Deuterium Isotope Exchange Reaction between Hydrogen and Water over Polyester-Supported Platinum Catalysts

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Deuterium transfer between hydrogen and water over polyester-supported platinum has been found to follow a two-step process, namely, an initial fast step followed by a slower one. The faster exchange step was more susceptible to water poisoning while the other step continued to be active for H/D exchange reaction during prolonged contact with liquid water. The results are in agreement with the existence of heterogeneous metal sites with varying degrees of catalytic activity and support the mechanism whereby the chemisorption of both the water and hydrogen molecules at metal sites leads to the deuterium exchange process. © 1990 Academic Press, Inc.

INTRODUCTION

The catalytic activity of Group VIII metals for isotopic exchange between hydrogen and water has been a subject of renewed interest in recent years (*1–13*), although much of the work has been concerned with the development of a suitable nonwetting (so-called hydrophobic) catalyst and is reported mostly as patent literature. Different views have been expressed on the mechanistic routes leading to deuterium exchange and on the role played by supports. Marginean and Olariu (*13*) have shown that the H–D exchange activity of nickel is strongly influenced by the nature of the oxide support, and the support surface was found to participate in the activation of the water molecules. Rolston and co-workers (*10, 11*) have also proposed that deuterium exchange takes place between chemisorbed hydrogen on a platinum surface and adsorbed water on the support surface. On the other hand, Temkin (*14*) considered the reaction as occurring in two steps, one step involving the oxidation of a vacant metal site followed by the reaction of chemisorbed oxygen with hydrogen.

In earlier work from this laboratory (*1, 2*), a comparative study was made of the deuterium exchange behaviour of platinum supported on activated charcoal, zeolites, and alumina. The effect on their exchange activity of coating these catalysts with a porous polytetrafluoroethylene (PTFE) film was also evaluated. The present paper deals with the deuterium exchange behaviour over platinum supported over polyester polymer in the form of chips and fibre. This support material was of particular interest since it has negligible water adsorptivity and practically no capability for activating the water molecule. Comparative evaluation of the HD/H$_2$O isotopic exchange parameters for platinum supported over the hydrophobic support and over a hydrophilic support also forms a part of this study. Pt on zeolite A was used as the hydrophilic catalyst.

EXPERIMENTAL

Catalysts

Pt/polyester catalysts were prepared by impregnating the fibrous or chip form of polyester support with an aqueous solution of chloroplatinic acid, drying in air at 373 K, and finally reducing in hydrogen at 425 K. A zeolite-5A-based Pt catalyst was similarly prepared, although the hydrogen re-

duction temperature in this case was 525 K. The details of the catalysts used are given in Table 1.

The polymer-based catalysts were studied by scanning electron microscopy for surface morphology. Figures 1a, 1b, and 2 show the secondary electron micrographs of the platinum-impregnated polyester fibre and polyester chip samples, respectively. These micrographs, which were obtained without giving any conductive coating to samples, show that the metal is distributed more uniformly over the fibre support than over the polyester chips. The same conclusions were also drawn from the macrooptical photographs of different samples.

Catalytic Reactor

Deuterium exchange rates were measured using two types of reactors, namely, (i) a closed reactor and (ii) a gas recirculation reactor.

Closed Reactor

The reactor design and the procedure are given elsewhere in detail (2). In this method, a known amount of catalyst sample was enclosed in a stainless-steel reactor of 135-ml capacity which had the facility for regular monitoring of pressure and temperature and for sampling ~0.3 ml of gas at desired intervals. After evacuation ($\sim 10^{-1}$ Torr) for 30 min, the reactor was filled with 11.15×10^{-3} mol of deuterated (250–400 ppm D) hydrogen. Water (150 ppm D) in equimolar ratio was then introduced into the reactor placed in a water bath at constant temperature. Hydrogen gas samples withdrawn periodically were cooled under liquid nitrogen for removal of any moisture and analysed for deuterium content using a double collector mass spectrometer. The gas analysis was continued until equilibrium was reached. To test for catalyst performance during prolonged contact with water, the experiment was repeated retaining the catalyst in the reactor, flowing hydrogen for few minutes, and then filling the reactor with a fresh batch of deuterated hydrogen. An equivalent amount of water was also introduced in the reactor. The catalyst sample was placed on a perforated PTFE platform about 2 cm above the reactor bottom to prevent submersion of the catalyst sample in water but at the same time keeping it wet. Specific rate constants were evaluated from semilog plots of $x_e/(x_e - x_t)$ versus time where x_e and x_t are the atom fractions of deuterium transferred at equilibrium and at any time t (2).

