Synthesis of hexagonal mesoporous aluminophosphate using Al dross

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Abstract−Hexagonal mesoporous aluminophosphate (HMA) materials were synthesized using cetyltrimethylammonium bromide as a structure directing agent and industrial aluminum dross powder or $Al(OH)_3$ extracted from Al dross as an aluminum source at room temperature. XRD confirmed the presence of ordered mesostructures in all of the prepared HMA samples, and textural properties of the prepared samples were close to those of HMA prepared using pure chemicals. Uniform pore structure of the materials prepared using the industrial Al dross was confirmed by TEM, and N_2 adsorption-desorption isotherms of the HMA samples showed type IV isotherms with surface area in the range of 410-560 m^2/g. Cr-containing HMA (CrHMA) samples were also prepared using industrial aluminum dross as an aluminum source, which demonstrated virtually identical catalytic performances in liquid phase tetralin oxidation reaction to those obtained over a CrHMA catalyst prepared using pure chemicals.

Key words: Aluminum Dross, Extraction, Hexagonal Mesoporous Aluminophosphate, Chromium

INTRODUCTION

Aluminum dross is made of free Al metal and nonmetallic substances such as oxides, nitrides, carbides, salts, and other metal oxides, which are produced during casting of aluminum or in the remelting step of recycling aluminum. From the global discharge of aluminum dross of ca. five million tons per year from the aluminum industry, only a small portion is re-used as a deoxidizer for steel making and cement mixture, while the remainder is treated by landfill [1]. Since disposal of these materials is a serious problem to the environment, developing new recycling technologies for aluminum dross has significant economic and environmental importance [2,3].

A large number of aluminophosphate molecular sieves in different framework structure have been used as adsorbents and catalysts [4], and more recently as a hard template for making single-walled carbon nanotubes [5]. Various aluminum sources have been utilized thus far for the synthesis of aluminophosphates [6,7], and Murayama et al. in 2006 reported a successful use of Al dross powder for making $AlPO_4$-5 [1]. It was established that mesoporous aluminophosphate molecular sieves incorporating various transition metal species (Ti, V, Zr, Cr, Mn, Fe, Co, and Ni) can be synthesized in the presence of a suitable surfactant as a template [8]. These mesoporous aluminophosphate materials were proven effective as catalyst by transforming large organic substrates through promoted access of bulky organic molecules to the inner catalytically active sites due to the presence of mesopores in aluminophosphates [9].

Oxidation of benzylic heterocyclic organic compounds has been extensively used in the synthesis of fine and specialty chemicals. Selective oxidation of tetralin, for example, produces α-tetralone

which is an important source of synthetic precursors for a wide range of compounds in steroids, dyes, drugs, and agrochemicals [10]. Cr-containing molecular sieves such as CrAPO-5 [11] and Cr-incorporated mesoporous materials [12] have been so far reported as active catalysts.

In the present study, preparation of hexagonal mesoporous aluminophosphate (HMA) from aluminum dross or $Al(OH)_3$ extracted from aluminum dross is reported for the first time. These materials were characterized by XRD, N_2 adsorption-desorption measurement, SEM, and TEM analyses, and the results are compared with those from an HMA sample synthesised from pure chemical $Al(OH)_3$. To verify the applicability of the HMA materials prepared in this work, we also prepared Cr-containing HMA samples using Al dross and compared their catalytic properties in liquid phase tetralin oxidation reaction against a reference CrHMA catalyst prepared using pure chemicals.

EXPERIMENTAL

1. Synthesis of HMA and CrHMA

Al dross used in this study was obtained from Novelis, Korea. A large granular mass of Al dross was ground thoroughly by a mixing-grinder. The Al dross powder obtained was sieved to particles with a mesh size less than 100 μm. For aluminum extraction, 4 g of the obtained fine powder was refluxed with 40 ml of 10 wt% NaOH solution at 100 °C for 48 h. The solution mixture was centrifuged and filtered to separate the suspended particles, and the supernatant was collected. As a seed, 0.08 g $Al(OH)_3$ was added to 100 ml of supernatant, and the mixture was stirred for 2 h. The pH of the supernatant was then adjusted to 1.5 using HNO_3 (65%) and the mixture was again stirred for 2 h to dissolve salt impurities. The pH of the mixture was subsequently adjusted to 8 by using a dilute NH_4OH (29%) solution and the mixture was further stirred for 2 h.

