

MECHANISM OF SILICA-IMMOBILIZED THIOANISOLE CONVERSION DURING AN AP-TPR-EXPERIMENT

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ABSTRACT

A kinetic study of the AP-TPR-profile of silica-immobilized thioanisole was carried out, resulting in a better understanding of the mechanistic behaviour of this model compound under the specified conditions. AP-TPR (Atmospheric Pressure - Temperature-Programmed Reduction) with potentiometric sulfur detection is a thermoanalytical method used to differentiate between sulfur forms in solids like coals. In this respect, silica-immobilized thioanisole was recorded as a nonmelting calibrant. Several kinetic methods exist to analyze a heterogeneous process involving a solid that is heated by a linear temperature programme. The isoconversional method can be considered as one of the most accurate. It was applied to the AP-TPR-profile of thioanisole, showing the reduction of this compound very quickly becomes a diffusion-controlled reaction. Kinetic parameters are reported for this process under the AP-TPR-conditions.

INTRODUCTION

Temperature-Programmed Reduction (TPR) of sulfur-containing solid samples under atmospheric pressure (AP), is a method to study different sulfur functionalities in the sample [1]. Knowledge of the distribution of sulfur functional groups in materials is of practical importance. For example, the ease with which sulfur is released from coal is determined by the functional form of the sulfur present. Thiols and sulfides are labile sulfur compounds and undesirable because of environmental consequences. Thiophenes on the other hand are more stable.

Recording of model compounds for sulfur functionality (in coal for example) is a key step in AP-TPR to evaluate characteristic temperature intervals where reduction of the specific sulfur group occurs.

A study of the AP-TPR-profiles of model compounds can also provide information about the mechanistic pathway of the occurring reactions that involve sulfur. In combination with other techniques a more detailed description can be given [2].

Also, a non-isothermal kinetic analysis of the AP-TPR-curves can be performed to get a better insight into the mechanism. A kinetic investigation of an AP-TPR-profile is different from conventional kinetics: the reaction studied is heterogeneous, a solid is involved and the temperature is raised during the experiment. Kinetic laws for homogeneous processes under isothermal conditions have been accurately determined. They can be considered as component parts of more complex kinetic models applied to heterogeneous processes [3].

For AP-TPR experiments, calibrants must neither melt nor evaporate before they are reduced in order that they remain in the reaction zone of the reactor. In this respect, nonmelting silica-immobilized (SI) substrates can be employed. It has been demonstrated the Si-O-C_{aryl} linkage is stable up to 500°C, even in reducing atmospheres [4].

In this work, AP-TPR-profiles of silica-immobilized thioanisole (\approx Ph-S-CH₃) are analyzed by non-isothermal kinetics, and more specifically by the isoconversional method [7].

EXPERIMENTAL

The AP-TPR-set-up is shown in figure 1. During an AP-TPR-experiment, the sample is located at the bottom of a quartz reactor, while H₂ gas is constantly flowing through it (fluidized bed system) at a rate of 50 ml/min. The oven is heated by a constant linear temperature programme, and the different sulfur functional groups are reduced in a characteristic temperature interval. The released H₂S is detected potentiometrically, resulting in a spectrum of H₂S evolution.

Silica-immobilized thioanisole was prepared from the sulfur-containing phenol (4-hydroxy-thioanisole, Aldrich Chemical Co.) and Cabosil fumed silica on a gram scale, as described previously for the synthesis of silica-immobilized diphenylalkanes [5].

For the AP-TPR-experiments, 20.0 mg SI thioanisole was used.

RESULTS AND DISCUSSION

Kinetic methods

Generally a simplified rate equation is used to describe reactions in solids [3]:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

where $\alpha = \frac{X_b - X}{X_b - X_c}$ is the degree of conversion (X is the measured quantity, e.g. mass sulphur in AP-TPR), normalised from 0 to 1, $k(T)$ is the Arrhenius rate constant, T is the temperature, t is the time and $f(\alpha)$ is a mathematical description of the reaction model. The form of $f(\alpha)$ is related to physico-geometric assumptions on the development of the reaction boundary between the initial solid substance and the product.

For non-isothermal conditions, when a constant heating rate $\beta = \frac{dT}{dt}$ is applied, eq. (1) is transformed:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

where E is the Arrhenius activation energy, A the pre-exponential factor and R the gas constant.

