

NOTES

INFLUENCE OF HYDROLYZED ZIRCONIUM SOLUTIONS ON THE OH-Zr-MONTMORILLONITE

CRISTINA VOLZONE¹ AND NORA ELBA HIPEDINGER²

Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC), C.C.49, Cno. Centenario y 506, (1897) M. B. Gonnet, Prov. Buenos Aires, Argentina

¹ Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET)

² Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC)

Key Words—Hydroxy-Interlayers, Intercalation, Montmorillonite, Smectite, Zirconium.

INTRODUCTION

Inorganic hydroxy metal interlayered smectites are used as catalysts, as adsorbents and in gas separation (Vaughan 1988; Yang and Baksh 1991). Inorganic hydroxy compounds used for intercalation are prepared from salts of Al, Ti, Cr and Zr cations. Yamanaka and Brindley (1979), Burch and Warburton (1986), Occelli and Finseth (1986), Bartley (1988) and Jones (1988) described the preparation of OH-Zr-smectites. They all observed differences in Zr-smectite properties with preparation method. Conditions such as temperature, aging time, pH and concentration affect the degree of polymerization of hydroxy Zr species in aqueous suspension and have an effect on the characteristics of intercalated smectites.

Jones (1988) measured the state of a $ZrOCl_2$ solution through conductance measurements and interaction with xylenol orange and mentioned that the complexity of Zr aqueous solutions requires considerable care in its analysis. Přebil and Veselý (1964) observed that the Zr determined by titration method of aged zirconium chloride solution was low. They attributed this behavior to the polymerization of Zr ions.

It is uncommon to find papers about OH-Zr-smectite that include the characterization of the Zr solution used; generally, the authors prepare it according to bibliographic data. The objective of this paper is to characterize the nature of various hydrolyzed Zr solutions and to evaluate the influence of these solutions on the structure of OH-Zr-montmorillonite.

MATERIALS AND METHODS

Different Zr solutions were prepared from a 0.1 M $ZrOCl_2 \cdot 8H_2O$ solution by hydrolysis under different conditions: 15 d and 15 mo at 20 °C (“15d/20” and

“15mo/20”, respectively) and 1 d at 60 °C (“1d/60”). The state of Zr in the solutions was determined by reacting the solutions with alizarin sulfonate (hereafter “alizarin”) based upon the colorimetric method developed by Green (1948). The measurements were carried out using a Hewlett Packard 8453 UV-visible diode array spectrophotometer. Each of the 0.1 M $ZrClO_2 \cdot 8H_2O$ solutions was diluted to 2×10^{-4} M and immediately added to the alizarin solution. The pH was adjusted to 1.5 with HCl to avoid hydrolysis of the Zr salt common at pH 2.8. Quality of chemicals used were Merck p.a. The alizarin solution without Zr was also adjusted to pH 1.5. Under this condition, the alizarin solution is yellowish and its UV-visible spectrum has a band with maximum of absorbance at 418 nm. A pink zirconium alizarin sulfonate complex (hereafter “Zr-complex”) is formed on reaction between Zr and alizarin. The maximum intensity of color development was obtained after 23 h at 520 nm.

The smectite sample used in the study was supplied by Georgia Kaolin Co. and was characterized in a previous work (Volzone et al. 1993). The smectite present was mainly montmorillonitic in nature. The montmorillonite was submitted to Na^+ exchange prior to intercalation. Then the homoionic montmorillonite was dispersed in distilled water (2% wt/wt) and after 1 d it was treated with the Zr solutions. The contact between the montmorillonite suspension and the hydrolyzed Zr solution was carried out at room temperature for 1 d. After treatment, the solid was washed with distilled water until free of electrolyte.

