

Hydrogen Temperature-Programmed Desorption (H_2 TPD) of Supported Platinum Catalysts

J. T. MILLER*¹ B. L. MEYERS,* F. S. MODICA,* G. S. LANE,* M. VAARKAMP,†
AND D. C. KONINGSBERGER‡

*AMOCO Research Center, P.O. Box 3011, Naperville, Illinois 60566-7011; †Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands; and ‡Debye Institute, Utrecht University, P.O. Box 80083, 3508 TB Utrecht, The Netherlands

Received March 3, 1993; revised May 28, 1993

Hydrogen temperature-programmed desorption (TPD) of supported platinum catalysts, Pt/K-LTL, Pt/H-LTL, Pt/K-MAZ, Pt/H-MAZ, Pt/ γ - Al_2O_3 , and Pt/SiO₂, was performed after hydrogen reduction at 300, 450, or 650°C. For all catalysts, reversible desorption of chemisorbed hydrogen occurred at approximately 175°C. In addition to chemisorbed H_2 , at least three peaks corresponding to higher temperature, irreversibly desorbed H_2 were observed and assigned to spillover hydrogen. The quantity of spillover hydrogen is related to the number of support hydroxyl groups and the maximum reduction temperature of the catalyst. It is suggested that the irreversibility of the spillover hydrogen results from dehydroxylation of the support at high temperature. The structure of Pt/K-LTL and Pt/H-LTL catalysts has been examined by EXAFS following reduction at 300, 450, and 600°C. After low-temperature reduction, it is proposed that a layer of spillover hydrogen is present between the platinum particle and the support. The distance between the platinum and the support (oxide) surface is ca. 2.6–2.7 Å. During high-temperature reduction, or during TPD, the interfacial hydrogen is irreversibly lost, and the platinum–oxygen distance decreases to 2.2 Å. The catalysts' turnover frequency (TOF) for propane hydrogenolysis was dependent on both the reduction temperature and the type of support. Platinum on acidic supports and reduced at the lowest temperature displayed the highest TOF. Qualitatively, the catalysts' hydrogenolysis activity increased with increasing amounts of spillover hydrogen. © 1993 Academic Press, Inc.

INTRODUCTION

The effect of reduction temperature on catalytic behavior has been the subject of numerous investigations. Many studies have shown both reduced catalytic activity (1–5) and reduced hydrogen chemisorption capacity (1, 7–10) after reduction in hydrogen at high temperatures (>500°C), however, a clear understanding of the phenomena involved is still lacking. Reduction at high temperatures may result in strongly chemisorbed hydrogen (2), may cause loss of spillover hydrogen altering the local charge transfer from the support to the metal at the particle boundary (4), may induce changes in morphology of the metal crys-

tallite (6), or may affect reduction of the support resulting in the formation of an alloy with atoms from the support, for example, Al or Ti (1, 7, 8).

Temperature-programmed desorption of hydrogen from supported and unsupported platinum, typically, shows multiple peaks above 100°C (2, 3, 8–11): one at low temperature (ca. 150°C) which is assigned to chemisorbed hydrogen on the metal surface (11), and one or more higher temperature peaks (ca. 300–500°C). These high-temperature peaks have been assigned by various authors to spillover hydrogen (4, 9, 13), to strongly chemisorbed hydrogen (2, 3, 12), to hydrogen in subsurface layers of the platinum (10), or to oxidation of the reduced metal by support protons (14, 15).

In this study, we compared the H_2 TPD

¹ To whom correspondence should be addressed.

spectra of platinum catalysts on acidic and nonacidic supports. The low-temperature desorption peak was assigned to reversibly chemisorbed hydrogen, and at least three high-temperature irreversibly desorbed hydrogen peaks were detected. Based on the EXAFS structural characterization of the Pt/K-LTL and Pt/H-LTL catalysts reduced at 300, 450, and 600°C, an assignment of the high-temperature hydrogen desorption peaks is proposed. Propane hydrogenolysis TOFs of the catalysts indicate that the specific activity is affected by both the support acidity and the reduction temperature.

EXPERIMENTAL

Catalyst preparation. Preparation of the zeolite catalysts is described elsewhere (16, 17). Briefly, the K-LTL was a commercial zeolite obtained from Union Carbide (now UOP). Excess alkali was reduced by water wash until the pH of the wash solution was 9.5 to give a K/Al molar ratio of 1.05 (elemental analysis: 11.8 wt% K and 7.7 wt% Al). An Na-omega (MAZ) was synthesized following reported methods (18) and calcined at 540°C for 16 hr prior to potassium exchange. The K-exchanged zeolite was given a final wash with dilute KOH at a pH of 9.5. The K-MAZ had a K/Al molar ratio of 1.08 (elemental analysis: 11.0 wt% K and 7.0 wt% Al).

An H-LTL was prepared by ammonium-exchange of K-LTL and subsequent calcination at 500°C. The K/Al molar ratio was 0.34. The H-MAZ was prepared by ammonium-exchange of Na-MAZ (with template). Following calcination, the H-MAZ contained 8.6 wt% Al and 106 ppm Na.

The SiO₂ was a commercial support (obtained from PQ Corporation) with a surface area of 215 m²/g and a pore volume of 1.0 cm³/g. A K-SiO₂ was prepared by washing the silica with dilute KOH until the pH remained 9.5. The K-SiO₂ contained 0.38 wt% K.

To each zeolite (or silica), platinum was impregnated using an aqueous solution of tetraammineplatinum (II) nitrate. Typically,

the platinum loading was 1.5 to 2.0 wt% for catalysts analyzed by TPD, while the loading was 1.2 wt% for the catalysts analyzed by EXAFS. The platinum/zeolite catalysts were dried at 120°C. The silica catalysts were calcined at 260°C.

A 1.0 wt% Pt/ γ -Al₂O₃ catalyst was prepared by impregnation of γ -alumina (Ketjen K300, 200 m²/g and 0.6 cm³/g) with an aqueous solution of H₂PtCl₆. The catalyst was dried by 120°C.

H₂ temperature-programmed desorption (TPD). H₂ TPD was performed on catalysts after an initial 300, 500, or 650°C reduction in H₂. Desorptions were programmed at 10°C per min to 700°C in flowing N₂. The H₂ and N₂ were purified by passing over oxygen and hydrocarbon traps. Cryogenic traps containing 5A molecular sieve were placed directly before and after, the furnace for water trapping. Desorbed gases were monitored by a thermal conductivity detector and periodically checked by independent gas chromatographic or mass spectroscopic analyses for H₂.

Following the first TPD, the catalyst was rereduced in H₂ for 1 hr at 700°C (or cooled to 300°C and rereduced at 300°C) and cooled to room temperature in H₂. A second H₂ TPD to 700°C was obtained as described above.

