Note

Gas chromatographic study of temperature–programmed desorption of hydrogen on platinum–alumina[*]

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Temperature-programmed desorption (TPD) or flash desorption is one of the most important methods in studies of the active centres of catalysts, adsorption, surface heterogeneity and catalytic reactions[1–3]. Amenomiya and Cvetanovic[4] suggested an adaptation of the TPD method, which consists in heating the catalyst with the gas adsorbed irreversibly at the lowest temperature of study at a programmed heating rate and measuring the gas desorbed continuously into the stream of an inert carrier gas by a gas detector. Their apparatus consisted of a static volumetric system for adsorption measurements and a flow system for TPD of the gases adsorbed irreversibly on the catalyst under reduced pressure. The catalyst was packed in a shallow-bed reactor. Komers *et al.*[5] extended the TPD technique to a metal catalyst with a small surface area of exposed metal and studied chemisorption and surface reactions of ethylene on platinum–silica.

In this study, a gas chromatographic technique with a catalyst packed in a long chromatographic column as a desorption reactor for TPD studies is described. The kinetic parameters of the desorption of hydrogen on a platinum–alumina catalyst have been determined by measuring the shift in the characteristic desorption temperature as a function of the linear heating rate.

EXPERIMENTAL

The TPD chromatograms for hydrogen on Engelhard RD-150 platinum–alumina reforming catalyst [containing 0.6% (w/w) of platinum and having a particle density of 1.35 g/cm^3, a pore volume of 0.37 cm^3/g and a porosity of 0.5] were obtained by measuring the hydrogen desorbed continuously in a stream of nitrogen with a thermal conductivity detector (TCD) using a Perkin-Elmer 900 gas chromatograph.

Two identical stainless-steel chromatographic columns (3 mm O.D. and 2 mm I.D.) (columns A and B) with a bed length of 90 cm, each packed with the same amount (2.53 g) of the platinum–alumina catalyst (heated in air at 500 °C for 4 h before used) in the form of particles of size 177–250 μm, were prepared and fitted to the chromatographic oven which was used for the linear temperature-programmed heating.

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The catalyst in both columns was reduced with hydrogen at 400 °C for 4 h. The hydrogen was then replaced with nitrogen (purified by passage over heated copper and molecular sieve to remove trace amounts of oxygen and moisture) and the catalyst was heated at 400 °C in the flow of nitrogen for 2 h. The dispersion of platinum in the catalyst was measured by the gas chromatographic pulse technique[6] based on the titration of chemisorbed oxygen with hydrogen, and was found to be $42 \pm 3\%$.

The catalyst in column A (connected to the sensitive section of the TCD) was used for the desorption studies. Column B (connected to the reference section of the TCD) was used as a dummy column. In order to check the stability of the baseline, several trial runs were carried out on the clean catalyst without desorption for each of the heating rates used in the study for the programmed heating range of 100–400 °C. Even though both columns were packed with the same amount of catalyst, there was a shift in the baseline, probably owing to unequal packing. Hence, the nitrogen flow-rate in the dummy column (B) was adjusted by trial and error until a steady baseline without a shift was obtained for the entire programmable temperature range at a fixed carrier gas flow-rate (170 ml/min) through column A.

The initial temperature chosen for the TPD run was 100 °C. Before starting the TPD, the catalyst in column A was saturated with hydrogen at this temperature by passing over it a number of pulses of hydrogen of known volume (0.25 ml) using a gas sampling valve. The amount of hydrogen irreversibly chemisorbed (or the initial surface coverage) was determined from these pulse experiments by a method described elsewhere[7]. The initial surface coverage was 0.063 ± 0.005 ml of hydrogen (at N.T.P.) per gram of catalyst for all of the TPD runs. This value does not include the residual hydrogen on the catalyst surface after desorption at 400 °C for 2 h.

The TPD chromatograms were obtained at six different heating rates in the range 4–24 °C/min and at a nitrogen flow-rate of 170 ml/min measured at room temperature (or 115–200 cm/sec, corrected for temperature variations).

The basic requirement of TPD is that the surface temperature of the adsorbent should be uniform throughout the bed at any instant of the heating period. This requirement can be met only if the heat transfer rate is very high. In this study, high heat transfer rates were expected because of the use of the well mixed (due to the rapid circulation of hot air) chromatographic oven, the long bed desorption reactor (with a small diameter) and the high gas flow-rate through the catalyst column. Another requirement for TPD is that the desorption process should be free from mass transfer limitations. Diffusional resistances to desorption, such as intraparticle diffusion and external film diffusion, were also eliminated by the use of small catalyst particles and a high linear carrier gas velocity, respectively.

