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Inverse Design of Porous Materials:

A Diffusion Model Approach

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Electronic Supplementary Information

Section S1. Details on ZeoDiff

Section S1-1. Data preparation

All three channels (energy/silicon/oxygen) comprising zeolite grids were normalized within the range of [-1, 1] and used as an input for the model. For energy grids, energy values were clipped to [-4000 K, 5000 K] before the normalization, as potential energy goes infinitely high for the region overlapped at the atom positions. A lower bound of the energy was set to be -4000 K since there was no grid point whose value was lower than -4000 K.

Data augmentation was implemented to impose translational and rotational invariance to the model. For rotation, one random axis (from [x, y, z]) was selected and the grids were rotated by 90 ° with respect to selected axis. For translation, one random displacement was selected (from [0~31, 0~31, 0~31]) and the grids were shifted accordingly with considering periodic boundary conditions. For each structure consisting the training dataset, two additional structures (one rotationally augmented structure and the other translationally augmented structure) were considered for the training.

Section S1-2. ZeoDiff architecture

ZeoDiff incorporates a U-Net as a model architecture, as shown in Figure S1. U-Net is one of the most widely used architecture in the field of image processing. In the context of ZeoDiff, U-Net components are slightly modified to handle three dimensional data (e.g. 2D Convolutional layer → 3D Convolutional layer). It is also noteworthy that, the convolutional layers of U-Net in ZeoDiff employ circular padding option to account for periodic boundary condition of zeolite grids.

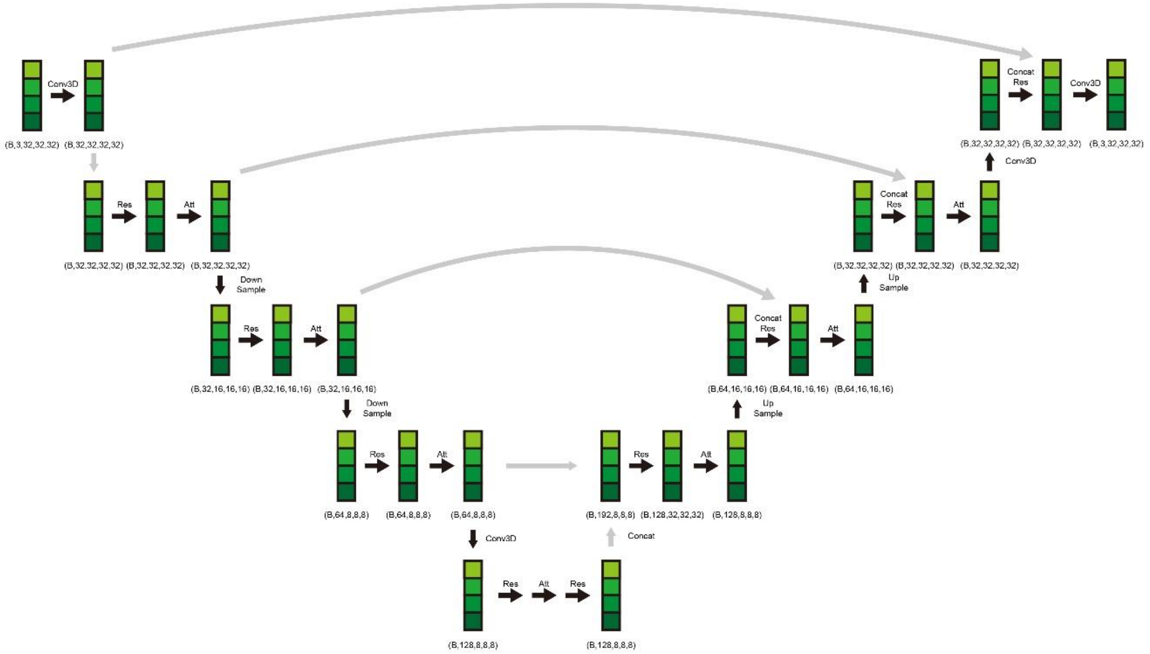


Figure S1. 3D U-Net architecture used in ZeoDiff. Original 2D U-Net was modified to handle zeolite grids (3D data with 3 channels). 'B', 'Res', 'Att' stand for batch size, resnet block and attention block, respectively. Number of trainable parameter of the model was 5.6 million.

Table S1. Hyperparameters used for ZeoDiff training

Hyperparameter		Value
Diffusion time steps		1500
Variance scheduling	β_1	0.0001
	β_T	0.02
	schedule type	linear
Batch size		128
Convolution kernel size		3 x 3 x 3
Learning rate		0.0001
Loss type		huber
Max epochs		2000
Early stopping criteria		50
Exponential Moving Average (EMA)		True
EMA ratio		0.9999

Section S1-4. Zeolite generation workflow

The overall workflow for zeolite generation is illustrated in Figure S2. As demonstrated in previous sections, ZeoDiff is used to generate realistic zeolite grids. Afterwards, an additional lattice regressor is utilized to predict the lattice parameters for the generated grids. The lattice regressor share the same U-Net architecture as ZeoDiff (Figure S1), but the only difference is that its output layer is designed to predict lattice parameters (l_x, l_y, and l_z). Finally, a post-processing is implemented (which will be discussed in more detail in the next section) to obtain perfect zeolite structures.

