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Effect of hydrogen treatments on ZrO_2 and Pt/ZrO_2 catalysts

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ZrO_2 and Pt/ZrO_2 catalysts have been investigated by TPR, hydrogen chemisorption, TPDH and in the conversion of *n*-hexane. At high temperature, ZrO_2 takes up hydrogen. High temperature hydrogen treatment is a precondition of the catalytic activity in the *n*-hexane conversion. Possibly, catalytically active acid sites are formed by this hydrogen treatment. The high temperature hydrogen treatment induces a strong Pt–ZrO_2 interaction.

Keywords: zirconia; platinum; hydrogen treatment; TPR; TPDH; H_2 chemisorption; *n*-hexane conversion; SMSI

1. Introduction

Due to its special physical and chemical properties, zirconia has been intensively investigated as a catalyst for a number of reactions, including hydrogenation or oxidation of CO, oxidation of hydrocarbons, polymerization of olefins and others [1]. Zirconia has been found to be a suitable carrier for supported metal catalysts, such as Ni/ZrO_2, Rh/ZrO_2, Cu/ZrO_2, Pd/ZrO_2, or Pt/ZrO_2, which are active, particularly, in reducing atmospheres [1–9]. Hence, it seemed to be interesting to investigate the influence of a reducing atmosphere on the catalytic behaviour of zirconia.

Moreover, metal–support interactions, which usually are generated by reducing hydrogen treatments, are of interest in the case of metal/zirconia systems, too. But, there are contradictory reports concerning this problem. On the one hand, metal–support interactions were reported to be responsible for modifications of the metal properties [9] as well as for increasing the reducibility and the acidity of ZrO_2 supports [6–8]. On the other hand, zirconia was believed to be hardly reducible and to be not reactive towards platinum in hydrogen atmosphere [10–13].

We investigated the influence of high temperature pretreatments in hydrogen on the catalytic properties of zirconia and on the interaction between zirconia and

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platinum by temperature programmed reduction (TPR), temperature programmed desorption of hydrogen (TPDH), and hydrogen pulse chemisorption. The catalytic properties of ZrO_2 and Pt/ZrO_2 were checked in the conversion of *n*-hexane. The results will show that a high temperature hydrogen pretreatment is a prerequisite of the catalytic activity of zirconia and that a strong Pt–ZrO_2 interaction is generated by such a pretreatment.

2. Experimental

2.1. CATALYST PREPARATION

The preparation of zirconia was performed via $ZrOCl_2$ hydrolysis, adding ammonia for 4 h to an aqueous $ZrOCl_2$ solution (final pH = 10). The $Zr(OH)_4$ precipitate was washed with water until the Cl^- test (addition of $AgNO_3$ to the washing water) was negative. The precipitate was dried at 120°C for 12 h. The material was calcined at 600°C in air for 4 h. XRD investigations showed that the resulting ZrO_2 consisted of a mixture of the monoclinic and the tetragonal phase.

In order to prepare the Pt/ZrO_2 catalysts, ZrO_2 was impregnated with a H_2PtCl_6 solution, dried at 120°C for 4 h and calcined at 500°C in air for 4 h. The Pt content amounted to 0.5 wt%.

2.2. TPR, HYDROGEN CHEMISORPTION AND TPDH

TPR, hydrogen chemisorption and TPDH measurements were performed by means of a quantitatively calibrated dynamic characterization system.

For TPR, the catalyst samples (500 mg) were heated up to 500°C in a dried air flow in order to remove water and organic contaminations. After cooling down to room temperature, TPR was carried out in an argon flow containing 5% hydrogen at a flow rate of 70 ml/min and a heating rate of 20 K/min.

For hydrogen pulse chemisorption on Pt/ZrO_2, the samples were reduced in hydrogen for 1 h at the desired temperature. The hydrogen flow was replaced by an argon flow of 70 ml/min and hydrogen was desorbed at 550°C for 0.5 h. Afterwards the sample was cooled down to 0°C, and 0.153 ml pulses of a 5% hydrogen/argon mixture were given onto the sample.

