

The Effect of Silane Modification on the Adsorptive Properties of Natural Pyrophyllite and Synthetic Titanium-Based Powders Prepared by the Sol-Gel Process

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Our aim was to improve the relatively poor adsorption characteristics of natural pyrophyllite and those of TiO_m and $Ti(OR)_x(OH)_y(O)_z$ obtained from titanium tetraisopropoxide (TTIP) by the sol-gel process. For this purpose, the surfaces of the above-mentioned adsorbents were coated with a surface modifier by dipping them in 1% and 50% (w/w) solutions of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DIAMO) in methanol. Realization of the coating processes was checked by FT-IR and SEM analyses. FT-IR analyses of the coated powders heat treated at 110 °C showed that condensation took place between OH groups of prehydrolyzed silane molecules and hydroxyl groups and/or oxygen atoms on the surface of the powders, ensuring the attachment of the silane molecules to the surface.

Adsorption properties of coated and uncoated adsorbents were compared. Adsorption percentage of natural pyrophyllite was 46.35% for 4-nitrophenol (4-NP) in aqueous solution, whereas 1% and 50% amino-coated pyrophyllite displayed 52.14% and 73.84% adsorption, respectively. The highest adsorption of 4-NP was realized when the calcinated powder obtained from the hydrolysis-condensation product of TTIP was coated with DIAMO from 50% solution.

Key Words: Aminosilane coupling agents, surface modification, 4-nitrophenol, adsorption.

Introduction

In surface modification, the most frequently applied agents are silane coupling agents of $(OR)_3-Si-X$ form, where X corresponds to the functional organic group linked to the Si atom by an alkyl chain, while OR corresponds to an easily hydrolyzable group^{1,2}. Anchoring of organosilanes onto the surface of oxide or clay is realized by a condensation reaction between OH groups present on the oxide or clay surface and silanol

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groups formed by the hydrolysis of organofunctional alkoxy silanes^{3–11}. Surface modification imparts some specific properties to the adsorbent through a mindful choice of organic functional groups. The presence of surface functional groups and the surface density of these groups affect the adsorption behavior. On the other hand, modification of natural silicate surfaces with coupling agents changes the hydrophobic character into hydrophilic^{12–15}. This in turn creates possibilities for their utilization for a multitude of purposes.

The sol-gel method has been intensively utilized in the synthesis of various functional coating films and preparation of featured materials^{16–19}. The use of sol-gel derived materials in various separation processes—from membranes to selective adsorbents—has been our major concern lately. In our laboratory a series of studies has been conducted to evaluate the possible of the use of sol-gel derived metal oxides for adsorption of organic and inorganic pollutants from aqueous solution^{20–24}.

In the present study, adsorption of 4-NP on both unmodified and modified powders prepared by the sol-gel method and on pyrophyllite was investigated. DIAMO was used as a surface modifier for both adsorbents. The effect of the modifier concentration on adsorption of 4-NP was also investigated.

Materials and Methods

Materials

Pyrophyllite (PYRO) samples were collected from a deposit mined in Malatya, Eastern Turkey. The sample consists of ~99% PYRO, and small quantities of kaolinite and quartz, as determined by X-ray diffraction analysis and chemical analysis.

Titanium tetraisopropoxide (TTIP) purchased from Fluka was used for the preparation of adsorbents and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane with the chemical formula $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ and described as DIAMO hereafter was used to prepare the coating solution. Methyl ethyl ketone (MEK) and methyl alcohol were used as solvents and stored over molecular sieves (Fluka 3Å XL8) for a day before use. The pure crystalline 4-nitrophenol (4-NP) was obtained from Merck. The solution of 4-NP of desired concentrations was prepared by dissolving the 4-NP in distilled water. The concentration of 4-NP in all aqueous solutions was analyzed using a Shimadzu 1601 model UV-visible spectrophotometer. A Mettler DL model 18 Karl–Fischer coulometric titrator was used to measure the amount of water consumed in the hydrolysis reaction of DIAMO and TTIP and to measure the amount of unreacted water. IR absorption spectra of solids were recorded on a Perkin-Elmer 283 model Fourier transformed infrared (FT-IR) spectrophotometer, using KBr pellets. A Perichrom Peri-2000 model gas chromatograph was employed to determine the amount of alcohol released in the hydrolysis reaction. Here isopropanol and MEK were used as internal standards. Elemental and TG-DTA analyses were carried out with a Perkin-Elmer model element analyzer and a Setaram A 24 model thermal analyzer, respectively. The surface morphology of the powders was analyzed using a Jeol model JXA-840A scanning electron microscope (SEM). Several surface characteristics of unmodified and modified powders were estimated by analysis of adsorption/desorption data, using a Micrometrics ASAP 2000 BET analyzer.

