Journal of Thermal Analysis, Vol. 27 (1983) 391–400

SOME EXPERIMENTAL ASPECTS OF THE DETERMINATION OF KINETIC PARAMETERS BY MEANS OF TEMPERATURE-PROGRAMMED DESORPTION

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(Received February 15, 1983)

The process of desorption of a gas from a catalyst surface, especially when temperature-programmed, can be affected by the occurrence of other chemical or physical processes.

On the basis of a simple method of analysis, which makes possible the examination of definite fractional areas of a peak, and therefore the examination of definite ranges of surface coverage during desorption, this paper examines two experimental cases of temperature-programmed desorption, relating to propylene metathesis on the practical catalysts, WO_3/SiO_2 and Re_2O_7/Al_2O_3.

Some particular methods and procedures for collecting TPD data and obtaining reliable kinetic results in the presence of multiple peaks, and therefore in the case of the overlapping of other physical phenomena, are developed: the results on the adsorptive and desorptive properties of the two catalysts are compared with the results reported in the literature, obtained from kinetic studies concerning propylene metathesis on the same catalysts.

Among the techniques for investigating and characterizing practical catalysts, temperature-programmed desorption (TPD) has become widespread in recent years. However, the obtaining of information on the nature of the interactions between adsorbed species and a catalyst surface requires the determination of reliable kinetic parameters and, in spite of the simplicity of the method, TPD spectra can be affected by many experimental factors (surface heterogeneity, diffusional resistances, desorption with readsorption or with reaction) in addition to those problems which derive from the use of a non-isothermal technique.

Many desorption processes are very complex and require a careful choice of the experimental conditions in order to obtain meaningful results: TPD is a typical non-isothermal method and has retained the "philosophy" of flash desorption, from which it was derived. However, much attention must be paid to the heating rate, the sample mass, the adsorption temperature and the carrier gas flow rate, which not only influence the occurrence of heat and mass transfer limitations and readsorption, mass transfer limitations and readsorption, but also determine the possibility of overlapping or separation of different desorption processes.

Many methods have been suggested [1–3], as far as the analysis procedure of the TPD spectra is concerned, to overcome these difficulties and to relate the kinetic parameters unambiguously and reliably to the rate-limiting process.

These methods are based on the analysis, from many spectra, of the shift of a TPD peak with changing heating rate, or on the analysis of the shape of a TPD peak in a single spectrum.

There is also the possibility of performing an analysis based on a differential method, similar to that used in differential scanning calorimetry [4], which has the advantages of simplicity and the possibility of examining even definite portions of a peak, and therefore of paying better attention to the possible variation of the kinetic parameters during the desorption process [5].

Experimental

The experiments were carried out in the apparatus shown in Fig. 1, whereby it is possible to perform pulse or continuous adsorption and to keep constant the flow rate of adsorbate and carrier gas both during adsorption and during desorption.

The reactor was a quartz tubular one, 1/4" in o.d., and the temperature was controlled by a coaxial thermocouple encased in a quartz tube inside the catalyst; the temperature was linearly programmed to a tubular furnace containing the reactor. The desorbed gas was monitored by means of a Dani hot wire detector provided with an HWD control.

The 7% WO_3/SiO_2 gel catalyst was prepared by impregnating silica gel (RP ACS C. Erba) 80–100 mesh, BET surface area 350 m^2/g, with an aqueous solution of ammonium tungstate (RP ACS C. Erba), followed by drying at 823 K for 3 h.

The 15% Re_2O_7/Al_2O_3 catalyst was prepared by impregnating alumina (Akzo Chemie) 80–100 mesh, BET surface area 307 m^2/g, with an aqueous solution of ammonium perrhenate (Ventron), followed by drying at 373 K and calcining at 823 K in dry air for 3 h.

The gases used were propylene N20 (SIO) and helium N45 (SIO): they were filtered on molecular sieve and helium was passed through a trap at liquid nitrogen temperature in order to dry it effectively.

Before every adsorption-desorption run the catalyst sample was pretreated "in situ" according to procedures reported in the literature [6, 7], which ensure the highest activity and selectivity for the metathesis of propylene:

$$2\,C_3H_6 \longrightarrow C_2H_4 + C_4H_8$$

The samples were then cooled down to the adsorption temperature, evacuated for 1 h at $2.5 \cdot 10^{-4}$ Torr for better cleaning of the surface, and afterwards adsorption was allowed by means of a mixture of helium and propylene flowing continuously for 1/2 h through the catalyst bed.

