Relationship between Surface Properties of Modified Titanooxides and Their Catalytic Performance in the Reaction of Ethylene Glycol Ethoxylation

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Abstract

Relationship of structure and surface properties of modified titanium dioxides, prepared by alkoxide method using derivatives of phosphoric acid as precursors, with their catalytic performance in the reaction of ethylene glycol ethoxylation was investigated. It was found, that such catalysts are mono-phase, nanocluster ones with anatase structure, and have uniform narrow pore distribution. Catalysts prepared using the amido-phosphite precursors provide high catalytic activity due to the high surface acidity, and high selectivity of diethylene glycol formation due to the "sieve effect" and concert acid-base mechanism of ethylene oxide addition.

INTRODUCTION

Reaction of ethoxylation of hydroxyl groups of alcohols is the basis of many large-scale industrial processes:

$$\mathrm{ROH} \xrightarrow[k_0]{\mathrm{C_2H_4O}} \mathrm{ROCH_2CH_2OH} \xrightarrow[k_1]{\mathrm{C_2H_4O}} \mathrm{RO(H_2CH_2O)_2} \xrightarrow[k_2]{\mathrm{C_2H_4O}} \ldots \quad (1)$$

in the case of ethylene glycol: R = $\mathrm{HOCH_2CH_2}-$

At the moment almost all such reactions are carried out in homogeneous conditions by acid-, base-catalyzed or noncatalytic way (Fig. 1). All the corresponding mechanisms have been well investigated [1–3].

The effectiveness of each of these three processes depends on two factors: the rate and selectivity of reaction. According to the reaction rates, these processes can be arranged in the following row:

Noncatalytic < *Base catalysis* < *Acid catalysis*

The selectivity of product's formation depends on the ratio of rates of consecutive stages of reaction (1) and usually is characterized by the distribution factor (C_i) [2, 4], which is equal to the ratio of rate constant of corresponding consecutive stage of reaction (1) to the rate constant of first stage:

$$C_i = k_i/k_0 \quad (2)$$

So the higher is value of C_i, the higher is selectivity of formation of corresponding product. For the three above mentioned mechanisms, average magnitudes of distribution factor for ethoxylation of primary alcohols are:

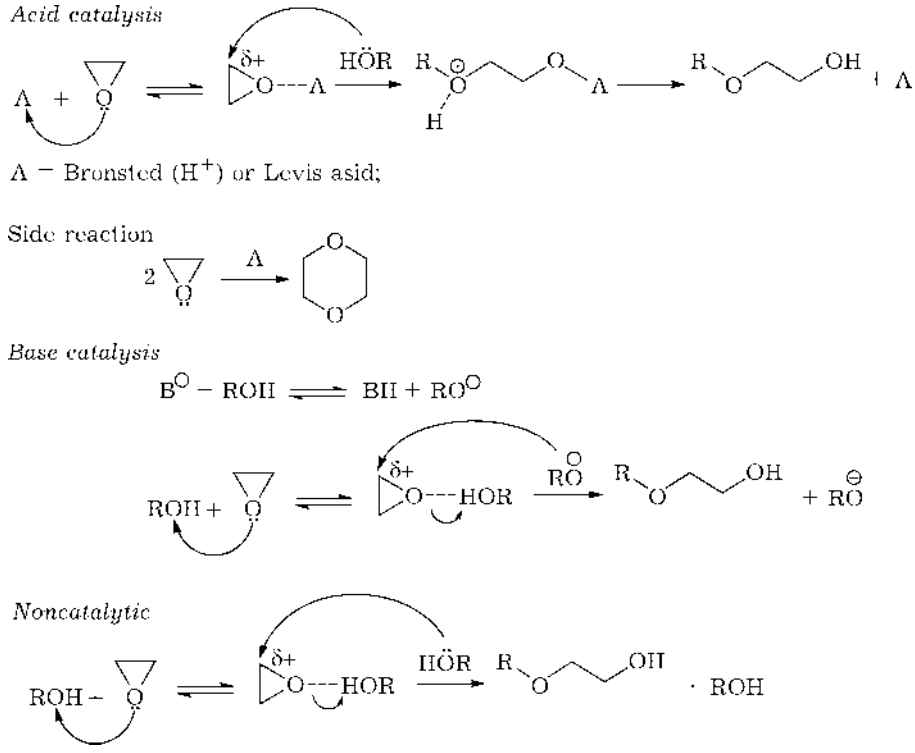


Fig. 1. Mechanisms of acid-, base-catalyzed and noncatalytic reaction of hydroxyl group ethoxylation in alcohols.

