J Health Scope.2012;**1**(1):7-11.

Health Scope

International Quarterly Journal

www.jhealthscope.com

Removal of Styrene From Air by Natural and Modified Zeolite

Hasan Asilian [1*], Ali Khavanin [1], Mahnaz Afzali [1], Saeed Dehestani [1], Ardalan Soleimanion [1]

[1] Environmental and Occupational Health Engineering Department, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, IR Iran

ARTICLE INFO

Article type:
Review Article

Article history:
Received: 25 Feb 2012
Revised: 02 Mar 2012
Accepted: 11 Mar 2012

Keywords:
Styrene
Zeolite
Trimethylchlorosilane
Adsorption

ABSTRACT

Context: Changing the surface characteristics of raw materials has created new prospects for catalysts and adsorption technology. Natural and modified zeolite with trimethylchlorosilane (TMSCI) has been used to adsorb styrene.
Evidence Acquisition: Dynamic adsorption tests were performed with a number of standard characterization techniques and zeolite particles were examined in three sizes: less than 1 mm, 1–2 mm, and 2–4 mm. The gas concentration was 20 ppm, 40 ppm, and 60 ppm. Three flow rates were tested in this study: 0.5 l/min, 0.75 l/min, and 1 l/min. The sorption of Styrene depended on the particle diameter size, gas flow rate, and inlet gas concentration.
Results: The optimum size for adsorption was less than 1 mm, the optimum flow rate was 0.5 l/min, and the optimum gas concentration was 20 ppm. The adsorption capacity decreased with increasing size, flow rate, and concentration of the pollutant.
Conclusions: The adsorption by the surface-modified zeolite increased by as much as 100% compared with natural zeolite. Therefore, the surface-modified natural zeolite may be utilized for many adsorption applications. This study shows the importance of chemical surface modification and confirms similar findings of other studies.

▸ *Implication for health policy/practice/research/medical education:*
This subject can be useful for styrene control in workplaces as a contaminant. It can be used for researchers who are interested in Air Pollution Control using zeolite as a adsorbent.

▸ *Please cite this paper as:*
Asilian H, Khavanin A, Afzali M, Dehestani S, A Sdeymanion. Removal of Styrene From Air by Natural and Modified Zeolite. *Health Scope*. 2012;**1**(1): 7-11.

1. Context

Styrene is a volatile organic compound and one of the most important monomers in industries. Human exposure to styrene occurs mainly in the reinforced plastics industry, particularly in developing countries. Styrene has been found to be hepatotoxic and pneumotoxic in humans and animals. Albumin and hemoglobin adduction derived from styrene oxide, a major reactive metabolite of styrene, has been reported in blood samples obtained from styrene-exposed workers (1). Although the styrene concentrations to which workers are exposed have been gradually decreasing in the past decade, styrene is still considered an excellent model compound for studying the mechanisms of genotoxicity (2, 3), lung impact (4), kidney and liver damage, and carcinogenicity (3, 5, 6). Styrene polymers and copolymers are used in an increasingly wide range of applications in many petrochemical and polymer processes in industries, and the liquid and gaseous effluents from many units in a petrochemical complex contain styrene. The most common uses of styrene are in plastics, paints and coatings, latex, PVC synthetic rubbers, styrene-alkyd coating, and polyesters. Of the top 50 chemicals produced worldwide, styrene was ranked twentieth in 1994, with a production of 11270 million pounds. Styrene is manufactured as an intermediate for the production of polystyrene (68%), styrene-butadiene (SBR) elastomers (6%), acrylonitrile-butadiene styrene (ABS) resins and styreneacrylonitrile (SAN) (9%), latexes (SBR latexes containing < 45% styrene and styrene-butadiene latexes containing > 45% styrene) (7%), unsaturated polyester resins (7%), and miscellaneous products (5, 7). Recently, the use of minerals and inexpensive materials for removing or

