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Hydrogen Temperature-Programmed Desorptions in Platinum Catalysts: Decomposition and Isotopic Exchange by Spillover Hydrogen of Chemisorbed Ammonia

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H_2-TPD of Pt/alumina catalysts display multiple hydrogen desorptions. In addition to chemisorbed hydrogen (Peak I) at approximately 175°C, there is a small hydrogen desorption (Peak II) at about 250°C and a large, irreversible hydrogen desorption (Peak III) at 450°C. The quantity of hydrogen associated with Peak III decreases with increasing precalcination temperature of the alumina. It is shown that the hydrogen from Peak III is caused by decomposition of ammonia chemisorbed on acid sites of the alumina, which are introduced during the catalyst's preparation. In the presence of Pt, the chemisorbed ammonia undergoes isotopic exchange with D_2 by a spillover hydrogen process, even in mixtures where chemisorbed ammonia and Pt are located on separate support particles. Although spillover hydrogen species affect deuterium exchange of ammonium ions, they do not contribute to the catalytic activity of platinum for neopentane hydrogenolysis or isomerization. © 1996 Academic Press, Inc.

INTRODUCTION

The mobility of adsorbed hydrogen species from supported metals onto the nonmetallic support has been known since the 1950's (1). Extensive research on these spillover hydrogen species has been the subject of numerous reviews (2–7). Spillover is known to affect changes in the catalyst, which may lead to modifications in the reactivity. For example, surface hydroxyl groups on alumina (8–10), silica (12, 13), and HNaY zeolites (14–16) undergo isotopic exchange with D_2 in the presence of metals, e.g., Pt, Pd, Rh, Ni, W. On the other hand, no exchange is observed in the absence of metal (17) or if the metal is poisoned, for example, by CO (18). Spillover hydrogen is thought to lower the reduction temperature in numerous metal oxides (2, 5, 19–22), including easily reducible supports like titania (23–25). These metal oxides may be fully or partially reduced, generating new catalytic centers that are not present in the absence of spillover hydrogen. In addition, the reactivity of the supported metal is strongly influenced by interactions with the support oxide (26, 27). Partial reduction of the support, therefore, may result in a large change in the metal–support interaction leading to a modification of the catalytic properties of the supported metal.

Spillover hydrogen has also been demonstrated to react with adsorbed organic species. For example, surface methoxy-silica groups react with spillover hydrogen to produce methane and Si–OH (28, 29). Similarly, spillover hydrogen reacts with activated carbon to produce methane (30) and has been proposed to affect the removal of coke deposits in reforming catalysts (31). Spillover hydrogen has also been reported to have catalytic activity similar to that of supported metals, for example, hydrogenation of ethylene (28, 32–34), isobutene (35), and benzene (36, 37).

Previously, we have reported multiple hydrogen desorptions in the temperature-programmed desorption (TPD) profiles from supported Pt/alumina, Pt/zeolite, and Pt/silica catalysts (27, 38, 39). In this earlier work, the high-temperature desorptions were proposed to be spillover hydrogen species. In the present work, these hydrogen desorptions have been more extensively studied and are now assigned to the decomposition of chemisorbed ammonia desorbed from the acid sites at high temperature. However, hydrogen spillover does occur on these catalysts, as evidenced by the isotopic exchange of the hydrogen atoms in the chemisorbed ammonia with gas-phase D_2. These spilled over hydrogen species, however, are unreactive for conversion of neopentane.

EXPERIMENTAL

Catalyst Preparation

The alumina supports were prepared by precalcination of Catapal SB pseudo-boehmite at 400, 550, or 700°C and Versal 150 pseudo-boehmite at 400°C. Catapal SB is a high-purity pseudo-boehmite, manufactured by hydrolysis of aluminum alkoxides. Versal 150 is a precipitated

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TABLE 1

Alumina Physical Properties

Alumina	Calcination temp. (°C)	Surface area (m^2/g)	Pore volume (cc/g)
Catapal SB	400	273	0.47
Catapal SB	550	216	0.47
Catapal SB	700	222	0.48
Versal 150	400	313	0.84

alumina with trace impurities (200 ppm Na_2O, 200 ppm SO_4, 600 ppm SiO_2, and 300 ppm Fe_2O_3). The γ-alumina BET surface areas and micropore volumes are given in Table 1. To each support, platinum was impregnated using an aqueous solution of tetraamine platinum (II) nitrate to a weight loading of 1.5 wt% Pt. The chloride level was adjusted by addition of dilute HCl during impregnation of platinum. The platinum-impregnated catalysts were dried and calcined in air at 250°C. The platinum dispersions were determined by hydrogen chemisorption after reduction at 250°C and are given in Table 2.

K-L zeolite (International Zeolite Association type LTL) was obtained from UOP and was exchanged at 80°C for 3 h with a 10-fold excess of 1 *M* NH_4NO_3. The NH_4-LTL was dried and calcined at 400°C for 3 h. The resulting H-LTL was impregnated with tetraamine platinum (II) nitrate to a weight loading of 3.0 wt% Pt.

Platinum in Na-A (IZA type LTA) zeolite was prepared according to published methods by addition of $Pt(NH_3)_4Cl_2$ during the zeolite synthesis (40). The Pt/LTA was washed thoroughly with distilled water and dried at 120°C. The resulting Pt/LTA contained 0.82 wt% Pt. Chemisorption of H_2 and CO revealed that most of the Pt was located within the pores of LTA (H/Pt = 0.41, CO/Pt = 0.03).