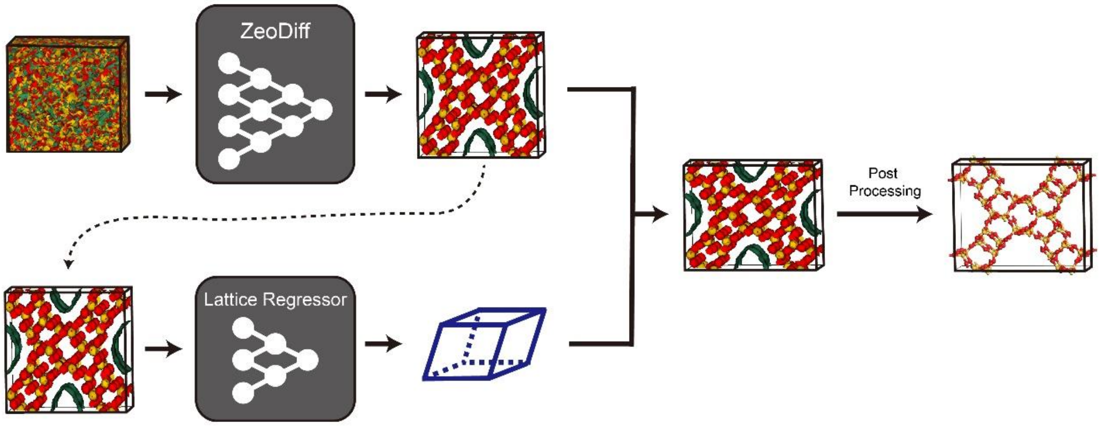


Figure S2. Overall workflow for zeolite generation. ZeoDiff and lattice regressor are used to generate zeolite grids with lattice parameters. Post-processing is implemented to obtain perfect zeolite structures from zeolite grids.

Section S2. Details on Post-Processing Procedure

The post-processing procedure is depicted in Figure 2 of the main text. In this section, we will discuss each step of the post-processing procedure in more detail.

Assigning Atom Coordinates

A volume-based method was used to assign atomic positions from the generated zeolite grids. Firstly, Gaussian volumes were detected using a flood-fill algorithm with a volume detection limit of 0.7. (Neighboring regions with Gaussian value larger than 0.7 was defined as Gaussian volumes.) After then, the atomic position was determined by calculating the weighted mean of the grid coordinates and their corresponding Gaussian values. This approach allowed for an accurate estimation of the atomic positions from noisy outputs of ZeoDiff.

