

Pt/SO₄²⁻-ZrO₂ catalysts prepared from Pt organometallic compounds

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Abstract

New Pt/SO₄²⁻-ZrO₂ catalysts were prepared using precalcined SO₄²⁻-ZrO₂ and organometallic Pt precursors. The objective was to obtain a bifunctional catalyst with improved metal properties, which are mostly suppressed in Pt/SO₄²⁻-ZrO₂ prepared in a standard fashion. The synthesis route used low temperatures to form the Pt particles in order to avoid sulfate decomposition and Pt poisoning. The use of precalcined zirconia decreased ionic diffusion, related to crystallization of the gel and encapsulation of Pt particles. As detected by TPR and cyclohexane dehydrogenation tests, after reducing at 270 °C, Pt on the new catalyst had metallic properties. Its dehydrogenation activity was higher than that of a standard Pt/SO₄²⁻-ZrO₂ catalyst (prepared from H₂PtCl₆). After activating in air at 300 °C, its activity for *n*-butane isomerization (300 °C, 1 atm., H₂:*n*-C₄ = 6, WHSV = 1 h⁻¹) was low, very likely because of incomplete elimination of adsorbed water. After activation in air at 600 °C, the isomerization activity was almost similar to that of standard Pt/SO₄²⁻-ZrO₂ but the dehydrogenation activity decreased to negligible values. The deleterious interaction between Pt and SO₄²⁻-ZrO₂ that occurred during calcination was possibly related to oxidation of the metal. On the other side, high reduction temperatures did not enhance the metal activity beyond the level obtained after reducing at 270 °C. On the contrary, the higher the reduction temperature, the lower the activity for cyclohexane dehydrogenation that was obtained. This effect was seemingly related to poisoning by sulfur compounds.

The new materials could be potentially useful for reacting systems needing a bifunctional catalyst and an acid function like SO₄²⁻-ZrO₂ but their operation is limited if high temperatures in air or H₂ are necessary for activation. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the past, the causes of the activity of sulfated-zirconia catalysts (SO₄²⁻-ZrO₂) have been studied [1–7] and it has been reported that active sites begin

to appear at a temperature of calcination of the sulfated gel, SO₄²⁻-Zr(OH)₄, of about 450–500 °C and that the activity reaches a maximum when calcining at 600–650 °C. The maximum temperature coincides with a maximum in tetragonal phase growth. Higher temperatures (*T* > 700–750 °C) produce the removal of sulfate groups, a tetragonal-to-monoclinic transition and a decrease in activity [6]. While the role of the crystalline structure is still not clear [7], the

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dominant structure in active catalysts is the tetragonal phase.

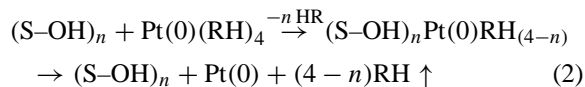
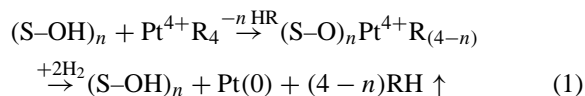
A loss of metallic properties occurs when Pt is supported on $\text{SO}_4^{2-}\text{-Zr(OH)}_4$ and the resulting catalyst ($\text{Pt/SO}_4^{2-}\text{-Zr(OH)}_4$) is calcined at the high temperatures (600°C) needed for the activation of the acid function. Pt is seemingly oxidized and loses capacity for de/hydrogenation of hydrocarbons and chemisorption of H_2 and CO . The effect has been addressed to encapsulation into the matrix of $\text{SO}_4^{2-}\text{-ZrO}_2$ [8,9], the formation of an oxidized layer of PtO_x over the metal Pt(0) particles [10,11], chemisorption of sulfur species [12], formation of Pt-S [13], and electron depletion by delocalized acidic protons [14,15].

Obtaining a $\text{Pt/SO}_4^{2-}\text{-ZrO}_2$ catalyst with an improved level of metallic properties could be important for its use in reacting systems needing a bifunctional catalyst and an acid function with the high selectivity to isomers of $\text{SO}_4^{2-}\text{-ZrO}_2$. In the case of the isomerization of *n*-butane, activity could be enhanced if reactive butenes were formed on metal sites and a bifunctional mechanism could take place. Hydrogen activation and spillover could also be increased on highly active Pt and in this way, the removal of coke precursors could be accelerated and the deactivation rate decreased.

Taking these facts into account and in order to try to avoid the problem of loss of metallic properties, a new formulation of $\text{Pt/SO}_4^{2-}\text{-ZrO}_2$ catalyst was tried. The basic idea consisted in the use of precalcined crystalline tetragonal materials ($\text{SO}_4^{2-}\text{-ZrO}_2$) for the impregnation of Pt. Tetragonal $\text{SO}_4^{2-}\text{-ZrO}_2$ was prepared by calcining $\text{SO}_4^{2-}\text{-Zr(OH)}_4$ at 600°C in air. Some advantages were thought to be obtained by using this crystalline material: (i) on this catalyst, the need for high activation temperatures could be less stringent because the support is already crystalline; (ii) lower sulfur losses are expected because the high ionic mobility in the zirconia lattice during crystallization does not occur and the sulfate groups have already been stabilized at 600°C , if less sulfur species are evolved Pt poisoning may be decreased; (iii) Pt encapsulation should be negligible for Pt deposited on crystalline zirconia because the effect is expected to occur mainly during crystallization of the $\text{SO}_4^{2-}\text{-Zr(OH)}_4$ gel. If surface reconstruction and diffusion onto Pt particles were however possible then low temperatures of calcination of $\text{Pt/SO}_4^{2-}\text{-ZrO}_2$ should be used.

If oxidation is likely to take place during activation in air at high temperatures, it could also be prevented by lowering the temperature of activation. A common sense objective was to lower the temperature of all activation treatments to values lower or equal than $270\text{--}300^\circ\text{C}$, the usual reaction temperature used in the isomerization of *n*-butane. In order to fulfill this requirement, the election of a suitable Pt precursor was important. An organometallic Pt complex was chosen because these materials can be decomposed and reduced at very low temperatures and do not leave adsorbed unwanted anions [16,17]. Organic non-aqueous solvents were used in order to avoid an early hydrolysis of the Pt complex.

