

**Supplemental Material to:**

**Insight into the Adsorption Mechanism of Benzene in HY zeolites:**

**the Effect of Loading**

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## 1. Models of HY zeolites

In this study, the chemical composition of HY zeolite  $\text{Si}_{192-x}\text{Al}_x\text{H}_x\text{O}_{384}$  was considered for  $x = 0, 14, 28, \text{ and } 56$ , namely 0Al, 14Al, 28Al, and 56Al, respectively, as shown in Table S11. In this manner, zeolite models with Si:Al ratios of  $\infty, 12.71, 5.86, \text{ and } 2.43$  were obtained, such that the 56Al model is in agreement with experimentally observed HY zeolite.<sup>1, 2</sup> Construction of the HY zeolite models can be divided into two steps: replacement of silicon atoms with Al atoms and compensation of H atoms ( $\text{H}_z$ ), which will be discussed, respectively.

The replacement of silicon atoms is relatively simple. At high Si:Al ratios, it is assumed that Si and Al are randomly distributed among the framework tetrahedral sites<sup>3, 4</sup>, with two rules govern the Si and Al distribution in zeolites: Löwenstein's rule<sup>5</sup> for avoidance of Al-O-Al linkages, and Dempsey's rule<sup>6</sup> requiring maximum separation of the Al atoms for a given Si:Al ratio. While Löwenstein's rule is generally accepted<sup>7</sup>, Dempsey's rule, which further limits the Si:Al ratio, is still debated and could be violated at low Si:Al ratios<sup>8, 9</sup>. Therefore, we strictly follow Dempsey's rule only for the 14Al model. For the 28Al and 56Al models having low Si:Al ratios, two Al atoms were allowed to occupy next nearest tetrahedral sites.

After Al atom substitution, the resulting negative charge is compensated by protons. As is known, there are four different positions for O atoms in the FAU framework ( $\text{O}_z$ )<sup>10</sup>, namely O1, O2, O3, and O4, and the  $\text{H}_z$ , which are attached to various  $\text{O}_z$  atoms, are denoted as H1, H2, H3, and H4. Based on previous neutron powder diffraction study of HY zeolites<sup>11</sup>, the site occupancy of  $\text{H}_z$  is as follows:  $\text{H1} > \text{H3} > \text{H2} > \text{H4}$ , with occupations of 28.6, 15.0, 9.5, and 0.0. In this study, the occupation of  $\text{H}_z$  for each model is based on that found in Ref 11 and has been idealized for simplicity. For the HY models, after the determination of the Si:Al ratios and percentages of H1, H2, and H3 atoms, the local charges of the frameworks can still be different based on the distribution of the  $\text{H}_z$  atoms. For example, for the 14Al model with seven H1 atoms in the framework, the relative positions of H1 atoms can be numerous. However, based on the experimental studies<sup>12-14</sup>, there are

no specific rules for the distribution of H<sub>z</sub> atoms. In our simulations, a relatively even distribution of the same kind of H<sub>z</sub> atoms was believed to be representative and typical.

**Table SII.** Detailed information of HY Models

Model	Si:Al ratio	Chemical composition	H1	H2	H3
0Al	∞	Si <sub>192</sub> O <sub>384</sub>	0	0	0
14Al	12.71	H <sub>14</sub> Al <sub>14</sub> Si <sub>178</sub> O <sub>384</sub>	7	3	4
28Al	5.86	H <sub>28</sub> Al <sub>28</sub> Si <sub>164</sub> O <sub>384</sub>	15	5	8
56Al	2.43	H <sub>56</sub> Al <sub>56</sub> Si <sub>136</sub> O <sub>384</sub>	30	10	16

<sup>a</sup> Idealized occupation of H<sub>z</sub> atoms.

