POROUS POLYMER COMPLEXES FOR GAS SEPARATIONS: MEMBRANE SEPARATIONS

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The Polymer–Metal Complex as a Gas Adsorbent

Solid adsorbents are promising materials for gas separation. A separation is achieved by selectively adsorbing one of the components of a gas mixture onto the surface of a solid adsorbent. To achieve an efficient separation, high selectivity towards the targeted gas against others is necessary. Some metal complexes are quite useful for this purpose. For example, gaseous molecules with non-bonding electrons or π-electrons such as carbon monoxide (CO), ethylene (C_2H_4), and nitrogen monoxide (NO) are co-ordinated reversibly on transition metals (Cu(I), Fe(II), Ag(I), and so on). Thus, solid adsorbents for these gases can be prepared conveniently by immobilizing the corresponding metal complexes on a polymeric resin. The polymer–metal complexes thus formed have good selectivity for the gaseous molecules. However, the polymer used as a support for the metal complex can significantly affect the adsorption properties. For instance, polymer–metal complexes acquire fairly high durability against undesirable molecules compared with the metal complexes without polymer support due to the polymer effect. Another important property of the polymer support is its *porosity*, which regulates the efficiency of the gas separation.

Importance of Porosity for the Efficient Gas Separation

Generally, porous structures are required for useful solid adsorbents. For example, metal complexes supported on a non-porous (gel-type) polymeric resin do not show rapid adsorption, although the metal complex itself binds smoothly to the target molecule. The same phenomenon is observed in conventional physical adsorption processes. The high adsorption capacity of active carbon is mainly attributed to the extremely large surface area of this material ($S \cong 1000\ \mathrm{m^2\,g^{-1}}$). Similarly, a porous structure is also essential for polystyrene resins which are applied industrially for separation processes. The same materials formed as round solid beads without physical pores are useless as adsorbents. The significance of the porous structure is well understood by the following simple calculation. In the case of a spherical polystyrene resin *without* porous structure, only the outer surface contributes to the surface area. The specific surface area per unit weight ($\mathrm{m^2\,g^{-1}}$) is expressed in the following equation as a function of the radius (r nm) of the resin:

$$S = 3 \times 10^3/(d \cdot r) \qquad [1]$$

where d is the density of the polystyrene resin (in this case, d is 1.04 $\mathrm{g\,cm^{-3}}$). To provide $100\ \mathrm{m^2\,g^{-1}}$ of S to the polystyrene resin, r would be as small as 29 nm which corresponds to the size of colloidal particles. A nano-sized polystyrene powder is practically useless as an adsorbent so that the technology to provide porous structure is of critical importance.

Preparation of Porous Polymer Complex Adsorbent

Crosslinked polystyrene resin (Pst) is normally used as a starting material of the porous polymer–metal complex. Ways for preparing porous polymer complexes from this resin are illustrated schematically in **Figure 1**. Primarily, polystyrene resin itself needs to have a porous structure as a matrix. Porous polystyrene resin can be synthesized through special polymerization techniques which are demonstrated below (step 1 in Figure 1). Certain metal ions can form complexes with aromatic hydrocarbons so that the obtained resin is also available as a support without further chemical modification. Complexation of metal ions with polystyrene resin provides the porous polymer–complex adsorbent.

Various organic ligands for the complexation with target metal ions can be also chemically introduced into the porous polystyrene resin (step 2). In this method the porous polymer–complex is obtained by simple complexation of the chelate resin with metal ions. However, porosity can then be further enhanced through complexation of multivalent metal ions and treatment with an organic solvent (step 3). In the following sections, steps 1 and 3 in Figure 1, which are very important processes to prepare porous polymer complex adsorbents, are described in detail.

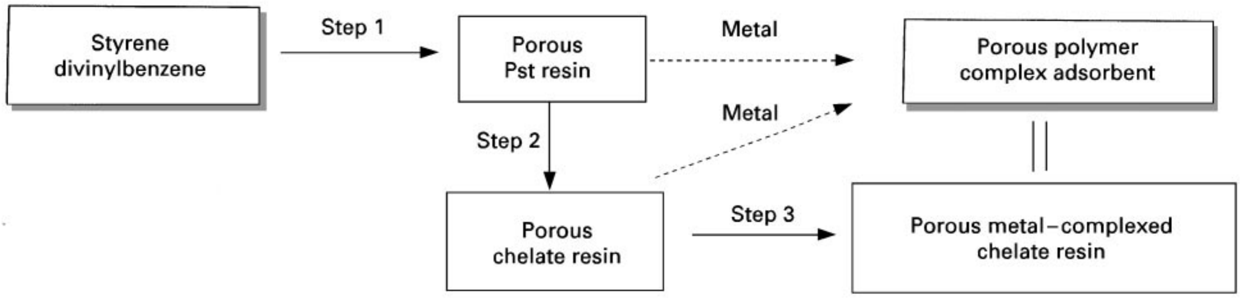

Figure 1 Processes for the preparation of porous polymer metal complexes.

