Advances in Environmental Technologies via the Application of Mesoporous Materials

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Abstract: This review describes (inorganic-organic hybrid) mesoporous silica and alumina preparation with a uniform pore structure, as well as some environmental applications. Functional organic groups can be incorporated in the mesoporous materials by grafting, co-condensation and imprinting methods, and these groups affect the hydrophilicity/hydrophobicity of the surface and its affinity for metal ions. Applications of mesoporous materials are highlighted, including catalysts for hydrogenation and hydrodechlorinatton, and the surface-to-volume ratios, these materials show superior catalytic activity and higher adsorption capacities than amorphous or non-porous materials.

Keywords: Adsorbents, Catalysts, Mesoporous materials, Nanotechnology, Templating method

Introduction

Nanotechnology is the paradigm in the new millennium as semiconductor technology was in the past. The latest advances in nanotechnology have generated materials and devices with new physical characteristics and chemical/biological functionalities that are useful in a wide variety of applications [1]. New synthesis processes involving nanotechnology have made nanostructured materials in a wide variety of compositions of metal oxides and metals supported on metal oxides available, which have led to recognition of their exceptional chemical, physical, and electronic properties [2].

Nanotechnology is a purpose oriented study in which the developed technology itself has applicability, and this can change an existing technology through yield improvement, energy saving, simplification of a process, and the realization of clean technology. Therefore, it is concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical, and biological properties. The following challenges have been identified as essential for the advancement of the field: nanostructured materials; nanoelectronics; optoelectronics and magnetics; advanced healthcare, therapeutics and diagnostics; nanoscale processes for environmental improvement; efficient energy conversion and storage; bio-nanosensors for communicable disease and biological threat detection [3].

Among the several novel materials used in nanotechnology, applications using mesoporous materials have not been studied extensively. Mesoporous materials have some unique characteristics as follows: uniform pore channel (1 ~ 10 nm), large surface area (~ 1000 m²/g), a 2D hexagonal structure or a 3D interconnected pore system, a high thermal stability, and ease of functionalization of internal and external surface using a self-assembled monolayer.

This review focuses on advances in environmental technologies via the application of mesoporous materials. In the first part, we describe functionalized mesoporous silicas, and several synthetic strategies associated with mesoporous alumina and hierarchical pore structure. The second part highlights environmental applications to catalysts and selective adsorbents using mesoporous materials.

Mesoporous Materials in the Fusion of NT and ET

Nanotechnology has the potential to significantly impact energy efficiency, storage, and production. It can be used
to monitor and remediate environmental problems, curb emissions from a wide range of sources, and develop green processing technologies that minimize the generation of undesirable by-product effluents [3].

In particular, (inorganic-organic hybrid) mesoporous materials are highlighted in the area of environmental technology due to their potential environmental applications such as catalysts for the recovery of resources from undesirable by-products and adsorbents for the remediation of toxic ions from waste solutions. Mesoporous materials possess an ultrahigh surface-to-volume ratio, which offer a greatly increased number of active sites for carrying out catalytic reactions and selective adsorption.

Mesoporous silicas and aluminas have been widely used in catalysis as an inert support for active metals and as a part of bifunctional catalysts [4]. Confinement of the metal catalyst in the mesoporous solid improves activity compared to attachment to amorphous or non-porous silicas. This is due to the enhanced selectivity in a sterically homogeneous environment and higher catalyst turnover, achieved by the stabilization of the catalyst within the pore channels [5]. To incorporate functional groups such as amines, thiols, etc., mesoporous supports are initially functionalized with organosilanes. These functional groups are then modified by wet impregnation or vapor deposition. Such mesoporous catalysts can be used to recover resources from industrial wastes.

The preparation of improved adsorbents, for removing toxic ions from aqueous solutions, has attracted considerable attention in the area of wastewater treatment. Several types of functionalized materials have been prepared by grafting chelating ligands (i.e., thiol, amine, etc.) to the surface of the supports to remove metal ions from aqueous solution. These include activated carbon, zeolites, clays and silica [6,7]. However, the small and irregular pore structures of the latter materials limit their access to the chelating ligands. This, in turn, lowers the metal loading capacities. To overcome these drawbacks, mesoporous molecular sieves can be used as adsorbents [8-11]. Feng and coworkers reported on a heavy metal ion adsorbent based on the thiol functionalization of calcined MCM-41 silica [8]. Mericier and coworkers prepared an analogous adsorbent by grafting thiol moieties to the pore channels of the hexagonal mesoporous silicas (HMS) [10]. Liu and coworkers prepared thiol- and amine-functionalized adsorbents using SBA-15 silica [11].