---

* *Corresponding author:* Environmental and Occupational Health Engineering Department, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, IR Iran. Tel: +98-2182883825, Fax: +98-2182883825.
E-mail: asilia_h@modares.ac.ir

reducing air pollution has increased. Zeolite is abundant in many areas of the world and has favorable physical characteristics. Zeolite is a well-known category of crystalline mineral that consists of hydrated aluminosilicates of alkaline and alkaline earth elements with a typical formula of Mx/n [(AlO_2)x(SiO_2)y] w.H_2O. Natural zeolite can be formed in active volcanic environments under hydrothermal conditions but can also have sedimentary origins. The use of natural zeolite as a sorbent has considerably increased in different industries (8, 9). Zeolites are suitable adsorbents for different polar and nonpolar molecules such as CO_2, SO_2, NO_2, NO, H_2S, NH_3, H_2O, aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, and other similar molecules. Zeolite with natural porosity and crystal structure in windows, cages, and supercages has shown the capability of selective ion exchange and can thus be used as a molecular sieve to adsorb molecules on its large internal area. Zeolite is metastable and stable when it is at a suitable temperature and pH. Within this range, it is unaffected by wide swings in temperature, pressure, and ionizing radiation. Different types of zeolite have windows from 0.3 to 3.0 nanometers (3 to 30 angstroms), but any one type has a nominally fixed window size. Changing the Si/Al ratio and exchanging ions can affect the size of the window (10, 11). Hydrophobic zeolite is currently used to concentrate VOCs before destruction (9). Hydrophobic zeolites can be very efficient at adsorbing and desorbing VOCs (12).

Chemical treatment is a common procedure for the purification of raw materials and the modification of surface properties for various purposes. The properties of zeolites can be changed by surface modification. This approach to zeolite surface modification has been studied extensively for the effective removal of some materials and hydrocarbons. Chlorosilanes are effective for the tuning of physical and chemical properties of organic and inorganic materials (13, 14), and for increasing catalytic properties (15). Zeolite modified with chlorosilan has already been used for the adsorption of different elements and substances such as hydrocarbons from water and wastewater (14, 16). Iranian natural zeolite (clinoptilolite) already been used for the adsorption of different substances (8, 17). The abundance of natural zeolite resources in many part of Iran could permit its development as a resource. The adsorption characteristics of modified zeolite for nonpolar hydrocarbons have been confirmed in some studies (14, 16, 18). The aims of this study were to surface-modify natural zeolite and to develop a surface adsorption rate suitable for adsorbing and degrading styrene as a VOC contaminant from the air.

2. Evidence Acquisition

2.1. Materials

The chemicals that were tested in this study were natural zeolite (clinoptilolite) obtained from the Semnan area in the center of Iran. Styrene was from Merck, purity: ≥ 99%. Trimethylchlorosilane was also from Merck, purity: ≥ 99%. The other materials used were toluene (Merck, purity: 99.7%), acetone (BDH-LTd England, purity: 99%) and hydrochloric acid (Merck, 37%-38%).

2.2. Physical and Chemical Methods

Representing natural zeolite, a clinoptilolite rich tuff was collected from Semnan (center of Iran). The collected samples of zeolite were ground and sieved to separate fractions with size ranges of 0.45-1 mm, 1-2 mm, and 2-4 mm. These particles were selected for this study and all of the sorption experiments were performed on a dynamic system. Flow rates were examined in 3 ranges: 0.5 l/mm, 0.75 L/min, and 1 L/min. The natural zeolite was dried in an oven at 105°C for 24 h. The zeolite was then kept in glass container for adsorption tests. Dried material (5 g) was placed into a glass tube. The glass tube had a height of 10 cm height and an internal diameter of 10 mm. Adsorption tests were conducted under atmospheric pressure and at 23-25°C. Each experiment was performed at least three times. The flow rate and gas concentration were measured and controlled before and after each examination. The inlet stream feed and flow rate were constant. The real-time device was a VOC Phochek 5000 (England). The chlorosilane used was trimethylchlorosilane (TMSCl) (14, 16, 19). Before modification with chlorosilane, the zeolite was treated with 2M hydrochloric acid for 1 hour at 70°C and then washed with distilled water until it reached natural pH (pH = 7). A typical modification procedure was applied as follows: 5g of the modified zeolite particles with hydrochloric acid were dispersed in 50 ml of toluene and trimethlchlrosilane in a tow-necked glass flask. The liquid-to-solid ratio in the flask was 50ml/1gr, and the materials were stirred at room temperature for 4 h. This mixture was refluxed under hydrogen at atmospheric pressure, and the whole experimental setup was designed to ensure anhydrous conditions to prevent the hydrolysis of the chlorosilane. After a reaction time of 4h, the solution was filtered and washed several times with toluene and acetone (10 cm^3). The obtained particles were subsequently dried in an oven at 110°C for 5h to remove the residual solvent (14, 19). A simple schematic representation of the designed system is shown in *Figure 1*. The adsorption of styrene was performed in a fixed bed, and the adsorption column was charged with the two different adsorbents prepared.

