Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Online publication date: 17 July 2000

To cite this Article Xia, Shuwei and Xia, Shaowu(2000) 'STUDY ON THE PHASE STATE OF ZIEGLER-NATTA IRON SYSTEM CATALYST $Fe(naph)_2$-$Al(i\text{-}Bu)_3$-CH_2=$CHCH_2Cl$ AND $FeCl_3$-$Al(i\text{-}Bu)_3$ Phen IN BUTADIENE POLYMERIZATION', Journal of Macromolecular Science, Part A, 37: 8, 927 — 941

To link to this Article: DOI: 10.1081/MA-100101132

URL: http://dx.doi.org/10.1081/MA-100101132

J.M.S.—PURE APPL. CHEM., A37(8), pp. 927–941 (2000)

STUDY ON THE PHASE STATE OF ZIEGLER-NATTA IRON SYSTEM CATALYST $Fe(naph)_2$-$Al(i\text{-}Bu)_3$-CH_2=$CHCH_2Cl$ AND $FeCl_3$-$Al(i\text{-}Bu)_3$Phen IN BUTADIENE POLYMERIZATION

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Key Words: Colloidal Catalyst, Tyndall Effect, Ultrafiltering, Butadiene Polymerization

ABSTRACT

By the Tyndall effect, the observation of electronic microscope and ultrafiltering experiment proved that both $Fe(naph)_2Al(i\text{-}Bu)_3CH_2$=$CHCH_2Cl$ catalyst and $FeCl_3Al(i\text{-}Bu)_3$Phen catalyst were colloidal disperse systems in butadiene, and contained hydrogenated gasoline solvent. Catalytic activity sites were located on the surface of colloidal particles. Therefore, both the catalysts were colloidal catalysts. The catalyst particles were amorphous. The ratio of catalyst components affected the shape of colloidal particles, among which the colloidal particles of the

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optimal ratio were small in size, even distributed, and with high catalytic activity.

The transition metal iron compound has been used to catalyze butadiene to polymerize since 1960. People have continuously researched the iron system mainly including the choice of the iron compound [1-10], the finding of the right matching [11-16], the stabilization of the active sites, the improvement of the catalytic activity [2, 13-16], and the synthesis of the high polymer [6, 17-20]. Many workers have studied the catalytic mechanism of the iron system [21-23] and obtained rich achievement. But until now, the phase state of the iron system catalyst has not been reported. Our group has first questioned the phase state of Ziegler-Natta iron system catalyst and carried out intensive research.

Herein, the phase state of the Ziegler-Natta iron system $Fe(naph)_2Al(i\text{-}Bu)_3CH_2{=}CHCH_2Cl$ catalyst and $FeCl_3Al(i\text{-}Bu)_3Phen$ catalyst was studied. The activity of both catalysts was high in butadiene polymerization with hydrogenated gasoline as solvent [14, 24]. The research of the phase state of the two catalysts has not been reported. It has always been regarded as homogeneous. But the preparative methods of the catalyst including ratio and adding order of the components and aging, etc., had considerable influence on the catalytic activity and molecular weight of polymer. These phenomena were similar to the characteristics of the preparative methods of solid catalyst. In this paper, the results of the Tyndall effect, the observation of electronic microscope and ultrafiltering experiment showed that the present catalysts dispersed in hydrogenated gasoline appeared to be colloidal disperse system. The diameter of catalytic particles was from 1 to 100 nm and the active sites of the catalyst were located on the surface of colloidal particles, therefore, these catalysts were colloidal catalysts. The exper-imental phenomena were explained reasonably according to the specific property of sol.

EXPERIMENTAL

Materials

The preparation of the catalyst and details of polymerization have been described previously [24, 25]. The hydrogenated gasoline solution of butadiene is briefly written as (Bd).

Tyndall Effect Experiment

The observed sample was added to the polymerization tube which had been dried and vacuumed. In a dark room, the Tyndall effect was observed with HJ-1B type He-Ne laser spectrometer with the incident light wavelength of 632.8 nm.