Mesoporous Materials: Silica, Alumina

Mesoporous Silica with Functional Groups

Following the discovery of the mesoporous molecular sieves [12,13], numerous research groups have investigated mesoporous molecular sieves. Mesoporous materials (MCM-x, FSM, SBA-x, HMS, MSU-x, etc.) have been synthesized using a metal alkoxide as a silica precursor in a template environment [12-17]. Methods of preparation of mesoporous silicas can be divided into an electrostatic assembly approach and a neutral templating route. The electrostatic assembly approach has been extended to other mesostructured compositions via the implementation of four synthetic routes which are complementary in nature [15]. The primary pathway involves the direct co-condensation of anionic inorganic species (I) with a cationic surfactant (S) providing assembled ion pairs of the type ST. Other types include S'I, S'XT' (where X = Cl or Br), and S'M'T (where M' = Na or K) assemblies. The neutral templating route is based on hydrogen bonding and self-assembly between neutral surfactant (S') and the neutral inorganic precursors (I'). This neutral S'I' templating route provided a distinguishable subset of hexagonal mesoporous molecular sieves with physical and catalytic properties which are different from those of the MCM-41 materials, prepared by electrostatic assembly.

Once the mesostructure is synthesized, template should be removed to give the desired pore structure. One method for the removal of the template is solvent extraction, in which the product is suspended in an ethanolic [15] or acidic [18] solution. The second method involves calcination, in which the product is heated under flowing air or oxygen, thus burning away the organic material. However, these methods are time-consuming procedures. Recently, microwave irradiation has been proposed to shorten the required time [19]. This method, however, depletes the surface hydroxyl groups of silica. In addition, it could not be applied to the organic-inorganic hybrid mesoporous materials synthesized via a co-condensation process, since it would also decompose the organic groups. Thus, it is necessary to extract the templates rapidly without the loss of surface hydroxyl groups and incorporated organic groups.

In order to incorporate a variety of functional groups onto the surface of mesopores, several methods have been proposed [8,20-28]. The first method is the post modification of pre-synthesized mesoporous silica, namely grafting by the attachment of organotrialkoxysilanes or organotrichlorosilanes to the surface of mesoporous silicas [8,20-28]. The silanol groups on the surface can be used as an anchor for organic groups. To obtain a high surface coverage of functional groups, it is necessary to minimize the loss of surface silanol groups using appropriate template removal methods. The second method, which involves the co-condensation of silica precursors and functional organosilanes with inorganic-organic hybrid networks, is one-pot synthesis or co-condensation method [23-25]. This method must avoid (i) phase separation of the precursors to obtain a uniform distribution of functional groups and (ii) Si-C bond cleavage during the sol-gel
reaction and template removal [5]. Hybrid organic-inorganic mesoporous silicas can be used in many applications, including catalysis, the sorption of metals, anions, and organics, reactors for polymerization, the fixation of biologically active species, and optical applications [5]. Lim and coworkers [23] synthesized vinyl functionalized MCM-41 using vinyltrialkoxysilanes by means of a postsynthesis grafting process and a direct co-condensation procedure, and compared the two synthetic procedures. Vinyl groups were distributed more homogeneously in the MCM-41 sample, that had been synthesized by co-condensation, compared to the product, synthesized by postsynthesis grafting. Vinyl functionalized MCM-41 was found to be more hydrothermally stable than the original MCM-41. However, the surface incorporation of organic groups and changes in the pore structures are dependent upon the types of functionalized organosilanes used in the process. An alternative procedure for separating heavy metal ions which have similar physical and chemical properties, a molecular imprinting method, or the introduction of target metal ions into the silica structure during the sol-gel process, has been proposed [26,27]. The molecular imprinting method leads to the formation of solid materials, which contain chemical functionalities that are spatially organized by covalent or non-covalent interactions with imprint (or template) molecules during their synthesis. The subsequent removal of the imprint molecules leaves behind designed sites that can recognize small molecules, thus making the material ideally suited for applications such as separations, chemical sensing and catalysis [28].

