

Synthesis and catalytic properties of iron - cerium phosphates with surfactant

(Síntese e propriedades catalíticas de ferro-fosfato de cério com surfactante)

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Abstract

Iron phosphate was prepared from iron nitrate and phosphoric acid with a surfactant, pentaethylene glycol mono dodecyl ether. The chemical composition of the obtained samples was estimated from ICP and XRD measurements. Particle shape and size distribution were observed by SEM images and laser diffraction / scattering methods. Further, the catalytic activity was studied with the decomposition of the complex between formaldehyde, ammonium acetate, and acetylacetone. The peaks of FePO_4 were observed in XRD patterns of samples prepared in $\text{Fe/Ce}=10/0$ and then heated at 600 °C. Other samples were amorphous in XRD patterns. Iron-cerium phosphates had high catalytic activity for the decomposition of the complex.

Keywords: iron phosphate, cerium substitution, surfactant, ICP analysis, catalytic property.

Resumo

Fosfato de ferro foi preparado a partir do nitrato de ferro e ácido fosfórico com um surfactante éter monododecil pentaetileno glicol. A composição química das amostras obtidas foi estimada a partir de medidas por ICP e DRX. A distribuição e forma das partículas foram observadas por imagens de MEV e o pelo método de espalhamento de laser. A atividade catalítica foi estudada com a decomposição do complexo entre formaldeído, acetato de amônio e acetilacetona. Os picos de FePO_4 foram observados nos padrões de DRX das amostras preparadas $\text{Fe/Ce}=10/0$ e então aquecidas a 600 °C. Outras amostras foram de padrões de DRX amorfo. Ferro-fosfatos de cério tiveram alta atividade catalítica para a decomposição do complexo.

Palavras-chave: fosfato de ferro, substituição do cério, surfactante, análises ICP, propriedade catalítica.

INTRODUCTION

Phosphates have been used for ceramic materials, catalysts, fluorescent materials, dielectric substances, metal surface treatment, detergent, food additives, fuel cells, pigments, etc. [1-3]. In these uses, catalyst is one of important applications of phosphate materials. Vanadium phosphate works as a catalyst for oxidation of butane [4]. Nickel phosphate works for oxidation of alcohol [5]. Iron phosphate works for oxidation of methane [6]. Aluminum phosphate works for dehydration of alcohol [7]. Other phosphates, zirconium, cobalt, potassium phosphates, and so on, are also important as a catalyst [8-10].

Transition metal phosphates sometimes have the different ratio of cation / phosphorus with the theoretical ratio of chemical composition, because of hydrogen cation, hydroxide anion, and so on. These hydrogen cation and hydroxide anion have influence on the catalytic activity of phosphate materials, because of the formation of hydrogen site on surface. These transition metal phosphates work as solid state acidic catalyst. Therefore, the synthetic process is

important to control the chemical composition of phosphate materials. Generally, the additives in preparation process were used to prepare the target particle of phosphate materials [11]. The spherical and porous particles of lanthanum phosphate were obtained by the addition of urea [12]. In this work, as a surfactant (sur), pentaethylene glycol mono dodecyl ether was used to prevent the aggregation in preparation process, which was one of the common anionic surfactant. This surfactant has 10.03 in Hydrophile-Lipophile Balance value [13].

Transition metal phosphates have a weak point to solve in acidic and basic solutions. In previous work [14], the substitution with rare earth cation inhibited the elution of phosphates. Therefore, rare earth substituted iron phosphates have a possibility to use as a catalyst in solutions.

In this work, iron - cerium phosphates were prepared from iron nitrate, ammonium cerium nitrate, and phosphoric acid with pentaethylene glycol mono dodecyl ether. The ratios of iron / cerium and phosphorus / pentaethylene glycol mono dodecyl ether (sur) were studied in this preparation. The obtained products were estimated from their particle

shape and size distribution, and catalytic activity. The purpose in this work is to clear the influence of cerium – substitution, surfactant, and heating temperature on chemical composition and catalytic activity of iron phosphates.

