

ION EXCHANGE PROPERTIES OF NOVEL
HYDROUS METAL OXIDE MATERIALS

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ABSTRACT

Hydrous metal oxide (HMO) materials are inorganic ion exchangers which have many desirable characteristics for catalyst support applications, including high cation exchange capacity, anion exchange capability, high surface area, ease of adjustment of acidity and basicity, bulk or thin film preparation, and similar chemistry for preparation of various transition metal oxides. Cation exchange capacity is engineered into these materials through the uniform incorporation of alkali cations via manipulation of alkoxide chemistry. Specific examples of the effects of Na stoichiometry and the addition of SiO₂ to hydrous titanium oxide (HTO) on ion exchange behavior will be given. Acid titration and cationic metal precursor complex exchange will be used to characterize the ion exchange behavior of these novel materials.

INTRODUCTION

MASTER

Hydrous metal oxide (HMO) materials were originally developed at Sandia National Laboratories as inorganic ion exchangers for high level nuclear waste incorporation [1]. This class of materials includes hydrous titanium, zirconium, niobium, or tantalum oxides, which are chemically synthesized using sol-gel methods. Cation exchange in these HMO materials is facilitated by the manipulation of alkoxide chemistry to produce a homogeneous distribution of ion exchangeable alkali cations that provide charge compensation to the metal-oxygen framework. In terms of the major types of inorganic ion exchangers defined by Clearfield [2], these amorphous HMO materials are similar to both hydrous oxides and layered oxide ion exchangers (e.g., alkali metal titanates).

For catalyst applications, the HMO material serves as an ion exchangeable support which facilitates the uniform incorporation of catalyst precursor species. Following catalyst precursor incorporation, an activation step is required to convert the catalyst precursor to the desired active phase. Considerable previous work on HMO materials has emphasized various forms of hydrous titanium oxides (HTOs) as catalyst supports for direct coal liquefaction, hydrotreating, and hydrogenation/dehydrogenation applications [3-8]. Additional studies have been performed to determine the titanium and oxygen coordination environments in these amorphous as-prepared (Na form) or acidified/cation-exchanged HTO materials [9-12], and these results have been coupled to a formal charge model [13,14] to predict possible cation and anion exchange sites. Although this work has demonstrated several promising correlations between HTO structure and ion exchange behavior, it is clear that additional studies are needed to provide further advances in this area. This paper describes acidification/cation exchange studies for amorphous HTO and improved silica-doped HTO (HTO:Si) materials with a range of Na:Ti ratios. These studies are intended to be initial efforts toward advancement in the understanding of the ion exchange behavior of these novel materials.

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EXPERIMENTAL

Bulk HTO-supported catalyst preparation involves a multiple step chemical procedure which begins with the synthesis of an HTO powder. Previous work has demonstrated that SiO_2 additions (Ti:Si molar ratio = 5:1) to HTO materials act to stabilize support surface area at high temperature ($\geq 500^\circ\text{C}$) [5,6]. Although previous workers have alluded to the fact that the added SiO_2 does not alter ion exchange behavior [5], no ion exchange data has been reported for these HTO:Si materials. The synthesis of either sodium titanate (HTO) or silica-doped sodium titanate (HTO:Si) involves a two step process, which is published in detail elsewhere [4-6,10], and will be summarized only briefly here. The first step of the reaction scheme involves adding the Ti (or mixed Ti-Si) alkoxide to a dilute (~10 wt.%) solution of sodium hydroxide in methanol, resulting in the production of a titanium tetramethoxide-like soluble intermediate species. Changes in the Na:Ti stoichiometry are easily accommodated over the range of $0 \leq \text{Na:Ti} \leq 0.5$. The soluble intermediate is subsequently hydrolyzed in a mixed water/acetone solution to precipitate the HTO or HTO:Si ion exchanger in bulk powder form. For simplicity, the various ion exchangeable supports synthesized and evaluated as part of this study will be referred to by the designations Na_xTi and $\text{Na}_x\text{Ti}:0.2\text{Si}$, where x represents the Na:Ti ratio. The precipitate is filtered, washed, and vacuum dried at room temperature to produce the material for subsequent acidification/cation exchange processing.

