

Selective Uptake of Phosphate Ions on Nanocomposite of ZrO₂ and Layered Double Hydroxide

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We synthesized novel nanocomposites (Zr-MgAl) of ZrO₂ and layered double hydroxide of Mg^{II} and Al^{III}, by adding a mixed solution of MgCl₂, FeCl₃, and ZrOCl₂ to distilled water, adjusting a constant pH value of 10 with another mixed solution of 1M Na₂CO₃ and 1M NaOH. The content of Zr in the Zr-MgAl was varied over 1-20 wt%. The Zr-MgAl exhibited only a poorly crystalline structure assigned to layered double hydroxide (LDH) from X-ray diffraction, with a decrease in strength with increasing the Zr content. XAFS characterization indicated that the Zr phase of the Zr-MgAl is almost identical with amorphous ZrO₂, with a similar local structure around Zr to cubic ZrO₂. The uptake of phosphate ions from P-enriched seawater (0.33 ppm-P) is strongly dependent on the Zr content, showing a maximal value of 18 mg-P/g at the Zr content of 14 wt%. The composite with a Zr content of 10-20 wt% exhibited a much greater uptake of phosphate ions than amorphous ZrO₂ and binary Mg-Al LDH. This interesting selectivity toward phosphate ions is probably due to a composite structure of nanoparticles of amorphous ZrO₂ with poorly crystalline Mg-Al LDH.

1. Introduction

The release of phosphate ions to surface waters causes eutrophication, and hyperphosphatemia results in ectopic calcification. The need for selective removal of phosphate ions at trace concentration levels has been growing. We have developed a novel material Zr-MgAl with the highest selectivity toward phosphate ions (Chitrakar et al., 2007), and recently have demonstrated that this material is a composite of amorphous ZrO₂ and layered double hydroxide (LDH) of Mg^{II} and Al^{III} (Mg-Al LDH) from X-ray absorption spectroscopy (Miyachi et al., 2009).

This study deals with the selective uptake of phosphate ions on the Zr-MgAl with a Zr content of 1-20 wt %, comparing with those of amorphous ZrO₂ and Mg-Al LDH.

2. Experimental

2.1 Synthesis of Samples

The Zr-MgAl samples were obtained by a coprecipitation method (Miyachi et al., 2009). In order to change the Zr content of the composite with the LDH phase of a constant Mg/Al molar ratio, a mixed solution (200 mL) prepared by diluting 1 M (mol/L) MgCl₂ (30 mL), 1 M AlCl₃ (5 mL), and 0.5 M ZrOCl₂ (0-22 mL) with distilled water was added drop-wise to 200 mL of deionized water, adjusting the pH value of ca. 10 by drop-wise addition of another mixed solution of 1M NaOH and 1M Na₂CO₃ (a vol/vol ratio of 4/1). The other preparation processes were the same as those described in the literature (Miyachi et al., 2009). The obtained samples are denoted as nZr-MgAl (n stands for the Zr content) and MgAl (prepared with no use of 0.5 M ZrOCl₂), and as nZr-MgAl-HT and MgAl-HT after hydrothermal treatment (HT) at 393 K of the former samples.

The ZrO₂ samples were prepared by the same method described previously (Miyachi et al., 2009) and denoted as ZrO₂ and ZrO₂-HT after HT. Stabilized zirconium oxides with 3 mol% Y₂O₃ (YSZ) and 3-5% CaO (CSZ), and monoclinic zirconium oxide (m-ZrO₂) were purchased commercially as references.

2.2 Selective Uptake of Phosphate Ions

Selective uptake of phosphate ions were carried out by stirring a sample (0.05 g) in 5 L of phosphate-enriched seawater (0.33 mg-P/L, pH=7.9) with NaH₂PO₄ at room temperature for 4 days to attain equilibrium. The concentrations of phosphate ions in the solution phase before and after uptake of phosphate ions were determined by a portable colorimeter (DR/700; HACH Co., USA).