Generally, three stages are involved in the preparation of organometallic compounds of transition elements: formation of surface organometallic complexes, formation of metal species in many oxidation states and finally, formation of metal particles upon reduction. For Pt complexes in the (0) and (4+) oxidation and having four ligands (charged R^- or neutral RH), the reaction is depicted by Eqs. (1) and (2):



(R = alkyl, allyl, alkoxy, etc.; S = support surface.)

The metal catalysts thus produced have two noteworthy features. First, the organometallic compounds have no anions which are difficult to remove. Secondly, the calcination in air which is common in the preparation of catalysts from H_2PtCl_6 can be avoided because organometallic compounds are easily decomposed by a treatment at low temperatures.

$\text{Pt/SO}_4^{2-}\text{-ZrO}_2$ catalysts prepared from crystalline $\text{SO}_4^{2-}\text{-ZrO}_2$ and from organometallic Pt compounds were synthesized and their activity in catalytic tests of the acid and metal functions (isomerization of *n*-butane, cyclohexane dehydrogenation, temperature programmed reduction (TPR)) was assessed. The properties of the catalysts were compared with those of standard $\text{Pt/SO}_4^{2-}\text{-ZrO}_2$ prepared with H_2PtCl_6 impregnated over sulfated zirconia in the amorphous state.

2. Experimental

2.1. Catalyst preparation

Zr(OH)₄ was prepared by precipitation of ZrOCl₂·8H₂O (Strem, 99.998+%) with concentrated NH₄OH (Merck, 35%). Details of the technique can be found elsewhere [18]. ZrO₂ was prepared by calcining Zr(OH)₄ at 600 °C for 3 h under flowing air (10 ml min⁻¹). Sulfated-zirconia (SO₄²⁻-Zr(OH)₄) was synthesized by impregnation of Zr(OH)₄ with a solution of 1N H₂SO₄ (immersion for 2 h, 10 ml g⁻¹). A portion of the SO₄²⁻-Zr(OH)₄ batch was calcined at 600 °C for 3 h in flowing air (10 ml min⁻¹) and the resulting crystalline material was named SO₄²⁻-ZrO₂. All the samples were dried at 110 °C overnight.

Pt⁴⁺ trimethylcyclo-pentadienyl and Pt(0) tetrakis triphenylphosphine were used as Pt precursors. Both materials were supplied by Aldrich. They were dissolved in benzene and impregnated by incipient wetness (0.5% Pt on final catalyst) over the SO₄²⁻-ZrO₂ support. The SO₄²⁻-ZrO₂ samples were first exposed to room humidity, dried at 110 °C and maintained in a desiccator before impregnating the organometal compounds. This procedure stabilized a minimum amount of OH groups on the catalysts in order to react with the Pt precursors. The catalysts were finally dried at 110 °C overnight. The catalysts thus obtained were named Pt(0)/SO₄²⁻-ZrO₂ and Pt(IV)/SO₄²⁻-ZrO₂. The notation highlights the original oxidation number of the Pt precursor salt. Samples of the Pt(IV)/SO₄²⁻-ZrO₂ and Pt(0)/SO₄²⁻-ZrO₂ catalysts were also calcined in air at 300 and 600 °C (air, 10 ml min⁻¹ g⁻¹) to see the influence of calcination on the reducibility of the catalysts.

Sulfate-free Pt over zirconia catalysts were prepared in the same fashion as Pt(0)/SO₄²⁻-ZrO₂ and Pt(IV)/SO₄²⁻-ZrO₂, but using ZrO₂ as support. The catalysts thus obtained were named Pt(0)-ZrO₂ and Pt(IV)-ZrO₂.

A standard Pt over SO₄²⁻-ZrO₂ catalyst was prepared by incipient wetness impregnation with chloroplatinic acid (0.5% Pt on final catalyst) of a dried sulfated-zirconia gel (SO₄²⁻-Zr(OH)₄). Then it was dried at 110 °C overnight and finally calcined at 600 °C for 3 h in air (10 ml min⁻¹ g⁻¹). The catalyst was named Pt*/SO₄²⁻-ZrO₂.

2.2. Characterization

TPR tests were performed in an Okhura TP2002S apparatus (200 mg per sample, 10 °C min⁻¹ heating rate, H₂:Ar = 4.08%). XRD spectra were recorded in a Shimadzu XD-1 equipment, using Cu K α radiation filtered with Ni. The samples were first dried in pure Ar at 110 °C before performing the test. The specific surface area was calculated by the BET method after adsorption of nitrogen at the temperature of liquid nitrogen with a static volumetric equipment (Quantachrome NOVA1000).

The dehydrogenating properties of the metal function were measured by the test reaction of dehydrogenation of cyclohexane. The reactant was injected in a hydrogen stream (WHSV = 10 h⁻¹; H₂/HC = 30), and reacted at 270 °C and atmospheric pressure over 30 mg of the catalyst ground to 35–80 mesh. The products were passed through a packed column of FFAP on Chromosorb W for their chromatographic analysis. Before the test, the samples were stabilized in H₂ at the reaction temperature (270 °C) for 30 min. Two Pt(IV)/SO₄²⁻-ZrO₂ samples were additionally reduced at 350 and 500 °C in order to see the influence of the reduction temperature.

For testing the isomerizing activity of the acid function of the catalysts, the reaction of *n*-butane isomerization was used. The reaction was performed both in a continuous flow and in a pulse reactor. All the catalysts used were ground and sieved to 35–80 mesh in both tests. The *n*-C₄ (99.9%), N₂ and H₂ were supplied by AGA. A packed column of dimethylsulfolane supported over Chromosorb P was used for the gas chromatographic analysis. Before starting the reaction, the catalysts were activated in air at different temperatures (10 ml min⁻¹ g_{cat}⁻¹) for 1 h (pulse test) or 2 h (continuous test). Then they were flushed with N₂ for 5 min (to remove adsorbed oxygen). In the case of the continuous test, they were further reduced in H₂ for 1 h at the reaction temperature. In the case of the continuous reaction test, a feed of *n*-C₄ was injected to a hydrogen stream (hydrogen/hydrocarbon molar ratio = 2 or 6, WHSV = 1 h⁻¹, 0.5 g of catalyst) and reacted at 300 °C and 1 atm. In the pulse test, the temperature and pressure were the same but one pulse (0.5 ml of pure *n*-C₄) was sent to a microreactor (loaded with 0.3 g of catalyst) by the carrier gas (N₂, 8 ml min⁻¹) every 5 min. The

reacted pulses were collected in gas-tight ampoules for analysis.