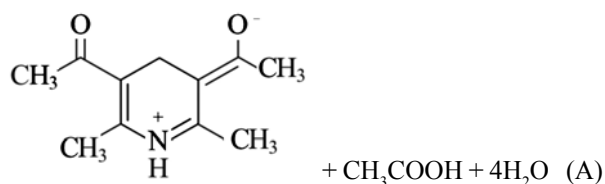
EXPERIMENTAL PROCEDURE

The 0.2 mol/L of iron nitrate, $\text{Fe}(\text{NO}_3)_3$, solution was mixed with 0.2 mol/L of phosphoric acid solution in the molar ratio of $\text{Fe}/\text{P}=1/1$. This ratio is settled from the chemical composition of iron orthophosphate, FePO_4 . Pentaethylene glycol mono dodecyl ether, $\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{H}$, (sur) was added to the mixed solution in $\text{P}/\text{sur}=10/0$, $10/1$, and $10/2$ to prevent the aggregation of particles. Then, the mixed solution was adjusted to pH 7 by ammonia solution. The precipitate was decanted off and dried at 60°C in air condition. The cerium - substituted samples were also prepared to compare with iron phosphates. A part of iron nitrate was substituted with ammonium cerium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, in $\text{Fe}/\text{Ce}=8/2$. The four iron (+III) cations were replaced with three cerium (+IV) cation. In this work, the ratio of $\text{P}/(3\text{Fe}+4\text{Ce})$ was $1/3$. All chemicals were of guaranteed reagents from Wako Chemical Industries Ltd. (Osaka, Japan) without further purification.

A part of the precipitates was dissolved in hydrochloric acid solution. The ratios of phosphorus, iron, and cerium in the precipitates were also calculated from Inductively Coupled Plasma (ICP) results of these solutions, using SPS1500VR, Seiko Instruments Inc. The thermal behavior of these materials was analyzed by X-ray diffraction (XRD). XRD patterns were recorded on a Rigaku Denki RINT 2000 X-ray diffractometer using monochromated $\text{CuK}\alpha$ radiation.

The powder properties of thermal products at 60 , 200 , 400 , and 600°C were characterized by particle shape and size distribution. Particle shapes were observed by scanning electron micrographs (SEM) using JGM-5510LV, Jeol Ltd. Particle size distribution was measured with laser diffraction / scattering particle size distribution Horiba LA-910.

Further, as an application of phosphates, the catalytic activity of these iron - cerium phosphates was studied with the decomposition of the following complex.



Formaldehyde was formed the complex with ammonium acetate and acetylacetone. This complex has the light adsorption at 415 nm . Samples were added in this solution and then shaken for 24 h. The strong catalyst decomposed this complex. Therefore, the adsorption at 415 nm became small. The catalytic activity of iron - cerium phosphate was

estimated from this adsorption at 415 nm .

RESULTS AND DISCUSSION

Chemical composition and powder properties of iron - cerium phosphates

All obtained samples were yellow powder in color, therefore the iron condition in precipitate is mainly trivalent state. Table I shows the chemical composition of precipitates from ICP measurements. Because the Fe/P ratio in iron phosphate, FePO_4 , is 1, samples contained a certain degree

Table I - Chemical composition of precipitates from ICP measurements.

[Tabela I - Composição química dos precipitados medidos por ICP.]

	Preparation		Precipitate, $\text{Fe}_x\text{Ce}_y\text{HzPO}_4$			
	Fe/Ce	sur/P	X	y	z	Fe/Ce
A	10/0	0/10	0.812	-	0.564	-
B	8/2	0/10	0.750	0.125	0.250	8/1.33
C	10/0	1/10	0.840	-	0.480	-
D	8/2	1/10	0.681	0.115	0.497	8/1.35
E	10/0	2/10	0.868	-	0.396	-
F	8/2	2/10	0.686	0.120	0.462	8/1.40

