Synthesis of Novel Manganese Aluminum Phosphate Violet Pigments

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Research Article

Keywords: Violet pigment, Phosphate materials, L*a*b* color phase

Posted Date: October 30th, 2020

DOI: https://doi.org/10.21203/rs.3.rs-98835/v1

Abstract

Novel violet pigments were synthesized from manganese oxide, aluminum hydroxide, and phosphoric acid by heating at several temperatures. The obtained materials were investigated by X-ray diffraction (XRD) analysis, infrared (IR) spectroscopy, ultraviolet–visible (UV–Vis) reflectance spectroscopy, and L*a*b* color space. Sample synthesized in this work showed no clear peak pattern on XRD analysis. At Mn/Al/P = 1/1/4, sample heated at 400 ° C showed the most violet color. The effect of heating time was small. In addition, the increasing the manganese ratio darkened the sample. Further, we examined the improvement of blue and red by replacing with copper and iron. The blue tint was improved by adding a small amount of copper. On the other hand, a high proportion of iron lost the violet color.

Introduction

The use of harmful metals is being restricted worldwide by various government regulations in an attempt to reduce and control the environment pollution. However, the lack of alternatives necessitates the use of materials containing harmful metals in many fields [1,2]. For example, inorganic color pigments with metals such as mercury, cadmium, and lead exhibit good properties, including high stability against radiation, heat resistance, coloring visibility, and low cost [3-5]. In addition, because of their low coloring and opacity, oxide pigments are not suitable for incorporation in paint and plastics [6]. Sulfate and nitride pigments have lower heat resistance than oxide pigments and also require harmful and/or combustible gas to synthesize. Furthermore, it is difficult to obtain sulfide and nitride pigments with repeatability [7,8]. Therefore, novel inorganic pigments with suitable properties and facile production methods are demanded.

Several kinds of inorganic red pigments are available for use, e.g., red iron oxide, red lead, cadmium red, vermilion, and cinnabar [9-12]. However, they all suffer from several disadvantages. For instance, red iron oxide exhibits only limited colorfulness, while other pigments contain harmful metals such as lead, cadmium, and mercury. Therefore, a novel red pigment that is economical and does not contain any harmful metals is required. We focus on the natural ore, natrophilite ($NaMnPO_4$), because it contains low-toxicity metals [13,14]. Natural ores have high stability against radiation and heat resistance. Furthermore, they exist in solid phase, which allows applications in plastics, paint, ceramics, etc. Natrophilite contains bivalent manganese ion. The valence of manganese is important to prepare these novel red pigments.

In previous works, we try to obtain manganese phosphate red pigments by heating, however only brown pigments were obtained as a result [15,16]. Therefore, we synthesize the inorganic pigments by further changing the mixing conditions, a red pigment was not obtained, but a violet pigment could be obtained [17]. However, this violet pigment is dark as a whole, and improvement in brightness is required. Therefore, in this study, a violet pigment whose brightness was improved by adding aluminum was produced.

Experimental

The 2 mL of phosphoric acid (14 mol/L) was diluted with 10 mL of water. The mixture of manganese dioxide and aluminum hydroxide was mixed with this phosphoric acid in the molar ratio of Mn/Al/P = 1/1/4. This mixture was kept for 1 day, and then heated at 300, 400, 500, 600, and 700ºC for 1, 6, 20 hours. The ideal chemical equations were follows.

$MnO_2 + Al(OH)_3 + 4H_3PO_4 \rightarrow Mn(+II)Al(H_2PO_4)_3(HPO_4) + 4H_2O + 1/2O_2$ (1)

$MnO_2 + Al(OH)_3 + 4H_3PO_4 \rightarrow Mn(+III)Al(H_2PO_4)_2(HPO_4)_2 + 9/2H_2O + 1/4O_2$ (2)

To obtain various kinds of pigments, we synthesized the materials at Mn/Al/P = 0.5/1.5/4, 0.75/1.25/4, 1.25/0.75/4, 1.5/0.5/4 in the same method. Further, copper oxide or iron powder was mixed in Cu or Fe/Mn/Al/P = 0.2/0.8/1/4, 0.2/1/0.8/4, 0.5/0.5//1/4, 0.5/1/0.5/4, and then heated at 400ºC for 1 hour for the purpose of improving blue and red. All chemicals were of commercial purity (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and were used without further purification.

The chemical compositions of these materials were determined by X-ray diffraction (XRD) analysis and infrared (IR) spectroscopy. The XRD patterns and IR spectra of the samples were recorded using an X-ray diffractometer (MiniFlex, Rigaku Corp., Akishima, Japan) with monochromatic CuKα radiation and HORIBA FT-IR 720 (Horiba Ltd., Kyoto, Japan) using the KBr disk method, respectively.

