Study of Metal-Humic Catalysts before and After the Gas Desulphurization Process Using Thermal Analysis

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Abstract. The study of metal-humic catalysts before and after the SO₂ conversion has been carried out using thermal analysis. The thermogravimetric analysis and differential thermal analysis has been carried out using Perkin-Elmer TGA 7 and DTA 7 equipment in an argonic atmosphere. The heating rate of samples in the DTA was 10 °C/min., and in the TGA 40 °C/min. The following catalysts have been chosen for analysis: H-Pb²⁺/450 °C, H-B/450 °C, H-Sn²⁺/450 °C, H-Ce⁴⁺. The study of metal-humic catalysts using thermal analysis has shown that, in the DTA curves of studied catalysts before SO₂ conversion, endothermic peaks related to decomposition of metal carbonates, melting of metals or decomposition of metal-humic bonding. In the DTA curves after the SO₂ conversion process, there are additional endothermic peaks related to the presence of sulphur in the metal-humic compounds and to thermal decomposition of those bonds.

1. Introduction
In 1887, Le Chatelier [1] published a paper entitled “The action of heat on clays” describing, for the first time, the thermal analysis method. The measurement consisted in recording the temperature of a heated clay sample using thermocouple and mirror galvanometer. It allowed to observe the behavior of the material during heating and to obtain, based on diagrams, the T = f(t) curve.

In time, this method was considerably modified. Using thermal analysis to study different materials has both scientific and practical applications. The development of thermal methods, along with technological progress, led to use of those methods for evaluation of those materials and their compounds both in quantitative and qualitative terms [2-3]. A combination of basic techniques of thermal analysis with mass atomic adsorption spectroscopy (AAS) and spectrometry, X-ray fluorescence spectrometry, (XRF), (MS), study of magnetic properties (TM), and mechanical properties (TMA) allows to obtain many information on the studied material at the same time. It is of particular importance in Earth sciences, especially in geochemistry [4].

Thermal methods are used to assess ceramic processes. An analysis of DTA and TG curves allows to identify clays and other materials [4, 5]. Anticipation of changes that may occur e.g. in production of clays allows to avoid generating a bad quality product [6].
In the glass industry, a lot of attention is paid to thermal properties of materials, and consequently, to the product obtained, i.e. glass. Physical, chemical and structural transformations during production decide on the generated product’s properties. Those transformations may be controlled using thermal analysis. A selection of adequate quantities of components allows to recognize transformations occurring during melting of quartz mixtures in comparison to potassium and lead silicate during glass production process.

In metallurgical processes, thermal analysis allows to evaluate phase transitions of material decomposition. Every sulphide mineral has a characteristic oxidation temperature. The technology of a metallurgical process of sulphides consists in a transition from sulphide to oxide. The transition level characterizes the sulphur content in the remaining material [7,8].

2. Experimental

2.1. Materials and methods of examination

The thermogravimetric analysis and the thermal differential analysis were carried out using the Perkin-Elmer equipment – TGA 7 and DTA 7 in an argon atmosphere. The heating rate was, in the case of the DTA – 10 °C/min., and TGA – 40 °C /min. Catalysts were studied before and after the SO2 conversion process. Catalysts that were most effective in the desulfurization process in selected temperatures were chosen for analysis, namely: H-Pb2+/450 °C, H-B/450 °C, H-Sn2+/450 °C, H-Ce4+.

2.2. Measurement results

2.2.1. Humic acid biochar

Humic acid biochar was a medium for metal-humic catalysts, and for that reason it was subjected to thermal analysis in order to compare it with obtained metal-humic catalysts (Table 1).

The TGA curve of humic acid biochar, before the desulfurization process, at 100-500 °C, shows a slight weight loss – ca. 3 %. At 500-1000 °C, the weight loss is more considerable (17.1%), as within this range, the humic substance is being decomposed – and the process is the more intense, the more the temperature of thermal analysis exceeds the temperature of humic acid carbonization (700 °C). The entire weight loss for humic acid biochar is 19.9 %. The DTA curve of humic acid biochar, before the SO2 conversion process, shows a small endothermic peak with minimum at 750°C.

After the desulfurization process at 25 °C, the weight loss of humic acid biochar up to the temperature of 500 °C is significantly higher than before the desulfurization process, reaching 6.5 %. At higher temperatures (500 °C), the TGA curve of the biochar is parallel to the TGA before the desulfurization process. It means that the bulk of the sulphur dioxide adsorbed is released in the temperature of up to 500 °C. It is confirmed by the DTA curve in which a clearly visible, deep endothermic peak with minimum at the temperature of 238 °C occurs, which is related to SO2 release. The entire weight loss in the catalyst, after the SO2 conversion, was approximately 23.6 %.

