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# Porous metal oxides derived from Cu–Al layered double hydroxide as an efficient heterogeneous catalyst for the Friedel–Crafts alkylation of indoles with benzaldehydes under microwave irradiation



Thanh-Truc Hoang Nguyen<sup>a</sup>, Xuan-Trang Thi Nguyen<sup>b</sup>, Chinh Quoc Nguyen<sup>a</sup>,  
Phuong Hoang Tran<sup>b,\*</sup>

<sup>a</sup> Department of Inorganic Chemistry, Faculty of Chemistry, University of Science, Viet Nam National University, Ho Chi Minh City, 721337, Viet Nam

<sup>b</sup> Department of Organic Chemistry, Faculty of Chemistry, University of Science, Viet Nam National University, Ho Chi Minh City, 721337, Viet Nam

\* Corresponding author.

E-mail address: [thphuong@hcmus.edu.vn](mailto:thphuong@hcmus.edu.vn) (P.H. Tran).

## Abstract

Four Cu-Mg-Al mixed metal oxides (MMO) were synthesized through the calcination of layered double hydroxides (LDHs). These catalysts were fully characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller surface area (BET), and inductively coupled plasma optical emission spectrometer (ICP-OES). The catalytic efficiency of porous metal oxides derived from LDHs has been tested successfully for the synthesis of bis(indolyl)methanes *via* the Friedel–Crafts alkylation of indoles with aromatic aldehydes under solvent-free microwave irradiation. The Cu-Al MMO showed the best catalytic activity to produce the expected products up to 98% yield and 100% selectivity for only 20 min under

solvent-free microwave irradiation. Moreover, the catalyst can be recovered quickly from the reaction mixture by filtration and reused several times without significant loss of the reactivity.

Keywords: Inorganic chemistry, Organic chemistry, Materials science

## 1. Introduction

Bis(indolyl)methanes are versatile synthetic intermediates for their biomedical applications in antitumor, antibacterial, antimicrobial, and antifungal activity [1, 2, 3, 4, 5]. Thus, the search for simple and efficient protocols for the selective synthesis of bis(indolyl)methanes has attracted much attention [3, 5, 6, 7]. Traditionally, three protocols have been developed for the synthesis of bis(indolyl)methanes including the condensation of indoles with alcohols or acetals under oxidative conditions [8, 9, 10], Bartoli reaction [11], and Friedel–Crafts alkylation of indoles with aldehydes [12, 13, 14]. Among these, Friedel–Crafts alkylation reaction is the favorable methodology with 100% atom economy and gives the high selectivity for desired product [15]. The synthesis of bis(indolyl)methanes occurs *via* the alkylation reaction between indoles and aldehydes has been studied intensively in the presence of an acid or base catalyst [7, 10, 16, 17]. Although various homogeneous and heterogeneous catalysts have been reported in the literature, there remain some drawbacks including long reaction time [7, 12], harmful organic solvent [18], and unrecyclable catalyst [18]. There, there is a demand to develop a new recyclable catalyst for the synthesis of bis(indolyl)methanes in high yield, short reaction time, and solvent-free condition.

Layered double hydroxides (LDHs) have been known as hydrotalcite-like compounds, which can be represented by the general formula  $[M_{(1-x)}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$  [19, 20, 21]. LDHs are composed of brucite-like layers in which a fraction of the divalent metal cations coordinated octahedrally by hydroxyl groups [19, 22, 23, 24]. When the divalent metal cations have been replaced by the trivalent metal cations, a positive charge is produced in the layer and balanced by an anion (*e.g.*, carbonate or hydroxyl) [25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. An advantage is that LDHs can be synthesized readily *via* coprecipitation, which is easy to scale up for industrial processes [25, 35, 36]. The mixed oxides can be synthesized by calcination of LDHs at 400–500 °C, and the thermal treatment of the LDHs materials destroys the lamellar structure to generate the porous mixed oxides [37]. Due to well-defined surface sites, there has been a rapid increase in publications related to the use of porous mixed oxide derived from LDHs as heterogeneous catalysts or catalyst supports in organic synthesis [38, 39, 40].

