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EFFECTS OF MODIFICATION AND CALCINATION CONDITIONS ON THE ADSORPTION PERFORMANCE OF RED MUD FOR LOW-CONCENTRATION FORMALDEHYDE IN AIR

The effects of modification and calcination conditions on the performance of red mud (RM) to absorb low-concentration formaldehyde in air were investigated using a fixed-bed flow reactor. The results show that the adsorption of RM for formaldehyde increases upon decreasing calcination temperature, with the optimum calcination temperature of 300 °C. H₂O₂ modification can improve the adsorption performance, with the optimum modification concentration at 20 wt. %. Pore structure analysis indicated that low-temperature calcination improves the formation of micropores (0.9 nm to 2.7 nm), and maximizes the specific surface area and total pore volume thereby facilitating formaldehyde adsorption.

1. INTRODUCTION

Formaldehyde is one of the most significant indoor air pollutants, which mainly comes from decorative materials such as wooden artificial boards, carpets, and plastic foam [1]. In recent years, the removal of formaldehyde from indoor air has become a focus of research in China. With respect to the indoor air formaldehyde removal, many techniques, including photocatalysis, non-thermal plasma and adsorption, have been investigated. However, low purification efficiency and high precious metal load of photocatalysis [2–5] and the high energy consumption and harmful byproducts of non-thermal plasma treatment [6, 7] limit the practical application of the catalysis and plasma methods.

Adsorption is one of the most effective methods of separating low-concentration pollutants from air, which has been successfully applied to the removal of organic compounds. However, traditional adsorbents are not suitable for the removal of indoor

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formaldehyde due to their low adsorptive rate and capacity. Therefore, research is needed to identify a low-cost alternative absorbent to remove formaldehyde from indoor air.

Red mud (RM) is a kind of high-alkaline solid residue produced by caustic digestion of bauxite ores during the production of alumina, being mainly composed of aluminum, iron, silicon, titanium oxides and hydroxides [8]. RM has become remarkably plentiful due to increasing alumina production. Due to its alkaline nature and the chemical and mineralogical species present in RM, this solid waste poses a significant threat to the environment, and the disposal of waste RM presents a huge challenge to the alumina industry. At present, RM produced from alumina plants is mostly treated by landfilling and ocean disposal [9]. However, the disposal cost is high, accounting for about 5% of alumina production [10]. Up to now, only a small amount of RM has been utilized for land composting [11], cement production [12], building material additives [13], and metal recovery [14].

In recent years, studies on RM as adsorbent and catalyst for wastewater treatment have been widely reported. It has been revealed that RM can be widely utilized to adsorb various aqueous pollutants with low cost and high efficiency. However, the use of RM in air purification has rarely been reported.

In this study, the removal of low-concentration formaldehyde in air by adsorption on the modified RM was investigated. The effects of modification and calcination conditions on the adsorption performance of RM for formaldehyde in air are investigated using a fixed-bed flow reactor. The relationship between pore structure and adsorptive property has also been established, based on the characterization and analysis of typical RM samples.

2. MATERIALS AND METHODS

Pretreatment of red mud. RM used in this research was procured from Shandong Aluminum Industry Co. Ltd. in China, and its main chemical composites are listed in Table 1.

Table 1

Composition of the red mud [%]

SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	TiO ₂	Ignition Loss
13.44	23.98	12.80	13.00	6.22	0.40	12.24	16.45

RM was first washed in water to remove fibrous debris and sand, and then dried at 105 °C for 12 h. After natural cooling to room temperature, it was ground and sieved. Finally, RM (20–40 mesh) was obtained and preserved for further modification.

The pretreated RM was soaked in H_2O_2 (from 0 to 30 wt. % at 50 °C) for 3 h. Then RM was mixed with deionized water and methyl cellulose at the weight ratio of 100:27:2.7.

The RM/water/methyl cellulose mixture was then calcined in a muffle furnace at 300–600 °C. Finally, the RM was ground and sieved into particular samples between 20 and 40 mesh.

Evaluation of adsorption performance. The adsorption properties of RM towards formaldehyde in air were evaluated in a continuous flow fixed bed reactor, with an adsorption tube diameter of 10 mm. A schematic diagram of the experimental system is shown in Fig. 1.