Acid catalysis − $C_i \approx 1$

Base catalysis − $C_i \approx 2-4$

Noncatalytic − $C_i \approx 1$

Moreover, the distinct feature of acid catalysis is side formation of 1,4-dioxane by dimerization of ethylene oxide.

Modified titanium dioxides synthesized by alkoxide method using the organic derivatives of phosphoric acid as precursors, as it was found by Tsodikov *et al.* [5, 6], are highly organized nanocluster materials. Thus, such method can be very suitable for the synthesis of TiO_2-like materials with controlled catalytic properties.

METHODS

Synthesis procedure

Modified titanium dioxides (Table 1) were prepared by the alkoxide method, in which chelation of titanium alkoxide with acetylacetone was used to stabilize the sol. For this purpose, an equimolar amount of acetylacetone was added to a 1.5 M solution of titanium tetra(*n*-butoxide). After stirring with a magnetic stirrer, Ar was bubbled through the solution, while 0.5 M benzene solutions of modifying components were added. Inorganic precursors dissolved in alcohol-water mixture were introduced into the initial organic solution.

The resulting sols were stirred for 30 min and then 80 % aqueous ethanol was added in such a way, that the amount of water was stoichiometric with respect to titanium alkoxide. The gels were then separated by evaporation of the solvents in rotary evaporator.

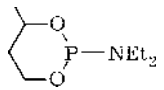
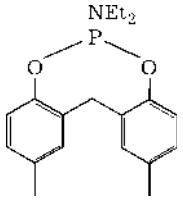
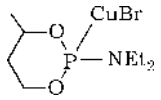
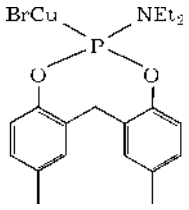
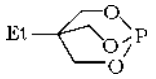
The gels were dried in vacuum at 90 °C; the final oxides were prepared by stepwise calcination from 100 to 500 °C over the period of 7 h.

Structure and porosity study

X-ray diffraction studies were carried out on a Dron-3M diffractometer using monochromatic CuK_α-radiation. The JCPDS−ICDD (1985−1995) data bank was used to identify the phases based on the interplanar spacings and the relative intensities of Bragg reflections. Positions of the lines characterizing tetragonal orientation of the structure ([200]

TABLE 1

Precursors, X-ray diffraction data and parameters of porous structure of modified titanium dioxides

Sample No.	Precursor	X-ray diffraction data			Parameters of porous structure		
		Oxide's composition	Lattice tetragonal parameter (C), nm	Average microcrystallite diameter (D), nm	S, m^2/g	V, cm^3/g	r, nm
1		$P_{0.07}Ti_{0.91}O_{2-\delta}$	0.945±0.002	7.7	91	0.11	0.8
2		$P_{0.07}Ti_{0.91}O_{2-\delta}$	0.941±0.002	7.6	160	0.12	0.9
3		$Cu_{0.07}P_{0.07}Ti_{0.88}O_{2-\delta}$	0.944±0.002	10.5	85	0.15	1.9
4		$Cu_{0.07}P_{0.07}Ti_{0.88}O_{2-\delta}$	0.945±0.002	12.9	93	0.26	1.8
5	$Ti(OBu)_4$	TiO_2 (anatase)	0.947±0.002	39.7	3.2	0.009	3.0
6		$P_{0.07}Ti_{0.94}O_{2-\delta}$	0.941±0.002	8.2	83	0.082	0.9
7	$Al_2(SO_4)_3 \cdot 18H_2O$	$Al_{0.09}Ti_{0.93}O_{2-\delta}(SO_x)_y$	–	–	–	–	–