In integral form:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} \equiv g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \equiv \frac{A}{\beta} I(E, T) \quad (3)$$

Equation (2) as well as numerous approximations of its integral form (3) underlie most of the methods of kinetic processing [3].

Most frequently, those methods are utilized that employ data obtained at one heating rate. Different reaction models are fitted to the dataset, the best $f(\alpha)$ is discriminated using some criterion, and the Arrhenius parameters are evaluated based on this choice. The problem [6] is that usually quite different reaction models fit the data equally well (from a statistical point of view), whereas the values of the corresponding Arrhenius parameters markedly differ. The ambiguity of the kinetic parameters obtained by these "discriminating" methods implies that their physical meaning is doubtful. Moreover [6] this type of analysis yields a single kinetic triplet (A , E and $f(\alpha)$) for the overall process of thermal transformation and doesn't allow the detection of a possible change of rate-limiting step (and associated Arrhenius parameters).

Overcoming these problems can be done by using methods that employ data at different heating rates, like isoconversional methods [7]. Without having to discriminate a reaction model, values of E are obtained at each given conversion α . The isoconversional method used in this work can be described as follows [7]:

assuming the reaction model is independent of the heating rate, eq. (3) can be written for a given conversion and a set of data obtained at different heating rates β_i ($i=1, \dots, n$):

$$\frac{A_\alpha}{\beta_1} I(E_\alpha, T_{\alpha,1}) = \frac{A_\alpha}{\beta_2} I(E_\alpha, T_{\alpha,2}) = \dots = \frac{A_\alpha}{\beta_n} I(E_\alpha, T_{\alpha,n}) \quad (4)$$

Strict fulfilment of eq. (4) results in:

$$\sum_{i=1}^n \sum_{j=1}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} = n(n-1) \quad (5)$$

where $j = 1, \dots, n$. Because the T_α values are measured with some experimental error, eq. (4) can only be satisfied as an approximate equality, in other words: eq. (5) can be met as a condition of minimum value:

$$n(n-1) - \sum_{i=1}^n \sum_{j=1}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} = \min \quad (6)$$

Substituting experimental values of T_α and β into eq. (6) and varying E_α to reach the minimum gives the value of the activation energy at a given conversion. The values of $I(E, T)$ are approximated.

Applying the isoconversional method to a multi-step process shows the dependence of E_α on α . This dependence can be used as a criterion for a multi-step process [8]. Moreover, the shape of the dependence can help to elucidate the mechanism of the occurring reactions [8].

Kinetic analysis of the AP-TPR profiles of silica-immobilized thioanisole

Several AP-TPR experiments for silica-immobilized thioanisole were performed at four different heating rates (3.5, 5, 8 and 12 °C/min). All profiles were normalised and converted to (α, T) dependences: see figure 2. Before 400 °C no reaction was detected. When the heating rate is increased, a shift of the profile is observed to higher temperatures [3].

Several combinations of curves at different heating rates were selected, and analyzed by the isoconversional method, resulting in a typical $E-\alpha$ dependence: see figure 3. At the very beginning of the process, values of E higher than 100 kJ/mol are observed, but immediately the activation energy reduces to values lower than 45 kJ/mol. These low values are typical for the diffusion of a gas in a solid [6, 9].

This $E-\alpha$ dependence can be interpreted as follows. The values of E (>100 kJ/mol) in the beginning refer to a chemical reaction that controls the rate. To determine what reaction is occurring, a comparison could be made with bond dissociation energies for the thioanisole compound. However, at very low values of α , the calculation of E is less accurate and an exact value of E can not be given. It can only be proven E -values typical for chemical reaction are seen here. Moreover, even at the beginning diffusion could influence the reaction rate, thus lowering the calculated E -values. Subsequently, the dependence shows a decrease of E to values lower than 45 kJ/mol. This means there is a transition from a reaction-controlled process to a regime that is completely controlled by diffusion of a gas in a solid. A possible explanation for this transition can be as follows. The sulfur-containing particles that can easily be reached by the H_2 gas react quickly to release H_2S with an activation energy $E > 100$ kJ/mol. The rate of the process is controlled by this hydrogenation. The rest of the particles that are not in direct contact with the H_2 gas, react next. But at this point, diffusion of H_2 or H_2S gas through the bulk of firstly reacted particles becomes the rate-limiting step. Another explanation for the transition to a diffusion regime involves reaction of the evolved H_2S with the siloxanes of the silica support to generate OSi-SH species that are then released slowly out of the solid.