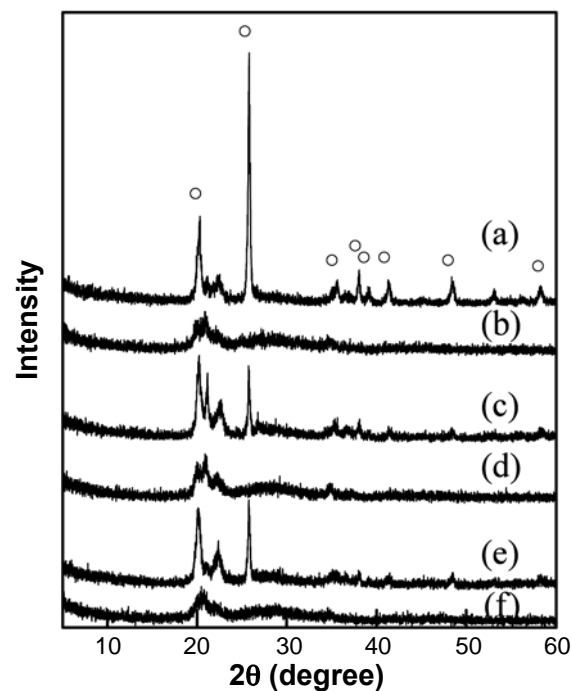


Figure 1: XRD patterns of samples heated at 600°C , (a) $\text{Fe}/\text{Ce}=10/0$, $\text{P}/\text{sur}=10/0$, (b) $\text{Fe}/\text{Ce}=8/2$, $\text{P}/\text{sur}=10/0$, (c) $\text{Fe}/\text{Ce}=10/0$, $\text{P}/\text{sur}=10/1$, (d) $\text{Fe}/\text{Ce}=8/2$, $\text{P}/\text{sur}=10/1$, (e) $\text{Fe}/\text{Ce}=10/0$, $\text{P}/\text{sur}=10/2$, and (f) $\text{Fe}/\text{Ce}=8/2$, $\text{P}/\text{sur}=10/2$, \circ ; FePO_4 .

[Figura 1: Difratoformas de raios X das amostras aquecidas a 600°C , (a) $\text{Fe}/\text{Ce}=10/0$, $\text{P}/\text{sur}=10/0$, (b) $\text{Fe}/\text{Ce}=8/2$, $\text{P}/\text{sur}=10/0$, (c) $\text{Fe}/\text{Ce}=10/0$, $\text{P}/\text{sur}=10/1$, (d) $\text{Fe}/\text{Ce}=8/2$, $\text{P}/\text{sur}=10/1$, (e) $\text{Fe}/\text{Ce}=10/0$, $\text{P}/\text{sur}=10/2$, e (f) $\text{Fe}/\text{Ce}=8/2$, $\text{P}/\text{sur}=10/2$, \circ ; FePO_4 .]

