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ARTICLES

Mechanism of the Optical Response of Mesoporous Silica Impregnated with Reichardt's Dye to NH_3 and Other Gases

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Neutral amines-templated mesoporous silica systems impregnated with Reichardt's dye are pink in color if previously dehydrated and white if still covered with hydroxyls: the pink coloration is, however, reversibly restored by exposing the latter sample only to NH_3 and amines. The mechanism of color change is discussed, and such systems are proposed as possible ammonia gas sensors.

Introduction

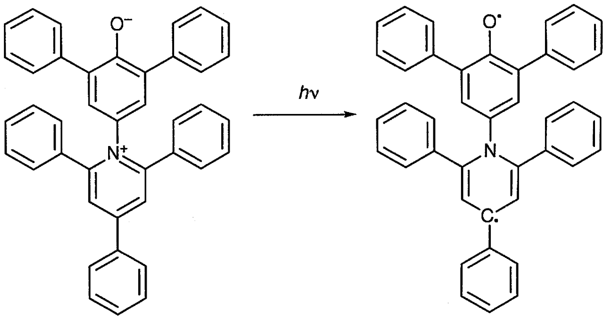
Ordered mesoporous silicas, because of highly uniform porosity, mechanical stiffness, and thermal stability, are of interest for several applications, such as separation, sorption, and catalysis.[1] Fairly recently, it is has been recognized that the porous nature makes them excellent hosts for sensing molecules, as the analyte can easily diffuse to the active center. As silica is transparent in the UV−visible range, these materials are ideal for sensors with an optical response.[2,3]

Reichardt's betaine dye [2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)-phenolate, represented in Scheme 1 and referred to hereafter as RD] is an excellent solvatochromic compound,[4] which has been already immobilized in polymeric substrates,[5,6] silica,[7] and glasses,[6] to obtain optochemical sensors for various vapors, including humidity. RD has a charge-transfer transition in the visible region, which is very medium dependent, because polar solvents stabilize the molecular electronic ground state more than the excited state, therefore increasing the energy of transition.

Several authors have used RD to study the polarity and the hydrogen-bond donor properties of different surfaces, among which are that of silica and MCM-41.[8−13] The present paper deals with the color changes of a RD-containing ordered mesoporous silica, caused by the contact with gaseous ammonia or amine vapors, which may be interesting for gas sensing applications.

The aspects related to hydration/dehydration of the solid and the presence of polar molecules in the surrounding atmosphere have also been examined because they interfere with the phenomena concerning ammonia.

SCHEME 1: Structure of the Ground and First Excited State of Reichardt's Dye



Experimental Section

The ordered mesoporous silica was prepared using neutral amines according to the recipe reported by Pinnavaia et al.,[14] and it is denoted hereafter as HMS. At room temperature, 2.33 g *n*-dodecylamine (Aldrich) was added to a solution made of 25 mL distilled water (Carlo Erba) and 25 mL absolute ethanol (Aldrich), under stirring. Tetraethyl orthosilicate (9.14 g, Aldrich) was then added. The solution was stirred for 18 h and yielded a thick white suspension. This was filtered and dried at 80 °C for 1 h. The amine was removed by heating the solid (ca. 0.5 g) under reflux in absolute ethanol (100 mL) for 6 h: the treatment was repeated two times. Thermal analysis (DTA-DTG Setaram92) and FT-IR characterization (Bruker FTIR Equinox 55 spectrometer, equipped with a MCT cryodetector) showed that the template was completely removed. The XRD pattern (Philips X'pert, Cu Kα radiation) showed the ordered structure of silica ($d_{100} = 3.4$ nm), and BET and BJH analysis of N_2 adsorption (Micromeritics ASAP2010) confirmed the high surface area (ca. 1000 m^2/g) and the mesoporosity (pore diameter = 2.5 nm).

The sample was dehydrated, either mildly at 300 °C or more severely at 600 °C: corresponding specimens are labeled HMS-

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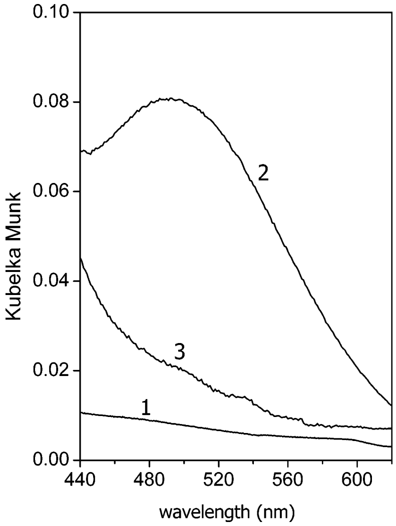


Figure 1. DR-UV−visible spectra of HMS (curve 1), R-HMS-600 (curve 2), and R-HMS-300 (curve 3).

