°. The solid solution of Ag in V_2O_5 forms a eutectic with β-$Ag_{0.3}V_{1.7}O_{4.25}$ (this compound will be referred to as the "β-phase") at 665° and a composition of about 3.5 mole % Ag_2O. The β-phase also appears as the first product of crystallization of the melt containing 14.8 mole % Ag_2O. However, on cooling, the meritectic reaction

$$\beta\text{-}Ag_{0.30}V_{1.70}O_{4.25} + \text{liquid} \rightleftharpoons Ag_2V_4O_{11} \qquad (1)$$

takes place at 550°.

Another meritectic reaction:

$$Ag_2V_4O_{11} + \text{liquid} \rightleftharpoons \beta\text{-}AgVO_3 \qquad (2)$$

occurs at 470° in the systems containing

33–55 mole % Ag_2O.

β-$AgVO_3$, corresponding to 50 mole % Ag_2O, forms a eutectic with Ag_3VO_4 at about 376° and a composition of about 64 mole % Ag_2O. The composition of Ag_3VO_4 corresponds to 75 mole % Ag_2O. When Ag_3VO_4 is heated, the probable reaction occurring at 450° is

$$Ag_3VO_4 \rightleftharpoons Ag + 1/2\,O_2 + \text{liquid} \tag{3}$$

Data on samples containing more than 80 mole % Ag_2O could not be obtained. These samples crept out of the crucible above 700°, thereby making the measurements unreliable. During the heating of Ag_2O, and endothermic effect could be observed at 440°, accompanied by a weight loss corresponding to the decomposition of Ag_2O.

For the samples containing 15–18 mole % Ag_2O, three endothermic effects were observed: at 550°, corresponding to reaction (1); at 654°–668° with a simultaneous sample weight increase of about 5%; and an endothermic effect above 700°, corresponding to melting. The interpretation of the effect at about 654–668° was by no means simple.

Samples with 15–18 mole % Ag_2O were heated and cooled down several times over a long period of time (see Figs. 2 and 3). This endothermic effect gradually diminished for the sample with 15 mole % Ag_2O and it disappeared completely for samples with 16 and 18 mole % Ag_2O. The X-ray diffraction reflections for samples with 15–18 mole % Ag_2O included two reflections from the V_2O_5 phase, and two reflections with $d = 2.36$ Å and 2.045 Å, which corresponded well to the strongest reflections of metallic silver. The presence of small amounts of V_2O_5 and Ag in the samples with 15–18 mole % Ag_2O explained the occurrence of endothermic effects at 654–668°. The reflection from V_2O_5 vanished for samples in which the endothermic effect at 654–668° was no longer present. The above temperature was not far from the melting point of pure V_2O_5 (672°) and the effect could be interpreted as corresponding to the fusion of V_2O_5 phase containing admixtures of Ag_2O in the form of solid solution. This interpretation was supported by the fact that the 654–668° endothermic peak was accompanied by a small increase in sample weight. Such an increase in weight on fusing is characteristic of V_2O_5, which in the liquid state dissolves a certain amount of oxygen.

In parallel with the disappearance of the V_2O_5 phase from the samples with 15–18 mole % Ag_2O on repeated heating and cooling, the reflections of metallic silver also vanished. As no presence of any new phase was recorded, this fact indicated that new portions of β-phase were being formed. However, this process was not a rapid one: prolonged heating was necessary.

The results obtained in the present investigation were in part consistent with the phase diagrams shown in [8, 9], which are distinctly different from each other. Fleury ascribed the formula AgV_7O_{18} to the compounds congruently melting at 732°. Wolkow [8] and the present work suggested that this compound is the β-phase of vanadia-silver oxide bronze.