2.3. IR measurements

The acidity of Pt loaded sulfate-zirconia (Pt(IV)/SO₄²⁻-ZrO₂) in dry and hydrated conditions was measured by adsorption of pyridine on self supported wafers (1 cm²) placed in a closed quartz cell. The amount of adsorbed pyridine was measured by absorption of infrared radiation in a Nicolet 5ZDX spectrometer, in the range 4800–400 cm⁻¹ with a resolution of 4 cm⁻¹. The self supported wafer was first maintained in a flow of dry air for 1 h at room temperature (hydrated sample), 300 °C (hydrated sample) or 600 °C (dehydrated sample). Then the sample was cooled to 150 °C and degassed at 10⁻⁶ Torr for 1 h. After recording the IR spectra, the sample was contacted with 30 Torr of pyridine for 10 min, degassed in the same way as before, and then a new spectrum was recorded. The absorbance of chemisorbed pyridine was obtained by subtraction of both spectra. All pretreatments (calcination in air, degassing, pyridine adsorption) were performed in situ in the quartz cell to avoid rehydration. IR spectra of the heat treated Pt(IV)/SO₄²⁻-ZrO₂ samples (room temperature, 300 and 600 °C) in the region of absorption of the OH groups were also recorded before the adsorption of pyridine.

3. Results

3.1. Surface area

Disregarding minor differences caused by the sulfate treatment and the Pt addition, the BET surface area of the different materials was: Zr(OH)₄ and SO₄²⁻-Zr(OH)₄ (285–325 m² g⁻¹); ZrO₂ (55 m² g⁻¹); SO₄²⁻-ZrO₂ and Pt/SO₄²⁻-ZrO₂ (110–120 m² g⁻¹). The amorphous uncalcined gels Zr(OH)₄ and SO₄²⁻-Zr(OH)₄ displayed the highest values of surface area. Calcination of these gels at 600 °C produced materials with lower area but the effect of sintering was diminished by the effect of the sulfate. ZrO₂ (obtained by calcination of Zr(OH)₄) had a much lower area than SO₄²⁻-ZrO₂ (obtained by calcination of SO₄²⁻-Zr(OH)₄). The effect of sulfate has been previously reported [2,7] and is related to a delay in

the crystallization temperature, a decrease in sintering and a preservation of part of the micropore volume of the gel, which contributes in a higher proportion to the total surface area.

3.2. Crystalline structure of zirconia

XRD spectra were recorded but they are not included for the sake of brevity. The ZrO₂ sample obtained by calcination of a hydroxide gel at 600 °C, was a mixture of the monoclinic (M) and tetragonal (T) phases, as seen by inspection of the peak at 28.5 addressable to the M phase and the peak at 30.5 addressable to the T phase. The sample was mainly monoclinic. SO₄²⁻-ZrO₂ was mainly tetragonal and the crystallinity was lower than ZrO₂. The lower crystallinity of the SO₄²⁻-ZrO₂ sample as compared to the ZrO₂ sample was addressed to the delay in the crystallization temperature, due to the interference of the adsorbed sulfate anion.

3.3. Choice of solvent for preparation

A solvent had to be chosen for the solubilization of the organometallic complexes during preparation. It should not be strongly chemisorbed on SO₄²⁻-ZrO₂, or should be easily desorbed by heating in an air stream. Fig. 1 is a plot of the initial activity (1st pulse of each run) in the test of isomerization of *n*-butane in the pulse reactor, as a function of the temperature of activation (air, 10 ml min⁻¹ g_{cat}⁻¹, 1 h) for the SO₄²⁻-ZrO₂ catalyst (precalcined at 600 °C) doped with several solvents. Doping was performed by incipient wetness impregnation (filling the pore volume) followed by drying in a stove (110 °C, 8 h). Low activity values were thought to be linked to strong chemisorption of the solvent, blocking the active sites. As it can be seen, acetyl-ketone was easily desorbed and even seemed to help in the removal of adsorbed water because the activity of the ketone doped catalyst was higher than the water doped one, for the same temperature of calcination. The activity of SO₄²⁻-ZrO₂ has been previously reported to be sensitive to the hydration state and the catalyst has been shown to partly deactivate upon adsorption of room humidity [4]. The *N*-butyl-amine was strongly adsorbed and the catalyst needed to be calcined at temperatures higher than 600 °C to recover its activity. Methanol also seemed to

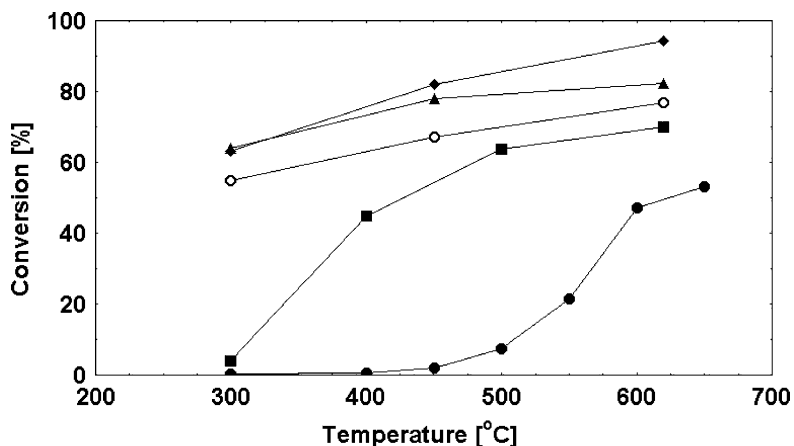


Fig. 1. Initial activity (first pulse) for isomerization of *n*-butane of $\text{SO}_4^{2-}\text{-ZrO}_2$ samples doped with several solvents and then activated in air (1 h, $10 \text{ ml min}^{-1} \text{ g}_{\text{cat}}^{-1}$) at different temperatures: *N*-butyl-amine (●); methanol (■); benzene (○); water (▲); and acetyl-ketone (◆).

act as a base but required lower temperatures for desorption. For its mild chemisorption on $\text{SO}_4^{2-}\text{-ZrO}_2$ and the good solubility of the organometallic precursors in it, benzene was chosen as the solvent for impregnation of the organometallic compounds. In this case, care was taken to always use air to activate the catalyst. Heating in an oxygen-free atmosphere has been reported to oxidize benzene to CO_2 and other products and reduce surface sulfates to SO_2 [19,20].

