

# Facile synthesis of novel heterogenous Rh/COF catalyst and its application in tandem selective transfer hydrogenation and mono-methylation of Nitro compounds with Methanol

Mingyue Zhang <sup>a,c</sup>, Jianguo Liu <sup>b\*</sup>, Nan Wang <sup>a,e</sup>, Xiuzhi Wei <sup>a,f</sup>, Bo Yang <sup>d\*</sup>, Longlong Ma <sup>a,b\*</sup>

<sup>a</sup> Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China.

<sup>b</sup> Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, PR China.

<sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

<sup>d</sup> Guangzhou Special Pressure Equipment Inspection and Research Institute, 9 Keyan Road, Guangzhou 510663, P.R. China.

<sup>e</sup> School of Environmental Science and Engineering, Tianjin University, Tianjin 300350, P. R. China.

<sup>f</sup> Department of Engineering Science, University of Science and Technology of China, Hefei 230026, P. R. China.

\* Corresponding author: liujg@ms.giec.ac.cn; mall@ms.giec.ac.cn

**Keywords:** *COF supported Rh catalyst; transfer hydrogenation; mono-methylation; nitro compounds*

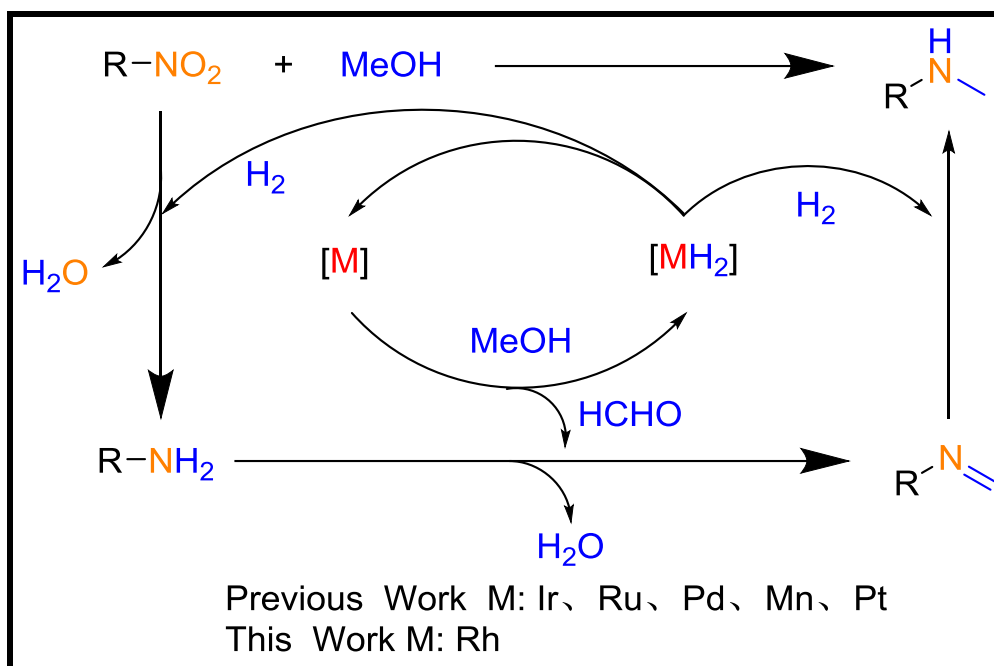
**Abstract:** The development of transition metal heterogeneous catalysts for economical and effective synthesis of N-methylamine, especially for the mono-methylation of amines is still challenging. Herein, two unprecedented Rh-supported COFs heterogeneous catalysts Rh/MelCOF was facile synthesized by Schiff base reaction using melamine as a precursor, and for the first time, it was successfully applied to the effective and high selective tandem reaction of transfer hydrogenation and mono-methylation of nitroaromatic hydrocarbons with methanol as C1 and hydrogenation source, with water as the only by-product. A series of nitroaromatic hydrocarbons, including heterocyclic or sterically hindered derivatives, can be well tolerated and the catalyst could also be reused 4 times without losing significant reactivity. At the same time, the study of the Rh/MelCOF mechanism supports the hydrogen borrowing mechanism and puts forward the reaction pathway of azobenzene as an intermediate, which is better than the hydrogen transfer pathway from N-phenylhydroxylamine to aniline directly. This work not only expands the COF family but also provides an effective way to obtain mono N-methylated amines from nitroaromatic hydrocarbons, as well as the detailed mechanism of Rh/COF catalyzed tandem transfer hydrogenation and mono-methylation of amines.

## 1. Introduction

N-methylamine is a high-value chemical product, which is widely used in the fields of drugs, bioactive products, dyes, preservatives, and agrochemicals[1-8]. Traditional synthesis methods require toxic and dangerous stoichiometric reagents, such as halogenated methane [9], dimethyl sulfate [10], or diazomethane[11]. Reactions using these reagents produce a large amount of waste and exhibit low selectivity due to excessive alkylation to N, N-dimethylamine. At present, more environmentally friendly methylating agents such as formaldehyde [12], formic acid [13, 14], and carbon dioxide [15-20] are also used to synthesize N-methylated amines, but the reaction requires excessive reducing agents or more stringent reaction conditions, such as high reaction temperature or excessive reducing sources, such as silane, molecular hydrogen, and so on. Therefore, in this case, direct and highly selective N-mono-methylation is a great challenge in drug synthesis chemistry. Nowadays, many homogeneous and heterogeneous metal catalysts have been developed for

selective N-methylation, such as Ir, Ru, Mn, Ni, and so on. But these methods generally use aliphatic amine or aromatic amine as the starting material.

