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Temperature Programmed Desorption of Triethylamine from Differently Pretreated Pd/Al_2O_3 Catalysts*

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The temperature programmed desorption (TPD) of triethylamine from alumina and two alumina-supported palladium catalysts of different metal loadings (0.3 and 2.77 wt.% Pd) confirmed the presence of strong Lewis acid sites in the samples subjected to high temperature reduction at 600°C. With increasing temperature during thermodesorption, triethylamine adsorbed on Lewis acid sites of alumina undergoes transformation, leading to desorption of several products, among which hydrogen, ethylene and acetonitrile predominate. However, introduction of increasing amounts of palladium to alumina makes the acidity probing difficult, because a considerable part of adsorbed triethylamine is decomposed on metal sites. Temperature programmed oxidation (TPO) shows that the organic coke left after TPD of triethylamine is associated with acid sites of alumina, not with palladium sites. Another observation that pure alumina and 0.3 wt.% Pd/Al_2O_3 retained larger amounts of coke than the 2.77 wt.% Pd/Al_2O_3 catalyst reveals a beneficial role of palladium in desorbing organic material in the course of TPD runs.

Key words: triethylamine, temperature programmed desorption (TPD), Lewis acid sites, alumina, effect of pretreatment, Pd/Al_2O_3, temperature programmed oxidation (TPO)

Temperature programmed desorption (TPD) of ammonia and various organic bases like pyridine, lutidine, isopropylamine or butylamine plays an important role in testing surface acidity of a great number of solid catalysts [1–3]. Occurrence of more or less intense desorption peaks with maxima at different temperatures serves for evaluation of acid sites densities. Obviously, the significance of such diagnosis is strengthened if TPD tests are accompanied by other data, *e.g.* IR spectra of adsorbed amines or the heats of adsorption at different amine coverages [1,4].

Recently we investigated Pd/Al_2O_3 catalysts subjected to different pretreatments [5–7]. Highly reduced Pd/Al_2O_3 catalysts at 600°C exhibited a considerable increase of isomerization activity in the reaction of 2,2-dimethylbutane (and n-hexane) with dihydrogen. Such an activity enhancement was correlated with the (Lewis) acidity of

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*Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

alumina, which is known to be greatly increased upon high temperature pretreatment [8–12]. To furnish additional evidence, expected changes in the acidity in Pd/Al_2O_3 catalysts were probed by temperature-programmed desorption of ammonia [6] and pyridine [7].

As far as interpretation of desorption of organic bases from acidic oxide supports seems to be rather straightforward, the presence of deposited metal would make TPD spectra much more complex. A stronger binding of nitrogen-containing compounds (through nitrogen lone pair) to metal sites [13–17], in combination with usually high dehydrogenating capability of transition metals, should lead to a massive liberation of H_2, and, in consequence, to the formation of hardly removable molecular fragments. For instance, in thermal decomposition of trimethylamine on Pt(111) the C–N bond cleavage is accompanied by a massive dehydrogenation [17]. However, neither N- nor C-containing residues were detected in thermal decomposition of methylamine on Pd(111), when a clean Pd surface stayed after each cycle of thermal desorption [18].

In this work we have used triethylamine for testing acidity of alumina-supported Pd catalysts subjected to various pretreatments. After TPD of triethylamine runs, the amount and form of carbon left on differently pretreated catalysts were examined by temperature programmed oxidation.

EXPERIMENTAL

Two chlorine-free Pd/Al_2O_3 catalysts were studied, 0.3 and 2.77 wt.% Pd/Al_2O_3. They were previously tested and characterized after different pretreatments [5–7]. Briefly, the catalyst support was γ-Al_2O_3, Alumina, Shell 618, acid washed and sieved (75–120 mesh). The Pd/Al_2O_3 catalysts were prepared by impregnation with palladium acetylacetonate (99.8%, Alfa Produkte, Karlsruhe, Germany) diluted in a benzene (analytical grade from POCh, Gliwice, Poland) solution according to Boitiaux *et al.* [19].