Herein, we disclose the preparation of various types of Mg–Cu–Al MMO and application as the catalysts for the preparation of bis(indolyl)methanes from the alkylation of indoles with aromatic aldehydes under solvent-free microwave irradiation. To the best of our knowledge, the catalyst has not been used as the catalyst for the synthesis of bis(indolyl)methanes. The LDHs were prepared with different mole ratio Mg–Cu–Al with a constant ratio of  $(\text{Mg} + \text{Cu})/\text{Al} = 3:1$ . The Mg–Cu–Al MMO were varied from 3:0:1, 2:1:1, 1:2:1, and 0:3:1 ratios respectively were prepared and tested the catalytic activity on the Friedel–Crafts alkylation of indole with aromatic aldehydes. This is the first time that the Mg–Cu–Al MMO have been used as a catalyst for the synthesis of bis(indolyl)methanes.

## 2. Experimental

### 2.1. Materials and characterizations

Mg, Cu and Al nitrates (99.8%), NaOH (99%) and  $\text{Na}_2\text{CO}_3$  (99%) were purchased from Merck. Indole (99%), benzaldehyde (99%), 4-methylbenzaldehyde (98%), 4-methoxybenzaldehyde (98%), 4-*tert*-butylbenzaldehyde (97%), 4-nitrobenzaldehyde (97%), 4-fluorobenzaldehyde (98%), 4-chlorobenzaldehyde (97%), 4-bromobenzaldehyde (99%), 3-chlorobenzaldehyde (97%), 2-chlorobenzaldehyde (99%) were purchased from Sigma-Aldrich. Silica gel 230–400 mesh for flash column chromatography, TLC plates (silica gel 60 F254), acetone, ethyl acetate, and petroleum ether were obtained from Merck. Deuterated solvent,  $\text{CDCl}_3$  was purchased from Cambridge Isotope Laboratories (Andover, MA) and used without further purification.

The reaction was carried out on a CEM Discover BenchMate apparatus which offered microwave synthesis with safe pressure regulation using a 10 mL pressurized glass tube with Teflon-coated septum. The GC analyses of products were performed on Agilent GC System 7890 equipped with a mass selective detector Agilent 5973N and a capillary DB–5MS column (30 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ). NMR spectra were recorded on Bruker Advance 500 MHz. The X-ray diffraction patterns of the materials were analyzed by an X-ray powder D2 Phaser diffractometer (Bruker) with  $\text{Cu K}\alpha$  radiation. Diffraction intensity was measured between  $5^\circ$  and  $85^\circ$ , with a  $2\theta$  step of  $0.02^\circ$  and a counting time of 9 s per point. In addition, the thermogravimetric analysis (TGA) was carried out with TGA-Q5000 machine from  $0^\circ\text{C}$  to  $800^\circ\text{C}$  and the scanning electron microscopy image (SEM) was recorded on a Hitachi Model FE-SEM S4800 (Japan). The elemental composition of catalyst was measured by using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 4300DY Perkin Elmer).

## 2.2. Preparation of catalysts

The Mg–Cu–Al LDHs were synthesized through the simplest co-precipitation method. Under vigorous stirring, an aqueous solution of metal nitrates (solution A, 50.00 mL) containing  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cu}^{2+}$  (total cationic concentration of 1.0 M) with the Mg:Cu:Al mole ratios of 3:0:1 (LDH-1); 2:1:1 (LDH-2); 1:2:1 (LDH-3); 0:3:1 (LDH-4) was slowly dropped in a solution (solution B, 500.00 mL) containing NaOH 1 M and  $\text{Na}_2\text{CO}_3$  0.4 M with a speed rate 1.5 mL/minute. The temperature was maintained at room temperature with a constant pH of 10. The resulting suspension was filtered with 0.2 mm membranes; the crude product was washed with deionized water and the filtered water was checked for almost neutral pH. The obtained slurry was aged at room temperature for 24 h and then dried at 80 °C for 24 h. The samples were calcined at 500 °C for 4 h to obtain the MMO.

