ISS AND TPD STUDY OF THE ADSORPTION AND INTERACTION OF CO AND H_2 ON POLYCRYSTALLINE Pt

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ABSTRACT

The adsorption and interaction of CO and H_2 on polycrystalline Pt has been studied using ion scattering spectroscopy (ISS) and temperature programmed desorption (TPD). The ISS results indicate that the initial CO adsorption on Pt takes place very rapidly and saturates the Pt surface with coverage close to a monolayer. ISS also shows that the CO molecules adsorb at an angular orientation from the surface normal and perhaps parallel to the surface. A TPD spectrum obtained after coadsorbing $^{12}C^{16}O$ and $^{13}C^{18}O$ on Pt shows no isotopic mixing, which is indicative of molecular CO adsorption. TPD spectra obtained after coadsorbing H_2 and CO on polycrystalline Pt provides evidence for the formation of a CO-H surface species.

INTRODUCTION

The adsorption characteristics of CO on polycrystalline Pt are of particular importance in understanding CO oxidation over Pt and Pt-containing catalysts such as Pt/SnO_x, which has been examined for use as a low-temperature CO oxidation catalyst in closed-cycle CO_2 lasers [1]. Although many studies have been carried out on CO adsorption on Pt, contradictory conclusions have been reached so important questions remain unresolved.

Furthermore, hydrogen is present at most if not all surfaces, but it is often neglected in surface studies because commonly used surface techniques such as electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) are relatively insensitive to surface hydrogen. Nevertheless, it can have a large influence on the chemical behavior of a surface. This has been demonstrated in a study of a Pt/SnO_x catalyst by Schryer et al [2]. For this catalyst the rate of CO oxidation depends strongly upon the surface hydroxyl group concentration. Using ESCA and electron stimulated desorption (ESD), Hoflund et al. [3] examined hydrogen at polycrystalline tin oxide surfaces and found that several different chemical states of hydrogen are present.

Hydrogen has also been shown to interact with CO during coadsorption on Pt to form a CO-H complex [4]. In temperature programmed desorption (TPD) and ESD experiments by Craig [5,6], CO and H_2 were coadsorbed on a polycrystalline Pt. A mass 2 TPD spectrum shows the evolution of a new feature when CO is added to the hydrogen dosing gas and a corresponding feature is also observed

in the ESD O^+ ion energy distribution. These additional peaks are attributed to the formation of a CO-H complex at the Pt surface. Based on these results and those of Schryer et al. (2), it is quite possible that the CO-H complex plays an important role in CO oxidation over Pt/SnO_x surfaces.

Although the molecular adsorption of CO on low index PT crystals is well documented and generally accepted, much controversy still exists in the literature regarding the adsorption of CO on high index Pt planes. Both molecular and dissociative adsorption of CO on high index planes have been reported. Iwasawa et al. (7) reported dissociation of CO at step and kink sites of a Pt(s) - 6(111) × (710) surface. In their experiment the adsorption of CO was monitored by ESCA, and the data show that the initial adsorption is dissociative as evidenced by the appearance of a carbide peak. Park et al. (8) have also reported dissociation of CO on Pt(410). In their ESCA data obtained from a CO-saturated Pt(410) surface, they observed C 1s and O 1s peak shifts. These peak shifts are similar to those observed during dissociation of CO on W(110) (9) and NO on Pt(100) (10). The O 1s peak shift is also characteristic of dissociative adsorption of O_2 on Pt. Li and coworkers (11, 12) determined by work function measurements obtained using field emission microscopy (FEM) that the dissociation of CO occurs at surface regions containing kinked edges including {210}, {320}, {430}, {520}, {310}, {410}, {741}, {321} and {1195}. They concluded that the extent of dissociation is proportional to the surface kink density which can depend upon the areas and structure of the terraces ({111}, {100}, {110}) and to the concentration of Si contamination.

