ХИМИЯ: ИТОГИ И ПЕРСПЕКТИВЫ

THERMAL STABILITY OF TiO_2-ANATASE PHASE DISPERSED IN SiO_2 MATRIX PREPARED BY THE SOL-GEL PROCESSING METHOD

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Представляем читателям статью крупного бразильского химика Йошитаки Гушикема, любезно написанную им с коллегами по предложению редколлегии.

Профессор Йошитака Гушикем родился 12 января 1942 года в городе Жетулина, штат Сан-Пауло, Бразилия. Степени бакалавра (1967) и доктора (1971) химии получил в университете Сан-Пауло. В 1971 году начал преподавать химию во вновь организованном университете Кампинаса (штат Сан-Пауло), где с 1987 года занимает должность профессора кафедры неорганической химии. В 1986-1988 возглавлял кафедру неорганической химии.

Йошитака Гушикем ведет активную научно-общественную деятельность, как член ИЮПАК, Бразильского химического общества, Японского химического общества, Бразильского общества развития науки, Национального научного совета, Фонда штата Сан-Пауло по финансированию научных исследований, Японского агентства по международному сотрудничеству. Член комитета министерства культуры и науки Бразилии.

Под руководством профессора Гушикема защищено более 26 диссертаций на соискание степени доктора химии и 14 магистерских диссертаций. Он опубликовал более 160 статей в международных научных изданиях, сделал 240 докладов на международных и национальных конференциях и симпозиумах.

Профессор Гушикем одним из первых в мировой науке два десятилетия назад приступил к исследованию по функционализации поверхности кремнезема. Последние десять лет в центре его научных интересов находится проблема создания, исследования и применения гибридных минеральных и органо-минеральных материалов, получаемых химической модификацией поверхности оксидов и целлюлозы, а также золь-гель методом. Основные области использования материалов нового поколения – сорбционное и ионообменное концентрирование и разделение и создание электрохимических сенсоров.

Женат, имеет двух дочерей.

Хобби: создание садов в японском стиле, рыбалка.

Редколлегия пользуется случаем пожелать профессору Гушикему здоровья и дальнейших творческих успехов.

Abstract

SiO_2/TiO_2 mixed oxide was prepared by the sol-gel processing method and presented the following compositions: SiO_2/6.0 wt%TiO_2, SiO_2/11.7 wt%TiO_2 and SiO_2/18.5 wt%TiO_2. The specific surface areas for all samples showed only small decreases after heat treatments from 333 up to 973 K while, above this temperature, the decrease became significant and at 1373 K a sintering of the material occurred. For the samples heat treated at temperatures > 1000 K, TiO_2 is observed as anatase phase islands. For bulk phase TiO_2 anatase phase, the transition to the rutile phase is usually observed at ca. 923 K. The reason for the observed stability of the anatase phase is the low thermal mobility, presumably due to Si-O-Ti bonds formed at the SiO_2/TiO_2 interface.

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Introduction

The chemical and structural characteristics of TiO_2 have been intensively investigated by using different synthetic routes aiming to obtain solids with a wide range of specific properties. The oxides obtained from these various methods have been used in catalysis, electrocatalysis and photoelectrocatalysis[1,2]. The sol-gel processing method has opened up the possibility to obtain binary mixed oxides of SiO_2/TiO_2, where TiO_2 presents suitable chemical properties of the bulk phase oxide with an advantage of being entrapped in a mechanically resistant matrix. [3-9] An additional advantage is that TiO_2 can be homogeneously dispersed in the mixed oxide system and the solid matrices can present reproducible compositions in several preparations, with controlled pores size.

Experimental Part

Preparations

The SiO_2/TiO_2 binary oxide was prepared in three steps, as follows: (1) 12 ml of 0.85 mol l^{-1} HNO_3 aqueous solution were added to 250 ml of 50% (v/ v) tetraethylorthosilicate (TEOS)/ ethanol solution, and the mixture was stirred at 353 K for 2.5 h. (2) Different volumes of titanium (IV) butoxide (TBO) and 490 ml of ethanol were then added and the mixture was stirred for 2 h at room temperature. (3) 66 ml of 0.6 mol l^{-1} HNO_3 solution was slowly added and the mixture was allowed to rest for gelation. The xerogels formed were ground, dried at 383 K for 24 h and sieved in order to obtain particles sizes between 75 and 250 μm.

In order to eliminate organic residues entrapped in the matrix, the SiO_2/TiO_2 was previously calcined at 773 K under air flux.

