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Adsorption and Thermogravimetric Methods for Monitoring Surface and Structural Changes in Ordered Mesoporous Silicas Induced by their Chemical Modification

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Abstract. The current work demonstrates that the standard adsorption analysis has a limited applicability for characterization of chemically modified porous silicas. Since low-pressure nitrogen adsorption isotherms are sensitive to the surface changes caused by chemical modification of silicas, these isotherms were successfully used to evaluate their surface heterogeneity during different stages of modification. The surface analysis was accomplished by using adsorption energy distributions and high-resolution comparative plots.

Keywords: MCM-41, bonding of organosilanes, surface analysis, adsorption energy distribution, pore structure analysis

Introduction

Nitrogen adsorption at 77 K is commonly used to evaluate the BET specific surface area, pore volume and mesopore size distributions of various porous solids (Gregg and Sing, 1982). However, a possibility of analysis of surface properties on the basis of low pressure nitrogen adsorption data is not fully recognized, despite the fact that many suitable methods of data analysis were developed and carefully examined in the past (see Kruk et al., 1997a; Jaroniec et al., 1997; Jaroniec and Kaneko, 1997 and references therein). Application of nitrogen adsorption technique for surface characterization has recently become much easier than before due to commercial availability of adsorption instruments capable of performing measurements starting from relative pressures as low as 10^{-7}. It was recently shown that low pressure adsorption on mesoporous silicas with physically coated and/or chemically bonded organic ligands depends strongly on the nature of these ligands and their surface coverage (Kruk and Jaroniec, 1999). These findings opened new opportunities for characterization of modified inorganic oxides on the basis of adsorption isotherms, providing the means for identification of certain surface functional groups and qualitative assessment of the surface coverage of immobilized ligands.

Chemical modification of siliceous nanoporous materials creates almost unlimited possibilities for altering their surface and structural properties and extends the range of their applications as highly efficient adsorbents, catalysts and separation media. It will be

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demonstrated that the standard adsorption analysis, which includes the evaluation of the BET specific surface area, pore volume and mesopore size distribution, provides limited information about chemically modified nanoporous silicas. Since in many cases chemical modification of silicas alters mainly their surface properties and to a smaller degree their structural properties, low pressure adsorption isotherms, e.g., for nitrogen at 77 K, are essential for monitoring the surface changes induced by this modification. These isotherms are very sensitive to the presence of organic ligands on the silica surface and can be successfully used to monitor the changes in the surface heterogeneity of silica samples during different stages of their modification. It will be shown in the current work that this monitoring can be accomplished by using the high resolution α_s-plot analysis and/or by comparing the adsorption energy distributions (AEDs) for unmodified and modified mesoporous ordered silicas, which recently attracted considerable attention (see review of Sayari, 1996 and references therein). The aforementioned adsorption characterization will be supplemented by thermogravimetric studies. The high resolution α_s-plot method (Jaroniec and Kaneko, 1997) appears to be very attractive to monitor the surface changes in the case of nanoporous silicas because they usually do not possess micropores and the observed curvature of this plot reflects only surface changes. Valuable information about surface properties can be also obtained by comparing adsorption energy distributions (Kruk et al., 1997a; Jaroniec et al., 1997a) for unmodified and modified silicas, but in contrast to the α_s-plot analysis, AEDs are model-dependent functions.

Experimental

A good quality MCM-41 described in (Kruk et al., 1997b) was used for chemical modification with alkylchlorosilanes. All silanes (trimethylchlorosilane, ethyldimethylchlorosilane triethyl-chlorosilane) were from United Chemical Technologies, Inc. (Bristol, PA), toluene and acetone were from Fisher (Pittsburgh, PA, USA). About 150 mg of MCM-41 was placed in a 25 ml round bottom flask, heated in an oven at 423 K for 3 h, capped with a glass stopper and allowed to cool to ambient temperature for about 30 min. 10 ml of dry toluene was added to the MCM-41 along with a magnetic stirrer, the flask was capped and contents stirred for about 5 min. Subsequently, 25 mmol of silane was added and the mixture was refluxed for 14 h. After cooling to ambient temperature for about 30 min, the volatiles (i.e., toluene and excess silane) were removed via the rotary evaporator at 343 K. The modified MCM-41 was washed 3 times with 10 ml of acetone (each wash was removed via the rotary evaporator at 343 K). Following the last wash the modified MCM-41 was heated in an oven at 423 K for 1 h. TGA analysis was performed on the dry product immediately after drying in oven to assess the degree of modification. The weight change curves were recorded on a TGA 2950 high resolution thermogravimetric analyzer from TA Instruments, Inc. (New Castle, DE, USA). In addition to TGA analysis, the carbon loading in the modified samples was obtained using a LECO CHNS-932 elemental analyzer (St. Joseph, MI, USA).