Several other studies (13-16), have concluded that CO does not dissociate on the stepped or kinked areas of Pt. Lang and Masel (16) reported that CO adsorbs molecularly on Pt(210) and desorbs without dissociation upon heating. Furthermore, they observed no shifts in the O 1s and C 1s ESCA peaks upon heating the Pt(210) surface, which is contrary to their observations on Pt(410) (8). Hayden et al. (13, 14) concluded that molecular CO adsorption occurs on Pt(533) initially in a linearly bonded configuration at sites associated with the steps and with subsequent adsorption on terrace sites with a reduced sticking coefficient. These controversial results seem to vary from one surface to another and may depend upon surface cleanliness.

EXPERIMENTAL

The AES, ion scattering spectroscopy (ISS) and TPD data were acquired in an UHV system described previously (17). AES and ISS data were taken using a Perkin Elmer PHI model 15-255GAR double pass cylindrical mirror analyzer containing an internal electron gun. AES was performed using a 3 keV primary beam and standard nonretarding mode parameters. ISS was also performed in the nonretarding mode using a 1 keV, 100 nA $^4He^+$ primary beam at a 151.3° scattering angle. Short scanning periods and a defocused primary ion beam were used to minimize sputter damage. This results in a low signal-to-noise ratio but no loss in spectral information. The TPD spectra were obtained using a quadrupole mass spectrometer controlled by a computer program which regulates the heating and data acquisition and allows for the rapid collection of a mass spectrum. $^{13}C^{18}O$ (99 at% ^{13}C and 96.6 at% ^{18}O) was obtained from Isotec, Inc., Miamisburg, Ohio. In order to ensure proper heating of the Pt sample during the TPD experiments, two pieces of tantalum foil were spotwelded to both ends of the Pt foil sample, and then the assembly was mounted in the

sample holder. The sample was heated resistively by passing a current through the heater leads attached to the sample holder, and the temperature was monitored using a 0.05 mm chromel-alumel thermocouple spotwelded to the back of the sample. The sample was cleaned using repeated cycles of sputtering with 2 keV Ar^+ and heating to 1100°C in 10^{-7} Torr of O_2. ISS and AES spectra taken from the cleaned sample are shown in figure 1. A small amount of background CO adsorbed on the surface during the collection of the Auger spectrum.

RESULTS AND DISCUSSION

A. ISS Results

The clean sample was exposed to 1×10^{-8} Torr of CO for several time periods, and the ISS spectra shown in figure 2 were collected after the various CO exposures. Peaks due to Pt, C and O appear in these spectra. The amount of adsorbed CO appears to saturate at an exposure period of 120 s (1.2 L), and no more CO adsorbs at larger exposures. The height of the Pt peak obtained from a CO-saturated surface is about one-fifth of that obtained from a clean surface using all of the same experimental settings and conditions. This implies that saturation coverage of the polycrystalline Pt surface by the CO is about 0.8 of a monolayer. Barteau et al. (18) reported an initial sticking coefficient close to 1 for CO on Pt(100) (5 × 20) up to coverages of approximately 15% of a monolayer after which a decline in the sticking coefficient is observed. McCabe and Schmidt (19) found a similar decline at approximately 20% of a monolayer. ISS can also be used to determine the sticking coefficient as a function of coverage, and such experiments are in progress.

Spectral features other than those due to elastic scattering are also observed in figure 2. The peak at about 25 eV is due to secondary ions. The SIMS cross section for Pt is quite small so the small SIMS peak observed in the ISS spectrum obtained from the cleaned Pt may be due mostly to contamination, such as hydrogen, which does not yield an elemental ISS peak at the scattering angle used in this study. The SIMS peak increases with CO exposure and, therefore, gives another measure of adsorbate surface concentration. The ISS background due to inelastically scattered primary ions gives a measure of the electron mobility of the near-surface region. The background is quite small for the metallic surface, which has a high electron mobility, and decreases with CO exposure as the adsorbate concentration increases resulting in a decrease in the electron mobility at the surface (20).