The SiO_2/TiO_2 solids obtained were analyzed using the X-ray fluorescence technique on a Tracor Northern 5000 apparatus, equipped with a berilium window under approximately 100 Pa pressure.

Physical Measurements

The specific surface areas, S_{BET}, were measured by using the multipoint technique on a Micromeritcs Flowsorb II 2300 connected to a flow controller apparatus. The average pore volume, Vp, was measured by using the Hg intrusion technique on a Micromeritics Pore Size 9300 apparatus.

The X-ray diffraction patterns, XRD, were obtained using Cu Kα (λ = 0.154 nm) radiation at 40 kV, with a current of 20 mA, on a Shimadzu XRD 6000 spectrometer. The scanning range was 15 - 60° (2θ) with a step size of 0.02° and a step time of 2.0 s. The identification of crystalline phases was accomplished by comparison with JCPDS file numbers 21-1272, 21-1276 and 39-1425 for TiO_2 in the anatase and rutile phases and for SiO_2 in the cristobalite phase, respectively.[10]

The average crystallite size was determined from the width of the line profiles defined, using Scherrer? equation. The broadening profile had to be corrected for instrumental broadening due to slit sizes and X-ray source characteristics. In order to measure instrumental broadening, a reference diffractogram was recorded from a standard specimen. Silicon powder with a ~5 μm grain size was used as a standard. The (111) reflection of silicon at 28.44° (2θ) was recorded using experimental settings similar to the recorded diffractograms of the material. From this line profile, the instrumental line broadening was determined as 0.16° (2θ).

The transmission electron microscopy measurements were made as HR-TEM (High resolution transmission electron microscop) at 300 kV on a JEOL JEM-3010 microscope from the Laboratory of Electronic Microscopy at the National Synchrotron Light Source Laboratory in Campinas, Brazil, with a point resolution of 0.17 nm. The powder was ultrasonically suspended in isopropyl alcohol and the suspension deposited on a copper grid previously covered with a thin layer of carbon.

The Raman spectra were recorded on a Bomem DA-08 spectrometer equipped with a Nd YAG laser. The Raman scattering data were collected between 750 and 150 cm^{-1} at room temperature with a laser beam of 1.064 μm.

Results and Discussions

Characteristics of the Material

Table 1 summarizes the chemical analyses results for the different samples of SiO_2/TiO_2 obtained as well as the specific surface areas and the average pore volumes. The sample containing the smallest amount of TiO_2 (6.0 wt%), thermally treated at 333 K presented the highest S_{BET} (824 $m^2\ g^{-1}$), which decreased 11 % only after calcination at elevated temperature, 973 K (Figure 1a). The other two samples (with 11.7 and 18.5 wt% of TiO_2), treated at the same temperature, also presented high S_{BET} (719 and 627 $m^2\ g^{-1}$, respectively) and a 12% average decrease in the specific surface area was also observed after the thermal treatment at 973 K (Figure 1b-c). A drastic surface area reduction was observed when the samples were thermally treated at 1273 K, when the S_{BET} values were at the lower detection limit of the equipment (8 $m^2\ g^{-1}$).

Table 1. Chemical analyses of SiO_2/TiO_2 samples, specific surface areas and average pore volumes

Ti / wt%	S_{BET} / m^2g^{-1}	V_p / $mL.g^{-1}$
6.0	824	0.47
11.7	719	0.39
18.5	627	0.31

We can conclude that, although the behavior of the S_{BET} curve shape according to the temperature of the treatment was similar for all the compositions, the SiO_2/TiO_2 system exhibited a dependence on the amount of TiO_2. The decrease of the S_{BET} of the samples thermally treated above 1273 K is a consequence of the sintering process.

X-Ray Diffraction Data

Table 2 reports the crystallographic phases observed by XRD analysis for $SiO_2/18.5$ wt%TiO_2 thermally treated in the range of 773-1473 K. Figure 2 shows the corresponding diffraction patterns. Even thought no defined peaks attributed to SiO_2 were observed, all the diffractograms presented a halo at ca. 21.3^o (2θ), which is very typical in the beginning of the silica crystallization process.[10] Figure 2a presents a broaden halo that was barely modified with increasing the temperature (Figure 2b-e). Moreover, no solid solution was observed since there was no change in the peak position of the anatase XRD pattern.

