

# Kinetic Investigation of the System $\text{Fe}_2\text{O}_3\text{-MnO-V}_2\text{O}_5\text{-SiO}_2$ , Using Waste Material

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**Abstract** - The kinetics of non-isothermal heating of the system  $\text{Fe}_2\text{O}_3\text{-MnO-V}_2\text{O}_5\text{-SiO}_2$  was investigated. Synthetic mixture of pure oxides included in the system and mixture containing waste vanadium catalyst (4.12%  $\text{V}_2\text{O}_5$ ) and manganese concentrate (44.56%  $\text{MnO}$ ) was used. The mixtures were characterized by DTA and X-ray diffraction analysis. From DTA and TG curves of the resulting thermograms, the average rate of the processes, rate constant and the activation energy was defined. Activation energy of mixture of pure oxides is  $E_{a1} = 7,876$  kJ/mol in the range up to 800K, and  $E_{a1} = 16,507$  kJ/mol to 1493K. For mixture containing waste vanadium catalyst  $E_{a2} = 5,604$  kJ/mol in the range up to 900K and  $E_{a2} = 10,119$  kJ/mol to 1493K. It has been found that the processes in the system take place in an external diffusion area.

**Key Words:** kinetics, process rate, activation energy, DTA

## 1. INTRODUCTION

Kinetics of processes in the system  $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MnO-SiO}_2$  is especially important. It is necessary to know in which range the phase transformation processes take place and which parameters should be changed in order to intensify the processes in this system. The obtained DTA, DSC and TG curves have been used to define activation energy. In the papers [1-3] DTA and TG curves are given in order to identify the reaction rate, and for calculation of the activation energy value.

Thermogravimetric analysis (TGA) of magnetite ( $\text{Fe}_3\text{O}_4$ ) oxidation to Hematite ( $\text{Fe}_2\text{O}_3$ ) was conducted at temperatures ranging from 750 to 900°C. The initial oxidation, which happened very quickly, was described using nucleation and growth processes with a low activation energy of about 4,21 kJ/mol. As the reaction developed on the surface, oxygen transported through the product layer and it became the rate controlling step with activation energy of 53,58 kJ/mol [4]. The kinetics and reaction mechanism of the transformation of the goethite to hematite are based upon the results from thermogravimetric analyzer [5]. M.Cornell and U. Schwertmann [6] determined the activation energy of  $\text{Fe}_2\text{O}_3$   $E_a = 47\text{-}50$  kJ/mol. Thermogravimetric analysis carried out in the presence of wet air was used to calculate the activation energy of  $E_a = 151$  kJ/mol [7]. The results is approximately to the one obtained by the authors [8, 9] -  $E_a = 134$  kJ/mol and  $E_a = 149$  kJ/mol, respectively.

During the decomposition of NO over  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  at 773K,  $\text{Mn}_2\text{O}_3$  has activation energy - 46 kJ/mol and  $\text{Mn}_3\text{O}_4$  -

63 kJ/mol [10]. TG, DSC and XRD curves are used to explain the mechanism of obtaining hausmanite in the thermal decomposition of manganese sulphate [11]. The apparent activation energy of dehydration at temperature range 200-400°C is 117,11 kJ/mol, and for the decomposition of  $\text{MnSO}_4$  to  $\text{Mn}_3\text{O}_4$  in the temperature range 750-1050°C, its value is 226,44 kJ/mol. With TG and DSC curves, the authors received the same results at non-isothermal  $\text{MnSO}_4$  heating. The kinetics of the cubic  $\text{Mn}_2\text{O}_3$  was described by reaction of the first order and its activation energy was 61,2 kJ/mol [12]. The  $\text{MnFe}_2\text{O}_4$  [13] had apparent activation energy 31,7 kJ/mol.

The oxidation kinetics of  $\text{FeV}_2\text{O}_4$  was studied using the methods of analysis for isothermal and non-isothermal conditions. It has been found [14] that the kinetics can be described from the point of view of three different overlapping processes.

The purpose of these studies is to identify some kinetic characteristics (activation energy, rate constant and rate of the processes), taking place in the system  $\text{Fe}_2\text{O}_3\text{-MnO-V}_2\text{O}_5\text{-SiO}_2$ , and to compare results between synthetic mixture of pure oxides Mix 1 and Mix 2 containing manganese concentrate, waste vanadium catalyst and  $\text{Fe}_2\text{O}_3$ .

## 2. EXPERIMENTAL WORK

### 2.1. Raw materials

#### *Manganese concentrate.*

The manganese deposit "Obrochiste" is located in Varna manganese-ore region and represents an area including a large ore formation in Bulgaria. The content of Mn is - 28,47%. The chemical composition of the manganese concentrate is shown in Table 1.