The color of the phosphate pigments was evaluated based on ultraviolet–visible (UV–Vis) reflectance spectra (UV2100; Shimadzu Corp., Kyoto, Japan) (reference compound: $BaSO_4$). The color of the pigments was also described using a TES135 plus color analyzer (TES Electrical Electronic Corp, Taipei, Taiwan). The L* value represents the whiteness of powder, in which 100 is white, while 0 is black. The a* value signifies the redness of the material, with positive (maximum; +128) and negative (-128) values corresponding to red and green, respectively [18]. The b* value denotes yellow intensity, in which positive (maximum; +128) and negative (-128) values correspond to yellow and blue, respectively.

Results And Discussion

Samples synthesized in Mn/Al/P=1/1/4

Figure 1 shows the XRD patterns of the samples prepared at various temperatures. All the samples were almost amorphous and did not show the peak pattern of the specific compound. Figure 2 shows the IR spectra of the samples prepared at various temperatures. Samples heated at low temperature showed the broad absorption peaks, while samples heated at high temperature showed the relatively clear peaks. It was considered that many compounds such as raw materials and products were contained at low temperature, whereas the raw material was lost at high temperature.

Figure 3 shows the photograph of the samples prepared at various temperatures. Sample heated at 300 ° C was dark, the sample heated at 400 ° C became purple, and became brighter by heating to a higher temperature. Figure 4 shows the UV-Vis reflectance spectra of the samples prepared at various temperatures. It was confirmed that all the samples had high reflectance near 400 nm and turned violet. The higher the heating temperature, the higher the overall reflectance, which corresponded to the whiteness. Figure 5 shows the photograph of samples prepared for various hours. The change in color due to the difference in heating time was small.

Table 1 shows the L*a*b* values of the samples prepared at various temperatures. Sample heated at 400 ℃ showed the highest a * value and the low b * value. Samples heated at 400 to 600 ℃ showed similar b * values, and had almost the same bluish color. The L * value increased as the temperature increased, which corresponded to the whitening of the sample powder. The a * value and the b * value decreased with increasing heating time. This indicated that redness was reduced and bluish was increased, which turned out to be more violet.

Samples synthesized in various Mn/Al/P ratios

Figure 6 shows the photograph of samples prepared in various Mn/Al/P ratios. It can be seen that the violet color becomes stronger as the proportion of manganese increases. This was a reasonable result given that the aluminum compound is white. Table 2 shows the L*a*b* values of sample prepared in various conditions. Samples with high manganese content showed low L * values. The change of a * value and b * value with respect to the change of manganese ratio was small. Increasing the proportion of aluminum only affected improving brightness, L * value.

Addition of CuO and Fe powder

Figure 7 shows the photograph of samples prepared in various Cu/Mn/Al/P ratios. Sample replaced with 20% of copper showed a strong purple color, while sample replaced with 50% had a weaker color. Figure 8 shows the photograph of samples prepared in various Fe/Mn/Al/P ratios. Sample substituted with 20% iron showed a purple color, while sample substituted with 50% became gray powder.

Table 3 shows the L*a*b* values of sample prepared in various conditions. Sample with 20% substitution with copper showed a lower b* value than sample without substitution, while the sample with 50% substitution showed a higher b * value. The 20% substitution with copper improved the blueness. On the other hand, sample with 20% substitution with iron showed almost the same a* value as sample without substitution. The redness could not be improved by replacing with iron.

Conclusions

Novel manganese aluminum phosphate violet pigments were obtained by heating a mixture of manganese dioxide, aluminum hydroxide, and phosphoric acid at various temperatures. Samples synthesized in this work did not show a clear peak pattern in XRD analysis. At Mn/Al/P = 1/1/4, sample heated at 400ºC showed the most violet color. The effect of heating time was small. Moreover, the sample became darker when the proportion of manganese was increased. Blue tint was improved by adding a small amount of copper. Also, at high iron ratio, the violet color was lost.