Hydrogen Temperature-Programmed Desorption (H_2-TPD)

Hydrogen TPD of Pt/alumina samples was performed on catalysts after reduction at atmospheric pressure in flowing H_2 at 250°C and cooling to room temperature in H_2. Desorptions were programmed at 10°C/min to 600°C in flowing N_2. The H_2 and N_2 were purified by passing over oxygen, hydrocarbon, and water traps. Desorbed gases were monitored by a thermal conductivity or a mass spectrometer detector. When the thermal conductivity detector was used, dry ice traps were also placed directly after the furnace.

TPD profiles on catalyst mixtures were obtained using equal weights of finely ground Pt/alumina (Versal alumina precalcined at 700°C and prereduced at 500°C) and H-LTL (precalcined at 400°C and containing no Pt). The mixture was reduced in flowing H_2 at 300°C for 1 h, cooled to room temperature in H_2 (or D_2), and programmed at 10°C/min to 700°C in N_2. The desorbed gases were analyzed by mass spectrometry. A TPD profile was also obtained for a mixture of equal weights of Pt/LTA and NH_4-LTL (no Pt).

The effects of oxygen on TPD profiles were measured using a Pt/alumina catalyst (Catapal SB precalcined at 400°C and containing 1.5% Pt and 1% Cl). The catalyst was reduced at 250°C for 1 h and cooled to 100°C in N_2. The reduced catalyst was exposed to flowing air at 100°C for 30 min and cooled to room temperature in N_2. A TPD profile was obtained as above. Separate samples of the same catalyst were reduced at 250°C for 1 h, oxidized with air at 100°C for 30 min, then rereduced at either 100 or 250°C for 30 min. Following the second reduction, the catalyst was cooled to room temperature in H_2 and the TPD was obtained as before.

Infrared Spectroscopy

Infrared spectra were obtained on Catapal SB alumina, without platinum or chloride, precalcined at 400, 550, or 700°C, or heated to 700°C under vacuum in the infrared cell. The sample was ground to a fine powder with an agate mortar and pestle and pressed in a $1\frac{1}{4}$-in. gold-plated stainless-steel die at 9 metric tons to form a thin self-supporting wafer (0.12 g). The wafer was trimmed and placed into a quartz sample holder and loaded into a quartz cell with CaF_2 windows. The cell was evacuated to less than 10^{-6} Torr at 400°C for 45 min. After drying, the sample was cooled and the

TABLE 2

Summary of H_2-TPD. 1.5 wt% Pt/Alumina Catalysts[a]

Alumina (calcination temp., °C)	Cl (wt%)	Pt dispersion (H/Pt)[b]	Total H_2 (cc/g)	Peak I (cc/g)[b]	Peak II (cc/g)	Peak III (cc/g)
Catapal SB (400)	0	0.82	2.21	0.71	0.23	1.27
Catapal SB (400)	1	0.95	2.71	0.81	0.31	1.59
Catapal SB (400)	2	0.95	2.35	0.81	0.31	1.23
Catapal SB (550)	1	0.82	2.15	0.71	0.32	1.12
Catapal SB (700)	1	0.70	1.21	0.60	0.00	0.61
Versal 150 (400)	1	0.80	2.07	0.68	0.17	1.22

[a] Catalysts reduced at 250°C.

[b] Determined from H_2 chemisorption.

spectrum (1024 scans) collected at room temperature with a Nicolet 740 FTIR using a liquid nitrogen-cooled detector. Background spectra were obtained with the sample removed from the infrared beam path.

Catalyst Tests

The conversion of neopentane was conducted at 350°C and atmospheric pressure in a fixed-bed reactor using 1.0 vol% neopentane in H_2. The catalyst was prereduced at the reaction temperature for 1 h, and the conversion was adjusted from 0.5 to 3.0% by varying the space velocity. Catalyst loadings were approximately 0.05 g. The turnover frequency (TOF) was calculated based on the volumetric hydrogen chemisorption and is reported as molecules/sec/surface Pt atom. The selectivity is calculated on a molar basis as the percentage of converted neopentane which is converted to isopentane (isomerization) and to isobutane plus methane (hydrogenolysis).

RESULTS

TPD Results

A typical TPD profile for Pt on alumina is shown in Fig. 1. As observed previously for Pt/alumina (38), broad overlapping hydrogen desorptions occur at about 175 (Peak I) and 250°C (Peak II) with the largest hydrogen desorption at 450°C (Peak III). Peaks I and II are similar to those observed previously on Pt/zeolites (38, 39) and represent hydrogen associated with the Pt, either chemisorbed on the Pt surface (Peak I) or held between the metal particle and the support surface (interfacial hydrogen). Peak III results from hydrogen species on the support distant from the Pt. When catalysts were reduced in D_2, the TPD profiles were identical to those reduced in H_2, except that all desorptions were D_2, with no H_2 detected. Similarly, for catalysts first reduced in H_2, then treated in D_2 for 30 min at 250°C, all TPD peaks were D_2. It was previously shown for Pt/zeolite catalysts that all hydrogen desorptions except Peak I (chemisorbed hydrogen) were irreversible, i.e., rereduction after the TPD did not restore the peaks on a second TPD (38). Identical behavior is observed on Pt/alumina. Following the first TPD to 600°C, the Pt/alumina catalyst was cooled to 300°C in N_2, rereduced for 1 h, and cooled to room temperature in H_2. Peaks II and III are absent in the second TPD, Fig. 1. The quantity of hydrogen desorbed in the second TPD was 0.93 cc/g compared to 2.71 cc/g in the first TPD and some sintering of the Pt has occurred as evidenced by a decrease in the size of Peak I.

