

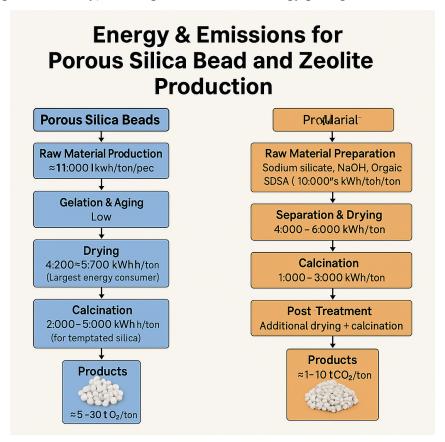
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Energy Requirements and Emissions for Porous Silica Beads and Zeolite Production

# Porous Silica Beads (Chromatography/Catalysis Grade)

Raw Material Production: Industrial porous silica beads are often derived from silica precursors like sodium silicate solution (waterglass) or tetraethyl orthosilicate (TEOS). The choice of precursor significantly affects energy usage. Producing sodium silicate via the high-temperature fusion of sand and soda ash is energy-intensive ( $\approx 5.37~\rm GJ$  per tonne of 48% Na<sub>2</sub>SiO<sub>3</sub> solution). This equates to roughly 1,490 kWh per tonne of solution, or about 11 GJ per tonne of silica *solids* after accounting for water content. By contrast, TEOS (an organosilicate used in sol-gel routes for high-purity or monodisperse silica) carries an even larger energy burden due to upstream silicon production. For example, reducing quartz to silicon metal for TEOS synthesis requires on the order of 13,000 kWh per tonne of Si ( $\approx 46.8~\rm GJ/ton$ ), highlighting the massive energy input for TEOS-based processes . Replacing TEOS with sodium silicate can therefore improve sustainability – studies show that using sodium silicate instead of TEOS in silica synthesis reduces overall environmental impact in large-scale production . If colloidal silica is used, its preparation involves concentrating dilute silica sol; evaporating water to raise silica content can demand  $\approx 11-36~\rm MJ$  per kg of silica (depending on efficiency) , adding  $\approx 3-10~\rm kWh$  of energy per kg before bead formation.



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**Sol-Gel Bead Formation and Aging:** Forming silica beads typically involves sol-gel chemistry (hydrolysis and condensation of silica precursors) and particle shaping (e.g. emulsifying sol into droplets or spray drying). These steps are usually conducted at mild conditions (ambient to ~90 °C) and are not the primary energy drivers compared to later thermal steps. Aging the silica hydrogel (to strengthen structure and control pore texture) may be done at warm temperatures for hours, but again consumes relatively low energy (mostly just heat to maintain e.g. 50–90 °C). In summary, the energy for mixing, reaction, and aging is modest compared to high-temperature drying or calcining steps.

Drying and Thermal Treatment: Drying is typically the single largest energy consumer in silica gel/bead production. The wet silica gel (often ~15–30% solid) must be dried by evaporating water, which requires a substantial heat input. Industrial data show 15-24 MJ per kg of final silica is needed just to dry silica gel or precipitated silica. This corresponds to roughly 4.2-6.7 kWh per kg (4,200-6,700 kWh per tonne) of silica product for the drying step alone. Hot air dryers (e.g. rotary or flash dryers) are commonly used, with inlet air heated to ~300 °C or more by natural gas combustion. The drying energy can vary with initial moisture content; for example, concentrating a silica sol from 10% to 20% solids was estimated at 11 MJ/kg in one case but up to 36 MJ/kg in a worst-case scenario. If the process uses an organic binder or template (as with specialized mesoporous silica), an additional high-temperature calcination step is required to burn out the organics. Calcination of silica (typically 450-600 °C in air for several hours) consumes a similar order of magnitude of energy as drying. In mesoporous silica syntheses, roughly half of the total energy can be in the calcination to remove the template. (For example, if  $\sim 50$  MJ/kg total, ~25 MJ/kg might be calcination.) If no organic template is used (e.g. traditional silica gel), then only a moderate heat treatment (if any) is applied after drying – often just a mild firing or activation at 100-200 °C to remove final traces of moisture. Table 1 (below) summarizes the energy usage by stage for silica bead production.

