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Preparation and characterization of novel porous metal/ceramic catalytic membrane materials

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Abstract

In order to obtain improved separation or catalytic activity, we propose a method to modify the surface of porous ceramic membranes by modifying the surface of sol particles. The key technical difficulty of this method is how to get appropriate ligands which can make metal ions adsorb on sol particles in the appropriate pH range in which the sol maintains its dynamic stability. Pd/γ-Al_2O_3 catalytic membrane materials with mesopore and a narrow pore size distribution were prepared by this method. Other kinds of metal/ceramic catalytic membrane materials such as Ni/γ-Al_2O_3, Pt/γ-Al_2O_3 can also be obtained by the same method.

1. Introduction

Separation systems are one vital part of most industrial processes. Inorganic membranes have the potential for providing separation systems particularly at high temperature. They can significantly reduce both the equipment and operating costs [1]. In addition, the performance of inorganic membrane reactors generally depends on the separation capability of inorganic membranes. So there has been a significant growth of interest in research and application of inorganic membranes.

The study of the potential feasibility of inorganic membranes in high-temperature petrochemical applications including hydrogen separation and membrane reaction concerning dehydrogenation is the aim of our work. So metal/ceramic catalytic membranes have been examined. According to the distribution pattern of the metal component, metal/ceramic catalytic membranes can be classified into three types (Fig. 1). In type 1, metals directly form dense or porous membranes which can be supported on porous ceramic membrane [2]. In type 2, metals are deposited inside the porous framework of ceramic mem-

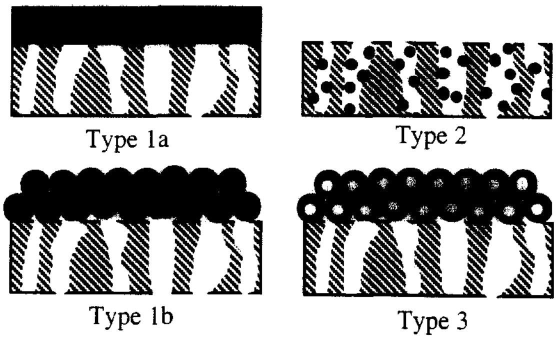

Fig. 1. The texture of the metal/ceramic catalytic membranes.

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branes [3]. In type 3, metals are coated on solid particles which are partly sintered into inorganic membranes [4]. In this paper, a method of modifying the surface of sol particles is proposed to get type 3 metal/ceramic catalytic membrane materials.

2. Experimental

2.1. Determination of the amount of adsorption as a function of pH

(1) Put 0.1–0.4 g solid particles into a conical flask and add a given volume of distilled water. In this way, one gets ten to fifteen samples. These samples are aged for about 4 h in order to hydrate the surface of solid particles.

(2) Add a given volume of the standard solution containing metal ions and ligands into the conical flasks in which the concentration of metal ions is ca. 10^{-4} M and the total volume of each sample is 100 ml.

(3) Adjust the pH of each sample to desired level with 0.1 M HAc or $NH_3 \cdot H_2O$ so that the pH of these samples is uniformly distributed in the designed range.

(4) The samples are shaken at constant room temperature for about 4 h in order to attain chemical equilibrium.

(5) The pH of each sample is measured using Cole Parmer 5986-50 pH meter with the combination glass electrode. The pH meter is corrected by NBS buffering standard solution. The equilibrium solution is separated from solid particles by centrifugation and used for quantitative analysis of metal ions by a spectrophotometric method. Percentage of adsorption can be calculated by the following equation. Lastly, E% vs. pH is plotted.

$$E\% = \{[X_{\text{total}}] - [X_{\text{equi}}]\} / [X_{\text{total}}] 100\%$$

$E\%$: Percent of adsorption
X_{total}: Total amount of metal ions in the suspension
X_{equi}: The amount of metal ions in the solution after adsorption equilibrium.

2.2. Preparation of metal/ceramic catalytic membrane materials

In principle, the method of modifying the surface of sol particles is based on adsorption of metal ions on sol particles. Metal ions and ligands are added into ceramic membrane precursor-sol. Adsorption of metal ions on sol particles takes place during stirring. This kind of sol is called modified sol. Modified sols are concentrated by drying at room temperature and converting into lyogel. Lastly, the resulting lyogel is calcined at 600°C for 3 h in air atmosphere to get metal/ceramic catalytic membrane materials.