In order to carry out TPDH measurements, the catalyst samples were pretreated in flowing hydrogen at the chosen temperature (350, 450 or 550°C) for 1 h. After cooling down the samples from the reduction temperature to room temperature in flowing hydrogen, the hydrogen flow was substituted by an argon flow (70 ml/min) and the temperature was linearly raised (20 K/min) up to 700°C.

2.3. *n*-HEXANE CONVERSION

The conversion of *n*-hexane was carried out on catalyst samples under normal pressure at 550°C (exceptions are given in the text) in a fixed-bed glass reactor, continuously fed with a hydrogen flow or a nitrogen flow, respectively, saturated at 17°C with *n*-hexane (corresponding to 14.3 kPa *n*-hexane). The catalyst samples were calcined in air at 300°C for 1 h in situ, followed by a hydrogen treatment at the desired temperature (mostly 550°C) for 1 h. The reaction products were analyzed using on line gas chromatography. With the aim of comparison with a well-known acid catalyst, *n*-hexane conversion was carried out under identical conditions also on a H-ZSM-5 sample, described more in detail in ref. [14].

3. Results

3.1. TEMPERATURE PROGRAMMED REDUCTION

The TPR profiles of zirconia and platinum supported on zirconia are shown in fig. 1. ZrO_2 exhibits a reduction peak at 660°C, which has been interpreted as a reversible hydrogen uptake of the ZrO_2 surface [7]. The spectrum of Pt/ZrO_2 consists of at least three signals with maxima at 280, 400 and 650°C. The peak at 280°C certainly is to be assigned to the reduction of Pt^{4+} to metallic Pt [15]. The high temperature peak at 650°C is far more intensive than the corresponding one with ZrO_2. This indicates that the hydrogen–zirconia interaction is strongly promoted by Pt. Perhaps, a hydrogen spillover from Pt to the ZrO_2 surface is the reason of the increase of the hydrogen amount taken up. The signal at 400°C and the shoulder at 500°C cannot be identified up to now; they illustrate the more complex nature of the hydrogen–zirconia interaction in presence of Pt.

3.2. HYDROGEN CHEMISORPTION

Table 1 contains the hydrogen chemisorption capacities of Pt/ZrO_2 samples, which had been reduced in hydrogen at 350, 450 and 550°C, respectively, before the

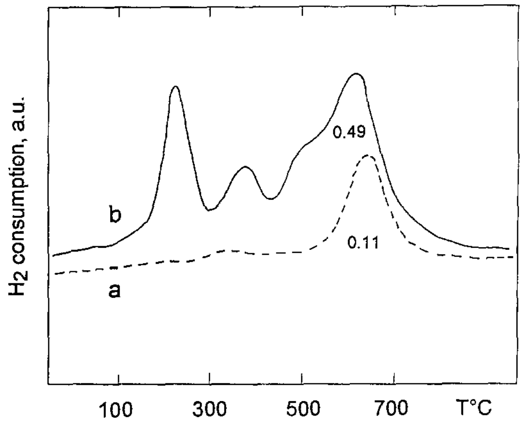

Fig. 1. TPR profiles of (a) ZrO_2 and (b) Pt/ZrO_2; the figures give the peak intensities in ml H_2/g catalyst.

Table 1
Hydrogen chemisorption capacities and H/Pt values of Pt/ZrO_2 catalysts after hydrogen treatments at different temperatures

Treatment temperature (°C)	H_2 chemisorption capacity ($ml\ H_2/g\ Pt$)	H/Pt
350	35.3	0.62
450	17.4	0.30
550	1.3	0.02

chemisorption procedure. A drastic decline of the Pt chemisorption capacity with increasing reduction temperature is observed. After reduction at 550°C, the hydrogen chemisorption is nearly totally suppressed.