300 and HMS-600, respectively. Both samples were then contacted with a dichloromethane solution of RD, which was green in color. The solution became colorless fairly rapidly, indicating a thorough adsorption of the dye on the mesoporous silica. After overnight stirring, samples were filtered, washed, and dried. These samples are referred to in the following as R-HMS-300 or R-HSM-600.

Diffuse reflectance UV−visible spectra were recorded on a Varian Cary 500 instrument. For FT-IR measurements, the powder was pressed into thin, self-supporting wafers; spectra were collected, at a resolution of 2 cm^{-1}, in the 4000−500 cm^{-1} range (128 scan). Adsorption of ammonia (Messer) was carried out using proper IR and UV−visible cells connected to a vacuum frame (residual pressure $<10^{-4}$ mbar).

Results and Discussion

Curve 1 in Figure 1 is the visible spectrum of both HMS and HMS-600, which, not exhibiting, as expected, absorption, represent the blank for the RD-containing HMS.

The sample R-HMS-600 has a marked pink coloration: the related visible spectrum taken in air, reported in the same figure as curve 2, shows a peak at 490 nm. It compares well with the values reported for RD adsorbed on silica, which range from 477 to 516 nm.[8−13] Such values are accounted for by a perturbation of the RD molecule by the underlying silica through van der Waals-like interactions and a probable H bond between an isolated silanol and the O^- atom in RD.

Curve 3 is the spectrum of R-HMS-300: the sample has no absorption in the visible region (a rise in the background suggests absorption in the nearby UV range); accordingly, the sample is white. The adsorbed RD molecule is in a colorless form, currently interpreted as arising from protonation to a phenolic species $H{-}RD^+$, not showing the CT band in the visible typical of RD.[8]

According to the literature, silica samples outgassed at 300 °C have a silanol content sizably higher than those outgassed at 600 °C. We have confirmed by IR spectra (not reported) that this is also the case with R-HSM-300 and R-HMS-600. It is inferred that a higher hydration of the silica surface inhibits the color. Isolated silanols are not able to transfer their proton: instead, closely packed patches of silanols may provide protons more acidic than those of isolated silanol.[19,20] The pK_a value of silanols in hydrated silica layer in contact with liquid water is estimated to be about 7[15] and that of HRD^+ 8.6.[16] The closeness of these values suggests that, although under different circumstances, competition for the proton may occur between the RD and the SiO^- group. If credit is given to the actual values, proton transfer to RD is fully accounted for. Protonation of RD by surface silanols has been already proposed in studies of surface polarity of silica,[8−12] and the role of chain terminals as most acidic silanols has been envisaged for protonation of Michler's ketone adsorbed on silica particles.[21,22]

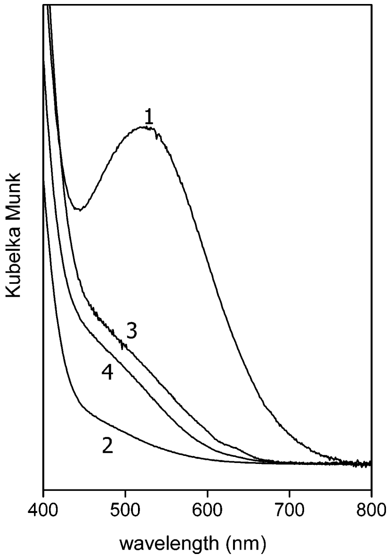
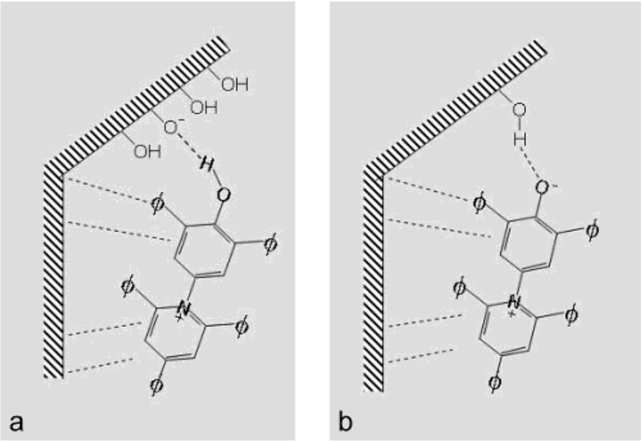


Figure 2. DR-UV−visible spectra related to HMS-300 after prolonged outgassing at RT (curve 1) and readmission of air (curve 2), ethanol (curve 3), and acetonitrile (curve 4).