Synthesis of Mesoporous Alumina

Aluminas have been used as an industrial catalysis, catalyst support, adsorbent and ion exchanger, because of their thermal, chemical, and mechanical stability and low cost. The performances, however, are limited due to the uncontrolled porosity, deactivation by coke formation and plugging in the micropore that hinders the diffusion of reactants and products. Thus, alumina supports with a narrow pore size distribution, uniform pore structure and high pore volume are required for practical industrial applications.

Mesoporous alumina has also been recently developed by several groups [4,29-37]. Ionic surfactants (carboxylic acid, sodium dodecylsulfate) [29,31] or neutral surfactants (tergitol, polypropylene oxide) [32] were used as chemical templates to prepare mesoporous alumina via a templating method. Mesoporous silicas such as MCM-41 and SBA-15 have a 1D or 2D hexagonal mesoporosity, while mesoporous aluminas are comprised of a 3D interconnected pore system in the form of a sponge-like structure, which is an advantage in catalyst reactions, such as the HDC reaction [4]. One limitation of the above synthetic strategies for mesoporous aluminas is that the rates of hydrolysis (and condensation) of aluminium alkoxides are much faster than that of the silicon alkoxides. Therefore, hydrolysis reactions in aqueous media also lead to the formation of lamellar hydrated hydroxides, even in the presence of a surfactant [32]. Amoros and coworkers [31] solved this problem by controlling the rate of hydrolysis of the aluminium suspension by adding hydrolysis inhibiting agents.

To develop an easy-and-fast method for preparing mesoporous alumina, a pre- and post-hydrolysis method was proposed using several different carboxylic acids as chemical templates at room temperature [4,29-37]. Stearic acid was used as the anionic surfactant to synthesize mesoporous aluminas, and aluminum sec-butoxide was used as an aluminum precursor. Oxidation reactions of aluminum alkoxide were minimized by controlling the pH of the synthesis medium [32,38], while mesoporous alumina prepared at pH 7 had a relatively well organized mesostructure. As shown in Figure 2, the pre-hydrolyzed aluminum precursor in the pre-hydrolysis method

![Figure 1. Schematic of the metal-imprinting method [26].](image)

![Figure 2. Comparison of pre- and post-hydrolysis methods used in the synthesis of mesoporous alumina [32].](image)
method condensed and formed an aggregated aluminum sol, leading to the production of a poorly organized mesoporous alumina [38]. In contrast, the post-hydrolyzed aluminum precursor produced by the post-hydrolysis method led to the production of well-ordered mesoporous alumina [33]. In the case of mesoporous alumina prepared using stearic acid via a post-hydrolysis procedure, the materials displayed a high degree of thermal stability, and the nickel impregnated mesoporous alumina had a low rate of deactivation and a high selectivity compared with those of commercial alumina for the conversion of hydrodechlorination of 1,2-dichloropropane to propylene [4].

The initial phase of the as-prepared mesoporous alumina was bayerite and/or (pseudo)boehmite, and was transformed into active alumina at 250°C, which remained thermally stable at temperatures up to 600°C [33]. Based on an $^{27}$Al MAS NMR analysis, calcined alumina prepared via a hydrothermal method contained a high ratio of $\text{Al}^{VI}$ to $\text{Al}^{IV}$ (~4.8), which is not fully transformed into active alumina, and aluminum hydroxide (AlOOH or Al(OH)$_3$) was detected. These results suggest that a high temperature is required to produce an active form of alumina, when the hydrothermal method is used [33,35]. Their pore properties could be controlled by adjusting the molar ratio of water to aluminum precursor, the carbon tail length of the alkyl carboxylate used, the preparation temperature, calcination conditions, and the pH of the reactants [4,29-37]. The pore size was adjustable from 2 to 7 nm, and the mesoporous alumina had a large surface area of 300–500 m$^2$/g and a narrow pore size distribution ($D_{WBM}<1$ nm). Pore properties are also controllable using isoctane, which is very hydrophobic and could be used as micelle structure reinforcement agent and swelling agent [34].