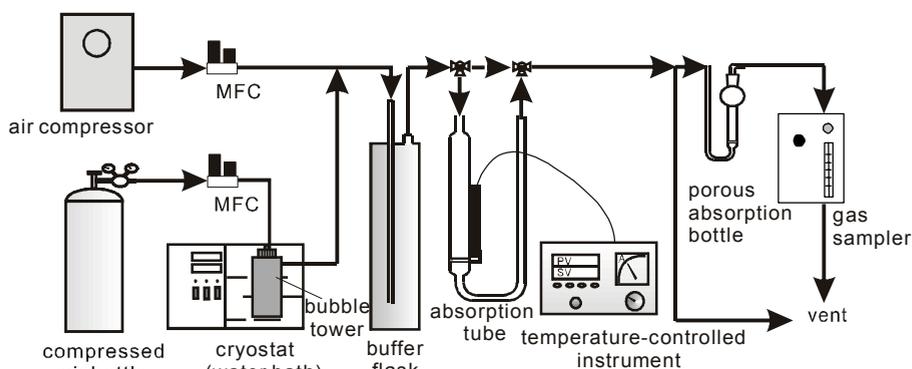


Fig. 1. Schematic diagram of RM adsorption evaluation system

Gaseous formaldehyde was introduced by passing dry air through a bubble tower containing 36 wt. % formaldehyde solution and then mixed with diluted air generated by an air compressor. The gas flow rate was controlled with a mass flow controller. The bubble tower containing formaldehyde solution was located in a thermostatic water bath with the temperature maintained at 13 °C to ensure the consistency of the formaldehyde concentration in the simulated air. The gas was completely mixed in a mixing chamber before introducing into the adsorption tube. The total gas flow rate was 600 cm^3/min , and the loading height and amount of absorbent were changed within the ranges of 1.0 cm to 2.5 cm and 0.60 g to 1.44 g, respectively, resulting in the space velocity of 1.83×10^4 – 3.18×10^4 h^{-1} . Operational temperature and relative humidity were 21 °C and 23%, respectively. The initial concentration of formaldehyde was 3.69 mg/m^3 .

The formaldehyde concentration in the gas stream was analyzed by the acetylacetone spectrophotometric method. The breakthrough curve of the RM was obtained by measuring the concentrations at the inlet and outlet of the adsorption tube vs. time. The breakthrough point was reached when the ratio of the outlet concentration (C) to

the inlet concentration (C_0) was 10%. The breakthrough time is defined as the time needed to reach the breakthrough point starting from the beginning of adsorption.

Sample characterization. Crystal morphology was identified using X-ray diffraction (XRD) equipment (Dmax-RB, Rigaku Company, Japan) with CuK_α radiation at 40 kV and 40 mA. The nitrogen adsorption-desorption isotherm was obtained using a NOVA 2200 e (Quantachrome, USA), Brunauer–Emmett–Teller (BET) calculations of a specific surface area, and Barrett–Joyner–Halenda (BJH) calculations of pore volume distributions from the desorption branch of the isotherm.

3. RESULTS AND ANALYSIS

3.1. EFFECTS OF H_2O_2 MODIFICATION ON ADSORPTION PERFORMANCE

The effects of H_2O_2 modification on the adsorption performance of RM were tested by comparing the RM modified with 20 wt. % H_2O_2 and calcined at $300\text{ }^\circ\text{C}$ with unmodified RM calcined at $300\text{ }^\circ\text{C}$. The breakthrough curves for each sample are presented in Fig. 2.

