Catalysis Letters 31 (1995) 165–172

Hydrogen spillover phenomena on Pt / ZrO_2

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Received 13 June 1994; accepted 15 December 1994

A Pt/ZrO_2 catalyst has been investigated by temperature-programmed reduction and temperature-programmed desorption of hydrogen. Hydrogen spills over from Pt onto the ZrO_2 surface at about 550°C. One part of spillover hydrogen is consumed by a partial reduction of zirconia. The other part is adsorbed on the surface and is desorbed at about 650°C. This desorption is a reversible one, i.e. it can be followed by a renewed uptake of spillover hydrogen. No connection between dehydroxylable OH groups and spillover hydrogen adsorption has been observed. The adsorption sites for the reversibly bound spillover hydrogen were possibly formed during the reducing hydrogen treatment.

Keywords: zirconia; platinum; hydrogen spillover; reversible desorption; TPR; TPDH

1. Introduction

Recently, Miller et al. [1] investigated the hydrogen adsorption properties of metallic Pt, supported on zeolites, γ-Al_2O_3 and SiO_2. With all these catalysts, they found chemisorption of hydrogen on metallic Pt, which was reversible at approximately 175°C. In addition to that hydrogen chemisorbed on Pt, spillover hydrogen was observed, which was desorbed from the support surface at essentially higher temperatures. The desorption proved to be "irreversible", i.e. the spillover of hydrogen from Pt onto the support surface could not be repeated after the high temperature desorption. Since the quantity of the irreversibly desorbed spillover hydrogen was found to be related to the number of surface OH groups, the authors suggested that the spillover hydrogen is stabilized by OH groups and that the irreversibility of the desorption, i.e. the non-repeatability of the adsorption, results from support dehydroxylation at high temperature.

Using temperature-programmed reduction (TPR), temperature-programmed desorption of hydrogen (TPDH), hydrogen chemisorption and *n*-hexane conversion as a catalytic test, we recently investigated the influence of hydrogen high temperature treatments on the properties of a ZrO_2 support and of a Pt/ZrO_2 catalyst

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[2]. In that paper, a hydrogen spillover from platinum onto the zirconia surface had already been suggested. However, in ref. [2] we did not examine the reversibility of the spillover hydrogen adsorption/desorption nor a possible connection between hydrogen spillover and dehydroxylation of the zirconia support.

In this paper we report some results of TPR and TPDH on another Pt/ZrO_2 catalyst sample. We shall demonstrate that the *hydrogen spillover adsorption after high temperature treatment is repeatable, which is in contrast to other systems* [1], and that the *hydrogen spillover adsorption is independent of the dehydroxylation state* of zirconia.

2. Experimental

2.1. CATALYST PREPARATION

Zirconia, containing 3.5% SiO_2 as a stabilizer, was supplied by MEL Chemicals, UK. The material was dried at 120°C for 12 h and thereafter calcined at 600°C in air for 4 h. The specific surface area amounted to 130 m^2/g. After TPDH1, the surface area decreased to 98 m^2/g, because of sintering at the high final temperature (800°C) of this procedure. X-ray diffraction proved a tetragonal structure of the material. The Pt/ZrO_2 catalyst was prepared by impregnating the calcined ZrO_2 with an aqueous $[Pt(NH_3)_4](NO_3)_2$ solution, drying at 120°C for 4 h and calcination at 500°C for 4 h. The Pt content amounted to 0.5 wt%.