Preparation of Porous Polymeric Resin

As mentioned in the previous section, the polymeric resin itself needs to have a porous structure to prepare porous polymer–metal complexes. Typically, high porosity is provided by the polymerization in the presence of a *porogen*. Generally, there are two methods for the preparation of porous polymers.

Addition of a precipitating solvent as a porogen This method is based on polymerization in the presence of a *precipitating solvent* (porogen) which solubilizes styrene but not polystyrene. Typical precipitating solvents include heptane, *tert*-amyl alcohol (2-methyl-2-butanol), 2-butanol, and isooctane (2,2,4-trimethylpentane). When polymerization is carried out in the presence of these solvents, nanosized microgels (polystyrene gel) are separated during the polymerization from the system as illustrated schematically in **Figure 2**(A). These microgels are connected with each other during the copolymerization and form the three-dimensional network of the polymer beads. The resin obtained is an opaque white colour due to the physical pores formed in the beads. In contrast, polystyrene resin prepared in the absence of the precipitating solvent is transparent. The nature of the beads (pore size distribution, specific surface area, and so on) can be regulated by the kind of porogen used, and various proportions of divinylbenzene and styrene.

Addition of a soluble linear polymer In this case, a molecular imprinting technique is applied for the pore generation. A soluble linear polymer (polystyrene) added as a template in the copolymerization system is incorporated into the resin. This linear polymer is finally eluted by the subsequent treatment of the resin with an appropriate solvent leaving a hole as illustrated in **Figure 2**(B). Instead of a linear polymer, a reverse micelle composed of a surfactant (such as sodium bis(2-ethylhexyl)sulfosuccinate) can also be used as a porogen. Pore size distribution, surface area and total pore volume can be elegantly controlled by the size of reverse micelle formed in the copolymerization system.

Formation of metal complex with porous polystyrene resin These porous polystyrene resins themselves

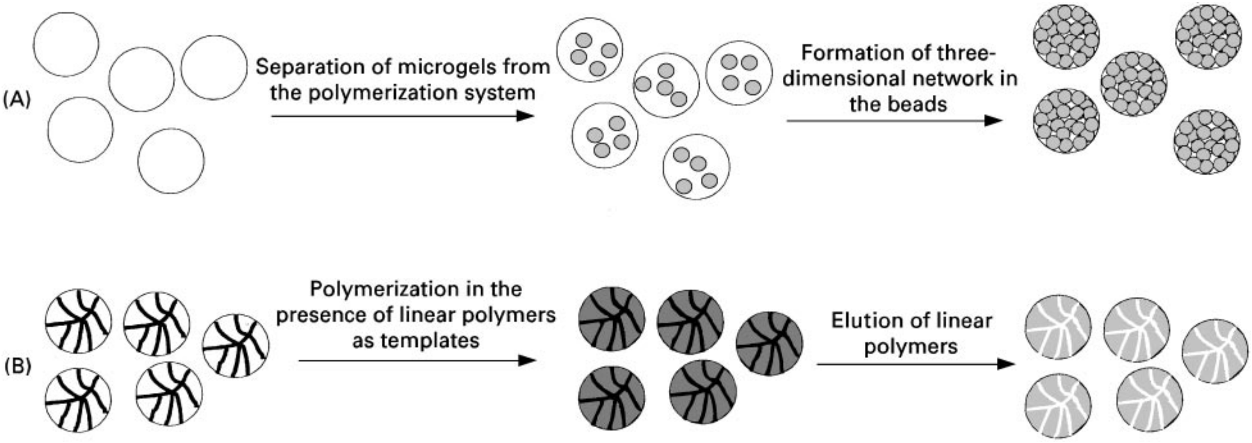

Figure 2 Schematic illustration of the procedures for the preparation of porous crosslinked polystyrene resin. (A) Addition of a precipitating solvent as a porogen. (B) Addition of a soluble linear polymer.

(without chemical modification) are excellent supports of the metal complexes when benzene moieties function as ligands. Double salts such as $AlCuCl_4$ and $AgAlCl_4$ are easily immobilized on the polystyrene beads because they preferentially form complexes with π-ligands such as benzene and toluene. For instance, a porous polymer–metal complex of $AlCuCl_4$ can be prepared by the treatment of $AlCuCl_4$ and porous polystyrene resin in dry carbon disulfide followed by the evaporation of the solvent. Although a toluene solution of $AlCuCl_4$ is very unstable to water, the polymer–metal complex has high water-resistivity due to the protection of the polystyrene matrices. This polystyrene resin-immobilized $AlCuCl_4$ complex functions as an excellent adsorbent of CO (*vide infra*).