Ultrafiltering Experiment

The improved A-A type stainless steel millipore filter was utilized and millipore filter film with aperture of 150 nm was made from the mixed cellulose ester provided by Shanghai Medical Industry Research Institute. After the equipment was vacuumed and purged by nitrogen in order to completely replace the air inside, a proper amount of $Fe(naph)_2$, $Al(i\text{-}Bu)_3$ and $CH_2{=}CHCH_2Cl$(or Phen, $FeCl_3$ and $Al(i\text{-}Bu)_3$) was injected, mixed quickly, and then pressed to filter with nitrogen gas. The filtrate was drawn from the receiver to detect its Tyndall effect and to be used in polymerization. The ultrafiltering experiments were conducted by blank test (no millipore filter film), four-layer filter, and eight-layer filter separately [26].

TEM and SEM Experiments

The Ampere tube was first vacuumed and purged by nitrogen and then a certain amount of hydrogenated gasoline was added before various catalyst components were added in the sequence of $Fe(naph)_2$, $CH_2{=}CHCH_2Cl$ and $Al(i\text{-}Bu)_3$(or Phen, $FeCl_3$ and $Al(i\text{-}Bu)_3$). Under nitrogen protection, a drop of catalyst sol was taken out and dripped on the filter screen pasted with filter. Then, also under nitrogen protection, the filter screen was placed into the sample stick and tested by an electron microscope. After ultrafiltering, the samples were taken out from each layer of filter, and sprayed on gold film, an SEM photograph was subsequently observed [27]. A JEM-2000EX electron microscope made in JDEL Company was used with an electric pressure of 120.0kV and a current density of $20x10^{-12} \sim 23x10^{-12} A{\bullet}cm^{-2}$.

RESULTS AND DISCUSSION

Tyndall Effect

The Tyndall effect of single-component, bicomponent and tricom-ponent of catalyst $Fe(naph)_2Al(i\text{-}Bu)_3CH_2{=}CHCH_2Cl$ were detected and given in Table

1. The Tyndall effect was not observed for $Fe(naph)_2$, CH_2=$CHCH_2Cl$, (Bd) and hydrogenated gasoline, a weak Tyndall effect could be observed for $Al(i\text{-}Bu)_3$; the bicomponent $Fe(naph)_2$ + CH_2=$CHCH_2Cl$ had no Tyndall effect, CH_2=$CHCH_2Cl$ + $Al(i\text{-}Bu)_3$ had weak Tyndall effect, but when $Fe(naph)_2$ and $Al(i\text{-}Bu)_3$ were mixed, scattered-light path appeared immediately and obviously. The tricomponent mixture $Fe(naph)_2$ + CH_2=$CHCH_2Cl$ + $Al(i\text{-}Bu)_3$ exhibited a stronger scattered-light path. The adding order of $Fe(naph)_2$, then CH_2=$CHCH_2Cl$ and then $Al(i\text{-}Bu)_3$ in polymerization was called the single adding, so No. 9 in Table 1 was also the Tyndall effect of single adding.

As shown in Table 2, single-component $FeCl_3$, bicomponent Phen + $FeCl_3$ and $FeCl_3$ + $Al(i\text{-}Bu)_3$ and tricompontent Phen + $FeCl_3$ + $Al(i\text{-}Bu)_3$ (i.e., Single adding in polymerization) presented strong a Tyndall effect; bicomponent Phen+$Al(i\text{-}Bu)_3$ had a weak Tyndall effect.

The substance of Tyndall effect is light scattering. The strength of scatter light is in direct proportion to the square of the particle volume under the condition of the specific number density [28]. It is well known that the system without the Tyndall effect or with very weak scattered-light is or is close to the molecular disperse system. The disperse system with the Tyndall effect is colloid. $Fe(naph)_2$ and $Al(i\text{-}Bu)_3$ or $FeCl_3$ and $Al(i\text{-}Bu)_3$, when mixed, immediately brought about the Tyndall effect, indicating that $Fe(naph)_2$ or $FeCl_3$ and $Al(i\text{-}Bu)_3$ reacted quickly and formed particles. Stronger scattered-light showed that there was an obvious interface between disperse phase(catalyst) and disperse medium(hydrogenated gasoline). Therefore, it was lyophobic colloid.