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Dissolved aluminum species was precipitated and then filtered, washed with copious amount of water, and dried at 100 °C for 12 h. The fine extracted Al precipitate was collected and used for the HMA synthesis.

The pure and chromium containing HMA samples were synthesized as described elsewhere [11,13]. In a typical synthesis of HMA, 1.74 g of Al dross or 3.46 g of extracted or pure Al(OH)$_3$ (Sigma-Aldrich) was slowly added to a solution of 2.5 ml phosphoric acid (85 wt%, Aldrich) dispersed in 25 g of water. This mixture was vigorously stirred to obtain complete dissolution of the aluminum source. The mixture was then combined with 4.0 g of cetyltrimethylammonium bromide (CTAB, Aldrich) dissolved in 30 g of water. The combined mixture was stirred for additional 3 h. For CrHMA samples, 0.325 g of chromium (III) acetate hydroxide dissolved in 15 g distilled water was added into the gel mixture. Tetramethylammonium hydroxide (TMAOH, 25 ml, 25 wt% solution in water, Merck) was slowly added to the above mixture until pH 9.5 was attained. The resulting mixture was then stirred for 72 h at room temperature. The solid product was recovered by filtration, washed several times with distilled water, dried at 80 °C for 24 h, and then calcined at 500 °C at a heating rate of 2 °C/min for 2 h under a nitrogen flow followed by 6 h in an oxygen flow to remove the surfactant molecules [13]. The gel composition of the above synthesis is Al$_2$O$_3$: P$_2$O$_5$: 0.04 Cr$_2$O$_3$: 0.5 CTAB : 8.5 TMAOH : 400 H$_2$O.

2. Characterization

The HMA samples were characterized by X-ray powder diffraction (XRD) with a Rigaku Miniflex diffractometer using CuK$_\alpha$ (λ= 1.54 Å) radiation. The morphology of the crystals was studied by scanning electron microscopy (SEM) using a Hitachi S-4200 electron microscope. Nitrogen adsorption and desorption properties were measured by a Micromeritics ASAP 2020 at liquid nitrogen temperature. The chemical composition of the Al dross and extracted Al(OH)$_3$ was measured by X-ray fluorescence (XRF) (PANalytical, Axios). An elemental analysis of the HMA samples was performed with a SEM-EDX (Hatachi S-4200). Transmission electron microscopy (TEM) measurements were taken on a JEOL JEM-2100F field-emission electron microscope with an acceleration volt-

age of 200 kV. UV-Vis diffuse reflectance spectroscopy of Cr-containing HMA samples was performed on a Varian CARY3E double beam spectrometer using MgO as a reference in the range of 200-750 nm in ambient conditions.

3. Catalytic Tetralin Oxidation

Catalytic reaction was carried out using a Chemistation PPS-2510 fitted with a condenser (Eyela) using 50 mg of the calcined catalyst, 5 ml of the chlorobenzene (solvent), and tetralin (8 mmol). In a typical reaction, a mixture containing the substrate, solvent, and catalyst was put into a Chemistation glass reactor and heated to 80 °C. The oxidant *tert*-butylhydroperoxide (TBHP) was then added through a septum to the reactant mixture and stirred at 600 rpm. Tetralin to TBHP molar ratio was kept to 1 : 2 and the reaction was continued for 8 h. The product sample obtained after removing the catalyst using a HPLC syringe filter was analyzed by GC (Acme 6000 Series, Younglin instruments) employing a HP-5 capillary column (60 m× 0.32 mm) and an FID. The reaction products were identified by a GC/MS (Varian 1200L) using authentic standard compounds.

RESULTS AND DISCUSSION

Chemical compositions of Al dross and extracted Al(OH)$_3$ were analyzed by XRF, which indicated that the elements Al, Mg, Cl, and Mn were present in amounts of 69, 25, 2, and 1.5 mol%, respectively, in the Al dross. There was also less than 1 mol% of Fe, Ca, Cu, Ti, S, Si, Na, V, Zn, and Ga found in the Al dross. The XRF results of the extracted Al(OH)$_3$ showed the presence of Al and Si at 96 and 2 mol%, respectively. Minor impurities of Na, Ca, Fe, Ga, V, and S in amounts less than 1 mol% were also present.