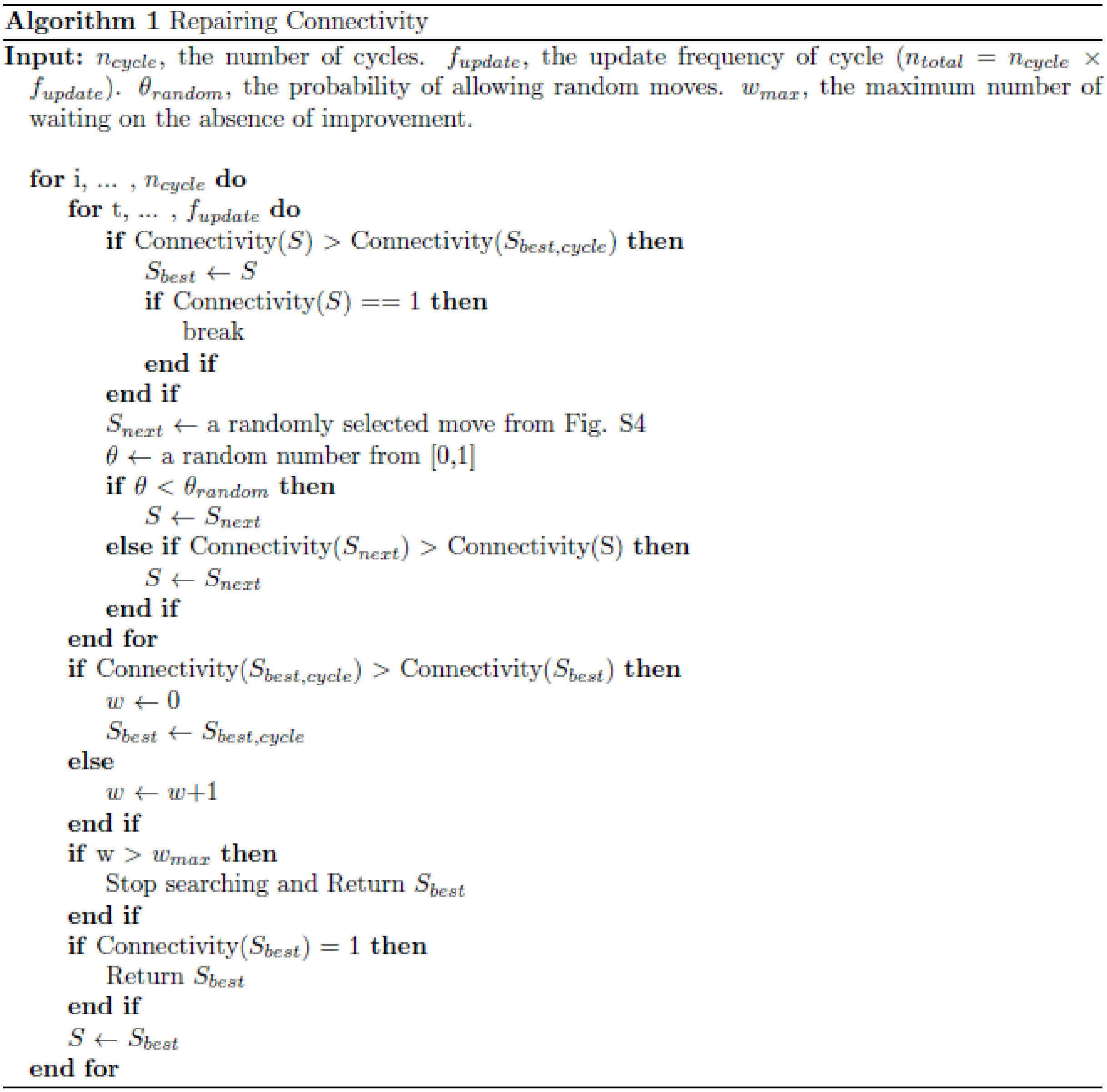
Determining Bond Connectivity

In the case of perfect zeolite structures, each silicon atom is bonded with four different oxygen atoms and each oxygen atom is bonded with two different silicon atoms. Therefore, in this work, the connectivity of the zeolite structure was defined as the ratio of atoms that possess the correct number of bonds (silicon: 4 bonds, oxygen: 2 bonds). To assess the bond connectivity of the generated structures, Si-O bond calculations were performed using a suitable bond threshold of 2.5 Å.

Repairing Bond Connectivity

The algorithm demonstrated in Table S2 was used for the bond restoration. Each move within the algorithm is illustrated in Figure S3.

Table S2. Connectivity Repair Algorithm.



Algorithm 1 Repairing Connectivity

Input: n_{cycle}, the number of cycles. f_{update}, the update frequency of cycle ($n_{total} = n_{cycle} \times f_{update}$). θ_{random}, the probability of allowing random moves. w_{max}, the maximum number of waiting on the absence of improvement.

```
for i, ... , $n_{cycle}$ do
    for t, ... , $f_{update}$ do
        if Connectivity($S$) > Connectivity($S_{best,cycle}$) then
            $S_{best} \leftarrow S$
            if Connectivity($S$) == 1 then
                break
            end if
        end if
        $S_{next} \leftarrow$ a randomly selected move from Fig. S4
        $\theta \leftarrow$ a random number from [0,1]
        if $\theta < \theta_{random}$ then
            $S \leftarrow S_{next}$
        else if Connectivity($S_{next}$) > Connectivity(S) then
            $S \leftarrow S_{next}$
        end if
    end for
    if Connectivity($S_{best,cycle}$) > Connectivity($S_{best}$) then
        $w \leftarrow 0$
        $S_{best} \leftarrow S_{best,cycle}$
    else
        $w \leftarrow w+1$
    end if
    if w > $w_{max}$ then
        Stop searching and Return $S_{best}$
    end if
    if Connectivity($S_{best}$) = 1 then
        Return $S_{best}$
    end if
    $S \leftarrow S_{best}$
end for
```

