

Synthesis and characterization of novel Ti-containing mesoporous silicas support

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Titanium-containing novel mesoporous silicas have been synthesized at ambient temperature by a sol-gel method using amines with alkyl chains of 10-16 carbon atoms as a templating surfactant. An identical synthesis procedure was followed together with the addition of different amounts of titanium (IV) source in the synthesis gels to obtain its titanium-containing silicate gels. Following this synthesis route, it was possible to prepare materials without forming extrawall TiO₂. The transparent gel formed as a precursor resulted in a relatively high titanium incorporation in the silicate framework of up to 0.4% Ti. The characterization results show that most Ti⁴⁺ are isolated and tetrahedrally incorporated into the framework of the silicate gel. Raman spectra and UV-vis spectra indicated that most Ti atoms were incorporated as isolated Ti sites into the silicate framework, and materials with a higher wt% Ti using relatively more coordination agent to prevent TiO₂ forming anatase.

Key words: Silica gel, Cethyltriethylammonium bromide, Titanium sulfate, Framework, Coordination agent.

Introduction

Microporous and mesoporous materials [1-3] have attracted widespread attention as adsorbents and catalysts because of their exceptional surface areas and well-defined pore sizes suitable for the diffusion of bulky adsorbate and substrate molecules. A variety of titanium-containing microporous zeolites, such as TS-1, TS-2, and Ti-, and mesoporous materials, such as Ti-MCM-41, Ti-HMS, and Ti-MCM-48, have been developed in recent years [4-6]. Because of the small pore size of TS-1 and other microporous zeolites, large organic molecules cannot access the active sites which are located inside the cavities and the channels of the zeolites. This limits the utilization of microporous titanium-containing zeolites to the selective oxidation of bulk organic compounds. Using a titanium-containing mesoporous molecular sieve can enlarge the opportunity for the selective oxidation of bulk organic compounds. So these new ordered mesoporous materials have stimulated great interest in the scientific community, principally, in the fields of catalysis and materials science [7-13]. Mesoporous silica, such as MCM-41 [14] and HMS [15], possess high thermal stability (up to 1198 K), large surface areas (above 1000 m²/g) and uniform-sized pores (about 40 Å). Titanium-containing mesoporous silica gels in which Si⁴⁺ is isomorphously substituted by Ti⁴⁺ ions in the silica gels framework is of great interest from both academic and industrial viewpoints because of their extraordinary potential as oxidation catalysts and in many other applications. It

seems therefore that incorporation of Ti⁴⁺ ions in mesoporous materials may enlarge considerably the possibilities of solid-catalyzed oxidation reactions in the liquid phase. Using a titanium-containing silicate gel was first proposed in this study. The titanium-containing zeolites have high wt% Ti, but in our study the wt% Ti is not as high as titanium-containing zeolites. The lower Ti mesoporous silica gel is very important as the support to a polyolefin catalyst. So the titanium-containing mesoporous silica gel was prepared with a wt% Ti of less than 1%. The restriction of titanium incorporation into the silicate network has been the formation due to reactivity differences between titanium and silicon soluble species [16-18]. By means of stabilizing Ti⁴⁺ with coordination agent (H₂O₂), the hydrolysis rate of Ti⁴⁺ in solution could be slowed down to avoid the formation of TiO₂ effectively during the synthesis of Ti-containing silicate gels. Incorporation of transition metal cations in these mesoporous structures is certainly a very interesting and promising field of research. Indeed, incorporation of Ti⁴⁺ ions in the framework of zeolites provides the latter with very interesting properties as catalysts in oxidation reactions with alkylperoxides [19-20]. In addition, it has been claimed that the photocatalytic activity of TiO₂ increased when it was loaded on zeolite or a mesoporous silica support [21-23].

In the present study, we describe a novel method to synthesize a low surface area as well as high titanium-containing silica gel with mesostructural units at ambient temperature by a sol-gel procedure. These mixed oxides prepared by a sol-gel procedure were noncrystalline materials with no regularity of the bulk and pore structure and had a relatively lower surface area of less than 300 m²/g. An advantage of these samples was that they could be prepared

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at ambient temperature, without the help of an autoclave.

In this study, we report in detail the synthesis and characterization of lower Ti-containing silicate gel prepared using cethyltriethylammonium bromide as templates. In particular, we have investigated the influence of the synthesis time, the coordination agent/Ti ratio, the wt% of Ti, and the dosage of templates. It has been pointed out that along with the increase of the wt% of Ti, the complexing agent/Ti ratio should increase. Nitrogen adsorption, Raman and UV-vis spectroscopy have been used to characterize the physicochemical properties of the products.