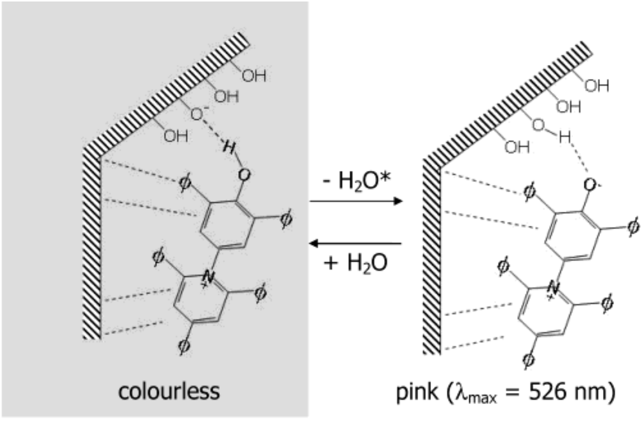
SCHEME 2: Structure of RD in R-HMS-300 (a) and R-HMS-600 (b)



The state of the RD molecule interacting with the hexagonal mesoporous silica wall in R-HMS-300 and R-HMS-600 is depicted in Scheme 2. Broken lines represent H bonding and van der Waals interactions.

Prolonged pumping of the sample R-HSM-300 in a vacuum at room temperature, which only brings about the removal of adsorbed molecular water, caused coloration of the sample, described by spectrum 1 in Figure 2 ($\lambda_{max} = 526$ nm). This effect is depicted in Scheme 3. Atmospheric water, probably adsorbed and therefore acting as a sort of solvent, stabilizes the $H{-}RD^+$ species, playing a role in the protonation of RD close to that observed for proton-transfer reactions in solutions.[4] Figure 2 shows that readmission of water (even in the form of atmospheric moisture) led to sample bleaching. The adsorption of other polar solvents (acetone, methanol, and acetonitrile) on

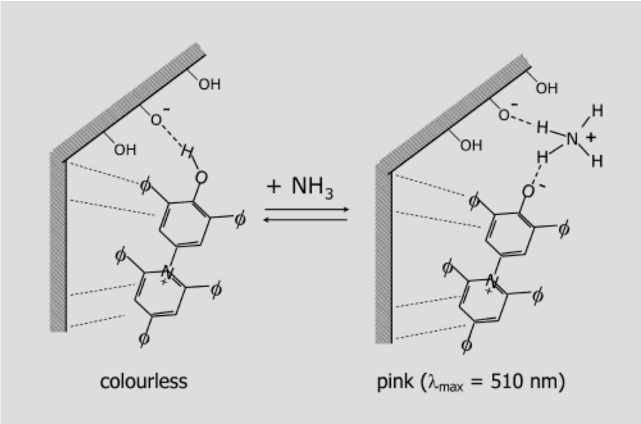
SCHEME 3: Effect of the Removal of Water or Polar Molecules from R-HMS-300[a]



* or other polar solvent

[a] Shadowing represents the presence of atmospheric water (or other polar solvents).

SCHEME 4: Effect of Interaction of Ammonia with R-HMS-300[a]



[a] Shadowing represents the presence of atmospheric water (or other polar solvents).

the same sample also caused the disappearance of color, whereas nonpolar solvents (e. g., tetrachloromethane and benzene) did not.

The effect of polar molecules on the state of RD adsorbed on poorly dehydrated silica has not been reported so far. Since it is not straightforward to describe the role (solvating?) of polar molecules on the RD-HMS-300 surface, their presence is represented in Schemes 2−4 by a mere shadowing.