#### *Waste vanadium catalyst.*

Vanadium catalyst is used for the sulfur acid production. It is deposited as waste product after its deactivation. Annually between 500 and 1000 tones vanadium catalyst are released from sulfur acid production and in the same time it contains significant quantity of deficit vanadium. The toxicity of the vanadium causes certain environmental problems which is an additional consideration to look for ways to utilize this valuable waste product. The chemical composition of waste vanadium catalyst is shown in Table 2.

**Table -1:** Chemical composition of manganese concentrate / mass. %

MnO	FeS <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>
44,56	2,25	1,79	12,4	2,00	3,90	2,10

**Table -2:** Chemical composition of the waste vanadium catalyst / mass. %

V <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>
4,12	3,4	57,12	6,71	3,93	0,82

Waste vanadium catalyst, manganese concentrate and chemically pure oxides of Fe<sub>2</sub>O<sub>3</sub>, MnO (MnO<sub>2</sub>), V<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> were used as materials for two mixture preparation.

Mixture 1 with the pure oxides were calculated and prepared in accordance with the percent correlation in the Mix 2 containing manganese concentrate, waste vanadium catalyst and Fe<sub>2</sub>O<sub>3</sub>.

## 2.2. Experimental data and discussion

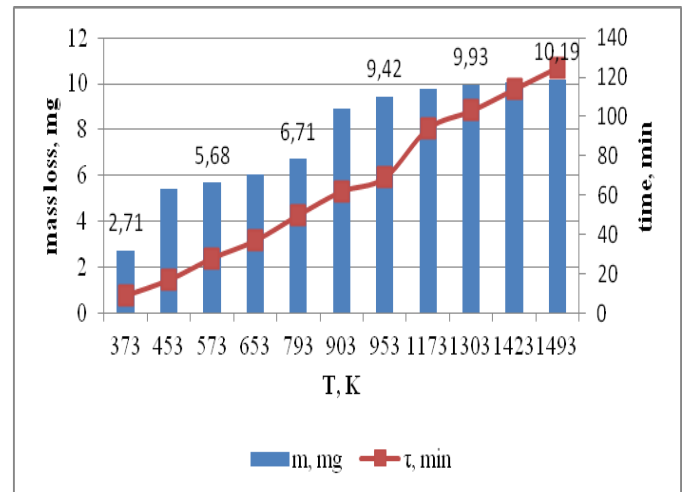
DTA and TG curves show that when the two mixtures were heated, the processes evolve in three stages.

**For Mix. 1:** I stage- 453-783 K; II stage-783-973 K and III stage- 1053-1423 K. In each stage, one endothermic peak associated with retention and reducing the sample mass was registered. The first interval is associated with the dissociation of MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub>, the second one - in the temperature range 783-973 K, a solid solution between Fe<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> from peritectical type is formed, which decomposes at ~ 1203K, and the third one, a partial dissociation of Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> takes place. XRD analysis of the products showed the presence mainly of rhombic hematite (Fe<sub>2</sub>O<sub>3</sub>), cubic Mn<sub>2</sub>O<sub>3</sub>, tetragonal hausmanite (Mn<sub>3</sub>O<sub>4</sub>) and cristallobite (SiO<sub>2</sub>).

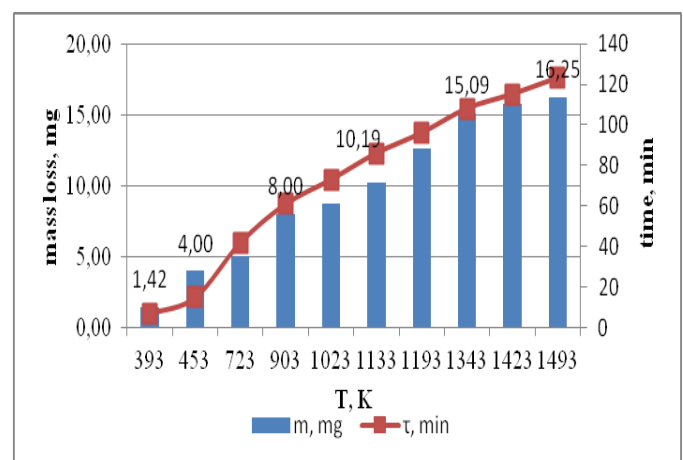
**For Mix 2:** I Stage - 463-733K; II - 733-1033 and III - 1033-1423K. As in Mix 1 in each stage, an endothermic peak associated with retention and reducing the mass of the sample was registered. The first two stages are associated with the behavior of the oxides in the waste vanadium catalyst and formation of FeV<sub>2</sub>O<sub>4</sub> or FeV<sub>2</sub>O<sub>6</sub>, and also with the formation of a solid solution of Fe<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> from peritectical type. The third stage involves the formation of a new phase Jacobsite. XRD analysis of the product showed the presence of Jacobsite (Mn<sub>6</sub>Fe<sub>4</sub>)(Mn<sub>4</sub>Fe<sub>1,6</sub>)O<sub>4</sub>, vanadium oxide (V<sub>3</sub>O<sub>4</sub>), coulsonite (Fe<sub>2</sub>VO<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub>.VO), hematite Fe<sub>2</sub>O<sub>3</sub> and α quartz.

