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Some Unusual Observations Concerning the Adsorption of Thiophene on Copper Chromite

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Adsorption of thiophene, a poison, on copper chromite catalyst has been studied at conditions close to those used in the reduction of nitrobenzene to aniline (i.e., at temperatures of 150° to 300°C and in the presence of excess hydrogen) by using pulse gas chromatographic technique. Both irreversible and reversible adsorption on a surface partially saturated with irreversibly adsorbed thiophene showed unusual behaviour: the rate of irreversible adsorption and the extent of reversible adsorption increased with initial surface coverage due to irreversible adsorption.

INTRODUCTION

Copper chromite catalyst is known to be poisoned by thiophene which is invariably present in traces in feeds of petrochemical origin. Earlier studies (*1*) on the poisoning of copper chromite catalyst by thiophene for the reduction of nitrobenzene to aniline revealed that both irreversible and reversible adsorption of thiophene on the catalyst play an important role in the poisoning. The present study has been undertaken to investigate the adsorption behavior of thiophene on copper chromite catalyst under reaction conditions (in the temperature range 150–300°C and in the presence of hydrogen) using the gas chromatographic pulse technique.

EXPERIMENTAL TECHNIQUE

The chromatographic adsorption data were collected using an NCL-AMIL dual column gas chromatograph equipped with a flame ionization detector (FID). Hydrogen (ultrahigh purity) was used as the carrier gas (and also as fuel for the detector).

A stainless-steel chromatographic column (6.0 mm o.d. and 60 mm length) was prepared by packing copper chromite catalyst ($CuO \cdot CuCr_2O_4$, developed in our laboratory for the vapor phase reduction of nitrobenzene to aniline) in the form of particles of average size 0.34 mm. The catalyst had the following properties: specific surface area, 54.0 m^2/g; porosity, 0.63; average pore radius, 108 Å.

After connecting the catalyst column to the gas chromatographic unit, the catalyst was reduced by passing a mixture of hydrogen and nitrogen (ultrahigh purity) (10% H_2) at 200°C for 2 hr and then finally at 300°C for 12 hr. The reduced form of the catalyst was 2 $Cu\text{–}Cr_2O_3$ as indicated by its loss in weight (10.5%) after reduction.

For the study of irreversible adsorption, the carrier gas flow (40 ml/min) was switched to catalyst column with the help of a two-way stopcock and the pulse experiments were carried out by injecting

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5.0 μl of thiophene into the catalyst column using a Hamilton microliter syringe and recording the elution chromatograms. The area under the peak of the pulse of thiophene in the absence of catalyst was obtained by switching the carrier gas to empty column and injecting the same amount of thiophene pulse into the empty column under identical conditions.

RESULTS AND DISCUSSION

Irreversible Adsorption

Irreversible adsorption of thiophene was detected by comparing the areas under the elution peaks obtained with and without the catalyst. The area of the former peak was found to be less than that of the latter at all the temperatures studied, thus indicating irreversible adsorption of thiophene on the catalyst. In order to measure the extent of irreversible adsorption quantitatively, a number of peaks were recorded by passing successively pulses of thiophene (each of 5.0 μl size) over the catalyst under the same experimental conditions. The amount of irreversibly adsorbed thiophene q_i during the passage of each pulse was estimated from

$$q_{\mathrm{i}} = \frac{Ve}{WM}\left[\frac{A^* - A}{A^*}\right] \qquad (1)$$

where A^* and A are the areas under the elution peaks in the presence and the absence of catalyst, respectively, V is the pulse size, W is the weight of catalyst, M is the molecular weight, and e is the density of thiophene.

Representative elution peaks of the successive thiophene pulses obtained on the catalyst at 150°C are presented in Fig. 1. At all the other temperatures of study, the elution curves obtained were generally similar to those at 150°C.

Figure 2a shows the variation of the peak area of the effluent pulse with pulse number at all the temperatures studied. At 150°C, as the pulse number increases, the peak area of the effluent pulse decreases initially, passes through a minimum (at pulse number 5) and then levels off. However, this trend is reversed at and above 200°C; the peak area of the effluent pulse increases initially, passes through a maximum near about a pulse number of $\frac{3}{4}$, and then levels off. It may also be noted that this reversal in trend takes place gradually with temperature.