TPD profiles for all the Pt/alumina catalysts are given in Figs. 2–4, showing the effects of the alumina source, chloride loading and alumina precalcination temperature. The quantities of hydrogen desorbed from each peak are given in Table 2. Since Peaks I and II are not resolved, the quantity of Peak I was taken as equal to the hydrogen chemisorption, and the area of Peak II was determined by subtraction of the hydrogen chemisorption from the sum of these two peaks. Peak III includes all hydrogen desorbed above 350°C in the TPD. Comparing the TPD profiles, one can observe the following trends:

(1) TPD profiles for the two aluminas are similar, but somewhat smaller for the Versal alumina (Fig. 2).

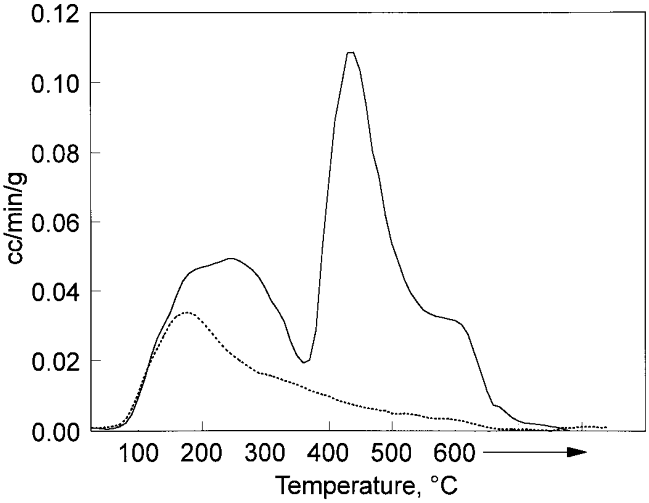

FIG. 1. H_2-TPD of Pt/alumina containing 1.5% Pt and 1% Cl supported on Catapal SB precalcined at 400°C. (—) TPD after reduction at 250°C, 2.71 cc H_2/g catalyst; (···) following the first TPD, the catalyst was cooled in N_2 and rereduced at 300°C, cooled in H_2, and second TPD, 0.93 cc H_2/g catalyst.

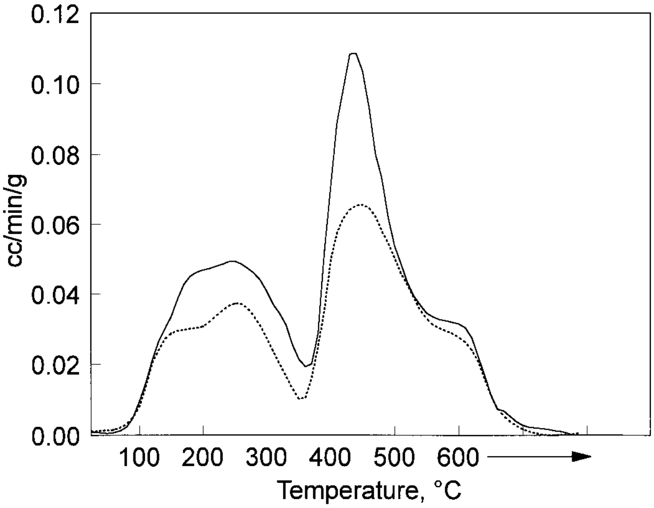

FIG. 2. The effect of the alumina source. H_2-TPD of Pt/alumina containing 1.5% Pt and 1% Cl supported on (—) Catapal SB, 2.71 cc H_2/g catalyst and (···) Versal, 2.07 cc H_2/g catalyst. Both aluminas were precalcined at 400°C and the catalysts reduced at 250°C.

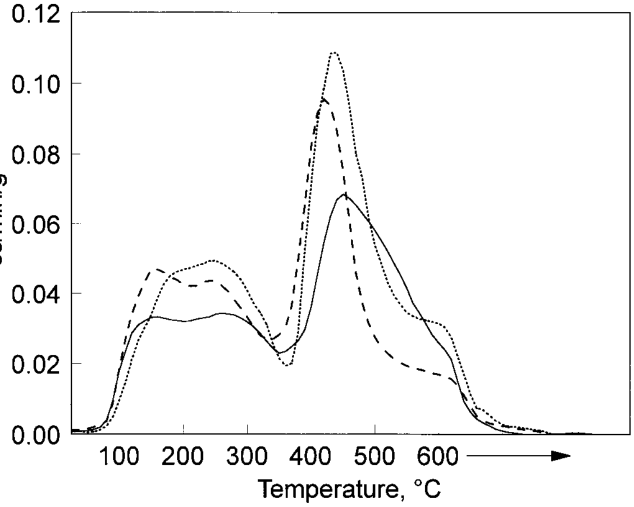

FIG. 3. The effect of chloride loading. H_2-TPD of Pt/alumina containing 1.5% Pt and (—) 0% Cl, 2.21 cc H_2/g catalyst, (···) 1% Cl, 2.71 cc H_2/g catalyst, and (- - -) 2% Cl, 2.35 cc H_2/g catalyst. The alumina was Catapal SB precalcined at 400°C and the catalysts were reduced at 250°C.