Preparation of powders

Hand specimen of pyrophyllite was first crushed with a hammer and then ground in a ceramic mill with ceramic balls as mill charge. Powdered pyrophyllite was then wet sieved and the sieve fraction with particle size distribution ranging from 150 to 212 μm , as determined using ASTM E11 test sieves, was utilized.

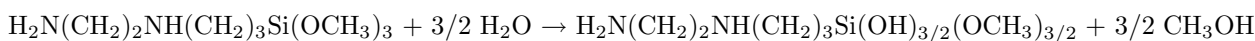
Before use, pyrophyllite (PYRO) was washed several times with distilled water until no suspended material was observed in the wash water and then it was dried at 110 °C and stored in a CaCl₂ desiccator until use.

The hydrolysis reaction of TTIP was performed without using a catalyst. The hydrolysis of TTIP was carried out using 1-4 moles of water per mole of alkoxide in MEK. After stirring the mixture for 60 min at room temperature, the amount of unreacted water was measured with a Karl-Fischer coulometric titrator. By removal of the solvent and isopropanol liberated during the hydrolysis-condensation reaction under vacuum, a solid product was obtained. The amount of alcohol liberated was determined by gas chromatography. The product was characterized by FT-IR, elemental and thermal analyses.

The hydrolysis product was dried in a vacuum sterilizer at 110 °C for 5 h. This product was ground and sieved to desired particle size (175-200 mesh). While one portion of the powdered material was used directly as adsorbent (T100), the other portion was also used for the same purpose (T900) after being calcinated at 900 °C in a muffle furnace. FT-IR and SEM analyses were used to check the realization of calcinations.

Modification of the powder surfaces

DIAMO was hydrolyzed by adding dropwise 3 moles of water per mole of DIAMO without solvent and catalyst. According to the Karl-Fischer titration, 1.5 moles of water were consumed per mole of DIAMO. The hydrolysis reaction of DIAMO can be represented as



The reaction was allowed to continue at ambient temperature until a clear and homogeneous solution occurred. Unreacted water and alcohol formed during the reaction were removed in vacuo. Thus, a viscous and colorless solution containing pre-hydrolyzed DIAMO was obtained. After diluting in dry methanol (1% and 50%, w/w), the solutions were used for the modification of T100, T900 and PYRO surfaces. Powders were added to the solution and the mixture was stirred at ambient temperature. After stirring for 1h, the solid phase was filtered and dried in a vacuum sterilizer for 90 min at 110 °C, resulting in a condensation reaction on the surface of the powders. Thus, powders coated with 1% solution of DIAMO, T100-1D, T900-1D and PYRO-1D, and the powders coated with 50% solution of DIAMO, T100-50D, T900-50D, PYRO-50D were obtained. Figure 1 shows the schematic illustration of the flow chart for the preparation of adsorbent powders. The powders were characterized by FT-IR and SEM analyses.

Adsorption experiments

After the optimization of parameters such as contact time, initial 4-NP concentration and amount of adsorbent, equilibrium adsorption experiments were batch performed. Briefly, 0.1 g of the powders was poured directly into a 50 mL beaker containing 10 mL of 10 mg/L 4-NP solution. The mixture was stirred on a magnetic stirrer at room temperature for 10 min at 300 rpm. The pH of 4-NP solutions was 6.8 ± 0.1 without further adjustment to simulate the natural aqueous solutions. Thereafter, the beaker was removed from the stirrer, and centrifuging at 2000 rpm for 5 min separated the aqueous and solid phases and using a Schleicher & Schuell 0.2 µm disposable filter unit then filtered the aqueous phase. The concentration of 4-NP in the clear solution was analyzed using the spectrophotometer by measuring the absorbency for 4-NP at 318 nm.