Fig. 1 shows the XRD patterns of aluminum dross and the HMA samples synthesized by using Al dross (HMA(D)), Al(OH)$_3$ extracted from Al dross (HMA(E)), and pure chemical Al(OH)$_3$ (HMA). In the aluminum dross, Al$_2$O$_3$, AlN, Al, (NO)$_2$Al$_{22}$O$_{34}$, NaAl$_{11}$O$_{17}$, MgAl$_2$O$_4$, and SiO$_2$ phases were present as reported earlier [1]. The XRD patterns of all the calcined HMA samples in (b) showed an intense diffraction peak due to (100) reflections at a 2θ value of 2.7, which is characteristic of a hexagonal mesoporous aluminophosphate. HMA (D) showed some additional crystalline phases due to impurities
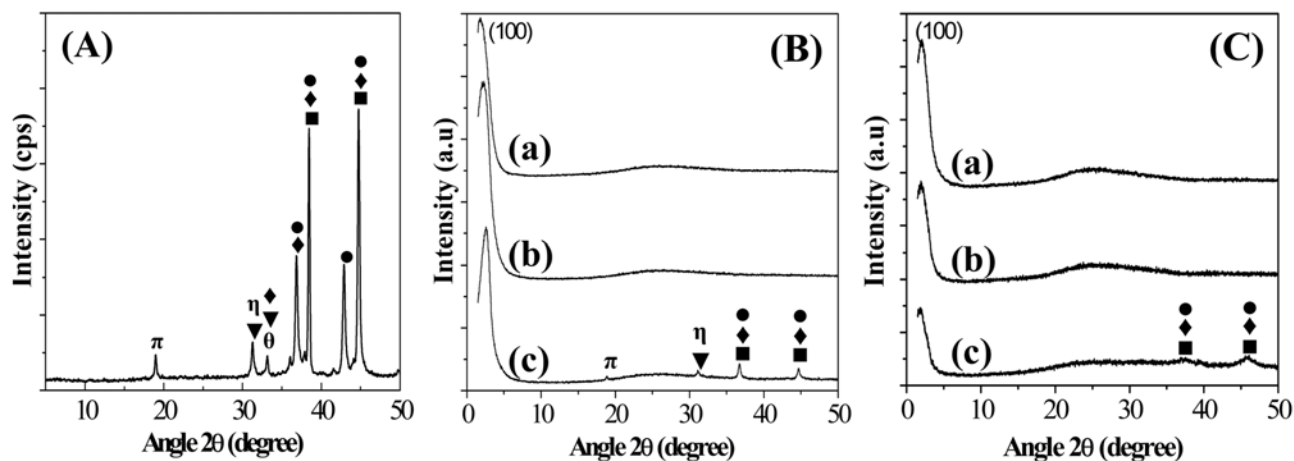

