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PREPARATION AND CHARACTERIZATION OF PLASMA-CHEMICALLY SYNTHESIZED NANODISPERSED POWDERS OF ZrO_2-Y_2O_3 AND SiO_2

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ABSTRACT. Nanodispersed oxides ZrO_2-Y_2O_3 and SiO_2 were successfully obtained by plasma-chemical synthesis in low-temperature plasma and plasma-forming gas argon. The ZrO_2-Y_2O_3 was synthesized by evaporation of a mixture with micron size – ZrO_2 (85%) and Y_2O_3 (15%) in argon plasma. The SiO_2 was obtained by evaporation of quartz in argon plasma. The phase composition, chemical composition, structure and morphology were investigated by X-ray diffraction, X-ray photoelectron spectroscopy, Infrared spectroscopy, Thermal analysis and Scanning electron microscopy. The specific surface area of the ZrO_2-Y_2O_3 and SiO_2 was measured. The plasma-chemical technology allowed the production of nanodispersed powders with unique properties.

ПОЛУЧАВАНЕ И ОХАРАКТЕРИЗИРАНЕ НА ПЛАЗМОХИМИЧНО СИНТЕЗИРАНИ НАНОДИСПЕРСНИ ПРАХОВЕ ОТ ZrO_2-Y_2O_3 И SiO_2

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РЕЗЮМЕ. Нанодисперсните оксиди ZrO_2-Y_2O_3 и SiO_2 бяха успешно получени чрез плазмохимичен синтез в условията на нискотемпературна плазма и плазмообразуващ газ аргон. ZrO_2-Y_2O_3 беше получен чрез изпаряване на смес с микронни размери – ZrO_2 (85%) и Y_2O_3 (15%) в аргонова плазма. SiO_2 е синтезиран чрез изпарение на кварц в аргонова плазма. Фазовият състав, химическият състав, структурата и морфологията са изследвани посредством рентгенофазов анализ, рентгенова фотоелектронна спектроскопия, инфрачервена спектроскопия, термичен анализ и сканираща електронна микроскопия. Измерена е специфичната повърхност на ZrO_2-Y_2O_3 и SiO_2. Плазмохимичната технология позволява получаването на нанодисперсни прахове със специфични свойства.

Introduction

The optical, magnetic, electronic, structural, mechanical, and chemical properties of nanoparticles are found to be almost invariably different from, and sometimes even superior to, those exhibited by their bulk counterparts of the same compositions (Gleiter, 1989; Ichinose et al., 1992; Shinde et al., 2000). Oxide nanomaterials are finding a wide range of applications as catalysts and starting materials for preparing advanced structural ceramics because they possess a unique property, i.e., high reactivity, resulting from their high specific surface area, controlled size, and distribution (Park et al., 2006).

The purpose of this work is to study plasma-chemical preparation of nanodispersed oxides ZrO_2-Y_2O_3 and SiO_2. The compounds were characterized and studied by X-ray diffraction, X-ray photoelectron spectroscopy, Infrared spectroscopy, Thermal analysis and Scanning electron microscopy. The specific surface area of the ZrO_2-Y_2O_3 and SiO_2 was measured. The data obtained allowed us to acquire new information concerning these nanodispersed powders (ZrO_2-Y_2O_3 and SiO_2).

Experimental

Nanodispersed powders of ZrO_2-Y_2O_3 and SiO_2 were synthesized in low-temperature plasma created by high-current electric arc. The ZrO_2-Y_2O_3 was synthesized by evaporation of a mixture with micron size – ZrO_2 (85%) and Y_2O_3 (15%). The SiO_2 was obtained by evaporation of quartz. The plasma-forming gas was argon (Vissokov et al., 1998; Vissokov et al., 2004). On Fig. 1 is shown the plasma-chemical installation used for the synthesis of nanodispersed powders (ZrO_2-Y_2O_3 and SiO_2).

The phase composition of the samples was determined by a X-ray diffraction analysis using apparatus "TUR-M62" with Breg Brentano geometry and a computer control of a goniometer HZG-3, Co-Kα radiation, a scanning step of spectra 0.05^0 and with an increased time for collecting of the impulses – 5 sec. A profile analysis of lines with a program "Fit", according to (Petkov and Bakaltchiev, 1990) was made of the experimental diffraction spectrum. The parameters of the elementary cell and an average size of the crystals were determined by program "PowderCell" (Kraus and Nolze, 1996).

