Characterization of the Polymer-Supported Phase Transfer Catalyst

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Synopsis

Polymer-supported phase transfer catalysts, which were prepared by immobilizing tributylamine on chloromethylpolystyrene, were characterized by optical microscope, SEM, EPMA, and ESCA. Both optical photograph and electron micrograph showed that the exterior surface of polymer support became wrinkly after immobilization in dry condition. The surface of the triphase catalyst may become smooth after being swelled by solvent. From the ESCA analysis in a depth of about 100 Å, it was found that 46.5% of covalent chloride in chloromethylpolystyrene had reacted with tributylamine and converted to quaternary ammonium chloride. However, the EPMA, which analyzed in a depth of about 1 μm, gave a value of only 31% and the titration method which was for the whole bead gave 14.3%. These results reveal that the catalyst has a higher content of quarternary ammonium chloride in the outer shell. It is concluded that the high activity of this catalyst is due to the fact that it contains both hydrophobic and hydrophilic groups on the exterior surface, and more active species in the outer shell.

INTRODUCTION

Because of the advantages of high reaction rate and product specificity, studies on the phase transfer catalysis have increased dramatically since its introduction in the latter 1960s.[1-6] Recently, Freedman[7] reports that over 65 different types of organic compounds can advantageously be synthesized by this new catalytic method. He also indicates that its industrial impact is significant and its potential is even more so.

It is well known that the solid-supported catalysts have their advantages of easy separation and reuse. After a fruitful development in phase transfer catalysts, the immobilization of phase transfer catalysts has been the research subject of many investigators.[8-12] The immobilized phase transfer catalyst, known as the triphase catalyst, was first investigated by Regen,[8,9] who also pointed out many potential applications of these catalysts. Among some materials, the polymer is the most suitable support for immobilizing the phase transfer catalysts.

In two previous studies[13,14] on the reaction between benzyl chloride and sodium bromide, we used two different phase transfer catalysts. One of these catalysts is tetrabutylammonium bromide (QBr), which is soluble in water and slightly soluble in toluene; hence the reaction system is two-phase (liquid–liquid). The other is a polymer-supported one, which is prepared by immobilizing tributylamine in chloromethylpolystyrene; hence the reaction

system is three-phase (triphase). We have found that the activation energy of the triphase reaction is lower than that of the liquid–liquid reaction and that the reaction rate of the triphase reaction is faster than that of the liquid–liquid reaction when the same milliequivalents of quarternary ammonium ions are used.

There are several possible reasons for the higher reaction rate constant (basis on the same milliequivalents), such as the following:

(1) In the liquid–liquid reaction, even under the condition that the third liquid phase presents,[15] only a small amount of QBr added takes part in the reaction, because most of the QBr still stays in the aqueous phase.
(2) The triphase catalyst particles tend to stay at the interface between the aqueous and organic phases and can react with benzyl chloride from the organic phases and sodium bromide from the aqueous phase easily.
(3) The triphase catalyst particles contain both hydrophobic and hydrophilic sites which can attract both toluene and water and hence have more chance to react with benzyl chloride and with sodium bromide.
(4) The active species (QBr and QCl) in this triphase catalyst are nonuniformly distributed. The outer shell is more active.

This work is for the purpose of understanding whether or not that the high activity of the triphase catalyst is due to the nonuniform distribution of active species and the capability to contact both organic and aqueous phases.

Many chemical reactions take place at the particle surfaces. Surface morphology and chemical nature are very important in the surface reactions. There are several techniques to characterize the heterogeneous catalysts.[16] Among those techniques, electron spectroscopy for chemical analysis (ESCA), ion scattering spectroscopy (ISS), secondary ion mass spectroscopy (SIMS), and Auger electron spectroscopy (AES) are usually used to measure the atomic composition of the surface. From ESCA analysis[17,18] we can get the valence state of elements of surface about 100 Å analysis depth. Those new surface characterization techniques were developed very fast in the last decade.

Although there were a tremendous number of studies on the surfaces of inorganic catalysts, the study of surface characterization of polymer supported catalyst[19] is just beginning. Reilley et al.[18] investigated the polymer-anchored metal complex. Tang et al.[20] used ESCA to characterize commercialized ion exchange resin.

Of course, there are several other techniques, such as scanning electron microscope (SEM), electron probe microanalyzer (EPMA), transmission electron microscope (TEM), and electron paramagnetic resonance (EPR), to characterize catalysts. Those techniques are helpful for the understanding of catalyst preparation, fabrication, and application.

In this work, the triphase catalyst which was prepared by quaternizing tributylamine in chloromethylpolystyrene was characterized by using optical microscope, SEM, EPMA, and ESCA.

EXPERIMENTAL

Preparation of the Triphase Catalyst

Chemicals

Tributylamine was purchased from Merck Co. Chloromethylpolystyrene crosslinked with 2% divinylbenzene (Merrifield polymer, 2.6 meq Cl/g, 200–400 mesh) was purchased from Fluka AG. Other chemicals and solvents were analytic grade. They were used without further purification.