For H-LTL, after an initial TPD to 700°C the catalyst was cooled to room temperature in N₂. H₂ was then pulsed (0.066 cm³ H₂/pulse) over the catalyst at 40°C until no further H₂ was consumed. The carrier gas was switched to 20% H₂ (in N₂) and a temperature programmed reduction to 700°C obtained.

Propane hydrogenolysis. The conversion of propane was conducted at 400°C and atmospheric pressure in a fixed-bed, bench-scale reactor using 3.78 vol% propane in H₂. The reaction temperature of 400°C was the lowest temperature at which all catalysts gave measurable propane conversion. The catalyst (0.01 to 0.2 g) was diluted with 2 g of α -alumina and prereduced at 450 or 600°C. The conversion was adjusted be-

tween 2 and 10% by changing the propane feed rate. The turnover frequencies (TOF) were determined on the basis of volumetric hydrogen chemisorption.

EXAFS. The EXAFS data were collected at the Synchrotron Radiation Source in Daresbury, U.K., Wiggler Station 9.2 using an Si (220) double crystal monochromator which was detuned to 50% intensity to minimize the higher harmonics present in the X-ray beam. The storage ring was operated with an electron energy of 2 GeV and a current between 120 and 250 mA. The estimated resolution at the Pt L_{III} edge (11,564 eV) is 3 eV. Self-supporting wafers (calculated to have an absorbance of 2.5) were reduced at 300, 450 (500), or 600°C in a controlled-atmosphere cell (19). Samples were cooled with liquid nitrogen to -130°C, and the data were collected in the presence of H₂. Measurements were made in transmission mode, and in order to reduce the noise, six scans were averaged. Standard procedures were used to extract the EXAFS data from the measured absorption spectra (20). The spectra were fitted with phase and amplitude functions extracted from the spectra of reference compounds (21).

RESULTS

Hydrogen temperature-programmed desorption (H₂ TPD). H₂ TPD profiles were obtained for six platinum catalysts, 2.0% Pt/K-LTL, 1.5% Pt/H-LTL, 2.0% Pt/K-MAZ, 1.5% Pt/H-MAZ, 1.0% Pt/ γ -Al₂O₃, and 3.3% Pt/SiO₂. The characteristic features of the hydrogen desorptions were determined, primarily, by the support acidity and reduction temperature; therefore, a detailed discussion of the TPD profiles are presented only for the Pt/K-LTL and Pt/H-LTL catalysts. H₂ TPD of the supports (no added platinum) gave no hydrogen desorptions.

A representative H₂ TPD profile for platinum supported on a non-acidic support is shown in Fig. 1a for 2.0% Pt/K-LTL reduced at 300°C. Broad, overlapping peaks are observed for H₂ desorptions at about

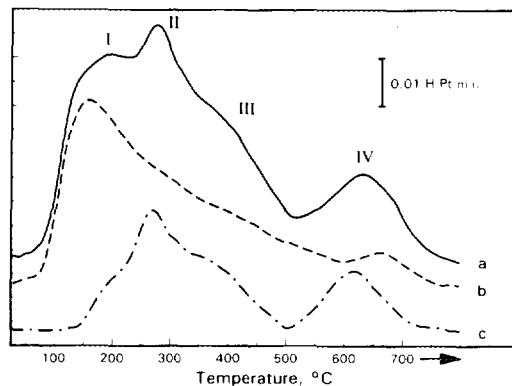


FIG. 1. 2.0% Pt/K-LTL reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 1.8; (b) following the first TPD, the catalyst was rereduced at 700°C, cooled in H₂, and second TPD to 700°C, H/Pt = 1.2; and (c) difference profile: (a) minus (b), H/Pt = 0.6.

150 (peak I) and 275°C (peak II) with some H₂ desorbing up to 400°C (peak III). In addition, there is a distinct desorption at 610°C (peak IV). The total H₂ desorption was 1.8 hydrogen atoms/platinum atom, H/Pt. Immediately after the first TPD, the catalyst was reexposed to H₂ at 700°C for 1 hr and cooled in flowing H₂ and a second TPD obtained. The second TPD, Fig. 1b, revealed only peak I with minor amounts of hydrogen desorbing at higher temperature. The total hydrogen desorption in the second TPD amounted to 1.2 H/Pt. Thus, only peak I is a reversible H₂ desorption, while, the higher temperature peaks (II-IV) correspond to H₂ irreversibly desorbed. The area of peak I (1.0 H/Pt) is in reasonable agreement with the amount of chemisorbed hydrogen determined volumetrically (0.97 H/Pt). Subtracting Fig. 1b from Fig. 1a yields Fig. 1c, which represents the irreversible hydrogen desorptions. Figure 1c clearly shows the presence of peaks II and III in the 200-500°C region, in addition to peak IV at 610°C. The measured N₂ micropore volume and surface area of the K-LTL zeolite was unchanged after the TPD experiment, indicating that there was no change in the crystallinity of the zeolite. Volumetric H₂ chemisorption declined only slightly, from 0.97 H/Pt in the

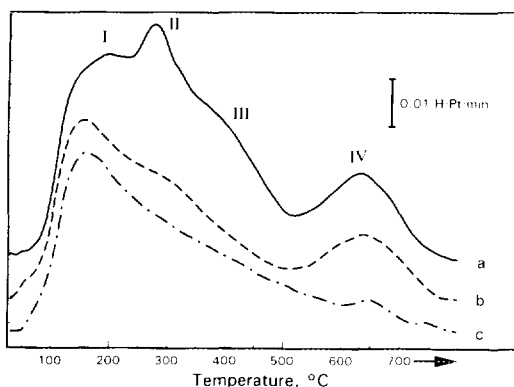


FIG. 2. 2.0% Pt/K-LTL reduced at (a) 300°C, H/Pt = 1.8; (b) 500°C, H/Pt = 1.2; and (c) 650°C, H/Pt = 1.1, cooled in H_2 , and TPD to 700°C.

fresh catalyst to 0.84 H/Pt after the first TPD, indicating only a small change in the platinum dispersion during the TPD experiment.

The effect of increasing reduction temperature on the TPD profiles is shown in Fig. 2 for Pt/K-LTL reduced at 300, 500 and 650°C. Reduction at higher temperatures progressively diminishes the total amount of hydrogen desorbed, from 1.8 H/Pt to 1.3 H/Pt to 1.1 H/Pt after reduction at 300, 500, and 650°C, respectively. After reduction at 500°C, the peaks corresponding to irreversible H_2 below 500°C are absent, e.g., peaks II and III, while the H_2 desorption at 610°C (peak IV) is unchanged. After reduction at 650°C, only the peak I remains. The spectra in Fig. 2 support the conclusion that the peak I corresponds to reversibly chemisorbed hydrogen, and the high temperature hydrogen desorptions are irreversible.