Experimental Section

Materials

Sodium silicate was donated from Petrochemical Research Center of Lanzhou, Petrochina. Cethyltriethylammonium bromide was obtained from Beijing Chemical Reagent Company (China), and titanium sulfate was purchased from Shanghai Chemical Reagent Company (China). They were of 98-99% purity and were used without additional purification. Distilled water was used throughout the study. Other chemicals and solvents were analytical grade and were all obtained from Tianjing Chemical Reagent Company (China).

Synthesis of the titanium-containing mesoporous silica

Titanium-containing mesoporous silica gel has been synthesized by a simple sol-gel method with cetyltrimethylammonium bromide as a template and with titanium sulfate and sodium silicate as framework sources. The procedure was as follows:

Solution A was prepared by mixing 25 ml sodium silicate solution and 5 ml distilled water into a stainless beaker at ambient temperature and blending fully with a mechanical stirrer. No isopropyl alcohol was added to the synthesis mixture.

A second solution (B) contained cethyltriethylammonium bromide dissolved in distilled water as the templating surfactant. The last solution contained titanium sulfate and complexing agent.

First, blending fully with 25 ml sodium silicate solution and distilled water in a transparent beaker and placed in a constant temperature water bath, running the blender and adjusting medium-speed stirring for 10 minutes to make the temperature consistent. A certain concentration of dilute sulfate solution (0.3-0.6 mol/L) was added by dripping into solution A under vigorous stirring. Then the pH was adjusted to 8.0-10.0 with dropwise addition of dilute sulfate solution (0.3 mol/L), and the gel was formed gradually. Second, solution B was poured into the new forming silicate gel under vigorous stirring, forming a system of equalities. Third, titanium sources were added into the synthesis gel, after that stirring at ambient temperature for about 30 minutes. Reactions proceeded at room temperature and the mixture was kept at pH 8.0-10.0 with stirring gently. Aging was performed by using an auto controlling

reactor under the conditions of pH 8.0-10.0 and a process heater from 35 °C to 80 °C in 5 h.

The homogeneous gel was further aged in turn for 1 hour at 40 °C, 2 hour at 50 °C, 1 hour at 60 °C, 1 hour at 70 °C. After finishing the above steps, the products were washed with distilled water until the pH of the washing solution was 7.0, the resulting product was filtered, washed 3-4 times to neutralize. Then the solid products dried in an oxygen atmosphere in turn for 1 hour at 50 °C, 1 hour at 80 °C, 1 hour at 100 °C, 1 hour at 120 °C, the solid products were put to mill powder into the bowl of crushed stone roller finally calcined in muffle at 650 °C for 6 h.

Characterization of the titanium-containing mesoporous silica

Raman spectra of the Ti-containing silicate gel were obtained using a continuous wave laser line at 325 nm as the excitation sources for 60 s. The wavelength was 100-1300 cm^{-1} . In this study, we used a Horiba Jobin Yvon LABRAM-HR800.

Diffuse reflectance UV-Vis spectroscopy is a very sensitive probe for the presence of extra framework Ti in zeolites. The measure of range was 220-700 nm. And the apparatus model was ZASCO UV-570.

The infrared spectra (FT-IR) of the Ti-containing silicate gels were recorded using a Nicolet NEXUS 670 FT-IR spectrophotometer, and the sample and KBr were pressed to form a tablet.

The average pore size of the Ti-containing silicate gel synthesized following the above procedures was determined by the Barrett-Joyner-Halenda (BJH) method, while the specific surface area was mensurated by the Brunauer-Emmett-Teller (BET) technique.

Results and Discussion

Synthesis of Ti-containing silicate gels with inorganic titanium sources

In the synthesis of the Ti-containing silica gels, control the rate of hydrolysis of titanium and silicate species is the key problem to decrease or avoid the formation of extra framework TiO_2 . In the synthesis of titanium-containing molecular sieves, one major disadvantage of using organic titanium sources is that a nonframework TiO_2 is unavoidably formed if the titanium source is not hydrolyzed carefully [24]. The rate of hydrolysis of titanium organics is usually far faster than those of silicon alkoxides, which makes it difficult to avoid the precipitation of TiO_2 [2]. Introducing inorganic titanium sources into a synthesis system may solve the above problem to a certain degree.