Quaternization of Tributylamine with Chloromethylpolystyrene

The triphase catalyst used in this study was prepared by quaternizing tributylamine with chloromethylpolystyrene. The procedure described as follows[21]: A mixture of 6.0 g of chloromethylpolystyrene and 12 g of tributylamine was deaerated under vacuum and heated at 65°C for 5 days. The resin was filtered and successively washed with water, methylene chloride, ethanol, methylene chloride, and methanol. After drying under vacuum at 60°C for 3 h, triphase catalyst was obtained.

Determination of Ionic Chloride Content

Weigh into 100 mL beakers about 0.5 g of the sample, the particle size of triphase catalyst being 200–400 mesh, add one drop of phenolphthalein indicator solution, and titrate the solution with $0.025N$ $Hg(NO_3)_2$ solution until a blue violet color, as viewed by transmitted light, persists throughout the solution for at least 15 s. The ionic chloride content measured is 0.37 meq/g.

Preparation of the Specimens for Surface Characterization

SEM Image Specimen

Because the electric charge will build up rapidly in a nonconducting specimen, it is necessary to deposit carbon on the surface of SEM specimen. A recommended way that we used to fix a powder is to shake some of it over a piece of double-sided adhesive tape. It should not be compressed or compacted, to prevent the morphology from changing. Specimens were measured with a JEOL JSM 35CF scanning electron microscope (resolution is about 60 Å).

EPMA Specimen and Operation

As the SEM image specimen, we must deposit carbon on the surface of the EPMA specimen. Samples for EPMA were mounted on NaBr (or KI etc.). This pellet size is 15 mm in diameter and about 5 mm in height. The specimen was also analyzed with a JEOL JSM 35 scanning electron microscope. The diameter of the electron probe is about 1 μm. We did quantitative analysis for

12 different points. The chloride was detected with WDS detector (use PET crystal). The operating condition was 18 keV for 20 s.

ESCA Specimen

The particle size of triphase catalyst is 200–400 mesh. The pressure of ultrahigh vacuum system of ESCA is very low. The catalyst must be mounted to prevent the catalyst from scattering around the vacuum system. The pellet size is 15 mm in diameter and about 5 mm in height. The specimen was analyzed with a Perkin-Elmer PHI/1905 ESCA. From the overall scan of ESCA, we can survey all the elements on the surface. Each sample took about 20 min for narrow scan of ESCA.

RESULTS AND DISCUSSION

Images of Optical Microscopy and Scanning Electron Microscopy

Figure 1 is the optical photograph of chloromethylpolystyrene which is used as the support. Figures 2(a)–2(c) show the optical photographs and electron micrographs of the triphase catalyst. Obviously the surface of this catalyst is quite different from that of the support (Fig. 1). From Figure 2(b) it is clear that there are a lot of wrinkles of the surface of this triphase catalyst in dry condition while the surface of support is relatively smooth.