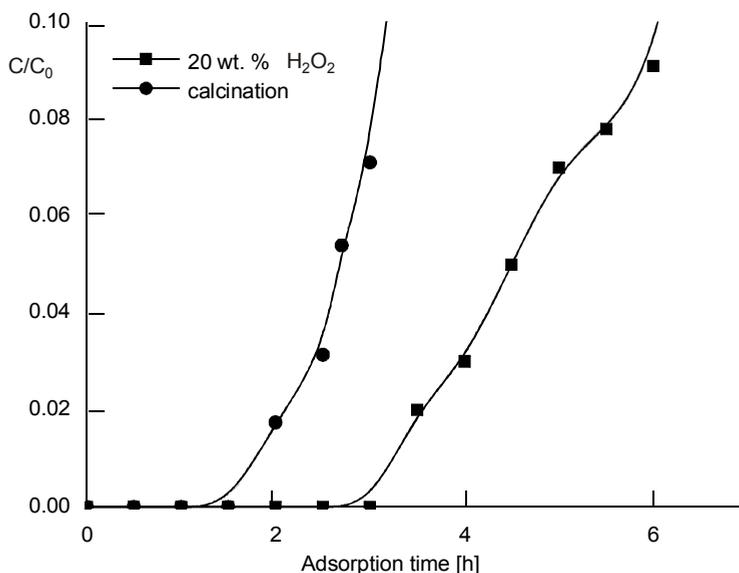


Fig. 2. Effect of H_2O_2 modification on adsorption performance; loading height – 1.0 cm, loading amount – 0.60 g, space velocity – $3.18 \times 10^4\text{ h}^{-1}$

The adsorption performance of the RM modified with 20 wt. % H_2O_2 is better than that of the unmodified RM, with breakthrough times of 6.2 h and 3.2 h, respectively.

H_2O_2 can significantly oxidize organic impurities of the RM, losing its structure and thereby facilitating the formaldehyde adsorption.

The effects of modification on the pore structure of RM were evaluated by comparing the two samples mentioned above by the BET nitrogen gas sorption method. The structural parameters are presented in Table 2. The variation in cumulative pore volume, with the pore diameter calculated using the BJH analysis method, is presented in Fig. 3.

Table 2

Pore structural parameters of the red mud samples at different modification conditions

Modification	Total pore volume $\times 10^{-2}$ [cm ³ /g]	Specific surface area [m ² /g]
Calcination at 300 °C	7.567	29.03
20 wt. % H_2O_2 and calcination at 300 °C	7.971	32.42

As seen in Table 2, H_2O_2 modification increases the specific surface area and total pore volume of the RM sample, thereby advancing the adsorption of formaldehyde and extending the breakthrough time.

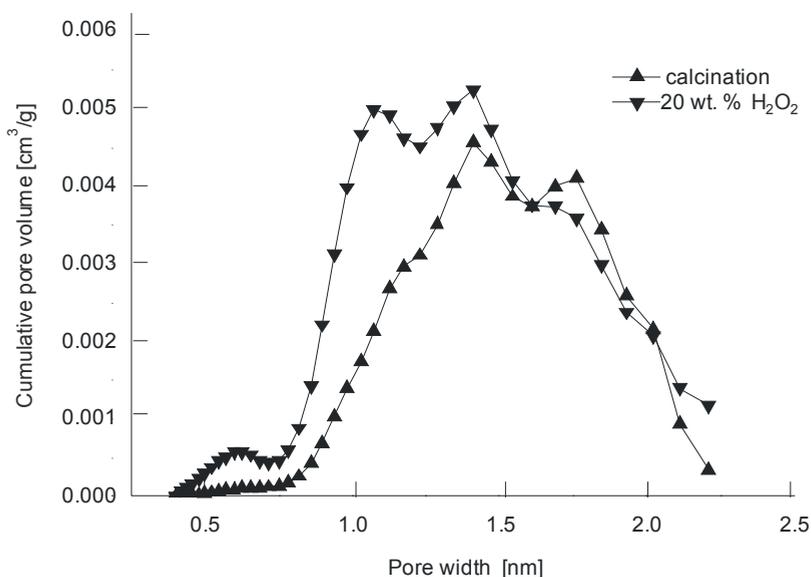


Fig. 3. Pore size distribution of RM samples at various modification conditions

As shown in Figure 3, the micropore distribution is higher in the sample modified with 20 wt. % H_2O_2 , which is consistent with the conclusion given by the pore structure parameters in Table 2. According to the results of the Lennard–Jones simulation

of potential energy, the potential adsorption energy of a parallel hole wall of the same diameter as the molecule is about 3.5 times greater than the energy of the surface of a single solid [15]. The diameter of formaldehyde molecules is approximately 0.45 nm [16]; overlaying adsorptive force fields on micropores with size ranges close to 0.45 nm can improve the thermal effect of physical adsorption of microporous materials due to the enhancement in adsorptive potential, and thus the adsorbent has a strong ability to capture formaldehyde molecules under relatively low pressure. The theoretical calculation indicates that slit type pores below two molecular diameters and circular type pores below six molecular diameters increase the of adsorption potential [17]. Therefore, microsors in RM, especially pores with diameters of 0.9 nm to 2.7 nm (two to six times of formaldehyde molecules), can greatly enhance the adsorption of formaldehyde.