2.2. CATALYST CHARACTERIZATION

TPR and TPDH. TPR and TPDH measurements were performed using the dynamic characterization system AMI-1 (Altamira, Inc.). Catalyst samples (500 mg) were heated to 500°C and kept at this temperature for 1 h in a dried flow of 20% O_2 in He, in order to remove water and organic contaminations. After this calcination, catalyst samples were cooled in a helium flow to room temperature and the first TPR run, TPR1, was carried out in an argon flow containing 5.17% hydrogen at a gas flow rate of 40 ml/min and a heating rate of 20 K/min. The TPR runs were finished by an isothermal period of 1.0 h at the final temperature of 550°C. Hydrogen consumption was detected by a thermal conductivity detector. After the TPR runs, the samples were cooled to room temperature in the hydrogen containing gas flow, with hydrogen being adsorbed at the respective temperatures. The adsorption was followed by the first TPDH run, TPDH1, in an argon flow (70 ml/min) at a heating rate of 20 K/min, up to 800°C. Desorbed gases were quantitatively monitored by a QMG-420C quadrupole mass spectrometer, QMS, (Balzers), which operated in the multiple ion detection mode. Catalysts were kept at 800°C for 30 min and cooled down again to room temperature in argon. After TPDH1, the second TPR run, TPR2, was performed under the conditions of TPR1, without the sample being contacted with air between TPDH1 and TPR2. TPR2 was followed by cooling down the samples in the hydrogen containing gas flow before the second TPDH run, TPDH2. This was carried out at the conditions of TPDH1.

3. Results and discussion

3.1. PRECEDING INVESTIGATION OF ZIRCONIA

Preceding TPR and TPDH experiments on the platinum free zirconia revealed differing behaviours of different zirconia types. In contrast to previous results obtained on a ZrO_2 sample prepared in our laboratory [2], the zirconia investigated in the present study surprisingly did not exhibit any hydrogen consumption during TPR and neither any hydrogen desorption during TPDH, see fig. 1, curve a and fig. 2, curve a. This differing behaviour may be due to the different structures of the two samples. The former sample was monoclinic, whereas the latter one was of tetragonal structure, probably because of the stabilizing action of the SiO_2 addition. It is known that the methods of preparation and certain additions can strongly influence the structure and, therefore, also the properties of zirconia [3–6].

3.2. TPR AND TPDH PEAK ASSIGNMENT

The TPR and TPDH profiles obtained on the Pt/ZrO_2 catalyst are shown in fig. 1, curves b and c, and in fig. 2, curves b and c, respectively, together with the corresponding amounts of hydrogen consumption or desorption.

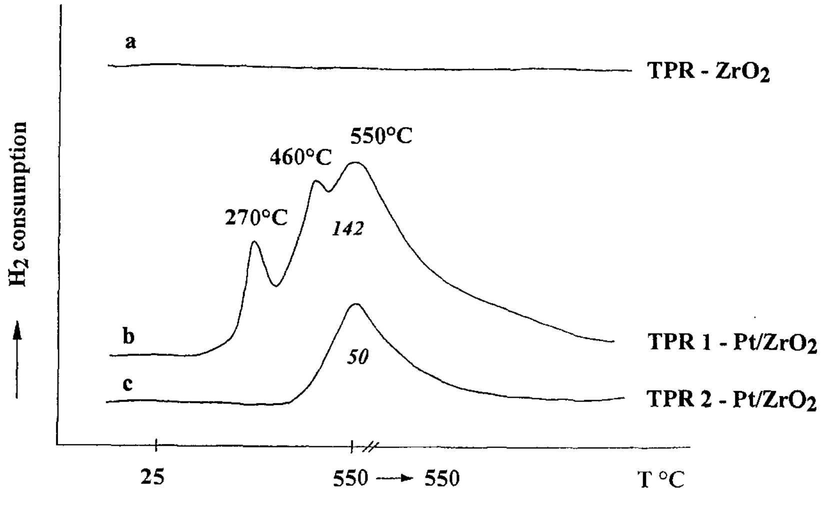

Fig. 1. TPR profiles of ZrO_2 (a); of Pt/ZrO_2 after calcination, TPR1 (b); and of Pt/ZrO_2 after TPDH1, TPR2 (c); the figures give the peak intensities in $\mu mol\ H_2/g_{cat}$.