(2) Addition of chloride to the alumina increased the dispersion of Pt from 0.82 to 0.95, with a corresponding increase in the size of Peaks I–II (Fig. 3). In addition, in the absence of chloride, the hydrogen desorption from Peak III occurs over a wider temperature range than observed for the chloride-containing catalysts. The area of Peak III is somewhat larger for the 1% Cl catalyst than for the other two chloride levels.

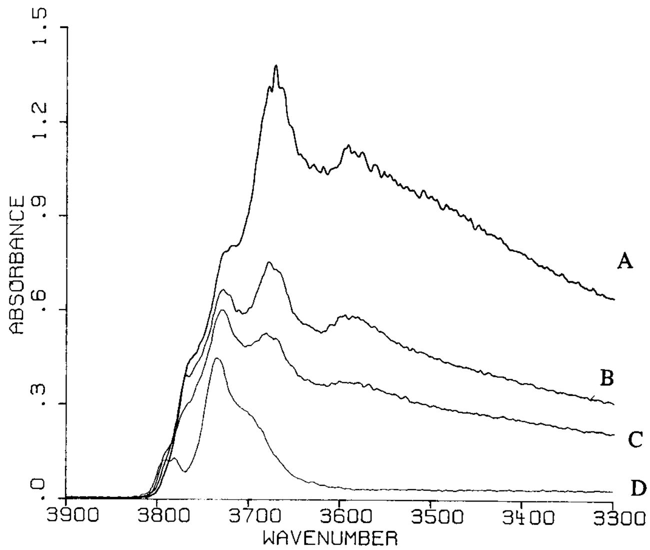

FIG. 5. The infrared spectra of the hydroxy region for Catapal SB (no Pt or Cl) precalcined at (A) 400°C, (B) 550°C, (C) 700°C, and (D) 700°C under vacuum.

(3) Increasing the alumina precalcination temperature decreases the Pt dispersion from 0.95 to 0.70, with a corresponding decrease in the size of Peaks I–II (Fig. 4). In addition, the area of Peak III also decreases significantly with increasing precalcination temperature.

The hydroxyl region of the infrared spectra of Catapal SB alumina (no Pt or Cl) calcined at 400, 550, and 700°C is shown in Fig. 5. The infrared spectra are similar to those previously reported for alumina (41–43) and the hydroxyl stretching frequencies are given in Table 3. As expected, increasing the alumina calcination temperature results in a decrease in the intensity of the hydroxyl bands, although a significant number of hydroxyl bands remain even after calcination at 700°C.

The reactivity of the various hydrogen species was investigated by reacting the reduced Pt/alumina catalyst with air at low temperature. TPD profiles of these samples after various air treatments and reductions are shown in Fig. 6, and the areas of the TPD peaks are given in Table 4. Figure 6 (solid line) shows the TPD profile after an initial reduction at 250°C. Following reduction at 250°C and treatment at 100°C in air, no hydrogen desorptions below 350°C were observed (Peaks I and II), but the large, high-temperature

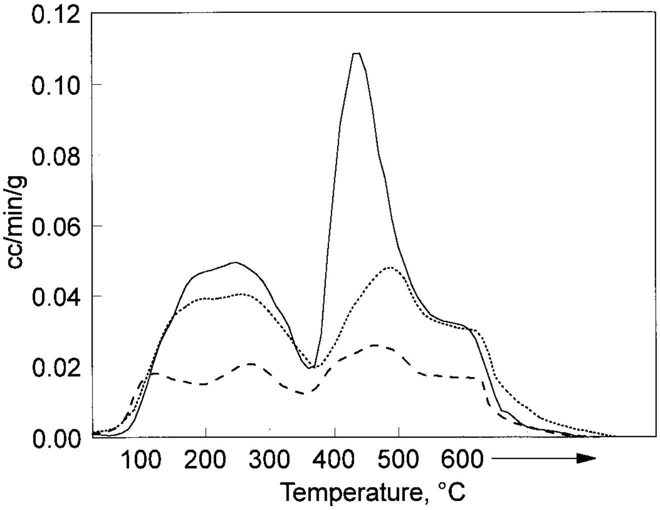

FIG. 4. The effect of alumina precalcination temperature. H_2-TPD of Pt/alumina containing 1.5% Pt and 1% Cl supported on Catapal SB precalcined at (—) 400°C, 2.71 cc H_2/g catalyst, (···) 550°C, 2.15 cc H_2/g catalyst, and (- - -) 700°C, 1.21 cc H_2/g catalyst. The catalysts were reduced at 250°C.

TABLE 3

Infrared Spectra of Catapal SB Alumina

Pretreatment	Peak positions (cm^{-1})				
400°C		3760	3720	3672	3590
550°C		3760	3728	3678	3595
700°C		3760	3730	3682	
700°C/Vacuum	3795	3780	3735	3698	