Fig. 1. X-ray diffraction patterns of (A) Al dross, (B) HMA, and (C) CrHMA synthesized from (a) pure chemicals, (b) extracted Al(OH)$_3$ and (c) Al dross. Key: (●) Al$_2$O$_3$, (◆) AlN, (■) Al, (▼) (NO)$_2$Al$_{22}$O$_{34}$, (θ) NaAl$_{11}$O$_{17}$, (η) MgAl$_2$O$_4$, and (π) SiO$_2$.
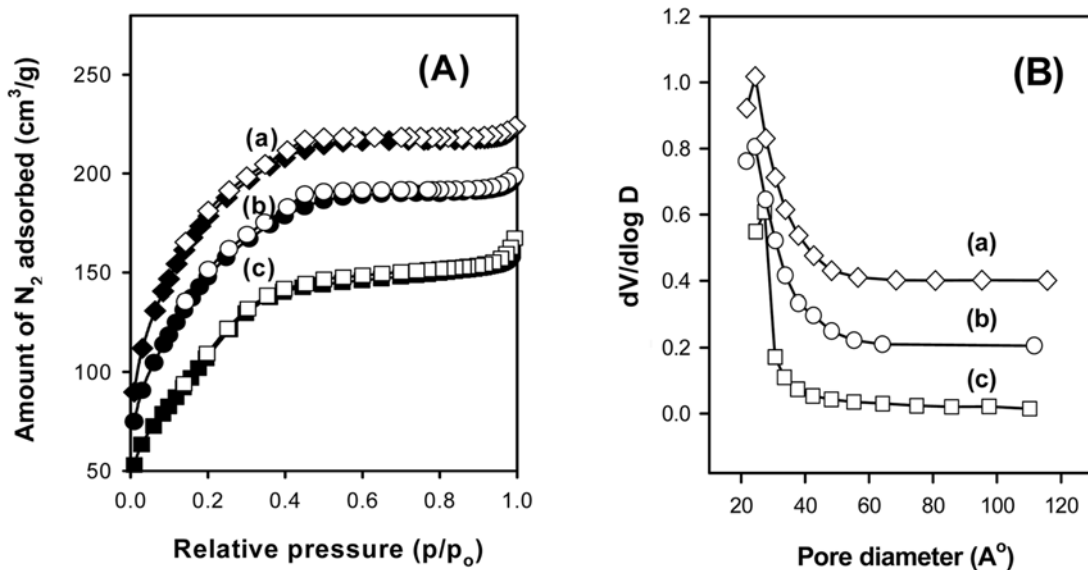
Fig. 2. (A) N_2 adsorption-desorption isotherms of (a) HMA, (b) HMA(E), and (c) HMA(D) (closed symbols: adsorption, open symbols: desorption), and (B) The BJH pore size distribution calculated from the adsorption branch of the isotherms. (For clarity, the pore size distribution curves were shifted by 0.2 units from their original values).

that were originally present in the Al dross [14]. Crystalline phases due to the impurities were not found in the HMA(E), suggesting that the extracted $Al(OH)_3$ precipitate used in the synthesis of HMA(E) contained mostly $Al(OH)_3$ while other impurities remained in the solution during the extraction process.

The N_2 adsorption isotherms and the BJH pore size distribution of HMA samples are shown in Fig. 2. The N_2 adsorption isotherms of all the HMA samples prepared are of type IV in the IUPAC classification, featuring a region of capillary condensation in mesopore

Table 1. Textural properties of mesoporous aluminophosphate synthesized from aluminum dross and pure chemical source

Sample	S_{BET} (m²/g)	V_p (cm³/g)	d_p (nm)
HMA(D)	412	0.24	2.4
HMA(E)	556	0.30	2.2
HMA	663	0.34	2.1

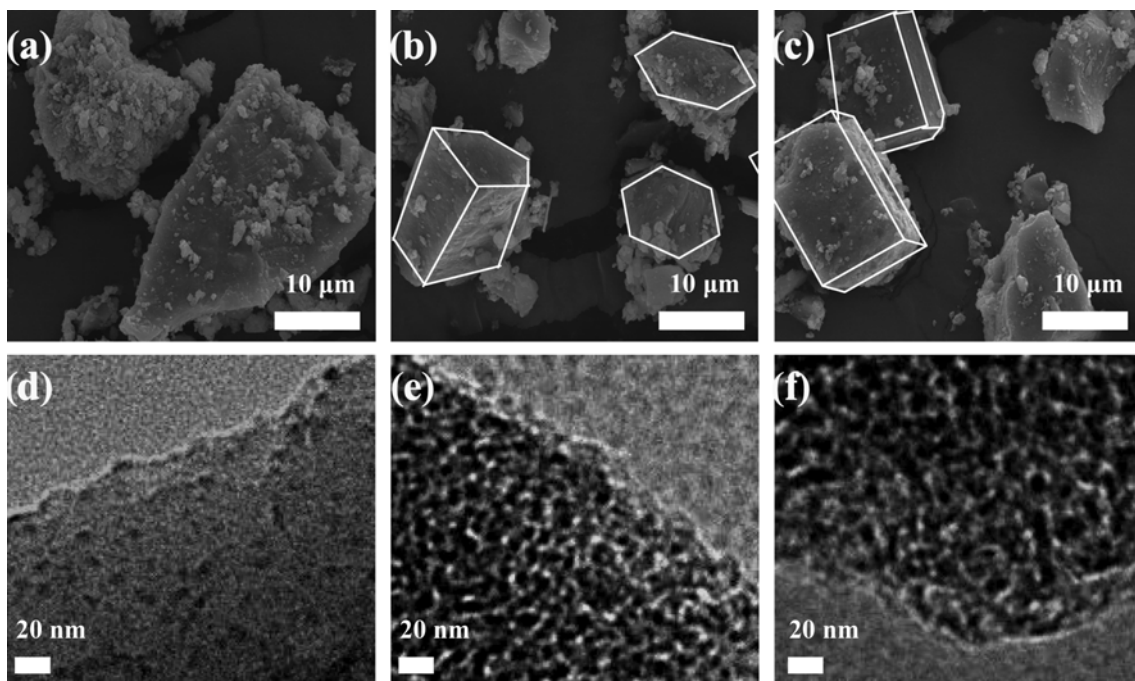S_{BET}=specific surface area, V_p=total pore volume, and d_p=pore diameter

