Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 177–181

REACTIVITY OF $Zn_3V_2O_8$ TOWARDS $ZnMoO_4$ IN THE SOLID STATE

M. Kurzawa and M. Bosacka

Department of Inorganic Chemistry, Technical University of Szczecin, Al. Piastów 42
71-065 Szczecin, Poland

Abstract

The reactivity of $Zn_3V_2O_8$ towards $ZnMoO_4$ was investigated by using DTA and XRD methods. A new compound of the formula $Zn_{2.5}VMoO_8$ was found. It crystallises in an orthorhombic system. The melting temperature was determinated to be 845±5°C.

Keywords: new compound of $Zn_{2.5}VMoO_{8,}$ $ZnMoO_4$, $Zn_3V_2O_8$

Introduction

It is known from the literature-scan-based information that some comprehensive studies have been undertaken recently, specifically aimed at searching for active and also selective oxide catalysts for oxidative dehydrogenation of light alkanes like propane, butane, etc. [1, 2]. Among the few compounds possessing such properties are numbered magnesium, cobalt(II), nickel(II) and zinc orthovanadates and molybdates [3–7]. Equally good catalytic selectivity in dehydrogenation of butane to butene can be attributed to the newly published compound, $Mg_{2.5}VMoO_8$, which is formed in the $Mg_3V_2O_8$–$MgMoO_4$ system [4–6].

Our preliminary researches on reactivity of $Co_3V_2O_8$ towards $CoMoO_4$ have also pointed out that a novel compound, which has not been yet described, $Co_{2.5}VMoO_8$, is formed in the $Co_3V_2O_8$–$CoMoO_4$ system [9]. The compound is isostructural with $Mg_{2.5}VMoO_8$, melts incongruently at 1085±5°C, depositing solid $CoMoO_4$ [9]. Literature survey provided only a reference to preparation of the two phases of a $M_{2.5}VMoO_8$ type, that is, $Mn_{2.5}VMoO_8$ and $Zn_{2.5}VMoO_8$ [6, 10]. Considering the exploitable catalytic properties of $Zn_3V_2O_8$ and $ZnMoO_4$, it seems that the information on mutual reactivity of the phases is not only essential from the cognitive point of view but also indispensable to the knowledge of mechanisms of their catalytic activity.

The structure and properties of $Zn_3V_2O_8$ and $ZnMoO_4$ are known. Zinc orthovanadate(V) occurs in two polymorphic forms: a low-temperature form α and a high-temperature form β. The reversible change of $\alpha \leftrightarrow \beta$ takes place at 795°C [11, 12]. α-$Zn_3V_2O_8$ crystallises in an orthorhombic system and belongs to a space

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

group Cmca [13]. The structure of β-$Zn_3V_2O_8$ has not been recognised yet. At 815±5°C β-$Zn_3V_2O_8$ decomposes into two solid phases: β-$Zn_2V_2O_7$ and $Zn_4V_2O_9$ [11, 12].

Zinc molybdate crystallises in a triclinic system, within a space group P1 [14]. Under atmospheric pressure $ZnMoO_4$ fails to display polymorphism. By recent information, $ZnMoO_4$ melts congruently at 1007°C [15].

Experimental

The samples for experiments were prepared from $Zn_3V_2O_8$ and $ZnMoO_4$, the reagents having been obtained by calcination of the suitable oxide mixtures. Thus $Zn_3V_2O_8$ was obtained by heating ZnO (analar, Reachim) with V_2O_5 (analar, Reachim) at the 3:1 molar ratio and temperatures: 600, 650 and 700°C for 24 h in each case. $ZnMoO_4$ was obtained by heating an equimolar mixture of ZnO and MoO_3 (analar, POCh) at 600°C for 24 h, and then at 660°C in two 24 hours' cycles.

The reagents weighed in appropriate proportions were homogenised by grinding and then shaped in pastilles and heated in a sylite furnace, in the air, in the following stages: 600°C (24 h)+650°C (24 h)+700°C (24 h×2). On each heating stage the samples were carefully cooled to ambient temperature; afterwards the pastilles ground again were examined by DTA and their contents were determined by the XRD method.

DTA examinations were made by using a derivatograph (MOM, Budapest). Samples with a mass of 1000 mg each were placed in quartz crucibles. All the measurements were made in air at the temperature range 20–1000°C and a heating rate of 10°C min^{-1}.

