Formation mechanism of metal–organic framework membranes derived from reactive seeding approach

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**Abstract**

Metal–organic framework (MOF) membranes have attracted great attention for their potential applications in gas and liquid separations. Recently, we have developed a novel reactive seeding (RS) method for the synthesis of MOF membranes, such as MIL-53 and MIL-96 membranes, on porous inorganic supports. By the RS method, a homogeneous seeding layer well bonding with the support could be formed for the secondary hydrothermal synthesis of high-quality MOF membranes. Our previous study demonstrated the RS approach was of versatility. However, the formation mechanism of MOF membranes derived from RS approach is unclear. In this work, taking MIL-96 as an example, we investigated the interactions between support and organic precursor and the differences between in situ synthesis and RS route. A formation mechanism of RS method was proposed. Based on the mechanism, the α-Al2O3 firstly reacted with H2O to produce γ-AlO(OH), and then the γ-AlO(OH) interacted with H3btc to form the MIL-96 seed crystals.

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**1. Introduction**

As a result of the enormous flexibility in design and functionalization of the skeleton construction through judicious choices of inorganic and organic components, metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) have shown potential applications in gas storage [1,2], gas adsorption and separation [3,4] and catalysis [5,6]. The well-defined pores and ultrahigh porosity endow MOFs with unlimited opportunities for selective filtration of various molecules. As a highly efficient and energy-saving technology, MOF-based membrane separations are considered as a highly efficient and effective alternative to traditional membrane separations with high reproducibility. However, the formation process of seeding layer using support as inorganic precursor is unclear. Moreover, it is difficult to understand the failure in fabricating the continuous MOF membrane by secondary growth method, the key point lies in the fabrication of an evenly distributed seeding layer which is bonded well with the porous support [7].

In our previous study, we reported a versatile reactive seeding (RS) method to synthesize MOF membranes on porous inorganic supports [28]. This method involves an in situ seeding process using porous support as inorganic precursor to react with organic precursor, followed by the secondary hydrothermal growth of a MOF membrane on the seeded support. This method realizes simultaneously even distribution of seeding layer and well bonding between seed crystals and support. Based on the produced seeding layer, high-quality MOF membranes could be synthesized with high reproducibility. However, the formation process of seeding layer using support as inorganic precursor is unclear. Moreover, it is difficult to understand the failure in fabricating the continuous MOF membranes by the in situ synthesis. The exploration on the in situ synthesis process is very crucial to the full understanding of the secondary hydrothermal growth step of RS procedure. In this work, taking the synthesis of MIL-96 membrane as an example, the formation process of MOF membranes by RS method was thoroughly analyzed. The reaction between α-Al2O3 support and organic precursor (1,3,5-benzenetricarboxylic acid, H3btc) for the seeding process was investigated in detail, and the formation of MIL-96 seeding layer was explored. Meanwhile, the interactions between α-Al2O3 support and H3btc in the presence of Al(NO3)3·9H2O and their influences on the growth of MIL-96 crystals on α-Al2O3 support surface were discussed for thorough...
2. Experimental

2.1. MIL-96 powder synthesis

To study the reaction between support and organic precursor, the MIL-96 powder was synthesized using different inorganic precursors, including the aluminum nitrate nonahydrate (Al(NO$_3$)$_3$·9H$_2$O, 98%, Alfa Aesar), $\alpha$-Al$_2$O$_3$ powder (99.99%, particle size of ~400 nm) and boehmite powder ($\gamma$-AlO(OH), 99.99%, particle size of ~20 nm) based on the same aluminum content. Typically, the synthesis solution consisted of 0.079 g 1,3,5-benzenetricarboxylic acid (trimesic acid, H$_3$btc, 98%, Alfa Aesar), 0.467 g Al(NO$_3$)$_3$·9H$_2$O and H$_2$O (10 ml, deionized water) was poured into a 50-ml Teflon lined stainless steel autoclave. The autoclave was sealed and subjected to heat treatment in an oven and the synthesis of MIL-96 powder was carried out at 210 °C for 24 h. After synthesis, the resulting sample was collected by centrifugation. Then the washed sample with abundant deionized water to dissolve the unreacted raw materials and removed them via centrifugation. This process was repeated three times to guarantee the complete removal of unreacted raw materials, finally dried the sample in 75 °C for 12 h.