Complexation of Porous Polymer to Improve Porosity

The second technique (step 3 in **Figure 1**) to provide high porosity is based first on complexation with metal ions and secondly subsequent treatment with an organic solvent. The porosity of the styrene–divinylbenzene copolymer having iminodiacetic acid (IDA) moieties (chelate resin; CR, see **Figure 5**A) can be regulated by complex formation with metal ions, followed by treatment with organic solvents. Maximum porosity is achieved by complex formation of Fe(III) with chelate resin in water and subsequent washing with methanol ($S = 329.2\ \mathrm{m^2\,g^{-1}}$), whereas no measurable pores are observed without this technique (specific surface area of the original sodium type of the resin is below $0.1\ \mathrm{m^2\,g^{-1}}$). In the following sections, this technique is described in detail.

Treatment with an organic solvent The network of the polymer is not too rigid, but rather flexible when a small amount of crosslinking agent (divinylbenzene for polystyrene resin) is used. Therefore, the porosity of the resin can be altered by solvent treatment before desiccation. Generally, the porosity decreases when the resin swollen with a good solvent (a solvent which has high affinity with the resin) is desiccated whereas it increases by desiccation after treating the swollen resin with a less-swelling solvent. In the case of polystyrene resin, the porosity decreases by the desiccation from toluene; a good swelling solvent. High porosity is obtained when the resin swollen with toluene is desiccated after having been washed with methanol or acetone in which polystyrene resin cannot swell. The same is true for chelate resin-immobilized metal complex (CR–Me). The chelate resin swells in water due to the hydrophilic IDA moieties so that chelate resin dried from water does not exhibit high porosity. A porous polymer–metal complex can be obtained by desiccation after having been washed with organic solvent such as methanol in which CR–Me cannot swell. For example, the specific surface area of CR–Fe(II) complex dried after treatment with methanol is $43.1\ \mathrm{m^2\,g^{-1}}$ whereas that dried from water is as low as $3.2\ \mathrm{m^2\,g^{-1}}$.

The increase in surface area on washing with an organic solvent is attributed to the suppression of shrinkage caused by the desiccation as illustrated in **Figure 3**. The CR–Me complex swollen in water keeps a rubberlike state (state A in **Figure 3**). When the solvent (water) in the resin is exchanged with an organic solvent miscible with water, many microgels are generated by a similar phenomenon to the 're-precipitation' of the polymer (state B). During exchange of the solvent, the resin complex is transformed from the rubberlike state into a glassy state because of the poor swelling in the organic solvent. In this glassy state, the shrinkage of the resin complex by desiccation is suppressed due to the low mobility of the polymer (state C). Consequently, surface area increases because pores produced in the resin complex remain. On the contrary, the resin complex swollen in water shrinks during the evaporation of water because the polymer chains have a high mobility in the rubberlike state (state D).

Efficient exchange of water in the resin with an organic solvent promotes the generation of microgels. Therefore, a solvent of high miscibility with water provides high porosity. The specific surface area of the CR–Fe(II) complex increases monotonously with increase in the solubility parameter δ as shown in **Figure 4**. Solvents with close δ values are very miscible with each other so that a large δ provides large porosity (note that δ of water is 47.9). Maximum porosity ($= 43.1\ \mathrm{m^2\,g^{-1}}$ for CR–Fe(II) complex) is obtained from methanol which has the closest δ value ($= 29.7$) to that of water.

Complexation with metal ions of high valency The porosity of the CR–Me complex is also affected by the metal ions bound on IDA moieties as shown in **Table 1**. Metal ions with high valency are quite effective for providing a large surface area. The CR–Fe(III) complex prepared by desiccation from methanol has a maximum porosity ($S = 329.2\ \mathrm{m^2\,g^{-1}}$), which is about 10 000 times larger than that of the original CR–Na(I) resin dried from water.

Metal ions (divalent and trivalent cations) are immobilized on CR through complex formation with IDA moieties, producing a 1 : 1 complex as shown in **Figure 5**(A). In addition to the solvent treatment, the electrostatic repulsion among the metal ions on IDA moieties also contributes to the suppression of the

