Hydrogen chemisorption on Pt/Al_2O_3: dependence of hydrogen desorption behaviour on its surface concentration, on adsorption temperature and on surface water

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The hydrogen chemisorption on Pt/Al_2O_3 was investigated by temperature programmed desorption. The activation energy of desorption strongly depends on the hydrogen surface coverage. The chemisorption process is shown to be activated. High temperature H_2 desorption (spilled-over hydrogen) is due to reoxidation of reduced parts of the carrier surface by water or –OH groups.

Keywords: hydrogen; chemisorption; temperature programmed desorption; temperature programmed reduction; platinum catalyst

1. Introduction

The quantitative determination of chemisorbed hydrogen by temperature programmed desorption (TPD) [1] and by pulse adsorption (PA) [2] are standard methods [3,4] to characterize the dispersion state of supported platinum. Assuming a certain (H/Pt = 1) stoichiometry, one can estimate the dispersion of the metal from the H/Pt ratio. The temperature programmed reduction (TPR) of freshly prepared catalysts allows one to easily value the percentage of Pt [5].

Thus, these methods are common in practice, but from the very beginning of their application [2,6] up to now an exact interpretation of such measurements is complicated. The results of the hydrogen chemisorption capacity measurement for a given catalyst often depend on the method used and also on the measurement conditions [7–12]. The reasons are probably different forms of chemisorbed hydrogen [9,10,12] and its energetic inhomogeneity, well established for platinum black [13,14] but shown also for supported platinum [10,15]. Often high temperature H_2 desorption (HTD) after high temperature reduction by hydrogen has been reported [15–17] and related to the existence of hydroxyl groups on the surface.

TPR of previously oxidized or freshly prepared platinum catalysts shows some kind of high temperature H_2 consumption [5,18,19]. This hydrogen consumption occurs additionally to the reduction of Pt^{IV} [20].

To estimate the reliability of hydrogen chemisorption measurements, sensitiveness of such experimental results against the experimental parameters must be considered. Thus, we studied by means of TPD the influence of the hydrogen surface concentration, of the adsorption temperature and of the surface water concentration on the hydrogen chemisorption characteristics.

2. Experimental

2.1. Catalyst and equipment

The Pt/Al_2O_3 catalyst has been described in ref. [5] as catalyst A. It has been prepared by impregnating "Condea" γ-alumina (190 m^2/g, 0.05 wt% Fe) with a solution of H_2PtCl_6 in dilute HCl and contained 0.50 wt% Pt.

Gases were taken from commercial cylinders (AGA or Messer Griesheim). Oxygen and water traces in argon were removed by passing the gas under pressure (0.5 MPa) through traps filled with reduced Cu/MgO catalyst (Leuna 4492) at 353 K and with molecular sieve at room temperature, respectively (Wolfen Zeosorb A4, outgassed previously at 673 K in an Ar stream). Hydrogen and hydrogen/argon mixture (5.0 vol% H_2) were passed at 0.5 MPa through a Pd/Al_2O_3 catalyst before being dried by the mentioned molecular sieve. At the inlet of the gas selection unit these gases passed special cartridges (Hewlett Packard Indicating Oxygen Trap) to remove oxygen traces. Oxygen and air were purified by molecular sieve traps as described above.

The TPD/TPR apparatus (fig. 1) was equipped with two quartz reactors, located in one oven unit (10 ml each, one for measurement and one as reference). To measure the H_2 content in the argon, we used a micro catharometer connected with a signal amplifier. The catharometer and the pulse loop were thermostated at 393 K. The reactor unit with a CO_2 cooled trap on the outlet was located between comparison side and sample side of the catharometer.

The apparatus was calibrated by defined Ar pulses in the H_2/Ar stream (5% H_2) and H_2/Ar pulses in the Ar stream (1.80 ℓ/h each). The calibration factors at 1000 mbar were: 1 μmol H_2 = 492 mV min in H_2/Ar, corre-