One of the other traditional synthetic ways for preparing aromatic amines uses inexpensive and readily available nitroarenes for reductive amination [21-24]. In these cases, with methanol as an economical and sustainable C1 source in the reaction for methylation and water as the sole byproduct, this method is more attractive and promising from both economic and environmental perspectives [22, 24-29]. Moreover, the dehydrogenation performance of methanol is much higher than that of higher alcohols such as ethanol and isopropanol. Therefore, it is of great practical importance to use a tandem and cost-effective one-pot method to selectively synthesize N-methylated amines using nitroarenes as the feedstock methanol as the methylation and hydrogenation source. The synthesis of N-methylated amines by such methods is less common although there have been a few reports in recent years (**Scheme 1**). First, the ruthenium NNN pincer complexes, which can efficiently catalyze the N-methylation of nitroarenes as well as vinyl nitro compounds into mono- and dimethylated amines, and the corresponding mechanisms pathways have been proposed [30]. Recent reports have also applied this tandem transformation system based on Ir, Ru, Pd, Mn, Pt. Among them, Ir is mainly based on functional NHC ligands, which confer Ir higher activity and selectivity, which improves the substrate application range of the series conversion system, in which N-heterocyclic carbene-iridium (NHC-Ir) coordination assemblies based on bis-pyrenoimidazolium salts are heterogeneous catalyst and has reusability [31-33]. The Ru catalyst system uses commercial precursor  $[\text{RuCl}_2(\text{p-cymene})_2]_2$  and NNN pincer (amine-pyridine-imine, API) as ligand to prepare the efficient catalyst in-situ[34]. The Pd based catalysts, which are generally referred to as a catalyst system composed of commercial catalyst Pd/C or Pd (OAc)<sub>2</sub> and ligand 1-[2-isopropyl (isopropyl) phenyl]-2-[tert-butyl (2-pyridinyl) phosphino]-1H-imidazole, usually require high catalyst loading, excessive auxiliary ligands, and longer reaction time[35, 36]. It has been reported that the synthesis catalyst [(N,N'-bis(diisopropylphosphino)-2,6-diaminopyridine)Mn(CO)<sub>3</sub>][Br] can obtain 90% separation yields after optimization, but the existence of alkali and molecular sieve with a high chemical equivalence ratio is necessary[37]. The previously reported Pt/C also gave high yields for this reaction, but it also required higher reaction temperatures and reaction times[38]. In summary, to make this series conversion reaction more widely used, the reaction conditions were milder and more sustainable, therefore, the heterogeneous catalysis of different metals was applied to the N-monomethylation of nitroaromatic hydrocarbons with methanol as methylation and hydrogenation source.



**Scheme 1.** Synthesis of N-methylamines by using methanol.

Covalent organic frame materials are a kind of periodic and crystalline organic porous polymers connected by covalent bonds. Because of its good thermal and chemical stability, ordered pore structure, good crystallinity, and designability of the unit structure, it has become a research hotspot in recent years. [39-45] Among them, the Schiff base COFs are connected by C=N, and both N in the precursor and N in the Schiff base can be used to anchor metal atoms to form strong coordination bonds. Nowadays, COFs are used in Suzuki reaction [46, 47], Sonogashira reaction [48], Diels Alder reaction [49], Michael addition reaction [50], and so on [46], but there are few reports on the application of COFs supported transition metal in N-methylation reaction. Specifically, when concerning the challenging tandem hydrogenation and N-mono-methylation of nitroaromatic hydrocarbons, especially when methanol served as both methylation and hydrogenation source, it undoubtedly requires that the transition metals should have the unique properties which can dehydrogenate methanol for reductive amination and further catalyze the N-methylation of amines selectively, and the precious metals are normally one of the choices. As mentioned above, catalyst stability and recyclability are of great importance facing the current environmental and economical issues. So, in combination with the advantages of both COF materials and precious transition metal, developing high and efficient heterogeneous catalysts can not only facilitate the challenging tandem experimental operation but also can recover the catalyst, this definitely will open COF supported transition metal catalyst wide application in both academic and industrial. Therefore, we designed and synthesized two kinds of Rh-anchored COFs using melamine as the precursor, and reported for the first time the tandem reaction of transfer hydrogenation and N-mono-methylation of nitroaromatic hydrocarbons with methanol as the methylation source. In addition, the catalyst is suitable for nitroaromatic hydrocarbons with various reaction functional groups and can be recycled without losing reactivity.

## 2. Experimental Section

### 2.1. Materials and Chemicals

All aromatic aldehydes and the chemical reagents were analytical grade and used directly without purification. The 1,3,5-trimethoxybenzene (99%) was purchased from Alfa Aesar Chemical

Co., Ltd.; MeOH, EtOH, THF, piperazine-1,4-dicarbaldehyde, Terephthalaldehyde was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.; CDCl<sub>3</sub> (99.8% D, containing 0.03% TMS, stabilized with Ag), Nitrobenzene (AR ≥ 99%), RhCl<sub>3</sub> (AR, 99%), Melamine was were obtained from Shanghai Macklin Biochemical Co., Ltd. Acetone was from the Guangzhou Chemical Reagent Factory. Cesium carbonate, CH<sub>2</sub>Cl<sub>2</sub> purchased from Energy-Chemical Co., Ltd.