2.3 Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2100 powder X-ray diffractometer with Ni-filtered Cu K α radiation. N₂ adsorption-desorption isotherms

Table 1: Elemental and Surface Analyses of the Zr-MgAl, ZrO₂, and MgAl Samples

sample	Zr (wt%)	Mg (wt%)	Al (wt%)	Mg/Al (mol/mol)	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	V_0^{a} (mL/g)
ZrO ₂	48.7	—	—	—	301	0.21
ZrO ₂ -HT	61.1	—	—	—	205	0.28
20Zr-MgAl	20.4	12.2	2.9	4.6	—	—
14Zr-MgAl	13.8	16.7	3.8	4.9	49	0.14
14Zr-MgAl-HT	16.0	15.5	4.6	3.7	154	0.28
9Zr-MgAl	8.6	17.2	4.1	4.7	—	—
5Zr-MgAl	4.9	18.8	4.7	4.4	—	—
1Zr-MgAl	1.0	20.5	4.6	5.0	—	—
MgAl	—	20.5	5.3	4.3	—	—
MgAl-r	—	21.5 ^a	8.2 ^a	2.9 ^a	73	0.20
MgAl-r-HT	—	22.5 ^a	8.9 ^a	2.8 ^a	59	0.18

a)Ref (Miyachi et al., 2009)

were measured at 77 K with a BEL JAPAN Inc.-made Belsorp 18A volumetric apparatus. All the samples were evacuated at 393 K for 2 h before adsorption measurement. The X-ray absorption experiments were carried out on the BL01B1 (Uruga et al., 1999) at SPring-8 (Hyogo, Japan. Proposal no. 2010A1334). The Zr K-edge X-ray absorption spectra were recorded in a transmission mode at room temperature using a Si (311) two-crystal monochromator.

3. Results and Discussion

3.1 Composite Structure of Zr-MgAl

Results of elemental analysis of the nZr-MgAl, MgAl, and ZrO₂ samples are listed in Table 1. It is noted that the Zr content of the nZr-MgAl is varied over 1-20 wt% under almost the same Mg/Al molar ratio of 4.7. The two extreme samples are the ZrO₂ with a Zr content of 48.7 wt% and the MgAl with a Mg/Al molar ratio of 4.3 close to those of the nZr-MgAl samples. The MgAl is a Mg^{II}-Al^{III} LDH with carbonate ions located between adjacent layers, the distance of which is given by $d(003) = 0.807$ nm, as shown in Figure 1g. The ZrO₂ is *amorphous* as in Figure 1a. The nZr-MgAl exhibits XRD signals characteristic of LDH, increasing the signal strength with a decrease in the Zr content in Figure 1b-f, but no XRD signal related to zirconium oxide, suggesting an amorphous phase.

In order to characterize the local structure around Zr in the nZr-MgAl, the k^3 -weighted Zr-K edge EXAFS spectra are shown in Figure 2 (left). The spectra of the nZr-MgAl with a Zr content ranging over 1.0-20.4 wt% are almost the same as each other, and quite close to that of the amorphous ZrO₂. Further they are quite similar to those of YSZ and CSZ characteristic of a cubic phase but different from that of m-ZrO₂ (Li et al., 1993). These results indicate that the Zr phase in the nZr-MgAl with a Zr content of 1.0-20.4 wt% is almost identical with the amorphous ZrO₂. The main EXAFS

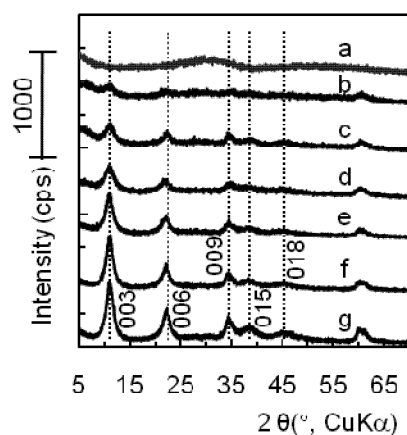


Figure 1: X-ray powder diffraction patterns of the samples: ZrO₂ (a), 20Zr-MgAl (b), 14Zr-MgAl (c), 9Zr-MgAl (d), 5Zr-MgAl (e), 1Zr-MgAl (f), and MgAl (g)

