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EVALUATION OF THERMAL DESORPTION SPECTRA FOR THE CHARACTERIZATION OF LOADED ACTIVE COKE AND OF ITS REGENERATION

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ABSTRACT

By thermal desorption spectrometry, not only desorption kinetics but also the amounts and kinds of adsorbed substances can be evaluated. Active coke loaded in flue gas cleaning experiments was investigated by this method and by chemical analysis. By thermal desorption, the state of the spent adsorbent is characterized more in detail, concerning not only adsorbed sulfuric acid and ammonia salts but also surface oxides of carbon.

INTRODUCTION

For many adsorption processes, it is important to know the state of the surface of the spent adsorbent, especially, when adsorption was accompanied by chemical reaction. If there is only interest in the kinds and amounts of the adsorbed substances, chemical analysis of the adsorbate is sufficient. Thermal desorption spectra give more information about complex binding mechanisms and their activation energies (e.g. adsorption of phenol cannot be described by a single binding force but by a binding force distribution evaluated from thermal desorption (ref.1)).

It is the classical method to carry out desorption experiments in a temperature-programmed differential reactor purged by an inert gas. For constant heating rates, the activation energy and the rate constant of desorption or decomposition can by determined directly (ref.2). A temperature-programmed batch reactor has been developed to evaluate desorption kinetics when gaseous desorption or decomposition products can react with adsorbed substances or the adsorbent itself (ref.3).

This paper compares results which were obtained for spent active coke by chemical analysis and by desorption spectrometry.

ADSORBENT

Active coke is a carbonaceous adsorbent produced from bituminous coal. The investigated samples had a BET surface area about 630 m²/g. Active coke is used for flue gas desulfurization and catalytical NO_x reduction after addition of NH_3.

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Ammonium salts are formed by a reaction of adsorbed sulfuric acid with NH_3 (ref.4).

The investigated samples were prepared by laboratory experiments. A gas mixture containing 1020 ppm SO_2, 720 ppm NO, 790 ppm NH_3, 6 % vol. O_2, 10 % by vol. steam and rest N_2 was forced through a fixed bed of active coke. The temperature was 393 K. The loading endured 9 h. The bed length was 1.0 m. One sample of loaded coke was taken from every 10 cm over the bed length.

EXPERIMENTAL

Chemical analysis was carried out for ammonium and sulfate.

Thermal desorption spectra were evaluated in a flush reactor (Fig.1a) and in a gradientless reactor with an internal gas circuit (Fig. 1b).

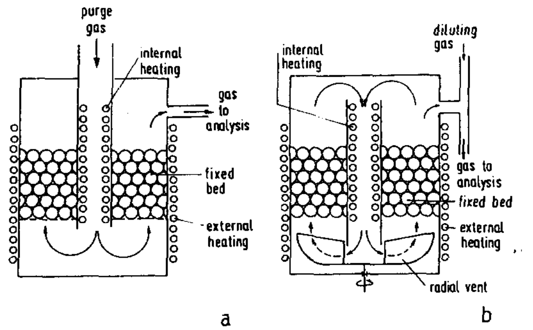

Fig.1:
Flow sheet of temperature-programmed reactors
a) Flush reactor
b) Gradientless reactor

Both reactors are described in detail (ref.3,4). They are heated time-linearly. The flush reactor was purged by He. The gradientless reactor which was operated like a batch reactor contained Ar in the gas volume at the beginning of the test. *During the test Ar becomes displaced by desorption products. The gases* leaving the reactor are fed to a He stream and analysed thereafter.

Experimental results

Desorption spectra were evaluated in the flush reactor for samples of loaded active coke from the first 40 cm of the bed. The gaseous desorption and decomposition products were determined by mass spectrometer. The desorption spectra are shown in Fig.2a/d. Physically adsorbed water vapour is desorbed first. At temperatures about 420 K N_2 is set free, in some cases together with NO. At temperatures about 570 K ammonium sulfate, ammonium bisulfate and sulfuric acid decompose forming water vapour, SO_2, NH_3, and (if NH_3 is not present) CO_2. At elevated temperatures surface complexes of carbon with oxygen and nitrogen decompose. CO, CO_2, and N_2 are the products.