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Tables

Table 1 L*a*b* values of sample prepared in various conditions (Mn/Al/P=1/1/4)

Temperature /ºC	Time /h	L*	a*	b*
300	1	24.26	6.95	-3.59
400	1	44.99	12.26	-14.13
500	1	50.79	8.47	-14.22
600	1	63.98	5.28	-14.36
700	1	66.05	2.76	-5.21
400	6	43.69	11.62	-15.83
400	20	40.16	10.13	-15.61

Table 2 L*a*b* values of sample prepared in various conditions (400ºC, 1 h)

Mn/Al/P	L*	a*	b*
0.5/1.5/4	43.57	11.84	-13.48
0.75/1.25/4	36.97	10.09	-11.32
1/1/4	44.99	12.26	-14.13
1.25/0.75/4	27.86	11.98	-12.87
1.5/0.5/4	25.72	12.76	-11.36

Table 3 L*a*b* values of sample prepared in various conditions (400ºC, 1 h)

	Cu or Fe/Mn/Al/P	L*	a*	b*
Cu	0.2/0.8/1/4	43.32	12.70	-15.18
Cu	0.2/1/0.8/4	40.03	13.87	-16.35
Cu	0.5/0.5/1/4	46.16	9.46	-11.28
Cu	0.5/1/0.5/4	36.91	12.11	-10.59
Fe	0.2/0.8/1/4	39.86	12.92	-13.07
Fe	0.2/1/0.8/4	37.64	12.73	-12.41
Fe	0.5/0.5/1/4	53.91	1.24	3.58
Fe	0.5/1/0.5/4	56.59	2.45	1.39

