

CHEMICAL UPGRADING OF SEDIMENTARY Na-CHABAZITE FROM BOWIE, ARIZONA

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Abstract—Natural zeolites may represent one of the greatest under-utilized resources of the mineral world. Even with their unique character and properties, issues of consistency, homogeneity and purity preclude them from many premium applications. We report a simple method to upgrade mineral sedimentary Na-chabazite from the well known Bowie, Arizona, deposit to near synthetic purity and consistency. During this alkaline-silicate digestion process, initially soft chabazite ore granules gain substantial mechanical strength. This may allow direct employment in adsorption and purification processes without the need for binding and forming. These granules manifest significantly improved adsorption properties, including enhanced water and CO₂ adsorptivity.

Key Words—Adsorption, Arizona, Bowie, Chabazite, Desiccant, Zeolite.

INTRODUCTION

Mineral chabazite is potentially the most polarizing of all known molecular sieve adsorbents, including synthetics. As such, it is a prime candidate for many gas-polishing applications and other uses where certain trace gases are to be collected and concentrated. Chabazite is such a strongly polarizing adsorbent (Maroulis *et al.*, 1987a) that it can cleanly separate oxygen from argon at ambient temperature by preferential interaction with the oxygen molecules (Maroulis *et al.*, 1987b). Due to its strongly polarizing surfaces, chabazite is finding new promise in fields from heavy oil cracking (Kuznicki *et al.*, 2006a) to bulk gas adsorption and new areas such as nano-metal templating and support (Kuznicki *et al.*, 2006b).

While samples of large crystals of essentially pure chabazite are well-known (*e.g.* from Wasson Bluff (Gottardi and Galli, 1985), Nova Scotia, Canada), large, commercially exploitable deposits, like that at Bowie, Arizona (Eyde *et al.*, 1987), invariably have the chabazite co-formed with significant amounts of other natural zeolites such as clinoptilolite and erionite, and other siliceous contaminants. Because of its high internal void volume of 0.47 cc/cc (Breck, 1974) comparable with the best synthetics, and its unusually strong interactions with appropriate adsorbates, pure chabazite, available on an industrial scale, could open many new opportunities for the commercial utilization of natural zeolites.

It is known that raw Bowie Na-chabazite ore can be recrystallized by caustic digestion into Al-rich analogs of the chabazite structure where the Si/Al ratio can approach 1.0 (Kuznicki and Whyte, 1988). The more siliceous

phases of the chabazite ore, clinoptilolite and erionite, selectively dissolve in the alkaline medium, reforming with the chabazite as an apparent structural template. While such semi-synthetic high-Al chabazite analogs manifest the expected increase in cation exchange capacity (to as high as 7.0 meq/g dry weight in the Na form) and demonstrate high selectivity towards heavy metals from solution, especially Pb (Kuznicki and Whyte, 1991), these Al-enriched materials are unstable toward rigorous dehydration, and therefore cannot be sufficiently activated to be employed as selective gas adsorbents.

We have found that Bowie Na-chabazite ore may be reformed and upgraded in an alkaline-silicate medium to a semi-synthetic, purified chabazite with elemental composition resembling the original chabazite components of the ore at Si/Al \approx 3.0 (Chipera and Apps, 2001), if substantial excess soluble silica is present in the reaction/digestion mixture. During this process, essentially all of the clinoptilolite and much of the erionite is dissolved and recrystallized into chabazite, but not at the high Al content found in solely caustic digestion. This new, semi-synthetic, purified and upgraded chabazite is stable towards the rigorous dehydration needed to activate it as an effective adsorbent. This chemical upgrading process represents a simple, cost-effective method that can transform raw chabazite ore to a product with purity comparable to many synthetics, but with the unique characteristics of mineral chabazite. Improving the consistency and performance of chabazite could dramatically increase its penetration into many industrial processes.