The variation in irreversible adsorption during the passage of each pulse of thiophene with pulse number can be readily obtained from the above figure and is shown in Fig. 2b. In this case, the trend of the curves (q_i vs pulse number) is exactly opposite to that of those shown in Fig. 2a. The nature of dependence of irreversibly adsorbed thiophene on pulse number (or on the extent of initial surface coverage) is quite unusual. A previous study (2) involving the adsorption of hydrogen on this catalyst had shown the usual adsorption behavior: The area of the elution peak increased gradually with peak number and finally reached a maximum or a constant value; hence the amount of irreversibly adsorbed hydrogen during the passage of each pulse decreased with pulse number.

Reversible Adsorption on Catalyst with Partially Saturated Irreversible Adsorption Sites

The retention volume of the adsorbate is a convenient measure of reversible adsorption. In the present study, retention volume is based on the first absolute moment (μ_1) of the chromatographic curves instead of the retention time (which is based on the peak maximum) because the retention data based on the first absolute moment give a more correct picture of reversible adsorption (*2*), particularly when the elution curves are asymmetric.

The values of μ_1 for thiophene were calculated from the chromatographic data by the usual method (*2*). Since it was not possible to obtain μ_1 for the inert gas experi-

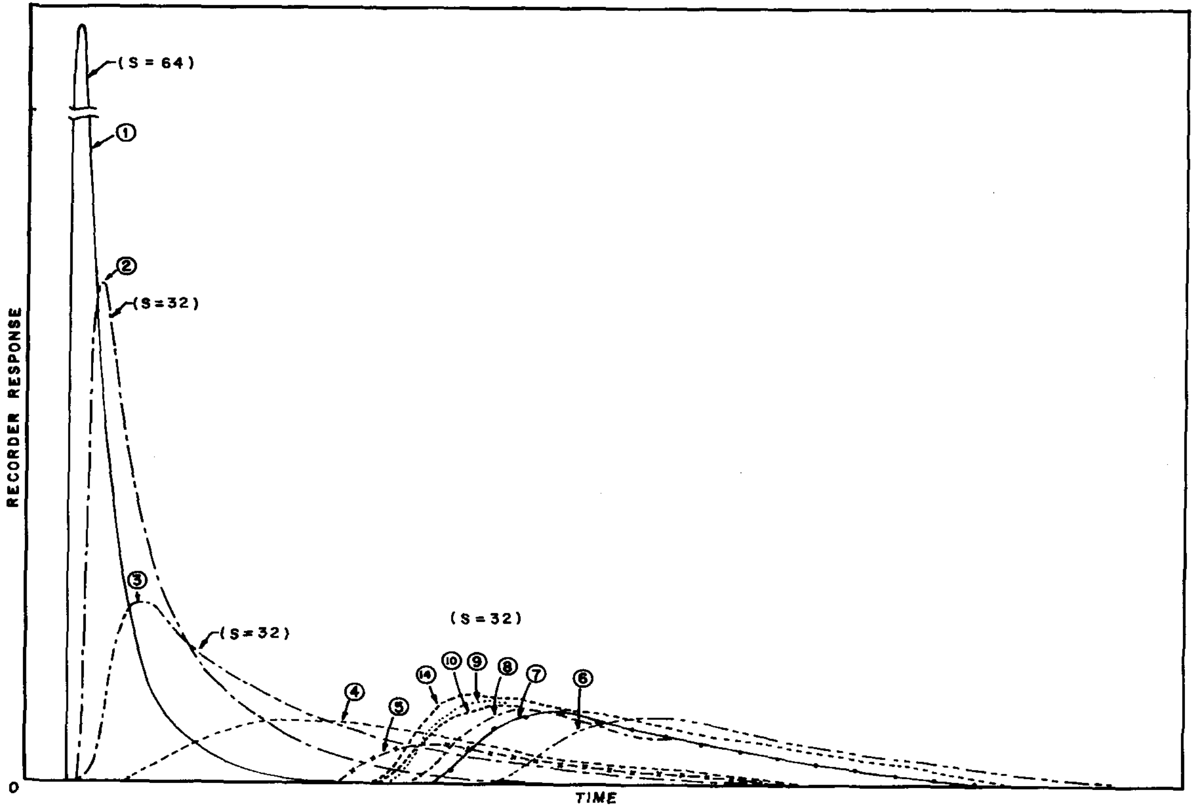

Fig. 1. Elution peaks of the successive thiophene pulses (each of size 5 μl) obtained on copper chromite at 150°C (S = sensitivity or attenuation).

