

Synthesis and Characterization of a Novel Heteropoly Acid/Hydrogel Composite

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Abstract Catalysis by Heteropoly acids (HPAs) and polyoxometalates (POMs) having a higher demand worldwide, as it can be designed to accelerate complex reactions and be more environmentally friendly. However, recycling of water-soluble solid catalysts remains a problem. The synthesis of a recyclable composite with catalytic properties is the key to better use of HPAs and POMs. Many researches have mentioned the method of synthesis by immersing a porous carrier in a supported solution. However, the catalytic stabilities of the previously studied composites after multiple uses have rarely been mentioned. In this research, a novel idea is proposed to synthesize a heteropoly acid supported composite. A complex hydrogel with catalytic properties was synthesized by mixing an anionic monomer with a heteropoly acid. The heteropoly acid particles were inserted inside the hydrogel by the interaction forces between the anions. Thus, preventing the water-soluble heteropoly acid from being lost during the catalytic reaction. The complex hydrogel is consisted of the anionic monomer 2-acrylamide-2-methylpropanesulfonic acid (AMPS) as a carrier, *N,N'*-Methylenebisacrylamide (MBAA) as crosslinkers and the typical Keggin-type HPA: $H_3PW_{12}O_{40}$. At last, a composite with $(NH_4)_3PW_{12}O_{40}$ particles was synthesized.

1 Introduction

Homogeneous catalysts usually bring excellent yield of production while causing environmental pollution, equipment corrosion and hard catalyst separation, which limit the extensive industrial application process of them.

Thus, the construction of high selective, active, stable, easily recyclable heterogeneous catalysts is a challenging goal of liquid phase oxidation catalysis (Cavani *et al.*, 2009; Clerici and Kholdeeva, 2013; Duprez and Kholdeeva, 2014).

Polyoxometalates (POMs) are discrete anionic metal oxide nanoclusters formed by early transition metals in their highest oxidation states (Pope and Müller, 1994). This family of compounds have been studied extensively because its chemical properties can be varied considerably due to the structure characteristics (Seaton *et al.*, 2017; Ma *et al.*, 2017), that makes them suitable for applications in fields like catalysis, energy, magnetism and materials science (Sécheresse, 2013).

In the catalysis field, the Keggin-type $[XM_{12}O_{40}]_n$ ($X=P, Si, Ge; M=W, Mo, etc.$) structure is the most common and stable structure (Pope *et al.*, 1983; Hill,

1998). The Keggin-type phosphotungstic acid $H_3PW_{12}O_{40}$ has high levels of acidity and thermal stability, that makes it widely used as a solid catalyst in gas phase or as a homogeneous catalyst in liquid phase (Kozhevnikov, 1998; Mizuno *et al.*, 1998).

Numerous studies have shown that the heteropoly acid could be converted into heterogeneous catalyst when it was supported on some supporters like silica, carbon and polymeric nanoparticles, and most of the heterogeneous catalysts showed better catalytic ability than heteropoly acid as a homogeneous catalyst (Huang *et al.*, 2018; Liao *et al.*, 2019).

$(NH_4)_3PW_{12}O_{40}$, is an ammonium salt with micropores defined as “sponge crystal” by Inumaru (Inumaru, 2006). $(NH_4)_3PW_{12}O_{40}$ also shows acid catalytic activity for conversion of methanol to hydrocarbons (Hayashi and Moffat, 1983) and conversion of methylethylbenzene (McMonagle and Moffat, 1984). $(NH_4)_3PW_{12}O_{40}$ has been prepared by neutralizing phosphotungstate acid with ammonium hydrogencarbonate, ammonium carbonate (Inumaru, 2006), or prepared by reaction of NH_4^+ with in-site

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generated $\text{PW}_{12}\text{O}_{40}^{3-}$ in a strongly acidic solution (Sahiro *et al.*, 2013).