MATERIALS AND METHODS

Materials

Sedimentary Na-chabazite from the deposit at Bowie, Arizona, was obtained from GSA Resources of Tucson, Arizona. Chemically upgraded chabazites were prepared

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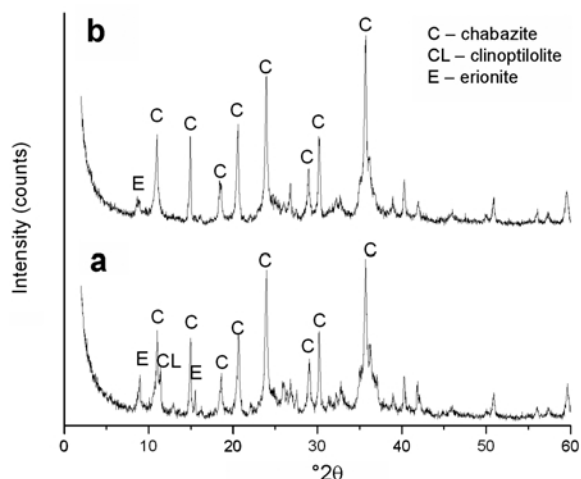


Figure 1. Powder XRD pattern of (a) raw and (b) upgraded Na-chabazite.

by prolonged digestion of the raw ore in an alkaline silicate mixture at temperatures varying from 60°C to 100°C for periods of 4 to 48 h.

A typical sample would be prepared by thoroughly mixing 30 g of Bowie Na-chabazite (as 20–50 mesh particles or –325 mesh fine powder) with 15 g of N-Brand sodium silicate (29% SiO₂, 9% Na₂O) and 3 g of NaOH with 30 g of water. The mixture would be stirred for 1 h, and then aged in a sealed plastic jar at 60°C for 16 h, followed by a static crystallization period of 8 h at 100°C. The resultant material would be thoroughly washed with de-ionized water, and dried in a forced-air oven at 100°C.

Characterization

Phase identification of mineral chabazite and upgraded materials were conducted by powder X-ray diffraction (XRD) analysis using a Rigaku Geigerflex 2173 vertical goniometer equipped with a graphite monochromator for filtration of K β wavelengths.

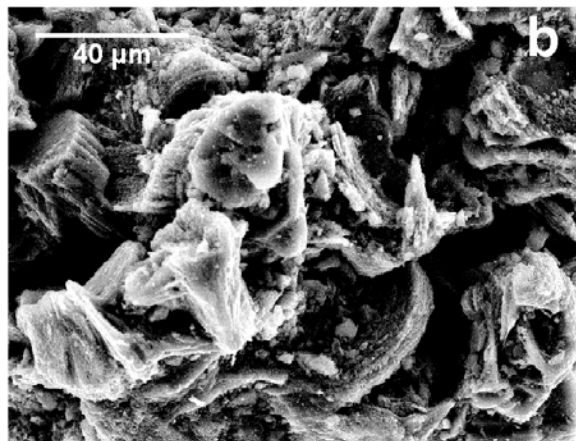
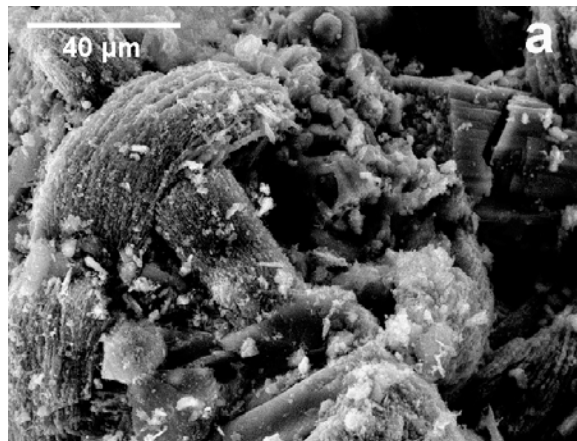


Figure 2. SEM images of (a) raw and (b) upgraded chabazite surfaces.

Table 1. Surface elemental compositions.

Sample	Average atomic conc. (%)		Si/Al ratio
	Si	Al	
Raw chabazite	77.69	22.31	3.48
Upgraded chabazite	75.97	24.03	3.16

Adsorption isotherms were measured using a VTI corporation system utilizing a Rubotherm magnetic suspension microbalance exhibiting an accuracy of $\pm 1 \mu\text{g}$. Samples (100 mg) were typically activated at 400°C for 6 h under vacuum ($<10^{-4}$ bar).