To investigate the possibility of exchange between the various forms of hydrogen identified by the TPD, a two-part TPD was performed. A fresh sample of Pt/K-LTL was reduced at 300°, and the TPD was conducted, programming only to 300°C and holding at this temperature for 1 hr (profile in Fig. 3b). The sample was cooled to room temperature under N_2 flow, and a second TPD to 700°C was obtained (Fig. 3c). The

catalyst was not exposed to hydrogen between the two TPD profiles. Total hydrogen desorption was 1.2 H/Pt in the low-temperature (ambient-300°C) TPD and 0.6 H/Pt in the second TPD, for a total of 1.8 H/Pt, which is in agreement with the 1.8 H/Pt obtained in a single TPD, i.e., Fig. 3a. The absence of peak I and II in the second TPD indicates that there is no exchange of hydrogen between the low temperature (<300°C) sites and the higher temperature sites. For example, after removal of the chemisorbed hydrogen in the low-temperature TPD, hydrogen does not migrate from the high-temperature sites back to the platinum surface and desorb at low temperature during the second TPD.

The TPD profiles for 1.5% Pt/H-LTL (Fig. 4) show desorption peaks at temperatures similar to those obtained for the Pt/K-LTL catalyst, but differing in the size of those peaks. Prominent in the spectra of Pt/H-LTL is the large desorption for peak IV at 625°C. The total hydrogen desorbed is 4.3 H/Pt. Following the first TPD, only the low-temperature H_2 desorption, peak I (H/Pt = 1.3), and minor amounts of H_2 desorbed at higher temperature are desorbed during the second TPD. For comparison, the volumetric hydrogen chemisorption of Pt/H-LTL

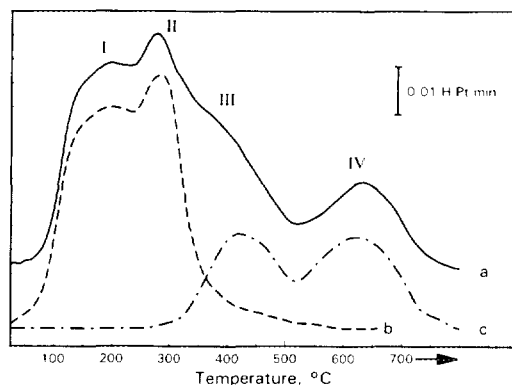


FIG. 3. 2.0% Pt/K-LTL reduced at (a) 300°C, cooled in H_2 , and TPD to 700°C, H/Pt = 1.8; (b) 300°C cooled in H_2 , and TPD to 300°C and held at 300°C for 1 hr, H/Pt = 1.2; and (c) sample in (b) was cooled in N_2 and TPD to 700°C, H/Pt = 0.6.

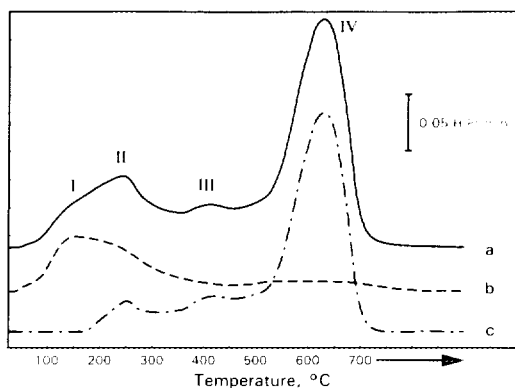


FIG. 4. 1.5% Pt/H-LTL reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 4.3; (b) following the first TPD, the catalyst was rereduced at 700°C, cooled in H₂, and second TPD to 700°C, H/Pt = 1.3; and (c) difference profile: (a) minus (b), H/Pt = 3.0.

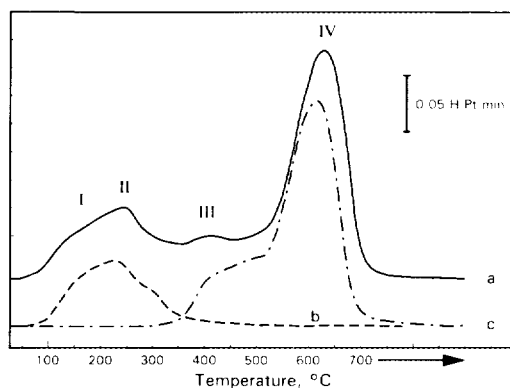


FIG. 6. 1.5% Pt/H-LTL reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 4.3; (b) 300°C, cooled in H₂, and TPD to 300°C and held at 300°C for 1 hr., H/Pt = 1.1; and (c) sample in (b) was cooled in N₂ and TPD to 700°C, H/Pt = 3.3.

reduced at 300°C was 1.10 H/Pt. Similar to Pt/K-LTL, peak I of the H₂ desorption from Pt/H-LTL corresponds to chemisorbed hydrogen, while higher temperature peaks represent irreversible hydrogen desorptions.

On both Pt/K-LTL and Pt/H-LTL, increasing the reduction temperature decreases the size of the irreversible desorption peaks below the reduction temperature. For example, after reduction of Pt/H-LTL at 500°C, Fig. 5b, the hydrogen desorptions corresponding to peaks II and III are absent,

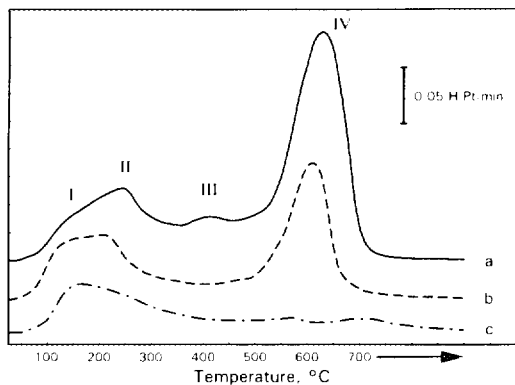


FIG. 5. 1.5% Pt/H-LTL reduced at (a) 300°C, H/Pt = 4.3; (b) 500°C, H/Pt = 2.6; and (c) 650°C, cooled in H₂, and TPD to 700°C, H/Pt = 1.2.

and much of the hydrogen associated with peak IV has been diminished. The total hydrogen desorption of Fig. 5b is 2.6 H/Pt. After reduction at 650°C, only the peak I (chemisorbed H₂) is present, Fig. 5c, with a total desorption of 1.2 H/Pt.

A two-part TPD was also conducted with the Pt/H-LTL catalyst (Fig. 6) using the same procedure describe above for Pt/K-LTL, for example Figs. 3b and 3c. Total hydrogen desorption was 1.1 H/Pt in the low-temperature (ambient–300°C) TPD, Fig. 6b, and 3.3 H/Pt in the second TPD, Fig. 6c, for a total of 4.4 H/Pt, which is in agreement with the 4.3 H/Pt obtained in a single TPD, Fig. 6a. As observed for Pt/K-LTL, the two-part TPD indicates that there is no exchange of hydrogen between the low temperature (<300°C) sites, corresponding to peaks I and II, and the higher temperature sites, corresponding to peaks III and IV.