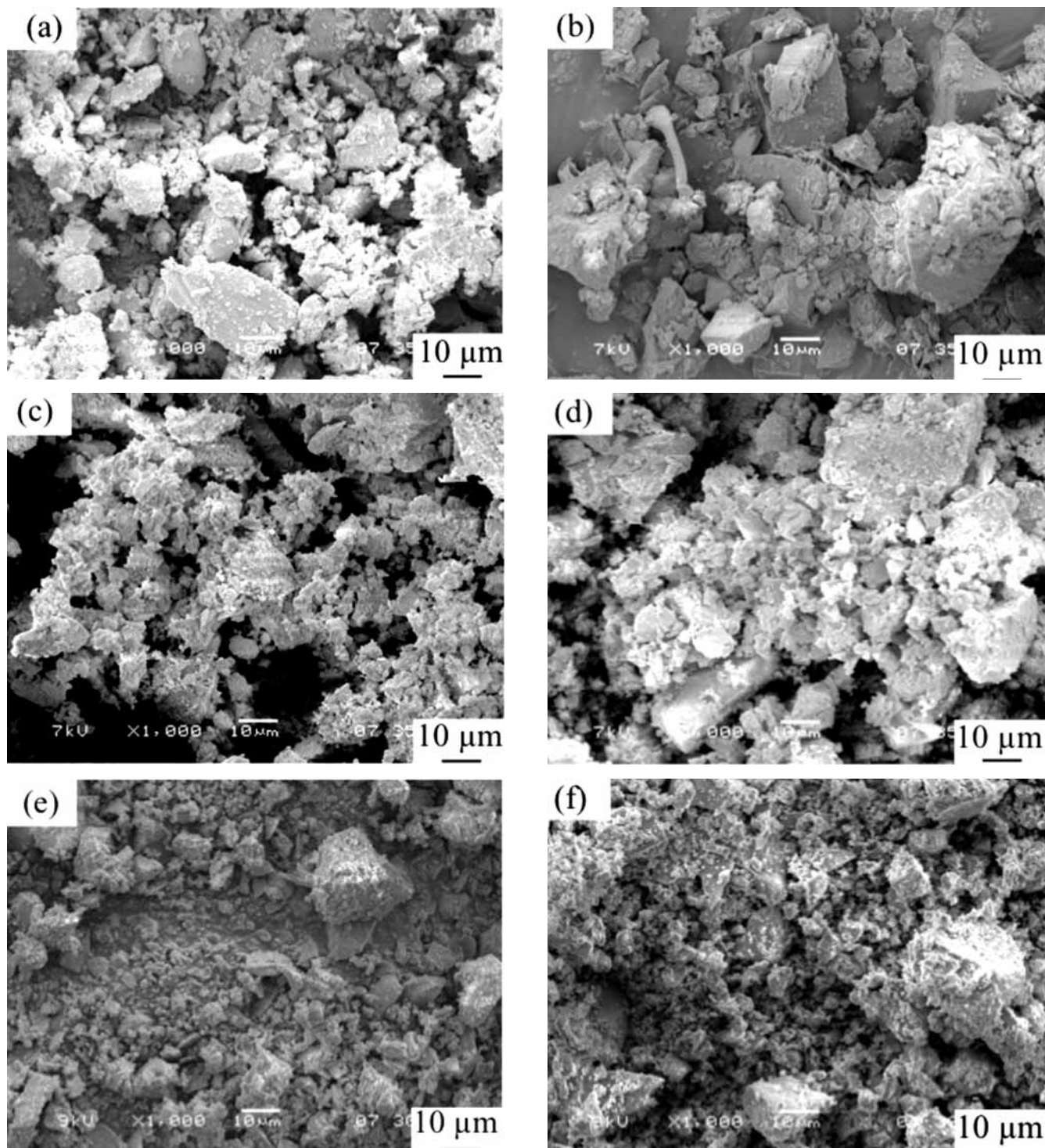


Figure 2: SEM images of samples, (a) Fe/Ce=10/0, P/sur=10/0, 60 °C, (b) Fe/Ce=8/2, P/sur=10/0, 60 °C, (c) Fe/Ce=10/0, P/sur=10/2, 60 °C, (d) Fe/Ce=8/2, P/sur=10/2, 60 °C, (e) Fe/Ce=10/0, P/sur=10/2, 600 °C, and (f) Fe/Ce=8/2, P/sur=10/2, 600 °C.

[Figura 2: Imagens de microscopia eletrônica de varredura das amostras (a) Fe/Ce=10/0, P/sur=10/0, 60 °C, (b) Fe/Ce=8/2, P/sur=10/0, 60 °C, (c) Fe/Ce=10/0, P/sur=10/2, 60 °C, (d) Fe/Ce=8/2, P/sur=10/2, 60 °C, (e) Fe/Ce=10/0, P/sur=10/2, 600 °C, e (f) Fe/Ce=8/2, P/sur=10/2, 600 °C.]

of proton, like $\text{Fe}_{0.812}\text{H}_{0.564}\text{PO}_4$. The presence of proton is important to use as a phosphate catalyst. The cerium ratio in precipitate was lower than that of preparation condition. In previous works [15, 16], lanthanum ratio in precipitates was higher than that in preparation condition. This difference

is considered to be form the valence state of rare earth cation. Cerium cation in this work is tetravalent one, on the other hand, lanthanum cation in previous works is trivalent one. Trivalent rare earth cation was much easy to react to phosphate materials. It is well known that trivalent rare

earth phosphates are a main composition of Monazite ore and insoluble for acidic and basic solution in the groups of phosphate materials. The addition of pentaethylene glycol mono dodecyl ether had less influence on the Fe/Ce ratio in precipitates.