Gas Recirculation Reactor

A schematic diagram of the reaction system, which enabled a continuous catalyst exposure to hydrogen gas and water mist, as suggested by Asakura et al. (15), is shown in Fig. 3. It consisted of a glass column packed with the catalyst, con-

TABLE 1

Characteristics of the Catalysts Used

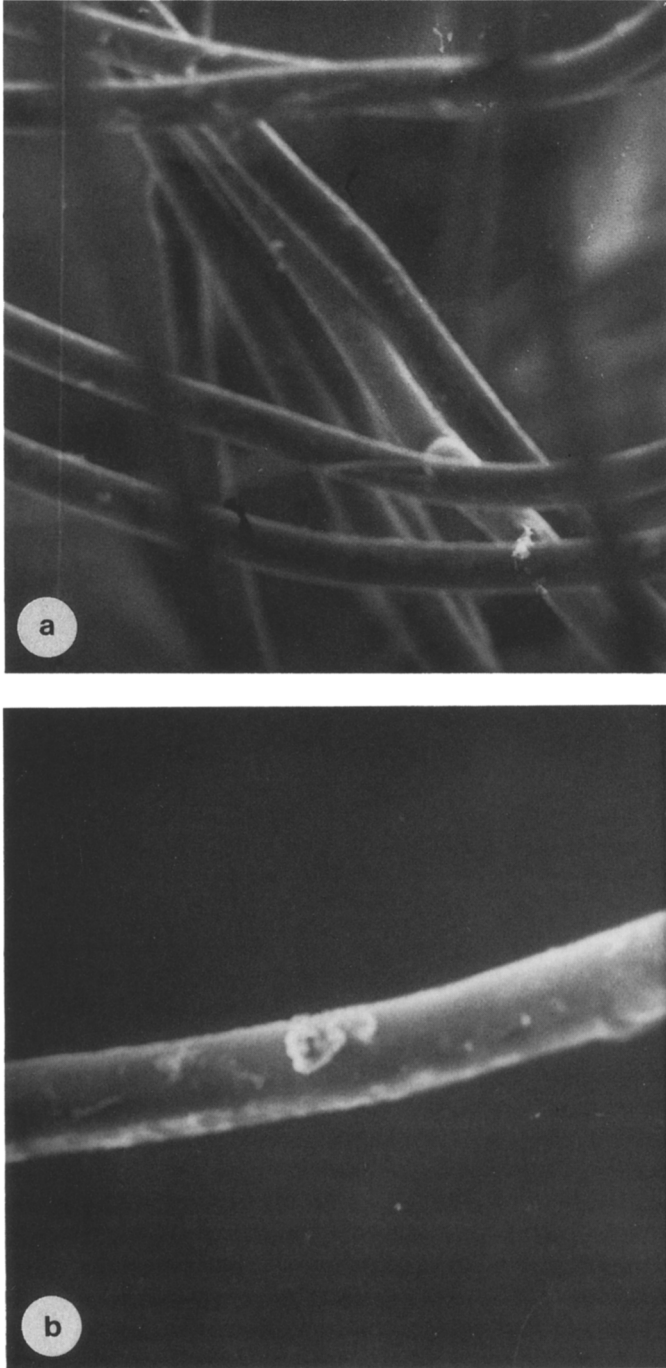| Support	Pt metal content (wt%)	BET surface area (m² g⁻¹)	H₂ chemisorption area (m² g⁻¹)	Nomenclature
1. Polyester chips (3 × 3 × 2 mm)	0.5	0.4[a]	0.17[a]	PPC
2. Polyester fibre (thickness ~15 μm)	0.7	4[a]	0.65[a]	PPF
3. Zeolite-5A (180–250 μm)	1.0	443	1.5[a]	PMS

[a] ±0.05.

