

Manifestation of the Effect of Strong Metal–Support Interaction in a Pt/TiO₂ Rutile Catalyst

Yu. M. Shul'ga*, I. N. Ivleva*, N. A. Gaidai**, T. A. Zav'yalov**, and E. N. Kurkin***

* Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

** Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 117913 Russia

*** Institute of New Chemical Problems, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

Received July 2, 1998

Abstract—Pt/TiO₂ catalysts supported on ultradispersed rutile are prepared. The effect of strong metal–support interaction (SMSI) in these catalysts is more pronounced than in Pt/TiO₂ catalysts with greater fractions of an anatase phase in the support. Mild oxidation of the rutile catalyst eliminates the SMSI effect.

INTRODUCTION

TiO₂ is the most typical and well-studied support for demonstrating the effect of strong metal–support interaction (SMSI) [1]. Analysis of published data indicates that the majority of studies concerning this effect in TiO₂ was performed with Degussa P 25 powder, which contains ~85% anatase and 15% rutile [2]. Rutile is the most thermodynamically stable structure of titanium dioxide. The anatase–rutile transition takes place at 1300 K; however, this temperature can be dramatically lowered in the case of fine particles of TiO₂ or in the presence of a metal that catalyzes the above transition. The heating of a Pt/TiO₂ catalyst in hydrogen to 773 K (a temperature typical of the transition of the catalyst to the SMSI state) results in a change in the phase composition of the Degussa P 25 support toward an increase in the rutile fraction. The relationship between the SMSI effect and the anatase–rutile phase transition was directly demonstrated in a number of recent papers (see, for example, [1]).

The aim of this work was to examine the SMSI effect by the example of Pt/TiO₂ catalysts in which specially prepared ultrafine rutile was used as a support. The catalyst activity was characterized by the rate of toluene hydrogenation. The toluene hydrogenation on a Pt/TiO₂ (Degussa P 25) catalyst was studied previously [3]. In this work, X-ray diffraction patterns were obtained and the magnetic susceptibilities of the supports and catalysts were measured at different steps of the treatment. Data on the magnetic susceptibility of a platinum/anatase catalyst were published in [4]. In this work, we studied changes in the activity of the rutile-based catalyst upon repeatedly performed low-temperature reduction–high-temperature reduction–mild oxidation (after the elimination of the SMSI effect) cycles. For comparison, we examined catalysts based on Degussa P 25 powders and pure anatase.

EXPERIMENTAL

Three types of titanium dioxide powder were used as supports. Powders I and III with specific surface areas of 95 and 65 m²/g, respectively, were prepared by vapor-phase decomposition of TiCl₄ according to a procedure described in [5]. The X-ray diffraction patterns of the initial supports (Fig. 1) indicate that their crystalline fraction primarily consists of rutile (powder I) or anatase (powder III). Support II was a commercial Degussa P 25 powder. According to our measurements, its specific surface area was ~40 m²/g.

Pt/TiO₂ catalysts supported on rutile (I) containing 1 and 3 wt % platinum metal were prepared by impregnating the support with a 0.5% (in terms of platinum) aqueous H₂PtCl₆ solution. Before impregnation, the support was calcined in an oxygen atmosphere ($P_{O_2} = 2.7 \times 10^4$ Pa) at 803 K for 3 h. After impregnation, the sample was dried in air upon continuous stirring with a quartz stick initially at 353–363 K for 3–6 h and then at

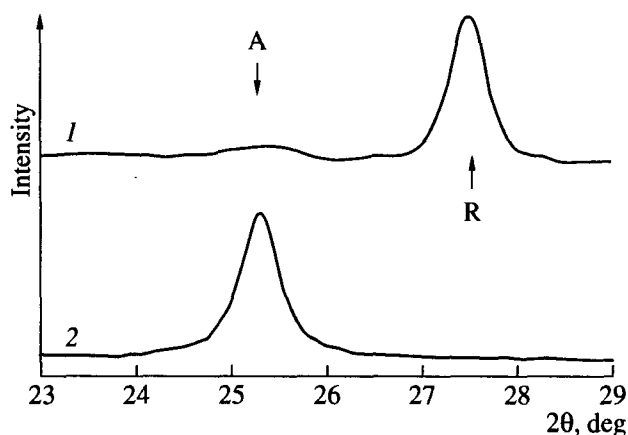


Fig. 1. Fragments of the X-ray diffraction patterns of (1) support I after calcination in an oxygen atmosphere at 803 K and (2) initial support III in the region of the most intense peaks of (A) anatase and (R) rutile phases.