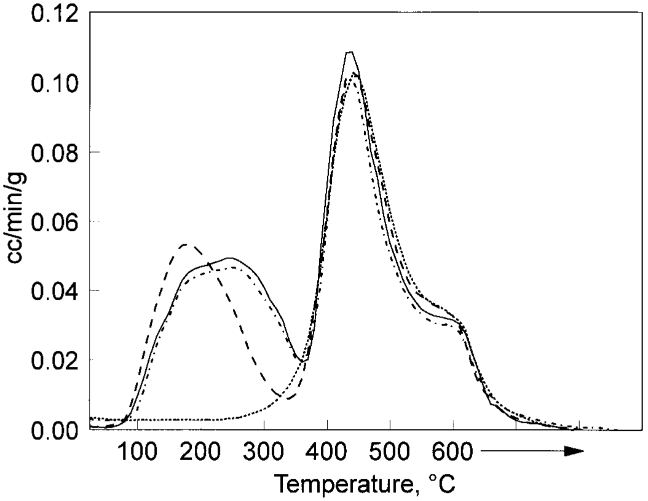

FIG. 6. The reactivity of hydrogen desorptions to air. H_2-TPD of Pt /alumina containing 1.5% Pt and 1% Cl supported on Catapal SB precalcined at 400°C and (—) reduced at 250°C, 2.71 cc H_2/g catalyst, (···) reduced at 250°C, cooled to 100°C in N_2 and exposed to air at 100°C, 1.64 cc H_2/g catalyst, (- - -) reduced at 250°C, cooled to 100°C in N_2, exposed to air at 100°C, and rereduced at 100°C, 2.56 cc H_2/g catalyst, and (-··-) reduced at 250°C, cooled to 100°C in N_2, exposed to air at 100°C, and rereduced at 250°C, 2.57 cc H_2/g catalyst.

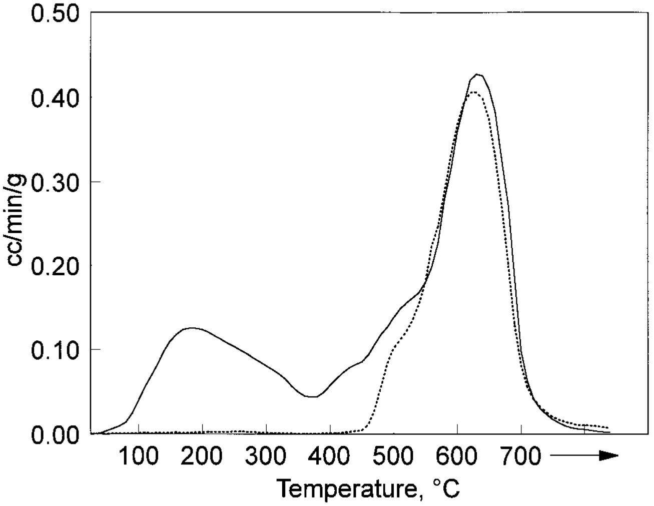

FIG. 7. H_2-TPD of 3% Pt/H-LTL (—) reduced at 250°C, 8.94 cc H_2/g catalyst and (···) pretreated at 300°C in N_2, 5.78 cc H_2/g catalyst.

desorption (Peak III) was unchanged (Fig. 6, dotted line). When the catalyst was reduced at 250°C, treated with air at 100°C, and then rereduced in H_2 at 100°C, the TPD profile (Fig. 6, dashed line) indicates that Peak I, but not Peak II, is restored by rereduction at 100°C. When the catalyst is rereduced at 250°C after air treatment (Fig. 6, dash-dotted line) all the peaks are restored, and the TPD profile is identical to that before air treatment (Fig. 6, solid line).

If the high-temperature desorptions observed in the TPD are due to spilled over hydrogen, as previously proposed (27, 38, 39), then these peaks should not be present in a catalyst that has never experienced hydrogen treatment. The H_2-TPD profiles of 3% Pt/H-LTL are shown in Fig. 7, after reduction in H_2 at 250°C (solid line) or after heating in N_2 at 300°C (no hydrogen reduction) (dotted line). As previously observed for Pt/H zeolite catalysts, four hydrogen desorptions are present after H_2 reduction, with the largest at 600°C (27, 38, 39). The total hydrogen desorption was 8.94 cc/g, with 7.10 cc/g in Peaks III and IV. In the catalyst that was treated only in N_2, Peaks I and II are absent, as expected, but Peaks III and IV are present at the same peak temperatures and only slightly smaller than after reduction in H_2 (5.78 cc/g). This result suggests that the hydrogen desorptions in the TPD result from the decomposition of a hydrogen-containing compound, which is present prior to reduction and desorbs from the support at high temperature.

TABLE 4

Reactivity of H_2-TPD Peaks with Air[a]

Treatment	Peak I and II (cc/g)	Peak III (cc/g)
Hydrogen 250°C	1.12	1.59
Hydrogen 250°C/Air 100°C	0.00	1.37
Hydrogen 250°C/Air 100°C Hydrogen 100°C	0.98	1.58
Hydrogen 250°C/Air 100°C Hydrogen 250°C	1.07	1.50

[a] Catalyst: 1.5% Pt/1% Cl-alumina, Catapal SB calcined at 400°C.

To confirm this observation and identify the species responsible for these hydrogen desorptions, TPD experiments were performed on a series of mixed catalysts. In the first series, TPD profiles were obtained on Pt/alumina (precalcined at 700°C and reduced at 500°C), H-LTL (no Pt), and a mixture of equal weights of these two. The resulting TPD profiles are shown in Fig. 8. In Fig. 8 (solid line) the small size of Peak I (chemisorbed hydrogen) for the Pt/alumina indicates extensive sintering of the Pt following the severe calcination and high-temperature reduction. Also, the high-temperature Peak III is quite small, consistent with previous results for Pt/alumina catalysts precalcined (Fig. 4) and reduced at high temperature (38). The total hydrogen desorption was 1.02 cc/g. The TPD profile of the H-LTL (no Pt) after H_2 reduction at 250°C gave no hydrogen desorptions (not shown). In the TPD profile of the mixture (Fig. 8, dotted line), new hydrogen desorptions that were not present in either sample individually are present. Peak I, which is due to chemisorbed hydrogen, is approximately comparable in size in both profiles and results from the desorption of chemisorbed hydrogen from the Pt/alu-