Figures

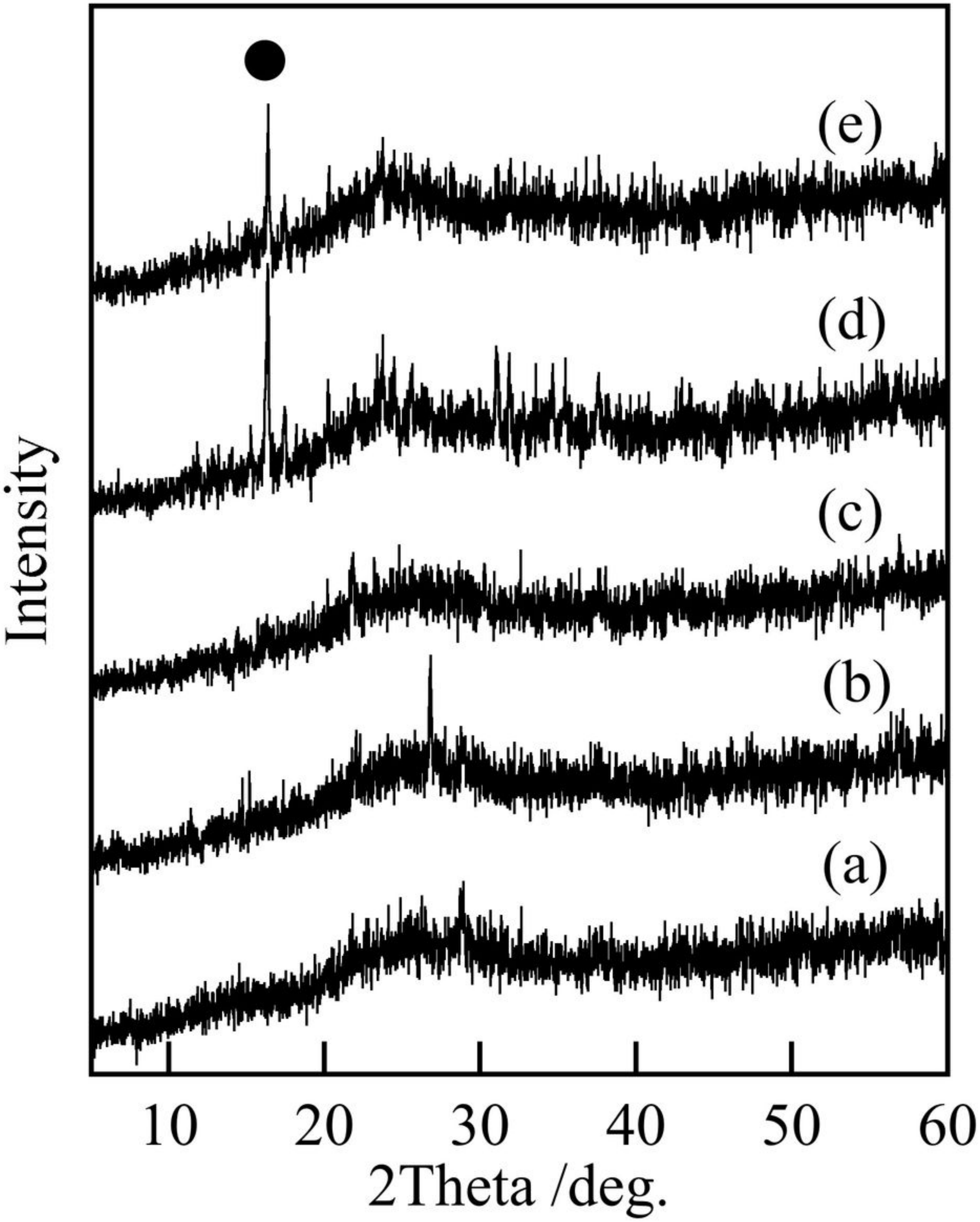
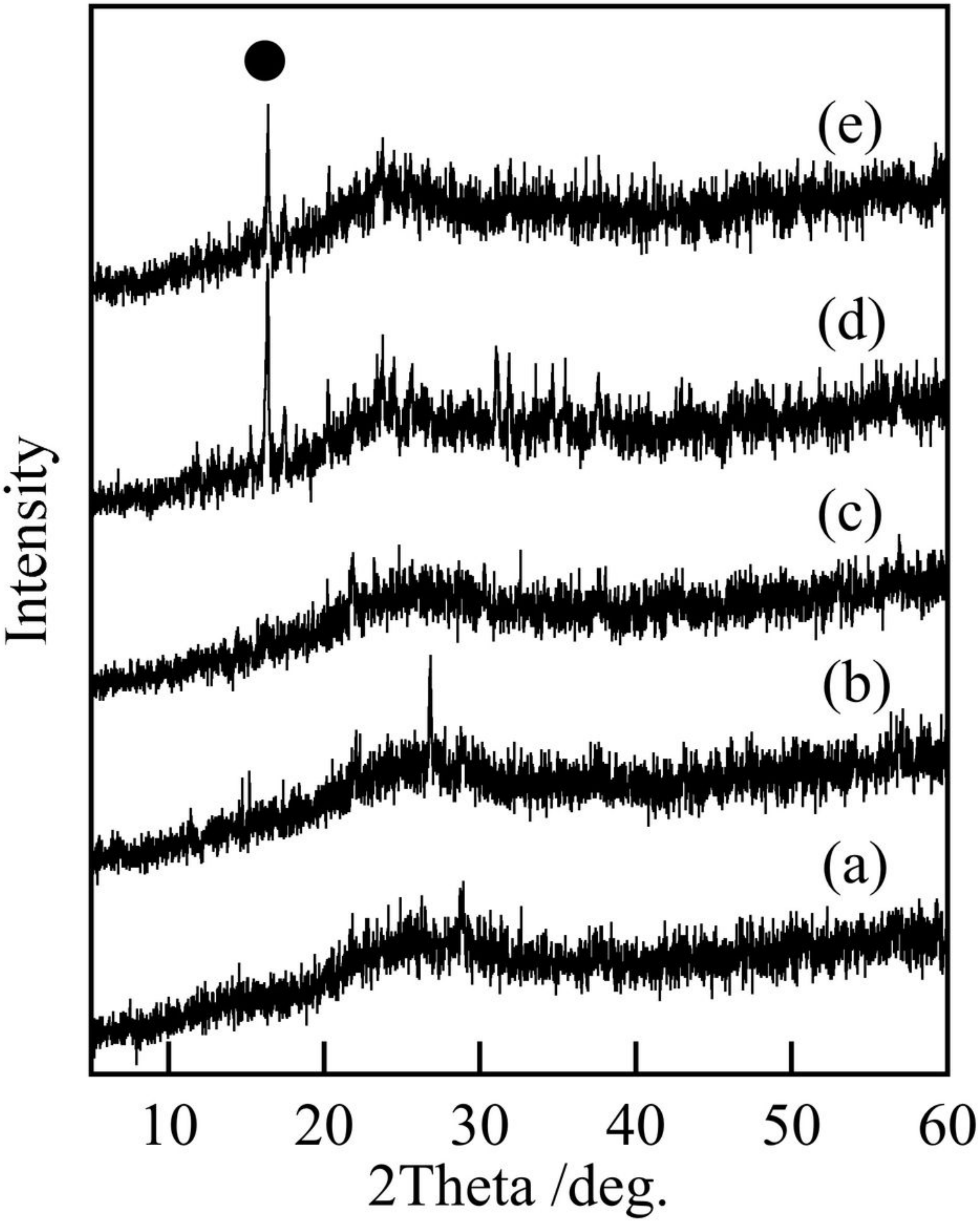


Figure 1

XRD patterns of samples prepared at various temperatures (Mn/Al/P=1/1/4, 1 h), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C, ●; MnHPO4.



