

## **PHYSICOCHEMICAL STUDIES ON THE TiO<sub>2</sub>-SILICA GEL SYSTEM**

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(Received March 1, 1993; in revised form November 7, 1993)

### **Abstract**

The physicochemical properties (crystal structure, surface acidity, surface area, catalytic activity and electrical conductivity) of TiO<sub>2</sub>-silica gel mixed oxides have been investigated. A series of mixed oxides of various compositions in the range of 0-100% for each component were prepared by calcining the mixed oxides in air at temperatures of 115, 300, 600 and 1000°C. The results obtained have been discussed and correlated.

**Keywords:** catalytic activity, crystal structure, electrical conductivity, surface, TiO<sub>2</sub>-silica gel system

### **Introduction**

Binary mixed oxides were found to have many important physical properties such as electrical and catalytic properties [1-5]. Such properties may be affected not only by the type of the starting compound, but also by the conditions of their preparation.

Several studies [6-10] showed the existence of a correlation between the catalytic activity and acidic properties of the solid surface for many pure and mixed oxides. Such studies may be helpful in determining the optimum catalytic properties of the oxides in terms of the acidic and basic properties of their solid surface. These interesting aspects of surface structure are also very important in the field of ion exchange.

In the present work we have studied the surface activity, surface area and catalytic activity for pure and mixed oxides of TiO<sub>2</sub> and silica gel. The electrical conductivity of these oxides has also been investigated.

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## Experimental

The binary oxides TiO<sub>2</sub>-silica gel were prepared in composition containing 0, 15, 30, 50, 70, 85 and 100 mol% TiO<sub>2</sub> from pure chemicals by impregnation technique. The impregnated oxides were dried at 115°C for 5 h. The samples thus obtained were ground and only the fractions collected between 100 and 150 mesh sieves were used. These powdered samples were calcined for 5 h at each of the following temperatures: 300, 600 and 1000°C. The samples after calcination were cooled in a desiccator and stored in covered glass tubes under vacuum.

The acidic groups attached to pure and mixed oxide surfaces were determined using the amine titration method developed by Johnson [11]. So 0.2 g of the mixed oxides suspended in benzene was titrated with a solution of 0.1 N *n*-butylamine in benzene using benzeneazo diphenyl-amine ( $pK_a=1.5$ ), *p*-dimethyl-amino azobenzene ( $pK_a=3.3$ ), methyl red ( $pK_a=4.8$ ), neutral red ( $pK_a=6.8$ ), dicinimal-acetone ( $pK_a=-3$ ), and benzylacetophenone ( $pK_a=-5.6$ ) as indicators. The surface acidity is expressed as mmol of *n*-butyl-amine (used in the titration for 1 g of the oxides).

DTA and TG experiments were carried out using a Shimadzu thermal analyser (model-30) at a heating rate of 10 deg·min<sup>-1</sup> in air on 20 mg samples.

The surface area of the binary mixed oxides was determined using a conventional BET-apparatus (BET micrometer 2000).

X-ray diffraction patterns of the oxides were obtained on a Philips unit type pW 2103/00, using copper target and nickel filter. The characteristic spacings and the relative intensities were compared with data in ASTM cards.

IR spectra of the oxides were recorded on a Beckman infrared spectrophotometer using the KBr pellet technique.

The decomposition of H<sub>2</sub>O<sub>2</sub> was selected for studying the catalytic reactivity of the catalysts and was conducted as described by Keating [12] in a temperature range of 35 to 65°C. The electrical conductivity of the oxides investigated was measured by a method reported elsewhere [13].

## Results and discussion

Figures 1, 2 represent the DTA and TG diagrams respectively for TiO<sub>2</sub>, SiO<sub>2</sub>·xH<sub>2</sub>O and SiO<sub>2</sub>·xH<sub>2</sub>O-TiO<sub>2</sub> mixtures. The DTA curve for TiO<sub>2</sub> shows two peaks at 430 and 1030°C. The first peak is accompanied by a loss in weight (~4%) due to the elimination of H<sub>2</sub>O molecules, while the higher temperature peak is accompanied by an increase in the weight of TiO<sub>2</sub>. This increase in weight may be attributed to a change in the stoichiometry of TiO<sub>2</sub> due to its interaction with oxygen at elevated temperatures [14].

