Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 865–869

THE REACTION MECHANISM AND KINETICS OF THE $Zn_{2.5}VMoO_8$ PHASE SYNTHESIS IN THE SOLID STATE[*]

P. Tabero, M. Bosacka and M. Kurzawa

Institute of Chemistry and Environment Protection, Technical University of Szczecin,
Al. Piastów 42, 71-065 Szczecin, Poland

Abstract

Studies on the reaction kinetics and mechanism of the synthesis of the $Zn_{2.5}VMoO_8$ compound in the solid state have been carried out in situ in a high-temperature X-ray diffraction attachment. The apparent activation energy, 212±26 kJ mol^{-1} was calculated by using the diffusion controlled Ginstling–Brounstein model. There was also determined a temperature dependence of unit cell parameters for $Zn_3V_2O_8$ and $Zn_{2.5}VMoO_8$.

Keywords: high-temperature XRD, isothermal kinetics, solid state reaction, $Zn_{2.5}VMoO_8$

Introduction

Vanadates(V) and molybdates(VI) of divalent metals, the structures of which are built of separate VO_4 or MoO_4 tetrahedra, display both a good selectivity and a high activity as catalysts in oxidative dehydrogenation of light alkanes [1, 2]. Such properties are exhibited by magnesium, cobalt(II) and zinc orthovanadates and molybdates [3–7] and $Mg_{2.5}VMoO_8$ – known since a short time [4–6]. The compound, crystallising in an orthorhombic system space group Pnma, melts incongruently at 1443 K to deposit $MgMoO_4$ [5]. Recently, other compounds of a $Mg_{2.5}VMoO_8$ type, where *M*=Mn, Zn, Co, were obtained [5, 8–12]. It is known from the published information available that the new family of compounds, isotypical with $Mg_{2.5}VMoO_8$, is an objective of dynamic and comprehensive investigations.

The studies include phase equilibria of the systems, in which the compounds originate their structure as well as thermal, magnetic and catalytic properties [5, 10–12]. It was only the reaction kinetics and mechanism of the synthesis of the $M_{2.5}VMoO_8$ type compounds that have not been studied yet. The aim of this work was to gain an insight into the reaction kinetics and mechanism of the $Zn_{2.5}VMoO_8$ synthesis. This compound, like other phases creating a family of a $M_{2.5}VMoO_8$ type, crystallises in an orthorhombic system. Parameters of a primitive unit cell are the fol-

---

[*] The paper was presented at Solid State Chemistry 2000.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

lowing: a=0.5069 nm, b=1.0420 nm, c=1.7586 nm; z=6 [9, 11]. $Zn_{2.5}VMoO_8$ melts incongruently at 1118 K, depositing solid $ZnMoO_4$ [11]. There is also known a diagram of phase equilibria established in the $ZnMoO_4$–$Zn_3V_2O_8$ system, where the compound is formed.

Experimental

For the experiments were used $ZnMoO_4$, $Zn_3V_2O_8$ and $Zn_{2.5}VMoO_8$, prepared by calcining oxides. Thus, $Zn_3V_2O_8$ was prepared by heating a mixture of an analar ZnO (REACHIM) with an analar V_2O_5 (REACHIM) at a 3:1 molar ratio at 873 K for 24 h, at 923 K for 24 h, at 973 K also for 24 h. $ZnMoO_4$ was prepared by heating an equimolar mixture of ZnO with an analar MoO_3 (POCh) at 873 K for 24 h and during two 24 h cycles at 933 K. $Zn_{2.5}VMoO_8$ was synthesized by calcining a $ZnMoO_4/Zn_3V_2O_8$ mixture at a 2:1 molar ratio at 873 K (24 h)+873 K (24 h)+973 K (48 h).

The investigations were carried out in a high-temperature X-ray attachment of a UVD-2000 type (Bourevestnik, Sankt Petersburg, Russia) linked to an HZG-4 diffractometer (Freiberger Prazisions-mechanik, Germany). The radiation source was a copper tube with a nickel filter (CuK_α/Ni). In the measurements the same nickel cuvette was used into which the examined samples were pressed. The angle position of diffraction reflexions and their intensities were determined by a step method (t=1 s, step 0.02°2θ). For calculating the degree of conversion a diffraction line (120), $d_{298\,K}$=0.3678 nm was employed, characteristic of $ZnMoO_4$, according to the relation:

$$\alpha = 1 - I^t/I^0 \tag{1}$$

where I^t is the diffraction line intensity after the reaction time t, I^0 is the diffraction line intensity for an initial reaction mixture.

The main kinetic measurements were made by isothermal method. Isothermal measurements were commenced (t=0) when the temperature setting for a given experiment was achieved in the high-temperature attachment. Examining the phase composition of a reaction mixture at 30 min intervals additionally monitored the reaction advance at an appropriate temperature.