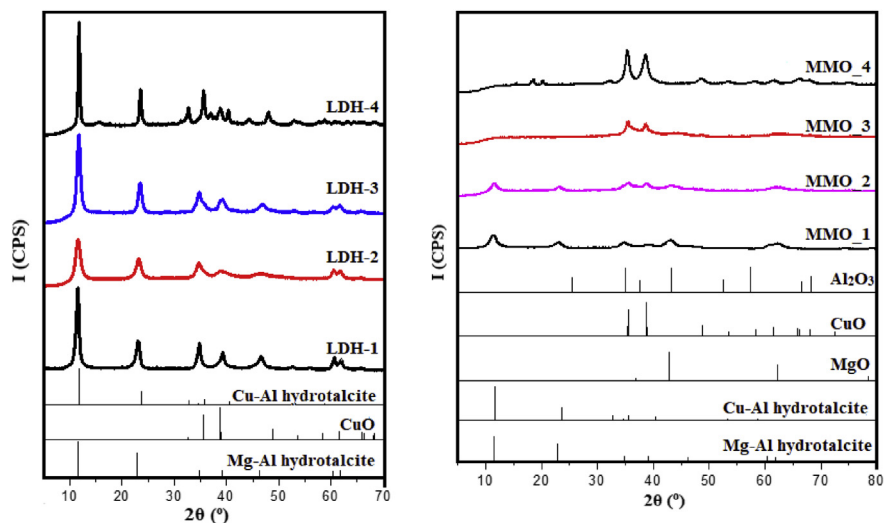
## 2.3. Bis(indolyl)methanes synthesis

The alkylation reactions were carried out in microwave oven with MMO as a catalyst. The mixture of benzaldehyde (0.106 g, 1.0 mmol), indole (0.234 g, 2.0 mmol), and MMO (0.02 g) was charged into a 10 mL pressurized glass tube and irradiated under microwave heating. After completion the reaction, the reaction mixture was diluted with ethyl acetate (5 mL) and the catalyst was filtered from mixture. The filtrate was diluted with ethyl acetate (10 mL), washed with  $\text{H}_2\text{O}$  ( $3 \times 20$  mL), dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was removed on a rotary evaporator. The purity and identity of the products were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and GC-MS spectrometry (please see in supporting information).

## 3. Results and discussion

### 3.1. Characterization of layered double hydroxides

The X-ray diffraction patterns of prepared Mg–Cu–Al LDHs with different molar ratios were shown in Fig. 1. The XRD pattern of the LDH-4 displays a range of typical diffraction peaks at  $2\theta$  11.7°, 23.5°, 32.6°, 35.5°, 40.3°, which are indexed to the (200), (400), ( $\bar{3}02$ ), (21 $\bar{1}$ ), (311) of Cu–Al hydrotalcite phase, respectively. CuO phase displays typical diffraction peaks at  $2\theta$  35.5°, 38.7° which are indexed to the (11 $\bar{1}$ ), (111) with low intensity. The XRD pattern of the LDH-1 shows a range of typical diffraction peaks at  $2\theta$  11.4°, 22.9°, 34.8°, 39.2°, 46.6°, 60.6°, 61.9° which are indexed to the (003), (006), (009), (015), (018), (110), (113) of Mg–Al hydrotalcite phase, respectively. The temperature of 500 °C was the best choice for the calcination of the catalysts to obtain MMO because there was the loss of crystal water and the loss of  $\text{CO}_2$  released from  $\text{CO}_3^{2-}$ . Those losses would be able to increase the surface areas of LDHs materials that making these materials become efficient catalysts. Representative XRD patterns of the MMO materials were shown in Fig. 1 (right).