FIG. 1. Secondary electron micrograph of Pt/polyester fibres. (a) Group of filaments, (b) single filament.
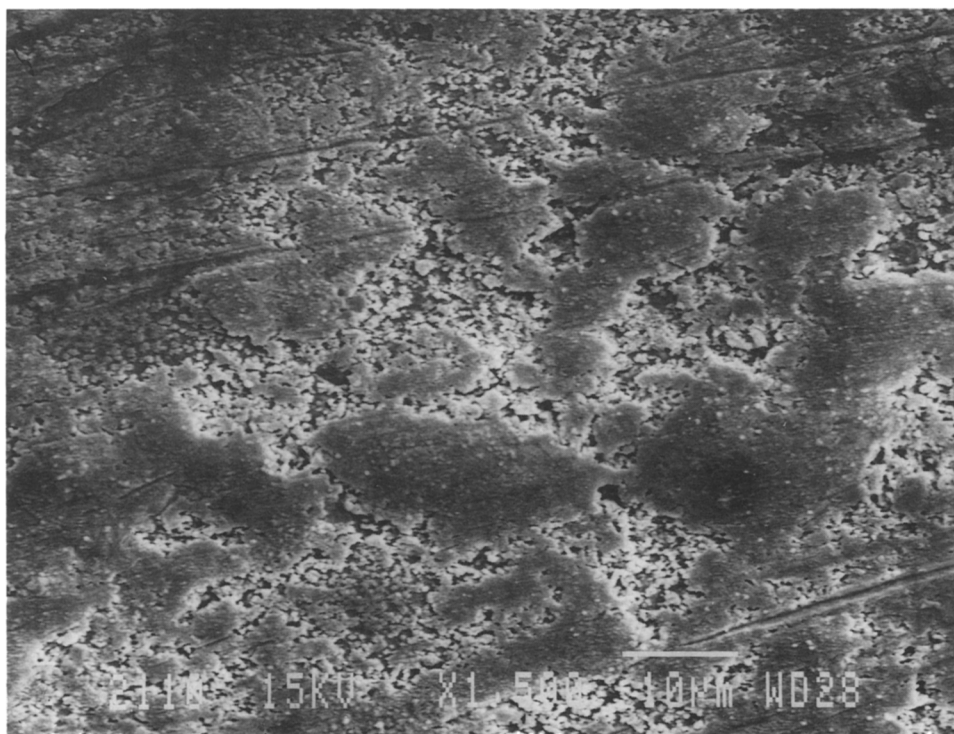
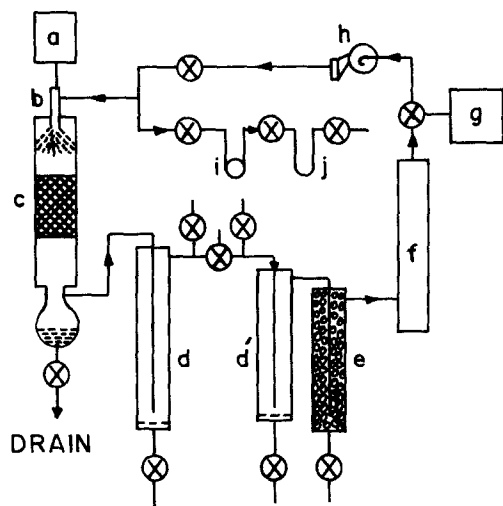FIG. 2. Secondary electron micrograph of a Pt/polyester chip.

FIG. 3. A gas recirculation catalytic reactor for evaluation of H–D exchange activity; (a) water tank, (b) atomiser, (c) catalyst column, (d) dehumidification column, (e) alumina trap, (f) H$_2$ reservoir, (g) H$_2$ generator, (h) metal diaphragm pump, (i) liquid nitrogen trap, (j) sample tube.

nected in series to dehumidifier columns, a compressor pump, and an atomiser. The total volume of the system was about 8 liters and it operated at near atmospheric pressure. The deuterated gas was circulated in a closed loop at the rate of about 4 liters min^{-1} using a metal diaphragm pump, and while flowing through the atomiser it was mixed with a fine spray of water before contacting the catalyst bed. The amount of water flowing over the catalyst bed in this manner was about 1 ml min^{-1}. In this form the catalytic reactor functioned as a constantly stirred static reactor where hydrogen gas could be replaced as and when desired while keeping the catalyst sample wet all the time and without exposing it to air in between. After completion of a day's experiment (~8 h), the catalyst was reused next day by replacing the H$_2$ gas and draining out the collected water. Since x_e changed in a particular experiment with

every cycle of H_2 flow through the catalyst column and also as the water amount was much in excess compared to the amount of H_2 gas, these results are expressed by plots of ln x_0/x' vs t where x_0/x' are the D atom fractions in the gas phase at time 0 and at any time t.

