FTIR spectra of TiO$_2$-SiO$_2$ nanocomposites

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Abstract In this work we have investigated SiO$_2$ xerogels doped with anatase TiO$_2$ nanopowder in different, very low concentrations. The nanocomposites were produced by mechanical incorporation of nanoparticles in gel matrix, using sol-gel process. The chemical and structural changes were investigated using Fourier transform infrared (FTIR) spectroscopy.

INTRODUCTION

Titania-silica (TiO$_2$-SiO$_2$ composite) represents a novel class of materials that have attracted much attention in recent years. Titania-silica materials have been extensively used as catalysts and supports for a wide variety of reactions. The applications of titania-silica materials as catalysts and supports fall into three categories based on their unique physico-chemical properties: (i) photocatalysis that is associated with the support effect and the quantum-size effect; (ii) acid catalysis that is related to the generation of new acid sites; and (iii) excellent catalytic support materials that possess enhanced thermal and mechanical stability due to SiO$_2$ while preserving the catalytic performance of TiO$_2$ [1].

TiO$_2$-SiO$_2$ composites are generally prepared by sol-gel method. Among the various preparation methods, sol-gel hydrolysis is most widely used due to its possible capability in controlling the textural and surface properties of the composite.

There are two types of interaction between TiO$_2$ and SiO$_2$: physically mixed (with interaction forces being nothing more than weak Van der Waals forces) and chemically bonded (i.e., the formation of Ti-O-Si linkages). When strong interaction results in chemical bonding, the physico-chemical/reactivity properties of titania-silica are very different from the simple combination of the individual phases (mechanical mixtures) [1].

The simplest way to examine the formation of Ti-O-Si bonds is to use infrared (IR) spectroscopy. The IR band observed at 910-960 cm$^{-1}$ is widely accepted as the characteristic vibration due to the formation of Ti-O-Si bonds, with the exact band position depending on the chemical composition of the sample as well as calibration and resolution of the instrument [1, 2]. In the spectral range from 500 to 1200 cm$^{-1}$ in titania-silica IR spectra appear modes connected with pure SiO$_2$: at 800 cm$^{-1}$ is mode associated with symmetric vibration of Si-O-Si, at 970 cm$^{-1}$ mode of SiOH, at about 1080 cm$^{-1}$ (AS1) and 1200 cm$^{-1}$ (AS2) are the modes connected with asymmetric Si-O-Si vibrations [3]. Kirk showed that AS1 mode is caused by antisymmetric stretching
of Si-O-Si bond, when oxygen atoms moves in the Si-Si direction in phase one to another, while AS2 is result of oxygen atoms moving in the same direction out of phase of 180° [4]. The AS2 mode is optically inactive but structure disorder activated it by coupling with strong AS1 mode [5]. In the same spectral range is positioned mode of pure TiO2 nanopowder at about 600 cm⁻¹ [6].

In this work we have presented FTIR spectra of TiO2-SiO2 composite synthesized by sol-gel process with very low amount of TiO2 (0.003-0.01%). The composites were prepared using mechanical incorporation of TiO2 nanopowder into silica matrix.

SAMPLE PREPARATION AND RESULTS

Anatase TiO2 nano powders were synthesized by laser induced pyrolysis, using titanium isopropoxide as liquid precursor. The dimension of TiO2 grains was about 16 nm, determined from XRD spectra using Scherrer method. The dimensions obtained by this method are underestimated. We compared this value with an estimation obtained from SEM photography, which give value of about 50 nm. We conclude that grain size of anatase TiO2 nanopowder has values between 30 and 50 nm. Specific surface area, obtained by BET method was 77 m²/gr.

The TiO2-SiO2 composites were obtained using sol-gel process. The precursors are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TEOS (tetraethilortosilicate) (gr)</th>
<th>EtOH (gr)</th>
<th>Water (gr)</th>
<th>HCl (gr)</th>
<th>Formamide (gr)</th>
<th>TiO2 (gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.666</td>
<td>5.769</td>
<td>3</td>
<td>0.03</td>
<td>2.377</td>
<td>0.0003</td>
</tr>
<tr>
<td>2</td>
<td>8.666</td>
<td>5.769</td>
<td>3</td>
<td>0.03</td>
<td>2.377</td>
<td>0.0009</td>
</tr>
<tr>
<td>3</td>
<td>8.666</td>
<td>5.769</td>
<td>3</td>
<td>0.03</td>
<td>2.377</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Weight amounts of TiO2 were 0.003 % (sample 1), 0.0045% (sample 2) and 0.01% (sample 3). Nano powder was added in the sol phase. The samples was gelated during 1 hour at 60 °C.,. The samples were dried at room temperature during 6 months. The shrinkage of the samples was about 50 %.

The FTIR spectra were measured in the spectral range from 500 to 3000 cm⁻¹, using BOMEM DA 8 spectrometer. Measurements were performed at room temperature. The FTIR spectra of TiO2-SiO2 composite samples and TiO2 pure nanopowder are presented in Figs. 1 and 2.

In the spectral range from 700 to 1200 cm⁻¹ which is interesting for our analysis, FTIR spectra of nano composite samples were fitted using three parameters model for dielectric function:

$$\varepsilon = \varepsilon_{\infty} + \sum_{j} \frac{S_j}{\omega_j^2 - \omega^2 + i\gamma_j \omega}$$
where $\omega_j$ is resonant frequency, $\gamma_j$ is damping parameter, $S_j$ is oscillator strength of $j$th oscillator and $\varepsilon_\infty$ is high frequency dielectric constant. This model is not suitable for fitting the spectra of TiO$_2$ nano powder [6]. In Fig. 3 are presented results of fitting procedure.

**DISCUSSION**

As we can see in Figs. 1 and 2 in the FTIR spectra of TiO$_2$-SiO$_2$ composite samples, appears mode connected with pure TiO$_2$ due to the presence of TiO$_2$ grains in the pores. However, modes at 918 and 952 cm$^{-1}$ assigned to Ti-O-Si vibration, show presence of chemical bonds between TiO$_2$ and SiO$_2$. In Fig. 4a we can see that oscillator strengths of these modes show same behavior as concentration of nanopowder. The mode at 967 cm$^{-1}$ connected with SiOH behaves differently. We assume that Ti-O-Si bonds have been created from TiOH presented at the surface of the grains and SiOH at the internal surface of the pores. Due to nano size of the TiO$_2$ grains, total boundary surface is large, despite the powder low concentration.
In the spectral range from 1000 to 1200 cm\(^{-1}\) appear only modes connected with asymmetric Si-O-Si vibration, AS1 and AS2. These modes are the measure of structural changes in silica matrix [5]. The oscillator strengths of AS1 and AS2 modes increases with concentration of TiO\(_2\). This means that filling of pores with TiO\(_2\) nanograins simulates densification of the Si-O-Si matrix. However, increasing of the AS2 mode oscillator strength indicates that disorder of the matrix become higher.

**CONCLUSION**

The observed nanocomposites, are produced by mechanical incorporation of nanoparticles in gel matrix, using sol-gel process. Analysis of FTIR spectra shows that in nanocomposite structure Ti-O-Si bonds have been formed, despite the synthesis method. The presence of the grains in the pores changes SiO\(_2\) matrix vibration activity.

**ACKNOWLEDGMENTS**

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**REFERENCES**