Table 1. Positions of the centers (*C*), half-widths (*W*), and integral intensities (*I*) of peaks in the X-ray diffraction patterns of test samples*

Sample	Treatment	Peak	<i>C</i> , degree	<i>W</i> , degree	<i>I</i>
TiO ₂ (I)	No treatment	A	25.38	0.807	0.33
		R	27.49	0.494	1.00
TiO ₂ (I)	O ₂ , 803 K	A	25.36	0.454	0.09
		R	27.51	0.375	1.00
3%Pt/TiO ₂ (I)	H ₂ , 773 K	A	25.38	0.362	0.05
		R	27.52	0.381	1.00
3%Pt/TiO ₂ (I)	After 6 cycles	A	Unchanged	Unchanged	>0.02
		R	27.65	0.309	1.00
TiO ₂ (III)	No treatment	A	25.29	0.432	1.00

* Henceforth, degrees are given on a 2θ scale.

393–403 K for 1 h. The final samples were light yellow. Catalysts based on anatase (powder III) were prepared by a similar procedure [4]. The catalyst on support II was prepared by Shpiro *et al.* [6].

The catalytic measurements under steady-state conditions were performed using a gradientless circulation reactor described in [7]. The reaction kinetics and the catalyst activity were studied at 403 and 433 K. The initial pressures of toluene and hydrogen were 1.16×10^{-3} and 0.99 atm, respectively. Before hydrogenation, the catalyst was reduced in a hydrogen flow directly in the reactor at $T_{\text{red}} = 473$ or 773 K.

For the magnetic susceptibility measurements, a catalyst reduced in a separate quartz vessel was sealed in a quartz ampule in a metal box with an inert atmosphere. The magnetic susceptibility was measured by the Faraday method at external magnetic field intensities of 4.1, 5.6, 6.3, 7.6, and 8.8 kOe using the instrument described in [8]. The scale of the Faraday balance was calibrated using Hg[Co(CNS)₄], for which the magnetic susceptibility was taken equal to 16.44×10^{-6} CGS units per gram ($\chi_{1/g}$) at $T = 293$ K. The precision of magnetic susceptibility measurements of the instrument was 2×10^{-9} CGS units at $H = 7.6$ kOe. The absolute accuracy of χ measurements primarily depends on the accuracy of weighing the test samples. In this study, the absolute accuracy of $\chi_{1/g}$ measurements for catalysts was 0.01×10^{-6} CGS units in the worst case.

The X-ray diffraction patterns of the catalysts were measured at all stages of the synthesis and treatment (a DRON ADP-1 instrument).

The specific surface area of TiO₂ powders was measured by the BET method using the low-temperature adsorption of krypton.

RESULTS AND DISCUSSION

Figure 1 demonstrates the diffraction patterns of supports I and III in the region of the most intense

peaks of rutile and anatase phases. The diffraction pattern of initial support I exhibits a broad peak (peak A), which results from an anatase impurity, apart from the main peak due to the presence of rutile (peak R). The calcination of powder in an oxygen atmosphere at 803 K resulted in a decrease in the relative intensity of peak A and in a decrease in the half-widths of both peaks (Table 1). In this case, the specific surface area decreased from 95 to 65 m²/g. Thus, as a result of the preliminary calcination of the initial powder in oxygen, the coherent scattering region of the component crystallites increased and the fraction of the impurity phase decreased; however, a reasonably high specific surface area was retained.

