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Note

Gas chromatographic technique for temperature-programmed desorption of reversibly and irreversibly adsorbed species

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Temperature programmed desorption (TPD) or flash desorption[1–3] is one of the most important methods employed in studies of active centres, adsorption, surface heterogeneity and catalytic reactions on solid catalysts. Amenomiya and Cvetanovic[4] have suggested an adaptation of the TPD technique: the catalyst (placed in shallow-bed reactor) with the gas adsorbed irreversibly on it at the lowest temperature of the study is heated at a programmed heating rate. The adsorbate desorbed continuously into the stream of an inert carrier gas is measured by a gas detector; a static volumetric system for adsorption measurement and a shallow bed reactor were used for this purpose. Recently, Choudhary[5] has described a gas chromatographic technique with catalyst packed in a long chromatographic column as a desorption reactor for such TPD studies. This technique offers many advantages for TPD studies.

The limitation of the TPD of irreversibly adsorbed species is that it gives information only on the sites that are involved in the irreversible adsorption at the lowest temperature of the TPD. These sites form only a small fraction of the total adsorption sites on the catalyst surface. Although much information can be derived from the TPD of strongly adsorbed species, the weak adsorption sites are not covered by the study and the above techniques are not very useful in studying the adsorption behaviour, surface heterogeneity and active centres for the actual reactants and the products of a particular reaction. As reversible adsorption of these species (*i.e.*, reactants and the products of the catalytic reaction) play an important role in the catalysis, the TPD of the reversibly adsorbed species would give a better understanding of the catalyst surface and its adsorption behaviour for a particular reaction. Further, by studying the TPD of reversibly and irreversibly adsorbed species separately, information on both reversible and irreversible adsorption sites could be obtained for a particular adsorbate.

This investigation was undertaken to extend the TPD method to include also the reversible adsorption sites on the catalyst, so that it is possible to study simultaneously the TPD on the species adsorbed irreversibly and reversibly at the lowest temperature of the TPD run. Such a study is essential for understanding the adsorption of weakly adsorbed species and/or the actual reactants and products of the catalytic

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reaction. A gas chromatographic technique with a catalyst packed in a long chromatographic column as a desorption reactor has been suggested for this purpose and the TPD of thiophene adsorbed reversibly and irreversibly on a reduced copper chromite catalyst has been studied concurrently.

GC METHOD FOR TPD OF IRREVERSIBLY AND REVERSIBLY ADSORBED SPECIES

The GC technique consists of introducing a continuous stream of adsorbate into a stream of carrier gas flowing over the catalyst packed in a long chromatographic column (which is used as a desorption reactor) at the lowest temperature of the TPD study. After the development of an adsorption front, the catalyst with the gas (or the vapour) adsorbed reversibly and irreversibly on it is heated at a programmed heating rate. The adsorbate desorbed continuously into the mixture of carrier gas and adsorbate (flowing continuously over the catalyst during the TPD run) is measured by a gas detector. The resulting chromatogram is due to the TPD of the species adsorbed irreversibly and reversibly at the lowest temperature of the TPD run.

The initial surface coverage due to irreversible adsorption before TPD can be determined by the usual pulse technique[6]. The reversible adsorption before TPD can be obtained from the adsorption front (*i.e.*, from a knowledge of the retention volume and concentration of adsorbate in the gas mixture flowing over the catalyst).

EXPERIMENTAL

The TPD chromatograms for reversibly and irreversibly adsorbed thiophene on the reduced copper chromite catalyst were obtained using an NCL-AIMIL gas chromatograph with a flame-ionization detector (FID). The experimental arrangement is shown in Fig. 1. Hydrogen (ultra-high purity) was used as the carrier gas (and also

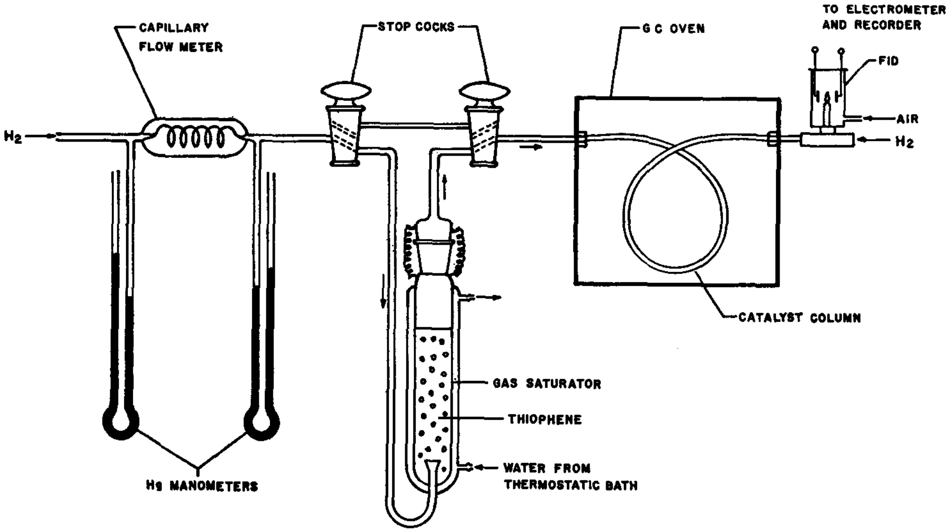

Fig. 1. Experimental arrangement for TPD studies.

