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Sorption of Benzene in CoAlPO$_4$-5 Molecular Sieves

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Abstract. The sorption isotherms of benzene in CoAlPO$_4$-5 at temperatures of 323–399 K were measured by the gravimetric technique. The sorption capacity and isosteric heat were estimated and interpreted on the basis of the pore topologies of the molecular sieves. The isotherms followed the typical Type-I shape, and could be well fitted with Langmuir and Dubinin-Radushkevich equations. The initial heats of sorption at zero coverage could be well explained by the surface curvature model. The isosteric heats of sorption varied with the coverage, which may suggest a shift of molecular packing manner in the sorbed phase.

Keywords: sorption, CoAlPO$_4$-5, benzene, sorption isotherms, heat of sorption

1. Introduction

AlPO$_4$-5, an aluminophosphate molecular sieve with the topological structure of AFI, consists of tetrahedral structure of AlO$_4$ and PO$_4$, which corner-share an oxygen atom and alternate strictly to build a three-dimensional framework with channels in the molecular dimension (Ribeiro et al., 1995). The framework of AlPO$_4$-5 has a hexagonal symmetry with a unit cell composition of $Al_{12}P_{12}O_{48}\cdot nH_2O$ and crystal parameters $a = b = 13.73$ Å, $c = 8.48$ Å, and $\gamma = 120°$, while the uni-directional cylindrical channel is composed of 12-membered rings with a uniform cross-section of 7.3 Å along the c axis (Wilson et al., 1982). The polar nature of its structure is expected due to the vertical alignment of P—O—Al bonds in one direction (Bennett et al., 1983; Choudhary et al., 1987).

The channel opening of AlPO$_4$-5 is comparable to the size of aromatics, which suggests its potential applications as catalysts and adsorbents. Furthermore, the neutral framework offers a unique opportunity to investigate the effects of molecular structure, size and shape on the sorbate-sorbent interactions. Knowledge on the sorption properties of AlPO$_4$-5 for the aromatic compounds is thus of great interest (Santilli et al., 1993). Choudhary et al., studied the sorption of hydrocarbons, water and alcohol in AlPO$_4$-5 at 313 K, and measured the sorption isotherms for *n*-hexane, benzene and pyridine in AlPO$_4$-5 at higher temperatures (523–673 K); the sorption of methanol, *n*-hexane and benzene at 313 K occurred via the volume filling mechanism and the total volume of the sorption

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space in $AlPO_4$-5 was found to be about 0.14 cm^3/g (Choudhary et al., 1988). Newalkar et al., reported that the initial heat of sorption for cyclohexane in $AlPO_4$-5 was higher than that for methyl cyclopentane, which reinforces the stronger influence of confinement effect on the cyclohexane molecule with a critical diameter of 6.9 Å than that on the methyl cyclopentane molecule with the critical diameter of 6.5 Å (Newalkar et al., 1999).

However, the strict alternation of Al and P in $AlPO_4$-5 results in the neutral and defect-free framework, and as a consequence, $AlPO_4$-5 does not possess any redox or acidic properties, which prohibits its further application. Much attention is then focused on the isomorphous substitution of P^{5+} and Al^{3+} by the transition metal ions such as Co^{2+}, Cr^{3+}, Fe^{3+} and Zn^{2+} (Kurshev et al., 1994; Uytterhoeven et al., 1994). The transition metal ions introduced into the framework of aluminophosphate bring along the acid and redox sites, and thereon the interesting catalytic properties. The isomorphous substitution of Al^{3+} or P^{5+} by Co^{2+} ($CoAlPO_4$-5) behaved excellently in the catalytic oxidation, for example, the selective oxidation of *n*-hexane to C_1–C_4 alcohols, aldehydes and ketones; and the terminal carbon in the alkane was preferentially oxidized (Thomas et al., 1999).

Although the effect of sorption on the reactivity and selectivity is particularly interesting because of the intense Coulomb force field within the intracrystalline pores (Chen et al., 1994), the study on the sorption properties of $CoAlPO_4$-5 was considerably limited compared to the extensive investigations on its synthesis, characterization and catalytic applications.

In this work, the sorption of benzene in $CoAlPO_4$-5 was investigated. The isotherms at temperatures of 323–399 K were measured by gravimetric technique. The sorption capacity and isosteric heat were estimated and interpreted on the basis of the pore topologies of the molecular sieves.

