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Research Article

PROBING THE CATALYTIC PERFORMANCE IN 4-NITROPHENOL REDUCTION OF TWO LANTHANIDE METAL-ORGANIC FRAMEWORKS

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ABSTRACT

The discharge of 4-nitrophenol (4-NP) into natural water has prompted scientific efforts for remediation. Many effective catalysts have been proposed to reduce 4-NP using sodium borohydride, highlighting factors like robust Lewis acidity, π-conjugate systems, and water stability to enhance 4-NP decomposition. To test whether these factors are sufficient to explain the catalytic performance of materials, two metal-organic frameworks (MOFs) that fulfilled these criteria were employed to catalyze the 4-NP reduction. We synthesized two Ln-MOF-589 (Ln = Ce, La) via a reported procedure and confirmed their identity using PXRD, SEM, IR, and TGA. Contrary to expectation, their catalytic performance in reducing 4-nitrophenol with sodium borohydride exhibited low efficiency, indicating that the presence of Lewis acid or π system is insufficient to predict the catalytic activities. Still, additional factors such as metal-linker collaboration, framework-embedded metal acidity, and structural porosity should also be considered. This result underscored the need to explore lanthanide-based MOFs and carbonized Ln-MOF-589 further to unravel the catalytic mechanisms involving metal-organic frameworks, particularly in 4-NP decomposition.

Keywords: 4-nitrophenol; lanthanide; MOF; reduction

1. Introduction

In the age of industrialization, besides undeniable economic benefits, environmental problems have always been of concern. One of these problems is the high level of chemicals in wastewater, especially those with aromatic rings, causing severe water pollution (Mejía & Reddy Bogireddy, 2022). 4-nitrophenol (4-NP), which is one of the most common intermediates used in dye, pharmaceutical, and pesticide industries. This has been reported to be harmful to the ecology due to its toxicity and carcinogen nature (Agency for Toxic Substances and Disease Registry, 2023). On that account, solutions to treating pollutants

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before discharging them into the environment have attracted many researchers, and most attention has been paid to electrochemical methods, adsorption, and chemical degradation (Din et al., 2020). Owing to the advantages of complete removal, simple working setups, and valuable reducing product (*i.e.*, 4-aminophenol), the chemical reduction method is considered a suitable solution.

The reaction between 4-NP and sodium borohydride ($NaBH_4$) as the reducing agent only occurs efficiently in the presence of nano-catalysts due to its high kinetic wall (Din et al., 2020). Several noble metal-based nanoparticles have shown magnificent catalytic performance in this reaction, but their high cost in synthesizing prompted the need for alternative materials (Abdelbasir & Shalan, 2019; J. Liu et al., 2020; Teimouri et al., 2018; Zakaria et al., 2020). Recently, scientists have exhibited many more cost-effective catalysts made from non-noble d- and f-group metals, e.g., copper(II)/cobalt(III)/iron(III)/nickel(II) oxide (Mandlimath & Gopal, 2011), CeO_2-supported nickel (She et al., 2018), cerium oxide (Keerthana et al., 2022), and lanthanum oxide (Ravi et al., 2019). However, their significant surface energy result in a high probability of aggregation, and this difficulty can be resolved by embedding the active metal atoms in a stable framework (Sun et al., 2016).

Metal-organic frameworks (MOFs), which are crystalline materials made of metal clusters and organic linkers, have emerged as favorable candidates for decomposing organic pollutants due to their distinctive features reported in many research works (Y. Liu et al., 2022). The catalytic reduction of 4-NP is suggested to follow the Langmuir–Hinshelwood mechanism, which consists of the adsorption of reactants as the first step, followed by the electron transfer to form products (Ahsan, Jabbari, et al., 2019). Since both 4-nitrophenolate (major species of 4-NP in basic medium) and BH_4^- are anions, it is predicted that positively charged metal ions are active sites for adsorption to occur. Moreover, as in the proposed catalytic mechanism for MOF UiO-66, transition metal nodes bearing Lewis acid nature also play the role of electron acceptors from BH_4^- whose electrons are then relayed to 4-NP. In other words, Lewis acidic sites promote hydride intermediate formation (Panda et al., 2022). Many other works also emphasized the significance of MOFs with Lewis acid in catalysis (Hu & Zhao, 2017; Wu & Yeow, 2022). Hence, MOFs constructed by metal clusters with strong Lewis acid characteristics show great potential for catalytic reduction of 4-NP (Zhang et al., 2021). Another critical criterion in choosing a catalyst for this reaction is its stability in aqueous solution when considering wastewater decontamination.