High-purity deuterated hydrogen gas was obtained by electrolysis of deuterated water using a Milton Roy hydrogen generator.

Thermal Analysis

The water sorption capacity of the catalysts and the heat of water desorption were evaluated using thermogravimetry (TG) and differential thermal analysis (DTA). About 100 mg of PPC or 50 mg of a PMS sample (Table 1) were heated at 385 K under vacuum for 16 h and exposed to water vapour over 2 M NaCl solution for 2–3 days before DTA and TG curves were recorded. The thermal analysis data were collected

under a helium carrier gas flow at 40 ml min^{-1} and with a heating rate of 10 K min^{-1} using a quadrupole mass spectrometer coupled thermobalance (Netzsch, Geratbau, West Germany).

RESULTS

Pt/Polyester Chips (PPC) Catalyst

Figure 4a shows the semilog plot of $x_e/(x_e - x_t)$ values versus reaction time when a fresh amount of 5 g PPC catalyst was equilibrated with hydrogen and water in the closed reactor. The data on this curve indicate that the deuterium transfer may be represented as a two-step process constituting two rate processes with specific rate constants k_1 and k_2 as 3.0 and 1.5 min^{-1} g^{-1} Pt. When the sample was reused next day without taking it out of the reactor and using the described procedure, the data shown in Fig. 4b were obtained. Curves c and d of
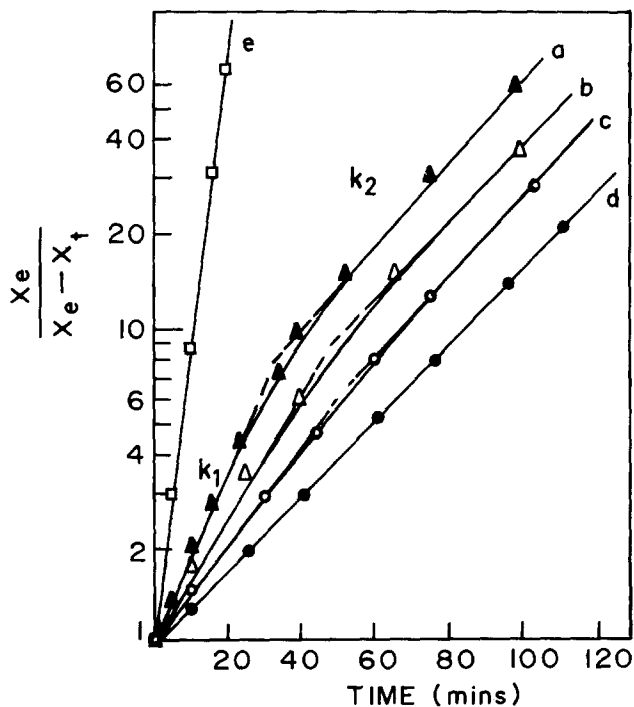

FIG. 4. Time-dependent deuterium transfer from hydrogen gas to water over Pt/polyester chips in a closed reactor system when the same 5-g catalyst was repeatedly used at 296 K without exposure to air or regeneration in between.

TABLE 2

Specific Rate Constants (Per Unit Metal Surface Area) for Deuterium Exchange Reaction over Pt (0.4%)
Polyester Chips and Pt (1%) Zeolite-5A Catalysts

Curve	Water exposure duration (days)	Pt/polyester chips[a]			Pt/zeolite-5A[b]		
		k_1	k_2	k_1/k_2	k_1	k_2	k_1/k_2
		(min^{-1} m^{-2} × 10^3)			(min^{-1} m^{-2} × 10^3)		
a	0	71.0	35.3	2	140.0	12.7	11
b	1	47.0	27.5	1.7	39.3	14.0	2.8
c	2	35.4	28.2	1.3	—	1.1	—
d	6	—	27.8	—	No activity	—	—

[a] Catalyst amount, 5 g; reaction temperature, 296 K; a_0, 330 ppm; x_0, 150 ppm; H$_2$, 0.012 mol; H$_2$O, 0.022 mol.
[b] Catalyst amount, 1 g; reaction temperature, 296 K; a_0, 300 ppm; x_0, 150 ppm; H$_2$, 0.011 mol; H$_2$O, 0.011 mol.