Water was also chemisorbed and $\text{SO}_4^{2-}\text{-ZrO}_2$ needed to be calcined at high temperatures in order to recover full activity, e.g. 620°C . The initial activity of the hydrated catalyst stabilized in air at 300°C was however fairly high, at least when measuring activity in the pulse reactor. $\text{SO}_4^{2-}\text{-Zr(OH)}_4$ amorphous catalysts are reported to be completely inactive for *n*-butane isomerization when activated at 300°C . This was in accord with our supposition that crystalline catalysts need lower activation temperatures, only related to removal of adsorbed water. In summary, strength of chemisorption of the solvent seemed to be related to its relative basicity, and followed the order: *n*-butylamine > methanol > benzene > water > acetyl-ketone.

Fig. 2 is a plot of conversion and selectivity to isobutane of a hydrated $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst (stabilized at 300°C in air, $10 \text{ ml min}^{-1} \text{ g}_{\text{cat}}^{-1}$, 1 h) and a dehydrated $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst (calcined at 600°C in air, $10 \text{ ml min}^{-1} \text{ g}_{\text{cat}}^{-1}$, 1 h), as a function of the

pulse number. A reaction test in pulse mode was chosen in order to accurately measure the conversion values of the fresh catalyst. The initial activity was fairly high for both catalysts. The catalyst activated at 600°C had approximately an initial conversion of 80% and the catalyst activated at 300°C an initial conversion of about 60%. The decay in conversion with the number of reacted pulses was however rapid for both catalysts and was due to formation of carbonaceous deposits. The decrease in *n*- C_4 conversion correlated with the increase in selectivity to isobutane. The main reaction product for the first pulses was propane and other smaller hydrocarbons were also present. The reaction of the last pulses yielded mainly isobutane and the remaining products were mainly propane and pentanes. The C_5/C_3 ratio was close to 1, indicating that most likely the reaction proceeded through a bimolecular alkylation-cracking mechanism, in which a branched C_8 adsorbed intermediate is either cracked symmetrically to produce butanes or asymmetrically to produce $\text{C}_3 + \text{C}_5$ [21].

The $\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts are deactivated by the deposition of carbonaceous deposits on the active sites and a stable conversion level can only be got in the presence of H_2 and a metal function, e.g. Pt. As seen in Fig. 2, deactivation of the Pt-free catalysts was evident and addition of Pt and the presence of H_2 was necessary to stabilize the conversion of the $\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts. The relatively high initial activity of

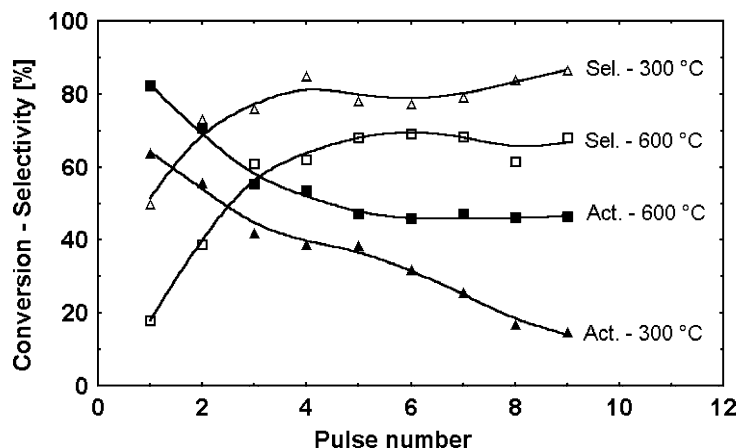


Fig. 2. Initial activity (full symbols) and selectivity to isobutane (hollow symbols) as a function of pulse number in the pulse reactor test. $\text{SO}_4^{2-}\text{-ZrO}_2$ catalyst firstly hydrated and then activated in air (1 h, $10 \text{ ml min}^{-1} \text{ g}_{\text{cat}}^{-1}$) at 300°C (\blacktriangle , \triangle) and 600°C (\blacksquare , \square).

$\text{SO}_4^{2-}\text{-ZrO}_2$ activated at 300°C encouraged us to think that if highly active Pt(0) could be formed in the Pt(0)/ $\text{SO}_4^{2-}\text{-ZrO}_2$ and Pt(IV)/ $\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts then a good level of $n\text{-C}_4$ isomerization activity should be achieved in the continuous flow test at a moderate $\text{H}_2/\text{hydrocarbon}$ ratio and without activating the catalysts at high temperatures.

3.4. TPR

Fig. 3 shows the TPR diagrams of different catalysts, Pt(IV)- ZrO_2 , Pt(0)/ $\text{SO}_4^{2-}\text{-ZrO}_2$ and

Pt(IV)/ $\text{SO}_4^{2-}\text{-ZrO}_2$. Hydrogen consumption peaks are indicated with different labels. Peaks due to sulfur reduction are marked with a black square label while those addressed to Pt reduction are marked with hollow circles. Each hydrogen consumption signal is further identified with the labels S(0), S(I), S(II), S(III) and S(IV).

On pure ZrO_2 , only high temperature reduction peaks were found (results not shown). A small peak at $100\text{--}120^\circ\text{C}$ was likely due to desorption of adsorbed water. Also small peaks at $550\text{--}575^\circ\text{C}$ were possibly linked to the reduction of Zr^{4+} to Zr^{3+} on the surface

