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Thermodesorption Analysis of Water Produced in H_2/O_2 Titrations on Pt and Rh Catalysts

Water produced in H_2/O_2 titrations performed upon metal catalysts supported on oxides such as alumina or silica is believed to remain adsorbed on the support: metal dispersions deduced from volumetric and gravimetric techniques are generally in good agreement (*1–3*). This article deals with a TPD analysis of these small quantities of water produced in H_2/O_2 titrations and adsorbed on the catalyst. The principle of the method is based on the reduction, by iron, of water desorbed from the catalyst during thermodesorption. Water is then analyzed as hydrogen in a catharometer with high sensitivity.

The apparatus is a gas chromatographic system used for the characterization of metal catalysts (*4, 5*). A 5 Å molecular sieve column (o.d. ⅛-in.; 1.5 m) is inserted between the reactor (Pyrex glass and i.d. 4 mm) and the TC detector to trap water when the device is used for performing a conventional thermodesorption (the relative molar response of water in argon is about eight times smaller than that of the hydrogen).

Catalysts are prepared by exchange from aqueous solutions of chloroplatinic acid and rhodium chloride hydrate. Rhone Poulenc GFS 400 γ-alumina is used as a support (210 m^2g^{-1}, mean micropore radius 5 nm, total impurities <500 ppm, iron <100 ppm, grain size 1.2 mm). Iron powder (99.9% Fe, grain size 50 μm), used for dissociating water into hydrogen, is located in the heated zone behind the catalyst. Separate runs are performed using a simple stainless-steel tube reactor as reducing system.

The standard procedure is the following. The sample (0.1 to 1 g is reduced under H_2 flow at 773 K for 15 h, flushed by a stream of ultrapure argon (total impurities <1 ppm) for 3 h and cooled to ambient temperature (Pt catalysts) or to 333 K (Rh catalysts). Hydrogen chemisorption (H_C) or a cycle H_C, O_T (oxygen titration) and H_T (hydrogen titration) is then performed; hydrogen is subsequently thermodesorbed at 20 K min^{-1} up to 773 K. The sample is then cooled to ambient temperature; iron powder (0.2 to 0.6 g) is inserted in the stream of the carrier gas below the catalyst sample and the same cycle of operations (reduction, flushing, chemisorption, titrations, and thermodesorption) is carried out again. A third series of experiments is performed using a stainless-steel reactor.

EFFECT OF TRAPPING OF WATER ON THE THERMODESORPTION PROFILES

The influence of the molecular sieve column used for trapping water in the thermodesorbed products is shown in Fig. 1. It is clear from the flat profile in the region 500–773 K that the trapping of water is satisfactory.

The first peak (T_M ~ 410 K) can be ascribed to hydrogen chemisorbed on the metal. The second peak appearing in profile b (T_M ~ 650 K) may be assigned to water produced in the titrations and desorbing from the support: this peak is eliminated by inserting the molecular sieve column between the catalyst cell and the detector (profile c).

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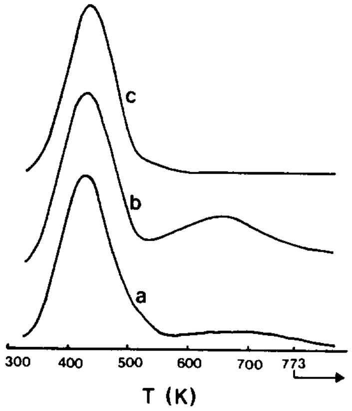

FIG. 1. Influence of the trapping of water on the thermodesorption profiles for H_2 from a 0.6% Rh/γ-Al_2O_3 catalyst: (a) direct thermodesorption after hydrogen chemisorption; (b) following a cycle H_C, O_T, H_T; (c) thermodesorption with trapping of water, following a cycle H_C, O_T, H_T.

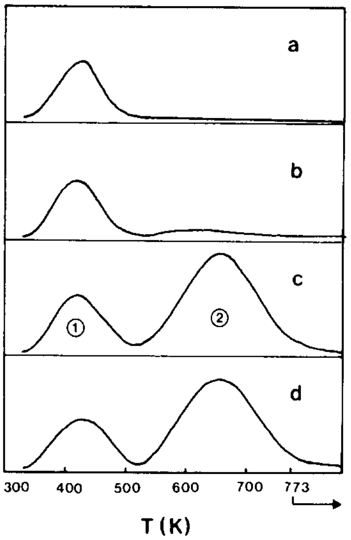

FIG. 2. Effect of a reducing system (iron or stainless steel) on the thermodesorption profiles for H_2 from 0.6% Rh/γ-Al_2O_3: (a) 0.5 g catalyst, following a cycle H_C, O_T, H_T; (b) 0.5 g catalyst + 0.5 g Fe, following H_C; (c) 0.5 g catalyst + 0.5 g Fe, following a cycle H_C, O_T, H_T; (d) 0.5 g catalyst, following a cycle H_C, O_T, H_T in a stainless-steel reactor.

