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Research Progress on Iodine Capture by Covalent Organic Framework Materials

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Abstract. With the development of nuclear power, the removal of radionuclides is an important responsibility and task. Radioactive iodine, as one of the most radionuclide in nuclear wastes, its safe disposal is essential to ensure the sustainable development of the nuclear industry. Covalent organic framework materials are crystalline organic porous materials, which were constructed by covalent bonds. Because of their regular pore structure, large surface area and high chemical stability, covalent organic framework materials are selected as an ideal iodine capturing materials due to their structural characteristics and the adsorption sites of covalent organic framework materials. In this paper, the research progress of covalent organic framework materials in iodine capture was briefly reviewed. Meanwhile, the prospect of high efficiency iodine-capture covalent organic framework materials on industrialized application is predicted.

Keywords: Covalent organic frameworks; Treatment and disposal; Iodine trapping; Radioactive substance; Adsorption site.

1. Introduction

Spent fuel reprocessing is a key link to ensure the sustainable development of nuclear energy as a clean energy. If concentrated nitric acid is used in the spent fuel treatment process, it will lead to strong acidity and high temperature, and a large amount of radioactive iodine will be released from the reprocessing facility. The main substances in the dissolved waste stream produced in this process are highly volatile diatomic element iodine and a small amount of organic iodine. ^{129}I and ^{131}I are typical nuclei waste radioisotopes (^{129}I has a half-life of 1.57×10^7 years)[1]. Radioactive iodine can quickly disperse into the air, resulting in continued radioactive contamination of the environment, an increased incidence of thyroid disease in humans, and harm the human reproductive and metabolic system. However, due to the complex situation of fuel retreatment exhaust gas, such as high system temperature, high ambient humidity, high irradiation intensity, extremely low iodine concentration and small partial system, there will be a large amount of acid gas. How to effectively remove radioactive iodine in the retreatment system is still a challenge. Therefore, it is important to strive to develop simple, efficient and easy method to develop iodine-absorbing materials. In recent ten years, porous materials as iodine adsorbents have been paid more attention by researchers, mainly including porous organic cage[2], ion exchange zeolite[3], silver-based zeolite[4] and activated carbon[5], etc. However, inorganic solid adsorbents such as silver-based zeolite have high cost, poor adsorption performance and adverse effects on the environment. Metal-organic frame materials (MOFs)[6] and porous organic polymers (POPs)[7] have a stronger ability to adsorb iodine than zeolite due to their high surface area, but are less stable at high temperatures and in solution for capturing iodine vapors. In the adsorption process, the complex and irregular pores in the material often lead to pore blockage, so the desired adsorption effect cannot be achieved. These disadvantages will limit their practical application in iodine capture. Covalent organic framework materials (COFs), as a new crystalline organic porous polymer formed by covalent bonds, have orderly internal structure and adjustable pore structure. Using COFs to adsorb iodine molecules in regular pores does not cause pore blockage. Because of its good thermal stability, iodine can be captured at high temperatures and in solution. In the process of irradiated nuclear fuel treatment, COFs can effectively adsorb part of long-lived radionuclides (VRL nuclides) from spent fuel. Therefore, COFs has great practical value in dealing

with emergency leakage of radioactive iodine or organic iodine in nuclear accidents or spent fuel reprocessing. Covalent organic framework materials with different pore sizes and polarities can be synthesized by selecting building units with high efficiency for iodine capture. Therefore, COFs material has great potential in capturing radioactive iodine and becomes an ideal material for capturing iodine. Since 2005, Yaghi and coworkers[8] successfully prepared COFs materials for the first time, it has gradually become a hot research field of current science and technology. This paper reviews the progress of iodine capture by COFs.

2. Iodine capture by different types of COFs

Because of its regular structure, easy surface modification, low density, large specific surface area and high chemical stability, COFs has attracted wide attention in the fields of gas adsorption storage, catalysis and optoelectronics, and has also aroused the research interest of scientists and researchers in other fields. In this paper, we will analyze the ability of different types of COFs to capture iodine from the perspective of structure, building units and introducing different functional groups to form functional organic ligands.

2.1. Imine bonding COFs

In 2016, Jiang and coworkers[9] synthesized chemically stable PBDMTP COF and TTA-TTB COF, and the iodine uptake capacity is as high as 6.26 and 4.95 g/g, respectively. This high adsorption capacity can be attributed to the one-dimensional channel of two-dimensional COFs that can fully enter the elemental iodine molecules.

