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THERMAL DESORPTION OF NITROGEN OXIDES FROM ACTIVATED CARBON

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ABSTRACT

The capacity for NO adsorption and the catalytic activity for NO oxidation of activated carbon are influenced by water vapour. Thermal desorption spectrometry is used to evaluate the state of adsorbed and chemisorbed species.

INTRODUCTION

Activated carbon is used as an adsorbent for the removal of nitrogen oxides from off-gases of chemical processes at ambient temperatures (ref.1). It is not possible to desorb NO and NO_2 completely by purging with nitrogen or air at adsorption temperature so that it is probable that these parts are chemisorbed (ref.2). Information is limited about the sorption mechanisms available from adsorption and desorption experiments at adsorption temperature. Additional information can be obtained by thermal desorption experiments.

ACTIVATED CARBON

The activated carbon D47/4 (Bergwerksverband, Essen) which had been produced from bituminous coal has a BET-surface of about 710 m^2/g. Nitrogen oxides were adsorbed on activated carbon in a fixed bed adsorber fed by a gas mixture containing 3.5 % by vol. O_2 and 0.1 % by vol. NO in nitrogen at 1.5 bar and 298 K. The gas of exp.1 was dry; the gas of exp.2 was saturated with water vapour at 298 K. The breakthrough curves of NO and of NO_2 formed by NO-oxidation are shown on Fig.1.
The adsorption capacity is high for dry gases. NO_2 from NO oxidation has a higher adsorption capacity. High relative humidities inhibit the adsorption and the catalytic oxidation of NO. Thus, the breakthrough of NO_x is earlier (ref.2).

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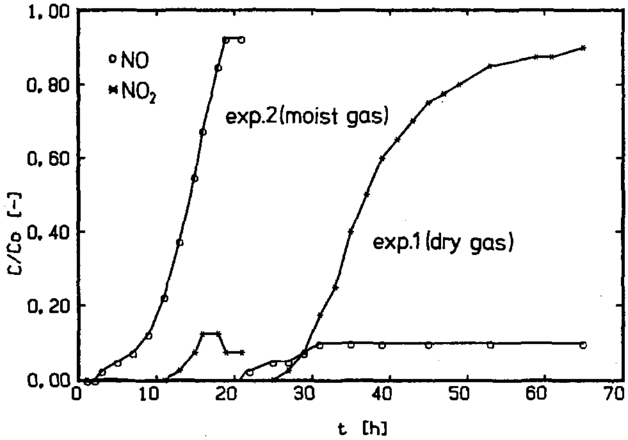

Adsorber volume:
0.00102 m^3
Feed rate:
1.45 m^3/h(STP)

Fig.1. Breakthrough curves of NO and NO_2 for exp.1 (dry gas) and exp.2 (moist gas).

Additionally one activated carbon sample soaked in diluted nitric acid is investigated for a better assignment of the desorbing species to known compounds. The samples are numbered as follows:

Sample 1	soaked in diluted nitric acid
Sample 2	loaded by NO in exp.1
Sample 3	loaded by NO in exp.2

EXPERIMENTAL

Thermal desorption spectra were evaluated in a differential flush reactor, whose temperature was raised time-linearly (5K/min). The reactor was purged by helium. The composition of the gas leaving the reactor was analysed by mass spectrometer. Additionally NO and NO_2 were analysed by a chemiluminescence analyzer (ref.3).

Experimental results

Water vapour adsorbed from humid air desorbs first from as received activated carbon used as a reference. CO and CO_2 desorbing over 700 K are decomposition products of carbon surface oxides.

The desorption spectrum of sample 1 (Fig.2) shows the decomposition of HNO_3 on a carbon surface. NO, NO_2, CO_2 and water vapour are the products of HNO_3 decomposition and of reaction of the products with carbon between 350 and 450 K. The desorption peaks of NO, NO_2 and CO_2 are temperature-shifted.

From sample 2 purged by N_2 after loading, the same gases except of water vapour are released (Fig.3). If the dry sample has rested for a longer time in ambient air, NO and NO_2 desorb at lower temperatures (Fig.4). If activated carbon has been loaded by NO in moist air (exp.2), the ratio of desorbed NO_2 to NO is the lowest one of the four experiments (Fig.5).