Fig. 3. SEM images of (a) HMA(D), (b) HMA(E), (c) HMA and TEM images of (d) HMA(D), (e) HMA(E), and (f) HMA.

channels [4] (shown in A). The corresponding BJH pore size distributions of HMA(D), HMA(E), and HMA are shown in (B). These materials have a narrow pore size distribution with an average pore diameter ≥21 Å. The textural properties of the prepared HMA samples are shown in Table 1. The surface area and pore volume of the HMA(D) sample were 412 m^2/g and 0.24 cm^3/g, whereas the corresponding textural properties of the HMA(E) sample were 556 m^2/g and 0.30 cm^3/g, respectively. These properties were again close in value to those of the HMA sample prepared from a pure chemical source, i.e., 663 m^2/g and 0.34 cm^3/g, respectively. The decrease in surface area and pore volume in the samples prepared by using aluminum dross appears to be due to the presence of impurities, which

Table 2. Elemental composition of HMA and CrHMA samples prepared using pure, extracted Al, and Al dross

Sample	Elemental composition (mol%)*			
	Al	P	Cr	Impurity**
HMA	53	46	N/D***	N/D
HMA(E)	52	47	N/D	0.28
HMA(D)	50	41	N/D	8.62
CrHMA	52	45	2.0	N/D
CrHMA(E)	51	46	2.0	0.29
CrHMA(D)	48	42	1.8	8.68

*SEM-EDX analysis, **mostly Mg (see text), ***N/D: not detected
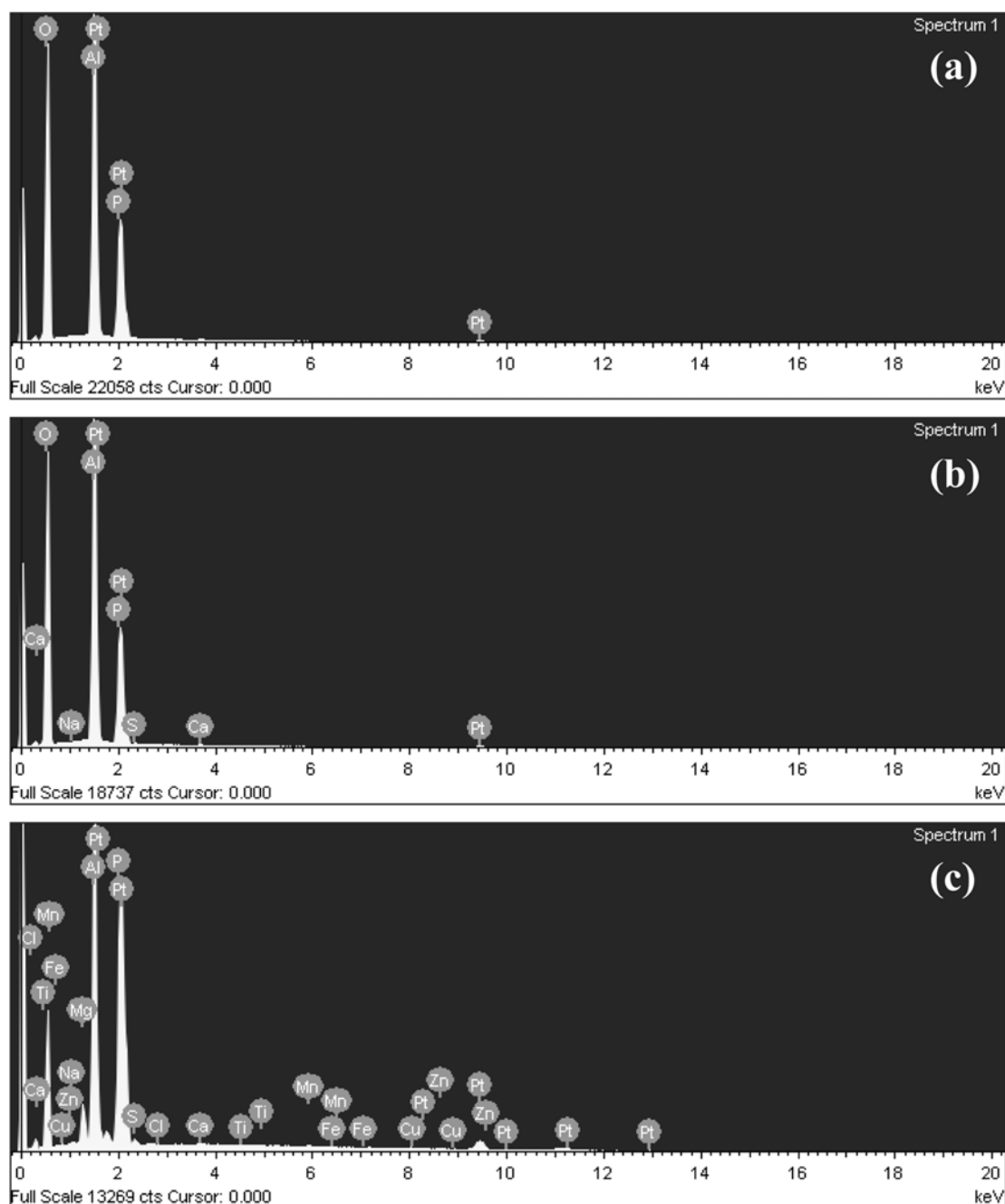
Fig. 4. EDX analysis of (a) HMA, (b) HMA(E), and (c) HMA(D).