and [004]) were used to calculate the unit cell constants [7]. The samples were scanned with a rate of 0.5° 2θ/min. The size of anatase microcrystallites (the region of coherent scattering) was determined from the line broadening [7]. To separate the effects of dispersion and microdistortions, the calculations were performed using two lines and the nomograms constructed beforehand, $m_1/\beta_1 = F(\beta_2/\beta_1)$ and $n_2/\beta_2 = F(\beta_2/\beta_1)$, where β_1 and β_2 are true physical line broadenings with d = 3.52 and 1.89 Å, respectively; m_1 and n_2 are the fractions of physical broadening caused by the dispersion and microdistortions, respectively.

The Ti K-edge EXAFS spectra for all samples were recorded at the EXAFS station of the Siberian Synchrotron Radiation Center using an electron beam energy of 2 GeV and an average current of 80 mA.

To record the data of temperature-programmed desorption (TPD) of NH_3 and CO_2, 0.2 g samples were held in a dry air stream for 2 h at 550 °C and in N_2 stream for 1 h at the same temperature, cooled to room temperature, and then treated with a 1:1 (v/v) mixture of N_2 and CO_2 (or NH_3) for 30 min. The samples were held for 1 h at 50 °C to remove the weakly bound adsorbate, cooled to room temperature, and then heated in a temperature-programmed mode at a rate of 8 K/min until the adsorbate was completely removed. The TPD data were processed by matching the experimental and calculated curves [8]. This method provides determination of the total number of adsorption sites and their distribution over the range of activation energies of desorption (E_d) between the minimum (E_{min}) and the maximum (E_{max}) values, and calculation of the average value for the whole range of desorption energies (<E>), which characterizes the average adsorption strength of the sites. The range of E_d was divided into equal sections (5 kJ/mol each). Within each section, the sites were considered uniform and their strength was represented by one average E_d corresponding to the middle of section.

Parameters of the porous structure were determined from N_2 vapor adsorption isotherms at 77 K. Experimental adsorption isotherms were measured using a Yravimat-4303 automated gravimetric setup (Netch, Germany) with a sensitivity of 1 μg for a sample up to 1 g at 77 K. The specific surface area (S) and pore volume (V) were calculated using the BET method [9]. The average pore radii (r) were found assuming a slot-like geometry of the pores.

Catalytic experiments

Catalytic activities of modified titanium dioxides in the ethylene glycol ethoxylation were studied in the laboratory manometric setup [10], where the rate of reaction is indicated by the decrease of ethylene oxide vapor pressure over the reaction mixture. The large excess of ethylene glycol provides kinetics of the first order with respect to ethylene oxide:

$$r = k_{exp} P_{EO} = (k + k_{cat}[Cat])P_{EO} \quad (3)$$

where: k_{exp} – experimental rate constant, 1/s; k – noncatalytic rate constant, 1/s; k_{cat} – catalytic rate constant, l/(g s); [Cat] – catalyst concentration, g/l; P_{EO} – ethylene oxide vapor pressure.

Catalytic rate constant was calculated as:

$$k_{cat} = (k_{exp} - k)/[Cat] \quad (4)$$

The reaction products composition of was investigated by gas-liquid chromatography using "Chrom–5" instrument equipped with glass-packed column (Inerton AW HMDC phase containing 15 % FFAP, 1 m × 3 mm) and a flame ionization detector. N_2 was used as a carrier gas. Chromatographic analysis was carried out in the temperature-programmed regime with temperature ramp 25 °C/min from 120 to 230 °C.