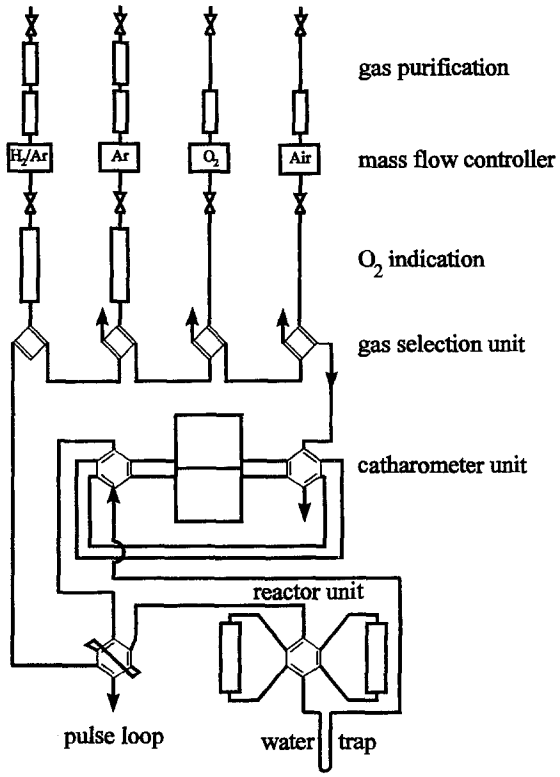


Fig. 1. Scheme of the apparatus.

sponding to 0.62 mV/ppm H_2; 1 μmol H_2 = 618 mV min in Ar, corresponding to 0.73 mV/ppm H_2. Ground fluctuation was about 0.1 mV.

Since the heating of the reactors causes a contribution to the gas flow, a "thermodesorption curve" of an empty reactor was to be expected. It equals 0.75 μmol H_2 and is to be considered. In TPR this thermic flow effect simulates a "negative consumption", but it is negligible in comparison with the TPR effects.

2.2. *Pretreatment of the samples*

Fresh samples (1 g) were outgassed and dried for 1 h at 473 K in an argon stream (1.8 ℓ/h), treated in oxygen (3.6 ℓ/h) for 1 h at 773 K and cooled down in oxygen to 373 K. After that, the gas feed was switched to argon and the reactor temperature decreased to 273 K.

In TPD experiments (heating rate 720 K/h) after oxygen pretreatment the sample was reduced in H_2/Ar at 773 K for 0.5 h. After reduction, the gas feed was switched to argon, a given adsorption temperature was established and then the argon flow was changed to H_2/Ar for 10 min. In this atmosphere the reactor was cooled down to 273 K. Before starting the temperature program, the sample was kept at 273 K for 10 min in the argon stream to displace the hydrogen/argon mixture.

PA experiments were performed after reduction at 773 K in H_2/Ar (0.5 h), followed by hydrogen desorption in an argon stream at the same temperature (1 h) and cooling down to 273 K. Reference pulses on the reference reactor were registered at the beginning and at the end of each experiment. The pulse loop was calibrated gravimetrically and contained 1.65 μmol H_2 (1.06 ml, 398 K, 1000 mbar, 5 vol% H_2/Ar).

TPR experiments were performed with a heating rate of 0.1 K/s (360 K/h) in a 1.80 ℓ/h stream of H_2/Ar (5% H_2).

3. Results

3.1. *Influence of hydrogen coverage on TPD*

To vary the hydrogen coverage we applied pulse adsorption (PA) at 273 K. Fig. 2 demonstrates the course of such an experiment. The catalyst chemisorbs about 3.5 pulses ($\sim$ 6 μmol H_2). Obviously, the hydrogen loaded catalyst influences the peak shape. The comparison pulses A–E are distinctly narrower and higher than the pulses 7–11 passing the hydrogen loaded catalyst. This effect, already mentioned by Freel [8], is caused by reversible adsorption/desorption processes and proves the existence of weakly bound hydrogen. In the peak maximum some hydrogen is adsorbed which gets desorbed later with the hydrogen concentration decreasing.

TPD profiles of hydrogen quantitatively characterize the desorption energy distribution [21,22]. The TPD patterns of the adsorbed hydrogen immediately after pulse sorption (fig. 3) are broad and poorly structured. Such spectra are also reported by other authors [9,10], and are interpreted as superimposition of different forms of chemisorbed hydrogen.