partially block the mesopores (see later).

Fig. 3 shows SEM and TEM images of the HMA(D), HMA(E), and HMA samples. HMA(D) shown in (a) has larger particles with a particle size >20 μm formed by aggregation of smaller particles of less than 1 μm size. The particle morphology of HMA(E) shown in (b) was characterized by cubic pentagonal and hexagonal phases with particles in excess of 10 μm size co-existing with a fraction of smaller particles of ca. 2 μm size. The SEM image of pure HMA shown in (c) indicates the presence of cubic rectangular particles of size greater than 15 μm together with aggregates of smaller particles with a particle size of ca. 2 μm. TEM image of HMA(D), which is shown in (d), shows disordered HMA channels with metal/metal oxide particles (black spots) blocking the pore entries. The TEM image of HMA(E) in (e) shows a uniform arrangement of disordered mesopore channels in the materials [4], which is closely in line with the features of the pure HMA sample shown in (f).

The elemental compositions of the synthesized HMA samples were examined by EDX analysis shown in Fig. 4, and the result is summarized in Table 2. For HMA(D), impurities of Mg, Mn, Ca, Ti, Fe, Cu, Zn, S, Cl, and Na at concentrations of 6.1, 0.75, 0.29, 0.14, 0.29, 0.09, 0.2, 0.4, 0.27, and 0.09 mol%, respectively, were detected. HMA (E) sample was also found to have Ca, S, and Na but at much lower levels (<0.3 mol%). Al/P ratios among the samples were close and fell in the range of 1.10 to 1.21.

Addition of 2 mol% Cr to the substrate mixtures produced virtually the same XRD patterns to HMA samples as shown in Fig. 1(c), which is in accordance with the known fact that aluminophosphates can accommodate various transition metals to relatively high concentrations into the structure [15]. While no deterioration in XRD diffraction pattern or impurity phases were detected in CrHMA(E), CrHMA(D) sample showed very low peak intensities of Al_2O_3, AlN, and Al impurity phases. As expected, CrHMA(D) had the same impurities found in HMA(D) comprised mostly of Mg, and CrHMA(E) also had a minor impurities as shown in Table 2.