X-ray photoelectron spectroscopy (XPS) measurements were carried out in the UHV chamber of the electron spectrometer ESCALAB-MkII (VG Scientific) with a base pressure of ~$5x10^{-10}$ mbar by using AlKα(1486.6 eV) radiation. The total instrumental resolution was ~ 1eV for all lines. The energy scale was calibrated by using C1s peak centered at 285 eV. The fitting of the recorded XPS spectra was performed, using a symmetrical Gaussian-Lorentzian curve fitting after Shirley-type subtraction of the background.

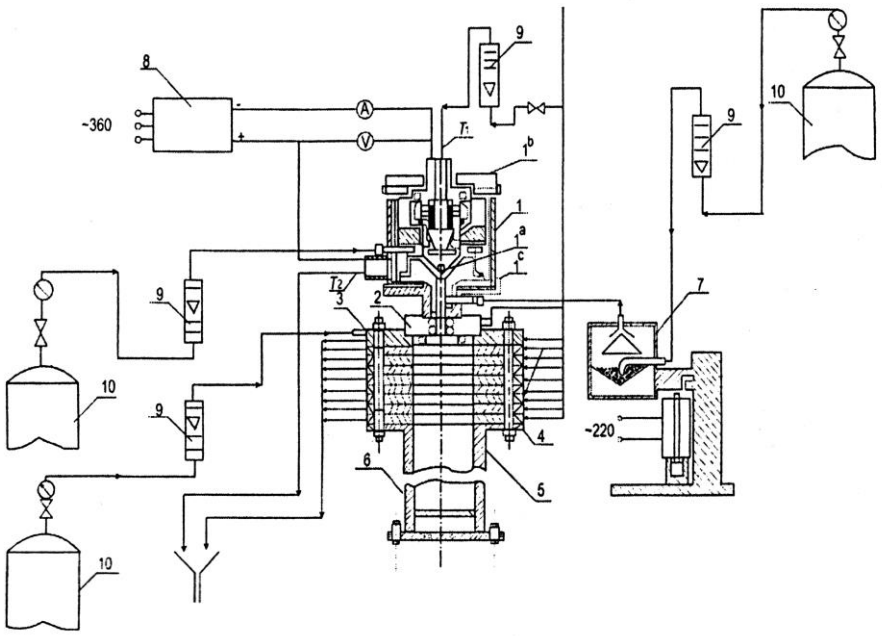

Fig. 1. Schematic diagram of plasma chemical installation for synthesis of nanodispersed powders.
1. Electric-arc D.C. plasmatron; 1^a. Thoriated tungsten cathode; 1^b. Copper water-cooled anode; 1^c. Plastic adjusting ring; 2. CW PCR; 3. Quenching device; 4. Copper water-cooled sections of the quenching device; 5. Powder-trapping chamber; 6. Filter; 7. Vibration powder-feeding device (if necessary, a piston type vibration powder-feeding device can also be used); 8. Current rectifier; 9. Flow rate meters; 10. Bottles with plasma forming, powder-carrying and quenching gases; T_1 – Temperature of inlet water; T_2- Temperature of outlet water.

The IR spectrum of the SiO_2 was recorded using the apparatus "FTIR Bruker Tensor 27". The sample for the IR spectroscopy analysis is prepared mixing 1 mg nanosized SiO_2 and 300 mg KBr and pressed in a tablet.

The Thermal analysis was carried out using a "Stanton Redcroft" (England) installation, connected to a PC at the following conditions: temperature interval of heating – 20 – 1100 ^{0}C; heating rate - 10 ^{0}C/min; sample mass - 10.00 mg; gaseous medium – 100% air, debit – 1l/h. Stabilized corundum crucible was used.

The SEM images of the ZrO_2-Y_2O_3 and SiO_2 were made by JEOL JSM 5300 SCANNING MICROSCOPE.

The specific surface area of the ZrO_2-Y_2O_3 and SiO_2 was measured with the FlowSorb 2300.