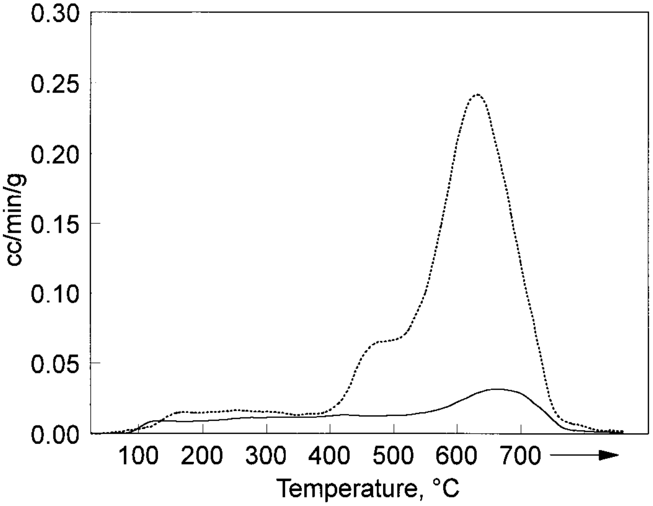

FIG. 8. H_2-TPD of (—) 1.5% Pt/alumina (1% Cl), Catapal SB precalcined at 700°C and the catalyst was prereduced at 500°C, 1.02 cc H_2/g catalyst and (···) a 1/1 mixture of Pt/alumina from 1.5% Pt/alumina and H-LTL (no Pt), rereduced at 250°C, 4.49 cc H_2/g catalyst.

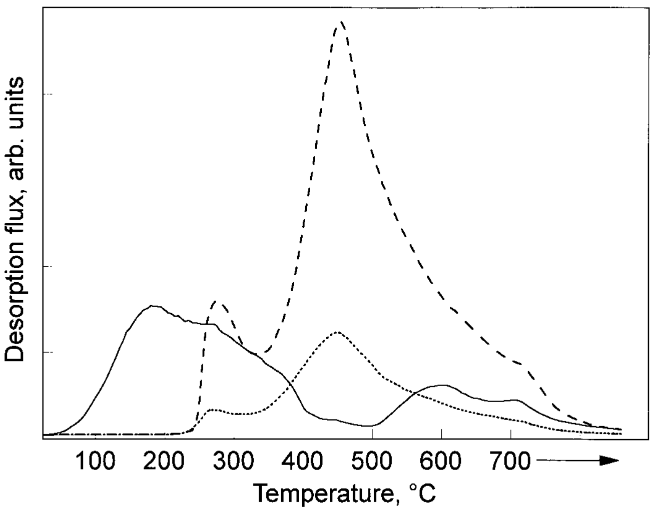

FIG. 9. H_2-TPD of a 1/1 mixture of Pt/LTA and NH_4-LTL (no Pt) reduced in D_2 at 300°C for 30 min. (—) D_2, 0.55 cc/g D_2, (···) mass 17, NH_3, and (- - -) mass 20, ND_3.

mina. Peaks III and IV, on the other hand, are quite large in the mixed catalyst and occur with desorption temperatures and sizes characteristic of Pt/H-LTL (see Fig. 7). Reduction of the mixture in D_2 gave the identical TPD profile, but with all peaks as D_2. Attributing all the hydrogen desorbed in Peaks III and IV to the H-LTL component of the mixture, the quantity of hydrogen is equivalent to 6.9 cc/g, which is in good agreement with the 7.1 cc/g obtained for these peaks in 3% Pt/H-LTL.

The second series of experiments was carried out on a mixture of equal weights of Pt/LTA and NH_4-LTL. The Pt in LTA was introduced into the catalyst during the synthesis. The low CO chemisorption capacity along with the high hydrogen chemisorption capacity of Pt/LTA indicates that the platinum is well dispersed within the zeolite cavities with little external platinum. As a result, the platinum is only accessible to very small molecules, such as hydrogen, that can diffuse through the small pore openings in LTA. In the TPD experiment, the mixture was reduced in D_2 at 300°C for 30 min, and the effluent was monitored by mass spectrometry (Fig. 9). Only small high-temperature D_2 desorptions were observed, at desorption temperatures characteristic of H-LTL. However, large quantities of ND_3 and a lesser amount of NHD_2 were observed, but with little NH_2D or NH_3. (The NHD_2 and NH_2D are omitted from Fig. 9 for clarity, but are similar in shape to ND_3 and NH_3.) The calculated D/H ratio of the ammonia species indicate approximately 80% deuterium exchange of the chemisorbed ammonium ions.

Catalytic Tests

Each Pt/alumina catalyst was evaluated for conversion of neopentane at 350°C and atmospheric pressure. Analysis of the reaction products indicates that methane, isobutane, and isopentane are primary reaction products. The catalyst TOF and isomerization selectivities are given in Table 5. There appears to be a small increase in the TOF as the chloride level increases from 0 to 2%, which may be due to a change in the support acidity, particle size, or some other subtle change. However, the TOF of all catalysts are otherwise very similar, indicating only small differences in the specific activity of the platinum on each alumina support. The isomerization selectivity is also very similar, at approximately 28%, for all catalysts, independent of the alumina precalcination temperature, support chloride level, platinum dispersion, or the size of the Peak III desorption in the TPD profiles.