Prior to TPD studies, the samples underwent three different pretreatments. First, they were subjected to low temperature reduction treatment (LTR), which was realized by precalcination under O_2 flow (25 cm^3/min) from room temperature (RT) to 400°C at 4°/min ramp, then cooling to RT in O_2 flow, and reduction in a 10% H_2/He stream (25 cm^3/min) with a temperature ramp of 8°/min to 300°C, and, finally cooled in helium to 100°C, which was selected as the temperature for adsorption of triethylamine. Second pretreatment was the high temperature reduction (HTR), which consisted in oxidizing the LTR sample under O_2 flow at 300°C for 0.5 h, and, after a short purge in He at 300°C, in reduction in H_2 flow at 600°C for 17 h. After reduction the sample was purged in He at 600°C for 1 h, and cooled to 100°C. Third pretreatment called “Regeneration“ denotes: sample investigated after HTR was oxidized under O_2 flow at 500°C for 1 h, then after a short purge in He at 500°C, reduced in H_2 at 300°C for 1 h, and, finally cooled to 100°C. The same sample pretreatments were applied prior to catalytic screening in alkane conversions [5–7] and metal dispersion measurements by hydrogen pulse chemisorption, as described elsewhere [6]. The LTR samples of 0.3 and 2.77 wt.% Pd/Al_2O_3 catalysts showed comparable metal dispersions, 0.23 and 0.3, respectively. Accordingly, they can be treated as suitable objects for our investigations, because the presence of similar in size Pd particles in two, differently metal-loaded catalysts, would help to obtain information about the acidity of alumina.

~0.26 g samples of Al_2O_3, 0.3 and 2.77 wt.% Pd/Al_2O_3 catalysts after different pretreatments were investigated by temperature programmed desorption of triethylamine (TEA, from Fluka, purum), using a mass spectrometer (M200 from Dycor-Ametek, Pittsburgh, PA) for identification of gaseous species liberated during the TPD run. After saturating a pretreated catalyst sample with TEA (in He stream) at 100°C, the flow of TEA was stopped and after half an hour purge in helium at 100°C, the catalyst was cooled to room temperature and the temperature was increased in a programmable fashion (10°C/min).

Next, the same samples were subjected to temperature programmed oxidation, (TPO, in 1% O_2/He, 25 cm^3/min, at 10°C/min ramp) to investigate the amount and form of carbonaceous species left after TPD runs. Main attention was focused at monitoring evolution of masses 44 (CO_2 formation)) and 32 (oxygen consumption). Changes in evolution of other masses (*e.g.* 18, 28 or 86) were negligible.

RESULTS AND DISCUSSION

All results of this work are presented graphically in Figures 1–6. Because identical mass signal intensity scale is used in each case and the same catalyst charges (~0.26 g) were studied, one can simply identify differences in the relative amounts of desorbed species. Subsequently, one can try to correlate obtained results with the palladium content in catalyst (0, 0.3 and 2.77 wt.%) and with the catalyst pretreatment (LTR, HTR and Regeneration). First, we present our results of TPD of triethylamine, then TPO studies of coke left on the catalysts subjected to TPD studies are discussed.

TPD of adsorbed triethylamine (TEA). Triethylamine is a stronger base than ammonia and, especially, pyridine, used by us in previous studies [6,7]. The use of molecules of different basicity would be advantageous in probing acid sites of variable distribution in differently pretreated alumina.

Fig. 1 shows TPD profiles of the most intense species liberated after adsorption of TEA on differently pretreated γ-alumina: hydrogen (m/z 2), acetonitrile (m/z 41), ethylene (m/z 28 confirmed by m/z 27) and TEA (m/z 86). The profiles for acetonitrile and ethylene were corrected by subtracting the intensity contribution of m/z 41 and

