React. Kinet. Catal. Lett., Vol. 34, No. 2, 413-419 (1987)

FORMATION OF THE ACTIVE COMPONENT OF A VANADIUM COMPLEX CATALYST FOR THE OXIDATION OF ANTHRACENE TO ANTHRAQUINONE

A. Spinzi[x] and P. Păuşescu[xx]
[x]Central Institute of Chemistry, Splaiul Independentei 202, Bucharest,
[xx]Central Institute of Physics, P.O. Box MG-06, Bucharest, Romania

Received October 2, 1986
Accepted November 20, 1986

The phase composition in various stages of preparation of the active material coating the catalyst for the partial oxidation of anthracene to anthraquinone was studied. The presence of an active phase was evidenced in the final active material as well in a precursor.

Исследовали фазовый состав на разных этапах обработки активного материала, входящего в состав катализатора для парциального окисления антрацена до антрахинона. Доказано присутствие активной фазы в конечном каталитическом материале, а также в его предшественнике.

INTRODUCTION

Typical catalysts for the partial oxidation of anthracene to anthraquinone in the vapor phase are obtained by coating an inert support with an active material.

The active material is a complex system formed in a liquid phase by interaction of some V, Fe, Mn, K salts [1,2]. The phase composition and the structure of this system have not been

Akadémiai Kiadó, Budapest

extensively studied. It has been reported that an active phase, still unidentified, is responsible for the catalytic activity [3]. The evolution of some physical properties (RES and Mössbauer spectroscopy) during the synthesis of this system was recently reported [4,5].

This letter presents the phase composition of the active material in various stages of its preparation, in order to give evidence of the active component and its formation in the system.

The synthesis of the active material was performed by a sequence of steps (Table 1) leading to interaction products of type V-K (A), V-K-Fe (B,C_o), V-K-Fe-Mn (C,F, F_o, K) in which the V/Fe/Mn molar ratio is constant. The samples are obtained by liquid phase precipitation at pH=7 except for the samples B and C (pH=1), drying and calcination at 380°C, by conventional procedures. The samples F_o and C_o are obtained by purification of sample F and B, respectively.

To specify the influence of the support, an active material obtained by stripping the support (K_d) has also been studied.

EXPERIMENTAL

X-ray diffraction analysis was carried out on a SIEMENS-KRISTALLOFLEX diffractometer, using a Cu anticathode. Assignments were based on the ASTM cards (up to card 24) or on the catalogs for at least eight diffraction lines.

The phase composition of the active material, dried or/and calcined, in various stages of preparation, is shown in Table 2.

The X-ray analysis of these samples show that during the precipitation of the vanadium salt with K, Fe, Mn compounds, amorphous-crystalline mixtures are formed in different ratios, with the equilibrium totally shifted towards either crystalline (A) or amorphous phase (C_o, F_o).

By calcination, the amorphous-crystalline equilibrium is modified within each sequence, the amorphous phase turning into well-crystallized products. In the sequence series $(A\text{-}K)_{380^\circ C}$, the amount of amorphous rises in the order:

Table 1

Various stages of the active material

Sample	Initial components
A	NH_4VO_3 + KHO
B	NH_4VO_3 + KOH + $Fe_2(SO_4)_3$
C_o	NH_4VO_3 + KOH + $Fe_2(SO_4)_3$
C	NH_4WO_3 + KOH + $Fe_2(SO_4)_3$ + $MnSO_4$
F	NH_4VO_3 + KOH + $Fe_2(SO_4)_3$ + $MnSO_4$
F_o	NH_4VO_3 + KOH + $Fe_2(SO_4)_3$ + $MnSO_4$
K	NH_4VO_3 + KOH + $Fe_2(SO_4)_3$ + $MnSO_4$ + K_2SO_4

$A_2 < B_2 < C_{o2} < F_2 < F_{o2} < K$.

The morphological aspect of the calcined samples show the existence of some small, almost undistinguishable crystallites (~50 Å) included in the amorphous and large, well-shaped crystallites (hundreds Å).

The appearance of the amorphous nucleus occurs on introducing $Fe_2(SO_4)_3$ into the system, evidenced by a broad maximum centered at $2\theta=32^o$. After formation, the amorphous nucleus including practically all the cations of the system (C_o, F_o) is maintained throughout all the subsequent reaction stages.

