

## TPD of cyclic hydrocarbons in silicalite-1 studied by intelligent gravimetry

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### Abstract

Temperature-programmed desorption (TPD) of cyclopentane, benzene and cyclohexane in silicalite-1 from room temperature to 400 °C at different loading has been investigated by intelligent gravimetry. TPD of cyclopentane and benzene at different heating rates (5, 10, 15 and 20 °C/min) has also been studied. There are two different peaks in cyclopentane and benzene TPD profiles at loading over four molecules per unit cell. Only one peak appears at loading lower than (or equal to) four molecules per unit cell in cyclopentane and benzene TPD profiles and in cyclohexane TPD profiles. The maximum desorption peak temperature increases with the increasing of initial adsorbate loading.

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### 1. Introduction

Silicalite-1, siliceous type of ZSM-5, consists of two types of intersecting channels of 10-membered ring openings. One channel system that is parallel to the [1 0 0] axis is sinusoidal with elliptical free apertures of 0.51 nm × 0.55 nm and the other one that is parallel to the [0 1 0] axis straight with free near-circular apertures of 0.54 ± 0.02 nm [1–3]. The pore diameters of silicalite-1 are close to the critical dimension of many important hydrocarbon molecules. This particular property leads to some interesting physical chemistry phenomenon when the adsorbate is present. Recent studies [4–7] have shown that adsorption isotherms of certain molecules in silicalite-1 exhibit a rather unusual behavior. This shows both the character of silicalite-1 framework and the proper-

ties of sorbates molecules determine their sorbing properties in silicalite-1.

TPD is not very accurate but is rapid and successful method to obtain information of adsorbate–adsorbent interactions of various hydrocarbon/zeolite system compared with isotherm determinations [4,5,8–11]. It is a good method especially for some adsorbates such as cyclohexane needing long equilibration time to determine accurate adsorption isotherms. To the best of our knowledge, the literature on the TPD of cyclopentane is sparse. In this paper, a very accurate, completely computer-controlled gravimetric technique, using the Intelligent Gravimetric Analyzer (IGA), Hiden Analytical Ltd., UK, has been applied to systematically investigate thermogravimetry properties of cyclopentane, benzene and cyclohexane in silicalite-1. Although the heats and activation energies of desorption are not to be tried to estimate, the qualitative desorption information obtained in this study will be of valuable assistance to understand the

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interactions of adsorbate–adsorbent and catalysis by zeolites with the ZSM-5/silicalite-1 framework.

## 2. Experimental

TPD or thermogravimetry (TG) measurements for cyclopentane, benzene and cyclohexane in silicalite-1 were carried out using the IGA supplied by Hiden Analytical Ltd. The IGA apparatus is an ultrahigh vacuum system which allows the adsorption–desorption isotherms and the corresponding kinetics of adsorption or desorption at each pressure step to be determined [12]. The system consists of a fully computerized microbalance which automatically measures the weight of the sample as a function of time with the gas vapor pressure and sample temperature under computer control. The microbalance had a long-term stability of  $\pm 1 \mu\text{g}$  with a weighing resolution of  $0.1 \mu\text{g}$ . The equilibrium pressures were determined by three, high-accuracy, Baratron pressure transducers with ranges of 0–2 mbar, 0–100 mbar and 0–10 bar, and maintained at the set-point by active computer control of the admittance/exhaust valve throughout the duration of the experiment. Buoyancy corrections were made on-line for sample and tare hang-downs and containers, and also the tare materials, sample and adsorbed gases. The sample temperature was also monitored throughout the adsorption process and regulated to  $\pm 0.1^\circ\text{C}$  by either a water bath or a furnace. The silicalite-1 sample ( $\sim 126 \text{ mg}$ ) was outgassed under a vacuum of  $< 10^{-5}$  mbar at  $400^\circ\text{C}$  for about 20 h. The sorbates were purified through several freeze-pump-thaw cycles where necessary. Before starting the TPD run, the adsorbent was saturated with the sorbate at room temperature at a specific pressure which was chosen from the isotherm to meet the required loading. The mass uptake was measured as a function of time and the approach to equilibrium monitored in real time with a computer algorithm. The system was then heated at different rates (5, 10, 15,  $20^\circ\text{C}/\text{min}$ ) from room temperature to  $400^\circ\text{C}$ . The pressure was maintained constant during the heating. The weight of the sorbent was recorded as a function of temperature from which TG and DTG (differential thermal gravimetry) data could be derived.