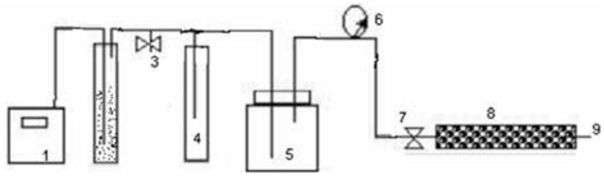


Figure 1. 1- Air supplier pump, 2- Humidity adsorbent (Cilicagel), 3 and 7- Valves and connections, 4- Styrene supplier, 5- Mixer of air and Styrene, 6- Flow meter, 8- Zeolites bed (column), 9- Styrene detector and Flow meter

3. Results

The adsorption capacities were determined by calculating the areas from the breakthrough and saturation curves. Results at identical flow rates with increasing adsorbent size showed a reduction in adsorption capacity. The optimum particle size for adsorption was less than 1 mm, i.e., U.S. standard mesh numbers of 20 and 30 (0.84 and 0.589 mm), and the optimum flow rate was 0.5 L/min. The adsorption breakthrough curves for clinoptilolite natural zeolite and modified zeolite at 0.5 L/min and a gas concentration of 20 ppm are shown in *Figure2* and *Figure 3* and *Figure 4*.

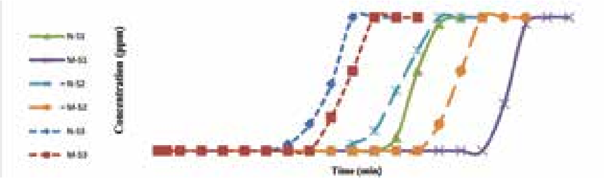


Figure 2. Adsorption Breakthrough Curves for Natural and Modified Zeolite at 0.5 l/min Flow rate and 20 ppm Styrene Concentration

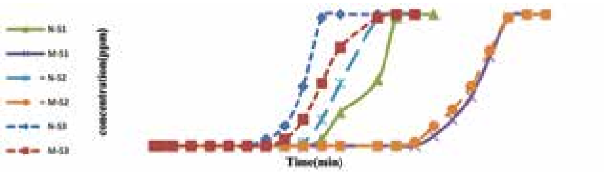


Figure 3. Adsorption Breakthrough Curves for Natural and Modified Zeolite at 0.5 l/min Flow Rate and 40 ppm Styrene Concentration

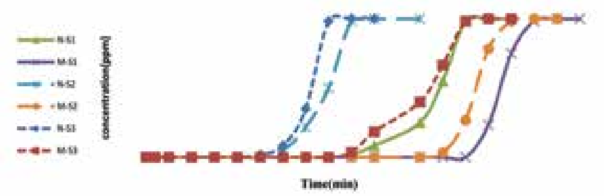


Figure 4. Adsorption Breakthrough Curves for Natural and Modified Zeolite at 0.5 l/min Flow Rate and 60 ppm Styrene Concentration

Surface Modification with Trimethylchlorosilane (TMSCl)

The surface modification of natural zeolite takes place through the reaction between zeolite and surface SiOH groups as follows:

$$\text{Si-OH} + \text{Cl-Si(CH}_3)_3 \rightarrow \text{Si-O-Si(CH}_3)_3 + \text{HCl}$$

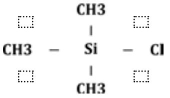
A monolayer of trimethylchlorosilane (TMSCl) groups is thus covalently attached to the pore surface of zeolite (16, 17). The chemical treatment or surface modification of natural zeolite increased the adsorption characteristics and also increased the its surface area. To characterize the zeolite samples, the X-ray fluorescence method (XRF) was used. XRF was used to determine the content of elements, and X-ray diffraction spectra (XRD) were obtained for the treated and untreated zeolite on oriented samples. The results from the chemical analysis of the samples are shown in *Table 1*.