Samples heated at 60, 200, and 400 °C had unknown small peaks in XRD patterns. A large part of these samples were amorphous state by XRD analysis. Generally, phosphate materials prepared in a solution are amorphous in XRD analysis. Amorphous phosphate materials expected to have various kinds of acidic sites to work as an acidic catalyst. Fig. 1 shows XRD patterns of samples heated at 600 °C. Samples prepared in Fe/Ce=10/0 had peaks of FePO₄ in spite of the surfactant ratio (Fig. 1a,c,e). On the other hand, samples prepared in Fe/Ce=8/2 were amorphous or had the small peaks in XRD patterns (Fig. 1b,d,f).

Fig. 2 shows SEM images of samples prepared in various conditions. No specified shapes were observed in this work. By the substitution with cerium cation, large particles formed (Fig. 2a,b). The addition of surfactant made the particle size of phosphates smaller (Fig. 2c,d). The heating temperature had no influence on particle shape of iron-cerium phosphates (Fig. 2e,f). Fig. 3 shows the particle size distribution of samples prepared in Fe/Ce=10/0 and 8/2. The particle size of iron – cerium phosphates were from 2 to 500 μm. The Fe/Ce ratio and P/sur ratio had small changes on particle size distribution of iron-cerium phosphates, because particle size was in a

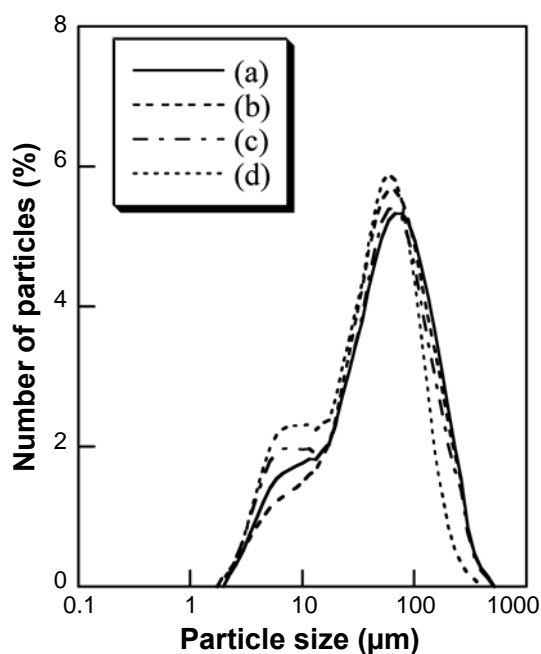


Figure 3: Particle size distributions of samples dried at 60 °C, (a) Fe/Ce=10/0, P/sur=10/0, (b) Fe/Ce=8/2, P/sur=10/0, (c) Fe/Ce=8/2, P/sur=10/1, and (d) Fe/Ce=8/2, P/sur=10/2.

[Figura 3: Distribuições de tamanho de partícula das amostras secas a 60 °C, (a) Fe/Ce=10/0, P/sur=10/0, (b) Fe/Ce=8/2, P/sur=10/0, (c) Fe/Ce=8/2, P/sur=10/1, e (d) Fe/Ce=8/2, P/sur=10/2.]

logarithm. Sample prepared without surfactant had larger particles than 100 μm in size by heating at 600 °C.