For the reliability of identification of phases at elevated temperatures, before starting the proper investigations, powder diffraction patterns of pure compounds: $ZnMoO_4$, $Zn_3V_2O_8$ and $Zn_{2.5}VMoO_8$ were recorded at 298, 473, 673, 873 and 1023 K. Next the shape of kinetic curves, (α=f(t)) was analysed, taking into account the known kinetic models [13, 14]. This procedure created a basis for the establishment of the process step determining a rate of the reaction under study. The reaction rate constant (k) and apparent activation energies (E) were calculated from the Arrhenius equation and from the relation characterising a given kinetic model.

Results and discussion

The works were commenced by monitoring the impact of temperature rise on the angle position of diffraction lines on powder diffraction patterns of reactants and products of the reaction under study. Next, on the evidence of powder diffraction patterns recorded at 298, 473, 673, 873 and 1023 K for $Zn_3V_2O_8$ and $Zn_{2.5}VMoO_8$ unit cells parameters were calculated with the aid of the program REFINEMENT. The results of calculation have been tabulated in Tables 1 and 2. The mean values of linear coefficients of thermal expansion for the examined compounds, were calculated from the relation [15]:

$$\beta = \frac{a_2 - a_1}{a_1(T_1 - T_2)} \qquad (2)$$

where β is the linear coefficient of thermal expansion of parameter a/1/K; a_1 is the value for the unit cell parameters at the temperature T_1/nm; a_2 is the value of the unit cell parameter at the temperature T_2/nm; T_1, T_2 are the temperatures of measurement in K.

Table 1 The unit cell parameters and volumes of the $Zn_{2.5}VMoO_8$ phase at different temperatures

No.	T/K	a/nm	b/nm	c/nm	V/nm^3
1	298	0.5051(1)	1.0417(2)	1.7580(3)	0.9250
2	473	0.5061(1)	1.0439(2)	1.7628(3)	0.9314
3	673	0.5075(1)	1.0459(1)	1.7657(3)	0.9373
4	873	0.5089(1)	1.0494(2)	1.7721(3)	0.9464
5	1023	0.5109(2)	1.0509(2)	1.7777(4)	0.9544

Table 2 The unit cell parameters and volumes of the $Zn_3V_2O_8$ phase at different temperatures

No.	T/K	a/nm	b/nm	c/nm	V/nm^3
1	298	0.6115(1)	1.1535(2)	0.8308(2)	0.5860
2	473	0.6145(2)	1.1564(1)	0.8328(1)	0.5918
3	673	0.6175(2)	1.1596(6)	0.8348(4)	0.5978
4	873	0.6210(3)	1.1624(6)	0.8371(5)	0.6043
5	1023	0.6233(3)	1.1656(5)	0.8368(4)	0.6080

The mean values of thermal expansion coefficients for $Zn_{2.5}VMoO_8$ in the temperature range 298–1023 K for unit cell parameters a, b and c were equal to $1.58\cdot10^{-5}$, $1.22\cdot10^{-5}$ and $1.55\cdot10^{-5}$, respectively. For the $Zn_3V_2O_8$ phase two temperature ranges were differentiated: 298–873 and 873–1023 K. The mean values of thermal expansion coefficients at the temperature range 298–873 K for unit cell parameters a, b and c were equal to $2.70\cdot10^{-5}$, $1.34\cdot10^{-5}$ and $1.32\cdot10^{-5}$ whereas at the temperature range 873–1023 K: $2.47\cdot10^{-5}$, $1.84\cdot10^{-5}$ and $-2.39\cdot10^{-6}$.

It follows from the data represented in Tables 1 and 2 that the relation between the unit cell parameters for $Zn_3V_2O_8$ and temperature is not linear over the temperature range, at which the measurements were carried out. Deviation of the temperature dependence of the unit cell parameters for $Zn_3V_2O_8$ from the straight line was observed above 873 K. Information about similar changes of the parameters for the $Zn_3V_2O_8$ unit cell in the temperature function has been given also by Fotiev and his associates [16]. It is known from the publications reviewed and from our own studies on thermal properties of $Zn_3V_2O_8$ [17] that this compound decomposes at 1073 K to two solid phases, i.e. β-$Zn_2V_2O_7$ and $Zn_4V_2O_9$. Thus in the light of the information assembled, a non-linear character of the temperature dependence of the $Zn_3V_2O_8$ unit cell parameters, observable at temperatures approximate to the temperatures of the $Zn_3V_2O_8$ thermal decomposition, pertains to the thermal stability of the compound in the solid state.

The results of experiments have shown the reaction of $ZnMoO_4$ with $Zn_3V_2O_8$ to start in the solid state at a measurable but very low rate at 873 K. Accordingly, the investigations were made under isothermal conditions at temperatures: 933, 973 and 1013 K. The synthesis of $Zn_{2.5}VMoO_8$ from a $ZnMoO_4/Zn_3V_2O_8$ mixture took place without intermediate products regardless the temperature at which it was carried out.

