Advanced Powder Technology 21 (2010) 169–174

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Synthesis and adsorption property of zinc rust of zinc hydroxynitrate

Hidekazu Tanaka [a,*], Ryohei Kaneda [a], Akiko Fujioka [a], Kazuhiko Kandori [b], Tatsuo Ishikawa [c]

[a] *Department of Material Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan*
[b] *School of Chemistry, Osaka University of Education, 4-698-1 Asahigaoka, Kashiwara, Osaka 582-8582, Japan*
[c] *Department of Education, Faculty of Human Development and Education, Kobe Shinwa Women's University, 7-13-1 Kita-machi, Suzurandai, Kita-ku, Kobe, Hyogo 651-1111, Japan*

ARTICLE INFO

Article history:
Received 12 July 2009
Received in revised form 12 October 2009
Accepted 29 October 2009

Keywords:
Zinc hydroxynitrate
Zinc rust
Rust layer
Atmospheric corrosion
Molecular adsorption

ABSTRACT

In order to clarify the formation condition of zinc rusts such as layered zinc hydroxynitrate ($Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$: ZHN), ZnO particles were aged with aqueous $Zn(NO_3)_2{\cdot}6H_2O$ solution at 6–140 °C for 48 h. Further, adsorption of H_2O and CO_2 on ZHN was examined for simulating study of atmospheric corrosion of galvanized steel. The ZHN was formed at 6 °C and the ZnO completely disappeared, meaning the hydrolysis of ZnO particles in aqueous $Zn(NO_3)_2{\cdot}6H_2O$ solution to recrystallize as ZHN. Increasing the aging temperature improved the crystallinity of layered structure of ZHN, showing a maximum at 85 °C. The formed ZHN was hexagonal plate-like particles. The particle size was dependent of the crystallinity of layered structure of ZHN. The specific surface area of ZHN was decreased on elevating the aging temperature, showing a minimum at 85 °C. The adsorption of H_2O and CO_2 was enhanced on increasing the crystallinity of layered structure of ZHN, meaning that these molecules are adsorbed not only on particle surface but also in interlayer of ZHN. These facts infer that the preferred orientation of plate-like ZHN particles leads to the formation of compact rust layer on galvanized steel and to the enhancement of corrosion resistance.

1. Introduction

In industry, steels are frequently galvanized to suppress the atmospheric corrosion of steels. Zinc rusts formed on the steels play an important role in protecting the steels from corrosion and contain various kinds of oxides, hydroxides and basic zinc salts (BZS) [1–9]. The corrosion resistance of zinc rusts was explained by the fact that the protecting property of BZS is related to the formation of a disordered layer structure producing adherent films [7]. It has been reported that the chemical composition of BZS depends on the exposure environment [1,4,8,9]. The zinc hydroxychloride ($Zn_5(OH)_8Cl_2{\cdot}H_2O$) is formed together with ZnO by exposing the galvanized steels to marine atmosphere [3]. Also, formation of zinc hydroxychloride by hydrolyzing the ZnO, which is one of the zinc rusts, in $ZnCl_2$ solution is recognized at $pH < 7$ [2]. The authors synthesized the zinc hydroxychlorides by hydrolyzing the ZnO at 6–140 °C and suggested that the phase transformation of ZnO to BZS in corrosive environment [10,11]. The zinc hydroxysulfate ($Zn_4SO_4(OH)_6{\cdot}nH_2O$) and $NaZn_4Cl(OH)_6SO_4{\cdot}6H_2O$ are generated in industrial district [1,4]. The initial zinc rust contains the hydrozincite ($Zn_5(OH)_6(CO_3)_2$) which is converted to other zinc rusts such as zinc hydroxychloride and $NaZn_4Cl(OH)_6SO_4{\cdot}6H_2O$ after exposing for a long periods [4]. On the other hand, zinc hydroxynitrate ($Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$: ZHN) was found on Zn plate exposed in humid air containing NO_2 gas in the laboratory test [12]. It seems, therefore, that the ZHN is a corrosion product of galvanized steels in industrial district in the presence of NO_x gas as well as zinc hydroxychlorides. The synthesis of ZHN has been reported by several researchers. Biswick et al. have synthesized the ZHN by aging the aqueous $Zn(NO_3)_2$ solutions above 150 °C [13]. The ZHN was obtained by addition of alkali solution such as NH_4OH and NaOH into $Zn(NO_3)_2$ solution [14,15]. Further, a few studies have been reported the synthesis of ZHN from ZnO particles using hydrolysis reaction by Feitknecht [16] and Stahlim and Oswald [17]. They succeeded the preparation of ZHN by the reaction of ZnO particles and aqueous $Zn(NO_3)_2$ solution. Nonetheless, the detailed formation condition of ZHN such as formation temperature, which corresponds to air temperature in corrosive environment, from ZnO particles has not been fully elucidated. Besides, clarifying the interaction between ZHN and corrosive gas molecules such as H_2O, CO_2, NO_x and SO_x is very important in simulating study for atmospheric corrosion of galvanized steel.

