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Preparation of Nano-TiO_2 from a Crude Solution Containing Ti(IV)–Fe(II) and H_2SO_4 with Extraction and Hydrolysis

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ABSTRACT

The extractions of TBP (or TOPO)–kerosene/a crude solution containing Ti(IV), Fe(II), and H_2SO_4 were studied for the separation of Ti/Fe. Nano-TiO_2 powder, about 20 nm, was prepared by hydrolysis of the middle phase microemulsion loading Ti(IV) obtained in TBP extraction system. By hydrolyzing the colloidal liquid aphrons (CLA) made by the extracted organic solution loading Ti(IV) in TOPO extraction system as the inner phase, a porous spherical TiO_2 was obtained. The contents of Fe in both products were less than 100 ppm.

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Key Words: Extraction; TiO_2; TBP; TOPO; The third phase; Colloidal liquid aphron.

INTRODUCTION

Nano-TiO_2 has excellent photical, mechanical, and electrical properties and is used in many fields, such as catalyst carrier, ultraviolet light absorbent, surface paint, and advanced ceramic additive. Many methods, such as hydrothermal, sol–gel, reversed micelle, or microemulsion and alkoxide hydrolysis, can be used for its preparation.[1] Nano-material can also be prepared by an extraction–hydrolysis method with both a two-phase and three-phase extraction system has been used.[2–4] The third phase formed in extraction system is similar to a middle-phase microemulsion in a typical surfactant system,[5] and study of its formation, structure, and application is in progress.[6]

Tri-butyl phosphate (TBP) and tri-octyl phosphinic oxide (TOPO) are two of commonly known neutral extractants, but they have very different extraction behaviors and phase behaviors in extracting Ti(IV) from H_2SO_4 aqueous solutions. In TBP–kerosene (40 or 60%, v/v)/$TiOSO_4$–H_2SO_4 system, the extraction of Ti(IV) was very low in the two-phase region when the acid concentration was lower ($C_{H_2SO_4,b} < 7.0\,mol/L$, where b represented the bottom phase). However, when $C_{H_2SO_4,b} > 7.0\,mol/L$, the third phase, began to form, and the extraction ratio raised sharply with increasing $C_{H_2SO_4,b}$. Ti(IV) was extracted mainly into the heavy organic phase (the middle phase) but not in the light organic phase (the upper phase).[3] This experiment indicated also that the concentration of Ti(IV) in the middle phase could reach 1 mol/L and more. TiO_2 particles with a narrow size distribution of about 20 nm were obtained by hydrolysis of the middle phase loaded Ti(IV). The third phase could also be formed in the TOPO–kerosene/Ti(IV)–H_2SO_4 system. Its phase behavior was almost the same as that in TBP system, but the extractive percentage in the two-phase region was much higher than in the three-phase region.[4] In the later study, stable colloidal liquid aphrons (CLAs) were prepared using the organic phase loaded Ti(IV) as the inner phase and the OP-10 (2%, v/v) aqueous solution as the outer phase. Ti(IV) in the oil core of CLAs was then hydrolyzed by ammonia solution, and a porous spherical TiO_2 powder smaller than 0.1 μ was obtained. Compared to other methods in colloid chemistry, the advantage of these two methods for preparing ultrafine powder was that the operating solution had a much higher metal content. These methods could be applied to the commercial manufacture of ultrafine powder.

In this study, Ti(IV) was extracted by TBP and TOPO from a crude solution containing Ti(IV), Fe(II), and H_2SO_4 supplied by a plant producing titanium white powder instead of from a solution made by chemical reagent.[3,4] The experiment results indicated that the contents of Fe in the produced TiO_2 powder were less than 100 ppm through one extraction–precipitation procedure.