The OH-Zr-montmorillonites were prepared using hydrolyzed 0.1 M Zr solutions 15d/20 and 1d/60, and the samples were named “M-15d/20” and “M-1d/60”, respectively. The amounts of Zr added in both

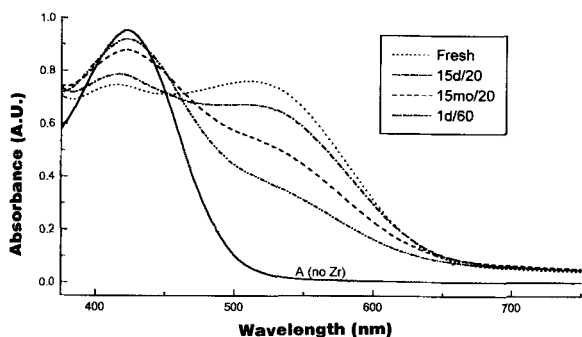


Figure 1. UV-visible absorbance spectra of alizarin solution without Zr (A, noZr) and after 23 h reacted with fresh and hydrolyzed $2 \times 10^{-4} M$ Zr solutions.

cases were 2.5 and 6.0 mmol Zr per gram of montmorillonite. The Zr retained by montmorillonite was determined by chemical analysis of the solid. The OH⁻ of OH-Zr-species retained by montmorillonite was calculated by determining the weight loss of the solid up to 500 °C and subtracting the amount of the original montmorillonite. These weight losses were obtained with a Thermal Analyse Netzsch STA 409 equipment.

The $d(001)$ spacings of all samples were measured on oriented slide specimens by scanning at $1^\circ 2\theta \text{ min}^{-1}$ between 2.5 and $12^\circ 2\theta$. X-ray diffraction (XRD) patterns were obtained with a generator and a Philips vertical goniometer (PW 1732/0 and PW 1050/70, respectively) using $\text{CuK}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$) and a Ni filter at 40 kV and 20 mA.

Surface area BET was calculated from the first part of the N_2 adsorption isotherm ($P/P_0 < 0.3$). The N_2 isotherms were obtained at liquid nitrogen temperature in a Micromeritics Accusorb equipment.

RESULTS AND DISCUSSION

Absorbances at 520 nm for solutions of the Zr-complex followed Beer's law in the range $1 \times 10^{-4} - 3 \times 10^{-4} M$ Zr using 89 mg alizarin L^{-1} .

Figure 1 shows the spectra of fresh and hydrolyzed Zr solutions after reaction with alizarin solution. An important amount of alizarin did not react with Zr present in 1d/60 and 15mo/20 solution because the absorbances at 520 nm were lower than the absorbance of fresh solution. However, considerable amount of Zr in the 15d/20 solution showed reaction with alizarin.

The percentages of the Zr-complex in the fresh, 15d/20, 15mo/20 and 1d/60 solutions were 100, 88, 71 and 52 respectively. These data were obtained by comparing the maximum absorbance at 520 nm for the hydrolyzed solutions with that obtained for fresh solution. If the Zr that did not react with the alizarin of the hydrolyzed solutions would be attributed to polymerization of Zr ions, then the 1d/60 solution showed a greater amount of Zr polymeric species than 15mo/20 and 15d/20. Přebil and Veselý (1964) mentioned

Table 1. Zr added and retained, Zr/OH retained, $d(001)$ spacing and surface area BET (S_{BET}) of the samples.

Sample	Zr added mmol g^{-1}	Zr retained mmol g^{-1}	Zr/OH retained molar ratio	$d(001)$ nm	S_{BET} $\text{m}^2 \text{g}^{-1}$
M	—	—	—	1.49	36
M-15d/20	2.5	0.78	0.28	2.02	190
M-15d/20	6.0	0.81	0.28	2.02	185
M-1d/60	2.5	1.01	0.32	2.08	203
M-1d/60	6.0	1.11	0.33	2.25	192

that the Zr ions of the aged and/or heated chloride solution that are not determined by titration method would correspond to polymeric species.

