Allene adsorption isotherms and active site determination on various titanium trichloride catalysts

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The techniques of gas–solid chromatography and temperature programmed desorption have been applied to the problem of evaluating the number of active polymerizing centres in variously prepared titanium trichloride catalysts. Using gas–solid chromatography the adsorption isotherms of allene on (i) hydrogen reduced $TiCl_4$ (Stauffer H), (ii) aluminium reduced $TiCl_4$ (Stauffer AA), (iii) Et_2AlCl activated Stauffer AA and (iv) Et_3Al activated Stauffer AA, have been obtained. The non-linear isotherms so derived have been analysed in terms of a two site Langmuir model from which the heats of adsorption and the number of adsorption sites have been evaluated. The number of surface sites is virtually identical on all four materials having values of 4.2×10^{13}, 5.3×10^{13}, 4.8×10^{13} and 4.9×10^{13} sites cm^{-2} respectively (~ 200 Å^2 per site), the majority of these sites ($> 90\%$) having heats of adsorption of 8 kcal mol^{-1}. Since these catalysts have different surface areas which varied from 2.5 $m^2 g^{-1}$ to 8.7 $m^2 g^{-1}$ the near identity of the site densities suggests that a fundamental property of the solid is being measured. The only observed effect of the aluminium alkyl activator on Stauffer AA was to reduce the heat of adsorption of the high energy site from 16.5 kcal mol^{-1} to 12.7 kcal mol^{-1} (Et_2AlCl) and to 9.3 kcal mol^{-1} (Et_3Al). Temperature programmed desorption experiments on Stauffer AA and Stauffer H confirmed the heat of adsorption and the site densities of the high energy sites showing coverages of 2.9×10^{12} and 2.6×10^{12} sites cm^{-2} respectively for these sites (identical to those predicted by the two site Langmuir adsorption model) and desorption activation energies of 18.8 and 17.8 kcal mol^{-1} respectively, inferring no activation energy to adsorption on to these sites.

Keywords Adsorption; allene; active site; titanium trichloride catalysts; isotherm

INTRODUCTION

Because of the factors outlined below, the unambiguous evaluation of the number of polymerizing centres on titanium trichloride based catalysts has proved difficult. This paper is an account of the evaluation of the number of polymerizing centres on different titanium trichloride catalysts by the determination of the adsorption isotherms of allene (corresponding to its reversible chemisorption) on these materials. The technique used is that of gas–solid chromatography[1–3], the allen being adsorbed on to the solid titanium trichloride from a dilute gas mixture in helium. Analysis of the temperature dependence of the line shapes of the isotherms allows evaluation of the heats of adsorption of allene on the titanium trichloride catalysts and also of the number of adsorption centres. The basic assumption used throughout is that since allene is a known poison in polymerization reactions, and since it, itself, polymerizes to a negligible extent, the sites corresponding to its reversible chemisorption are therefore those for propylene (say) adsorption and polymerization.

The model due to Cossee[4] provides an adequate mechanism for olefin polymerization on aluminium alkyl activated titanium trichloride catalysts. In it the active centre is considered to be a titanium ion in an octahedral environment, having an alkyl group substituted for one of the halogen ions and an empty t_{2g} orbital. Polymer initiation is begun by coordination of the monomer olefin to the vacant orbital through a π-bond, which destabilizes the metal to alkyl bond, allowing the alkyl group to migrate and to form a σ-bond to the monomer. As a result of this the monomer becomes σ-bonded to the titanium ion. This process releases a new vacant position for another olefin coordination and repetition of the whole procedure.

In the absence of complicating features such as chain transfer reactions or energetically heterogeneous surfaces, the Cossee mechanism implies a rate of polymerization given by the expression:

$$\begin{array}{c}\text{Rate of polymerization} \\ (\text{molecules cm}^{-2}\,\text{s}^{-1})\end{array} = k_p \frac{\delta K c}{1 + K c} \qquad (1)$$

where k_p is the propagation rate constant, having units of reciprocal seconds, and given by $e^{-E_p/RT}$ (E_p therefore is the activation energy for chain, or alkyl, migration to the monomer), K is the equilibrium constant for chemisorption of the monomer, given by $Ae^{-\Delta H/RT}$ (ΔH is therefore the bond strength of the π-bonded monomer), c is the concentration of the monomer in solution or in the gas phase (mol cm^{-3}), and δ is the vacant site density (sites cm^{-2}).

The expression (equation (1)) explicitly separates the chemisorption of the monomer (bond strength ΔH) from

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the propagation step (activation energy E_p) and shows that, if the activation energy for chain (or alkyl) migration is unaffected by the chemisorption of the monomer, then at low surface coverages, the overall activation energy for polymer propagation is reduced by increasing the heat of adsorption of the monomer. (It may well be that the stronger the heat of adsorption of the monomer the lower is the activation energy for the propagation/migration step, i.e. the higher the heat of adsorption of the monomer the greater is the destabilization of the alkyl/polymer bond strength.) Furthermore expressing the number of active centres as a site density (sites cm^{-2}) is particularly apt, since if their method of determination actually measures an intrinsic property of the solid before polymerization has begun, the value will remain unaltered after polymerization has induced fragmentation of the solid, a greater number of the same crystallographic faces having the same intrinsic site density simply being exposed. Nevertheless no evaluation of the activation energy for chain propagation, E_p, nor of the heat of adsorption of the monomer, ΔH, has yet been achieved, while in the evaluation of the number of polymerizing sites, the numbers produced are a function of the method employed[5-8].

Kissin *et al.*[5], using the lattice parameters, have calculated that the area associated with each titanium atom on the basal plane of $TiCl_3$ is 16 Å^2. (This plane constitutes 95% of the $TiCl_3$ surface area.) However, experimentally, using a methanol pretreated $TiCl_3$ to inhibit active site formation on treatment with $AlEt_3$ (and thereby to inhibit polymer formation), he calculates the area per active site to be 35 Å^2. The methanol molecule is adsorbed on the $TiCl_3$, and then migrates to the $TiCl_3,AlEt_3$ complex causing it to be blocked off for polymer formation. Should the methanol interact with the $TiCl_3$ or the $AlEt_3$ in any way, their value of the number of sites (2.9×10^{14} sites cm^{-2} on a 7 $m^2\ g^{-1}$ surface area catalyst) will be an over-estimate.

The molar number of active centres per mole $TiCl_3$ is:

$$\frac{\text{Number of centres per gramme catalyst} \times \text{gramme molecular weight}}{\text{Avogadro's Number}}$$

$$= \frac{2.9 \times 7 \times 1.544 \times 10^{20}}{6.023 \times 10^{23}} \text{mole centres/(mole } TiCl_3)$$

$$= 5.2 \times 10^{-3}$$

This might be regarded as an upper limit due to the possibility of the over-estimate of the active site density. However it cannot be used as such, since the calculation of the number of mole centres per mole $TiCl_3$ is a linear function of the catalyst surface area, and, in the sense, is a misleading figure since it is particular to the catalyst of that given surface area and does not relate to an intrinsic property of the solid structure and its ability to form a surface complex.