Fig. 4 shows the TPD curves after the adsorption of different numbers of hydrogen pulses (0–4 pulses,

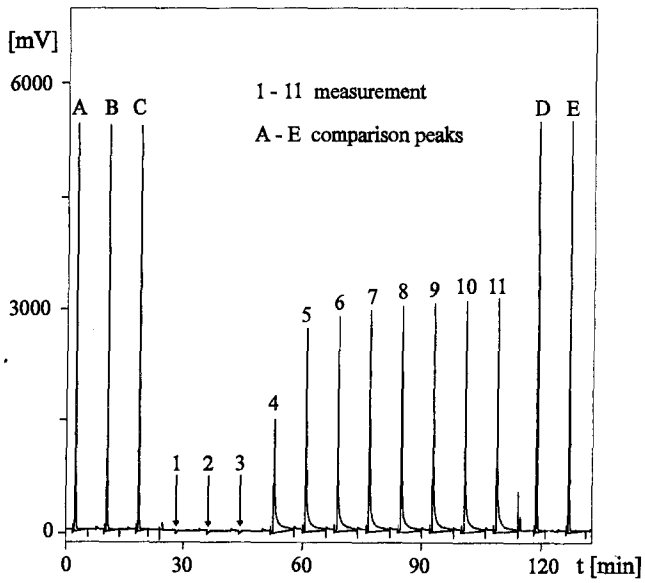


Fig. 2. Pulse adsorption on reduced Pt/Al_2O_3.

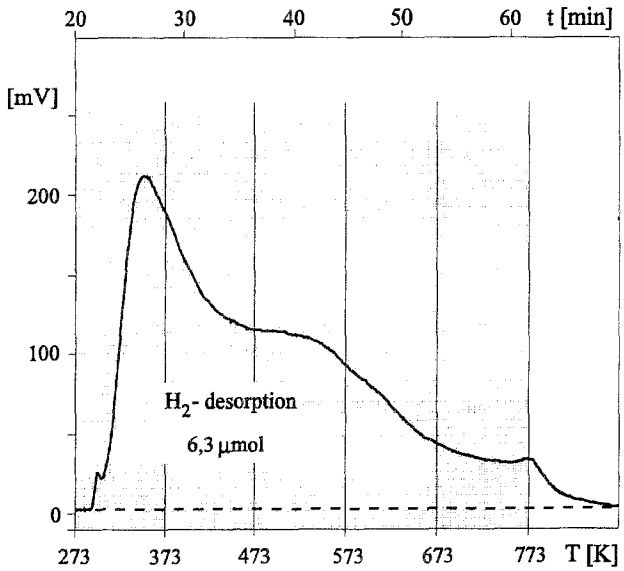


Fig. 3. Pulse adsorption on Pt/Al_2O_3, TPD after adsorption (H-loaded catalyst).

1.65 µmol H_2 each). Table 1 presents the relation between adsorbed and desorbed hydrogen amounts. The differences are due to H_2 desorption at high temperature.

3.2. *Influence of adsorption temperature*

With the hydrogen chemisorption on Pt/Al_2O_3 occurring without activation energy, the hydrogen–catalyst system is unambiguously determined by the chemisorption equilibrium conditions (H_2 pressure, chemisorption energy distribution, temperature). Its state would not depend on the way this equilibrium is attained. On the other hand, any dependence of the state of the system on the way to the TPD starting conditions indicates that either the hydrogen–metal interaction is an activated process or that the catalyst changes non-reversible with changing adsorption conditions.

Table 1
Relation between adsorbed and desorbed hydrogen amounts

Pulse	Adsorbed	µmol H_2 adsorbed	µmol H_2 desorbed	Difference (µmol)
0	0	0	0.3	+0.3
1	1	1.7	2.3	+0.6
2	2	3.3	4.0	+0.7
3	3	5.0	5.3	+0.5
4	3.6	5.9	6.1	+0.2
15 min exposition to H_2/Ar at 273 K, followed by 10 min blowing out H_2 in the Ar stream			7.6	

We performed measurements at different adsorption temperatures. Results are given in fig. 5. The shapes of the curves strongly depend on the adsorption temperatures (curve 1 773 K, curve 2 473 K, curve 3 273 K). This has been reported already by Tsuchiya [23] and Moger [24].

When rising the adsorption temperature from 273 to 473 K, the low temperature desorption peak at 360 K decreases, giving rise to the second peak at 500 K. The high temperature adsorption at 773 K results in a certain high temperature desorption (HTD) range ($T > 623$ K) with a peak maximum at 760 K. These effects do not depend on the sequence of the experiments, each adsorption temperature results in its typical TPD pattern.