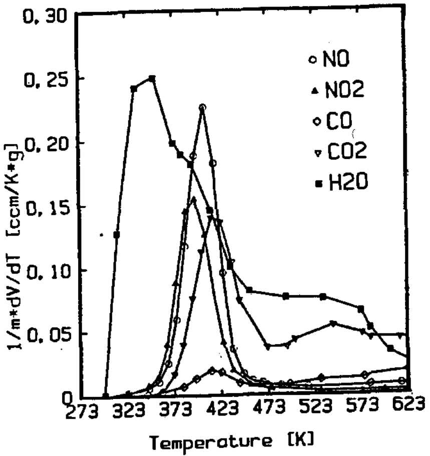

Fig.2. Desorption spectrum for sample 1

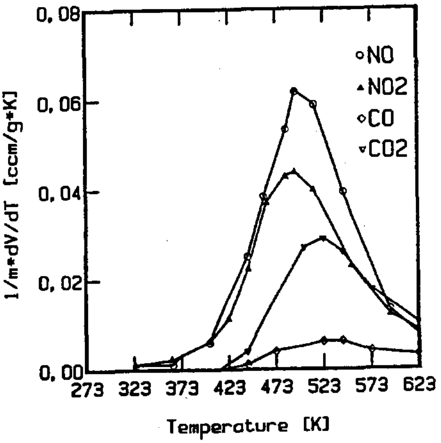

Fig.3. Desorption spectrum for sample 2 purged by N_2

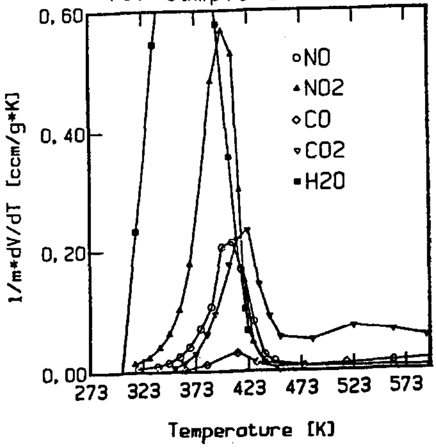

Fig.4. Desorption spectrum for sample 2 after exposure to air

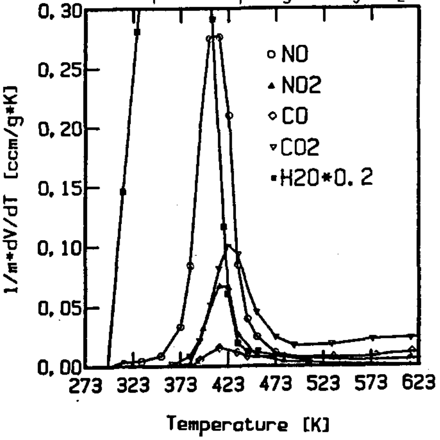

Fig.5. Desorption spectrum for sample 3

DISCUSSION

The amounts of gases released during thermal desorption are a direct measure for the adsorbed amounts if the species are not converted by chemical reactions during temperature rise. The chemical reactions must be known before assertions on the adsorbed species can be made. Carbon takes part in most of these reactions. The reduction of NO to N_2 as well as the formation of CO are negligible. Parts of adsorbed NO_2 are reduced forming NO and CO_2 or carbon surface oxides. The later can decompose immediately or at elevated temperatures (ref.4). Carbon participates in the decomposition of nitric acid:

$$2\ HNO_3 + C \longrightarrow H_2O + NO + NO_2 + CO_2$$

The desorption spectra verify the results of the adsorption tests: the adsorption and the oxidation of NO are inhibited by water vapour. Only smaller amounts of NO_2 are set free from sample 3 (Fig.5) while larger amounts of NO_2 are released or reduced from sample 2 loaded by dry gas (Fig.3 and 4).

As a rule, species which are adsorbed with higher interaction forces, like NO_2 compared to NO, are desorbed at higher temperatures (ref.3). This is evident for the dry sample 2 purged by N_2 (Fig.3).

If water vapour is adsorbed additionally, the desorption temperatures are lowered. This effect is independent of the temporal sequence of the adsorption of the respective species: Mainly NO is released at temperatures about 373 to 423 K from sample 3 loaded by moist gas (Fig.5); mainly NO_2 is released rather at the same temperatures from sample 2 loaded by dry gas and succeedingly by moisture (Fig.4). Nitric acid may have been formed from adsorbed NO_2 and water vapour in the later case, as nitric acid decomposes in the same temperature interval. But only small amounts of nitric acid prevail because less CO_2 is released from the dry loaded sample 2 exposed to moist air than from sample 1. Thus, the desorption spectra approve the adsorption/reaction mechanisms derived from adsorption tests.

CONCLUSIONS

The results are important for regenerative adsorption of NO_x from the moist off-gases of nitric acid plants. The disadvantage of lower adsorption capacity for NO_x from moist gases is overcompensated by the lower temperature needed for thermal regeneration.

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