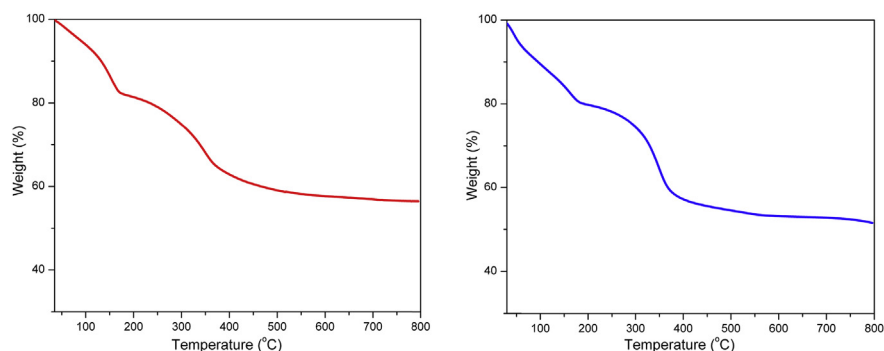


**Fig. 1.** The XRD patterns of the uncalcined (left) and calcined (right) Mg–Cu–Al LDHs.

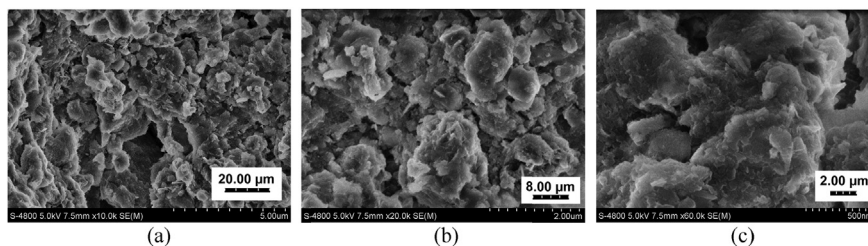
After calcination, four samples exhibit the poor characteristic peaks of poorly crystalline hydrotalcite phase at the samples MMO-1 and MMO-2 and show mixed oxides MgO, CuO, Al<sub>2</sub>O<sub>3</sub>.

The thermogravimetric analyses (TGA) for different LDHs are presented in Fig. 2. The TGA showed three prominent weight-loss steps. The first one is in the range of 50–190 °C due to the elimination of interlayer water molecules. The second weight-loss step occurred in the temperature range of 200 °C–500 °C, where there was the dehydroxylation of the metal hydroxide layers and decarbonation in the interlayer space as a charge-balancing anion. Additionally, the Mg:Cu:Al mole ratios analyzed by ICP-OES were slightly different from the pre-calculated mole ratios. The molar ratios of LDH-1, LDH-2, LDH-3, LDH-4 were 2.9:0:1, 1.9:1:1, 1:2:1, and 0:2.9:1, respectively.

The surface morphology of MMO-4 sample was confirmed by scanning electron microscopy (SEM). The results were shown in Fig. 3. The particles of MMO-4 sample



**Fig. 2.** TGA of LDH-1 (left) and LDH-4 (right).



**Fig. 3.** SEM images of calcined layered double hydroxide MMO-4, magnification (a) 10000 times (b) 20000 times (c) 60000 times.

was variable size and shapes. It consisted of a relatively uniform hexagonal platelet-like structure, which was typical for layered material.

The specific surface area for all calcined and uncalcined LDHs samples was presented in Table 1. The calcined LDHs samples exhibited a higher surface area than that of uncalcined ones. The release of CO<sub>2</sub> would result in the more porous surface of MMO, followed by the increase in MMO surface area. Moreover, the surface area of samples increased presumably due to the increase of Cu concentration. All the calcined samples showed very good BET surface area between 100 and 244 m<sup>2</sup>/g.