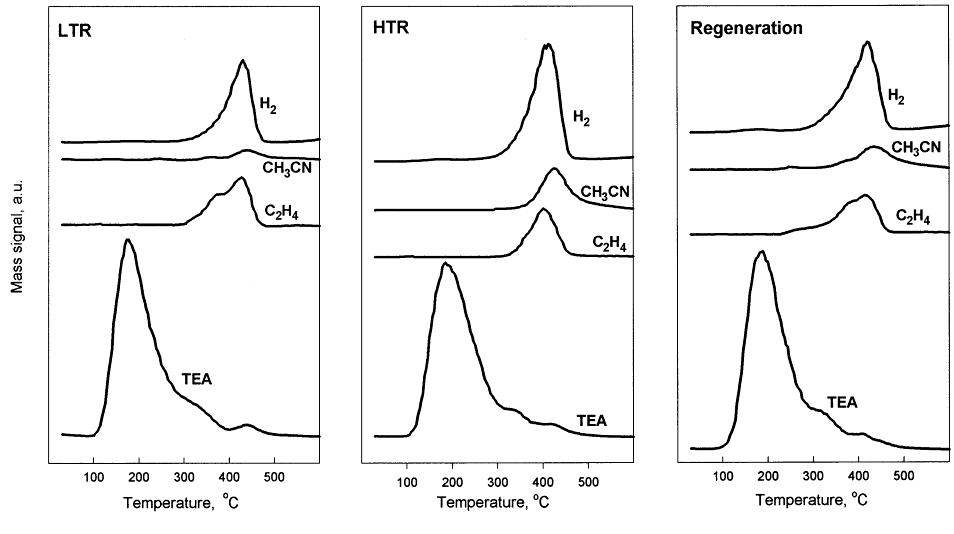

Figure 1. Temperature programmed desorption of TEA from γ-alumina after: LTR (left section), HTR (middle section) and Regeneration (right section). The intensities of liberated ethylene (from m/z 28) and acetonitrile (from m/z 41) were corrected by subtracting respective traces of m/z 28 and m/z 41 originated from the mass signal of released TEA.

m/z 28 from TEA. Fig. 1 demonstrates that much larger amounts of desorbing species are released after HTR and Regeneration than after LTR. The most important difference is seen in the intensities of desorbed acetonitrile and hydrogen. Neither ammonia nor nitrogen were detected among thermodesorption products. Evidently, the presence of strong Lewis acid sites in the HTR sample of alumina results in transformation of TEA, *via* a reaction similar to the Hoffman elimination reaction [20]:

$$(CH_3CH_2)_3N_{(ad)} \rightarrow CH_3CH_2N{=}CHCH_{3(ad)} + H_{2\,(g)} + CH_2{=}CH_{2\,(g)}$$

$$CH_3CH_2N{=}CHCH_{3\,(ad)} \rightarrow CH_2{=}CH_{2\,(g)} + CH_3CN_{(g)} + H_{2\,(g)}$$

Similar results were obtained in a static desorption study by Sokoll *et al.* [20] who also obtained considerable amounts of acetonitrile, hydrogen and ethylene desorbed at 325°C (desorption peak maxima) from highly pretreated alumina. The presence of adsorbed imine ($CH_3CH_2N{=}CHCH_3$) was substantiated by IR [20]. In our case, the maxima of desorbing species (H_2, CH_3CN and C_2H_4) are located at somewhat higher temperatures (maximum at $\geq$ 400°C) but the difference between our and Sokoll *et al.* results can be caused by different experimental conditions (flow *vs.* static desorption, different catalyst pretreatments and different sources of alumina used in both works).

Introduction of palladium to the catalysts makes the TPD spectra more complex (Fig. 2 and 3). A greater number of species, not detected in the desorption profile from alumina, are released. In some cases the presence of liberated NH_3, N_2, CH_4 and HCN is manifested. Although overall amounts of desorbed material (as judged from the