### 2.2 Catalyst Preparation

Melamine (500mg) and piperazine-1,4-dicarbaldehyde (1139mg) were added to 60 ml DMSO at a molar ratio of 2:3 and ultrasonic until the precursor was completely dissolved. Then nitrogen protective condensation refluxed was carried out at 180 °C for 72 hours. Then the white sediment was collected and washed with ethanol, acetone, tetrahydrofuran, and dichloromethane respectively. Finally, vacuum drying at 90 °C for 8 h, and expressed as MelCOF-1. For comparison, MelCOF-2 was synthesized using melamine (500mg) and terephthalaldehyde (1074mg) at the same molar ratio of 2:3 and the same method. To prepare Rh-anchored COF, the RhCl<sub>3</sub> methanol solution is introduced into the pre-synthesized COF with a metal content of 5wt% and stirred at room temperature for 24 hours. After the reaction, the excess unloaded RhCl<sub>3</sub> was removed by Soxhlet extraction, and then dried in a vacuum at 80 °C for 12 h.

### 2.3 Catalyst Characterization

The crystal structure of the catalyst was recorded by X-ray powder diffraction using Cu-K $\alpha$  radiation, with  $2\theta$  ranging from 5° to 80°. X-ray photoelectron spectroscopy (XPS) was carried out using AXIS Ultra DLD (Kratos, Britain), and the standard C1s peak is used as a reference for correcting the shifts. Field emission scanning electron microscope (FESEM) images and transmission electron microscope (TEM) images were performed to determine the morphology of the catalyst. These images were taken by JEOL JSM-6700 and JEM-2010 electron microscopes. After vacuum degassing at 90 °C for 15 hours, the adsorption-desorption isotherms of N<sub>2</sub> samples were measured by Tristar3010 isothermal nitrogen absorption analyzer (Micromeritics, USA) at 77 K. The <sup>1</sup>H NMR spectrum is carried out on Bruker400 with reference to the use of tetramethylsilane by 400MHz in CDCl<sub>3</sub>. The <sup>13</sup>C SSNMR spectrum was recorded on the Bruker AVANCE III spectrometers.

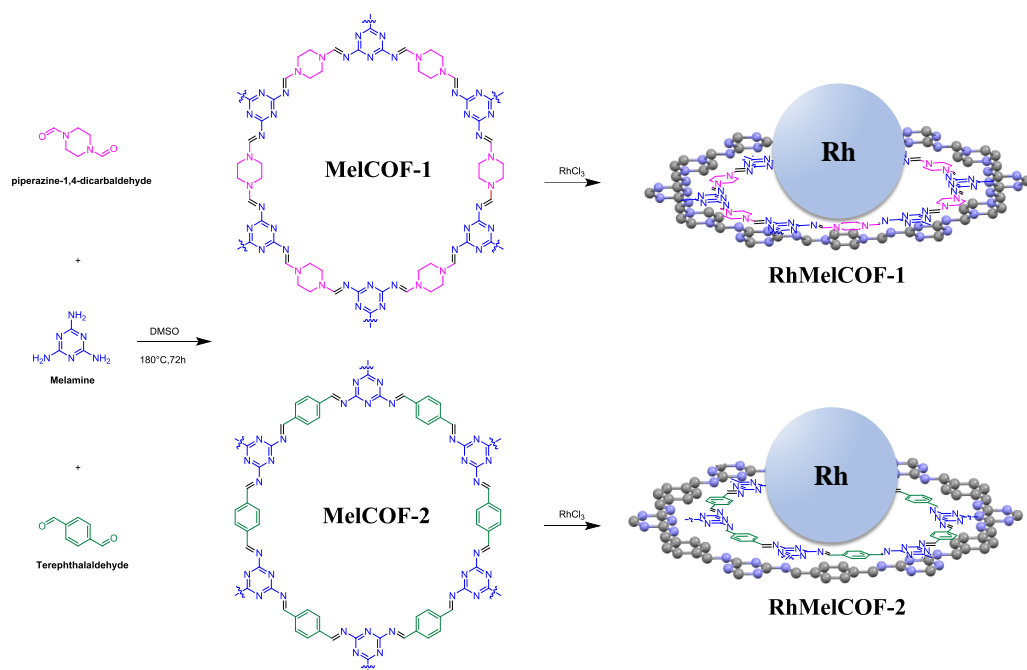
### 2.4 Catalytic Tests

The methylation of nitroaromatic hydrocarbons is carried out in a pressure tube. The 3 mg catalyst is usually placed in the pressure tube together with 0.2 mmol nitroaromatics 2.4 mmol cesium carbonate and 2 ml methanol. And put it into the preheated oil bath pot, magnetic stirring heating for the corresponding time. After the reaction time is over, the pressure tube is removed and cooled to room temperature, and the solid catalyst is separated by a 0.22  $\mu$ m filter membrane. The mixture was analyzed by GC or GC-MS and quantitatively analyzed by the normalization method.

