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CHARACTERIZATION, CORRELATION AND KINETICS OF DOLOMITE SAMPLES AS OUTLINED BY THERMAL METHODS

M. V. Kök[1*] *and W. Smykatz-Kloss*[2]

[1]Department of Petroleum and Natural Gas Engineering, Middle East Technical University, 06531 Ankara-Turkey
[2]University of Karlsruhe, Mineralogisches Institut der Universität, Kaiser str. 12, 76131 Karlsruhe, Germany

In this study, the decomposition behavior of four dolomite samples of different origin was studied by X-ray diffractometer and simultaneous TG-DTA experiments. Three different decomposition regions were determined known as dehydration of inter-particle water, formation of MgO and calcite and decomposition of calcite. Kinetic analysis of these decomposition regions was analyzed and the related activation energies are determined. It was observed that the activation energies were in the range of 48–137 kJ mol^{-1}.

Keywords: *chemical structure, decomposition, dolomite, thermal analysis, X-ray*

Introduction

The study of clays and silicate minerals plays an important role in the propagation of the thermal analysis techniques. The reactions which occur in a mineral or other chemical substance during thermal treatment and the mass-energy changes can be identified and measured very clearly by thermal analysis methods. Dolomite is a double salt of calcium and magnesium carbonate and is one of the two forms of limestone. The thermal decomposition of dolomite shows different characteristics depending on the atmosphere.

Makó and Juhász [1] studied the crystal structure deformation of dolomite caused by intensive grinding by X-ray and thermal analysis. Structurally deformed dolomite crystallites developed due to mechanical treatment decomposed in two stages at a higher and lower CO_2 partial pressure. It was observed that the proportion of structurally distorted dolomite increases with grinding time. Dollimore [2] showed that TG reveals the extent of the hydration product portlandite $Ca(OH)_2$ in the sample, the amount of $CaCO_3$ present and the amount of dolomite. X-ray studies confirm the presence of these materials. Kök and Smykatz-Kloss [3] studied the regular and iron-bearing dolomites based on decomposition temperatures. The mass% FeO of all the dolomite samples was identified by DTA and the results are confirmed by atomic absorption spectrophotometer experiments. Bogahawatta *et al.* [4] studied the effect of particle size and heat treatment on partial decomposition of dolomite for the extraction of calcite. Isothermal firing trials varying the soaking period were performed for dolomite at temperatures between 740–760°C according to schedules derived from thermogravimetric analysis (TG). A single processing cycle performed under the optimized conditions coupled with relatively short periods of hydration and re-carbonation (24 h, 15 min) yielded $CaCO_3$ with 7.5% MgO from a dolomite containing 23.6% MgO. Samtani *et al.* [5] studied the decomposition mechanism of dolomite in an atmosphere of CO_2. The energy of activation obtained for the isothermal experiments was determined to be 424.97 kJ mol^{-1}, while the value for the rising temperature experiment was 647.20 kJ mol^{-1}. Similarly, the In A-value for the isothermal experiments was found to be 49.22, while the In A-value for the rising temperature experiment was 74.20. The effect of procedural variables on the thermal behavior of dolomite in a nitrogen atmosphere is also investigated. Avial *et al.* [6] applied thermogravimetry to investigate the effects of temperature and atmosphere on conversion of sulfur dioxide absorbed by limestone. Ranges of temperature and particle size were studied, typical of fluidized-bed coal combustion. Isothermal experiments were performed at different temperatures in dynamic atmospheres of air and nitrogen. The maximum conversion was 29% higher in nitrogen atmosphere than in air atmosphere. Maitra *et al.* [7], investigated the kinetics of dolomite decomposition to study the effects of different parameters. It has been observed that pure dolomite decomposed in only two steps. Calcite decomposed to CaO between 900 and 960°C and under air, simultaneous formation of $CaCO_3$, CaO and MgO accompanied dolomite decomposition between 700 and 740–750°C. At the latter temperature, the calcite began to decompose even though a significant amount of dolomite was still present and simultaneous decomposition of the two carbonates was terminated at 780°C. Also, changes in decomposition rates of the various phases correlated with changes in the rate of mass loss determined by derivative thermogravimetric analysis. Mericboyu and Kucukbayrak [8] investigated