It is widely known that lanthanide metal ions act as forceful Lewis acids; hence they have been utilized as catalysts for acid-facilitating reactions (Fukuzumi et al., 2017; X. Wu & Yeow, 2022). Scientists presented several works with lanthanide-based MOFs (Ln-MOFs), most of which contributed to providing proof that Lewis acidity of Ln ions acted as the reaction accelerator (D’Vries et al., 2012; Zhang et al., 2021). Since 2018, Dang et al. (2019) have synthesized a series of Ln-MOFs, with Ln = Nd, Eu, Tb (Nguyen et al., 2018), Ce and La (denoted as Ln-MOF-589) (Dang et al., 2019; Tran & Nguyen, 2021), from benzoimidephenanthroline tetracarboxylic acid (H_4BIPA-TC), a bis(imide) linker, by solvothermal method. They reported that these Ln-MOF-589 had high stability in aqueous solution, which is proved by the experiments of Ce-MOF (termed Ln-MOF-589 catalyzing the Fenton-type decomposition of methylene blue with hydrogen peroxide (Dang et al., 2019). Moreover, the BIPA-TC linker, with the π conjugated system in the naphthalene rings, can further attract anion adsorption through anion-π interaction, which also helps Ln-MOF-589 become promising catalysts for the 4-NP decomposing process (Al Kobaisi et al., 2016).

These lanthanide-based MOFs, Ln-MOF-589 (Ln = Ce, La), show ultimate catalytic activities in methylene blue decomposition and olefins oxidation reaction but have not been investigated into 4-NP degrading experiments (Dang et al., 2019; Tran & Nguyen, 2021). Based on the above hypothetic mechanism, Ln-MOF-589, characterized by strong Lewis acid metal nodes, π-conjugate system promoting anion adsorption, and high stability in water, seems to be a potential candidate for catalytic reduction of 4-nitrophenol. Herein, we synthesized Ln-MOF-589 (Ln = Ce, La) from the H_4BIPA-TC linker following the procedure reported by Dang et al. (2019), then probing their catalytic activity in decomposing 4-nitrophenol with sodium borohydride to test whether the Lewis acidity and π conjugate system are sufficient to determine the activity of MOFs.

2. Experiment

2.1. Materials and general procedures

2.1.1. Chemicals

1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) was purchased from Tokyo Chemical Industry Company. 5-aminoisophthalic acid (AIA) was obtained from Ark Pharm Inc. Lanthanum(III) nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, 99.9%) and cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.9%) were purchased from Merck KGaA. N, N-dimethylacetamide (DMA, $\geq$ 99.0%) was acquired from Acros Organics. N, N-dimethylformamide (DMF, $\geq$ 99.8%) was purchased from VWR International. Finally, absolute ethanol (C_2H_5OH, 99.5%) was obtained from VN Chemsol, and acetic acid (CH_3COOH, $\geq$ 99.5%) was obtained from Xilong Scientific Company. All chemicals were used without further purification.

2.1.2. Analytical techniques

Powder X-ray Diffraction (PXRD) measurements were performed on an X-ray diffractometer (D8 Advance Eco of Bruker) with Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å) operated at 40 kV and 25 mA (1000 W). Samples of as-synthesized and activated Ln-MOF-589 (Ln = Ce, La) were successively mounted on zero background holders and then well-flattened. The PXRD patterns were recorded in the range of 2θ from 3° to 30°, a step size of 0.01°, with a count time of 0.25 s per step.