An estimate of the numbers of centres effecting polymerization has been achieved by injecting labelled carbon monoxide (^{14}CO) into the reacting medium and measuring the activity of the quenched polymerization reaction extrapolated to zero exposure time[6-8] (the radio-activity of the polymer was found to increase with increasing time of exposure to the ^{14}CO).

With unactivated $TiCl_2$[6] the number of sites on the most active catalyst (surface area 25 $m^2\ g^{-1}$) was 2.6×10^{-5} mole sites (mole $TiCl_2)^{-1}$, i.e. mole sites (mole $TiCl_2)^{-1}$ = surface area g^{-1} × mole sites m^{-2} × mole wt $TiCl_2$, or

$$\text{sites cm}^{-2} = \frac{\text{Avogadro's Number} \times (\text{mole sites (mole } TiCl_2)^{-1})}{(\text{surface area g}^{-1}) \times \text{mole wt } TiCl_2}$$

$$= 5.27 \times 10^{11} \text{ centres cm}^{-2} \text{ (0.08\% of the surface Ti atoms)}$$

or area per site $= 1.9 \times 10^4$ Å^2 per site.

(Addition of the diethyl aluminium chloride activator to this material was reported to have reduced the number of sites to 31% of its maximum value. However the fall in the numbers of centres on addition of activator was noted only when propylene monomer was used; no change in the active centre density was noted upon the addition of diethyl aluminium chloride to the $TiCl_2$ when ethylene monomer was used.) The value obtained by the ^{14}CO method was one hundred and twenty times less than these experimenters obtained by the use of tritiated methanol and five hundred times less than the value obtained by Kissin *et al.*[5] using methanol inhibition for the same monomers.

When the labelled carbon monoxide method is applied to titanium trichloride based catalysts the estimate of the number of active centres increases markedly[6]. (Here however with $TiCl_2$ catalysts, the number of centres was observed to be greater for ethylene than for propylene when their polymerization reactions were quenched by ^{14}CO. In $TiCl_3$ based catalysts the order was reversed, propylene polymerization inexplicably producing a greater number of centres than the smaller ethylene molecule.) The catalyst of maximum activity—$TiCl_3$, $0.3AlCl_3 + AlEt_3$—had a value of the number of centres of 1.5×10^{-2} mole centres (mole Ti)$^{-1}$ on a surface area (measured by BET) of 20 $m^2\ g^{-1}$. This corresponds to a site density of 2.27×10^{14} sites cm^{-2} or an area of 44 Å^2 per site, a value which is larger than the 35 Å^2 obtained by Kissin[5], and indeed larger than the 16 Å^2 estimated from crystal geometry. When the crystallite size of the catalyst (the ultimate size after polymerization induced fragmentation and not the BET value) is used to determine the catalyst area, a value of 200 $m^2\ g^{-1}$ is obtained and the site density is now 2.3×10^{13} sites cm^{-2} or 441 Å^2 site^{-1}. Nevertheless depending on the degree of fragmentation, which will be a function of the length of time allowed for polymerization before ^{14}CO quenching, an uncertainty will exist as to the actual surface area to be used in the calculation of the site density.

In *Table 1* an evaluation is made of the site densities (site cm^{-2}) and the site areas (Å^2 site^{-1}) for the different techniques cited above. This is done to put the estimates of the numbers of active centres on a consistent and comparable footing.

No clear pattern can be seen to emerge. Conflicting results are obtained (i) by the use of different monomers—are there more or less centres per unit area produced by ethylene monomer or propylene monomer, (ii) whether or not activator is used and (iii) by the method employed (a) ^{14}CO, (b) CH_3O^3H, and (c) CH_3OH pretreatment.

This paper is an account of the application of the technique of gas adsorption chromatography[1-3] to the problem of determining the number of active centres on $TiCl_3$ (hydrogen reduced $TiCl_4$ (Stauffer H), and

Table 1 Determination of the active centre density (centres cm^{-2}) using labelled CO, CO$_2$, and CH$_3$OH

	Crystallographic analysis		^{14}CO quench		^{14}CO$_2$ quench		CH$_3$O^{3}H quench		CH$_3$OH pretreatment		Monomer	Reference
	Area per site (Å^2 site^{-1})	Site density (sites cm^{-2})	Area per site (Å^2 site^{-1})	Site density (sites cm^{-2})	Area per site (Å^2 site^{-1})	Site density (sites cm^{-2})	Area per site (Å^2 site^{-1})	Site density (sites cm^{-2})	Area per site (Å^2 site^{-1})	Site density (sites cm^{-2})		
TiCl$_3$ (Stoichiometric basal plane)	16	6.3×10^{14}	—	—	—	—	—	—	—	—	—	5
TiCl$_3$.AlEt$_3$ (7.0 m^2 g^{-1} BET)	—	—	—	—	—	—	—	—	35	2.9×10^{14}	Propylene	5
TiCl$_3$.0.3AlCl$_3$ AlEt$_3$ (20 m^2 g^{-1} BET)	—	—	44.1	2.27×10^{14}	—	—	—	—	—	—	Propylene	7
(200 m^2 g^{-1} X-ray diffraction)	—	—	441	2.27×10^{13}	—	—	—	—	—	—	Propylene	7
TiCl$_2$ (25 m^2 g^{-1} BET)	—	—	19000	5.3×10^{11}	17 000	5.9×10^{11}	—	—	—	—	Ethylene	6
TiCl$_2$ + AlEt$_2$Cl (25 m^2 g^{-1} BET)	—	—	19000	5.3×10^{11}	22 000	4.5×10^{11}	136	7.3×10^{13}	—	—	Ethylene	6
TiCl$_2$ (25 m^2 g^{-1} BET)	—	—	—	—	92 000	1.1×10^{11}	—	—	—	—	Propylene	6
TiCl$_2$ + AlEt$_2$Cl	—	—	—	—	300 000	3.4×10^{10}	2530	4.0×10^{12}	—	—	Propylene	6

aluminium reduced TiCl$_4$ (Stauffer AA)) and on differently activated TiCl$_3$ (Stauffer AA) catalysts. Using it the isotherms for the reversible chemisorption of allene (a poison for ethylene or propylene polymerization[9]) have been obtained. Analysis of these isotherms has allowed evaluation of the heats of adsorption of the allene and also of the numbers of centres for its chemisorption. Since allene is a poison used to quench the polymerization reaction and thereby measure the number of active centres[10], the former will be an upper limit on the heats of adsorption of propylene. The latter will be the number of active centres for polymerization since the Langmuir point for 100% adsorption of allene has been shown to lie close to the point for 100% loss of polymerizing activity[10]. The method offers the possibility of being able to evaluate the intrinsic numbers of active centres on a catalyst whose surface area has been measured *in situ*, polymerization induced fragmentation, which would result in an undetermined change in surface area, being excluded.

