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DEVELOPMENT OF DODECANIOBATE KEGGIN CHAIN MATERIALS AS ALTERNATIVE SORBENTS FOR SR AND ACTINIDE REMOVAL FROM HIGH-LEVEL NUCLEAR WASTE SOLUTIONS

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INTRODUCTION

Polyoxometalates (POMs—metal oxo clusters composed predominantly of WO_6, MoO_6, NbO_6, VO_6 or TaO_6 octahedra) or POM-based materials have been considered as potential sequestering reagents or sorbents for removing radionuclides from nuclear waste solutions.[1-5] The metal-binding capabilities of POMs are owed to their negative charge and their geometry. In particular, the lacunary POMs with vacant octahedral sites have particularly good metal binding capabilities since have both higher negative charge and sites with ideal geometries for binding metals. The drawback of the POMs as reagents for nuclear waste cleanup is that the majority of POMs (WO_6 and MoO_6 POMs) are unstable in basic solutions and most of the nuclear wastes stored at U.S. sites are highly caustic. The NbO_6 and TaO_6 POMs, on the other hand, are stable in basic solutions; but the chemistry of these POMs is much less developed than that of the WO_6 and MoO_6 POMs. Recently, we have succeeded in forwarding the field of polyoxoniobate chemistry, both as clusters and extended solids.[6-8] In addition to being base-stable, these polyoxoniobate materials are advantageous for radionuclide binding due to their higher negative charge per cluster than the related polyoxomolybdates and polyoxotungstates. We present here the synthesis and structural characterization of a family of α-Keggin ion $[TNb_{12}O_{40}]^{16-}$ (T=Si, Ge) based ion exchanger materials that have excellent ion exchange capabilities and good selectivity for sorption of Sr and actinides from highly caustic, high ionic strength nuclear wastes.

RESULTS

All the α-Keggin ion $[TNb_{12}O_{40}]^{16-}$ (T=Si, Ge) based ion exchanger materials discussed in this presentation were synthesized hydrothermally using amorphous metal oxide and metal alkoxide precursors in basic Na- or K- containing solutions. Five different compositions/phases have been produced. The compositions, space group and unit cell parameters are summarized in **Table 1**. The structure of $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]\bullet 16H_2O$ was determined from single-crystal X-ray data and the structures of the Na-analogues (which are all isostructural with each other) were determined from X-ray powder data. All the Keggin chain materials have tetragonal symmetry and feature Keggin ions that are bicapped with NbO_6 or TiO_6 octahedra. These NbO_6 or TiO_6 octahedra link the Keggin ions together by edge-sharing, forming a $[Nb_2O_2]^{6+}$ or $[Ti_2O_2]^{4+}$ bridging unit. The chains extend infinitely in the z-direction and are not linked within the *xy* plane. This allows rapid and complete exchange of the charge-balancing K- and Na- cations that reside between the chains. The structures of the K-analogue and Na-analogues differ in the arrangement of the chains with respect to each other and the degree of hydration of the charge-balancing alkali cations. SEM images of the K-analogue and a typical Na-analogue are shown in **Figure 1**.

Table 1. Composition and Crystallographic Information for the Keggin Chain Materials

Composition	Z	Space group	*a* Å (error)	*c* Å (error)	Volume A^3 (error)
$K_{12}[Ti_2O_2][SiNb_{12}O_{40}]\bullet 16H_2O$	4	*P-4c2*	15.972 (4)	22.956 (6)	5856 (2)
$Na_{12}[Ti_2O_2][SiNb_{12}O_{40}]\bullet 4H_2O$	2	*I –4 m 2*	14.2701(5)	11.2923(7)	2299.5(2)
$Na_{10}[Nb_2O_2][SiNb_{12}O_{40}]\bullet 6H_2O$	2	*I –4 m 2*	14.2649(4)	11.3575(5)	2311.1(1)
$Na_{12}[Ti_2O_2][GeNb_{12}O_{40}]\bullet 4H_2O$	2	*I –4 m 2*	14.2852(5)	11.3222(7)	2310.5(2)
$Na_{10}[Nb_2O_2][GeNb_{12}O_{40}]\bullet 6H_2O$	2	*I –4 m 2*	14.2633(3)	11.3947(3)	2318.2(1)