Table 1. Chemical Composition of the Zeolite Samples by X-Ray Fluorescence

Components	Contents	Wt, %
	Natural Zeolite	Modified Zeolite
SiO_2	61.696	80.543
Al_2O_3	9.678	8.283
Fe_2O_3	1.229	0.714
TiO_2	0.212	O.224
CaO	2.846	2.242
MgO	0.831	0.536
Na_2O	2.528	0.198
K_2O	4.374	2.647
P_2O_5	0.034	-
L.O.I	11.86	6.55
SO3	4.284	0.04
CL	0.385	-
Sr	0.026	0.009
Zr	0.016	0.015
Total	99.999	101.77

The chemical treatment of the natural zeolite sample used hydrochloric acid to complete the removal of any carbonaceous minerals (calcite and aragonite), thereby increasing the purity before surface modification. As shown in *Table.1*, the SiO2/ Al2O3 ratio increased from 6.37 before modification to 9.72 after surface modification.

The empirical formula for trimethylchlorosilane (TMSCl) is C3H9ClSi, and the headgroup is:



$$\begin{array}{ccccc} & & \text{CH3} & & \\ & & | & & \\ \text{CH3} & - & \text{Si} & - & \text{Cl} \\ & & | & & \\ & & \text{CH3} & & \end{array}$$

The basic silanization reaction for zeolite is shown in *Figure 5*.

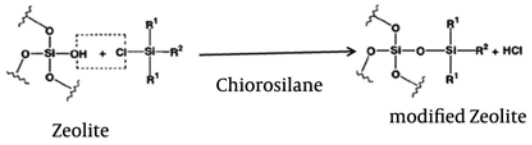


Figure 5. Reaction Scheme for the Surface Modification of Zoelite using Chlorosilane (14).

4. Conclusions

This study aimed to develop a new method to generate an adsorbent capable of removing styrene as a contaminant from air. Experiments were thus performed to test the adsorption capacity of natural (clinoptilolite) and modified zeolite (chemically modified with trimethylchlorosilane) for styrene removal. Pre- and post-modification XRD and XRF measurements showed an increase in the SiO_2/Al_2O_3 ratio, which indicates that the surface modification by trimethylchlorosilane was achieved successfully. It was also found that by increasing the sorbent

Table 2. Breakthrough and Saturation Points and Adsorption Capacity of Natural Clinoptilolite for STYRENE. (T = 25°C, Amount of Zeolite in Each Column 5g, Particle Size U.S. Standard Mesh Numbers of 20 and 30 (0.84 and 0.589 mm). Flow Rate, 0.5 L/min

Zeolite	Concentration, ppm	Gas Flow, L/min	Breakthrough Time, min	Saturation Time, min	Adsorption Capacity to Breakthrough Point, mg/g	Adsorption Capacity to Saturation Point, mg/g
Natural	20	0.5	55	70	0.050	0.567
	40	0.5	45	60	0.041	0.996
	60	0.5	45	65	0.095	1.632
Modified	20	0.5	80	90	0.240	0.729
	40	0.5	70	85	0.007	1.445
	60	0.5	65	80	0.39	2.008

Table 3. Breakthrough and Saturation Points and Adsorption Capacity of Natural Clinoptilolite for STYRENE. (T = 25°C, amount of Zeolite in Each Column 5g, Particle Size U.S. Standard Mesh Numbers of 20 and 30 (0.84 and 0.589 mm). Flow Rate, 0.75 L/min

Zeolite	Concentration , ppm	Gas Flow , L/min	Breakthrough Time , min	Saturation Time , min	Adsorption Capacity to Breakthrough Point , mg/g	Adsorption Capacity to Saturation Point , mg/g
Natural	20	0.75	50	65	0.030	0.79
	40	0.75	45	60	0.027	0.549
	60	0.75	35	45	0.047	1.694
Modified	20	0.75	75	80	0.146	0.972
	40	0.75	65	75	0.166	1.868
	60	0.75	40	50	0.024	1.883

Table 4. Breakthrough and Saturation Points and Adsorption Capacity of Natural Clinoptilolite for STYRENE. (T = 25°C, amount of Zeolite in Each Column 5g, Particle Size U.S. Standard Mesh Numbers of 20 and 30 (0.84 and 0.589 mm). Flow rate, 1 L/min