Transmission electron microscopy (TEM) was performed on a Philips Tecnai F20 Twin FEG, equipped with EDX, EFTEM/EELS, annular dark-field detector (ADF), and high-angle tilting capability located at the University of Calgary. The microscope was operated in scanning transmission (STEM) mode.

Surface elemental analysis of mineral and upgraded chabazite samples was conducted by X-ray photoelectron spectroscopy (XPS) utilizing a Kratos AXIS 165 spectrometer, and operated in a wide-scan mode.

Scanning electron microscopy (SEM) was performed on a Hitachi S2700 equipped with an X-ray EDS detector.

RESULTS AND DISCUSSION

As expected for samples from the Bowie, Arizona, deposit (Eyde, 1987), a powder XRD pattern (Figure 1) shows the raw ore to be highly zeolitized with chabazite being the major component. It is also clear from the XRD patterns that clinoptilolite and erionite are present as significant contaminants. Digestion in the alkaline-silicate media as described above completely removes the clinoptilolite and substantially removes the erionite while increasing chabazite content as is also seen in Figure 1. It is believed that in this digestion procedure the

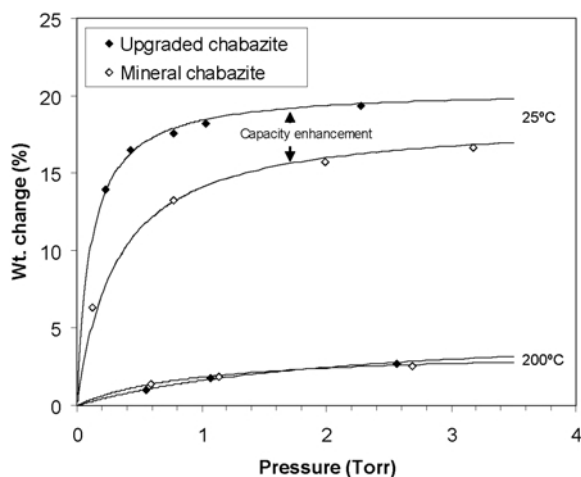


Figure 3. Low-pressure water capacity isotherm for raw and upgraded chabazite.

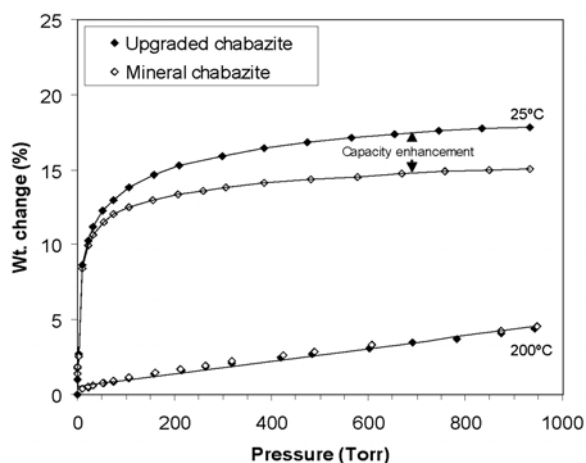


Figure 4. CO₂ isotherm for raw and upgraded chabazite.

more siliceous phases of the chabazite ore, erionite and clinoptilolite (Si/Al \sim 5.0) (Neuhoff and Ruhl, 2006), selectively dissolve, reforming with the chabazite as an apparent structural template at Si/Al \approx 3.0. Table 1 shows that surface Si/Al ratio declines slightly during the recrystallization process, approaching a level expected for pure chabazite (Passaglia and Sheppard, 2001). The Si/Al ratio of the finished product is controlled by the levels of excess caustic and silica in the solution. The excess silica buffers the alkalinity and increases the average silica chain length in the solution phase. Without this buffering effect, the Si/Al ratio of the finished product would be expected to decline dramatically, approaching 1.0 at maximum Al enrichment (Kuznicki and Whyte, 1988).

Analysis by SEM shows increased surface homogeneity of the finished product as the contaminant

phases decline (Figure 2). Grains or granules of the raw ore, which are normally of low mechanical integrity as mined, gain substantial mechanical strength as the material is upgraded. We believe that this results from interlocking crystals as the contaminant phases reform to chabazite from solution.