Structural information can also be deduced from the ISS data shown in figure 2. Several possible bonding structures for CO on Pt are depicted in figure 3 along with the expected ISS spectra which would be obtained from each structure assuming that ISS detects only the outermost atomic layer. If the CO bonds vertically and completely covers the Pt, then only an O peak should be observed in ISS. If the Pt is not completely covered, then both an O and a Pt peak would be observed. In the case that CO bonds dissociatively or molecularly at an angle (perhaps parallel) to the surface, then both C and O peaks would be observed, and the size of the Pt peak would depend upon coverage. Furthermore, the ISS cross section is a strong function of mass and scattering angle. Since C and O have similar masses, their cross sections are not very different, but Pt is much more massive and has an ISS cross section which is

at least 40 to 80 times that of C or O. Thus, even when the outermost atomic layer contains mostly C and O, the Pt peak may be predominant. The ISS spectra shown in figure 2 suggest that the CO bonds either molecularly at some angle parallel to the surface, or dissociatively, and that the Pt is not completely covered as stated above. The results of the isotopic TPD experiments described below indicate that CO bonds molecularly to polycrystalline Pt. This and the fact that the C and O peaks are nearly the same size suggest that the CO bonds molecularly and probably parallel to the polycrystalline Pt surface. Using electron stimulated desorption-ion angular distribution (ESDIAD), CO bonded nonvertically to several surfaces has been reported; Mo(100) (21), W(100) (22), W(111) (23, 24), Pd(210) (25), Ni(110) (26), Pt(111) (27) and Pt(110)-(1x2) (14).

Figure 4 shows ISS data which were taken from a CO-saturated Pt surface after exposure to 1×10^{-8} Torr of O_2 at room temperature for various times. It appears that very little change occurs with exposure of this surface to O_2 at room temperature. In fact, any reduction in the amount of adsorbed CO is probably due to loss by ion sputtering. This experiment is consistent with the well-known result that metallic Pt does not catalyze CO oxidation at room temperature because the CO essentially saturates the surface so that O_2 cannot adsorb and react with the adsorbed CO by a Langmuir-Hinshelwood mechanism. Attempts were also made to adsorb O_2 on a cleaned Pt surface at 20 to 300°C and up to 10 Torr, but adsorbed oxygen could not be detected with ISS.

B. TPD Results

The TPD spectra shown in figure 5 were obtained by dosing the cleaned polycrystalline Pt surface with CO at 1×10^{-8} Torr for various periods. The predominant desorption peak occurs at 276°C regardless of coverage. This is characteristic of a first-order desorption process. With a heating rate β = 9.8 degrees/sec and assuming a frequency factor $\nu = 10^{13}$ sec^{-1} (28), the desorption energy of CO is 33.2 kcal/mole. A second lower-temperature desorption peak emerges at exposures greater than 0.6 L, which is consistent with previous TPD studies of CO from polycrystalline Pt (4-6, 14, 18). Although the origin of this peak is unclear, Hayden and coworkers (14) have attributed it to a phase transition in the CO overlayer at overages $\theta > 0.5$ which involves the onset of strong lateral interactions and tilting of the CO molecules.

Figure 6 shows a 2 amu TPD spectrum obtained after dosing the cleaned polycrystalline Pt surface with 9 L of H_2 at room temperature. In this case only one desorption peak appears regardless of coverage, and the desorption process is first order with a desorption energy of 22.4 kcal/mole. As expected, a similar TPD spectrum is obtained using D_2 rather than H_2.

Two and 28 amu TPD spectra obtained after dosing the cleaned polycrystalline Pt surface with a 3.6 L exposure of a 1:1 mixture of H_2 and CO at room temperature are shown in figure 7. In addition to the predominant peaks seen in figures 5 and 6 from adsorbed CO and adsorbed H_2, new peaks appear in the 2 amu spectrum at about 280°C, the CO desorption temperature, and in the 28 amu spectrum at about 101°C, the H_2 desorption temperature. These two new features indicate the formation of a surface CO-H complex, which is consistent

with the findings of Kawasaki (4) and Craig (5, 6). This experiment was repeated by coadsorbing D_2 and CO, and similar results were obtained as shown in figure 8.

The ISS data indicate that the CO covers about 80% of the Pt surface and that it bonds at an angle and possibly parallel to the surface or dissociatively. An isotopic TPD experiment was carried out to determine if the adsorption is molecular or dissociative. Using two separate leak valves, $^{12}C^{16}O$ (28 amu) and $^{13}C^{18}O$ (31 amu) were admitted into the system each at a partial pressure of 1×10^{-8} Torr. During the TPD experiments, the 30 amu signal due to $^{12}C^{18}O$) and 29 amu signal (due to $^{13}C^{16}O$) were monitored, but no isotopic mixing was found. This result demonstrates that CO adsorption on polycrystalline Pt is molecular. Unfortunately, it was not possible to determine the various surfaces and step and kink concentrations at this polycrystalline Pt surface.