EFFECT OF THE REDUCING SYSTEM (IRON POWDER) ON THE THERMODESORPTION PROFILE

In the following, the molecular sieve column is permanently inserted in the carrier gas stream. Typical thermodesorption profiles for H_2 from 0.6% Rh/γ-Al_2O_3 are shown in Fig. 2. The same sequence of experiments has been performed on 1.12% Pt/γ-Al_2O_3 and has led to very similar results. When the desorption is performed in the glass reactor without the reducing system, the profile of H_2 comprises one single peak at about 390–410 K (Fig. 2a). On the other hand, in the presence of the reducing system (Fe powder) added to the catalysts, another important peak appears on the thermodesorption spectrum (Fig. 2c, Peak 2) when, and only when, a complete cycle H_C, O_T, H_T has been performed before desorption. A quite similar peak is obtained when the chemisorption, titrations and desorption cycle is carried out in a stainless steel reactor (Fig. 2d). The presence of Peak 2 in the TPD profile is clearly related to the formation of water on the catalyst by titration before thermodesorption (Fig. 3). Under our experimental conditions, the stoichiometries $H_C/O_T/H_T$ have been found to be close to 1/2/4 for Rh catalysts (*4*, *6*) and to 1/1.5/3 for Pt catalysts (*3*, *4*, *7*, *8*). In that case, the theoretical production of water

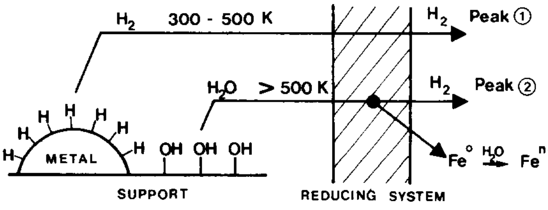

FIG. 3. Scheme of the thermodesorption analysis of H_2 and H_2O from a supported-noble metal (Rh or Pt) catalyst.

TABLE 1

Chemisorption (H_C), Titrations (O_T and H_T) and Thermodesorption (H_2 peaks) on Rh and Pt Catalysts (μmol H_2, O_2, or H_2O per g of catalyst)

Catalyst	H_C	O_T	H_T	H_2O formed	Thermodesorption		
					Peak 1	Peak 2	(Peak 2)/(Peak 1)
0.18% Rh	9.0	17.5	34.0	34	8.6	33	3.93
0.58% Rh	25	51	98	99	24	93	3.88
0.60% Rh	27	56	109	110	26	100	3.85
4.82% Rh	104	211	412	414	98	377	3.85
10.3% Rh	328	620	1252	1249	335	1195	3.57
0.58% Pt	12	16.5	35	34	11.5	34	2.96
1.12% Pt	22	30	61	60	20.5	60	2.93
4.36% Pt	95	122	259	254	90	246	2.74

during the titrations would be $O_T/2 + 3\ H_T/4$ for Rh catalysts and $2(O_T + H_T)/3$ for Pt catalysts. Results concerning adsorption and titrations data for the two series of Rh and Pt catalysts are reported in Table 1. Also reported in this table are the quantitative results concerning the thermodesorption profiles for H_2, using the above method of analysis.

It is clear that the amount of H_2 desorbed beyond 500 K is close to the theoretical value of H_2O formed during the titrations. Another important point is provided by the ratio of Peak 2 to Peak 1 which should be equal to 4 and 3 for Rh and Pt catalysts, respectively. The experimental results are in good agreement with these values except for the highly loaded catalysts. Nevertheless, it must be pointed out that, for these catalysts, Peaks 1 and 2 are not so well-separated as for the 0.6% Rh sample (Fig. 4).

The iron powder used in this study possesses a geometrical surface area of about 150 $cm^2\ g^{-1}$ corresponding to about 0.4 μmol of surface Fe atoms per g. The capacity of the powder to reduce water has separately been measured by injecting series of pulses of water (27 μmol H_2O per pulse) on 0.2 g of powder at different temperatures. Beyond a certain degree of oxidation, the Fe powder sample can no longer reduce water and the production of H_2 falls to zero. At 723 K, the oxidation capacity of the iron powder is about 1000 μmol $H_2O\ g^{-1}$. At 523 K, the oxidation capacity is still higher than 200 μmol g^{-1}. It is thus clear that, under our usual conditions, the thermodesorption analysis of water is not limited by the oxidation capacity of the redox material. Another relevant result of this study is provided by Fig. 2d which shows that a stainless-steel tube heated above 500 K may dissociate water and provoke a strong alteration of the H_2 thermodesorption profiles from metal catalysts.