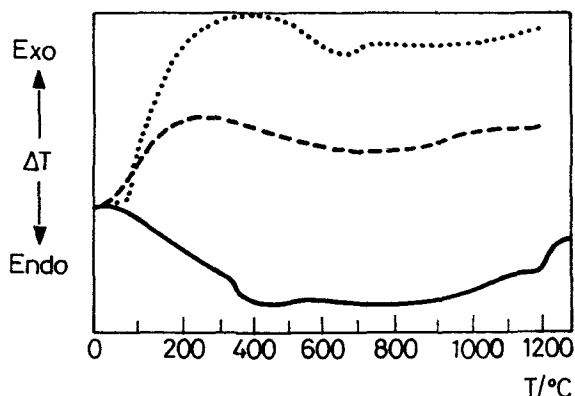


Fig. 1 DTA curves of the  $\text{TiO}_2\text{-SiO}_2\cdot x\text{H}_2\text{O}$  system calcined at  $300^\circ\text{C}$   $\text{TiO}_2$  (—),  $\text{SiO}_2\text{-TiO}_2$  (1:1 molar ratio) (- - -),  $\text{SiO}_2$  (⋯)

The TG curve of silica gel in Fig. 2 shows a continuous decrease in the weight in the temperature range of  $30\text{--}1200^\circ\text{C}$ , whereas the DTA curve shows two endothermic peaks at  $70$  and  $600^\circ\text{C}$ . The first small peak appearing at  $70^\circ\text{C}$  may be attributed to the desorption of water molecules from the surface of the oxide while the second peak appearing at  $600^\circ\text{C}$  is explained on the basis of the transformation of silica gel to  $\text{SiO}_2$ . This transformation was also reported by other authors [15–19].

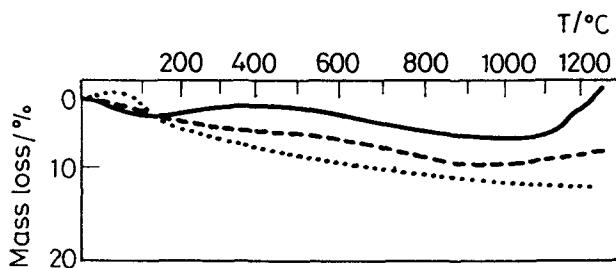


Fig. 2 TG curves of the  $\text{TiO}_2\text{-SiO}_2\cdot x\text{H}_2\text{O}$  system calcined at  $300^\circ\text{C}$   $\text{TiO}_2$  (—),  $\text{SiO}_2\text{-TiO}_2$  (1:1 molar ratio) (- - -),  $\text{SiO}_2$  (⋯)

The DTA–TG diagrams of  $\text{TiO}_2\text{-SiO}_2\cdot x\text{H}_2\text{O}$  mixture (1:1 molar ratio) showed only the same peaks characteristic of the pure oxides, which means that no chemical reaction occurs between the two oxides in the investigated temperature range.

Figure 3 shows the IR spectra of  $\text{TiO}_2$ , silica gel and their mixtures (1:1 molar ratio). The spectra of pure samples showed bands at  $4300$  and  $1630\text{ cm}^{-1}$  attributed to an adsorption of water on the surface of the oxides. The intensity of