2.3. Characterization

Particle size of the sols is measured by Zetasizer 3 (Malvern Instruments) using photon correlation spectroscopy with measuring sol particle diameters in the range from 5 to 5000 nm.

Nitrogen adsorption–desorption isotherms at 77 K are obtained with ASAP 2000 (Micrometerics Corporation). The pore size distribution analysis is performed following Kelvin equation. According to BET theory, specific surface areas are calculated.

3. Results and discussion

3.1. Adsorption of metal ions on solid particles as a function of pH

The method of modifying the surface of sol particles has some technical difficulties. This is because some metal ions cannot, to practical extent, adsorb on sol particles in the pH range in which ceramic membrane precursor-sol maintains its dynamic stability. So it is necessary to find some compounds which can complex with metal ions in order to enhance adsorption of metal ions on sol particles in acidic solution. In this case, percent of adsorption of metal ions as a function of pH in the presence of different ligands was

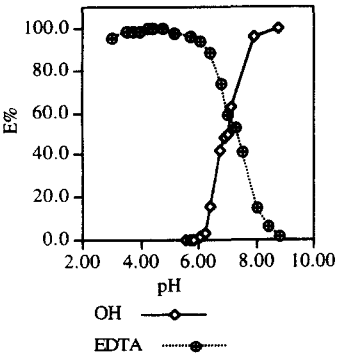

Fig. 2. Adsorption of Ni^{II} on solid particles as a function of pH in presence of different ligands.

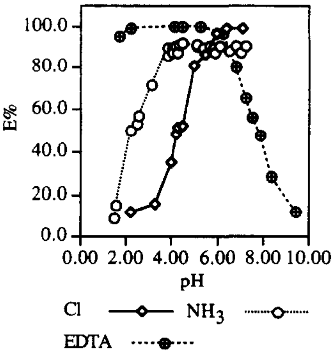

Fig. 3. Adsorption of Pd^{II} on solid particles as a function of pH in presence of different ligands.

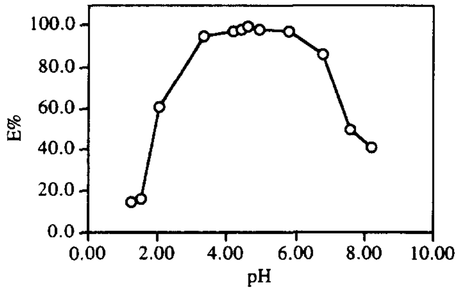

Fig. 4. Adsorption of Pt^{IV} on solid particles as a function of pH in presence of ligand Cl^-.

determined in order to find the above mentioned compounds.

γ-Al_2O_3 is one of the most important supports for catalysis. Moreover, γ-Al_2O_3 membranes are commercially available. Nickel, palladium and platinum are catalysts for hydrogen-concerned reactions. So our investigation focused on how to obtain Ni/γ-Al_2O_3, Pd/γ-Al_2O_3 or Pt/γ-Al_3O_3 catalytic membranes.

Fig. 2 shows that there exist two kinds of *E%* vs. pH. In the presence of OH^-, percent of adsorption of Ni^{II} on γ-Al_2O_3 particles vs. pH looks like a shaped S, in this way, this kind of *E%* vs. pH is named ‘type S’. In the contrary, percent of adsorption of Ni^{II}-EDTA on γ-Al_2O_3 particles vs. pH is just like a reverse shaped S, which is called ‘type reverse S’. As shown in Fig. 2, Ni^{II}-EDTA can adsorb as much as 100% in the pH range from 3 to 4 in which boehmite sol maintains its dynamic stability. Therefore, EDTA meets the requirement of the method of modifying the surface of boehmite sol particles to obtain Ni/γ-Al_2O_3 catalytic membranes.

In Fig. 3, percent of adsorption of Pd^{II}–Cl^- or Pd^{II}–NH_3 on γ-Al_2O_3 particles vs. pH is type S. But using EDTA, the type reverse S was obtained. So, NH_3 and EDTA can be used to prepare Pd/γ-Al_2O_3 catalytic membranes.