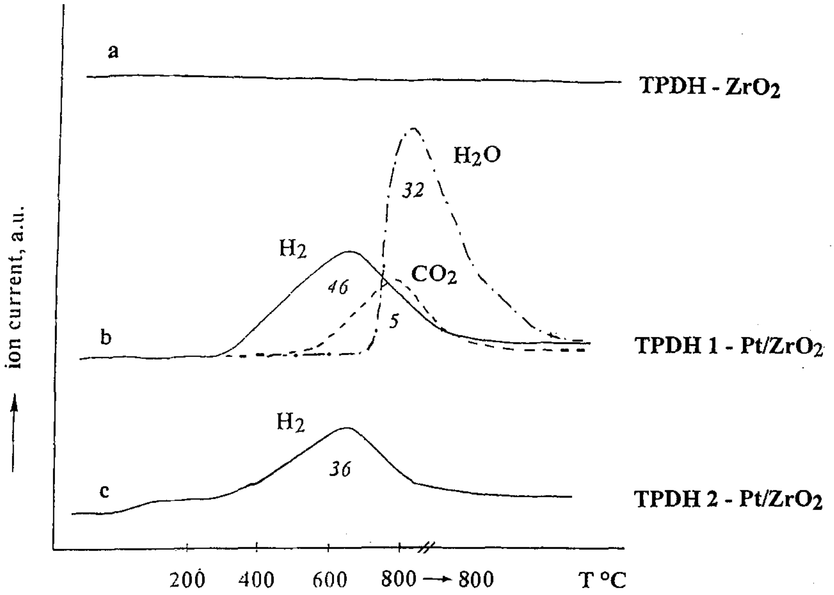

Fig. 2. TPDH spectra of ZrO_2 after TPR and hydrogen adsorption (a); of Pt/ZrO_2 after TPR1 and hydrogen adsorption, TPDH1 (b); and of Pt/ZrO_2 after TPR2 and hydrogen adsorption, TPDH2 (c); the figures give the eluated amounts of H_2, CO_2 and H_2O in μmol/g_{cat}.

The TPR1 profile, fig. 1, curve b, consists of three peaks, the total intensity of which amounts to 142 μmol H_2/g_{cat}. The first peak centered at 270°C is certainly to be assigned to Pt^{2+} reduction and corresponds to the reduction of ca. 58% of the Pt^{2+} ions loaded on the ZrO_2 support. The second one at 460°C should be due to the reduction of the rest of Pt^{2+} ions. The appearance of two Pt reduction peaks gives a hint to a complicated reduction behaviour of zirconia supported platinum. As the Pt free zirconia support used in this study does not exhibit any hydrogen consumption at this temperature (curve a), the third hydrogen consumption peak centered at 550°C must be connected with the presence of platinum. But, the reduced platinum itself can be ruled out as a hydrogen consumer at this temperature [1]. Hence, the third peak should be assigned to a hydrogen consumption of the ZrO_2 support, mediated by platinum. In the cases of Pt/ZrO_2 [2] and Rh/ZrO_2 [7], it has been shown that the metals are able to activate hydrogen, which spills over onto the zirconia surface in the temperature range around 550°C. Therefore, we assume that the background of the third peak in TPR1 is hydrogen spillover. This peak assignment is supported by the result of TPDH1, shown in fig. 2, curve b. The TPDH1 spectrum exhibits a hydrogen desorption peak at 650°C. According to Miller et al. [1], hydrogen desorption at such high temperatures cannot be ascribed to the desorption of hydrogen, strongly chemisorbed on Pt, or of hydrogen, which spilled over *back* from the support surface to platinum. Thus, in accordance with refs. [1,2] and with the above TPR1 peak assignment, the hydrogen desorption at

650°C is due to the desorption of spillover hydrogen from the zirconia surface, which was adsorbed there during the TPR1 procedure.

Beyond the spillover hydrogen, the desorbed gases of TPDH1 contained 5 μmol CO_2/g_{cat} and 32 μmol H_2O/g_{cat}, both desorbed at nearly 800°C. The CO_2 peak surely is due to a thermal decomposition of carbonates in the zirconia, which were formed during its preparation and/or by contact with the surrounding atmosphere. The H_2O peak is doubtless caused by the dehydroxylation of the zirconia surface [8,9]. Eluations of CO and CH_4 [10] were not observed, neither with the ZrO_2 sample nor with the Pt/ZrO_2 catalyst. From a methodological point of view, the desorption of other molecules than H_2 demonstrates that mass spectrometric analysis is highly desirable with TPDH investigations on zirconia.