2.2. MIL-96 membrane preparation

MIL-96 membrane was synthesized according to our reported method (i.e. RS method) [28] with minor modification. Self-made porous disk-shaped $\alpha$-Al$_2$O$_3$ with an average pore size of ca. 110 nm and a porosity of ~35% was used as support for preparing the MIL-96 membrane. One side of the support was polished using 1200-mesh SiC sandpaper. The 0.01 mol L$^{-1}$ H$_3$btc solution was transferred into a Teflon-lined autoclave containing the $\alpha$-Al$_2$O$_3$ disk on the bottom. And then the autoclave was heated for seeding in an oven at 210 °C for 12 h. After that, the sample was washed with deionized water and dried at 50 °C for 12 h prior to the MIL-96 membrane preparation. To observe the MIL-96 seed crystals on the support, an H$_2$btc solution with higher concentration (0.048 mol L$^{-1}$) was used to seed the $\alpha$-Al$_2$O$_3$ support at 210 °C for 24 h.

A synthesis solution was prepared by mixing the H$_3$btc (0.059 g) and Al(NO$_3$)$_3$·9H$_2$O (0.349 g) in H$_2$O (15 ml). The mixing solution was directly poured into a 50-ml Teflon-lined autoclave in which the seeded support was fixed vertically in the autoclave for the preparation of MIL-96 membrane. The autoclave was sealed and heated in an oven at 210 °C for 24 h. After crystallization, the as-prepared membranes were cleaned with deionized water and stored in an oven at 100 °C for 12 h. For comparison, the in situ growth method was also applied to prepare MIL-96 membranes on the $\alpha$-Al$_2$O$_3$ supports under identical hydrothermal conditions.

2.3. Characterization

The crystal structures of the synthesized powder and membrane samples were determined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation (D8-advance, Bruker, Germany) in reflection mode at room temperature. The microstructures of the MOF membrane samples were observed through scanning electron microscopy (SEM) (FEI, Model Quanta-200, Holland). Fourier transform infrared spectroscopy (FT-IR) spectra of MIL-96 crystals, $\alpha$-Al$_2$O$_3$ powder and powder scaled off from the surface of the seeded $\alpha$-Al$_2$O$_3$ support were separately recorded in a FT-IR spectrophotometer (AVATAR-FT-IR-360, Thermo Nicolet, USA) with the range 3000–600 cm$^{-1}$, using the KBr disk technique. The single gas permeation was conducted according to the previously reported procedure [28].

The pervaporation (PV) experiment of MIL-96 membranes was conducted on a homemade apparatus [31]. The feed solution was continuously circulated from a feed tank through the membrane surface using a variable speed feed pump. Vacuum on the permeate side was maintained at below 200 Pa and was monitored by a digital vacuum gauge. The effective membrane area was ca. 4 cm$^2$. At steady state, the weight of permeated vapor collected in the cold trap was measured to obtain the total flux.

The flux $J$ and separation factor $\alpha$ are defined as:

$$J = \frac{M}{A \times t}$$  \hspace{1cm} (1)

$$\alpha = \frac{X_w}{1 - X_w}$$  \hspace{1cm} (2)

where $M$ (kg m$^{-2}$ h$^{-1}$) is the total mass permeated during the experiment time interval $t$ (h), and $A$ is the effective membrane area (m$^2$). $X_w$ and $Y_w$ refer to the weight fractions of water in the feed and permeate samples, respectively.