### Table 1. Thermogravimetric analysis and thermal differential analysis of the humic acid biochar

| Curve peaks desulfurization | Weight loss visible on curves | Temperature range, °C | TGA, % wt. desulfurization |
|-----------------------------|-----------------------------|-----------------------|---------------------------|
| Curve peaks DTA, °C Before | Curve peaks DTA, °C After | Weight loss visible on curves TGA, % wt. desulfurization |
| 120 Before | 150 After | 150 | 100-500 | 2,8 |
| 238 Before | 200 After | 200 | 500-1000 | 17,1 |
| 750 Before | 647 After | 650 | 630 | 17,1 |

| Total weight loss to temperature ratio | 1000 °C | 19,9 | 23,6 |

2.2.2. H-B catalyst

The DTA curve of the H-B catalyst, before the desulfurization process, at a temperature of 600 °C, has shown one endothermic peak with two minima at 481 °C and 655 °C (Table 2). It is possible that the first one corresponds to melting temperature B2O3 (Tm 450 °C). The weight loss in the TGA curve in
600 °C was 6.3 % by mass, and within the temperature range of 600-1000 °C, it reached 7.5 %. The DTA curve of the catalyst after the desulfurization process has shown one endothermic peak with minima at 794 and 857 °C. Total weight loss on the catalyst after conversion was considerably smaller than before the conversion and reached 8.7 %. It means that the sulfated catalyst is stable in temperatures of up to 1000 °C, and consequently, that it forms permanent bonds with sulfur dioxide.

### Table 2. Thermogravimetric analysis and thermal differential analysis of the H-B catalyst.

| Curve peaks DTA, °C before desulfurization | Curve peaks DTA, °C after desulfurization | Weight loss visible on curves TGA,% wt. before desulfurization Temperature range, °C |
|------------------------------------------|------------------------------------------|------------------------------------------|
| Before 481 230                           | After 655 430                            | 120-130 1,7                               |
| Before 794 770                           | After 857 820                            | 600-1000 7,5                              |
| 1000 Total weight loss to temperature ratio 1000 °C | 14,8 8,7                                 |

2.2.3. **H-V catalyst**

The DTA curve of the H-V catalyst shows two endothermic peaks (Table 3). The first significant peak with minimum at 511 °C finds its equivalent in the DTA curve of the catalyst after the SO2 conversion at 534 °C. The second endothermic peak starts at 850 °C and reaches its minimum at 951 °C for the sample before and after conversion. Both peaks are accompanied by weight loss in TGA curves, within the temperature range of 500-1000 °C in the quantity of 3.5 % by mass. Weight loss in the TGA curve of the catalyst, before the conversion, within the temperature range of 750-1000 °C, appearing also in the TGA curve of the catalyst after conversion, might be a result of decomposition of the vanadyl sulphate applied in H-V catalyst processing. Total catalyst weight loss after SO2 conversion exceeded by 3.7 % the weight loss of the catalyst before conversion, and the bulk of the weight loss occurred at 500-1000 °C, which suggests that a part of the reacted SO2 may be released in that temperature range.

### Table 3. Thermogravimetric analysis and thermal differential analysis of the H-V catalyst.

| Curve peaks DTA, °C before desulfurization | Curve peaks DTA, °C after desulfurization | Weight loss visible on curves TGA,% wt. before desulfurization Temperature range, °C |
|------------------------------------------|------------------------------------------|------------------------------------------|
| Before 511 230                           | After 534 230                            | 100-500 3,5                               |
| Before 799 520                           | After 952 850                            | 500-800 6,9                               |
| 1000 Total weight loss to temperature ratio 1000 °C | 16,7 20,4                                 |

2.2.4. **H-Ag catalyst**

The DTA curve of the H-Ag catalyst before the conversion shows one large, broad peak related to the so-called baseline float, and another, clearly visible, with a minimum at 950 °C, corresponding to the melting temperature of silver (960.8) (Table 4). It occurs also in the DTA curve of the catalyst after conversion. TGA curves show that weight loss of the catalyst before and after conversion are similar, reaching approximately 4.6-4.8 %. Exceptionally low weight loss in the H-Ag catalyst proves a strong impact of the addition of silver ions on the thermal resistance of the catalyst compared to humic acid
biochars. As the H-Ag catalyst conversion was not significant, the difference in the catalyst weight loss before and after conversion is slight – 0.2 % by mass.