In this research, a novel technique is proposed to synthesize a heteropoly acid supported composite. A complex hydrogel with catalytic properties was synthesized by mixing an anionic monomer AMPS with a heteropoly acid. The heteropoly acid particles were inserted inside the hydrogel by polymer chains and interaction forces between the anions. Thus, preventing the heteropoly acid from being lost during the catalytic reaction. Here, we present this method by reaction of NH_4^+ with in-site generated $\text{PW}_{12}\text{O}_{40}^{3-}$ in a free radical polymerization process. The synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ particles were well kept in the hydrogel structure has been confirmed by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Thermogravimetric analysis (TGA).

2 Experimental

2.1 Materials

Monomer: AMPS (2-Acrylamido-2-methylpropane sulfonic acid) was obtained from Tokyo Chemical Industry Co., Ltd. Crosslinker: MBAA (*N,N'*-Methylenebisacrylamide) was obtained from Sigma Aldrich Co., Ltd. Initiator: $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and Accelerator: Na_2SO_3 were obtained from Nacalai Tesque, INC. PTA ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) was obtained from Nippon Inorganic Colour & Chemical Co., Ltd. All chemicals were reagent-grade and used as supplied. Water used in all the experiments was distilled water.

2.2 Synthesis of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /hydrogel composite

All AMPS/ $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ composites were synthesized by free radical polymerization method. 0.025 mol AMPS, 0.00125 mol MBAA, 0.0005 mol Na_2SO_3 and 0.0005 mol PTA were mixed together in one container, while 0.0005 mol $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was in another container. Distilled water was added to make total solution volume 25 mL, the consisted of 5 mL for the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and 20 mL for mixture of AMPS, MBAA, Na_2SO_3 , and PTA. The obtained mixtures were homogenized and bubbled with nitrogen gas to remove dissolved oxygen for 1 hour, then poured into the polytetrafluoroethylene (PTFE) tube of 6 mm inner diameter. Reaction was conducted at 50°C for 24 hours. After composites were synthesized, they were cut into 3 mm segments and washed by methanol using Soxhlet extractor for 24 hours. Finally, the hydrogel composites were air dried at room temperature for 1 day then followed by further drying at 50°C for 1 day in a drying oven. Then, dried hydrogel composites were washed by deionized water at room temperature and dried for every 24 hours.

2.3 Characterizations

FT-IR spectra were recorded on an IRPrestige-21 (SHIMADZU) Fourier transform infrared spectrophotometer with 2 cm^{-1} resolution.

Powder X-ray diffraction (XRD) patterns were measured with a MiniFlex600 (RIGAKU) diffractometer by using $\text{Cu K}\alpha$ radiation at ambient temperature. And crystallite sizes were calculated by using Scherrer's equation (1).

$$d = \frac{B\lambda}{\beta \cos \theta} \quad (1)$$

Surface morphology was observed using an S-5200 (HITACHI High-Technologies) field-emission scanning electron microscopy at an acceleration voltage of 1.0 kV. The samples for the SEM analysis were dusted on adhesive conductive carbon paper attached to a brass sample mount.

High-resolution transmission electron microscopy (TEM) were obtained using a JEM-2010 (JEOL Ltd.) electron microscope operated at 200kV for obtaining TEM images. The samples for the TEM analysis were prepared on perforated carbon film mounted on a copper grid.

Thermogravimetric analysis (TGA) were measured by a TGA-50 (SHIMADZU) thermogravimetric analyzer. The samples (ca. 20 mg) were heated in a flow of air at 20 K min^{-1} from room temperature to 873 K and kept at 873 K for 10 mins.

3 Result and Discussion

3.1 Synthesis and characterization

The $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ was produced by reaction of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ during the free radical polymerization of the AMPS hydrogel.

Figure 1 shows FT-IR spectra of the hydrogel, composites and PTA.