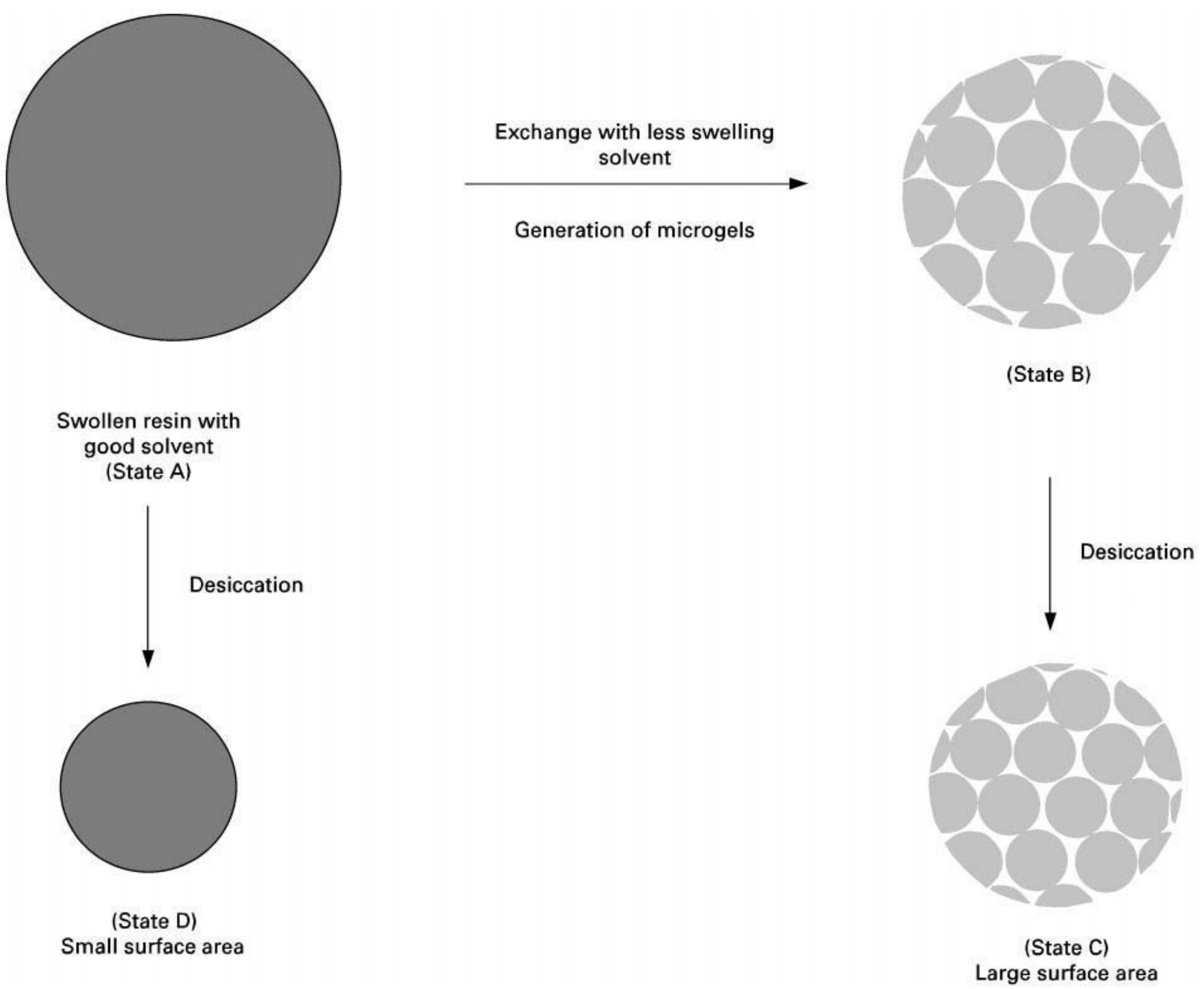

Figure 3 Effect of solvent treatment of the swollen resin on the porosity.

shrinkage, which provides much higher porosity. Since interaction on a molecular level creates these pores, the size of pores generated by this method is smaller than 2.5 nm.

This phenomenon is characteristic of a chelate resin with IDA moieties. The reverse tendency is observed on crosslinked polystyrene sulfonate or polyacrylate. The porosities of these resins is decreased by high valent metal ions because anionic residues are crosslinked by the metal ions through electrostatic interaction as illustrated in **Figure** 5(B), which promotes shrinkage of the resin.

Gas Separation by Porous Polymer–Metal Complexes

Porous polymer–metal complexes prepared as above are available for efficient gas separation. High porosity directly contributes to the rapid adsorption of target gaseous molecules. In addition, the polymer matrix provides the adsorbent with durability against contamination compared with the corresponding monomeric system. In the following subsections, separations of CO, ethylene, and NO are demonstrated in detail.

Adsorption of CO and C_2H_4 by Porous Polystyrene–Immobilized Metal Complex

A toluene solution of $AlCuCl_4$ reversibly absorbs gaseous CO molecules through co-ordination on Cu(I). Thus, immobilization of $AlCuCl_4$ on polystyrene resin provides an excellent solid adsorbent of CO. The adsorbent composed of porous crosslinked polystyrene beads (Bio-Beads SM-2, surface area $300\ m^2\ g^{-1}$) and $AlCuCl_4$ rapidly adsorbs an equimolar amount of CO to the charged Cu(I) within 10 min at 20°C as shown by the solid circles in **Figure 6**. In contrast, it takes more than a day to reach equilibrium when a gel-type resin (Bio-Beads S-X1) is used as a support (open circles).