Table 1 shows the structural montmorillonite characteristics before and after treatment with hydrolyzed Zr solutions. A high Zr and Zr/OH were retained by the montmorillonite after treatment with 1d/60 solution. These behaviors could be attributed to high amount of Zr polymeric species contained in 1d/60 (mentioned above and in Table 1). The interlayer $d(001)$ spacing of the original montmorillonite (M) was increased from 1.49 to around 2.00 nm after hydrolyzed Zr solution treatment. Under these conditions, the Zr polymeric species of the Zr solutions would be responsible for montmorillonite expansion. Higher $d(001)$ spacing value of montmorillonites was obtained after treatment with 1d/60 solution. Yamanaka and Brindley (1979) obtained 1.88 nm basal spacing of montmorillonite after treatment with fresh 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution. Burch and Warburton (1986) reported different $d(001)$ value according to the preparation method using refluxed 0.1 M Zr solution.

Surface area BET of montmorillonite was increased from $36 \text{ m}^2 \text{g}^{-1}$ to around $200 \text{ m}^2 \text{g}^{-1}$ after treatment with hydrolyzed Zr solutions. A slight increase of the surface area of montmorillonite after treatment with 1d/60 Zr solution was obtained with respect to the montmorillonite treated with 15d/20 solution. Bartley and Burch (1985) and Bartley (1988) reported that intercalation of the montmorillonite with fresh zirconium chloride solution had a lower surface area ($117 \text{ m}^2 \text{g}^{-1}$) than after treatment with Zr polymers obtained using 0.1 M ZrOCl_2 aged 1 d at 100 °C ($147 \text{ m}^2 \text{g}^{-1}$). Similar structural characteristics of the OH-Zr-montmorillonite were obtained after 2.5 and 6.0 mmol of Zr were added per gram of montmorillonite.

The Zr retained, the Zr/OH molar ratio, the $d(001)$ spacing and the surface area of the montmorillonite increased with the amount of Zr polymeric species added. Although it was not possible to determine the type of the polymeric species, the different Zr/OH molar ratios retained in the montmorillonite after treatment with different hydrolyzed Zr solutions would indicate that the Zr species in such solutions were different.

The intercalated montmorillonites with different hydrolyzed Zr solutions originated OH-Zr-montmorillonites with different textural and structural characteristics. Larger basal spacing (≈ 2.00 nm) and surface area BET (≈ 200 m² g⁻¹) of the montmorillonite were obtained after treatment with hydrolyzed Zr solutions. The montmorillonite treated with hydrolyzed 0.1 M zirconium chloride solution during 1 d at 60 °C showed more basal spacing and surface area than one treated with hydrolyzed solution during 15 d at 20 °C.

REFERENCES

- Bartley GJJ. 1988. Zirconium pillared clays. *Catal Today* 2: 233–241.
- Bartley GJJ, Burch R. 1985. Zr-containing pillared interlayer clays. Part III. Influence of method of preparation on the thermal and hydrothermal stability. *Appl Catal* 19:175–185.
- Burch R, Warburton CI. 1986. Zr-containing pillared interlayer clays. I. Preparation and structural characterisation. *J Catal* 97:503–510.
- Green DE. 1948. Colorimetric microdetermination of zirconium. *Anal Chem* 20:370–372.
- Jones SL. 1988. The preparation and solution chemistry of Al(III) and Zr(IV) pillaring species. *Catal Today* 2:209–217.
- Ocelli ML, Finseth DH. 1986. Preparation and characterization of pillared hectorite catalysts. *J Catal* 99:316–326.
- Přibil R, Veselý V. 1964. Contributions to the basic problems of complexometry. XIV: Determination of zirconium, thorium and titanium in the presence of each other. *Talanta* 11:1197–1202.
- Vaughan DEW. 1988. Pillared clays—A historical perspective. *Catal Today* 2:187–198.
- Volzone C, Cesio AM, Torres Sánchez RM, Pereira E. 1993. Hydroxy-chromium smectite. *Clays Clay Miner* 41:702–706.
- Yamanaka S, Brindley GW. 1979. High surface area solids obtained by reaction of montmorillonite with zirconyl chloride. *Clays Clay Miner* 27:119–124.
- Yang RT, Baksh MSA. 1991. Pillared clays as a new class of sorbents for gas separation. *AIChE J* 37:679–686.

(Received 9 December 1997; accepted 1 September 1998; Ms. 97-113)