Silicalite-1 are of research grade cubic with a size of  $4 \mu\text{m} \times 3 \mu\text{m} \times 4 \mu\text{m}$  and with Si/Al ratio  $> 1000$ . Such sufficiently low content of aluminium makes the possibility of catalytic reactions unimportant under the conditions used in the TPD experiments. Prior to using for the adsorption studies, the sample was calcinated at  $550^\circ\text{C}$  for 10 h in a hot-air oven. The crystal was heated from room temperature to  $550^\circ\text{C}$  at  $2^\circ\text{C}/\text{min}$ . The morphology of the crystal can be seen from the SEM in Fig. 1. Cyclopentane was obtained from Fluka Chemie AG; benzene was obtained from Chemical Company of Agents, Shanghai, China; and cyclohexane was supplied by the No. 1 factory in Shanghai, China. All these chemicals have purity  $> 99.0\%$ .

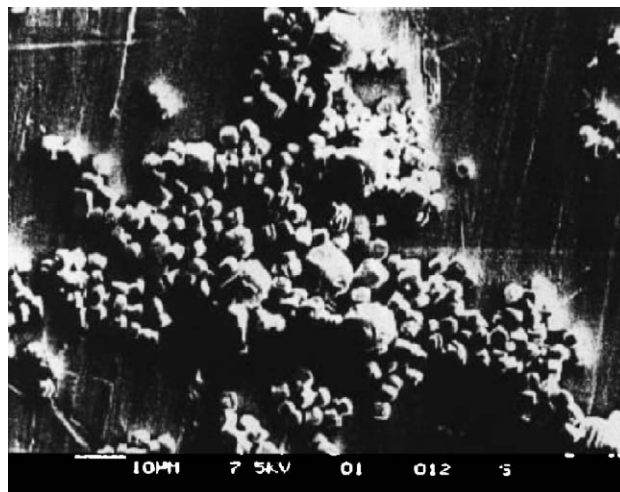


Fig. 1. SEM of silicalite-1 zeolite.

## 3. Results and discussion

The TPD curves for cyclopentane, benzene and cyclohexane at different loadings at a heating rate  $20^\circ\text{C}/\text{min}$  are shown in Figs. 2–4, respectively. The differential curves (DTG) give a clear indication of the differences exhibited by these three sorbates in silicalite-1. Both cyclopentane and benzene demonstrate one-peak desorption profiles at the initial loading less than (or equal to) four molecules per unit cell and double peak profiles at higher loading. Although their maximum loadings differ, it is interesting to note that there is an inflection point in the TG profiles when the initial loadings of cyclopentane and benzene are larger than four molecules per unit cell. And the loading at the inflection point is always about four molecules per unit cell. Cyclohexane produces only single desorption peak profiles. At full loading, only

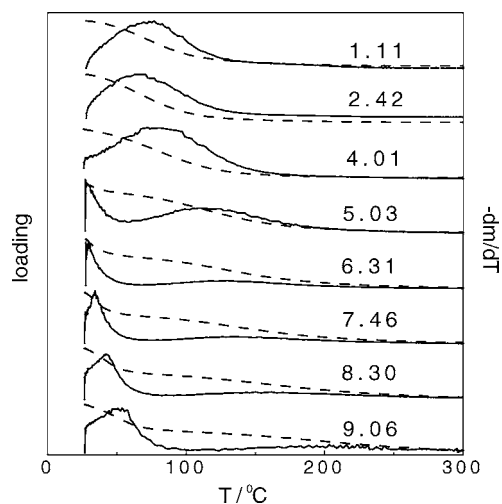


Fig. 2. TG and DTG curves for cyclopentane in silicalite-1 at different initial adsorbate loadings in molecules of cyclopentane per unit cell (linear heating rate  $20^\circ\text{C}/\text{min}$ ).