Zeolite	Concentration, ppm	Gas Flow, L/min	Breakthrough Time, min	Saturation Time, min	Adsorption Capacity to Breakthrough Point, mg/g	Adsorption Capacity to Saturation Point, mg/g
Natural	20	1	45	50	0.189	0.810
	40	1	25	30	0.105	0.996
	60	1	15	25	0.063	1.255
Modified	20	1	55	70	0.044	1.134
	40	1	45	65	0.036	2.158
	60	1	40	50	0.136	2.510

particle size from a range of 425 μm to 1 mm to a range of 1–2 mm and then to 2–4 mm, the adsorption capacity and breakthrough time were considerably decreased, although a decrease in the particle size caused an increase in the pressure drop of the system. These investigations also showed that, in the same conditions, an increase in the gas flow rate causes a decrease in the breakthrough and saturation time. The investigated Iranian natural clinoptilolite zeolites are suitable adsorbents for the removal of styrene from the polluted air streams in some industries, especially at lower flow rates, and the present results are superior to those of some previous studies [20]. The following conclusions can be drawn from the experimental investigation. The maximum increase in breakthrough capacity was for modified zeolite at an inlet gas concentration of 20 ppm with a flow rate of 0.5 L/min and 0.75 L/min. The minimum increase in the breakthrough capacity was for modified zeolite at an inlet gas concentration of 40 ppm and a flow rate of 0.5 L/min. The maximum increase in the saturation capacity was for modified zeolite at inlet gas concentrations of 60 ppm and 40 ppm and a flow rate of 1 L/min. It can thus be concluded that the modification increased the breakthrough capacity for a lower inlet concentration and flow rate and increased the saturation capacity for a maximum inlet concentration and average flow rate. The modification did not increase the time of breakthrough to saturation time at lower flow rates, but the maximum gap between the breakthrough and saturation capacity was for modified zeolite at an inlet gas concentration of 40 ppm and a flow rate of 1 L/min. The minimum gap between the breakthrough and saturation capacity for modified zeolite was observed with the lowest inlet gas concentration and average flow rate, i.e., 20 ppm at 0.75 L/min, and that for natural zeolite was observed at 20 ppm and 40 ppm with a flow rate of 1 L/min. The results of this study show that the surface groups of clinoptilolite modified with TMSCl have good affinity for styrene as a VOC compound. The adsorption results demonstrate that surface-modified zeolite has a good capability to adsorb organic compounds, with the adsorption improving by as much as 100% for a lower concentration of gas and decreased flow rate. These findings are of particular importance in designing selective adsorbents for environmental applications, such as the removal of VOCs and styrene in industries. The surface chemistry of zeolite could be effectively modified to be more adsorbent by the chemical attachment of organic species (silylation). The free and germinal silanol groups over zeolite surfaces are responsible for such active modifications. Although more research is necessary, chlorosilane-modified clinoptilolite is a potential sorbent for aromatic organic compounds with applications in air pollution control or permeable reactive barriers. This study showed good agreement with other studies (16, 17). To optimize the conditions of the removal process, further studies should be performed for other gases in VOC groups.

Acknowledgements

The authors are grateful to Dr. Yamini and Dr. Alizadeh, Chemistry Department of Tarbiat Modares University, who advised on chemical problems; Dr. Zaree for his professional help in this study; Oslob San'at Mad Co. and Dr.Mahmodaadbadi for providing natural zeolites; and Mr. Solaimanian for his professional help in the laboratory.

Authors' Contribution

A.B. conceived the study aims and design, contributed to the systematic review and data extraction, performed the analysis and interpreted the results. G.T. and Y.B. drafted the manuscript, contributed to the data extraction and to the revision of the manuscript.

Financial Disclosure

None declared.

Funding/Support

None declared.

