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Temperature Programmed Desorption of Pyridine and 2,6-Dimethylpyridine from Differently Pretreated Pd/Al_2O_3 Catalysts

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The temperature programmed desorption (TPD) of pyridine and 2,6-dimethylpyridine from alumina and two alumina-supported palladium catalysts of different metal loadings (0.3 and 2.77 wt.% Pd) confirmed the presence of strong acid sites in the samples subjected to high temperature reduction at 600°C. Roughly similar amounts of both organic bases were desorbed from the catalysts which underwent similar pretreatments. However, 2,6-dimethylpyridine appears less strongly bonded than pyridine to Lewis acid sites in alumina, apparently because of some steric hindrance produced by the presence of methyl substituents in 2- and 6-position to the nitrogen lone pair. Thus, pyridine is better suited for probing evolution of Lewis acidity in alumina, brought about by high temperature reduction at 600°C. With increasing temperature during thermodesorption, both organic bases adsorbed on palladium-containing samples undergo transformation, leading to desorption of several products, among which hydrogen and nitrogen predominate. Introduction of increasing amounts of palladium to alumina makes the acidity probing difficult, because a considerable part of adsorbed organic base is decomposed on metal sites. Decomposition of pyridine and 2,6-dimethylpyridine may serve as a convenient probe of availability of palladium surface. After high temperature reduction of Pd/Al_2O_3 a considerable part of Pd surface is blocked by support species.

Key words: pyridine, 2,6-dimethylpyridine, temperature programmed desorption of (TPD), acid sites, alumina, effect of pretreatment, Pd/Al_2O_3

Adsorption and temperature programmed desorption (TPD) of ammonia and various organic bases like pyridine, lutidine, isopropylamine or butylamine play an important role in testing surface acidity of a great number of solid catalysts [1–5]. 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 [4,5].

Recently, we investigated Pd/Al_2O_3 catalysts subjected to different pretreatments [6–9]. Highly reduced Pd/Al_2O_3 catalysts at 600°C exhibited a considerable increase of isomerization activity in the reaction of C_6-alkanes with dihydrogen. Such an activity enhancement was correlated with the acidity of alumina, which is known to be greatly increased upon high temperature pretreatment [10–14]. To furnish additional evidence, expected changes in the acidity in Pd/Al_2O_3 catalysts were probed by temperature programmed desorption of ammonia [7] and triethylamine [8].

In this work, we decided to test acidity changes in differently-pretreated Al_2O_3 and Pd/Al_2O_3 catalysts, using two organic bases: pyridine (Py) and 2,6-dimethylpyridine (DMPy). Benesi [15] suggested that a direct comparison of interaction of these two bases with acid sites would distinguish between protonic (Brønsted) and aprotonic (Lewis) acidity of solids. It was considered, that the ability of DMPy to identify Lewis acid sites should be significantly constrained, because of a steric hindrance produced by two methyl substituents in 2- and 6-position to the nitrogen lone pair. In effect, DMPy would titrate mainly Brønsted acid sites. Consequently, the concentration of Lewis acid sites would be derived from the difference between the amount of adsorbed Py (total acidity) and the amount of adsorbed DMPy. Following Benesi [15], several workers have used substituted pyridines to probe acid sites in various solid oxides; even though Knözinger and Stolz [16] showed that 2,4,6-trimethylpyridine can still be (albeit more weakly) coordinated to Lewis acid sites in alumina. More recently, Aramendía *et al.* [17] and Haneda *et al.* [18] used the suggestion of Benesi to determine acid sites in various solids, including alumina. Satsuma *et al.* [19] showed that the level of purging temperature after DMPy adsorption on oxidic supports is important to discriminate between Brønsted and Lewis acid sites. After purging at relatively low temperature (*i.e.* below 250°C), the amount of (weakly) adsorbed DMPy is quite large. The spectrum after purging at 150°C shows a sharp desorption peak, having a maximum at ~220°C [19].