Two types of acidification experiments were performed as part of this study. In the case of the $\text{Na}_{0.5}\text{Ti}$ and $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ materials, 1 g samples were mixed with 100 ml of aqueous HCl solutions ranging in concentration from 0 to 0.04 M. This follows the previous procedure used for potentiometric titration of $\text{Na}_{0.5}\text{Ti}$ materials [4,10]. Following equilibration overnight while shaking, the final equilibrium slurry pH was measured and the solids were separated from the supernate by filtration. Atomic absorption spectrophotometry (AAS) was used to determine the partitioning of Na^+ between the supernate and the solid phase. In an effort to streamline this overall effort, an autotitration system was evaluated for measuring the equilibrium pH versus acid content for these materials. For these experiments, 1 g samples were initially mixed with 100 ml of deionized H_2O and loaded onto the titration system. At 10 min intervals, 0.1 ml aliquots of 1.0 M HCl were dosed into the slurry, with pH measurements recorded continuously. These autotitration experiments allowed the rapid screening and comparison of various materials in terms of their potentiometric titration curves.

The final experiments focused on performing equilibrium cation exchange experiments using the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ support. For these cation exchange experiments, $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ was chosen as the catalyst precursor since the cationic $[\text{Pt}(\text{NH}_3)_4]^{+2}$ species is stable over a wide range of pH. These experiments were performed in the same manner as the equilibrium potentiometric titration experiments described above, with the following exceptions: 1) HNO_3 was used as the acid to provide a common anion with respect to the catalyst precursor; and 2) a constant amount of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, equivalent to the total number of moles necessary for complete cation exchange of $[\text{Pt}(\text{NH}_3)_4]^{+2}$ for Na^+ , was added. The $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ powder was added directly to the mixed $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$ solution to allow a direct competition between the $[\text{Pt}(\text{NH}_3)_4]^{+2}$ and H^+ species for Na^+ sites in the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$. The equilibrated Pt-containing slurries were evaluated against equilibrated control samples which contained only $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$, H_2O , and HNO_3 , similar to the original equilibrium experiments described previously. After filtering the solids from the supernate, the partitioning of both $[\text{Pt}(\text{NH}_3)_4]^{+2}$ and Na^+ between these two phases was evaluated by AAS. This experiment allowed the evaluation of the competition between H^+ and $[\text{Pt}(\text{NH}_3)_4]^{+2}$ for cation (Na^+) exchange sites over a wide range of slurry pH (4-11).

RESULTS AND DISCUSSION

Previous work has shown that amorphous $\text{Na}_{0.5}\text{Ti}$ materials behave as weak polyfunctional acids, represented as $\text{Na}^+(\text{Ti}_2\text{O}_5\text{H})^-$, which upon dissociation of their ionic components yield mobile cations and fixed colloidal anions [4]. Figure 1 shows the combined results for equilibrium and controlled acidification measurements with $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ and $\text{Na}_{0.5}\text{Ti}$ materials, and compares these results with the historical equilibrium results obtained for $\text{Na}_{0.5}\text{Ti}$. For simplicity, these historical results are illustrated in Figure 1 by means of the solid vertical lines at meq H^+ /meq Na^+ values of 0.33 and 1.0. These two lines represent the sharp equivalence points interpreted/observed previously for equilibrium measurements with $\text{Na}_{0.5}\text{Ti}$ [4,10]. The first observation to make regarding this new data is that, in contrast to the earlier work, two sharp equivalence points are not observed in the equilibrium titration curve for the $\text{Na}_{0.5}\text{Ti}$ material. Rather, a single relatively sharp equivalence point is observed at a nominal meq H^+ /meq Na^+ value of 1.0. The existence of this particular equivalence point is consistent with previous work, and it is clear that it is associated with the transition of the $\text{Na}_{0.5}\text{Ti}$ material from a cation to an anion exchange regime [4,10]. However, it is felt that the new equilibrium data for this material is more representative of actual material performance since a larger number of meq H^+ /meq Na^+ values were evaluated over the range of cation exchange interest. The equilibrium data agrees well with the controlled acidification data generated using the autotitration system (solid curved line). Note that the solid curved line in Figure 1 representing the controlled acidification data is actually a composite of two separate autotitration profiles. This result shows that the 10 min period between acid aliquot additions in the controlled acidification procedure was sufficient to reach equilibrium or near-equilibrium conditions.