References

1. Yuan W, Jin H, Chung JK, Zheng J. Evidence for cellular protein covalent binding derived from styrene metabolite. *Chem Biol Interact*. 2010;**186**(3):323-30.
2. Vodicka PA, Koskinen MI, Arand MI, Oesch FR, Hemminki KA. Spectrum of styrene-induced DNA adducts: the relationship to other biomarkers and prospects in human biomonitoring. *Mutat Res*. 2002;**511**:239-54.
3. Rueff J, Teixeira JP, Santos LS, Gaspar JF. Genetic effects and biotoxicity monitoring of occupational styrene exposure. *Clin Chim Acta*. 2009;**399**(1-2):8-23.
4. Kaufmann W, Mellert W, van Ravenzwaay B, Landsiedel R, Poole A. Effects of styrene and its metabolites on different lung compartments of the mouse--cell proliferation and histomorphology. *Regul Toxicol Pharmacol*. 2005;**42**(1):24-36.
5. Emery AS, Kong J, Mark A, Bahner RT. Assessment of Styrene Emission Controls for FRP / C and Boat Building Industries. *USEPA*. Washington; 1998.
6. EPA.Air Quality Guidelines.Styrene. 2000; 1-31]. Available from: http://books.google.com/books?id=WVg8CYswPu4C&pg=PA106&lpg=PA106&dq=Air+Quality+Guidelines+%2B+Styrene&source=bl&ots=zLDrsZscdE&sig=mHbtofv1RHiVgwsIIOsHP7biju8&hl=en&sa=X&ei=C6FdT5WnKcfm4QT3o-TVDw&ved=0CE8Q6AEwAw#v=onepage&q=Air%20Quality%20Guidelines%20%2B%20Styrene&f=false.
7. EPA.Locating And Estimating Air Emissions From sources Of Styrene.final report. 1993; 1-167]. Available from: http://www.epa.gov/nscep/index.html.
8. Asilian HA, Mortazavi SB, Kazemian HO, Phaghiehzadeh S, Shahtaheri SJ. Removal of Ammonia from Air, using Three Iranian Natural Zeolites. *Iraninan J Publ Health*. 2004;**33**(1):45-51.
9. Khan FA, Ghoshal AL. Removal of Volatile Organic Compounds from polluted air. *J Loss Prev Process Ind*. 2000;**13**:527-45.
10. Modhera BK, Chakraborty M, Bajaj HC, Parikh PA. Influences of Mesoporosity Generation in ZSM-5 and Zeolite Beta on Catalytic Performance During n-Hexane Isomerization. *Catal Lett*. 2011;**141**(8):1182-90.
11. Sa CN, Chimica D, Sapienza UL, Moro PA. Effects of the Si / A1 atomic ratio on the activity of Cu-ZSM-5 catalysts for nitric oxide decomposition. *Catal Lett*. 1994;**23**:135-40.
12. EPA.Office of Air Quality Planning and Standards . ZEOLITE, VERSATILE, and Air Pollutant Adsorber. 1998; 1-18]. Available from: http://www.epa.gov/nscep/index.html.
13. Han X, Wang L, Li J, Zhan X, Chen J, Yang J. Tuning the hydrophobicity of ZSM-5 zeolites by surface silanization using alkyltrichlorosilane. *Appl Surf Sci*. 2011;**257**:9525-31.
14. Huttenloch PE, Roehl KA, Czurda KU. Sorption of nonpolar aromatic contaminants by chlorosilane surface modified natural minerals. *Environ Sci Technol*. 2001;**35**:4260-4.
15. Igarashi NA, Hashimoto KA, Tatsumi TA. Catalytical studies on trimethylsilylated Ti-MCM-41 and Ti-MCM-48 materials. *Micropor Mesopor Mater*. 2007 **104**:269-80.
16. Impens N, van der Voort P, Vansant EF. Silylation of micro-, meso- and non-porous oxides. *Micropor Mesopor Mater*. 1999;**28**(2):217-32.
17. Rahmani AR, Samadi MT, Ehsani HR. Investigation of Clinoptilolite Natural Zeolite regeneration by Air Stripping Followed by ION Exchange for Removal of Ammonium From Aqueous Solutions. *Iran J Environ Health Sci Eng*. 2009;**6**(3):167-72.
18. Northcott KA, Bacus J, Taya N, Komatsu Y, Perera JM, Stevens GW. Synthesis and characterization of hydrophobic zeolite for the treatment of hydrocarbon contaminated ground water. *J Hazard Mater*. 2010;**183**(1-3):434-40.
19. Wouters BH, Chen T, Dewilde M, Grobet PJ. Reactivity of the surface hydroxyl groups of MCM-41 towards silylation with trimethylchlorosilane. *Micropor Mesopor Mater*. 2001;**44-45**:453-7.