In connection with the present study of Pd/Al_2O_3 catalysts, it must be noticed that the presence of palladium deposited on alumina support would make TPD spectra of adsorbed bases much more complex than in the case of Pd-free alumina. A stronger binding of nitrogen-containing compounds (through nitrogen lone pair) to metal sites [20–23], in combination with usually high dehydrogenating capability of transition metals, should lead to a massive liberation of nitrogen and hydrogen, and, in consequence, to the formation of hardly removable carbon-containing molecular fragments. A preliminary part of TPD of Py from differently pretreated Pd/Al_2O_3 catalysts study has been published in [24].

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 [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.* [25].

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 to 400°C at 4^o/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^o/min to 300°C, and, finally cooled in helium to 100°C, which was selected as the temperature for adsorption of Py (DMPy). 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 [6–8] and metal dispersion measurements by hydrogen pulse chemisorption, as described elsewhere [7]. 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.

~0.27 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 Py (>99%, P.P.H. POCh "Naftochem", Kraków, Poland) or DMPy (>99%, BDH Chemicals Ltd., Poole, UK) 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 Py(DMPy) in a helium stream at 100°C, the flow of organic base was stopped and after half an hour purge in He at 100°C, the catalyst was cooled to room temperature and the temperature was increased in a programmable fashion (10°/min).

In the case of Py desorption, our main attention was focused at monitoring evolution of masses: 79 (Py), 28 (N_2), 2 (H_2) and 44 (CO_2). Evolution of Py was backed by other masses characteristic for this compound (*e.g.* 52, at ~80% abundance). In the case of DMPy desorption the m/z chosen were: 107 (DMPy, the base peak, backed by m/z 66), 28 (N_2), 2 (H_2) and 44 (CO_2). Changes in water evolution (masses 17 and 18) were also monitored.

RESULTS AND DISCUSSION

The use of molecules of different basicity would be advantageous in probing acid sites of variable distribution in differently pretreated alumina. DMPy (pK_a 6.7) is a stronger base than Py (pK_a 5.2) and for this reason the TPD of Py would be more informative in titration of stronger acidic centers. All basic results of this work are presented graphically in Figures 1 and 2. Because identical mass signal intensity scale is used in each case and the same catalyst charges (~0.27 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 Py, then those of DMPy.

TPD of adsorbed pyridine. The results of TPD of adsorbed Py are shown in Fig. 1. It may be seen that for all tested samples, *i.e.* pure alumina (Fig. 1(a)) and two Pd/Al_2O_3 catalysts (Fig. 1(b)and (c)), more Py desorbs after HTR than after LTR (peak maximum located at <200°C). In the case of pure Al_2O_3, HTR increases the amount of desorbed Py by *ca.* 30%, whereas for 0.3 wt.% Pd/Al_2O_3 the analogous change attains *ca.* 50%. Because this difference largely results from changes in the shape of the right-branch of TPD peak, at the 300–450°C range, it is considered that HTR generates stronger acid sites in alumina.