### Table 4. Thermogravimetric analysis and thermal differential analysis of the H-Ag catalyst.

| Curve peaks |
|-------------|
| DTA, °C     |
| Before      | After      |
| 590         | 140        |
| 640         | 756        |
| 956         | 956        |

| Weight loss visible on curves |
|------------------------------|
| Temperature range, °C TGA,% wt. |
| Before          | After          |
| 100-680         | 2,0            |
| 680-1000        | 2,6            |
| 800             | 2,5            |

| Total weight loss to temperature ratio 1000 °C |
|-----------------------------------------------|
| 4,6                                           |

#### 2.2.5. H-Sn catalyst

DTA curves of H-Sn preparations, both before and after conversion, show an endothermic peak with a minimum at 235 °C, corresponding to the melting temperature of tin (Table 5). It is sharp and clearly visible; nevertheless, in the catalyst curve before the conversion, it is more pronounced than in the catalyst after conversion, which may suggest that a part of the sulphur dioxide reacted with tin. Another endothermic peak occurs at 650-800 °C, accompanied by a significant weight loss in the TGA curve. Within that temperature range, sulphur dioxide may be released, most likely bound in the form of tin (IV) sulphite. Total catalyst weight loss in the catalyst after conversion was two times higher than the weight loss in the catalyst before the desulfurization process – the difference was 11.4 %.

### Table 5. Thermogravimetric analysis and thermal differential analysis of the H-Sn catalyst.

| Curve peaks |
|-------------|
| DTA, °C     |
| Before      | After      |
| 103         | 99         |
| 235         | 235        |
| 717         | 736        |

| Weight loss visible on curves |
|------------------------------|
| Temperature range, °C TGA,% wt. |
| Before          | After          |
| 100-600         | 2,0            |
| 600-800         | 8,0            |
| 800-1000        | 2,6            |

| Total weight loss to temperature ratio 1000 °C |
|-----------------------------------------------|
| 12,6                                          |

#### 2.2.6. H-Fe²⁺ and H-Fe³⁺ catalysts

Both preparations may be analyzed together, as the nature of their thermal analysis curves is similar (Table 6). It is related to the fact that Fe³⁺ may be reduced to Fe²⁺. At 411 °C, the DTA curve of the catalyst after the SO₂ conversion shows a slight endothermic peak, accompanied by a slight weight loss of 5.56 % in the TGA curve at 300-690°C, which is probably a result of sulfur dioxide release from the surface of the catalyst. DTA curves, before and after conversion, show sharp, clear peaks within the temperature range of 750-850 °C, which might be a result of reduction of iron oxides. The Fe₂O₃ oxide is probably reduced to FeO and Fe₃O₄ oxides, and the FeO oxide is subject to further reduction to metal. Those peaks are characteristic of DTA curves for iron-humic preparations [7,8]. Weight loss in the catalyst after the conversion was higher by 2.3 % than in the catalyst before the conversion.
Table 6. Thermogravimetric analysis and thermal differential analysis of the H-Fe$^{2+}$ and H-Fe$^{3+}$ catalysts.

| Curve peaks DTA, °C | Curve peaks DTA, °C | Weight loss visible on curves TGA, % wt. desulfurization |
|---------------------|---------------------|----------------------------------------------------------|
| Before              | After               | Temperature range, °C Before | After |
| 91                  | 103                 | 130-300                                                  | 0,5   |
| 411                 | 400                 | 300-690                                                  | 4,2   |
| 784                 | 780                 | 690-1000                                                 | 15,2  |
|                     | 850                 |                                                          | 15,0  |

Total weight loss to temperature ratio 1000 °C 19,9 22,2

2.2.7. H-Mg catalyst

The TGA of the studied catalyst, before the desulfurization process, shows a relatively small, but continuous weight loss at 700 °C, reaching 8.2 %. Above 700 °C, the loss is 5.5 %, which reflects the decomposition of magnesium-humic bonds. The DTA curve, in temperatures of up to 700 °C, shows a large endothermic peak, and above that temperature, a slow return to the baseline occurs.

In the DTA curve of the H-Mg catalyst, after the desulfurization process, at 25 °C, three small endothermic peaks with minima at 579, 821, 933 °C may be distinguished. From 500 °C, in the TGA curve, a clearly increasing weight loss is visible, which in the DTG curve is characterized by two minima at ca. 600 °C and 650 °C, and a minimum at approx. 900 °C. The difference in weight loss before and after desulfurization is 9.8 %. It means that the SO$_2$ adsorbed at 25 °C does not form permanent bonds with the surface of the catalyst and that it is released at 500-800 °C.