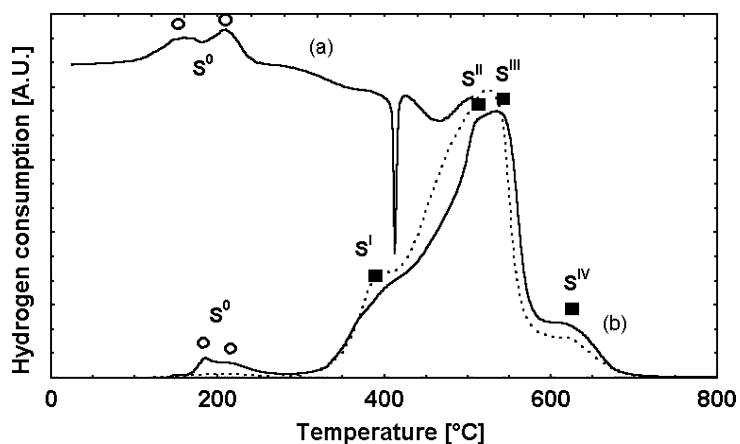


Fig. 3. TPR tests: (a) Pt(IV)- ZrO_2 dried at 110°C ($\times 3$); (b) Pt(IV)/ $\text{SO}_4^{2-}\text{-ZrO}_2$ dried at 110°C (continuous line); Pt(0)/ $\text{SO}_4^{2-}\text{-ZrO}_2$ dried at 110°C (dotted line).

and in the bulk. The magnitude of all these reduction peaks was completely negligible when compared to those of Pt (curve (a) in Fig. 3) and sulfate (curve (b) in Fig. 3). For this reason, the results of ZrO₂ reduction were not plotted.

In the case of Pt(IV)-ZrO₂ (curve (a), Fig. 3), a zone of reduction can be seen at 125–225 °C (indicated with circles) addressed to both the decomposition of the organometallic compound and the reduction of Pt⁴⁺ to Pt⁰. Desorption of hydrogen was detected by the presence of a sharp peak at 415 °C. In the case of Pt(0)-ZrO₂ (results not plotted), the pattern was similar though the area of the 125–225 peak (signal S(0)) was about three times smaller. The smaller S(0) peak was likely due to decomposition of the complex only and without Pt reduction because the Pt precursor was already in the zero oxidation state (see Eq. (2)). The sharp peak at about 400 °C was present on both catalysts. This peak is not found in common Pt-ZrO₂ catalysts (prepared in aqueous medium from common inorganic salts) and therefore we suppose that it could be related to a reaction of adsorbed solvent (e.g. benzene ↔ cyclohexane + H₂). The broad peak at 450 °C could be related to desorption of spilt over hydrogen but it can not be confirmed without further experimental evidence. Fig. 3 (b) contains the TPR profiles of Pt(IV)/SO₄²⁻-ZrO₂ (continuous line) and Pt(0)/SO₄²⁻-ZrO₂ (dotted line) while the different positions of the reduction peaks for catalysts calcined at different temperatures are indicated in Table 1. Values corresponding to the standard Pt*/SO₄²⁻-ZrO₂ catalyst prepared from H₂PtCl₆ and calcined at 600 °C, used as a reference, are also included in the table. Different reduction peaks are indicated with labels (S(0), S(I)–S(IV)). S(0) is addressed to the decompo-

sition of the organometal compound and the reduction of Pt to the metal state. The other signals are related to reduction of different groups of surface sulfate on SO₄²⁻-ZrO₂. The main peak, S(III), is big and broad. It has two smaller peaks mounted on, S(I) and S(II), related to sulfate groups of greater reducibility. It can be firstly remarked that no S(0) signal was present in the TPR profile of Pt(0)/SO₄²⁻-ZrO₂. The size and position of the S(I)–S(IV) signals was the same for both the Pt(0)/SO₄²⁻-ZrO₂ and Pt(IV)/SO₄²⁻-ZrO₂ catalysts. Absence of Pt reduction in the case of Pt(0)/SO₄²⁻-ZrO₂ was easily interpreted by supposing that the complex was in the zero oxidation state.

Table 1 contains the position of the peaks of reduction (in the TPR tests) of the Pt(0)/SO₄²⁻-ZrO₂ and Pt(IV)/SO₄²⁻-ZrO₂ catalysts, dried at 100 °C or calcined at higher temperatures. An inspection of the values indicates that there is a shift of the peaks of reduction upon calcination of the support in air. The shift is toward higher temperature and shows a degradation of the reducibility of the catalyst. The upward shift in peak S(III) was of 100 °C in the case of Pt(IV)/SO₄²⁻-ZrO₂ when calcination was performed at 300 °C. The shift grew to about 140 °C when calcination was performed at 600 °C. The shift was of 100 °C for Pt(0)/SO₄²⁻-ZrO₂ at both temperatures of calcination.

The degradation of the reducibility of the Pt(IV)/SO₄²⁻-ZrO₂ and Pt(0)/SO₄²⁻-ZrO₂ catalysts was addressed to a loss of Pt metal catalytic properties. The inhibition of the formation of atomic hydrogen would preclude the early reduction of sulfur. The effect on the organometallic catalysts was more severe than that found in Pt*/SO₄²⁻-ZrO₂ standard catalysts calcined at 600 °C. The S(III) peak, related to most of the

Table 1

Location of reduction peaks during TPR of Pt*/SO₄²⁻-ZrO₂, Pt(0)/SO₄²⁻-ZrO₂ and Pt(IV)/SO₄²⁻-ZrO₂ (influence of calcination temperature)

Sample (calcination temperature)	Peak S(0) (°C)	Peak S(I) (°C)	Peak S(II) (°C)	Peak S(III) (°C)	Peak S(IV) (°C)
Pt*/SO ₄ ²⁻ -ZrO ₂ (600 °C)	–	325	–	530	–
Pt(IV)/ SO ₄ ²⁻ -ZrO ₂ (110 °C)	190–210	395	510	535	630
Pt(IV)/ SO ₄ ²⁻ -ZrO ₂ (300 °C)	–	450	550–590	600–620	710
Pt(IV)/ SO ₄ ²⁻ -ZrO ₂ (600 °C)	–	470	590	670	710
Pt(0)/ SO ₄ ²⁻ -ZrO ₂ (110 °C)	–	395	485	525	625
Pt(0)/ SO ₄ ²⁻ -ZrO ₂ (300 °C)	–	450	585	625	695
Pt(0)/ SO ₄ ²⁻ -ZrO ₂ (600 °C)	–	425	–	590–630	–

