

Pore Size and its Effect on Molybdenum Retention in Mesoporous Alumina

R. Hepburn, Ph.D.* and S. Tsubota**

*Fujimi Corporation, NBD, Wilsonville, OR, USA, bhepburn@fujimico.com

**Fujimi Incorporated, ATRC, Gifu, Japan, tsubotas@fujimiinc.co.jp

ABSTRACT

Mesoporous alumina is used as the adsorbent for retaining molybdenum-99 in the molybdenum/technetium generators used for medical imaging. However, in 2012 an initiative [1] was agreed upon to minimize and then eliminate the use and production of highly enriched uranium (HEU) for non-military applications. In general, when non-uranium production methods are employed, there is a lower concentration of molybdenum-99 generated. This has created a need for a mesoporous alumina that can retain more molybdenum.

Our research has shown that the pore size of the mesoporous alumina and not the surface area is more predictive of the molybdenum retention performance. Mesoporous alumina with pore sizes ranging from 5nm to 19nm have been evaluated and the retention of molybdenum increased by a factor of 6. A variety of pore forming agents and templating materials were chosen to modulate the pore size.

Keywords: mesoporous, alumina, retention, molybdenum, isotope

1 INTRODUCTION

Technetium-99m (^{99m}Tc) is one of the most commonly used materials for nuclear medical imaging, accounting for up to 85% of the procedures performed worldwide [2]. Until recently, almost all of the ^{99m}Tc used for medical imaging was produced by processing highly enriched uranium (HEU). Many of the reactors used for this purpose are nearing the end of their useable service life [3]. This has resulted in supply interruptions of $^{99}\text{Mo}/^{99m}\text{Tc}$ due to planned and unplanned shutdowns of the reactors. Due to the relatively short half life of ^{99}Mo , 66hr, it is not possible to stockpile the material in anticipation of a planned supply shortage.

Additionally, in 2012, the American Medical Isotopes Production Act emphasized the need to eliminate the usage of HEU for non-military applications. A significant amount of effort was spent to convert HEU production to low enriched uranium (LEU) production. While others have been developing techniques to manufacture ^{99m}Mo without the need for uranium at all [4, 5]. It is these non-uranium based production methods that would benefit from the use of a higher performance adsorbent to compete competitively with the LEU based method.

2 EXPERIMENTAL SECTION

Two different HPLC style columns were used to evaluate the performance of the different mesoporous aluminas for this study. One column is a 4 x 40 mm constructed of PEEK and the other type of column is 4.6 x 50mm made out of 316 stainless steel. In all cases, an HPLC pump was used to pass the solution through the column into a collection vessel. Flow rates from 0.1 to 10mL/min were employed and the resultant back pressure was monitored.

Sodium molybdate was sourced from Sigma Aldrich and used as a non-radioactive surrogate for ^{99m}Mo . Concentrations of sodium molybdate varied from 0.05 wt% to 30 wt% and the pH was varied between 2.5 and 12. Dilute nitric acid was used to lower the pH and dilute sodium hydroxide was used to raise the pH of the solutions. Solutions were analyzed with an inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine the amount of alumina and molybdenum in the solution before and after being passed through the column. Molybdenum retention tests should be assumed to performed at 0.25 wt% molybdate at a pH of 2.5 unless otherwise noted.

Initial efforts to synthesize mesoporous alumina followed the method provided by Xu et al. [6], 32 g of aluminum isopropoxide (Sigma Aldrich) was added to 1 L of aqueous solution containing 30 g of glucose (Sigma Aldrich). This mixture was stirred for 24 hours and then dried at 80 °C. The solid was then calcined at 600°C for 24 hours to ensure complete removal of the glucose template. The resultant material was crushed and sieved for a final product size of 150 to 300 μm . Brockmann acidic alumina was obtained from Sigma Aldrich to use as baseline mesoporous alumina to compare the performance of our materials against.

The structure of the material was imaged with a scanning transmission electron microscope (STEM) and the porosity and surface area were determined with a Quantachrome Nova Win2.

3 RESULTS AND DISCUSSION

3.1. Mesoporous Aluminas With Saccharide Template

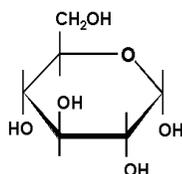
Following the method provided by Xu et al. [6] material was produced that had the porosity as shown in Figure 1.



