Magnetic susceptibility of ultradispersed rutile and related Pt/TiO_2 catalysts

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The magnetic susceptibilities of ultradispersed rutile and catalysts 1% Pt/TiO_2 and 3% Pt/TiO_2 were measured. Rutile-based catalysts are paramagnetic, and their magnetic susceptibilities increase as the platinum content increases.

Key words: Pt/TiO_2 catalysts, ultradispersed rutile; magnetic susceptibility; X-ray photoelectron spectra.

Pt/TiO_2 catalysts with a pronounced effect of strong metal—support interaction (SMSI) are usually prepared from TiO_2 powders consisting of anatase (the main phase) and rutile.[1] The rutile structure is thermodynamically more stable. The anatase—rutile transition occurs at ~1300 K. This temperature can be considerably lower for powders with large specific surfaces. Some metals, including platinum, accelerate this phase transition.[2,3] The SMSI effect in Pt/TiO_2 catalyst is observed at ~800 K. At the same temperature, the fraction of rutile in the sample studied is often increased. Based on this fact, some researchers indicate a possible relation between the SMSI effect and the anatase—rutile phase transition for Pt/TiO_2 catalyst.[4] It seems promising to use ultradispersed rutile as the support in order to reveal the role of the phase transition during the formation of the SMSI state in the Pt/TiO_2 catalyst.

In this work, we studied the magnetic susceptibility of ultradispersed TiO_2 powder, whose main phase is rutile, and Pt/TiO_2 catalysts based on it. It has been previously shown[5] that an increase in the temperature of reduction of the "anatase" Pt/TiO_2 catalyst results in an increase in its paramagnetic susceptibility. It was of interest to compare the magnetic properties of the anatase- and rutile-supported Pt/TiO_2 catalysts.

Experimental

Ultradispersed TiO_2 powder with a specific surface of 95 $m^2\,g^{-1}$ obtained by vapor-phase decomposition of $TiCl_4$ was used as the support. The diffraction pattern of the support (Fig. 1, curve *1*) indicates that its crystalline part is mainly rutile. The support was pre-calcined in an O_2 atmosphere for 3 h ($p = 2.7 \cdot 10^4$ Pa) at 803 K.

Catalysts containing 1 and 3 wt.% Pt were prepared by impregnation with an aqueous solution of H_2PtCl_6. Then the samples were dried in air with continuous stirring for 3—6 h at 353—363 K and for 1 h at 393—403 K. The catalysts thus prepared were light-yellow.

The catalysts (weighed sample 100 mg) were reduced by dihydrogen ($p = 2.7 \cdot 10^4$ Pa) in a quartz vessel designed as a

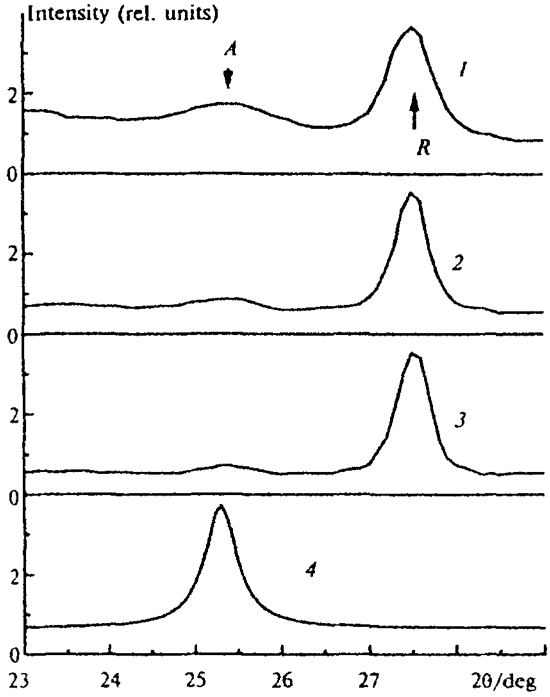

Fig. 1. Diffraction patterns of powders: *1*, starting TiO_2 (S_{sp} = 95 $m^2\,g^{-1}$); *2*, sample calcined in O_2 at 803 K (S_{sp} = 65 $m^2\,g^{-1}$); *3*, 3% Pt/TiO_2 catalyst reduced in H_2 at 773 K; and *4*, TiO_2—anatase (S_{sp} = 55 $m^2\,g^{-1}$).

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tube (diameter 3 cm, length 20 cm, volume ~120 cm^3) with a ground joint. Before heating, the tube was pumped out to ~0.2 Pa, filled with dihydrogen to ~9 · 10^4 Pa, evacuated to 0.2 Pa, and again filled with dihydrogen to 2.7 · 10^4 Pa. At this pressure, the molar amount of dihydrogen in the tube exceeded the molar amount of platinum by three orders of magnitude. After H_2 was fed, the samples changed color from yellow to dark-gray even at room temperature.

Heating was carried out using a tube furnace mounted at a ~10° angle to the horizontal. The bottom part (~10 cm) of the quartz tube with a thermocouple, whose junction was above the reduced sample, was placed in the furnace. The upper part of the quartz tube was isolated by an asbestos tissue. This installation provided convection mixing of the gas in the tube. The treatment of the sample with dihydrogen at 473 K practically did not change its color. After reduction at 773 K, the color of the sample became lighter, which is especially pronounced in the case of the 1% catalyst.

