

NOTES

EFFECT OF MINERAL HOST ON SURFACE ACIDITY OF HYDROXY-Cr INTERCALATED CLAYS

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INTRODUCTION

The speciation of hydroxychromium complexes in solution has been extensively studied and the acidities of various polymer species reported (Baes and Mesmer 1976; Stunzi and Marty 1983). In Table 1, we present the values of pK_a (where K_a is acidity constant) of Cr^{III} oligomers according to Stunzi and Marty (1983). When incorporated between clay layers, these species can change the total acidity of the material. Depending on the nature of the clay surface and the treatment of the intercalated material, the pK_a of Cr polymers may change when compared to their counterparts present in solution (Drljaca et al. 1992). Moreover, the hydroxy-chromium interlayers may consist of 1 or more polymeric complexes, depending on preparation conditions and clay material used as the host (Carr 1985).

The objective of this study is to assess the acidity of hydroxychromium intercalated clays of natural and synthetic origin in terms of the distribution of species characterized by their pK_a values. Such characterizations have been recently reported in the literature for various solids such as activated carbons, pillared clays or soils (Bandosz et al. 1993, 1994, 1995; Jagiełło et al. 1995; Nederlof et al. 1993). Our laboratory analyses are based on a comparison of the pK_a values obtained for our pillared Cr sorbents to the pK_a values of polymeric species present in solution.

EXPERIMENTAL

Materials

Hydroxychromium solutions of composition $OH/Cr = \sim 2$ were prepared by slowly titrating 400 mL of 0.1

M $CrCl_3$ solution with 270 cm³ of 0.1 M NaOH and then diluting to 2 L. One-half L of hydroxy-Cr solution was added slowly, with continuous stirring, to a 5% water suspension of Wyoming bentonite (Black Hill) and a 3% water suspension of the synthetic mineral lithium taeniolite (Shell and Ivey 1969). The suspensions were aged for 36 h. The pH of the intercalating solution and the pH of the obtained suspension were measured. The resulting solids were washed several times to remove excess exchange solution (until the $AgNO_3$ test for Cl^- was negative) and air-dried in an oven at 393 K. The samples obtained are designated WCR2 and TCR2, where W and T represent the parent mineral (W = bentonite, T = taeniolite). A portion of the samples was heated at 573 K for 10 h in air. The heat-treated samples are referred to as "WCR2-H" and "TCR2-H".

Potentiometric Titration

Potentiometric titration measurements were performed with a 665 Dosimat (Brinkmann) combined with a Accumet pH meter model 50 equipped with a combination glass electrode (Corning). Subsamples of the studied materials of approximately 0.100 g in 50 mL 0.01 N $NaNO_3$ were placed in a container with the electrolyte solution thermostated at 298 K and equilibrated overnight. The mineral suspension was stirred throughout the measurements. Dilute solutions of NaOH and HNO_3 (0.1 N) were used as titrants. The experiments were done in the pH range 3–10 to minimize dissolution of mineral layers (Wehrli et al. 1990). Each sample was titrated by both acid and base starting from the initial pH of the suspension.

RESULTS AND DISCUSSION

General Features of the Materials

The pH of the intercalating solution was 4.7. When solutions were mixed with a suspension of the mineral,

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Table 1. pK_a values of chromium(III) oligomers (Stunzi and Marty 1983).

| Composition | Monomer Cr^{III} | Dimer $Cr_2(OH)_2^{IV}$ | Trimer $Cr_3(OH)_3^{V}$ | Tetramer $Cr_4(OH)_6^{VI}$ |
|---------------|-----------------------|----------------------------|----------------------------|-------------------------------|
| pK_a values | 4.29 | 3.68 | 4.35 | 2.55 |
| | 6.10 | 6.04 | 5.63 | 5.08 |
| | | | 6.00 | |

the pH increased to 6.4 for the WCR2 sample and 7.4 for the TCR2 sample. The resulting solids had a light green color which, after heat treatment in air, became dark olive, almost brown. Changes in color of the materials can be explained by mutation in the surface chemistry and oxidation of Cr^{III} to Cr^{VI} . Similar changes were also observed by Bornholdt et al. (1991), whose extended X-ray absorption fine structure (EXAFS) study indicated the possibility of conversion of Cr^{III} to a mixed-valence compound, $Cr^{III}_2Cr^{VI}_3O_{12}$, upon partial oxidation.