The XRD data for the sample revealed the presence of only one crystallographic phase, TiO_2-anatase (with the main peak at 25.4 / 2θ). This state was determined by comparison with JCPDS file number 21-1272.[11] This phase can be well identified after thermal treatment of the sample at 772 K (Figure 2a), but the corresponding diffraction peaks were sharper and distinguishable only after 1373 K (Figure 2d). Despite the higher temperature of treatment (1473 K), the anatase phase remained very stable, without any crystallographic transformation (Figure 2e).

The anatase - rutile transformation is related to the degree of packing of the particles, the transformation begins with the nucleation of rutile on anatase and the rutile nuclei grow throughout the anatase particle until completion.[12] High surface area titania is commonly formed by the anatase phase which, under thermal treatment above 800 K, transforms into the more stable rutile form with extensive surface area loss.[12, 13]

Anatase is a metastable TiO_2 polymorph and it tends to transform into the rutile phase, decreasing the surface area, inducing a loss of catalytic activity.[14] Some properties of TiO_2 are very sensitive to its structure. Since the anatase phase is chemically and optically active, it is suitable for use as catalysts and supports,[12,13] while the rutile phase has the highest refractive index and ultraviolet absortivity among the titania phases; thus it is employed in pigments, paints, ultraviolet absorbents.[12]

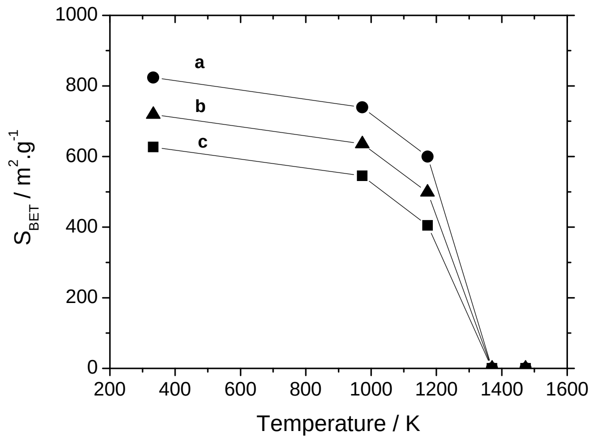

Fig.1. Specific surface areas (BET) of SiO_2/TiO_2 samples thermally treated in the range of 333-1473 K as a function of TiO_2 amount: (a) 6.0 wt%, (b) 11.7 wt% and (c) 18.5 wt%.

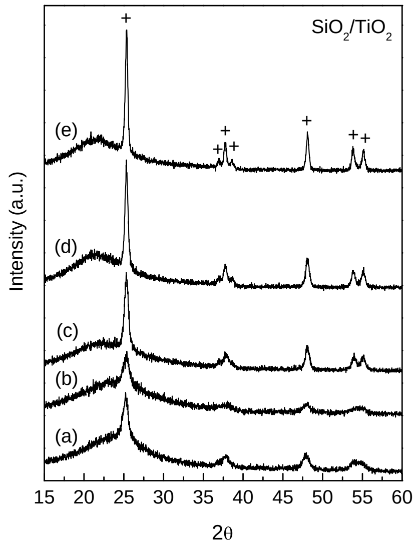

Fig.2. X-ray diffraction patterns of SiO_2/18.5%TiO_2 sample thermally treated at: (a) 773 K, (b) 973 K, (c) 1173 K, (d) 1373 K and (e) 1473 K. (+) TiO_2- anatase phase.

Table 2. Anatase crystallite sizes estimated through Scherrer's equation for SiO_2/18.5 wt%TiO_2 thermally treated between 773 and 1473 K

Temperatures of treatment / K	Anatase particle sizes / nm
773	5
973	5
1173	13
1373	15
1473	22

Our XRD results shows that titania in the anatase phase is very well stabilized on the silica surface after a thermal treatment at 1473 K. Corroborating the stable behavior of anatase are the particle sizes, estimated from Scherrer's equation (Table 2) for the SiO_2/18.5 wt%TiO_2 sample heat treated at various temperatures, since an increase is observed for the anatase crystallite size.

Raman spectroscopy data

Figure 3 shows the Raman spectra for TiO_2 anatase and rutile phases, compared to the SiO_2/ 18.5w%TiO_2 heat treated sample at 1473 K. The TiO_2 powder phase presents a well defined Raman scattering bands due to the anatase phase.[15, 16] Anatase is tetragonal and belongs to the space group D_{4h}^{19} whose optically active lattice modes[17] are listed in Table 3. Although it is known that bulk TiO_2 undergoes a phase transition to rutile upon heating at 1473 K, in the sol gel matrix the Raman frequency of such a phase transition could not be observed, confirming the observations from XRD measurements.

