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Short communication

Adsorption of benzene and cyclohexane on γ-Al_2O_3 and Pd/γ-Al_2O_3 at elevated temperature and pressure

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Abstract

Adsorption of benzene and cyclohexane on catalyst supports γ-Al_2O_3 and catalyst pellets Pd/γ-Al_2O_3 was studied from 393 to 453 K over an adsorbate relative pressure range of 0.2–1.0. The corresponding adsorption isotherms, which were experimentally measured in the range of the relative pressure p/p^0 larger than 0.2, were considered to be type IV, and can be simulated by a simple adsorption model. The adsorption isotherm of benzene was similar to that of cyclohexane. Compared with the adsorption isotherm of benzene on γ-Al_2O_3, a similar one was obtained on Pd/γ-Al_2O_3 except that the hysteresis loop appeared a little bit earlier. As far as adsorption of benzene on γ-Al_2O_3 was concerned, only physisorption was involved. But when it came to Pd/γ-Al_2O_3, both chemisorption and physisorption occurred, and the chemisorption process facilitated the formation of monolayer, multilayer and capillary condensation in spite of the lower metal loading of the catalyst.

Keywords: Adsorption; Benzene; Cyclohexane; Catalyst; Chemisorption

1. Introduction

Being a good probe molecule, benzene or cyclohexane has often been used to characterize porous adsorbents. Previous studies on adsorption of benzene or cyclohexane on porous media are mainly conducted at normal temperature and pressure. Nguyen et al. [1] studied adsorption of benzene on a series of MCM-41 samples at lower temperatures. Similarly, Shim et al. [2] measured adsorption isotherms of benzene on palletized MCM-48 materials at normal temperature. Adsorption of benzene on silicalite-1 was studied by Ban et al. [3], however, capillary condensation was not involved because of the micropore framework of silicalite-1 used. Although Asnin et al. [4] investigated adsorption of benzene on γ-Al_2O_3 at a higher temperature range of 413–572 K, the partial pressure of benzene was no higher than 1000 Pa. As far as the industrial application is concerned, such as benzene hydrogenation to cyclohexane, knowledge of adsorption of reactants on catalyst pellets at elevated temperature and pressure is actually interesting for chemical engineers since the overall mass transfer of reactants is controlled to some extent by the vapor–liquid equilibrium in the catalyst, which is associated with the adsorption behavior of reactants [5]. Unfortunately, few pertinent results have been reported so far.

Another aspect, to be paid much attention to, is the effect of the active metal atoms distributed on the support surface on the adsorption isotherms of reactants. Compared to adsorption of gases on catalyst supports, adsorption of reactants on catalyst pellets exhibits more or less different behaviors on account of the active metal atoms on the surface of the catalyst. As a result, the adsorption isotherms for the two cases may be different. Many studies were reported on adsorption of different adsorbates on catalysts, e.g., H_2S on a sulfided CoMo/Al_2O_3 catalyst [6], *n*-alkanes (C_8–C_{12}) on a commercial Pd/Al_2O_3 catalyst [7], 2,2,4-trimethylpentane and toluene on a monolithic light-off catalyst [8], etc., however, only monolayer adsorption in these cases was taken into account due to the much lower partial pressure of adsorbate. The subsequent multilayer adsorption and capillary condensation at higher partial pressure were not investigated. Nevertheless, a complete adsorption isotherm, especially in the case of multilayer adsorption and capillary condensation, is very useful particularly for those reactions where reactants are apt to condense in capillary pores [9,10]. Therefore, an investigation on the effect of active metal atoms on capillary condensation of reactants will be very attractive.

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In our previous paper [11], some preliminary results of adsorption of benzene and cyclohexane on Pd/γ-Al_2O_3 at higher temperature and pressure were reported for the first time, in which adsorption isotherms of benzene and cyclohexane were experimentally measured, and a simple model combining multilayer adsorption and capillary condensation was derived to correlate the adsorption equilibrium data. In context to the previous work, the objective of this contribution is to further study adsorption of benzene, cyclohexane and their mixtures on a commercial hydrogenation catalyst and its support at elevated temperature and pressure, and qualitatively analyze the impact of chemisorption caused by the active metal atoms on the adsorption isotherm by comparison of the results obtained between the catalyst and the catalyst support. These results will conduce to some insight into this complex process accompanied by chemisorption, monolayer and multilayer adsorption as well as capillary condensation.