Potentiometric Titration

Information about the nature of chemical species present on the clay surface can be obtained from potentiometric titration (Bandosz et al. 1994; Bandosz et al. 1995; Jagiełło et al. 1995). In our approach, it is assumed that the system under study consists of acidic sites characterized by their K_a . It is also assumed that the population of sites can be described by a continuous pK_a distribution $f(pK_a)$. The experimental data can be transformed into a proton binding isotherm, Q , representing the total amount of protonated sites, which is related to the pK_a distribution by the following integral equation:

$$Q(pH) = \int_{-\infty}^{\infty} q(pH, pK_a) f(pK_a) dpK_a \quad [1]$$

We use the numerical procedure SAIEUS (Jagiełło 1994). The solution is obtained using regularization combined with non-negativity constraints. The choice of the degree of regularization/smoothing is based on the analysis of a measure of the effective bias introduced by the regularization and a measure of uncertainty of the solution. SAIEUS was tested using simulated data and experimental titration data of organic standards, and it was demonstrated that this method can completely resolve peaks that are less than 1 pK_a unit apart (Jagiełło 1994; Jagiełło et al. 1994; Jagiełło et al. 1995).

Proton Binding Isotherms

Figure 1 shows the proton binding isotherms obtained for hydroxy-chromium intercalated clays. The solid lines represent the fitting of the experimental points to Equation [1]. The shape of the isotherms indicates the existence of different degrees of surface heterogeneity. We find that the isotherms for the 2 un-

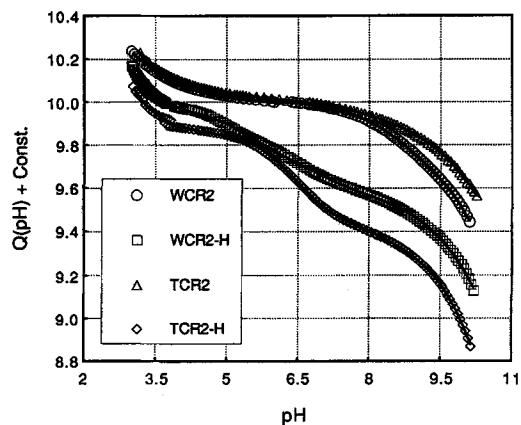


Figure 1. Proton binding isotherms. Solid lines indicate the fit of the experimental points to Equation [1].

treated samples are similar between pH 2 and 8, despite differences in the chemical composition of the parent mineral; heat treatment, however, changes their shape significantly, suggesting corresponding changes in surface chemistry and in the distribution of Cr species.

pK_a Distributions

The proton affinity distributions for the hydroxy-chromium intercalated clays are presented in Figures 2 and 3; Table 2 shows the results obtained from our analysis. A peak position is given as a value of its first order moment; the number of species given in parentheses is the value of the integral of the peak. In all cases the root mean square error (rms) of fitting the data to Equation [1] was relatively small. For all samples, peaks at the ends of the experimental window were observed. We did not analyze these results, due to uncertainty caused by possible dissolution of the mineral (Wehrli et al. 1990).

Comparison of the distributions obtained for the WCR2 and TCR2 samples indicates only a small difference in species present on the surface of bentonite and taeniolite. It is assumed that strong acidic centers come predominantly from the presence of interlayer material (Bandosz et al. 1994; Bandosz et al. 1995). The pK_a values obtained are compared to those of Cr polymeric species present in solution (Stunzi and Marty 1983), which serve as a reference (Table 1).

The positions of peaks obtained are similar for both minerals; however, in the case of the taeniolite-based sample, 1 additional peak at pK_a 5.82 is detected. This suggests an influence of mineral type on creation of a new population of polychromium species. Based on the results of Stunzi and Marty (1983), peaks at pK_a values <7 are attributed to the presence of hydroxy-chromium polymers (Tables 1 and 2). The values of pK_a obtained suggest the presence of trimers; however, due to the broadness of the distribution and similarities

Table 2. Peak positions and the number of groups (in parentheses; mmol g⁻¹) for materials studied.

| Sample | pH† | pK _a 3-4 | pK _a 4-5 | pK _a 5-6 | pK _a 6-7 | pK _a 7-8 | pK _a 8-9 | pK _a 9-10 | rms error |
|--------|-----|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|----------------------|-----------|
| WCR2 | 6.1 | ‡ | 4.79 (0.056) | | | 7.53 (0.069) | 8.86 (0.266) | ‡ | 0.002 |
| WCR2-H | 4.0 | ‡ | | 5.54 (0.220) | | 7.10 (0.159) | 8.76 (0.106) | ‡ | 0.005 |
| TCR2 | 6.5 | ‡ | 4.39 (0.067) | 5.82 (0.025) | | 7.66 (0.075) | 8.96 (0.124) | ‡ | 0.001 |
| TCR2-H | 3.8 | ‡ | | | 6.47 (0.425) | | 8.49 (0.150) | ‡ | 0.004 |

† Initial pH of the mineral suspension used for titration.