Neither TPDH1 nor TPDH2, fig. 2, curve b, exhibit any desorption signal in the low temperature range below 200°C, i.e. in the range usual for desorption of hydrogen from the metallic Pt surface. This confirms our recent results, according to which platinum suffers a total loss of hydrogen chemisorption capacity in Pt/ZrO_2 after hydrogen treatments at 550°C [2]. This behaviour might be explained by a Pt–ZrO_2 strong metal–support interaction. With Rh/ZrO_2 an analogous loss of hydrogen adsorption capacity has been observed and interpreted as metal–support interaction [7]. With Pt/ZrO_2, the situation concerning SMSI like effects is not quite clear, probably because of differing materials or working conditions. After reduction of Pt/ZrO_2 at only 500°C, only a weak loss of hydrogen chemisorption capacity has been observed [11]. Concerning a decoration of the metal surface by migrating ZrO_x species, different conclusions have been drawn [7,11–13]. On the other hand, Pt–Zr alloy formation in Pt/ZrO_2 has been demonstrated [14], which is another possible reason for decreased hydrogen adsorption.

3.3. ACTIONS OF SPILLOVER HYDROGEN

According to the above peak assignment, the third peak in the TPR1 spectrum is due to spillover hydrogen, which is desorbed at 650°C during TPDH1. But, one can see from figs. 1 and 2 that there is a remarkable difference between the amounts of hydrogen, spilled over during TPR1 on the one hand and desorbed during TPDH1 on the other hand. In recent papers on Rh/ZrO_2 [7] and Pt/TiO_2 [15], it has been suggested that the hydrogen, which spilled over from the metals onto the supports can cause a partial reduction of the support. On the basis of this assumption, we are able to differentiate between spillover hydrogen, which is irreversibly consumed for a partial reduction, and spillover hydrogen, which is reversibly adsorbed on appropriate sites of the support. The intensity of the third peak in TPR1, ascribed to hydrogen spillover, was estimated under the precondition that the platinum is fully reduced from Pt^{2+} to Pt^0 during TPR1. This reduction, which proceeds within the first and the second TPR1 peak would consume 26 μmol H_2/g_{cat}. Consequently, the intensity of the third peak corresponds to a hydrogen consumption of $142 - 26 = 116$ μmol H_2/g_{cat}. Then, it follows:

total spillover hydrogen onto support, see above (TPR1)	116 μmol H_2/g_{cat}
spillover hydrogen desorbed from support (TPDH1)	– 46 μmol H_2/g_{cat}
difference: spillover hydrogen consumed for partial ZrO_2 reduction	70 μmol H_2/g_{cat}.

3.4. REVERSIBILITY OF SPILLOVER HYDROGEN DESORPTION

According to Miller et al. [1], spillover hydrogen is stabilized on the surfaces of zeolites, γ-Al_2O_3 and SiO_2 by OH groups and is irreversibly desorbed, if the support surface is dehydroxylated. Our results demonstrate that this assumption does not apply to zirconia as a support:

(i) The TPDH1 profile, fig. 2, curve a, unambiguously shows that most of the hydrogen desorption took place already before the water desorption started. That means that the spillover hydrogen desorption started before the surface dehydroxylation of the zirconia and that, therefore, there is no connection between dehydroxylation state and spillover hydrogen, with zirconia as a support. This is in direct contrast to what was found by Miller et al. [1] with other supports. These authors observed desorption of water over the same temperature range as desorption of hydrogen.

(ii) It is a consequence of (i) that the desorption of spillover hydrogen must be reversible, i.e. a renewed spillover hydrogen adsorption must be possible even on a catalyst sample, which had been dehydroxylated by a preceding thermodesorption procedure. This is proved by the experiments: Our catalyst had essentially been dehydroxylated during TPDH1. This can be concluded from the intensive dehydroxylation peak, fig. 2, curve a, and from the fact that during the second TPDH procedure, TPDH2, fig. 2, curve b, no further dehydroxylation could be observed. Nevertheless, the sample was again able to take up spillover hydrogen during TPR2, see fig. 1, curve c. Also from these results, no connection between dehydroxylation state of zirconia and hydrogen spillover can be concluded.

