Numerical Adsorption Simulation of Low-Concentration Ammonia

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Abstract

In numerical simulations to predict breakthrough behaviors of a detoxifier to remove trace ammonia remaining in hydrogen produced by ammonia cracking, the equilibrium adsorption amount has been determined from the fitting equation of adsorption isotherm, but for low-concentration gases, the prediction accuracy of breakthrough time is low. In this study, several measurements with varying dose pressure and temperature were carried out to measure the ammonia adsorption isotherms of zeolite that can correspond to low-concentration gas breakthrough experiments. These isotherms were formulated by Roginsky's dispersion function method. This allowed us to predict breakthrough time for low-concentration gas on the order of ppm.

1. Introduction

Hydrogen has been gaining attention in recent years due to its environmentally friendly nature and the fact that its heat of combustion per unit mass is the highest among all chemical fuels. However, its critical temperature is extremely low at 33 K, and its critical pressure is also relatively low at 1.3 MPa. As a result, the energy per unit volume of hydrogen is very small at room temperature. Additionally, hydrogen has a wide flammability range of 4% to 75%, making it highly explosive, and its flame is both high-temperature and invisible. Therefore, techniques for storing hydrogen more safely and at higher densities are required.

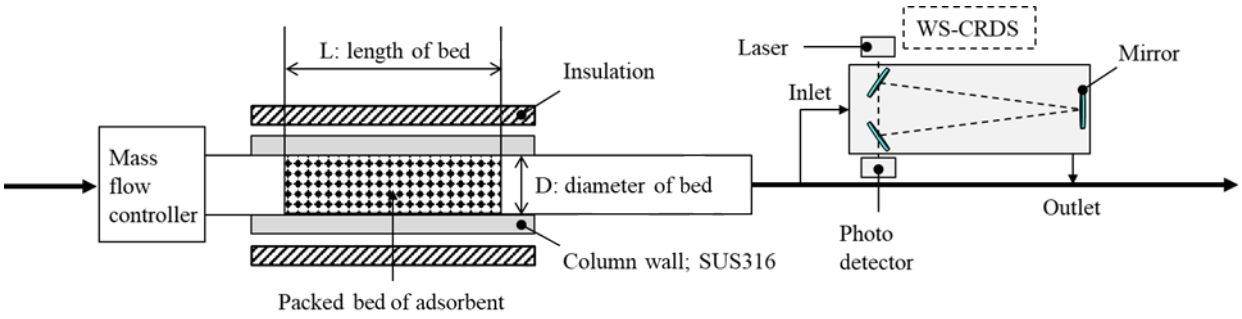
As means of storing and transporting hydrogen energy, the use of hydrogen compounds such as metal hydrides, ammonia borane, and methylcyclohexane is being explored[1,2]. Among these, liquid ammonia has attracted attention due to its ability to liquefy easily at 1 MPa even at room temperature and its high combustion heat per unit volume[3]. Furthermore, since the number of hydrogen atoms per unit volume is 1.5 times that of liquid hydrogen, it possesses excellent characteristics as a hydrogen carrier. However, since ammonia has high toxicity and corrosiveness even at low concentrations in the ppm range, any residual ammonia must be removed, whether it is cracked into hydrogen or used directly. In terms of level, when using it as a hydrogen source for polymer electrolyte fuel cells, which are also installed in fuel cell vehicles, the residual ammonia concentration must be reduced to 0.1 ppm or lower to suppress fuel cell degradation caused by poisoning[4]. There are various ways to remove ammonia, but adsorption-based decontamination using an adsorbent was adopted as a method capable of handling low-concentration ammonia while allowing for a large processing capacity[5-9]. Aisan Industry Co., Ltd. has a proven track record in designing and manufacturing charcoal canisters as gasoline vapor adsorption devices, and its expertise is also expected to be applicable. An important factor in designing a decontamination device is predicting the breakthrough characteristics, which describe the time dependence of ammonia that flows downstream of the device. Numerous studies have reported the use of numerical simulations to predict the breakthrough characteristics of volatile organic compounds and carbon dioxide adsorption. However, characteristics on the order of ppm have not been examined[10-14]. This study focuses on the adsorption behavior of low-concentration ammonia on zeolite and develops a simulation model of an adsorption tower capable of predicting breakthrough characteristics at the ppm level, which are generally difficult to predict.

