Journal of Thermal Analysis, Vol. 23 (1982) 45—50

INVESTIGATION OF THE CHEMISORPTION OF PROPYLENE ON ZINC OXIDE BY TEMPERATURE-PROGRAMMED DESORPTION

R. SPINICCI and A. TOFANARI

Istituto di Chimica Applicata dell'Università di Firenze — Via S. Marta, 3 50139 Firenze Italy

The interactions of propylene with zinc oxide have been studied by temperature-programmed desorption (TPD) under experimental conditions free of inter- or intraparticle limitations or readsorption phenomena.

The results indicate that propylene is adsorbed on two types of active sites, and the Arrhenius parameters for the corresponding desorption processes have been calculated; moreover, on the basis of these results, important hypotheses can be made regarding the reaction mechanisms of the total oxidation and the dehydroaromatization of propylene on zinc oxide.

The experiments confirm that thermal methods can be successfully used in the interesting and important field of heterogeneous catalysis.

It is now generally accepted that the selective oxidation of propylene to acrolein, or its oxidative dehydroaromatization to benzene over zinc oxide, proceed via the formation of a symmetric π-allylic intermediate [5].

The possibility of formation of these two different products, added to the possibility of total oxidation to carbon dioxide, indicates that more than one type of active site may exist on the catalyst surface, or alternatively that propylene can follow different reaction mechanisms on a certain type of active site.

However, it is difficult to obtain any meaningful information about active sites and about their relative contribution to the catalyst activity from steady state reaction kinetics, especially if the active sites are energetically heterogeneous and if the reaction rate is controlled by the desorption of the products.

A reasonable approach to the investigation of different types of active sites on a catalyst surface is the temperature-programmed desorption (TPD) technique, developed from both experimental and theoretical points of view by Cvetanovic and Amenomiya and improved by many other researchers [1—3].

The basic features of this thermal method are the desorption of the chemisorbed gas into a stream of carrier gas by heating the catalyst in a programmed manner, and the detection of the desorbed gas in the carrier followed by its analysis. The shapes of the peaks and their position on a temperature scale are related in a fundamental way to the desorption process and therefore provide information on the adsorption process, too.

Experimental

The catalyst was prepared by decomposing basic zinc carbonate (RP ACS, C. Erba) for 2 hr at 400° and by decomposing zinc hydroxide (previously prepared by precipitation of zinc nitrate in an ammonia solution) with the same procedure. The catalyst sample was pretreated in situ by heating at 550° for 5 hr in a stream of dried air.

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 tubular one and the temperature was controlled by a coaxial thermocouple whose tip was placed inside the catalyst: the temperature was linearly programmed by means of a Setaram PRT 540 C programmer slightly modified to give heating rates up to 25°/min.

The detector was a Dani hot wire detector provided with a HWD control. After the pretreatment procedure the catalyst was cooled down to the adsorption temperature (in the range 19 – 22°) and the propylene adsorption was followed catha-

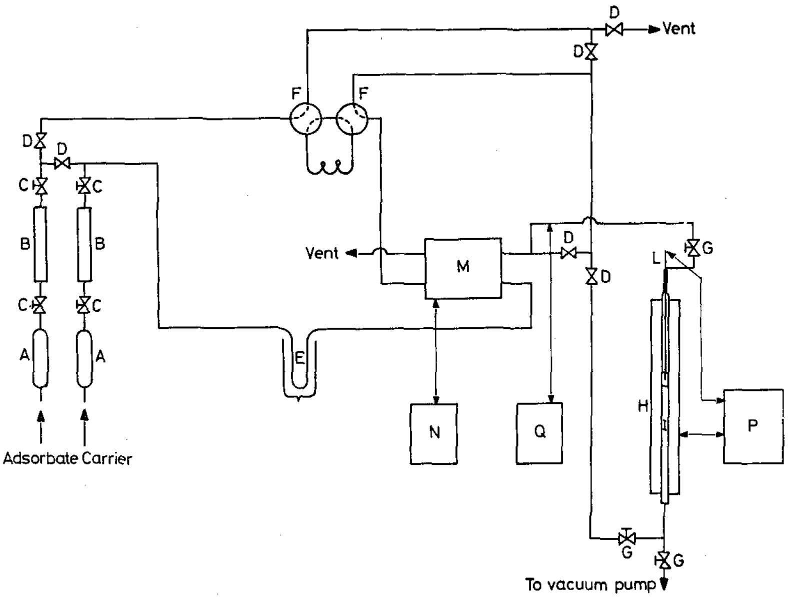

Fig. 1. Schematic diagram of TPD apparatus; A = filter, B = rotameter, C = mass flow controllers, D = on-off valve, E = trap, F = four-way valve, G = needle valve for vacuum, H = furnace, I = tubular stainless steel reactor, L = thermocouple, M = HWD detector, N = HWD control, P = temperature programmer, Q = temperature regulator for heating the line between the reactor and the detector

rometrically under either pulse or continuous flow conditions, in order to be able to study a wide variety of surface coverages.