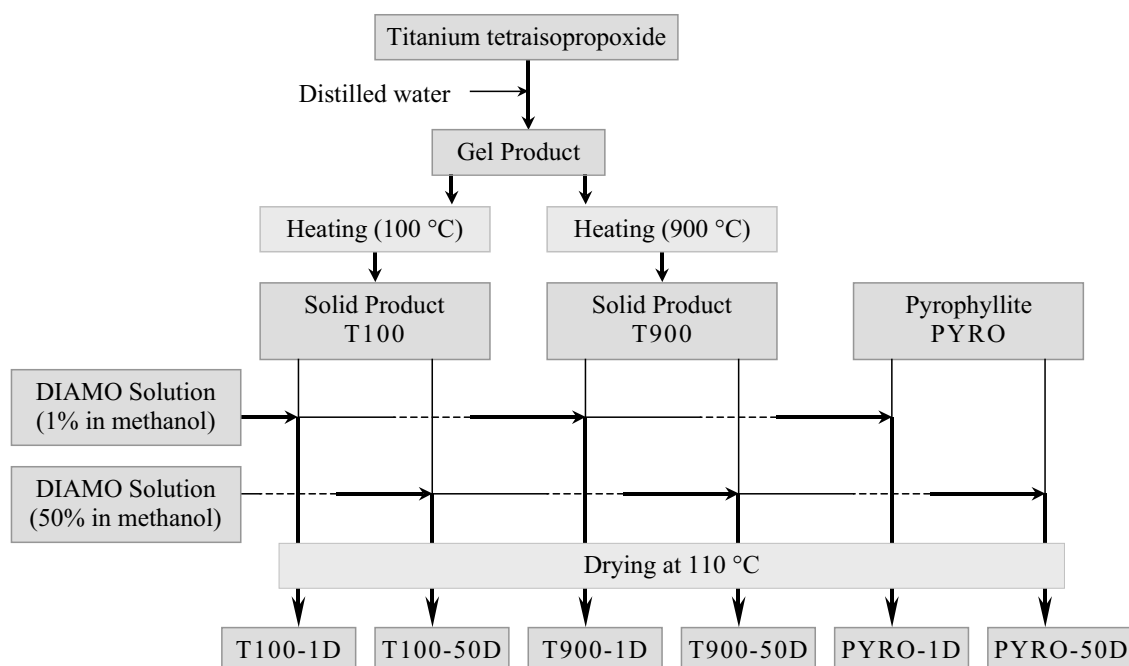
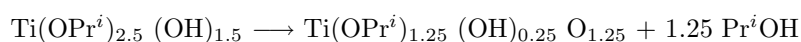
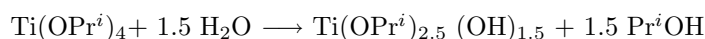


Figure 1. The flow-chart for the preparation of adsorbent powders by sol-gel method.

Results and Discussion

According to the Karl-Fischer titrations and GC measurements, 1.5 moles of water were used per mole of TTIP and 2.75 moles of isopropanol were liberated in the hydrolysis-condensation reaction of alkoxide. Thus the hydrolysis-condensation reaction of TTIP can be shown as follows:



In the FT-IR spectrum of the hydrolysis-condensation product, the broad band at $3010\text{-}3400 \text{ cm}^{-1}$ and the weak band at 1600 cm^{-1} are attributed to the stretching and bending vibration of the OH group in the hydrolyzed product and adsorbed water. Ti-O and Ti-O-C vibrations were observed at $581\text{-}650 \text{ cm}^{-1}$ and 1260 cm^{-1} , respectively. These vibrations clearly indicate that alkoxide groups bonded to titanium were not completely removed after hydrolysis.