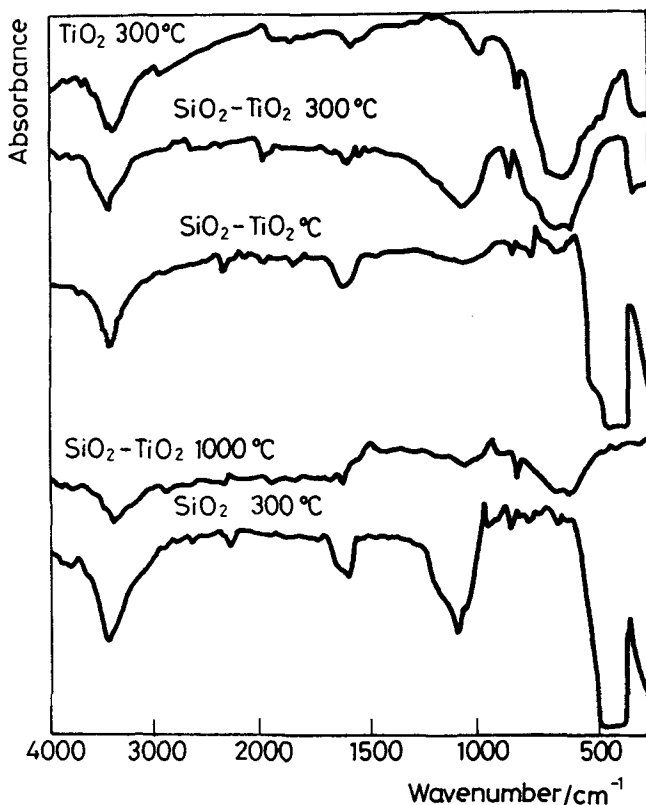


Fig. 3 IR spectra of TiO<sub>2</sub>, SiO<sub>2</sub> and the TiO<sub>2</sub>-SiO<sub>2</sub>·xH<sub>2</sub>O (1:1 molar ratio) system calcined at different temperatures

these peaks decreased with increasing calcination temperature. The IR spectra of TiO<sub>2</sub> showed also peaks at 1460 and 1100 cm<sup>-1</sup> due to the presence of some carbonate impurity on the surface [20] and Si-O vibration respectively. In the IR spectra of the oxide mixtures no new peaks could be detected but they showed only the peaks observed for the pure individual components. This agreed with the above thermal results (i.e. no reaction occurred between the oxides).

Figure 4 shows the X-ray diffraction patterns of the pure materials and the products of thermal treatment of TiO<sub>2</sub>-silica gel at different calcination temperatures. All calcined samples of TiO<sub>2</sub> and its mixtures with silica gel showed diffraction lines at 3.5, 2.38, 1.89, 1.70 and 1.68 Å, which are characteristic of the rutile structure of TiO<sub>2</sub> [21]. The absence of new X-ray diffraction lines for the investigated product indicates that no reaction has occurred between

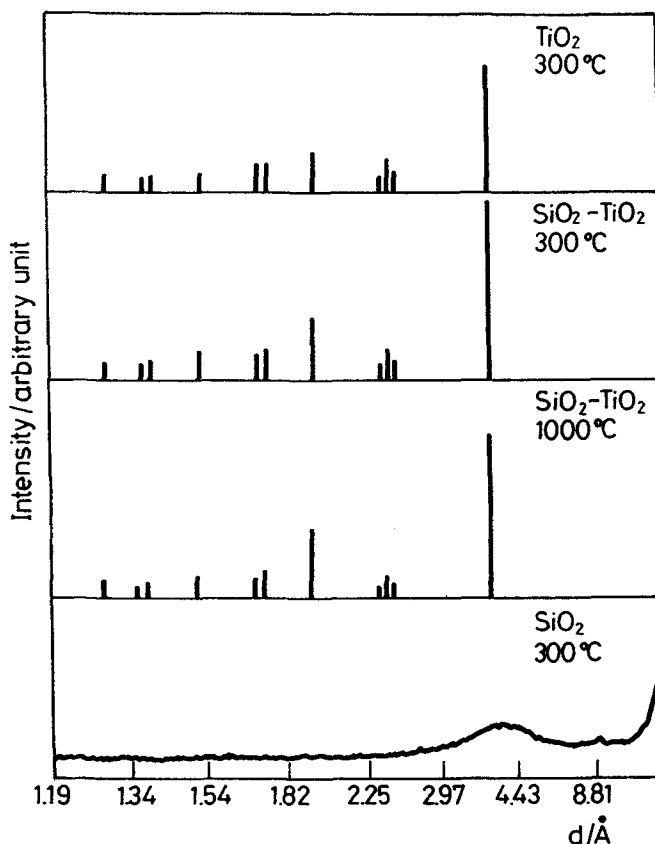


Fig. 4 X-ray diffraction patterns of  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{TiO}_2\text{-SiO}_2\cdot x\text{H}_2\text{O}$  (1:1 molar ratio) calcined at different temperatures

$\text{TiO}_2$  and  $\text{SiO}_2\cdot x\text{H}_2\text{O}$  at the calcination temperatures (300, 600 and 1000 °C) applied.