TPR after oxygen treatment shows at this high temperature range some hydrogen consumption. The reduc-

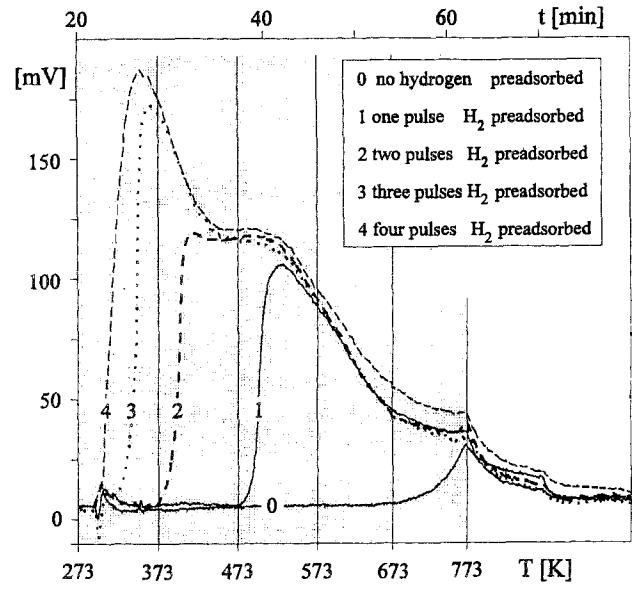


Fig. 4. Pulse adsorption on Pt/Al_2O_3, TPD after preadsorption of different amounts of hydrogen.

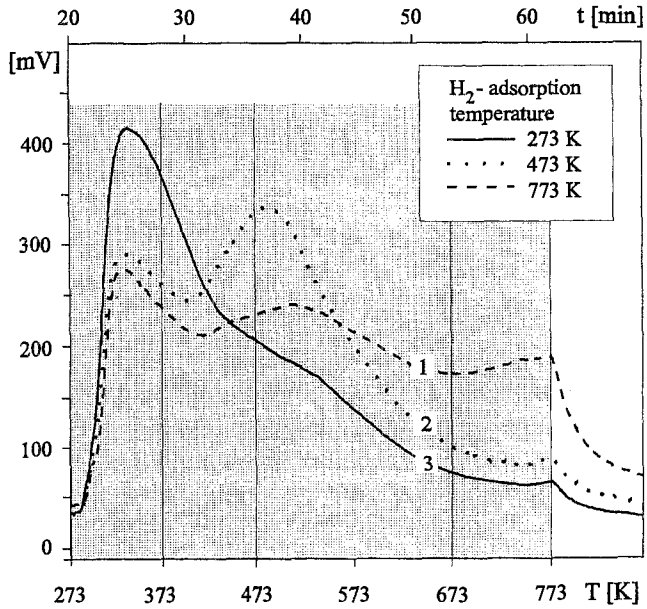


Fig. 5. Dependence of hydrogen TPD on the adsorption temperature.

tion peak of Pt (maximum temperature 530 K) merges into a broad shoulder (fig. 6). The total hydrogen consumption equals 59 μmol/g catalyst, with the reduction of Pt^{IV} requiring only 51 μmol/g.

3.3. *Effect of water*

The HTD of hydrogen occurs near the maximum temperatures the catalyst was exposed to. At these conditions the Al_2O_3 surface –OH groups become movable and could interact with reduced species on the carrier surface. In such case, water added to the catalyst should raise the HTD of hydrogen. Thus, we modified the adsorption temperature series of experiments: At the end of the exposure of the sample to the (dry) H_2/Ar stream at 273 K, the gas stream was saturated at room temperature with water (about 3 vol%) during the last 3 min before switching the gas line to argon. The dosage of water equals 10^{-4} mol or 3–4% of a monolayer (based on 10^{19} water molecules per m^2 and 190 m^2/g catalyst).

The results of the TPD after such water treatment compared to the "dry" experiments are shown in figs. 7–9. In every figure the solid line represents the "dry" and the dotted line the "wet" experiment. For all adsorption temperatures the HTD of H_2 is increased significantly. The 773 and 473 K experiments (figs. 7 and 8) additionally show a noticeable increase in the low temperature desorption area.

We provided an additional experiment using an oxidized sample with water dosage as mentioned. The TPD curve is identical to that of an empty reactor and shows, that our HTD areas are not caused by any water breakthrough.

TPD was provided also without previous hydrogen adsorption: The oxygen treated catalyst was reduced during 30 min at 773 K by the H_2/Ar mixture and then treated with argon at this temperature for 30 min to desorb any chemisorbed hydrogen. After that the catalyst was cooled down to 273 K and TPD was started. In a second run the sample was exposed additionally to wet argon for 3 min at 273 K. Fig. 10 shows that this exposure to water causes a remarkable amount of HTD hydrogen (dotted line).