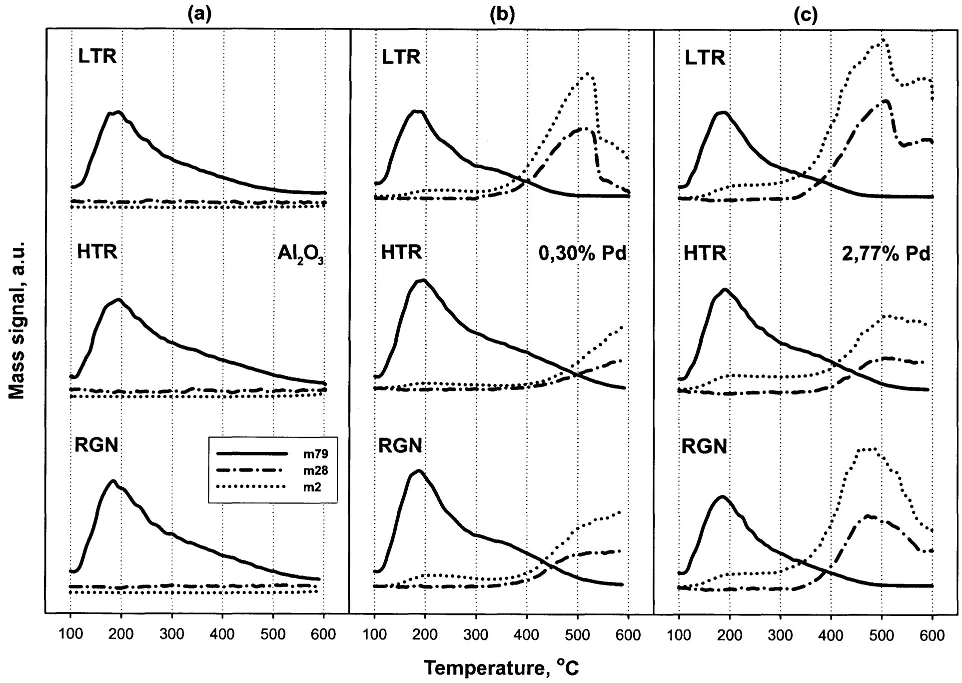

Figure 1. Temperature programmed desorption of pyridine (Py) from γ-alumina and two Pd/Al_2O_3 catalysts subjected to various pretreatments (LTR, HTR and "Regeneration" (RGN), for pretreatment code see text). Sections: (a) Al_2O_3, (b) 0.3 wt.% Pd/Al_2O_3 and (c) 2.77 wt.% Pd/Al_2O_3. Evolution of pyridine (mass 79), hydrogen (mass 2) and nitrogen (mass 28) are shown.

It is seen, that during TPD runs with differently pretreated alumina, only desorbed Py was detected in the gas phase (Fig. 1 (a)). On the other hand, for Pd-containing samples a significant portion of adsorbed Py is decomposed leading to a release of nitrogen, and, especially, hydrogen (Fig. 1 (b), (c)). Decomposition of adsorbed Py during TPD runs was found for several metal surfaces [26–32]. A part of Py adsorbed at low temperatures on Pt(111) surface desorbs after heating to room temperature, however, a significant part (50%) of this amine decomposes giving α-pyridyl fragment and hydrogen, which desorbs in few steps: at ~60°, ~240° and ~350°C [27]. In the present study, a massive release of hydrogen is noticed at well above 400°C and desorption of N_2 accompanies the hydrogen release. Three observations can be made here. First, the amount of hydrogen (and nitrogen) released during TPD from LTR samples seems to be directly correlated with the amount of metal in the sample. Therefore, we conclude that Py decomposition occurs on palladium surface. Second, the Pd/Al_2O_3 catalysts subjected to HTR liberate much less H_2 and N_2 than the LTR samples. It suggests that a considerable part of Pd surface is blocked in effect of HTR. Thus, it looks like the TPD of Py is a sensitive method in probing availability of exposed palladium surface. Third, in line with the previous suggestion, we conclude that "Regeneration" of HTR samples restores, to a considerable extent, accessibility of palladium surface, because hydrogen release is again well observed during TPD runs. This effect is better seen for the catalysts of a higher metal loading, *i.e.* for 2.77 wt.% Pd/Al_2O_3 (Fig. 1(c)) than for 0.3 wt.% Pd/Al_2O_3 (Fig. 1 (b)).

For the sake of clarity, CO_2 evolution (mass 44) is not presented in Fig. 1. Its liberation to the gas phase was only seen in the case of LTR and Regenerated Pd/Al_2O_3 samples. It suggests that oxidation of carbonaceous material (from Py) does not occur on highly dehydroxylated (*i.e.* HTR) samples.

Summing up, the TPD study of adsorbed Py furnished significant results, which are of a considerable value in diagnosing changes in differently pretreated alumina-supported metal catalysts. These changes concern both the state of metal and alumina support.