Fourier transforms infrared spectra (FT-IR) were recorded on a Jasco FT/IR-6600typeA spectrometer. Activated Ln-MOF-589 samples were prepared using potassium bromide pellets before performing FT-IR spectrometry with a scanning speed of 2 mm s^{-1} and resolution of 2 cm^{-1}.

Thermogravimetric analysis (TGA) was performed on a Labsys Evo TG-DSC under dry air flow. Samples of 8-mg activated Ln-MOF-589 were held in platinum pans and heated to 800 °C to record the TGA traces.

Scanning electron microscopic (SEM) images were captured with a JSM-IT500 InTouchScope™. Activated Ln-MOF-589 samples were captured using a Scanning electron microscope with magnifications of 100, 200, and 500 times.

The catalytic performance of the materials was investigated through the absorbance of reaction mixtures over time with a Jasco V730 UV-visible spectrophotometer.

2.2. Synthesis of H_4BIPA-TC linker

Benzoimidephenanthroline tetracarboxylic acid (H_4BIPA-TC) was synthesized by a one-step condensation reaction following the reported procedure by Nguyen et al. (2018) with slight modification. An amount of 1.35 grams of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA, 0.503 mmol) and 1.82 grams of 5-aminoisophthalic acid (AIA, 1.00 mmol) were added into a 100-mL round-bottom flask, accompanied by 10 mL of N, N-dimethylformamide (DMF). The mixture was continually stirred and heated under reflux at 120°C for nine hours. In the first hour of the reaction, DMF was added into the flask three times, with 2-3 mL each time, to dissolve the solid floating on the surface of the mixture. After being allowed to cool to ambient temperature, the mixture was filtered under low pressure to obtain the bright brown solid. This solid was then washed with DMF in a 5-mL beaker and filtered; the procedure was repeated until the bright yellow solid was obtained. The solid was washed once with ethanol, a volatile solvent, before being dried at 85°C for one hour to acquire the final product.

2.3. Ln-MOF-589 (Ln = Ce, La) synthesis and activation

The synthetic procedure of Ce-MOFs was modified from the procedure used by Dang et al. (2019 and Tran and Nguyen (2021). Before synthesis, 0.01 M stock solutions of Ce(III) were prepared from an exact amount of $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in distilled water; 0.01 M stock solution of the linker was prepared by dissolving H_4BIPA-TC in DMA. To an 8-mL vial, 2 mL of 0.01 M Ce(III) solution, 2 mL of 0.01 M linker solution, 2 mL of distilled water, and 0.6 mL of acetic acid were added. The vial was sealed and heated at 120°C for 24 hours to yield a yellow crystalline solid. The as-synthesized Ce-MOF was activated by soaking in DMF (5 mL, three times per day for two days), followed by exchanging in absolute ethanol (5 mL, three times for one day). The resulting solid was dried at 50°C for three hours to obtain activated material. La-MOF was synthesized and activated according to a similar procedure to Ce-MOF, except for $La(NO_3)_3 \cdot 6H_2O$ being used to prepare stock solution instead of $Ce(NO_3)_3 \cdot 6H_2O$.

2.4. Probing the catalytic 4-NP reduction

The catalytic performance of Ln-MOF-589 (Ln = Ce, La) in 4-nitrophenol reduction was tested through UV-vis absorption of 4-NP. For that purpose, a 2-ppm solution of 4-NP and 1 mg Ln-MOF-589 were added to a quartz cuvette and then sonicated for two minutes. After that, 4 mg of $NaBH_4$ in water was added, and the cuvette was immediately recorded its absorbance at a wavelength range of 200 – 800 nm every two minutes, using a Jasco V730 UV-vis spectrometer.

3. Results and discussion

3.1. Ln-MOF-589 synthesis and structural confirmation

After the synthesis following the above procedures, the obtained materials appeared as yellow rectangular crystals under an optical microscope and in SEM images (Figure 1), despite some cracked crystals due to the activation process. This result confirmed the shape similar to that of La-MOF-589 reported previously (Dang et al., 2019; Nguyen et al., 2018; Tran & Nguyen, 2021).