EXPERIMENTAL

Catalysts

Four TiCl$_3$ materials were investigated. They were: (i) hydrogen reduced TiCl$_4$ (Stauffer H), (ii) aluminium reduced TiCl$_4$ (Stauffer AA), (iii) Et$_2$AlCl activated Stauffer AA and (iv) Et$_3$Al activated Stauffer AA. Equal amounts of activator were added to a given weight of Stauffer AA. They were 13 cm^3 (1.5 M) Et$_2$AlCl to 10.82 g Stauffer AA and 20 cm^3 (1.54 M) Et$_3$Al to 17.2 g Stauffer AA, which were added by syringe to a hexane slurry of the TiCl$_3$. The excess activator was removed by repeated washings with hexane, finally removing the hexane itself under vacuum.

The catalysts were loaded, under dry nitrogen, into weighed glass U-tubes which were then sealed and re-weighed prior to connecting to the gas adsorption chromatography apparatus.

Gas adsorption chromatography apparatus

The equipment used to obtain both the surface areas and the adsorption isotherms of allene on these catalysts is shown in *Figure 1*.

The catalyst (in a glass U-tube, held in place by glass beads) was housed in a normal gas chromatographic oven (Servomex Ltd). It was maintained at constant temperatures 77, 225, 273, 283, 293 and 303K, using a vacuum flask containing liquid nitrogen, the appropriate slush bath or the appropriate water mixture, or by using the oven heater itself. The detectors, a katharometer (Servomex microkatharometer) and a flame ionization

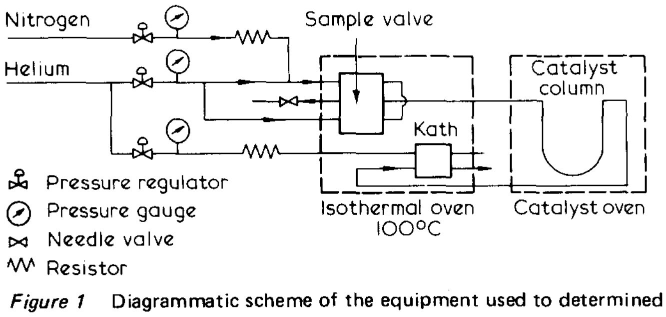

Figure 1 Diagrammatic scheme of the equipment used to determined the catalyst surface areas and the allene adsorption isotherms

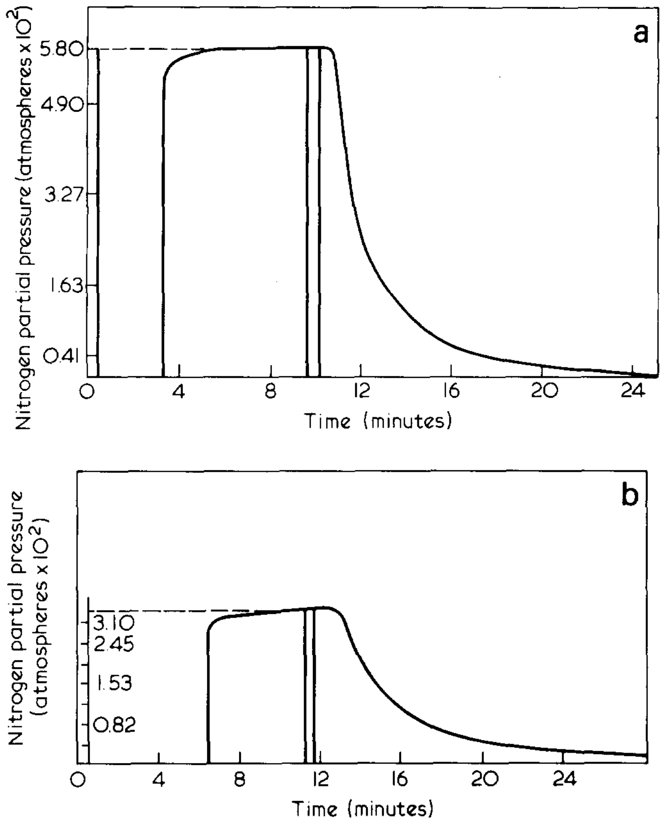

Figure 2 Frontal chromatograms of nitrogen (5.8% N_2 in helium) at −196°C on (a) the Et_2AlCl activated Stauffer AA and (b) the Et_3Al activated Stauffer AA

detector were housed in a separate gas chromatographic oven (Servomex Ltd) at 100°C.

The six port pneumatic valve was used in one of two modes: (i) as a flow switching device by means of which the gas flow over the catalyst could be changed from pure helium to mixtures of either nitrogen in helium ($\sim 6\%$ N_2) in He maximum, 1 atmosphere total pressure) or of allene in helium (0.1%, 1 atmosphere total pressure), (ii) as a pulsed injection device, introducing a known amount of allene on to the catalyst by sweeping out a calibrated loop (0.487 ml) through which flowed a constant stream of allene in helium. (The quantity of allene introduced using this method was varied by varying the dilution of the allene in the helium stream.

Gaseous purities

The gases used were helium, nitrogen and allene. The helium (British Oxygen Company) was purified by passing through a 'Rare Gas Purifier' (British Oxygen Company, Mk 3) which contained, in series, columns containing titanium granules at 973K to remove nitrogen and oxygen, copper oxide (also at 973K) to remove hydrocarbons, hydrogen and carbon monoxide, and molecular sieve (at ambient temperature) to remove water and carbon dioxide. The oxygen content in the exit gas was unmeasurable (i.e. less than 1 ppm) on a Hersch Oxygen Meter (Englehard Industries Ltd).

The nitrogen (British Oxygen Company 'White Spot') was passed through a molecular sieve (5 Å) at room temperature prior to use. Its oxygen content was measured at 4 ppm and the remaining impurities were listed as: $CO < 5$ ppm, $CO_2 < 5$ ppm, $H_2O < 6$ ppm, hydrocarbons < 5 ppm. The allene (Cambrian Gases, Croydon) was used direct from the cylinder. Its listed purity was:oxygen 2.5×10^3 ppm, nitrogen 8×10^3 ppm, CO_2 4.8×10^3 ppm, propylene 5.6×10^3 ppm, and methyl acetylene 6.8×10^3 ppm. Since the maximum allene content in the helium was only 24% and since the volume injected was only 0.487 ml, the activated catalysts were exposed to negligible quantities of impurities which might have a deleterious effect on the $TiCl_3$/aluminium alkyl complex.

RESULTS AND DISCUSSION

Surface area measurements

Figure 2 shows a typical frontal chromatogram obtained when a stream of nitrogen in helium is diverted over the catalysts to replace a helium stream at −196°C. The time of switching from the helium stream to the helium/nitrogen stream is set at zero on the abscissa, while the vertical line after approximately 30 s delay (t_0) is the sweep-out time of the dead volume of the systems at the flow rates used. The integrals of the areas from t_0 to the nitrogen breakthrough is proportional to the volume of nitrogen adsorbed (the uptake) on the catalyst and glass beads (whose surface area had been determined separately) in equilibrium with the gas phase nitrogen partial pressure given by the ordinate value of the plateau of the square wave. (The uptake volume will correspond to the catalyst surface area only when the nitrogen partial pressure used corresponds to monolayer coverage. However the uptake method is a rapid *in situ* method to check for fragmentation induced increase in surface area.)