Since $AlCuCl_4$ complex reversibly coordinates C_2H_4, the same polystyrene–immobilized $AlCuCl_4$

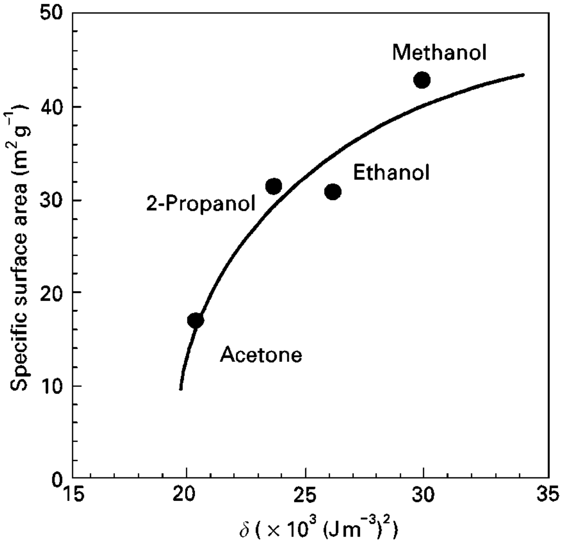

Figure 4 Relationship between the specific surface area and the solubility parameter (δ) of the solvent used for washing the water-swollen CR–Fe(II) complex. The parameter δ corresponds to the square root of the cohesive energy density $(E/V)^{1/2}$, where E and V are the cohesive energy (energy of vaporization) and volume of unit weight of the solvent, respectively. If the δ solubility parameters of the two solvents are close to each other, it indicates that they have high mutual miscibility. Note that the δ value of water is 47.9. (Reproduced with permission from Toshima N, Asanuma H and Hirai H, *Bulletin of the Chemical Society of Japan* 62: 893–902 (1989), p. 901 by courtesy of the Chemical Society of Japan.)

complex also functions as a solid adsorbent of C_2H_4. The same porous solid adsorbent binds 1.40 times as much C_2H_4 as the charged Cu(I) under the identical conditions of CO adsorption described above. Since a double salt of $AgAlCl_4$ binds C_2H_4 reversibly, porous polystyrene–immobilized $AgAlCl_4$ prepared in a same manner as $AlCuCl_4$ system also functions as a solid adsorbent of C_2H_4. In this case, selective adsorption towards C_2H_4 against CO is achieved because it does not show binding activity to CO. Both $AlCuCl_4$ and $AgAlCl_4$ are so water-sensitive that toluene solutions of these double salts lose 70% of gas-binding activity by contact with 9000 ppm of water vapour for 10 min. In contrast, polystyrene-immobilized double salts maintain their initial gas-binding activities after contact with water vapour, due to the protection of the metal complex by the hydrophobic polystyrene.

Adsorption of NO by Porous Chelate Resin–Immobilized Fe(II) Complex

CR–Fe(II) complex The complex of Fe(II) and a polyamine *N*-carboxylate [ethylenediaminetetraacetate acid (EDTA), nitrilotriacetate acid (NTA), and IDA] can bind NO through complex formation. Their aqueous solutions themselves are promising candidates for the absorption of NO because of their high capacity. A solid adsorbent of NO can be prepared by immobilization of above ligand on a polymer chain. For this purpose, the chelate resin involving IDA moieties is available. The porous polymer beads of the chelate resin–Fe(II) complexes which have been demonstrated in the previous section are quite useful as an adsorbent for NO.

Porous chelate resin–immobilized Fe(II) (CR–Fe(II)) complexes are prepared by desiccation of the complex after washing with methanol ($S = 43.1\ \mathrm{m^2\,g^{-1}}$). The CR–Fe(II) complex shows such high NO adsorption capacity that almost all the NO is removed from 6 dm^3 of nitrogen containing 1000 ppm of NO within 25 min, as shown by the solid circles in **Figure 7**. On the other hand, the CR–Fe(II) complex prepared by washing with water ($S = 3.2\ \mathrm{m^2\,g^{-1}}$) does not exhibit such a high adsorbing capability (open circles). The adsorption rate of NO linearly increases with an increase in the specific surface area of CR–Fe(II) complex. This fact clearly demonstrates that the improvement of the porosity contributes directly to rapid adsorption of NO. The adsorbent is completely regenerated by desorption treatment such as keeping the CR–Fe(II)–NO at 90°C under 3 mmHg for 3 h. The CR–Fe(II) complex can be repeatedly used for NO adsorption without significant deterioration.

Nitrogen monoxide is co-ordinated on the Fe(II) ion through 1 : 1 complex formation so that the following Langmuir adsorption isotherm can be applied for the detailed analysis of adsorption properties:

$$\text{CR–Fe(II)} + \text{NO} \overset{K}{\rightleftharpoons} \text{CR–Fe(II)–NO} \qquad [2]$$

$$1/K = (P/[\text{CR–Fe(II)–NO}])[\text{CR–Fe(II)}] - P \qquad [3]$$

where P is the partial pressure of NO (atm) and [CR–Fe(II)–NO] is the amount of the NO adsorbed at equilibrium (mmol). From the linear plots of P against P/[CR–Fe(II)–NO], the effective Fe(II) and the dissociation constant (1/K; atm) can be calculated from the slope and the intercept of the ordinate, respectively. **Table 2** shows the results of Langmuir analyses of CR–Fe(II) complexes with different washing solvents (i.e. different surface area). The K values of each CR–Fe(II) complex is around $8 \times 10^3\ \mathrm{atm^{-1}}$, which does not depend on the washing solvents. The equilibrium constant (K) is even larger than that of an aqueous solution of the Fe(II)–EDTA complex ($5.6 \times 10^3\ \mathrm{atm^{-1}}$). By contrast, the amount of effective Fe(II) ion increases proportionally with the speci-

