



# Adsorption process of phenol on silicalite-1 and crystal structure of phenol8.0–silicalite-1 using a single crystal X-ray diffraction method

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## ABSTRACT

The adsorption process of phenol on silicalite-1 was studied by single-crystal X-ray diffraction. The loading of phenol on silicalite-1 was performed for 24, 48, 72, and 168 h. Phenol molecules first diffused through the intersection forming hydrogen bonds with the oxygen atoms of the framework and then subsequently turned into the sinusoidal channel. As adsorption progressed, phenol molecules were located at the intersection and in the sinusoidal channel, and these two kinds of phenols interacted with each other. High-loaded phenol–silicalite-1 (8.0 molecules/unit cell) was obtained after 168 h of adsorption. It is clear that hydrogen bonds were present in the framework, based on the results of the single-crystal XRD measurements and an IR study.

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## 1. Introduction

Phenol is known to be toxic and is typically found in effluent wastewater from industrial plants. Consequently, various removal technologies for phenol have been developed. Currently, there are a few methods available for the removal of pollutants, for example, decomposition by microorganisms and extraction using organic solvents. Although these methods are widely used in sewage-treatment plants, they have problems such as the disposal of the resulting sludge and high cost. In addition, adsorption methods have attracted interest for the removal of pollutants and the application of various adsorbents has been extensively studied [1]. Activated carbon is widely used for the adsorption of organic compounds [2,3], but the regeneration cost is high and the regeneration process is difficult. Therefore, many scientists have been interested in and have explored the use of zeolite for adsorption of organic compounds. The adsorption capacity of synthetic zeolites for phenol has also been reported. Na-Y zeolite (Si/Al  $\approx$  2.3) adsorbs 0.8 mmol/g of phenol molecules on the framework [4] and the amount of adsorbed phenol in Na-X zeolite (Si/Al  $\approx$  1.2) is about 1 molecule/supercage [5]. Damjanovic et al. studied phenol adsorption by H-ZSM-5 zeolite and they reported that the higher the Si/Al ratio, the higher the adsorption of phenol [6]. In this study, silicalite-1 zeolite was adopted as a sorbent because it has the highest Si/Al ratio among all zeolites.

The adsorption properties of the MFI framework are very important in order to discuss the catalytic reaction. The crystal

structures of sorbate-ZSM-5 and sorbate-silicalite-1 have been previously reported using various methods. The single-crystal X-ray diffraction (XRD) method was adopted in several studies of the MFI crystal structure with adsorbed aromatic molecules [7–12]. These studies show the equilibrium state of the adsorbed aromatic compounds. However, the adsorption process of these compounds for the zeolite framework has not yet been reported by single-crystal XRD because the saturated vapor pressure of almost all aromatic compounds is high and their adsorption reaches the saturation state immediately (for example, pyridine: 20.68, toluene: 28.47, chlorobenzene: 11.98 Torr, at 293 K). The saturated vapor pressure of phenol is low, 0.35 Torr, compared to the above compounds because of the formation of intermolecular hydrogen bonds in phenol. Thus the phenol molecule is suitable for observation of the adsorption process of sorbates by XRD.

The crystal structure of phenol–silicalite-1 was solved by single-crystal XRD to understand the adsorption process of phenol in the zeolite framework. In addition to structure analysis, infrared spectra (IR) were obtained to prove the presence of a hydrogen bond between hydroxyl groups of phenols and the framework of zeolite.

## 2. Experimental

### 2.1. Preparation of phenol–silicalite-1

Silicalite-1 crystals were synthesized as described in our earlier report [13]. The reaction mixture had the following molar composition: 3SiO<sub>2</sub>–8KOH–10TPABr–500H<sub>2</sub>O. The mixture solutions were transferred to a Teflon-coated stainless steel autoclave at