Phases occurring in the samples were identified depending on the results of the X-ray phase analysis (a diffractometer DRON-3, CoK_α radiation, Fe filter) and on the data included in PDF cards [16], and publications [4–6, 11].

Results and discussion

Table 1 shows results obtained by the XRD method for a sample containing 33.33 mol% of $Zn_3V_2O_8$ and 66.67 mol% of $ZnMoO_4$ in its initial mixture on the successive stages of the synthesis. On the diffraction pattern of a sample obtained after 24 h heating at 600°C there was recorded, apart from the diffraction lines characteristic for $Zn_3V_2O_8$ and $ZnMoO_4$, also a diffraction line set, imperceptibly different from the set characteristic of the compound, $Co_{2.5}VMoO_8$, which crystallises in a quasi-binary $Co_3V_2O_8$–$CoMoO_4$ section of the CoO–V_2O_5–MoO_3 system [4]. Diffraction patterns of that sample made after two consecutive heating stages show that intensities of the new diffraction lines are distinctly increased, while the lines characteristic of $Zn_3V_2O_8$ and $ZnMoO_4$ are perceptibly diminished. No initial reagents have been found in the sample on the final stage of heating, and its diffraction pattern included only a new set of diffraction lines. It has been recognised that the diffraction line set is characteristic of the compound $Zn_{2.5}VMoO_8$, the receiving of which has been reported [3].

Table 1 X-ray phase analysis of a sample containing 33.33 mol% of $Zn_3V_2O_8$ and 66.67 mol% of $ZnMoO_4$, on successive stages

No.	Temperature/°C	Time/h	Phases identified
1	600	24	$ZnMoO_4$, $Zn_3V_2O_8$, LN^*
2	650	24	LN^*, $ZnMoO_4$, $Zn_3V_2O_8$
3	700	24	LN^*, $ZnMoO_4$ – traces
4	700	24	LN^*

LN^* – a phase characterized by a set of new diffraction lines

The X-ray phase analysis of samples containing 15.00 and 25.00 mol% of $Zn_3V_2O_8$ in their initial mixtures, made on the last heating stage shows that two phases, e.g. $ZnMoO_4$ and $Zn_{2.5}VMoO_8$ occur. Other samples with the $Zn_3V_2O_8$ content being 40.00, 60.00 and 80.00 mol% on the final heating stage are composed of zinc orthovanadate and $Zn_{2.5}VMoO_8$. These results show that $Zn_3V_2O_8$ and $ZnMoO_4$ are not inert towards each other in the solid state, but interreact to form a compound, $Zn_{2.5}VMoO_8$, according to the equation:

$$2ZnMoO_{4\,(s)}+Zn_3V_2O_{8\,(s)}=2Zn_{2.5}VMoO_{8\,(s)} \qquad (1)$$

Table 2 shows results of indexing the first 20 lines of the powder diffraction pattern of $Zn_{2.5}VMoO_8$, the angle position of which was determined on the basis of a diffraction pattern made for a sample against an internal reference standard (KCl). The parameters

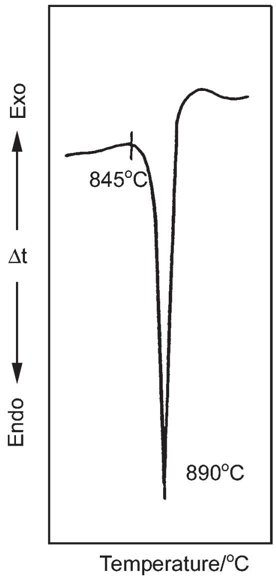

Fig. 1 DTA curve of $Zn_{2.5}VMoO_8$

calculated of an orthorhombic unit cell are the following: a=0.50639, b=1.04202, c=1.75861 nm. A type of the cell: P, Z=6, density calculated: ρ_{rtg}=4.70 g cm^{-3}. Experimental density, ρ_{exp}=4.63 g cm^{-3} was found by the method described in [17]; $\Delta\rho$=0.07.