Results and discussion

The registered lines in a XRD spectrum (Fig. 2) of ZrO_2-Y_2O_3 corresponded to these which belong to the ZrO_2 or some intermetallic oxides in the system ZrO_2-Y_2O_3. For example the lines completely corresponded to $Zr_{0.8}Y_{0.2}O_{1.9}$. This sample is a well glacial substance. A phase composition, a size of crystals and parameters of the elementary cell are $Zr_{0.8}Y_{0.2}O_{1.9}$, 100 wt%, D = 25 nm, a=b=c= 5.1325 Å.

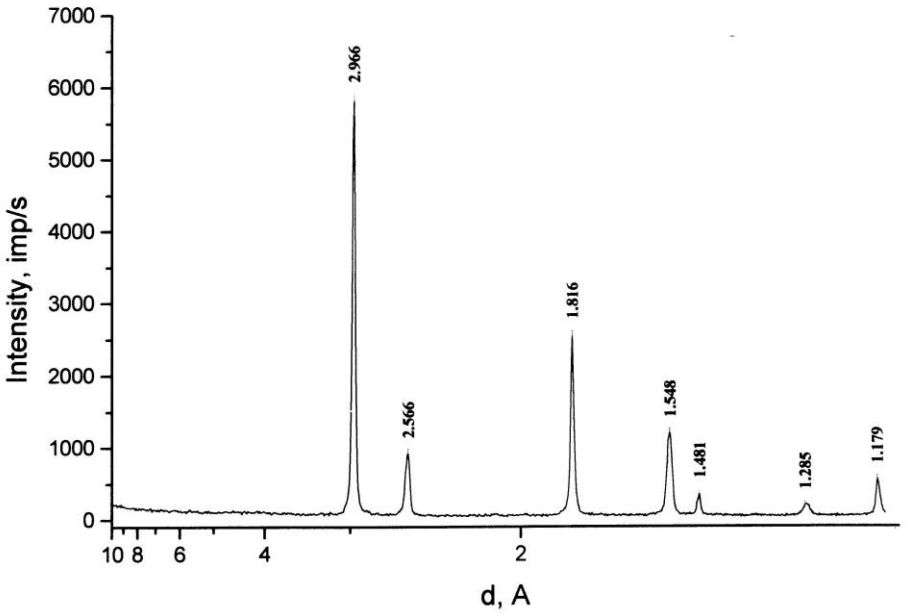

Fig. 2. XRD spectrum of the sample ZrO_2-Y_2O_3.

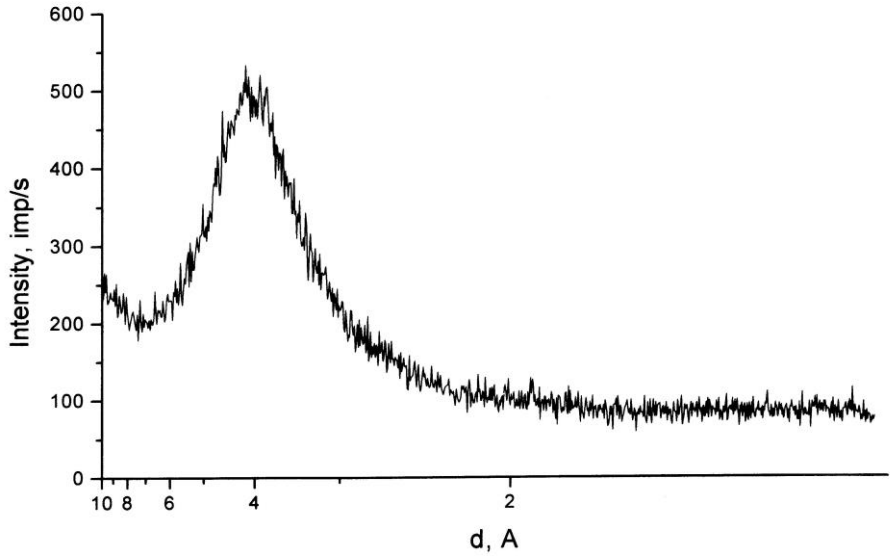

Fig. 3. XRD spectrum of the sample SiO_2.

The XRD spectrum (Fig. 3) of a sample SiO_2 shows the absence of crystalline phases. The registered halo – peak is insufficient for a detailed analysis.