The integration of the amounts of gases released over the whole temperature range results in the initial load if no reactions of the substances occur

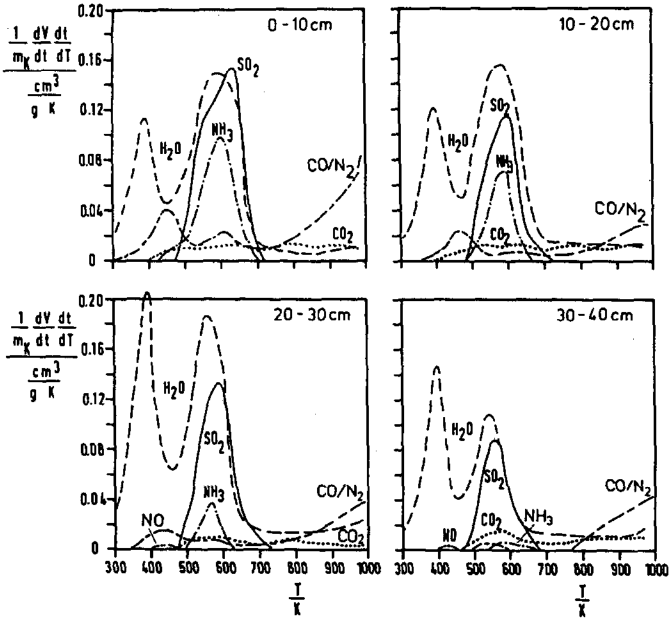

Fig. 2. Temperature-programmed desorption spectra for loaded active coke from different regions of a fixed bed reactor.
Reactor: Flush reactor; Heating rate: 10 K/min.

during the experiment. For the four samples, the total number of moles of SO_2 and of NH_3 released during thermal desorption is plotted in Fig.3. It is evident that the load of ammonium and sulfate decreases with the bed length and that much more SO_2 is released than NH_3.

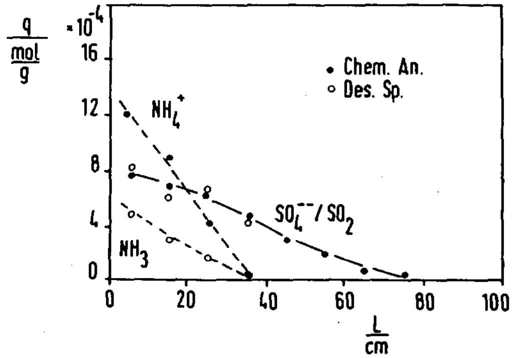

Fig. 3:
Amounts of ammonia/ammonium and sulfur dioxide/sulphate from active coke as a function of bed length determined by desorption spectrometry in the flush reactor (Des.Sp.) or wet chemical analysis (Chem.An.).

Chemical analysis of the loaded active coke samples show results which are identical in the amounts of sulfate. But they differ with respect to the amount of ammonium on the loaded samples which is more than twice as much as the amount of NH_3 released. Test by differential scanning calorimetry (Fig.4) show endotherm effects at temperatures about 623 K and exothermic effects at tempe-

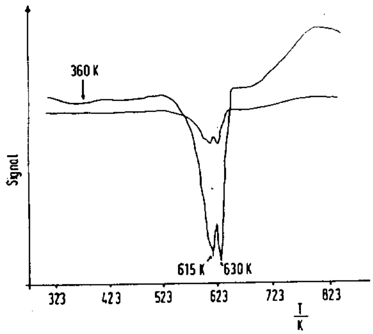

Fig. 4. DSC investigation of loaded active coke

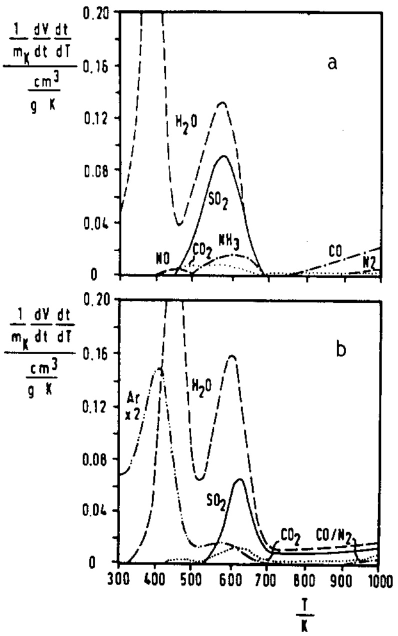

Fig. 5. Comparison of temperature-programmed desorption spectra from flush reactor (a) and gradientless batch reactor (b) experiments. Active coke loaded for 6 h.

ratures over 660 K. The corresponding reactions can be evaluated only from the desorption spectra.

A comparison of thermal desorption spectra obtained by tests in the flush reactor with those obtained by tests in the gradientless reactor shows that released ammonia is consumed in a consequetive reaction. Experimental results for a mean sample from the first 40 cm of the fixed bed are shown in Fig. 5: (a. flush reactor, b. gradientless batch reactor). NH_3 is consumed in the gradientless reactor so that only negligible amounts leave the reactor (the same is true for NO).