as the fuel for the detector). The carrier gas flow-rate was measured using a glass capillary flow meter provided with mercury manometers.

A stainless-steel chromatographic column (60 cm × 4 mm I.D.) was prepared by packing 11.53 g of copper chromite catalyst ($CuO \cdot CuCr_2O_4$, developed in our laboratory for the vapour-phase reduction of nitrobenzene to aniline) having the following properties: particle size, 0.34 mm; 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 in a stream of hydrogen, initially at 200° for 2 h and finally at 300° for 12 h.

Nitrogen (ultra-high purity) was also passed through the column during reduction in order to remove the high heat of catalyst reduction. The weight loss of the catalyst due to the reduction was about 10.5%.

TPD of irreversibly adsorbed thiophene

The initial temperature chosen for the TPD run was 40°. Before starting the TPD, the catalyst in the column was saturated with thiophene by passing a mixture of hydrogen and thiophene vapours (by bubbling hydrogen through thiophene in a gas saturator at 30.5°) over the catalyst for about 1 h. The gas saturator was then bypassed and the reversibly adsorbed thiophene was desorbed in the stream of hydrogen for 30 min. The TPD chromatogram for the irreversibly adsorbed thiophene at 40° was then obtained by measuring the thiophene desorbed continuously in the stream of hydrogen (at a flow-rate of 100 ml/min) by the detector at a heating rate of 20°/min.

TPD of irreversibly and reversibly adsorbed thiophene

At the lowest temperature chosen for the TPD run, the irreversible adsorption sites for thiophene on the catalyst surface were saturated by passing thiophene vapour together with the carrier gas for about 1 h. The reversibly adsorbed thiophene was then desorbed in the flow of hydrogen for 30 min. The hydrogen was replaced with a mixture of hydrogen (100 ml/min) and thiophene vapour (partial pressure of thiophene: 100 mmHg). After development of the adsorption front of the reversible adsorption of thiophene, the TPD chromatogram was started at a heating rate 20°/min. The thiophene desorbed continuously in the carrier gas stream (consisting of the mixture of hydrogen and thiophene vapour) was measured by the detector.

RESULTS AND DISCUSSION

The TPD chromatograms for thiophene adsorbed both irreversibly and reversibly (at 40° and 100°) and irreversibly alone (at 40°) at a heating rate of 20°/min are shown in Fig. 2. It can be seen that the TPD of thiophene adsorbed irreversibly and reversibly on the catalyst surface shows multillicity in the desorption process, as indicated by the multiple desorption peaks.

The TPD of thiophene adsorbed irreversibly at 40° on the catalyst occurs in three stages, as indicated by the three major desorption peaks (one at 115°, the second at 140° and the third at 180°) on the chromatogram (Fig. 2a).

In the case of thiophene adsorbed reversibly at 40° (initial surface coverage of reversibly adsorbed thiophene $3.9 \cdot 10^{-4}$ mole/g) and at 100° (initial surface coverage