## 3. Results and Discussion

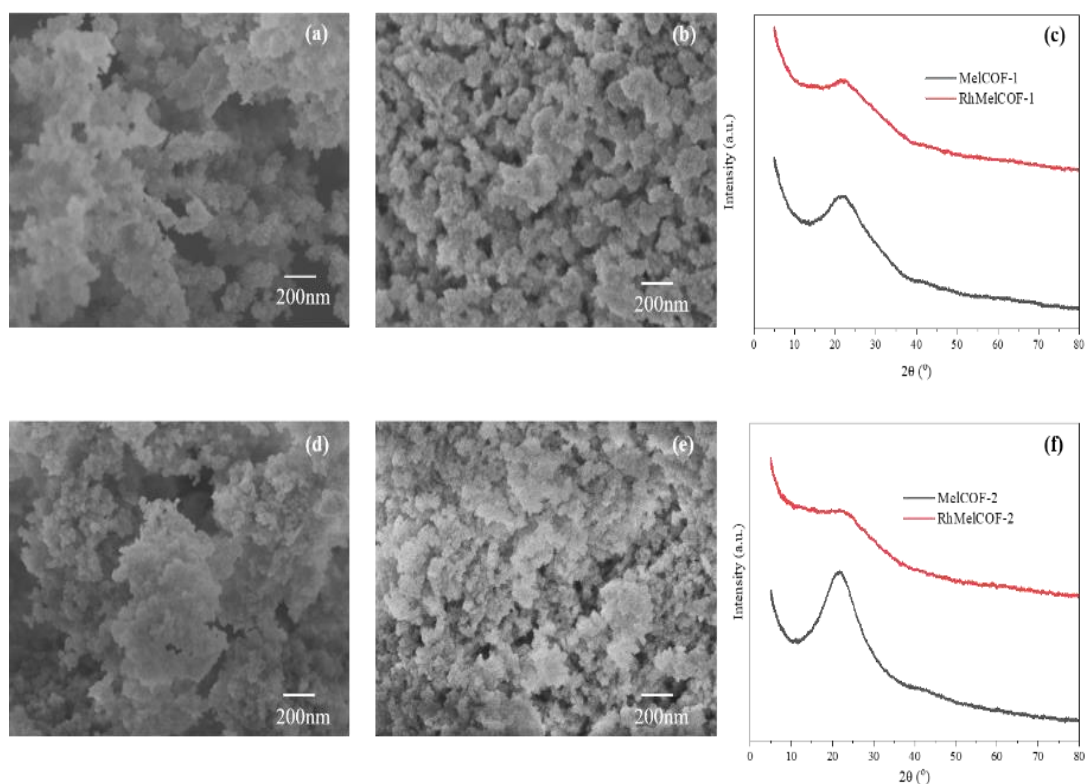
### 3.1 Characterization and analysis of catalysts

Both COFs catalysts were synthesized by simple stirring, and the synthesis process was as shown in **Scheme 2**. Melamine was used as a monomer to react with piperazine-1,4-dicarbaldehyde or terephthalaldehyde in DMSO to obtain MelCOF-1 or MelCOF-2. Then the metal ions were introduced into the COFs by the strong coordination interaction between the metal ions and the N in the substrate of the COFs, and the Rh/MelCOF-1 or Rh/MelCOF-2 was obtained.



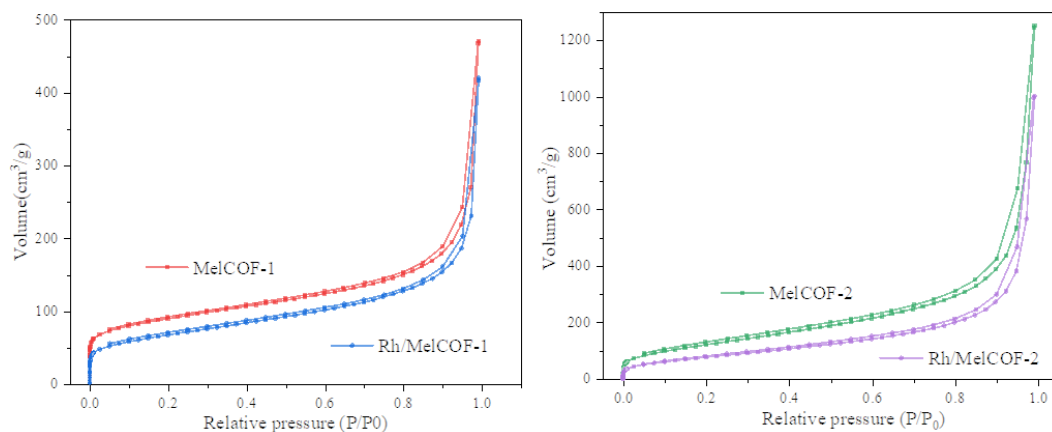
**Scheme 2.** Representation of the synthesis of Rh/MelCOF.

The synthesized MelCOF and Rh/MelCOF were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). Typical SEM images, as shown in **Figure 1** a, b, d, e, revealed that MelCOF and Rh/MelCOF showed the irregular shape of 200nm, and the introduction of Rh did not destroy the structure of COF, but made the whole structure of COF more agglomerated, forming a compact state, resulting in the decrease of its morphology and size. In order to understand the crystal structure of the synthesized COF, powder X-ray diffraction (PXRD) was carried out. **Figure 1** c, 1f shows the PXRD diffraction spectra of the amorphous MelCOF and the corresponding Rh/MelCOF. As expected, since there is no regular nm-level morphology in SEM, and Rh riveted MelCOF is in ionic form, the diffraction peak of COF in the low angle range and the diffraction peaks of Rh are not observed. The relatively wide signal at  $22^\circ$  coincides with the reflection (001), which is attributed to the  $\pi$ - $\pi$  accumulation between the ordered adjacent layers of COF sheets.