The time from t_0 after the switch out of the nitrogen/helium stream (and its replacement by the helium stream) to the trailing edge of the eluted pulses is proportional to the differential of the adsorption isotherms. Integration of these differentials of the isotherm by normal stripwise integration of the trailing edges[2,3] gives the nitrogen adsorption isotherm shown in *Figure 3*. These isotherms are used to obtain plots of $\frac{P/P_0}{V(1-P/P_0)}$ *versus* P/P_0 (where V is the volume of gas adsorbed in equilibrium with partial pressure, P, and P_0 is the saturation vapour pressure) from which V_m, the volume corresponding to monolayer coverage, is derived from the slope, $\frac{1}{V_mC}(C-1)$, and the intercept, $\frac{1}{V_mC}$, C being a constant[11]. *Table 2* lists the uptake volumes, the volumes corresponding to monolayer coverage, and the surface areas for each catalyst.

Allene adsorption isotherms and active centre determination for the Et_2AlCl and Et_3Al activated Stauffer AA catalysts

Different samples of the same catalysts used in the surface area experiments of the previous section were used for the determination of the allene adsorption isotherms so as to avoid the possibility of impurity contamination/decomposition of the active centres in the surface area experiments. The apparatus for these gas adsorption chromatography experiments was the same as that used in the surface area experiments except for a slight modification to the sample valve which allowed a pulse of an allene/helium mixture (23.7% allene in helium) to be injected on to the catalyst by sweeping out a calibrated loop (0.487 ml) through which the mixture had flowed. The temperature dependence of the eluted peak shapes is shown in *Figures 4a* (Et_2AlCl activated Stauffer AA) and *4b* (Et_3Al activated Stauffer AA).

As in the analysis of the trailing edges of the frontal chromatograms so the retention times $(t_c - t_0)$ of the trailing edges of the gas adsorption chromatography peak shapes are proportional to the differential of the isotherms at concentration c. (The origin of the abscissa of *Figures 4a* and *4b* is t_0.)

The retention times of the peak trailing edges were logged on a PDP 11 computer, one hundred points being taken for each trailing edge. Confirmation that adsorption equilibrium had been achieved was obtained in experiments in which different quantities of allene were injected, superposition of the trailing edges for the different amounts injected showing equilibrium[3].

Figures 5a and *5b* plot every fifth one of the retention times of the trailing edges logged by the PDP 11 computer (crosses) together with the fit to these (solid line) obtained by a least squares optimization of the six parameters, δ, A_1, ΔH_1, A_2, ΔH_2 and α of the differential of a two site Langmuir model[2,12] i.e.

$$\begin{matrix}\text{Retention time to} \\ \text{concentration } c\end{matrix} = \frac{C_s\delta}{F}\left[\frac{\alpha K_1}{(1+K_1c)^2} + \frac{(1-\alpha)K_2}{(1+K_2c)^2}\right] \tag{2}$$

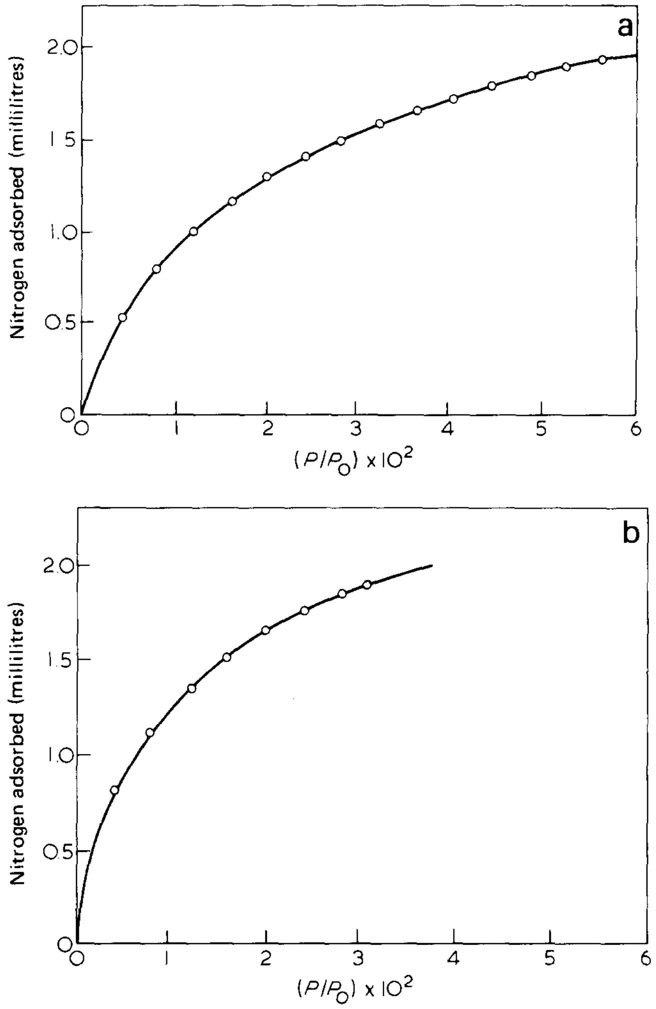

Figure 3 Adsorption isotherms of nitrogen at 77K on (a) the Et_2AlCl activated Stauffer AA and (b) the Et_3Al activated Stauffer AA derived by integration of the trailing edge of the frontal chromatogram

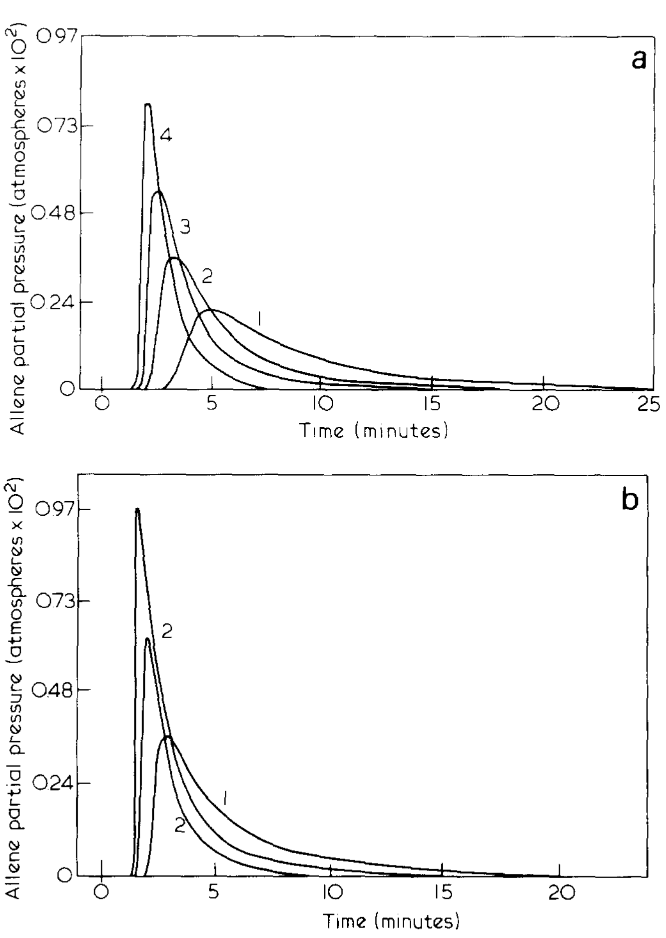

Figure 4 Temperature dependence of the gas adsorption peak shapes of allene pulsed isothermally over two catalysts: (a) Et_2AlCl activated Stauffer AA, 273K – curve 1, 283K – curve 2, 293K – curve 3, 303K – curve 4, (b) Et_3Al activated Stauffer AA, 273K – curve 1, 283K – curve 2, 293K – curve 3