The surface acidity results of various compositions of  $\text{TiO}_2$ -silica gel calcined at different temperatures are represented in Fig. 5. The results show that all samples have weak acidic sites for indicators having  $pK_a$  values of 1.5, 3.3, 4.0 and 4.8, and showing also a change in the surface acidity with changing composition of the solids. The maximum number of acidity sites were observed at 50 mol%  $\text{TiO}_2$ . The change in the surface acidity with the calcination temperature showed maximum at 600 °C for all the compositions investigated. The acidity of pure silica gel has completely disappeared for the sample calcined at 1000 °C.

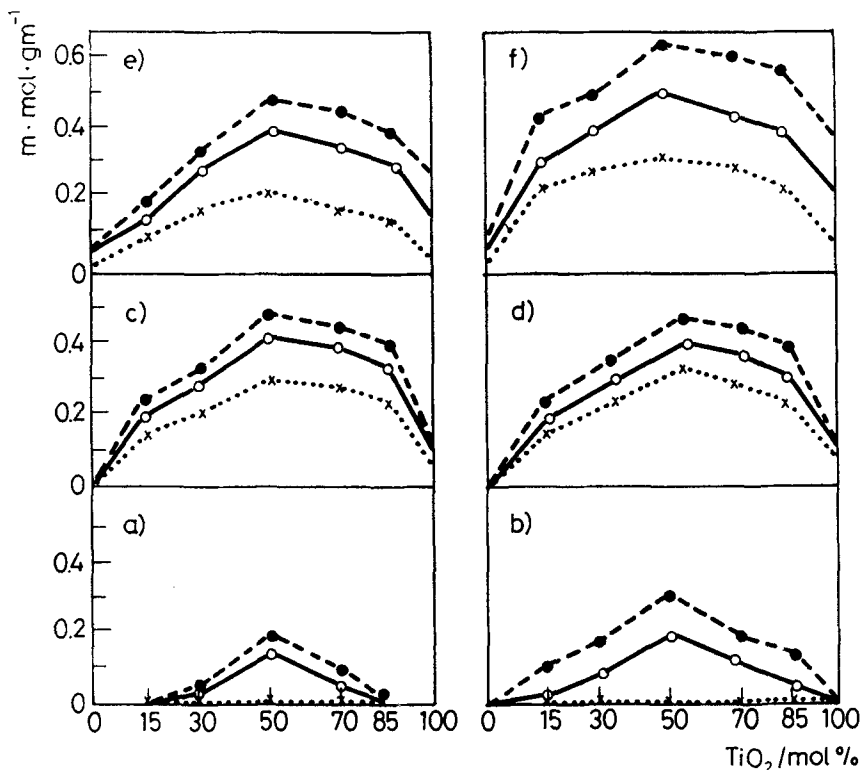
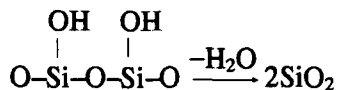


Fig. 5 Effect of composition on the acidic properties of the  $\text{TiO}_2\text{-SiO}_2\cdot x\text{H}_2\text{O}$  system; (o)  $300^\circ\text{C}$ ; ( $\bullet$ )  $600^\circ\text{C}$ ; (x)  $1000^\circ\text{C}$

The change in the acidity sites on the surface of silica gel with increasing calcination temperature could be explained according to the following dehydration process:



As the temperature of heat treatment is raised, a water molecule is removed from two hydroxyl groups attached to silicon atoms at the Si-O-Si link. The Si-O-Si link is readily formed between neighbouring Si-OH groups in the early stages of dehydration, but the distortion between them becomes progressively greater with further dehydration of the Si-O-Si link (which is responsible for the acid strength).