With analogous experiments, on ZrO_2, free of Pt, not any hydrogen adsorption was observed.

3.3.TEMPERATURE PROGRAMMED DESORPTION OF HYDROGEN

Fig. 2 shows TPDH spectra including peak intensities of ZrO_2 and Pt/ZrO_2, with the samples being pretreated in hydrogen at the given temperatures and cooled down afterwards in hydrogen to room temperature.

Not depicted here and in accordance with its TPR spectrum, ZrO_2 does not desorb any hydrogen after a hydrogen treatment at 350°C. After a treatment at 550°C, i.e. about the peak maximum temperature of TPR, an intensive desorption

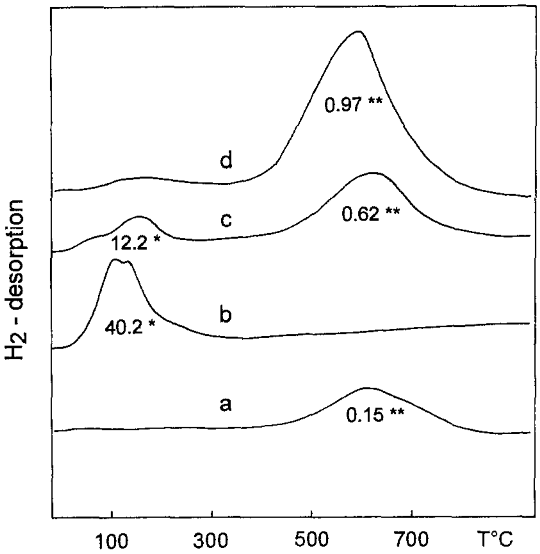

Fig. 2. TPDH spectra of ZrO_2 and Pt/ZrO_2 samples, pretreated in hydrogen at the following temperatures: (a) ZrO_2, 550°C; (b) Pt/ZrO_2, 350°C; (c) Pt/ZrO_2, 450°C; (d) Pt/ZrO_2, 550°C. The figures in the peak areas give the peak intensities as follows: * $ml\ H_2/g\ Pt$; ** $ml\ H_2/g$ catalyst.

peak is observed, the amount of which is comparable with the hydrogen consumption measured in the corresponding TPR experiment, see curve a. Seemingly, that hydrogen amount which was taken up during the pretreatment was desorbed in the TPDH experiment. Hence, this hydrogen desorption into an inert gas seems to be the reversal of the high temperature hydrogen uptake, which was observed in the TPR experiments.

With Pt/ZrO_2 (curves b–d), two desorption peaks were observed. The low temperature peak (*) around 100°C certainly is to be assigned to the desorption of hydrogen from metallic Pt. The amounts of hydrogen desorbed sufficiently agree with the corresponding chemisorption results in table 1 and, consequently, they exhibit the same drastic decline with increasing hydrogen pretreatment temperature. As with ZrO_2, the high temperature peak at about 600°C (**) could be observed only with samples pretreated at least near the temperature range of the ZrO_2 hydrogen uptake observed by TPR. In line with the TPR experiments, the desorption intensity from Pt/ZrO_2 significantly exceeds the corresponding intensity with ZrO_2, indicating a promotion of the formation of desorbable hydrogen species by Pt via hydrogen spillover, as mentioned above.

3.4. *n*-HEXANE CONVERSION

In fig. 3, catalytic total activities of ZrO_2 are depicted, of samples differently pretreated and in different reaction atmospheres.