Temperature dependence and mass loss of the studied mixtures are shown in Chart 1 and Chart 2. The results of the mass loss indicate that up to 1000 K synthetic Mix 1 and Mix 2 containing waste vanadium catalyst have similar changes. The losses at this temperature reach up to 15%. That is a result from dehydration processes (evaporation of

dampness and oxides dissociation), which is accompanied by endothermic effects. In comparison with the synthetic mixture, mass losses of the second one are significantly higher at temperatures above 1100 K. In Mix 2, mass loss of 25,2% was registered at temperature 1493 K, which is the result of the impurities in the vanadium catalyst and manganese concentrate (mainly related to the sulfur in the sulphides and sulphites).



**Chart -1:** Dependence of mass loss on temperature and time of synthetic mix. 1



**Chart -2:** Dependence of mass loss on temperature and time of mix. 2.

Based on the results of the obtained derivatograms, the rate constant, activation energy and process rate were determined. To this end, the dependence  $\lg m - 2\lg T = f(1/T)$  was proposed, as shown in Chart 3 and Chart 4. Using equation (1) [15] the apparent activation energy was calculated.

$$E = 8,31,2,3 \cdot 10^{-3} \cdot (y_1 - y_2 / x_1 - x_2), \text{ kJ/mol} \quad (1)$$

A comparative chart of apparent activation energy values for two mixtures is shown in Chart 5. The heating process of the test mixtures took place in the diffusion area in the whole temperature range.

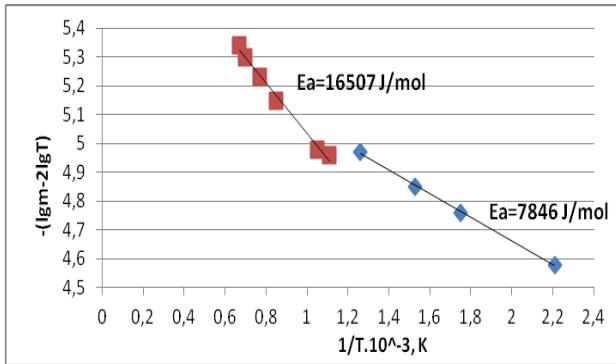


Chart -3: Dependence  $\lg m - 2\lg T = f(1/T)$  of synthetic mix. 1.

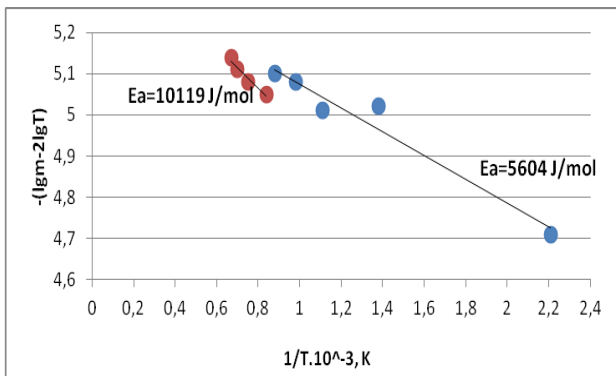


Chart -4: Dependence  $\lg m - 2\lg T = f(1/T)$  of mix. 2

The low values of the activation energy in the temperature range up to 800 K are due to the processes of nucleation and growth of new phases, occurring on the surface due to the dissociation processes. The obtained apparent activation energies at temperatures over 900 K are lower compared with the values of pure oxides obtained from various authors [3, 4, 6, 10, 12, 14]. Lower values of activation energy in the studied system are due to formation of new phases ( $\text{FeV}_2\text{O}_4$ ,  $\text{FeV}_2\text{O}_6$ ,  $(\text{Mn}_6\text{Fe}_4)(\text{Mn}_4\text{Fe}_{1.6})\text{O}_4$ ).