The sample mass was kept to a minimum (0.1 g) to avoid temperature gradients within the catalyst bed. During desorption, the gas flow was trapped immediately after the detector and analyzed by means of a Hewlett Packard 5750 gas chromatograph, to characterize the recorded peaks. It must be stressed that the dead space

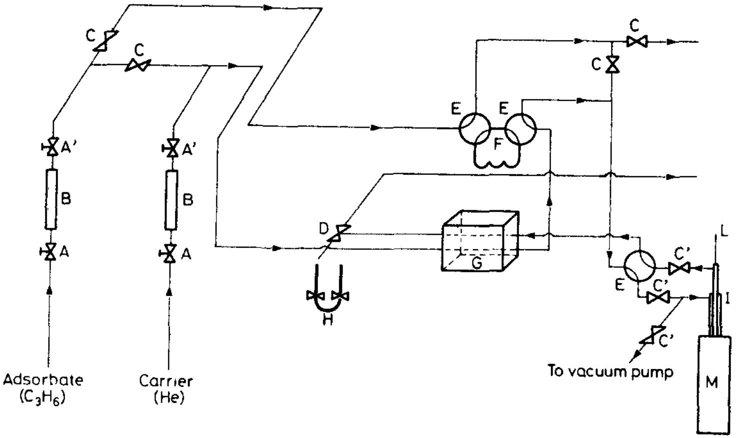

Fig. 1 A schematic diagram of the TPD apparatus: A = upstream mass flow controller; A' = downstream mass flow controller; B = rotameters; C = on-off valve; C' = on-off valve for vacuum; D = three-way valve; E = four-way valve; F = gas sampling loop; G = hot wire detector; H = trap for GC analysis; L = thermocouple; I = reactor; M = furnace; (traps for condensing impurities in gases are inserted before upstream mass flow controllers)

between the reactor and detector was taken into account, as well as the thermocouple lag, in order to obtain correct temperature values.

On the other hand, the absence of mass transfer limitations was preliminarily checked by means of runs at different grain sizes of the catalyst powders; the absence of heat transfer limitations was preliminarily checked by determining the lowest heating rate at which variations of the sample mass did not cause variations in the shape of the considered peak and in its position on the temperature scale.

Results and discussion

The greatest part of the discussion will be devoted to the results obtained from desorption runs on WO_3/SiO_2 gel catalyst, because of the peculiarities of the results.

The initial runs were performed using room temperature as adsorption temperature, and a high carrier gas flow rate during desorption to avoid readsorption phenomena; the features of the corresponding desorptograms are shown in Fig. 2.

The presence of two shoulders near the maximum of the first peak does not allow any conclusion from the symmetry and from the shape of this peak.

On the other hand, the gas-chromatographic analysis of the effluent showed that only propylene desorbs from the catalyst when this peak is recorded. It is therefore possible to deduce that this peak monitors three different forms of adsorbed propylene: the desorption processes of the second and third forms of adsorbed propylene overlap at a high heating rate.

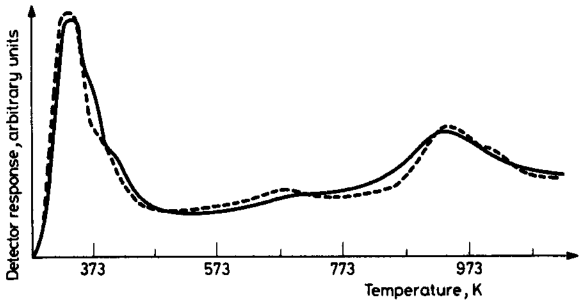

Fig. 2 TPD spectrum obtained by means of high carrier gas flow rate after room temperature adsorption of propylene on WO_3/SiO_2 (— — — — high heating rate; ——— low heating rate)