The uncalcined product A is completely crystallized as KVO_3 (I and II). The I and II structures are similar yet different with respect to line intensities and consequently to the location of atoms in the lattice. The crystallographic system has not been identified. By calcination, polyvanadates of V_2O_5/K_2O ratio equal to 5/3 and 5/2 are formed.

One can notice that in stage B, unlike the C_o,F and F_o stages, the amorphous nucleus incorporates only partially vanadium and separates it on calcination, as well-crystallized sulfur and vanadium polyanhydrides.

Table 2

Phase composition of the active material in various stages of preparation

System	Sample	$t = 110^{o}C$ Phase comp.	Sample	$t = 380^{o}C$ Phase comp.
V-K	A	KVO_3(I) KVO_3(II) unident.lines	A_2	$K_3V_5O_{14}$ $K_4V_{10}O_{27}$ VO_2
V-K-Fe	B	amorphous $V_{10}O_{24} \cdot 12\ H_2O$	B_2	amorphous $K_3Fe(SO_4)_3$ $KFe(SO_4)_3$ $K_2V_6S_2O_{22}$ $K_5V_2S_{19}O_{69}$ α-Fe_2O_3 V_2O_5
V-K-Fe	C_o	amorphous	C_{o2}	amorphous $K_2V_8O_{21}$ $KFe(SO_4)_3$ V_2O_3
V-K-Fe-Mn	F	amorphous K_2SO_4	F_2	amorphous K_2SO_4 α-Fe_2O_3 D phase

(continued)

(Table 2 contd.)

V-K-Fe-Mn	F_o	amorphous	F_{o2}	amorphous α-Fe_2O_3 $K_2V_{18}O_{45}$
V-K-Fe-Mn	K	amorphous K_2SO_4 VO_2	K_2	amorphous K_2SO_4 VO_2 D phase
K stripped	K_d	amorphous K_2SO_4 V_4O_{11}	K_{d2}	amorphous K_2SO_4 D phase

Beginning from stage F, K_2SO_4 is separated from the amorphous nucleus. The disappearence of the K_2SO_4 from the F_o phase is explained by its total elimination, following purification of the sample.

On calcination, the amorphous phase becomes partially ordered by removing the vanadium as sulfur and vanadium polyanhydrides and the iron as mixed sulfates and/or α-Fe_2O_3.

The appearance of an unidentified crystalline phase, called phase D, is noted in the intermediate (F_2) and in the final product before coating (K_2) and after stripping (K_{d2}) of the support. According to interplanar distances d and to relative intensities I_{rel} this phase corresponds to the D phase mentioned by Kursheva et al. [3]. Table 3 lists comparatively, our data and Kursheva's data concerning the D phase.

These authors consider that phase D is the active component of the V-Fe-Mn-K system for the partial oxidation of anthracene

Table 3

Interplanar distances and relative intensities of the D phase

Sample F_2		Ref.3	
d(Å)	I/I_o	d(Å)	I/I_o
3.46	10	3.50	20
3.22	50	3.26	65
3.14	100	3.16	100
3.06	100	3.07	95
2.13	10	2.12	25
		2.08	20
1.99	5	2.01	20
1.95	10	1.95	15
1.65	15	1.65	30
		1.43	20

to anthraquinone. The compound has not been identified, but it was suggested that it contains the vanadium stabilized as V^{5+}, probably, as VO_3^- or VO_4^- groups.

Data in Table 2 show that the appearance of the D phase takes place only in the stage F, which suggests that the catalytically active compound is separated only after introduction of the manganese salt into the system. The above data support the hypothesis that the manganese is the promoter of the active phase formation, typical for this system.

It is worth noting that in sample F_{o2}, corresponding to sample F_2 from which the K_2SO_4 was completely removed by purification, phase D was hardly detected. Conversely, when the K_2SO_4 is reintroduced into the system (K_2) the D phase distinctly reappears.

This finding allows us to correlate in a first hypothesis, the appearence of the D phase not only with the content of manganese but with that of K_2SO_4 as well; this latter seems to favor crystallization of the active phase.

REFERENCES

1. URSS 238,526 (1969).
2. Ger. 1,147,213 (1963).
3. G.A. Kursheva, O.Ia. Polotniuk, D.I. Konysheva, Z.I. Eikova, B.E. Zaitsev: Kinet. Katal., 13, 459 (1972).
4. A. Spinzi, E. Burzo, M. Rogalski: React. Kinet. Catal. Lett., 28, 181 (1985).
5. E. Burzo, M. Chipara, A. Spinzi: React. Kinet. Catal. Lett., 28, 203 (1985).