TPD of adsorbed 2,6-dimethylpyridine. The results of TPD of adsorbed DMPy are shown in Fig. 2. Again, as in the case of TPD of Py, massive amounts of hydrogen (and nitrogen) are liberated for Pd-containing samples, especially after LTR and "Regeneration". Also, restoration of H_2 and N_2 evolution by "Regeneration" is more complete for the catalysts of a higher metal loading, *i.e.* for 2.77 wt.% (Fig. 2 (c)) vs. 0.3 wt.% (Fig. 2 (b)). It should be noticed that hydrogen (and nitrogen) release

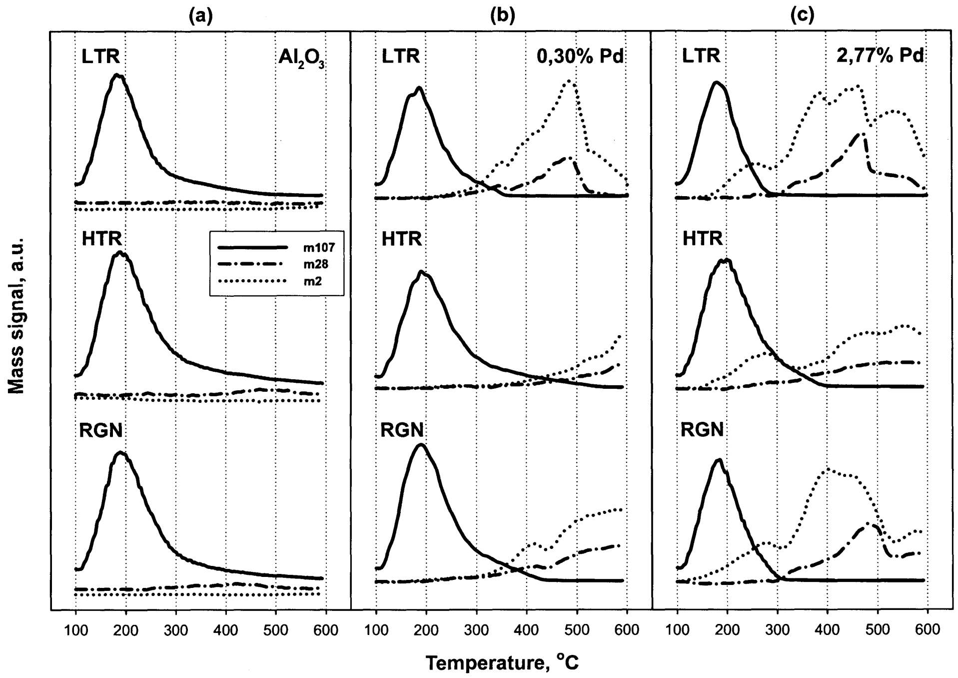

Figure 2. Temperature programmed desorption of 2,6-dimethylpyridine (DMPy) from γ-alumina and two Pd/Al_2O_3 catalysts subjected to various pretreatments (LTR, HTR and "Regeneration" (RGN), for pretreatment code see text). Sections: (a) Al_2O_3, (b) 0.3 wt.% Pd/Al_2O_3 and (c) 2.77 wt.% Pd/Al_2O_3. Evolution of 2,6-dimethylpyridine (mass 107), hydrogen (mass 2) and nitrogen (mass 28) are shown.

commences at lower temperature than the same observable fact when desorption of Py has been studied. This difference would indicate, that palladium interacts stronger with DMPy than with Py.

There are some similarities in Py and DMPy desorption. First, the amounts of released amines are similar. Also, the maximum of TPD peak of DMPy is located at <200°C, like in the case of Py desorption. However, the desorption peaks of DMPy are taller and sharper, *i.e.* a large right-branch tail seen in Py desorption does not occur for DMPy. This result would be rationalized using earlier findings of Knözinger and Stolz [16]. It seems, that DMPy can still be bonded to alumina, nevertheless its bonding to Lewis acid sites (Al^{3+} species) is weaker, due to some steric hindrance produced by methyl substituents. It is recalled that DMPy adsorption (and purging after adsorption) was realized at a relatively low temperature (100°C). Satsuma *et al.* [19] showed, that the level of purging temperature after DMPy adsorption on oxidic supports is important to discriminate between Brønsted and Lewis acid sites. After purging at relatively low temperature (*i.e.* below 250°C), then the amount of (albeit rather weakly) adsorbed DMPy is quite large.

Such results are in full agreement with our earlier data [6,7,9], 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. The Lewis acidity of alumina increased upon high temperature reduction is a source of enhanced isomerization activity exhibited by Pd/Al_2O_3 catalysts.