High temperature hydrogen desorptions in the TPD have been reported in the literature as being due to oxidation of the metal by support protons (14, 15). In order to evaluate this possibility, a fresh sample of Pt/H-LTL was subjected to a H₂ TPD to 700°C, Fig. 7a. Following the TPD, the sample was cooled in N₂ to 40°C and pulsed with H₂. The quantity of hydrogen consumed at 40°C

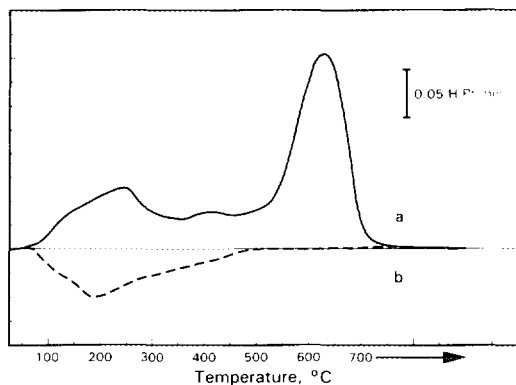


FIG. 7. 1.5% Pt/H-LTL reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 4.3; (b) following the first TPD, the catalyst was cooled in N₂ to 40°C, H/Pt = 0.88, and pulsed with hydrogen until saturation (not shown); TPR in 20% H₂/80% N₂ to 700°C; desorption = 0.91 H/Pt.

was 0.88 H/Pt. Subsequent temperature program reduction (TPR) of this sample to 700°C, Fig. 7b, resulted in the *desorption* of hydrogen equal to 0.91 H/Pt, which is in agreement with the pulsed chemisorption above and is also consistent with volumetric hydrogen chemisorption on the fresh catalyst. In addition, the peak desorption temperature during the TPR (185°C) was similar to desorption temperature for chemisorbed hydrogen (175°C) in the TPD. If the high-temperature desorptions in the TPD represent reversible oxidation of platinum, then the amount of hydrogen consumed in the pulsed reduction/chemisorption should have been approximately 4.3 H/Pt as observed in the TPD. The quantity of hydrogen consumed during the pulsed chemisorption, however, is only 0.9 H/Pt and is consistent with chemisorbed hydrogen. Thus, the high-temperature hydrogen desorptions in the TPD are *not* a result of oxidation of platinum by support protons.

In summary, the H₂ desorptions for Pt/K-LTL and Pt/H-LTL are qualitatively similar, but the quantity of irreversible hydrogen, peaks II–IV, is significantly higher for Pt/H-LTL. In addition, for both catalysts, the hydrogen present on the low-tempera-

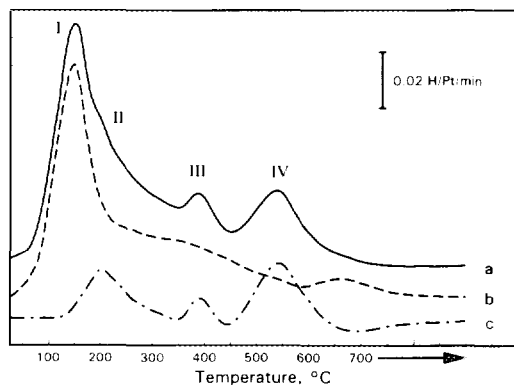


FIG. 8. 2.0% Pt/K-MAZ reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 1.9; (b) following the first TPD, the catalyst was rereduced at 700°C, cooled in H₂, and second TPD to 700°C, H/Pt = 1.3; and (c) difference profile: (a) minus (b), H/Pt = 0.6.

ture (<300°C) sites and the higher temperature sites do not readily exchange, and the quantity of irreversibly desorbed H₂ decreases with increasing reduction temperature.

The H₂ TPD profiles of 2.0% Pt/K-MAZ and 1.5% Pt/H-MAZ are shown in Figs. 8–11. The profiles are similar to those for Pt/K-LTL and Pt/H-LTL, although the total hydrogen desorptions were slightly higher. For Pt/K-MAZ, the total hydrogen desorp-

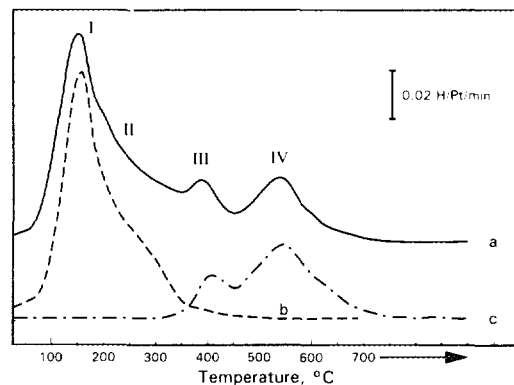


FIG. 9. 2.0% Pt/K-MAZ reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 1.9; (b) 300°C, cooled in H₂, and TPD to 300°C and held at 300°C for 1 hr, H/Pt = 1.3; and (c) sample in (b) was cooled in N₂ and TPD to 700°C, H/Pt = 0.6.

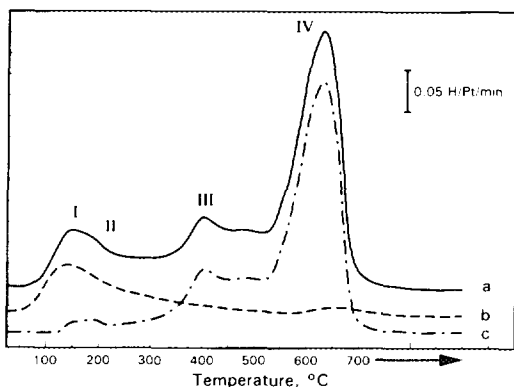


FIG. 10. 1.5% Pt/H-MAZ reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 5.6; (b) following the first TPD, the catalyst was rereduced at 700°C, cooled in H₂, and second TPD to 700°C, H/Pt = 1.4; and (c) difference profile: (a) minus (b), H/Pt = 4.2.

tion was equivalent to 1.9 H/Pt, compared to 1.7 H/Pt for Pt/K-LTL. Hydrogen desorption from Pt/H-MAZ was 5.6 H/Pt, compared to 4.3 H/Pt for Pt/H-LTL. For both catalysts, peaks II–IV were absent during a second TPD (Figs. 8b and 10b), and results for the two-part TPD (Figs. 9b and 9c and 11b and 11c) indicate that hydrogen from the higher temperature sites does not exchange with the lower temperature sites.

Hydrogen TPD for platinum on amor-

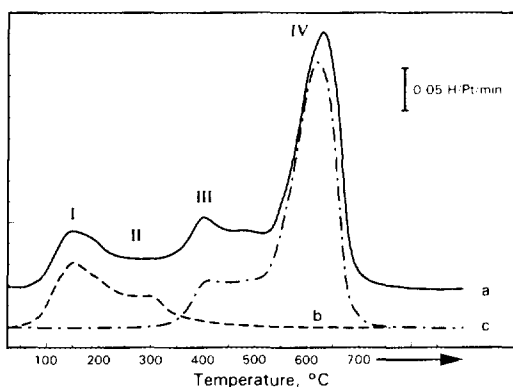


FIG. 11. 1.5% Pt/H-MAZ reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 5.6; (b) 300°C, cooled in H₂, and TPD to 300°C and held at 300°C for 1 hr, H/Pt = 1.4; and (c) sample in (b) was cooled in N₂ and TPD to 700°C, H/Pt = 4.0.