After the desulfurization process, at 300 °C, in DTA curves of the H-Mg catalyst, there are three endothermic peaks with minima at 605, 772, and 907 °C. The bulk of the weight loss in TGA curves occurs at 550-1000 °C and reaches 9.7 %. The difference in weight loss in the catalyst before and after the desulfurization process at 300 °C is marginal – 0.2% - which indicates that at 300 °C, permanent bonds are formed between the H-Mg catalyst and sulphur dioxide.

2.2.8. H-Pb catalyst

The DTA curve of the H-Pb preparation before the conversion shows a large, broad endothermic peak starting at 200 °C with a minimum at 495 °C (Table 7). It is probably due to decomposition of carbonates (especially the alkaline lead carbonate). In the DTA curve of the catalyst after conversion, the peak is merely apparent. The bulk of the weight loss in the TGA curve for the H-Pb catalyst after the SO$_2$ conversion occurs in two temperature ranges. The first one at 400-650 °C is 8.0 %, the second one at 650-1000 °C reaches 8.7 %. Most likely, in higher temperature ranges, a decomposition of lead (IV) sulphites or (VI) sulphites takes place.

Table 7. Thermogravimetric analysis and thermal differential analysis of the H-Pb catalyst.

| Curve peaks DTA, °C desulfurization | Curve peaks DTA, °C desulfurization | Weight loss visible on curves TGA, % wt. desulfurization |
|-------------------------------------|-------------------------------------|----------------------------------------------------------|
| Before                              | After                               | Temperature range, °C Before | After |
| 90                                 | 90                                  | 120-400                                                   | 1,3   |
| 495                                | 496                                 | 400-650                                                   | 8,0   |
| 700                                | 806                                 | 650-1000                                                  | 8,7   |
|                                     | 850                                 |                                                          |       |
|                                     | 1000                                |                                                          |       |

Total weight loss to temperature ratio 1000 °C 18,0
2.2.9. H-Ce catalyst
An analysis of the number of conversions of sulphur dioxide in the H-Ce catalyst shows that it bound large quantities of SO$_2$ (166.5 mg/g category at 450 °C) (Table 8). However, the difference in weight loss between the catalyst before the conversion is marginal – 0.4% - which means that sulphur dioxide is permanently bound to the metal-humic substance.

The DTA curve of the preparation before the conversion shows one large endothermic peak with a minimum at 617 °C, which may reflect the decomposition of the metal-humic substance.

The DTA curve of the catalyst after conversion shows two small endothermic peaks at 567 and 778 °C, accompanied by weight losses in the TGA curve within the temperature range of 400-650 °C (9.2 %) and 650-1000 °C (9.3 %). It is probable that in those two stages, sulphur dioxide is released from the cerium sulfate created in the desulfurization process, which is proven by endothermic peaks in the DTA curve. Total weight loss in the catalyst after conversion is 22.5 % by mass.

| Curve peaks | Curve peaks | Weight loss visible on curves |
|-------------|-------------|-----------------------------|
| DTA, °C     | DTA, °C     | Temperature range, °C        |
|             |             | TGA, % wt.                   |
| Before      | After       | Before                      | After                      |
| 112         | 112         | 150                         | 160                        | 100-300                     | 4.8                         |
| 567         | 617         | 230                         | 250                        | 100-400                     | 4.0                         |
| 778         | 650-700     | 450                         | 550                        | 300-620                     | 9.4                         |
|             | 810         | 800                         | 900                        | 620-1000                    | 8.0                         |
|             |             |                             |                             |                            | 9.3                         |

2.2.10. H-Ba catalyst
Both DTA curves of the H-Ba catalyst before the SO$_2$ conversion show a large, deep endothermic peak starting at 400 °C and reaching its minimum at 753 °C, and another one, merely apparent, at 865 °C (Table 10). Those temperatures probably correspond to the decomposition of barium carbonate. The weight loss observed in the TGA curve of the catalyst before the conversion is highest at 600-1000 °C and reaches 15.8 %.