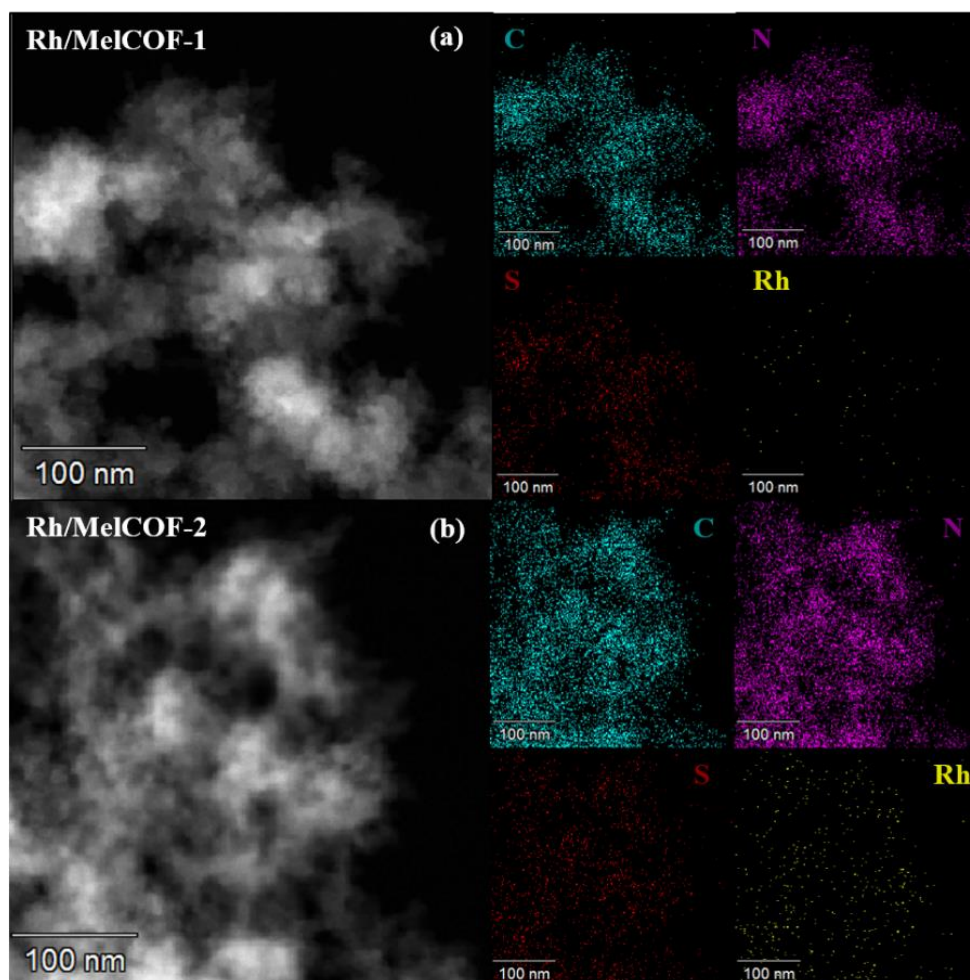
**Figure 1.** SEM images of MelCOF-1(a), Rh/MelCOF-1(b), MelCOF-2(d), Rh/MelCOF-2(e) and XRD pattern of as-synthesized MelCOF and Rh/MelCOF(c,f).

The adsorption-desorption isotherms of MelCOF and corresponding Rh/MelCOF are shown in **Figure 2**. It was found that the Brunauer-Emmett-Teller (BET) surface areas of MelCOF-1 and Rh/MelCOF-1 were  $357\text{m}^2\text{g}^{-1}$  and  $239\text{m}^2\text{g}^{-1}$  respectively. The BET surface areas of MelCOF-2 and Rh/MelCOF-2 were  $457\text{m}^2\text{g}^{-1}$  and  $284\text{m}^2\text{g}^{-1}$ , respectively. In addition, according to the Barrett-Joyner-Halenda (BJH) method, the load Rh reduces the  $V_{\text{pore}}$  of MelCOF-1 and MelCOF-2 from  $0.339\text{cm}^3$  and  $0.827\text{cm}^3$  to  $0.289\text{cm}^3$  and  $0.592\text{cm}^3$ , respectively. The reduction of specific surface areas and pore volume can be attributed to the successful encapsulation of ionic rhodium in MelCOF channels after the introduction of Rh. The relatively narrow pore size distribution of Rh/MelCOF-1 and Rh/MelCOF-2 is concentrated between 1.5 nm-5.7 nm, and the pore size changes slightly compared with the carrier MelCOF, indicating that the existence of Rh does not block the cavity channel of Rh/MelCOF.



**Figure 2.** Nitrogen adsorption-desorption isotherms of MelCOF and Rh/MelCOF.

In addition, the Rh/MelCOF-1 and Rh/MelCOF-2 supported by MelCOF materials are further analyzed by EDS. As shown in **Figure 3**, there exist S elements in addition to C and N of synthetic COF materials. Although a variety of solvents are used to wash the COF material carrier in the synthesis process, and Soxhlet extraction is used in the process of loading Rh, there is still a small amount of DMSO unwashed, so some S elements is detected. At the same time, the Rh element was also observed. It can be seen that Rh was uniformly loaded into MelCOF, but the content of Rh (1.32Wt%) in Rh/MelCOF-1 was significantly lower than that in Rh/MelCOF-2 (5.86Wt%).