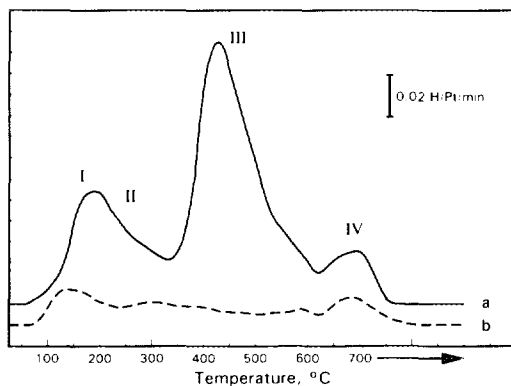


FIG. 12. 1.0% Pt/ γ -Al₂O₃ reduced at (a) 300°C, cooled in H₂, and TPD to 700°C, H/Pt = 3.6; (b) following the first TPD, the catalyst was rereduced at 700°C, cooled in H₂, and second TPD to 700°C, H/Pt = 0.6.

phous supports also shows multiple high-temperature desorption peaks similar to those observed with zeolite supports. The H₂ TPD of 1.0% Pt/ γ -Al₂O₃ reduced at 300°C (Fig. 12a) displays three peaks centered at around 180°C (peak I), 420°C and 700°C. As with the zeolite supports, the low temperature peak corresponds to chemisorbed hydrogen, and its size is consistent with the amount of chemisorbed H₂ measured volumetrically (H/Pt = 0.94). Some sintering of the platinum particles is apparent in the repeat TPD (Fig. 12b), as the size of the chemisorption peak is diminished. Pt/ γ -Al₂O₃ appears similar to the acidic zeolite supports in that the total H₂ desorption is large (3.6 H/Pt). However, unlike the zeolite supports, the largest peak (1.9 H/Pt) for Pt/ γ -Al₂O₃ is observed near 400°C, while the highest temperature peak is small.

The H₂ TPD profile of 3.3% Pt/SiO₂ reduced at 300°C is given in Fig. 13. The peaks in this profile are much less distinct, but a chemisorption peak at 150°C (peak I) and a higher temperature desorption at 550°C can be clearly seen.

Deuterium labeling. Hydrogen TPD profiles were obtained on Pt/K-LTL, Pt/H-LTL, and Pt/ γ -Al₂O₃ reduced at 300°C in D₂. In these experiments, the cryogenic (water) traps were removed and the desorbed hy-

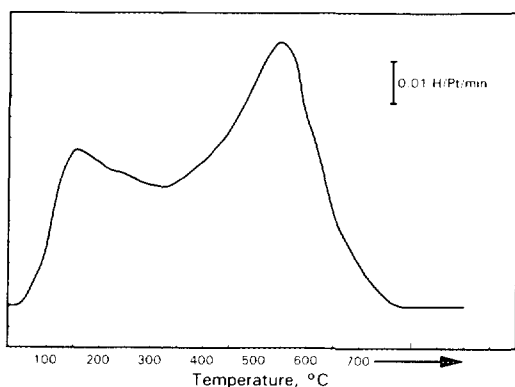


FIG. 13. 3.3% Pt/SiO₂ reduced at (a) 300°C, cooled in H₂, and TPD to 700°C.

drogen was detected by mass spectrometry. The TPD profiles were identical to those presented above (Figs. 1a, 4a, and 12a), and all of the peaks for each catalyst were D₂. No H₂ was detected. In addition to desorption of D₂, large quantities of H₂O desorbed over the same temperature range (450–600°C). Approximately 1% of the water was HDO. Since most of the desorbed water is H₂O while the desorbed hydrogen is D₂, we conclude that the hydrogen desorptions do not result from oxidation of platinum by water at high temperature.

Additionally, Pt/H-LTL was reduced at 300°C in H₂ for 1 hr. At 300°C, the reducing gas was switched to D₂ for 30 min (a large excess of D₂) and cooled to ambient temperature in D₂. In the subsequent TPD, all of the desorptions were D₂ with only traces of H₂ or HD detected.

EXAFS. A full EXAFS analysis of Pt/K-LTL and Pt/H-LTL is presented elsewhere (22). The Pt–Pt phase and amplitude corrected k^3 -weighted Fourier transform of the EXAFS data of Pt/K-LTL reduced at 300, 450, and 600°C is presented in Fig. 14. Qualitative inspection of Fig. 14 shows that metallic Pt is present in all samples as indicated by the Pt/Pt bond distance of 2.77 Å. In addition, as the reduction temperature is increased, the amplitude of the Pt/Pt peak increases, indicating growth of the platinum

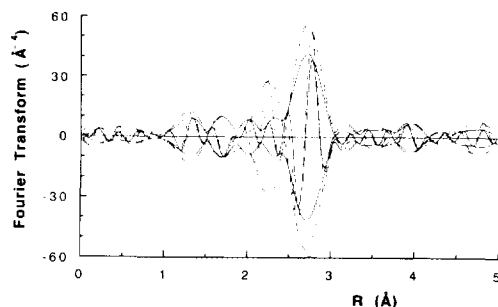


FIG. 14. k^3 -weighted Fourier transform of EXAFS spectra of 1.2% Pt/K-LTL reduced at (a) 300°C (solid line), (b) 450°C (dotted line), and (c) 600°C (dashed line).

particle. For all reduction temperatures, however, the platinum particles are relatively small as denoted by the absence of higher Pt–Pt shells. The EXAFS spectra were fit in both k - and r -space, and Table 1 summarizes the results.

For Pt/K-LTL reduced at 300°C, the Pt–Pt coordination number corresponds to an average particle size of six atoms ($N = 4.0$). With increasing reduction temperature the particle size increases. At 450°C the average particle size is ca. ten atoms ($N = 4.8$), while at 600°C the particle size is near 12 atoms ($N = 4.9$). In all of the catalysts, the particle size is sufficiently small to observe a contribution to the EXAFS from the oxygen atoms of the support. For Pt/K-LTL reduced at 300°C, the Pt–O coordination is 1.4 and the platinum–oxygen distance is 2.73 Å. For Pt/K-LTL reduced at 450°C, there is a

TABLE 1

EXAFS Coordination Parameters for Pt/K-LTL			
Reduction temperature (°C)	Backscatter	N	R (Å)
300	Pt	4.0	2.74
	O	1.4	2.73
450	Pt	4.8	2.74
	O	1.3	2.77
600	O	0.4	2.20
	Pt	4.9	2.75
	O	1.3	2.24

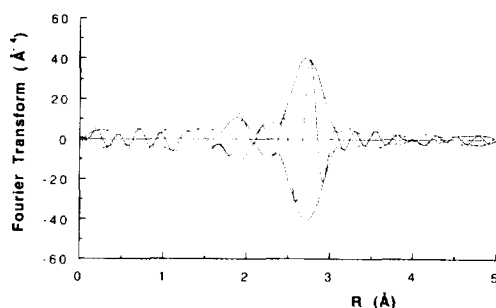


FIG. 15. k^3 -weighted Fourier transform of EXAFS spectra of 1.2% Pt/H-LTL reduced at (a) 300°C (solid line) and (b) 500°C (dotted line).

second Pt-O coordination at a distance of 2.20 Å with a total Pt-O coordination number of 1.7. After reduction at 600°C, only one Pt-O contribution at a distance of 2.20 Å is present with a Pt-O coordination number of 1.3.