The X-ray photoelectron spectroscopy shows that the measured lines of yttrium stabilized zirconium dioxide (Fig. 4) are with energy for Zr3d – 182.3 eV, Y3d – 157.3 eV and O1s – 530.0 eV and 531.8 eV. The peaks of Zr and Y are symmetrical and their half-widths are 1.7 eV for Zr3d and 2.0 eV for Y3d. The peaks composing oxygen line are with half-widths 1.8 eV for peak with energy 530.0 eV (78%) and 2.3 eV for a peak with energy 531.8 eV (22%). The ratio between atomic percentages of Zr3d, Y3d and O1s is Y3d:Zr3d:O1s=1:5.5:11.2. From position of the peaks and their half-widths, as well as from ratio of the concentrations on surface of the respective elements follows that the investigated sample is zirconium dioxide with inserted yttrium in his lattice. This conclusion comes from the higher energy with 0.5 eV of a peak Y3d in the sample than Y_2O_3. The presence of a peak with a high energy in the line of O1s shows an adsorbed oxygen out of the lattice or OH group over the surface. On the

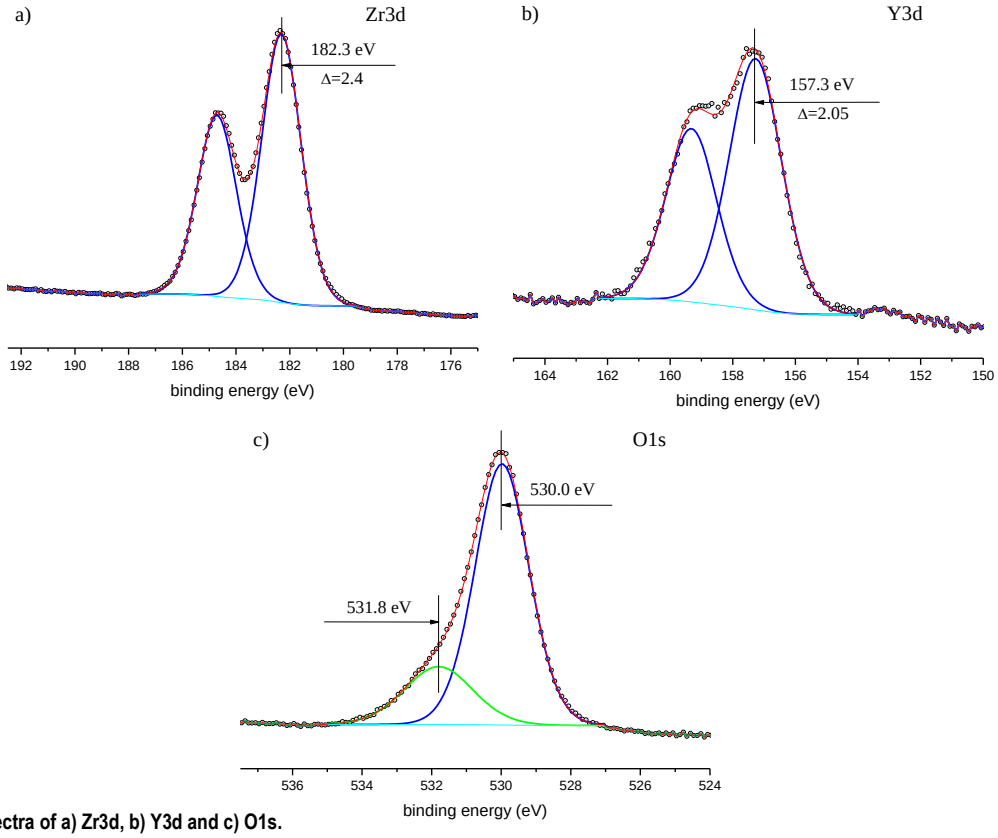

Fig. 4. XPS spectra of a) Zr3d, b) Y3d and c) O1s.

surface of the investigated sample has adsorbed hydrocarbons, which give line C1s. Their presence presses the oxygen, the zirconium and the yttrium in different way. At working of the spectra leave the influence on adsorbed hydrocarbons out of account.