TEM Observation

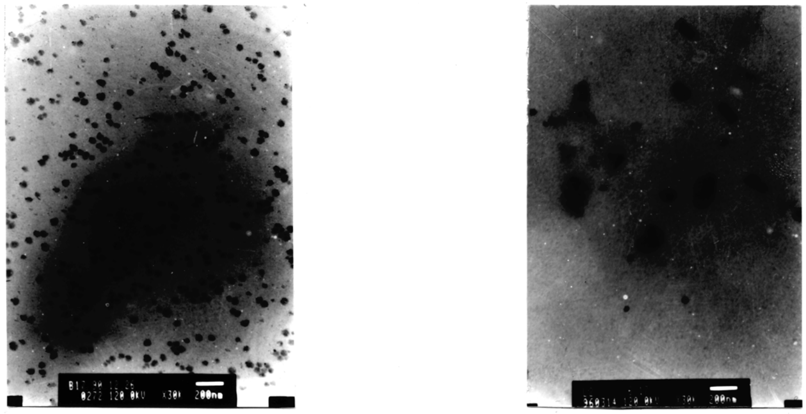
The polymerization results showed that the catalytic activity of $Fe(naph)_2Al(i\text{-}Bu)_3CH_2$=$CHCH_2Cl$ was the highest at the ratios CH_2=$CHCH_2Cl/Fe(naph)_2$=2.5, $Al(i\text{-}Bu)_3/Fe(naph)_2$=20 [14], which was called the optimum ratio. The electronic microscope (TEM) photograph of a catalyst prepared in optimum ratio in single adding (no butadiene in solution) was shown in Figure 1(a). The catalyst particles were small and even dispersed, most of them were approximate 50 nm in diameter in the range of colloid. However, in other ratios the catalyst particles were usually bigger and uneven dispersed, most of them were above 100 nm in diameter in excess of the range of colloid [29]. The optimum ratio of catalyst $PhenFeCl_3Al(i\text{-}Bu)_3$ was given in No. 7 of Table 2. Its TEM photograph was shown in Figure 1(b). The size of the particles was ranged from 30 nm to 100 nm.

TABLE 1. Experimental Results of Tyndall Effect of $Fe(naph)_2$-$Al(i\text{-}Bu)_3$-CH_2=$CHCH_2Cl$ Catalytic System

No.	Sample	C/ $mol \cdot dm^{-3}$	n($Fe(naph)_2$): n(CH_2=$CHCH_2Cl$): n($Al(i\text{-}Bu)_3$)	Tyndall effect
1	$Fe(naph)_2$	7.4×10^{-4}	1:0:0	no
2	CH_2=$CHCH_2Cl$	1.85×10^{-3}	0:1:0	no
3	$Al(i\text{-}Bu)_3$	1.48×10^{-2}	0:0:1	weak
4	hydrogenated gasoline	—	—	no
5	(Bd)	1.85	—	no
6	CH_2=$CHCH_2Cl$+$Al(i\text{-}Bu)_3$	same as (2,3)	0:1:8	weak
7	CH_2=$CHCH_2Cl$+$Fe(naph)_2$	same as (1,2)	1:2.5:0	no
8	$Fe(naph)_2$+$Al(i\text{-}Bu)_3$	same as (1,3)	1:0:20	strong
9	$Fe(naph)_2$+CH_2=$CHCH_2Cl$+ $Al(i\text{-}Bu)_3$	Same as (1,2,3)	1:2.5:20	very strong

TABLE 2. Experimental Results of Tyndall Effect of $FeCl_3$-$Al(i\text{-}Bu)_3$-Phen Catalytic System