The Pt-Pt phase and amplitude corrected k^3 -weighted Fourier transform of the EXAFS data of Pt/H-LTL reduced at 300 and 500°C is presented in Fig. 15. In both catalysts, small, metallic Pt particles are present as indicated by the Pt-Pt bond distance of 2.77 Å. The EXAFS spectra were fit in both k - and r -space, the results are given in Table 2.

For Pt/H-LTL reduced at 300°C, the Pt-Pt coordination number of 4.1 corresponds to an average particle size of approximately seven atoms. In addition, a long Pt-O distance of 2.65 Å with a coordination number of 1.2 is detected. Increasing the

TABLE 2

EXAFS Coordination Parameters for Pt/H-LTL

Reduction temperature (°C)	Backscatter	N	R (Å)
300	Pt	4.1	2.73
	O	1.2	2.65
500	Pt	4.4	2.72
	O	1.5	2.24

TABLE 3

Propane Hydrogenolysis^a

Catalyst support ^b	TOF ^c (molecules/sec/surface Pt atom)
K-LTL (450°C)	0.064
K-LTL (600°C) ^d	0.022
K-MAZ	0.032
K-SiO ₂	0.0074
SiO ₂	0.19
H-LTL (450°C)	0.53 ^e (0.40) ^f
H-LTL (600°C) ^d	0.14 ^e (0.10) ^f
H-MAZ	0.37 ^e (0.27) ^f
Al ₂ O ₃	0.62

^a Atmospheric pressure and 400°C.

^b Catalysts reduced at 450°C.

^c Based on H₂ chemisorption.

^d Catalysts reduced at 600°C.

^e Initial TOF.

^f TOF after 10 min.

reduction temperature to 500°C increases the Pt-Pt coordination number to 4.4, or approximately a nine atom cluster. After reduction at 500°C, the Pt-O distance is 2.24 Å, and the Pt-O coordination number is 1.5.

Propane hydrogenolysis. For each catalyst, hydrogenolysis of propane yielded methane and ethane in equal molar amounts. The TOFs at 400°C are given in Table 3. For Pt/K-LTL, Pt/K-MAZ, Pt/SiO₂, and Pt/ γ -Al₂O₃, there was little deactivation. For Pt/H-MAZ and Pt/H-LTL, however, deactivation was more rapid. The conversion, therefore, was determined as a function of time (at one space velocity) and extrapolated to zero time, i.e., no deactivation. For these two catalysts, since the activity was changing rapidly during the first few minutes, the initial TOF and the TOF after 10 min are reported in Table 3.

DISCUSSION

Temperature-programmed desorption of hydrogen indicates that in the absence of platinum no hydrogen desorptions are observed from any of the supports. By contrast, there are several types of hydrogen on platinum catalysts. In addition to chemi-

sorbed hydrogen, three higher temperature hydrogen desorptions (peaks II–IV) are also observed at temperatures from about 250 to 650°C. It has been proposed that high-temperature reduction (HTR) can result in the formation of subsurface hydrogen (10), i.e., hydrogen present in the platinum lattice just below the surface platinum atoms. The platinum–platinum distances measured by EXAFS are identical to those observed for bulk platinum and do not change with reduction temperature. These results rule out the presence of subsurface hydrogen or platinum hydrides. In addition, it has been proposed that HTR can lead to the formation of platinum–aluminum alloys (1, 7, 8). Since no backscattering by aluminum neighbors was detected in the EXAFS, these alloys are not responsible for any of the peaks in the TPD. Also, HTR has been suggested to produce strongly chemisorbed hydrogen (2, 3, 12), leading to high-temperature peaks during TPD. In the present study, higher reduction temperatures resulted in less high-temperature, irreversible hydrogen in the TPD. The high-temperature TPD peaks, therefore, are not due to strongly chemisorbed hydrogen.

Since the higher temperature desorptions do not result from hydrogen at the platinum particles, e.g., strongly chemisorbed hydrogen, subsurface hydrogen, metal hydrides, or platinum–aluminum alloys, we conclude that they result from desorption of hydrogen located on the support. In addition, since these hydrogen desorptions do not result from platinum oxidation by support protons, or desorbed water, this hydrogen must be present as neutral species, i.e., spillover hydrogen.

Although the spillover hydrogen is initially formed at 300°C, desorption of the spillover hydrogen does not occur until much higher temperatures. Once the spillover hydrogen has been desorbed from the support, either during a high temperature reduction or a TPD, spillover hydrogen can no longer be formed by reexposure to hydrogen. The desorption of spillover hydrogen,

therefore, is irreversible. Since there have been only minor changes in the dispersion, chemisorption, and structure of the platinum particles, the irreversibility of hydrogen desorption is likely due to a change in the structure of the support. Stabilization of spillover hydrogen is believed to require the presence of support hydroxyl groups (23–25) and zeolites begin to dehydroxylate above 500°C (26, 27). Desorption of water was detected over the same temperature range as desorption of hydrogen from peak IV. We propose, therefore, that the inability to form spillover hydrogen after high temperature treatments results from irreversible dehydroxylation of the support.

Qualitatively, the number and temperature of peaks in the TPD profiles for platinum on nonacidic and acidic zeolites are similar. As discussed above, the total amount of spillover hydrogen is dependent on the extent of support dehydroxylation. Likewise, the amount of spillover hydrogen is also strongly dependent on the support acidity, as shown in Table 4. The effect of support acidity is most dramatically shown by the size of peak IV in the TPD profiles, and this peak is largest for platinum on acidic supports. Table 4 summarizes the total amount of hydrogen desorbed in the TPD profile for platinum supported on various acidic and nonacidic zeolite supports. In the first TPD, both reversible (chemisorbed) and irreversible (spillover) hydrogen are measured, while in the second TPD, only reversible (chemisorbed) hydrogen is observed. The difference between the two TPD profiles represents the irreversible (spillover) hydrogen on the catalyst, i.e., peaks II–IV. The data in Table 4 clearly show that the amount of spillover hydrogen is much larger for platinum on acidic supports than on nonacidic supports. For example, the amount of spillover hydrogen is equivalent to 3.0 H/Pt for Pt/H-LTL but only 0.7 H/Pt for Pt/K-LTL.