CONCLUSIONS

ISS and TPD have been used to examine the adsorption and coadsorption of CO and H_2 on a sputter-cleaned and annealed polycrystalline Pt surface. The data indicate that CO adsorbs molecularly and probably parallel to the surface with an average sticking coefficient $S \geq 0.8$ and a saturation coverage of about 80%. Exposure of a CO-saturated Pt surface to O_2 results in no loss of adsorbed CO. This finding is consistent with the fact that Pt does not catalyze CO oxidation at room temperature. The coadsorption experiments indicate that a CO-H surface complex forms on polycrystalline Pt.


ACKNOWLEDGMENTS

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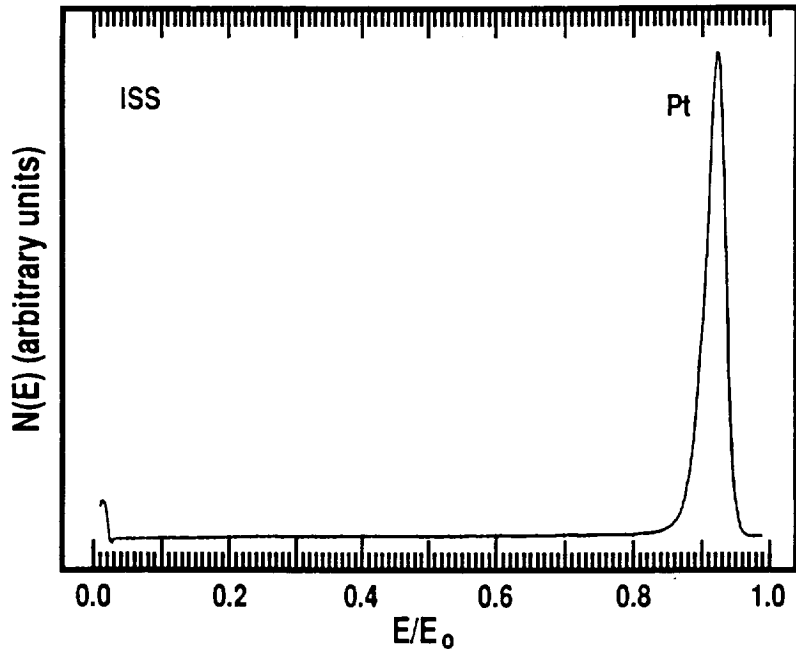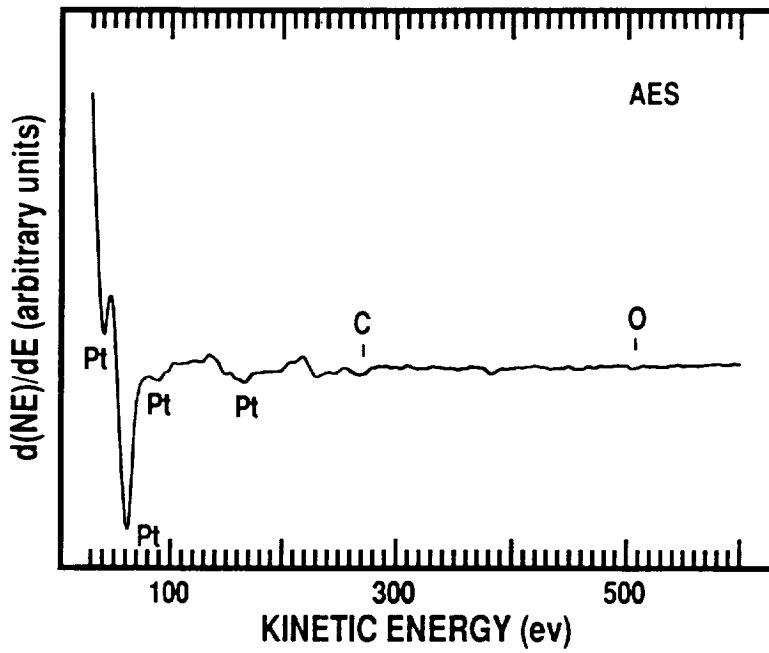
Figure 1. (A) ISS and (B) AES spectra taken from the cleaned polycrystalline Pt surface.