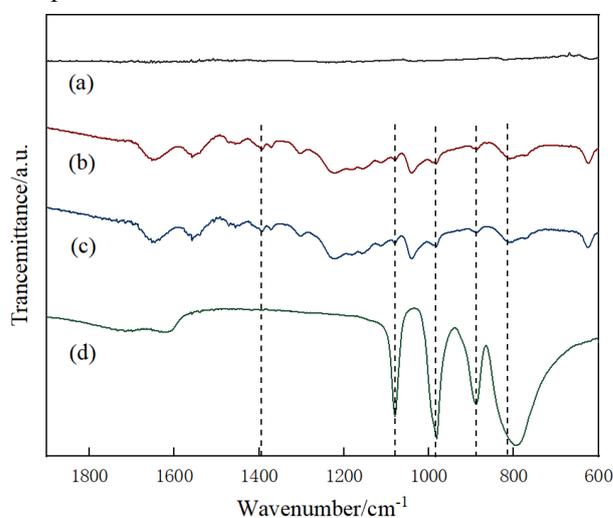


Figure 1. FT-IR spectra of sample AMPS hydrogel (a), synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite (b), synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite after 96 h washed (c), and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (d)

Although the characteristic bands were much weaker than pure PTA, in both composites, characteristic bands of Keggin-type phosphotungstate $[\text{PW}_{12}\text{O}_{40}]^{3-}$ at 1080, 983, 887, and 810 cm^{-1} could be observed, and a band corresponding to bending vibration of NH_4 at 1396 cm^{-1} was also observed. Comparing samples (b) and (c), the positions and intensities of characteristic bands were almost the same, it showed that the $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ particles in the composite were no chemical constitution changing during the washing process. These data indicated that the $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ was contained in the composite and remained at a stable chemical state inside the composite.

Figure 2 shows XRD patterns of the AMPS hydrogel, obtained composites and PTA. XRD patterns of synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite and composite after 96 h washed showed almost the same characteristic peaks, but different peak intensities. And both of composites had stronger peak intensities than pure PTA. In figs 2b and 2c, the peaks at $2\theta = 22.3, 27.1, 31.3$ and 36.6 were consistent with previous research (Sahiro *et al.*, 2013). In particular, the strong peak at $2\theta = 26.5$ is a significant marker of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ crystal. Crystallite sizes were calculated by using Scherrer's equation, the sizes were 8.9 nm (b) and 14.0 nm (c), respectively. It indicated that $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized crystallites were formed in the composite, however, the crystallites became larger when the washing time increased.

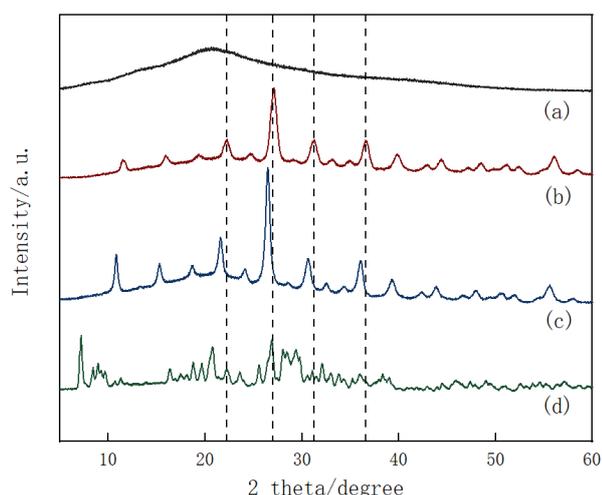


Figure 2. XRD patterns of sample AMPS hydrogel (a), synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite (b), synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite after 96 h washed (c), and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (d)

Figure 3 shows SEM images of the AMPS hydrogel and obtained composites. Smooth surface was observed in AMPS image (a). On the other hand, a lot of small white particles were observed on the surface of the composites in (b), (c) and (d). In image (c), the higher magnification was used to observe the synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite, many white particles could be clearly observed on the surface of composite. Comparing the red frame areas in (b) and (d), the white particles in (d) were more clearly observed than those in (b). It showed that these white particles in the washed composites were larger than those in the unwashed ones.