2.4. Estimating of the weights of synthesized MIL-96 and unreacted $\alpha$-Al$_2$O$_3$

To study the influence of pH value of synthesis system on the yield of MIL-96 crystals using $\alpha$-Al$_2$O$_3$ as inorganic precursor, the weights of the synthesized MIL-96 and unreacted $\alpha$-Al$_2$O$_3$ were estimated according to the following procedure. The collected powder samples were washed using H$_2$O along with a heating process to fully dissolve and remove the residual H$_3$btc by centrifugation. After removing the guest molecules by heating at 150 °C for 24 h, the weights of these powder samples containing activated MIL-96 and unreacted $\alpha$-Al$_2$O$_3$ were recorded. These samples were further heated at 800 °C with a heating (cooling) rate of 5 °C/min for 6 h in the air to guarantee the synthesized MIL-96 crystals entirely decompose, and these mass losses before and after decomposition were also recorded. From the structural formula of MIL-96, it was calculated that 1 g activated MIL-96 crystals after complete decomposition would lose the mass of about 0.654 g. According to these data, the weights of synthesized MIL-96 (activated sample) and unreacted $\alpha$-Al$_2$O$_3$ could be estimated.

3. Results and discussion

3.1. Preparation and characterization of MIL-96 membranes

The $\alpha$-Al$_2$O$_3$ powder instead of Al(NO$_3$)$_3$·9H$_2$O was used as inorganic precursor, which reacted with H$_3$btc to produce a MIL-96 seeding layer. This process was proved by the reaction between $\alpha$-Al$_2$O$_3$ powder and H$_3$btc under identical conditions. The resulting XRD pattern (Fig. 1c) shows that the crystal structure of the powder product using the $\alpha$-Al$_2$O$_3$ powder as inorganic precursor is consistent with the reported XRD pattern (Fig. 1a) obtained by simulation from Mercury Software.

The morphology of the seeded $\alpha$-Al$_2$O$_3$ support is shown in Fig. 2a. No obvious seed crystals were observed on the support because of the small crystallite size. However, this seeding layer is enough to construct a high-quality and thin MIL-96 membrane. The formation of seeding layer was affected by the synthesis parameters, such as the concentration of H$_3$btc solution and the seeding time. As shown in Fig. 2b, obvious MIL-96 crystal can be
observed on the support surface when 0.048 mol L$^{-1}$ H$_3$btc solution was used to react with $\alpha$-Al$_2$O$_3$ support for 24 h. These effects were further discussed in Section 3.3.

Based on the prepared seeding layer, MIL-96 membrane was synthesized by hydrothermal growth. Fig. 3c shows the XRD pattern of the prepared MIL-96 membrane. The crystal structure is consistent with that of MIL-96 crystal reported in the literature (Fig. 3a) [32], and no other phase is observed except the $\alpha$-Al$_2$O$_3$ support. Fig. 4a and b display the surface and cross section images of MIL-96 membrane fabricated by the RS method. The MIL-96 polycrystalline layer on the support is highly integrated, and no obvious defects were observed. The membrane layer with a thickness of approximately 6 $\mu$m is bonded well with the support.

For comparison, a preliminary attempt to construct the MIL-96 membrane by the in situ synthesis was conducted. According to the XRD pattern as shown in Fig. 3b, MIL-96 crystalline layer can be synthesized by in situ route on the $\alpha$-Al$_2$O$_3$ support. However, the SEM results (Fig. 4c and d) demonstrate that the crystalline layer is discontinuous. The typical flat hexagonal-shape MIL-96 crystals with an average size of 15 $\mu$m scatter on the support surface. This result indicates that the MIL-96 crystals are inclined to grow in the bulk solution rather than on the support during the in situ crystallization. The exploration on the in situ synthesis process will be discussed in Section 3.4.

It has been reported that the carboxylate-based MOF crystals are easy to nucleate and grow on the supports with hydroxyl groups [32]. To further confirm that the seeding layer instead of the hydroxyl groups plays a key role in the formation of integrated MIL-96 membrane a verification experiment was carried out. The $\alpha$-Al$_2$O$_3$ support after hydrothermal treatment without organic ligand (to increase the concentration of hydroxyl groups on the support) was used for the preparation of MIL-96 membrane. The microstructure of the obtained MIL-96 membrane (Fig. 4e) was discontinuous and similar with that in Fig. 4c. This result suggested that the seed crystals formed during the reactive seeding process not the hydroxyl groups are responsible for the membrane synthesis. In addition, we also attempted to deposit H$_3$btc molecules on the support for synthesizing integrated MIL-96 membrane. The deposition process was conducted by immersing the $\alpha$-Al$_2$O$_3$ support into the H$_3$btc solution (0.01 mol L$^{-1}$) for 24 h at room temperature. However, on the treated support, the synthesized MIL-96 membrane is still discontinuous.