Optional Post-Processing (Functionalization): Additional processing like surface functionalization or ion-exchange is sometimes done on silica supports (e.g. bonding of organic groups for chromatography media). These steps tend to be low-temperature and have relatively small energy requirements. For instance, grafting organosilanes to silica might be done in solvent at <120 °C, followed by curing and drying at ~100 °C. The energy for such steps is on the order of a few MJ/kg – minor compared to initial drying. In cases where silica is used as a catalyst support that is impregnated with metal salts, an extra drying and a light calcination (to convert the salts to oxides) are needed. Each such cycle adds perhaps 10–20% to the total energy (since another ~15 MJ/kg may be spent in drying/calcining the impregnated material). Overall, post-treatment steps do contribute some energy and emissions, but unless multiple cycles are performed, they are typically small compared to the primary drying (and calcining) energy.

## Cage-Structured Silicates (Zeolites) for Catalysis

Raw Material Preparation: Zeolites are crystalline aluminosilicates, so their precursors include silica and alumina sources plus alkali. Commonly, sodium silicate provides silica, and sodium aluminate (or alumina hydroxide with NaOH) provides alumina,

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in a high-pH synthesis gel. The upstream energy for these precursors is significant. As noted, waterglass production is  $\sim$ 5.4 GJ/ton , and **sodium hydroxide** is even more energy-intensive ( $\sim$ 20.5 GJ per ton NaOH) , largely due to caustic soda being made by electrolysis. In fact, life-cycle analyses have found that producing NaOH (and other chemicals) dominates the energy and carbon footprint for zeolite manufacturing . One study of zeolite A highlighted that NaOH input was a major hotspot, contributing heavily to environmental impact in both batch and continuous processes . If organic structure-directing agents (OSDAs, e.g. tetrapropylammonium bromide for ZSM-5 or other quaternary amines) are used, their production adds further upstream energy and emissions. These organics are typically synthesized from petrochemical feedstocks in multi-step processes, so they carry a non-trivial energy/CO2 footprint . In summary, just assembling the raw materials (silicate, aluminate, NaOH, OSDA, etc.) to feed a zeolite reactor can indirectly account for a large share of the total energy per ton of product.

Hydrothermal Synthesis (Crystallization): Zeolites are produced by hydrothermal crystallization, which involves heating an alkaline gel of the precursors in autoclaves or reactors for extended periods. Industrial crystallization temperatures range from about 90 °C (for zeolite A) up to ~150–200 °C (for many high-silica zeolites), under autogeneous pressure . The synthesis time can be 1–2 hours for some easily crystallized zeolites, or as long as several days for more complex frameworks. This step requires substantial thermal energy to heat and hold the slurry: steam or hot oil heating is typically used, often via natural gasfired boilers. The energy to heat large reactors (and their contents) is nearly independent of yield, so low space-time-yield translates to high energy per unit product. For a conventional batch process, the *crystallization stage* is a major energy consumer (along with drying and calcining). A BASF industry review noted that heating the autoclaves often results in "well above 1 kg CO<sub>2</sub> per kg" of zeolite product from this step alone (depending on gel concentration and cycle time). This implies on the order of >1 MJ of fossil energy per kg, often much more. For example, a long 100 h synthesis at 180 °C will consume hundreds of MJ/kg in heating and stirring. To improve efficiency, manufacturers optimize recipes to increase solid yield and shorten crystallization time. Techniques include seeding, higher initial solids content, aging steps at lower temperature, or using continuous and microwave/ultrasound-assisted reactors. Such measures can drastically cut the per-ton energy. (One pilot continuous process for zeolite A achieved notable energy and emissions reductions versus a traditional batch, mainly by recycling mother liquor and reducing waste heat-up of large batches .) Still, under typical conditions, the hydrothermal synthesis contributes a sizable fraction of the total energy.