RESULTS AND DISCUSSION

The TPD chromatograms for hydrogen on the platinum–alumina catalyst at different heating rates are shown in Fig. 1. The desorption appears to be first order because the chromatograms are asymmetric. Further, there is only one peak for the desorption, which indicates the involvement of only one type of active centre in the desorption process.

The characteristic desorption temperatures (T_m) at which the desorption rate is
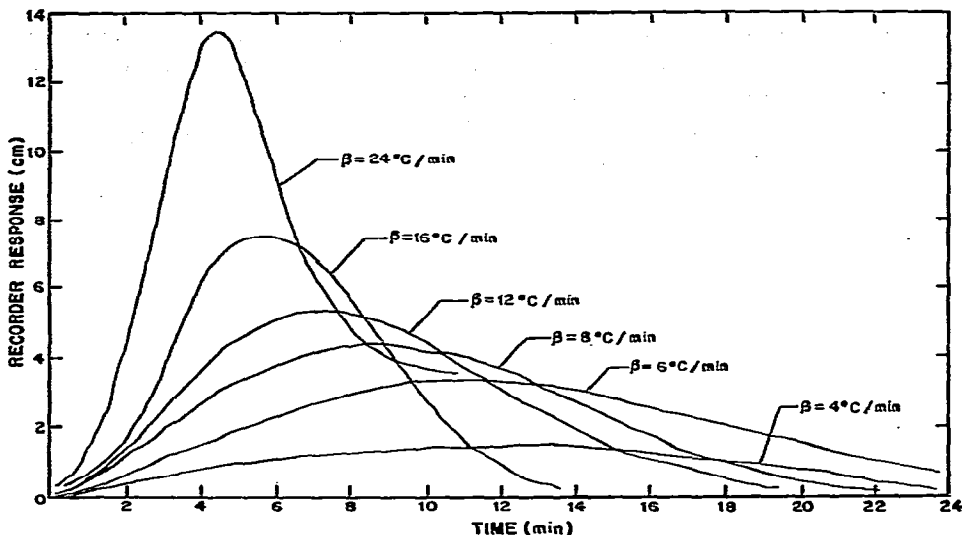
Fig. 1. TPD chromatograms for hydrogen of platinum–alumina. Carrier gas, nitrogen.

maximal for different heating rates are listed in Table I. It can be seen that there was a shift in T_m from 424 to 481 °K when the heating rate (β) was increased from 4 to 24 °C/min.

The activation energy for desorption was obtained from these data by using the relationships developed by Redhead[8], Carter[9] and Amenomiya and Cvetanovic[4] for the first-order desorption process when readsorption does not occur and assuming that the activation energy for desorption is independent of the surface coverage:

$$(k_d)_m = \frac{\beta E_d}{R T_m^2} = A \exp\left(-E_d/R T_m\right) \tag{1}$$

or

$$\log\left(T_m^2/\beta\right) = \frac{E_d}{2.303\,R}\left(\frac{1}{T_m}\right) + \log\left(\frac{E_d}{AR}\right) \tag{2}$$

TABLE I

RESULTS OF TPD OF HYDROGEN ON PLATINUM–ALUMINA

Heating rate, β (°C/min)	Temperature of peak maximum, T_m (°K)	Desorption rate constant at T_m, k_d (sec^{-1})
4	424	$1.98\cdot10^{-3}$
6	437	$2.80\cdot10^{-3}$
8	443	$3.63\cdot10^{-3}$
12	459	$5.08\cdot10^{-3}$
16	469	$6.49\cdot10^{-3}$
24	481	$9.25\cdot10^{-3}$
Activation energy of desorption (E_d)		10.7 kcal/mole* 10.5 kcal/mole**
Pre-exponential factor (A)		602 sec^{-1}

* Obtained from eqn. 2.
** Obtained from eqn. 3.