Also shown in Figure 1 is the equilibrium acid titration curve for the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ material. This titration curve is very similar in shape to that of the $\text{Na}_{0.5}\text{Ti}$ material, although the whole curve is displaced to slightly more acidic conditions. This displacement is probably due to the higher acidity of SiO_2 than TiO_2 , as well as the lower overall Na^+ content of the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ material. The lack of a single sharp equivalence point at higher pH in the acid titration curves for all of these materials seems consistent with their amorphous nature.

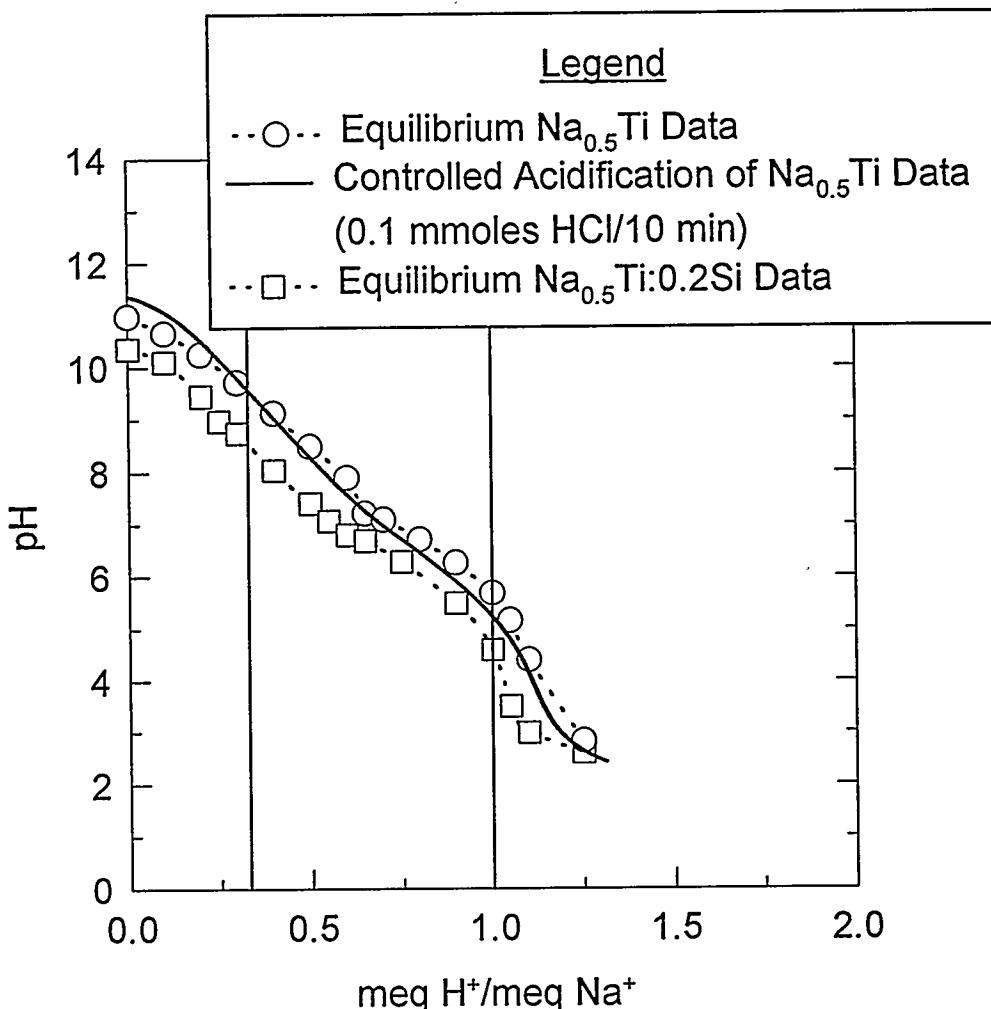


Figure 1. Equilibrium potentiometric titration and controlled acidification data of $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ and $\text{Na}_{0.5}\text{Ti}$ materials.

Figure 2 shows the results of controlled acidification experiments performed with the autotitration system on various Na_xTi materials. As in the case of Figure 1, the lines representing the different Na_xTi materials are composites from a minimum of two titration experiments. As the $\text{Na}:\text{Ti}$ ratio increases the amount of total exchangeable Na^+ increases, as does the amount of Na^+ which is exchangeable at higher pH conditions. It is also noted that the characteristic equivalence point observed at a nominal $\text{meq H}^+/\text{meq Na}^+$ value of 1.0 is consistent with all Na_xTi materials regardless of their exact $\text{Na}:\text{Ti}$ ratio. Previous studies have shown that decreasing the $\text{Na}:\text{Ti}$ ratio from 0.5 to 0.25 correlates well with an interesting structural change, the disappearance of non-bridging oxygen species. Since these species are likely cation exchange sites [13,14], particularly at high pH, this previous work correlates well with our acid titration results.

Figure 3 shows the results of equilibrium experiments involving competitive cation exchange between $[\text{Pt}(\text{NH}_3)_4]^{+2}$ and H^+ using the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ support material. These results show that after cation exchange at high pH conditions ($\text{meq H}^+/\text{meq Na}^+$ values ≤ 0.5 , $\text{pH} > 6.5$), $\sim 50\%$ or more of the original Na^+ sites in the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ material are occupied by $[\text{Pt}(\text{NH}_3)_4]^{+2}$ species (assuming a stoichiometry of 1 $[\text{Pt}(\text{NH}_3)_4]^{+2}$ replacing 2 Na^+). Under these conditions,