**Separation and Drying:** Once crystallization is complete, the zeolite crystals are separated (e.g. by filtration) from the mother liquor and then washed. The wet filter cake contains a lot of water – for instance, it may be 50–70% water by weight. **Drying this zeolite cake is another major energy stage**, analogous to silica gel drying. Industrially, zeolite powders are often dried in **spin-flash dryers or spray dryers** with inlet air of 300–500 °C. The water removal demand is similar: on the order of **15–24 MJ per kg** of dried zeolite if a large amount of water must be evaporated (several kg H<sub>2</sub>O per kg product). In practice, energy-conscious plants may do partial mechanical dewatering (e.g. pressing) to reduce moisture before thermal drying. Even so, thousands of kWh per ton are expended in drying.

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For example, using waste heat integration (using hot exhaust air to preheat incoming air) can trim some energy, but drying remains one of the "major energy consumers" in zeolite production. Notably, if the synthesis slurry is very dilute, the drying energy skyrockets – so modern processes try to crystallize at higher solids to avoid "drying all that excess water." In summary, drying 1 ton of zeolite product can require on the order of 4,000–6,000 kWh of heat input (comparable to silica gel drying) in conventional setups.

Calcination (Template Removal): Many zeolites intended for catalysis are made with organic templates (OSDAs) or require activation steps. Calcination is a hightemperature step (typically 500-650 °C in air) used to burn off organic species occluded in the zeolite pores. This step is crucial for materials like ZSM-5, Beta, Y, etc., to open their pore structure or convert to the H-form (after ammonium exchange). Calcination is normally done in large ovens, rotary kilns (residence  $\sim 0.5-2$  h), or belt furnaces ( $\sim 4-6$  h). The energy required depends on furnace efficiency, batch size, and the exothermicity of burning the organics. Often, burning the template releases heat, but not enough to self-sustain the 500 °C temperature, so external heating is needed throughout. This calcining stage is the third major energy consumer (with crystallization and drying) identified in zeolite manufacturing . While exact values vary, it's on the order of magnitude of the drying energy. For example, in lab-scale mesoporous silica, the energy to calcine (remove surfactant) was roughly equal to the energy to dry the material. In industrial zeolite plants, calcination might add several GJ per ton. One older reference for fumed silica (which is produced by high-temp oxidation of SiCl<sub>4</sub>) notes 15–18 MJ/kg for that process, which is in a similar ballpark. New technologies are being explored to reduce calcination energy: one idea is flash calcination, where a wet zeolite slurry is directly atomized into a hot stream, so that droplets dry and combust their template in milliseconds. Such combined steps could eliminate a lengthy oven bake. In conventional practice, however, calcination remains energy-heavy and also creates emissions (the off-gas requires scrubbing for HCl, NO<sub>x</sub>, etc., if halide templates or nitrates were present).

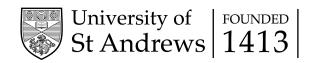
Post-Synthesis Ion Exchange and Finishing: After drying/calcination, additional treatments may be applied to zeolites, especially for catalysts. A common step is ion exchange – e.g. converting a Na-form zeolite to the NH<sub>4</sub>-form (then H-form) or exchanging metal cations (Cu<sup>2+</sup>, Fe<sup>2+</sup>, etc.) into the structure. Ion exchange is done by slurrying the zeolite in a salt solution at ~60–100 °C for a few hours. The energy for heating and stirring these exchangers is relatively low (perhaps a few MJ per kg). However, after ion exchange, the material must be filtered, washed, and dried again. Thus, each ion exchange cycle introduces another drying step (and sometimes a calcination). For example, producing an H-zeolite usually entails drying the NH<sub>4</sub>-zeolite and then calcining it to drive off ammonia. This secondary calcination is at similar temperature (~500 °C) but often shorter duration (since the zeolite is already mostly dry and only NH3 needs removal). Still, it can add a significant energy increment – on the order of hundreds of kWh per ton extra. If a metal doping is done via impregnation, likewise a drying and maybe a moderate calcine (to decompose precursors to oxide) is done. In sum, each additional post-synthesis cycle (ion exchange + drying + calcine) can add perhaps 10–30% more to the total energy required per ton. Industrial catalysts may undergo one or two such cycles, so it's a noticeable but not primary contributor. Table 1 below gives an approximate breakdown.