Figure 3 shows the surface of support. Figure 3(a) is the image of the backscattered electron of SEM. Those surfaces of the specimen facing the electron source appear bright, while those facing away from the electron source are nearly completely black. Figures 3(b) and 3(c) are the images of the secondary electron of SEM. We can find that there are a lot of micropores on
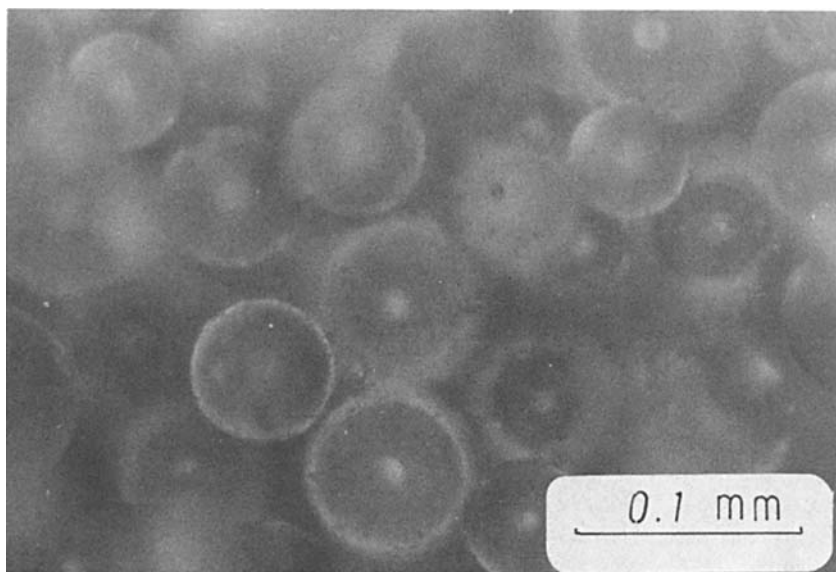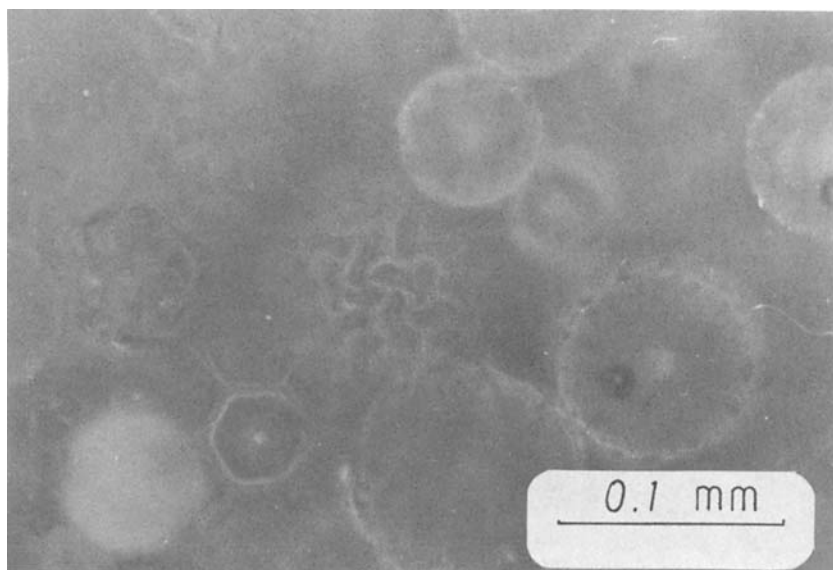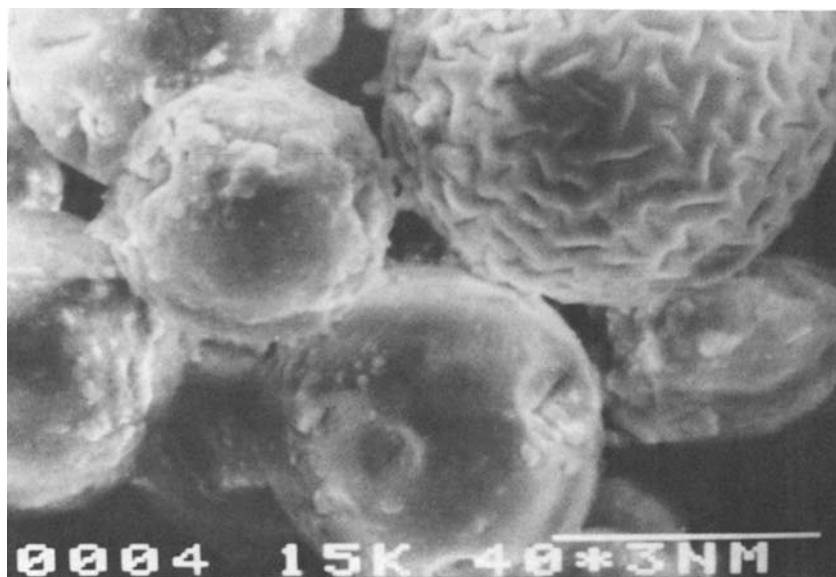

Fig. 1.   Optical photograph of chloromethylpolystyrene (the catalyst support).

(a)

(b)

Fig. 2. Optical photograph and electron micrographs of the triphase catalyst: (a) optical photographs; (b, c) SEM images.

the surface of support. It is quite different from the surface of the triphase catalyst which has wrinkles and cracks on its surface in dry condition. In wet condition the triphase catalyst will be swelled by solvent so that the surface may become smooth. Figure 4 is the topograph of the triphase catalyst. Samples for ESCA were mounted on NaBr (or KI etc.). Figure 5 is the optical microscopy of ESCA sample.
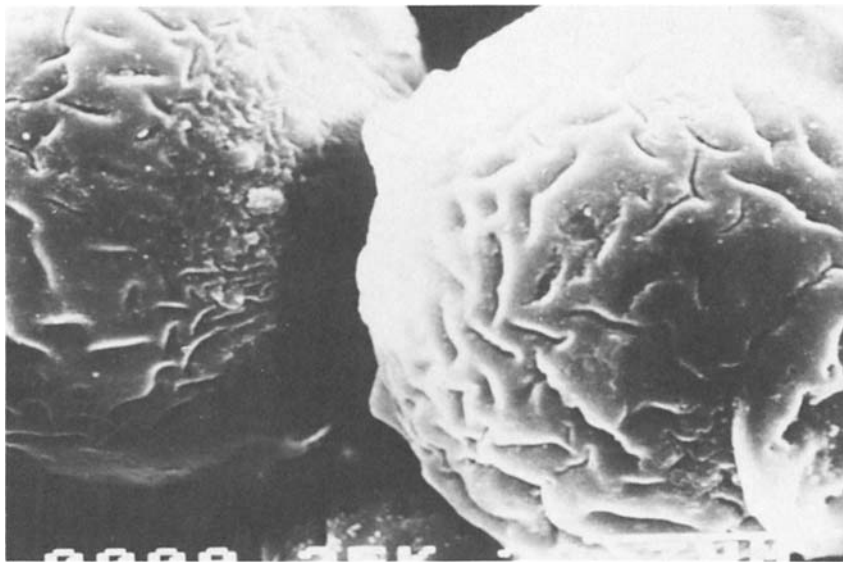
(c)

Fig. 2. (*Continued from the previous page.*)

Electron Spectroscopy for Chemical Analysis ESCA [X-Ray Photoelectron Spectroscopy (XPS)]

From this surface technique we can get the valence state and elements of surface about 100 Å analysis depth. Since the triphase catalyst is prepared from tributylamine, chloromethyl-polystyrene, and divinylbenzene, the support is composed of carbon, hydrogen, and chlorine. The line positions from Mg X-rays are as follows: C ls 287eV, N ls 402 eV, Cl 2p 199 eV, Br 3d 69 eV.

