Colloids and Surfaces A: Physicochem. Eng. Aspects 375 (2011) 136–140

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

# Comparative study of phenol compounds adsorption on mesoporous sieves with different degrees of modification

Jiawei Fu, Qihui He, Rui Wang, Bo Liu, Baixing Hu*

*School of Chemistry and Chemical Engineering, Nanjing University, 22 Hankou Road, Nanjing, 210093 Jiangsu, China*

ARTICLE INFO

*Article history:*
Received 20 July 2010
Received in revised form 13 October 2010
Accepted 28 November 2010
Available online 9 December 2010

*Keywords:*
Surface modification
Adsorption
Phenol
Hydroquinone

## ABSTRACT

Mesoporous sieves MCM-41 modified by trimethylchlorosilane and methyltrimethoxysilane were prepared by postsynthesis grafting (PSG) process and further characterized by thermogravimetric (TG) analysis, FTIR spectroscopy, and nitrogen sorption experiments. Adsorption experiments of phenol and hydroquinone in solutions were carried out. The surface properties of silica were found to be the key factors for the phenol compound adsorption in low concentration solutions. Results showed that the modification of alkyl groups did enhance the loading amount of phenol by employing both the van der Waals force and hydrogen bonds, but it also reduced the adsorption amount of hydroquinone by covering oxygen atoms and hydroxyl groups on the surface when hydrogen bond was a dominant factor due to the specific structure of hydroquinone.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Ordered mesoporous silica, MCM-41, and its modified compounds have long been studied in the applications of catalysis [1,2], removal of heavy metal ions [3–7], desulfurization [8,9], drug delivery [10], and more importantly the adsorption of organic pollutants like phenol and other derivative compounds from waste water, which has recently become a hot focus due to the great environmental concerns [11–13]. Zeolites have been reported to adsorb the nitrogen compounds [11,13], but MCM-41 also exhibits its superiority by its uniform structure with favorable pore sizes and capacity for desired modification design.

The surface properties of mesoporous silica, including surface area, grafted groups and hydrophobicity, all exert great influence to the adsorption behaviors of phenol compounds, because those small molecules are very sensitive to the adsorption sites on the mesoporous sieves. Unmodified MCM-41 usually exhibits high hydrophilicity due to the existing surface hydroxyl groups, while the hydrophobic aromatic or alkyl groups in phenol may lead to relatively low adsorption efficiency of organic pollutants in waste water. On the other side, it is also an effective way to improve the loading amount by appropriate modification of the mesoporous sieves, and further explore the relationship between adsorption properties and the modification of mesoporous sieves.

This article is dedicated to the comparative study of the adsorption behaviors of phenol and hydroquinone on both pristine large pore MCM-41 and those modified by different organic molecules, such as trimethylchlorosilane and methyltrimethoxysilane. A postsynthesis grafting (PSG) process was employed and for those samples modified by methyltrimethoxysilane, different surface coverages were obtained by controlling different experimental conditions. The relationship between adsorption properties and the modification of mesoporous sieves was later investigated comprehensively by various analytical methods such as thermogravimetric (TG) analysis, FTIR spectroscopy, and nitrogen sorption experiments.

## 2. Experiment

### 2.1. Materials

Sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS), cetyltrimethyl ammonium bromide (CTAB), mesitylene, hexane, phenol, hydroquinone, trimethylchlorosilane, and methyltrimethoxysilane were purchased from Sinopharm Chemical Reagent Co. Limited (Scheme 1).

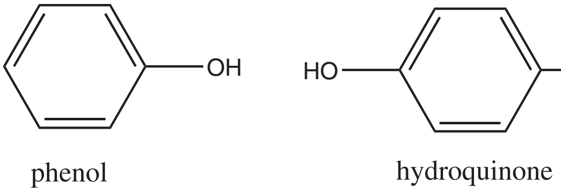
### 2.2. Synthesis of large pore MCM-41

A similar method with Ref. [14] was employed to prepare the mesoporous sieves. 22.5 mL TEOS was added quickly to a solution (4.38 g CTAB in 200 mL distilled water) containing 1.13 g NaOH. Then 10 mL mesitylene and 5 mL hexane were added to the mixture as pore-expanders [15]. After stirring at 60 °C for several hours, the mixture was sealed in Teflon autoclaves and maintained at 110 °C for 48 h. An ion-exchange method [16] was used to remove the

---

* Corresponding author. Tel.: +86 25 83592878; fax: +86 25 83592878.
*E-mail address:* hubx@nju.edu.cn (B. Hu).

0927-7757/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2010.11.078



**Scheme 1.** Molecular structures of phenol and hydroquinone.

surfactant molecules in order to contain the hydroxyl groups, for calcination at high temperature would destroy most of them.

### 2.3. Surface silylation of MCM-41 with trimethylchlorosilane

The mesoporous silica was dried at 105 °C for 12 h, later soaked in a toluene solution of trimethylchlorosilane at 60 °C for a desired time [17]. The sample was finally washed with toluene and acetone and denoted as MCM-41-rA.