Low pressure nitrogen adsorption measurements were carried out at 77 K on an ASAP 2010 volumetric adsorption analyzer from Micromeritics (Norcross, GA, USA). Prior adsorption measurements the samples were outgassed at 423 K for 2 h.

Results and Discussion

Structural properties of the MCM-41 used to bond short-chain alkylchlorosilanes were described in our previous work (Kruk et al., 1997b), where it is listed as #4A2 sample. It was shown that the sample exhibited high hydrothermal stability and a significant degree of ordering. Table 1 contains numerical values of surface and structural parameters, which are commonly used to characterize unmodified and modified porous silicas. Four columns following sample codes in Table 1 contain parameters evaluated from nitrogen adsorption isotherms: the specific surface area S_{BET} evaluated according to the BET method (Gregg and Sing, 1982), the total pore volume V_t and the pore

Table 1. Surface and structural parameters of the unmodified MCM-41 and MCM-41 samples modified with trimethylchlorosilane (TMS), ethyldimethylchlorosilane (EDMS) and triethylchlorosilane (TES).

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	V_t (cm^3/g)	w (nm)	%C	η (μmol/m^2)
MCM-41	860	0.64	0.84	3.82	—	—
TMS	580	0.40	0.54	3.48	9.07	3.59
EDMS	700	0.48	0.63	3.50	5.87	1.59
TES	770	0.53	0.68	3.51	5.35	0.95

volume V_p of primary mesopores determined by the single-point method and α_s-plot method, respectively (Kruk et al., 1997b), and the mesopore diameter w was estimated according to the method proposed in our previous study (Kruk et al., 1997c). Last two columns in this table contain the percentage of carbon in the bonded ligands determined by elemental analysis and the coverage density η. The latter was calculated on the basis of $\%C$ and S_{BET}. As expected the covalent bonding of alkylsilyl ligands to MCM-41 led to a decrease in the specific surface area, total pore volume, volume of primary mesopores and mesopore diameter of this sample. The largest change is observed for the sample modified with trimethylchlorosilane (TMS), smaller—for the sample modified with ethyldimethylchlorosilane (EDMS) and the smallest—for the sample having triethylsilyl (TES) ligands. Normally, a largest decrease in the surface area and pore volume should be observed for ligands of larger size provided that the bonding density is similar. This unusual behavior is caused by the fact that the coverage density for the samples studied decreased with increasing ligand size (see Table 1).

Thermogravimetric weight change curves for the materials under study are shown in Fig. 1. The first weight loss (below 473 K) reflects thermodesoption of physically adsorbed water. The largest value of this weight loss, as expected, is observed for MCM-41. Also, a relatively large weight loss was for the sample modified with TES, which had the smallest bonding density, i.e., the largest amount of unreacted surface silanols. The second weight loss observed for modified samples about 673 K reflects decomposition of the bonded phase. It should be noted that at temperatures above 473 K the weight of the unmodified MCM-41 still decrases indicating a significant amount of surface silanols.

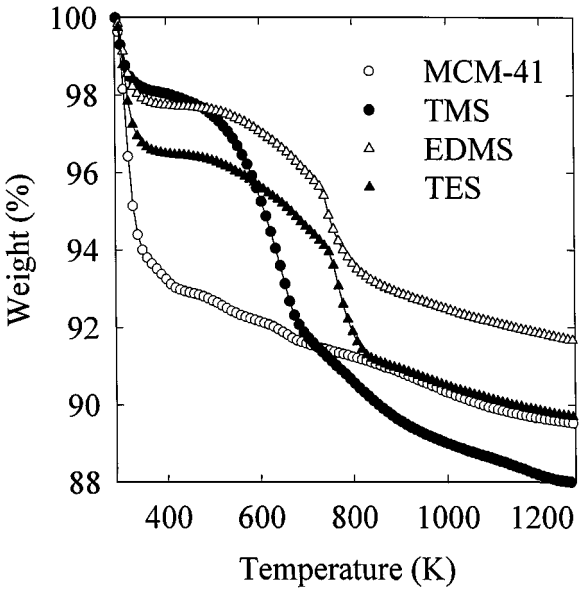

Figure 1. Thermogravimetric weight change curves for the unmodified MCM-41 and the samples modified with alkylchlorosilanes.

