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LASER-INDUCED REACTION
A tool to analyse laser-induced reactions with solid phase participation

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Several experiments have shown that inorganic salts may be decomposed to oxides by irradiating them with a continuous-wave CO_2 laser. The process is characterized by an extremely high heating rate which develops within the impact region of the laser beam with the substance. For comparison, salts were also decomposed under controlled heating conditions. Knowledge of the intermediate steps stresses the importance of the positive and negative feedback mechanisms which control the laser-induced reactions. The present paper reviews results obtained by us for more complete descriptions of laser-induced reactions.

Keywords: laser-induced reactions

Introduction

Laser energy, emitted within a narrow spectral range, leads to strong and localized heating. Consequently laser-induced chemical reactions are characterized both by high temperature gradients and by particular features resulting from absorption properties of reagents and reaction products. The laser is a unique device both for synthesis of new materials and for improvement of classical synthesis methods. Several experiments on decomposition of inorganic salts with the aid of a continuous-wave CO_2 laser [1–4] have used the experimental device shown immediately in Fig. 1.

The inorganic salt is present as a layer of controlled thickness, h, in the reaction cell, N, which passes with a constant but adjustable speed, v, through the laser beam whose power is measured by the powermeter PM. After each passage the reaction cell is weighed and the operation is repeated until constant weight is weighed. The temperature within the laser impact area is measured by an optical

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pyrometer. The change of temperature with time is plotted in Fig. 2, together with the corresponding weight change, for a typical decomposition reaction.

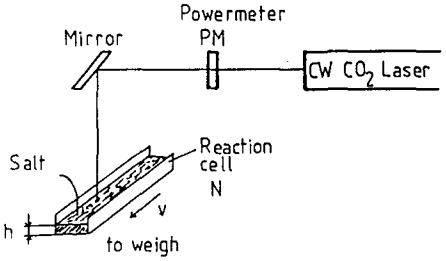

Fig. 1 The experimental system

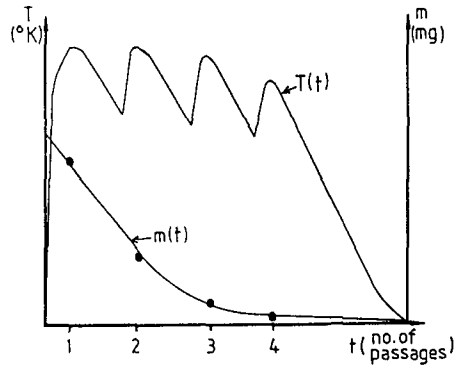

Fig. 2 Typical temperature and weight evolution curves during laser experiments

Temperatures of the peaks in Fig. 2 depend on the laser power and on the absorptivity of the laser quanta (which, for the *cw* CO_2 laser is 10.6 μm) by both the initial salt and the reaction products.

As a result of differences in absorptivity properties there are two general types of feedback mechanisms which may develop during a laser experiment [5]:

i) A positive feedback mechanism which acts when the absorptivity of quanta by the reaction products is higher than that of the initial reagent; consequently, temperatures of the peaks in Fig. 2 constantly increase with number of passages as more products are formed.

ii) A negative feedback mechanism which acts when the absorptivity of quanta by the reaction products is lower than those of the initial salt; consequently, temperatures of the peaks in Fig. 2 decrease and the reaction rate diminished.

Obviously the absorption properties of the intermediate products play an important role in these mechanisms and, therefore, it is necessary to know these products.

The use of thermal analysis to explain feedback mechanisms

Knowledge of the intermediate reaction products is required to explain the action of the positive/negative feedback mechanisms described above. The appearance of intermediate products which absorb the 10.6 μm quanta less leads to a negative feedback which may even stop the reaction at the intermediate step which generates it. This effect is amplified when the end-product does not absorb the radiation.

This phenomenon was noticed when $LiOH \cdot H_2O$ laser-induced dehydration was investigated [2]. The TG curve allows detection of the reactions occurring upto 1000°C:

$$2LiOH \cdot H_2O \xrightarrow{-2H_2O} 2LiOH \xrightarrow{-H_2O} Li_2O$$

Since both LiOH and Li_2O do not absorb 10.6 μm radiation the reaction stops with LiOH as the major end-product [2]. These results allowed us to conclude, also, that laser-induced reactions follow the same decomposition route as those thermally induced [4].

Influence of heating rate on physical form of final products

The heating rate of laser-induced reactions is strongly related to the number of quanta absorbed by the substance (i.e. to the absorptivity of the salt at 10.6 μm), to the power of the source, to the speed of the cell through the laser beam, etc. As shown by various experiments [1, 3], heating rate influences the physical form of the final products.

Nickel and copper oxides obtained from the salts listed in Table 1 have been investigated using X-ray diffraction and differences in size and isotropy of oxide crystallites for laser-obtained products as compared to those obtained by controlled heating have been noticed. The magnitude of the differences depends on the absorptivity of the laser radiation by the initial salt [3, 4], as Figs 3 and 4 show.

