Organic–Inorganic Cooperative Molecular Recognition in Nanostructure of Alkyl-grafted MCM-41

Kei Inumaru,* Yuta Inoue, Shintaro Kakii, Tomoyasu Nakano, and Shoji Yamanaka
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527

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Molecules having hydrophobic and hydrophilic groups such as 4-*n*-heptylaniline and 4-nonylphenol, an endocrine disrupter, fit the organic–inorganic nanostructure in alkyl-grafted MCM-41, interacting with the inorganic walls as well as the organic moiety, and thus the adsorbent achieves high molecular adsorption selectivity.

Grafting of organic groups on inorganic porous materials is a powerful method for creating organic–inorganic nanostructures with new functions.[1–4] Recent studies succeeded to functionalize nanometer size pores of mesoporous silicas (MCM-41 or FSM-16)[5,6] as catalysts,[7,8] heavy metal ion adsorbents,[9–11] and photocontrollable molecular storage materials.[12] However, these chemical functions are mainly ascribable to the organic moiety, leaving the inorganic walls as just a framework to maintain the structure and restrict functional diversity.

Molecular recognition is becoming increasingly important for environmental protection. Extremely specific molecular selectivity is required for the removal of highly diluted pollutants in water, otherwise many coexisting compounds with higher concentrations will saturate the adsorption capacity.

We previously reported that alkyl-grafted mesoporous silica showed excellent performance for molecular selective adsorption of diluted 4-nonylphenol, an endocrine disurupter.[13] This was the first application, to our knowledge, of organo-grafted mesoporous silica to selective adsorption of organic molecules in water. Other scientists reported that micelles in as-synthesized MCM-41 efficiently absorbed organic compounds such as chlorophenols, and the function was ascribed only to hydrophobicity of the organic micelles.[14,15]

Here we report evidence of a novel type of molecular recognition in the nanostructure where the inorganic part contributes directly to the function. Alkyl-grafted MCM-41 recognizes hydrophobic and hydrophilic groups of a molecule simultaneously through the inorganic walls and the organic moiety in the nanostructure, and thus achieves high adsorption molecular selectivity.

Hexagonal mesoporous pure silica (designated Si-M) and silica–alumina (Si/Al = 100 and 37, designated M(100) and M(37)) were prepared at 303 K and in hydrothermal conditions, respectively. $n\text{-}C_{16}H_{33}(CH_3)_3NBr$ was used as the template for all materials. Alkyl grafting was carried out as described elsewhere[15] using *n*-pentyltriethoxysilane, *n*-octyltriethoxysilane, or *n*-dodecyltriethoxysilane. In typical adsorption experiments with organic compounds, several mg of the adsorbent was added to 60 g of an aqueous solution of phenol, alkylphenols and/or alkylanilines (2–7 ppm. The pH is ca. 6–7 and thus neutral molecules are predominant). The time courses of the residual amounts in the liquid phase were traced by a liquid chromatograph with a UV detector. For IR spectra measurements, the samples were filtered after the adsorption of organic compounds, and then were casted on Si wafers followed by drying in an ambient atmosphere.

Comparison of nitrogen (77 K) and water (293 K) adsorption isotherms reveals the formation of highly hydrophobic nanospaces in the pores for the alkyl-grafted samples. For example, the *n*-octyl grafted sample (C8-M(100)) still adsorbs half as much nitrogen as adsorbed by non-grafted sample (M(100)). This means that large spaces among alkyl groups are available for molecular adsorption (ca. $0.3\,cm^3\,g^{-1}$ for C8-M(100)), even after the alkyl grafting. This is consistent with the large distance between the alkyl groups (ca. 1.2 nm in average, estimated from the carbon content and the surface area of MCM-41). On the other hand, water adsorption isotherm of the same sample shows little adsorption and no condensation (at least up to $P/P_o = 0.9$), despite the large spaces detected by nitrogen adsorption. These results demonstrate that the nanospaces in the mesopores are extremely hydrophobic.

Figure 1 shows adsorption isotherms of several kinds of compounds from aqueous solutions for the adsorbent C8-M(100). The adsorption amount of 4-nonylphenol is as large as $6 \times 10^{-4}\,mol\,g^{-1}$ even at the low concentrations of $10^{-6}\,mol\,dm^{-3}$, which is comparable to the performance of activated carbon.[13] 4-*tert*-Amylphenol ($CH_3CH_2(CH_3)_2CC_6H_4OH$) shows adsorption amounts much smaller than 4-nonylphenol. The uptake of phenol is undetectable (not shown). The order of the selectivity for these 4-alkylphenols (4-nonylphenol > 4-*n*-heptylphenol ≫ 4-*tert*-amylphenol > phenol) can be explained in terms of the hydrophobicity of the alkyl groups of the molecules: as molecules having large alkyl group (i.e., highly hydrophobic) are preferably adsorbed. This molecular selectivity was also confirmed by adsorption from mixed solution (da-

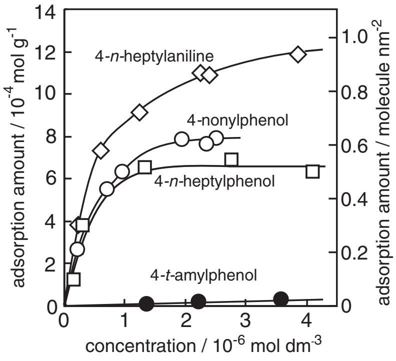

Figure 1. Adsorption isotherms of some organic molecules on C8-M(100). The scale on the right side is normalized using the surface areas of the inorganic moieties contained in the alkyl-grafted sample.

ta not shown). It is notable that the adsorbent clearly recognizes the difference between the heptyl group and the *tert*-amyl group.