Table 2 Nitrogen uptake and surface area measurements

Catalyst	Nitrogen partial pressure (atm x 10^2)	Weight of catalyst (g)	Weight of glass beads (g)	Uptake volume (ml)	V_m (ml)	Volume correction for glass beads (ml)	Surface area (m^2 g^{-1})
(Et_2AlCl activated Stauffer AA)	5.8	1.0455	5.3420	1.96	2.34	7.92 x 10^{-2}	8.72
(Et_3Al activated Stauffer AA)	3.1	1.5945	4.2909	2.09	2.60	6.40 x 10^{-2}	6.41
Stauffer AA	5.4	1.32	4.7806	–	2.80	7.09 x 10^{-2}	8.50
Stauffer H	5.2	1.08	5.0181	0.68	–	7.44 x 10^{-2}	2.54

where $K_1 = 10A_1 e^{\Delta H_1/RT}$ and $K_2 = 10A_2 e^{\Delta H_2/RT}$ are the equilibrium constants, α is the fraction of the adsorption centres subtending a heat of adsorption of ΔH_1, δ is the total number of adsorption centres for allene adsorption, C_s is the recorder chart speed, c is the gas phase concentration of allene in mol cm^{-3} units and F is the carrier gas flow rate.

The integrated form of equation (2) is the familiar two site Langmuir adsorption isotherm[13], this model of the adsorption being used on the basis of the following considerations: (i) the non-Gaussian peak shapes indicate some form of heterogeneous[12] or coverage dependent heat of adsorption, (ii) consideration of the nature of the bond involved—a weak π-complex—suggests we should be considering this heterogeneity as deriving from discrete energies rather than invoking a through-the-solid type of coverage dependence, (iii) the low coverages involved suggest that an account of the heterogeneity in repulsive interactions between the adsorbate molecules producing some coverage dependent heat of adsorption is implausible.

The value of the 'best fit' parameters for the two catalysts are listed in *Table 3* and the transformation of the trailing edges of *Figures 5a* and *5b* to the isotherms (by 'stripwise' integration[2,3]) is shown in *Figures 6a* and *6b* (the crosses are every fifth experimental point taken, and the solid lines are the isotherms produced by the best fit parameters listed in *Table 3*).

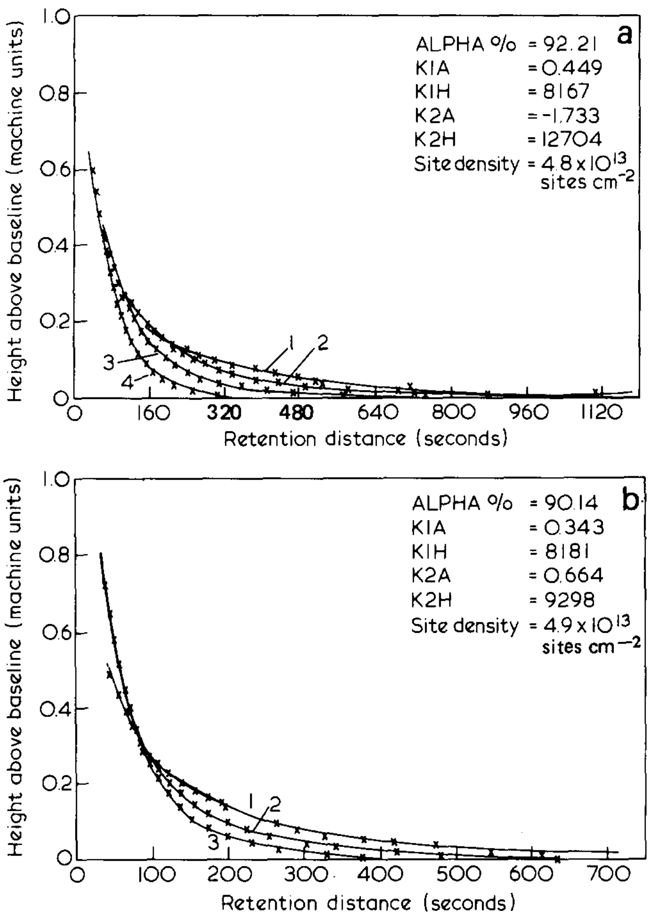

Figure 5 Fit to the allene peak trailing edges on the basis of optimizing the six parameters (numbers of sites heats of adsorption, and pre-exponential terms) of a differentiated two site Langmuir adsorption isotherm, crosses = experimental points, solid line = prediction. (a) Et_2AlCl activated Stauffer AA, 273K – curve 1, 283K – curve 2, 293K – curve 3, and 303K – curve 4. (b) Et_3Al activated Stauffer AA, 273K – curve 1, 283K – curve 2, 293K – curve 3. (The value of the 'best fit' parameters are listed in *Table 3*)

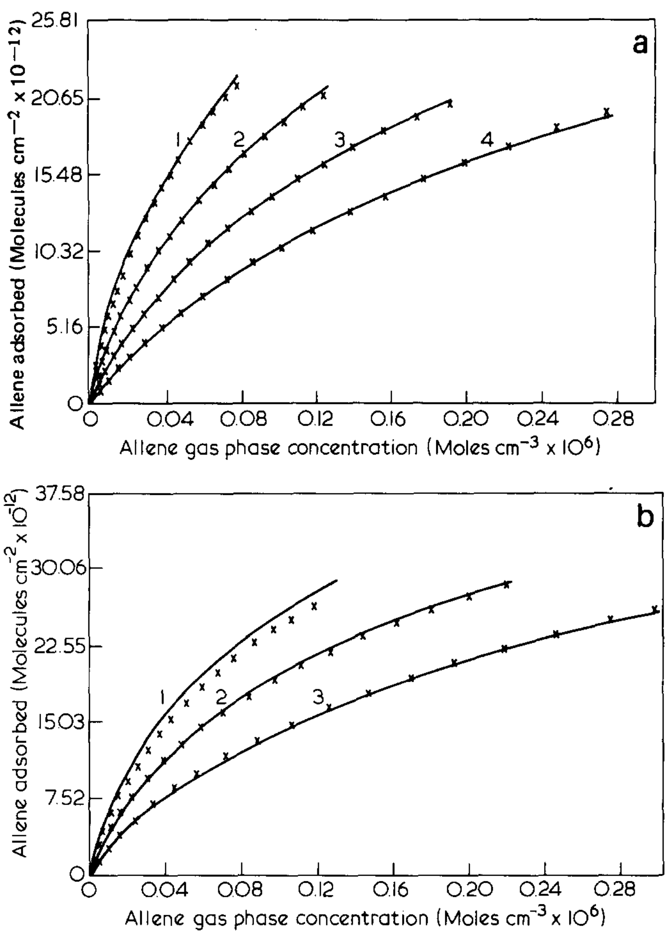

Figure 6 Allene adsorption isotherms on (a) Et_2AlCl activated Stauffer AA, 273K – curve 1, 283K – curve 2, 293K – curve 3, 303K – curve 4. (b) Et_3Al activated Stauffer AA, 273K – curve 1, 283K – curve 2, 293K – curve 3 (crosses = experimental points, solid lines = prediction) obtained by 'stripwise' integration of the allene peak trailing edges of *Figure 5*