2. Experiment and Simulation

2.1. Experimental Method

Various adsorbents are suitable for ammonia adsorption; however, in this study, we used Na-exchanged X-type zeolite (NaX; F9-HA; Tosoh Corporation), which is inexpensive, has a high adsorption capacity, and allows desorption of adsorbed ammonia simply by heating[15]. The breakthrough experiment was conducted using the apparatus shown in Figure 1. Most parts of the apparatus were the same as those used in the previous study by Miyaoka et al.[16]. The column had an inner diameter of 25 mm, and the zeolite was measured and packed to achieve a packed bed length of 100 mm. The packed bed was fixed using glass wool, a perforated metal plate, and a coil spring. As a pretreatment for the breakthrough experiment, the column was heated to 350°C while flowing argon at 100 L/h until the ammonia concentration meter indicated less than 0.1 ppm, after which it was cooled to the experiment temperature. The ammonia gas mixture used in the experiment was a pre-adjusted gas with a composition ratio of 74.9% hydrogen,

Figure 1 Schematic diagram of breakthrough experiment apparatus



25% nitrogen, and 1000 ppm ammonia. The breakthrough curve represents the time dependence of the ammonia concentration in the gas exiting the column and the residence time.

The ammonia adsorption isotherm was measured using a BELSORP-max (MicrotracBEL). In this apparatus, the sample tube containing zeolite was evacuated, and pure ammonia was dosed in small increments. The amount of adsorption was then calculated based on the equilibrium pressure before and after the dosing of ammonia in the sample tube and the apparatus piping.

2.2. Simulation Method

The simulation is based on a model that simultaneously solves the adsorption isotherm, mass conservation law, energy conservation law, and adsorption rate equation. Calculations were performed using Dymola 2017 by Dassault Systems. This model is based on the following assumptions:

(1) The supplied gas is an ideal gas composed of two components: ammonia and a carrier gas.
(2) Local thermal equilibrium is assumed, meaning the gas and the adsorbent at a given location have the same temperature.
(3) The molecular diffusion term in the mass conservation and energy conservation equations is considered negligible compared to the advection term.
(4) The adsorption rate equation is expressed using the linear driving force approximation.
(5) Zeolite adsorbs only ammonia, while adsorption of the carrier gas is neglected.
(6) The initial temperature and pressure within the column are uniform.
(7) The dependence of physical quantities on the radial direction of the column is ignored.
(8) The porosity within the column, the bulk density of the adsorbent, and the specific heat capacities of both the column and the adsorbent are constant.

Based on these assumptions, the following set of equations was derived.

The law of mass conservation is expressed as follows:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial (u\rho)}{\partial x} - \frac{\hat{\rho}_z}{\varepsilon}\frac{\partial q}{\partial t} \tag{1}$$

where $\rho\ (\mathrm{kg/m^3})$, $u\ (\mathrm{m/s})$, $t\ (\mathrm{s})$, $x\ (\mathrm{m})$, ε, $q\ (\mathrm{kg/kg\ NaX})$ and $\hat{\rho}_z\ (\mathrm{kg/m^3})$ represent the density of the mixed gas, the superficial velocity, time, the coordinate along the column axis, the porosity, the amount of ammonia adsorbed per unit mass of zeolite, and the bulk density of the zeolite, respectively.