FT-IR spectroscopy was also used to analyze the seeded $\alpha$-Al$_2$O$_3$ support surface. The powder scaled off from the seeded $\alpha$-Al$_2$O$_3$ support surface was collected for the FT-IR analysis. Fig. 5b is the resulting FT-IR spectrum. For comparison, the FT-IR spectra of MIL-96 crystals and $\alpha$-Al$_2$O$_3$ powder were recorded and shown in Fig. 5a and c, respectively. The FT-IR spectrum of MIL-96 crystals (Fig. 5a) is in good agreement with the literature data [32]. The vibrational bands in the range 1400–1700 cm$^{-1}$ were assigned to the carboxylic function of MIL-96. Two absorption bands, located at 1596 and 1610 cm$^{-1}$, are assigned to symmetric $–$CO$_2$ stretching, whereas the absorption bands between 1458 and 1385 cm$^{-1}$ were attributed to symmetric $–$CO$_2$ stretching. From Fig. 5b, the
vibrational bands of MIL-96 in the range 1400–1700 cm\(^{-1}\) for carboxylic function were also observed in the powder collected from the surface of the seeded support, indicating that the MIL-96 seed crystals were indeed produced on the \(\alpha\)-Al\(_2\)O\(_3\) support after the hydrothermal treatment of H\(_3\)btc solution.

The as-synthesized MIL-96 membrane was gas-tight because its cavities were occupied fully by the guest molecules. After activation by heating, the membrane was tested by single gas permeation experiments at room temperature. The single gas permeation (SGP) results of H\(_2\), CH\(_4\), N\(_2\), and CO\(_2\) through the membrane under a constant transmembrane pressure drop of 1 bar are shown in Fig. 6. The permeances of these gas molecules increase linearly with the increase in the square root of their molecular weights, indicating that the permeation of these gas molecules through the MIL-96 membrane mainly follows the Knudsen diffusion. The N\(_2\) permeances through the support and the membrane were also measured under different transmembrane pressure drops. The N\(_2\) permeances through the \(\alpha\)-Al\(_2\)O\(_3\) markedly increase with increasing pressure drops (Fig. 6) due to the substantial contribution of viscous flow to the total flow that resulted from the large pore size of the support. The N\(_2\) permeances through the membrane are almost independent of the transmembrane pressure drops, suggesting the negligible defects in the MIL-96 membrane. As for the pervaporation dehydration
The $\alpha$-Al$_2$O$_3$ is very inert ceramic material; however, the reaction between $\alpha$-Al$_2$O$_3$ and H$_3$btc solution for synthesizing MIL-96 crystals was indeed observed (Fig. 1c). The exploration on the detailed reaction process is therefore very significant for an in-depth knowledge of the seeding step of the RS route. According to the formula of MIL-96, the synthesis of MIL-96 via the reaction between $\alpha$-Al$_2$O$_3$ and H$_3$btc could be summarized as reaction 3:

$$\begin{align*}
7\alpha - Al_2O_3 + 6H_3btc + 29H_2O &\rightarrow Al_{12}O_3(OH)_{18}(H_2O)_{14}(Al_3(OH)_{18})[btc]_{18} \cdot 24H_2O \\
&\text{(3)}
\end{align*}$$

From the reaction 3, it can be seen that H$_2$O takes part in the reaction. The solid $\alpha$-Al$_2$O$_3$ could not react directly with H$_3$btc, so we inferred that the $\alpha$-Al$_2$O$_3$ will firstly interact with H$_2$O and transform into the hydrated Al$_2$O$_3$. Desset et al. have proved that the surface of Al$_2$O$_3$ can transform into aluminium hydroxide gibbsite (i.e. Al(OH)$_3$) during the hydrothermal treatment (ageing in H$_2$O at 100 °C) [34]. The possible hydration process of $\alpha$-Al$_2$O$_3$ during the hydrothermal reaction was therefore explored.