Figures 6 and 7 are the ESCA results of support and catalyst. Figure 6(a) reveals that the elements of C, Cl, Si, and O are present on the surface of catalyst. Figure 6(b) is the narrow scan of ESCA; it shows that the line position of covalent chlorine is 203 eV. From the narrow scan we can recognize the position of the peak and distinguish different valence states of element. Figure 7 is the surface analysis of the triphase catalyst. We can split Cl 2p lines into two peaks for covalent chlorine and ionic chlorine, respectively.

The elements present in a specimen could be identified by the directly or indirectly excited X-ray spectra. The area analyzed is quite large (about 1 mm^2). On the other hand, a focused electron beam was used to excite a very small area on a specimen for the EPMA (about 1 μm^2). We can see that the ESCA result of surface composition is more reliable.

Figure 7(a) is the overall scan of ESCA. It shows the surface condition of the immobilized catalyst. There are C, Cl, Si, O, and N elements on the surface. The analysis of ESCA spectra into two components is based on a Gaussian line shape. After the curve fitting, we observed that the peak position of covalent chlorine is 203 eV and the peak position of ionic chlorine is 201.6 eV. It means that the binding energy of ionic chlorine is lower than the binding energy of covalent chlorine.

From Figures 6 and 7 it is easy to find the difference between the support and the triphase catalyst. According to the result of ESCA there are 46.5%
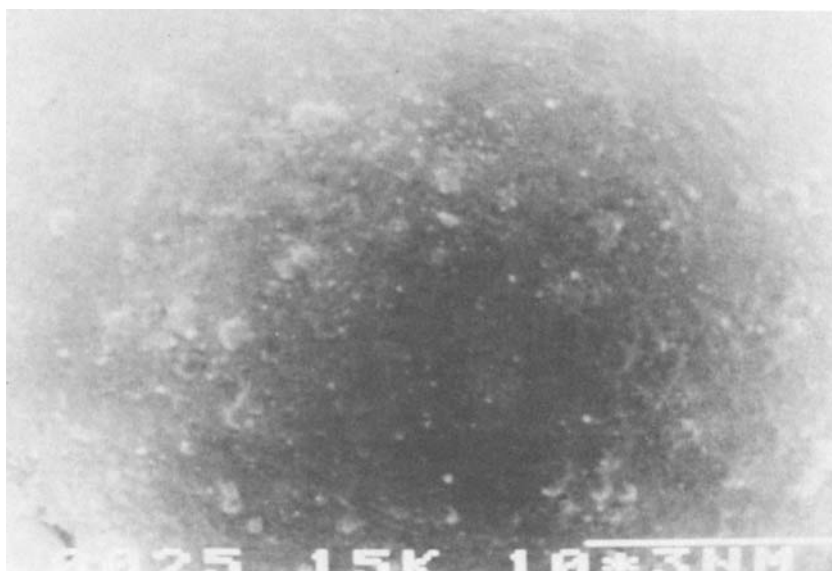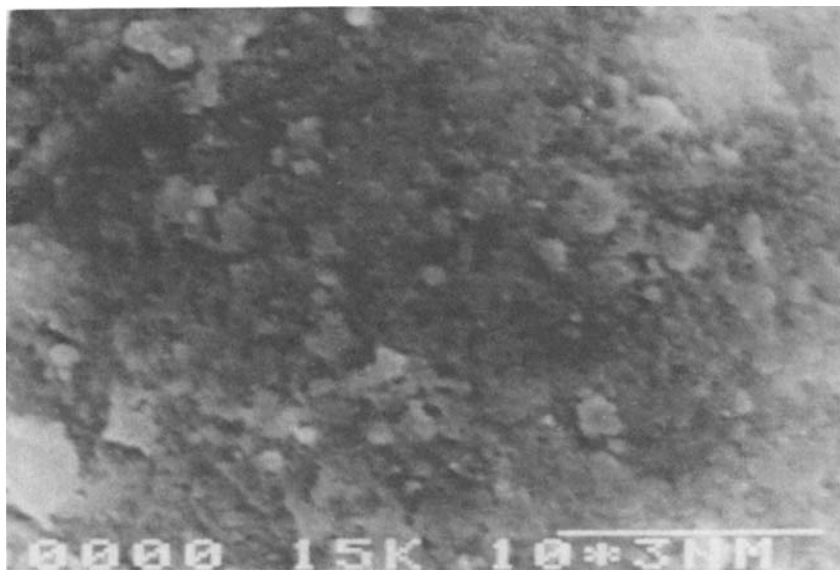
(a)
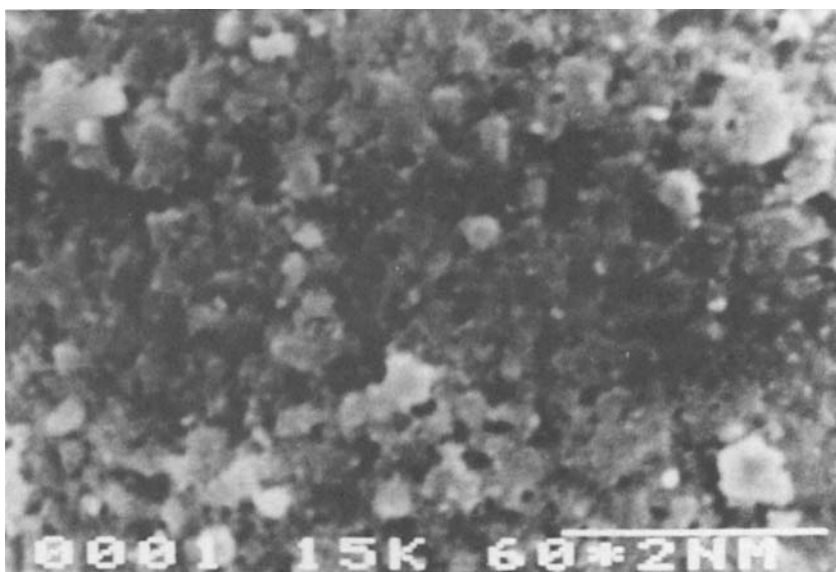
(b)