Distribution factors (C) were calculated by solving the system of Weibull–Nicander equations, used for the description of products composition when $k_0 \neq k_1 = k_2 = ... = k_n$ [4]:

$$\begin{aligned}\left[HOCH_2CH_2O\left(CH_2CH_2O\right)_n H\right] &= -\left[HOCH_2CH_2OH\right]^C \\ &\times\left\{\frac{C^{n-1}}{S\left[HOCH_2CH_2OH\right]_0^S}\sum_{i=0}^{n-1}\frac{1}{S^{n-1-i}}\frac{z^i}{i!}\right\} \\ &+\left\{\frac{C^{n-1}}{S^n}\right\}\left[HOCH_2CH_2OH\right]\end{aligned} \quad (5)$$

where: [ ] – molar concentrations of original ethylene glycol and its ethoxylation products;

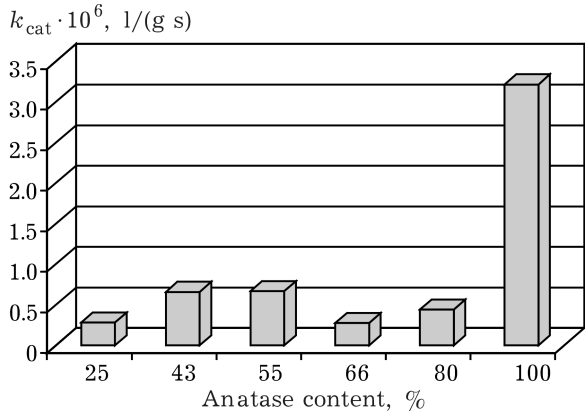


Fig. 2. Dependence of the rate constant of catalytic reaction of ethylene glycol ethoxylation *vs.* the anatase content in Cu-modified titanium dioxides.

$C = k_n/k_0$ – distribution factor; $S = C - 1$ for $C \neq 1$; $z = \ln([HOCH_2CH_2OH]_0/[HOCH_2CH_2OH])$.

Selectivity of the formation of first product of ethylene oxide addition – diethylene glycol (DEG), relative to the ethylene oxide (EO), was calculated as:

$$S_{DEG}^{EO} = [DEG]/([EO]_0 - [EO]) \quad (6)$$

RESULTS AND DISCUSSION

The series of kinetic experiments with Cu-modified titanium dioxides, differing in the ratio of rutile and anatase, showed that sample with 100 % anatase structure has the highest catalytic activity (Fig. 2). Therefore, only the catalysts with 100 % anatase structure were prepared for all the following experiments.

The precursors which where used for the preparation of modified titanium dioxides, their phase composition and crystal lattice parameters determined by X-ray diffraction are listed in Table 1.

According to the X-ray diffraction data, mixed titanium dioxides obtained using the organic and inorganic precursors were single-phase systems with anatase structure. Furthermore, two important observations were made: first, incorporation of modifiers leads to the remarkable decrease of microcrystallite diameters in the studied oxides, to the values less than 15 nm, hence all these oxides are nanocluster systems; second, existence of modified (doped) component leads to the change of lattice tetragonal parameter *c* only; parameter *a* was determined as (0.378 ± 0.002) nm for all the samples.

Parameters of the porous structure determined by N_2 vapor adsorption isotherms are listed in Table 1 as well. The isotherms of polymolecular adsorption, calculated using the BET method and plotted in coordinates "experimental amount of adsorbate *vs.* number of monomolecular layers", are given in Fig. 3. Presence of the only single break on the isotherms shows, that all samples are characterized by uniform distribution of pore radii: about 0.8–0.9 nm for phosphorus-containing ones (samples 1, 2, 6) and about 1.8–1.9 nm for metal-containing ones (samples 3, 4).