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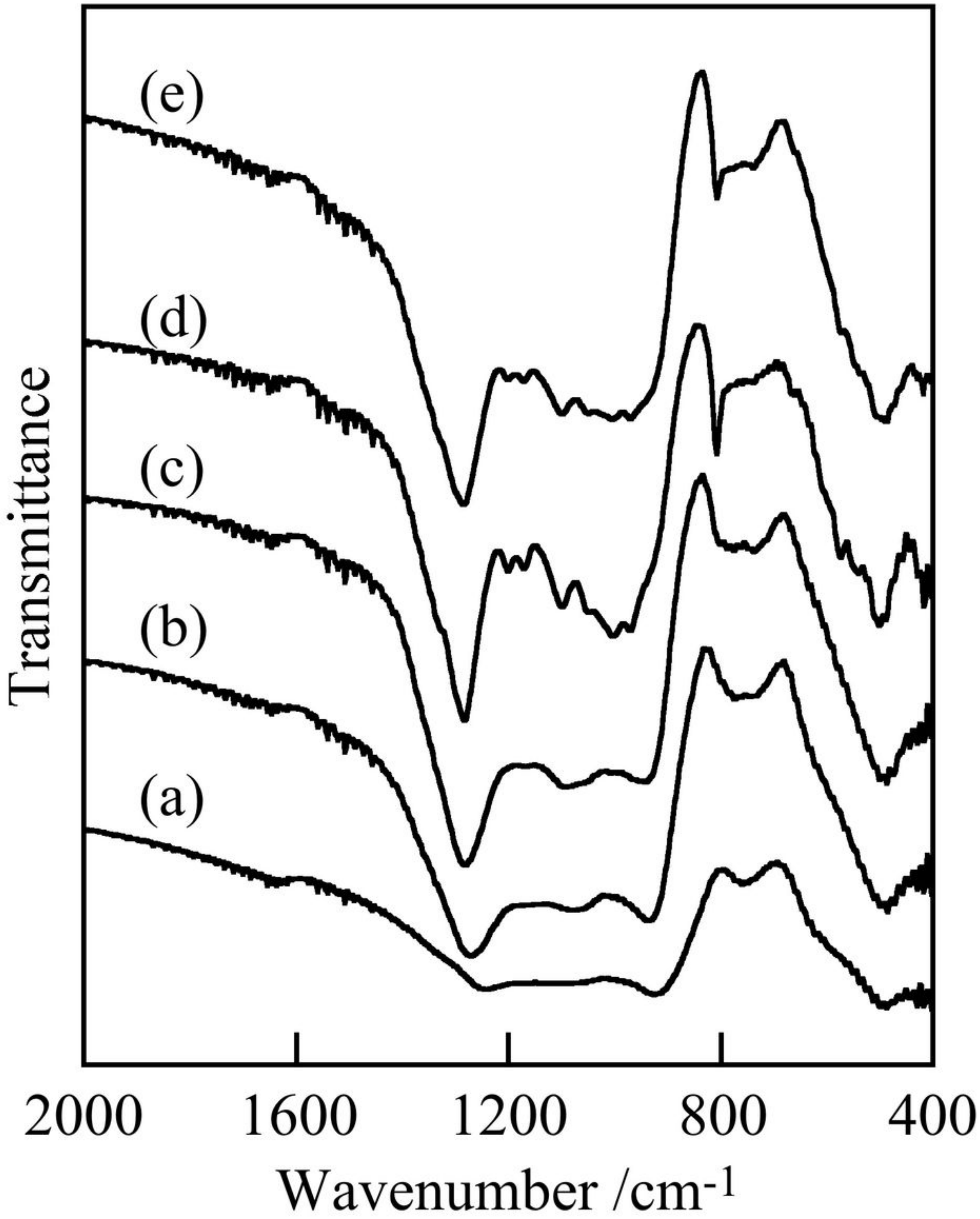
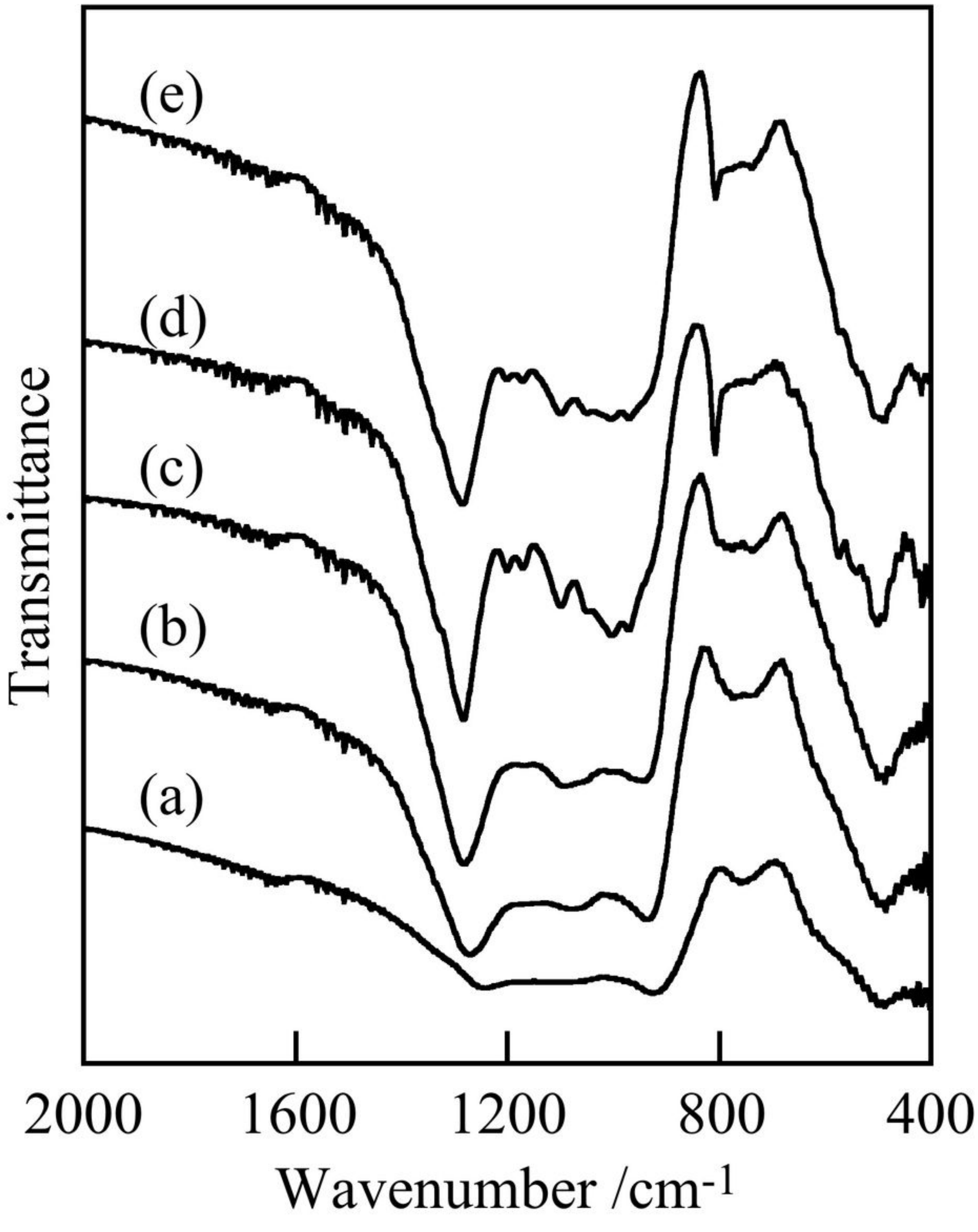