Fig. 3.   SEM images of the catalyst support: (a) backscattered electron; (b) secondary electron; (c) secondary electron.

(c)

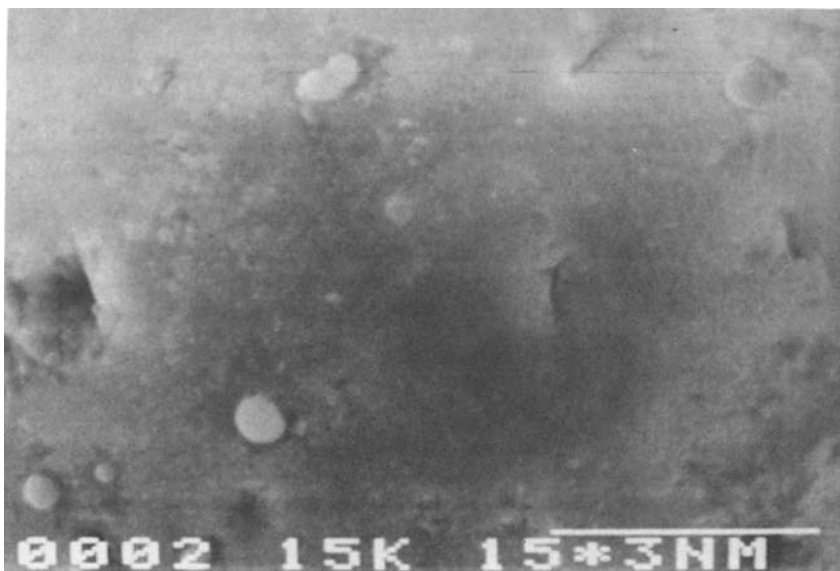Fig. 3. (*Continued from the previous page.*)
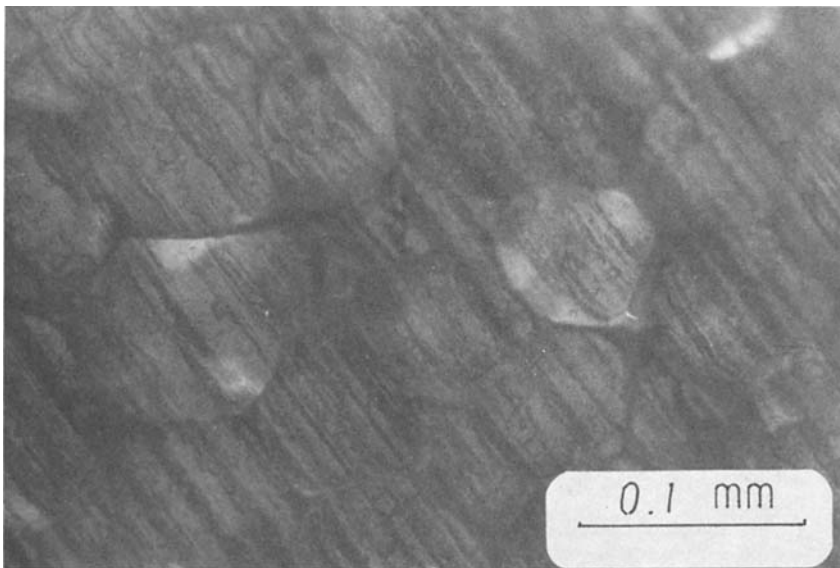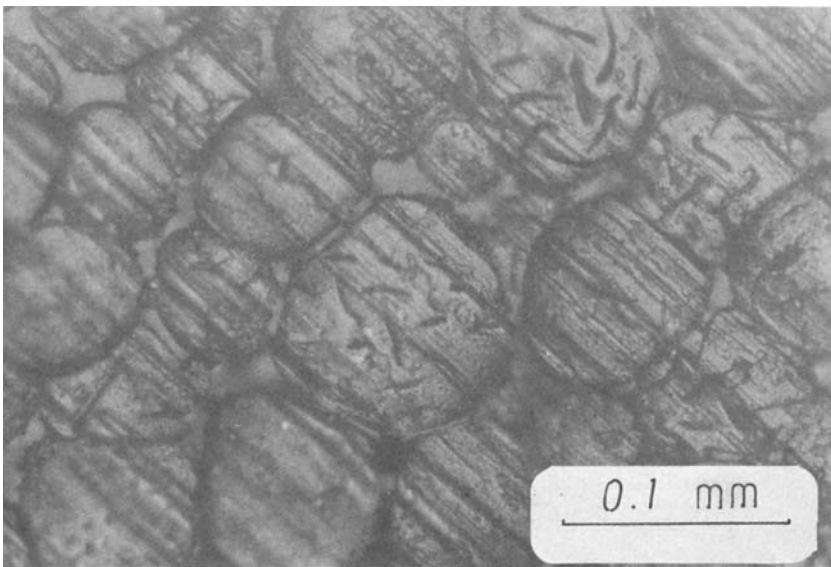