### 3.2. Synthesis of bis(indolyl)methanes using calcined LDHs as catalysts

The activity of prepared MMO-4 derived from LDH-4 was next tested in the model reaction of indole (2 mmol) and benzaldehyde (1 mmol) under solvent-free microwave irradiation. As shown in Table 2, the reaction occurred smoothly in the presence of 10 mg of MMO-4, afforded the desired product in 98% yield without any side-products (Table 2, entry 7).

Next, various LDHs including LDH-4, MMO-1, MMO-2, MMO-3, MMO-4 were also tested under the optimized condition and the desired products were afforded in low yields (Table 3, entries 1–5). As seen in Table 3, the uncalcined LDHs (entry 1) provided the lower yield than the MMO. The difference in the product yield between calcined and uncalcined LDHs could be explained by a significant change in

**Table 1.** BET surface area values of layered double hydroxides.

Entry	Uncalcined samples	BET (m <sup>2</sup> /g)	Calcined samples (500 °C)	BET (m <sup>2</sup> /g)
1	LDH-1	48.6097	MMO-1	101
2	LDH-2	51.6732	MMO-2	196
3	LDH-3	66.8227	MMO-3	198
4	LDH-4	74.9816	MMO-4	234

**Table 2.** An initial survey of reaction conditions for reaction of indole with benzaldehyde.

Entry	Temperature (°C)	Catalytic amount (mg)	Mole ratio indole:benzaldehyde	Time (min)	Yield <sup>a</sup> (%)
1	100	10	2:1	10	30
2	120	10	2:1	10	57
3	140	10	2:1	10	62
4	160	10	2:1	3	83
5	160	1	2:1	10	68
6	160	5	2:1	10	80
7	<b>160</b>	<b>10</b>	<b>2:1</b>	<b>10</b>	<b>98</b>
8	160	10	3:1	10	90
9	160	10	4:1	10	90

<sup>a</sup> Isolated yield.

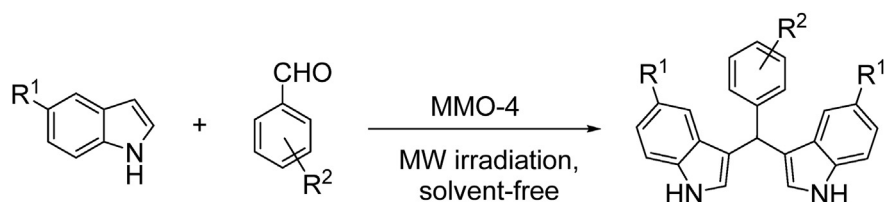
the surface area of the LDHs material under calcination procedure, in which the MMO samples could reach surface areas from 100 m<sup>2</sup>/g to 234 m<sup>2</sup>/g while the uncalcined LDHs samples could only attain surface areas of 75 m<sup>2</sup>/g. Remarkably, when the Cu concentration of samples increased, the yields of the desired product were improved significantly (Table 3, entries 2–5). LDHs were heated by the calcination at the temperature of 500 °C; they would be transformed into MMO. To confirm the catalytic activity of MMO, the control experiment with CuO/Al<sub>2</sub>O<sub>3</sub> (Cu<sup>2+</sup>: Al<sup>3+</sup> = 3:1) was also investigated, and the expected product was afforded in 16% yield (Table 3, entry 6). Consequently, the MMO have displayed the high catalytic activity in the bis(indolyl)methane synthesis.

With the optimized conditions in hands, we then conducted the reactions on a variety of reactants to explore the scope of this method (Fig. 4). As shown in Table 4, a variety of aromatic aldehydes smoothly reacted with indoles to produce bis(indolyl) methanes under solvent-free microwave irradiation, and the desired products were obtained in the range of 71%–98% yields. For the substituted benzaldehydes bearing

**Table 3.** The effects of samples in the reaction of indole with benzaldehyde.<sup>a</sup>

Entry	Catalyst	Isolated yield (%)
1	LDH-4	33
2	MMO-1	53
3	MMO-2	58
4	MMO-3	87
5	MMO-4	98
6	CuO and Al <sub>2</sub> O <sub>3</sub>	16

<sup>a</sup> Reaction condition: indole (2 mmol), benzaldehyde (1 mmol), catalyst (10 mg), solvent-free microwave irradiation at 160 °C, 10 min.