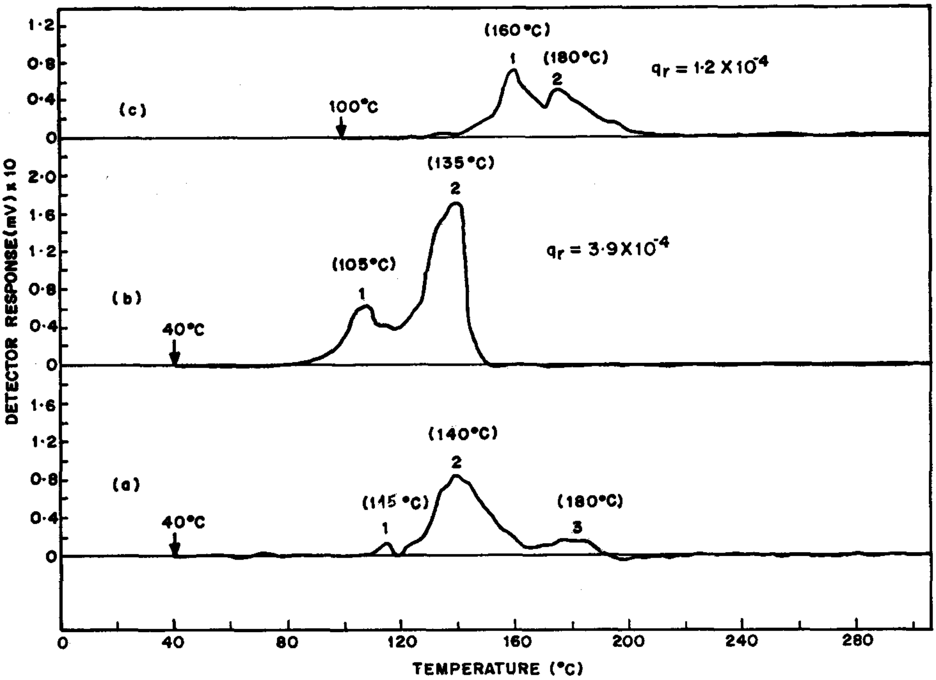

Fig. 2. TPD chromatograms for thiophene on copper chromite (heating rate: 20°/min). (a) TPD of thiophene adsorbed irreversibly at 40° (detector attenuation: 8); (b) TPD of thiophene adsorbed reversibly at 40° (detector attenuation: 128); (c) TPD of thiophene adsorbed reversibly at 100° (detector attenuation: 32). q_r = Amount of thiophene adsorbed reversibly (mole/g).

of reversibly adsorbed thiophene $1.2 \cdot 10^{-4}$ mole/g), the TPD of thiophene was found to occur in two distinct stages, as indicated by two major desorption peaks (Fig. 2b and c). For the TPD of thiophene adsorbed reversibly at 40°, the first desorption peak occurred at 105° and the second at 135° (Fig. 2b), while for that at 100° the first peak occurred at 160° and the second at 180° (Fig. 2c). Further, the desorption of thiophene did not start immediately after the start of the temperature-programmed heating. The desorption started from 80° for the TPD of thiophene adsorbed reversibly at 40° and from 140° for the TPD of thiophene adsorbed reversibly at 100°. These results indicate that the reversible adsorption of thiophene at 40° and 100° was mostly due to reversible chemisorption. In the case of physical adsorption, the desorption would have started immediately after the start of temperature-programmed heating.

It may be noted that the TPD of reversibly adsorbed species at the lowest temperature of study will also include the desorption of the species adsorbed irreversibly on the catalyst surface. However, the extent of the contribution made by desorption of irreversibly adsorbed species to the overall TPD would depend on the extent of the irreversible adsorption in comparison with the reversible adsorption. In the present case, the TPD chromatogram of thiophene adsorbed reversibly at 40° (Fig. 2b) is largely due to the desorption of reversibly adsorbed thiophene. As can be seen from Fig. 2b (chromatogram obtained at detector attenuation 128) and Fig. 2a (chromatogram obtained at detector attenuation 8), the contribution due to the desorption of irreversibly adsorbed thiophene to the overall desorption is negligibly small.

The multiplicity in the TPD of both irreversibly and reversibly adsorbed thiophene on the reduced copper chromite catalyst is probably due to the site heterogeneity on the catalyst surface. The copper chromite catalyst used in this study was an equimolar mixture of CuO and $CuCr_2O_4$. The weight loss of the catalyst (10.5%) on reduction with hydrogen at 300° indicated that the final form of the catalyst was $2Cu \cdot Cr_2O_3$. The study on the reduction of copper chromite catalyst at about 280° by Chistyakova *et al.*[7] supports this view. As the reduced catalyst consists of copper (metal) and Cr_2O_3 (semiconductor), there must exist at least three distinct types of active centres, the first on copper, the second on Cr_2O_3 and the third at the interface of copper and Cr_2O_3. Kinetic multiplicity indicating surface-site heterogeneity has also been observed for both adsorption[8] and desorption[9] of hydrogen on this catalyst in the temperature range 50–300°.

CONCLUSIONS

A gas chromatographic method has been suggested for studying the TPD of both irreversibly and reversibly adsorbed species. With this technique, it is possible to study the adsorption behaviour, surface heterogeneity and active sites of solid catalysts for both irreversible and reversible adsorption. Reversible adsorption is very important in catalysis and hence this technique is useful in studying the reversible adsorption of actual reaction species (*i.e.*, reactants and products of catalytic reactions) at the reaction conditions (or close to the reaction conditions). Further, it is possible to distinguish between physical adsorption and reversible chemisorption.

The application of this technique to the adsorption of thiophene (a catalyst poison) on copper chromite indicated that the irreversible adsorption occurs on three distinct active sites. The reversible adsorption is mostly due to reversible chemisorption and occurs on two distinct active sites.

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