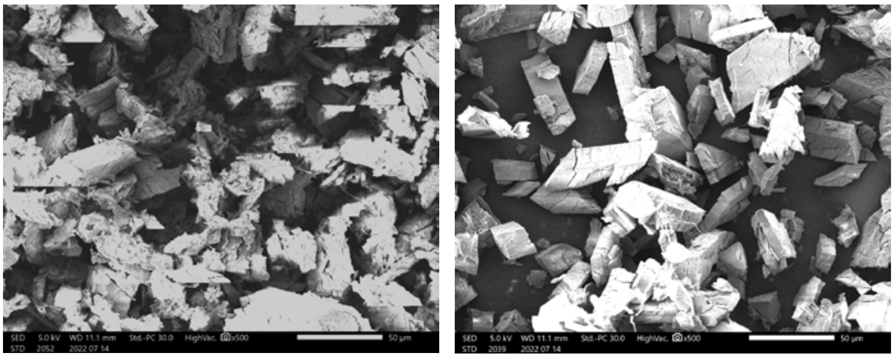

Figure 1. *Scanning electron microscopic images of Ce-MOF-589 (left) and La-MOF-589 (right) with a magnification of 500 times*

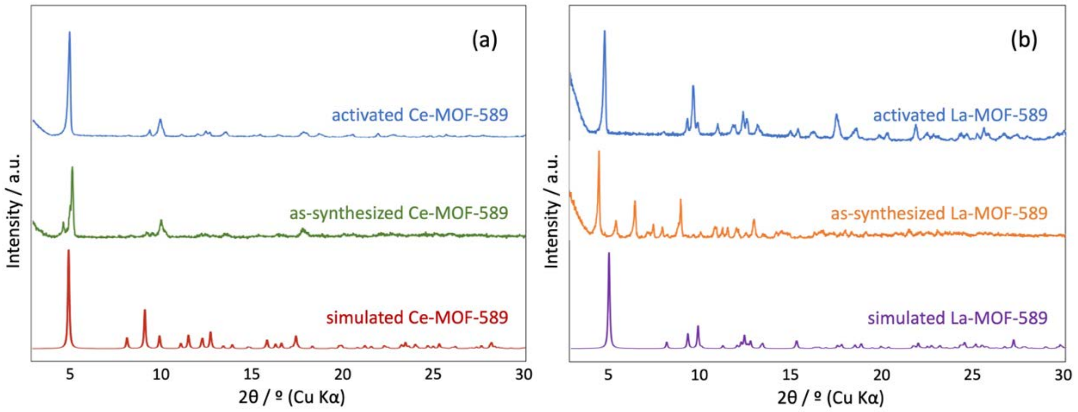

Figure 2. *Powder X-ray diffraction patterns of activated, as-synthesized, and simulated (a) Ce-MOF-589; (b) La-MOF-589*

The successful synthesis of the bulk Ln-MOF-589 was confirmed by the similarity of their PXRD diagrams to the simulated diagrams (Figure 2). As shown in Figure 2a, the patterns of as-synthesized and activated Ce-MOF-589 are in good agreement with the simulated diagram, especially the peaks at 2θ = 5° with the highest intensity. This similarity proved that the synthetic bulk material is identical to Ce-MOF-589 reported by Dang et al. (2019). Figure 2b shows the agreement of PXRD patterns of as-synthesized, activated La-MOF-589 with the simulated diagram. There is a match in peak values, among which the peak at about 5° has the highest intensity. The shift of the peaks in the as-synthesized diagram compared to the simulated pattern may be due to the solvent and guest molecules left in the sample, causing the deviation in the crystal structure. After the activation process, these guest molecules were eliminated, leading to the PXRD pattern of activated La-MOF having good matching with the simulation, which confirmed the synthesis of La-MOF-589 reported by Tran and Nguyen (2021). The coincidence of peak positions of activated and as-synthesized MOFs proved the structural maintenance of two Ln-MOF-589 after activation processes.