The high-purity $\alpha$-Al$_2$O$_3$ powder was directly treated under hydrothermal condition at 210 °C for different time. Each sample was 0.1 g, together with 15 ml H$_2$O. The treated $\alpha$-Al$_2$O$_3$ powders after drying at 75 °C for 12 h were tested by XRD, and the results were shown in Fig. 7. Apart from the characteristic XRD peaks of $\alpha$-Al$_2$O$_3$, the XRD peaks derived from boehmite ($\gamma$-AlO(OH)), a hydrated form of Al$_2$O$_3$, were observed. This result reveals that part of $\alpha$-Al$_2$O$_3$ powder has transformed into the $\gamma$-AlO(OH) after the hydrothermal treatment. The intensity of XRD peaks of the $\gamma$-AlO(OH) increases significantly with increasing treatment time. Additionally, no impurity phases from other hydrated Al$_2$O$_3$ were observed during the hydrothermal treatment processes. In the hydrolysis reaction of $\alpha$-Al$_2$O$_3$, the formation process of $\gamma$-AlO(OH) is expressed as reaction 4:

$$\alpha - Al_2O_3 + H_2O \rightarrow 2\gamma - AlO(OH)$$

$$\text{(4)}$$

The $\gamma$-AlO(OH) is not so inert as $\alpha$-Al$_2$O$_3$, and it is able to react with carboxylic acids even in a milder condition [35–37]. The $\gamma$-AlO(OH) powder was directly used to synthesize the MIL-96 crystals under identical hydrothermal condition. Fig. 1d shows the XRD pattern of collected powder. The crystal phase of MIL-96 can be seen clearly, suggesting that the MIL-96 could also be synthesized using $\gamma$-AlO(OH) as inorganic precursor. This hydrothermal synthesis process is described as reaction 5:

$$\begin{align*}
14\gamma - AlO(OH) + 6H_3btc + 22H_2O &\rightarrow Al_{12}O_3(OH)_{18}(H_2O)_{14}(Al_3(OH)_{18})[btc]_{18} \cdot 24H_2O \\
&\text{(5)}
\end{align*}$$

According to the Reactions (4) and (5), a two-step reaction mechanism was suggested to understand the formation of MIL-96 crystals using $\alpha$-Al$_2$O$_3$ as inorganic precursor. The $\alpha$-Al$_2$O$_3$ first transforms into the hydrated $\gamma$-AlO(OH) in the presence of H$_2$O, and then the hydrated $\gamma$-AlO(OH) reacts with H$_3$btc solution to produce the MIL-96. The two-step reaction mechanism could be expressed as follows:

$$\begin{align*}
\alpha - Al_2O_3 + H_2O &\rightarrow \gamma - AlO(OH) \\
\gamma - AlO(OH) + H_3btc &\rightarrow Al_{12}O_3(OH)_{18}(H_2O)_{14}(Al_3(OH)_{18})[btc]_{18} \cdot 24H_2O \\
&\text{(6)}
\end{align*}$$

From the above research results, the formation mechanism of MIL-96 seeding layer on the $\alpha$-Al$_2$O$_3$ support surface was illustrated in Fig. 8. The $\alpha$-Al$_2$O$_3$ support surface layer firstly interacts with H$_2$O to form the $\gamma$-AlO(OH) (reaction 4), and the $\gamma$-AlO(OH) immediately reacts with H$_3$btc to form the MIL-96 seeding layer (reaction 5).