As shown in Fig. 4, the amount of adsorption of Pt^{IV}–Cl^- on γ-Al_2O_3 particles attains to maximum in the pH range from 3 to 4. In this way, Cl^- also meets the requirement to modify the surface of boehmite sol particles.

3.2. Preparation of Pd/γ-Al_2O_3 catalytic membrane materials

The experimental results mentioned above were obtained in the systems of metal ions —γ-Al_2O_3 particles. Does the difference between γ-Al_2O_3 particles and boehmite sol particles limit the application of the experimental results? In consideration of this, without or with the ligand EDTA, adsorption of Ni^{II} on boehmite sol particles was examined. The equilibrium solution was separated by cellulose nitrate filter with pore diameter 20 nm (Sortorius, Germany). The pH of the equilibrium solution is 3.51. Without EDTA, percent of adsorption of Ni^{II} on boehmite sol particles is less than 5%. But with EDTA, it is more than 65%. This result is similar to that in Fig. 2. Therefore, the interaction between Ni^{II} and boehmite sol particles is comparable to that between Ni^{II} and γ-Al_2O_3 particles.

In this paper, Pd/γ-Al_2O_3 catalytic membrane materials were prepared as an example of metal/

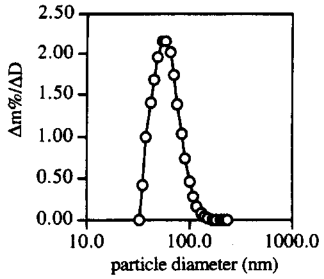

Fig. 5. Particle size distribution of Pd^{II}-modified boehmite sol (2% Pd wt./γ-Al_2O_3 wt.).

Table 1
Particles size and their distribution of modified-sols

Pd (Pd wt./γ-Al_2O_3 wt.)	1	2	3	4
D^a (nm)	59.6	83.5	98.1	95.4

[a] Diameter of sol particles.

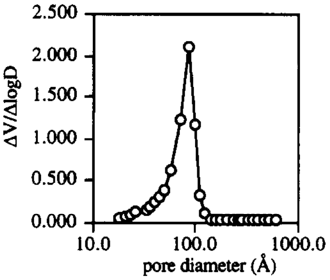

Fig. 6. Pore size distribution of catalytic membrane material (2% Pd wt. /γ-Al_2O_3 wt.).

Table 2
Pore size and their distribution of Pd/γ-Al_2O_3 catalytic membrane materials

Pd (Pd wt./γ-Al_2O_3 wt.)	0.5	1.0	1.5	2.0
P^a (nm)	5.48	5.56	6.45	6.47
S (m^2/g)	267	271	240	253
V (cm^3/g)	0.474	0.483	0.472	0.497

[a] Pore diameter.

ceramic catalytic membrane materials by modifying the surface of sol particles.

Four samples of Pd^{II}-modified boehmite sol with different palladium concentrations were prepared. Pd^{II}-modified boehmite sol shows a narrow particle size distribution up to 4% (w/w) Pd/γ-Al_2O_3 (Fig. 5). The sol particle diameter increases from 59.6 to 95.4 nm with increasing Pd^{II} concentration (Table 1). Moreover, Pd/γ-Al_2O_3 catalytic membrane materials were obtained for pore size and their distribution analysis. Fig. 6 shows that Pd/γ-Al_2O_3 catalytic membrane material possesses very narrow pore size distributions corresponding to its sol particle size distribution. As shown in Table 2, the average pore size of Pd/γ-Al_2O_3 catalytic membrane materials (ca.6 nm) is not obviously affected by addition of palladium salt. It is expected that other kinds of metal/ceramic catalytic membranes such as Ni/γ-Al_2O_3, Pt/γ-Al_2O_3 can be prepared by the same method.

4. Conclusion

Pd/γ-Al_2O_3 catalytic membrane materials with mesopore and a narrow pore size distribution can be prepared by a method of modifying the surface of sol particles. Other kinds of metal/ceramic catalytic membrane materials can also be obtained by the same method. Because metal ions adsorb on sol particles in advance, metal ions do not affect the substrate during slipcasting. Their hydrogen separation and catalytic performance will be examined.

Acknowledgements

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