The results of surface area measurements are given in Table 1. It shows a change in the surface area with changing oxide composition in a manner similar to that obtained in the results of surface acidity i.e. maximum surface area at 50 mol% TiO<sub>2</sub>.

**Table 1** Surface area of TiO<sub>2</sub>-SiO<sub>2</sub> calcined at 600°C

Composition of oxides / mol %TiO <sub>2</sub> .	100	85	70	50	30	15	0
Surface area / m <sup>2</sup> .g <sup>-1</sup>	77.9	210	245	340	237	225	220

The results of decomposition of H<sub>2</sub>O<sub>2</sub> over TiO<sub>2</sub>-SiO<sub>2</sub>.xH<sub>2</sub>O are shown in Fig. 6 and summarized in Table 2. The results show that pure silica gel is less active in catalysing the reaction due to the presence of the weakly acidic surface SiOH groups [22]. The rate of H<sub>2</sub>O<sub>2</sub> decomposition changes with increasing concentration of TiO<sub>2</sub> and has a maximum value at 50 mol% TiO<sub>2</sub> due to the greatest number of acidity sites and the greatest surface area (Table 1) found for this mixture.

**Table 2** Activation parameters of H<sub>2</sub>O<sub>2</sub> decomposition over TiO<sub>2</sub>-SiO<sub>2</sub>

Calcination temp.	300°C		600°C		1000°C	
	E / kJ.mol <sup>-1</sup>	A / min <sup>-1</sup>	E / kJ.mol <sup>-1</sup>	A / min <sup>-1</sup>	E / kJ.mol <sup>-1</sup>	A / min <sup>-1</sup>
0	21.8725	0.4535	25.3082	1.2748	27.2157	1.3385
15	20.6792	0.2857	24.6199	1.3512	38.3637	5.8654
30	20.6234	0.4595	12.3573	3.1351	29.0909	2.8692
50	16.6203	1.4838	9.5058	3.9173	24.7368	1.6219
70	18.4505	1.0734	13.5152	2.7073	21.7070	0.3094
85	18.4505	1.0734	13.5152	2.7073	21.7070	0.3094
100	20.7937	0.6660	15.5857	1.9993	24.1746	0.2332

The electrical conductivity,  $\sigma$ , of calcined samples of TiO<sub>2</sub>, SiO<sub>2</sub> and their mixtures was measured as a function of temperature in the range 25 to 600°C. The results obtained are represented by plotting  $\ln \sigma$  vs.  $1/T$ . A typical plot is shown in Fig. 7. Each plot showed many straight lines with different slopes. In the lower temperature range, the conductivity was found to decrease with increasing temperature due to the continuous elimination of water molecules on heating, as confirmed by IR spectra. On the other hand, in the higher temperature range the conductivity increased with increasing temperature. The tem-

perature  $T_b$ , at which the break in the  $\sigma$ -values appears is shifted to lower values with increasing calcination temperature for most of the samples investigated.

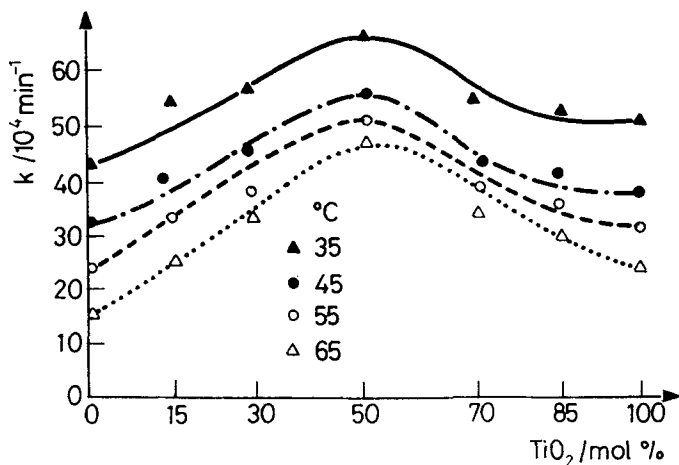


Fig. 6 Variation of the rate constant of  $H_2O_2$  decomposition with the composition of the  $TiO_2-SiO_2 \cdot xH_2O$  system calcined at  $600^\circ C$