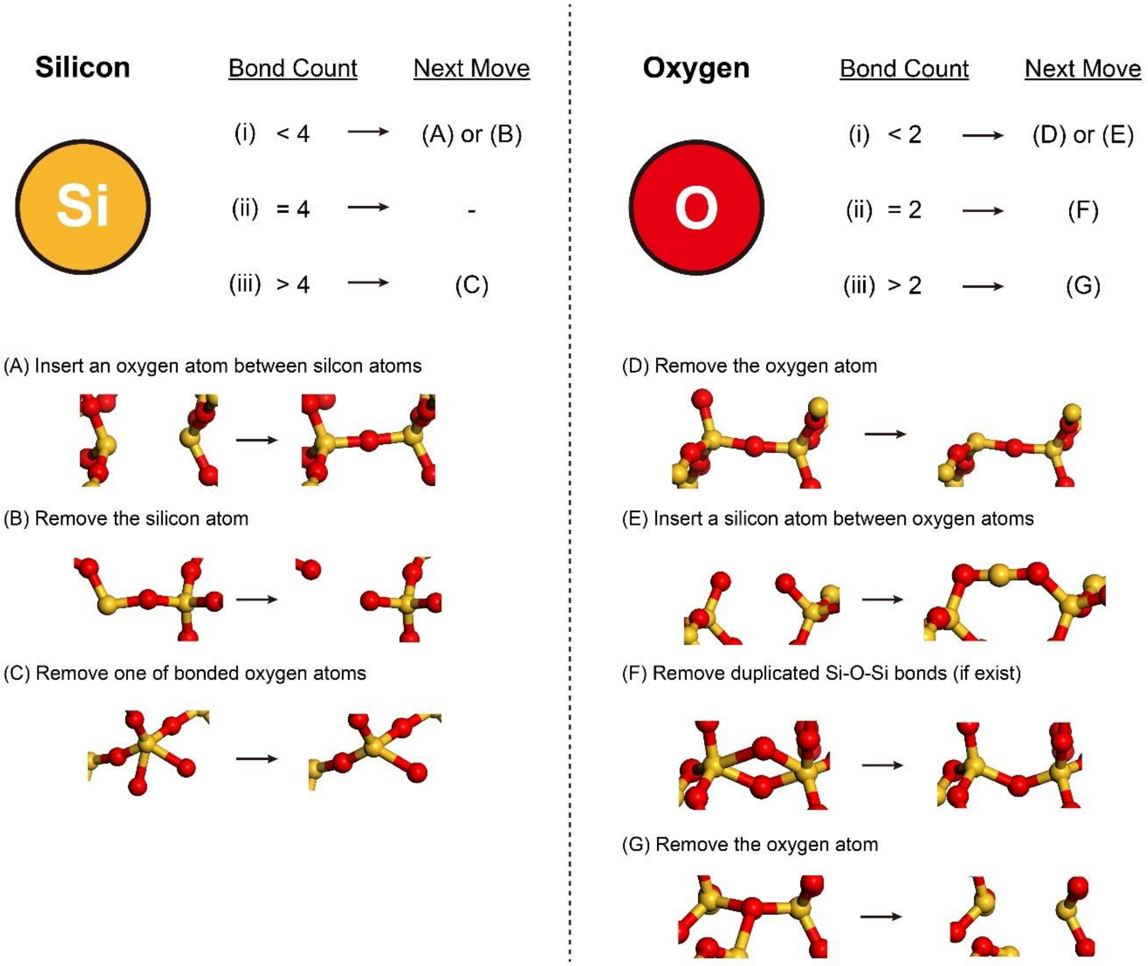
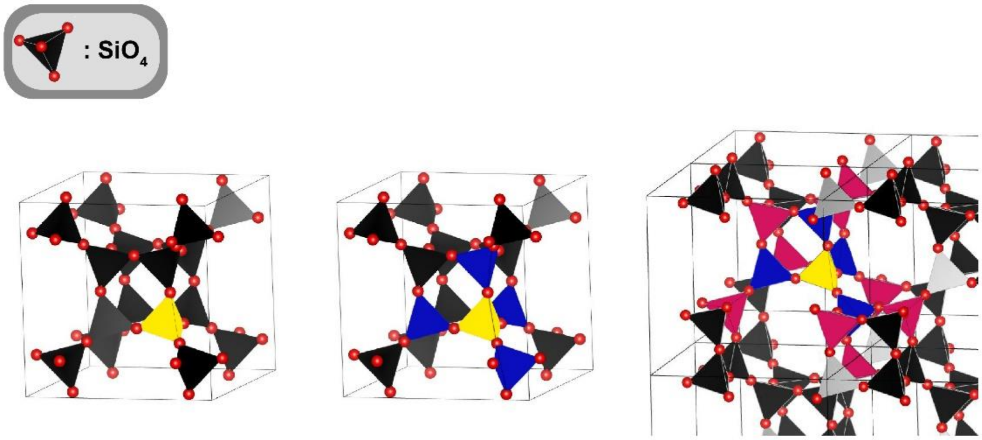


Figure S3. Possible moves for the connectivity repair algorithm. Possible moves for the connectivity repair algorithm explained in Table S2. (A) For an unsaturated silicon atom, a new oxygen atom is inserted at the midpoint with another unsaturated silicon atom. (B, D, G) Atoms with incorrect bond count are deleted. (C) For a silicon atom with more than 4 bonds, one of its bonded oxygen atoms is removed. (E) For an unsaturated oxygen atom, a new silicon atom is inserted at the midpoint with another unsaturated oxygen atom. (F) If Si-O-Si bond is duplicated between same silicon atoms, one of them is removed.

Counting the Number of Unique T atoms

Unique T atom is defined as a Si atom within a pure silica zeolite that exhibits distinct topology compared to others. It is worth noting that the majority of the experimentally synthesized zeolites and all of the hypothetical zeolites in PCOD database possess fewer than 10 unique T atoms.[1] The number of unique T atoms of given structures was counted by comparing the coordination sequence of each Si atom (Figure S4). The coordination sequence is defined as the number of neighboring Si atom it is directly bonded to, arranged in increasing order of distance. If two Si atoms are unique T atoms, then those two Si atoms exhibit different coordination sequences. In this work, the coordination sequence was considered up to the 10th nearest neighbors. (The coordination sequence was also used to check the identity between the structures.)