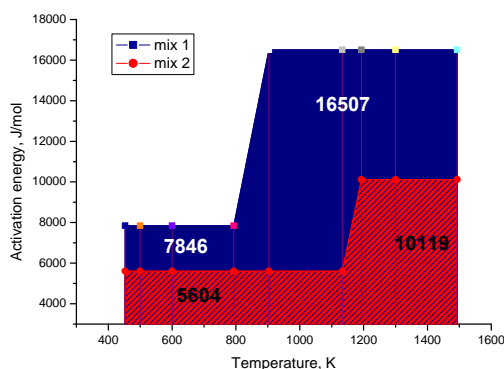


Chart -5: Comparison diagram of the activation energy changing at non-isothermal heating for mix 1 and mix 2.

Rate constant equations are derived based on experimental data.

For mix 1:

$$\lg k_1 = \frac{409}{T} - 5,48; R^2 = 0,999; \text{Temp. range } T = 453\text{K} - 793\text{K}.$$

$$\lg k_2 = \frac{873}{T} - 5,91; R^2 = 0,991; \text{Temp. range } T = 903\text{K} - 1493\text{K}$$

For mix 2:

$$\lg k_1 = \frac{288}{T} - 5,36; R^2 = 0,956; \text{Temp. range } T = 453\text{K} - 1133\text{K}$$

$$\lg k_2 = \frac{506}{T} - 5,47; R^2 = 0,945; \text{Temp. range } T = 1193\text{K} - 1493\text{K}$$

The process rate was calculated by equation (2)

$$v = \pm \frac{\Delta m}{\Delta \tau \cdot m_0}, \text{ mg/min} \quad (2)$$

,where  $v$  is the average process rate g/min;  $\Delta m$  is the change of the mass of the mixture, mg;  $\Delta \tau$  - change over time, min;  $m_0$  - the initial mixture mass, g.

A comparison of change of rate processes in mixtures 1 and 2 heated to 1493K is shown in Chart 6.

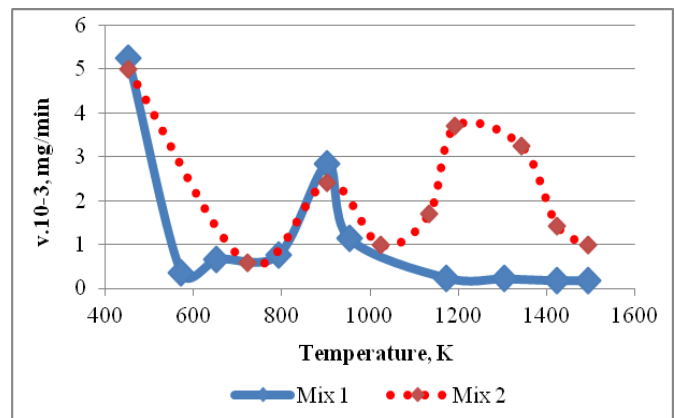


Chart -6: Dependencies of the heating rate on temperature for mix 1 and 2.

The results show that for Mix 1, the maximum rate was reached at  $T \sim 903\text{K}$  whereas for Mix 2 at  $T \sim 1193\text{K}$ . On the rate curves there is one maximum peak for Mix 1 and two for Mix 2. The first maximum of mixture 2 is similar to that of Mix 1 ( $T \sim 930\text{K}$ ), which show that at this temperature the same process occurs. This maximum corresponds to the rate of formation of solid solution between  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  from peritectical type. For the first mixture there is a subsequent decomposition whereas for the second mixture there is a subsequent decomposition as well as Coulsonite ( $\text{Fe}_2\text{VO}_4$ ) phase formation. The second maximum of the rate for mix 2 is associated with the formation a new phase Jacobsite ( $(\text{Mn}_6\text{Fe}_4)(\text{Mn}_4\text{Fe}_{1.6})\text{O}_4$ ).

### 3. CONCLUSIONS

It was found out, analyzing the DTA and TG curves of two mixtures, that the processes took place in three stages. The first stage involved the dissociation of  $MnO_2$  (mix 1) and vanadium oxides from the waste vanadium catalyst (mix 2). Typical of the second stage is the formation of a solid solution of  $Fe_2O_3$  and  $Mn_2O_3$  from peritectical type that subsequently decomposes. In the second stage of mix 2, a new phase  $FeV_2O_4$  or  $FeV_2O_6$  was also formed. In the third stage, new phases hausmanite  $Mn_3O_4$  (mix 1) and Jacobsite  $(Mn_6Fe_4)(Mn_4Fe_{1.6})O_4$  (mix 2) were formed.

The apparent activation energy of the two mixtures was determined experimentally. Activation energy for mix 1 is  $E_{a1} = 7,876$  kJ/mol in the range up to 800K, and  $E_{a1} = 16,507$  kJ/mol to 1493K. For mixture 2  $E_{a2} = 5,604$  kJ/mol in the range up to 900K and  $E_{a2} = 10,119$  kJ/mol to 1493K. The activation energy values show that heating processes run in an external diffusion area.

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