2. Experimental

The experimental setup is given schematically in Fig. 1. Experiments were conducted in a fixed bed from 393 to 453 K over an adsorbate relative pressure range of 0.2–1.0. The adsorption bed was put in an oil bath where variations in temperature can be controlled within 0.2 °C. The temperature was measured by a calibrated nichrome nickel–copper thermocouple (0–600) °C, which had an accuracy of ±0.5 °C by comparison with a platinum resistance thermometer.

The adsorption bed was preheated to a desired temperature under N_2 protection, and then nitrogen was shut off, and the porous adsorbent was degassed with a vacuum pump for 5 h. Finally, the liquid adsorbate, benzene or cyclohexane or their mixture was introduced at a certain flow rate using a metering pump. The adsorbate was vaporized and preheated to a desired temperature before leading to the adsorption bed. After passing through the adsorption bed at a given pressure, the extra adsorbate was condensed and collected in a sample tank. The weight variation of the condensed adsorbate was measured by an electronic balance, whose accuracy was of the order of 0.0001 g. The system pressure was exactly controlled by a back-pressure regulator.

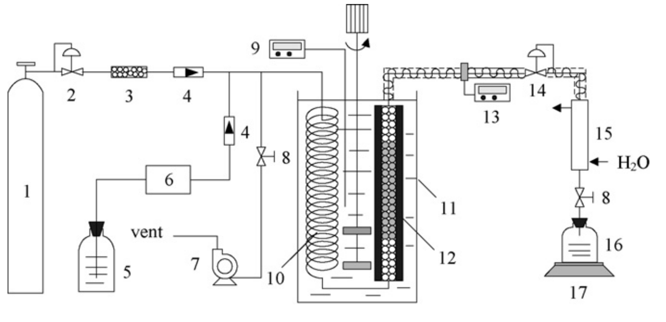

Fig. 1. Schematic diagram of the experimental apparatus. (1) Nitrogen, (2) pressure regulator, (3) dehydrator, (4) check valve, (5) liquid tank, (6) metering pump, (7) vacuum pump, (8) valve, (9) temperature controller, (10) evaporator, (11) oil bath, (12) adsorption bed, (13) manometer, (14) back-pressure regulator, (15) condenser, (16) sample tank, and (17) electronic balance.

The equilibrium adsorption quantity equaled the difference between the accumulative amount of inlet adsorbate and that of outlet adsorbate minus the amount of the adsorbate occupying the vacant volume of the system.

The commercial Pd/γ-Al_2O_3 catalyst and its support γ-Al_2O_3 were supplied by Shanghai HengYe Molecular Sieve Co. Ltd., and the palladium content was 0.5 wt.%. The catalyst was reduced by hydrogen at 473 K for 12 h prior to adsorption experiments. Benzene and cyclohexane were purchased from Sinopharm Group Chemical Reagent Co. with specified minimum mass fraction purities of 0.995. They were used without further purification. The physical properties of benzene and cyclohexane are provided in the literature [12,13].

3. Results and discussion

Pore size distribution of the catalyst and its support is measured by the standard nitrogen adsorption–desorption method with a Micrometrics ASAP 2010 apparatus. As seen from Fig. 2, pore size distribution of catalyst pellets is approximately the same as that of catalyst supports, which can be ascribed to the lower metal loading as well as the impregnation method used for preparing the catalyst.

Fig. 3 presents the adsorption isotherm of benzene on γ-Al_2O_3 at different temperatures. A short segment of the adsorption isotherm corresponding to the lower relative pressure ($p/p^0 = 0$–0.2) is not measured due to the experimental method used in this work. The solid line in Fig. 3 is calculated by a simple adsorption model [11]. Taking into account multilayer adsorption and capillary condensation, this model combines a modified Halsey equation and the Kelvin equation. The good agreement between the measured data and the predicted indicates that the adsorption model is favorable. It is clear that the adsorption isotherm of benzene on γ-Al_2O_3 is type IV. The beginning point of the hysteresis loop (shown by C) moves backwards in terms of the relative pressure with temperature variation from 393 to 453 K. Moreover, the size of the hysteresis loop becomes narrower with increased temperature. These phenomena are justifiable because the critical pore radius above which capillary condensation can occur increases with temperature [14].