The diffraction patterns of Pt/TiO₂ catalysts based on support I both before and after reduction in hydrogen at 473 K are almost identical to the diffraction pattern of the support precalcined in oxygen at 803 K. Minor changes can be observed only in the diffraction patterns of catalysts reduced at 773 K (Table 1). These changes consist in a further decrease in the anatase fraction and, in general, provide support for the published data that platinum catalyzes the anatase–rutile phase transition. In the case of support I, preliminary calcination in oxygen dramatically decreased this effect.

The phase composition of support II is well known [2]. It is also known that high-temperature reduction of catalysts based on support II (catalysts II) significantly increased the fraction of a rutile phase [2]. The reduction of Pt/TiO₂ catalysts (III) at 774 K dramatically decreased the specific surface area (to ~20 m²/g) and increased the intensity of peak R in the diffraction pattern.

The following equation that describes the rate of toluene hydrogenation on Pt/TiO₂ catalysts in the temperature range 403–453 K was given in [3]:

$$r = k(P_t P_H^n) / (P_H^{0.5} + k_1 P_H + k_2 P_t)^2, \quad (1)$$

where P_t is the pressure of toluene; P_H is the pressure of hydrogen; n is the exponent equal to 1 or 2 depending on the temperature for the preliminary reduction of the catalyst [3]; and k , k_1 , and k_2 are constants. With $P_t = P_{t0}(1 - x)$, equation (1) can be presented as

$$r = A(1 - x)/(B - x)^2, \quad (2)$$

where x is the fraction of reacted toluene, $A = kP_H^n/k_2^2P_{t0}$, and $B = 1 + P_H^{0.5}/k_2P_{t0} + k_1P_H/k_2P_{t0}$. Thus, using the experimental data and the condition that the reaction rate is equal to zero at $x = 1$, we can find A and B by the least-squares technique and hence determine the rate of hydrogenation at the conversion equal to zero: $r(0) = A/B^2$.

Figure 2 demonstrates the experimental data on the kinetics of toluene hydrogenation on catalyst II. It can be seen that function (2) adequately describes the experimental results. The experimental data obtained on other catalysts were treated in a similar manner. Table 2 summarizes the results of calculations. The catalysts on supports II and III exhibited the highest and lowest activities, respectively, at a treatment temperature of 473 K. The rate of hydrogenation on all of the three types of catalysts decreased as the temperature of catalyst reduction increased. However, the activity of catalyst III insignificantly decreased as the reduction temperature increased from 473 to 773 K, whereas this effect in catalyst I was considerable. We failed to detect toluene transformations after the catalyst reduction at 773 K, whereas the reaction kinetics could be followed using the same portion of the catalyst reduced at 473 K. The rate of toluene hydrogenation on an anatase catalyst (support III) at 433 K decreased from 1.30 to ~ 0.9 mmol g⁻¹ h⁻¹ as the reduction temperature increased from 473 to 773 K. Thus, the SMSI effect was most pronounced in the case of catalyst I and least pronounced in the case of catalyst III.

The SMSI effect can result from both reversible and irreversible processes occurring during the reduction of catalysts. To examine the reversibility of these processes, the sequence of low-temperature (473 K) and high-temperature reductions (773 K) is usually completed by mild oxidation of the catalyst. It was postulated in the literature that a reversible component of the SMSI effect disappears after mild oxidation; that is, the catalyst activity after repeated low-temperature reduction returns to the initial level. Table 2 summarizes the values of $r(0)$ for catalysts I and II reduced at 473 K after oxidation with the air at 473 K. These experiments were not performed with catalyst III because the SMSI effect for this catalyst was extremely low even in the first cycle. The returning of $r(0)$ to the initial level was never observed. However, the value of $r(0)$ for catalyst I in the second cycle was lower than that in the first cycle, whereas the opposite situation took place for catalyst II. This finding stimulated us to study the changes in $r(0)$ on catalyst I upon repeatedly performing the following cycles: reduction at 473 K–activity test in the reaction