The law of energy conservation is expressed as follows:

$$C_{P,z}\hat{\rho}_z\frac{\partial T}{\partial t} = -\varepsilon C_{P,g}\rho u\frac{\partial T}{\partial x} + Q_{in} + W \tag{2}$$

where $C_{P,z}\ (\mathrm{J/kg/K})$, $C_{P,g}\ (\mathrm{J/kg/K})$, $C_{P,g}\ (\mathrm{J/kg/K})$, $T\ (\mathrm{K})$, $Q_{in}\ (\mathrm{W/m^3})$ and $W\ (\mathrm{W/m^3})$ represent the specific heat of zeolite, the specific heat of the mixed gas, the temperature of the mixed gas, the heat influx from the column wall, and the adsorption heat, respectively.

The adsorption rate equation is given as follows:

$$\frac{\partial q}{\partial t} = k_f\hat{\rho}_{\mathrm{NH_3}}\left(\frac{P_{\mathrm{NH_3}} - P^*_{\mathrm{NH_3}}}{P}\right) \tag{3}$$

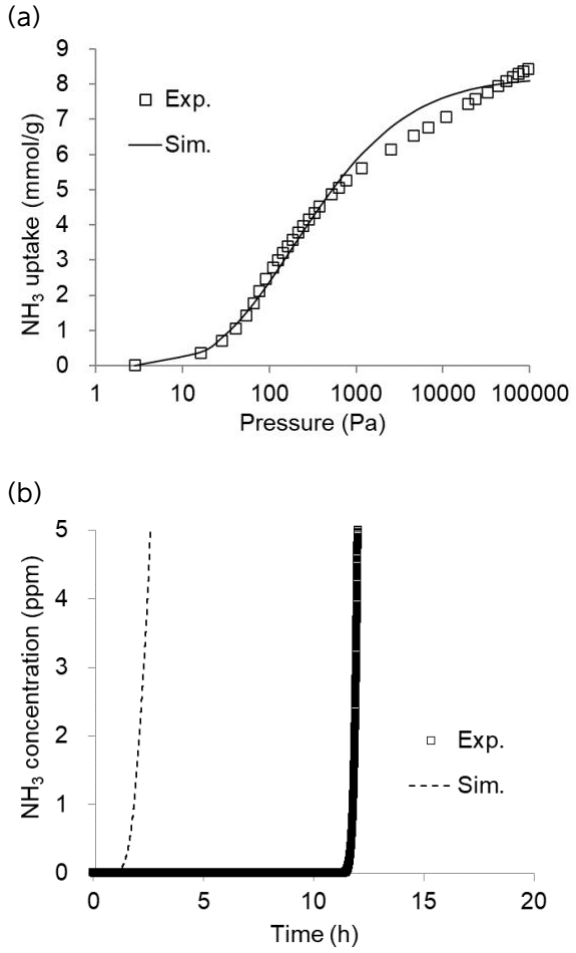
where $\hat{\rho}_{\mathrm{NH_3}}\ (\mathrm{kg/m^3})$, $P^*_{\mathrm{NH_3}}\ (\mathrm{Pa})$ and $P_{\mathrm{NH_3}}\ (\mathrm{Pa})$ represent the density of pure ammonia gas, the interfacial partial pressure of ammonia, and the partial pressure of ammonia, respectively. The interfacial partial pressure of ammonia refers to the hypothetical ammonia partial pressure that would be in equilibrium with the adsorbed amount q. k_f is the adsorption rate coefficient, and in this model, Yoshida's equation is adopted[17]:

$$(k_f/u)(\mathrm{Sc})^{2/3} \propto [\mathrm{Re}/(1-\varepsilon)]^{-0.51} \tag{4}$$

where Re and Sc represent the Reynolds number and the Schmidt number, respectively.