The shape of kinetic curves ($\alpha=f(t)$) was analysed with taking into account the following kinetic models: D1, D2, D3, D4, D5, F1, R2, R3, A2, A3, A4, T3, T4 and T5 [13, 14].When the integral function form $g(\alpha)$ characteristic of the given kinetic model is properly chosen, the plot of $g(\alpha)$ *vs*. time should be linear and the reaction mechanism can be confirmed from $g(\alpha)$ form. The regression analysis of $g(\alpha)$ at various temperatures *vs*. time was performed in the least square method. With the use of the values of the correlation coefficients as a criterion, the form of $g(\alpha)$ function was selected and the reaction mechanism was determined. Figure 1 shows kinetic curves $\alpha=f(t)$ at the set temperatures. Analysis of the curves made with the use of various kinetic models has shown that the $\alpha=f(t)$ curves can be almost equally well described

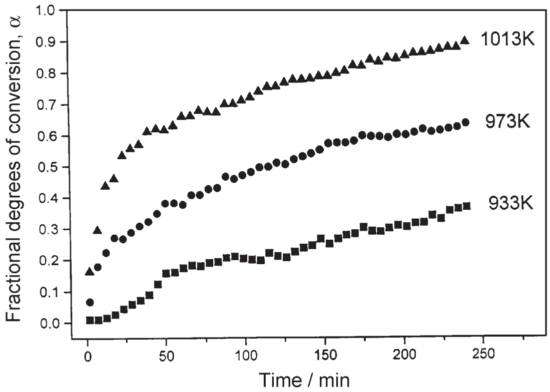

Fig. 1 The fractional degree of conversion *vs*. reaction time curves of $Zn_{2.5}VMoO_8$ formation

by the diffusion controlled models. The best fit was received for the Ginstling–Brounstein model (D4) [13, 14]:

$$kt=1-2/3\alpha-(1-\alpha)^{2/3} \qquad (3)$$

where k is the reaction-rate constant (min^{-1}); t is time (min); α is fractional degree of conversion.

The calculated mean value for correlation coefficients of this equation is $R=0.9869$.

It shows that it is well possible that the synthesis reaction mechanism of $Zn_{2.5}VMoO_8$ phase corresponds to the D4 model, that is, diffusion is the rate controlling step of the reaction. The rate constants calculated according to relation (3) for temperatures: 933, 973 and 1013 K are $7.0\cdot10^{-5}$, $2.7\cdot10^{-4}$ and $6.1\cdot10^{-4}$, respectively. The calculated value for the reaction-activation energy of the $Zn_{2.5}VMoO_8$ synthesis equals to 212±26 kJ mol^{-1} and calculated value for pre-exponential factor A equals to $5.8\cdot10^{7}$ (min^{-1}).

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 U. A. Doroshenko, L. P. Shapovalova and D. N. Tmentov, Zh. Prikl. Khim., 55 (1982) 80.
4 W. W. Harding, H. H. Kung, V. L. Kozhevnicov and K. R. Poppelmeier, J. Catal., 144 (1993) 597.
5 V. G. Zhubkov, J. 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 M. Kurzawa, Book of Abstracts, IVth European Conference on Solid State Chemistry, Zurich 1997, PB 108.
9 X. Wang, K. R. Heier, C. L. Stern and K. R. Poppelmeier, J. Alloys. Comp., 255 (1997) 190.
10 X. Wang, K. R. Heier, C. L. Stern and K. R. Poppelmeier, J. Alloys. Comp., 267 (1998) 79.
11 M. Kurzawa and M. Bosacka, J. Therm. Anal. Cal., 60 (2000) 177.
12 M. Kurzawa and M. Bosacka, J. Therm. Anal. Cal., 56 (1999) 211.
13 J. Beretka and T. Brown, J. Am. Ceram. Soc., 66 (1983) 383.
14 J. J. Zhang, L. G. Ge, X. L. Zhang, Y. J. Dai, H. L. Chen and L. P. Mo, J. Therm. Anal. Cal., 58 (1999) 269.
15 International Tables for X-ray Crystallography, Vol III, Physical and Chemical Tables, Eds K. Lonsale, C. H. Macgorillany and G. G. Rieckj; The kynoch Press, Birmingham 1968.
16 T. I. Krasnenko, O. A. Burneiko, O. A. Zabara, A. Yu. Popkov and A. A. Fotiev, Neorg. Mater., 5 (1993) 29.
17 M. Kurzawa, I. Rychłowska-Himmel, M. Bosacka and A. Błońska-Tabero, J. Therm. Anal. Cal., in press.