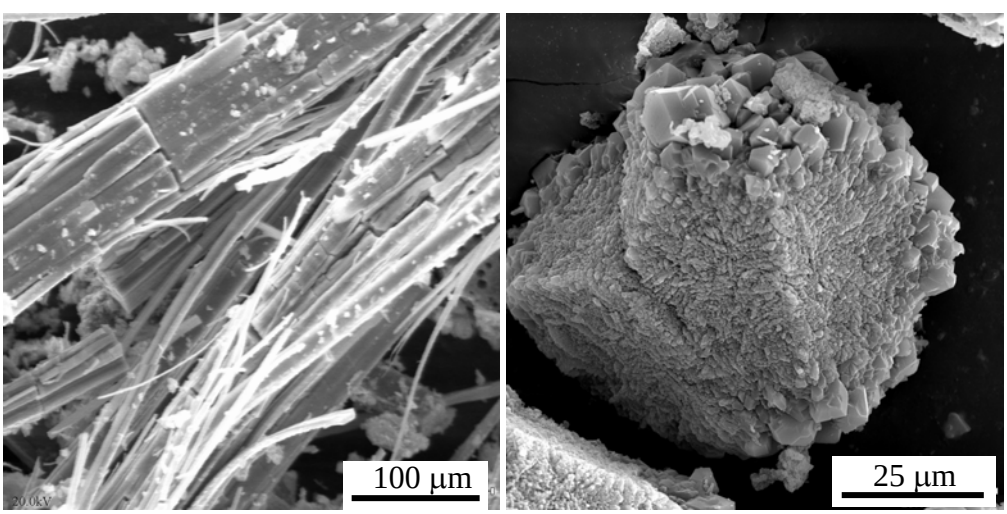

Figure 1. Left: SEM image of $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]\bullet 16H_2O$
Right: SEM image of $Na_{10}[Nb_2O_2][GeNb_{12}O_{40}]\bullet 6H_2O$.

The K^+ of the K-analogue can be exchanged almost completely for Sr^{2+}, but the structure undergoes alteration and crystallinity becomes rather poor. On the other hand, the Na^+ of the Na-analogues can be exchanged completely for Sr^{2+} without degradation of the structure. The unit cell parameters of the Sr-exchanged, Na-analogues were also determined and the coordination of the Sr was examined. The Sr^{2+} binds to both bridging and terminal oxygens of the Keggin chains as well as the oxygens of the $[Nb_2O_2]^{6+}$ or $[Ti_2O_2]^{4+}$ bridges.

SUMMARY

These new dodecaniobate Keggin chain materials are excellent ion exchangers and potential sorbents for selective removal of radionuclides from the highly basic wastes stored in locales such as SRS and Hanford. Since they are 1-dimensional materials, the framework is flexible with easy access to the exchange tunnels. This results in a high capacity, rapid ion exchange material. Since size-selectivity is improbable with these materials, the origin of selectivity is presumably related to the chemical interaction between the sorbates and the negatively-charged framework of the sorbent.

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References

1. Bion, L.; Moisy, P.; Madic, C. *Radiochim. Acta* 1995, **69**, 251-257.
2. Kamoshida, M.; Fukasawa, T.; Kawamura, F. *J. Nucl. Sci. Technol.* 1998, **35**, 185-189.
3. Besserguenev, A. V.; Dickman, M. H.; Pope, M. T. *Inorganic Chemistry* 2001, **40**, 2582-2586.
4. Katsoulis, D. E. *Chem. Rev.* 1998, **98**, 359-387.
5. Pope, M. T.; Muller, A. *Angew. Chem. Int. Ed. Engl.* 1991, **30**, 34-48.
6. Nyman, M.; Bonhomme, F.; Alam, T. M.; Rodriguez, M. A.; Cherry, B. R.; Krumhansl, J. L.; Nenoff, T. M.; Sattler, A. M. *Science* 2002, **297**, 996-998.
7. Nyman, M.; Criscenti, L. J.; Bonhomme, F.; Rodriguez, M. A.; Cygan, R. T. *Journal of Solid State Chemistry* 2003, **176**, 111-119.
8. Nyman, M.; Bonhomme, F.; Alam, T. M.; Parise, J. B.; Vaughan, G. M. B. *Angew. Chem. Int. Ed.* 2003.