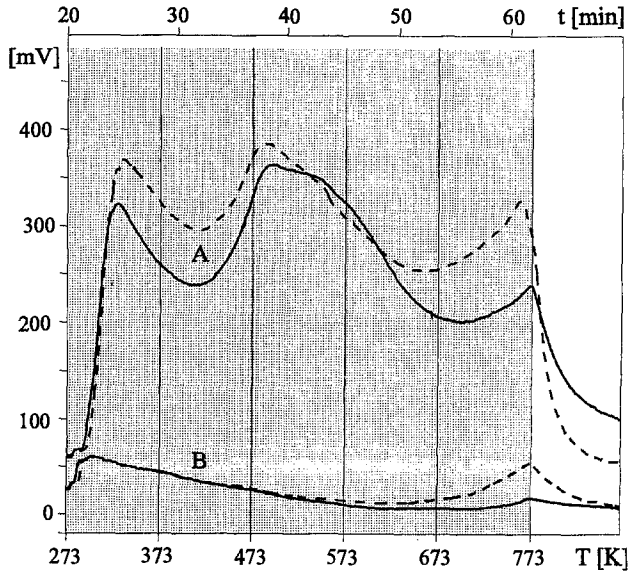


Fig. 7. Water influence on Pt/Al_2O_3 hydrogen chemisorption, adsorption temperature 773 K, (A) catalyst, (B) carrier, (——) "dry" experiment, (– – –) 100 μmol H_2O added at 273 K.

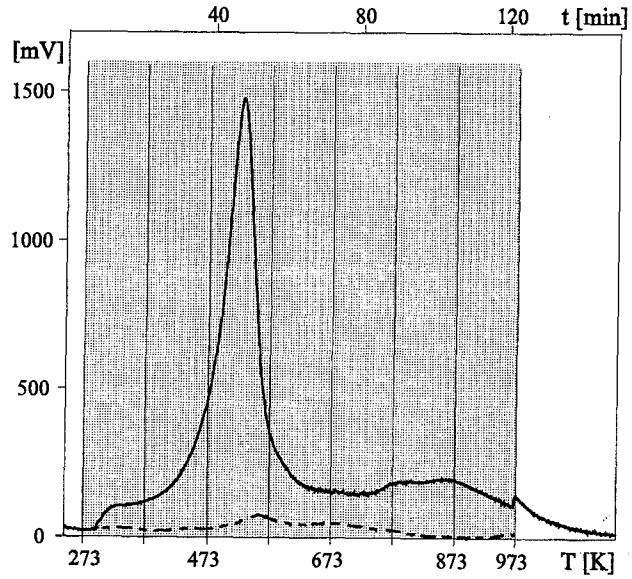


Fig. 6. TPR of the catalyst in comparison to the alumina carrier, (——) Pt/Al_2O_3, (– – –) Al_2O_3.

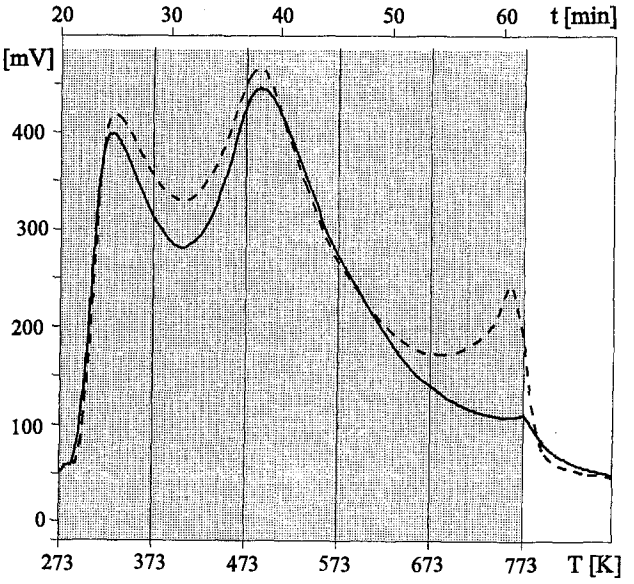


Fig. 8. Water influence on Pt/Al_2O_3 hydrogen chemisorption, adsorption temperature 473 K, (——) "dry" experiment, (– – –) 100 μmol H_2O added at 273 K.