where $(k_d)_m$ is the desorption rate constant at T_m, T_m is the temperature corresponding to the maximum desorption rate, E_d is the activation energy for desorption, β is the linear heating rate, A is the pre-exponential factor and R is the gas constant. The plot of log (T_m^2/β) against $1/T_m$ was a straight line (Fig. 2). The activation energy (E_d) and the pre-exponential factor (A) were obtained from the slope of the linear plot and by substituting the value of E_d in eqn. 1, respectively. The values of k_d, E_d and A are listed in Table I.
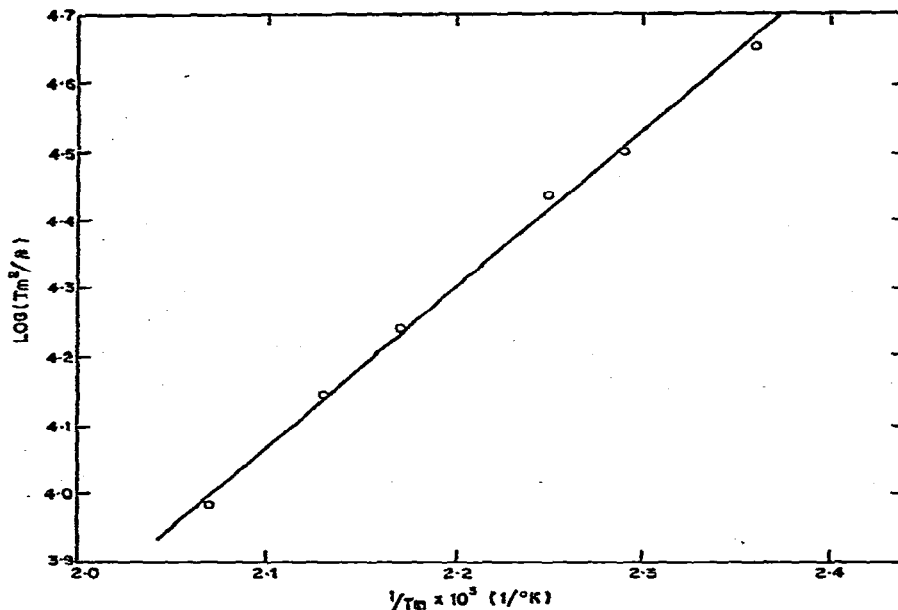

Fig. 2. Graph of log (T_m^2/β) versus $1/T_m$.

The activation energy can also be obtained[8] by plotting log β against log T_m and using the equation

$$\left(\frac{E_d}{R\,T_m}\right) + 2 = d(\log \beta)/d(\log T_m) \tag{3}$$

The values of E_d obtained by means of eqns. 2 and 3 are very similar (Table I).

It should be noted that the values of E_d and A given in Table I are valid for first-order desorption when no readsorption occurs. In this work, as the initial surface coverage is very small and the desorption is carried out in the stream of inert gas flowing over the catalyst at a very high rate, the concentration of the desorbed gas is extremely small and the assumption that readsorption does not take place during the TPD is valid.

The value of E_d (10.7 kcal/mole) obtained in this work is very close to the value of ΔH (10 kcal/mole) for the adsorption of hydrogen on platinum–alumina [0.5% (w/w) of platinum] determined by Gruber and Hausen[10] by gas chromatography from the temperature dependence of the retention volume at low surface

coverage. Tsuchiya et al.[11] investigated the chemisorption of hydrogen on a platinum black catalyst over the temperature range −196–400 °C by TPD and observed four different states (α, β, γ and δ) of chemisorbed hydrogen with different activation energies. Only one state of chemisorbed hydrogen on alumina-supported platinum was observed from the present TPD studies in the temperature range 100–400 °C, because the preadsorption temperature and the catalyst pre-treatment before starting the TPD runs were different in the two studies. However, a comparison between these two studies shows that the hydrogen chemisorbed in the present investigation corresponds to the γ-hydrogen of the previous study[11], which was also found to follow a first-order desorption process.

Gas chromatography with a catalyst packed in a long column with a small diameter offers many advantages for TPD studies, such as the elimination of mass transfer and heat transfer resistances for achieving a uniform temperature throughout the catalyst bed at any instant of the heating period, and the applications of the well established gas chromatographic methods[7,12] for determining the initial surface coverages (i.e., irreversible or reversible adsorption) and the physico-chemical surface properties of the catalyst under study. Thus, the requirement of an additional static volumetric system with a high-vacuum arrangement for measuring adsorption in TPD studies is eliminated. The problem of a shift in the baseline during temperature programming can be avoided by using a flame-ionization detector, which is not sensitive to small changes in the flow-rate, for studying the TPD of hydrocarbons or other detectable adsorbates. Further, this technique can be extended to study the TPD of reversibly adsorbed species.

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