2. Experimental

2.1. Material

$CoAlPO_4$-5 was synthesized according to the method described in the literature (Fan et al., 2001). The XRD patterns indicated that the sample was in a single phase with good crystallinity. The incorporation of Co^{2+} into the framework was confirmed by the diffuse reflectance spectroscopy (DRS). The compositions of $CoAlPO_4$-5 were determined by inductively coupled plasma (ICP) and listed in Table 1.

Table 1. Chemical compositions of $CoAlPO_4$-5.

Co/Al*	Co^T (mol.%)	Co^F (mol.%)	Co^{EF} (mol.%)	(Co + Al)/P	(P − Al)/P	Co^F (%)	Co^{EF} (%)
0.12	0.0994	0.0831	0.0163	1.021	0.107	83.6	16.4

Note: F, framework; EF, extraframework; T, total; *, in the framework.

It was found that the ([Co] + [Al])/[P] ratio was close to unity, which suggested the isomorphous substitution of Al^{3+} by Co^{2+}. The substitution extent estimated in terms of the ([P] − [Al])/[P] ratio was about 10.7%, which was higher than the value 6% reported by Uytterhoeven (Uytterhoeven et al., 1994). It was then inferred that the Co^{2+} presented at the ion-exchange sites was probably in the forms of cobalt oxide and/or dense-phase cobalt phosphate.

2.2. Sorption Measurements

The sorption was measured by IGA (Intelligent Gravimetric Analysis, Model 002/3, Hiden Analytical Limited, UK) with computer-controlled microbalance and stainless steel vacuum pressure vessel. Benzene (A.R. grade, ≥99.5%, Shanghai Chemical Reagent Co., China) was used as adsorbate without further purification. The dissolved air in the sorbate was removed by a freeze-thaw cycle. The adsorbent ($CoAlPO_4$-5, ca. 150 mg) was placed in a stainless steel (SS316LN) sample container and degassed in situ at 723 K (heating rate 5 K/min) under the ultra-high vacuum of 10^{-7}–10^{-9} bar for 500 min. The temperature of the samples during the isotherm measurement was controlled by a water bath or furnace. The equilibrium pressure was measured with a transducer in the ranges of 0–2, 0–100 or 0–10000 mbar. The accuracy of isotherm data was estimated as ±0.1 K for the temperature, ±0.1 Pa for the pressure, and ±0.1 μg for the mass of the adsorbate.

2.3. Data Transaction

The sorption isotherms in this work were described by Langmuir isotherm model

$$\frac{p}{W} = \frac{1}{B} + \frac{p}{V_m} \tag{1}$$

and Dubinin-Radushkevich isotherm model

$$\ln W = \ln W_0 - D\left(\ln \frac{p_s}{p}\right)^2 \tag{2}$$

where p and p_s are equilibrium and saturation pressure of sorbate at the test temperature T, W is the sorbed amount, B and D are model constants, V_m and W_0 are the sorption capacities. D can be expressed as $A \cdot T/\beta^2$, where A is a characteristic of sorbent pore structure and independent of temperature, and β is the affinity coefficient.

The isosteric heat Q was estimated from the branch of adsorption by the Clausius-Clapeyron equation

$$\left(\frac{\partial \ln p}{\partial T}\right)_W = \frac{Q}{RT^2} \tag{3}$$

3. Results and Discussion

3.1. Sorption Isotherms and Capacities

The sorption isotherms for benzene in CoAlPO$_4$-5 at different temperatures were shown in Fig. 1. All the isotherms followed the typical type-I shape. A sharp rise on the isotherms at low-pressure region was observed, which indicated the presence of micropore filling (Newalkar et al., 1999). The hysteresis in the branch of desorption may be due to the extremely slow desorption rate during the measurement.

The isotherms could be well fitted with Langmuir and Dubinin-Radushkevich equations. The values of sorption capacities V_m and W_0 and constants B and D of benzene in CoAlPO$_4$-5 along with the relative coefficient for the correlation were given in Table 2, which showed a good consistency between two models, although a better fit by Langmuir isotherm model was observed. The sorption capacities of benzene in CoAlPO$_4$-5 decreased with temperature.