Table 1 Specific surface area of various chelate resin–immobilized metal complex

Metal	*Specific surface area* ($m^2\ g^{-1}$)*		*Molar ratio of immbolized metal ion to IDA moieties*
	Water†	*Methanol*†	
Li(I)	1.1	6.8	2.0
Na(I)	<0.1	3.3	2.0
K(I)	<0.1	1.6	2.0
Mg(II)	2.5	22.6	1.0
Ca(II)	3.6	33.3	0.94
Sr(II)	3.2	25.1	1.0
Ba(II)	3.5	19.0	1.0
Al(III)	4.7	54.1	0.77
Fe(III)	5.9	329.2	1.0

*BET surface area per 1 g of the chelate resin in the sodium form.
†Solvent used for washing the resin–immobilized metal complex. (Reproduced with permission from Toshima N and Asanuma H, *Polymers for Gas Separation*, p. 157 by the courtesy of VCH Publishers.)

fic surface area caused by washing with an organic solvent. Thus, wash-treatment does not raise the complex formation constant K, but raises the amount of effective Fe(II) ions through an increase in the surface area.

Immobilization of Fe(II) complex on the polymeric resin has another advantage compared with the aqueous Fe(II) complex. As mentioned at the beginning of this section, the complexes of Fe(II) and polyamine *N*-carboxylates (for example, IDA) themselves are promising candidates for the absorption of NO. But an aqueous solution of Fe(II)–IDA, a monomeric model of the CR–Fe(II) complex, readily deteriorates with oxygen through oxidation of Fe(II) to Fe(III) which does not absorb NO. In contrast, the CR–Fe(II) complex has some durability in the presence of oxygen. Both CR–Fe(II) complex and Fe(II)–IDA (each has 16.2 mmol of Fe(II)) can remove more than 90% of NO from 6 dm^3 of nitrogen containing 1000 ppm of NO at room temperature before contact with air. In the case of Fe(II)–IDA complex, however, the amount of adsorbed NO decreases below 20% after contact of the complex with air for 60 min. About 80% of Fe(II) ions are oxidized by this treatment. In contrast, a decrease in the amount of adsorbed NO with the CR–Fe(II) complex is scarcely observed, and more than 50% of initially immobilized Fe(II) ions remain without oxidation. This distinct durability of CR–Fe(II) complex to oxygen is mainly attributed to the absence of water. The oxidation of Fe(II) is accelerated by the presence of water according to the following equation:

$$\mathrm{Fe(II)} + \tfrac{1}{4}\mathrm{O_2} + \tfrac{1}{2}\mathrm{H_2O} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^-} \qquad [4]$$

In the case of Fe(II)–IDA complex, water is inevitably required as a solvent so that oxidation of Fe(II) ions