No.	Sample	C/ $mol \cdot dm^{-3}$	$n(FeCl_3) : n(Phen) : n(Al(i\text{-}Bu)_3)$	Tyndall effect
1	$FeCl_3$	5.55×10^{-2}	1:0:0	strong
2	Phen	9.26×10^{-2}	0:1:0	no
3	$Al(i\text{-}Bu)_3$	3.73	0:0:1	weak
4	Phen + $FeCl_3$	same as (1, 2)	1:1.67:0	strong
5	Phen + $Al(i\text{-}Bu)_3$	same as (2, 3)	0:1:40	weak
6	$FeCl_3$ + $Al(i\text{-}Bu)_3$	same as (1, 3)	1:0:66.7	strong
7	Phen + $FeCl_3$ + $Al(i\text{-}Bu)_3$	same as (1, 2, 3)	1:1.67:66.7	very strong



(a)

$n(Fe(naph)_2) : n(CH_2{=}CHCH_2Cl) : n(Al(i\text{-}Bu)_3) = 1 : 2.5 : 20$,

$[Fe(naph)_2] = 7.4 \times 10^{-4} mol \cdot dm^{-3}$, 15℃, 7h

(b)

$n(FeCl_3) : n(Al(i\text{-}Bu)_3) : n(Phen) = 1 : 1.67 : 66.7$,

$[FeCl_3] = 5.5 \times 10^{-2} mol \cdot dm^{-3}$, 30℃, 5h

Figure 1. TEM photograph of the catalysts at optimum ratio.

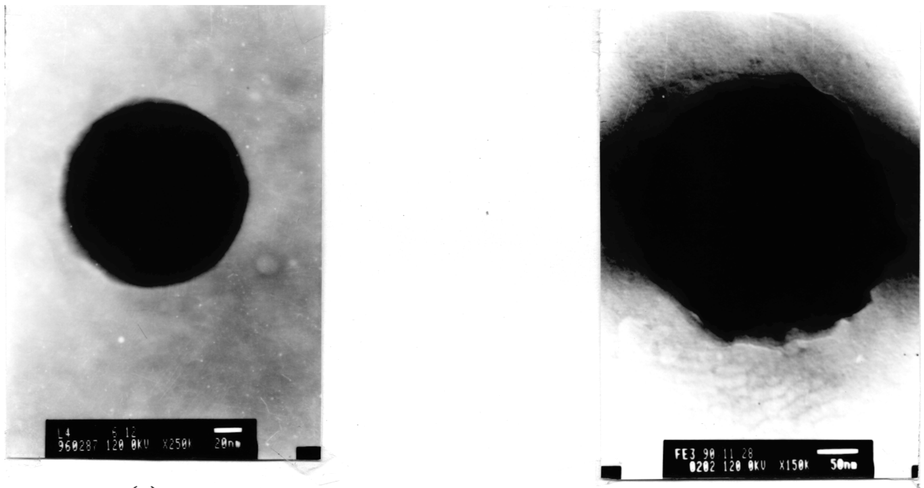
The polymerization experiment indicated that the catalyst in the optimum ratio presented a conversion of 90%, while in other ratios the conversion was less than 20%.

TEM observation showed that the catalyst existed as particles. The catalyst particles prepared in the optimum ratio were in the range of colloid and the conversion was high. This indicates that the shape of catalyst particles influences the catalytic activity and in one aspect, it demonstrates that the active site is located on the surface of catalyst particles.

Figure 2(a,b) presented the photograph of catalyst particle of Figure 1(a,b) magnified by 150,000 times. It can be seen that it is coalesced by tiny particles. It is amorphous.

Ultrafiltering Experiment

The ultrafiltering experiment was conducted to further examine where the active site of catalyzed polymerization is located, on the surface of colloidal particles or soluble in disperse medium. Three components $Fe(naph)_2$, $CH_2{=}CHCH_2Cl$ and $Al(i\text{-}Bu)_3$ were mixed and ultrafiltered at 0°C. Some of the filtrate was taken out to observe the Tyndall effect, the other was to carry out polymerization. The results were summarized in Table 3.