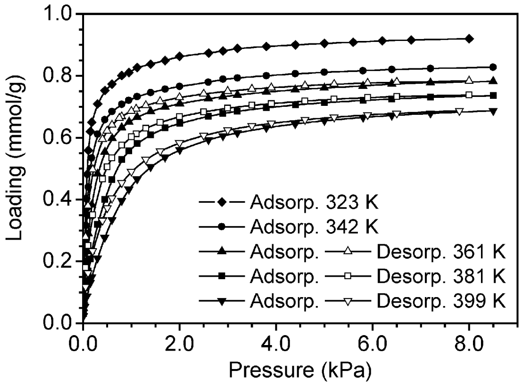

Figure 1. Adsorption and desorption isotherms of benzene in CoAlPO$_4$-5 at 323, 342, 361, 381 and 399 K.

Since benzene is a flat molecular with a thickness of about 4 Å and length of 6.6 Å, which is smaller than the channel dimension of AlPO$_4$-5. The kinetic diameter of benzene is 5.85 Å (Talu et al., 1989). Thus benzene molecules could rotate freely in the channel of CoAlPO$_4$-5 molecular sieves. The most favorable conformation of benzene adsorbed in the molecular sieves would be in an orientation concentric to the T12 ring (Chang et al., 1991). In such an orientation, all the hydrogen atoms will be in an equal distance from the pore wall. Since each unit channel consists of two T12 rings with asymmetric alternations of Al and P atoms, there might be two minimum energy sites in each channel. It was also reported that benzene and ethylbenzene molecules had only a very weak interaction with AlPO$_4$-5 framework (Mallmann et al., 1989). The repulsive force between the π bonds of nearby benzene molecules should be a more important factor than the interaction with the T12 ring, especially under the saturation condition.

Table 2. Sorption capacity estimated for benzene in CoAlPO$_4$-5 by Langmuir and Dubinin-Rudushkevich isotherm models.

	Langmuir			Dubinin-Radushkevich		
Temperature (K)	V_m (mmol g^{-1})	B × 10^2 (mmol g^{-1} Pa^{-1})	R^2	W_0 (mmol g^{-1})	D × 10^2	R^2
323	0.925	0.915	0.999	0.961	1.44	0.995
342	0.834	0.671	0.999	0.907	1.38	0.982
361	0.794	0.405	0.999	0.867	1.18	0.992
381	0.766	0.214	0.999	0.843	1.16	0.989
399	0.746	0.107	0.999	0.836	1.05	0.991

3.2. Heat of Sorption at Zero Coverage

As estimated by linear regression of van't Hoff equation (Newalkar et al., 1999), the heat of sorption at zero coverage for benzene in CoAlPO$_4$-5 was −36.2 kJ/mol, which is determined by the nature of sorbate, structure of molecular sieves and the sorbate-sorbent interactions within the channels. As benzene is a nonpolar molecule with little polarisability, the interaction of benzene with the surface of CoAlPO$_4$-5 is due to the dispersion and repulsion forces between the benzene molecules and the lattice oxygen, framework cobalt, aluminium and phosphates atoms in the sorbent (Newalkar et al., 1997).

On the other hand, the heat of sorption at zero coverage could also be estimated by the confinement theory deduced from the surface curvature model (Derouane et al., 1987). By the confinement theory, the heat of sorption at zero coverage for molecules within zeolite pore is described as

$$Q_0 = RT + C_z C_m W_r(s) \tag{4}$$

where

$$W_r(s) = \left(1 - \frac{1}{2}s\right)^{-3} \tag{5}$$

and C_z is a molecular constant characterizing the molecular sieves and C_m combines the molecular parameters polarizability and van der Waals radius of the sorbed molecules. $W_r(s)$ is the relative physisorption energy that depends only on the curvature parameter $s = d/a$, where a is the zeolite pore radius and d is the sorption distance. With the parameters C_z, C_m, d and a being 98.9, 0.19045, 3.79 Å (Derouane et al., 1987) and 7.3 Å, respectively, the heat of sorption at zero coverage for benzene in AlPO$_4$-5 estimated with the surface curvature model was −49.1 kJ/mol, which was in good agreement with the data in the literature (Choudhary et al., 1988; Stach et al., 1993; McCullen et al., 1993).