TEM analysis

The TEM images of the SiO_2/TiO_2 sample thermally treated at 1473 K were obtained and one of the images is shown in Figure 4. The micrographs revealed the presence of nanocrystallites of TiO_2 anatase phase since it distinguished the presence of three fringes attributed to this phase. These fringes have the crystallographic planes (h k l) equal to (101), (200), and (004), corresponding to the main diffraction peaks of TiO_2-anatase observed by

XRD. Figure 4 presents two different distances for the atomic planes, 3.6 and 2.5 Å (with (h k l) indexes equal to (101) and (004), respectively). The average crystalline size was 19.9 nm for the SiO_2/18.5 wt%TiO_2 sample thermally treated at 1473 K, in good agreement to the size estimated by Scherrer's equation.

No crystallite due to the rutile phase could be identifiede in the sample heated at 1473 K.

Table 3. Raman vibrational frequencies (cm^{-1}) and assignments for SiO_2/18.5 wt%TiO_2 sample and TiO_2-anatase phase

TiO_2 Anatase phase	SiO_2/18.5wt%TiO_2 Sample heated at 1473 K	Assignments Ref. 17
636	634	E_g*
513	509	A_{1g}, B_{1g}**
196	196$^{\#}$	E_g

*Irreducible representations, **accidental degeneracy, # very weak

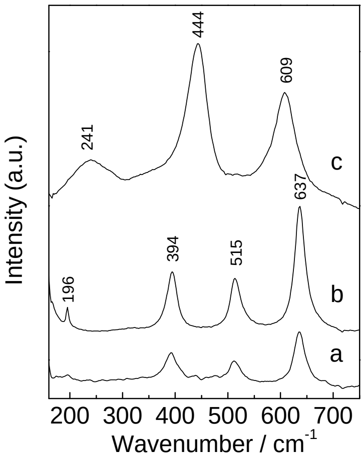

Fig.3. Raman spectra of: (a) SiO_2/18.5%TiO_2, preheated at 1463 K, (b) TiO_2 anatase phase, (c) TiO_2 rutile phase.

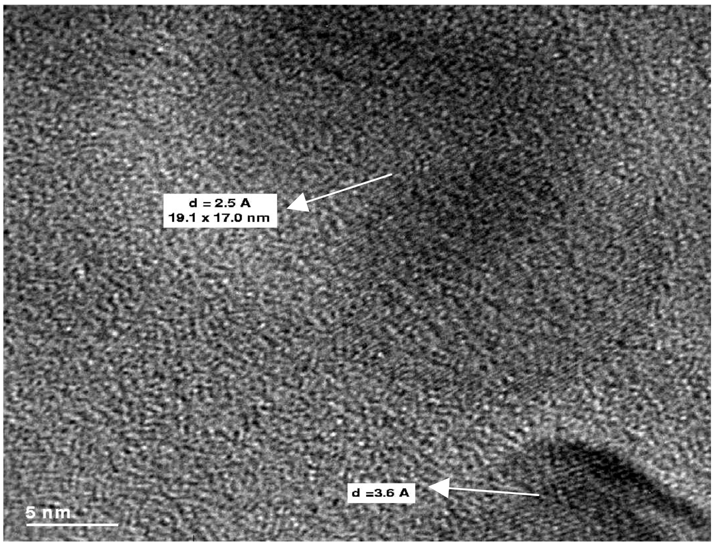

Fig.4. Transmission electron micrograph of SiO_2/18.5%TiO_2 sample thermally treated at 1473 K.

Conclusions

The structural and superficial behaviors of SiO_2/TiO_2 mixed oxides were studied with the objective to better understand metal oxide dispersion in the SiO_2/TiO_2 system. TiO_2 particles are observed as crystallites presenting sizes between 5 and 22 nm for the sample with 18.5 wt% of Ti loading on the silica surface. The TEM image clearly showed in this case that TiO_2 appeared as separated islands of anatase phase. For samples with lower TiO_2 loadings, TEM and XRD measurements were not carried out because the particle dimensions are smaller in size than the lower limit to obtain microscopy images or XRD scattering patterns. The low thermal mobility of this phase is presumably due to the formation of Si-O-Ti bonding at the SiO_2/TiO_2 interfaces since, as observed, even after heating the material at 1473 K, no segregated rutile phase was observed even thought, for bulk phase TiO_2, the phase transition anatase → rutile occurs at ca. 923 K.[12,13,18]

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