(a) (b)

Figure 2. TEM photograph of colloidal particle in high magnification.

Table 3 presents a comparison of single adding, aging, and ultrafiltering experiment. According to the conditions shown in Table 3, the conversion of single adding is up to 92.5%, the conversion of aging for 5 minutes at room temperature is 14.0%, of blank filtrate is 14.3% and the Tyndall effect of the filtrate is obvious. The conversion of blank filtrate is similar to that of aging but much lower than single adding. To blank filter, it would take 5 minutes for the three components $Fe(naph)_2$, $CH_2{=}CHCH_2Cl$ and $Al(i\text{-}Bu)_3$ to mix and filter, which may correspond to aging 5 minutes. Therefore, the two conversions are very close. The filtrate passing four layers of filter cannot catalyze butadiene to polymerize within 7 hours, indicating that the filtrate has no activity. The filtrate exhibiting a weak Tyndall effect suggests that most colloidal particles are hindered and only an extremely small amount of colloidal particles with very small volume passes the filter. Thus, it can be understood that it could not exhibit the catalytic activity.

Without a stabilizer, as soon as the three components were mixed, a precipitate appeared immediately, indicating that the catalyst system was a coalescence unstable system. So, during the aging period, colloids coalesce and grow quickly causing the specific surface area to decrease sharply, and the shape of colloidal particles may be changed. Thus, the catalytic activity decreases greatly, aging only 5 minutes makes the conversion drop to 14%. Single adding is that three components of the catalyst are successively injected into the butadiene-

TABLE 3. Comparison of the Results of Single Adding, Aging, and Ultra-filtering of $Fe(naph)_2$-$Al(i\text{-}Bu)_3$-CH_2=$CHCH_2Cl$ Catalytic System

	Single adding (not to filter)	Aging (not to filter)	Blank filtering (no filtering film)	Filtering with four layers of film
Operating	tricomponent was added into tube in order	ticomponent was mixed, aging for 5 min and then added into tube	ticomponent was mixed and immediately filtered	ticomponent was mixed and immediately filtered
Tyndall effect	very strong	very strong	very strong(filtrate)	weak(filtrate)
Conversion/%	92.5	14.0	14.3	0

Polymerization condition: n($Fe(naph)_2$) : n(CH_2=$CHCH_2Cl$) : n($Al(i\text{-}Bu)_3$) =1 : 2.5 : 20,

[$Fe(naph)_2$]=7.4×10^{-4}mol·dm^{-3}, 15℃, 7h containing tube. The catalyst immediately forms colloidal particles which instantaneously results in the polymerization of butadiene. The polymer exists around the colloidal particles to prevent them from coalescing and hence increases the stability of the sol. Therefore, the catalytic activity is high. The filtrate passing four layers of filter has no activity, leading to the conclusion that the active site is not in the medium but on the surface of colloidal particles.

Three components Phen, $FeCl_3$, $Al(i\text{-}Bu)_3$ were mixed and ultrafiltered at 15°C. The results were given in Table 4. Similar to the aging filtrate, the purplish red blank filtrate has obvious Tyndall effect and can catalyze butadiene to polymerize. Its conversion is 94.6% approach to that of aging (95.2%). The filtrate passing eight layers of film has no color and Tyndall effect, which cannot make butadiene polymerize showing that the filtrate has no activity. It also proves that the active site is not in the medium but on the surface of colloidal particles.