Fig. 4. Topograph of the triphase catalyst.

(a)

(b)

Fig. 5.   Optical photographs of the specimens for ESCA and EPMA: (a) catalyst support; (b) triphase catalyst.
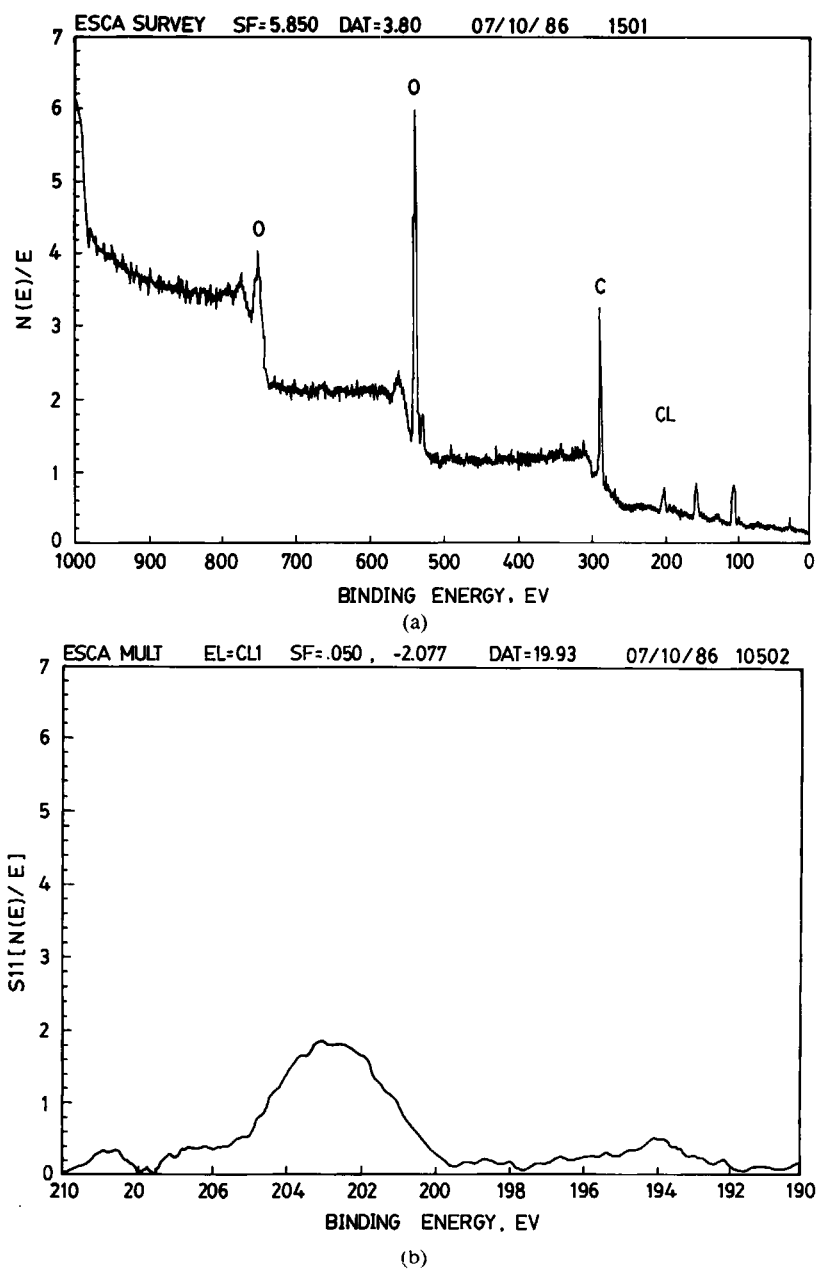
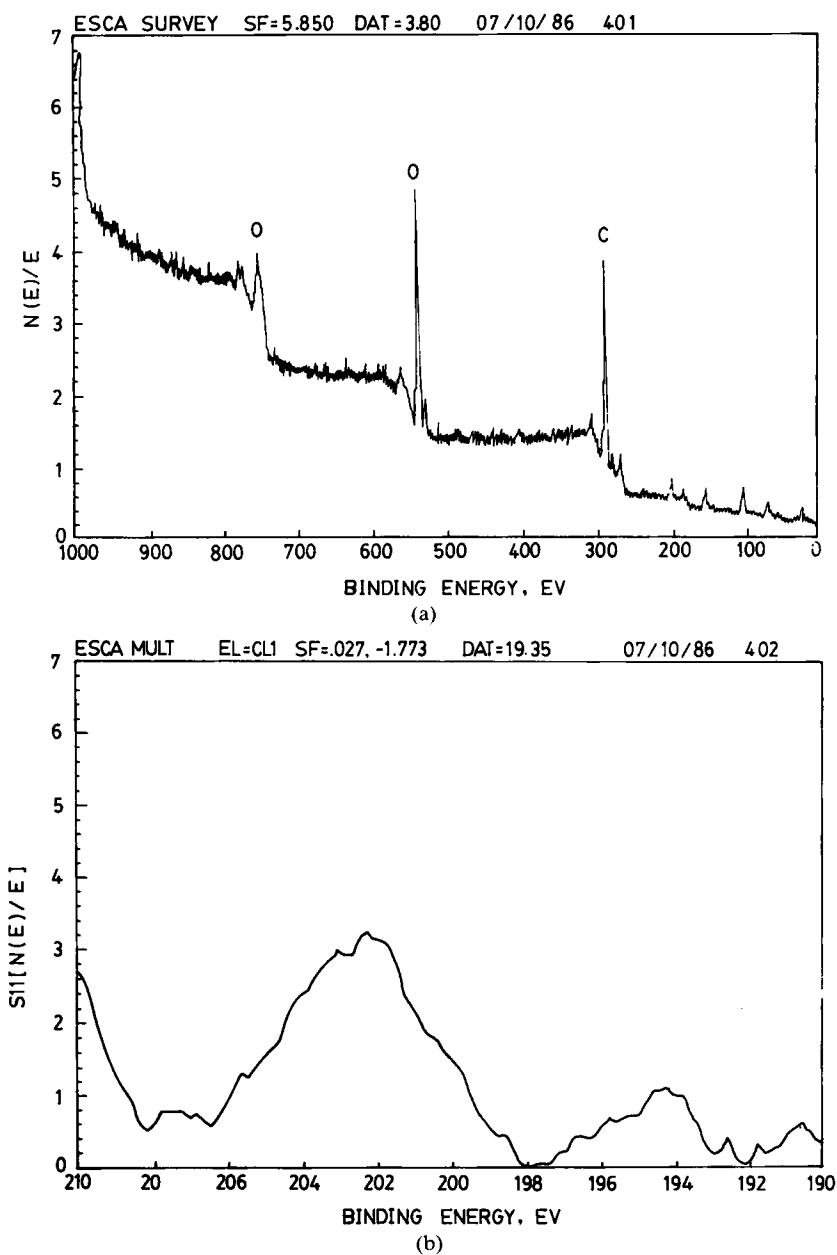Fig. 6.   ESCA spectra of the catalyst support: (a) overall scan; (b) narrow scan.