### 3.3. Effects of synthesis time, concentration and pH value

The effects of several controllable parameters such as the synthesis time, concentration and the pH value of synthesis system on the production of MIL-96 crystals using $\alpha$-Al$_2$O$_3$ powder as inorganic precursor were investigated. Fig. 9a shows the XRD patterns of MIL-96 powders from different synthesis time. The intensity of XRD peaks of $\alpha$-Al$_2$O$_3$ is almost independent of the synthesis time, while the XRD intensity derived from the MIL-96 significantly increases with increasing synthesis time. For the synthesis of MIL-96 with different H$_3$btc concentrations, the similar results were obtained. As shown in Fig. 9b, the increase of H$_3$btc concentration results in the obvious increase of XRD signals of MIL-96, suggesting the increase in the MIL-96 yield.
The pH value of synthesis solution was adjusted by HCl solution (1 mol L\(^{-1}\)) and its influence on the yield of MIL-96 crystals was studied. As shown in Fig. 10, after reaction the amount of total powder sample collected from the autoclave firstly increases rapidly (0 < pH < 1), then reaches a maximum (pH = 1), and finally gradually decreases (1 < pH < 7). According to the reaction 3, the weight of synthesized MIL-96 and the unreacted \(\alpha\)-Al\(_2\)O\(_3\) could be estimated. The amount of the produced MIL-96 displays a similar variation tendency to that of the total powder sample. The amount of the unreacted \(\alpha\)-Al\(_2\)O\(_3\) increases gradually with the increase in the pH value. When the pH value of the synthesis system is 0, nothing is collected. This result implies that the extreme acidity strongly prevents the formation of MIL-96. This may be caused by the fact that lots of hydroxide groups exist in the building unit of MIL-96. We also found that both MIL-96 and \(\alpha\)-Al\(_2\)O\(_3\) powders could be thoroughly consumed in the hydrothermal environment of pH = 0. When the pH value is in the range of 0–1, the \(\alpha\)-Al\(_2\)O\(_3\) does not completely dissolve into the solution. The produced aluminium ion clusters could react with H\(_3\)btc to synthesize MIL-96. When the pH value is one, the yield of MIL-96 reaches the highest. More and more unreacted \(\alpha\)-Al\(_2\)O\(_3\) will be collected in the autoclave for the steady increase of pH value (1 < pH < 7). Meanwhile, the amount of MIL-96 decreases gradually due to the fact that the high pH value of the synthesis system suppresses the dissolution of \(\alpha\)-Al\(_2\)O\(_3\).

In a word, the synthesis time, concentration and the pH value of synthesis system are key factors to influence the reaction between \(\alpha\)-Al\(_2\)O\(_3\) and H\(_3\)btc. And the seeding process on the support could be regulated by these synthesis parameters.

3.4. Differences between in situ synthesis and RS route

For the in situ synthesis, several reactions involving the H\(_3\)btc, Al(NO\(_3\))\(_3\), H\(_2\)O and \(\alpha\)-Al\(_2\)O\(_3\) support could take place in the synthesis system. The Reactions (4) and (5) are two established chemical processes that occurred on the \(\alpha\)-Al\(_2\)O\(_3\) support surface, and they
could be considered as one process, namely reaction 3 (seen in the Section 3.2). Meanwhile, Al(NO$_3$)$_3$ also react with H$_3$btc to produce MIL-96 crystals, and this process is described as reaction 6:

$$14\text{Al(NO}_3\text{)}_3 + 6\text{H}_2\text{btc} + 50\text{H}_2\text{O} 
\rightarrow \text{Al}_2\text{O(OH)}_6(\text{H}_2\text{O})_3(\text{Al}_2(\text{OH})_6)\text{btc}_6 \cdot 24\text{H}_2\text{O} + 42\text{HNO}_3$$ (7)

The Reactions (3) and (7) could simultaneously occur in the regions A and B (Fig. 11) respectively. As for the desired in situ synthesis route, the reaction 3 ought to carry out firstly in the region A using $\alpha$-Al$_2$O$_3$ support as inorganic precursor. After reaction 3, a homogeneous MIL-96 seeding layer could be produced on the support surface. Then the seeding layer could obtain enough nutrient via reaction 6 to generate an integrated MIL-96 membrane. This seems to be feasible if the rate of reaction 3 is fast enough, so after the formation of seeding layer there is still adequate nutrient supplied from the region B for the reaction 6. In fact, however, the fact is contrary to our expectation. The rate of reaction 6 using free aluminium ions provided by Al(NO$_3$)$_3$9H$_2$O as inorganic precursor is much faster than that of reaction 3. After the formation of seeding layer, there is no enough nutrient in the region B for the secondary growth of MIL-96 membrane.