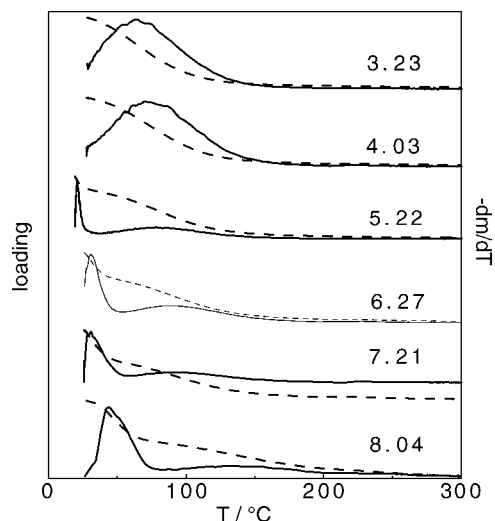


Fig. 3. TG and DTG curves for benzene in silicalite-1 at different initial adsorbate loadings in molecules of benzene per unit cell (linear heating rate 20 °C/min).

about four cyclohexane molecules sorb per silicalite-1 unit cell, which is consistent with the results reported by Song et al. [13], and by Magnalhães et al. [14].

With cyclopentane and benzene system, the desorption rate of the first desorption region is larger than that of the second, which suggests the adsorption energy of cyclopentane and benzene at high loading must be weaker than that at low loading, consistent with that reported by Olson and Reischman [4]. Weaker adsorption in the 4-saturation range means that Gibbs free energy,  $\Delta G$ , is less negative in this range than that in the 0–4 range. The heats of adsorption,  $-\Delta H$ , of cyclopentane and benzene, presented in Fig. 5,

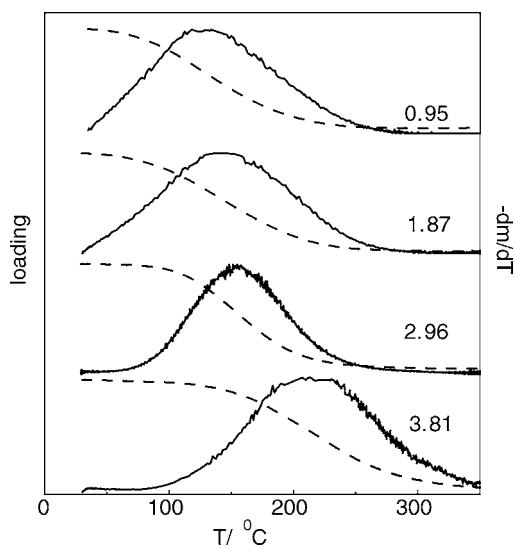


Fig. 4. TG and DTG curves for cyclohexane in silicalite-1 at different initial adsorbate loadings in molecules of cyclohexane per unit cell (linear heating rate 20 °C/min).