Even though formation of spillover hydrogen occurs at 300°C, it does not desorb at 300°C in flowing N₂, even after 1 hr. Fur-

TABLE 4
Total Hydrogen Desorption (H/Pt) by H₂ TPD

Catalyst	K-LTL	H-LTL	K-MAZ	H-MAZ
H/Pt first TPD ^a (Rev + Irrev)	1.8	4.3	1.9	5.6
H/Pt second TPD ^b (reversible)	1.2	1.3	1.3	1.4
Difference (irreversible)	0.6	3.0	0.6	4.2

^a Catalyst reduced at 300°C, cooled in H₂, and TPD to 700°C.

^b Following the 1st TPD, the catalyst was rereduced at 700°C, cooled in H₂, and TPD to 700°C.

thermore, it also does not migrate back to the platinum under these conditions. Once formed on the support, spillover hydrogen seems to be quite stable. At 300°C, however, the spillover hydrogen does completely exchange with excess, gas-phase D₂ within 30 min. It is commonly assumed that H-D exchange of spillover hydrogen occurs by migration of the spillover hydrogen to the platinum particles followed by exchange of spillover hydrogen with chemisorbed deuterium. However, since spillover hydrogen does not migrate to vacant platinum sites at 300°C, it seems unlikely that the spillover hydrogen would migrate to the platinum particles and exchange with chemisorbed deuterium. It is possible that the exchange takes place by direct reaction between the spillover hydrogen and the gas phase deuterium, without the participation of the platinum.

For all reduction temperatures, the platinum particles are small enough to reside within the zeolite pores. Because of the very small metal particle size, oxygen atoms from the support are detected by EXAFS. After high-temperature reduction (HTR) (>500°C) the measured Pt-O distance is 2.2 Å, which is approximately equal to the sum of the covalent radii of the two atoms. This is consistent with platinum atoms in direct contact with the oxide ions of the zeolite surface.

Reduction at 300°C (LTR), on the other hand, results in a longer Pt-O distance of 2.77 Å. Based on the absence of additional backscatters, it has been suggested that this

long Pt-O distance results from the presence of hydrogen between the platinum atoms and the oxide support (22, 28, 29). The interfacial hydrogen may be either chemisorbed hydrogen trapped at the interface during the initial reduction, or hydrogen from the support hydroxyl groups (29). At intermediate reduction temperatures there is a mixture of both the long and short Pt-O distances. Thus, as the reduction temperature is increased there is the progressive loss of the long Pt-O distance with the simultaneous formation to the short Pt-O distance. Comparison of the H₂ TPD with EXAFS indicates several desorption peaks (peaks II and III) in the same temperature range observed for the conversion of the long Pt-O distance to the short Pt-O distance. These peaks may, therefore, correspond to the loss of interfacial hydrogen. Both the desorption temperature and the large quantity of H₂ desorbed for peak IV in acidic catalysts makes it unlikely that this peak is associated with loss of interfacial hydrogen.

In summary, we assign the irreversible, high temperature H₂ desorptions to spillover hydrogen stabilized by support hydroxyl groups, both acidic and nonacidic. Peaks II and/or III may be spillover hydrogen located at the interface between the platinum particles and the support. Peak IV likely represents spillover hydrogen on acidic hydroxyl groups.

Effects on catalysis. Similar to other studies (15, 30, 31), the propane hydrogenolysis activities are determined predominantly by

the acidity of the support. The TOFs for platinum on acidic supports, e.g., Pt/H-LTL, Pt/MAZ, and Pt/ γ -Al₂O₃ were more than an order of magnitude higher than on the nonacidic supports, e.g., Pt/K-LTL and Pt/K-MAZ. The TOF for Pt/SiO₂, a weakly acidic support, was intermediate between the acidic and non-acidic supports. Neutralization of the silica by addition of alkali, i.e., Pt/K-SiO₂, strongly reduced the hydrogenolysis TOF.

In previous studies, the increase in hydrogenolysis activity for metals on acidic supports has been attributed to electron-deficient platinum. The electron deficient platinum can result from donation of platinum electron density to the support (30), or result from the formation of metal-proton adducts (15, 34). Results of a recent study suggest that the electron deficient nature of the platinum is an intrinsic property of the small metal particles (32). A series of Pt/Y catalysts was investigated by several techniques, including XANES, where it was concluded that all of the observations ascribed to electron deficiency were the result of the intrinsic properties of the very small platinum particles which form on acidic supports. In our study, the platinum particle size of Pt/K-LTL, Pt/H-LTL and Pt/ γ -Al₂O₃ (17, 23) are very similar with the particle size in all catalysts from seven to ten atoms. It is unlikely, therefore, that the particle size alone can account for the differences in hydrogenolysis activities.

While we have previously proposed that platinum on acidic supports is electron deficient (33), in the present study we have found that the most active catalysts are those which have the largest amount of spillover hydrogen, i.e., platinum on acidic supports. As the support acidity decreases, both the propane hydrogenolysis TOF and the quantity of spillover hydrogen also decrease in the same order, e.g., acidic supports > silica > nonacidic supports. The specific activity, however, does not parallel the acid strength. For example, the acid strength of Pt/ γ -Al₂O₃ compared with Pt/H-

LTL is much weaker. On the other hand, the specific activities for the two catalysts are very similar. Although the acid strengths of Pt/ γ -Al₂O₃ and Pt/H-LTL are very different, the quantity of spillover hydrogen per surface platinum atom on the two catalysts is similar. These results suggest that the amount of spillover hydrogen and the specific hydrogenolysis activity are influenced by the number of hydroxyl groups, rather than their acid strength.

In addition to the support acidity, the hydrogenolysis TOF is also affected by the reduction temperature. For Pt/K-LTL and Pt/H-LTL, as the reduction temperature increased, both the specific activity and the amount of spillover hydrogen decreased. After HTR, there are at least three changes in the catalyst which may affect the specific activity. First, the TPD indicates that there is little spillover hydrogen on the catalyst. This also implies that there are few surface hydroxyl groups, which are necessary for stabilization of the spillover hydrogen. Dehydroxylation of the support leads to a change in the surface structure resulting from the loss of both oxygen and hydrogen atoms. HTR also induces changes in the structure of the metal-support interface leaving platinum atoms in direct contact and interacting more strongly with the oxygen atoms of the support. Comparison of the hydrogenolysis TOFs for catalysts reduced at 600°C, where spillover hydrogen is absent from both Pt/H-LTL and Pt/K-LTL, indicate that the specific activity for platinum on acidic supports is still much higher than platinum on a nonacidic support. These differences are consistent with differences in electronic properties of the metal induced by the support as previously proposed (15, 30, 31, 33). However, at 600°C the absence of hydroxyl groups necessary to stabilize spillover hydrogen suggests that the electronic modifications result from interaction of the platinum with oxygen atoms in addition to the interaction of platinum with support protons (15, 34).