Table 3 Optimal parameters of a two site Langmuir adsorption model for allene adsorption on alkyl activated Stauffer AA's

Catalyst	A_1	ΔH_1 (kcal mol^{-1})	A_2	ΔH_2 (kcal mol^{-1})	α Fraction of sites having ΔH_1	δ Maximum site density (sites cm^{-2})
Et_2AlCl activated						
Stauffer AA	0.449	8.17	−1.733	12.7	0.92	4.8 x 10^{13}
(1.0706 g)	±5.8 x 10^{-2}	±8.3 x 10^{-2}	±6.38 x 10^{-1}	±8.9 x 10^{-1}	± 3.4 x 10^{-3}	±5.2 x 10^{11}
Et_3Al activated						
Stauffer AA	0.343	8.18	0.664	9.30	0.90	4.9 x 10^{13}
(1.1205 g)	±5.4 x 10^{-2}	±7.3 x 10^{-2}	±4.8 x 10^{-3}	±6.6 x 10^{-1}	±2.6 x 10^{-3}	±2.0 x 10^{11}

Table 4 Parameter correlation matrices

Et$_2$AlCl activated Stauffer AA	α	A_1	ΔH_1	A_2	ΔH_2	δ
α	1.0					
A_1	−0.23	1.0				
ΔH_1	0.39	−0.98	1.0			
A_2	−0.48	0.63	−0.69	1.0		
ΔH_2	0.51	−0.63	0.69	−0.99	1.0	
δ	−0.73	0.17	−0.35	0.40	−0.43	1.0

Et$_3$Al activated Stauffer AA	α	A_1	ΔH_1	A_2	ΔH_2	δ
α	1.0					
A_1	−0.25	1.0				
ΔH_1	0.34	−0.99	1.0			
A_2	0.39	0.73	−0.75	1.0		
ΔH_2	0.42	−0.73	0.75	−0.99	1.0	
δ	−0.72	0.27	−0.13	0.11	−0.13	1.0

Inspection of *Figures 5a*, *5b*, *6a*, and *6b* shows the fit to be within experimental error. Other indicators, such as the experimental correction to the standard deviation and the sum of the squares of the residuals, confirm this.

The values obtained for δ, the site density, are virtually identical for both catalysts, being 4.8×10^{13} sites cm^{-2} for the Et$_2$AlCl activated TiCl$_3$ and 4.9×10^{13} sites cm^{-2} for the Et$_3$Al activated material, and are 20% of those obtained by Zakharov *et al.*[7] for ostensibly the same TiCl$_3$ catalyst using the labelled CO method. The correspondence of this result for two separate catalysts, differently activated, in separate experiments, suggests we are measuring an intrinsic property of the solid. This, and the similarity of our values with that of Zakharov, infers that the method is a valid (and ready) means of measuring active site density on a catalyst of well defined surface area.

The heats of adsorption of allene on these activated TiCl$_3$ catalysts predicted by the model are of interest. On both catalysts it is predicted that 90% of the adsorbing surface subtends a heat of adsorption of 8.2 kcal mol^{-1} for allene adsorption. Again the identity of this result for two completely separate and differently activated catalysts is surprising. (Indeed the allene probe molecule appears unable to distinguish between the two activators.) Nevertheless, since allene is a poison for propylene polymerization by being adsorbed preferentially and not polymerizing, the value of 8.2 kcal mol^{-1} must represent an upper limit on the heat of adsorption of propylene.

It might be mooted that the clear distinction between the two catalysts is the considerably different energies of the higher energy site, 12.7 kcal mol^{-1} for the Et$_2$AlCl activated catalyst and 9.3 kcal mol^{-1} for the Et$_3$Al activated material, and consideration of indicators such as the parameter correlation matrix (*Table 4*) and the standard errors of the best fit parameters (*Table 3*) suggests that this is valid. The parameter correlation matrix for example shows that there is a strong correlation between the parameters A_1 and A_2 (>0.7 for Et$_3$Al and 0.63 for Et$_2$AlCl) and also between their ΔH values which comprise the equilibrium constants. Therefore if we change A_2 (Et$_2$AlCl) from -1.733 to 0.664, a value which is well outside the error limits listed in *Table 3*, we must also change A_1 by an equally significant amount and, in consequence, alter the isotherm totally, so that the predicted values would not correspond (within experimental error) with the experimental points. One can conclude then that the real differences between the two catalysts is in the heat of adsorption of allene on the scarce (8% of the adsorbing surface, Et$_2$AlCl; 10% of the adsorbing surface Et$_3$Al) high energy site (12.7 ± 1.1 kcal mol^{-1}, Et$_2$AlCl; 9.3 ± 0.67 kcal mol^{-1}, Et$_3$Al).

If, as we have supposed, allene is bonded to the activated catalyst similarly to propylene (in some form of π-complex) and, in being a poison, is only more strongly bonded, then propylene will also show weaker, but heterogeneous, bonding to the activated catalysts. The majority of the adsorbed propylene should therefore have the same bond—corresponding to the 8.2 kcal mol^{-1} bond—on both Et$_2$AlCl and Et$_3$Al activated TiCl$_3$, 0.3AlCl$_3$, but a small fraction will be differently bonded—corresponding to the 12.7 kcal mol^{-1} bond and the 9.3 kcal mol^{-1}. In these differently adsorbed states it is reasonable to expect different reactivities giving rise to different molecular weight distributions at these centres.

It should be noted, however, that in these adsorption experiments a certain quantity of the allene appeared to be 'irreversibly' adsorbed, i.e. the eluted pulse was always less than that of the calibration. The amount of irreversibly held allene was quantified for the Et$_2$AlCl activated TiCl$_3$ at 300K. In a sequence of ten consecutive pulses the amount of allene 'irreversibly' held was: 98.5, 75, 60.2, 64.7, 69, 55.9, 51.5, 47.1, 42.7, and 41.1% of the injected pulse—a total of 1.38×10^{19} molecules— an average of 3 molecules per adsorption site. The amount of allene irreversibly held therefore decreased with increasing pulse number but also varied as a function of the time interval between individual pulses, so that it can be seen that the amount of irreversibly held allene increased from 60.2% to 64.7% between pulses three and four where the time interval between these pulses was 20 min compared with 10 min between pulses two and three when the amount irreversibly adsorbed decreased from 75% to 60.2%. It must be emphasized, however, that the trailing edges of all of these eluted pulses containing differing quantities of allene were completely superimposable indicating that the isotherm itself was unaffected by this irreversible adsorption.