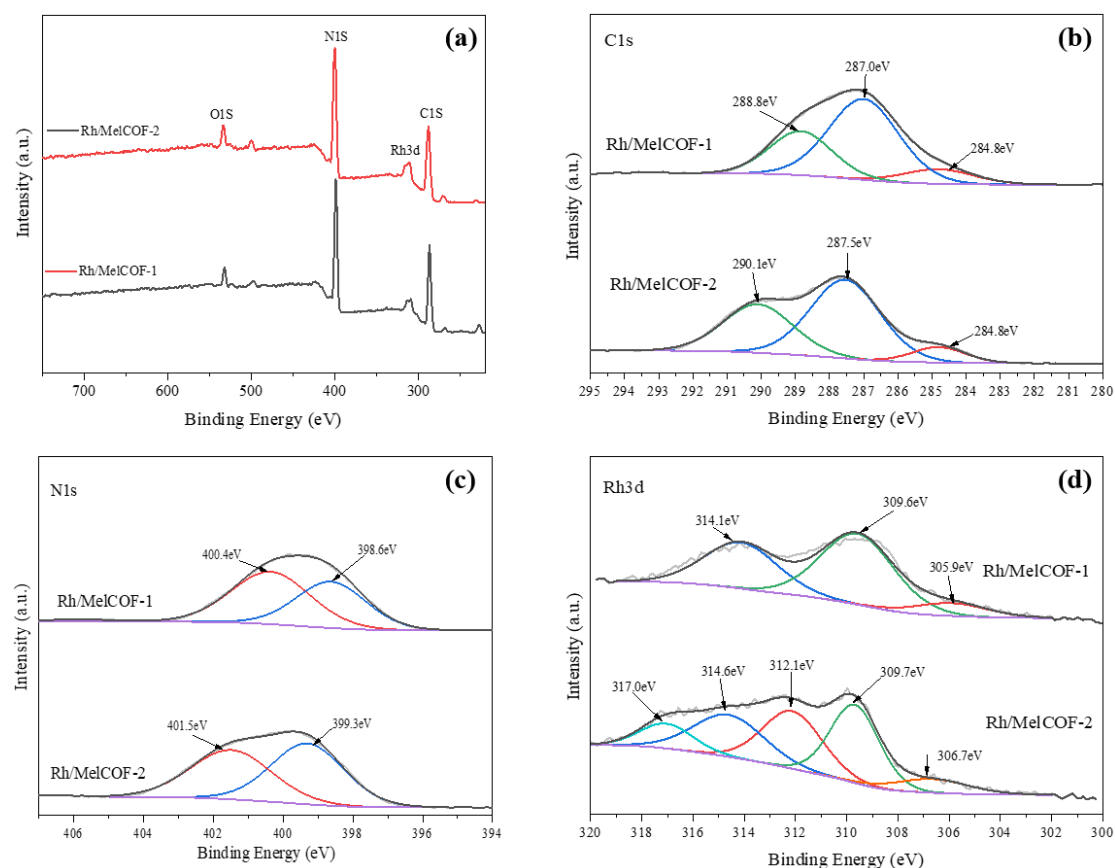


**Figure 3.** EDS mapping of Rh/MelCOF.

At the same time, the surface composition and element valence of the synthesized Rh/MelCOF-1 or Rh/MelCOF-2 were analyzed by X-ray photoelectron spectroscopy (XPS). **Figure 4** (a) clearly shows the signals of Rh3d, N1s, C1s, and O1s. C1s is used as a reference to correct the binding energy of XPS analysis under 284.8 eV and used for analysis. The corresponding high-resolution C1s spectra of Rh/MelCOF-1 and Rh/MelCOF-2 in **Figure 4** (b) show that the peaks centered by 287.0 eV and 287.5 eV follow the sp<sup>2</sup>-coordinated C=N bond on COF materials[51]. In addition, the two peaks fitted by the N1s spectra **Figure 4** (c) of the two kinds of Rh/MelCOF also belong to sp<sup>2</sup> hybrid nitrogen, corresponding to the environment of C-N=C and C-N, respectively. Then the most important thing is the Rh3d XPS spectrum. From **Figure 4** (d), Rh/MelCOF-1 can see that the binding energy spectrum has two peaks in 309.6 eV and 314.1eV, which are Rh3d<sub>3/2</sub> (Rh-N<sub>x</sub>) and Rh3d<sub>5/2</sub> (Rh-N<sub>x</sub>) energy levels belonging to Rh (III) species. At the same time, the 305.9 eV satellite peak of Rh is also observed. There is also a corresponding peak in Rh/MelCOF-2. In



addition, compared with Rh/MelCOF-1, the Rh/MelCOF-2 has more signal peaks of 317.0 eV and 312.1 eV, which is attributed to the peak of rhodium chloride that is not strongly coordinated with N in the COF ligand. Thus it can be seen that the Rh species mainly exist in the form of Rh-NX in Rh/MelCOF-1, while in the Rh/MelCOF-2 catalyst, in addition to Rh-NX, there is rhodium chloride that filled in the MelCOF2 channel. Therefore, although the amount of rhodium chloride used in the synthesis process of the two COF catalysts is the same, the content of Rh on the actual load MelCOF-2 is higher than that of MelCOF-1, which also confirms the results of EDS characterization. The binding energy of rhodium chloride decreases from 317.0 eV and 312.1 eV energy to 314.6 eV and 309.7 eV respectively, which indicates the electron transfer from N to Rh and reveals the strong metal-carrier interaction between Rh and MelCOF.