The DTA curve of the H-Ba catalyst after the SO$_2$ conversion shows two endothermic peaks. The first one occurs at 600-700 °C with a minimum at 650 °C, which is probably where SO$_2$ release occurs. Another peak occurring in the temperature range of 700-1000°C with a minimum at 768 °C might be responsible for the barium carbonate decomposition. Weight losses observed in the TGA curves are highest at 600-1000 °C and reach, respectively, 15.8 % for the catalyst before conversion, and 21.7 % by mass for the catalyst after conversion. The difference in weight loss reaching 6.5 % is probably due to SO$_2$ release from the surface of the catalyst. The weight loss in the catalyst after conversion, reaching 8.4 %, occurs at 750-100 °C. Those inflections are accompanied also by peaks in
the DTA curve at 798 and 886 °C. Within that range, the aluminium sulphate generated in the desulfurization process is probably decomposed. Total weight loss in the catalyst after conversion is 19.5 by mass and is 6 % higher than the weight loss in the catalyst before the desulfurization process.

3. Discussion of the results

Metal-humic catalysts obtained by introducing metal ions into the ion exchange process or humic acid complexation and their carbonization at 700 °C, show a higher conversion in the gas desulfurization process at a temperature exceeding 150 °C in comparison to biochars of those humic acids.

A study of metal-humic catalysts using thermal analysis has shown that the addition of metal ions to humic acids causes the appearance of additional endothermic peaks in DTA and TGA curves. Endothermic peaks occurring within the temperature range of 110-130°C are related to evaporation of hygroscopic moisture. Peaks occurring in higher temperatures have different origins. DTA curves of some of the studied catalysts before the SO₂ conversion show endothermic peaks related to decomposition of metal carbonates that are created as a result of a reaction between CO₂ and CO generated during decomposition of the humic substance with metal ions. Other peaks correspond to the melting temperature of metals that have been introduced in the humic substance and whose oxides were reduced to metal on a strongly reductive carbon medium. Furthermore, there are peaks that are difficult to interpret, which probably originated from the metal and humic substance compounds. Humic acid biochar up to 1000 °C has shown a weight loss of 20 % before the conversion, whereas weight loss in metal-humic catalysts before the SO₂ conversion fluctuated heavily – from 4.6 % to 22 % by mass. Generally, however, most catalysts show smaller weight loss than the humic acid biochar itself. It means that introduction of metal ions into the humic substance causes the thermal stability of humic catalysts to increase.

DTA curves of catalysts after the SO₂ conversion process show additional peaks related to the presence of sulphur compounds in the structure of metal humates and to thermal decomposition of those bonds. Sulphur may be bound to the catalyst in the form of sulphites (IV, VI). A strongly reductive carbon medium may also reduce the sulphur dioxide to metal sulphides or to elemental sulphur. Weight losses in the catalysts after the desulfurization process range between 4.8-27.2 % by mass and are generally smaller than in the humic acid biochars after the desulfurization process (23.6 % by mass), but higher than in the biochars before the conversion. The only exception is the H-B catalyst whose weight loss after the conversion was 6.1 % smaller than before the conversion. Large weight losses in catalysts after conversion occurred within the temperature range of 600-1000 °C. Those losses are due to thermal decomposition of abovementioned compounds that may be generated in the desulfurization process.

A comparison of thermal analysis results and the SO₂ metal-humic catalyst conversion results shows that the entire amount of reacted SO₂ is released from the H-V, H-Ba and H-Fe³⁺ catalysts at the temperature of up to 1000 °C. On the other hand, only a part of the SO₂ is released from H-Sn, H-Mg (70-73 %), H-Al (39 %) and H-Fe²⁺ (26%) catalysts. From catalysts such as H-B, H-Ce, H-Ag, no sulfur dioxide is released up to 1000 °C.

Weight loss in the TGA curves of catalysts after the desulfurization process (temp. up to 1000 °C) is generally higher than amounts of SO₂ released during thermal regeneration of catalysts, and those differences may be due to a much lower temperature in which regeneration was conducted (800 °C).

4. Conclusions

A study of metal-humic catalysts using thermal analysis has shown that DTA curves of studied catalysts before the SO₂ conversion show endothermic peaks related to decomposition of metal carbonates, metal melting or decomposition of metal-humic bonds.
In DTA curves of catalysts after the SO\textsubscript{2} conversion process, additional endothermic peaks appear, due to the presence of sulphur compounds in the metal-humic compound structures, and to the thermal decomposition of those bonds.

Significant weight losses in TGA curves of catalysts after the SO\textsubscript{2} conversion occur at 600-1000 °C and are related to sulphur dioxide release, which may be bound to the catalyst in the form of (VI and V) sulphites or be reduced to metal sulphides.

Sulphur dioxide, up to 1000 °C, creates thermostable bonds with H-B, H-Ce, and H-Ag catalysts, whereas the SO\textsubscript{2} reacted on H-V, H-Ba and H-Fe\textsuperscript{3+} catalysts is fully released within the temperature range of 600-1000 °C.

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