Fig. 4 show the data obtained on repeating the process on the third and fourth day, respectively. The data obtained on subsequent days followed curve d. The specific rate (k_1, k_2) values expressed in terms of per unit metal surface area for these data are given in Table 2.

After these experiments, when the catalyst was oven dried at 400 K and evacuated in the reaction cell prior to activity evaluation, the data shown by curve a were again observed.

In experiments carried out at temperatures greater then ~335 K, the data points could be fitted into a single straight line as shown by Fig. 4e for experiments performed at 348 K.

When the successive cycles of experiments were similarly carried out using 50 g of PPC catalyst in a gas recirculation reactor (Fig. 3), the data shown in Fig. 5 were obtained. Curve a in this figure shows the room temperature data obtained on the first experiment day while curve b represents the data of the second and consecutive test days. In all these experiments the procedure followed was similar to that mentioned above, i.e., before beginning each day's experiment, the depleted hydrogen and the water collected in the reactor column were drained out.

When the metal-free polyester chips were employed, no deuterium transfer between hydrogen and water was detectable under both sealed and gas-recirculation conditions.

Pt/Polyester Fibre (PPF) Catalyst

Similar catalyst behaviour was observed when the polymer fibre-based catalyst (PPF) was used. The data given in Fig. 6 show the day-to-day room temperature catalytic activity using 2 g of PPF in a recirculation reactor. In the case of the fibre-based sample, the ratio of the slopes of the fast and of the slow steps was comparatively less compared to those of the PPC sample (Fig. 5). Also the deactivation rate was slower in PPF than in PPC catalyst.