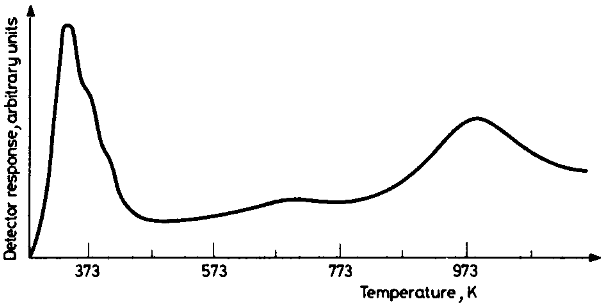

Fig. 3 TPD spectrum obtained by means of low carrier gas flow rate after room temperature adsorption of propylene on WO_3/SiO_2

Subsequently, runs were performed by decreasing the carrier gas flow rate, to check if readsorption had to be taken into account; however, as shown in Fig. 3, the maximum of the first peak and its two shoulders are not significantly shifted on the temperatures scale at corresponding heating rates, and this seems to confirm the absence of readsorption phenomena.

The features of the spectra in the range of higher temperatures are similar, aside from the experimental conditions: a low and broad peak with a maximum at about 673 K, and another peak with a maximum at about 973 K, are shown.

Gas-chromatographic analysis shows that both are related to desorption processes with reaction, and indeed metathesis products are associated with the first of these two peaks: 673 K is a typical mean temperature for the metathesis of propylene over WO_3/SiO_2 gel. Products of metathesis, dimerization and cyclodimerization, and also carbon dioxide, are associated with the second of these two peaks.

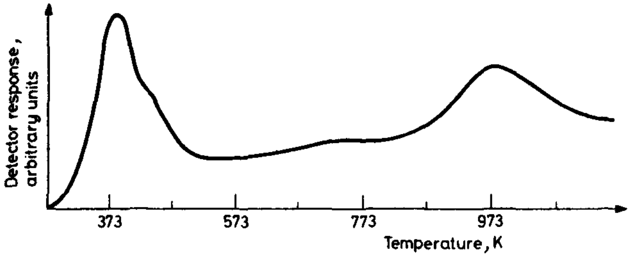

Fig. 4 TPD spectrum obtained after isothermal desorption at 52.5°C, related to adsorption of propylene on WO_3/SiO_2

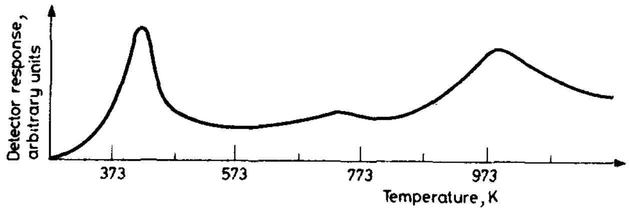

Fig. 5 TPD spectrum obtained by means of adsorption at 128°C of propylene on WO_3/SiO_2 and using high carrier gas flow rate

In order to perform as complete as possible a kinetic analysis on the first peak (at lower temperatures), it was terefore useless to work only at low heating rates, because overlapping was only reduced (this choice must be recommended, however, to avoid heat transfer limitations and large temperature lags).

The desorption of adsorbed propylene of form I was therefore studied by means of adsorption runs at temperatures of about 313 K, and by a subsequent temperature-programmed desorption (see Fig. 4).

Runs were then performed to study the desorption of adsorbed propylene of form III by means of adsorption at higher temperatures (about 403 K), followed by temperature-programmed desorption at a high carrier gas flow rate to avoid readsorption (see Fig. 5).

(It is obvious that it was impossible to characterize in a reliable way the kinetic parameters relating to the desorption of adsorbed propylene of form II, because it was impossible to avoid even a minimum overlapping with the other desorption processes.)

By means of the already mentioned procedure [5] now applied to isothermal desorption, and considering that:

$$\text{rate of desorption} = -\frac{d\Theta}{dt} = \frac{d(1-\Theta)}{dt} \quad \text{and} \quad \frac{d(1-\Theta)}{dt} = k\Theta^n$$

where Θ = surface coverage, we obtain

$$\ln\left(\frac{d(1-\Theta)}{dt}\right) = \ln k + n \ln \Theta$$

Thus, a plot of $\ln\left(\frac{d(1-\Theta)}{dt}\right)$ *vs.* $\ln \Theta$ will give a straight line with slope n and intercept $\ln k$. This plot and the subsequent Arrhenius plot show that this desorption process follows first-order kinetics with an activation energy of 52.5 kJ/mole and a pre-exponential factor of $2.7 \cdot 10^6$ s^{-1}. As far as the peak relating to adsorbed propylene of form III is concerned, we checked above all the possible presence of a surface heterogeneity.