EXPERIMENTAL

Equipments and Reagents

- JEM-100CX Electro microscope (Joel company, Japan).
- 721 Spectrophotometer (Shanghai No. 3 Equipment Factory, China).
- SiC high temperature furnace.
- TOPO (with commercial name of Cyanex 921) was kindly supplied by Cytec Canada, Inc., Niagra Falls, Ontario, Canada.
- TBP, H_2SO_4, H_2O_2, NaF and all other reagents were AR grade.
- The crude solution of Ti(IV) with major compositions of $C_{H_2SO_4} = 1.85\,\text{mol/L}$, $C_{Ti} = 2.71\,\text{mol/L}$, and $C_{Fe} = 0.67\,\text{mol/L}$, respectively, was supplied by Jinan Yuxing Chemical Plant in China.

Kerosene was sulphonated, washed by NaOH solution and water, subsequently, and then distilled, taking the fraction of 180 to 200°C for experiments.

Experimental Method

The extraction process was undertaken in 10-mL stoppered tubes. Organic and aqueous solutions were mixed and shaken for 10 minutes, then equilibrated at 298 K for over 24 hours. The volumes and compositions of each phase were determined. The concentration of Ti(IV) in the aqueous phase was analyzed by spectrophotometry with H_2O_2. Fe(II) was determined by spectrophotometry with phenanthroline. The concentrations of H_2SO_4 in the bottom phase could not be determined by titration with standard NaOH solution in the presence of NaF as seen by Hu et al.[3], because the precipitation interference of both Ti(IV) and Fe(II) could not be prevented. Hence, $SO_4{}^{2-}$ was analyzed by gravimetric method. The contents of all components in the organic phase (two-phase region) or in the middle phase (three-phase region) were calculated by the differences. Our experiments indicated that the light organic solutions in the three-phase region contained no metal and H_2SO_4.

RESULTS AND DISCUSSION

TBP–Kerosene/Crude Solution Extraction System

Pretreatment of the Crude Solution

The previous study for the system of TBP–kerosene/Ti(IV)–H_2SO_4 indicated that the third phase was not formed when $C_{H_2SO_4,b} < 7.0\,\mathrm{mol/L}$ Ti(IV) was extracted mainly the middle phase, when $C_{H_2SO_4,b} > 7.0\,\mathrm{mol/L}$.[3] So the crude solution must be pretreated to increase its H_2SO_4 concentration. In this study, reduced pressure distillation was first used to concentrate the crude solution. After about 20% of water was distill from the crude solution at 80°C, 125 mL of concentrated H_2SO_4 was added to 250 mL of the distillated crude solution, noted as No. 1 solution, and 80 mL of concentrated H_2SO_4 was added to 250 mL of the distillated crude solution, noted as No. 2 solution. Both No. 1 and No. 2 solutions were kept at 0°C for 12 hours and some $FeSO_4$ was crystallized. Then the solutions were analyzed after filtration and the results were as follows:

No. 1 solution: $C_{H_2SO_4} = 8.60\,\mathrm{mol/L}$, $C_{Ti} = 2.74\,\mathrm{mol/L}$, $C_{Fe} = 0.469\,\mathrm{mol/L}$.

No. 2 solution: $C_{H_2SO_4} = 7.10\,\mathrm{mol/L}$, $C_{Ti} = 3.09\,\mathrm{mol/L}$, $C_{Fe} = 0.542\,\mathrm{mol/L}$.

If more water was distillated off, the crude solution would be too viscous for an extraction operation.

Removal of Fe(II) by Extraction

Extraction data of the middle phase obtained in the 60% TBP–kerosene (v/v), the pretreated solution (No. 1 or No. 2) at various phase volume ratios (v_o/v_a) are listed in Table 1, where the separation coefficient, β, represents the ratios of C_{Ti}/C_{Fe} values after and before extraction.

Table 1 shows that the extraction percentage of Ti(IV) into the middle phase is obviously higher when $C_{H_2SO_4,b} = 8.6\,\mathrm{mol/L}$ in No. 1 than in No. 2,

Table 1. Extraction data for 60% TBP–kerosene/pretreated crude solution.