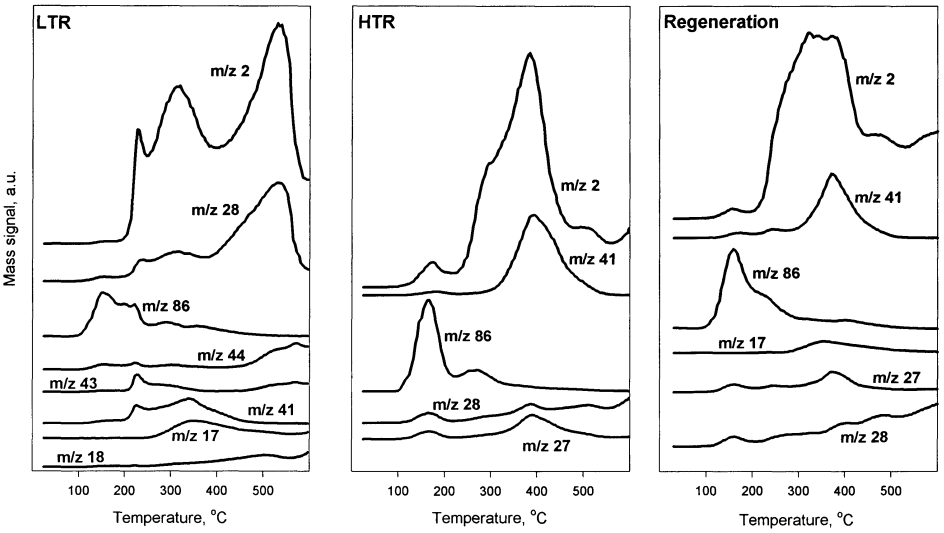

Figure 2. Temperature programmed desorption of TEA from 0.3 wt.% Pd/Al_2O_3 after: LTR (left section), HTR (middle section) and Regeneration (right section).

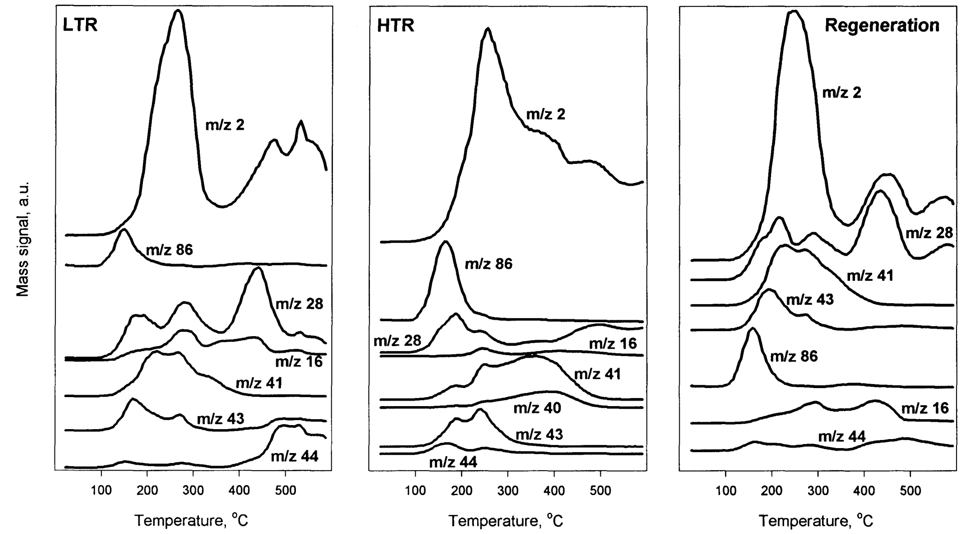

Figure 3. Temperature programmed desorption of TEA from 2.77 wt.% Pd/Al_2O_3 after: LTR (left section), HTR (middle section) and Regeneration (right section).

areas of desorption peaks) are roughly similar for all tested samples, nevertheless, apart from evolution of m/z 2 (H_2), 86 (TEA) and 28 (N_2, C_2H_4), the intensities of a vast majority of masses are rather low. This leads to some uncertainty in product identification.