SEM Analysis

To examine whether the filtering film could hinder catalyst colloidal particles, SEM observation was conducted for the unused and used various filtering films, respectively. The results of $Fe(naph)_2CH_2{=}CHCH_2ClAl(i\text{-}Bu)_3$ catalyst were presented in Figure 3, including four SEM photographs magnified by 6000 times. A-0 is the photograph of the original filter film (without using for filter), on which the little dark points are filtering holes with an aperture diameter of approximately 150 nm. A-1 is the photograph of the first layer film in four layers of filtering films. Almost all the surface of the film was covered by catalyst colloidal particles, so that filtering holes could not be observed. But several crackles were produced due to the evaporation of the solvent. A-2 is the photograph of the second layer filtering film. A part of the region of the film was still covered by the catalyst. The observable little dark points are smaller than those in A-0, which reveals that filtering holes are partly clogged by the catalyst colloidal particles. A-3 is the photograph of the third layer filtering film. There is no covered region as in A-2, only the dark points are much smaller, indicating that the colloidal particles are gathered around filtering holes resulting in the decrease of bore. The SEM photograph of the fourth layer filtering film which is almost identical to that of the unused filtering film(A-0) is not presented.

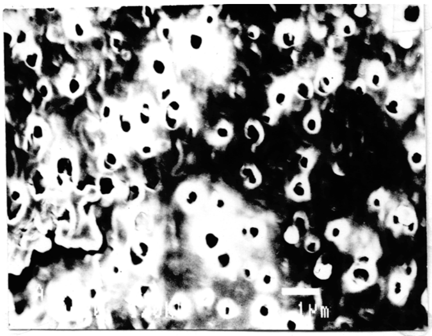
The SEM photographs of $FeCl_3Al(i\text{-}Bu)_3$Phen catalyst were shown in Figure 4. B-1 is the photograph of the first layer film in eight layers of filtering films. Similar to the A-1 of Figure 3, the film was covered by catalyst colloidal particles. B-2 is the photograph of the second layer filtering film. Part region of

TABLE 4. Comparison of the Results of Single Adding, Aging and Ultrafiltering of $FeCl_3Al(i\text{-}Bu)_3$Phen Catalytic System

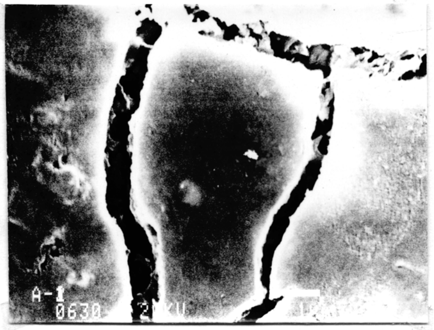
	Blank filtration (no filtering film)	Aging (not to filter)	Filering with eight layers of film
Operating	ticomponent was mixed and immediately filtered	ticomponent was mixed, aging for 10min and then added into tube	ticomponent was mixed and immediately filtered
Tyndall effect	very strong(filtrate)	very strong	no(filtrate)
Conversion/%	94.6	95.2	0

Polymerization condition: $n(FeCl_3) : n(Al(i\text{-}Bu)_3) : n(Phen) = 1 : 1.67 : 66.7$,

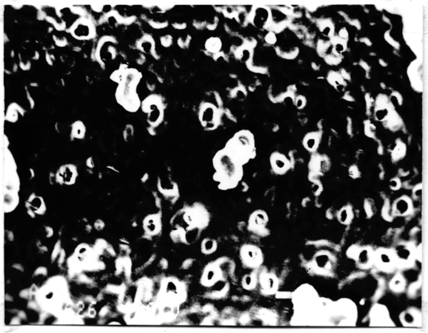
$[FeCl_3]=5.5\times10^{-2} mol\cdot dm^{-3}$, 30℃, 5h