	Solution no. 1				Solution no. 2			
Vo/Va	$C_{Ti,m}$	$C_{Fe,m}$	β	Extraction percentage	$C_{Ti,m}$	$C_{Fe,m}$	β	Extraction percentage
4	0.387	0.0032	20.7	53.6	0.270	0.0028	16.9	34.3
2.33	0.700	0.0033	36.4	55.1	0.501	0.0031	28.2	36.3
1.5	0.940	0.0034	47.4	46.8	0.652	0.0037	30.7	29.1
1	1.20	0.0035	58.8	38.2	0.772	0.0039	34.5	22.9
0.67	1.26	0.0039	55.4	27.4	0.841	0.0043	34.1	16.8

The unit for all concentrations is mol/L, m represents the middle phase.

with $C_{H_2SO_4,b} = 7.1\,mol/L$. It is consistent with the data reported by Hu et al. for the study of a TBP–kerosene/Ti(IV)–H_2SO_4 extraction system. Fe(II), therefore, does not interfere the extraction of Ti(IV). Moreover, the ratio of $C_{Ti,m}/C_{Fe,m} > 100$ shows that Fe(II) is seldom extracted by TBP. The small Fe(II) content in the third phase may originate from the solubilized H_2O in the middle phase microemulsion.

The extraction percentage of Ti(IV) increases with the increase of phase–volume ratio and reaches up to a maximum value at $V_o/V_a = 2.33$, but the concentration of Ti(IV) in the middle phase is lower because the middle phase volume is greater. It is good to the increase of the loading concentration of Ti(IV) in the middle phase at a lower phase volume ratio, but the extracted solution is too viscous to be handled. In this experiment, the proper phase ratio of 1 to 1.5 was chosen.

Table 2 gives the extraction data at various temperatures. With increasing temperature, the extraction percentage of Ti(IV) decreases, the volume of the middle phase increases slightly, and the viscosity decreases, but the content of

Table 2. Extraction data of TBP–kerosene/pretreated no. 1 solution system at various temperatures ($Vo/Va = 6\,mL/4\,mL = 1.5$).

Temperature	20	45	70
V_m/mL	5.46	5.47	5.69
$C_{Ti,m}/mol\,L^{-1}$	0.94	0.79	0.66
$C_{Fe,m}/mol\,L^{-1}$	0.0034	0.0052	0.0073

Fe(II) in the middle phase increases, which may be attributed to the more solubilized H_2O in the middle phase with more attaching Fe(II) ions.

Preparation of TiO_2 Powder

To achieve a good separation of Ti/Fe and a suitable viscosity, a temperature of 45°C was chosen in the extraction experiments. The middle phase with extracted Ti(IV) was slowly titrated into a 1:1 ammonia solution under rapid magnetic stirring until a film of kerosene in the beaker appears. The formed precipitates were separated by centrifugation and washed with alcohol and distilled water three times, respectively, and then washed with acetone. After that, the precipitates were filtered and dried to obtain a white powder. Analysis indicated that the content of Fe in the powder was less than 90 ppm.

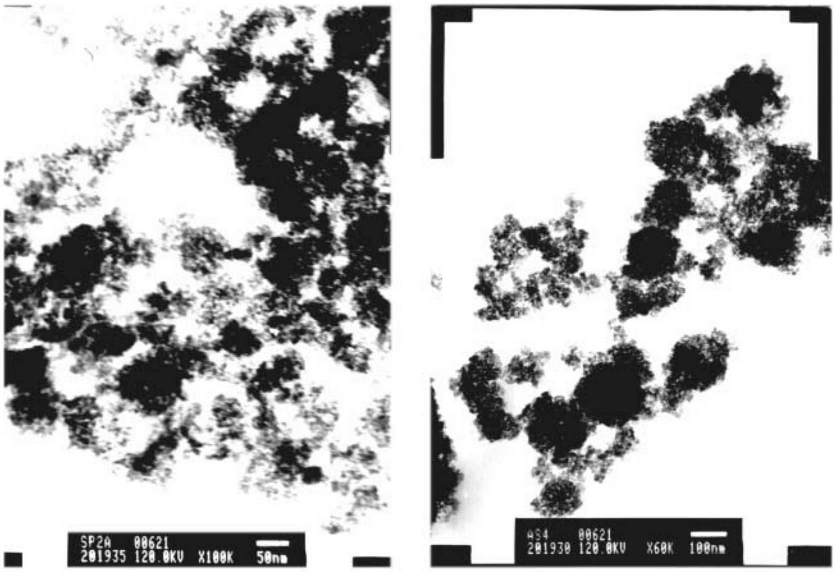
The white powder was calcinated at 600°C and 1200°C, respectively, in a muffle furnace. The powder was whiter in the former than in the latter. TEM images of these two powders showed that the former was a spherical particle, sized about 20 nm, with a good shape (see Fig. 1a), but the latter was agglomerated to about 200 ppm or more. The TEM image was very similar to that of TiO_2 prepared by pure $TiOSO_4$.[3] X-ray diffractions of the powders show that the calcinations at 600°C give anatase but rutile at 1200°C.