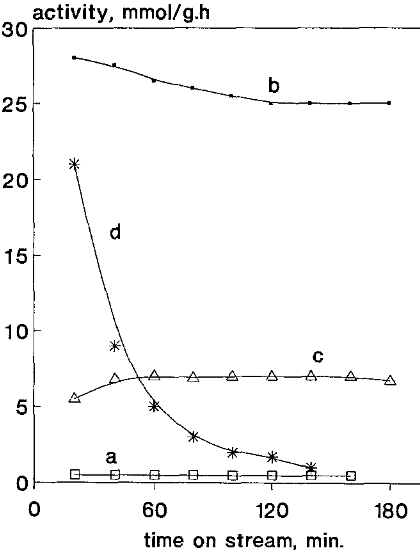

Fig. 3. Catalytic activities of ZrO_2 samples, differently pretreated and in different reaction atmosphere: (a) pretreated in nitrogen at 550°C, reaction in N_2/*n*-hexane at 550°C; (b) pretreated in hydrogen at 550°C, reaction in H_2/*n*-hexane at 550°C; (c) pretreated in hydrogen at 450°C, reaction in H_2/*n*-hexane at 450°C; (d) pretreated in hydrogen at 550°C, reaction in N_2/*n*-hexane at 550°C.

Without hydrogen pretreatment, ZrO_2 is completely inactive in N_2/n-hexane at 550°C, see curve a. After a pretreatment in hydrogen at 550°C, ZrO_2 exhibits a remarkable and stable catalytic activity in H_2/n-hexane at the same reaction temperature, curve b. With a hydrogen pretreatment at only 450°C and a reaction temperature of 450°C, a stable but drastically lower activity in H_2/n-hexane was observed, curve c. Finally, in N_2/n-hexane, a sample pretreated in hydrogen at 550°C shows an initially high, but steeply decreasing catalytic activity, curve d.

With all catalysts investigated, we observed only cracking products (C_1–C_4 alkanes, C_2–C_4 alkenes) and C_6–C_8 aromatics, but no hexenes, see fig. 4. Fig. 4a compares product selectivities on ZrO_2 and on the acid H-ZSM-5 catalyst at 550°C. Except the higher aromatization selectivity of H-ZSM-5, the selectivities with respect to saturated and olefinic cracking products roughly correspond. Fig. 4b shows that also the distribution of aromatics is very similar with ZrO_2 and H-ZSM-5. This indicates the acid nature of the catalytically active sites formed during the high temperature hydrogen treatment.

In fig. 5, yields of products at 550°C are given for ZrO_2 and Pt/ZrO_2, with the samples always being pretreated in hydrogen at 550°C. The Pt containing catalyst exhibits a higher total activity and additionally a remarkable selectivity towards aromatic hydrocarbons.

4. Discussion

4.1. ACTION OF HYDROGEN TREATMENT ON THE CATALYTIC ACTIVITY

The TPR and TPDH results show that at high temperature, zirconia is able to bind hydrogen reversibly, i.e. it takes up hydrogen and seems to release it in the same temperature range, if the surrounding atmosphere is changed from a hydrogen containing one to an inert one. These results confirm recent reports [4,7]. Dall'Agnol et al. [7] regard their results as consistent with an increase of the concentration of OH^- surface groups, due to the surface reaction $Zr{-}O{-}Zr + H_2 \rightarrow ZrOH + Zr\ldots H$ at high temperature. The formation of surface OH^- groups when treating ZrO_2 with hydrogen had already been suggested by He and Ekerdt [4].

What is important to emphasize here is that the high temperature hydrogen treatment of zirconia obviously is connected with its catalytic activity. Samples without hydrogen treatment do not exhibit any catalytic activity, if exposed to N_2/n-hexane atmosphere. Only after a hydrogen treatment and in H_2/n-hexane atmosphere is a stable activity observed, with this activity being strongly dependent on the pretreatment temperature and being high only after hydrogen treatments in the temperature range of the hydrogen uptake around 550°C. The connection between hydrogen uptake and catalytic activity is once demonstrated by the finding that a hydrogen pretreated sample loses its catalytic activity under