An explanation of this behaviour is to be found in the postulate that certain oligomerization sites exist on the surface, not associated with those sites on which reversible adsorption occurs, where limited polymerization of the allene occurs. This results in a lowering in the standing allene concentration in the gas phase. In this lower concentration gas phase allene the higher energy adsorption sites are preferentially populated and as the oligomerization sites are blocked by the growing polymer chain, more allene is available in the gas phase for reversible chemisorption progressively populating the lower energy sites. The reversible isotherm (the possible source of the allene to the oligomerizing site) is therefore unaffected. Desorption of the oligomer appears to be both feasible and slow resulting in the observed time dependence of the amount of irreversible adsorption, i.e. the dependence of the amount of irreversibly held allene on the time elapsed between pulses.

The model which emerges then is that three sites (at least) exist on the surface, two which adsorb allene reversibly and which probably are the polymerizing sites for propylene and a third one on which allene oligomerizes rapidly and which also probably polymerizes propylene rapidly.

Allene adsorption isotherms and active centre determination on Stauffer AA and Stauffer H $TiCl_3$

Since the oligomerization described above may have derived from the involvement of the alkyl activator, the adsorption isotherms of allene on Stauffer AA and Stauffer H $TiCl_3$ (which had not been treated with aluminium alkyls) were determined. The aim was to investigate the role of the alkyl in respect of the energetics and site densities of the reversible allene chemisorption and also in respect of the oligomerization reaction. Comparison of the Stauffer H with the Stauffer AA, would allow investigation of the possible role of aluminium itself in the oligomerization.

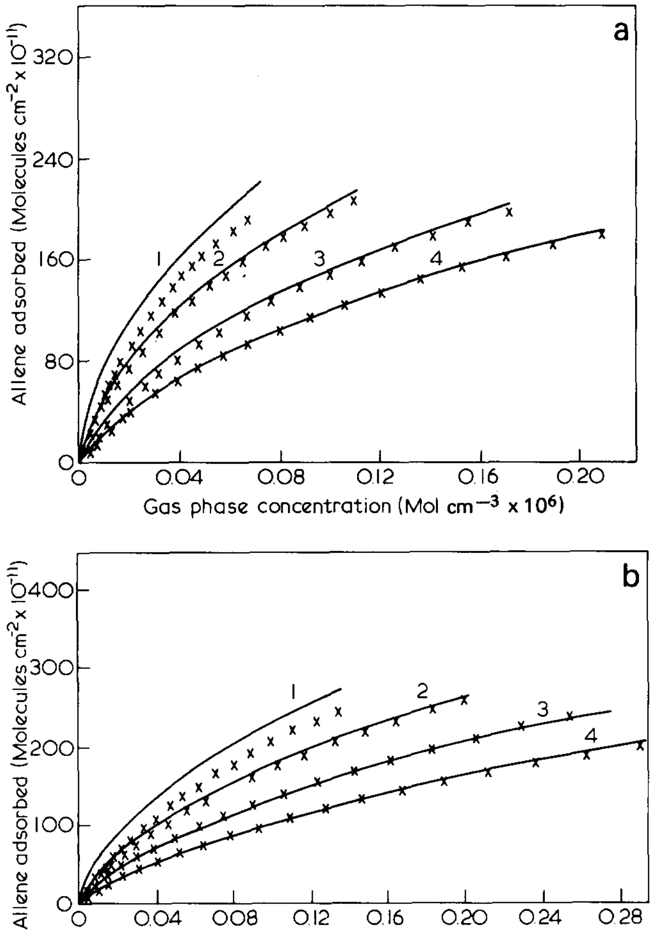

Figure 7 Allene adsorption isotherms on (a) Stauffer AA and (b) Stauffer H, 273K – curve 1, 283K – curve 2, 293K – curve 3, 303K – curve 4

The allene isotherms obtained by the stripwise integration of the gas adsorption peak shapes at 273,283, 293 and 303K on Stauffer AA and Stauffer H are shown in *Figures 7a* and *7b* respectively. The crosses are the experimental points (only every fifth point being plotted) while the solid lines are the predicted isotherms obtained by the fit to the peak trailing edges for a two site Langmuir model, the best fit parameters of which are listed in *Table 5*.

Comparison of the results for Stauffer AA (*Table 5*) with those of the aluminium alkyl activated Stauffer AA's (*Table 3*) shows the aluminium alkyl activator to affect only the high energy adsorption site; the adsorption site density, the heat of adsorption of allene on the lower energy site, and the fraction of the adsorbing surface subtending the lower energy site all remain unaltered. The activator appears only to reduce the heat of adsorption of the allene on the higher energy site from 16.5 kcal mol^{-1} to 12.7 kcal mol^{-1} for Et_2AlCl and to 9.3 kcal mol^{-1} for Et_3Al.

If, as is the contention, these allene adsorption sites are the sites for propylene adsorption and polymerization, then in the absence of aluminium alkyl activator the Stauffer AA would be expected to produce a highly inhomogeneous polymer due to the large difference in the energetics of the adsorption sites. Addition of the activator has a moderating effect on the energetics of the less populous site producing an energetically more homogeneous surface and possibly a more homogeneous polymer.

Equally the presence of the aluminium alkyl activator has no effect on the rate of the oligomerization reaction, the amount of irreversibly held (oligomerized) allene being identical at 7.9×10^{13} molecules cm^{-2} (or 2 molecules per adsorption site) for Stauffer AA and for the Et_2AlCl activated Stauffer AA after the injection of equal quantities of allene. While it might be argued that the presence of the aluminium in the cocrystalline $TiCl_3$, $0.33AlCl_3$ complex which comprises Stauffer AA is responsible for producing the oligomerizing site, the results of the adsorption studies on Stauffer H disprove this—for slighly lower allene loadings than for Stauffer AA, Stauffer H oligomerized 1.4×10^{14} molecules cm^{-2} or about 3 molecules per site.