In our experiments, the difference in the reaction rates using different inorganic sources to synthesize MIL-96 was indirectly expressed by the yield of MIL-96. The MIL-96 crystals were synthesized by Al(NO$_3$)$_3$9H$_2$O (0.698 g) and H$_3$btc (0.118 g) in H$_2$O (30 ml) at 210 °C for different time (24, 12, 8, 4, 2, 1.5 and 1 h). The reactant concentration is same as that used for the preparation of MIL-96 membrane. The relationship between the weight of synthesized MIL-96 powder (after activation at 150 °C for 24 h) and synthesis time is illustrated in Fig. 12. Within 4 h, the synthesis of MIL-96 crystals has completed, and the yield trends to a constant after 4 h. The crystal structure of the sample synthesized for only 2 h was confirmed to be MIL-96 (Fig. 13b). For comparison, $\alpha$-Al$_2$O$_3$ (0.095 g) was also used to synthesize MIL-96 at 210 °C for 4 h. The content of aluminium in the $\alpha$-Al$_2$O$_3$ is same as that in the used Al(NO$_3$)$_3$9H$_2$O. After reaction, the resulting powder after drying was analyzed by XRD, the collected pattern is shown in Fig. 13a. Only a very weak peak (102) of MIL-96 was observed, indicating that a small number of MIL-96 crystals produced in the reaction process. Compared with the synthesis of MIL-96 using Al(NO$_3$)$_3$9H$_2$O, the generation rate of MIL-96 using $\alpha$-Al$_2$O$_3$ is indeed much lower.

During the in situ synthesis system, H$_3$btc is the shared reagent of Reactions (3) and (7); the competition between them is inevita-

![Diagram](image.png)

Fig. 11. The schematic diagram of two regions for the occurrences of Reactions (3) and (7) in the in situ synthesis system used for the synthesis of MIL-96 membrane.

![Diagram](image.png)

Fig. 12. The weights of activated MIL-96 powders synthesized at 210 °C for different time. The synthesis process of MIL-96 crystals could be divided into three stages. In the stage I, no MIL-96 crystals were collected; the growth of most MIL-96 crystals has been achieved in stage II; in the stage III, almost no crystals formed and the yield of MIL-96 crystals trended to a constant.

![Diagram](image.png)

Fig. 13. XRD patterns of MIL-96 powders synthesized (a) using $\alpha$-Al$_2$O$_3$ powder as inorganic precursor at 210 °C for 4 h and (b) using Al(NO$_3$)$_3$9H$_2$O as inorganic precursor at 210 °C for 2 h.
4. Conclusions

The formation mechanism of MOF membrane by RS approach was elaborated. A two-step reaction mechanism was proposed for the formation of MIL-96 seeding layer. First, the $\alpha$-Al$_2$O$_3$ reacted with H$_2$O to produce $\gamma$-AlO(OH); Second, $\gamma$-AlO(OH) interacted with H$_3$btc to form the MIL-96 seed crystals. The synthesis time, concentration and the pH value of synthesis system are key factors to control the reaction between $\alpha$-Al$_2$O$_3$ and H$_3$btc. In the secondary growth step of RS approach, the interaction between $\alpha$-Al$_2$O$_3$ and H$_3$btc was strongly suppressed because a homogeneous MIL-96 seeding layer has formed on the $\alpha$-Al$_2$O$_3$ support. On the basis of the seeding layer, an integrated MIL-96 membrane could be directly synthesized. In addition, the in situ route is proved to be hard to synthesize an integrated MIL-96 membrane on the $\alpha$-Al$_2$O$_3$ support because of the fact that the MIL-96 crystals are easier to crystallize and grow in the bulk solution rather than on the support surface. This work could offer some guidance for the preparation of high-quality MOF membranes using RS method.

Acknowledgements

This work was supported by the National Basic Research Program of China (No. 2009CB623406); National Natural Science Foundation of China (No. 20990222, No. 21006047, No. 21176115); and the China Postdoctoral Science Foundation (No. 201003581).

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