On the other hand, BZS has recently attracted much attention in application of new functionalized nano-material. Since the BZS possesses the basal nano-sheets mainly composed of Zn(II) octahedron and tetrahedron and the anions and H_2O molecules exist in the layer [17,18], the material is anticipated to be available for anion exchangers, adsorbents for gases and so forth. Wypych et al. have reported that the intercalation of mono- and di-carbox-

---

[*] Corresponding author. Fax: +81 852 32 6823.
E-mail address: hidekazu@riko.shimane-u.ac.jp (H. Tanaka).

0921-8831/$ - see front matter
doi:10.1016/j.apt.2009.10.013

ylic acids in ZHN layer [19]. Also, Newman and Jones have intercalated the organic anions acetate, terephthalate and benzoate by exchange of the interlayer nitrate anions [20]. Ishikawa et al. have reported the anion exchange property of zinc hydroxychloride [21]. Also, Zhang and Yanagisawa [22], Fuji and co-workers [23] and the authors [24] synthesized the ZnO particles with various morphologies such as nano-sheet, tube and plate from BZS.

The aim of this study was to elucidate the formation condition of zinc rust of ZHN and to clarify the adsorption property of H_2O and CO_2 on ZHN for simulating study of atmospheric corrosion of galvanized steel. Hence, we tried to synthesize the ZHN by aging the ZnO particles in aqueous $Zn(NO_3)_2{\cdot}6H_2O$ at different aging temperatures of 6–140 °C. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), inductively coupled plasma emission spectroscopy (ICP-AES), adsorption of N_2, H_2O and CO_2, and so on. The formation condition and molecular adsorption properties of ZHN are discussed in this article based on the results obtained.

2. Experimental

2.1. Synthesis of ZnO particles

ZnO particles were synthesized by the following wet method. An aqueous solution of 0.05 mol/dm^3 $Zn(NO_3)_2{\cdot}6H_2O$ was prepared and the pH of the solution was adjusted to 9.0 by adding a 28% aqueous NH_3 solution under stirring condition. The resultants were aged at 50 °C for 24 h in a sealed polypropylene vessel without stirring. After aging, the resulting precipitates were filtered off, thoroughly washed with deionized-distilled water and finally dried at 50 °C in an air oven for 24 h.

2.2. Synthesis of ZHN particles

Preparation of ZHN particles was carried out by the same method of synthesis of zinc hydroxychloride as reported previously [10,11]. The synthetic ZnO particles (16.0 mmol) were added into 50.0 ml of 0–2.0 mol/dm^3 aqueous $Zn(NO_3)_2{\cdot}6H_2O$ solutions in a sealed polypropylene vessel or a stainless-steel autoclave and they were aged at 6–140 °C for 48 h without stirring. The products were filtered off, washed with acetone and finally dried *in vacuo* at 50 °C for 24 h.

2.3. Characterization

The materials thus obtained were characterized by a variety of conventional techniques. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered Cu Kα radiation (30 kV, 16 mA). Particle morphology was observed by a TOPCON Transmission electron microscope (TEM). Transmission IR spectra were recorded with a resolution of 4 cm^{-1} using a KBr method by a JASCO Fourier transform infrared (FTIR) spectrometer. Zn and NO_3 contents in the material were respectively assayed by a Seiko inductively coupled plasma atomic emission spectrometer (ICP-AES) and a Yokogawa ion-chromatograph. The samples were dissolved in aqueous HCl solutions. Specific surface area was obtained by fitting the BET equation to the N_2 adsorption isotherms measured by a Quantachrome volumetric apparatus at the boiling temperature of liquid nitrogen. Adsorption isotherms of H_2O were determined at 25 °C by a gravimetric technique. Adsorption isotherms of CO_2 were measured at 25 °C with an automatic volumetric apparatus assembled in our laboratory. Prior to the adsorption measurements, the samples were treated at 100 °C under 10^{-5} Torr for 2 h.