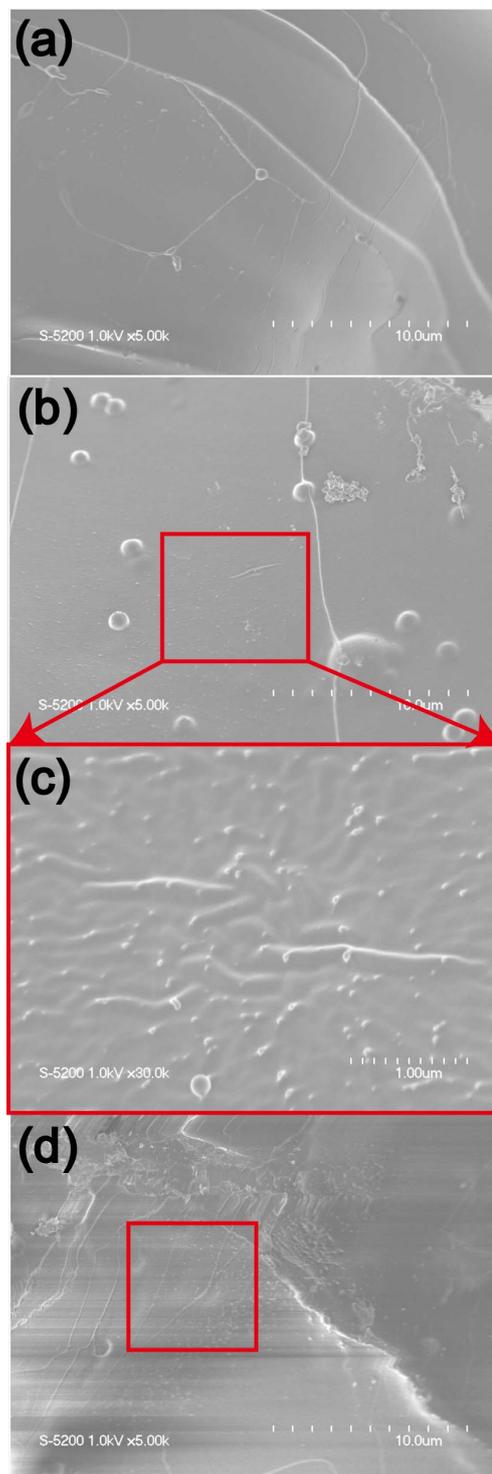


Figure 3. SEM images of sample AMPS hydrogel $\times 5.0\text{k}$ (a), synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite $\times 5.0\text{k}$ (b), synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite $\times 30.0\text{k}$ (c), and synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ /AMPS composite after 96 h washed $\times 5.0\text{k}$ (d)

This result might be caused by nanosized particle agglomeration. During the washing process, the AMPS hydrogel absorbed water and swelled, so that the polymeric structure became loose. It led to the nanosized particles agglomerating easily. These results indicate that the small particles were dispersed in the composites at first. However, with the washing time increasing, the

particles became larger. It conjectured that these white particles were clusters which were aggregated by $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized crystallites, with the washing time increasing, the nanosized crystallites agglomerated and formed larger clusters. In order to verify this conjecture, the TEM analysis was performed.

Figure 4 shows TEM images of the obtained composite. (a) and (b) show synthesized composite in different magnifications, (c) and (d) show washed composite in different magnifications. In the TEM images, both samples showed the similar particle agglomerated states. Although the particles had an agglomerated state, primary crystallites could still be observed. It suggested that the growth of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized crystallites was suppressed by an interaction between polymer chains and crystallites. The crystallites sizes increased slightly from 8.9 nm to 14.0 nm after 96 h washing. It was also proved by the results in XRD analysis as expressed in Figure 2.