Fig. 7. ESCA spectra of the triphase catalyst: (a) overall scan; (b) narrow scan for Cl element.
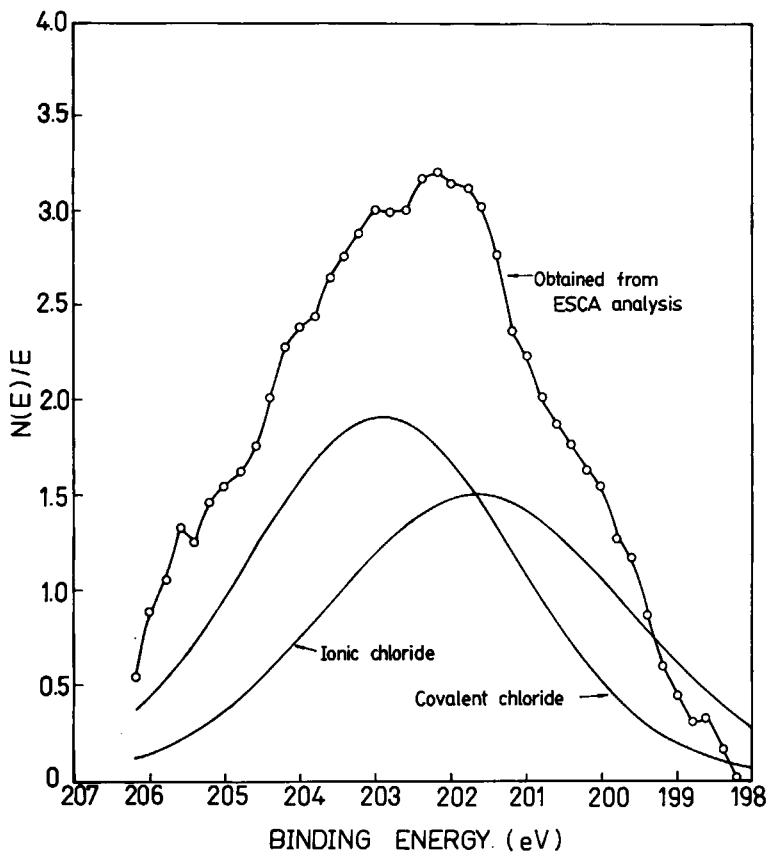
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Fig. 8. Curve fitting of the ESCA spectrum for chlorides based on a Gaussian line shape.

covalent chlorine to react with tributylamine on the surface (calculated from Fig. 8). In addition, chlorine in the support is covalent while that in the catalyst may be ionic or covalent. The existence of an N element in the catalyst shows that tributylamine had been immobilized.