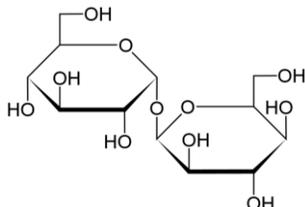
Figure 1: STEM image of mesoporous alumina

In an attempt to increase the pore size, sugars other than glucose were chosen to be the templating material, as shown in Figure 2. The following commercially available sugars were obtained: trehalose and pullulan.

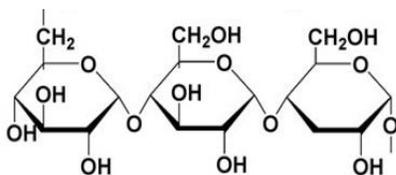
Mesoporous alumina samples were made using the different sugars as templating materials. In addition to changing the template, the amount of the templating material was also adjusted to determine what that effect would be on the structure of the material.



(A) Glucose, a monosaccharide



(B) Trehalose, a disaccharide



(C) Pullulan, a trisaccharide

Figure 2. Different sugars used as templating agents for mesoporous alumina. (A) Glucose, (B) Trehalose, and (C) Pullulan

Each material was produced in a similar manner to that described in the previous section. Samples were then analyzed for pore size distribution and surface area and the results are shown in Figure 3 and Table 1.

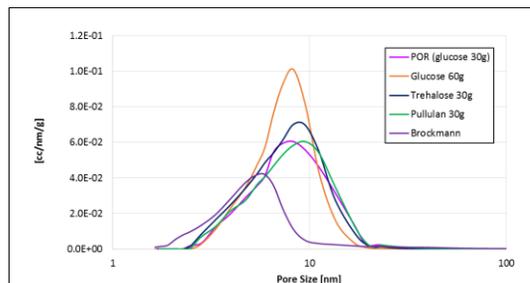


Figure 3. Pore size distribution with different sugars used as templating agents.

There was not a significant difference in the pore size distribution for the different types of saccharides. However, there was a shift from the pore diameter of the Brockmann, approximately 5nm, to the saccharide templated samples, approximately 9nm.

	POR (glucose 30g)	Glucose 60g	Trehalose 30g	Pullulan 30g	Brockmann
Surface Area[m ² /g]	264	312	291	268	154
Pore Volume [cc/g]	0.58	0.61	0.60	0.60	0.25
Pore Diameter DV(d)	8.3	8.3	8.3	9.6	6.0

Table 1. Summary of the pore size and surface area for the materials made with different saccharides for templating.

Surface area of the saccharide templated materials was much higher than that of Brockmann's commercially available alumina. There was no obvious trend between the saccharide type and the surface area.

Figure 4 shows the STEM image of the mesoporous alumina made with 60 g of glucose. Figure 5 shows the STEM image from material templated with 60 g of pullulan. Although the pore structures are similar it does appear that there is a slightly more open structure when the pullulan was used as the templating material.

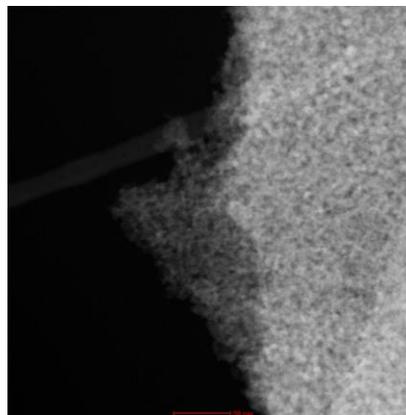


Figure 4. STEM image of mesoporous alumina made with 60 g of glucose as the templating agent.

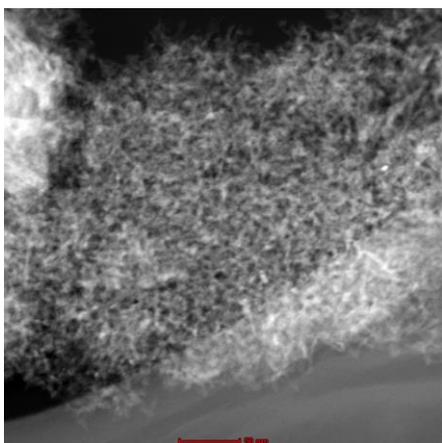


Figure 5. STEM image of mesoporous alumina made with 60 g of pullulan as the templating agent.