Pt/Zeolite 5A Catalyst

A two-step time-dependent deuterium exchange between HD and H$_2$O was also observed using the Pt/zeolite catalyst. Curve a of Fig. 7 shows the semilog plot of $x_e/(x_e - x_t)$ values versus reaction time when a fresh amount of 1 g PMS catalyst was equilibrated with hydrogen and water in the closed reactor. Curves b and c show the data when the sample was reused on the next 2 successive days. Corresponding rate constant values k_1 and k_2 are given in Table 2. It was observed that the zeolite-based catalyst lost its activity within 2 days (Fig. 7) while the polymer-based sample main-
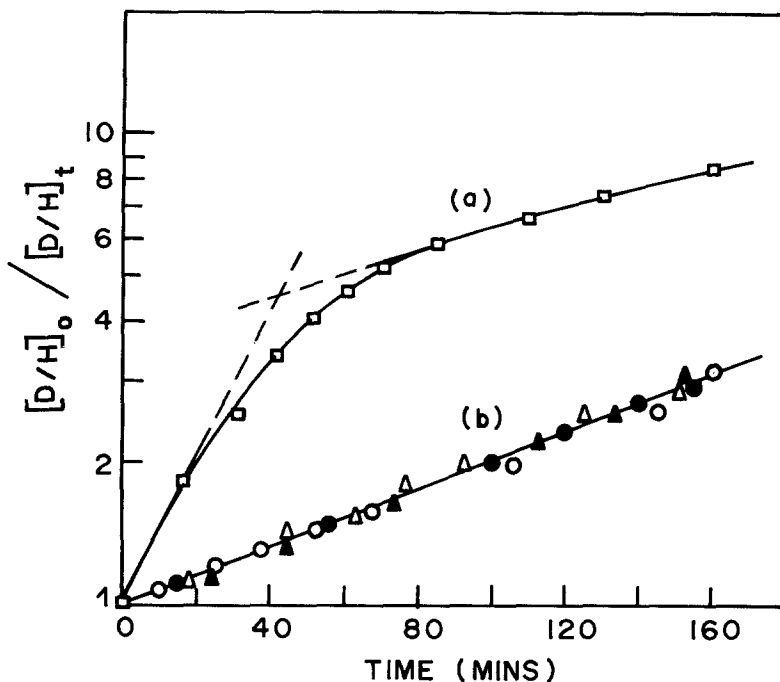
FIG. 5. Time-dependent deuterium transfer from hydrogen gas to water over 50-g Pt/polyester chips in a gas recirculation reactor measured consecutively over several days at 296 K while maintaining a wet catalyst at all times. (□) First day with fresh catalyst; (○) second day; (●) third day; (△) ninth day; (▲) sixteenth day.
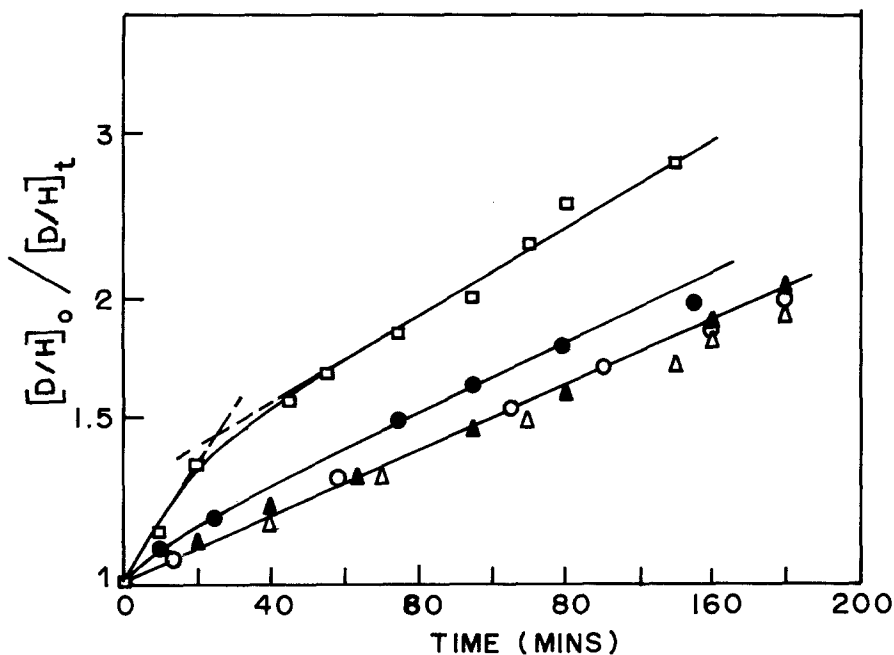

FIG. 6. Time-dependent deuterium transfer at 296 K from hydrogen gas to water over 2-g Pt/polyester fibre in a gas recirculation reactor. Activity was measured consecutively on several days without air exposure or activation of the catalyst in between. (□) First day with fresh catalyst; (●) third day; (○) sixth day; (△) eighth day; (▲) sixteenth day.
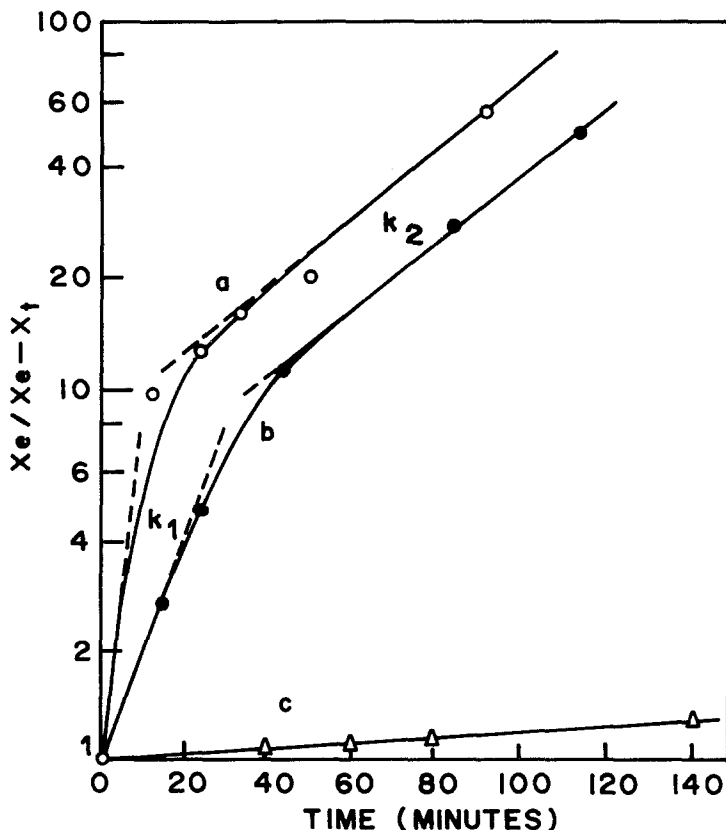
FIG. 7. Time-dependent deuterium transfer from hydrogen gas to water over 1 g of Pt/zeolite-5A catalyst in a closed reactor when the same catalyst was used at 296 K on (a) the first, (b) the second, and (c) the thrid successive day without exposure to air or regeneration in between.