Catalytic properties of iron-cerium phosphates

Fig. 4 shows the catalytic activity of samples prepared in Fe/Ce=10/0 and 8/2 from the adsorption at 415 nm. The residual ratio in absorbance was calculated on the basis of that without catalyst. The low residual ratio means high catalytic activity of iron-cerium phosphates. Sulfuric acid, as one of common acidic catalysts, had about 30% of the residual ratio in this reaction. Some iron – cerium phosphates indicated higher catalytic activity than that of sulfuric acid. Samples prepared in Fe/Ce=8/2 had higher catalytic activity than that in Fe/Ce=10/0. In previous work [17], iron phosphates heated at 60 and 600 °C indicated low catalytic activity. Because samples heated at 60 °C had large particles, the amount of acidic sites on surface of particles was small. From the results of samples heated at 600 °C, the crystalline iron phosphate was considered to have little catalytic activity. In this work, samples heated at 60 and 600 °C indicated low catalytic activity, considered in relation to that of iron-cerium phosphates as a whole. These results had same tendency with previous work. The influence of surfactant was not clear on the catalytic activity of iron-cerium phosphates.

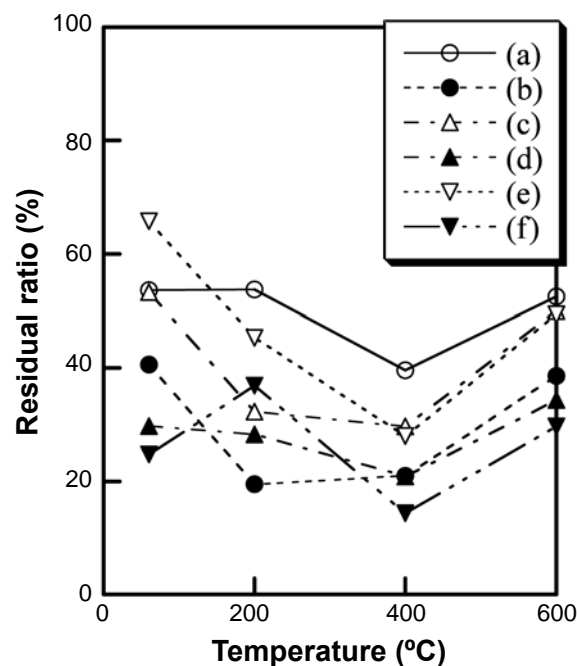


Figure 4: Catalytic activity of samples prepared in various conditions, (a) Fe/Ce=10/0, P/sur=10/0, (b) Fe/Ce=8/2, P/sur=10/0, (c) Fe/Ce=10/0, P/sur=10/1, (d) Fe/Ce=8/2, P/sur=10/1, (e) Fe/Ce=10/0, P/sur=10/2, and (f) Fe/Ce=8/2, P/sur=10/2.

[Figura 4: Atividade catalítica das amostras preparadas em varias condições, (a) Fe/Ce=10/0, P/sur=10/0, (b) Fe/Ce=8/2, P/sur=10/0, (c) Fe/Ce=10/0, P/sur=10/1, (d) Fe/Ce=8/2, P/sur=10/1, (e) Fe/Ce=10/0, P/sur=10/2, e (f) Fe/Ce=8/2, P/sur=10/2.]

CONCLUSIONS

Iron-cerium phosphates were prepared from iron nitrate, ammonium cerium nitrate, and phosphoric acid with a surfactant, pentaethylene glycol mono dodecyl ether. The obtained phosphates were yellow powder in color, therefore the iron condition in precipitate is mainly trivalent state. All samples had high hydrogen ratio in spite of the changes of the cerium and surfactant ratios. The peaks of FePO₄ were observed in XRD patterns of samples prepared in Fe/Ce=10/0 and then heated at 600 °C. Other samples were near amorphous states in XRD patterns. The particle size of iron-cerium phosphates was from 2 to 500 μm. Samples prepared in Fe/Ce=8/2 indicated higher catalytic activity than that in Fe/Ce=10/0 for the decomposition of the complex from formaldehyde, ammonium acetate, and acetylacetone.

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