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[*] Author for correspondence: kok@metu.edu.tr

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

the calcinations kinetics of six dolomite samples originating from different parts of Turkey by using the non-isothermal thermogravimetry technique. TG curves of samples were obtained under two different atmospheres of pure nitrogen and a mixture consisting of 15 vol.% CO_2 and 85 vol.% dry air, by using a constant heating rate of 10°C min^{-1}. Arrhenius parameters E and A and the model function $f(\alpha)$ that best describes the reaction mechanism were evaluated for the decomposition reactions of both $MgCO_3$ and $CaCO_3$ components of samples. It was observed that besides differences in the chemical composition of samples, gaseous atmosphere and the method of calculation influenced the results obtained. Samtani *et al.* [9] studied the decomposition of dolomites via a single stage process in an atmosphere of nitrogen. The thermal behavior and the kinetics of decomposition were studied using the Arrhenius equation applied to solid-state reactions. It was found that calcite and dolomite supposedly decompose via a zero order mechanism while magnesite decomposes via a first order process. The energy of activation for the decomposition of magnesite, calcite and dolomite were 226.34, 192.50 and 175.05 kJ mol^{-1}, respectively. The three procedural variables studied included flow rate, heating rate and sample size. The kinetic parameters and mechanism remain unaffected by a change in these variables. Yener *et al.* [10] studied the thermal behavior of a mineral mixture of sepiolite and dolomite using X-ray diffraction and thermal analysis techniques (TG and DTA). The temperature ranges were determined for the dehydrations of interparticle water and zeolitic water. The changes in the specific surface area with the increase in temperature were discussed according to dehydrations and dehydroxylation of the sepiolite.

Experimental

The dolomite samples used in this research is collected from different geological formations. Lump samples were ground to and size fraction <60 meshes are collected for experiments. All samples were dried at 120°C and kept in desiccators prior to use. Simultaneous TG-DTA experiments were carried out at a linear heating rate of 10°C min^{-1} over the temperature range of ambient and 1200°C, under flowing air with a rate of 100 mL min^{-1}. Prior to experiments, TG-DTA equipment was calibrated and experiments were performed twice for repeatability. X-ray diffraction patterns were recorded on a diffractometer, using Ni-filtered CuK_α radiation. Room temperature diffractograms were recorded at a scanning speed of 0.002° 2θ per second. The X-ray diffraction patterns of the samples are given in Fig. 1.

Results and discussion

Thermal analysis techniques in combination with X-ray and chemical analysis are a novel technique in the determination of minerals in solid mixtures. In general, the decomposition of a pure, disordered crystal by means of heat will occur spontaneously. This will be reflected in the DTA curve by a very sharp en-