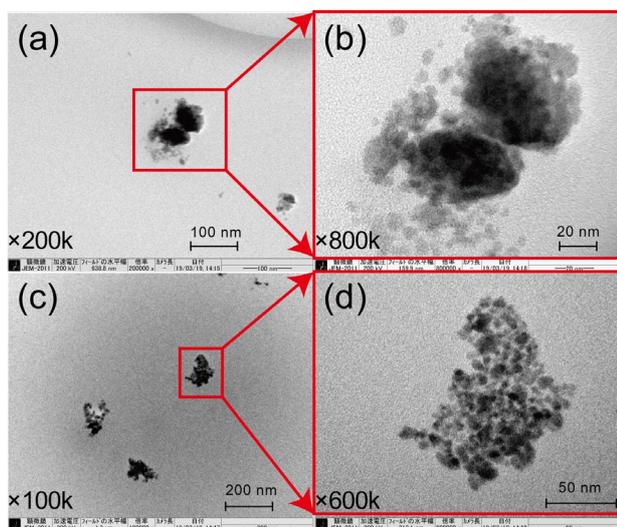


Figure 4. TEM images of sample synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}/\text{AMPS}$ composite $\times 200\text{k}$ (a), $\times 800\text{k}$ (b), and synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}/\text{AMPS}$ composite after 96 h washed $\times 100\text{k}$ (c), $\times 600\text{k}$ (d)

3.2 Catalyst stability and recoverability

Figure 5 shows particle contents of the composites obtained by TGA. During the washing process, the particle contents were kept at about 17%, while the mass fraction of PTA in the materials solution was about 20% before preparation of the composites. It suggested that hydrogel supporter played an important role to keep particle content at a high level. In composites, the average size of clusters which were aggregated by nanosized catalyst particles was about 100 nm, and in other researches indicated, the hydrogel network mesh size was usually smaller than 100 nm (Han *et al.*, 2014; Munoz-Pinto *et al.*, 2015). In this case, clusters couldn't escape from the composite, so the particle content could be kept at a high level. It indicated that the $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized particles could be kept in the composite during the washing process and be recovered easily.

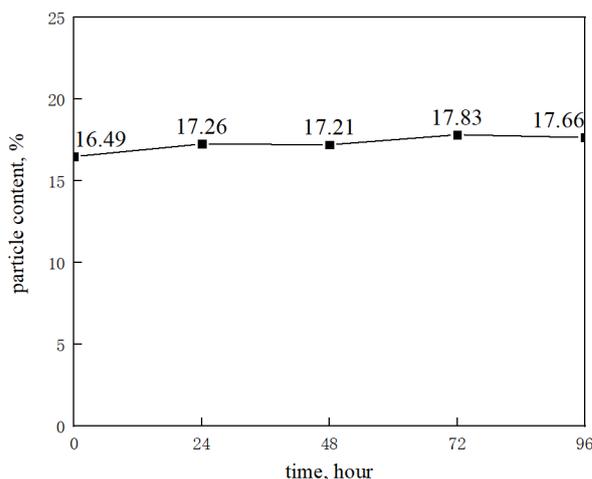


Figure 5. Particle content of synthesized $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}/\text{AMPS}$ composite after 0, 24, 48, 72, 96 washed by deionized water

4 Conclusions

This study presented a novel technique to synthesize a $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized particles supported composite. FT-IR and XRD experiments indicated that the $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized crystallites were formed in the composite and remained at a stable chemical state inside the composite. SEM and TEM experiments indicated that the clusters agglomerated by $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized crystallites were well dispersed in the composites, and the growth of $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ nanosized crystallites was suppressed by an interaction between polymer chains and crystallites. TG analysis indicated that the $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ particles could be kept in the composite during the washing process and be recovered easily. These results proved that the novel synthesis technique for synthesizing a heteropoly acid / hydrogel composite was feasible. In our next study, we will examine the catalytic performances of the composite in practical applications.

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