Evolution of TEA (mass 86) is rather modest, especially for lowly pretreated Pd/Al_2O_3 catalysts, as compared to the situation with pure alumina. Therefore, the TEA adsorbed on palladium-containing catalysts must experience large transformations. Fig. 2 and 3 display very large amounts of liberated hydrogen (m/z 2) indicating massive dehydrogenation of the amine. Another large difference between TPD spectra of TEA from alumina and Pd-based samples is evolution of m/z 28. In the case of TPD from alumina, this mass (assisted by the trace of m/z 27) was unequivocally ascribed to desorption of ethylene (Fig. 1, especially middle and right sections). For Pd-containing catalysts, the m/z 28 follows from liberation of N_2, ethylene and, most probably, some not identified organic amine. Interestingly, the LTR samples of both Pd/Al_2O_3 catalysts and regenerated sample of 2.77 wt.% Pd/Al_2O_3 show massive desorption of m/z 28 at higher temperatures (> 400°C). Since evolution of this mass is accompanied by m/z 44, 18 and 43 (Fig. 2), we can cautiously consider desorption of some smaller alkylamine, like dimethylamine. Such belief should not be surprising because desorption of methane (m/z 16 assisted by m/z 15, not shown) and ethylene (m/z 28 assisted by m/z 27) were also found.

In effect, the presence of palladium complicates the acidity assessment in highly reduced Al_2O_3-supported catalysts. This problem is less severe in the case of the low metal-loaded, 0.3 wt.% Pd/Al_2O_3, catalyst where evolution of m/z 41 (acetonitrile) accompanied by m/z 2 (H_2) and 28 (ethylene) at 380–390°C resembles the analysis of Lewis acidity of highly reduced alumina (*vide supra*). In addition, similarly to the situation with alumina, Regeneration of the HTR sample of 0.3 wt.% Pd/Al_2O_3 brings about only modest decrease of acidity, assuming that acetonitrile evolution (at ~400°C) can be regarded as evidence for this property. For 2.77 wt.% Pd/Al_2O_3 subjected to HTR, acetonitrile (m/z 41 assisted by m/z 40, Fig. 3b) also desorbs at similar temperature. However, after Regeneration, m/z 41 appears at lower temperature, < 300°C (Fig. 3c), resembling the situation of the LTR sample (Fig. 3a). Such results are in full agreement with our earlier data [6,7], when the behaviour of differently pretreated Pd/Al_2O_3 catalysts in the reactions of 2,2-dimethylbutane and n-hexane with hydrogen was investigated.

TPO of residues left after TPD of TEA. Figures 4, 5 and 6 show TPO spectra from differently pretreated samples of alumina, 0.3 wt.% Pd/Al_2O_3 and 2.77 wt.% Pd/Al_2O_3, catalysts which were subjected to TPD of triethylamine. Only very small amounts of coke from the LTR sample of Al_2O_3 are burned off as CO_2 at ~500°C (Fig. 4, left section). We shall refer to this form of coke as to "hard coke". HTR (at 600°C) results in much more serious carbiding (Fig. 4, middle section), which is essentially unchanged after Regeneration (Fig. 4, right section). Introduction of small amounts of Pd (0.3 wt.% Pd/Al_2O_3) produces noticeable changes in TPO spectra (Fig. 5). After HTR and Regeneration, in addition to the hard coke, some amounts of coke are oxidized at much lower temperature, *i.e.* at ~270°C. Because this low-temperature form of coke was not observed in Fig. 5 (left section), we speculate that this coke must be still *associated with alumina*, not with palladium surface. Fig. 6 seems to confirm such an assumption. TPO of coke from the HTR-pretreated 2.77 wt.% Pd/Al_2O_3 also shows two forms of coke, but now the low-temperature form of coke dominates over the hard one (Fig. 6, middle section). And, analogously to the behaviour of 0.3 wt.% Pd/Al_2O_3, LTR of 2.77 wt.% Pd/Al_2O_3 shows the presence of hard coke, in small amount, comparable to that present in 0.3 wt.% Pd/Al_2O_3. We suggest that the low-temperature form of coke is deposited on the surface of alumina, which is located very close to metal particles. Our speculation is based on the following grounds: First, the absence of low-temperature form of coke in LTR samples of 0.3 and 2.77 wt.% Pd/Al_2O_3 catalysts (left sections of Fig. 5 and 6) allows us to disregard any presence of coke on palladium. This conclusion is in accord with recent work of Chen and Winograd [18], who showed that after TPD of methylamine adsorbed on Pd(111), the Pd surface stayed clean. Then, we find that the amount of low-temperature form of coke is correlated with the amount of metal in catalyst (Fig. 5 *vs*. Fig. 6, middle sections). It must recalled that our two differently metal-loaded catalysts (0.3 and 2.77 wt.% Pd) showed similar Pd particle sizes (see Experimental). The last observation leads to conclusion that the catalyst with a ten times higher metal loading (2.77 wt.%) must have roughly ten times larger Pd-Al_2O_3 boundary (per g_{cat}), so oxygen atoms produced *via* dissociative chemisorption of O_2 on palladium have a better access to larger portions of carbided alumina (*via* spillover). Carbonaceous species deposited on a more distant (from