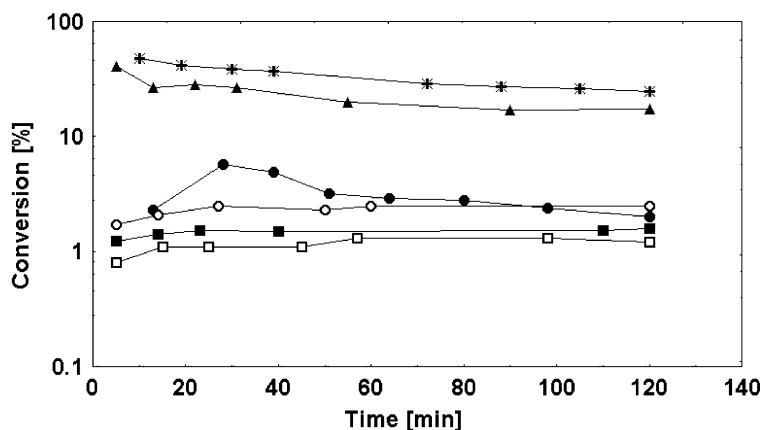


Fig. 4. Conversion of *n*-C₄ as a function of time-on-stream (continuous flow test, 300 °C, WHSV = 1 h⁻¹). Pt(0)/SO₄²⁻-ZrO₂ activated in air for 1 h at 300 °C: H₂/*n*-C₄ = 2 (●); H₂/*n*-C₄ = 6 (■). Pt(IV)/SO₄²⁻-ZrO₂ activated in air for 1 h at 300 °C: H₂/*n*-C₄ = 2 (○); H₂/*n*-C₄ = 6 (□). Pt*/SO₄²⁻-ZrO₂ calcined in air at 600 °C for 1 h: H₂/*n*-C₄ = 6 (*). Pt(0)/SO₄²⁻-ZrO₂ calcined in air at 600 °C for 1 h: H₂/*n*-C₄ = 6 (▲).

sulfate groups, was located at 530 °C in the case of Pt*/SO₄²⁻-ZrO₂ and at the same temperature of the organometallic catalysts dried at 110 °C.

3.5. Isomerization of *n*-butane

Fig. 4 is a plot of the conversion of *n*-C₄ in the continuous flow test in the presence of H₂. Pt*/SO₄²⁻-ZrO₂ was calcined at 600 °C in air for 2 h, then flushed with N₂ for 5 min and reduced in H₂ 1 h before the test. This sample had the highest activity in isomerization. The selectivity to isobutane was always high (>80%) regardless of the value of conversion. Selectivity was about 80–85% for a conversion of 30–50% and about 90–95% for a conversion lower than 20%.

The high conversion raised concerns on the possible presence of diffusion limitations to mass transfer inside the porous particles of the catalysts. The Weisz–Prater modulus (Φ) was calculated in order to check this point.

$$\Phi = \frac{R^2 r_v}{(CD_{\text{eff}})} = 0.002 \ll 1$$

(no diffusional limitations)

R is the particle radius (<0.025 cm); D_{eff} the effective diffusivity ($\approx 0.036 \text{ cm}^2 \text{ seg}^{-1}$); r_v the observed

reaction rate per unit volume ($\approx 2.0 \mu\text{mol seg}^{-1} \text{ ml}^{-1}$); C the concentration of the reactant ($\approx 20 \mu\text{mol ml}^{-1}$).

D_{eff} was calculated from the expression for the Knudsen coefficient because the mean Wheeler pore radius ($r_p = 12 \text{ nm}$) was smaller than the mean free path between molecular collisions as calculated by the kinetic theory.

In order to fulfill the restriction set for the activation conditions of Pt/SO₄²⁻-ZrO₂, the catalysts prepared from precalcined zirconia and organometallic Pt were activated in air at 300 °C for 2 h, then flushed with N₂ for 5 min (to remove adsorbed oxygen) and reduced at the reaction temperature for another 1 h in H₂ (10 ml min⁻¹ g_{cat}⁻¹) before being tested. These pre-treatments were performed in situ to avoid rehydration. Two different H₂/hydrocarbon molar ratios were used, 2 and 6. The latter is the minimum ratio to be used in the stable operation of common Pt*/SO₄²⁻-ZrO₂ catalysts [22]. The conversion of *n*-butane was very low (1–3%). The reason for the low activity was supposed to be linked to the incomplete elimination of adsorbed water or humidity at the temperature of activation. It has been reported that water requires high temperatures to be desorbed completely [4]. The activity was increased upon calcination at 600 °C (Fig. 4, triangles), but the conversion level was lower than that of Pt*/SO₄²⁻-ZrO₂ activated at the same temperature.

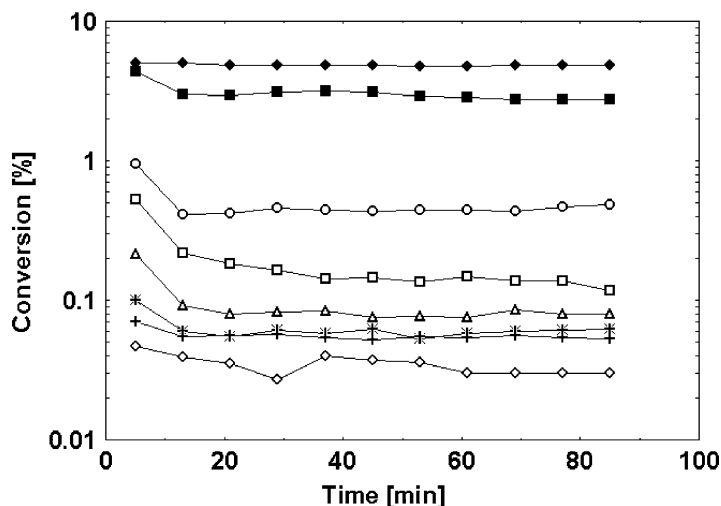


Fig. 5. Catalytic activity in dehydrogenation of cyclohexane on $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts reduced for 1 h in H_2 at different temperatures before the test. $\text{Pt}(0)\text{-ZrO}_2$ (270 °C) (◆). $\text{Pt}(0)/\text{SO}_4^{2-}\text{-ZrO}_2$ (270 °C) (○). Pt(IV)-ZrO_2 (270 °C) (■). $\text{Pt(IV)/SO}_4^{2-}\text{-ZrO}_2$ (270 °C) (□). $\text{Pt(IV)/SO}_4^{2-}\text{-ZrO}_2$ (350 °C) (△). $\text{Pt(IV)/SO}_4^{2-}\text{-ZrO}_2$ (500 °C) (◇). $\text{Pt}^*/\text{SO}_4^{2-}\text{-ZrO}_2$ (270 °C) (*). $\text{Pt}(0)/\text{SO}_4^{2-}\text{-ZrO}_2$ calcined at 600 °C in air and reduced at 270 °C (+).