In addition, inexpensive mesoporous alumina can be used in the preparation of industrial catalysts, since these materials are prepared using stearic acid salts such as magnesium or sodium stearate. These materials also show similar physical properties with respect to pore size and surface area to those of mesoporous alumina prepared using stearic acid [35,37]. Other stearic acid salts may also be used as chemical templates in the preparation of mesoporous alumina. When nickel stearate is used as a chemical template and nickel source, the Ni/Al$_2$O$_3$ catalyst can be prepared easily and quickly after continuous calcination and reduction without the need for an additional impregnation step [35].

In addition to unimodal mesoporous alumina, hierarchical meso- and macroporous alumina can be prepared [36]. The framework of the porous alumina is prepared via a chemical templating method using alkyl carboxylates. As a physical template for macropores, polystyrene beads (PS) or a silica gel (200 mesh) are employed (Figure 3). Micro- and mesopores are able to selectively accommodate guest molecules, while additional macropores reduce transport limitations and enhance the accessibility of a molecule to the active sites [39]. As theoretically proven by Levenspiel, the bimodal catalyst can guarantee a high diffusion efficiency [40]. For example, a cobalt catalyst supported on bimodal silica showed a remarkably high activity in a liquid-phase Fischer-Tropsch synthesis [41].

Important trends in the $N_2$ isotherm when the PS beads are used as a physical template are shown in Figure 4. P1
Applications to Catalysts

Hydrodechlorination

From an environmental point of view, the catalytic hydrodechlorination of chlorinated organic compounds has an advantage over the conventional incineration process, which requires harsh operation conditions and produces secondary pollutants. In addition, the catalytic process has an economic merit of producing useful hydrocarbons.

The hydrodechlorination of chlorinated alkanes over supported Ni catalysts has been widely studied by a number of researchers [42-45]. Choi and coworkers [42] reported that a considerably high selectivity for propylene was obtained with Ni/SiO₂ in the hydrodechlorination of 1,2-dichloropropane. One research group [43,44] carried out the dehalogenation of cyclohexyl chloride over supported Ni catalysts. They reported that unsaturated hydrocarbons such as cyclohexene were formed via dehydrochlorination. Ni catalysts used in the hydrodechlorination of chlorinated organic compounds were mostly supported on silica and zeolite, while very limited studies of the hydrodechlorination of chlorinated organic compounds over Ni/Al₂O₃ catalysts have been reported [45].

Mesoporous molecular sieves are attractive as a catalyst support due to their desirable properties such as large surface area, well defined pore channels and narrow pore size distribution. In addition, mesoporous silicas can be easily functionalized with organic or inorganic chemicals by a grafting method. Numerous studies have been performed to develop a hydrodechlorination catalyst using noble or transition metals supported on SiO₂ [46-48] and Al₂O₃ [4].

A nickel catalyst supported on SBA-15 type mesoporous silica was synthesized by the grafting of 1,3-bis[3-trimethoxysilylpropyl]ethylene diamine triacetate acid salt (EDTA) onto the surface of SBA-15, followed by the adsorption of nickel ions and calcination (Ni-E-SBA) [47,48]. While nickel particles loaded on catalysts (Ni-WI-SBA) prepared by the wet impregnation method were found to be aggregated on the outer wall of the support, they were finely dispersed on the surface of the mesopores in the Ni-E-SBA catalyst. The catalytic performances of the prepared catalysts were evaluated using the hydrodechlorination (HDC) of 1,1,2-trichloroethane (TCEa) as a model reaction. As shown in Figure 5, the results show that the Ni-E-SBA catalyst had the highest activities of the catalysts, compared to conventional catalysts (Ni-WI-JRC, Ni-WI-SBA) [46].

**Figure 5.** Catalytic activity of the prepared catalysts with respect to time-on-stream at 573 K: (a) Ni-E-SBA, (b) Ni-WI-SBA and (c) Ni-WI-JRC [46].