The RM samples used to evaluate the effects of H_2O_2 concentration on adsorption performance of RM were soaked in 10 wt. %, 20 wt. % and 30 wt. % H_2O_2 , respectively. The calcination temperature was 300 °C. The breakthrough curves are presented in Fig. 4.

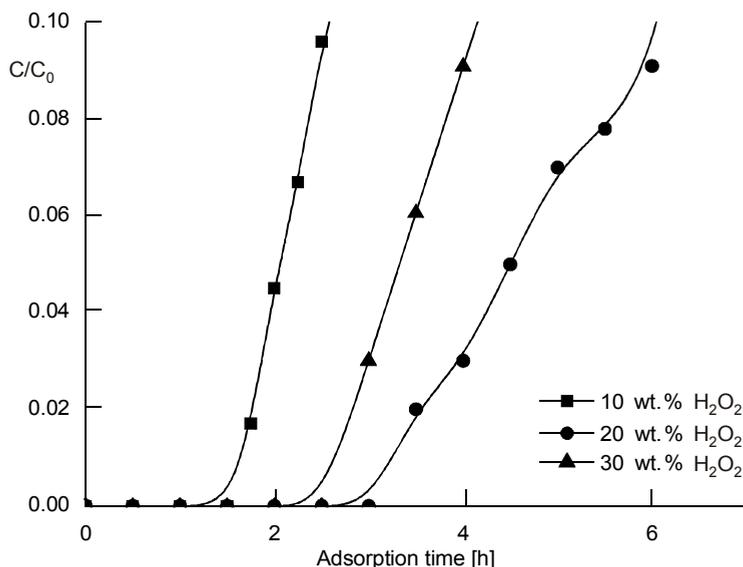


Fig. 4. Effects of H_2O_2 concentration on adsorption performance; loading height – 1.0 cm, loading amount – 0.60 g, space velocity – $3.18 \times 10^4 \text{ h}^{-1}$

As seen in Figure 4, the breakthrough times of the samples are 2.2 h, 6.2 h and 3.7 h, respectively. It can be deduced that modification by H_2O_2 at low concentrations is insufficient to oxidize the RM completely and the optimum pore structure cannot be formed. Inversely, excessive concentrations of H_2O_2 may destroy the micropore struc-

ture of the adsorbent. Thus, optimum H_2O_2 concentration is 20 wt. % at the calcination temperature of 300 °C.

3.2. EFFECTS OF CALCINATION TEMPERATURE ON ADSORPTIVE PERFORMANCE

The adsorptive performance of RM at various calcination temperatures was studied. The RM samples were calcinated at 300 °C, 400 °C, 500 °C, 600 °C, respectively, with a fixed H_2O_2 concentration of 20 wt. %. The breakthrough curves are presented in Fig. 5.

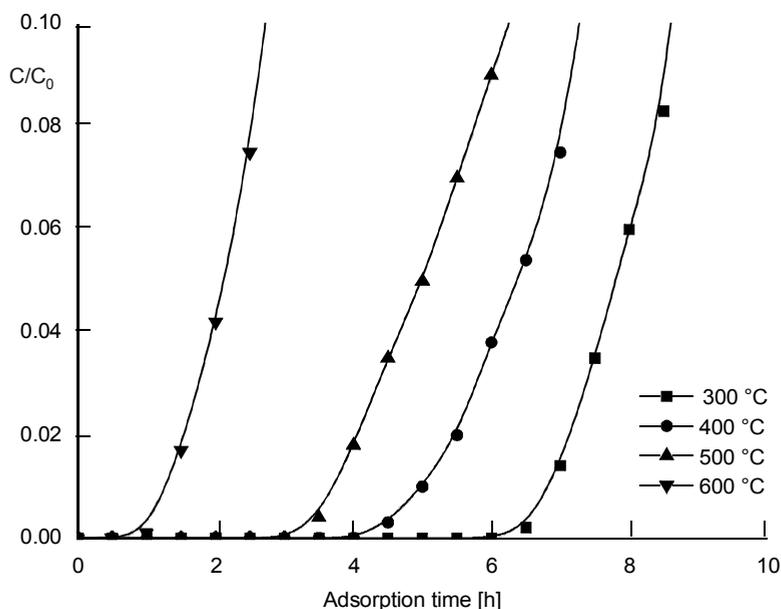


Fig. 5. Effects of calcination temperature on adsorptive performance; loading height – 2.5 cm, loading amount – 1.44 g, space velocity – $1.83 \times 10^4 \text{ h}^{-1}$