In the upgrading process, substantial improvements in adsorption properties are observed. As seen in Figure 3, water adsorption capacity, especially at low partial pressures, is substantially improved. Low partial pressure adsorptivity is especially important in deep desiccation processes where an ultra-dry product is needed such as in drying natural gas before pipelining. The CO₂ adsorption behavior, while improved, is qualitatively different from that seen for water, as is evident in Figure 4. CO₂ capacities for the upgraded

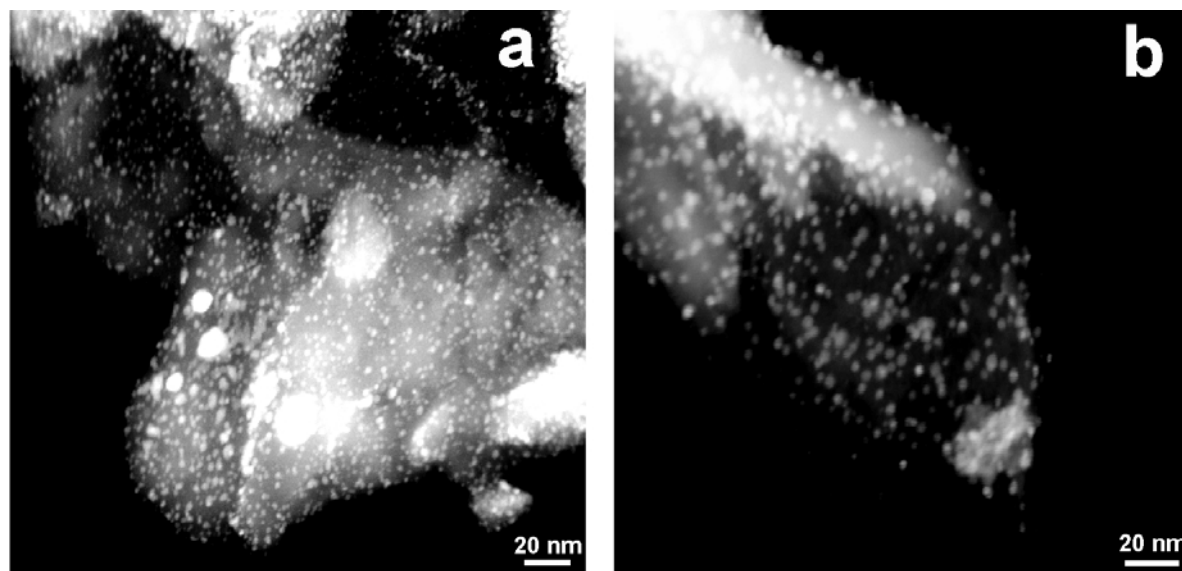


Figure 5. Silver nanoparticulates on (a) raw and (b) upgraded chabazite surfaces.

material increase over the raw ore as the CO₂ partial pressure increases. This could be advantageous in bulk CO₂ removal processes.

A further demonstration of the increased surface homogeneity of the upgraded material can be found in the manner in which nanodots of metals such as silver form on the upgraded material's surface compared to the raw ore (Figure 5). While both materials induce the formation of high concentrations of nanodots of silver in the 3 nm regime on their surfaces upon thermal reduction of silver exchanged cations, the upgraded sample clearly shows a more uniform distribution without large ensembles as seen in the raw ore. The inhomogeneity of the particles on the raw ore is almost undoubtedly due to the inhomogeneity of the surface on which they are formed. Increased surface homogeneity makes the upgraded material a much more attractive catalyst and support than the as-mined raw ore.

CONCLUSIONS

We have shown that chemically upgraded chabazite, stable to dehydration, may be prepared by a simple, caustic-silica digestion of raw Na-chabazite ore. During this digestion, contaminants such as clinoptilolite and erionite are significantly reduced while chabazite concentration increases. These upgraded materials not only show a substantial increase in adsorption properties, they also show an increase in mechanical integrity. Granules of such upgraded materials may well be directly useable in industrial adsorption processes without the cost and performance loss associated with the forming and dilution with a binder generally employed to make adsorbent aggregates. With increased purity and surface homogeneity, chabazite may challenge, or even outperform, synthetic molecular sieves on many fronts.

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