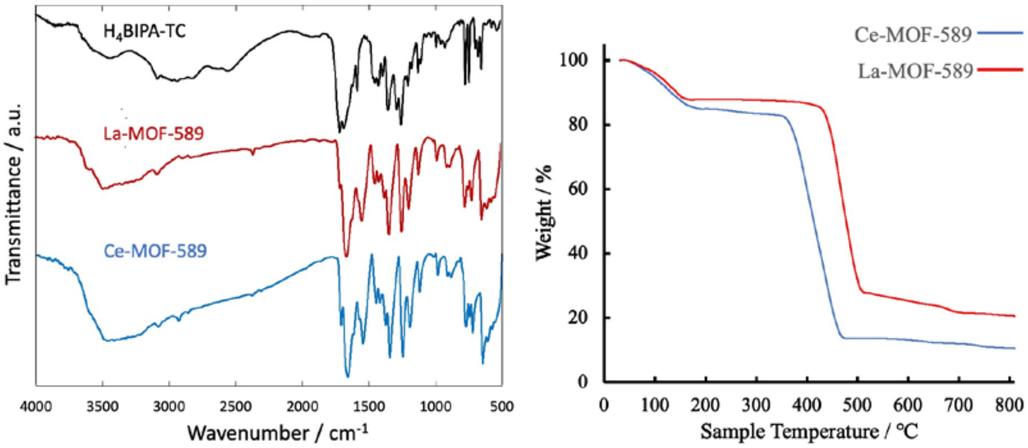

Figure 3. *Fourier transform infrared (FT-IR) spectra (left) and thermogravimetric analysis (TGA) (right) of Ln-MOF-589*

FT-IR and TGA analysis of the synthesized Ln-MOF-589 are shown in Figure 3. The striking similarities between the spectra of Ce-MOF and La-MOF, especially in the fingerprint region (1500-400 cm^{-1}), are apparent, which indicates the presence of the same functional groups in these two materials. The 1658 cm^{-1} peak appears in the three spectra, proving the presence of carbonyl amide groups in the free linker and Ln-MOFs. This observation indicates that the linker maintained its structure during the Ln-MOF synthesis and activation. Moreover, the peak at 1711 cm^{-1}, according to the carboxyl group (-COOH), appears as a strong and sharp peak in the linker spectrum but medium and weak absorption in Ln-MOF spectra, which proves the formation of metal-carboxylate coordination. This analysis was similar to the FT-IR analysis reported by Tran and Nguyen (2021), which confirms the agreement between synthesized materials and reported MOFs. In addition, the two MOFs were reported to have high thermal stability, and this feature was also confirmed by TGA patterns, from which one can infer that two Ln-MOF-589 can maintain their structure in a condition of up to about 400ºC.

3.2. Probing the catalytic performance in 4-NP reduction

The absorbance of 4-nitrophenol in the presence of sodium borohydride and Ln-MOF-589 is shown in Figure 5.

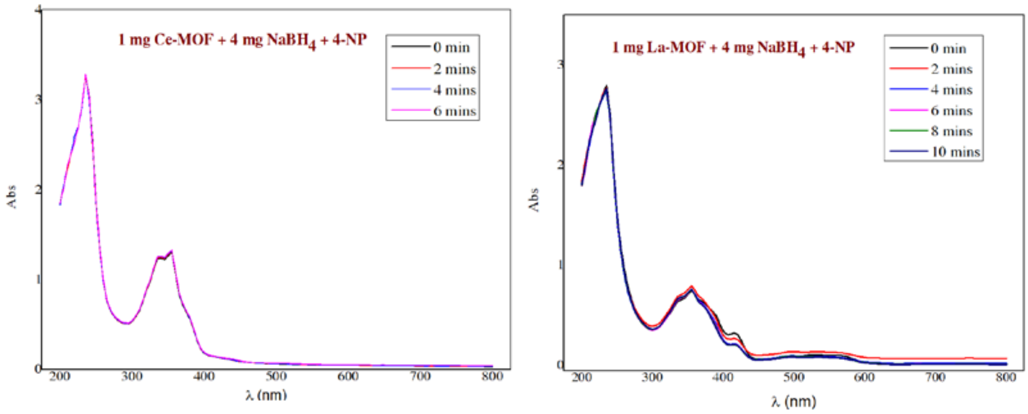

Figure 4. *Time-dependent UV-Vis absorption spectra of 4-NP solution in the presence of $NaBH_4$ and Ce-MOF-589 (left) or La-MOF-589 (right)*