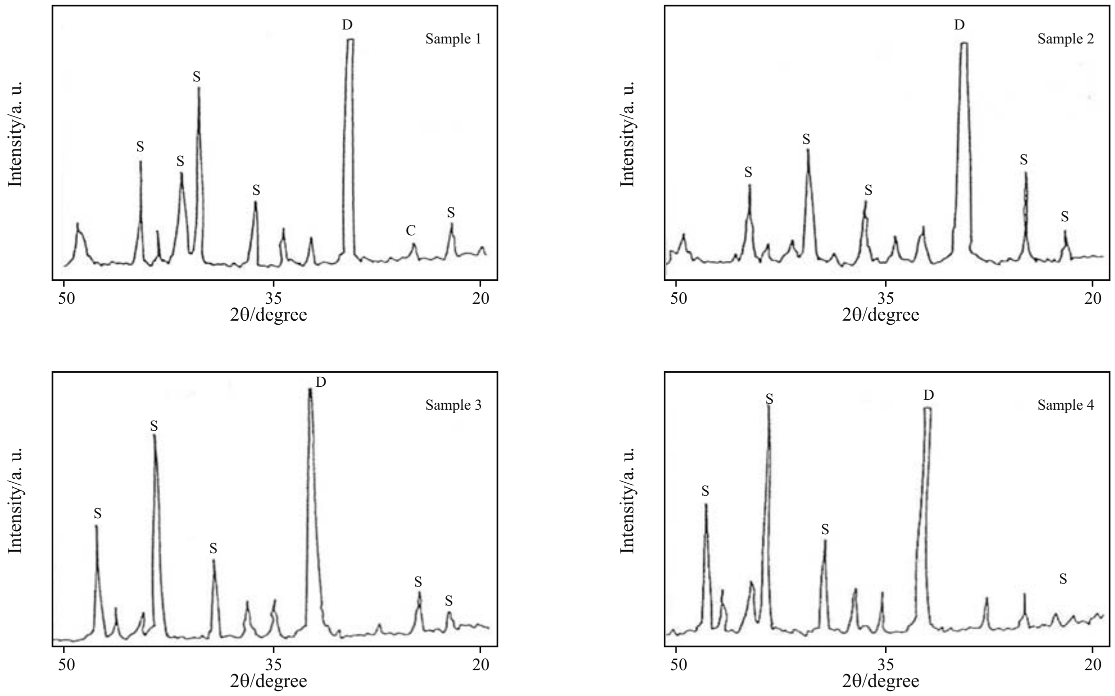

Fig. 1 X-ray diffraction patterns of the dolomite samples

Table 1 Temperature interval and maximum rate temperatures of the decomposition regions

Sample	Decomp. region I/°C	Max. decomp. temp. I/°C	Decomp. region II/°C	Max. decomp. temp. II/°C	Decomp. region III/°C	Max. decomp. temp. III/°C
1	20–300	100	695–805	760	805–910	860
2	20–315	110	740–800	780	800–900	870
3	20–310	105	690–820	790	820–900	875
4	20–305	100	770–820	765	820–920	865