The adsorption isotherm expresses the equilibrium relationship between pressure and adsorption amount, which is necessary for determining the interfacial partial pressure of ammonia, and various equation models exist. The Dubinin–Astakhov model[18] was used to design the charcoal canister, assuming that gasoline vapor is adsorbed in liquid form. On the other hand, in the case of ultra-low concentration ammonia adsorption, the adsorption amount is small, causing ammonia molecules to be directly adsorbed onto the zeolite surface. Based on previous research on hydrogen adsorption, it is expected that the adsorption state on the outermost surface of the adsorbent will not be able to be considered a liquid[19]. Therefore, in this study, a specific adsorption model was adopted. Furthermore, since ammonia, like water, is a polar molecule, previous research by Shirono et al. on water molecule adsorption onto zeolite was also referenced[20]. Shirono et al. demonstrated through molecular simulations that NaX zeolite possesses three types of cations, but only two

Figure 2 (a) Adsorption isotherm of ammonia at T = 298 K, (b) Breakthrough curve of ammonia at T = 298 K



function as adsorption sites. These two adsorption sites do not interact with ammonia molecules in a one-to-one manner; rather, adsorption can also occur at intermediate positions between the two sites. Taking these factors into account, this study developed a model incorporating specific adsorption heterogeneity, referring to the method by Roginsky et al.[21]. The distribution function of adsorption sites follows a Gaussian distribution with respect to adsorption energy. Assuming that this distribution is independent of temperature, the equation for equilibrium adsorption capacity is given as follows:

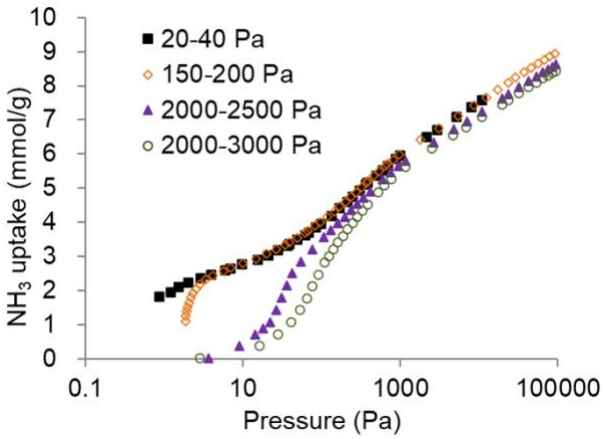
$$q = q_t \left[1 - \frac{1}{2}\mathrm{erfc}\left(-\frac{\tilde{E}}{\sqrt{2}}\right)\right] \tag{5}$$

where q_t (kg/kg-NaX) represents the maximum adsorption capacity, erfc is the complementary error function, and ($\tilde{E}$) is given by:

$$\tilde{E} = \frac{-RT\ln K_0 P^*_{\mathrm{NH_3}} - E_0}{\sigma} \tag{6}$$

where E_0, σ^2, and K_0 are parameters corresponding to the mode, standard deviation, and equilibrium coefficient, respectively. R is the gas constant. In this model, the adsorption heat is expressed as:

Figure 3 Adsorption isotherm of ammonia measured at T = 298 K with varying dosing pressures



$$W = -\frac{1}{\hat{V}_{\mathrm{NH_3}}}\frac{\partial q}{\partial t}\left[RT\ln K_0 P^*_{\mathrm{NH_3}}\right] \tag{7}$$

where $\hat{V}_{\mathrm{NH_3}}$ $(\mathrm{m^3/mol})$ is the molar volume of pure ammonia gas.

Equation (5) for the adsorption isotherm contains three parameters. However, since predicting these values theoretically is difficult, in practice, the adsorption isotherm is experimentally measured, and the results are fitted to formulate the equation and apply it to the simulation model.

3. Results and Discussion

3.1. Exploratory Experiment Results

A mixed gas was supplied to a column filled with zeolite at a flow rate of 275 L/h (stp). The temperature was 298 K, and the pressure was 114 kPa. A numerical simulation was conducted under the same conditions as this experiment to verify the validity of the model. Figure 2a shows the measured adsorption isotherm used in the simulation along with the fitting results, while Figure 2b presents the breakthrough experiment results and the simulation results. In Figure 2b, regardless of the value of the fitting parameter k_f, the simulation results indicate that the ammonia concentration begins to increase much earlier than the experimental results. This suggests that the amount of adsorption in the simulation is smaller than the actual adsorption amount. Since the adsorption amount in the simulation is determined based on the adsorption isotherm, and the isotherm appears to be well-fitted in Figure 2a, this result implies that the static adsorption amount obtained from the adsorption isotherm measurement and the dynamic adsorption amount obtained from the breakthrough experiment may differ.