Because of the high catalytic activity of Pt/alumina for conversion of neopentane, it is difficult to determine if there is a contribution to the conversion from spillover hydrogen

TABLE 5

Conversion of Neopentane[a]

1.5% Pt/alumina catalyst	TOF (molecules/sec/$Pt_{exposed}$)	Isomerization selectivity (%)[b]
0% Cl/Catapal SB (400°C)	2.2×10^{-2}	25
1% Cl/Catapal SB (400°C)	3.0×10^{-2}	28
2% Cl/Catapal SB (400°C)	5.2×10^{-2}	26
1% Cl/Catapal SB (550°C)	4.0×10^{-2}	25
1% Cl/Catapal SB (700°C)	2.5×10^{-2}	30
1% Cl/Versal (400°C)	2.3×10^{-2}	30

[a] Reaction conditions: atmospheric pressure, 350°C and 1.0 vol% neopentane in H_2.

[b] Determined at 0.5% conversion.

species. To evaluate the contribution of spillover to the conversion of neopentane the reaction was conducted over Pt /LTA and a mixture of Pt/LTA with H-LTL (no Pt). No measurable neopentane conversion was observed with either the pure Pt/LTA or its mixture with H-LTL at reaction temperatures up to 450°C.

DISCUSSION

Previous H_2-TPD of Pt/zeolite and Pt/alumina catalysts indicated that there are several types of surface hydrogen (27, 38, 39). Peak I was shown to be due to reversibly chemisorbed hydrogen. Peak II was speculated to be due to interfacial hydrogen, i.e., a layer of chemisorbed hydrogen between the platinum particles and the support. Previous EXAFS structural studies (44) indicate that the high-temperature desorptions are not due to platinum–hydrogen species, for example, platinum hydride or subsurface hydrogen (45). It was concluded, therefore, that the high-temperature hydrogen desorptions (Peak III in Pt /alumina and Peaks III and IV in Pt/zeolites) were derived from species remote from the platinum clusters, i.e., hydrogen species located on the support. Furthermore, since the quantity of hydrogen desorbed from Peak IV increased as the number of acid sites on Pt/H-LTL increased, it was concluded that this hydrogen was associated with and stabilized by the acidic hydroxyl groups from the support (27, 39). Because the hydrogen species from Peaks III and IV were located distant from the platinum clusters and underwent isotopic exchange with D_2, these desorptions were thought to be spillover hydrogen (38).

The results of this study are in agreement with our earlier TPD studies (27, 38, 39) but lead to an alternate interpretation of the origin of the high-temperature hydrogen desorptions. For example, as observed for Peak IV on Pt/ zeolite catalysts, the amount of hydrogen desorbed from Peak III in Pt/alumina catalysts increases as the number of support hydroxyl groups increases. On zeolites, the number of support hydroxyls was varied by changing the extent of ion exchange. In the alumina catalysts of this study, the number of surface hydroxyl groups was varied by changing the support precalcination temperature. As the calcination temperature increased, the number of hydroxyl groups decreased as evidenced by infrared spectroscopy. Similarly, the quantity of hydrogen desorbed from Peak III decreased with increasing support precalcination temperature. Despite the differences in the nature of support hydroxyl groups in acidic zeolites and alumina, the quantity of desorbed hydrogen in both catalysts appears to be related to the number of surface hydroxyl groups.

In previous studies of Pt/LTL catalysts, it was suggested that the spilled over hydrogen was stabilized by support hydroxyl groups and that removal of these hydroxyls by thermal treatment led to an inability of the support to hold spilled over hydrogen (27, 38, 39) during a subsequent reduction. This mechanism was proposed to explain the loss of high-temperature hydrogen TPD peaks after high-temperature reduction or precalcination. Identical behavior is observed with Pt/alumina. Following high-temperature calcination of the alumina the hydrogen desorption from Peak III is greatly reduced and is absent entirely after a first TPD. However, the TPD for Pt/alumina was only to 600°C where at least some of the surface hydroxyl groups remain, as shown by infrared spectroscopy. If the previously proposed model was correct, at least some spilled over hydrogen should be observed in the second TPD of Pt/alumina, albeit in lower amounts.

The presence of high-temperature H_2 desorptions in the TPD profile of Pt/H-LTL, which has been heated only in N_2, suggests that a chemisorbed (molecular) hydrogen species is already present on the catalyst before reduction and that the H_2 peaks do not result from desorption of spilled over hydrogen species. The lack of reactivity to air at 100°C with the hydrogen species that produce Peak III in the TPD also supports this conclusion. For example, if the spillover hydrogen was a molecular species, it would be expected to desorb at a temperature much lower than that observed in the TPD, while spilled over atomic hydrogen species would be expected to be highly reactive with oxygen.