Table 2 Results of indexing the first 20 lines of the powder diffraction pattern of $Zn_{2.5}VMoO_8$

No.	*h k l*	I/I_o	$d_{obs.}$/nm	$d_{calc.}$/nm	*F. M.*
1	0 2 2	10.7	0.44724	0.44823	20
2	1 0 2	10.3	0.44047	0.43882	13
	0 0 4			0.43965	51
3	1 2 1	5.9	0.35546	0.35563	20
4	0 3 1	19.2	0.34118	0.34076	30
5	1 2 2	100.0	0.33569	0.33563	25
	0 2 4			0.33601	74
6	1 0 4	52.8	0.33192	0.33199	56
7	0 3 2	6.0	0.32268	0.32305	40
8	1 1 4	14.1	0.31581	0.31632	64
9	0 3 3	21.0	0.29899	0.29882	63
10	0 0 6	14.3	0.29321	0.29310	157
11	1 3 1	31.3	0.28254	0.28271	36
	0 1 6			0.28215	163
12	1 2 4	29.2	0.27976	0.27998	78
13	1 1 5	20.2	0.27832	0.27838	111
14	1 3 2	6.5	0.27328	0.27235	46
	0 3 4			0.27255	91
15	0 4 0	11.5	0.26065	0.26050	52
16	0 4 1	47.2	0.25727	0.25769	55
	1 3 3			0.25735	69
17	0 2 6	15.2	0.25565	0.25545	178
18	1 0 6	34.5	0.25352	0.25367	165
19	2 0 0	31.1	0.25300	0.25319	127
20	0 4 2	18.1	0.24972	0.24977	73

The melting temperature of $Zn_{2.5}VMoO_8$, read from the DTA curve as an endothermic effect onset, is 845°C (Fig. 1). The X-ray phase analysis of $Zn_{2.5}VMoO_8$ melted at 880°C and then rapidly cooled to ambient temperature afterwards has shown that $Zn_{2.5}VMoO_8$ melts incongruently, depositing a solid phase – $ZnMoO_4$.

Conclusions

The reactivity between $Co_3V_2O_8$ and $CoMoO_4$ were studied in air up to 1000°C using XRD and DTA methods. The following conclusions can be drawn from these studies:

- In the solid state $Co_3V_2O_8$ and $CoMoO_4$ are not inert to one another but interreact to form a new phase, $Zn_{2.5}VMoO_8$.
- The compound $Zn_{2.5}VMoO_8$ melts incongruently at 845°C to deposit a solid $ZnMoO_4$.

References

1 M. A. Chaar, D. Patel, M. C. Kung and H. H. Kung, J. Catal., 105 (1987) 483.
2 A. Corma, J. M. Lopez Nieto and N. Paredes, J. Catal., 144 (1993) 425.
3 V. A. Doroshenko, L. P. Shapovalova and D. N. Tmenov, Zh. Prikl. Khim., 55 (1982) 80.
4 W. D. Harding, H. H. Kung, V. L. Kozhevnikov and K. R. Poppelmeier, J. Catal., 144 (1993) 597.
5 V. G. Zhubkov, I. A. Leonidov, K. R. Poppelmeier and V. L. Kozhevnikov, J. Solid State Chem., 111 (1994) 197.
6 X. Wang, C. L. Stern and K. R. Poppelmeier, J. Alloys Comp., 243 (1996) 51.
7 S. C. Chang, M. A. Lenger and M. R. Bore, J. Phys.Chem., 96 (1992) 10358.
8 K. Nakamura, K. Eda, S. Hasegawa and N. Sotani, Appl. Catal., 178 (1999) 167.
9 M. Kurzawa, Book of Abstracts IVth European Conference on Solid State Chemistry, Zurich 1997, PB 108.
10 X. Wang, K. R. Heier, Ch. L. Sern and K. R. Poppelmeier, J. Alloys Comp., 255 (1997) 170.
11 V. A. Makarov, A. A. Fotiev and L. N. Serebriakova, Zh. Neorg. Khim., 16 (1971) 2849.
12 G. M. Clark and A. N. Pick, J. Thermal Anal., 7 (1975) 289.
13 R. Gopal and C. Calvo, Can. J. Chem., 49 (1971) 3056.
14 S. C. Abrahams, J. Chem. Phys., 46 (1967) 2052.
15 T. Söhnel, W. Reichelt, H. Oppermann, H. J. Mattausch and A. Simon, Z. anorg. allg. Chem., 622 (1996) 1274.
16 Joint Committee of Powder Diffraction File: 35-765, 34-378.
17 Z. Kluz and I. Waclawska, Rocz. Chem., 49 (1975) 839.