It is shown, that starting from the same initial coverage, a particular value of the actual surface coverage is reached at different temperatures if different heating rates are used. Arrhenius plots can therefore be drawn [8, 9] for fixed values of the surface coverage, obtaining the activation energy corresponding to those values of the surface coverage, with subsequent checking of the dependence of the activation energy on the surface coverage: in this case no variation has been observed.

We checked which law (first or second-order law with or without readsorption, diffusion law) gives the best Arrhenius plot when the logarithm of the rate at determined temperature values T (deduced from the height of the peak at that temperature) is plotted $1/T$.

In Fig. 6 an Arrhenius plot is given to show that, over a large range of surface coverage, desorption follows second-order kinetics: the activation energy is 116.5 kJ mole and the pre-exponential factor is $1.5 \cdot 10^{12}$ s^{-1}.

As far as propylene desorption over Re_2O_7/Al_2O_3 is concerned, we must note that the most important characteristics of its TPD spectrum can be studied by varying the partial pressure of propylene in the adsorption gas mixture, thereby varying the initial surface coverage. Figure 7 shows two typical desorptograms, starting from low and from higher initial surface coverage: in the second instance a shoulder appears near the maximum of the first peak. However, it is very difficult to obtain kinetic parameters relating to the desorption process for in this instance the gas-chromatographic analysis monitors the presence of metathesis products in the gaseous stream coming from the reactor.

(We must stress here that the optimum temperature range for the metathesis reaction over Re_2O_7/Al_2O_3 is 323–353 K.)

Therefore, only in the first instance it was possible to extract meaningful kinetic parameters, and it was found that desorption follows second-order kinetics, characterized by two distinct intervals: the first ($0.95 < \Theta < 0.85$) with an activation energy of 43.7 kJ/mole, and the second ($0.85 < \Theta < 0.09$) with an activation energy of 35.5 kJ/mole. We are therefore dealing first with a more activated mechanism, and

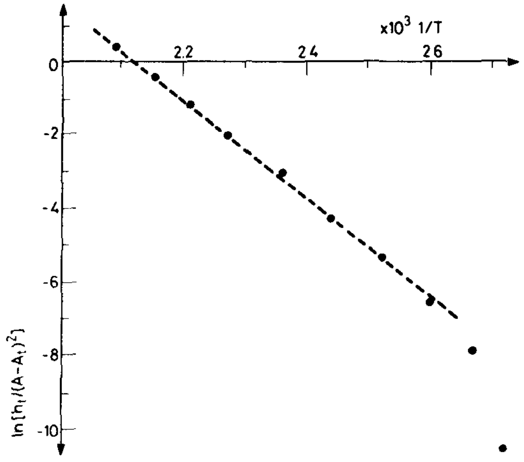

Fig. 6 Arrhenius plot related to the TPD peak of the form III of propylene previously adsorbed at 128°C on WO_3/SiO_2

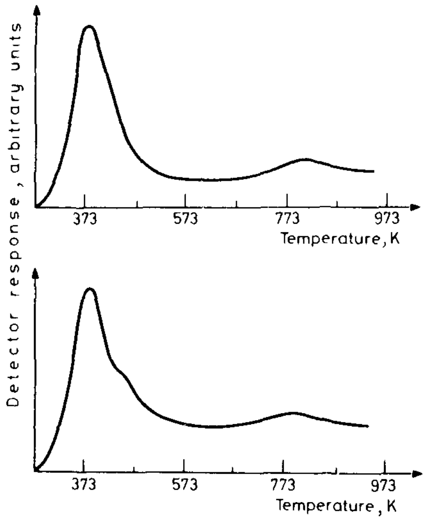

Fig. 7 TPD spectrum of propylene adsorbed on Re_2O_7/Al_2O_3 with low (a) and high (b) initial surface coverage

subsequently with a less activated one, but both can be described by second-order kinetics (see Fig. 8).