Since 4-*n*-heptylaniline has an amino group ($–NH_2$), which is much more strongly hydrophilic (and basic) compared to the phenolic hydroxyl group (–OH), the behavior of this compound provides information about the effect of the hydrophilic group in the molecule on adsorption selectivity. In light of the results for alkylphenols, 4-*n*-heptylaniline is expected to be adsorbed in a lower amount than 4-*n*-heptylphenol and 4-nonylphenol because the aniline is much more hydrophilic than the alkylphenols. (Indeed, the solubility of 4-*n*-heptylaniline in water is much higher than that of 4-nonylphenol. Note that 4-*n*-heptylaniline and 4-*n*-heptylphenol have the same molecular structure except the hydrophilic part.) However, as shown in Figure 1, the adsorbent C8-M(100) shows a larger uptake of 4-*n*-heptylaniline than those of the alkylphenols; as the material preferably adsorbs molecules having a highly hydrophilic group. That is, this adsorbent simultaneously recognizes the hydrophilic group of the molecules as well as the hydrophobic group. The adsorption amount of 4-*n*-heptylaniline is much larger than the Al content ($1.4 \times 10^{-4}\,\mathrm{mol\,g^{-1}}$). Samples without alkyl-grafting show very low adsorption amounts of *n*-heptylaniline.

The IR spectra provided evidence that the amino group of the 4-*n*-heptylaniline molecule interacts with the inorganic wall in the nanostructure; Figure 2 shows the spectra in the N–H stretching region of 4-*n*-heptylaniline adsorbed in these materials. The liquid sample of *n*-heptylaniline (Figure 2c) shows absorption peaks due to its NH_2 stretching vibrations at around 3446 (asymmetric mode) and around $3347\,\mathrm{cm^{-1}}$ (symmetric mode). The broadness is ascribable to weak intermolecular hydrogen bonds. For the *n*-heptylaniline molecules that are adsorbed on C8-M(100), the two peaks are observed at the much lower frequencies of 3386 and $3320\,\mathrm{cm^{-1}}$ (Figure 4a), which are very close to the peaks of aniline adsorbed on silica (3388 and $3319\,\mathrm{cm^{-1}}$).[16] These large shifts toward lower frequencies are due to the strong hydrogen bonding of the amino groups to the inorganic surface. Further support is derived from the peak positions being dependent on the inorganic composition (the right panel in Figure 2). As Al content is increased, the two peaks shift monotonically to lower frequencies. Considering that aniline adsorbed on Al_2O_3 gives two NH_2 peaks at lower frequencies than those on SiO_2 by ca. $70\,\mathrm{cm^{-1}}$,[16] the observed shift is evidence that the amino group interacts with the inorganic walls.

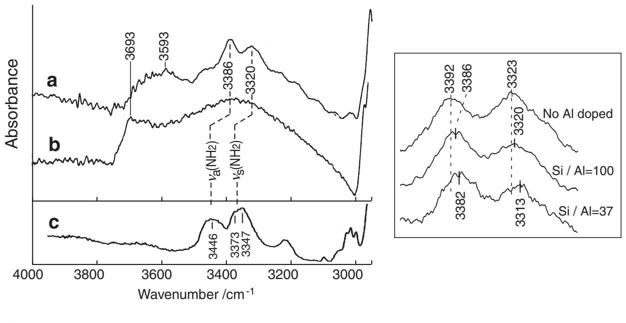

Figure 2. IR absorption spectra in the NH stretching region of *n*-heptylaniline adsorbed in C8-M(100) (a), fresh C8-M(100) (b), and of liquid *n*-heptylaniline (c). The right panel shows the magnified peaks of *n*-heptylaniline adsorbed in samples having different Si/Al ratios. The adsorption amounts for the three samples were adjusted to be $0.4–0.6\,\mathrm{molecules\,nm^{-2}}$.

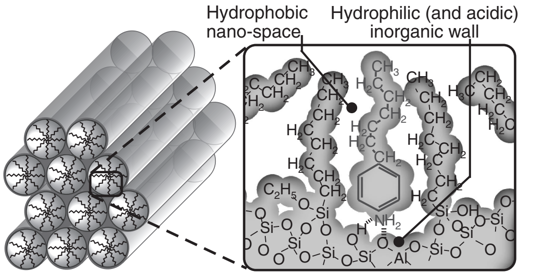

Figure 3. Schematic illustration of a molecule adsorbed in the nanostructure.

In addition, a new broad band is observed around $3593\,\mathrm{cm^{-1}}$ in Figure 2a. For the samples before *n*-heptylaniline adsorption, only weakly hydrogen-bonded Si–OH is observed at around $3693\,\mathrm{cm^{-1}}$ (Figure 2b). The broad band at $3593\,\mathrm{cm^{-1}}$ is presumably ascribable to surface Si–OH strongly hydrogen-bonded to the amino group, which is consistent with the above results. Though the acidity of Si–OH groups is weak, it may contribute to the interaction with the basic molecules.

The above results when taken together demonstrate that organic and inorganic moieties cooperate in molecular recognition; the recognized molecules having a direct interaction with the inorganic inner surfaces (Figure 3). In the solid materials currently studied for molecular recognition, even for those based on inorganic materials,[4,17] the molecules recognized in the cavities interact with just organic functionalities bound to the materials. We believe that a strategy such as ours, which designs cooperative functions for organic and inorganic moieties, heralds the development of more sophisticated nanomaterials.

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