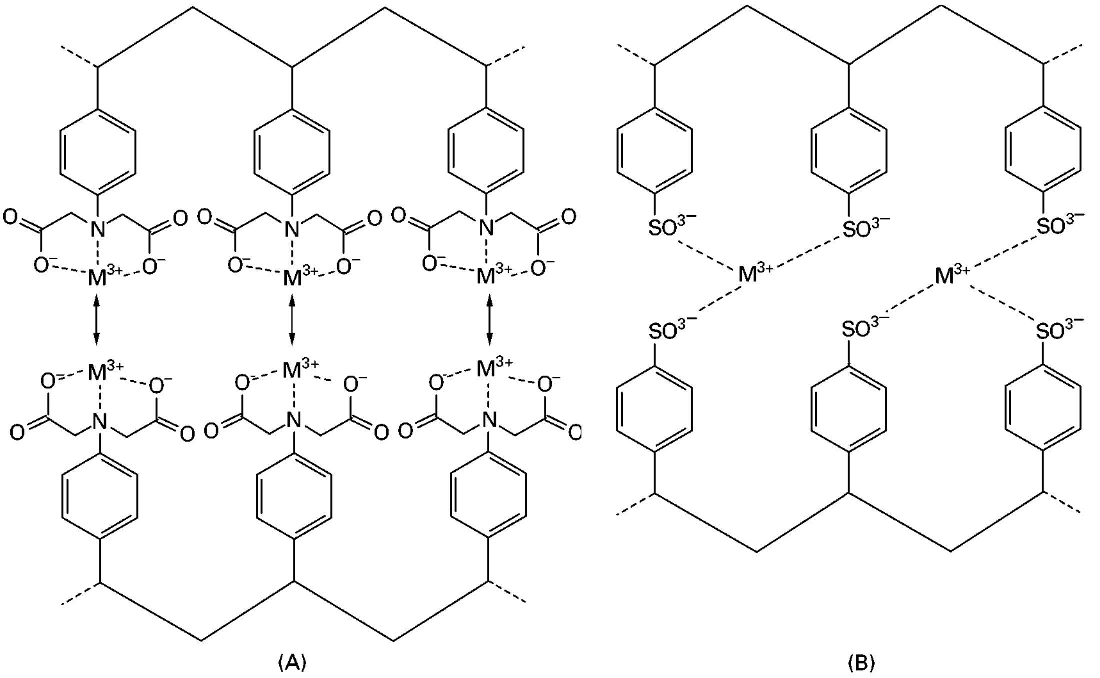

Figure 5 Schematic illustration of the resin–immobilized trivalent metal complex. (A) Chelate resin–immobilized trivalent metal complex. Metal ions are bound to IDA moieties through 1 : 1 complex formation. (B) Polystyrene sulfonate resin–immobilized trivalent metal complex. Ionic moieties are crosslinked by trivalent metal ions through electrostatic interaction. (Reproduced with permission from Toshima N and Asanuma H, *Polymers for Gas Separation*, p. 159 by the courtesy of VCH Publishers.)

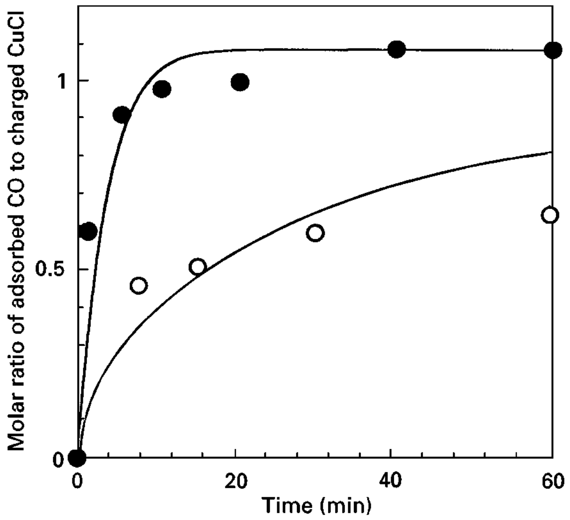

Figure 6 Adsorption of CO by the $AlCuCl_4$ complex supported on the porous polystyrene resin (●) and gel-type polystyrene resin (○) under 1 atm of CO at 20°C. (Reproduced with permission from Toshima N and Asanuma H, *Polymers for Gas Separation*, p. 152 by the courtesy of VCH Publishers.)

proceeds rapidly. The polymer–metal complexes do not need solvents since metal complexes are dispersed on polymeric matrices. This is one of the advantages of polymer–metal complexes. Furthermore, oxidation of Fe(II) ions in CR–Fe(II) is suppressed even in the presence of water, probably due to the protection of the metal complex by the polymer matrix.

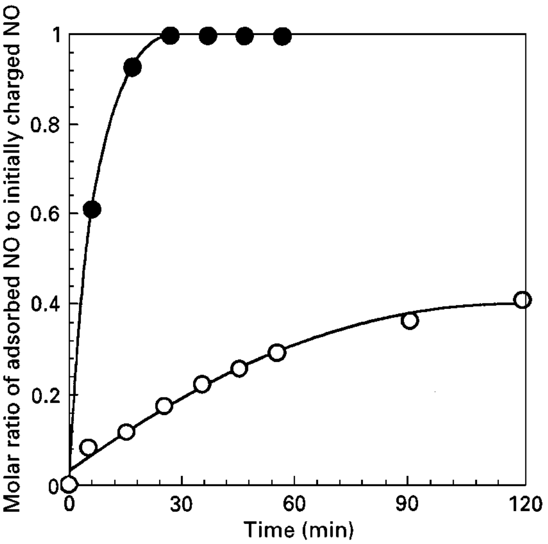

Figure 7 Adsorption curves for NO by the CR–Fe(II) complex prepared by drying after washing with methanol (●) and water (○). These CR–Fe(II) complexes are composed of 8.0 g of chelate resin (involving 21.0 mmol of IDA moieties) and 16.2 mmol of Fe(II) ions. The adsorption experiments are carried out by circulating 6 dm^3 of nitrogen containing 1000 ppm of NO at room temperature at the rate of 1.6 $dm^3\ min^{-1}$. (Reproduced with permission from Toshima N, Asanuma H and Hirai H, *Journal of Polymer Science, Part A Polymer Chemistry* 28: 907–922 (1990), p. 912 by the courtesy of John Wiley.)

Table 2 Effect of the washing solvent on the complex formation constant (K) at room temperature and the effective amount of Fe(II) ions

Solvent	*Effective Fe(II) (mmol g^{-1})*	*Surface area (m^2 g^{-1})*	*K* (10^3 atm^{-1})*
Methanol	0.282	43.1	8.33
Ethanol	0.197	31.1	8.33
Acetone	0.144	17.1	6.67

*Binding constant CR–Fe(II)–NO complex formation as determined from Langmuir plots based on eq. [3]. (Reproduced with permission from Toshima N and Asanuma H, *Journal of Polymer Science, Part A Polymer Chemistry* 28: 907–922 (1990), p. 918 by courtesy of John Wiley.)