It can be seen from the spectra that there is no significant change in the absorption band of 4-NP over time in the presence of Ln-MOF-589, indicating that both Ce- and La-MOF-589 show weak catalytic activity in the 4-NP reduction reaction. Considering the Langmuir-Hinshelwood mechanism mentioned at the beginning, one can infer that Ln-MOF-589 would be favorable to catalyzing the reduction of 4-NP since they met the proposed criteria: Ce^{3+} and La^{3+} are strong Lewis acid, the π system of the linker induces anion adsorption and electron relay, and the framework is stable in aqueous medium. Therefore, this surprising result suggests that there are other undefined factors controlling the catalytic activities of metal-organic frameworks. In comparison to other nanomaterials reported to speed up this reaction (Table 1), herein we point out some possible explanations and suggestions:

- Ln-MOF-589 is tightly structured, with narrow window dimensions and a modest surface area (Dang et al., 2019; Tran & Nguyen, 2021). This low porosity suggests that the interaction between the material and substrates mainly occurs on the outermost surface, decreasing the aid of active metal sites on the reaction rate. However, Ce-MOF-589 effectively catalyzes the degradation of methylene blue in the presence of peroxide, so the size of the pores may not be the critical factor in catalysis properties.
- The metal ions and the linker, if considered individually, may favor the reaction. However, several works predict that the cooperation of metal clusters and organic linkers may partially decide the functions of MOFs (Dang et al., 2019; Panda et al., 2022). This result likely supports the hypothesis of this link, but more investigation should be conducted to confirm the mechanism.

- Comparing the conversion percentage and time in Table 1, one can find that some cerium and lanthanum-based materials show weaker activity than other catalysts. It is worth noting that Lewis acidity depends on several factors, including the linker, the material structure, or the surface (Hu & Zhao, 2017). What needs to be further investigated is whether cerium and lanthanum are unlikely to catalyze 4-NP reduction, or whether the framework formation diminishes the activities of these metal ions.
- The series of C@Me (with Me = Fe, Ni, Cu, Co) listed in Table 1, researched by Ahsan and his colleagues, showed incredible results in facilitating the reaction rate. These nanocarbons, in addition to many other materials, do not contain the π conjugate system as in Ln-MOF-589, contrary to the hypothesis of anion-π interaction augmenting the adsorption and reaction process. Another exciting feature of these nanocarbons is that they are all made by carbonizing related MOFs. In recent years, MOF-derived nanocarbons have emerged as new nanomaterials showing high thermal stability and good catalytic performance; in some cases, they offer better activity than their MOF precursors (Kharissova et al., 2020). Hence, further research should be done to reveal if lanthanide nanocarbons derived from Ln-MOF-589 enhance the catalytic performance in decomposing 4-nitrophenol.

Table 1. *Catalytic performance towards nitroarenes decomposing reactions of some reported nanomaterials*

No.	Material	Metal node	Pi conjugate system	Yield (%)	Time required (min)	Reference
1	Au-Ag/GO (I)	Au, Ag	Graphene	100	0.5	(T.Wu et al., 2013)
2	C@Fe	Fe	No	100	4	(Ahsan et al., 2019)
3	C@Ni	Ni	No	98.25	1	(Ahsan et al., 2019)
4	C@Cu	Cu	No	95.35	1	(Ahsan et al., 2019)
5	C@Co	Co	No	99.34	2	(Ahsan et al., 2019)
6	MOF UiO-66	Zr (strong Lewis acid)	Benzene	100	10	(Panda et al., 2022)
7	CeO_2	Ce	No	50	45	(Keerthana et al., 2022)
8	Hf^{3+}-doped La_2O_3	Hf, La	No	85	90	(Ravi et al., 2019)
9	MOF RPF-16	La	No	15	60	(D’Vries et al., 2012)