As shown in Fig. 5, the removal of formaldehyde increases with the decrease of calcination temperature when the H_2O_2 concentration is consistent. The breakthrough times for formaldehyde calcinated at 300 °C, 400 °C, 500 °C, 600 °C were 9 h, 6.8 h, 5.9 h, and 2.5 h, respectively. Thus, modification under low calcination temperature facilitates the adsorption of formaldehyde when the H_2O_2 modification is constant. However, when calcination temperature decreases below 250 °C, the performance of pore-forming agent (methyl cellulose) can hardly work, which may make it difficult for the RM to be granulated by grinding after being tableted and calcined. Therefore, the selected optimum calcination temperature is 300 °C.

The pore structure of the samples soaked in 20 wt. % H_2O_2 and calcined at 300 °C, 400 °C, 500 °C, and 600 °C were also analyzed. The pore structure parameters and cumulative pore volumes of four RM samples are shown in Table 3 and Fig. 6, respectively.

Table 3
Pore structural parameters of the red mud samples
calcined at various temperatures

Calcination temperature [°C]	Total pore volume $\times 10^{-2}$ [cm ³ /g]	Specific surface area [m ² /g]
300	7.971	32.42
400	7.683	29.43
500	7.443	26.35
600	7.211	25.81

As seen in Table 3, the specific surface area and total pore volume increase as the calcination temperature decreases. As temperature decreases from 600 °C to 300 °C, the specific surface area increases from 25.81 m²/g to 32.42 m²/g, and the total pore volume increases from 7.211×10^{-2} cm³/g to 7.971×10^{-2} cm³/g. Calcination at 300 °C can transform pore structures into micropores. However, excessively high calcination temperatures may destroy the micropore structures of the adsorbent.

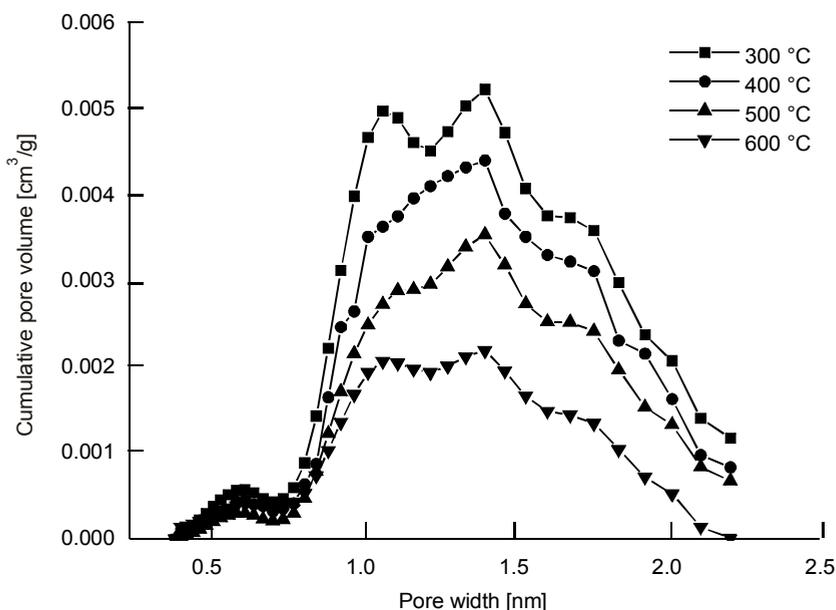


Fig. 6. Pore size distribution diagram of RM samples calcined at different temperatures

As seen in Figure 6, cumulative pore volumes from 0.50 nm to 2.25 nm in RM increase with the decrease of calcination temperature, Combined with the adsorptive performance of RM, low-temperature calcination of RM enhances the adsorption of formaldehyde, indicating that adsorption efficiency increases with microporous distribution in RM. The existence of micropores has great positive effects on the adsorption of formaldehyde using RM.