**Figure 4** (a) XPS spectra of survey patterns, (b) C XPS spectra, (c) N XPS spectra, and (d) Rh XPS spectra of the synthesized Rh/COFs.

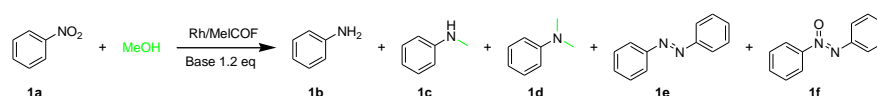
### 3.2 Study on Catalytic performance

The catalytic applicability of two kinds of Rh/MelCOF-1 or Rh/MelCOF-2 was studied by investigating the single N-methylation of nitrobenzene as a model reaction (**Table 1**). In the initial condition screening process, we used Rh/MelCOF-2 with a relatively high content of Rh load, and the substrates were 2 mmol nitrobenzene, 2 ml methanol and 1.2 eq base. With the increase of reaction time, the conversion of reactant 1a increased, while the selectivity of by-product 1e and 1f decreased, while the selectivity of main product 1c increased, so it was inferred that 1e and 1f were possible intermediates. The reaction temperature has a great influence on catalytic performance. When the reaction temperature increases from 90 to 130 degrees Celsius, the conversion rate of 1c is also greatly increased to 98%. At the same time, it is observed that only 1e and 1f are formed at 90 degrees Celsius, indicating that these two substances are preferentially formed under the catalysis



of Rh/MelCOF, which provides an important idea for the kinetic analysis in the following article. In order to confirm whether the reaction was catalyzed by Rh or MelCOF in Rh/MelCOF, other comparison experiments were conducted and found that 1c was not formed in the reaction without catalyst, or only using RhCl<sub>3</sub> or MelCOF<sub>2</sub> as the catalyst. Then the effects of different bases on the reaction were evaluated at 130 °C for 16 h. Different from the effects of different kinds of bases in the existing literature, almost all inorganic bases had good selectivity, such as Cs<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, KO<sup>t</sup>Bu, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and there was no methylation. The formation of 1d was mainly the selective competition between 1b and 1c. However, the conversion of organic alkali Et<sub>3</sub>N is low due to its weak basicity. For this reason, under the optimum reaction conditions of 130 °C, 16 h and Cs<sub>2</sub>CO<sub>3</sub>, the 1c selectivity is lower when using the Rh/MelCOF-1 than that of use Rh/MelCOF-2.