Figure 2

IR spectra of samples prepared at various temperatures (Mn/Al/P=1/1/4, 1 h), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.



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IR spectra of samples prepared at various temperatures (Mn/Al/P=1/1/4, 1 h), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.

Figure 3

Photograph of samples prepared at various temperatures (Mn/Al/P=1/1/4, 1 h), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.

Figure 3

Photograph of samples prepared at various temperatures (Mn/Al/P=1/1/4, 1 h), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.

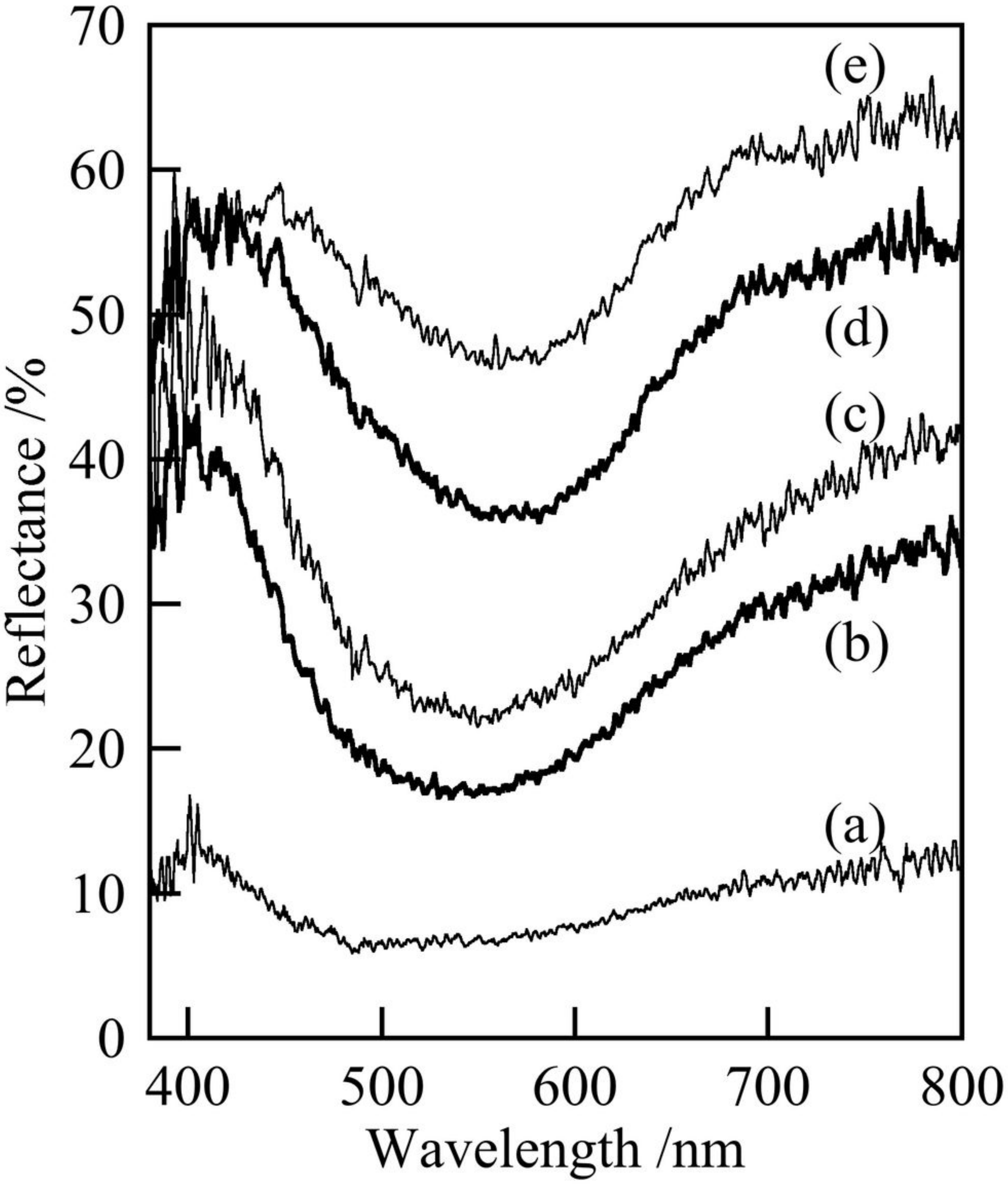

Figure 4

UV-Vis reflectance spectra of samples prepared at various temperatures (Mn/Al/P=1/1/4, 1 h), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.