Each material was also used to test the molybdenum retention at 30 wt% molybdate solution at a pH of 7. In Figure 6, one can see that increasing the amount of the template material and increasing the size of the template molecule had a positive impact on the amount of molybdenum that could be absorbed on to the material.

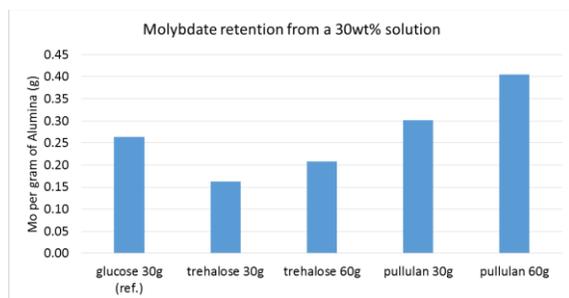


Figure 6. Comparing the molybdate retention performance of mesoporous aluminas made with different templating agents and amounts.

3.2. Mesoporous alumina with ammonium carbonate as the pore former

Sumitani and Izutsu [7] showed that mesoporous aluminas with surface areas greater than 400 m²/g could be produced by using ammonium carbonate as an inorganic pore former combined with an aluminum salt. Our attempt to use ammonium carbonate with aluminum isopropoxide did not produce a mesoporous alumina with a larger surface area than the material produced with saccharides. However, there was an unexpected significant increase in the size of the pores and that resulted in superior molybdate retention.

Figure 7 shows the STEM image of the material made with ammonium carbonate. The structure of this material is different from the aluminas created with saccharides as the template. While many of the pores are of comparable size, there are pores present that are much larger than 10nm. There also appears to be some short fibrils scattered

throughout this material, which are not present in the saccharide templated material.

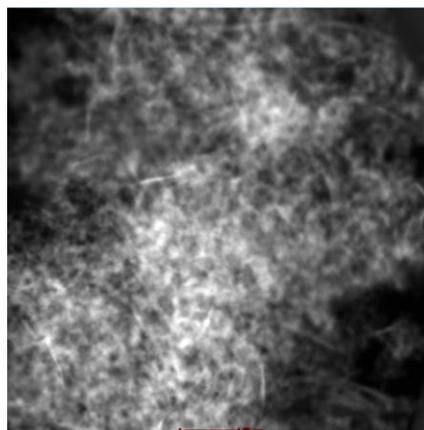


Figure 7. STEM image of mesoporous alumina created with aluminum isopropoxide and ammonium carbonate.

Surface area and pore size were also measured for this new material and is shown in Figure 8. The new method of production results in an increase in pore size up to approximately 16nm.

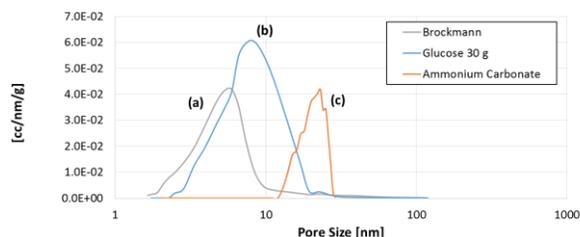


Figure 8. Pore size distribution comparing three different aluminas, (a) Brockmann, (b) Glucose 30 g, and (c) Ammonium Carbonate.

However, as shown in Table 2, there was not significant increase in the surface area of the new material.

	Brockmann	Glucose 30g	Ammonium Carbonate
Pore Diameter (nm)	6.0	8.3	16.6
Surface Area (m ² /g)	81	263	265

Table 2. Comparing the pore size and surface area of the various types of different mesoporous alumina.

Figure 9 shows the molybdate retention performance of this new material against Brockmann across the pH range at 0.25 wt% molybdate concentration. At a pH of 2.5 the new material can hold triple the amount of molybdate as Brockmann.