After the adsorption was completed, the carrier gas was allowed to flow inside the catalyst bed at room temperature for detection of the amount of propylene which had been reversibly adsorbed: subsequently the temperature was increased linearly and many heating rates were used to deduce the values of the kinetic parameters.

The amount of catalyst was kept to a minimum (0.5 g), which yielded reliable desorption peaks, and at the same time the flow rate of the carrier gas during desorption was kept very high (100 cm^3/min): these two experimental procedures were used to avoid readsorption phenomena. On the other hand, the absence of mass transfer limitations was checked by varying the catalyst grain size.

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.

Moreover, the dead space between the reactor and the detector was taken into account to assign a correct value to the temperature of every peak maximum, and therefore to deduce correct kinetic data.

Results and discussion

The most significant features of a TPD spectrum of propylene with helium as carrier gas are shown in Fig. 2. It presents a low-temperature desorption peak due to a weakly-bound reversibly chemisorbed form of propylene, and a high-temperature desorption peak due to a strongly-bound form, which desorbs only with reaction and appears to be due to benzene.

Both peaks are symmetrical, which indicates that the sites involved are energetically homogeneous.

Initial tests were performed to determine the effect of the amount of adsorbed propylene, but no effect on the position of the peaks was observed: the desorption

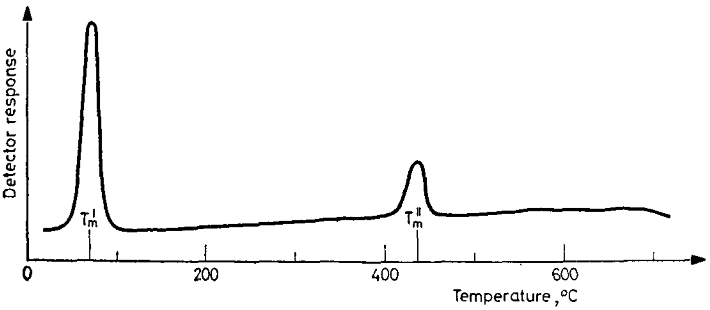

Fig. 2. Desorption spectrum of propylene with helium as carrier gas at a heating rate of 14.5 degree/min — propylene ($T_m' = 76.5°$; $T_m'' = 441°$)

processes therefore follow a first-order kinetics. The activation energies for the two processes were calculated using the following equation for a number of heating rates:

$$2 \ln T_m - \ln \beta = \frac{E_d}{R \cdot T_m} + \ln \frac{E_d}{R \cdot A}$$

where T_m is the temperature at the peak maximum, β is the heating rate in degrees per sec, E_d is the activation energy, R is the gas constant and A is the pre-exponential factor.

The values obtained were: for the first peak, $E_d = 68.9$ kJ/mole and $A = 4 \cdot 10^8$ sec^{-1}; for the second, $E_d = 175.9$ kJ/mole and $A = 2 \cdot 10^{11}$ sec^{-1}. These values were derived by plotting ($a \ln T_m - \ln \beta$) against $1/T_m$ and A calculating E_d from the slope and the intercept, respectively of the straight line.

In order to gain a deeper insigth into the nature of the desorption processes, runs were performed using oxygen as carrier gas: the corresponding TPD spectrum is shown in Fig. 3.

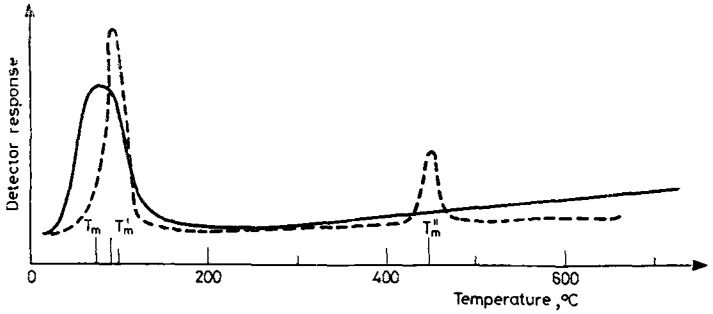

Fig. 3. Desorption spectrum of propylene with oxygen as carrier gas at a heating rate of 15.1 degree/min; — carbon dioxide ($T_m = 81°$); — — — beneze ($T'_m = 95°$; $T''_m = 449$)

It may be seen that the peak of the weakly-bound reversibly chemisorbed propylene is smaller than when helium is used as carrier; a new peak is formed at temperature intermediate between the temperatures of the two peaks formed with helium as carrier: this corresponds to the desorption of carbon dioxide.

This seems to indicate that a fraction of the weakly chemisorbed propylene desorbs with reaction as carbon dioxide by means of the intervention of the gas phase or adsorbed oxygen, while benzene must be produced via the intervention of lattice oxygen.