Since the breakthrough experiment is conducted using a mixed gas, the total pressure remains above atmospheric pressure even when the partial pressure of ammonia is low. On the other hand, the adsorption isotherm measurement is performed using pure ammonia gas. For realizing the low partial pressure of ammonia, the total pressure should be low.

Figure 4 (a) Adsorption isotherms at various temperatures (plotted points represent measured values, while the solid lines indicate the approximation formula), (b) Distribution of adsorption sites calculated from adsorption isotherms

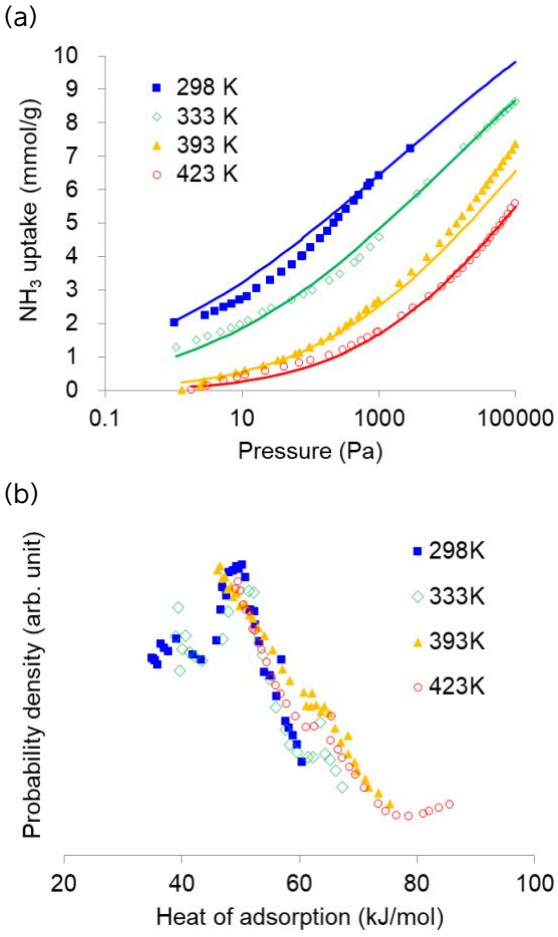
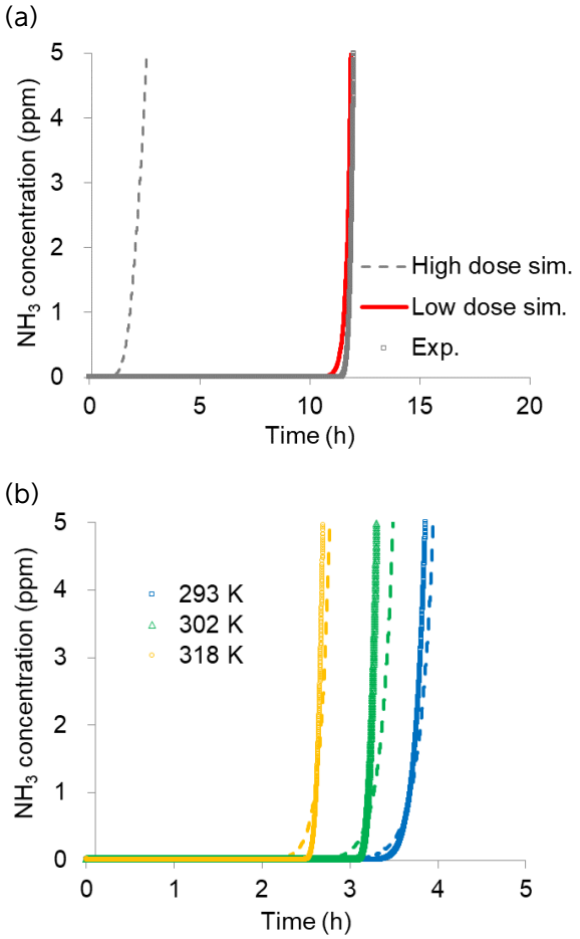


Figure 5 (a) Breakthrough curve using the improved (Low dose) model, (b) Breakthrough curves at various temperatures. The solid lines indicate measured values, while the dashed lines indicate simulation predictions.