Electron Probe Microanalyzer (EPMA)

The electron probe microanalyzer is one of the most powerful instruments for the microanalysis of inorganic and organic materials. Quantitative analysis can be obtained at many different points with a precision about 1–2%. The usefulness of the EPMA is that compositional information, using characteristic X-ray lines, with a spatial resolution of the order of 1 μm can be obtained from a sample. An electron probe has a diameter of approximately 0.1–1 μm on the specimen. It means electrons produce X-rays from a volume often exceeding 1 μm in diameter and 1 μm in depth.

There are two different X-ray spectrometers. The operating character of WDS (wavelength dispersive spectrometers) is crystal diffraction and of EDS (energy dispersive spectrometers) is silicon energy dispersive. The minimum useful probe size is about 2000 Å for WDS and is about 50 Å for EDS. The distinct advantage of WDS is its good resolutions (about 5 eV). The resolution

TABLE I
Analysis of Ionic Chloride in the Triphase Catalyst

Analytical method	Titration	EPMA	ESCA
Analysis depth			
beneath the surface	All bead	1 μm	100 Å
Percentage			
of quaternization	14.3%	31%	46.5%

of EDS is 150 eV. The best features of the EDS is its speed, which can result in a qualitative analysis in a matter of minutes. For WDS it will take 10 min to 1 h.

For quantitative X-ray microanalysis we use a WDS spectrometer. From the experimental result of chlorine it shows there are 31% active positions immobilized with tributylamine. The active species also have nitrogen element, but nitrogen is a light element. The mass absorption coefficients for long wavelength X-rays (such as the long wavelength Kα lines of the light elements) are not well known. For the light element it is not easy to get a precise quantitative analysis by EPMA. From the result of ESCA and EPMA it shows that more tributylamine has been immobilized near the support surface.

The Ionic Chloride Content in Triphase Catalyst

The ionic chloride content of the triphase catalyst used in the study is measured as 0.37 meq Cl/g. Because chloromethylpolystyrene contains 2.6 meq Cl/g, the percentage of quaternization is only about 14.3%, which is the percentage of chloride in the whole bead converted to the ionic ones. From the results of ESCA and EPMA it is known that the percentages of quaternization are 46.5 and 31%, respectively. These results reveal that the outer shell of the triphase catalyst has more ionic chloride than the inner core because the values of 46.5 and 31% are much higher than 14.3%, which is of the whole bead. It means that the active species are not uniformly dispersed (Table I) throughout the support. This kind of distribution is good for reaction because most of active species is in the outer shell.

Hydrophilicity and Ionic Chloride Content

Chloromethylpolystyrene is a hydrophobic polymer support though less hydrophobic than polystyrene. However, it becomes less hydrophobic when it is quaternized with tributylamine. Whether it is hydrophobic or hydrophilic depends on the extent of quaternization. The hydrophilicity of this triphase catalyst plays an important role in two physical processes in the phase transfer catalysis. These two physical processes are the contact of triphase catalyst with organic and aqueous phases and the diffusion of the organic and inorganic reactants in the catalyst pores. If the catalyst has a "proper" hydrophilicity, then it can attract both organic and inorganic reactants and both organic and inorganic reactants can diffuse into the pores more easily by

surface migration no matter whether the pores are occupied by organic or aqueous solutions; hence the catalyst will catalyze the reaction more easily.

The result of ESCA shows that the ionic chloride is about 46.5% of total chloride. In other words, 46.5% of chloromethylpolystyrene is quaternized with tributylamine. This value may be close to a "proper" percentage, which gives a "proper" hydrophilicity for the triphase catalyst to catalyze the reaction. The coexistence of hydrophobic and hydrophilic groups on the catalyst surface are helpful to preserve both water and organic drops and hence enhance the reaction rate.

CONCLUSIONS

Surface characterization of catalyst supported by polymeric materials is still in its infancy. In this work, the optical microscope and SEM are employed to inspect the surface of triphase catalysts. Both ESCA and EPMA are used to evaluate the content of active species via the measurement of ionic chloride.

In summary, the distribution of active species in this triphase catalyst is not uniform. Most of the active species are in the outer shell; hence they can catalyze the reaction more easily. The coexistence of hydrophilic and hydrophobic groups provides a good environment for the catalyst to contact with both aqueous and organic phases. The density of the triphase catalyst is between those of aqueous and organic (toluene in this study) phases; hence the triphase catalyst particles can contact both phases. All these three facts result in a high reaction rate for this triphase catalysis.

It is quite obvious that the hydrophilicity is a very important property of the triphase catalyst. Because the hydrophilicity depends on the extent of quaternization, the effect of quaternization on the hydrophilicity and, in turn, on the reaction rate of triphase catalysis should be elucidated. For this purpose, reaction catalyzed by the catalyst with various extent of quaternization should be carried out. As an optimal extent of quaternization for the highest reaction rate might exist, it is valuable to search for it.

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