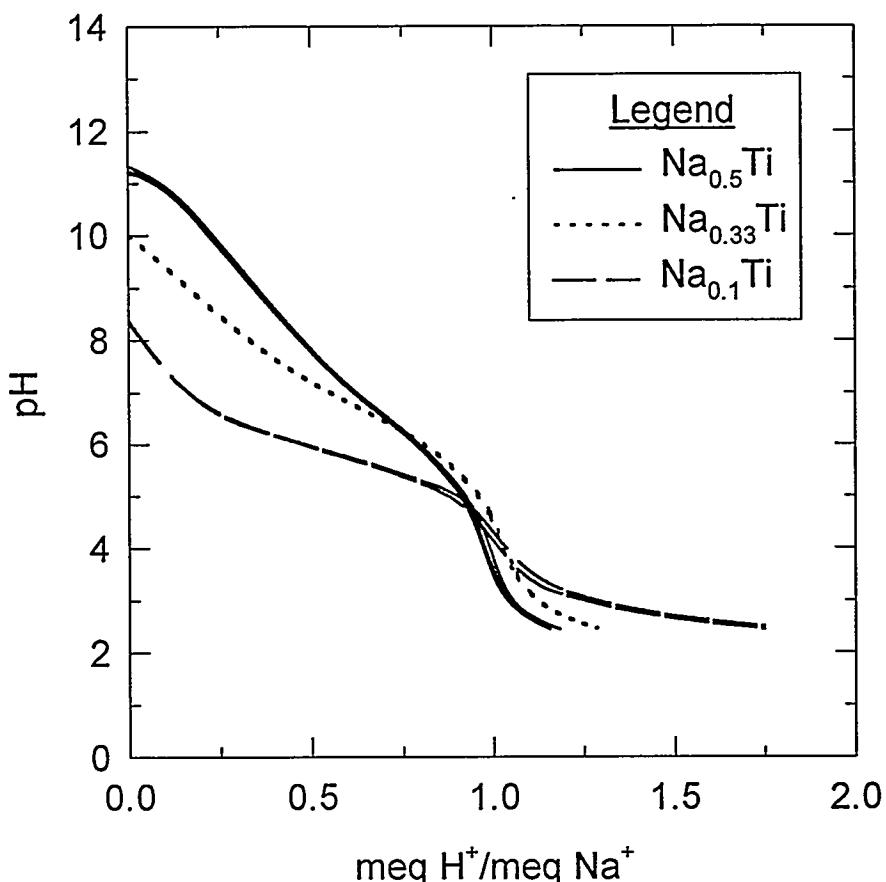


Figure 2. Controlled acidification data of Na_xTi materials as a function of Na:Ti ratio. Note that the characteristic titration curve shown for each material is actually a composite of at least two replicate runs.

uptakes of $[\text{Pt}(\text{NH}_3)_4]^{+2}$ on the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ support following cation exchange are large, with final Pt metal loadings >18 wt.% (calcined basis). These uptakes do not approach theoretical limits as evidenced by the presence of significant quantities of unexchanged Na^+ sites in the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ support following the experiment. At more acidic conditions ($\text{meq H}^+/\text{meq Na}^+ > 0.50$, $\text{pH} < 6$) $[\text{Pt}(\text{NH}_3)_4]^{+2}$ species do not compete effectively with H^+ for the Na^+ exchange sites. This is clearly shown in Figure 3 by the H^+ site dominance at high $\text{meq H}^+/\text{meq Na}^+$ values. Comparison of the data shown in Figure 3 to the control data (no Pt addition, data not shown) indicated that H^+ for Na^+ exchange is clearly dominant, being only slightly decreased by the presence of the $[\text{Pt}(\text{NH}_3)_4]^{+2}$ species. This observation is reinforced by the fact that where $[\text{Pt}(\text{NH}_3)_4]^{+2}$ and H^+ species approach equal concentrations ($\text{meq H}^+/\text{meq Na}^+ > 0.50$), H^+ for Na^+ cation exchange is dominant.

Previous work has demonstrated that competition between H^+ and Ni^{+2} for cationic ion exchange sites in $\text{Na}_{0.5}\text{Ti}$ can be significant [15]. This work slightly differed from this previous work in that the initial exposure of both the $[\text{Pt}(\text{NH}_3)_4]^{+2}$ and H^+ cationic species to the $\text{Na}_{0.5}\text{Ti}$ was simultaneous, while in the previous work the $\text{Na}_{0.5}\text{Ti}$ was initially partially protonated by adjusting slurry pH conditions to prevent Ni^{+2} hydrolysis under cation exchange conditions [16]. Further work needs to be pursued to continue investigation of H^+ vs. M^{+n} species competition during cation exchange procedures with Na_xTi and $\text{Na}_x\text{Ti}:0.2\text{Si}$ materials.