Coordination Sequence of Zeolite ACO

	N_0	N_1	N_2	N_3	N_4	N_5	N_6	N_7	N_8	N_9	N_{10}
CS	1	4	9	19	35	52	72	100	131	163	201

Figure S4. Coordination Sequence. The coordination sequence for each silicon (Si) atom refers to the number of neighboring silicon atoms it is directly bonded to, arranged in increasing order of distance. In other words, it describes the number of silicon atoms surrounding a particular Si atom at different distances.

Structure Relaxation

Structures generated from the workflow were relaxed by using sequential optimization steps. In the first step, as a pre-relaxation, structures were optimized using Forcite module of the Material Studio[2] using UFF (Universal Force Field[3]) with the van der Waals cutoff radius of 12.5 Å. Smart minimizer algorithm was used with the moderate accuracy option. After then, structures were optimized again with the SLC force field[4] using GULP software[5]. Pre-relaxation step was required to overcome the distance sensitivity of the SLC potential.

Section S3. Details on Unconditional Generation

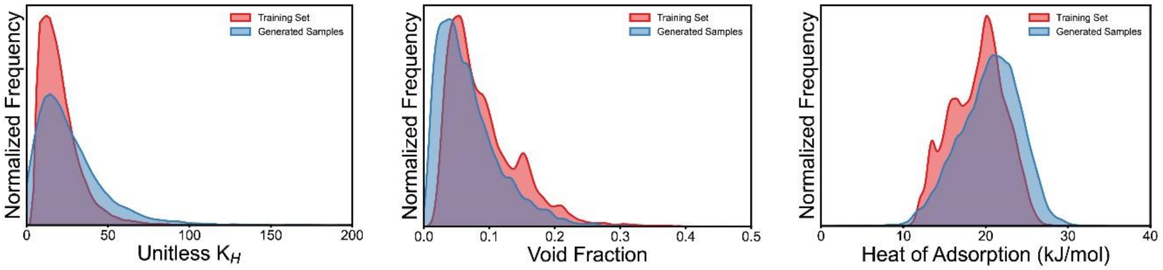


Figure S5. Distribution of chemical properties of unconditionally generated samples. The distribution of the Henry coefficient, void fraction and heat of adsorption of unconditionally generated 10,000 samples with comparison of training dataset.

Thermodynamic Stability

Thermodynamic stability of the generated zeolite structures were examined using the metric proposed by Deem and coworkers[1] which assessed the thermodynamic stability of the structure by calculating the relative energy to α-quartz (the most common polymorph of the silica). The structures were optimized using the SLC force field[4], and classified as 'thermodynamically accessible' or 'thermodynamically inaccessible' depending on whether the relative energy is smaller than 30 kJ/mol Si or not.

We applied the same metric to the structures generated in an unconditional manner to assess the thermodynamic stability of the generated samples. 1D and 2D structures were excluded as their optimization process was not simulated properly with SLC force field, and the number of the samples was 146. As illustrated in Figure S6, 91.1 % of the samples exhibited the relative energy lower than 30 kJ/mol Si, which satisfied thermodynamic stability metric of Deem. One interpretation of this lager proportion of stable structures is that, as we apply additional post-processing procedure (Figure 2), those structure which energetically unstable would be excluded in advance.

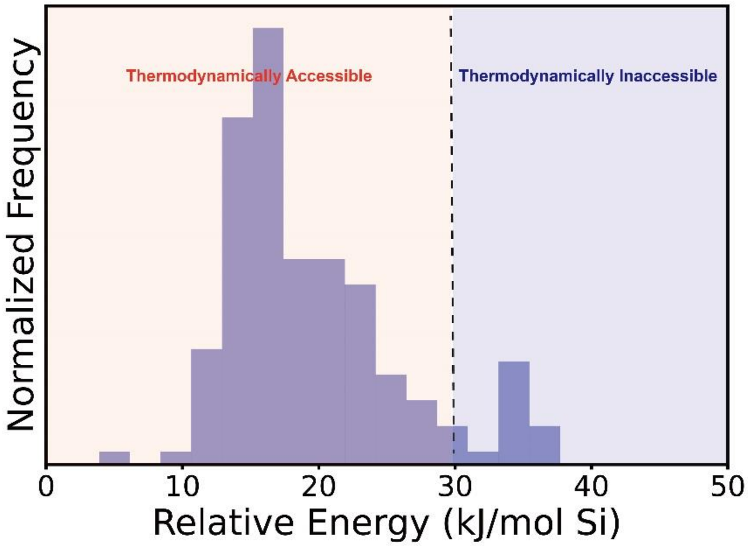


Figure S6. Relative energy of the unconditionally generated structure to α-quartz. Structures with relative energy lower than 30 kJ/mol Si were deemed to be thermodynamically accessible.