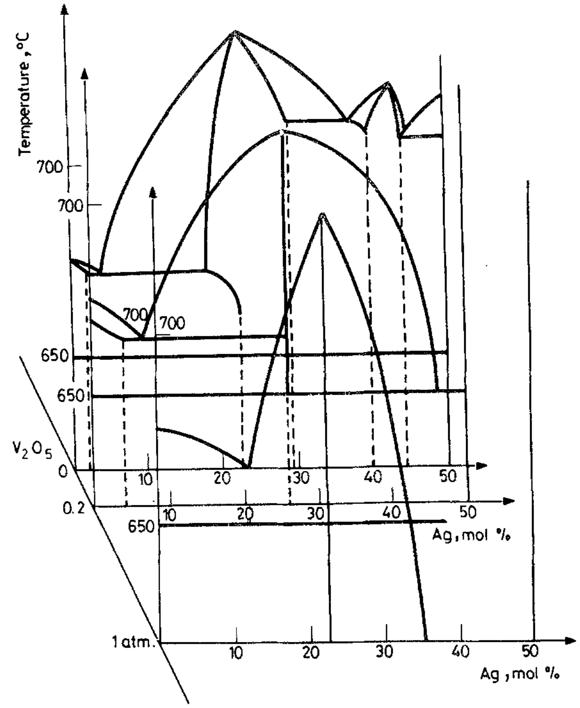

Fig. 4 A hypothetical diagram of three component V_2O_5—Ag—O system constructed on the basis [8] (0 atm O_2), present work (0.2 atm O_2), and [9] (1 atm O_2)

In the present work it was found that $Ag_2V_4O_{11}$ and β-$AgVO_3$ melt incongruently, in contrast to [9]. In the latter paper the following reactions were reported:

$$\alpha\text{-}AgVO_3 \xleftrightarrow{372^\circ} \beta\text{-}AgVO_3 \xleftrightarrow{473^\circ} \gamma\text{-}AgVO_3,$$

which were not found in the present work. No thermal effect was observed at 400° either for the samples with more than 66 mole % Ag_2O. The shape of the liquidus in the range 12–35 mole % Ag_2O was different too. Apart from the mentioned dissimilarities between [9] and the present work, the other parts of the two diagrams were consistent.

The diagram shown in [8] was quite different from that obtained in [9] and the present work, except for the range 0–10 mole % Ag_2O. This was probably due to the absence of oxygen during the preparation of the samples. The dissimilarities between the diagrams stemmed from the fact that the investigated system is in fact a three-component system: V_2O_5—Ag_2O—O_2.

On the basis of the results from [8, 9] and our own investigation, a hypothetical diagram of the three-component V_2O_5—Ag_2O—O_2 system was constructed and is shown in Fig. 4.

At a low concentration of Ag, eutectic lines and surfaces are distinctly visible. The eutectic composition changes from about 4 to about 12 mole % Ag. The range of solubility of Ag_2O in V_2O_5 also changes. At an oxygen pressure of 1 atm, silver does not dissolve in the V_2O_5 phase; in the course of decrease of the oxygen pressure, the solubility of Ag_2O increases.

Determination of the phase equilibrium in a further part of the diagram would require additional data for the range 0–0.2 atm oxygen.

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Zusammenfassung — Phasengleichgewichte im V_2O_5—Ag_2O-System wurden bei konstantem Sauerstoffdruck (0.2 atm) untersucht. Das unter diesen Bedingungen erhaltene Phasendiagramm wurde mit den Ergebnissen derjenigen Autoren verglichen, die das gleiche System im Vakuum und bei einem Sauerstoffdruck von 1 atm untersucht hatten. Auf all diesen Ergebnissen basierend wurde der Versuch unternommen, das hypothetische Diagramm des Systems V_2O_5—Ag_2O—O_2 zu konstruieren.

Резюме — Исследовано фазовое равновесие системы V_2O_5—Ag_2O при постоянном давлении кислорода (0,2 атм.) и найденная при этом фазовая диаграмма сопоставлена с таковой в вакууме и при давлении кислорода в 1 атм. На основе этих трех данных сделана попытка построить предположительную диаграмму для системы V_2O_5—Ag_2O—O_2.