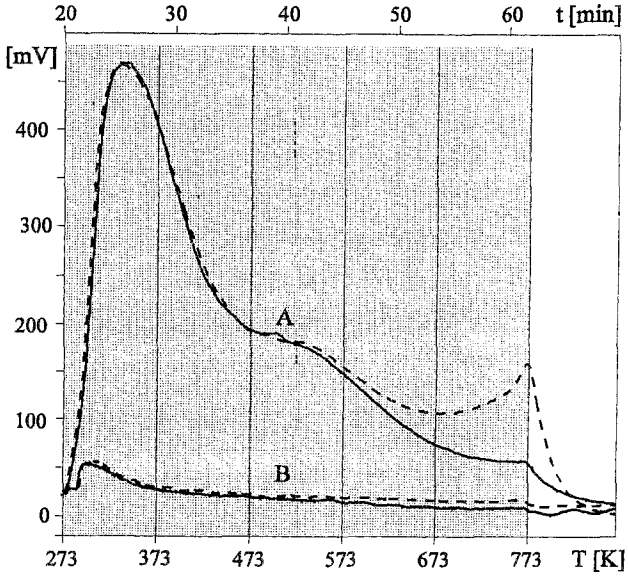


Fig. 9. Water influence on Pt/Al_2O_3 hydrogen chemisorption, adsorption temperature 273 K, (A) catalyst, (B) carrier, (——) "dry" experiment, (– – –) 100 μmol H_2O added at 273 K.

4. Discussion

As shown by the pulse experiments, the desorption energy of hydrogen strongly depends on the degree of surface coverage. The desorption curves in fig. 4 clearly prove the stepwise filling of an inhomogeneous adsorption area. In the case of two defined species of adsorbed H we would observe a stepwise growing up of the low temperature peak [14] after the high temperature peak is filled, as shown, for instance, in ref. [4].

Similar TPD patterns were reported by Gianantonio et al. [10]. These authors conclude, that it is, at least, necessary to differentiate between strongly and weakly adsorbed hydrogen. The problem one is faced with is, how to define the frontier between weak and strong adsorption. The methods, recommended by these authors, do not solve the problem.

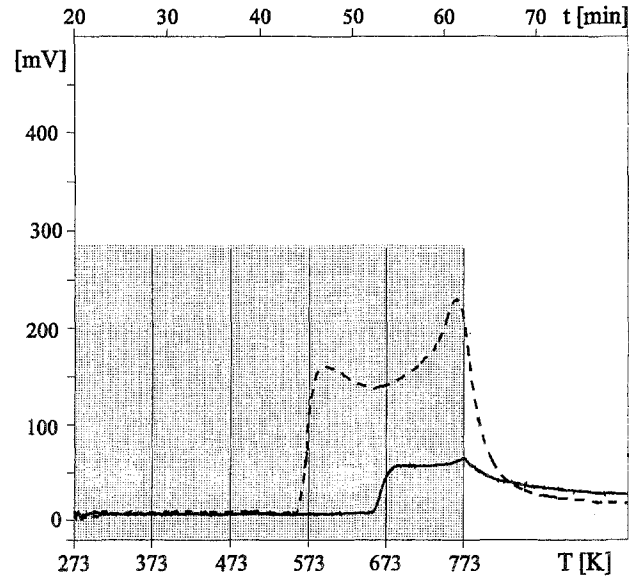


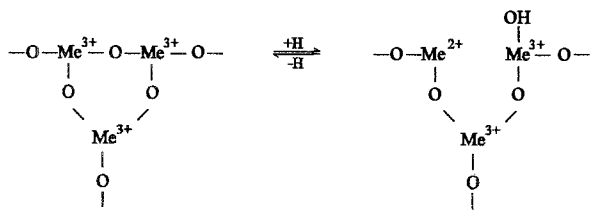
Fig. 10. Water effect on reduced Pt/Al_2O_3: hydrogen desorption without previous adsorption, (——) "dry" experiment, (– – –) 100 μmol H_2O added at 273 K.