In 2020, Sun and coworkers[10] synthesized three COFs (COF-TpgDB, COF-TpgBD and COF-TpgTd) using 2,4,6-trihydroxy-benzene-1,3,5-triosan aldehyde (Tpg) and linear amino linkage units (DB, BD and Td) at ambient temperature and pressure. This class of COFs has strong binding ability to I_2, I^+, I^{3-} and I^{5-}. DFT calculations show that the benzene ring, C=O and -C-(NH)-C- units in COFs have strong interactions with iodine. It is found that the three COFs have large surface area, high chemical stability and high thermal stability. In addition, COF-TpgDB, COF-TpgBD and COF-TpgTd achieved high adsorption capacities of 260, 181 and 166 wt % of iodine, respectively. The outstanding contribution of this research group lies in the study of adsorption sites of different iodine substances in COFs by theoretical calculation method. The relationship between different functional groups and different iodine substances is clearly explained, which provides a basis for designing and developing more advanced iodine adsorbent materials.

In 2021, Chen and coworkers[11] reported on a highly efficient iodine adsorber TAPB-BPDA COF that synthesized from the condensation reaction of 1,3,5-tri(4-aminophenyl) benzene (TAPB) and 4,4'-diphenyl aldehyde (BPDA). The weak interaction between benzene ring and iodine molecule and the electron transfer between nitrogen atom and iodine can enhance the iodine adsorption property of the material. The iodine adsorption capacity of the material can reach 988.17 mg/g in aqueous solution at room temperature.

In 2021, Song and coworkers[12] successfully synthesized a series of imine bond connected COFs (TFB-DB COF, TFB-BD COF and TFB-Td COF). The results show that the larger pore sizes of the three COFs allow iodine to pass through the one-dimensional open channel of COFs, and the Lewis acid-base interaction between the polar C-N bond and iodine molecules also increases the ability to capture iodine. The iodine capacity of TFB-DB COF, TFB-BDCOF and TFB-Td COF were 6.4, 6.23 and 4.97 g/g, respectively, and reached 99.9, 99.8 and 99.8 mg/g in *n*-hexane solution, respectively. In addition, after five iodine adsorption cycles, the three COFs can still remove more than 99% of the iodine in *n*-hexane solution, which indicates that the three COFs have good recyclability in the adsorption of iodine in vapor and solution. The results showed that the iodine adsorption capacity of the three COFs was affected by the different binding energy of the three COFs due to different pore sizes. Therefore, further theoretical calculation of suitable pore size is an important challenge in the development of efficient iodine adsorbents.

In 2021, Zhai and coworkers[13] synthesized two new types of TTA-TMTA-COF and TTA-FMTA-COF with large porosity and good chemical stability by introducing methoxy functional groups into the framework. This kind of material has higher specific surface area and larger pore volume and high chemical stability. Because the electron cloud density on the benzene ring skeleton in the molecule is more density under the action of the pushed electron of methoxy group, and the large polar methoxy functional group can enhance the adsorption performance of iodine molecules in organic solvents, so that the obtained COFs material has a high iodine adsorption capacity. The adsorption capacity of TTA-TMTA-COF and TTA-FMTA-COF for iodine was 3.21 and 5.07 g/g, respectively.

In 2021, Zhao and coworkers[14] designed and synthesized a new double iodine-absorbing adsorbent COF-PA containing quinoline and phenylacetylene units through post-modification. The adsorption rate of iodine in the solution and iodine in the material is very fast, and the adsorption amount of iodine in the solution reaches 1.3 g/g. When the weight ratio of adsorbent to iodine is 1:1, the adsorption efficiency of COF-PA reaches 90%. And COF-PA soaked in organic solvents, strong acids and strong bases for a week, can still maintain good crystallinity. In addition, COF-PA can emit bright yellow fluorescence under ultraviolet light (UV) excitation at 365 nm, and the fluorescence is quickly extinguished when iodine is added, thus verifying the effectiveness of iodine adsorption. So this stability COFs with strong, high adsorption capacity and sensitive detection function will have great application prospects in industry in the future.

In 2021, in order to enhance the host-guest interaction between the COFs skeleton and iodine, He and coworkers[15] chose 2,2'-bipyridine-5,5'-aldehyde as the functional ligand and constructed two-dimensional two-pore SCU-COF-20. The experimental results show that the absorption capacity of SCU-COF-2 at 348 K is up to 5.1 g/g at 24 h and the maximum absorption at 96 h. The amount is 6.0 g/g. The excellent iodine capture capability of SCU-COF-2 was demonstrated by breakthrough experiments at high humidity and temperature. The absorption capacity of SCU-COF-2 at 348 K is up to 5.1 g/g at 24 h, and the maximum absorption amount at 96 h is 6.0 g/g. The excellent iodine capture capability of SCU-COF-2 was demonstrated by breakthrough experiments at high humidity and temperature. The absorption capacity of SCU-COF-2 at 348 K is up to 5.1 g/g at 24 h, and the maximum absorption amount at 96 h is 6.0 g/g. The excellent iodine capture capability of SCU-COF-2 was demonstrated by breakthrough experiments at high humidity and temperature.