## 2. Partial Charges:

The partial charges placed on the atoms of benzene and HY zeolite models was taken from Ref<sup>15</sup> as shown in Table SI2, which were restricted by two relations:

$$q(\text{Si}) + 2q(\text{O}(\text{Si-O-Si})) = 0 \quad (1)$$

$$q(\text{Si}) + 4q(\text{O}(\text{Si-O-Si})) = q(\text{Al}) + q(\text{H}) + 3q(\text{O}(\text{Si-O-Al})) + q(\text{O}(\text{Si-OH-Al})) \quad (2)$$

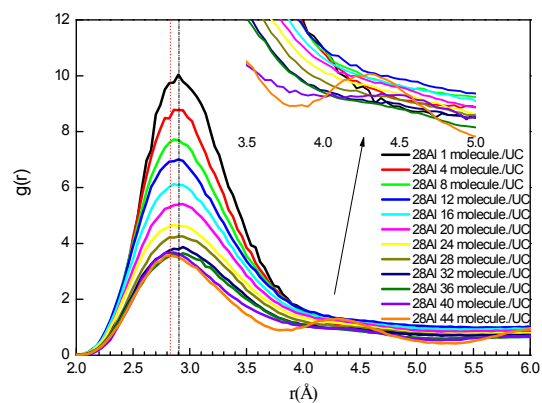
**Table SI2.** Partial Charges for Benzene-Zeolite Potentials

	Si	Al	O(Si-O-Si)	O(Si-O-Al)	O(Si-OH-Al)	H
0Al	+1.6  e	+1.2 e	-0.8 e	/	/	+0.2 e
14Al	+1.6  e	+1.2 e	-0.8 e	-0.9 e	-0.3 e	+0.2 e
28Al	+1.6  e	+1.2 e	-0.8 e	-0.9 e	-0.3 e	+0.2 e
56Al	+1.6  e	+1.2 e	-0.8 e	-0.9 e	-0.3 e	+0.2 e
Benzene	C	-0.153 e				
	H	+0.153 e				

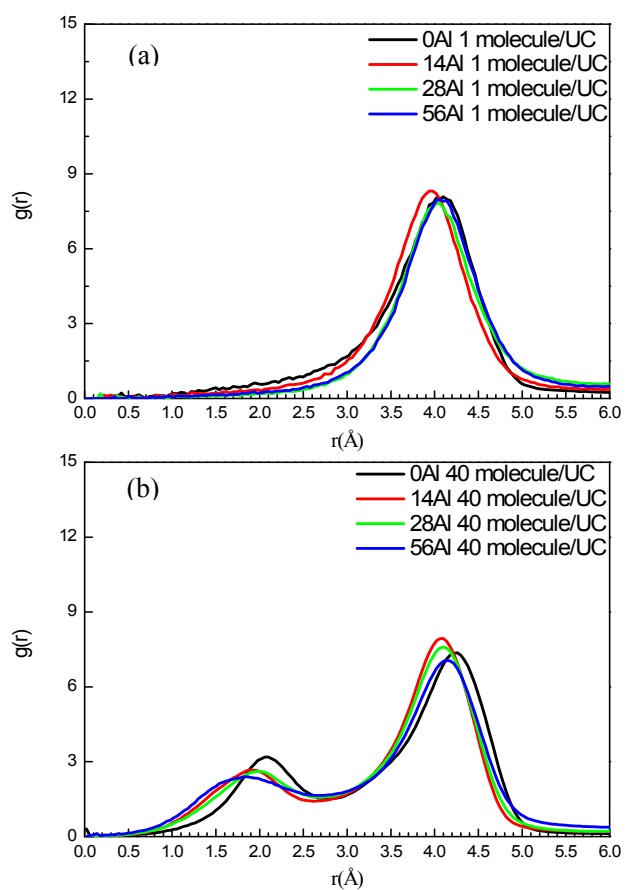
## 3. Radial distribution functions (RDFs):

The RDFs of COM and H1 protons of HY zeolite in Figure SI1 is shown to verify that inserted benzene molecules at loadings higher than the I-P push adsorbed molecules towards the zeolite framework. The RDFs of C<sub>ben</sub>-Supercage<sup>c</sup> in Figure SI2 and the insert of Figure SI1 show obvious new peak centered at loadings above the I-P, which represent insertion molecules inside the

supercage.



**Figure S11.** Radial distribution functions of COM-H1 for 28Al at various loadings.



**Figure S12.** Radial distribution functions of  $C_{ben}$ -Supercage<sup>c</sup> at: (a) 1 molecule/UC, (b) 40 molecule/UC, for 0Al, 14Al, 28Al, and 56Al models.

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