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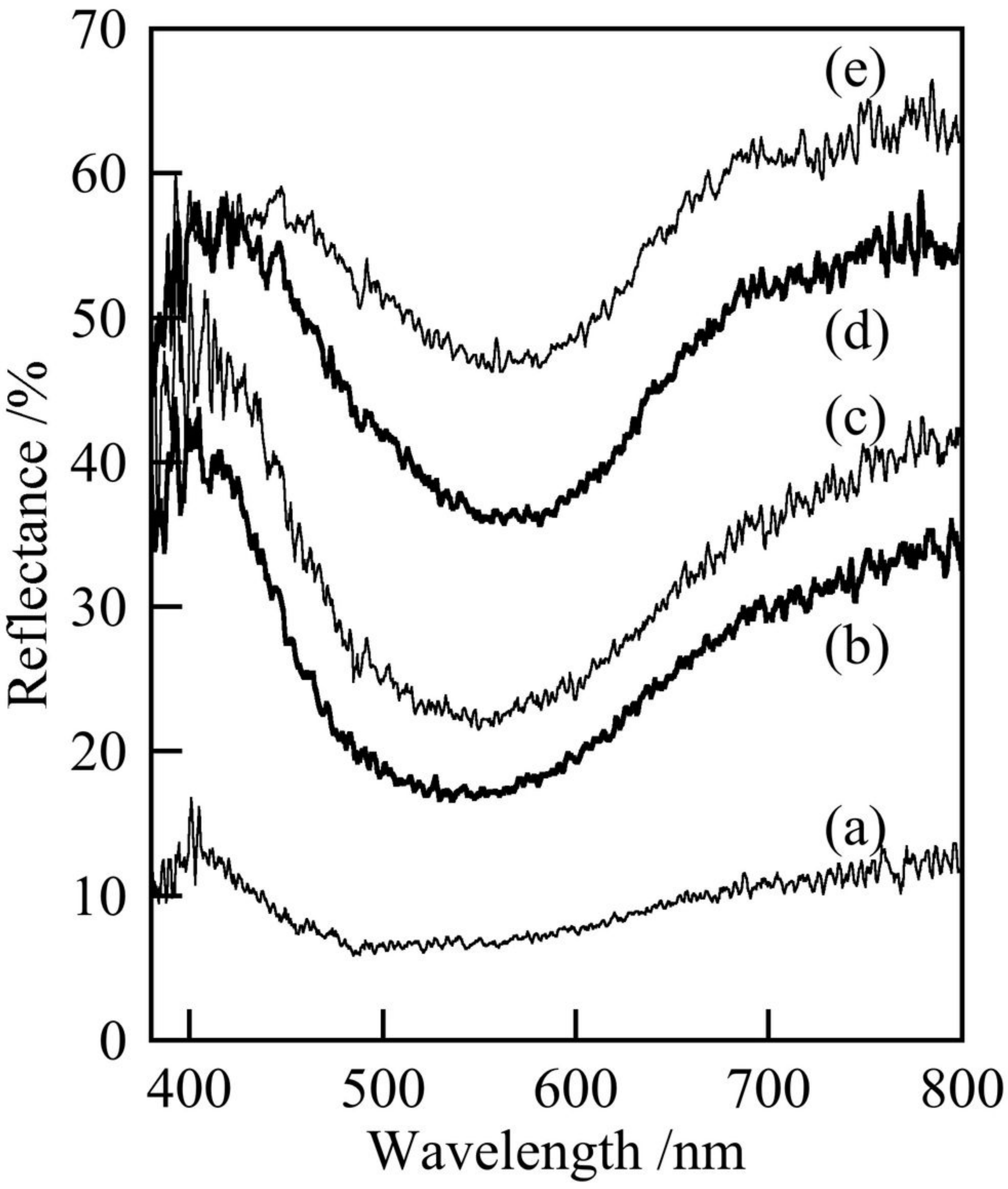

Figure 4

UV-Vis reflectance spectra of samples prepared at various temperatures (Mn/Al/P=1/1/4, 1 h), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.

Figure 5

Photograph of samples prepared for various hours (Mn/Al/P=1/1/4, 400ºC), (a) 1 h, (b) 6 h, and (c) 20 h.

Figure 5

Photograph of samples prepared for various hours (Mn/Al/P=1/1/4, 400ºC), (a) 1 h, (b) 6 h, and (c) 20 h.

Figure 6

Photograph of samples prepared in various Mn/Al/P ratios (400ºC, 1 h), (a) 0.5/1.5/4, (b) 0.75/1.25/4, (c) 1/1/4, (d) 1.25/0.75/4, and (e) 1.5/0.5/4.

Figure 6

Photograph of samples prepared in various Mn/Al/P ratios (400ºC, 1 h), (a) 0.5/1.5/4, (b) 0.75/1.25/4, (c) 1/1/4, (d) 1.25/0.75/4, and (e) 1.5/0.5/4.

Figure 7

Photograph of samples prepared in various Cu/Mn/Al/P ratios (400ºC, 1 h), (a) 0.2/0.8/1/4, (b) 0.2/1/0.8/4, (c) 0.5/0.5/1/4, and (d) 0.5/1/0.5/4.

Figure 7

Photograph of samples prepared in various Cu/Mn/Al/P ratios (400ºC, 1 h), (a) 0.2/0.8/1/4, (b) 0.2/1/0.8/4, (c) 0.5/0.5/1/4, and (d) 0.5/1/0.5/4.

Figure 8

Photograph of samples prepared in various Fe/Mn/Al/P ratios (400ºC, 1 h), (a) 0.2/0.8/1/4, (b) 0.2/1/0.8/4, (c) 0.5/0.5/1/4, and (d) 0.5/1/0.5/4.

Figure 8

Photograph of samples prepared in various Fe/Mn/Al/P ratios (400ºC, 1 h), (a) 0.2/0.8/1/4, (b) 0.2/1/0.8/4, (c) 0.5/0.5/1/4, and (d) 0.5/1/0.5/4.