In addition, we use a type of coordination agent, when using an adequate coordination agent, the coordination agent will complex with excess hydrolyze titanium and only leave a few titanium hydrate combinations in the silicate-oxygen system, i.e. the Ti^{4+} is released step by step from the compound system. When a coordination agent was used in the titanium salts solutions, all of the solutions containing

Ti⁴⁺ remained clear even when the solutions were adjusted to pH = 9.5, This shows that the presence of coordination agent could prevent effectively the precipitation of Ti⁴⁺ in a basic solution.

Characterization by raman spectra, and UV-vis spectra, nitrogen adsorption, FT-IR spectra

Raman spectra of Ti-containing silicate gel

Fig. 1 shows the Raman spectra of the sample of the Ti-containing silica gel, Anatase is known to have strong Raman scattering properties, and this is readily detected by the intense Raman bands at 395, 515, and 640 cm⁻¹. The interpretation of Raman bands at 395, 515, 640 cm⁻¹ is complicated in the Ti-Si mixed oxide because amorphous silica also possesses Raman features at ~410, ~487, ~607, and ~802 cm⁻¹. However, the large peak at 150 cm⁻¹ is a sensitive indicator of the presence of anatase [26]. The sample exhibits no trace of the 150 cm⁻¹ band as shown in Fig. 1, indicate that most of Ti species have come into the silica gel framework. The resonance enhanced Raman bands at 490, 530, and 1125 cm⁻¹ can be attributed to framework titanium species in tetrahedral sites. These vibrational modes can be assigned simply from the analysis of the local unit of a [Ti (OSi)₄], denoted as Ti-O-Si in this paper. The bands at 490 and 530 cm⁻¹ are respectively assigned to the bending and symmetric stretching vibrations of the framework Ti-O-Si species and the band at 1125 cm⁻¹ is attributed to the asymmetric stretching vibration of the Ti-O-Si [27-30]. The band at 1125 cm⁻¹ is most enhanced in the UV resonance Raman spectrum because this vibration mode is more sensitive to the charge-transfer transition of Ti-O-Si.

UV-vis spectra of Ti-containing silicate gel

The DR UV-Vis spectra of the mesoporous Ti-containing silica gel samples are shown in Fig. 2. All of the titanium-containing silica gel samples above showed a weak band centered at ca. 210 nm together with an intense shoulder at 260-270 nm. The band at 210 nm is assigned to isolated

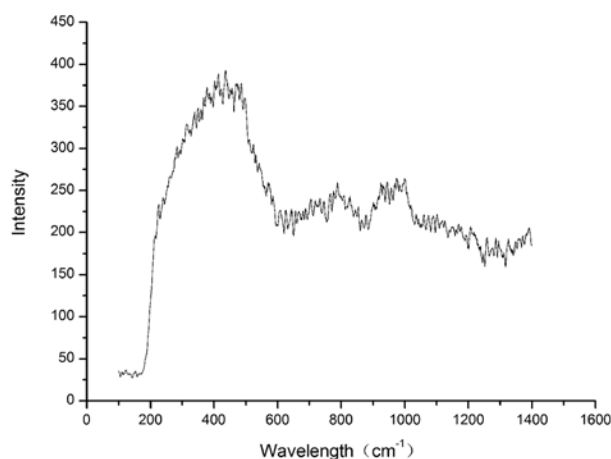


Fig. 1. Raman spectra of Ti-containing silica gel.

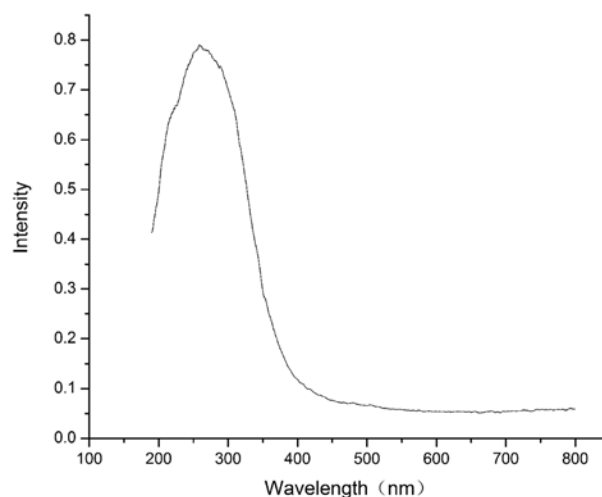


Fig. 2. UV-Vis spectra of Ti-containing silica gel synthesized with cetyltrimethylammonium bromide as the template.

framework titanium in tetrahedral coordinated sites [31, 32]. The shoulder at 260 nm probably corresponds to partially polymerized Ti species (ve and six-coordinated) in small titania nanodomains. The absence of the 330 nm peak for the mesoporous Ti-containing silica gel indicates that no bulk titanium dioxide is formed. The above results suggest that most of the Ti atoms occupy a site-isolated position in the silica framework of the Ti-containing silica gel synthesized with inorganic titanium sources.