Hydrogenation of Linoleic Acid

Nickel stearate was used as a chemical template and
Figure 6. Conversion of 1,2-dichloropropane and propylene selectivity over supported mesoporous Ni/Al₂O₃ catalysts as a function of time on stream [4].

metalsource for the easy-and-fast preparation of Ni/Al₂O₃ catalyst with a mesoporous structure [35]. Ni-Nx and Ni-Hx were prepared using an NH₃OH-treated precipitate and HCl-treated solution as a chemical template, respectively, and these materials show only the effect of the chemical template, a regular pore size distribution. Ni-Nx with both a developed framework and textural porosity show a larger surface area and pore volume but a less irregular pore structure than Ni-Hx which shows a well-developed framework porosity. An ²⁷Al MAS NMR analysis showed that nickel oxide supported on active alumina allows Ni²⁺ ions to diffuse into the surface lattice vacancies of the alumina spinel structure. Such a migration of metal ions may be limited to the first few layers of the supports, but leads to the production of a difficult-to-reduce metal oxide (i.e. a high metal-support interaction). Ni-Nx was also found to have a more dispersed nickel particle configuration than Ni-Hx after reduction.

A catalyst prepared by the traditional method (i.e. metal impregnation onto mesoporous alumina [4] has features similar to the Ni-Hx catalyst prepared by the one-pot method as described in this work. These materials showed aggregated and large nickel particles on the pore and/or surface of the structure, while the Ni-Nx catalyst showed small and highly dispersed nickel particles. The Ni-H1 and Ni-N2 catalysts have the same metal content (8 wt%), and thus, were tested in a hydrogenation reaction of linoleic acid (C₁₈:2, n₀=1.469) as a potential application. Linoleic acid contains 2 unsaturated (9C and 12C) bonds. In this reaction the acid would be saturated with hydrogen and changed into oleic acid (C₁₈:1, n₀=1.459) or stearic acid (C₁₈:0), and thus, the degree of saturation would be increased. At the beginning of the hydrogenation, almost all of the double bonds are present in the cis form. At the termination, most of the C₁₈:2, however, was converted to C₁₈:1 and C₁₈:0, and small portion of C₁₈:1 or C₁₈:0 were saturated, forming C₁₈:0 [49,50]. Therefore, the selective hydrogenation of linoleic acid to oleic acid was achieved.

As shown in Figure 7, Ni-N2 is a more reactive catalyst than Ni-H1 due to the high dispersion of metal particles, the high surface area, and many active sites for hydrogenation. This reaction showed that the N-N2 with highly dispersed metal is a more suitable and efficient catalyst for the hydrogenation of fats than the one-pot synthesized mesoporous alumina (e.g. Ni-H1) or metal impregnated mesoporous alumina, which contains large metal particles.

Figure 7. Hydrogenation of linoleic acid using (a) Ni-H1 and (b) Ni-N2 catalysts [34].

Applications to Selective adsorption

Removal of Heavy Metal Ions

The first attempt to use mesoporous materials as an environmental remediation method involved the removal of toxic heavy metal ions from an aqueous solution. Functional groups (amine, thiol, and imidazol), which are known to have selective adsorption properties with respect to specific metal ions, are incorporated on the surface of the mesoporous materials. For example, a thiol group has a high affinity for mercury, lead and cadmium, while an amine group shows high copper removal efficiency [51-58].

Bi-functional porous silicas were also used as heavy metal ion adsorbents [27,59]. To prevent the loss of co-condensed functional groups on the surface of silicas by calcination, a neutral surfactant was used as a template, which was later removed by ethanol extraction. High concentrations of organic groups (organic group/TEOS=1:4) were used to couple the functional groups to the wall of the porous silica by co-condensation. This resulted in a high concentration of mercapto-functionalized silica (2.4 mmol/g). This adsorbent also had highly selective adsor-
orption properties for mercury, compared to other heavy metal ions in aqueous solutions. The surface hydrophilicity of the adsorbent was improved by the introduction of amino groups. However, the introduced amino groups decreased the hydrothermal stability and metal adsorption capacities of the adsorbents. Process optimization between the hydrophilicity of adsorbents and the metal loading capacity should be taken into account when hydrophilic adsorbents are used in a continuous process.