The X-ray photoelectron spectroscopy shows that the measured lines of the silicon dioxide (Figure 5) are with energy for Si2p – 103.3 eV and O1s – 532.7 eV. The peaks are symmetrical and their half-widths are 2.5 eV for the two lines. The ratio between atomic percentages of Si2p and O1s is 0.55. From position of the peaks and their half-widths as well as from ratio of the concentrations on the surface of the respective elements follows that the investigated sample is SiO_2. On the surface of the investigated sample has some atomic percentages from adsorbed hydrocarbons which give a line C1s. Their presence presses the oxygen and the silicon in SiO_2 in different way and has a little diversion from the theoretically correlation (0.5) between atomic percentages of the oxygen and the silicon. At working of the spectra of silicon and the oxygen leave the influence on adsorbed hydrocarbons out of account.

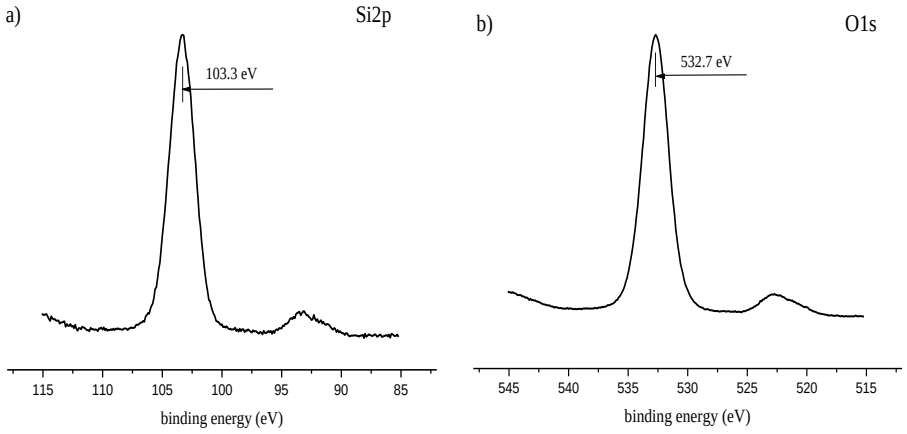

Fig. 5. XPS spectra of the sample SiO_2 a) Si2p and b) O1s.

In IR spectrum of the SiO_2 (Figure 6) has bands:at 3448 cm^{-1} characteristic for vibration of O-H_2 bonds in adsorbed H_2O molecules, at 1636 cm^{-1} characteristic for vibrations of O-H bonds in OH groups and at 1102 cm^{-1} characteristic for vibration of Si-O bonds.

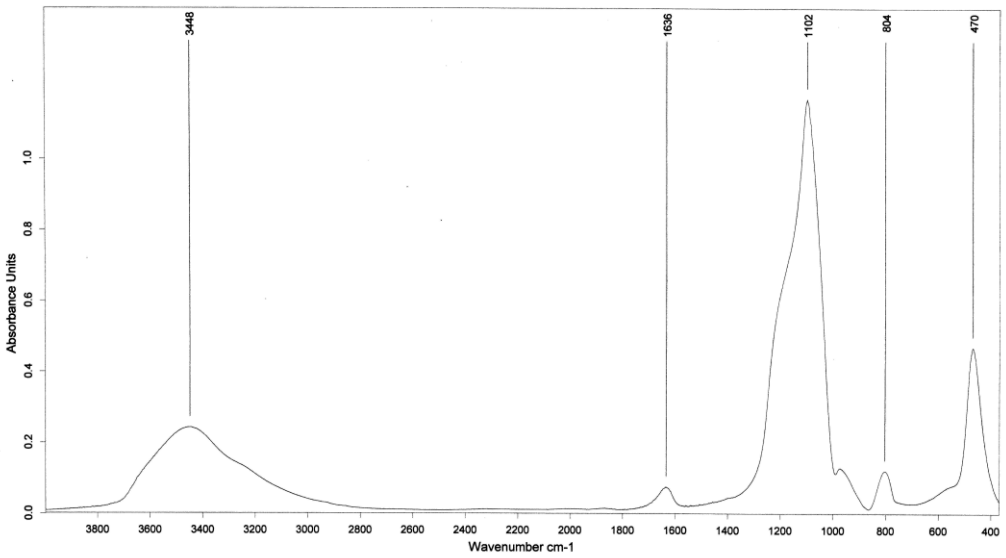

Fig. 6. IR spectrum of the sample SiO_2.