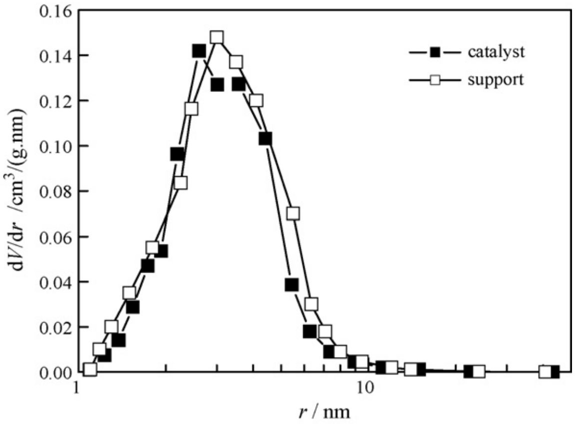

Fig. 2. Pore size distribution of catalyst pellets and catalyst supports.

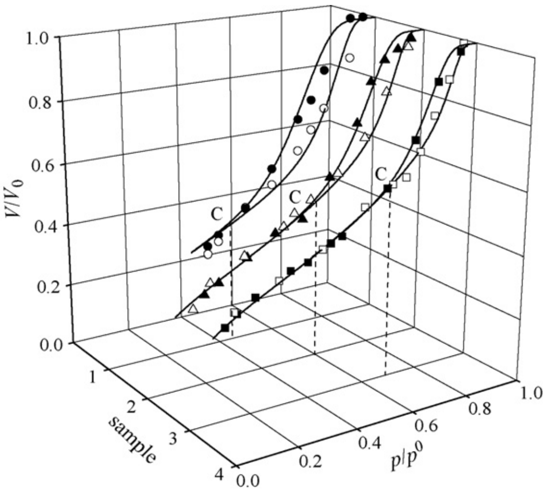

Fig. 3. Adsorption isotherm of benzene on γ-Al_2O_3. (●,○) 393 K; (▲,△) 433 K; (■,□) 453 K; (—) predicted.

A comparison of adsorption of benzene and cyclohexane on γ-Al_2O_3 at 433 K is presented in Fig. 4. Apparently, the adsorption isotherm of benzene at $p/p^0 = 0.2$–1.0 is similar to that of cyclohexane, which can be attributed to their similar properties. This similarity was also observed on a mesoporous silica gel at 298 K [15] or on MCM-48 at (303.15, 313.15 and 323.15) K [16]. However, it should be noted that this similarity is present only in the relative high-pressure region, and it may be not the case in the low-pressure region. It is well known that the adsorption of cyclohexane on γ-Al_2O_3 is non-specific adsorption, where only dispersion and repulsive forces are involved, whereas for benzene, it is specific adsorption, where Coulombic contributions are present additionally [15,17]. Therefore, in the low-pressure region, especially in the region where monolayer adsorption is occurred, the adsorption isotherm of benzene on γ-Al_2O_3 is most likely different from that of cyclohexane due to the different forces involved. This result has indeed been proved by the adsorption of benzene and cyclohexane on a mesoporous silica gel at 298 K [15], where the isotherms of benzene and cyclohexane are different in the low-pressure region (the isotherm of benzene is concave to the pressure axis, whereas for cyclohexane, its isotherm is convex), but they are similar in the high-pressure region. Unfortunately, the isotherms of benzene and cyclohexane in the low-pressure region ($p/p^0 = 0$–0.2) cannot be measured by the present experimental method in this study.