3. Results and discussion

3.1. Influence of $Zn(NO_3)_2{\cdot}6H_2O$ concentration and aging temperature on the formation of ZHN

To verify the influence of $Zn(NO_3)_2{\cdot}6H_2O$ concentration in the starting solution on the formation of ZHN, synthetic ZnO particles were aged at various $Zn(NO_3)_2{\cdot}6H_2O$ concentrations ranging from 0 to 2.0 mol/dm^3 at 85 °C for 48 h. Hereafter, $Zn(NO_3)_2{\cdot}6H_2O$ concentration was abbreviated as $[Zn^{2+}]$. Fig. 1 shows the XRD patterns of the products at different $[Zn^{2+}]$. Pattern ***a*** is the synthetic ZnO particles used as a raw material of ZHN (JCPDS No. 36-1451). When the ZnO is aged at $[Zn^{2+}] = 0$ and 0.2 mol/dm^3, no remarkable difference in XRD patterns is recognized as compared with pattern ***a*** (patterns ***b*** and ***c***). At $[Zn^{2+}] = 0.5$ mol/dm^3, the peaks of ZnO faintly weaken and new peaks mainly develop at $2\theta = 9.1°$, 18.2°, 26.9° and 34.5°. All of the new peaks can be ascribed to ZHN (No. 72-627). On increasing the $[Zn^{2+}]$, the diffraction intensity of ZHN peaks increases and that of ZnO peaks falls. The ZnO peaks completely disappear at $[Zn^{2+}] = 1.5$ mol/dm^3 while the diffraction intensity of ZHN is a maximum at $[Zn^{2+}] = 2.0$ mol/dm^3. The Zn and NO_3 contents of the product at $[Zn^{2+}] = 2.0$ mol/dm^3 were 8.13 and 3.26 mmol/g, respectively. These values are almost identical with theoretical Zn (8.07 mmol/g) and NO_3 contents (3.25 mmol/g) calculated from the chemical formula of ZHN. Nevertheless, aging at $[Zn^{2+}] = 2.0$ mol/dm^3 and 85 °C without ZnO particles formed no ZHN. It is, therefore, indicative that the formation of ZHN requires the ZnO particles. These facts allow us to infer that the ZnO particles are hydrolyzed in aqueous $Zn(NO_3)_2{\cdot}6H_2O$ solution to recrystallize as ZHN by the following reactions:

$$ZnO + H_2O \rightarrow Zn^{2+} + 2OH^-$$

$$5Zn^{2+} + 8OH^- + 2NO_3^- + 2H_2O \rightarrow Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O \text{ (ZNH)}$$

To elucidate the influence of aging temperature on the formation of ZHN, ZnO particles were aged at $[Zn^{2+}] = 2.0$ mol/dm^3 and different temperatures from 6 to 140 °C for 48 h. The XRD patterns

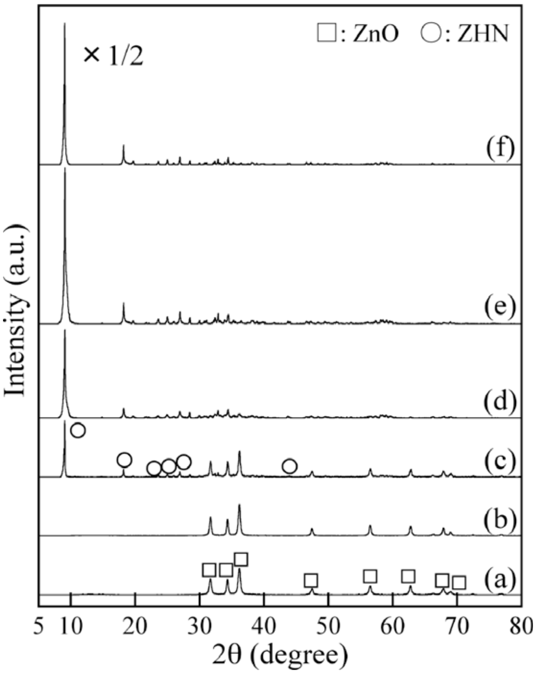

Fig. 1. XRD patterns of the products at different $[Zn^{2+}]$ and 85 °C for 48 h. $[Zn^{2+}]$ (mol/dm^3): (a) 0, (b) 0.2, (c) 0.5, (d) 1.0, (e) 1.5 and (f) 2.0.