UV-Vis spectra of the calcined CrHMA samples are shown in Fig. 5. All the samples, irrespective of the aluminum sources used, showed the same spectral features; the absorption bands around 270 and 350 nm are due to the two charge transfer transitions of Cr(VI) [16] and those at 460 and 620 nm due to Cr(III) in distorted octahedral coordination [17]. The spectrum of the as-syn CrHMA shows only two intense bands at ca. 440 and 610 nm due to the spin-allowed d-d transitions $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$, respectively. As explained
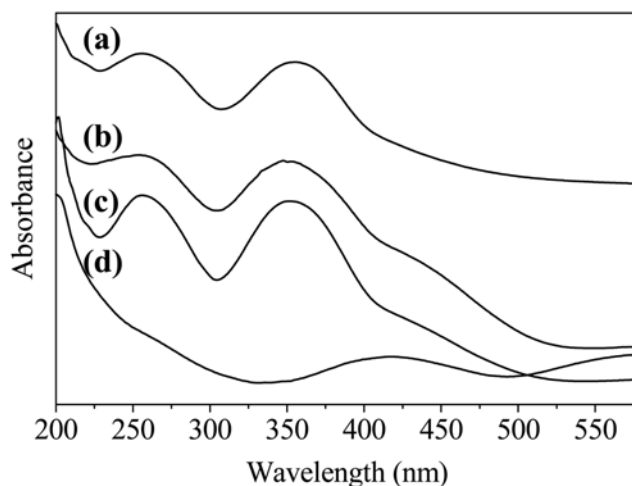

Fig. 5. UV-Visible spectra of (a) CrHMA, (b) CrHMA(D), (c) Cr-HMA(E), and (d) as-syn. CrHMA.

by Weckhuysen and Schoonheydt for CrAPO-5 [18], Cr(III) seems to be quantitatively oxidized to Cr(VI) in the calcined CrHMA samples.

Catalytic performance of the CrHMA samples was tested for liquid phase tetralin oxidation using TBHP as an oxidant. We conducted the reaction using the catalysts pre-washed with ammonium acetate solution (3 M) at room temperature to remove the less stable Cr species from CrHMA [19]. Tetralin conversion and product distribution obtained for each catalyst are summarized in Table 3. α-Tetralone was the major product followed by α-tetralol, naphthalene, and α-napthol. All three kinds of CrHMA catalysts performed very closely with high selectivity (>84%) to α-tetralone at 45-47% conversion level. It seems tetralin conversion was mostly controlled by Cr level in the CrHMA samples, but apparently those impurities present in CrHMA(D) did not cause any serious adverse effect either on conversion or product selectivity.

CONCLUSIONS

Aluminum dross was successfully used as an aluminum source for preparing hexagonal aluminophosphates under basic conditions. HMA(D) sample prepared from ground Al dross powder showed somewhat lower specific surface area and pore volume due to the

Table 3. Performance of tetralin oxidation by CrHMA catalysts

Catalysts	Tetralin conversion (%)	Product selectivity (%)			
		Naphtalene	Tetralone	α-Tetralol	α-Naphthol
CrHMA(D)	45	1.3	84.4	8.1	6.2
CrHMA(E)	47	1.2	86.0	7.1	5.7
CrHMA	47	1.0	86.5	7.3	5.2

Reaction conditions: 5 ml chlorobenzene, 8 mmol tetralin, 16 mmol TBHP per 50 mg catalyst, 80 °C, 8 h
Reaction pathway of tetralin oxidation
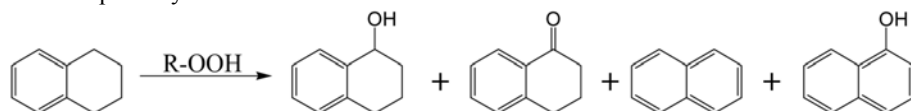
presence of metal/metal oxide impurities. HMA(E) prepared from extracted Al(OH)$_3$, on the other hand, was mostly free from metal and other metal oxides. TEM analysis confirmed that these materials have disordered uniform pore structures. CrHMA samples were also prepared in the same manner as in HMA using either Al dross powder or an extracted Al(OH)$_3$ from the dross. These materials had shown comparable catalytic properties to the CrHMA sample prepared by using pure chemicals in the liquid phase oxidation of tetralin with TBHP as an oxidant.

ACKNOWLEDGMENT

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