By exposing the R-HSM-300 sample to ammonia vapors, the color turns immediately to a strong pink. The same effect was obtained with primary amines in the vapor phase, whereas many other polar substances (alcohols, thiols, and phosphines) were ineffective. This means that ammonia does not act by virtue of its polar nature, which would instead favor even more the protonated form of RD, but because of its basic nature. As a relatively *strong base*, it is able to strip a proton from the H−RD$^+$ species, bringing back the charge-transfer transition in the visible spectrum. The interaction with ammonia is reversible, and the color readily fades away if the sample is not in contact with ammonia vapors. Figure 3 illustrates the exposure of the R-HMS-300 sample to ammonia under controlled circumstances. After insertion into a UV−visible cell, the sample is briefly pumped at ambient temperature and exposed to NH_3 at increasing pressures. A band at 510 nm appears, the intensity of which grows steadily with pressure. A slight red shift is seen at higher pressures, which probably monitors a change in the environment along the experiment.

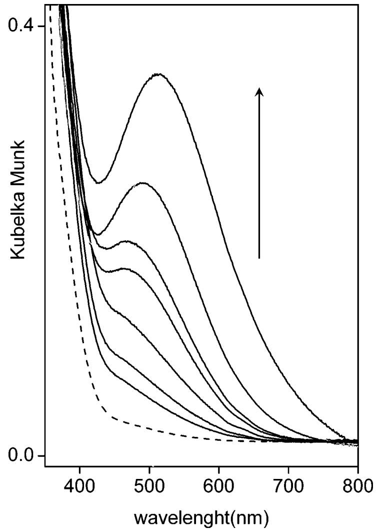


Figure 3. DR-UV−visible spectra related to the exposure of R-HMS-300 to NH_3 (broken curve: before exposure to NH_3; the arrow indicates NH_3 pressure increasing from 1.0×10^{-1} to 10 mbar).

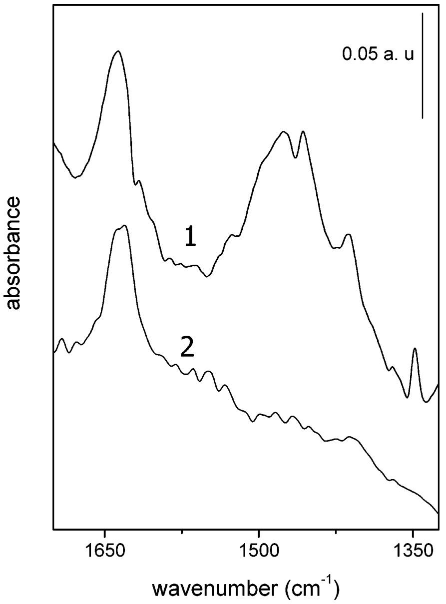


Figure 4. Difference FTIR spectra related to the adsorption of NH_3 on R-HMS-300 (curve 1) and HMS-300 (curve 2).

Note that the different environment of Reichardt's dye (presence/absence of ammonia and/or water) is reflected in the different wavelength of the absorption maximum in the visible spectrum, as a consequence of different polarity and H bonding interactions.[16]

A behavior with gaseous ammonia similar to that reported has been observed for Reichardt's-dye−polymer composites treated with hydrochloric acid: the acid protonates the dye to a white form,[17] as silanols do with R-HMS-300, and ammonia brings back the color.

Direct evidence that on R-HMS-300 the reaction occurring is

$$HRD^+ + NH_{3(g)} = RD + NH_4^+$$

comes from the infrared spectrum of the sample (Figure 4); in the presence of ammonia, a band is seen at 1465 cm^{-1}, typical of the NH_4^+ species (curve 1).[18] The band at 1635 cm^{-1} is due to the asymmetric bending mode of adsorbed molecular ammonia. Both bands disappear when ammonia is removed. As well known in the surface chemistry of silica, the same experiment conducted on a HMS sample without RD does not lead to any ammonium ions. Indeed, spectrum 2, referring to HSM-300, only shows the bending mode of molecular ammonia, so confirming that the formation of NH_4^+ species is due to the presence of the dye.

A possible structure for the RD-colored species under these circumstances is given in Scheme 4, in which the ammonium species is assumed to interact with both the silanolate of the silica walls and the phenolic oxygen of the dye.

Conclusions

In the presence of polar molecules acting as solvents, such as atmospheric water, methanol, acetonitrile, or acetone, RD on a highly hydrated HMS surface strips a proton from a SiOH in a patch of silanols, so becoming colorless. A base stronger than RD (ammonia or amines) captures the proton, giving rise to the appearance of color. The process is fully reversible. This feature, together with the rapidity of the optical response and its dependence on NH_3 pressure (Figure 3), makes this material promising for optical sensing applications.

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