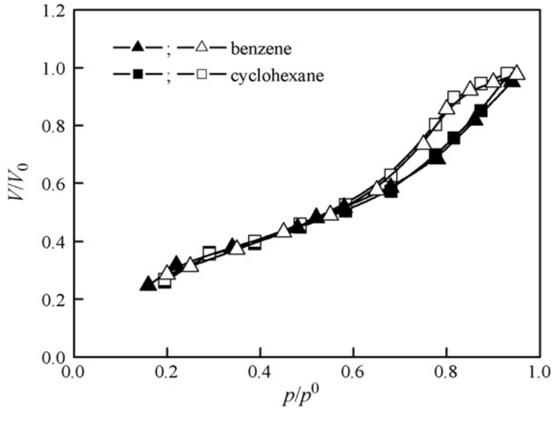

Fig. 4. Comparison of adsorption of benzene and cyclohexane on γ-Al_2O_3 ($T = 433$ K).

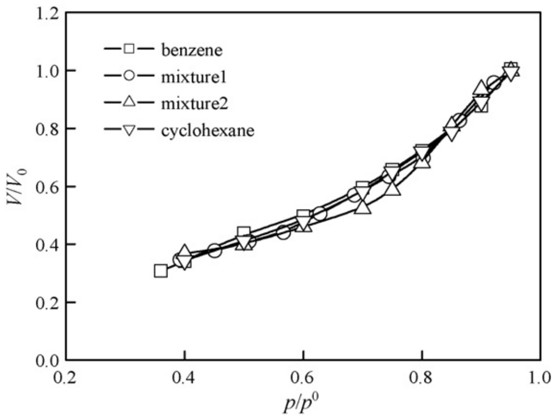

Fig. 5. Comparison of adsorption of benzene, cyclohexane and their mixture on γ-Al_2O_3 ($T = 393$ K).

To further clarify the similarity of adsorption of benzene and cyclohexane on γ-Al_2O_3, two kinds of mixtures of benzene and cyclohexane were used as adsorbate with benzene/cyclohexane molar ratio of 1:1 (mixture 1) or 7:3 (mixture 2). In these experiments, two separate steps were carried out. One step was that the outlet adsorbate was regularly analyzed using a gas chromatography (GC6890, Agilent) instead of being weighed for measuring the adsorption isotherm, while the other step was just contrary. In both cases, the experimental procedure and operation parameters were kept identical.

It is very interesting that the composition of outlet adsorbate is almost identical with that of inlet adsorbate. The composition of the adsorbate is not changed after passing through the adsorption bed, which indicates that adsorption of benzene and cyclohexane on γ-Al_2O_3 is noncompetitive. Fig. 5 shows the adsorption branches of benzene, cyclohexane and their mixtures. It is obvious that the adsorption branches of these adsorbates are very similar. All of these demonstrate that benzene and cyclohexane can be regarded as one and the same component in the case of adsorption of these adsorbates on γ-Al_2O_3.

The adsorption isotherm of benzene on catalyst pellets is measured by the same procedure above-mentioned. As seen from Fig. 6, the adsorption isotherm of benzene on catalyst supports at 393 K (Fig. 6(a)) is similar to that on catalyst pellets except that the beginning point of the hysteresis loop (shown by S) for catalyst pellets appears a little bit earlier than for catalyst supports. A similar result is also obtained at 433 K (Fig. 6(b)). It seems that the palladium atoms supported on the internal surface of the catalyst pellet facilitate capillary condensation of benzene in the pore.

Adsorption of benzene on γ-Al_2O_3 is indeed different from that on Pd/γ-Al_2O_3. In the former case, only physical adsorption (physisorption) occurs, while in the latter case, both physisorption and chemical adsorption (chemisorption) take place because of the formation of strong chemical bond between the benzene