**Fig. 4.** Synthesis of various bis(indolyl)methanes.

electron-donating groups, such as alkyls on the aromatic ring, good yields of the product were obtained for 15 min (Table 4, entries 2–4). Benzaldehyde with halogen group at the *para* position provided the expected product in moderate yields (Table 4, entries 5–7). For the chloro substituted in the *ortho*, *meta* and *para* positions (Table 4, entries 6, 8–9), *o*-chlorobenzaldehyde afforded the desired product in excellent yield (95%) due to the increase of negative inductive effect. Nitrobenzaldehyde accommodated the desired product in excellent yield due to strong electron-withdrawing substituent (Table 4, entry 10). To further investigate the scope of indole, variously substituted indoles including 5-nitroindole, 5-chloroindole, and 5-methylindole were studied for their reactivity under present method. The electron-withdrawing substituent such as NO<sub>2</sub> provided the desired product in a lower yield than the unsubstituted indole (Table 4, entries 1, 11), while electron-donating substituents gave the product in high yield (Table 4, entries 12–15).

**Table 4.** Synthesis of various bis(indolyl)methanes using MMO-4 as a catalyst.

Entry	R <sup>1</sup>	R <sup>2</sup>	Conditions	Isolated yield (%)
1	H	H	160 °C, 10 min	98
2	H	4-CH <sub>3</sub>	160 °C, 15 min	83
3	H	4- <i>t</i> -Bu	160 °C, 15 min	80
4	H	4-OCH <sub>3</sub>	160 °C, 15 min	87
5	H	4-F	160 °C, 15 min	81
6	H	4-Cl	160 °C, 20 min	71
7	H	4-Br	160 °C, 20 min	73
8	H	3-Cl	140 °C, 10 min	92
9	H	2-Cl	140 °C, 10 min	95
10	H	4-NO <sub>2</sub>	140 °C, 20 min	98
11	NO <sub>2</sub>	4-H	160 °C, 10 min	83
12	Cl	4-CH <sub>3</sub>	160 °C, 20 min	84
13	Cl	4- <i>t</i> -Bu	160 °C, 20 min	86
14	CH <sub>3</sub>	4-CH <sub>3</sub>	160 °C, 15 min	93
15	CH <sub>3</sub>	4- <i>t</i> -Bu	160 °C, 15 min	90



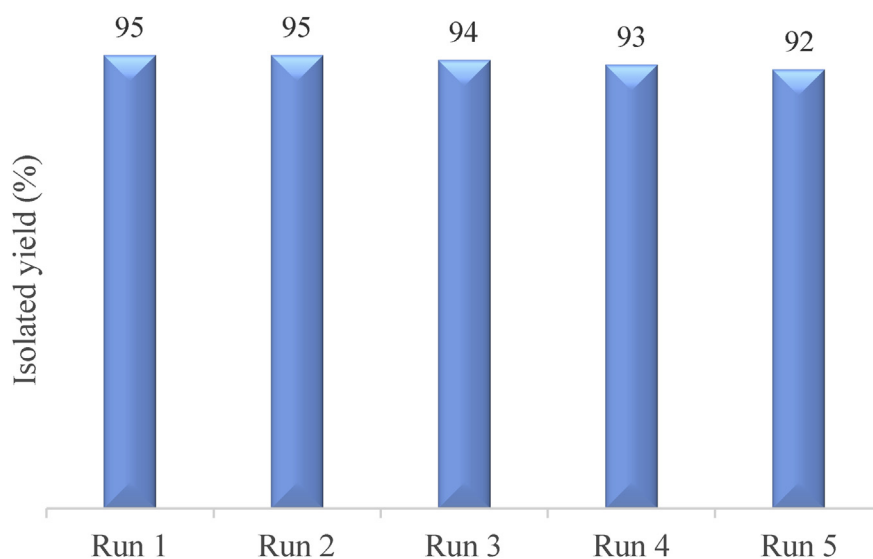


Fig. 5. Reusability of MMO-4.