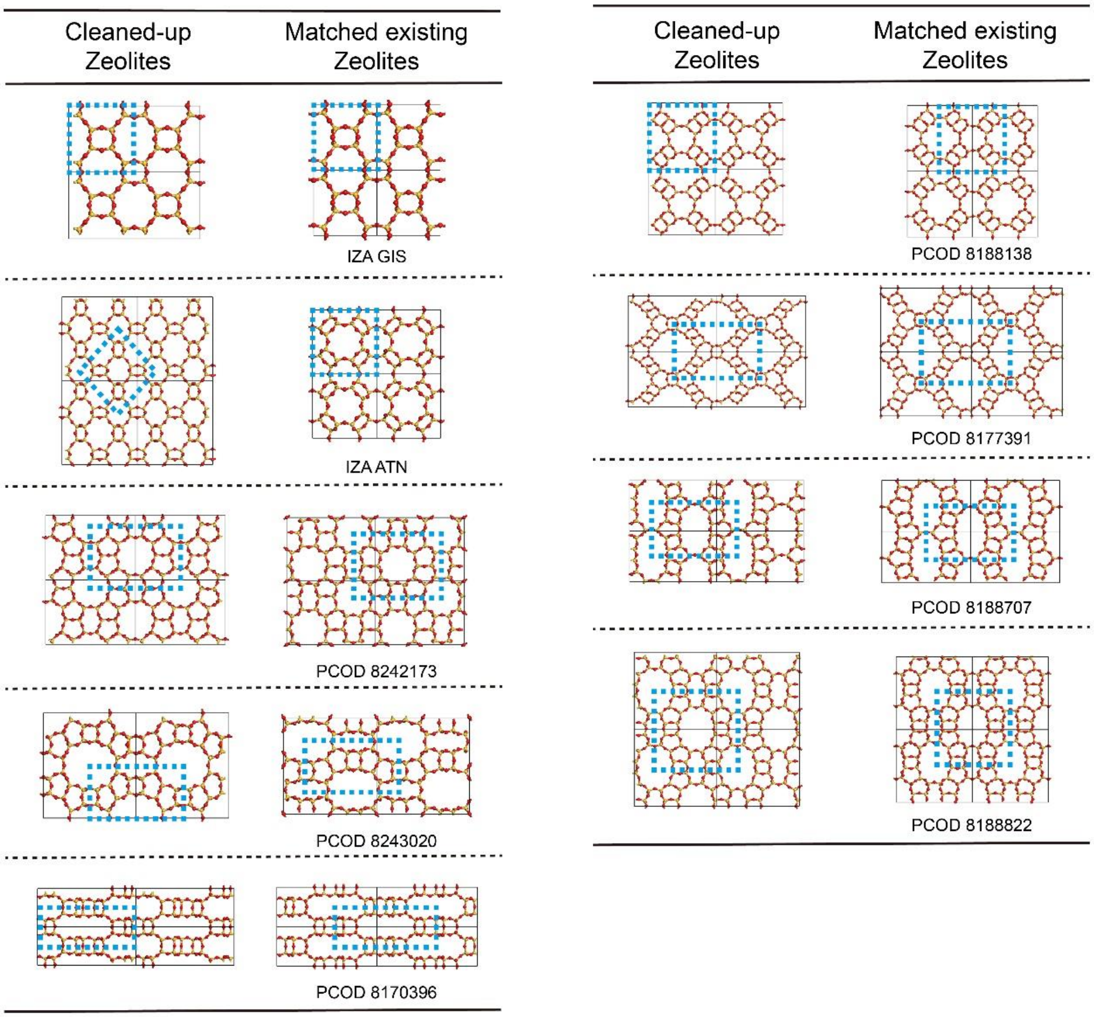


Figure S7. Zeolites generated using ZeoDiff and their corresponding structures in training dataset (IZA/PCOD). Dashed blue line indicates the matching portion within the structures.