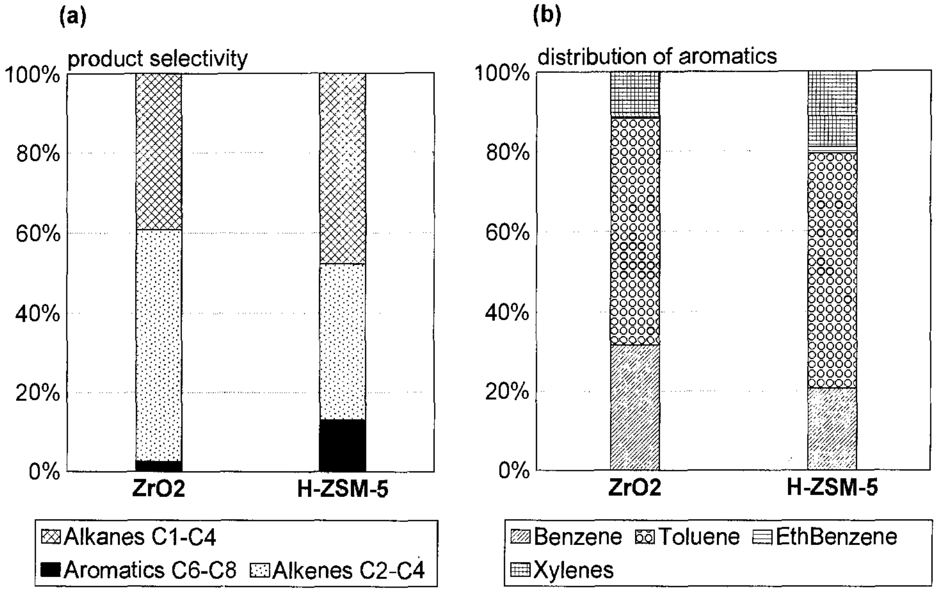

Fig. 4. Comparison of selectivities on ZrO_2 and H-ZSM-5; (a) cracking products and aromatics, (b) distribution of the aromatics formed.

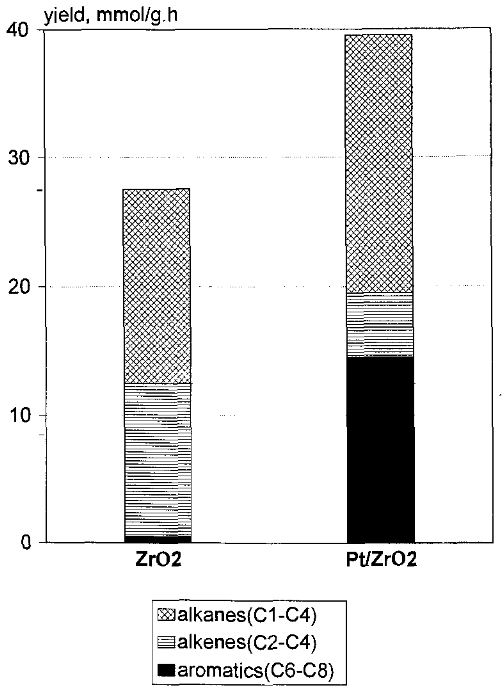

Fig. 5. Product yields of *n*-hexane conversion in H_2/*n*-hexane at 550°C on ZrO_2 and Pt/ZrO_2 catalysts, pretreated in hydrogen at 550°C.

the conditions of hydrogen desorption: in nitrogen atmosphere and at high temperature. The catalytic activity seems to disappear corresponding to the extent of hydrogen desorption.

It seems plausible to assume that the catalytic activity is originated by acid sites, e.g. OH^- groups or Zr^{x+} Lewis sites, which were formed during the hydrogen treatment, possibly according to the mechanism cited above [7]. The product spectra of our catalytic experiments are compatible with alkane cracking reactions on acid catalysts, which are initiated, as known, via protonation or via hydrid abstraction on acid sites, resulting in a mixture of light alkanes and light olefins in the first step [16,17].