A comment can be made here on the use of this model compound (SI thioanisole) for AP-TPR calibration. Since the hydrogenation is only rate-determining at the beginning of the process under AP-TPR-conditions, only the rate at the beginning is reproducible. The rest of the AP-TPR-rate-profile (differential form) is diffusion controlled, and can vary according to the specific conditions inside the AP-TPR-reactor. Because the sample amount used is very small (20 mg), and the experimental AP-TPR conditions are almost invariant, the differential profiles of thioanisole are very similar. Still, the diffusion-control has to be taken into account. This means that only the onset temperature can be used as a calibrant temperature for this thioanisole model compound. Additional studies have to be done to see if this conclusion also holds for other model compounds.

CONCLUSIONS

Application of the AP-TPR-technique in combination with non-isothermal kinetic analysis, is an efficient tool to study mechanistic pathways of reduction of sulfur in model compounds. The term "mechanism" indicates a kinetic scheme in this context, and not a sequence of elementary steps, because only those reactions can be seen in AP-TPR that induce the change in the measured quantity.

The results for silica-immobilized thioanisole show a transition from a (chemical) reaction-controlled process to a regime that is completely controlled by diffusion of a gas in a solid. Kinetic analyses of other model compounds like cysteine and silica-immobilized phenylbenzylsulfide will be discussed later.

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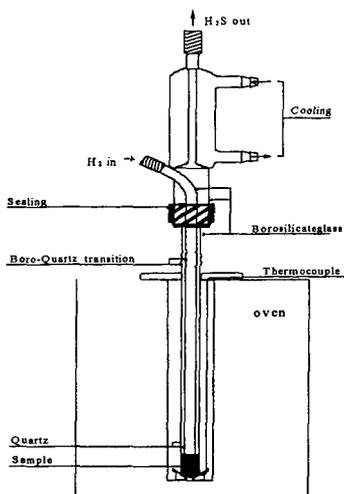


Figure 1: AP-TPR set-up

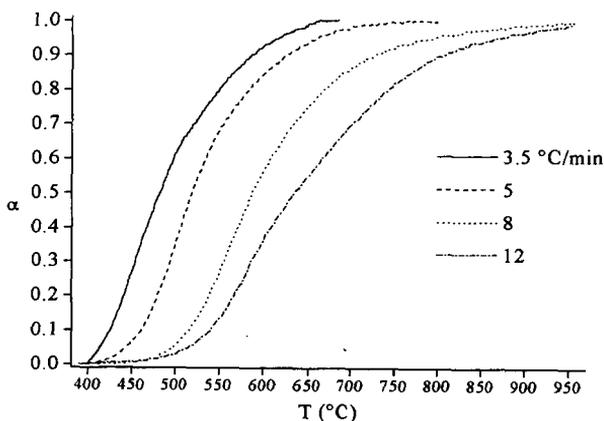


Figure 2: AP-TPR profiles of SI thioanisole shown as α , T dependences for 4 heating rates

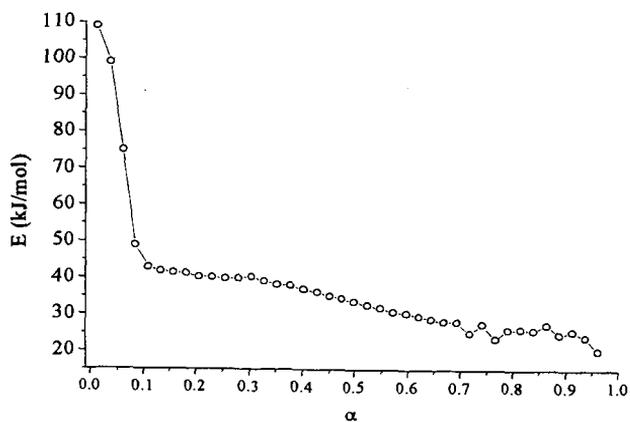


Figure 3: Typical E, α dependence for AP-TPR profiles of SI thioanisole