Tetrathiofuvalene (TTF) derivatives, as superior electron donors, can form radical cations with accepter I_2 through reinforcement interactions. In 2022, Wang and coworkers[16] successfully synthesized TTF-TD-COF and by introducing functional groups of tetrathiofuvalene into the building unit TTF-TAPT-COF. It is calculated that the BET surface area of TTF-TD-COF and TTF-TAPT-COF are 235 and 461 m^2/g, respectively, the pore volume of TTF-TD-COF is about 0.23 cm^3/g, and the pore volume of TTF-TAPT-COF is about 0.28 cm^3/g. The high BET surface area and large pore volume indicate the porosity of the COFs obtained. The maximum iodine adsorption capacity of COF and TTF-TD-COF at 348 K ambient pressure was 5.02 and 4.38 g/g, respectively, which exceeded most other materials reported at present, and the adsorption capacity remained high after six cycles. In addition, the experimental results show that iodine molecules will disperse into the pores of COFs to produce electron transfer substances (I_3^- and I_5^-). The synergistic effect of physical adsorption and chemisorption will accelerate the transport rate and adsorption rate of iodine molecules, because TTF groups can enhance the lipophilicity of the framework and thus enhance the active site in contact with iodine molecules. Because of its high adsorption capacity and strong recovery, it provides a feasible method for rational design and construction of novel and effective iodine adsorbents. The study also provides fundamental guidance for designing and exploring advanced crystalline porous materials to adsorb radioactive iodine and other harmful molecules quickly and efficiently.

In 2022, Liu et al[17] developed a mild and efficient microwave radiation method instead of the traditional solvothermal method to prepare the covalent organic framework Cux Pc-COFs based on copper phthalocyanine within only 15 min. Nitrogen-rich 1,2,4,5 - tetramethylbenzene (TCNB) was selected as the only organic ligand to construct 2D COFs of copper phthalocyanine. The obtained

Cux Pc-COFs showed a good iodine adsorption capacity of 2.99 g/g for volatile iodine and 492.27 mg/g for cyclohexane solution, which was better than most reported porous adsorbents. Spectral analysis and DFT calculation show that this good adsorption performance is due to the charge transfer between the nitrogen-rich phthalocyanine structure and the iodine molecule. In addition, the strong electrostatic interaction between Cu(II) and polyiodoanion (I_x^-) in the chelating center also plays an important role in the capture of radioactive iodine. Based on the experimental data and theoretical calculation analysis, there are three interaction mechanisms of Cu_xPc-COFs on the adsorption of iodine: charge transfer between the nitrogen atom and the electron-rich π conjugation system on the imine bond and the iodine molecule; electrostatic interaction of Cu-N_4 structure with polyiodide anion; trace REDOX reaction (cuprous iodide). In addition, Cu_xPc-COFs is considered to be a promising host material for the absorption of radioactive iodine from nuclear waste due to its rigid structure and non-uniformly charged two-dimensional conjugated network structure. The success of this experiment also provides a simple and intelligent method to achieve effective adsorption of iodine by metal-based COFs.

In 2022, Zhang et al[18] followed the same idea and successfully prepared a 2D COFs material with high stability, high specific surface area and specific iodine adsorption, named JUC-609. JUC-609 has high crystallinity and a large specific surface area. Under 353 K and high pressure, the adsorption capacity of JUC-609 for iodine distillation is 5.9 g/g. In addition, JUC 609 can be recycled several times, and the crystal structure and morphology have not changed. The high adsorption capacity can be attributed to the combination of large porosity, effective adsorption sites and extended π-conjugated structures.

In 2022, Wen et al[19] developed ETTA-PyTTA-COF through the Schiff base condensation reaction. Due to its high BET surface area (1519 m^2/g), large π-conjugated structure and a large number of imine groups in the covalent organic framework as effective iodine adsorption sites, the iodine adsorption can reach 4.6 g/g at 348 K, which is the best among all reported porous adsorbents. In addition, after the first cycle, the adsorption capacity of iodine only decreased from 4.6 g/g to 3.9 g/g, and after repeated cycles, the adsorption capacity of iodine of the material almost remained unchanged, which indicates that ETTA-PyTTA-COF material has good recyclability.