4. Conclusion

The decline in water quality due to toxic industrial discharge, including 4-nitrophenol, has posed challenges to scientists in finding solutions. Among suggested approaches in removing 4-NP, the method of chemical reduction using $NaBH_4$ stands out thanks to its high-yield conversion to useful 4-aminophenol, but heterogeneous catalysts are required. Hundreds of excellent catalysts for this reaction have been reported in several works, many of which proposed that robust Lewis acidity, the presence of the π-conjugate system, and water stability are favorable to accelerate the decomposition of 4-NP. The two lanthanide-based metal-organic frameworks constructed with the H_4BIPA-TC linker denoted as Ln-MOF-589 (Ln = Ce, La), satisfied the above criteria and therefore were used to probe for their catalytic activities towards 4-NP reduction, which has not been conducted before.

We synthesized two Ln-MOF-589 (Ln = Ce, La) by applying the procedures by Tran and Nguyen (2021) and confirmed the successful synthesis of these materials by PXRD, SEM, IR, and TGA. We probed their catalytic activity in reducing 4-nitrophenol with sodium borohydride and found that both Ln-MOF-589 showed critically low efficiency towards this reaction. This result revealed that the above criteria are insufficient to rationalize the mechanism of catalysts in 4-NP reduction; at the same time, other factors may be attributed to the properties of MOFs, namely metal-linker cooperation, Lewis acidity of framework-embedded metals, and structural porosity. This result recommended that further research into the catalytic activity of other lanthanide-based MOFs and carbonized Ln-MOF-589 should be conducted to uncover the myths in the catalyzing mechanism of metal-organic frameworks in general and, in particular, the 4-NP decomposition.

- ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*
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THĂM DÒ HOẠT TÍNH XÚC TÁC PHẢN ỨNG KHỬ 4-NITROPHENOL CỦA HAI VẬT LIỆU KHUNG HỮU CƠ-KIM LOẠI NHÓM LANTHANIDE

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TÓM TẮT

Tuy là một hoá chất quan trọng trong công nghiệp, vấn đề ô nhiễm nước do sự tồn tại của 4-nitrophenol (4-NP) trong nước thải đã thúc đẩy các nỗ lực khoa học nhằm xử lí hoá chất này trước khi bị đưa vào nguồn nước tự nhiên. Nhiều chất xúc tác hiệu quả đã được đề xuất để khử 4-NP bằng cách sử dụng sodium borohydride, dự đoán rằng các yếu tố như tính Lewis acid mạnh, hệ liên hợp π và tính bền trong nước quyết định khả năng phân hủy 4-NP. Để kiểm chứng các yếu tố này có đủ để giải thích hiệu suất xúc tác của vật liệu hay không, hai vật liệu khung hữu cơ-kim loại (MOF) đáp ứng các tiêu chí này đã được sử dụng để xúc tác cho quá trình khử 4-NP. Chúng tôi đã tổng hợp hai Ln-MOF-589 (Ln = Ce, La) thông qua quy trình đã được công bố và xác định bằng PXRD, SEM, IR và TGA. Trái ngược với mong đợi, hai vật liệu này thể hiện hoạt tính xúc tác kém trong phản ứng khử 4-nitrophenol bằng sodium borohydride, cho thấy rằng sự hiện diện của Lewis acid hoặc hệ thống liên hợp π là không đủ để dự đoán hoạt tính xúc tác. Bên cạnh đó, các yếu tố khác như tương tác của tâm kim loại và cầu nối hữu cơ, lực acid của kim loại trong cấu trúc vật liệu và độ xốp cũng cần được xem xét. Kết quả này nhấn mạnh sự cần thiết phải nghiên cứu thêm các MOF tổng hợp từ kim loại lanthanide và vật liệu Ln-MOF-589 carbon hóa để làm sáng tỏ các cơ chế xúc tác liên quan đến vật liệu MOF, đặc biệt là trong phản ứng phân hủy 4-NP.

Từ khoá: 4-nitrophenol; lanthanide; MOF; reduction