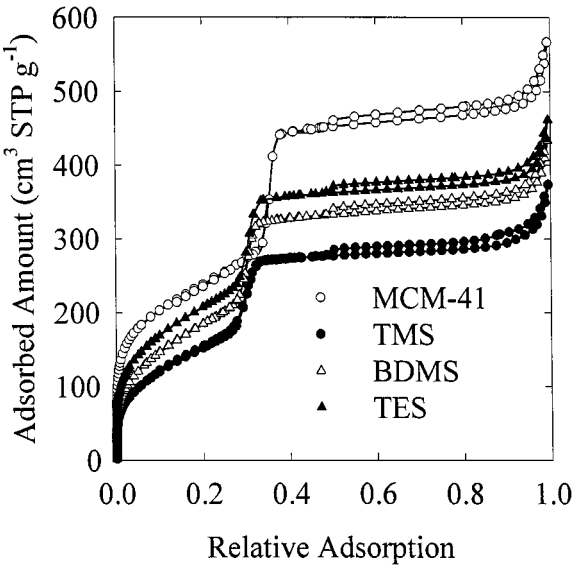

Figure 2. Nitrogen adsorption isotherms for the unmodified MCM-41 and the samples modified with alkylchlorosilanes.

Nitrogen adsorption isotherms and mesopore size distributions for the samples studied are shown in Fig. 2. One can notice that the step of nitrogen condensation in primary mesopores is very sharp for MCM-41 proving a good quality of this sample. After modification of MCM-41 with alkylchlorosilanes this step is shifted in direction of lower pressures indicating a decrease in the mesopore diameter. A comparison of mesopore size distributions (calculated according the method described in the work of Kruk et al., 1997c) shows that the mesopore diameters for all modified samples are very similar due to the compensation effect of ligand size and bonding density (see Fig. 3).

The effect of modification of the MCM-41 sample on its surface properties is presented in Figs. 4 and 5, which show adsorption energy distributions and α_s-plots, respectively, for all samples studied. Adsorption energy distributions were calculated by inverting the integral equation of adsorption (Jaroniec and Madey, 1988; Szombathely et al., 1992), whereas α_s-plots

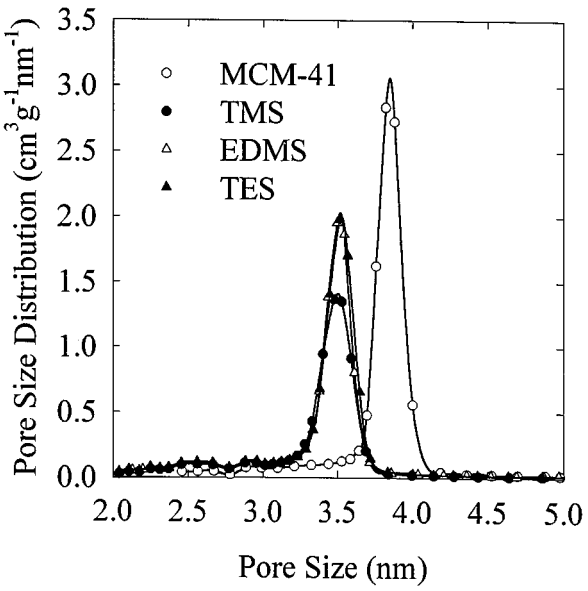

Figure 3. Mesopore size distributions for the unmodified MCM-41 and the samples modified with alkylchlorosilanes.

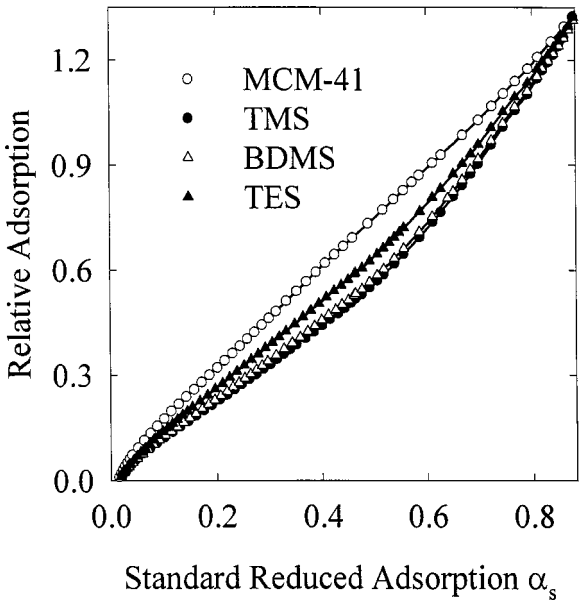

Figure 5. α_s-plots for the unmodified MCM-41 and the samples modified with TMS, EDMS and TES agents.