We have noticed also that the speed of passage through the laser beam influenced the size of the resulting crystallites. Two nickel oxides, obtained from two different salts, nickel hydroxycarbonate, which has an absorptivity of 42%, and nickel nitrate which absorbs only 2%, have been investigated. It would be expected, according to the above considerations, that a change in speed of the cell

Table 1 Nickel and copper salts decomposed during laser experiments

Salt	Code	Absorptivity / %	End-product
$Ni_2CO_3(OH)_2 \cdot H_2O$	K	42	NiO
$NiSO_4 \cdot 7H_2O$	S	8	NiO
$Ni(NO_3)_2 \cdot 6H_2O$	A	2	NiO
$NiCl_2 \cdot 6H_2O$	C	≈ 0	NiO
$Cu_2CO_3(OH)_2$	K	15	CuO
$CuSO_4 \cdot 5H_2O$	S	10	CuO
$Cu(CH_3COO)_2$	A	5	CuO
$CuCl_2 \cdot 2H_2O$	C	≈ 0	CuO

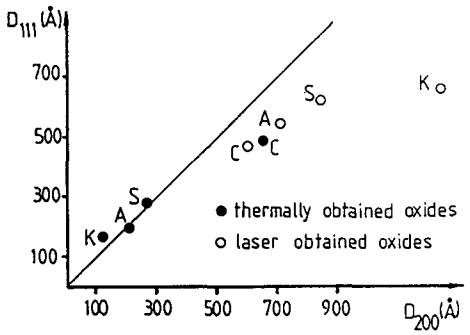

Fig. 3 XRD data for nickel oxide crystallites

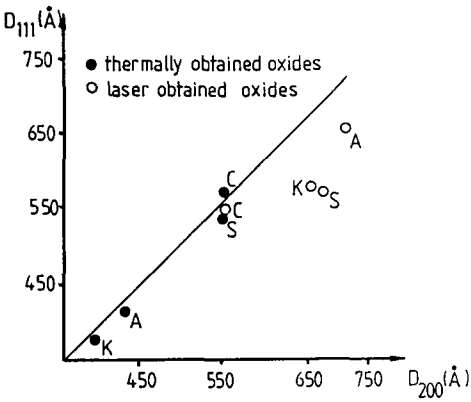

Fig. 4 XRD data for copper oxide crystallites

through the laser beam would lead to a more significant change in heating rate for the salt with higher absorptivity. The results of the experiments are given in Fig. 4.

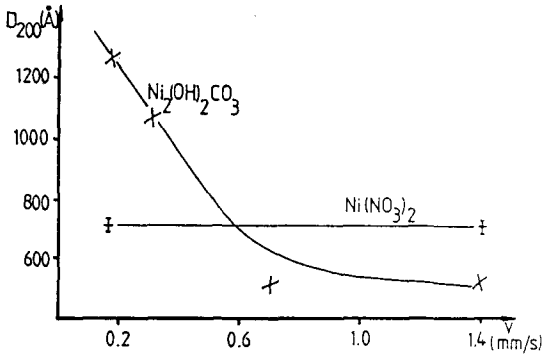

Fig. 5 Dependence of size of nickel oxide crystallites on speed of passage through laser beam

The explanation of these results may be based on the fact that high temperature gradients are induced in high-absorptivity salts. As a consequence the resulting crystallites are characterized by large size and anisotropy. The gradients decrease either when the initial salt absorptivity is low or when the speed of passage through the laser beam is high. In the latter case the whole reaction cell is probably heated uniformly. Consequently the crystallites obtained are similar to those obtained by controlled heating treatments.

Conclusions

Non-isothermal kinetic models offer a proper framework for better understanding of laser-induced reactions. Thermogravimetric analysis allowed characterization of the intermediate steps, and calculation of their kinetic parameters. In addition, it helps to explain some results due to the effect of feedback mechanisms and to the temperature gradients which are locally induced during laser experiments.

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Zusammenfassung — In einigen Experimenten wurde gezeigt, daß anorganische Salze unter Einstrahlung mit einem CW CO_2-Laser zu Oxiden zersetzt werden. Der Prozeß ist durch eine extrem hohe Aufheizgeschwindigkeit gekennzeichnet, die sich in der Region des Einfallen des Laserstrahles in der Substanz aufbaut. Zum Vergleich wurden die Salze auch unter kontrollierten Aufheizbedingungen zersetzt. Das Wissen um die Zwischenschritte hebt die Bedeutung des positiven und negativen Feedback-Mechanismus hervor, welcher die laserinduzierten Reaktionen beherrscht. Vorliegende Arbeit gibt einen Überblick über eigene Ergebnisse für eine bessere Beschreibung laserinduzierter Reaktionen.