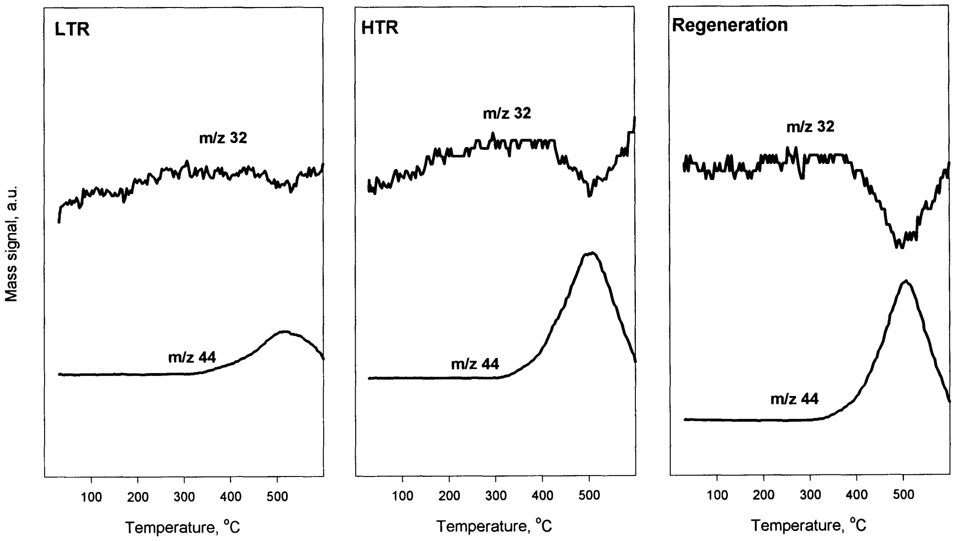

Figure 4. Temperature programmed oxidation of coke left after thermodesorption of TEA from differently pretreated γ-alumina. After: LTR (left section), HTR (middle section) and Regeneration (right section).

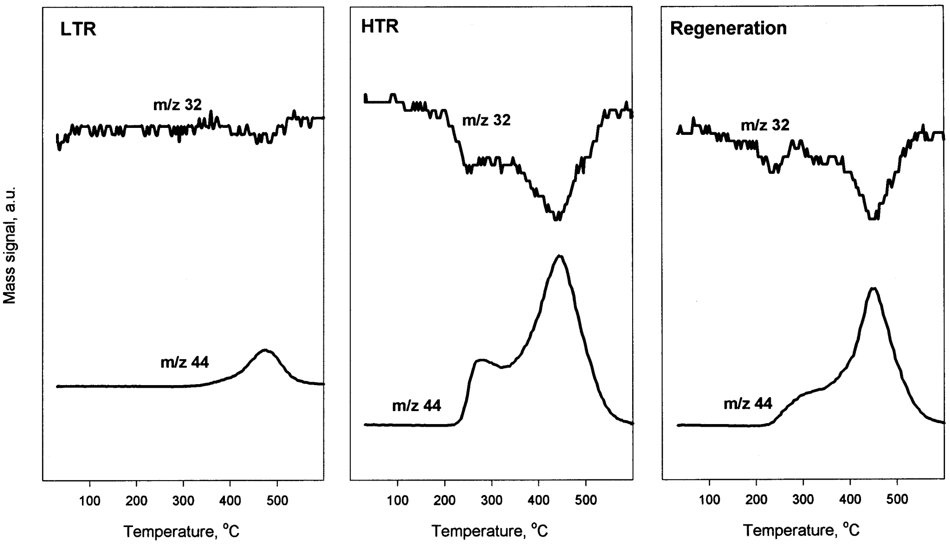

Figure 5. Temperature programmed oxidation of coke left after thermodesorption of TEA from differently pretreated 0.3 wt.% Pd/Al_2O_3. After: LTR (left section), HTR (middle section) and Regeneration (right section).