In a previous study by Shirono et al., it was suggested that when water is adsorbed onto zeolite, it may form clusters around adsorption sites[20]. Since ammonia, like water, has strong polarity and is considered to form clusters in a similar manner, it is suggested that when the total pressure is low, these clusters prevent ammonia molecules from diffusing into the interior of the zeolite crystal, potentially reaching equilibrium with most adsorption sites remaining unused.

3.2. Experiment Results After Modification

Regarding diffusion inhibition, a similar phenomenon has been reported in the hydrogen storage process of palladium-coated magnesium[22]. Considering this analogy, the cause of clustering is presumed to be rapid adsorption. Therefore, during the measurement of the adsorption isotherm, an experiment was conducted in which the amount of dosed ammonia was reduced. The results of adsorption isotherm measurements conducted while varying the dosing pressure are shown in Figure 3. From these results, it can be observed that the adsorption amount in the region 10 Pa or below varies significantly depending on the dosing pressure. In the breakthrough experiment, ammonia is thought to have sufficiently diffused into the interior of the zeolite crystals. Therefore, the adsorption isotherm measured under the smallest dosing pressure, where adsorption is also expected to progress into the interior of the crystals, was deemed suitable for simulation. The results of adsorption isotherm measurements conducted while lowering the dosing pressure and further varying the temperature are shown in Figure 4a. The distribution function of adsorption sites was calculated based on these adsorption isotherms, yielding Figure 4b. This function was then fitted using a Gaussian distribution, formulated, and applied to numerical simulations.

Next, a simulation was conducted under the same conditions as the previous experiment, with a flow rate of 275 L/h (stp), a temperature of 298 K, and a pressure of 114 kPa, to determine the value of the fitting parameter k_f. As shown in Figure 5a, when the adsorption isotherm measured at a lower inlet pressure was applied to the simulation model, a solution emerged in which the breakthrough characteristics matched the experimental results. To verify the usefulness of the developed simulation model, breakthrough experiments were conducted under different conditions and compared with the simulation predictions. Figure 5b presents the results of a breakthrough experiment performed at a flow rate of 900 L/h (stp) and a pressure of 190 kPa, along with the corresponding

simulation predictions. The time required for a breakthrough concentration of 0.1 ppm was found to match within a margin of error of approximately 10%, even with variations in temperature and flow rate, demonstrating the model's ability to accurately predict breakthrough characteristics even at low ppm-level concentrations. Although the results are omitted here, the model also successfully predicted breakthrough characteristics in experiments where the column inner diameter and packed bed length were varied.

4. Conclusion

In this study, an unexpected result was obtained in the measurement of adsorption isotherms using the constant-volume method, where the adsorption amount varied depending on the dosing pressure. Among these adsorption isotherms, simulation results indicated that the isotherm measured at a lower dosing pressure corresponds to the breakthrough experiment. This dosing pressure dependency of the adsorption isotherm suggests the possibility of ammonia molecule clustering, but further detailed investigation is required. Additionally, the newly developed adsorption isotherm model formula is considered applicable to adsorbents with multiple types of adsorption sites and is expected to be useful not only for zeolites but also for other adsorbents such as MOFs and PCPs.

By incorporating two key factors, the measurement of adsorption isotherms corresponding to breakthrough experiments and the formulation of adsorption isotherms considering the heterogeneity of adsorption sites, it has become possible to develop a simulation model that accurately predicts breakthrough characteristics even at low concentrations on the order of ppm. These results can be utilized in techniques for the safe use of ammonia as a hydrogen carrier and are expected to contribute to the realization of a future hydrogen society.

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