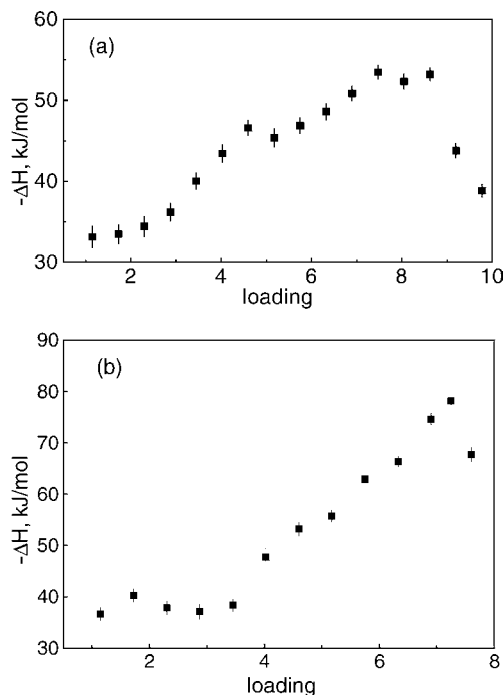


Fig. 5. Isosteric heats of adsorption,  $-\Delta H$ , of cyclopentane (a) and benzene (b) in silicalite-1 as a function of loading in molecules per unit cell; typical error bars shown.

have been calculated from the isotherms measured gravimetrically in our laboratories. On the whole, the isosteric heat of cyclopentane and benzene increases in magnitude with increasing loading except when the loading is close to the saturation amount, which shows  $\Delta H$  becomes more negative in the 4-saturation range. Thus, only when  $(-T \Delta S)$  must be more positive with the increasing of loading, may  $\Delta G$  be less negative according to equation  $\Delta G = \Delta H - T \Delta S$ . That is to say, the final entropy must be significantly lower than the initial entropy in the 4-saturation molecule region relative to the 0–4 molecule region, i.e.,  $S(4\text{-saturation}) < S(0\text{--}4)$ . Previous paper [15] has reported the same phenomenon, i.e., a more ordered state for the latter molecules of adsorbates relative to the first four molecules. Therefore, it can be concluded that entropic changes are the possible cause of the weaker adsorption at high loading. The adsorption state of sorbates can be known from the TPD profiles.

Two desorption peaks are corresponding to the two thermodesorption processes, consistent with two-site adsorption mechanism reported by Karli et al. [16]. It was previously noted that TPD spectra of organic compounds from microporous silicalite frequently display two-stage desorption processes due to self-blocking of the channel network by flexible molecules bending through 90° at intersections of the channel system. But this was considered as an oversimplistic description of the desorption process [9]. In fact, the desorption of adsorbate molecules should be along the easiest path available. It is possible that desorption occurs simultaneously from both types of channels in silicalite-1.

It has been reported [7,17,18] that cyclopentane (or benzene) molecules adsorbed in ZSM-5/silicalite-1 are localized at channel intersections when loadings are lower than four molecules per unit cell. Rearrangement then occurs to give a more efficient packing at higher filling. Computer simulation calculations and XRD techniques have shown that the intersections, of which there are four per unit cell in silicalite-1, are the most preferred sorption sites for these cyclic hydrocarbon molecules and the equivalent aromatics [7,19–23]. Therefore, the desorption from silicalite-1 at loading less than or equal to four molecules per unit cell can be assigned to the cyclopentane (or benzene or cyclohexane) molecules that are known to be located in the intersection sites.

There will be considerable exchange of molecules between the different adsorption sites as the TG measurement is performed. Further, there may also be a change in the preferred adsorption sites as the loading is reduced during the TPD experiment [24]. The first desorption peak, therefore, cannot be simply imposed on desorption from a state of adsorbate molecules located in zigzag channel or straight channel at high loading. It is impossible for molecules to desorb from a site in the zigzag channel (or straight channel) without passing through the channel intersection sites due to the microporous channel structure as mentioned in Section 1. Thus, it can be seen that the first desorption peak should correspond to desorption from a state of more than four cyclopentane (or benzene) molecules per unit cell, i.e., the process of loss of loading >4 down to four molecules per unit cell. When the loading has been reduced to four molecules per unit cell, the remaining four molecules relocate preferentially at the channel intersection sites, and their desorption peaks in the second desorption region in Figs. 2 and 3.