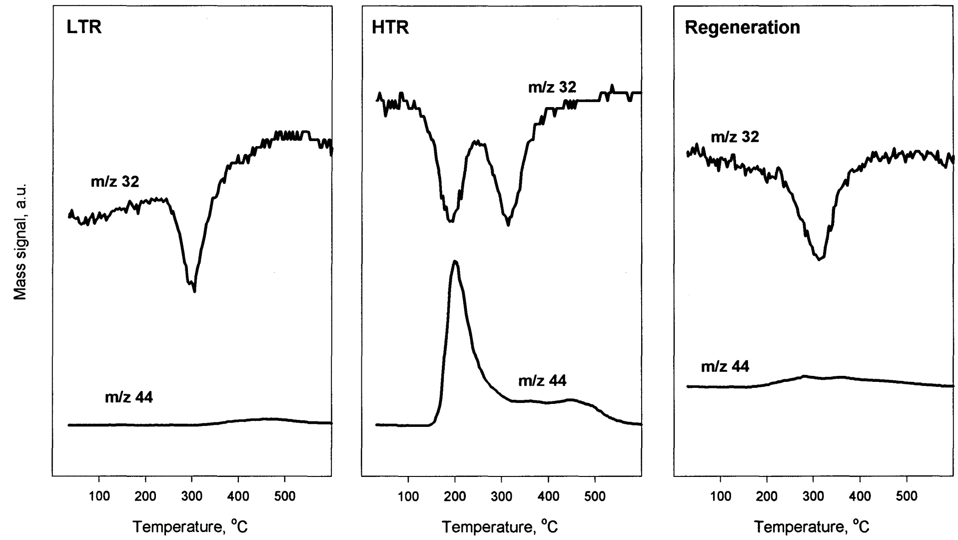

Figure 6. Temperature programmed oxidation of coke left after thermodesorption of TEA from differently pretreated 2.77 wt.% Pd/Al_2O_3. After: LTR (left section), HTR (middle section) and Regeneration (right section).

Pd) area of alumina become inaccessible for relatively short living oxygen atoms. Thus, this type of deposit (hard coke) can be removed by oxygen only at much higher temperatures.

Regeneration of 2.77 wt.% Pd/Al_2O_3 leads to a different result than the same pretreatment of 0.3 wt.% Pd/Al_2O_3, when the differences between TPO after HTR and Regeneration were rather small. As our previous results indicate [5,6], Regeneration returns the LTR behaviour for the high metal loaded Pd catalyst, *i.e.* almost completely removes the acidity generated upon HTR.

So far, we have not mentioned some additional oxygen consumption at 300–320°C, seen in Fig. 5 and 6. This effect, proportional to the amount of metal in catalyst, is associated with bulk oxidation of palladium and, of course, has not any mirror image in CO_2 formation.

CONCLUSIONS

The temperature programmed desorption of triethylamine from γ-Al_2O_3 and Pd/γ-Al_2O_3 catalysts showed the appearance of strong Lewis acid sites in the samples prereduced at 600°C. During thermodesorption, the presence of such acid centers is manifested by transformation of adsorbed triethylamine to several products, among which hydrogen, ethylene and acetonitrile predominate. Addition of palladium to alumina makes the acidity probing difficult, because a substantial part of adsorbed triethylamine is decomposed on palladium sites. Temperature programmed oxidation experiments showed that the organic coke left after thermodesorption of triethylamine is associated with acid sites of alumina, not with palladium sites.

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