2.2. Composite COFs

In 2020, Li and coworkers[20] successfully prepared COFs@cotton composite materials by post-modification method. The surface of cotton fiber is oxidized with $NaIO_4$ to obtain aldehyde group, and then COFs material is connected to the backbone of cotton fiber by Schiff base reaction. The composite material has a high specific surface area and good pore structure, and also has a high absorption capacity of iodine in solution. It can show a fast adsorption rate, and the iodine adsorption capacity can reach 533.9 mg/g, which is much higher than that of untreated cotton fiber.

2.3. Three dimensions(3D) COFs

Three-dimensional covalent organic frameworks (3D COFs) have attracted much attention due to their high specific surface area and open pore structure. In 2018, Wang and coworkers[21] explored and discovered an adamantane structure, which is able to maintain a robust porous framework due to its rigid structure and chemical stability. Using this feature, the research group designed and synthesized 3D COF-DL229 containing the adamantane building unit. The material has an eight-fold interspersed diamond topology with ordered one-dimensional nanochannels. In addition, the edge portion has a phenyl group connected by two imine bonds, giving the skeleton structural flexibility. These characteristics determine that this is an ideal iodine adsorption porous material, iodine adsorption capacity can reach 4.7 g/g at 75 ℃ and ambient pressure.

2.4. Ionized COFs

A series of ionic COF (iCOF) for iodine capture were designed and synthesized by using the "multivariate" strategy combined with post-modification method. This kind of material has unique

structure and composition characteristics. In 2021, Xie and coworkers[22] optimized COFs through several experiments, and finally obtained ionic COFs (iCOF-AB-50). First, the materials exhibit high crystallinity and a large specific surface area (> 2000 m^2/g), which ensures that significant porosity can be maintained after ion modification. Secondly, there is a high density of imine and triazine groups throughout the framework, thus providing a large number of binding sites for I_2. The experimental results show that the static I_2 absorption capacity of iCOF-AB-50 at 75 ℃ is 10.21 g/g, and the dynamic absorption capacity of ICOF-AB-50 at 25 ℃ is 2.79 g/g, which far exceeds the performance of the adsorbent under similar conditions previously reported. In addition, iCOF-AB-50 has fast adsorption kinetics, good moisture resistance and full reusability. Ionic COFs will also occupy a place in future industrial development as high iodine adsorbents.

3. Conclusion

In this paper, based on the structural design of COFs, the high efficiency of iodine adsorption by different types of COFs and the change of iodine adsorption in different environments are discussed in detail. The performance of COFs material for adsorbing and removing iodine from solution has been fully proven, its maximum adsorption capacity can reach more than 6 times the mass of the adsorbent itself, and it also has a very fast kinetic process, and the adsorption effect is far better than existing commercial adsorbents. Many researchers have great strides in the direction of efficient iodine adsorption. However, COFs still faces challenges in iodine adsorption. In order to be applied in the actual environment as soon as possible, COFs still needs to solve a series of potential problems: such as harsh synthesis conditions of COFs, poor stability of COFs in strong radiation environment, complex environmental factors affecting the amount of iodine adsorption, and whether the highly efficient iodine adsorbent can be recycled many times. In the previous design ideas of iodine adsorption materials, iodine molecules are mostly filled into open spaces and achieving high adsorption capacity under static conditions. However, when iodine is at low concentrations, this leads to relatively weak host-guest interactions, and poor specificity selectivity when coexisting gaseous molecules are present in large numbers. Therefore, in the future, for the research and development of highly efficient iodine adsorption COFs materials, from the laboratory test stage to the actual industry should focus on solving the following three problems: First, the solvent used to synthesize COFs materials is mostly harmful to the human body organic solvents, so the green and simple synthesis path should be selected; Second, although COFs has obtained excellent adsorption capacity for iodine in solution, its application in the actual water environment needs to be explored. In order to improve the adsorption capacity, metal atoms, electron rich atoms and electron donor groups can be introduced into COFs to improve the electron density around the active site, strengthen the interaction between host and guest, and thus improve the adsorption capacity of iodine. Third, the laboratory usually uses strong acid and alkali solutions to treat the COFs after adsorption of iodine, but these strong acid and alkali solutions may have a certain risk in practical application, and the concentration should be reduced or replaced by milder regeneration reagents in future studies. In addition, due to the rapid development of the application of COFs materials in the environmental field, the relevant ecological risk assessment has yet to be carried out. With the further understanding of COFs materials, COFs materials are expected to play a more important role in iodine treatment technology.

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