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REFERENCES

1. Malinowski S. and Marczewski M., in *Catalysis*, (Specialist Periodical Reports, The Royal Society of Chemistry, Cambridge), Vol. 8, 107 (1989).
2. Amenomiya Y., Chenier J.H.B and Cvetanović R.J., *J. Phys. Chem.*, **68**, 52 (1964).
3. Gorte R.J., *Catal. Lett.,* **62**, 1 (1999).
4. Knözinger H., *in* „Handbook of Heterogeneous Catalysis“ (G. Ertl, H. Knözinger, and J. Weitkamp, Eds.), Vol. 2, Chap. 3.2.3.3., p. 706, Wiley-VCH, Weinheim, 1997.
5. Kijeński J. and Baiker A., *Catal. Today*, **5**, 1 (1989).
6. Skotak M. and Karpiński Z., *Polish J. Chem*., **75**, 839 (2001).
7. Skotak M., Łomot D. and Karpiński Z., *Appl. Catal. A: General,* **229**, 103 (2002).
8. Skotak M., Kijeński J. and Karpiński Z., *Polish J. Chem.*, **77**, 757 (2003).
9. Skotak M., Karpiński Z., Juszczyk W., Pielaszek J., Kępiński L., Kazachkin D.W., Kovalchuk V.I., and d'Itri J.L., *J. Catal*., accepted.
10. Peri J.B., *J. Phys. Chem.,* **69**, 220 (1965).
11. Pines H. and Haag W., *J. Am. Chem. Soc.,* **82**, 497 (1960).
12. Knözinger H. and Ratnasamy P., *Catal. Rev. Sci. Eng.,* **17**, 31 (1978).
13. Morterra C. and Magnacca G., *Catal. Today,* **27,** 497 (1996).
14. Busca G., *Catal. Today,* **41**, 191 (1998).
15. Benesi H.A., *J. Catal*., **28**, 176 (1973).

16. Knözinger H. and Stolz H., *Ber. Bunsenges. Phys. Chem.* **75**, 1055 (1971).
17. Aramendía M.A., Borau V., Jiménez C., Marinas J.M., Porras A. and Urbano F.J., *Rapid Commun. Mass Spectrom*., **8**, 599 (1994).
18. Haneda M., Joubert E., Ménézo J.-C., Duprez D., Barbier J., Bion B., Daturi M., Saussey J., Lavalley J.-C. and Hamada H., *Phys. Chem. Chem.Phys*., **3**, 1366 (2001).
19. Satsuma A., Kamiya Y., Westi Y. and Hattori T., *Appl. Catal. A: General,* **194**–**195**, 253 (2000).
20. Kishi K., Kikui F. and Ikeda S., *Surf. Sci.,* **99**, 405 (1980).
21. Inamura K., Inoue Y., Ikeda S. and Kishi K., *Surf. Sci.,* **155**, 173 (1985).
22. Nakayama T., Inamura K., Inoue Y., Ikeda S. and Kishi K., *Surf. Sci.,* **179**, 47 (1987).
23. Albert M.R., *Appl. Surf. Sci.,* **158,** 120 (2000).
24. Skotak M. and Karpiński Z., *Chem. Eng. J*., **90**, 89 (2002).
25. Boitiaux J.P., Cosyns J. and Vasudevan S., in: *Preparation of Catalysts III* (Elsevier, Amsterdam), p. 123, 1983.
26. Di Nardo N.J., Avouris Ph. and Demouth J.E., *J. Chem. Phys*., **81**, 2169 (1984).
27. Grassian V.H. and Muetterties E.L., *J. Phys. Chem*., **90**, 5900 (1986).
28. Jacob P., Lloyd D.R. and Menzel D., *Surf. Sci*., **227**, 325 (1990).
29. Cohen M.R. and Merill R.P., *Surf. Sci*., **245**, 1 (1991).
30. Davies P.R. and Shukla N., *Surf. Sci*., **322**, 8 (1995).
31. Erley W., Xu R. and Hemminger J.C., *Surf. Sci*., **389**, 272 (1997).
32. Nunney T.S., Birtill J.J. and Raval R., *Surf. Sci*., **427**–**428**, 282 (1999).