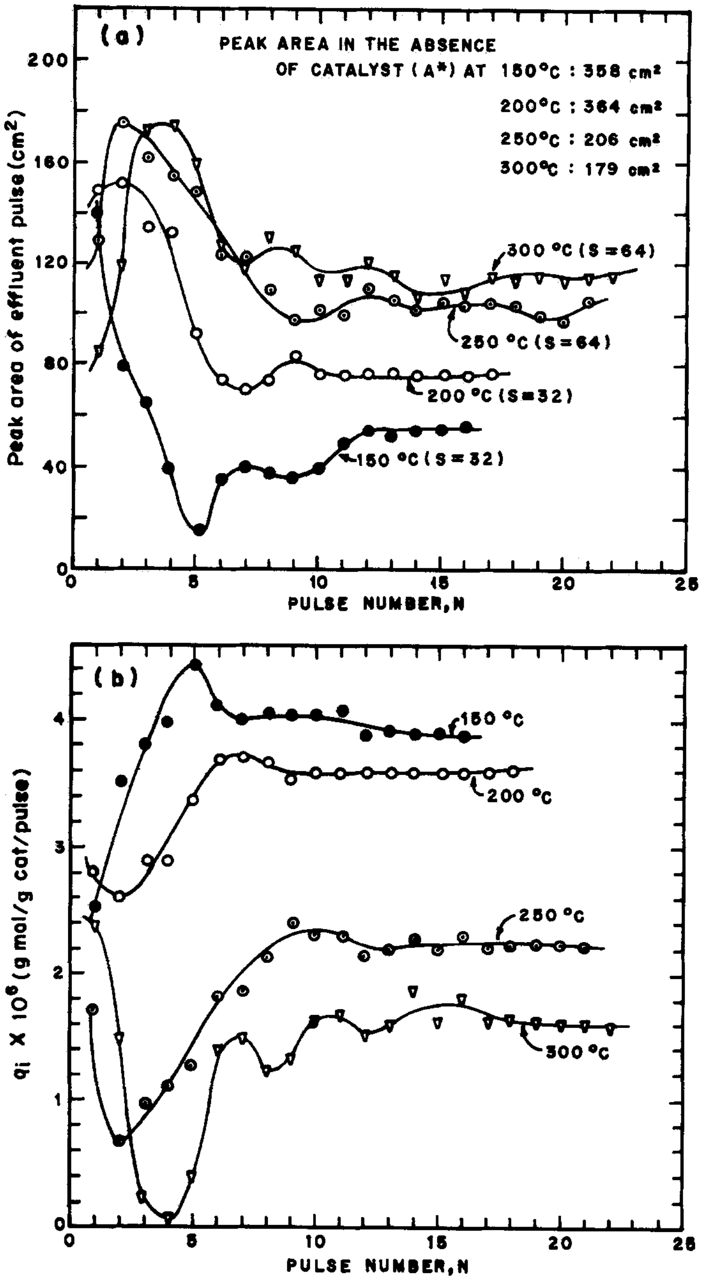

FIG. 2. Effect of initial surface coverage on the irreversible adsorption of thiophene during the passage of each pulse.

mentally (because of the use of FID), the values of $\mu_{1(\text{inert})}$ were calculated (*3*) from a knowledge of carrier gas flow rate and column characteristics.