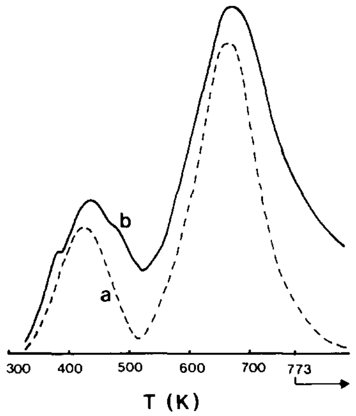

FIG. 4. Thermodesorption of H_2, following a cycle H_C, O_T, H_T: (a) 0.5 g 0.6% Rh/Al_2O_3 + 0.5 g Fe; (b) 0.1 g 10.3% Rh/Al_2O_3 + 1.0 g Fe.

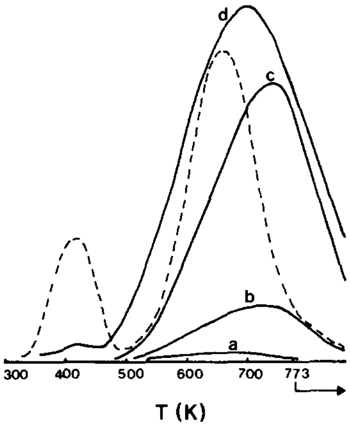

FIG. 5. Thermodesorption of water from γ-Al_2O_3: (a) 0.5 g Al_2O_3, injection 10 μmol H_2O; (b,c,d) 0.5 g Al_2O_3 + 0.5 g Fe; (b) injection 10 μmol H_2O; (c) injection 50 μmol H_2O; (d) injection 100 μmol H_2O. Dashed line is the TPD profile for H_2 from the 0.6% Rh catalyst following a cycle H_C, O_T, H_T.

ANALYSIS OF WATER CHEMISORBED ON BARE ALUMINA

The fact that chemisorbed water desorbs from alumina at a temperature higher than 500 K was a key to a good separation of the chemisorbed hydrogen and the hydrogen resulting from the decomposition of water. Blank experiments have been performed to characterize the peak of water thermodesorbed from bare alumina. The support is pretreated as the metal catalyst (H_2, 773 K, 15 h) and known amounts of water are introduced in the stream of carrier gas ahead of the alumina. Water is subsequently thermodesorbed and analyzed in the H_2 form using the standard reducing system (iron powder). Results are shown in Fig. 5. In this, the TPD profile from 0.6% Rh/γ-Al_2O_3 after a cycle $H_C/O_T/H_T$ (dashed line) is also represented. It is clear that the thermodesorption of water from alumina corresponds to the high-temperature peak in the TPD profile from the metal catalyst. Nevertheless, a slight increase of the temperature of the maximum, about 30 to 40 K, is observed on bare alumina (compare the thermogram given by the dashed line with the thermogram c which corresponds to the same amount of chemisorbed water). It may be considered that the presence of metal on the support slightly increases the rate of desorption of water from the catalyst.

EFFECT OF WATER ON THE THERMODESORPTION PROFILES FOR H_2 FROM METAL CATALYSTS

Water formed in H_2/O_2 titrations desorbs above 500 K and the corresponding peak is clearly observable on the H_2 thermodesorption spectrum (Fig. 1b). The presence of a reducing system (Fe) strongly enhances this high-temperature peak (Fig. 2c) because water is dissociated into H_2 which is detected with a much higher sensitivity. Recently Jóźwiak and Paryjczak (*9*) have reported a thermodesorption study of H_2 from Rh/γ-Al_2O_3. The TPD spectra comprise two major peaks (at 400 and 870 K) and a minor peak at 620 K. The peak at 870 K is strongly altered by repeated cycles of H_2/O_2 titrations before desorption. We did not observe this peak at 870 K which desorbs at a too high temperature. On the other hand, the peak at 620 K is likely to correspond with our high-temperature peak desorbing in the region 500–773 K. Thermodesorption of H_2 from Pt catalysts has been extensively studied. As a rule, a single peak at about 380–420 K is observed when, and only when, chemisorption is performed at room temperature (*10, 11*). On the other hand, when chemisorption is performed at high temperature (e.g., sample reduced at 650–800 K and cooled under H_2 flow) a second diffuse peak is observed above 550 K which is generally ascribed to H_2 chemisorbed on the support by spillover (*11, 12*). The present study refers to the first case (chemisorption at room temperature) and a spectrum with a single peak at 410 K is always obtained following hydrogen chemisorption. Water formed *in situ* by H_2/O_2 titrations generates a second peak above 500 K which may be suppressed by trapping water before detection or, on the contrary, which may be enhanced in the presence of a reducing compound such as Fe or stainless steel, by dissociation of water into hydrogen. In the last case, the amounts of hydrogen desorbing at low and high temperature are found to be well correlated with the stoichiometries $H_C/O_T/H_T$, which supports our interpretation.

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