tained its activity during prolonged contact with water although at a reduced level.

Thermal Analysis

Figure 8 shows the heating cycle DTA and TG curves for water desorption from PPC and PMS catalysts. The TG and DTA curves obtained from metal-free polyester chips were similar to those shown in Figs. 8a and 8b. A large baseline shift in DTA curve b of Fig. 8 is due to mismatch of the heat capacity of the sample and that of reference alumina and also due to loose sample packing. The total amount of water desorbed from the sample was evaluated to be about 0.4 wt% (curve a).

DISCUSSION

Several studies on metal-catalysed deuterium isotope exchange between hydrogen and water have been reported in the literature, and these are concerned mainly with the effect of the support (5, 13), with preadsorbed species (2, 6, 7), and with the effect of different reaction parameters (10, 11).

Studies of this laboratory using platinum supported on activated charcoal and γ-alumina (1, 2) have shown that the deuterium exchange follows a two-step process, the faster step being more susceptible to water poisoning (2) as is also revealed in the data of Fig. 7 for a Pt/zeolite catalyst. A similar two-step process is observed using a fresh polymer-supported catalyst (Figs. 4–6).
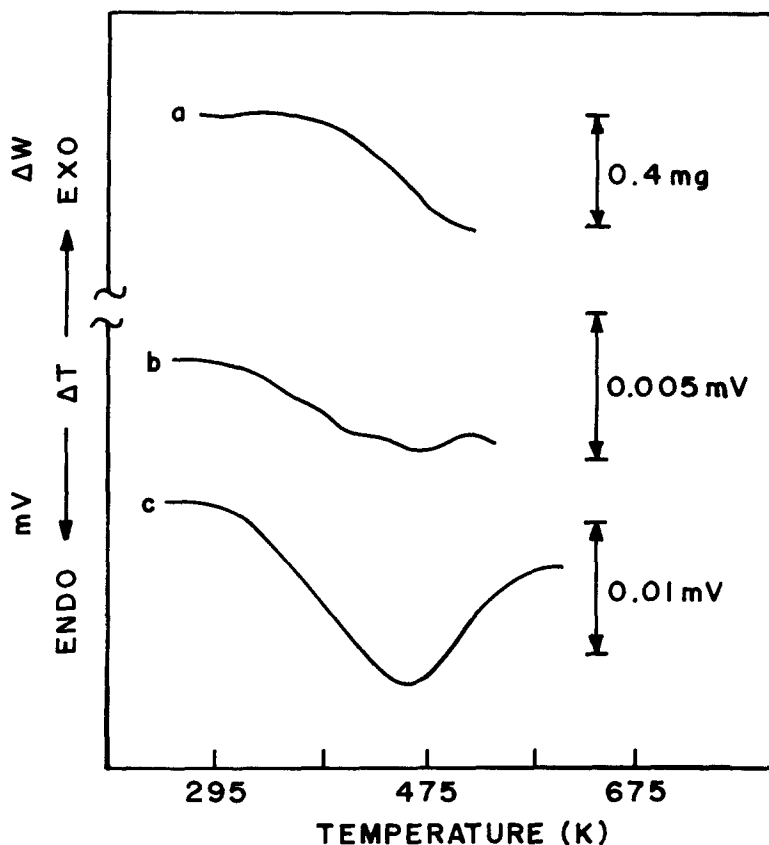
FIG. 8. TG (a) and DTA (b) curves for water desorption from 100-mg PPC catalyst exposed to 2 M NaCl aqueous solution. Curve c shows DTA curve for water desorption from 50-mg zeolite-based Pt catalyst.

