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## GAS CHROMATOGRAPHIC STUDY OF ADSORPTION ON COPPER CHROMITE CATALYST\*

### I. ADSORPTION OF HYDROGEN

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#### SUMMARY

The irreversible and reversible adsorption of hydrogen on copper chromite catalyst has been studied at 30–350° using gas chromatographic techniques. The reversible adsorption was found to be an activated process. The retention isobar, obtained by the pulse technique using the first absolute moment of the chromatographic peak, and the adsorption isobar, determined using the frontal adsorption-desorption method, exhibit similar trends, with one maximum and two minima.

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#### INTRODUCTION

Gas chromatography (GC) provides simple and rapid techniques<sup>1</sup> for studying the adsorptive properties of solid catalysts and adsorbents under their operating conditions. The present investigation concerns the adsorption of hydrogen on copper chromite catalyst at 30–350°. This catalyst is known<sup>2</sup> for its ability to hydrogenate selectively the side groups of benzene, leaving the nucleus intact, and is employed in the commercial process for the vapour phase reduction of nitrobenzene to aniline.

#### EXPERIMENTAL

The chromatographic retention and adsorption data were collected using an NCL-AIMIL dual-column gas chromatograph equipped with a thermal conductivity detector. The detector response was found to be linear with respect to the pulse size and concentration. The carrier gas was nitrogen. The hydrogen and nitrogen used were high-purity gases obtained from Indian Oxygen (Bombay, India) and were further purified by passing the hydrogen over Pd-Al<sub>2</sub>O<sub>3</sub> (0.5% Pd) at 100° and the nitrogen over copper at 400° to remove trace amounts of oxygen, and passing both gases over silica gel to remove traces of moisture.

A stainless-steel chromatographic column (78 cm × 6 mm) was packed with

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copper chromite ( $\text{CuO-CuCr}_2\text{O}_4$ , developed in our laboratory for the vapour phase reduction of nitrobenzene to aniline) in the form of particles (250–500  $\mu\text{m}$ ). The catalyst has the following properties: surface area, 54.1  $\text{m}^2/\text{g}$ ; porosity, 0.634; average pore radius, 108 Å. The catalyst was reduced in a stream of hydrogen at 350° for 16 h and its weight after the reduction was 13.5 g. No change in weight was observed when the catalyst was heated further in the stream of hydrogen at 350°.

The pulse experiments were carried out by introducing 5.0 ml of hydrogen or a mixture of hydrogen and nitrogen (or argon) into the catalyst column using a gas-sampling valve and recording the eluted chromatographic peak on a chart until the recorder pen had reached the baseline.

The frontal adsorption–desorption experiments were carried out by switching over from nitrogen carrier gas to hydrogen for a fixed time (9 min) and then desorbing the adsorbed hydrogen by passage of nitrogen. The desorption chromatogram was recorded until the recorder pen had returned to the baseline.

The area under the elution peak or the desorption chromatogram was determined by the cut-and-weigh procedure. The adsorption on the column wall was found to be negligible. The pressure drop across the catalyst column was within 7% of the outlet pressure (715 mm Hg).

## RESULTS AND DISCUSSION

### *Irreversible adsorption*

The irreversible adsorption of hydrogen was detected by comparing the area under the elution peak of a pulse of hydrogen passed over the catalyst with that obtained with an empty column under identical experimental conditions. The area of the former peak was found to be smaller than that of the latter at all of the temperatures studied. In order to determine the amount of irreversible adsorption, a number of peaks were recorded, one after another, by passing pulses of hydrogen over the catalyst after it had first been heated at 350° in the presence of nitrogen for 4 h to desorb the adsorbed hydrogen. Sufficient time was allowed between two successive pulses for desorption of the hydrogen adsorbed during the passage of the previous pulse. The area of the elution peak was found to increase gradually with the peak number for the first 10–12 peaks and then reach a maximum value ( $A^*$ ), which remained constant for the subsequent peaks. The amount of irreversibly adsorbed hydrogen ( $x$ ) was estimated from

$$x \text{ cm}^3 = V \Sigma(A^* - A_n)/A^* \quad (1)$$

where  $A^*$  is the maximum area of the peak (which was also equal to that of the peak obtained using the empty column under the same experimental conditions),  $A_n$  is the area of the  $n$ th peak and  $V$  is the volume of the hydrogen pulse in  $\text{cm}^3$ . The temperature dependence of the irreversible adsorption of hydrogen is given in Fig. 1a. The amount of hydrogen adsorbed irreversibly is exclusive of the residual hydrogen on the catalyst surface after desorption in a stream of nitrogen at 350° for 4 h.