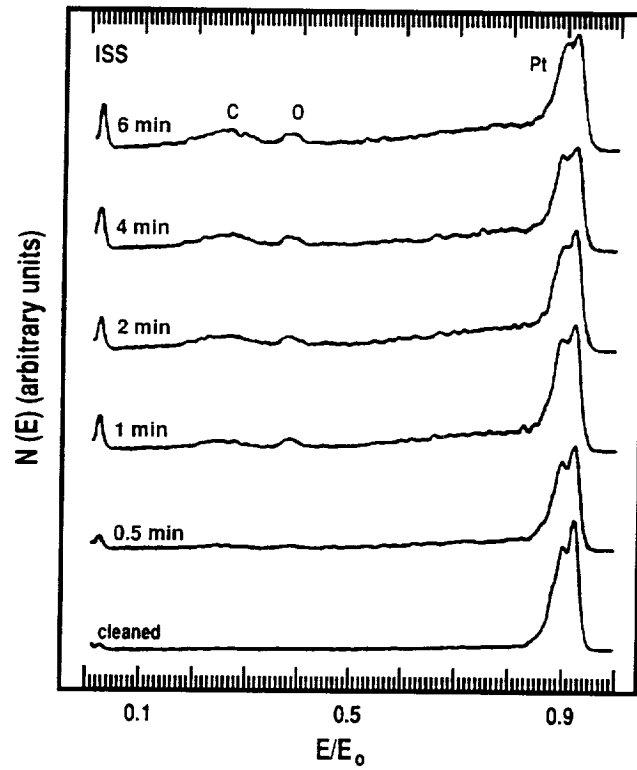Figure 2. ISS spectra taken from the polycrystalline Pt surface before and after exposure to 1×10^{-8} Torr CO at room temperature for 30 s (0.3 L), 60 s (0.6 L), 120 s (1.2 L), 240 s (2.4 L) and 360 s (3.6 L).
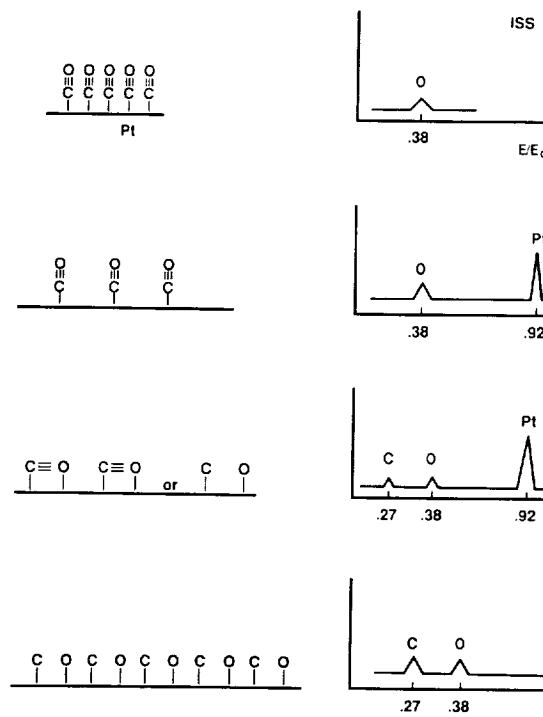