The heat of sorption at zero coverage for benzene in AlPO$_4$-5 from the surface curvature model was higher than that in CoAlPO$_4$-5 in the present work. Because of the little difference in the pore dimensions between the CoAlPO$_4$-5 and AlPO$_4$-5 molecular sieves, the variances of the sorption properties due to the pore size could be excluded. The tetrahedral Co in the framework coexisted with the octahedral ones that might present as cobalt oxide, and/or dense-phase cobalt phosphate. The lower heats of sorption for benzene in CoAlPO$_4$-5 than that in AlPO$_4$-5 could presumably result from the variance in the electric field caused by the substitution of cobalt.

3.3. Isosteric Heat of Sorption with the Coverage

The dependence of isosteric heat of benzene sorption in CoAlPO$_4$-5 on the loading was shown in Fig. 2. The isosteres were also shown in Fig. 3, which indicated the good consistency of the sorption data obtained in this work.

As shown in Fig. 2, the heat of sorption for benzene in CoAlPO$_4$-5 did not depend markedly on the sorption loading up to 0.45 mmol/g due to that the interactions between benzene molecules were marginal in

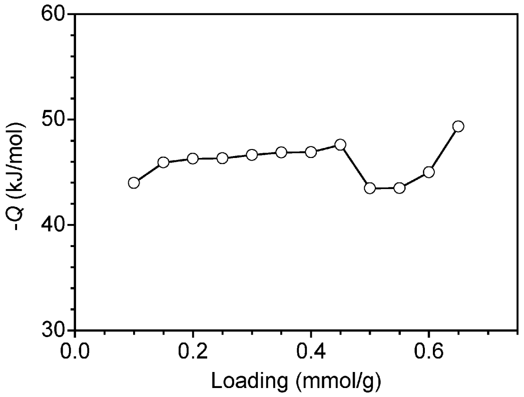

Figure 2. Dependence of isosteric heat of sorption for benzene in CoAlPO$_4$-5 on the loading.

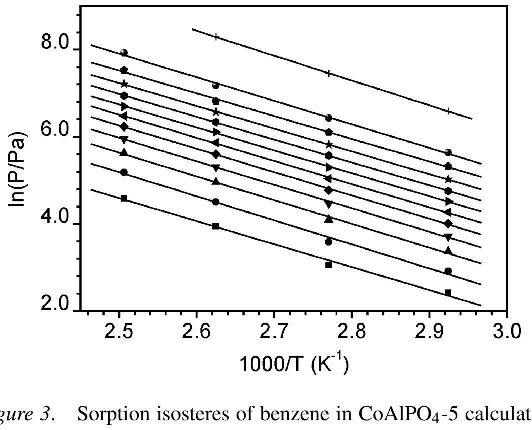

Figure 3. Sorption isosteres of benzene in CoAlPO$_4$-5 calculated from the sorption isotherms using Clausius-Clapeyron equation: the loading of benzene increased in the sequence of 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6 and 0.7 mmol/g (from bottom to top).

the channels. This reflected an energetically uniform surface within the CoAlPO$_4$-5 channels. The subsequent variation in the heat of sorption with the loading higher than 0.45 mmol/g implied the importance of sorbate-sorbate interactions; it seemed to be associated with a cooperative redistribution and/or reorientation of sorbed molecules, for example, the formation of benzene dimmers (Thamm et al., 1987).

4. Conclusion

The sorption isotherms of benzene in CoAlPO$_4$-5 at temperatures of 323–399 K were measured by gravimetric technique. The isotherms followed the typical type-I shape, and could be well fitted with Langmuir and Dubinin-Radushkevich equations. The sorption capacity and isosteric heat were estimated and interpreted on the basis of the pore topologies of the molecular sieves.

The sorption capacity decreased with the increase of temperature. The isosteric heats of sorption varied with the coverage, which may suggest a shift of sorbate-sorbent interactions and molecular packing manner in the sorbed phase.

Nomenclature

a	Zeolite pore radius (Å)
B	Langmuir constant (mmol g^{-1} Pa^{-1})
C_m	Parameters for the sorbed molecule
C_z	Molecular constant characterizing the zeolite
d	Sorption distance (Å)
D	Dubinin-Raduskavich constant
p_s	Saturation pressure of sorbate (Pa)
p	Equilibrium pressure (Pa)
Q	Heat of sorption (kJ/mol)
R	Gas constant (J mol^{-1} K^{-1})
S	Curvature parameter
T	Temperature (K)
V_m	Langmuir sorption capacity (mmol/g)
W	Amounts sorbed (mmol/g)
W_0	Dubinin-Raduskavich sorption capacity (mmol/g)

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