Allene was dosed on to Stauffer AA and Stauffer H catalysts at low temperatures (255 and 225K) in an attempt to stop the oligomerization reactions. This was unsucccessful, although the amount of oligomerization was reduced by a factor of 10 at the lowest temperature. Nevertheless these experiments allowed direct evidence to be obtained for the value of the heat of adsorption and of the population of the high energy sites on Stauffer AA and on Stauffer H. After dosing the allene at 225K, the catalyst and adsorbate were purged with helium for given lengths

Table 5 Optimal parameters of a two site Langmuir adsorption model for allene adsorption on Stauffer AA and Stauffer H

Catalyst	A_1	ΔH_1 (kcal mol^{-1})	A_2	ΔH_2 (kcal mol^{-1})	α Fraction of sites having ΔH_1	δ Maximum site density (sites cm^{-2})
Stauffer AA	0.409 $\pm 9.14 \times 10^{-2}$	8.45 $\pm 1.18 \times 10^{-1}$	-4.1 ± 1.02	16.49 ± 1.35	0.92 $\pm 2.5 \times 10^{-3}$	4.2×10^{13} $\pm 2.2 \times 10^{11}$
Stauffer H	0.757 $\pm 6.42 \times 10^{-2}$	7.54 $\pm 8.4 \times 10^{-2}$	-6.50 $\pm 8.5 \times 10^{-1}$	19.40 ± 1.15	0.95 $\pm 1.65 \times 10^{-3}$	5.3×10^{13} $\pm 4.2 \times 10^{11}$

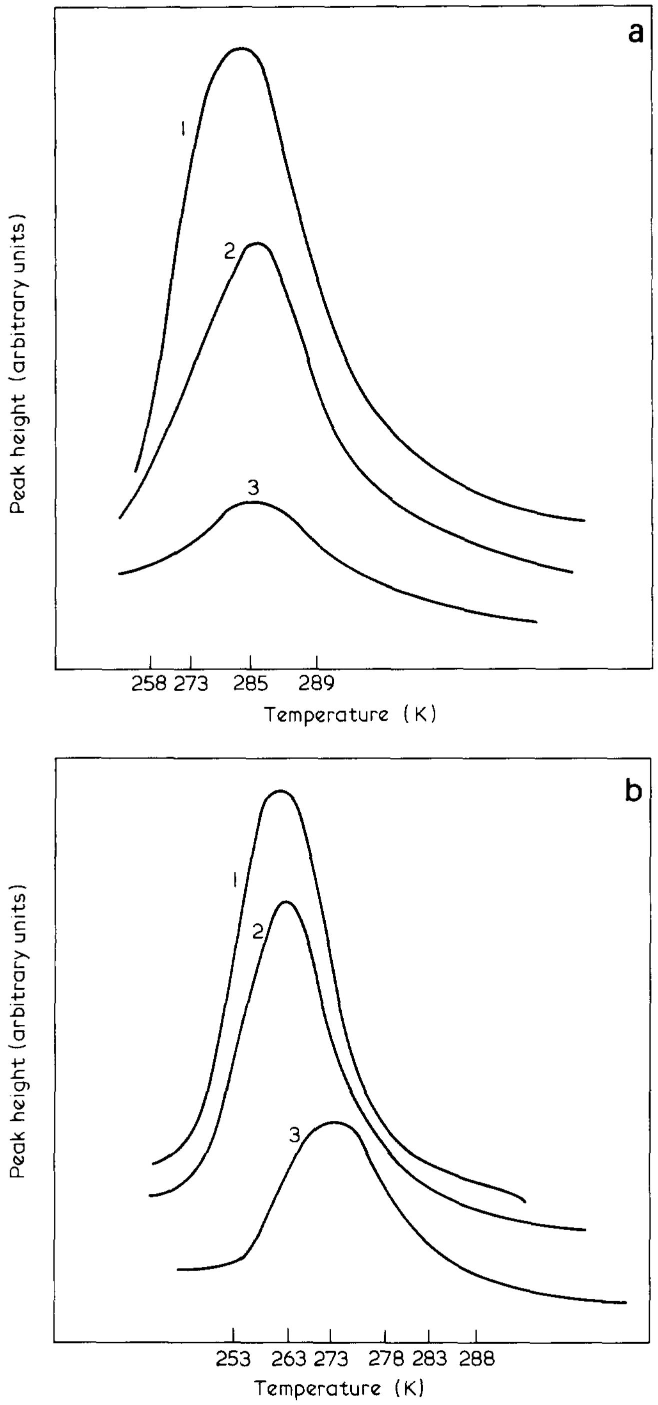

Figure 8 Allene desorption spectra for an adsorption temperature of 225K. (a) Stauffer AA. Temperature programming begun after a helium purge time of 13 min – curve 1, 40 min – curve 2, and 78 min – curve 3. (b) Stauffer H. Temperature programming begun after a helium purge time of 6 min – curve 1, 26 min – curve 2, and 77 min – curve 3. The baselines of the desorption peaks obtained at different coverages are displaced for clarity

Table 6 Allene coverages and desorption activation energies from Stauffer AA and Stauffer H catalysts

Catalyst	Duration of helium purge (min)	Coverage (molecules cm^{-2})	T_{max} (K)	Desorption activation energy, E_d (kcal mol^{-1})
Stauffer AA	13	1.6×10^{13}	281	18.4
"	40	1.1×10^{13}	284	18.6
"	78	2.9×10^{12}	286	18.8
Stauffer H	6	6.2×10^{12}	263	16.8
"	26	4.4×10^{12}	268	17.2
"	77	2.6×10^{12}	273	17.8

of time at 225K, the remaining adsorbate being desorbed by programmed increase of the temperature of the catalyst.

Figures 8a and *8b* are the allene desorption spectra from Stauffer AA and Stauffer H respectively, the catalysts having been closed at 225K by diverting an allene helium stream (~0.1% allene in helium) over them for 50 min. The different quantities of allene adsorbed indicated by the integral of the desorption peak were obtained by varying the length of time of helium purge at 225K after stopping the flow of the dosing mixture prior to programmed temperature increase[15]. The coverages so obtained and the desorption activation energies derived by solution of the Redhead equation[15] (equation (3)) are listed in *Table 6*:

$$E_d/RT_m^2 = (A/\beta)\exp(-E_d/RT_m)^2 \qquad (3)$$

where E_d is the desorption activation energy (cal mol^{-1}), T_m is the temperature of the peak maximum (K), A is the Arrhenius pre-exponential factor ($= 10^{13}$ s^{-1} assumed).

The desorption activation energies are within 1 kcal of the heats of adsorption of the high energy sites listed in *Table 5* while the coverages of the catalyst by these sites as obtained in experiments using the longest duration of helium purge (78 min—Stauffer AA, 77 min—Stauffer H) are virtually identical to the values predicted by analysis of the isotherm: 3.36×10^{12} sites cm^{-2} predicted (i.e. $0.08 \times 4.2 \times 10^{13}$) *versus* 2.9×10^{12} experimental for Stauffer AA and 2.65×10^{12} sites cm^{-2} predicted (i.e. $0.05 \times 5.3 \times 10^{13}$) *versus* 2.6×10^{12} experimental for Stauffer H. The close agreement of the predicted and experimental site population and heats of adsorption is strong evidence for the validity of the analysis of the isotherm. However the larger coverages obtained from the shorter duration of helium purge and the movement of the peak maximum temperature to lower values (lower desorption energies) suggest that the surface may be more complicated than simply having two heats of adsorption, since the desorption half life at 225K for an 8 kcal mol^{-1} heat of adsorption is 4×10^{-6} s and therefore the coverage at 6, 13, 26, and 40 min should simply be that of the high energy site and should be identical to the 77, 78 min value. For the Stauffer H the addition of a small number of sites of heat of adsorption of about 16.5 kcal mol^{-1} would probably suffice for a totally consistent description of the isotherm and the desorption spectra but would lead to an overdefinition of the equation required for the definition of the isotherm, i.e. there would be too many parameters to describe the curve resulting in some of the parameters being linearly related to each other.

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