TOPO–Kerosene/Crude Solution Extraction System

Pretreatment and Extraction–Separation of the Crude Solution

The extraction behavior of the TOPO–kerosene/Ti(IV)–H_2SO_4 system is very different from that of a TBP system. In a TOPO–kerosene/Ti(IV)–H_2SO_4 system, there is a high extraction percentage (higher than 80%[4]) in the two-phase region when $C_{H_2SO_4,b} = 3-8\,\mathrm{mol/L}$. In this experiment, the crude solution supplied by the plant was then diluted and its acidity adjusted by H_2SO_4 solution. The compositions of the pretreated solutions were $C_{Ti} = 0.542\,\mathrm{mol/L}$, $C_{Fe} = 0.134\,\mathrm{mol/L}$, and $C_{H_2SO_4} = 2-6\,\mathrm{mol/L}$. Equal volumes of 0.5 mol/L TOPO–kerosene solution and the pretreated solution were mixed, shaken for several minutes, and then equilibrated at 298 K for 24 h. The volumes and concentrations of each phase are given in Table 3.

The concentration of Ti in the organic phase increased with the increase of the initial aqueous concentration of H_2SO_4 and reached a maximum value at $C_{H_2SO_4,ini} = 4.5\,\mathrm{mol/L}$. After that, $C_{Ti,org}$ remained almost constant, but



(a) (b)

Figure 1. TEM images of nano-TiO_2 calcinated at 550–600°C obtained from (a) the hydrolyzed middle phase in TBP–kerosene/crude solution extraction system; and (b) the hydrolyzed CALs in TOPO–kerosene/crude solution extraction system.

the content of Fe(II) in the organic phase increased with the increase of the acid concentration. It is, therefore, unfavorable for the separation of Ti/Fe at a higher acidity. When $C_{H_2SO_4,ini}$ was 3 mol/L, the separation coefficient reached a maximum value of 21, and C_{Ti}/C_{Fe} in the organic phase was 88, which is 20 times higher than that in the initial aqueous solution ($C_{Ti/Fe} = 4$). To obtain a good separation efficiency for Ti/Fe, $C_{H_2SO_4,ini}$ was selected as 3 mol/L in the subsequent experiments.

Preparation of TiO_2 by CLAs Method

The pretreated crude aqueous solution with $C_{H_2SO_4,ini} = 3\,\mathrm{mol/L}$ was extracted by 0.5 mol/L TOPO–kerosene solution. The obtained organic phase with loaded Ti(IV) (2% Tween-80, v/v, is first added) was slowly titrated into an aqueous solution of surfactant (2% polyoxyethylene (10) octylphenol ether, v/v)

Table 3. Extraction data of 0.5 mol/L TOPO–kerosene/Ti(IV)–Fe(II)–H_2SO_4 system (Vo/Va = 1, T = 20°C).