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Table 1 – Approximate Energy Usage by Production Stage (in kWh per ton product, for industrial-scale processes):

Stage	Porous Silica Beads (SiO2)	Zeolites (Aluminosilicate)
Precursor Production	Sodium silicate route: ~1,500 kWh/ton (5.4 GJ/ton). TEOS route: substantially higher (e.g. silicon reduction ~13,000 kWh/ton Si), equating to many thousands of kWh per ton SiO <sub>2</sub> .	Silica & alumina sources: ~1,500 kWh/ton for Na <sub>2</sub> SiO <sub>3</sub> ; NaOH: ~5,700 kWh/ton (20.5 GJ/ton) (allocated per ton NaOH). OSDA organics add further upstream energy (varies by chemical)
Mixing/Gelation (Synthesis)	Typically low – sol-gel reactions at <100 °C. Minor energy for stirring and maybe heating (~10s of kWh/ton).	Hydrothermal heating 120–200 °C for hours-days: major heat input. Often on the order of <b>0.5–1.5 GJ/ton</b> (140–420 kWh/ton) <i>per day</i> of synthesis. Optimized processes cut time to reduce this. (Crystallization can emit >1 kg CO <sub>2</sub> /kg, indicating high energy use).
Drying	<b>4,200–6,700 kWh/ton</b> (15–24 MJ/kg) to remove water . Hot air ~300 °C; usually the largest energy stage.	Similar magnitude: on the order of 4,000–6,000 kWh/ton if cake is ~50% water. Drying is one of the major energy loads (e.g. spray drying at 300–500 °C). Heat recovery and higher solids content can improve this slightly.
Calcination	If no organics (e.g. plain silica gel): negligible or low (perhaps 100–200 kWh for final 200 °C activation). If <b>template or surfactant used:</b> comparable to drying energy (often ~50% of total process energy) . E.g. 2,000–5,000 kWh/ton range typical for calcining mesoporous silica.	If OSDA/template present: high-temperature calcination 500–650 °C for 1–6 h. This is a major energy stage (order of a few GJ/ton, i.e. ~1,000–3,000+ kWh/ton). Longer or multi-step calcinations (with controlled ramping, etc.) push this higher. (Zeolite A, made without organics, requires no such calcination.)
Post-treatment (Ion Exchange, etc.)	Generally minor. An exchange at 60–80 °C plus an extra drying step might add on the order of 200–500 kWh/ton. Surface functionalizations (curing at ~100 °C) also in the low hundreds of kWh/ton at most.	Additional ion exchange cycles and subsequent drying/calcining can add ~10–20% to total energy per cycle. For instance, an ammonium exchange + recalcination to H-form might consume another ~1,000 kWh/ton combined. Doping steps similarly add some energy,



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Stage

Porous Silica Beads (SiO<sub>2</sub>)

**Zeolites (Aluminosilicate)** 

though often less than the primary calcination.

*Note:* The figures above are broad estimates. Actual values vary with process specifics (concentration of reactants, dryer efficiency, heat recovery, etc.). Nonetheless, it is clear that **drying and calcination dominate the energy profile** for both silica and zeolites, while raw material production and crystallization contribute significantly to zeolites' energy use.