The data in Figs. 4–7 and those in Table 2 show that although the specific activity of the zeolite-based catalyst is higher initially, the polymer-based catalysts maintain much higher activity under prolonged contact with water. However, the rate constant k_1 for the faster D-exchange step decreases, albeit slowly, even in the case of a polymer-based catalyst, and eventually the isotopic exchange appears to follow a single-step process (Figs. 4–6). The ratio k_1/k_2 in the case of PPC and PPF catalysts was found to be less than 2 (Table 2) while the value in the case of the zeolite-based catalyst was about 11 and lay in the range 8–30 for other large-area catalysts (2). The present data are in agreement with the proposed existence of energetically heterogeneous Pt sites (1, 2), the energy difference between different sites being less in the case of low-surface-area supports such as polyester. This is further supported by the fact that with a slight increase in reaction temperature, the two steps tend to merge with each other in the case of the polymer-based samples (Fig. 4e).

The data in Fig. 8 show that not only is a lesser amount of water adsorbed but also water is held less strongly over polyester-based catalysts than it is over the zeolite-supported sample. Studies in Ref. (2) have confirmed that the samples which show strong catalyst–water interaction are more prone to poisoning. It may thus be surmised that in the case of polymer-based catalysts only a fraction of Pt sites having higher af-

finity for H$_2$O chemisorption and hence higher catalytic activity is rendered ineffective due to water poisoning, thus accounting for a partial deactivation of catalyst activity as observed in this study (Figs. 4–6). Heterogeneity of sites has been found to be responsible for the varying degrees of catalytic activity shown by transition metals for reactions such as H$_2$–D$_2$ exchange (16).

Polyester, being an almost nonpolar material, would be incapable of activating water molecules at its surface. Thermal analysis (Fig. 8) confirmed that our samples have negligible affinity for water adsorption. It is therefore apparent that the activation of water molecules by the support, as proposed by Marginean and Olariu (12), is less likely to play an important role. The exchange of chemisorbed hydrogen with water vapour following an Eley–Rideal mechanism is also less likely to be responsible for catalytic activity under present experimental conditions where the catalyst surface is completely covered with a liquid water film. The results obtained in this study thus appear to support the view that the chemisorption of both the hydrogen and water at adjacent metal sites leads to the isotopic exchange process.

REFERENCES

1. Belapurkar, A. D., Gupta, N. M., and Iyer, R. M., *Appl. Catal.* **43**, 1 (1988).

2. Gupta, N. M., Belapurkar, A. D., Rama Rao, K. V. S., and Iyer, R. M., *Appl. Catal.* **43**, 15 (1988).

3. Rae, H. K., *Amer. Chem. Soc. Symp. Ser.* 68 (1978), p. 1.

4. Sagert, N. H., and Pouteau, R. M. L., *Canad. J. Chem.* **52**, 2960 (1974).

5. Sagert, N. H., and Pouteau, R. M. L., *Cand. J. Chem.* **51**, 4031 (1973).

6. Iida, I., and Tamaru, K., *J. Catal.* **56**, 229 (1979).

7. Iida, I., and Tamaru, K., *Z. Phys. Chem. N.F.* **107**, 231 (1977).

8. Iida, I., Kato, J., and Tamaru, K., *Z. Phys. Chem. N.F.* **107**, 219 (1977).

9. Iida, I., Kato, J., and Tamaru, K., *Bull. Chem. Soc. Japan* **49**, 3433 (1976).

10. Rolston, J. H., and Goodale, J. W., *Canad. J. Chem.* **50**, 1900 (1972).

11. Rolston, J. H., den Hartog, J., and Butler, J. P., *J. Phys. Chem.* **80**, 1064 (1976).

12. Marginean, P., and Olariu, A., *J. Catal.* **8**, 359 (1967).

13. Marginean, P., and Olariu, A., *J. Catal.* **95**, 1 (1985).

14. Temkin, M. I., *Dokl. Akad. Nauk. SSSR* **161**, 160 (1965).

15. Asakura, Y., Isuchiya, H., Yusa, H., and Matsuda, S., *Nucl. Sci. Eng.* **79**, 49 (1981).

16. Bernasek, S. L., and Somorjai, G. A., *J. Chem. Phys.* **62**, 3149 (1975).