$C_{H_2SO_4,ini}$/ mol L^{-1}		V/mL	C_{H2SO4}/ mol L^{-1}	$C_{Ti(IV)}$/ mol L^{-1}	$C_{Fe(II)}$/ mol L^{-1}	Extraction percentage	$\beta_{Ti/Fe}$
2.0	u	5.46	0.11	0.201	0.0029	40.5	17.1
	b	4.54	2.07	0.355	0.144		
3.0	u	5.47	0..27	0.219	0.0025	44.2	21.1
	b	4.53	2.99	0.334	0.145		
3.5	u	5.48	0.34	0.235	0.0043	47.5	13.5
	b	4.52	3.46	0.315	0.143		
4.5	u	5.48	0.41	0.302	0.0051	61.1	14.6
	b	4.52	4.45	0.233	0.142		
5.5	u	5.48	0.55	0.303	0.010	61.0	7.49
	b	4.52	5.41	0.232	0.136		

The unit for all concentrations is mol/L, u represents the top phase and b, the bottom phase.

under rapid magnetic stirring until the phase volume ratio, PVR, reached 5. Stable CLAs were formed. Colloidal liquid aphrons (CLAs)[7] are oil aphrons dispersed in a continuous water phase. Each aphron consists of an oil droplet containing an oil-soluble surfactant and a thin aqueous soapy film with a water-soluble surfactant. Ammonia solution (1:3) was then titrated slowly into the prepared CLAs under stirring until the pH of the continuous aqueous phase was up to 8. The system was kept at 100°C for 1 hour for hydrolysis of Ti(IV). The precipitates obtained were filtered, washed with distilled water, alcohol, and acetone twice, respectively, and dried at room temperature to obtain TiO_2 powder.

The powders were calcinated at 550°C and 1200°C, respectively. X-ray diffractions of the powders demonstrated that the anatase powder was obtained at 550°C and rutile powder, at 1200°C. The contents of Fe impurity were less than 100 ppm.

The TEM image of the obtained anatase powder is shown in Fig. 1b. It is similar to that of the TiO_2 prepared by pure $Ti(SO_4)_2$ by Shi et al. It demonstrates that the diameters of the powder are about 50 to 100 nm, with a good shape. Each spherical particle seems to be composed of many smaller units and porous. Considering the structure of CLA, it can be predicted that the hydrophilic group of TOPO–Ti(IV) extracted complex is located at the internal surface of the shell, so that the hydrolysis must occur there. The hydrolyzed Ti(IV) leaves the surface to deposit in the oil core, and unhydrolyzed Ti(IV) gradually diffuses toward the surface. The disorderly deposition of TiO_2 leads to the formation of the porous structure. The sizes of the aggregated spherical TiO_2 are attributed to the different quantities of Ti(IV) in the oil cores.

The small iron content in TiO_2 prepared by both two methods might not be a bad thing. Some metal, including Fe(III) dopaned TiO_2, could increase its photocatalytic reactivity. Bahneman et al.[8] reported that the photocatalytic reactivity for the photodegradation of dichloroacetic acid increased four times. Choi et al.[9] found that the efficiency of the photocatalytic decomposed reaction of CCl_4 and $CHCl_3$ increased greatly if 0.5% Fe(III) was dopaned in TiO_2.

CONCLUSION

A crude solution containing Ti(IV), Fe(II), and H_2SO_4 supplied by a plant was extracted by TBP–kerosene solution. The obtained middle phase loaded Ti(IV) was hydrolyzed to TiO_2 powder with a narrow size distribution of 20 nm. The content of iron in the product was less than 90 ppm through only one stage of extraction and hydrolysis.

The crude solution was also extracted by TOPO–kerosene solution. The obtained organic solution loaded Ti(IV) was used to prepare stable colloidal liquid aphrons as the inner phase. Under favorable hydrolysis conditions, a porous spherical TiO_2 of about 50 to 100 nm was obtained. The content of iron in the product was less than 100 ppm.

In brief, the primary advantage of these two methods for preparing ultrafine powder TiO_2 is that the processing solution has a rather higher metal content than any other methods reported before in colloidal chemistry. Furthermore, the process is simple, requiring only one stage of extraction for efficient separation of Ti/Fe and a precipitation. It is, therefore, predicted that these methods could be applied for the commercial manufacture of TiO_2 ultrafine powder.

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