According to the thermogravimetric analysis (TG), the weight loss of the hydrolysis-condensation product of TTIP was 26.32% at $420 \text{ }^\circ\text{C}$. This value corresponds to 73.68% for TiO_2 content. The weight loss was due to the removal of water and organic constituents in the product of the hydrolysis-condensation. In the elemental analysis of the product, the amounts of TiO_2 and Ti were 72.03% and 43.18%, respectively. In the differential analysis (DTA) of the hydrolysis-condensation product of TTIP, the peaks at $135 \text{ }^\circ\text{C}$ (endothermic), $255 \text{ }^\circ\text{C}$ (exothermic) and $430 \text{ }^\circ\text{C}$ (exothermic) can be ascribed to the removal of water attached to the compound and the combustion of the organic groups.

Table 1 lists the FT-IR vibration band positions and their assignments of PYRO, T900, 50% DIAMO solution, PYRO-50D and T900-50D. Depending on the FT-IR vibration band positions listed in Table 1, it was realized that the bands of DIAMO are also observed on the spectrum of PYRO-50D and T900-50D as

evidence of a surface reaction with DIAMO. It can be suggested that after treatment with DIAMO solution heat treatment at 100-110 °C for drying results in a condensation reaction between the OH groups of the DIAMO molecules and the hydroxyl groups and/or oxygen atoms on the PYRO and T900 surface, causing attachment of DIAMO to the surface of the powder. The reaction between the powder surface and the prehydrolyzed DIAMO molecule can be schematically represented as follows:

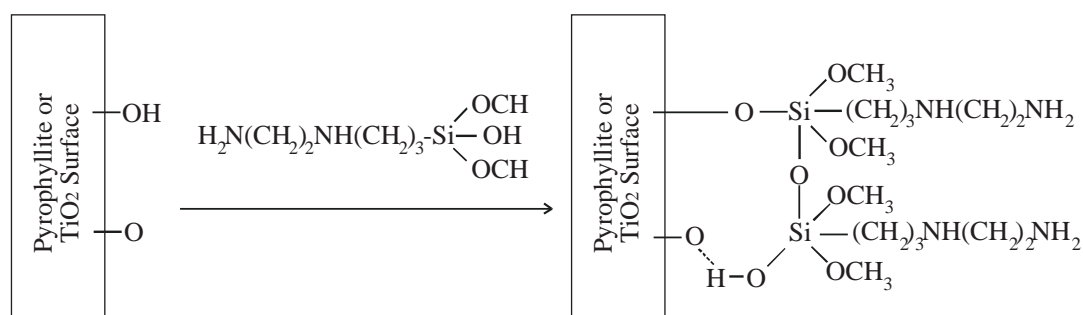


Table 1. The FT-IR vibration band positions and their assignments for PYRO, T900, 50% DIAMO solution, PYRO-50D and T900-50D.

	Band position, cm ⁻¹	Vibration assignment
PYRO	3674	O-H stretching vibration of OH groups bonded to Al ions within layer structure
	3179	H bonded OH stretching
	1145, 1015	Si-O stretching
	955	OH bending vibration of Al-OH groups
	554	Si-O-Al stretching
	465, 440	Bending of Si-O groups
T900	1260	Ti(O-C) stretching
	930	Ti-O-Ti stretching
	581-650	Ti-O stretching
50% DIAMO Solution	3591, 3211	-OH and -NH ₂ stretching
	2955-2837	Aliphatic CH ₂ - stretching
	1482	-CH ₂ bending
	1150-1043	Si-O stretching
PYRO-50D	3610-3256	-NH ₂ stretching
	2955	Aliphatic -CH ₂ stretching
	1621	-NH bending
	1510	HNC bending
	1126-1066	Si-O stretching
T900-50D	3468	-NH ₂ stretching
	1649	-NH bending
	1494	-CH ₂ bending
	1130	Si-O stretching
	577-608	Ti-O-Si stretching

Figure 2 shows SEM images of PYRO and T900 particles before and after treatment with 50% DIAMO solution. It was observed that pyrophyllite almost loses its foliated structure and gains a more homogeneous morphology, whereas T900 particles becomes more aggregated.