Figure 7 and Figure 8 show the changes in the thermal behaviour of a sample at given experimental conditions by changes of the mass (TG), a rate of the thermal reactions (DTG), a qualitative characterization of the calorific effects which attend the thermal reactions with a mark for a direction of the endothermic and exothermic effects (DTA) and the temperature dependency (T) with the time in minutes.

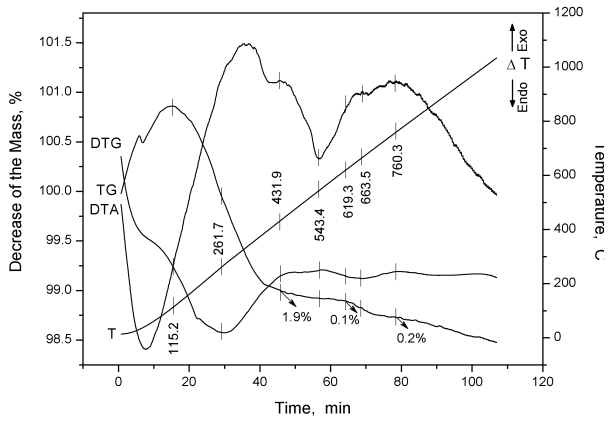

Fig. 7. TG, DTG, DTA and T (time) curves of the sample ZrO_2-Y_2O_3.

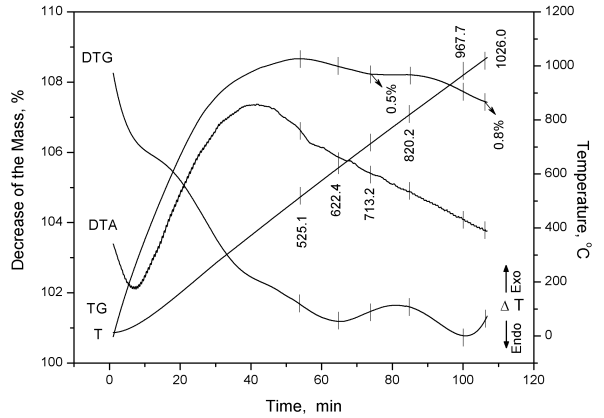

Fig. 8. TG, DTG, DTA and T (time) curves of the sample SiO_2.

The SEM images (Figure 9 and Figure 10) show that have small and large particles. The large particles are composed of small particles.

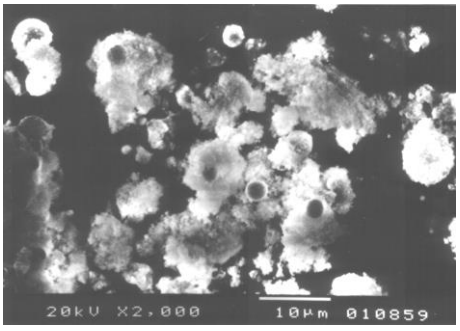

Fig. 9. SEM image of the sample ZrO_2-Y_2O_3.

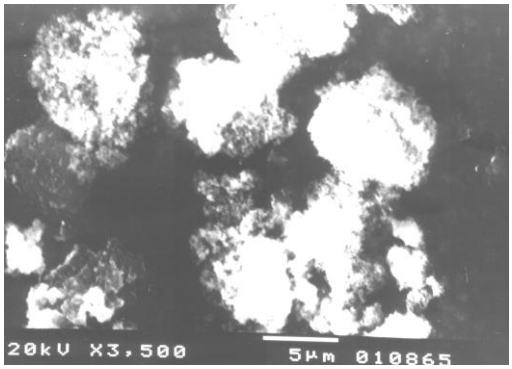

Fig. 10. SEM image of the sample SiO_2.

The specific surface area is 14 m^2/g (ZrO_2-Y_2O_3) and 244 m^2/g (SiO_2).

Conclusion

Nanosized powders of ZrO_2-Y_2O_3 and SiO_2 were prepared using plasma-chemical technique. The X-ray diffraction, X-ray photoelectron spectroscopy, Infrared spectroscopy, Thermal analysis and Scanning electron microscopy were used to characterize the structure of the ZrO_2-Y_2O_3 and SiO_2. The prepared nanostructured materials are promising for many applications. They can be used as supported catalysts. The nanodispersed SiO_2 can be introduced to textile materials and their properties change for the better.

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