The TPD of NH_3 data (Fig. 4) allow to determine the concentration of acid sites on sur-

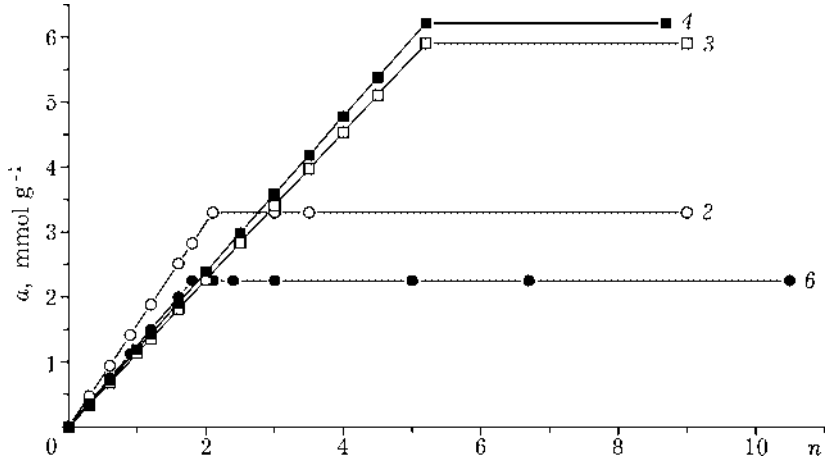


Fig. 3. Isotherm dependencies of the amount of N_2 adsorbed on the sample *vs.* the number of monomolecular layers (number of isotherm designates the number of sample).

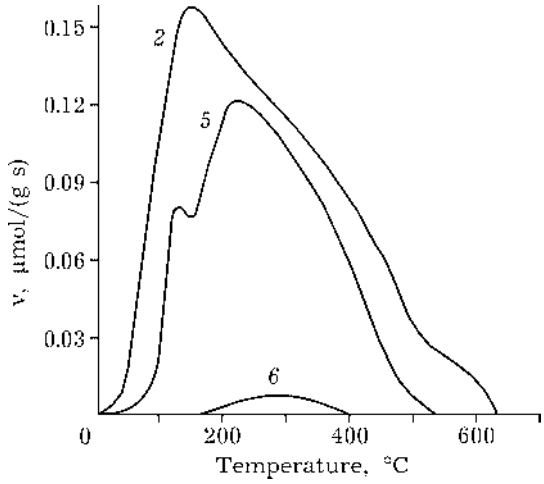


Fig. 4. Temperature-programmed desorption of NH_3 (number of curve designates the number of sample).

face of samples (Table 2). As it follows from Table 2, the use of amidophosphite precursors leads to the rise of modified titanium dioxide acidity. All acid sites were divided into three categories, depending on the activation energy (E_d) of NH_3 desorption: $E_d \leq 90$ kJ/mol – weakly acidic sites; 90 kJ/mol $< E_d <$ 130 kJ/mol – moderately acidic sites; $E_d \geq 130$ kJ/mol – strongly acidic sites (see Table 2).

The TPD of CO_2 data show, that amidophosphite precursors decrease the overall basicity compared with pure anatase, and result in the appearance of narrow peak in the region of weakly basic sites (Fig. 5).

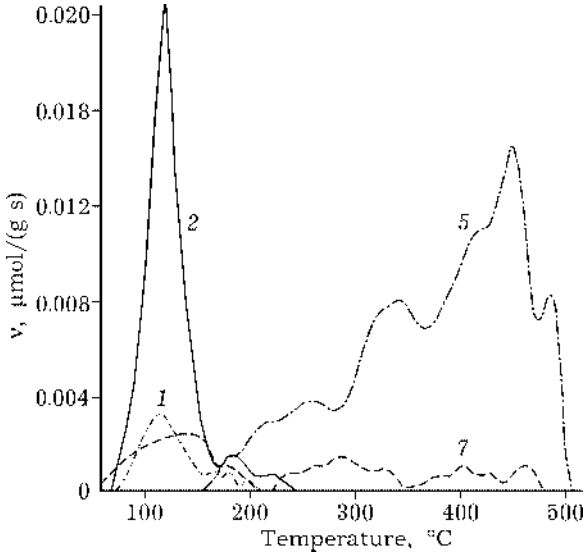


Fig. 5. Temperature-programmed desorption of CO_2 (number of curve designates the number of sample).