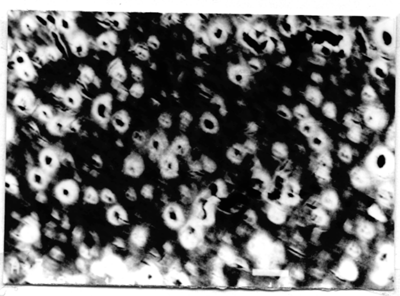
A-0 photograph of unused filter film



A-1 photograph of the first layer of filtering film



A-2 photograph of the second layer of filtering film

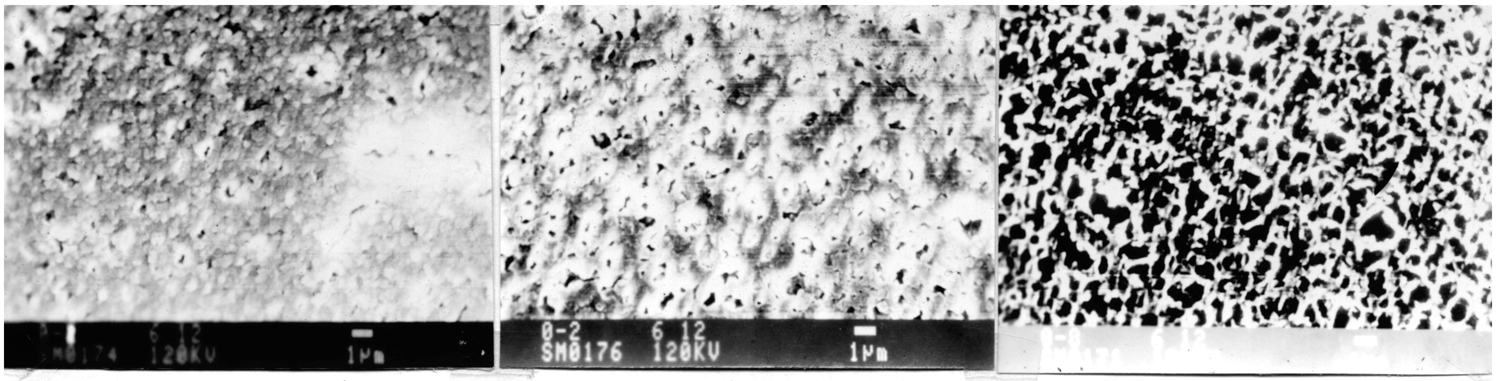


A-3 photograph of the third layer of filtering film

Figure 3. SEM photographs of filtering film of $Fe(naph)_2CH_2{=}CHCH_2ClAl(i\text{-}Bu)_3$ catalytic system. B-1, photograph of the first layer of filtering film; B-2, photograph of the second layer of filtering film; B-3, photograph of the eighth layer of filtering film.

the film was covered by the catalyst. B-3 is of the eighth layer filtering film which is almost identical to that of A-1 in Figure 4.

The above microscope photographs show that four layers filtering films can hinder most of the catalyst colloidal particles. The results that the filtering film was observed by an electron microscope fully confirmed the reliability of ultrafiltering experiment.



B-1 photograph of the first layer of filtering film   B-2 photograph of the second layer of filtering film   B-3 photograph of the eighth layer of filtering film

Figure 4. SEM Photographs of Filtering Film of FeCl3-Al(i-Bu)3-Phen Catalytic System. A-0, photograph of unused filter film; A-1, photograph of the first layer of filtering film; A-2, photograph of the second layer of filtering film; A-3, photograph of the third layer of filtering film.

CONCLUSION

From the Tyndall effect, ultrafiltering experiment and the observation of electronic mircoscope, etc., it was found that the iron catalyst system Fe(naph)2–Al(i-Bu)$_3$–CH_2=$CHCH_2Cl$ catalyst and $FeCl_3$–Al(i-Bu)$_3$–Phen catalyst were dispersed as colloidal particles in hydrogenated gasoline, i.e., they were colloidal catalysts, belonging to a multiphase catalyst. The colloidal particles of the catalyst was aggregated from tiny particles. The component ratios influence the form and homogeneity of catalyst and then influence the catalytic activity. It is obvious that in the view of colloidal catalyst, diffusion, adsorption and surface reaction, etc. should be considered in the kinetics study. It is necessary to study the novel kinetic character by the specific property of nanometer particles such as surface effect, volume effect, etc.

ACKNOWLEDGEMENT

Project 29373106 was supported by the National Nature Science Foundation of China.

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Received November 30, 1999
Revision received March 20, 2000