Figure 3. Various models for the adsorption of CO on a Pt surface and schematic ISS spectra which would be obtained from each bonding structure.
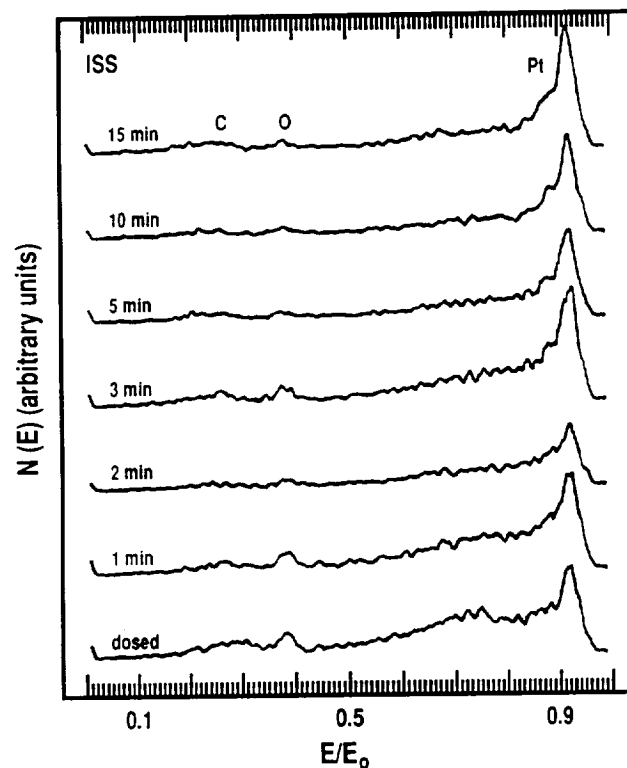
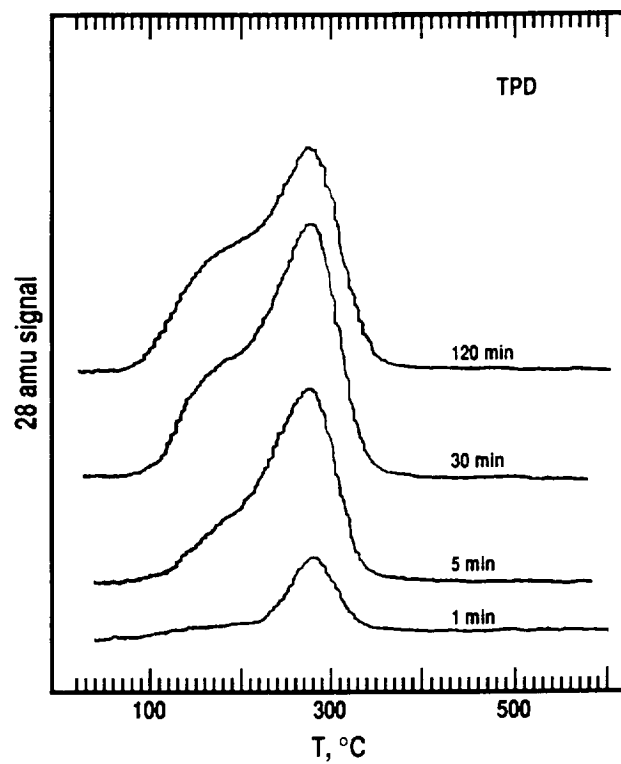Figure 4. ISS spectra taken from a CO-saturated polycrystalline Pt after exposure to
1×10^{-8} Torr of O_2 for various periods.

Figure 5. 28 amu TPD spectra obtained after exposing polycrystalline Pt to CO at
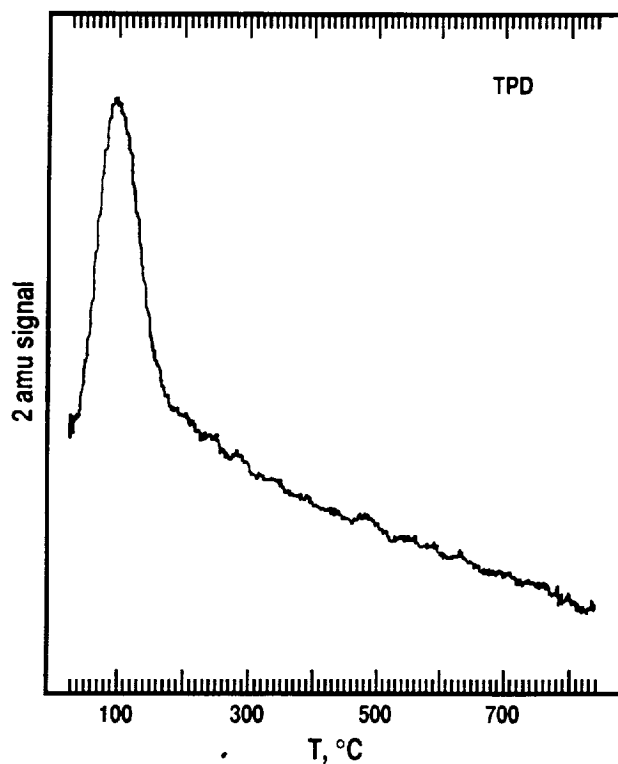1×10^{-8} Torr and room temperature for various periods.