On the whole, we could show that the hydrogen treatment of zirconia at high temperature probably is a prerequisite of its catalytic activity in hydrocarbon conversions. Probably, this hydrogen uptake leads to the formation of catalytically active acid sites. It is a future task to detect and to characterize these sites by appropriate methods more in detail.

4.2. PLATINUM–ZIRCONIA INTERACTION

As was demonstrated by the TPR and TPDH experiments, platinum significantly enhances the reversible high temperature hydrogen uptake of ZrO_2. This behaviour is analogous to the system Rh/ZrO_2, which has been studied by Dall'Agnol et al. [7]. The authors concluded that the hydrogen desorbed from Rh/ZrO_2 comes from the same type of binding sites as with ZrO_2. Rh is assumed to promote the hydrogen uptake by a hydrogen spillover onto the support. It promotes, therefore, the desorbed hydrogen amount, too. We propose that Pt in our Pt/ZrO_2 samples acts analogously.

The catalytic total activity of ZrO_2 is increased by Pt. This might be due to its inherent catalytic activity and/or to an increase of the number of acid sites by increased hydrogen uptake. The selectivity is significantly changed in presence of Pt, too. A remarkable aromatization activity is observed. This might be the consequence of an efficient bifunctional cooperation of acid and metallic sites, e.g. [18], or of direct metal-catalyzed dehydrocyclization of *n*-hexane [19].

Another effect of the high temperature hydrogen treatment of Pt/ZrO_2 is the total loss of the ability of Pt to adsorb hydrogen at low temperature, proved by the results of the hydrogen chemisorption as well as by the disappearance of the low temperature TPDH peak after high temperature hydrogen treatment. This finding is analogous to what was found by Dall'Agnol et al. with the system Rh/ZrO_2 [7]. But, this behaviour does not correspond with results on Pt/ZrO_2 by Yoshitake and Iwasawa [20], who found no remarkable loss of hydrogen chemisorption capacity with increasing reduction temperature in hydrogen. Maybe that the zirconia used by the authors differed from ours. It seems that a strong metal–support interaction was generated by hydrogen at high temperatures. Assuming a behaviour analogous to the system Rh/ZrO_2, the nature of this SMSI effect could consist in the formation of Zr–O–Pt entities [7], partly covering the Pt particles. On the other hand, a Pt–Zr alloy formation, which was reported some years ago [9], could explain the disappearance of hydrogen adsorption, too.

A SMSI effect, e.g. generated by a covering of the Pt surface by ZrO_x species or by Pt–Zr alloy formation, should hinder hydrogenolysis reactions, see e.g. refs. [19,21], because large metallic ensembles, necessary for the structure sensitive hydrogenolysis, would be destroyed by Zr species. But, due to the presence of hydrogen at the high temperature of 550°C during our catalytic test, we could not compare our catalyst with a SMSI free system and, therefore, a possible suppress of hydrogenolysis by SMSI could not be proved.

5. Conclusions

– With hydrogen treatments of ZrO_2 and Pt/ZrO_2 at high temperatures, a hydrogen uptake occurs. Desorption is observed at the uptake temperatures, when changing the surrounding atmosphere from hydrogen to inert gas. Pt promotes this process, possibly via a spillover mechanism. These findings are analogous to the system Rh/ZrO_2 [7].

– High temperature hydrogen treatment is a precondition of the catalytic activity of ZrO_2 in *n*-hexane conversion. The catalytic activity disappears under the conditions of hydrogen desorption. The product spectra of the catalytic investigations are compatible with the assumption that catalytically active acid sites are formed during the high temperature hydrogen treatment.

– The high temperature hydrogen treatment induces a strong Pt–ZrO_2 interaction, indicated especially by the loss of hydrogen chemisorption capacity. This SMSI effect might be due to a decoration of Pt by Zr species or by a Pt–Zr alloy formation.

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