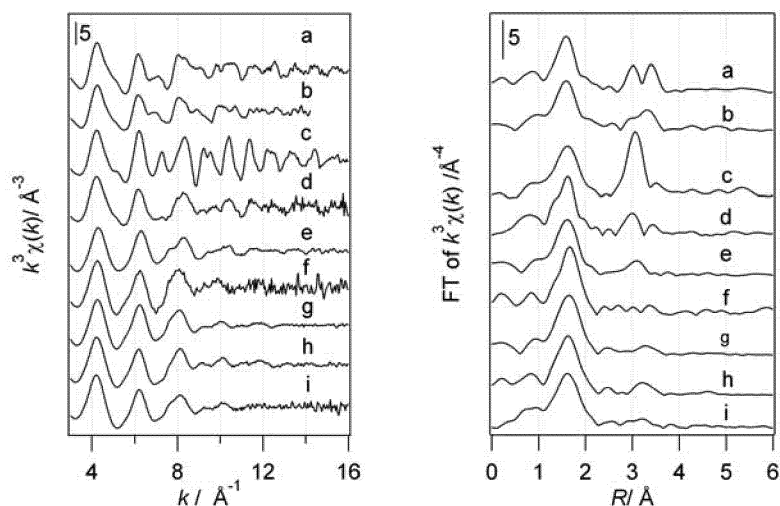


Figure 2: k^3 -weighted Zr-K edge EXAFS spectra (left) and their Fourier transforms (right) in the k -range of 3-16 \AA^{-1} of the samples: ZrO_2 (e), ZrO_2 -HT (d), 1Zr-MgAl (f), 5Zr-MgAl (g), 14Zr-MgAl (h), and 20Zr-MgAl (i), as well as YSZ (a), CSZ (b) and $m\text{-ZrO}_2$ (c) as references.

oscillation less than 10\AA^{-1} is similar to that of cubic ZrO_2 . Figure 2 (right) shows radial structure functions (RSFs) obtained by Fourier transforms of k^3 -weighted EXAFS spectra in the k -range of 3-16 \AA^{-1} region. The RSFs of the Zr-MgAl samples exhibit only the first coordination sphere around 1.7 \AA corresponding to Zr-O pairs, while that of the ZrO_2 possesses not only the similar first coordination sphere but also the second coordination sphere around 3.0 \AA relating to Zr-Zr pair (Li et al., 1993). The nZr-MgAl and ZrO_2 obtained in this study are much less ordered than the similar composites analyzed by Intissar et al. (2003), because of the appearance of distinct RSF signals due to Zr-Zr pair around 3.2 \AA on the latter samples. Thus all the above results show that the nZr-MgAl with a Zr content of 1.0-20.4 wt% is a composite of amorphous ZrO_2 and poorly-crystalline Mg-Al LDH with CO_3^{2-} ions between the layers. The impossibility of incorporation of Zr^{IV} into LDH layers even in the 1Zr-MgAl with an extremely small Zr-content is probably due to greater repulsive interactions between Zr^{IV} s because even the Mg/Al ordering in Mg-Al LDH is determined through interactions between Al^{III} s with a smaller charge (Sideris et al., 2008).

3.2 Pore Structure of Zr-MgAl

Figure 3 shows the pore size distribution of the 14Zr-MgAl, the MgAl-r with a different Mg/Al molar ratio from the MgAl, and the ZrO_2 samples obtained from desorption branches of N_2 adsorption-desorption isotherms by the Barrett-Joyner-Halenda (BJH) method. The amorphous ZrO_2 exhibits a mesoporosity with pore diameters (D_p) smaller than 5 nm; and its mesopore size significantly increases to $D_p = 5.01 \text{ nm}$ after hydrothermal treatment (HT), indicating a growth in particle size. The MgAl-r shows a mesopore size distribution centered at $D_p = 4.18 \text{ nm}$. It is interesting that its mesopores

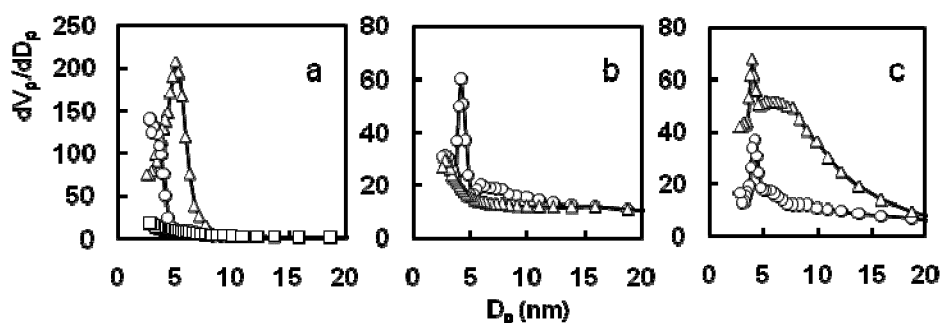


Figure 3: Pore size distribution curves of the samples: ZrO_2 (a), $MgAl-r$ (b), and $14Zr-MgAl$ (c). Symbols (\circ and \triangle) represent the results before and after hydrothermal treatment, respectively. The results of $m-ZrO_2$ as a reference are shown by plots (\square).