Table 1 lists a summary of the TPD experiments at a heating rate of 20 °C/min. It can be observed from Table 1 that the variation of maximum desorption peak temperature with the initial adsorbate loading for cyclopentane, benzene and cyclohexane. The first and the second desorption peak temperatures (including the peak temperature at loading less than or equal to four molecules per unit cell) of cyclopentane and benzene increase with sorbate loading increasing. As mentioned in Ref. [18], rearrangement occurs due to the interaction of sorbate–sorbate at high filling. The interaction of sorbate–sorbate becomes stronger, followed by the larger entropy lost, with the increasing of loading. Those latter molecules, therefore, must have enough gains in entropy on desorption as the main driving force. Thus, the higher desorption temperature will be required with increase in the initial loading. The increase in temperature of the second desorption peak corresponding to desorption of molecules adsorbed in the channel intersection sites arises from the increase in equilibrium pressure that is maintained in these DTG measurements as the initial loading increases (see Section 2). For cyclohexane, molecule rearrangement does not occur in the adsorption process at room temperature [7]. Adsorption is dominated by the interactions between cyclohexane molecules and the silicalite surface and not enhanced even by

Table 1  
Summary of TPD results for a heating rate of 20 °C/min

Initial loading <sup>a</sup>	<i>T</i> of the first desorption (°C)	<i>T</i> of the second desorption (°C) <sup>b</sup>	Loading at inflection point <sup>a</sup>
<b>Cyclopentane</b>			
1.11	–	65.6	–
2.42	–	70.7	–
4.01	–	80.9	–
5.03	27.2	110.3	3.94
6.31	27.6	130.0	3.95
7.46	34.3	133.0	3.96
8.30	42.1	151.0	3.89
9.06	54.7	223.4	4.21
<b>Benzene</b>			
3.23	–	65.0	–
4.03	–	69.5	–
5.22	20.6	78.1	3.97
6.27	30.5	84.3	3.85
7.21	31.0	94.1	3.87
8.04	43.6	128.5	3.85
<b>Cyclohexane</b>			
0.95	–	106.6	–
1.87	–	118.7	–
2.96	–	146.7	–
3.81	–	220.7	–

<sup>a</sup> Molecules per unit cell.

<sup>b</sup> *T* of the second desorption peak including the desorption temperature of molecules at loading less than or equal to four molecules per unit cell.

the presence of sodium ions [25]. The interactions between cyclohexane molecules and the channels of silicalite-1 will become more pronounced due to the more chance of interaction of sorbate–sorbent with the increasing of the loading. The desorption peak temperature therefore increases from 106.6 to 220.7 °C when the loading increases from 0.95 to 3.81 molecules per unit cell.

Comparing the DTG profiles of cyclopentane, benzene and cyclohexane in this study at specific loading, it is not difficult to find that the maximum desorption temperature of cyclohexane is higher than that of cyclopentane and benzene, which suggests that the affinity, *A<sub>T</sub>* [26], of cyclohexane is the highest. The critical diameter for cyclohexane is 0.69 nm, slightly larger than that for cyclopentane, 0.64 nm and for benzene, 0.664 nm. This increase in critical diameter from cyclopentane, benzene to cyclohexane implies that interactions between the sorbent and sorbate will increase [13]. Moreover, the additional interactions of the extra hydrogen atoms of the cyclohexane molecules with the framework oxygen in silicalite-1 structure may be the most probable reason. This finding indicates that the size of sorbate molecules plays a crucial role in the desorption properties of these systems.

In a previous study [27], the TPD profile of benzene from silicalite exhibited only one peak at a heating rate 10 K/min. It was obvious (see Fig. 1 of Ref. [27]) that the starting temperature (80 °C) was higher than the temperature of the first peak (43.6 °C) in our study at the maximum saturation loading. Although the samples may be different, this result shows