### *Reversible adsorption*

The reversibility of the hydrogen adsorption was tested as follows. The catalyst

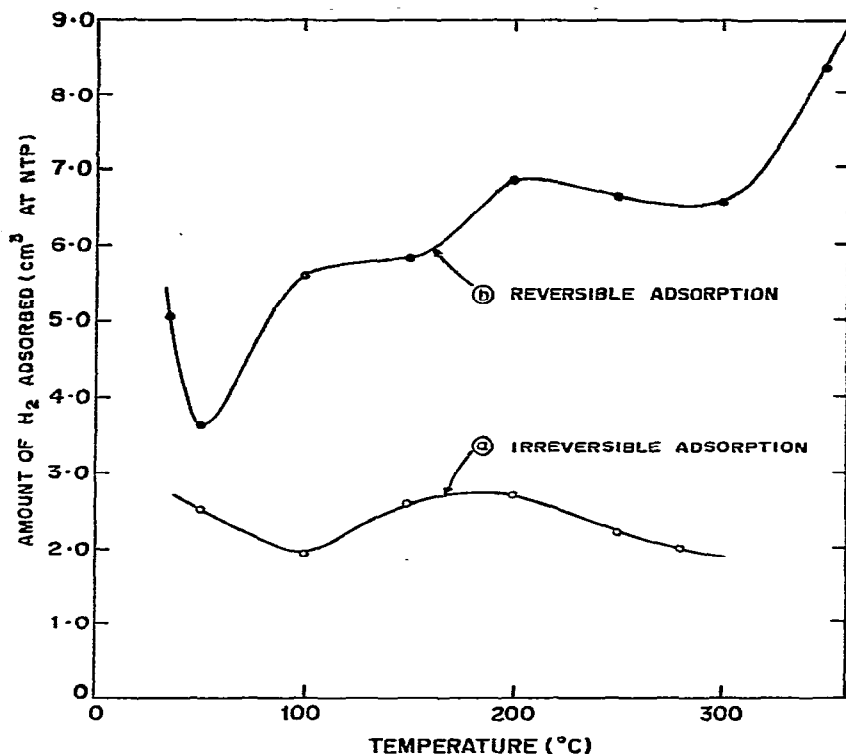


Fig. 1. Adsorption isobars.

was treated with hydrogen for 2 h at the temperature of study in order to saturate the irreversible adsorption sites. This was followed by the desorption of reversibly adsorbed hydrogen in a stream of nitrogen for 30 min. A pulse consisting of hydrogen-argon (1:1) was then introduced into the catalyst column. The chromatograms of the elution pulse at different temperatures are presented in Fig. 2. It is clear that the molecules of hydrogen are retarded in their passage over the catalyst by adsorption on the catalyst surface since the chromatogram consists of two peaks, the first being that of argon (no adsorption) and the second that of hydrogen (reversible adsorption).

The nature of the reversible adsorption, *i.e.*, whether it is an activated or non-activated process, was established by two independent chromatographic techniques (pulse and frontal adsorption-desorption) by studying the variation of the pulse retention and the amount of reversibly adsorbed hydrogen with temperature.

The retention volumes of the gas pulses introduced are the basis of information about the activated process<sup>3</sup>. The retention isobars,  $(t_{m(H_2)} - t_{m(Ar)})F$  vs.  $T$  and  $(\mu_{1(H_2)} - \mu_{1(Ar)})F$  vs.  $T$ , are presented in Fig. 3.  $t_m$  is the retention time corresponding to the peak maximum,  $\mu_1$  is the first absolute moment of the chromatographic peak and  $F$  is the carrier gas flow-rate corrected for the pressure drop across the catalyst column and the column temperature ( $T$ ). The chromatograms were obtained by injecting a pulse consisting of hydrogen-nitrogen (1:1) into the nitrogen stream passing over the catalyst, the active sites for the irreversible adsorption having previously