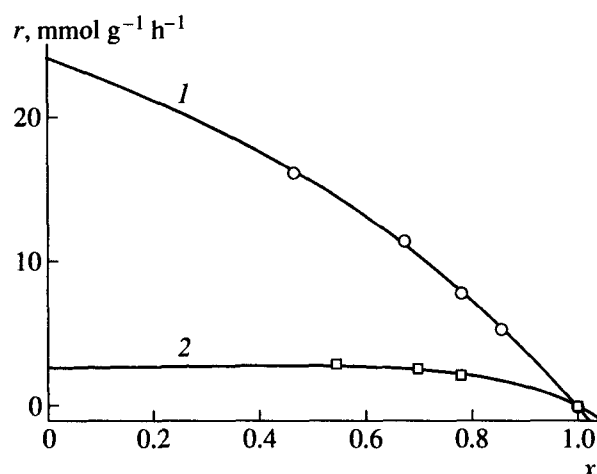


Fig. 2. Rate of toluene hydrogenation on 1%Pt/TiO₂ (II) as a function of conversion at 403 K after preliminary reduction of the catalyst at (1) 473 or (2) 773 K. Points indicate the experimental data, and lines correspond to calculations by equation (2).

of toluene hydrogenation under standard conditions—reduction at 773 K–activity test–oxidation and reduction at 473 K–activity test. Figure 3 illustrates the data obtained. Curves 1 and 2 correspond to catalysts reduced at 473 and 773 K, respectively. The first point in curve 1 (the first cycle) was obtained after the reduction of a fresh catalyst at 473 K; the catalyst activity was equal to zero after reduction at 773 K (curve 2). After the oxidation and repeated reduction of this catalyst at 473 K, its activity was higher than the initial level, and the activity after oxidation and repeated reduction at 773 K was higher than zero, although very small (cycle 2). Further repeated oxidation and reduction at 473 K (cycles 3–5) brought the reaction rate of toluene hydrogenation under standard conditions closer to the initial level. A dramatic decrease in $r(0)$ was observed only after the sixth cycle. The rate of the reaction on a catalyst reduced at 773 K remained almost unchanged in repeated cycles. An analysis of the X-ray

Table 2. Rate of toluene hydrogenation on 1 wt % Pt/TiO₂ catalysts at $x = 0$

T_{red}, K	$r(0), \text{mmol g}^{-1} \text{h}^{-1}$			
	catalyst I		catalyst II, 433 K	catalyst III, 433 K
	403 K	433 K		
473	5.0	6.9	24.0	1.30
573	2.01	2.61	—	—
673	0.35	0.38	—	—
773	<0.03	<0.03	3.96	0.92
473	8.7*	10.6*	2.59*	—

* The rate of toluene hydrogenation after the second cycle of the catalyst pretreatment (see the text).

Table 3. Magnetic susceptibility of test samples

Sample no.	Sample	Treatment	Time of contact with air, min	$\chi_{1/g} \times 10^6$, CGS units	
				290 K	80 K
1	TiO ₂ (I)	No treatment		-0.11	
2	TiO ₂ (I)	O ₂ , 803 K	60	-0.12	
3	1%Pt/TiO ₂ (I)	No treatment	1440	+0.11	
4	1%Pt/TiO ₂ (I)	H ₂ , 473 K	0	+0.38	+0.89
5	1%Pt/TiO ₂ (I)	H ₂ , 473 K	30	+0.12	
6	1%Pt/TiO ₂ (I)	H ₂ , 473 K	1440	+0.07	
7	1%Pt/TiO ₂ (I)	H ₂ , 773 K	0	+0.17	+0.30
8	1%Pt/TiO ₂ (I)	H ₂ , 773 K	30	+0.10	
9	1%Pt/TiO ₂ (I)	H ₂ , 773 K	1440	+0.07	
10	3%Pt/TiO ₂ (I)	No treatment	1440	+0.20	
11	3%Pt/TiO ₂ (I)	H ₂ , 473 K	0	+0.47	+0.75
12	3%Pt/TiO ₂ (I)	H ₂ , 473 K	30	+0.16	
13	3%Pt/TiO ₂ (I)	H ₂ , 473 K	1440	+0.10	
14	3%Pt/TiO ₂ (I)	H ₂ , 773 K	0	+0.33	+0.66
15	3%Pt/TiO ₂ (I)	H ₂ , 773 K	30	+0.10	
16	3%Pt/TiO ₂ (I)	H ₂ , 773 K	1440	+0.07	
17	TiO ₂ (III)	No treatment		-0.14	
18	TiO ₂ (III)	O ₂ , 773 K	1440	-0.16	
19	1%Pt/TiO ₂ (III)	H ₂ , 473 K	0	+0.07	
20	1%Pt/TiO ₂ (III)	H ₂ , 473 K	>3	+0.07	
21	1%Pt/TiO ₂ (III)	H ₂ , 773 K	0	+0.17	
22	1%Pt/TiO ₂ (III)	H ₂ , 773 K	>3	+0.07	