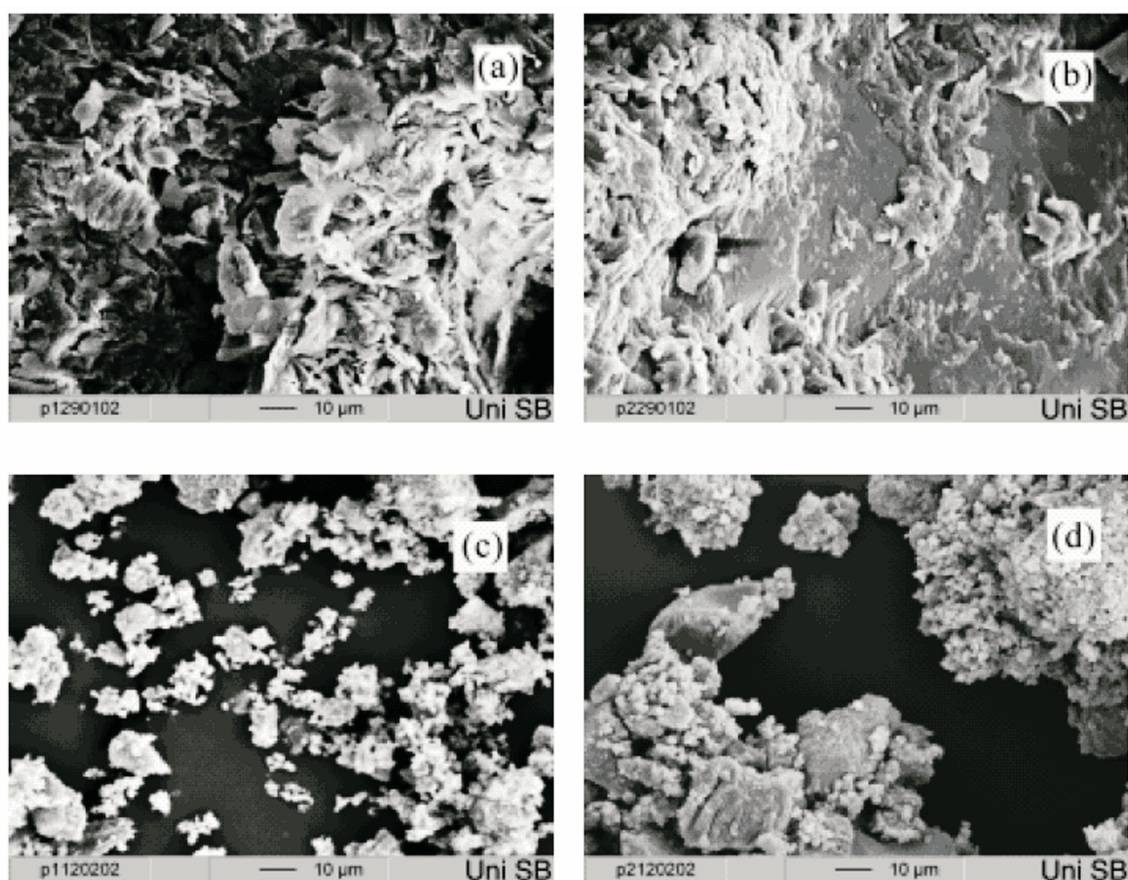


Figure 2. The SEM microphotographs for (a) PYRO, (b) PYRO-50D, (c) T900 and (d) T900-50D after drying at 110 °C.

The results obtained by batch adsorption tests for the removal of 4-NP by adsorption onto unmodified and modified pyrophyllite and sol-gel obtained powders are listed in Table 2. It is generally reported that the adsorption properties of a material subjected to surface modification with silanes are influenced by many factors, such as (a) the concentration of silane solution used in modification, (b) the thermal treatment temperature for the adsorbent before and after modification, (c) the surface area and pore diameter of the adsorbent, (d) the type, molecular size and acidity of adsorbate, (e) the type, acid-base properties and the amounts of groups bonded to the surface of adsorbent, (f) the amounts of adsorbent and adsorbate, (g) pH of aqueous medium, (h) contact time of adsorbent with aqueous medium, (i) temperature of adsorption. For instance, according to the results given in Table 2, as the calcination temperature applied to the hydrolysis-condensation product of TTIP was increased from 100 to 900 °C, the BET surface area drastically decreased from 623.88 to 1.08 m²/g; however, average pore diameter increased from 2.82 to 22.21 nm. This decrease in the surface area and increase in the average pore diameter could result from agglomeration and/or crystallization and growth of titania particles. The surface area and pore diameter of T100 slightly changed after it was treated with as much as 1% DIAMO solution. This shows that DIAMO molecules on the surface of the powder are in a very thin film form. When powders were treated with 50% DIAMO solution, it is likely that the thickness of the film increased, giving rise to more available functional adsorption sites on the surface of all powders.