The variation of the retention volume $[F(\mu_{1\,(\text{thiophene})} - \mu_{1\,(\text{inert})})]$ of thiophene with pulse number is shown in Fig. 3a. In order to emphasize the dependence of the retention volume on the initial surface coverage (due to irreversible adsorption), the total amount of irreversibly adsorbed thiophene (q_{it}) as a function of pulse

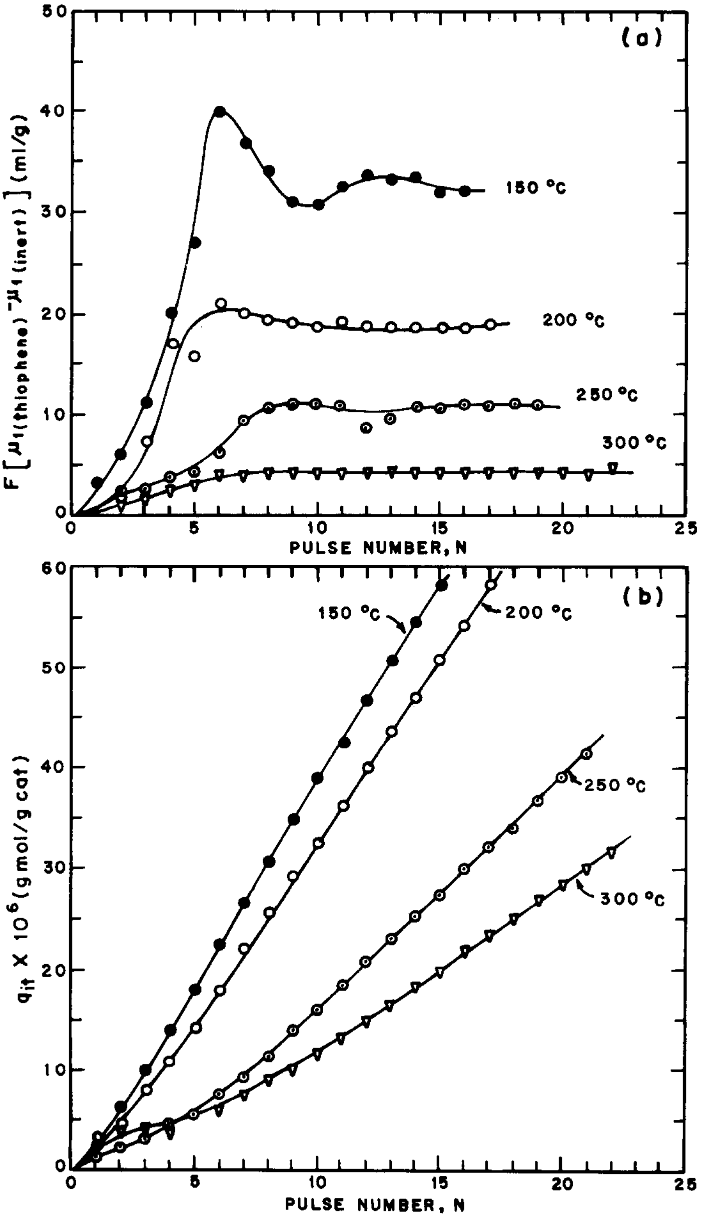

FIG. 3. Effect of initial surface coverage of irreversibly adsorbed thiophene on the extent of reversible adsorption of thiophene on copper chromite.

number is shown in Fig. 3b. It can be seen from these plots that, as the initial surface coverage increases, the retention volume (and therefore the extent of reversible adsorption) increases initially, passes through a maximum (except at 300°C) and then levels off. It may also be noticed that the plots of retention volume vs pulse number show a typical trend which gradually changes with temperature.

Examples of unusual adsorption behavior such as enhancement in the amount adsorbed and/or of the rate of adsorption due to the presence of the same species or some other species on the catalyst surface are very few. In the present case, the adsorption of thiophene on copper chromite involves an enhancement (i) in the rate of irreversible adsorption as indicated qualitatively by the pulse experiments (Fig. 2b), and (ii) in the extent of reversible adsorption with increase in the surface coverage due to irreversible adsorption (Fig. 3a). Such enhancing effects on adsorption due to the presence of the same adsorbate are very rare, e.g., H_2 on iron (*4*), copper (*5*), and nickel (*6*).

The unusual trend in the irreversible and reversible adsorption of thiophene on a partially covered catalyst surface, which changes gradually with temperature (an additional peculiarity), may probably be explained by considering the possibility of the modification of existing sites and/or creation of new adsorption sites during the process of irreversible adsorption.

The gas chromatographic pulse flow technique seems to be unique, particularly in the study of reversible adsorption at various initial surface coverages due to the irreversible adsorption of the same species or some other species. It can also be conveniently employed for studying the effect of various preadsorbed species on the irreversible adsorption of a particular adsorbate.

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