diffraction patterns of catalyst **I** after the sixth cycle demonstrated that it almost completely consists of rutile. In addition to the peaks of rutile, the diffraction pattern exhibits rather intense peaks due to the presence of platinum metal. The peak at $2\theta = 39.75^\circ$ exhibits a maximum intensity (particle diameter of 2.265 Å). The specific surface area of the catalyst after the sixth cycle was as low as 26 m²/g.

We failed to compare the magnetic properties of catalysts of all types because a catalyst based on the Degussa P 25 powder contained a detectable amount of ferromagnetic impurities. Table 3 summarizes the results of measurements of the magnetic susceptibility

of catalysts **I** and **III**. The TiO₂ powders prepared by us are diamagnetic. Calcination of the powders in oxygen left their magnetic susceptibility almost unaffected. All Pt/TiO₂ catalysts are paramagnetic. A contact with the air decreased a paramagnetic component of the susceptibility. The paramagnetic susceptibility of catalyst **III** reduced at a high temperature decreased more rapidly than in the case of catalyst **I**. However, the susceptibility of catalyst **III** reduced at a low temperature remained unchanged in contact with the air. All of the reduced rutile catalysts acquire a weak paramagnetic state with time. Catalyst **I** reduced at 473 K exhibits a specific susceptibility higher than that of the catalyst reduced at 773 K. In this respect, a rutile catalyst is different from an anatase one, whose susceptibility monotonically increased as the reduction temperature was increased. We also found that the paramagnetic susceptibility of reduced catalysts **I** increased with the decreasing temperature of the measurements (Table 3).

Let us consider these data within the framework of two simple models.

Model 1: The reduction results in the formation of platinum metal clusters, and the support remains unaffected. Then, the magnetic susceptibility of a 1%

Table 4. Treatment of the data on the magnetic susceptibility of catalysts **I** by equation (3)

Catalyst	T_{red} , K	C	$\chi_{\text{ti}} \times 10^6$, CGS units	$N \times 10^{-19}$
1%Pt/TiO ₂	473	56	0.19	8.3
1%Pt/TiO ₂	773	12	0.15	1.8
3%Pt/TiO ₂	473	31	0.36	4.6
3%Pt/TiO ₂	773	36	0.20	5.4

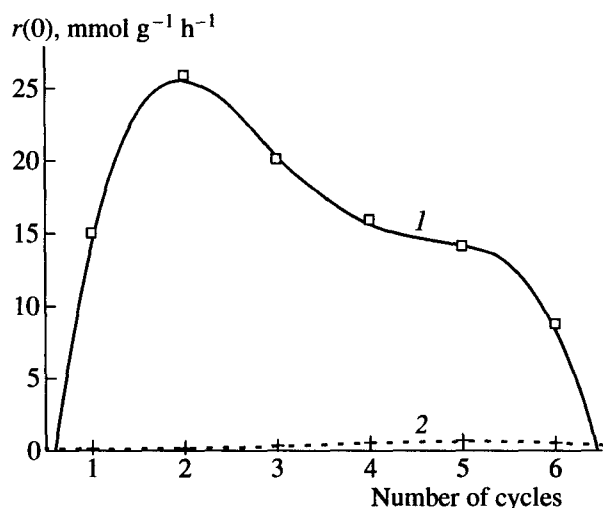


Fig. 3. Dependence of $r(0)$ at 403 K on the number of reduction-oxidation cycles of a 3%Pt/TiO₂ catalyst: (1) preliminary reduction at 473 K and (2) preliminary reduction at 773 K.