The experimental values of rate constants of catalytic reaction of ethylene glycol ethoxylation (k_{cat}) at 115 °C, distribution factors (*C*) and selectivities of ethylene oxide conversion to diethylene glycol (S^{EO}_{DEG}), at the initial molar ratio (ethylene oxide) : (ethylene glycol) = 0.5, are listed in Table 2. The data for homogeneous conditions are also included for comparison.

Table 2 shows, that modified titanium dioxides which have maximum number of acid sites (samples 1, 2, 7) provide the highest catalytic activity. However, in contrast to P-modified samples, the Al-modified one (sample 7) yields 1,4-dioxane, which indicates that the nature of surface acidity of these two types of catalysts is different. This observation corresponds to the fact, that during the NH_3 TPD experiment on sample 7 certain amount of NH_3 did not desorb even at temperature 600 °C and higher.

Regarding the selectivity of reaction of ethylene glycol ethoxylation, the distribution factor for Al-modified titanium dioxide (sample 7) is 1.02, that is close to the experimental one for homogeneous acid-catalyzed reaction (see Table 2).

The information given above allows to suggest the existence of strong Bronsted acid sites on the surface of Al-modified catalyst.

The unique selectivity was obtained in the case of amidophosphite-modified titanium dioxides. The distribution factors for samples 1–4 are in the range of 0.37–0.52. Such values can not be achieved neither due to the acidic nor basic homogeneous catalysis (see Table 2).

We propose two explanations of such high selectivity.

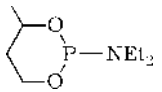
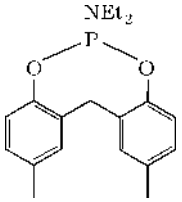
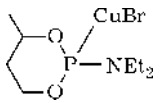
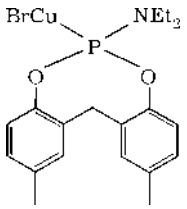
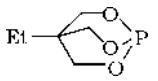
The first is so-called “sieve effect”, which is caused by the uniform mesoporous structure of catalysts.

The second is probable concert acid-base mechanism of ethylene oxide addition, when epoxide oxygen can be activated via the strong acid sites provided by titanium cations, and alcohol hydroxide group can be activated via weak basic sites provided by surface oxygen anions (Fig. 6).

To estimate the contribution of each type of acid sites (see Table 2) into the overall catalytic activity, the experimental rate con-

TABLE 2

Precursors, acidity properties and catalytic performance of modified titanium dioxides in ethylene glycol ethoxylation

Sample No.	Precursor	Distribution of acid sites by the activation energy of desorption (E_d) of NH_3				$k_{cat} \cdot 10^{-4}$, l/(g s)	Distribution factor, C	Selectivity, S_{DEG}^{EO}
		NH_3 overall capacity (a_0), μmol/g	$E_d \leq 90$ kJ/mol	90 kJ/mol $< E_d <$ 130 kJ/mol	$E_d \geq 130$ kJ/mol			
1		386	67	306	13	2.1	0.38	78.9
2		660	148	493	19	2.4	0.51	74.3
3		324	71	249	4	0.3	0.52	73.7
4		300	78	222	0	0.5	0.37	79.3
5	$Ti(OBu)_4$	–	–	–	–	0.00008	0.9	62.9
6		–	–	–	–	0.0015	0.78	65.9
7	$Al_2(SO_4)_3 \cdot 18H_2O$	–	–	–	–	6.1	1.02	60.2 (Dioxane formation)
–	Homogeneous conditions					H+	1.0	60.8 (Dioxane formation)
						OH^-	0.85	64.2
						Noncatal.	0.93	62.3

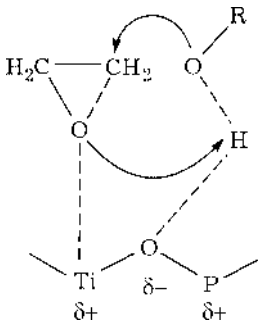


Fig. 6. Scheme of the proposed ethylene oxide addition reaction mechanism.

stant of catalytic reaction was described by the following equation using least-squares method:

$$k_{\text{cat}} = \sum_{j=1}^{3} a_j k_{aj} \qquad (7)$$

where: a_j – concentration of acid sites of the j-th region, μmol/g; k_{aj} – specific rate constant over the j-th region, l/(μmol s).