It is to be stressed, however, that in the first interval uncertain evidence of a rectilinear plot of second-order kinetics with readsorption seems to justify these conclusions.

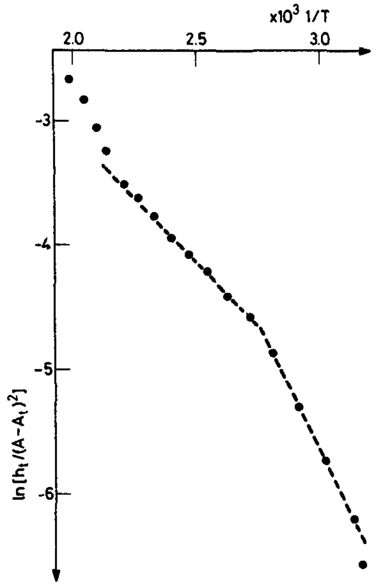

Fig. 8 Arrhenius plot related to the TPD peak of Fig. 7a at lower temperature

Conclusions

Temperature-programmed desorption was introduced as a complementary technique in catalysis studies, to characterize catalysts and allow a deeper insight into their active centres: the results of the analysis of a TPD spectrum must therefore be of use towards a better understanding of the mechanism of activity and selectivity of the catalyst in a well-determined reaction. As far as the WO_3/SiO_2 gel catalyst is concerned, adsorbed propylene of form III appears to be the most important, because the peaks at higher temperatures (desorption with reaction) seem to be related to this form: indeed, these peaks disappear only when the adsorption temperatures are fixed above the desorption temperatures of this form of propylene.

Moreover, the area of the two peaks at higher temperatures (and therefore the volume of the desorbed gases) is practically constant when forms I and II are adsorbed and when these forms are not adsorbed.

For both catalysts, the most important peak relating to desorption without reaction shows a general trend to follow second-order kinetics.

This is surely related to the manner of adsorption of propylene on these catalysts, which is dissociative adsorption with formation of an allylic fragment, leading to associative desorption.

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Zusammenfassung — Der Vorgang der Desorption eines Gases von einer Katalysatoroberfläche, besonders wenn er temperaturprogrammiert ist, kann durch das Vorkommen von anderen chemischen oder physikalischen Vorgängen beeinflusst werden.

Auf Grund einer einfachen, analytischen Methode, die die Untersuchung bestimmter Teilgebiete eines Peaks, und dadurch die Untersuchung bestimmter Bereiche der Oberflächendeckung während der Desorption ermöglicht, untersucht diese Arbeit zwei Versuchsfälle der temperaturprogrammierten Desorption, bezüglich der Propylen-Austauschreaktion mit den praktischen Katalysatoren WO_3/SiO_2 und Re_2O_7/Al_2O_3.

Einige spezielle Methoden und Verfahren zum Sammeln der TPD-Daten, und um vertrauenswürdige kinetische Ergebnisse in der Anwesenheit von mehreren Peaks und dadurch im Falle der Überdeckung anderer physikalischer Erscheinungen zu erhalten, wurden entwickelt: Die Ergebnisse über die adsorptiven und desorptiven Eigenschaften der zwei Katalysatoren wurden mit denjenigen in der Literatur mitgeteilten Ergebnissen verglichen, die während kinetischer Untersuchungen bezüglich der Propylen-Austauschreaktion mit denselben Katalysatoren erhalten wurden.

Резюме — Процесс десорбции газа с поверхности катализатора, особенно в случае запрограммированной температуры, может затрагиваться наличием других химических и физических процессов. На основе простого метода анализа, представляющий возможным исследовать определенные частичные площади пиков, в результате чего и исследование определенных областей поверхности охвата во время десорбции, в статье исследуются два экспериментальных случая температурно-запрограммированной десорбции, касающейся реакции обмена пропилена на катализаторах WO_3/SiO_2 и Re_2O_7/Al_2O_3. Разработаны специальные методы и методики сбора данных ТПД и получения надежных кинетических результатов в присутствии многочисленных пиков и в случае наложения других физических явлений. Полученные результаты по адсорбционным и десорбционным свойствам двух катализаторов сопоставлены с литературными данными, полученными при изучении кинетики реакции обмена пропилена на тех же самых катализаторах.