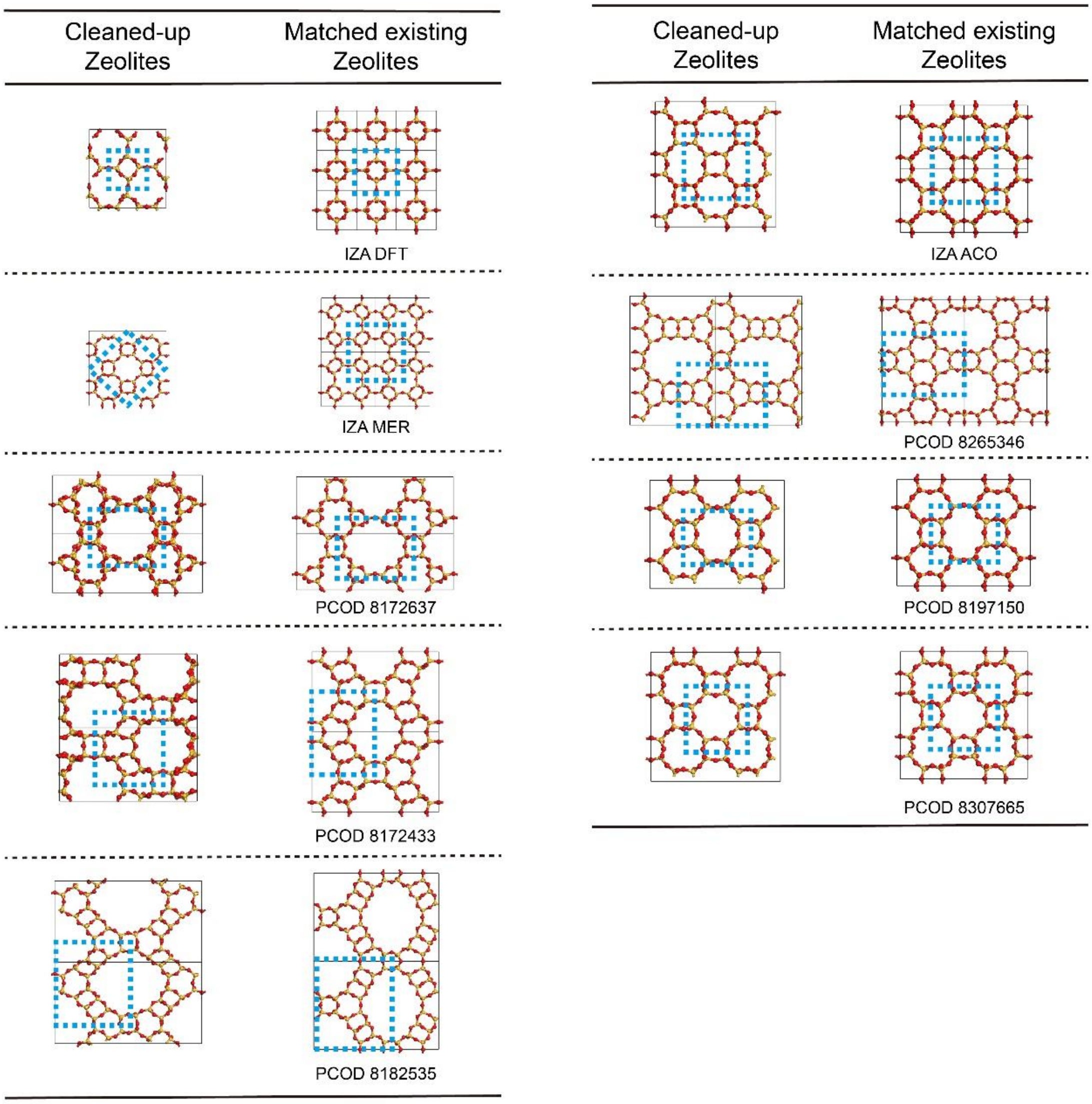


Figure S8. Zeolites generated using ZeoDiff and their corresponding structures in test dataset (IZA/PCOD). Dashed blue line indicates the matching portion within the structures.

Impact of Post-processing Procedure on Chemical Properties

In our workflow, energy grids generated from the diffusion model were directly used to calculate the chemical properties. However, during the post-processing procedure (Figure 2), modifications in atomic coordination take place, leading to alterations in energy grids and chemical properties of the output structures. To assess the impact of the post-processing step on the chemical properties, for the 102 structures generated in an unconditional manner, we re-calculated the chemical properties from the cleaned-up structures and compared them with values computed from the diffusion-generated grids. As depicted in Figure S9, minimal differences in values were observed before and after post-processing for relatively simple chemical properties (e.g. void fraction). In contrast, discrepancies appeared for relatively sensitive or complex properties (e.g. Henry coefficient). This suggests that discrepancies could become more pronounced when dealing with more challenging gases, such as CO_2, or with structurally complex substances like MOFs.

This discrepancy is directly correlated with the performance of the diffusion model. If the model's performance is excellent and all the generated samples are highly realistic, the structural changes during the post-processing procedure would be minimized, resulting in a decrease in the discrepancy. Therefore, the most straightforward way to address this issue would be to enhance the performance of the diffusion model by utilizing advanced algorithms and/or training with a higher-quality dataset.

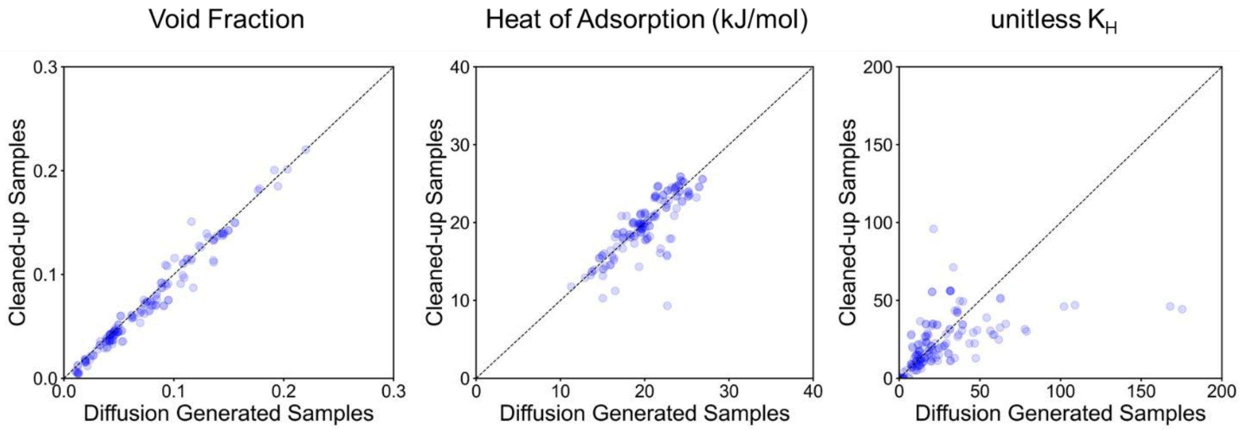


Figure S9. Parity plot between the chemical properties calculated from the energy grids obtained from the diffusion model and those calculated from the cleaned-up structures.