A further question is connected with the difference between pulse adsorption and "long-time" hydrogen exposure, shown in table 1. 10 min of hydrogen outblowing should be enough to loose weakly adsorbed species. It seems that at 273 K the chemisorption is not quick enough to reach equilibration values for the pulses passing through the catalyst layer. Already in 1973 Karnauchov [25] published isobars of hydrogen chemisorption with a maximum at 350 K and recommended adsorption measurement at higher temperature (520 K). The adsorption temperature influences not only the amount of chemisorbed hydrogen. The distribution of desorption energy strongly depends on it, too. With rising adsorption temperature the desorption energy distribution shifts to higher values.

The most exciting question is the origin of the hydrogen desorbed at high temperatures. The HTD of hydrogen becomes noticeable with H_2 adsorption at enhanced temperatures only. At these temperatures we noticed some hydrogen consumption additionally to the Pt^{IV} reduction. Obviously, this excess consumption of hydrogen (8 μmol) is caused by reduction of surface impurities. The Condea γ-Al_2O_3 contains about 10 μmol Fe/g. Experiments with the carrier result in hydrogen consumption of about 5 μmol H_2. Reduction of the carrier surface itself cannot be excluded but seems not very probably.

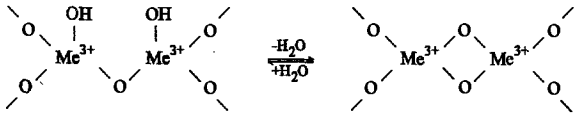
Exposure of the catalyst to dry argon at high temperatures decreases the amount of HTD of hydrogen. Exposure of reduced catalyst to water traces even results in hydrogen desorption, if no hydrogen was adsorbed previously.

All these facts can be simply explained: Under high temperature reduction conditions the alumina surface (impurities on it) is reduced by spillover hydrogen, forming –OH groups, as shown by the following scheme:



Thus, this hydrogen accumulation on the catalyst surface proceeds via a reversible redox reaction. *The spilled-over hydrogen consists of –OH groups and reduced cations (or metal atoms).* In the absence of H_2 and at temperatures equal to that of the previous pretreatment or higher, surface –OH groups can oxidize the reduced centres, releasing hydrogen.

The decrease of high temperature H_2 desorption after high temperature argon pretreatment (fig. 5, curves 2 and 3) can be interpreted as a result of surface dehydration. The –OH groups formed by surface reduction transform to –O– bridges:



This reaction occurs in every dry gas flow, but in H_2 containing atmosphere, the water production by reducing the surface of the carrier is particularly compensating the water loss. Dry argon, therefore, causes more effective dehydration.

In this context it is worth mentioning, that the high temperature hydrogen desorption has been usually connected with the existence of –OH groups or water:

– In recent papers [16,17] Modica, Miller, Meyers and Koningsberger have investigated K-containing Linde LTL zeolites. The amount of high temperature desorbed hydrogen strongly depended on the K/Al ratio and the H_2 desorption temperature was similar to the dealumination temperature of such kind of zeolite. For a given zeolite module the K/Al ratio defines the amount of the acid –OH groups and the dealumination would produce water.

– Boron modification of the Pt/Al_2O_3 catalysts also increases the –OH surface concentration [26] and the high temperature H_2 desorption [27].

In our opinion, the hydrogen activated by Pt (spill-over hydrogen) causes the surface reduction: As shown above in fig. 6, the high temperature reduction shoulder occurs only in the TPR of the Pt-containing catalyst. The TPR of the carrier does not show any high temperature hydrogen consumption.

The high temperature H_2 desorption (usually interpreted as spilled-over hydrogen) occurring under TPD conditions is the result of the reoxidation of reduced surface sites by water or –OH groups.

The catalytic effect of spilled-over hydrogen, reported for instance in ref. [17], can be connected with the appearance of moderate base–acid site pairs, as shown by the scheme above, and, may be, with the general decreasing of the acidity because of the surface reduction. Hydrogen desorbed during surface reoxidation by water can be rather reactive on the analogy to hydrogen in statu nascendi.

Exposition of the reduced surface to a dry argon stream decreases the amount of high temperature H_2 desorption and increases the activity for methylcyclohexene dehydrogenation [12]. This could be due to an increase of the amount of Lewis sites on the surface, generated by dehydration.

The hydrogen chemisorption on Pt/carrier catalyst is a complex process without simple stoichiometry. Dispersion values obtained this way must be interpreted with caution. To exclude the superimposition of hydrogen desorbed from the metal and hydrogen released by the interaction of the reduced carrier with water, more detailed investigations of hydrogen chemisorption are to be performed.