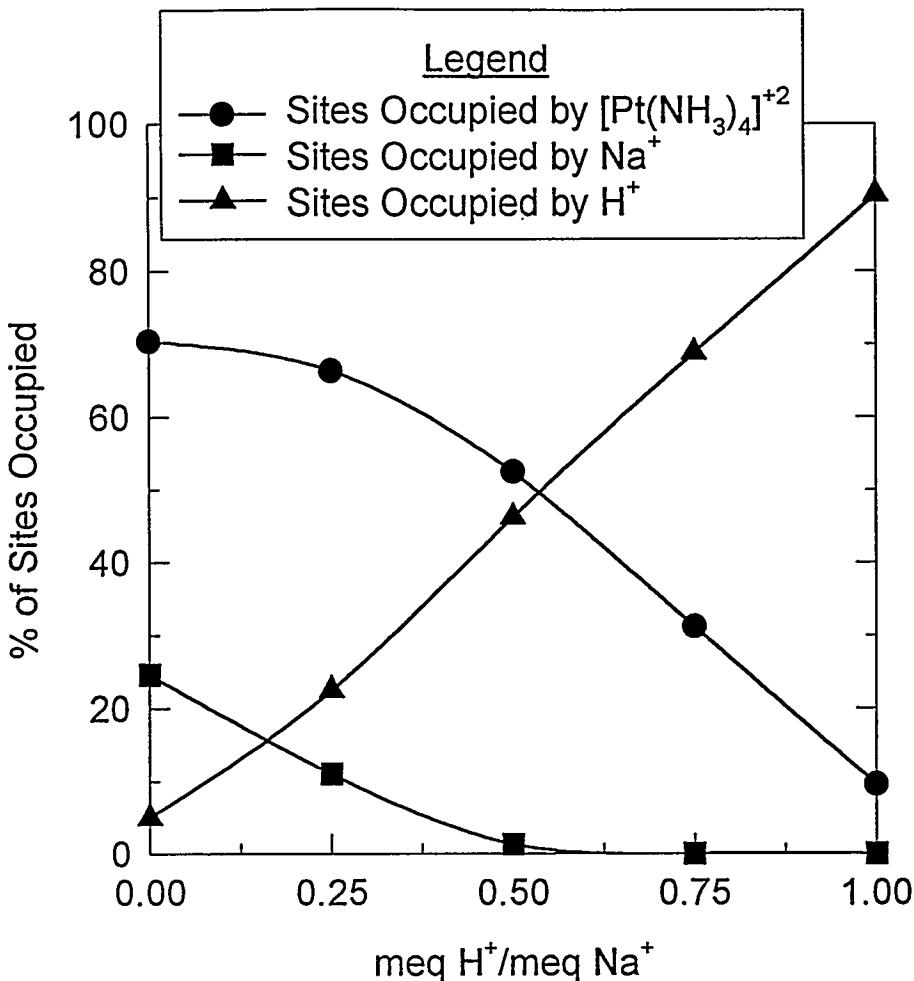


Figure 3. Equilibrium cation exchange results illustrating the competition between $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and H^+ for cation exchange sites in the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ material. The results are shown in terms of the percent of original Na^+ sites in the $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ material occupied by $[\text{Pt}(\text{NH}_3)_4]^{2+}$, H^+ , and unexchanged Na^+ in the final, equilibrated, cation-exchanged materials.

SUMMARY

This work has resulted in several observations regarding the cation exchange behavior of hydrous titanium oxide (HTO) and silica-doped hydrous titanium oxide (HTO:Si) materials. In contrast to previous work, we find that the characteristic potentiometric titration curves for a range of Na_xTi and $\text{Na}_x\text{Ti}:0.2\text{Si}$ materials exhibit a single equivalence point near H^+/Na^+ values of 1. The lack of a distinct equivalence point at higher pH is consistent with the amorphous nature of these materials, perhaps indicating that a range of different sites exist at higher pH. As the Na:Ti ratio of the Na_xTi materials is increased, we find an increase in the amount of cation exchangeable Na, which manifests itself in the higher pH portion of the titration curve. Finally, equilibrium experiments involving the competitive exchange of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and H^+ cationic species for Na^+ in $\text{Na}_{0.5}\text{Ti}:0.2\text{Si}$ materials clearly showed that although large $[\text{Pt}(\text{NH}_3)_4]^{2+}$ uptakes were possible under high

pH conditions, H^+ for Na^+ cation exchange dominates under conditions where H^+ concentrations approach or exceed $[\text{Pt}(\text{NH}_3)_4]^{+2}$ concentrations.

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