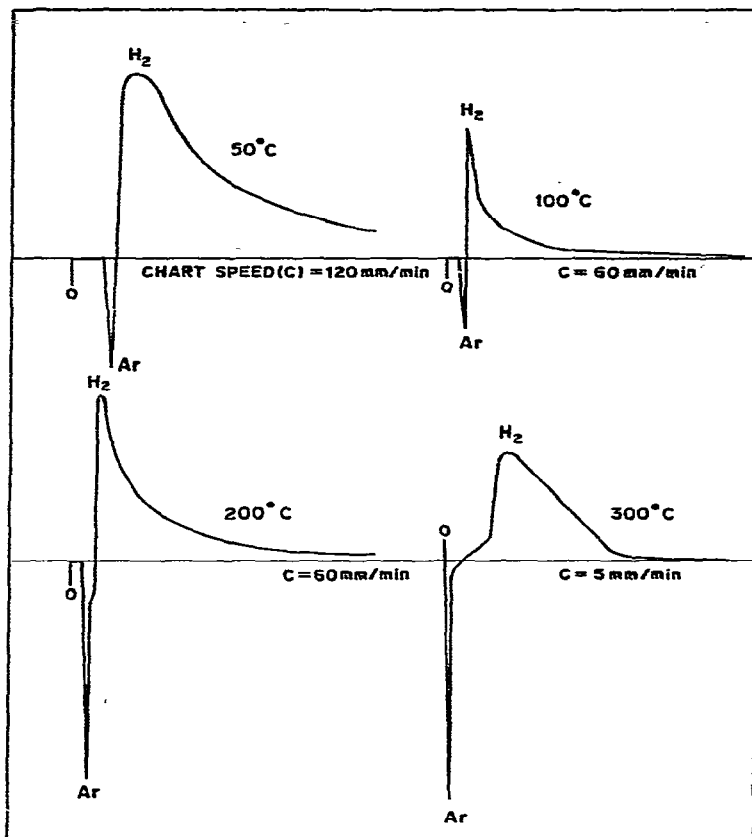


Fig. 2. Chromatograms of hydrogen and argon at different temperatures.

been saturated with hydrogen. The first absolute moment,  $\mu_1$ , of the elution peak is given by

$$\mu_1 = \frac{\int_0^{\infty} t c(t) dt}{\int_0^{\infty} c(t) dt} \quad (2)$$

where  $c(t)$  is the height of the abscissa at the time  $t$ . The integrals were evaluated from the chromatographic data [ $c(t)$  vs.  $t$ ] using the trapezoidal rule on an electronic desk calculator (MOSCAL 1080PS).

It can be seen from Fig. 3 that the retention isobars are different. The isobar  $(\mu_{1(H_2)} - \mu_{1(Ar)})F$  vs.  $T$  represented by the curve b has two minima (one at 50° and the second at 290°) and one maximum (at 230°). This indicates that the reversible adsorption is an activated process. In the case of the isobar  $(t_{m(H_2)} - t_{m(Ar)})F$  vs.  $T$ , represented by curve a, the retention volume is nearly zero between 30 and 80° and increases continuously with temperature. It is very unlikely that the amount of hydrogen adsorbed (which is proportional to the retention volume) is zero, and it has been shown in a separate experiment (discussed later) that the adsorption is appreciable. All of these facts indicate that the use of  $t_m$  in the retention isobar does not give the correct picture