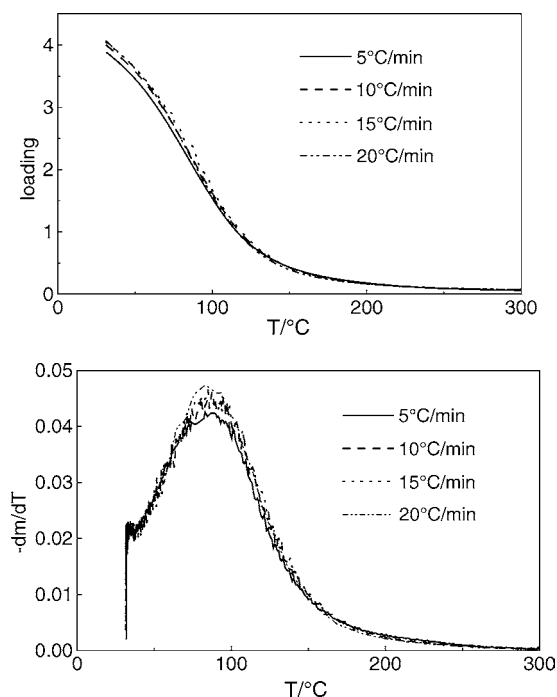


Fig. 6. TG and DTG curves of cyclopentane in silicalite-1 at different heating rates at initial loading about 4.03 molecules per unit cell.

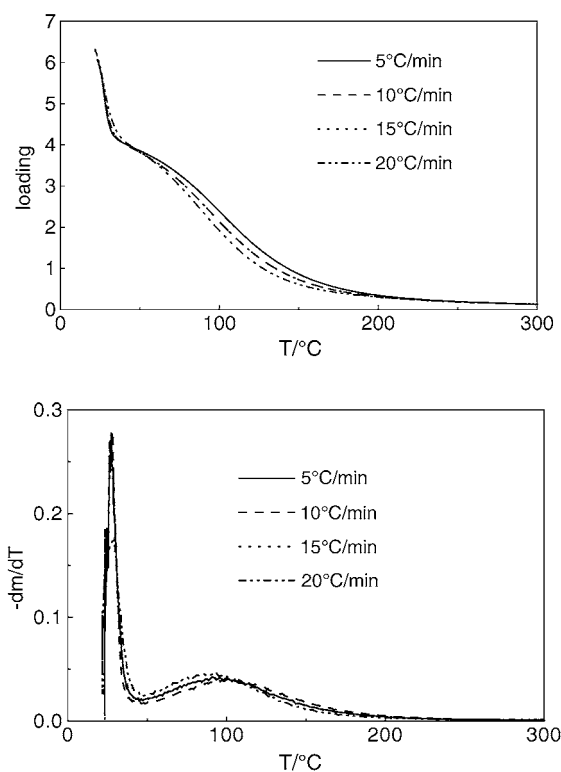


Fig. 7. TG and DTG curves of benzene in silicalite-1 at different heating rates at initial loading about 6.31 molecules per unit cell.

that many factors may have influence on the TG/DTG curve, such as initiative desorption temperature (i.e., the temperature at which the adsorbed adsorbate start desorbing), heating rate, etc.

Figs. 6 and 7 show TG/DTG profiles obtained for cyclopentane loaded about 4.03 molecules per unit cell and benzene loaded about 6.31 molecules per unit cell at different heating rates (5, 10, 15, and 20 °C/min, respectively). The desorption patterns do not change significantly with different heating rates, but the peak temperatures change slightly. This result suggests the heating rate has little effect on the TPD studies in this study.

#### 4. Conclusions

The TPD of cyclopentane and benzene in silicalite-1 reveals that desorption occurs in two distinct processes at loading larger than four molecules per unit cell. And an inflection point exists in about four molecules per unit cell. TPD of cyclopentane and benzene in this case does not directly measure desorption from specific adsorption sites, but detects the presence of different overall adsorption states.

The TG/DTG profiles of cyclopentane, benzene and cyclohexane which exhibit energetic heterogeneity of the pore in silicalite-1 give evidence of the existence of energetically favoured adsorption sites with an adsorption capacity of four molecules per unit cell.

The different heating rate has less influence on the pattern of DTG profiles. But only the desorption peak temperatures change slightly.

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