Section S4. Details on Conditional Generation

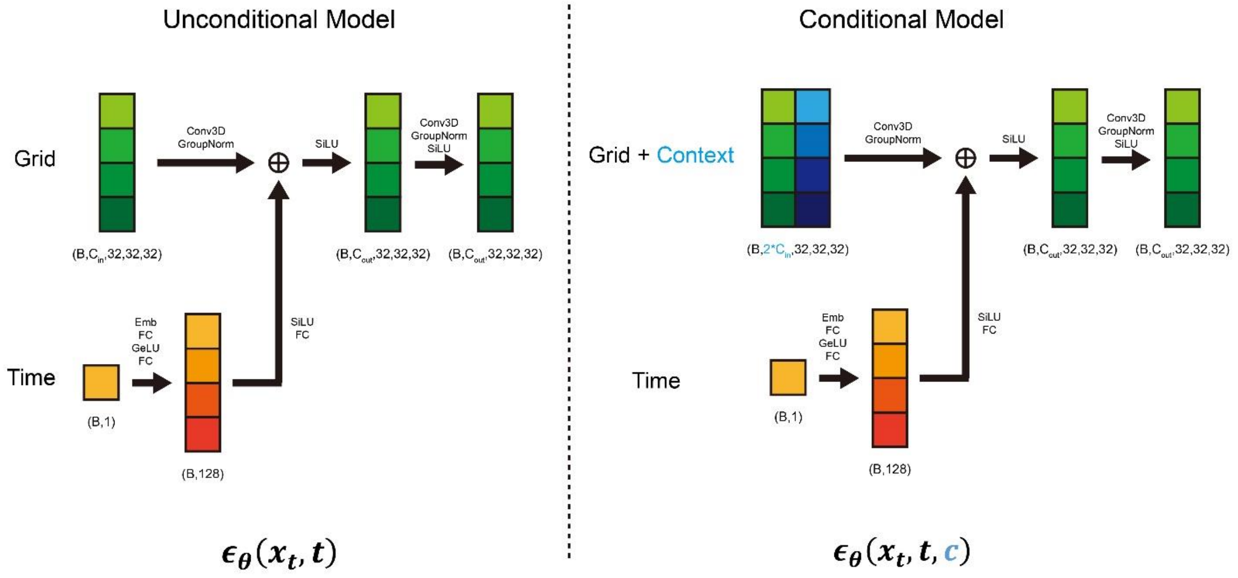


Figure S10. Difference in model architecture between the unconditional and conditional ZeoDiff models. Only the first block of the U-Net architecture is represented. As can be checked, the conditional model takes additional context as an input and the only difference between the two models is the dimensionality of the input.

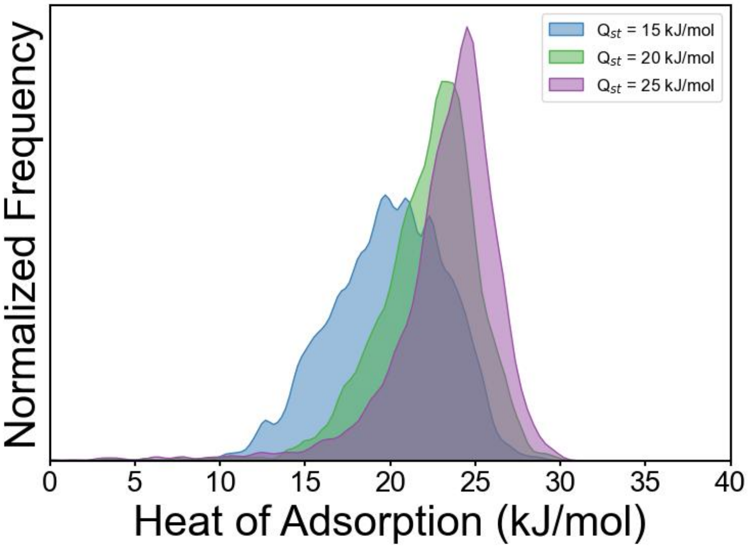


Figure S11. Inverse design targeted on heat of adsorption with an additional Boltzmann grid. To compare with the model trained without Boltzmann grid (Figure 5b), no prominent enhancement on the model's performance was observed. This implies that, the representation of three channels (Energy, Si, and O) still provides the model with sufficient information to understand the relationship between the structure and the heat of adsorption.

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