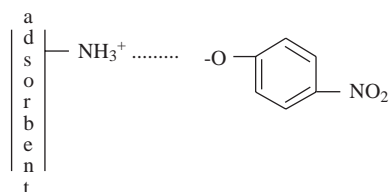
Table 2. Some of the surface properties of unmodified and modified natural pyrophyllite and sol-gel derived synthetic powders as obtained by BET surface analysis and batch adsorption tests.

Material	BET surface area m ² /g	Average pore diameter nm	4-NP Adsorption* %
PYRO	-	-	46.35
PYRO-1D	-	-	52.14
PYRO-50D	-	-	73.84
T100	623.88	2.82	11.80
T100-1D	600.35	2.75	49.40
T100-50D	-	-	59.94
T900	1.08	22.21	43.15
T900-1D	1.06	21.05	57.60
T900-50D	-	-	70.85

*Batch adsorption test conditions

Contact time	10 min
Initial 4-NP concentration	10 mg/L
pH of the solution	6.8 ± 0.1
Temperature	25 ± 1 °
Amount of powder	0.1 g

Surface modification with either 1% or 50% DIAMO solution increases the adsorbed amount of 4-NP molecule, by means of gaining more attractive adsorption sites for 4-NP on the powder surface. A change in the DIAMO concentration of the solution used for modification also increases the amount of adsorption by increasing the numbers of active adsorption sites. Moreover, it was found that thermal treatment of titanium-based powder before silane treatment has a more significant positive effect for the removal of 4-nitrophenol from aqueous solution. The adsorption of 4-NP onto the powders can be explained in 3 ways: (1) 4-NP molecules can fit the pores of the adsorbent, (2) retention of 4-NP by adsorbent perhaps involves a H-bonding interaction between hydroxyl or the nitro group of 4-NP and amino groups on the modified adsorbent surface, or (3) amino groups on the coated adsorbent surface may be protonated thus, gaining a cationic character, whereas the 4-NP molecule is anionic at the study pH. Therefore, the retention of 4-NP by adsorbent involves H-bonding interactions between anionic 4-NP molecules and protonated amino groups attached to the adsorbent surfaces. The third phenomenon can be represented as



Conclusions

From the results presented the following conclusions may be drawn:

Surfaces of either natural (such as pyrophyllite) or synthetic (such as titanium-based) powders obtained by the sol-gel processing of TTIP can be easily modified by silane molecules that have inherent functional groups.

After treatment of the powders with amino functional silane solution, DIAMO, a condensation reaction occurs between the surface and the DIAMO molecule, transferring DIAMO to the powder surface as a coating by curing at 110 °C. During this procedure, siloxane bonds are formed by the condensation of hydroxyl groups as well as methoxy groups.

The condensation reaction proceeds between the hydroxyl groups of the hydrolyzed DIAMO molecule and the hydroxyl groups and/or oxygen atoms present on the surface of pyrophyllite and titanium-based powders. This is the main mechanism for the surface functionalization.

The significant improvement in the adsorption of 4-NP is mainly due to the polar character of the modified powder surfaces. H-bonding interactions between anionic 4-NP molecules and the protonated amine group drive the adsorption process.

It was concluded that the adsorptive properties of natural and synthetic materials, which have oxygen atoms and/or hydroxyl groups on their surfaces, could be more easily improved by coating with silanes. The proposed modification method is simple, economical and fast, and can be performed at room temperature.

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