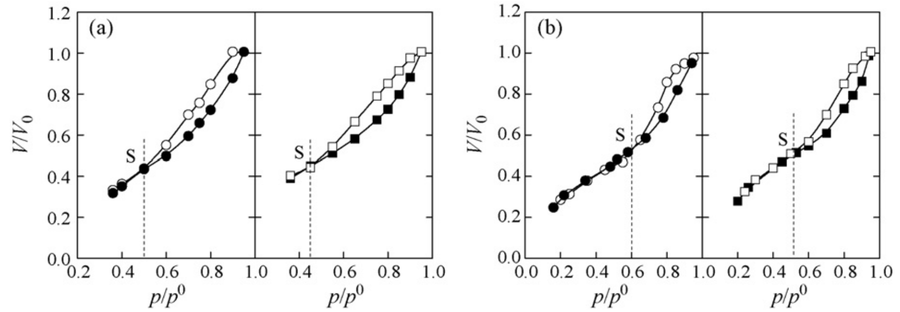

Fig. 6. Comparison of adsorption of benzene on γ-Al_2O_3 and Pd/γ-Al_2O_3. (a) 393 K; (b) 433 K; (○,●) γ-Al_2O_3; (■,□) Pd/γ-Al_2O_3.

molecule and the palladium atom on the surface of the catalyst. With regard to the strong chemisorption of benzene on active metals such as palladium or platinum, many meaningful researches have been done [18,19]. However, none is concerned with the impact of chemisorption on the isotherm of benzene or cyclohexane.

Considering that the adsorbate pressure needed for the formation of a monomolecular adsorbed layer in the chemisorption process is much lower than that in the physisorption process [20], chemisorption of benzene on active sites of the catalyst firstly occurs at a lower relative pressure, and then physisorption of benzene on the remained surface starts with an increase in relative pressure. Therefore, in contrast to the single physisorption process, combination of chemisorption and physisorption process makes easier the monolayer formation of benzene on Pd/γ-Al_2O_3, which in turn accelerates the multilayer formation and capillary condensation. In a similar case, a comparison of adsorption isotherms of *n*-decane between Pd/Al_2O_3 and Al_2O_3 proved that the catalyst performed better as an adsorbent than alumina [7]. Kruk and Jaroniec [21] also pointed out that low-pressure hysteresis may arise when physisorption was accompanied to some extent by chemisorption process.

The reason why the difference between the adsorption isotherm of benzene on γ-Al_2O_3 and that on Pd/γ-Al_2O_3 is very small is that the metal loading of the catalyst is too low, which is only 0.5 wt.%. Given the uniform dispersion of the palladium atoms on the surface of the catalyst, the surface area occupied by the palladium atoms can be easily calculated using the following expression:

$$S_{\mathrm{Pd}} = \frac{wN_{\mathrm{A}}}{M}\pi r^2 \qquad (1)$$

where w is the metal loading, N_{A} Avogadro constant, M the molecular weight, and r the atomic radius of palladium, $r = 1.79$ Å. The calculated S_{Pd} is 2.85 m^2/g, which is only 1% of the total surface area of the catalyst. Thus, although chemisorption has an effect on the adsorption isotherm, the lower palladium loading makes its effect weakened. It can be anticipated that the higher the loading quantity of palladium in the catalyst is, the earlier the hysteresis loop arises.

Just as shown elsewhere [11], in the viewpoint of engineering application, the aforementioned adsorption model is still capable of describing adsorption of benzene or cyclohexane on Pd/γ-Al_2O_3 (Pd: 0.5 wt.%) by neglecting the chemisorption effect. However, it should be kept in mind that the chemisorption process plays a more and more important role with the increased metal loading of the catalyst.

4. Conclusion

Adsorption of benzene and cyclohexane on catalyst pellets Pd/γ-Al_2O_3 and catalyst supports γ-Al_2O_3 is studied at elevated temperature and pressure in this work. In contrast to previous studies, which have examined monolayer adsorption of adsorbate molecules in the low relative pressure region, this study investigates the multilayer adsorption and capillary condensation at the high relative pressure of adsorbate. Moreover, the effect of chemisorption on the capillary condensation of adsorbate is elucidated.

It is shown that the adsorption isotherm of benzene at $p/p^0 = 0.2$–1.0 is very similar to that of cyclohexane. The hysteresis loop of the adsorption isotherm is found to appear slightly earlier for catalyst pellets than for catalyst supports, which can be ascribed to the chemisorption process between the adsorbate and the palladium atoms as well as the physisorption process. The chemisorption process has a positive effect on the formation of monolayer, multilayer and capillary condensation of the adsorbate.

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