### 2.4. Surface silylation of MCM-41 with methyltrimethoxysilane

Modification of MCM-41 with different coverages of surface hydroxyl groups could be obtained by varying the experimental conditions [3,18]. The proper amount of adsorbed water on the surface is the key factor of obtaining samples with different coverages. Enough adsorbed water would give rise to hydrolysis reactions to form monolayer, but excessive free water is detrimental due to polymerization of methyltrimethoxysilane in solutions. For low coverage sample, 2 g MCM-41 was suspended in 100 mL distilled water and refluxed for 4 h before placement at ambient temperature overnight. Then the silica was suspended in 100 mL toluene containing 10 mL methyltrimethoxysilane and refluxed for 4 h. The sample was later washed by chloroform and denoted as MCM-41-rB. For high coverage sample, about 1.5 mL distilled water was added dropwise into 100 mL toluene with 2 g MCM-41 suspended, and the mixture was then refluxed for 1 h. Afterwards 10 mL of methyltrimethoxysilane was added and another 5 mL was added 3 h later. After being refluxed for a desired time, the sample was then washed with 2-propanol copiously and denoted as MCM-41-rC.

### 2.5. Adsorption of phenol compounds

Phenol and hydroquinone solutions were prepared at the concentration range of 50–400 mg/L. The adsorption experiments were carried out in a water batch at 40 °C for 1 h with approximately 0.1 g mesoporous sieves as adsorbents. The solutions after filtration were obtained for further UV analysis.

### 2.6. Characterization

TG measurement (NETZSCH STA 449C thermogravimeter) was employed to investigate the weight increase after silylation. Samples were heated from ambient temperature to 800 °C in nitrogen atmosphere. FTIR was performed on the NICOLET NEXUS 870 spectrometer from 400 to 4000 cm$^{-1}$ by dried KBr pellet and the nitrogen sorption experiments were carried out on Micromeritics ASAP 2010 accelerated surface area and porisimetry adsorption analyzer with $N_2$ as adsorbate at 77 K. All samples were degassed at 110 °C for 8 h in vacuum. Brunauer, Emmett and Teller (BJH) method was employed to calculate the pore size distribution (PSD). Concentration changes of phenol solutions were detected using SHIMADZU UV-3600 spectrophotometer by identifying peak values at certain wavelengths (269.5 nm for phenol and 288.5 nm for hydroquinone).

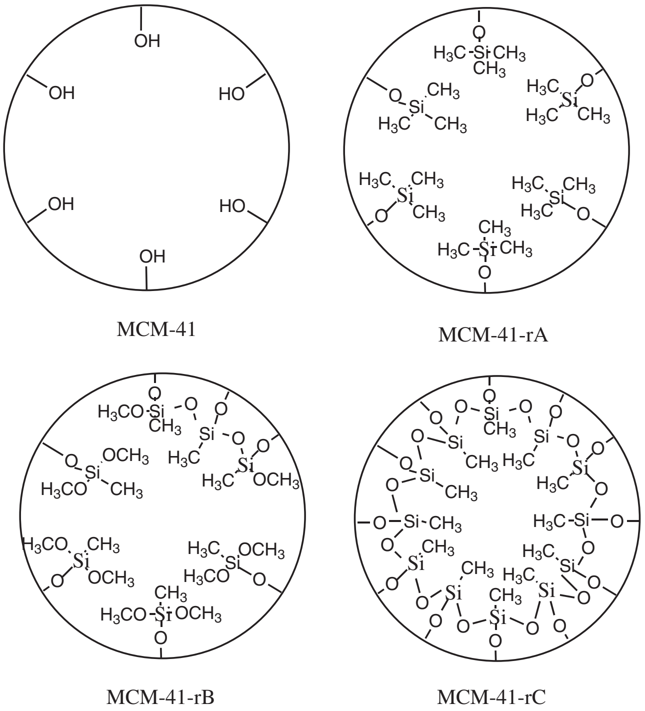


**Fig. 1.** Molecular structures of the modified samples.

## 3. Results and discussion

### 3.1. Surface modification

The molecular structures of modified MCM-41 surface under different conditions have been discussed in other literature [3,17] and are listed in Fig. 1. Through the following reactions [17], trimethylsilyl groups are covalently attached onto the surface of MCM-41.

$$\text{Cl–Si(CH}_3)_3 + \text{–Si–OH} \rightarrow \text{–Si–O–Si(CH}_3)_3 + \text{HCl} \qquad (1)$$

For those modified by methyltrimethoxysilane, samples with different surface hydroxyl group coverages are successfully obtained by controlling the amount of adsorbed surface water and hydrolysis reactions of organic molecules. A large portion of organic groups on the surface of MCM-41-rB is isolated while only a few groups are cross-linked to each other, which leads to a relatively low surface coverage. On the other hand, organic groups form a uniform monolayer on the surface of MCM-41-rC with the existence of proper amount of adsorbed water. Generally all modified samples exhibit relatively high hydrophobicity due to the replacement of hydroxyl groups by alkyl groups on the surface, and the surface coverage also exerts important influence on this aspect.

### 3.2. FTIR investigation

Modification of MCM-41 by surface silylation can be confirmed by identifying the presence of specific peaks of the employed organic molecules in IR spectra (Fig. 2). The peak at 461 cm$^{-1}$ represents the rocking of Si–O–Si, 802 cm$^{-1}$ is Si–O symmetric stretching, 968 cm$^{-1}$ is Si–O–H stretching, 1085 cm$^{-1}$ is asymmetric Si–O–Si stretching and the wide band from 3100 cm$^{-1}$ to 3700 cm$^{-1}$ is due to the O–H stretching. O–H bending from adsorbed water [19] gives rise to the peak at 1640 cm$^{-1}$. After silylation, intensity of peak at 1640 cm$^{-1}$ and wide band over 3000 cm$^{-1}$ decreased dramatically due to a great loss of adsorbed water when the mesoporous sieves became much more hydropho-

Download English Version:

https://daneshyari.com/en/article/595008

Download Persian Version:

https://daneshyari.com/article/595008

Daneshyari.com