In an interpretation of high affinity of thiol-functionalized porous silicas for mercury to other metals, Marcus [60] examined the thermodynamics of the solvation of metallic ions, and established that the experimental values of the molar Gibbs energy of hydration, \(-\Delta_{\text{hyd}}G^\circ\) [kJmol\(^{-1}\)] (Hg\(^{2+}\) = 1760, Ni\(^{2+}\) = 1980, Cu\(^{2+}\) = 2010), and the standard molar enthalpy changes of hydration, \(-\Delta_{\text{hyd}}H^\circ\) [kJmol\(^{-1}\)] (Hg\(^{2+}\) = 1853, Ni\(^{2+}\) = 2119, Cu\(^{2+}\) = 2123), are in the sequence Hg\(^{2+}\) < Ni\(^{2+}\) < Cu\(^{2+}\). These results indicate that on increasing \(-\Delta_{\text{hyd}}G^\circ\) and \(-\Delta_{\text{hyd}}H^\circ\), the interaction capacity of the metal ions with the mercapto-modified surface is reduced [61]. In addition, interaction enthalpy values between mercapto-modified silica surface and metal ion solution, \(-\Delta_{\text{hyd}}H^\circ\) were in the sequence Hg\(^{2+}\) > Cu\(^{2+}\) > Ni\(^{2+}\). These thermodynamic properties are consistent with results reported here on the selective adsorption of mercury ions. This difference in adsorption selectivities is shown schematically in Figure 8. Mercury ions are adsorbed to the inner surface of the pore, whereas other metal ions are adsorbed to the outer surface of pore or near the pore entrance. This schematic is consistent with the thermodynamic data described above. Metals such as Cu, which have high \(-\Delta_{\text{hyd}}G^\circ\) and low \(-\Delta_{\text{hyd}}H^\circ\), do not diffuse into the pore and are adsorbed on the outer surface of pore instead of inner surface. However, mercury ions, which have a low \(-\Delta_{\text{hyd}}G^\circ\) and high \(-\Delta_{\text{hyd}}H^\circ\), diffuse into the pore and is adsorbed on the inner surface.

Functionalized mesoporous silica is a fine powder, which makes it difficult to recover metal ions loaded in the adsorbents in batch tests. This can be overcome through the magnetic separation of the metal loaded adsorbent. Basically, this method involves the incorporation of magnetic materials into non-magnetic materials to increase their magnetic susceptibility and allow these agglomerates to be separated by magnetic separation. There have been many reports of the preparation of magnetic iron oxide composites embedded in silica or zeolite matrix [62-64]. Magnetite (core) was used as a magnetic carrier material for magnetic separation, while an amine-functionalized mesostructured silica (shell) was used as a heavy metal ion adsorbent as shown in Figure 9 [65]. Metal uptake capacity was dependent on the content of functional groups on the surface of the support. The use of an adsorbent with 2.43 mmol/g of amine-functional group showed a 0.11 mmol/g Cu ion uptake, and the molar ratio of the adsorbed copper ion to the amine-functional group was 0.045. After coming into contact with a copper solution, the adsorbents were collected by a magnet. The magnet attracted the adsorbsents from the solution and consequently, the solution became clear. The recovery process of the metal ion loaded adsorbents by the magnetic or electromagnetic force is very rapid and effective.

Regarding mesoporous silicas as adsorbents, it is interesting to note that the thiol concentration showed a low correlation with pore size and the surface area of the supports, but was strongly dependent on the framework pore volume [66]. The concentration of the grafted functional groups increased with increasing framework pore volume. Therefore, mesoporous silica, which has a well-developed framework porosity, was able to accommodate a larger concentration of functional groups on the adsorbents. The mercury ion uptake capacity of adsorbents with only a framework porosity increased with increasing concentration of functional groups, while that with a large textural porosity remained constant with increasing functional group concentration. An irregular pore channel structure, such as amorphous silica, caused pore blockage. Therefore, a large proportion of the grafted functional groups in the textural pores appear to be underutilized. The metal ion uptake capacities of SBA having long range 2-D pore channels were small compared with those of HMS, with short range interconnected 3-D pore channels. It was concluded that framework pores increased the loading of functional groups, while additional textural pore enhanced the accessibility of a molecule to the active site [67].

Figure 8. The difference in adsorption properties between mercury ions and other metal ions [49].

Figure 9. Schematic diagram of a mesostructured silica-shell (HMS) containing a magnetite-core structure [55].
The removal capacity of mesoporous silica is 5~8 times larger than that of conventional silica with irregular pore structure. This can be attributed to its large surface area and uniform pore structure. A semibatch reactor using fixed-bed was used to examine the characteristics of mesoporous silica for mass transfer. The external mass transfer coefficient was estimated by correlation and the effective diffusivity was calculated from the known tortuosity of conventional silica [67]. The experimental result and model prediction were in a good agreement. The results of a sensitivity analysis indicate the both external mass transfer and the diffusion are not rate determining steps. Because hydrophilic functionalizing agents were used, there was no the eternal mass transfer resistance.