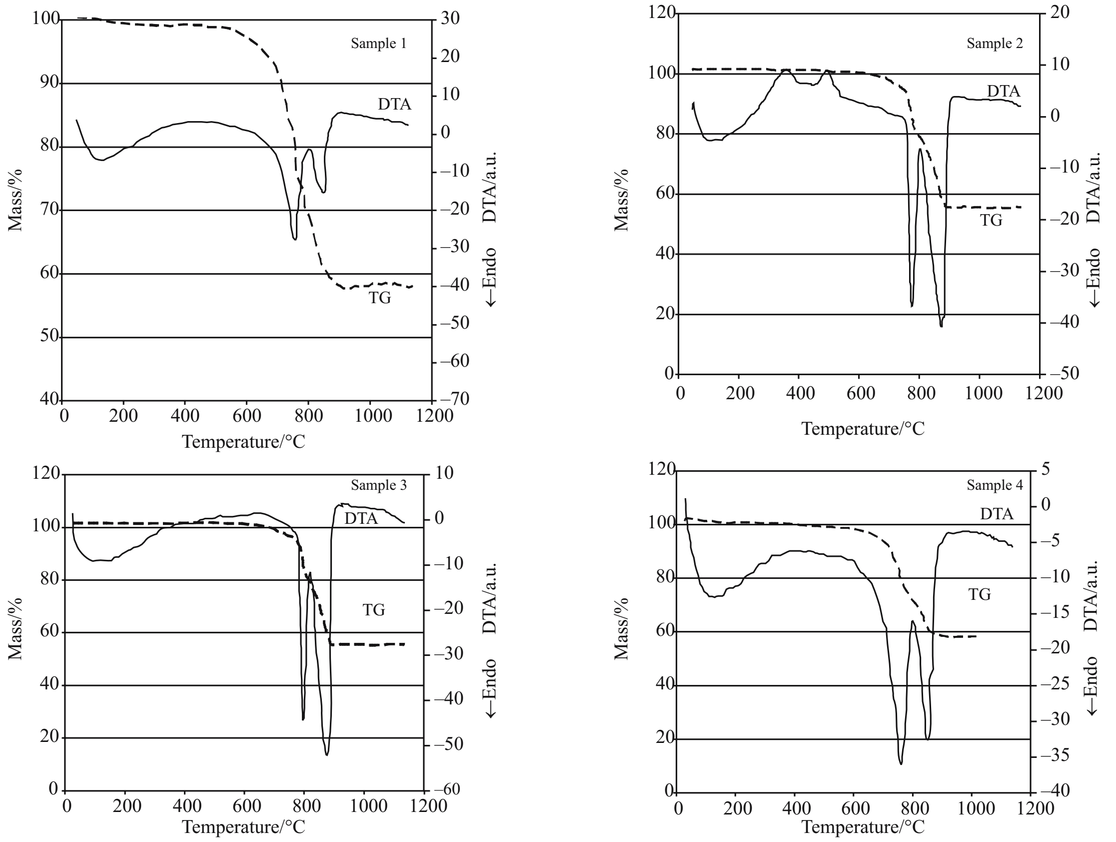

Fig. 2 TG-DTA curves of the dolomite samples

dothermic peak with relatively large temperature difference. Compared with the sharp decomposition peak of a pure crystal, the DTA curve of the same mineral that is impure or disordered only shows a broad deflection of lower intensity without as distinct endothermic minimum [3, 11].

The TG-DTA curves of dolomite samples for the temperature range of 20–1200°C are given in Fig. 2. The first endothermic mass loss which is observed in the temperature range of 20–315°C is due to the dehydration of inter-particle water known as moisture. The major endothermic mass loss of the dolomite sample was observed in the temperature range of 690–920°C and this might be divided in two different temperature ranges as 690–810°C and 810–920°C. The first temperature range can be assigned to the formation of MgO and calcite and the second range was assigned to the decomposition of calcite [12].

Table 2 Activation energies of the samples

Sample	Decomp. region II/°C	E_a decomp. region II/kJ mol^{-1}	Decomp. region III/°C	E_a decomp. region III/kJ mol^{-1}
1	695–805	88	805–910	104
2	740–800	72	800–900	137
3	690–820	67	820–900	134
4	770–820	48	820–920	96

The temperature interval and maximum rate temperature of the endothermic changes are given in Table 1.

Non-isothermal kinetic study of mass loss by thermal analysis techniques (DSC, TG and DTA) is extremely complex for solid particles and mineral because of the numerous complex components and their parallel and consecutive reactions. The thermal characteristics of different samples and minerals were determined using different types of kinetic models and results showed that there are significant differences in the thermal characteristics and kinetics of the samples and minerals according to origin, different size fractions and heating rates [13–21].

The rate equation of thermal decomposition of dolomite is given by;

$$\mathrm{d}\alpha/\mathrm{d}t=\mathrm{k}\alpha^{\mathrm{n}} \tag{1}$$

where α is the amount of sample undergoing the reaction, n is the order of reaction and k is the specific rate constant. The temperature dependence of k is expressed by the Arrhenius equation:

$$k=A_{\mathrm{r}}\exp(-E/RT) \tag{2}$$

In Arrhenius model [18], rate of mass change with respect to time is equal to:

$$\mathrm{d}W/\mathrm{d}t=kW^{\mathrm{n}} \tag{3}$$

$$k=A_{\mathrm{r}}\exp(-E/RT) \tag{4}$$

Assuming first-order kinetics,

$$\log[(\mathrm{d}W/\mathrm{d}t)1/W]=\log A_{\mathrm{r}}-E/2.303\,RT \tag{5}$$

where $\mathrm{d}W/\mathrm{d}t$ is the rate of mass change, E is the activation energy, T is the temperature and A_{r} is Arrhenius constant.

When $\log[(\mathrm{d}W/\mathrm{d}t)1/W]$ is plotted *vs.* $1/T$, a straight line is obtained which will have a slope equal to $E/2.303R$ where activation energy can be obtained.

The kinetic study was carried out for two different temperature ranges as 690–810°C and 810–920°C. These were the zones for formation of MgO along with calcite and the formation of calcite. It was observed that the calculated activation energies were in the range of 48–88 kJ mol^{-1} in the region for formation of MgO and 96–137 kJ mol^{-1} in the region for formation of calcite (Table 2) which is in good order with literature [7].

Conclusions

In this research, characterization, correlation and kinetics of dolomite samples were investigated by X-ray and thermal methods. Decomposition mass loss regions and corresponding maximum rate temperatures were determined. Kinetic analysis of the dolomite samples was also studied and it was observed that the activation energies were in the range of 48–137 kJ mol^{-1}.

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