The TPDH2 experiment illustrates at the same time that the spillover hydrogen taken up during TPR2 can be desorbed in the same way and at the same temperature (650°C) as with TPDH1. The desorbed amount (36 μmol H_2/g_{cat}) is somewhat lower than with TPDH1 (46 μmol H_2/g_{cat}). This difference could be explained by the presence of 3.5% stabilizing SiO_2. A portion of spillover hydrogen could have been adsorbed during TPR1 on silica surface OH groups, as suggested by Miller et al. [1]. This portion of hydrogen could have been irreversibly desorbed, when the SiO_2 surface was dehydroxylated at the high final temperature of TPDH1 (800°C). On the other hand, the difference could also be explained by the moderate sintering of zirconia [16,17] at that high temperature, mentioned in section 2.

As a matter of fact, the results of TPR2 (50 μmol H_2/g_{cat}) and of TPDH2 (36 μmol H_2/g_{cat}) should essentially coincide, according to our approach. Also this difference cannot be explained with certainty, up to now. We cannot exclude that during TPR2 a further irreversible reduction took place, which seized perhaps also the zirconia bulk.

On basis of the results presented, only assumptions are possible about the mechanism of the processes observed as well as about the species involved. The high temperature hydrogen treatment leads to a partial zirconia reduction, which is not reversible under TPDH conditions, and at the same time to a reversible spillover hydrogen adsorption. Because OH groups should be excluded as stabilizing sites for spillover hydrogen according to our experiments, one can assume on trial that these stabilizing sites were created by the partial reduction. The existence of Zr^{3+} after high temperature treatments or hydrogen treatments of ZrO_2 is well established [18–21]. For highly reduced TiO_2, there are proposals, according to which stable hydride species Ti^{4+}–H are formed from Ti^{3+} ions and hydrogen, which decompose only at temperatures above 500°C [22]. The formation of analogous Zr^{4+}–H species on ZrO_2 surfaces [18], in e.g. ref. [7] combined with the formation of ZrOH species, has already been discussed. In principle, equilibria of the type $H + Me^{4+} \rightleftharpoons H^+ + Me^{3+}$, e.g. ref. [15], could also explain a reversible hydrogen uptake. But, unlike the above model, which *presupposes* a reduction to Me^{3+} for the spillover hydrogen stabilization, the latter model *leads* to a simultaneous zirconia reduction and hydrogen uptake, and the relevance of such equilibria at high temperatures is uncertain, to our best knowledge. These questions as well as a possible catalytic role of the spillover hydrogen in zirconia supported catalysts must be a subject of further investigations.

4. Conclusions

– TPR and TPDH investigations on a Pt/ZrO_2 catalyst demonstrated that hydrogen spills over at temperatures around 550°C from metallic Pt onto the zirconia surface.

– A part of the spilled-over hydrogen seems to be consumed for a partial reduction of zirconia, the other part is adsorbed on the zirconia surface. The adsorption sites for spillover hydrogen on zirconia are possibly formed by that partial reduction.

– Spillover hydrogen adsorbed on the zirconia surface is desorbed at about 650°C. Surface dehydroxylation is observed only at still higher temperatures. In contrast to other supports with dehydroxylable surfaces like zeolites, Al_2O_3 and SiO_2, this high temperature desorption is reversible with zirconia. This means that zirconia, essentially dehydroxylated during a preceding thermodesorption, can again adsorb spillover hydrogen during a following high temperature hydrogen treatment. On the whole, on Pt/ZrO_2 no connection between spillover hydrogen adsorption and dehydroxylation of the support is observed.

Acknowledgement

The authors are grateful to MEL Chemicals, Manchester, UK, for supplying them with the zirconia support as well as to Mrs. S. Evert and Mrs. K. Struve for technical assistance.

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