Removal of Noble Metal ions
Little research has been reported relative to the adsorption of noble metal ions using mesoporous silica. Talanova and coworkers [68] reported that polymeric extractants with heterocyclic amine units resulted in the efficient adsorption of Pd(II) and Pt(II) from aqueous solutions, and Liu and coworkers [69] reported that polymers containing functional groups with donor N and S atoms were promising adsorbents for noble metal ions. It has been shown in a previous study that polymeric extractants containing heterocyclic amine units adsorb Pt and Pd efficiently from aqueous solutions and it has also been reported that polymers containing functional groups with nitrogen and sulfur donor atoms are promising adsorbents for noble metal ions. The majority of these studies, however, were conducted under strongly acidic conditions (pH<1). Mesoporous adsorbents functionalized with a chelating ligand (imidazole group) via a grafting method were synthesized and applied to the adsorption of noble metals in aqueous solutions [70-72]. This preparation technique and its applicability to trap noble metal ions onto mesoporous silica as a molecular unit appear to be a useful tool for other research areas, such as the selective concentration of metal ions from process streams, metal-dispersed catalysts, and the heterogenization of catalytic complexes of noble metal ions. It should also be noted that thiolated mesoporous adsorbents may be applicable to drug-delivery systems in that the interparticle migration of cis-platin [cis-Pt(NH3)Cl2] can be achieved via the use of thiol-modified silica [72]. Noble metal ion (Pt2+, Pd2+) adsorbents with uniform mesopore channels were prepared by grafting a thiol functional group onto ordered mesoporous silica, SBA-15. Table 1 summarizes the values for the distribution constant (Kd) of thiolated SBA-15 toward Pt2+ obtained in the presence of other metal ions. SBA-15 had little or no binding affinity for Ni2+, Cu2+, Cd2+ in buffer solutions at pH 4.01. High selectivity of the adsorbents was maintained, although the adsorbents were contacted with solutions such as 1 mM of Pt2+, 10 mM of Ni2+, Cu2+, Cd2+ or 1 mM of Pd2+, 10 mM of Ni2+, Cu2+, Cd2+ ions. Although alkyl sulfides are known to be soft bases which preferably bind to soft acids such as Cu2+ and Cd2+ from Pearson's hard and soft acid and base principle, the thiol-functionalized SBA-15 exhibited low adsorption capacities toward Cu2+ and Cd2+ [70-72].

Removal of Anion
Activated alumina (AA) is the most commonly used sorbent for removing arsenic from aqueous solutions. Conventional porous solids, including AA have ill-defined pore structures and typically low adsorption capacities, and act in a kinetically slow manner. An ideal adsorbent should have uniformly accessible pores, an interlinked pore system, a high surface area, and physical and/or chemical stability. It has been reported that aminosilane-grafted mesoporous silica showed a high uptake capacity [73]. MCM-41, with a one-directional pore structure adsorbed 110 mg of As(V)/g, while SBA-1 with an interlinked pore system adsorbed 260 mg As(V)/g. After aminosilane-grafting, the surface area of the two materials was 481 m2/g and 126 m2/g, respectively. In addition, a uniform pore structure with well-defined channels has been shown to have a great advantage over a disordered pore network in terms of the access of guest species to the binding sites [74]. Therefore, the surface area of the adsorbent is likely to be wide, but the pore structure, i.e., regular interlinked pore system is the most important issue for arsenic removal. The mesoporous alumina used had a 7 times higher uptake capacity (121 mg As(V)/g and 47 mg As(III)/g in Figure 10) than that of AA [75]. This high

| Table 1. Competitive Binding Behavior of SBA-15 and Thio-SBA-15 for Pt2+ [62] |
|-----------------------------|-----------|------------|------------|--------------|-------------|-----------|
| Solution 1st                | % Pt2+Abs | Kd (Pt2+) (mL/g) | Kd (Ni2+) (mL/g) | Kd (Cu2+) (mL/g) | Kd (Cd2+) (mL/g) |
| SBA-15                      | 15.95     | 38         | 13.1       | 14.0         | 15.2        |
| Thio-SBA-15                 | 99.48     | 3.8 × 104  | 9.4        | 17.2         | 14.0        |
| Solution 2nd                | 97.74     | 8.7 × 103  | 6.4        | 6.0          | 5.0         |