Pt/TiO₂ catalyst is $\chi_{1/g} = 0.99\chi'_{1/g} + 0.01\chi''_{1/g}$, where $\chi'_{1/g}$ and $\chi''_{1/g}$ are the magnetic susceptibilities of TiO₂ and platinum metal, respectively. The susceptibility $\chi'_{1/g}$ is known (sample 2 in Table 3). According to [9], $\chi''_{1/g} = 0.97 \times 10^{-6}$ CGS units for platinum metal. Consequently, in terms of this model, Pt/TiO₂ $\chi_{1/r} = -0.11 \times 10^{-6}$ CGS units for the 1% Pt/TiO₂ catalyst, and this value is independent of the reduction and measurement temperatures, in contrast to experimental results.

Model 2: The support is partially reduced simultaneously with the reduction of platinum (Ti³⁺ is formed). It is well known that the magnetic susceptibility of trivalent titanium obeys the Curie law ($\chi = C/T$) down to very low temperatures [9]. The treatment of the results of susceptibility measurements at two temperatures using the equation

$$\chi = C/T + \chi_{ti}, \quad (3)$$

where χ_{ti} is a temperature-independent part of χ , gives positive values for both parameters (Table 4). We can estimate the number N of Ti³⁺ ions per gram of the catalyst from the relation

$$C = N(\mu_{\text{eff}})^2/k_B, \quad (4)$$

where μ_{eff} is the effective magnetic momentum, and k_B is the Boltzmann constant assuming that $\mu_{\text{eff}} \approx 1.8\mu_B$. Table 4 summarizes the values of N thus found. The total number of titanium atoms in 1 g of a 1% Pt/TiO₂ catalyst is equal to 7.5×10^{21} , and the number of platinum atoms is 3.1×10^{19} . Consequently, the paramagnetic Ti³⁺ ions can, in principle, affect the electronic properties of platinum particles because their number is comparable to the number of platinum atoms. A positive and reasonably high value of χ_{ti} can be indicative, for example, of a great number of free electrons in the sample. The χ_{ti} values for reduced catalysts cannot be explained only by free electrons of platinum clusters, in particular, if the diamagnetism of an ionic framework is taken into account. It is believed that free electrons are present in areas adjacent to platinum clusters on the support. It is likely that paramagnetic centers formed upon reduction of the support interact with one another, and platinum particles participate in the exchange interaction as bridging structures.

To elucidate the question concerning the exchange interactions in reduced Pt/TiO₂ catalysts, it is necessary to examine the temperature dependence of the magnetic susceptibility in more detail.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 96-03-34125).

REFERENCES

1. Ermolov, L.V. and Slinkin, A.A., *Usp. Khim.*, 1991, vol. 60, no. 4, p. 689.
2. Haller, G.L. and Resasco, D.E., *Adv. Catal.*, 1989, vol. 36, p. 173.
3. Novikov, P.B., Gaidai, N.A., Nekrasov, N.V., et al., *Proc. 3rd Eur. Congr. on Catalyst*, Krakow, 1997, vol. 2, p. 582.
4. Shul'ga, Yu.M., Ivleva, I.N., Borod'ko, Yu.G., et al., *Kinet. Katal.*, 1997, vol. 38, no. 6, p. 935.
5. Troitskii, V.N., *Tekhnol. Legkikh Splavov*, 1996, no. 6, p. 15.
6. Shpiro, E.S., Dyubensina, B.B., Tkachenko, O.P., et al., *Kinet. Katal.*, 1986, vol. 27, no. 3, p. 638.
7. Novikov, P.B., Gaidai, N.A., Nekrasov, N.V., et al., *Proc. 8th Int. Symp.*, Bulgaria, 1996, pt. 1, p. 117.
8. Kolesov, Yu.R., Ivleva, I.N., Zelenov, N.A., et al., *Prib. Tekh. Eksp.*, 1973, no. 1, p. 217.
9. Kittel, Ch., *Introduction to Solid State Physics*, New York: Wiley, 1977.