TEST EVALUATION

Jüntgen and van Heek (ref.2) have shown that in very many cases the rate r_i of thermal desorption and decomposition can be described for a substance A_i by:

$$r_i = \frac{d\bar{c}_i}{dt} = -k_i^\circ \exp(-E_i/RT)\,\bar{c}_i \qquad (1)$$

$\bar{c}_i$ are the concentrations of the adsorbed or solid substances, k_i° the frequency factor and E_i the activation energy. The latter two can be evaluated directly

from flush reactor experiments for a single desorption. For complex mechanisms a reaction model is needed (ref.4). Then the mass balances for the test reactors must be solved and the parameters must be evaluated by curve fitting.
Based on the experimental results, the reaction scheme (Fig.6) has been derived by Jung (ref.5); showing the temperatures at which the desorptions and reactions occur. The gaseous state is indicated by a circle.

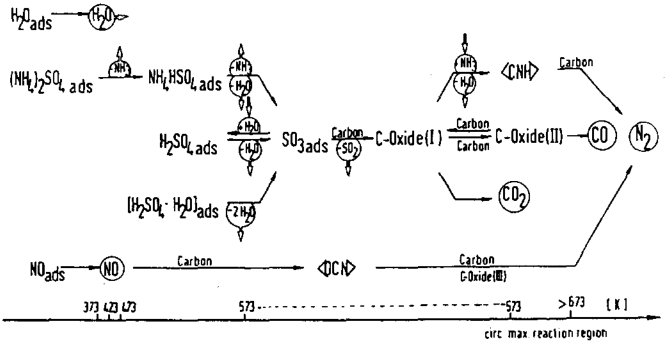

Fig. 6. Reaction scheme of thermal regeneration of active coke

The frequency factors and the activation energies for these reactions have been evaluated simultaneously for a large number of active cokes loaded at different conditions (ref.4).

DISCUSSION

As a first step for the characterization of loaded adsorbents, chemical analysis of the adsorbate is needed if adsorption has been accompanied by chemical reaction. Chemical analysis of the loaded adsorbents gives no special information if only single components, e.g. organic vapours, have been adsorbed. Information from wet chemical analysis is limited as not the substances themselves ($(NH_4)_2SO_4$, NH_4HSO_4, H_2SO_4) but only ions (NH_4^+ and $SO_4^=$) can be determined. In most cases, X-ray diffraction and IR-analysis cannot be applied because the adsorbed substances prevail finely dispersed on the surface, so that the weak signal is overlayed by the signals from the active coke and its surface oxides. Thus the information from chemical analysis of spent adsorbents is limited.

Nevertheless, it is an important aid for thermal desorption spectrometry as long as it is not known which gaseous desorption and decomposition products must be analysed. Desorption spectrometry needs big efforts for the fast and precise analysis of the released gases. For the gradientless reactor, the mass balances which are needed for test evaluation can only be solved if all the products are analysed (ref.4). On the other hand, it is possible to predict the decomposition and desorption products with some accuracy if the conditions for the previous loading of the adsorbent are known.

It is difficult to recover secondary reactions by desorption spectrometry if the chemical state of the loaded adsorbent is not known: in the experiments described above (Fig.2/3) less NH_3 was detected by desorption spectrometry than NH_4^+ was prevailing on the respective sample. Thus, integration of the desorbed gas leads to wrong values for the adsorbed amounts. The easiest way to detect secondary reactions is to compare results from flush reactor and gradientless reactor tests because the latter exhibits much higher concentrations of the gaseous products around the desorbing material (thus increasing the reaction rate).

By comparison of the thermal desorption spectra of the investigated samples with those from adsorbents loaded with pure substances (e.g. H_2SO_4), it is possible to determine the substances on the loaded adsorbent more precisely. Desorption scanning calorimetry gives only a global information as simultaneously occuring parallel reactions of surface complexes cannot be detected, if the initial load is not known (parallel ractions can occur on active coke in many cases when surface complexes have been formed during adsorption which can decompose at the same temperatures as the adsorbed substances). Modeling of the thermal desorption spectra gives additional information about the frequency factors and the activation energies of desorption and of complex decomposition reactions.

For the design of a regeneration process the latter ones are unconditionally necessary. The conditions prevailing in the gradientless reactor are quite similar to those in regeneration reactors where high concentrations of the desorbed gases are demanded for to make further processing of these products easier.

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