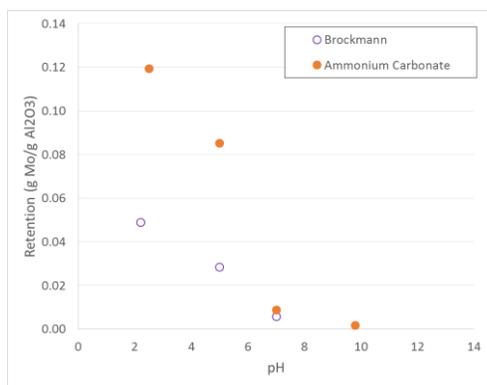


Figure 9. Comparing the molybdenum retention at various pH at 0.25 wt% molybdate concentration of Brockmann and ammonium carbonate aluminas.

Figure 10 summarizes the molybdate retention performance of many of the aluminas that were studied during this investigation. The test conditions were at 30 wt% molybdate and a pH of 7.

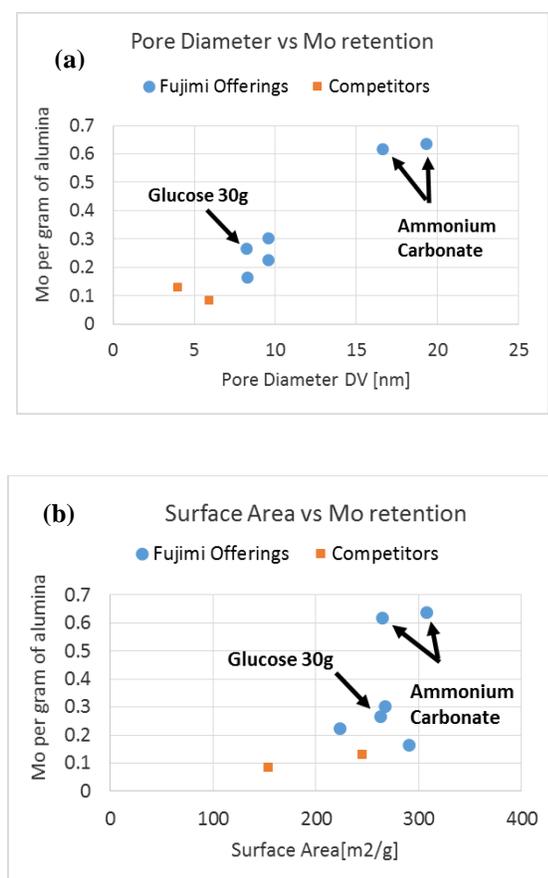


Figure 10. Molybdenum retention as a function of (a) pore diameter and (b) surface area.

4 CONCLUSIONS

In summary, the pore size of mesoporous alumina can be adjusted based on the template or pore former used during the production of the material. Increases in pore size did not necessarily correlate with increases in surface area. Furthermore, it was the pore size and not the surface area that was a better predictor of how well the material would retain molybdate.

5 ACKNOWLEDGEMENTS

Fujimi Incorporated is acknowledged for their support of this research.

6 AUTHOR INFORMATION

Corresponding Author

*Tel.: +1-503-682-7822,

E-mail: bhepburn@fujimico.com

REFERENCES

- [1] U. S. C. Senate., *American Medical Isotopes Production Act of 2012*.
- [2] W. C. Eckelman, "Unparalleled Contribution of Technetium-99m to Medicine over 5 Decades," *J. Am. Coll. Cardiol. Img.*, vol. 2, p. 364, 2009.
- [3] P. Gould, "Medical Isotope Shortage Reaches Crisis Level," *Nature*, vol. 460, p. 312, 2009.
- [4] M. R. A. Pillai, A. Dash and F. F. J. Knapp, "Sustained Availability of Technetium-99m: Possible Paths Forward," *J. Nucl. Med.*, vol. 54, p. 1, 2013.
- [5] M. Lyra, P. Charalambatos, E. Roussou and S. B. L. Fytros, "Alternative Production Methods to Face Global Molybdenum-99 Supply Shortage," *Hell. J. Nucl. Med.*, vol. 14, p. 49, 2011.
- [6] B. Xu, T. Xiao, Z. Yan, X. Sun, J. Sloan, S. Gonzalez-Cortes, F. Alshahrani and M. Green, "Synthesis of Mesoporous Alumina with Highly Thermal Stability Using Glucose Template in Aqueous System," *Micropo. Mesopor. Mat.*, vol. 91, p. 293, 2006.
- [7] S. Sumitani and H. Izutsu, "Method for Manufacturing Mesoporous Alumina". Japan Patent 5802124, 4 September 2015.