On the other hand, in order to clarify the effects of variations in calcination temperatures on RM crystal structures, four samples calcined at 300 °C, 400 °C, 500 °C, and 600 °C were selected to conduct XRD scanning analysis. However, the results show that the major mineral components are quartz, hematite, calcite and sodalite, with no significant differences in the mineral compositions of the samples. These results indicate that the differences in formaldehyde adsorptive performance of all samples are not caused by differences in the crystalline phase.

3.3. EFFECTS OF SPACE VELOCITY ON ADSORPTIVE PERFORMANCE

The RM sample obtained at the optimum modification conditions (20 wt. % H₂O₂, calcination temperature 300 °C) was used to test the effects of space velocity on adsorptive performance. The breakthrough curves are presented in Fig. 7.

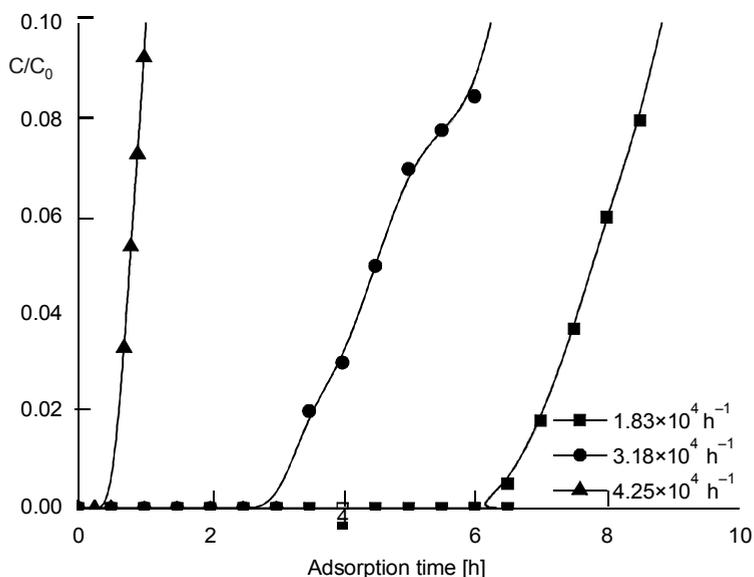


Fig. 7. Effects of space velocity on adsorptive performance

As seen in Fig. 7, the breakthrough times of formaldehyde at space velocities of $1.83 \times 10^4 \text{ h}^{-1}$, $3.18 \times 10^4 \text{ h}^{-1}$ and $4.25 \times 10^4 \text{ h}^{-1}$ are 9 h, 6.5 h, and 1.5 h, respectively. The

breakthrough time decreases as the space velocity increases which is attributed to the existence of a laminar boundary layer on the surface of adsorbent when the space velocity remains low. This layer becomes thinner as the space velocity increases, resulting in the decreased external diffusion resistance and increased external diffusion mass transfer coefficient. However, the contact time decreases with the increasing space velocity, and therefore the formaldehyde in the gas flow cannot have a good contact with the bed. The results show that this factor has an important positive effect on the adsorption of formaldehyde using RM.

4. CONCLUSIONS

- H_2O_2 modification can enhance the adsorptive performance of RM for formaldehyde. The optimum H_2O_2 concentration is 20 wt. % when calcination temperature is 300 °C. The effects of modification conditions on adsorption of formaldehyde by RM are due to the modification of microporous structure of RM. H_2O_2 modification integrates with calcination process and calcination alone can both create abundant micropores in RM, and thus achieve similar formaldehyde removal efficiency.

- Calcination temperature is an important factor on the adsorption of formaldehyde. The adsorptive performance of formaldehyde by RM increases with the decrease of calcination temperature due to the formation of abundant micropores under low calcination temperature in RM.

- Developing micropores in RM, especially pores with the diameters from 0.9 nm to 2.7 nm (from two to six lengths of formaldehyde molecules) can enhance the adsorption of formaldehyde.

- The adsorption of formaldehyde on RM after H_2O_2 modification integrated with calcination is mainly physical adsorption.

- The breakthrough time of formaldehyde decreases as space velocity increases.

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