For studying the magnetic susceptibility, the catalyst reduced in H_2 was placed in a sealed quartz ampule in a metallic box with an inert atmosphere. The contents of O_2 and H_2O in the atmosphere of the box were maintained at a low level by P_2O_5. The magnetic susceptibility was measured by the known method[6] at an intensity of the external magnetic field equal to 4.1, 5.6, 6.3, 7.6, and 8.8 kOe. The scale of the Faraday balance was calibrated by $Hg[Co(CNS)_4]$ for which the value χ_g = 16.44 · 10^{-6} CGS at 293 K was accepted. The absolute accuracy of χ_g measurements determined mainly by the accuracy of weighing of the sample under study was ±0.01 · 10^{-6} CGS.

The preparation of samples for studying XPE spectra has been previously described in detail.[7] The Al-Kα radiation ($h\nu$ = 1486.6 eV) was used. The Ti $2p_{3/2}$ peak (458.8 eV) was used for calibration of XPS. This corresponds to the bond energy E_b = 284.9 eV of the C 1s peak of hydrocarbons adsorbed on the surface of the starting catalyst.

A DRON UM-3 instrument was used for recording diffraction patterns.

The specific surface of TiO_2 powders was determined by the BET method from the low-temperature adsorption of krypton.

Results and Discussion

The diffraction pattern for the starting TiO_2 (see Fig. 1, curve *1*) exhibits, along with the peak of the main phase rutile (peak *R*), the broad peak *A* of the anatase admixture. The latter is confirmed by the diffraction pattern of anatase (see Fig. 1, curve *4*). Calcination of the starting TiO_2 powder in the O_2 atmosphere at 803 K results in a decrease in the relative intensity of peak *A* from 33—38 to 9—12% and a decrease in the half-widths of both peaks (Table 1). The specific surface of the powder decreases from 95 to 65 m^2 g^{-1}. Thus, after calcination of the starting sample in dioxygen, the average size of the crystallites that compose the sample increases, and the fraction of the anatase phase decreases, but, nevertheless, a sufficiently high specific surface is retained.

Table 1. Positions of the center (C/deg) and half-width (Δ/deg) and integral intensities (I) of peaks in the diffraction patterns presented in Fig. 1

Sample (conditions of treatment)	Peak	Gaussian[a]			Lorentzian[a]		
		C	Δ	I	C	Δ	I
TiO_2	*1*	25.42	1.021	0.38	25.38	0.807	0.33
(starting)	*2*	27.49	0.536	1.00	27.49	0.494	1.00
TiO_2	*1*	25.34	0.634	0.12	25.36	0.454	0.09
(O_2, 803 K)	*2*	27.50	0.406	1.00	27.51	0.375	1.00
3%Pt/TiO_2	*1*	25.38	0.554	0.08	25.38	0.362	0.05
(H_2, 773 K)	*2*	27.51	0.405	1.00	27.52	0.381	1.00
TiO_2[b]	*1*	25.29	0.469	1.00	25.29	0.432	1.00

[a] Approximation function. [b] Anatase.

The diffraction patterns of the Pt/TiO_2 catalysts before and after the reduction in H_2 at 473 K are almost the same as the diffraction pattern of the calcined TiO_2 powder (see Fig. 1, curve *2*). Slight changes (a decrease in the intensity of *A*) are observed only in the diffraction patterns of the catalysts reduced at 773 K (see Fig. 1, Table 1). The high-temperature reduction of the 1% Pt/TiO_2 catalyst results in smaller changes in its diffraction pattern as compared to those for 3% Pt/TiO_2. These changes confirm, as a whole, the data[2,3] that platinum catalyzes the anatase—rutile phase transition. However, the calcination of TiO_2 in O_2 decreases substantially the value of this effect. It is possible to select the conditions of pre-treatment of the TiO_2 powder studied, which makes the catalyst almost completely monophase with retention of the high specific surface.

As is expected, the starting ultradispersed TiO_2 powder is diamagnetic. Its calcination in dioxygen practically did not change the magnetic properties (Table 2).

Unlike TiO_2, Pt/TiO_2 catalysts are paramagnetic, and their magnetic susceptibilities at 290 K increase as the platinum content increases (see Table 2). The magnetic susceptibilities of the Pt/TiO_2 samples, which were obtained by the impregnation of the support by an