Nitrogen adsorption and desorption isotherms of Ti-containing silicate gel

From the isotherms, a hysteresis loop is observed, it is a type of Langmuri, this is characteristic of nitrogen adsorption and desorption isotherms for a mesoporous material. When P/PO is lower than 0.2, the quantity of nitrogen adsorption and desorption will increase gradually along with the increase of P/PO. This is because of the N₂ at the pore surfaces. The capillary action of N₂ in pores make the quantity of nitrogen adsorption and desorption increase sharply, which make isotherms have obvious speed between 0.3~0.45. Whereafter, the long adsorption and desorption indicate that the saturation of nitrogen adsorption in the capillaries. The porous properties revealed in Table 1.

Infrared spectra of Ti-containing silicate gel

The evidence of this isomorphous substitution of Si by Ti is usually taken from the Si-O-Ti vibration band at ca. 960 cm⁻¹ in the FT-IR absorption spectrum [33, 34]. We could detect the band at ca. 960 cm⁻¹ for Ti-containing silica gel shown in Fig. 3.

Table 1. The Porous Properties of sample TSG-1-008

sample number	Bulk density (g/cm ³)	Specific surface area (m ² /g)	Pore Volume (cm ³ /g)	Aperture (nm)
TSG-1-008	0.38	429.5	1.576	10.02

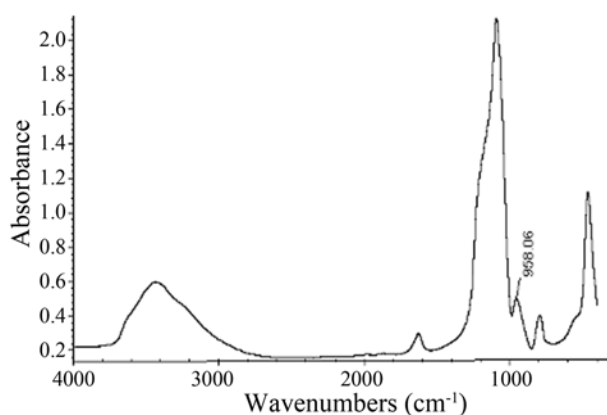


Fig. 3. FT-IR Spectra of the Ti-containing silica gel.

Optimum amount of Ti/Si ratio

In this study, we prepared Ti-containing silica gels containing from 0.1-0.4 wt% Ti. As shown in the Fig. 4, all samples have been characterized using Raman spectra, and this detection technique has been used extensively for the characterization of the nature and coordination of Ti^{4+} ions in zeolites [35].

From Fig. 4, with the wt% Ti increase, a part of the Ti species forms Anatase.

The situation of Ti into the framework properties is revealed in Table 2.

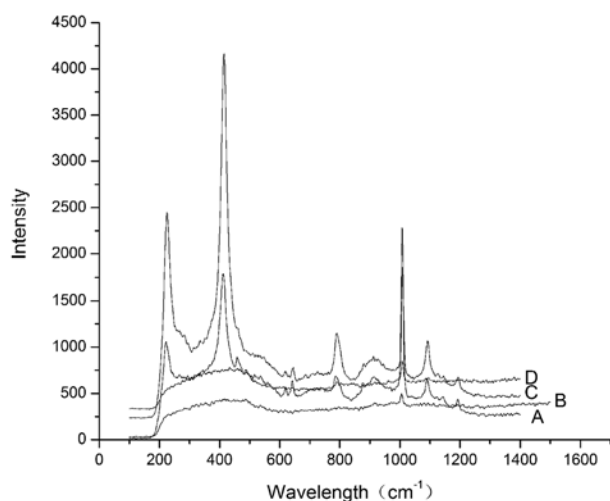


Fig. 4. Raman spectra of samples TSG-1-008; TSG-1-031; TSG-1-034; TSG-1-037 (A: TSG-1-008 with wt% Ti is 0.4; B: TSG-1-031 with wt% Ti is 0.3; C: TSG-1-034 with wt% Ti is 0.2; D: TSG-1-037 with wt% Ti is 0.1).