The diagram in Fig. 7 shows satisfactory correspondence of the experimental and calculated rate constants of catalytic reaction for samples with high acidity.

The calculated values of k_{aj} are: $k_{a1} = 3\ 10^{-8}$; $k_{a2} = 2.3\ 10^{-17}$; $k_{a3} = 1.5\ 10^{-5}$ l/(μmol s). As it follows from these results ($k_{a3} >> k_{a1} >> k_{a2}$), strong acidic sites are the ones that provide dominating contribution to the overall catalytic activity of modified titanium dioxides in the reaction of ethylene glycol ethoxylation.

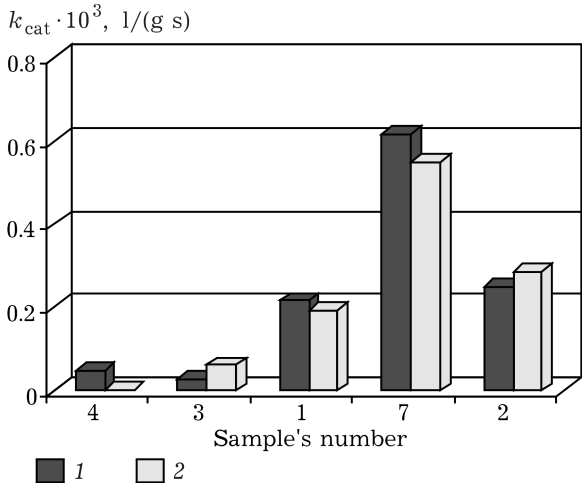


Fig. 7. Comparison of the experimental (*1*) and calculated (*2*) reaction rate constants of catalytic ethylene glycol ethoxylation for different samples of modified titanium dioxides.

CONCLUSION

It can be concluded, that modified titanium dioxides prepared by alcoxide method with derivatives of phosphoric acid as precursors are mono-phase, nanocluster materials with anatase structure and have uniform narrow pore distribution.

At the same time, the use of amidophosphite precursors leads to significant increase of sample acidity and to the appearance of narrowly distributed weak base sites.

Alcoxide method was found to be very suitable to control catalytic properties of modified titanium dioxides in the reaction of ethylene glycol ethoxylation. Samples prepared using the amidophosphite precursors provide high catalytic activity due to the high surface acidity, and high selectivity of diethylene glycol formation due to "sieve effect" and concert acid-base mechanism of ethylene oxide addition.

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REFERNCES

1 N. Schounfeldt, Grenzflachenaktive Athylenoxid, MBH, Stuttgart, 1976.
2 M. Nico, V. Os, Nonionic Surfactants, Surfactant Sci. Ser., vol. 72, Marcel Dekker Inc., New York, 1998.
3 N. N. Lebedev, V. P. Savelyanov, Yu. I. Baranov, *Zhurn. prikl. khimii*, 42 (1969) 1815.
4 B. Weibull, B. Nycander, *Acta Chim. Scand.*, 8 (1954) 847.
5 M. V. Tsodikov, O. V. Bukhtenko, E. B. Slivinskiy *et al., Izv. RAN. Ser. khim.*, 11 (2000) 1829.
6 M. V. Tsodikov, E. B. Slivinskiy, V. V. Yushchenko *et al., Ibid.*, 12 (2000) 2037.
7 S. S. Gorelik, L. N. Rastorguev, Yu. A. Skakov, Rentgenograficheskii i electronoopticheskii analiz [X-Ray Diffraction and Electron-optical Analysis], Metallurgiya, Moscow, 1970, pp. 83, 143.
8 V. V. Yushchenko, *Zhurn. fiz. khimii*, 71 (1997) 628.
9 S. J. Gregg, K. S. W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982.
10 V. F. Shvets, N. N. Lebedev, *Kinetika i Kataliz*, 9 (1968) 504.