3.6. Cyclohexane dehydrogenation

Fig. 5 shows a low level of conversion for all the catalysts tested in our experimental conditions. $\text{Pt}(0)\text{-ZrO}_2$ (reduced at 270 °C for 1 h in H_2 before the reaction) had the highest level of dehydrogenating activity (about 5%). In the case of Pt(IV)-ZrO_2 , the conversion of cyclohexane was lower (about 3%). For all catalysts tested the selectivity to benzene (under the used reaction conditions) was greater than 99% and only a very small contribution of cracking to lower hydrocarbons was detected.

For all the organometallic Pt based, sulfate doped catalysts the performance was better than that of $\text{Pt}^*/\text{SO}_4^{2-}\text{-ZrO}_2$ calcined at 600 °C, for similar crystal properties (all of them are tetragonal) and calcination temperature of the support. The conversion of $\text{Pt}(0)/\text{SO}_4^{2-}\text{-ZrO}_2$ and $\text{Pt(IV)/SO}_4^{2-}\text{-ZrO}_2$ was one order of magnitude higher than the conversion of standard $\text{Pt}^*/\text{SO}_4^{2-}\text{-ZrO}_2$. Their activity was however lower than that corresponding to $\text{Pt}(0)\text{-ZrO}_2$ or Pt(IV)-ZrO_2 . This effect could be a priori addressed to the presence of sulfur poisoning, since it seems difficult that oxidation of the Pt particles may occur at 300 °C. According to our experience, sulfur poisoning of Pt in the presence of $\text{SO}_4^{2-}\text{-ZrO}_2$

and H_2 can occur at temperatures as low as 100 °C [23].

Depending on the reduction temperature the conversion varied. A trend of decreasing activity at higher calcination temperatures was clear, as can be seen from the dehydrogenation conversion values for $\text{Pt(IV)/SO}_4^{2-}\text{-ZrO}_2$. At 350 °C activity decreased to a great extent, and at 500 °C conversion was already negligible.

3.7. IR measurements

The spectra of pyridine adsorption of $\text{Pt(IV)/SO}_4^{2-}\text{-ZrO}_2$ in three different hydration states are presented in Fig. 6 (b). The total acidity of the uncalcined sample (maintained at room temperature) was $157 \mu\text{mol pyridine g}_{\text{cat}}^{-1}$. The inspection of the peaks due to pyridine coordinatively adsorbed over Lewis sites ($1430\text{--}1460 \text{ cm}^{-1}$) and to pyridinium ions adsorbed over Brønsted sites ($1520\text{--}1560 \text{ cm}^{-1}$) indicates that heat treatments performed at successively higher temperatures reduce the amount of Brønsted acid sites. As expected from the hydration equilibrium between Brønsted and Lewis sites, the reduction in the intensity of the $1520\text{--}1560 \text{ cm}^{-1}$ band was correlated with a parallel augment in Lewis acidity.

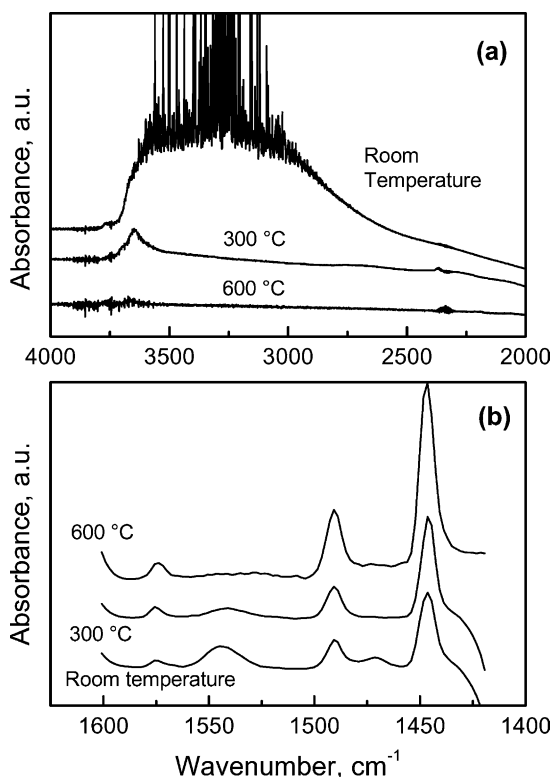


Fig. 6. IR spectra of a Pt(IV)/SO₄²⁻-ZrO₂ catalyst previously calcined in situ in air at different temperatures (room temperature, 300 and 600 °C). (a) After degassing in vacuo at 150 °C. (b) After adsorption of pyridine and degassing in vacuo at 150 °C.

Finally, the sample calcined at 600 °C had practically no Brønsted sites and all remaining acid sites were of the Lewis type. IR spectra in the zone of absorption of OH groups are plotted in Fig. 6 (a). In the case of the untreated sample, only maintained at room temperature, the high frequency spectral range (4000–2500 cm⁻¹) was dominated by a broad and unresolved absorption band at $\nu < 3600$ cm⁻¹, due to OH stretching modes of both undissociated water molecules and OH species interacting by H bonding. In the case of the OH groups vibrations due to tri-coordinated OH (3630–3720 cm⁻¹), di-coordinated OH (3740–3770 cm⁻¹) and mono-coordinated OH (3770–3810 cm⁻¹) have been reported on zirconia. Upon dehydration at 300 °C of the Pt(IV)/SO₄²⁻-ZrO₂ sample, the broad envelope disappears and the bands due to OH groups are visible. The band of

tri-coordinated OH groups dominates the spectrum at this temperature of pretreatment. Upon thorough dehydration at 600 °C, the previous band was reduced to less than one tenth its size and two other small bands due to di- and mono-coordinated OH appeared, possibly as a result of the conversion of tri-coordinated groups into OH groups of lower coordination.

4. Discussion

An alternative solution for the problem of the anomalous state of Pt on SO₄²⁻-ZrO₂ was tried, which consisted in the synthesis of new catalysts from organometallic Pt precursors and precalcined SO₄²⁻-ZrO₂. Activation at low temperatures was expected to sidestep the oxidation of the metal, a process thermally activated, and some other processes possibly taking place at high temperatures, such as Pt encapsulation and poisoning.

