Research Article

Preparation and Catalytic Properties of Iron-Cerium Phosphates with Sodium Dodecyl Sulfate

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Received 28 August 2012; Accepted 12 September 2012

Academic Editors: S. Gutzov and P. Thavorniti

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Iron phosphate was prepared from iron nitrate and phosphoric acid with sodium dodecyl sulfate at various stirring hours. 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.

1. Introduction

Phosphates have been used for ceramic materials, catalysts, fluorescent materials, dielectric substances, metal surface treatment, detergent, food additives, fuel cells, pigments, and so forth [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 an additive, sodium dodecyl sulfate (SDS) was used to prevent the aggregation in preparation process, which was one of the common anionic surfactant.

Transition metal phosphates have a weak point to solve in acidic and basic solutions. In previous work [13], 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 sodium dodecyl sulfate. The ratios of iron/cerium and sodium dodecyl sulfate/phosphorus were studied in this preparation. The obtained products were estimated from their particle shape, size distribution, and catalytic activity. The purpose in this work is to clear the influence of cerium substitution, SDS, and heating temperature on chemical composition and catalytic activity of iron phosphates.

2. 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

FIGURE 2: SEM images of samples (60°C), (a) Fe/Ce = 10/0, SDS/P = 0/10, (b) Fe/Ce = 8/2, SDS/P = 0/10, (c) Fe/Ce = 8/2, SDS/P = 1/10, and (d) Fe/Ce = 8/2, SDS/P = 2/10.

FIGURE 3: Particle size distribution of samples (60°C, SDS/P = 0/10), (a) Fe/Ce = 10/0 and (b) 8/2.

precipitate was lower than that of preparation condition. In previous works [14, 15], lanthanum ratio in precipitates was higher than that in preparation condition. This difference is considered to be from 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

FIGURE 4: Catalytic activity of samples (SDS/P = 0/10), (a) Fe/Ce = 10/0 and (b) 8/2.

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 sodium dodecyl sulfate had less influence on the Fe/Ce ratio in precipitates.

Samples heated at 60, 200, and 400°C were amorphous in XRD patterns. Generally, phosphate materials prepared in a solution are amorphous in XRD analysis. Amorphous

FIGURE 5: Catalytic activity of samples (Fe/Ce = 10/0), (a) SDS/P = 0/10, (b) 1/10, and (c) 2/10.

phosphate materials were expected to have various kinds of acidic sites to work as an acidic catalyst. Figure 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 SDS ratio (Figures 1(a), 1(c), and 1(e)). On the other hand, samples prepared in Fe/Ce = 8/2 were amorphous or had small peaks in XRD patterns (Figures 1(b), 1(d), and 1(f)).

Figure 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 were formed (Figures 2(a) and 2(b)). The addition of sodium dodecyl sulfate made the particle size of phosphates smaller (Figures 2(b), 2(c), and 2(d)). The heating temperature had no influence on particle shape of iron-cerium phosphates. Particle size distribution of samples was estimated for catalytic reaction in the complex solution. Figure 3 shows the particle size distribution of samples prepared in Fe/Ce = 10/0 and 8/2. The particle sizes of samples were from 2 to 800 μm. Sample prepared in Fe/Ce = 8/2 had larger particles than 100 μm in size. The amount of large particles became smaller by the addition of sodium dodecyl sulfate (not shown). The heating temperature had little change on particle size distribution of iron-cerium phosphates.

3.2. Catalytic Properties of Iron-Cerium Phosphates. Figure 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. In previous work [16], 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 prepared in Fe/Ce = 10/0 and then heated at 60 and 600°C indicated low catalytic activity. These results had same tendency with previous work. Samples prepared in Fe/Ce = 8/2 and then heated at 60, 200, and 600°C had high catalytic activity. The substitution with cerium prevented the crystallization of iron phosphate, therefore, sample heated at 600°C (Fe/Ce = 8/2) indicated high catalytic activity. Figure 5 shows the catalytic activity of samples prepared with various SDS ratios. Samples prepared with SDS/P = 1/10 and 2/10 had higher catalytic activity than sample prepared without sodium dodecyl sulfate. Because samples prepared with sodium dodecyl sulfate had smaller particles, the complex came into contact with phosphate catalysts.

4. Conclusions

Iron-cerium phosphates were prepared from iron nitrate, ammonium cerium nitrate, and phosphoric acid with sodium dodecyl sulfate. 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 Fe/Ce and P/SDS 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 amorphous in XRD patterns. The particle size of samples prepared in Fe/Ce = 8/2 was larger than that in Fe/Ce = 10/0. Samples prepared in Fe/Ce = 8/2 and then heated at 60, 200, and 600°C indicated high catalytic activity for the decomposition of the complex from formaldehyde, ammonium acetate, and acetylacetone.

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