The TPD technique can be used to study the energetics of a surface reaction if the appearance of a product peak is controlled by the surface reaction and not by the product desorption: this prompted us to perform desorption runs on preadsorbed carbon dioxide and benzene, respectively, and to compare them with the propylene desorptogram obtained under the same conditions.

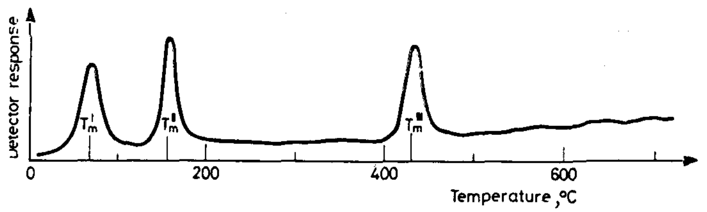

Fig. 4. Desorption spectra of preadsorbed benzene and carbon dioxide at a heating rate of 15.7 degree/min and respectively of 14.1 degree/min; ——— propylene ($T'_m = 74°$; $T''_m = 158°$; $T'''_m = 435°$)

The results, shown in Fig. 4, indicate that carbon dioxide desorption results only in a peak at low temperature, which therefore appears to be related to a reversibly chemisorbed form of carbon dioxide.

The desorption of benzene is characterized by two peaks, at lower and at higher temperatures: this second peak appears at the same temperature as the benzene produced from adsorbed propylene: this suggests that the appearance of benzene in the gas phase is controlled by the rate of desorption and therefore the activation energy found by means of propylene thermal desorption must be related to the desorption process.

The overall experimental results must be related to the studies on the catalytic activity of zinc oxide towards the oxidative dehydroaromatization of propylene [4] which are now in progress in the authors' laboratory in order to explain some of the observed and reported peculiarities of this heterogeneous catalytic reaction.

Above all, it is to be stated that the low activity of the catalyst is due (in addition to its relatively low surface area) to the fact that the majority of the propylene is adsorbed in a weakly and reversibly bound form, which desorbs at lower temperatures and therefore does not interact with the surface of zinc oxide at the temperatures of the dehydromatization runs (450–550°).

Moreover, it should be stressed that the TPD runs confirm that the total oxidation is favoured by a large amount of oxygen in the gas phase and requires oxygen-rich sites; in contrast the oxidative dehydroaromatization requires sites with low oxygen content, in order to exploit the electron excess (Zn^+, Zn^0) which favours dimerization and aromatization: however, this oxidative process requires the consumption of oxygen and therefore the activity would fall quickly without the presence of a relevant amount of oxygen in the reactant mixture. This explains the unavoidable presence of carbon dioxide as reaction product [4, 5].

References

1. R. J. Cvetanovic and Y. Amenomiya, Advan. Catal., 17 (1967) 103.
2. J. M. Criado, P. Malet and G. Munuera, Thermochim. Acta, 33 (1979) 345.
3. E. E. Ibok and D. F. Ollis, J. Catal., 66 (1980) 391.

4. R. Spinicci and A. Tofanari, submitted for publication to Applied Catalysis.
5. T. Seiyama, N. Yamazoe and M. Egashira, Proc. 5th Int. Congr. Catal. 1972, Florida, 1973, Vol. 2, p. 997.

Zusammenfassung — Die Wechselwirkungen von Propylen mit Zinkoxid wurden durch temperaturprogrammierte Desorption (TPD) unter Versuchsbedingungen frei von inter- oder intrapartikulären Begrenzungen oder Readsorptionserscheinungen untersucht.

Die Ergebnisse zeigen, daß Propylen an zwei Typen von aktiven Stellen adsorbiert wird. Die Arrhenius-Parameter für die entsprechenden Desorptionsprozesse wurden berechnet. Aufgrund dieser Ergebnisse können wichtige Hypothesen bezüglich des Reaktionsmechanismus der totalen Oxidation und der Dehydroaromatisierung von Propylen an Zinkoxid aufgestellt werden.

Die Versuche bestätigen, daß thermische Methoden auf dem interessanten und wichtigen Gebiet der heterogenen Katalyse mit Erfolg eingesetzt werden können.

Резюме — Взаимодействие пропилена с окисью цинка было изучено с помощью температурно-программированной десорбции в экспериментальных условиях, свободных от меж- и внутричастичных ограничений и явления реадсорбции.

Результаты показали, что пропилен адсорбируется на двух типах активных сторон. Вычислены аррениусовские параметры для соответствующих процессов десорбции. На основании полученных результатов, представлена гипотеза о механизме реакции окисления и дегидроароматизации пропилена на окиси цинка. Эксперименты подтвердили, что термические методы успешно могут быть использованы в интересной и важной области гетерогенного катализа.