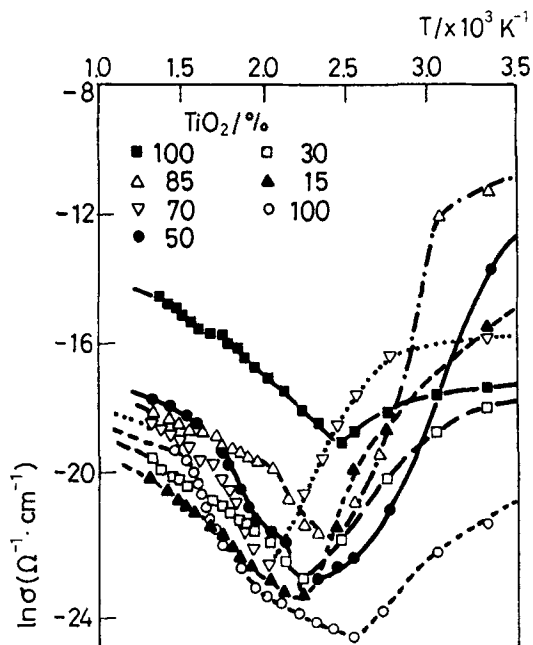


Fig. 7 Effect of temperature on the electrical conductivity of the  $TiO_2-SiO_2 \cdot xH_2O$  system calcined at  $1000^\circ C$



The activation energies,  $E_a$ , of the conductivity process are calculated from the linear plots represented in Fig. 7. All the conductivity results obtained are summarized in Table 3.

**Table 3** The activation energy ( $E_a$  in  $\text{kJ}\cdot\text{mol}^{-1}$ ) of electrical conductivity of the  $\text{TiO}_2$ - $\text{SiO}_2$  system for  $T > T_b^*$

Composition / $\text{TiO}_2$ mol %	$T_b^*$ / $^{\circ}\text{C}$	Calcination temperature		
		$300^{\circ}\text{C}$	$600^{\circ}\text{C}$	$1000^{\circ}\text{C}$
0	280	41.7	76.6	43.2
15	200	49.1	25.7	42.9
30	240	39.9	48.6	31.2
50	260	118.3	49.3	50.6
70	140	87.9	29.3	49.9
85	160	89.4	34.0	28.1
100	240	62.4	47.7	29.4

\*  $T_b$  – break temperature appearing in conductivity data

The conductivity results showed lower  $\sigma$ -values for pure and mixed oxides calcined at  $1000^{\circ}\text{C}$  compared with those found for samples calcined at  $300$  and  $600^{\circ}\text{C}$ . For pure  $\text{TiO}_2$ , this can be attributed to the change in its stoichiometric composition [23], while for silica gel this decrease in  $\sigma$ -values may be explained on the basis of the removal of OH-groups on heating the samples at higher temperatures. Therefore the decrease in  $\sigma$ -values of the mixed oxides can be attributed to both of these factors.

Conductivity results in Table 3 show a maximum in  $E_a$  at 50 mol%  $\text{TiO}_2$ . This refers to a decrease in the concentration of charge carriers in the pure compounds due to the addition of one component to the other. The above results indicate that in spite of the absence of any indication on the formation of new compounds in the system investigated (according to DTA, IR and X-ray results) but the higher change in physical properties (conductivity, catalytic activity, surface acidity) gives an evidence for the formation of new phases or new components in very low concentrations. These changes are too low to be observed by DTA, IR or X-ray diffraction techniques.

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**Zusammenfassung** — Es wurden die physiko-chemischen Eigenschaften (Kristallstruktur, Oberflächenazidität, Oberflächengröße, katalytische Aktivität und elektrische Leitfähigkeit) von  $\text{TiO}_2$ -Kieselgel Mischoxiden untersucht. Eine Reihe dieser Mischoxide verschiedener Zusammensetzung im Bereich 0 bis 100% für jede der Komponenten wurde durch Kalzinieren der Mischoxide in Luft bei Temperaturen von 115, 300, 600 und 1000°C hergestellt. Die erhaltenen Ergebnisse werden diskutiert und miteinander korreliert.