Table 2. The Properties of sample TSG-1-008; TSG-1-031; TSG-1-034; TSG-1-037

Sample number	TSG-1-008	TSG-1-031	TSG-1-034	TSG-1-037
wt% Ti	0.1	0.2	0.3	0.4
Property of Ti into the framework	Better	Better	Good	Bad

Optimum amount of the coordination agent

All samples were prepared according as described above, and the results from Raman spectra are shown in Fig. 5. If samples were to have a higher wt% Ti, relatively more coordination agent would need to be used to avoid the formation of extra framework TiO_2 .

All of the samples show that most Ti species enter into the framework of the silica gel.

The situation of Ti into the framework properties is revealed in Table 3.

Optimum reaction temperature

All samples were prepared according as described in addition to the reaction temperature being changed. The situation of Ti into the framework properties is revealed in Table 4.

On the basis of the thermal and mechanical stability demonstrated in air, in combination with the other stability features and the structural and properties previously reported [36], it is demonstrated that all the Ti-containing silica gel materials prepared with different titanium contents are thermally stable in air up to high temperatures. The thermal

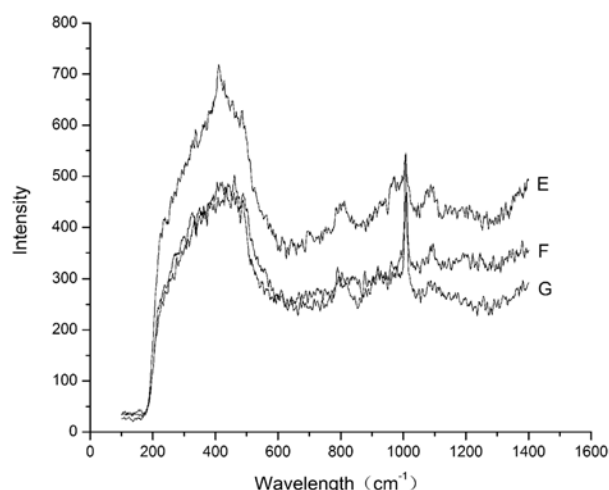


Fig. 5. Raman spectra of samples TSG-1-014; TSG-1-037; TSG-1-040 (E: TSG-1-014 with wt% Ti is 0.4 and the coordination agent/Ti ratio is 30; F: TSG-1-037 with wt% Ti is 0.1 and the coordination agent/Ti ratio is 10; G: TSG-1-040 with wt% Ti is 0.3 and the coordination agent/Ti ratio is 20).

Table 3. The Properties of sample TSG-1-014; TSG-1-037; TSG-1-040

Sample number	TSG-1-014	TSG-1-037	TSG-1-040
coordination agent/Ti ratio	10	20	30
Property of Ti into the framework	Bad	Good	Good

Table 4. The Properties of sample TSG-1-037; TSG-1-038; TSG-1-039

Sample number	TSG-1-037	TSG-1-038	TSG-1-039
Reaction Temperature (°C)	30	40	50
Property of Ti into the framework	Better	Good	Good

stability was found to be practically independent of the Si/Ti molar ratios and of the alkyl chain of the cetyltriethylammonium bromide used in the synthesis.

Uniform design (UD) to the preparation of Ti-containing silica gels

UD is precisely a technique for experimental designs, emphasizing the uniformity of space filling in the experimental domain. With uniform design, we can find the optimal condition is that the reaction temperature is 40 °C, the coordination agent /Ti ratio is 15, the Ti/Si ratio is 0.35%, and the optimum pH is 9.5.

Conclusion

Titanium-containing novel mesoporous silicas have been synthesized, and the Raman spectra, FT-IR spectra and UV-vis spectra, all indicate that most of Ti species enter the silica gel framework. Nitrogen adsorption shows that Ti-containing silica gels have larger surface areas and well-defined pore sizes. Using a coordination agent can avoid the formation of non framework TiO₂. The titanium dioxide distribution in the titania-silica support depends on the method of support preparation the less wt% Ti, the finer capability of the samples, and as the quantity of titanium increases, so does the quantity of the coordination agent needed to avoid the formation of extra framework TiO₂. We may conclude that this synthesis method performed in a short period of time at ambient temperature and pressure, using cetyltrimethylammonium bromide titanium sulfate and cationic surfactants, is a valid alternative to obtain Ti-containing silica gel materials. The as-synthesized materials will be very valuable in applications as polyolefin catalyst carriers.

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