The recovered catalyst was tested in the model reaction of indole and benzaldehyde under the optimized conditions. The results were presented in Fig. 5. The slight decrease observed in the catalytic activity due to the weight loss in the work-up process. PXRD showed that the crystallinity and integrity of MMO-4 were maintained after the fifth cycle (Fig. 6). The high catalytic activity and easy recycling of MMO-4 are promising for the application on industrial processes.

LDHs display both basic and acidic properties [41]. After calcination of LDH at high temperatures, MMO is obtained with the large surface area and many  $M^{2+}$ ,  $M^{3+}$  Lewis acidic sites [42]. Base on our experiments and previous literature [15, 16, 43, 44], a proposed mechanism for MMO-catalyzed the Friedel–Crafts alkylation of indoles with aromatic aldehydes is presented in Fig. 7. The electrophilicity of carbonyl carbon is activated in the presence of MMO and readily reacted with indole

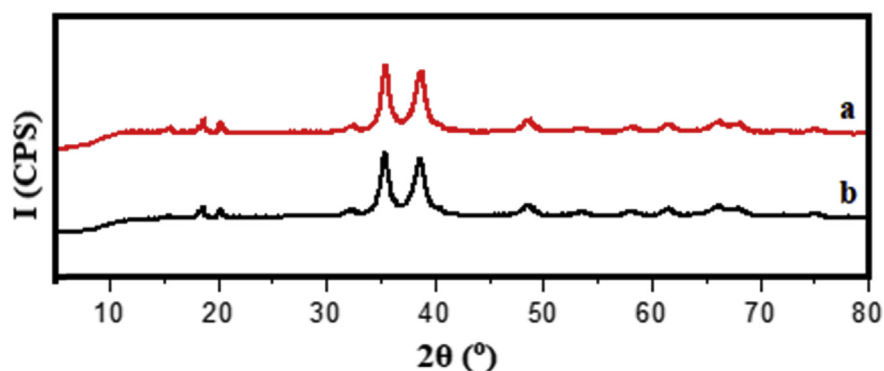
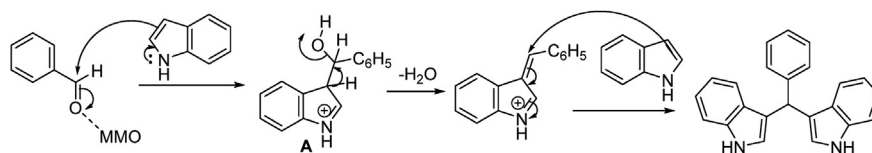


Fig. 6. The XRD patterns of (a) the reused MMO-4 after fifth time recycling, (b) fresh-prepared MMO-4.



**Fig. 7.** The proposed mechanism of Friedel–Crafts alkylation of indole with benzaldehyde.

to provide the intermediate (A), followed by dehydration of (A). Finally, the nucleophilic addition of another mole of indole afforded the expected product.

## 4. Conclusions

We have developed the first MMO as heterogeneous catalysts for the synthesis of bis(indolyl)methanes under solvent-free microwave irradiation. The inexpensive and non-toxic, recyclable MMO efficiently promoted the Friedel–Crafts alkylation of indole with aromatic aldehydes in high yields within short reaction times. This method contributes a low-cost and straightforward pathway to obtain bis(indolyl)methanes which are essential units in medicinal chemistry.

## Declarations

### Author contribution statement

Thanh-Truc H. Nguyen, Chinh Q. Nguyen, Xuan-Trang T. Nguyen: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Phuong H. Tran: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

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