While there seems to be a general correla-

tion between the specific hydrogenolysis activity and the amount of spillover hydrogen, the role of spillover hydrogen (if any) on the rate of hydrogenolysis is uncertain and several possibilities exist. The quantity of spillover hydrogen may simply parallel the number of support hydroxyl groups and be an indirect measure of the support acidity, and hence, may be a relative measure of the electronic effects induced by the support. Understanding the role of spillover hydrogen on catalyst activity (and selectivity) will be the subject of future investigations.

CONCLUSIONS

The H₂ TPD indicates that several types of hydrogen exist on platinum catalysts. In addition to chemisorbed hydrogen on the platinum, several types of spillover hydrogen are present on the support. The quantity of spillover hydrogen is dependent on the number of support hydroxyl groups and is largest for platinum on acidic supports reduced at low temperature. Spillover hydrogen is irreversibly desorbed at high temperatures since the support is irreversibly dehydroxylated.

We propose that after low temperature reduction, a layer of spillover hydrogen is located between the platinum particles and the support (oxide) surface. The platinum-oxygen distance is ca. 2.7 Å. Reduction of the platinum at higher temperatures results in the progressive loss of the interfacial hydrogen. At reduction temperatures above 500°C, all of the interfacial hydrogen is lost, and the platinum is in direct contact with the oxygen atoms of the zeolite support as indicated by a platinum-oxygen distance of 2.2 Å. In the TPD, two hydrogen desorption peaks observed at temperatures from 300 to 500°C may correspond to the loss of interfacial hydrogen detected by EXAFS.

The catalysts' specific activities for hydrogenolysis were affected by both the support acidity and the reduction temperature. Platinum on acidic supports and reduced at lowest temperature were the most active. Qualitatively, the hydrogenolysis activity

increased with increasing amounts of spillover hydrogen, although the role of spillover hydrogen in affecting the catalytic activity is uncertain.

ACKNOWLEDGMENT

The authors acknowledge the contribution to this work of Ronald Kurek, who built the TPD/TPR apparatus and provided the TPD data presented in this manuscript.

REFERENCES

1. den Otter, G. J., and Dautzenberg, F. M., *J. Catal.* **53**, 116 (1978).
2. Menon, P. G., and Froment, G. F., *J. Catal.* **59**, 138 (1979).
3. Menon, P. G., and Froment, G. F., *Appl. Catal.* **1**, 31 (1981).
4. Kramer, R., and Fischbacher, M., *J. Mol. Catal.* **51**, 247 (1989).
5. Bonneviot, L., and Haller, G. L., *J. Catal.* **130**, 359 (1991).
6. Kunimori, K., Okouchi, T., and Uchijima, T., *Chem. Lett.*, 1513 (1980).
7. Kumimori, K., Ikeda, Y., and Soma, and Uchijima, T., *J. Catal.* **79**, 185 (1983).
8. Kunimori, K., and Uchijima, T., in "Spillover of Adsorbed Species" (G. M. Pajonk, S. J. Teichner, and J. E. Germain, Eds.), Studies in Surface Science and Catalysis, Vol. 17, p. 197. Elsevier, Amsterdam, 1983.
9. Dou, L.-Q., Tan, Y.-S., and Lu, D.-S., *Appl. Catal.* **66**, 235 (1990).
10. Levy, P.-J., and Primet, M., *Appl. Catal.* **70**, 263 (1991).
11. Foger, K., and Anderson, J. R., *J. Catal.* **54**, 318 (1978).
12. Szilagyi, T., *J. Catal.* **121**, 223 (1990).
13. Kramer, R., and Andre, M., *J. Catal.* **58**, 287 (1979).
14. Dalmon, J. A., Mirodatos, C., Turlier, P., and Martin, G. A., in "Spillover of Adsorbed Species" (G. M. Pajonk, S. J. Teichner, and J. E. Germain, Eds.), Studies in Surface Science and Catalysis, Vol. 17, p. 169. Elsevier, Amsterdam, 1983.
15. Homeyer, S. T., Karpinski, Z., and Sachtler, W. M. H., *J. Catal.* **123**, 60 (1990).
16. Lane, G. S., Miller, J. T., Modica, F. S., and Barr, M. K., *J. Catal.* **141**, 465 (1993).
17. Vaarkamp, M., Miller, J. T., Modica, F. S., and Koningsberger, D. C., *Jpn. J. Appl. Phys.* in press.
18. Breck, D. W., "Zeolite Molecular Sieves, Structure, Chemistry and Use," p. 306. Wiley, New York, 1974.
19. Kampers, F. W. H., Maas, T. M. J., van Grondelle, J., Brinkgreve, P., and Koningsberger, D. C., *Rev. Sci. Instrum.* **60**, 2635 (1989).

20. Cook, J. W., Jr., and Sayers, D. E., *J. Appl. Phys.* **52**, 5024 (1981).
21. van Zon, J. B. A. D., Koningsberger, D. C., van't Blik, H. F. J., and Sayers, D. E., *J. Chem. Phys.* **12**, 5742 (1985).
22. Vaarkamp, M., Modica, F. S., Miller, J. T., and Koningsberger, D. C., submitted for publication.
23. Altham, J. A., and Wevv, G., *J. Catal.* **18**, 133 (1970).
24. Levy, R. B., and Boudart, M., *J. Catal.* **32**, (1974).
25. Ambs, W. J., and Mitchell, M. M., Jr., *J. Catal.* **82**, 226 (1983).
26. Hughes, T. R., and White, H. M., *J. Phys. Chem.* **71**, 2192 (1967).
27. Datka, J., *J. Chem. Soc. Faraday Trans. 1* **77**, 2877 (1981).
28. Kampers, F. W. H., and Koningsberger, D. C., *Faraday Discuss. Chem. Soc.* **89**, 137 (1990).
29. Koningsberger, D. C., and Gates, B. C., *Catal. Lett.* **14**, 271 (1992).
30. Dalla Betta, R. A., and Boudart, M., in "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 2, p. 1329. North-Holland, Amsterdam, 1973.
31. Naccache, C., Kaufherr, N., Dufaux, M., Baudiera, J., and Imelik, B., *ACS Symp. Ser.* **40**, 538 (1977).
32. Samant, M. G., and Boudart, M., *J. Phys. Chem.* **95**, 4070 (1991).
33. Vaarkamp, M., Miller, J. T., Modica, F. S. Lane, G. S., and Koningsberger, D. C., in "Tenth International Congress on Catalysis, Proceedings, Budapest, Hungary, 1992," in press.
34. Tzou, M. S., and Sachtler, W. M. H., "Catalysis 1987" (J. W. Ward, Ed.), p. 233. Elsevier, Amsterdam, 1988.