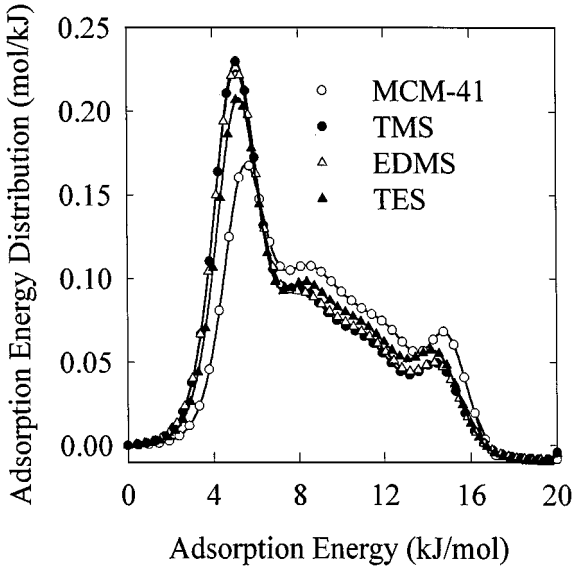

Figure 4. Adsorption energy distributions for the unmodified MCM-41 and the samples modified with TMS, EDMS and TES agents.

were constructed as reported elsewhere (Jaroniec and Kaneko, 1997). The Fowler-Guggenheim equation was assumed to represent the local adsorption isotherm, which is unknown subintegral function. Note that the α_s-plot analysis does not require this type of assumption. For the samples studied both the energy distributions and α_s-plots provide information about surface properties only because there is no evidence for micropores and the observed changes on the energy distributions and α_s-plots reflect only changes generated on the silica surface by its chemical modification.

The comparison of the adsorption energy distributions presented in Fig. 4 shows that the attachment of alkylsilyl ligands to the MCM-41 pore walls causes a decrease in the relative amount of high-energy adsorption sites. This decrease is not significant due to a small size of bonded ligands, low bonding densities in the case of the samples modified with EDMS and TES, and relatively high hydrophilicity of the MCM-41 sample. It was shown elsewhere (Kruk et al., 1997a; Jaroniec et al., 1997; Kruk and Jaroniec, 1999) that the attachment of ligands of larger size (e.g., octyldimethylsilyl groups) causes more dramatic changes on the adsorption energy distributions in the range of high adsorption energies. Moreover, it was often possible to attribute certain ranges of adsorption energies to the presence of specific groups on the silica surface and/or in the structure of bonded or coated phases (Kruk and Jaroniec, 1999).

In order to further demonstrate the effects of surface modification α_s-plots were drawn to compare adsorption properties of these samples with those for a macroporous reference silica gel. It can be seen that the amount adsorbed of nitrogen at its low surface

coverages for the unmodified MCM-41 is almost directly proportional to the amount adsorbed on the reference solid (at this same pressure values). However, comparative plots for the modified samples are bent downwards, which reflects weaker interactions of nitrogen molecules with these samples in comparison to those observed for the reference silica. Another words, the average adsorption energy of nitrogen with modified surfaces is smaller than that with the unmodified reference silica (Jaroniec and Kaneko, 1997).

Conclusions

It was shown that low pressure nitrogen adsorption isotherms can be successfully used to characterize the surface properties of conventional and ordered mesoporous silicas modified with organosilanes. These isotherms allows to calculate adsorption energy distributions, which at the range of high energies gradually decrease when surface silanols are replaced by hydrophobic ligands. Also, the submonolayer α_s-plots for chemically modified mesoporous silicas show downward deviations, the magnitude of which depends on the properties of bonded ligands and their surface coverage. In contrast to the adsorption energy distributions, the calculation of which requires the assumption of a model for the local adsorption isotherm, the α_s-plot analysis is model independent. Since nitrogen adsorption is very sensitive on the presence of bonded alkyl ligands on the silica surface, the α_s-plots method is extermely useful for monitoring surface changes in mesoporous silicas caused by organosilane modfication.

Acknowledgment

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Nomenclature

S_{BET}	BET specific surface area, m^2/g
V_p	Primary mesopore volume, cm^3/g
V_t	Total pore volume, cm^3/g
w	Maximum of the pore size distribution calculated from the BJH method, nm
$\%C$	Weight percent of carbon, %
α_s	Standard reduced adsorption
η	Surface coverage of bonded ligands, $\mu mol/m^2$

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