# CO<sub>2</sub> Emissions per Tonne of Product

The energy-intensive nature of these processes translates to substantial **carbon dioxide emissions**, especially if fossil fuels provide the heat or if energy-intensive feedstocks are used. In addition, some chemical reactions (like soda ash use) release CO<sub>2</sub> directly. Below are typical CO<sub>2</sub> emission figures reported for porous silica and zeolite production:

- Silica Gel/Precipitated Silica: The cradle-to-gate carbon footprint is on the order of a few tonnes of CO<sub>2</sub> per tonne of silica. A recent "verified" industry estimate for precipitated silica (food additive grade E551) is about 5.0 kg CO<sub>2</sub> per kg of silica. This ~5 tCO<sub>2</sub>/ton result includes all production energy and inputs at an average factory. It aligns with the fact that drying uses large amounts of natural gas (which emits ~56 kg CO<sub>2</sub> per GJ) and that sodium carbonate use yields ~0.15 kg of chemical CO<sub>2</sub> per kg silica (from the calcination of Na<sub>2</sub>CO<sub>3</sub>). By comparison, advanced mesoporous silica made via organic-templating can have a much higher CO<sub>2</sub> footprint due to additional organic reagents and calcination: one LCA found 31 ± 18 kg CO<sub>2</sub> per kg (i.e. ~31 tCO<sub>2</sub>/ton) for mesoporous material in a scaled-up scenario . (Lab-scale processes were even higher at ~54 kg/kg, showing the penalty of inefficient small-scale operations .) Thus, "typical" silica gel lies at the lower end (~5 tCO<sub>2</sub>/ton), while specialty high-porosity silicas with surfactants can emit tens of tonnes CO<sub>2</sub> per tonne product if not optimized.
- Zeolites: Conventional zeolite manufacturing also carries a significant CO<sub>2</sub> footprint, though generally a bit lower than the extreme case of surfactant-templated silica. A large portion of emissions comes from energy use (fuel combustion for heat and electricity generation). For example, heating an autoclave with natural gas and drying with gas-fired air will emit CO<sub>2</sub> on site. As noted, just the crystallization step can easily exceed 1 kg CO<sub>2</sub> per kg zeolite, meaning >1 tCO<sub>2</sub>/ton from that step alone if using fossil energy. The total cradle-to-gate GHG emissions for a base zeolite (like Zeolite A or X) are typically in the low single-digit tonnes CO<sub>2</sub> per tonne. (In a 1990s European Zeolite A study, the overall energy was 22.4 GJ/ton; if one assumes roughly half electricity, half natural gas, the associated emissions would be on the order of 2–3 tCO<sub>2</sub>/ton of zeolite.) Modern LCAs corroborate this scale: one analysis of a Cu-exchanged Y zeolite showed ~15 kg CO<sub>2</sub> eq for 0.3 kg of product (which suggests around 50 kg CO<sub>2</sub> per kg, but that scenario included use-phase CO<sub>2</sub> capture, so it's not straightforward). A clearer indication comes from industry:



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"Conventional zeolite processes are highly energy-intensive and come with a significant CO2 footprint." Improvements like continuous processing, waste heat reuse, and switching to renewable electricity can cut this footprint appreciably. For instance, the continuous pilot for zeolite A reduced overall impacts relative to a batch baseline, but the production of NaOH remained a big contributor to GHG emissions. In regions with cleaner energy grids (or if electrification of heating is combined with renewable power), the CO2 per ton can be brought down. One case study claims that using hydroelectric power for a fumed silica process could achieve ~1 kg CO2 per kg product, illustrating the importance of energy source. Generally, one can expect 1—5 tCO2 per ton for many synthetic zeolites under typical conditions, with the lower end achievable in efficient plants with greener energy, and higher values if lots of organic template or high fuel use is involved.