‡ Uncertainty of the peak position and the number of groups due to the limit of the experimental window.

in pK_a of particular Cr oligomers, the presence of dimers and monomers cannot be excluded from our interpretation. It is also likely that observed pK_a values are shifted to higher values compared to the oligomers present in the solution, due to mineral layer influence (Drljaca et al. 1992). Peaks at pK_a of approximately 7.5 and 9, in the case of the WCR2 sample, can be the result of the combined influence of either: 1) both protonation of AlOH groups of edge surfaces of the mineral and AlOH groups on the basal gibbsite layers, or 2) new species created by inner-sphere complexation of Cr with O in the silicate layers (Dubbin and Goh 1995; Drljaca et al. 1992). Schindler and Stumm (1987) estimated the pK_a values of Al layers as 6.31, 8.69 (edge surface) and 4.04, 7.04 (basal gibbsite layers). The pK_a distributions obtained for smectite and taeniolite samples intercalated with hydroxyaluminum and hydroxy-aluminum zirconium polycations showed 1 common well-defined peak at pK_a approximately 9 (Bandosz et al. 1994; Bandosz et al. 1995), regardless of the composition of the octahedral layers. This previous observation suggests that the peak at pK_a approximately 7.5 (almost identical for both hydroxychromium intercalated samples) may represent the inner-sphere complexation of Cr with O from silicate layers (Dubbin and Goh 1995; Drljaca et al. 1992).

Heat treatment revealed dramatic differences between taeniolite- and bentonite-based samples. The WCR2-H sample became more heterogeneous than TCR2-H, with 3 peaks at 5.54, 7.10 and 8.76. The species, which we assume characterize octahedral layers at pK_a 8.76, decreased in population, whereas the number of species at pK_a 7.10 increased significantly with a shift toward higher acidity compared to WCR2. This is probably the result of changes in the environment of the inner-sphere complexes of Cr with siloxane O (Dubbin and Goh 1995). The new peak at 5.54 is proposed to be due to oxidation of Cr^{III} to Cr^{VI} (Bornholdt et al. 1991). The presence of Cr^{VI} would account for the high acidity of the material, since chromic acid is a strong acid with one of its pK_a values at 6.5 (Baes and Mesmer 1976). The observed shift toward a lower value could be the result of the influence of layers, changes in the chemical environment or only a partial oxidation of Cr compounds (Bornholdt et al. 1991). On the other hand, in the case of TCR2-H, a significant population of groups, represented by a peak at 6.47, is in excellent agreement with a pK_a of chromic acid. In fact, after heat treatment, virtually all of the Cr appears to be converted to Cr^{VI}, which suggests that, for taeniolite, there is a weaker interaction of the intercalate pool with the mineral layers. The acidity

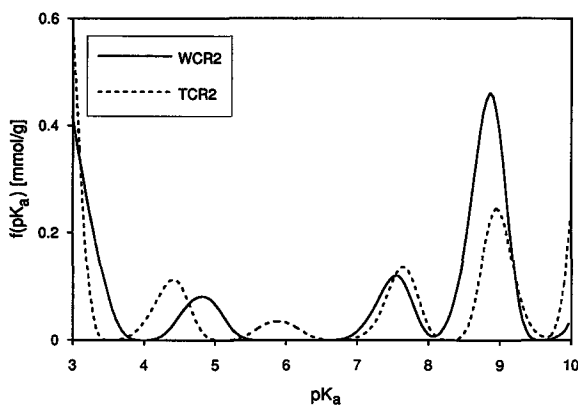


Figure 2. Comparison of pK_a distributions for the WCR2 and TCR2 samples.

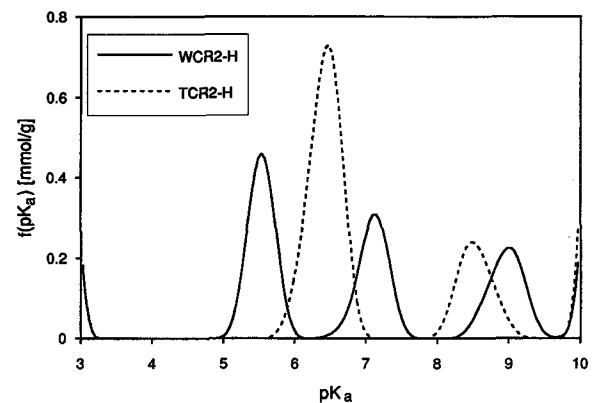


Figure 3. The pK_a distributions of heat treated samples.

coming from the octahedral layers remains almost unchanged after this modification.

CONCLUSIONS

The results demonstrate that potentiometric titration combined with the SAIEUS procedure is a useful tool to assess the surface acidity of minerals. The values of pK_a obtained for hydroxychromium clays of different origin are in relatively good agreement with those pK_a values that characterize Cr oligomers present in solution. Since the distributions obtained are rather broad and some Cr oligomers have similar pK_a values, it is difficult to make a precise assignment of each peak to a particular polymeric species. However, changes in the pK_a distributions obtained showed that the population and strength of acidic species depend on the chemical environment (nature of mineral) and also on the history of the sample (heat treatment in oxidizing atmosphere).

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(Received 15 February 1996; accepted 8 April 1996; Ms. 2739)