Table 2. Magnetic susceptibility (χ_g) of samples under study

Sample	Treatment		Time of contact	χ_g · 10^{-6} CGS	
	Medium	*T*/K	with air/h	80 K	290 K
TiO_2[a]	—	—	—	—	−0.11
	O_2	803	1.0	—	−0.12
1%Pt/TiO_2	—	—	24.0	—	0.11
1%Pt/TiO_2	H_2	473	0	0.89	0.38
1%Pt/TiO_2	H_2	473	0.5	—	0.12
1%Pt/TiO_2	H_2	473	24.0	—	0.07
1%Pt/TiO_2	H_2	773	0	0.30	0.17
1%Pt/TiO_2	H_2	773	0.5	—	0.10
1%Pt/TiO_2	H_2	773	24.0	—	0.07
3%Pt/TiO_2	—	—	24.0	—	0.20
3%Pt/TiO_2	H_2	473	0	0.75	0.47
3%Pt/TiO_2	H_2	473	0.5	—	0.16
3%Pt/TiO_2	H_2	473	24.0	—	0.10
3%Pt/TiO_2	H_2	773	0	0.66	0.33
3%Pt/TiO_2	H_2	773	0.5	—	0.10
3%Pt/TiO_2	H_2	773	24.0	—	0.07
TiO_2[b]	O_2	803	24.0	—	−0.14

[a] Starting. [b] Anatase.

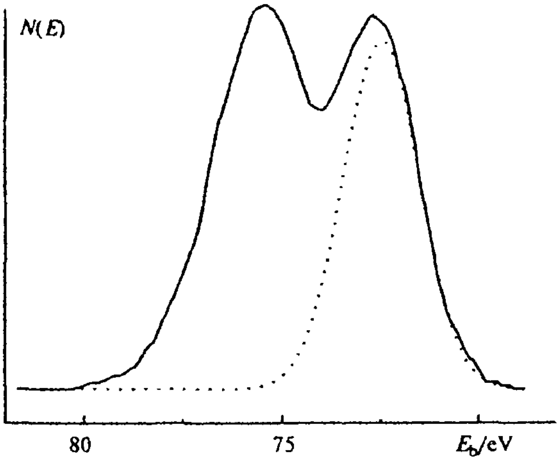

Fig. 2. XPE Pt 4*f* spectrum of the nonreduced 3% Pt/TiO_2 catalyst (Pt $4f_{7/2}$ component is shown by the dotted line).

aqueous solution of H_2PtCl_6 followed by drying in air, are higher than the susceptibilities of similar catalysts after prolonged (days and more) contact with air. As can be seen in Table 2 contact with air decreases the paramagnetic component of the susceptibility. It decreases with time to the χ_g value $(0.07-0.10) \cdot 10^{-6}$ CGS, which is close to that for all reduced catalysts.

As follows from the data presented in Table 2, the Pt/TiO_2—rutile catalysts reduced at a lower temperature have a higher specific susceptibility than those of the samples treated with H_2 at 773 K. This distinguishes rutile-containing catalysts from similar catalysts based on anatase, which exhibits an increase in the magnetic susceptibility with an increase in the reduction temperature.[5]

As the measurement temperature decreases from 290 to 80 K, the paramagnetic susceptibility of the reduced Pt/TiO_2 catalysts also increases (see Table 2).

The changes in the susceptibility considered above can be explained in terms of two simple models.

Model I. The reduction results in the formation of metallic platinum clusters, while the support remains unchanged. The 1% Pt/TiO_2 catalyst has the following magnetic susceptibility: $\chi = 0.99\chi' + 0.01\chi''$, where χ' and χ'' are the magnetic susceptibilities of TiO_2 and platinum metal, respectively. The magnetic susceptibility χ'_g is equal to $-0.12 \cdot 10^{-6}$ CGS (see Table 2). For platinum metal, $\chi''_g = 0.97 \cdot 10^{-6}$ CGS.[8] Therefore, in terms of this model for the 1% Pt/TiO_2 catalyst, $\chi_g = -0.11 \cdot 10^{-6}$ CGS and is independent of the temperatures of reduction and measurement, which disagrees with the experimental results.

Model II. The partial reduction of the support (the formation of Ti^{3+}) occurs simultaneously with the reduction of platinum. Titanium(III) is known[8] to possess a moment caused only by spin and to obey the Curie law ($\chi = C/T + B$) down to very low temperatures. However, processing of the results of measuring the susceptibility using this law (Table 3) gives positive *B* values for all of the four samples instead of the expected value $\chi_g = -0.12 \cdot 10^{-6}$ CGS (the magnetic susceptibility of the starting support).

[Pt] (%)	*C*		*B*	
	473 K	773 K	473 K	773 K
1	56	12	0.19	0.15
3	31	36	0.36	0.20

Thus, the data on the magnetic susceptibilities of the reduced Pt/TiO_2 catalysts do not fit the simple schemes. This can be explained by the fact that paramagnetic centers, some of which interact with each other, are formed during the reduction of the Pt/TiO_2 catalysts. It is also probable that the magnetic properties of small platinum particles differ from those of platinum bulk metal.

The XPE Pt 4*f* spectrum of the nonreduced 3% Pt/TiO_2 catalyst is presented in Fig. 2. According to the position of the main peak, in this catalyst platinum is in the form of Pt^{2+} (E_b Pt $4f_{7/2}$ = 72.5 eV). Therefore, the starting Pt^{4+} is reduced during the preparation of the catalyst. It can be assumed that the support can also be partially reduced during prolonged drying of the catalyst in air, which is the reason for the noticeable magnetic susceptibilities of these samples.

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