disappear after HT, probably due to an increase in crystallinity of Mg-Al LDH by HT (Miyachi et al., 2009) by the repairing of defects. The pore size distribution of the $14Zr-MgAl$ exhibits some characteristic features due to composition of amorphous ZrO_2 and Mg-Al LDH phases. The sharp pore size distribution with D_p around 4.0 nm remains even after HT, suggesting strong interactions between the two phases. Furthermore, a broad pore size distribution with a greater D_p (ranging over 5 nm) was formed after HT, probably due to the formation of a secondary house-of-cards aggregate structure consisting of LDH layers and ZrO_2 nanoparticles.

3.3 Uptake of Phosphate Ions on Zr-MgAl

The selective uptake of phosphate ions on the $nZr-MgAl$ was considered with phosphate-enriched seawater, which is suitable for evaluation of competitive uptake of phosphate ions among other ions. The uptake of phosphate ions is plotted against the Zr content in Figure 4a. It is emphasized that the uptake on the $nZr-MgAl$ with a Zr content of 10-20 wt% is greater than that on the amorphous ZrO_2 , although the latter is a principle constituent for uptake of phosphate ions. Then the molar ratio of phosphate ions captured to Zr content (P/Zr) is evaluated against the Zr content in Figure 4b. Figure 4a reveals a slight contribution of uptake of phosphate ions from the MgAl phase, which is more significant with decreasing the Zr content. The corrected P/Zr of the $nZr-MgAl$ increases with a decrease in the Zr content, greater than the amorphous ZrO_2 with a Zr content of 48.7 wt%, and up to 0.80 at the Zr content of 1.0 wt%. Interestingly the corrected Zr/P values exhibit a plateau close to 0.35 in the Zr content of 5-15 wt%, indicative of formation of a dinuclear-bidentate inner-sphere complex.

The ZrO_2 phase in the $nZr-MgAl$ is quite similar to the amorphous ZrO_2 in Figure 2. However the composition suppresses significantly the growth in the particle size of the ZrO_2 phase as compared with the amorphous ZrO_2 sample as shown in Figure 3, and disturbs the crystallization of the phase. These provide more active sites on the surface for uptake of phosphate ions, and probably are principal reasons why the $14Zr-MgAl$ exhibits the most selective uptake of phosphate ions among the $nZr-MgAl$, ZrO_2 , and MgAl samples.

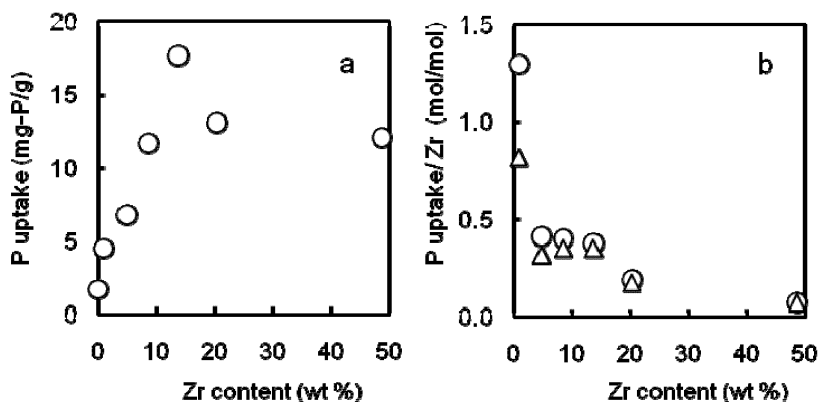


Figure 4: Uptake of phosphate ions on the $n\text{Zr-MgAl}$, the MgAl , and the ZrO_2 . The plots (Δ) show the results obtained by correcting the contribution from the LDH phase.

4. Conclusions

We synthesized the Zr-MgAl composite with a Zr content of 1-20 wt% which consists of nanoparticles of amorphous ZrO_2 and poorly crystalline Mg-Al LDH with a Mg/Al molar ratio of ca. 4.7. This composite exhibits the most selective uptake toward phosphate ions, at the Zr content of 14 wt%, probably due to its composite structure.

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