Figure 6. 2 amu TPD spectrum obtained after exposing polycrystalline Pt to 1×10^{-8} Torr of H_2 for 15 minutes at room temperature.
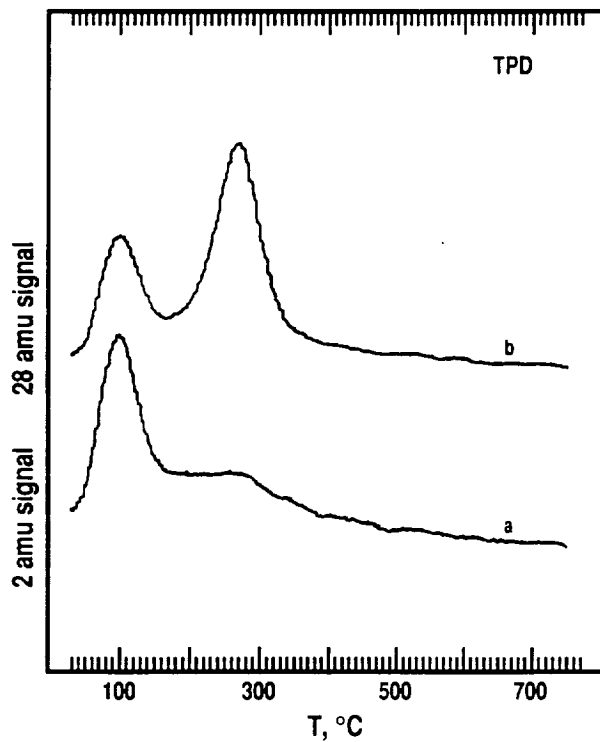

Figure 7. (a) 2 amu and (b) 28 amu TPD spectra obtained after exposing polycrystalline Pt to a 1:1 mixture of H_2 and CO for 3.6 L at room temperature.
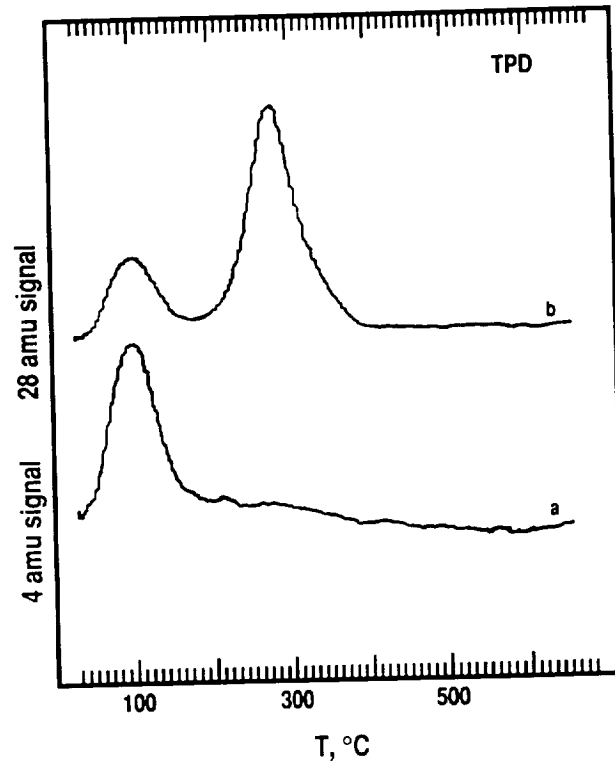
Figure 8. (a) 4 amu and (b) 28 amu TPD spectra obtained after exposing polycrystalline Pt to a 1:1 mixture of D_2 and CO for 3.6 L at room temperature.