Pt was supposed to be reduced to Pt(0) at temperatures lower than 300 °C on both sulfate-free and sulfate-doped catalysts as seen from the TPR results of Pt(IV)/SO₄²⁻-ZrO₂, Pt(0)-ZrO₂ and Pt(IV)-ZrO₂. If the first TPR peak of Fig. 3 (b) of catalyst Pt(IV)/SO₄²⁻-ZrO₂ was due to Pt(*n*+) reduction, sulfur poisoning seemed undoubtedly to affect the Pt(0) particles because the activity in cyclohexane dehydrogenation was only one fifth that of the sulfur-free catalyst Pt(IV)-ZrO₂. The same comparison can be made between the activity in dehydrogenation of Pt(0)-ZrO₂ and Pt(0)/SO₄²⁻-ZrO₂. A series of Pt(IV)/SO₄²⁻-ZrO₂ catalysts (see Fig. 5) was further subjected to reduction at increasing temperatures before the test in order to check if the low activity in dehydrogenation could have been due to incomplete reduction. Not only the activity was not improved but increasing reduction temperatures lowered the dehydrogenation capacity. Activity for conversion of cyclohexane was lower after reducing at 350 °C and negligible after reducing at 500 °C. This trend is easily explained by considering that sulfate groups are reduced to SO₂ and then migrate to the surface of Pt where they are further reduced to H₂S and elemental sulfur which are strongly chemisorbed and block the active sites [24,25].

When activating Pt(IV)/SO₄²⁻-ZrO₂ and Pt(0)/SO₄²⁻-ZrO₂ at 270 °C, we found that the catalytic

activity of the metal function was higher than that of the standard Pt*/SO₄²⁻-ZrO₂ catalyst. However, the new catalyst was not very active for the isomerization of *n*-C₄ at this temperature of activation. The low activity in isomerization of *n*-C₄ when activating at 270 °C was supposed to be due to incomplete dehydration of the surface and/or incomplete removal of benzene. We saw in Fig. 2 (pulse reaction with pure *n*-C₄) that the initial activity of a hydrated catalyst activated at about 300 °C was fairly high. The initial conversion was about 60% and was not drastically lower than that of the dehydrated catalyst activated at 600 °C (approximately 80%). The comparison of the conversion values of the 9th pulse was less even. The conversion of the hydrated catalyst was less than 20% and was still decreasing while the conversion of the dehydrated catalyst calcined at 600 °C was more than 40% and more stable.

The result might indicate that Lewis acid sites are the main active sites in the reaction. It can be supposed that the hydrated catalyst had only a small number of free Lewis sites, while most of them had been converted to the Brønsted type or had water on them acting as a coordinatively bonded Lewis base. In the case of the dehydrated catalyst, there must have been more free Lewis sites present, because Brønsted sites transform to Lewis ones upon dehydration at high temperatures and evaporation of coordinated water leaves uncoordinated Zr⁴⁺ cations (Lewis sites) behind. This easily explains the results of Fig. 2, when only pure *n*-butane was used as reactant and Pt-free SO₄²⁻-ZrO₂ was the catalyst.

In the case of Pt loaded SO₄²⁻-ZrO₂ catalysts, they have been reported to produce H⁺ from H₂ [11]. Direct heterolytic dissociation is not likely and dissociation of H₂ into atomic H• over a few active Pt metal sites could be the first step, followed by electron abstraction over surface Lewis sites [26]. These protons have been posed to be the source of activity of the catalyst for activation of *n*-butane while atomic H• is supposed to hydrogenate coke precursors and stabilize the conversion level. Even in this case, our hypotheses that the presence of a high concentration of Lewis sites in the most active catalysts was the decisive factor, seems to be valid. Without active Lewis sites protonic acidity coming from reduction of H• is not feasible. From this point of view, it seems reasonable that the new Pt/SO₄²⁻-ZrO₂ activated

at low temperature had lower activity because the concentration of surface Lewis sites was too low.

It could be however possible that the catalyst were much more active for some other reaction demanding a bifunctional catalyst and a less active acid function, e.g. the one-step hydroisomerization of benzene to methylcyclopentane [27]. However, no new attempts with other reactions were done in this work.

Concerning the phenomena that led to a loss of metal properties of the Pt(0)/SO₄²⁻-ZrO₂ catalyst after calcination in air at 600 °C (loss of cyclohexane dehydrogenation activity, Fig. 5), encapsulation in the zirconia matrix, as stated in [8,9] seems not likely because ionic mobility is only important during crystallization and the SO₄²⁻-ZrO₂ catalysts were already crystalline. One explanation could be that sulfate groups were decomposed to SO₂ and were chemisorbed over the Pt particles. During reduction the adsorbed species would have been further reduced to H₂S and elemental sulfur, thus blocking the active sites for de/hydrogenation. Oxidation of the Pt particles to form surface PtO_x during calcination in air was also likely. The one electron transfer, oxidizing ability of SO₄²⁻-ZrO₂ catalysts has been highlighted by many authors [7,28,29] and has been posed as the key feature for activation of light inert alkanes. However, the mechanism by which this oxidation might take place on the Pt particles is unclear in this case.

5. Conclusions

Calcination of sulfated zirconium hydroxide at 600 °C, impregnation of the crystalline obtained material with an organometallic Pt complex and reduction of this material at a temperature lower than 300 °C yields a catalyst which has a non-negligible level of metal activity for cyclohexane dehydrogenation, much higher than that of standard SO₄²⁻-ZrO₂ supported Pt catalysts. At low temperatures of activation in air, the activity of the acid function for *n*-C₄ isomerization is however low, likely because of incomplete surface dehydration.

Upon calcination in air at high temperature (600 °C) the dehydrogenation properties of the supported metal Pt particles are lost but the acid function attains full capacity for alkane isomerization. Reduction of the catalysts at successively higher temperatures produces

a decrease in metal activity for cyclohexane dehydrogenation; it is negligible after reduction at 500 °C in H₂. The results indicate that the loss of metal properties of Pt supported over SO₄²⁻-ZrO₂ is not related to phenomena occurring during crystallization but to sulfur poisoning in a reducing atmosphere or oxidation in air at high temperatures.

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