These and previous results indicate that the high-temperature H_2 desorptions observed in the TPD likely result from the decomposition of hydrogen-containing species, which are strongly chemisorbed on the support. Following their desorption, either during the pretreatment or a TPD, these hydrogen-containing species are not restored by rereduction in H_2. Mass spectroscopic analysis of the desorbing gases, however, did not detect any hydrocarbon compounds. On the other hand, significant quantities of ammonia were desorbed from all catalysts. We propose that the adsorbed species is ammonia originally present as amine ligands from the tetraammine platinum nitrate and/or from exchanged ammonium ions in the case of the acidic zeolites. To obtain a high platinum dispersion, these catalysts were calcined at 250°C, which is apparently too low to decompose or desorb all of the ammonia. At about 450°C in the TPD of Pt/alumina, or 600°C in the H-LTL, the ammonia is desorbed and is subsequently decomposed to N_2 and H_2 on the Pt surface (46–48). When the Pt was encapsulated in the small pores of LTA, the ammonia that was desorbed from NH_4-LTL did not decompose and was detected as ammonia, with little H_2 observed. It was previously observed that the desorption temperatures for the high-temperature peaks increase as the support acid strength increases in the order. Pt/silica $<$ Pt/alumina $<$ Pt/H zeolite (38). It was also observed that the quantity of hydrogen desorbed from Peak IV for Pt/H-LTL was proportional to the number of acid sites and the metal loading (39). All of these observations are consistent with the conclusion that the high-temperature hydrogen desorptions are due to the desorption and decomposition of chemisorbed ammonia from acidic support hydroxyl groups.

Although the hydrogen desorptions are not spillover hydrogen species, the hydrogen atoms of the chemisorbed ammonia do undergo isotopic exchange by D_2 in the presence of Pt, even when the Pt and the ammonia are on separate support particles in mixtures. For example a physical mixture of Pt/alumina and H-LTL shows a hydrogen desorption at 600°C, characteristic of ammonia desorption from the H-LTL support. After treatment in D_2 at 300°C, only D_2 is observed, indicating complete exchange of the hydrogen in the chemisorbed ammonia. Although the H-LTL was calcined at 400°C, TPD analysis revealed that small amounts of NH_3 are desorbed above 400°C. Similarly, small amounts of strongly chemisorbed ammonia are still present in H–Y after calcination at 450°C (49). Since these remaining NH_4^+ ions in H-LTL have survived 400°C calcination and do not desorb until about 600°C in the TPD, it is unlikely that the NH_4^+ ions are mobile during D_2 treatment at 300°C. It can be concluded, therefore, that the isotopic exchange occurs via deuterium spilled over from the Pt on to the alumina, migrating across particle boundaries and exchanging with the chemisorbed ammonia on the H-LTL zeolite. Similar mechanisms have been proposed to explain the isotopic exchange of support hydroxyl groups (12, 50).

Similarly, in the mixture of Pt/LTA with NH_4-LTL, the ammonium ions exchanged on the LTL zeolite (no Pt) undergo isotopic exchange with D_2. However, since the small pores of Pt/LTA prevent access of the ammonia to the platinum, the desorbed ND_3 is not decomposed to D_2 and N_2. This also implies that the hydrogen–deuterium exchange must occur at some site other than the platinum surface. While ammonia is too large to access the platinum, the ability of Pt/LTA to chemisorb hydrogen indicates that the Pt is accessible to hydrogen. Thus, it appears likely that the exchange of the N–H bonds for deuterium must involve mobile (spilled over) deuterium species, which migrate from the LTA support surface to the LTL support with the chemisorbed ammonia.

Spillover hydrogen has been reported to have catalytic activity similar to that of supported metals, for example, hydrogenation of ethylene (28, 32–34), isobutene (35), and benzene (36, 37). Also, we previously observed a correlation between the size of the high-temperature H_2-TPD peaks and the activity for hydrogenolysis in Pt/LTL catalysts (38). In the current study, activity for neopentane conversion was measured for Pt/alumina catalysts with widely varying properties, for example, alumina source, alumina surface area, precalcination temperature, chloride level, platinum dispersion, and with differing amounts of high-temperature desorbed hydrogen. Despite the large differences in the amount of high-temperature hydrogen desorptions, there is little difference in TOF or selectivity for neopentane conversion among these catalysts. The size of the high-temperature H_2-TPD peaks, therefore, is unrelated to the catalyst performance.

The observed isotopic exchange of ammonia in mixtures of Pt/LTA and NH_4-LTL confirms that spillover does take place under conditions similar to those for hydrogenolysis of neopentane on Pt/alumina. In addition, because neopentane is too large to diffuse through the small pores of LTA, any reaction of neopentane in such mixtures can be attributed to participation by the spilled over hydrogen. No conversion of neopentane, however, was observed for either Pt/LTA alone, or a mixture of Pt/LTA with H-LTL, at temperatures up to 450°C. Thus, although spillover hydrogen is present on the support surface, these spillover hydrogen species do not contribute to the catalytic reaction of neopentane on Pt/alumina at 350°C.

CONCLUSION

High-temperature, irreversible hydrogen desorptions on supported Pt catalysts result from the desorption of chemisorbed ammonia and its subsequent decomposition on the Pt surface into H_2 and N_2. The ammonia is introduced during the catalyst preparation and remains chemisorbed on the support acid sites when low calcination and reduction temperatures are used. The size of the hydrogen desorptions is determined by the number of acidic support hydroxyl sites and, for alumina, decreases with increasing precalcination temperature. While the quantity of chemisorbed ammonia determines the amount of high-temperature hydrogen in the TPD, the acid strength determines the desorption temperature, which increases as the acid strength of the support increases. The hydrogen atoms of the chemisorbed ammonia undergo isotopic exchange with D_2 by a spillover process in the presence of Pt, even in mixtures where the chemisorbed ammonia and Pt are located on separate support particles. These spilled over hydrogen species, however, do not contribute to the catalytic performance of platinum for neopentane hydrogenolysis or isomerization.

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