Highly porous CR complex with mixed valences of Fe(II) and Fe(III) The CR–Fe(II) complex efficiently adsorbs NO, however, the ratio of the effective amount of Fe(II) ions with respect to total immobilized ions is only 0.14, indicating that the CR–Fe(II) complex does not fully exhibit its potential adsorbing capacity. To obtain the potential ability of CR–Fe(II), further enhancement of porosity is effective. Thus, Fe(III) is incorporated into the CR–Fe(II) complex in order to make the complex more porous. The chelate resin–mixed valence iron complex can be prepared by immobilizing both Fe(II) and Fe(III) ions simultaneously. Immobilization of a large amount of Fe(III) ions is preferable for high porosity. The mixed valence complex composed of 1.27 mmol of Fe(III) and 0.44 mmol of Fe(II) (per 1 g of the chelate resin involving 2.6 mmol of IDA moieties) adsorbs NO much more rapidly as expected. Specific surface area of the mixed valence complex is as large as 128.0 $m^2\ g^{-1}$. Without Fe(III) ions (with 0.62 mmol of Fe(II) ions per 1 g of CR), rapid adsorption is not achieved due to the small porosity ($S = 5.3\ m^2\ g^{-1}$). Langmuir analysis (see **Table 3**) clearly demonstrates the role of each iron ion. Since the binding constant K of NO adsorption by the mixed valence complex is almost the same as that of the CR–Fe(II) complex, the active centre for NO adsorption of the mixed valence complex is identical with that of CR–Fe(II). The amounts of the effective Fe(II) ions for the mixed valence complex and CR–Fe(II) (determined from Langmuir plot) are 0.12 and 0.28 mmol, respectively as listed in Table 3. The value of the efficiency, R, of Fe(II) ions can be estimated from the ratio of the amount of effective Fe(II) to the amount of immobilized Fe(II). The efficiency R of the mixed valence iron complex is larger than that of the CR–Fe(II) complex due to an

Table 3 Amount of effective Fe(II) ions on CR–Fe(II) and mixed valence complex

Complex	*Immobilized ion*		*Surface area* ($m^2\,g^{-1}$)	*K** (10^3 atm^{-1})	*Effective Fe(II)* ($mmol\,g^{-1}$)	*R†*
	Fe(III) ($mmol\,g^{-1}$)	*Fe(II)* ($mmol\,g^{-1}$)				
CR–Fe(II)	0	2.01	43.1	8.33	0.28	0.14
CR–Fe(II), Fe(III)	1.27	0.44	128.1	10.0	0.12	0.26

*Binding constant of CR–Fe(II)–NO complex formation as determined from Langmuir plots based on eqn [3].

†Efficiency of Fe(II) immobilized on chelate resin determined as the ratio of effective Fe(II) to the amount of immobilized Fe(II). (Toshima N and Asanuma H, *Journal of the Chemical Society, Chemical Communications* 1989: 1075–1076, p. 1076 by the courtesy of Royal Society of Chemistry.)

increase in the surface area, demonstrating that the Fe(III) ions work by making the resin porous. The use of these two metal ions enables efficient NO adsorption.

The polymeric resin as well as the metal complex itself greatly affects the adsorbing ability for the target gas molecules as described in the case of CO, C_2H_4, and NO adsorption. It has been demonstrated clearly that large surface area directly contributes to the rapid adsorption of gaseous molecules. In some cases, the nature of the support dominates the whole adsorption property of the polymer–metal complex rather than the nature of the metal complex. Therefore, further regulation of porosity (e.g. pore size distribution) is quite significant in order to achieve efficient separation of the target gas. Metal complexes are promising compounds for reversible coordination of gaseous molecules so that metal complexes immobilized on polymeric supports with properly regulated porosity will provide further useful materials for efficient gas separation.

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POROUS POLYMERS: LIQUID CHROMATOGRAPHY

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Introduction

Polymers have been used as stationary phases in liquid chromatography (LC) for nearly 40 years. Initially they were used for size exclusion chromatography (SEC), a noninteractive means of separating molecules based on their size. This technique was originally applied to water-soluble macromolecules and is often referred to as gel filtration chromatography (GFC). Gel filtration describes the process particularly well: the stationary phase originally described was a lightly cross-linked agarose in bead form, although other polysaccharides and also acrylamide-based materials are still employed today.

Characteristically such microporous gels are extremely soft and can easily be crushed. They do not possess a fixed pore structure and analytes can diffuse in and out of the aqueous swollen polymer particles. As a consequence column pressures must be minimized; reduced liquid flow rates and wide-bore columns are a necessity, resulting in extremely long run times. By 1964 a new polymeric stationary phase had been introduced based on cross-linked polystyrene. This material had sufficient cross-linker (in this case divinylbenzene) to ensure a high degree of physical strength when compared with earlier microporous