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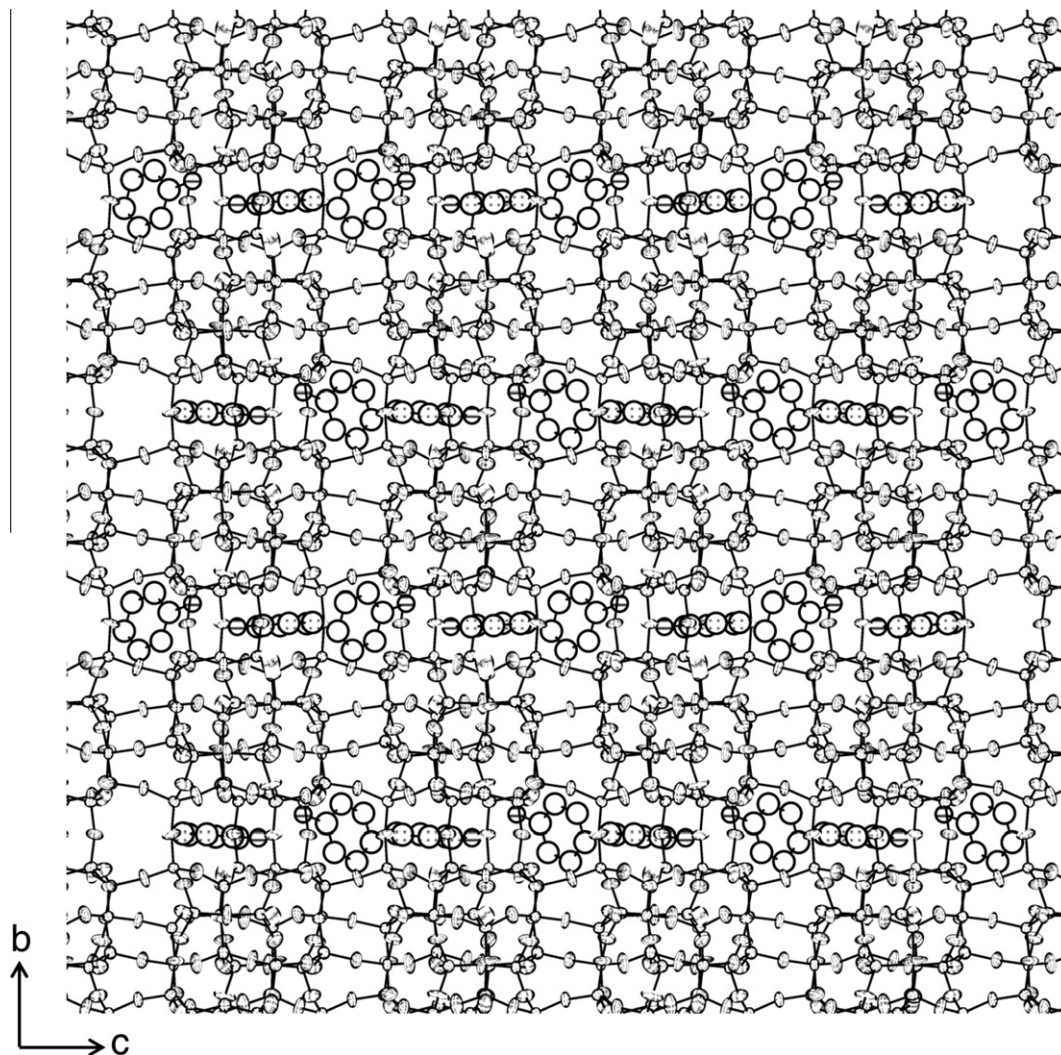
**Table 1**  
Experimental details of XRD measurements for the 168-h adsorption condition.

Empirical formula	2.0C <sub>6</sub> H <sub>5</sub> OH·Si <sub>24</sub> O <sub>48</sub>
Formula weight	6481.18
Temperature	293 K
Crystal system	Orthorhombic
Space group	<i>Pn</i> 2(1) <i>a</i>
<i>Unit cell dimensions</i>	
<i>a</i> = 20.016(4) Å	$\alpha = 90^\circ$
<i>b</i> = 19.801(4) Å	$\beta = 90^\circ$
<i>c</i> = 13.412(3) Å	$\gamma = 90^\circ$
Volume	5315.7(19) Å <sup>3</sup>
Z	4
Density (calculated)	2.025 Mg/m <sup>3</sup>
Absorption coefficient	0.693 mm <sup>-1</sup>
Crystal size	0.1 × 0.08 × 0.05 mm <sup>3</sup>
Theta range for data collection	1.83°–28.73°
Index ranges	–27 ≤ <i>h</i> ≤ 26, –26 ≤ <i>k</i> ≤ 26, –17 ≤ <i>l</i> ≤ 17
Reflections collected	60,605
Independent reflections	12,967 [R(int) = 0.1266]
Completeness to theta = 28.73°	96.4%
Absorption correction	Analytical
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Observation [ <i>I</i> ≥ 2σ( <i>I</i> )]	5882
Data/restraints/parameters	5882/13/675
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.897
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0660, <i>wR</i> 2 = 0.1802
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1424, <i>wR</i> 2 = 0.2433
Absolute structure parameter	0.6(4)
Largest diff. peak and hole	1.420 and –0.795 e Å <sup>-3</sup>

453 K for 12 day under static conditions. The obtained samples were washed with distilled water and dried at 388 K for 1 day. The as-synthesized crystals were treated with NaClO<sub>4</sub> and then calcined at 763 K in air for 1 h [12]. The silicalite-1 crystals after calcination were exposed to saturated phenol vapor in a vacuum vessel for 24 h, 48 h, 72 h, or 168 h at room temperature.

## 2.2. Single-crystal X-ray diffraction analysis

Single-crystal XRD analysis was carried out at room temperature using a SMART APEX II CCD X-ray diffractometer (Bruker AXS Co., Ltd.) with Mo K $\alpha$  radiation and a carbon monochromator. The crystal structures for various samples were refined by the full-matrix least-squares method [14]. The space group of the crystals was orthorhombic, *Pn*2<sub>1</sub>*a* (No. 33), for all adsorption periods. For the 24-, 48-, and 72-h adsorption periods, the crystal data for phenol-silicalite-1 was incomplete because these were not the equilibrium structures. However, some adsorption sites were relatively stable and they could be observed by XRD before equilibrium. After the 168-h adsorption period, high-loaded phenol-silicalite-1 was obtained. The full experimental details of the sample in this condition are listed in Table 1 and the crystal structure obtained is shown in Fig. 1. The final *R* value, a measure of the agreement between the crystallographic model and the experimental XRD data, was 0.066 using 5882 observations with *I* ≥ 2σ(*I*) and 0.142 for all 12,967



**Fig. 1.** Packing structure of high-loaded phenol-silicalite-1 (after adsorption for 168 h).

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