5. Conclusions

The TPD spectra of hydrogen chemisorbed on Pt/Al_2O_3 demonstrate the complex character of the surface–hydrogen interaction:

– The hydrogen, chemisorbed on Pt/Al_2O_3, is energetically inhomogeneous.

– The hydrogen desorption energy distribution is a steady non-discrete function of the hydrogen surface concentration.

– This energy distribution function strongly depends on the adsorption temperature and gives evidence for activated chemisorption processes.

– This energy distribution function depends also on the surface water content.

– High temperature hydrogen desorption (> 650 K) takes place only after high temperature surface reduction (> 450 K). It occurs as the result of surface reoxidation by water or –OH groups.

Any quantitative interpretation of hydrogen chemisorption experiments must consider not only the amount of hydrogen chemisorbed but also its chemisorption energy distribution.

References

[1] G. Ehrlich, Adv. Catal. 14 (1963) 255.
[2] H.L. Gruber, Anal. Chem. 34 (1962) 1828.
[3] J.R. Anderson and K.C. Pratt, *Introduction to Characterization and Testing of Catalysts* (Academic Press, New York, 1985) chs. I, V.
[4] G.K. Boreskov, *Geterogennyj Kataliz* (Heterogeneous Catalysis) (Nauka, Moscow, 1986) ch. V.
[5] H. Lieske, G. Lietz, H. Spindler and J. Völter, J. Catal. 81 (1983) 8.
[6] S.D. Robertson, B.D. Mc Nicol, J.H. de Baas, S.C. Kloet and J.W. Jenkins, J. Catal. 37 (1975) 425.
[7] J. Prasad and P.G. Menon, J. Catal. 44 (1976) 314.
[8] J. Freel, J. Catal. 25 (1972) 139, 149.
[9] E. Rockova, J. Catal. 48 (1977) 137.
[10] R. Gianantonio, V. Ragaini and P. Magni, J. Catal. 146 (1994) 103.
[11] A. Frennet and P.B. Wells, Appl. Catal. 18 (1985) 243.
[12] A. Rochefort, F. Le Peltier and J.-P. Boitiaux, J. Catal. 145 (1994) 409.
[13] D.V. Sokolskij, *Gidrirovanie v Rastvorach* (Hydrogenation in Solutions) (Izdatel'stvo Akademii Nauk Kazachskoj SSR, Alma Ata, 1962).
[14] V.I. Jakerson and V.V. Rozanov, *Issledovanie Katalitičeskich Sistem Metodami Termodesorbcii i Termochromatografii* (VINITI, Moscow, 1974) p. 114.
[15] P.G. Menon and G.F. Froment, J. Catal. 59 (1979) 138; Appl. Catal. 1 (1981) 31.

[16] J.T. Miller, B.L. Meyers, F.S. Modica, G.S. Lane, M. Vaarkamp and D.C. Koningsberger, J. Catal. 143 (1993) 395.
[17] S. Modica, J.T. Miller, B.L. Meyers and D.C. Koningsberger, Catal. Today 21 (1994) 37.
[18] P. Birke, D. Bohm and S. Engels, Z. Chem. 25 (1985) 74.
[19] S. Engels, J. Haupt and H. Lausch, Z. Phys. Chem. 269 (1988) 463.
[20] H. Ehwald, U. Kürschner and G. Alscher, XXVI Jahrestreffen deutscher Katalytiker 1993, Preprints p. 75.
[21] K. Hashimoto, T. Masuda and T. Mori, Stud. Surf. Sci. Catal. 28 (1994) 503.
[22] M. Arai, Y. Nishiyama, T. Masuda and K. Hashimoto, Appl. Surf. Sci. 89 (1995) 11.
[23] S. Tsuchiya, Y. Amenomiya and R.J. Cvetanovic, J. Catal. 44 (1970) 314.
[24] D. Moger, M. Hegedüs, G. Besenyei and F. Nagy, Act. Chim. (Budapest) 93 (1977) 289.
[25] A.P. Karnauchov, *Investigation Methods for Catalysts and Catalytic Reactions*, Vol. 4 (Institute of Catalysis, Siberian Branch of the Academy of Science of USSR, Novosibirsk, 1971) p. 96, in Russian.
[26] V. Vorobev, A. Agzamkhodzhaeva, V. Mikita and M. Abidova, Kinet. Katal. 25 (1984) 190.
[27] C. Li, Appl. Surf. Sci. 74 (1994) 171.