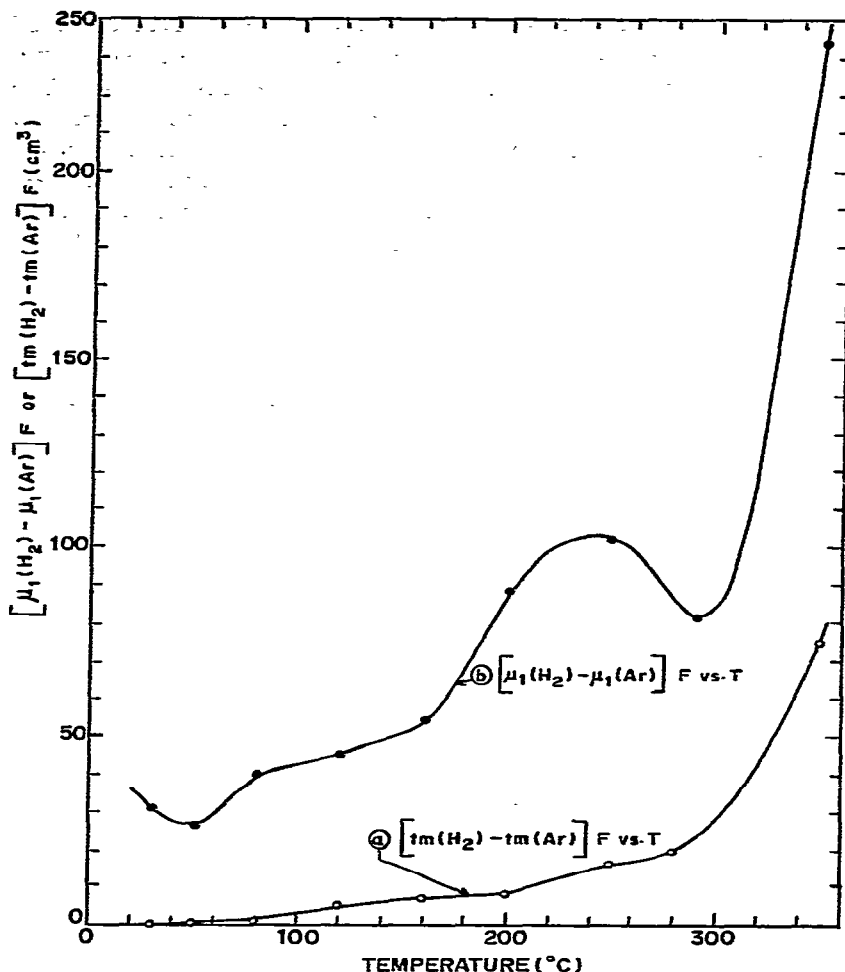


Fig. 3. Retention isobars.

of the activated process. It is recommended that the first absolute moment is used, which corresponds to the centroid of the area under the chromatographic elution curve (which generally differs from  $t_m$ ) and depends only on the values of the equilibrium constant and the porosity of the adsorbent.  $\mu_1$  has a definite physical meaning, while  $t_m$  has less significance because it is not possible to give it a simple physical interpretation and it is also influenced by the longitudinal diffusion<sup>4</sup>.

The hydrogen adsorption isobar was obtained from the frontal adsorption-desorption measurements. The amount of hydrogen adsorbed ( $y$ ) in a fixed time (9 min) when it was passed over the catalyst at different temperatures was determined from the desorbed hydrogen in the stream of nitrogen using the relation

$$y \text{ cm}^3 = A_d V / A_p \quad (3)$$

where  $A_d$  is the area under the desorption curve and  $A_p$  is the area of the peak obtained when a hydrogen pulse of volume  $V$  was passed through the empty or catalyst column under identical experimental conditions of temperature and carrier gas flow-rate. The adsorption isobar is given in Fig. 1b. It has one maximum (at 210°) and two minima (one at 50° and the second at 290°). A comparison of the adsorption isobar (Fig. 1b) with the retention isobar (Fig. 3b) obtained using  $\mu_1$  shows that both the isobars exhibit similar trends in adsorption. This also indicates that  $\mu_1$  is preferable to  $t_m$  in the determination of the retention isobar for ascertaining the activated process of adsorption.

## CONCLUSIONS

Gas chromatography can be successfully used for detecting the reversibility of adsorption, for separately determining irreversible and reversible adsorption and for ascertaining the activated process of adsorption on solid catalysts at temperatures which approach those used in commercial processes.

The adsorption of hydrogen on copper chromite catalyst from 30 to 350° occurs by both irreversible and reversible processes, the latter being an activated process, as suggested by Taylor<sup>5</sup>. It is recommended that the first absolute moment of the chromatographic peak is used instead of the peak maximum to obtain the retention isobar. The former approach is one of the important ways of determining whether the adsorption is activated or not.

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