Table 2 provides a summary of representative CO<sub>2</sub> emission intensities for silica and zeolite products (per tonne):

Table 2 – Typical CO<sub>2</sub> Emissions per Tonne of Product

Product	Approx. CO <sub>2</sub> Emissions (kg CO <sub>2</sub> per ton product)	Notes/Source
Silica gel / precipitated silica (traditional)	$\sim$ 5 × 10 <sup>3</sup> kg CO <sub>2</sub> /ton (i.e. $\sim$ 5 tCO <sub>2</sub> /ton)	Representative industry footprint . High emissions due to drying energy and $CO_2$ from soda ash usage.
Mesoporous silica (templated)	$\sim$ 3.1 × 10 <sup>4</sup> kg CO <sub>2</sub> /ton (up to 30+ tCO <sub>2</sub> /ton)	LCA for large-scale synthesis with TEOS + surfactant . (Much higher if small-scale or inefficient).
Zeolite (conventional, e.g. Zeolite A/X)	$\sim 1 \times 10^{3}$ to $3 \times 10^{3}$ kg CO <sub>2</sub> /ton (1–3 tCO <sub>2</sub> /ton)	Estimated range for common zeolites.  Crystallization often >1 kg CO <sub>2</sub> /kg product just from fuel use . Total includes drying & calcining; exact value depends on energy sources (could be lower with green energy).
Zeolite with organic template (e.g. ZSM-5, Beta)	$2 \times 10^{3}$ to $1 \times 10^{4}$ kg CO <sub>2</sub> /ton (2–10 tCO <sub>2</sub> /ton)	Higher silica zeolites require template burn-off and typically more energy. If made in inefficient batch mode with organic SDA, emissions can reach the upper end. (No direct single-source value; extrapolated from energy use and analogies to mesoporous silica).

(Note: CO<sub>2</sub> figures above are rough and assume conventional energy mixes. Actual emissions can be lower with decarbonized energy or higher if processes are not heat-integrated. The data illustrates the magnitude rather than precise numbers.)

## **References and Recent Developments**

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Recent (post-2015) sources consistently highlight the energy and CO<sub>2</sub> intensity of porous material manufacturing, spurring research into greener methods. For silica, attention is on using bio-derived silicas or improving drying efficiency. For zeolites, researchers and industry are pursuing: process intensification (e.g. continuous flow reactors, microwave heating to speed crystallization), solid-state or solvent-free syntheses (which avoid boiling large water masses), and template-free routes or template recycling to cut calcination needs. BASF's perspective suggests even merging drying and calcination in one step to save energy. These efforts aim to reduce the cradle-to-gate energy per ton – moving from tens of GJ down into single-digit GJ if possible – and to lower CO<sub>2</sub> emissions in line with climate goals. In summary, producing porous silica and zeolites at industrial scale requires on the order of 20–40 GJ/ton (5,500–11,000 kWh/ton) of material in well-optimized settings, and emits a few tonnes of CO<sub>2</sub> per ton product under typical conditions. Both energy use and emissions are dominated by thermal steps (drying, calcining) and the production of chemical precursors, so innovations targeting those areas are key to more sustainable chromatography and catalyst materials in the future.

### **Sources:**

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- Roes et al. (2010) nanocomposites LCA citing drying energy for silica (15–24 MJ/kg)
- Fawer et al. (1999) life-cycle inventory data for sodium silicate and NaOH production
- Fawer et al. (1998) Zeolite A LCI (22,400 MJ/ton)
- Grimaldi et al. (2021) Continuous vs batch Zeolite A LCA (hotspots: NaOH, etc.)
- Parvulescu & Maurer (BASF) (2022) Zeolite manufacturing sustainability (energy-intensive steps and CO<sub>2</sub> footprint)
- Green Chemistry (2024) LCA of mesoporous silicas (high energy and GHG impact of TEOS + template, ~31 kg CO<sub>2</sub>/kg)
- CarbonCloud database Silica (E551) carbon footprint ~5 kgCO<sub>2</sub>/kg.
- Pyrogenesis Inc. (2021) claim of ~1 kgCO<sub>2</sub>/kg fumed silica with hydroelectric power.
- Additional data embedded in text from references as cited above.