*Solutions containing a mixture of ca. 1 mM of Pt2+, Ni2+, Cu2+, and Cd2*, *Solution containing a mixture of ca. 1 mM of Pt2+ and each ca. 10 mM of Ni2+, Cu2+, and Cd2*, Percentage of metal ion adsorbed.
capacity for arsenic is due to the interlinked pore system of mesoporous alumina, as in SBA-1. In addition, the advantage of the MA adsorbent is that no post-treatment such as functionalization of the surface is needed, compared with mesoporous silica.

Consequently, a regular pore structure (prefer to interlinked pore system) was found to be the most critical factor for the removal of arsenic using mesoporous material, and the pore volume of the adsorbent also acted as a controlling factor in cases of mesoporous material with the same surface area.

**Removal of Organic Dye**

It is possible to apply mesoporous materials as an organic adsorbent [36]. Wang and coworkers [76] showed that siliceous materials adsorbed organophilic compounds after treatment with a cationic polymer and oppositely charged surfactant micelles. The organic removal reaction is known to be a fast and reversible ion-exchange reaction. The cationic charge site (N⁺) in PDDA (polydiallyldimethylammonium chloride) reacts with anionic charge site (SO₃⁻) of dye through charge matching.

In the case of mesoporous aluminas (unimodal P2 and bimodal P4), more than 90% of the acid red 44 (C₂₀H₁₄N₂O₂S₂, crystal scarlet) in aqueous solution was removed within 10 min, and the adsorption feature of PDDA/P4 is faster than that of PDDA/P2. The rate constant for intraparticle diffusion (k_d) is given by Weber and Morris [77]:

\[
q = k_d t^{1/2}
\]

As shown in Figure 11, an initial steep-sloped portion at the point of intraparticle diffusion is seen, followed by a plateau at equilibrium. The initial steep-sloped portion (from 0 to 10 min) can be attributed to surface adsorption and intraparticle diffusion. The plateau to equilibrium suggests that the intraparticle diffusion starts to slow down due to the extremely low solute concentration in the solution [77]. The intraparticle diffusion rate of PDDA/P4 is faster than that of PDDA/P2, indicating that acid red 44 ion is more easily diffused and transported into P4 than P2 due to the presence of macropores in the PDDA/P4. This provides evidence to show that the macropores reduced the transport limitation and enhanced the accessibility to the active site. In addition, the elution of the adsorbed dye was easy and fast when 0.5 M HNO₃ solution was applied.

**Conclusions**

With advances in nanotechnology, significant impacts on the area of environmental technology, such as energy storage, monitor, and remediation can be foreseen. In addition, a large number of novel techniques for the synthesis of mesoporous materials have been developed in recent years. These mesoporous materials hold promise as catalysts and adsorbents for environmental applications. The flexible choice of functional organics, inorganic precursors and templates allows the characteristics of mesoporous materials to be easily adjusted for desired applications. Their uniform pore structure, large surface area and adjustable mesoporosity are matched with the properties of an ideal support for catalysts and adsorbents. One can expect the fabrication of more complicated materials with hierarchical pore structures and highly selective materials. It should be accompanied with studies of the physicochemical properties for further appropriate applications with the developed materials.

In addition to environmental applications, mesoporous materials are used for the replication of mesoporous carbon [78], optical applications [79], and polymerization reactors [80]. Mesoporous carbon prepared by the replication
method using mesoporous silica can be used as an electrode in fuel cells. Suitably functionalized mesoporous materials are promising candidates for lasers, light filters, solar cells, and photocatalysts. In addition, it has been used as hosts for polymerization reaction through extrusion.

Thus, research on the synthesis and application of mesoporous materials continues to expand. However, mesoporous materials have not yet been commercialized in any environmental processes, while this will happen in the near-future due to the high adsorption capacity and superior catalytic activity of mesoporous materials compared to amorphous or non-porous materials.

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**References**