**Table 1** Optimization of Single N-methylation of Nitrobenzene in One-Pot to Produce N-Methylaniline<sup>a</sup>.



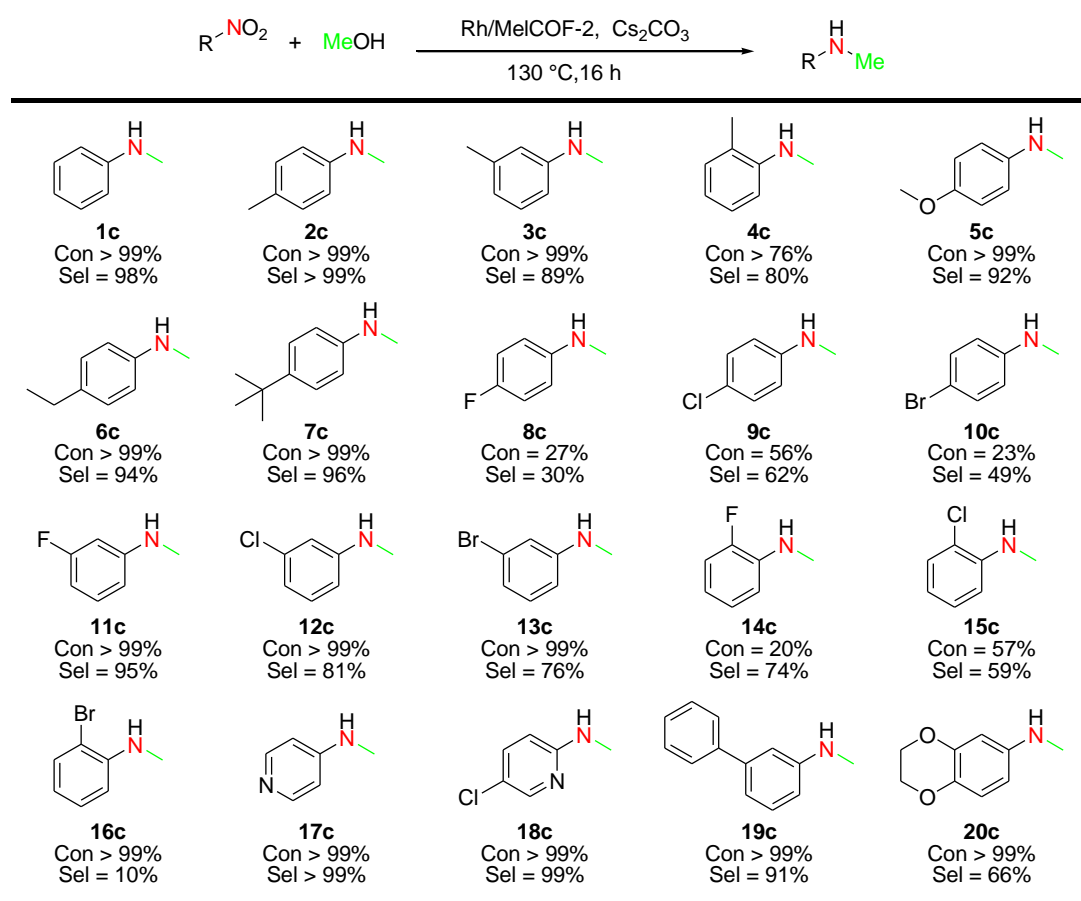
Entry	Catalysts	Base	T (°C)	Time (h)	1a Con (%) <sup>b</sup>	Sel (%) <sup>b</sup>				
						1b	1c	1d	1e	1f
1	Rh/MelCOF-2	Cs <sub>2</sub> CO <sub>3</sub>	110	14	>99	8	81	0	9	3
2	Rh/MelCOF-2	Cs <sub>2</sub> CO <sub>3</sub>	110	16	>99	9	85	0	4	2
3	Rh/MelCOF-2	Cs <sub>2</sub> CO <sub>3</sub>	110	18	>99	8	90	0	1	1
4	Rh/MelCOF-2	Cs <sub>2</sub> CO <sub>3</sub>	90	16	38	0	0	0	50	50
5	Rh/MelCOF-2	Cs <sub>2</sub> CO <sub>3</sub>	130	16	>99	2	98	0	0	0
6	Rh/MelCOF-2	NaOH	130	16	>99	5	94	0	1	0
7	Rh/MelCOF-2	KOH	130	16	>99	3	97	0	0	0
8	Rh/MelCOF-2	KO <sup>t</sup> Bu	130	16	>99	2	97	0	1	0
9	Rh/MelCOF-2	NaOMe	130	16	96	4	88	0	4	4
10	Rh/MelCOF-2	Na <sub>2</sub> CO <sub>3</sub>	130	16	>99	3	97	0	0	0
11	Rh/MelCOF-2	K <sub>2</sub> CO <sub>3</sub>	130	16	>99	2	98	0	0	0
12	Rh/MelCOF-2	Et <sub>3</sub> N	130	16	19	43	38	0	13	6
13	Rh/MelCOF-1	Cs <sub>2</sub> CO <sub>3</sub>	130	16	>99	10	72	0	9	9

<sup>a</sup>Reaction conditions: 3 mg catalyst, 2 mmol nitrobenzene, 2 mL MeOH, 1.2 eq base. <sup>b</sup>Conversion and selectivity were determined by GC. The types of products were confirmed by GCMS and <sup>1</sup>H NMR.

Then, based on the optimized conditions of methylation and hydrogenation of nitroaromatic hydrocarbons using methanol as the source of methylation and hydrogenation, it is proved that Rh/MelCOF is generally applicable in the synthesis of N-monomethylamine substrates. As shown in **Table 2**, 2 mmol substrates, 3 mg Rh/MelCOF-2 catalyst and 2.4 mmol Cs<sub>2</sub>CO<sub>3</sub> (1.2eq) are used for COF supported Rh catalyzed tandem hydrogenation and mono-methylation in 2 ml MeOH at 130 °C for 16 h. It can be seen that many nitro compounds with different functional groups have good tolerance, which proves their universal application in mono-N methylation. Among them, the substrates with para-electron donor groups have good reaction selectivity, and all of them are quantitatively converted into monomethylated derivatives (2c, 5c, 5c, 6c, 7c). However, the electron donor groups on the m and ortho-position will lead to the decrease of selectivity and even incomplete conversion, and the main competitive product is aniline aromatics, which may be attributed to the increase of spatial shielding of nitro functional groups. As a result, the transfer hydrogenation step

is inhibited (3c). However, the conversion and selectivity of electron-withdrawing halogen-substituted derivatives at the para-position are poor, and the main competitive products are aniline aromatics, azobenzene, and azobenzene oxide homologs (8c, 9c, 10c). On the other hand, the reaction effect of the meta-electron-absorbing group is better than that of the para-substituent, the conversion can reach more than 99%, and the selectivity is also higher, which may be attributed to the synergistic effect of electron synergy and space effect (11c, 12c, 13c). On the other hand, the spatial effect of ortho-electron-absorbing halogen-substituted derivatives is stronger than that of electron synergism, which leads to a decrease in the yield of N-monomethylamine (14c, 15, 16c). However, heterocycles, biphenyl rings, and substrates with steric hindrance all have good reactivity (17c, 18c, 19c, 20c). Moreover, according to the reaction law, the effect of electronic synergy on the methylation and hydrogenation of nitroaromatic hydrocarbons using methanol as a methylation source is higher than the spatial effect, and heterocyclic compounds can counteract the effect of electronic synergy. These prove that the prepared Rh/MelCOF heterogeneous catalyst can obtain hydrogen directly from methanol resources and carry out the mono-N methylation, and highly selective synthesize the challenging N-mono-methylamine products via the tandem transfer hydrogenation and mono-metylation of amine.

**Table 2.** Rh/MelCOF-2 catalyzed N-mono-methylation of Various Nitroaromatic Hydrocarbons

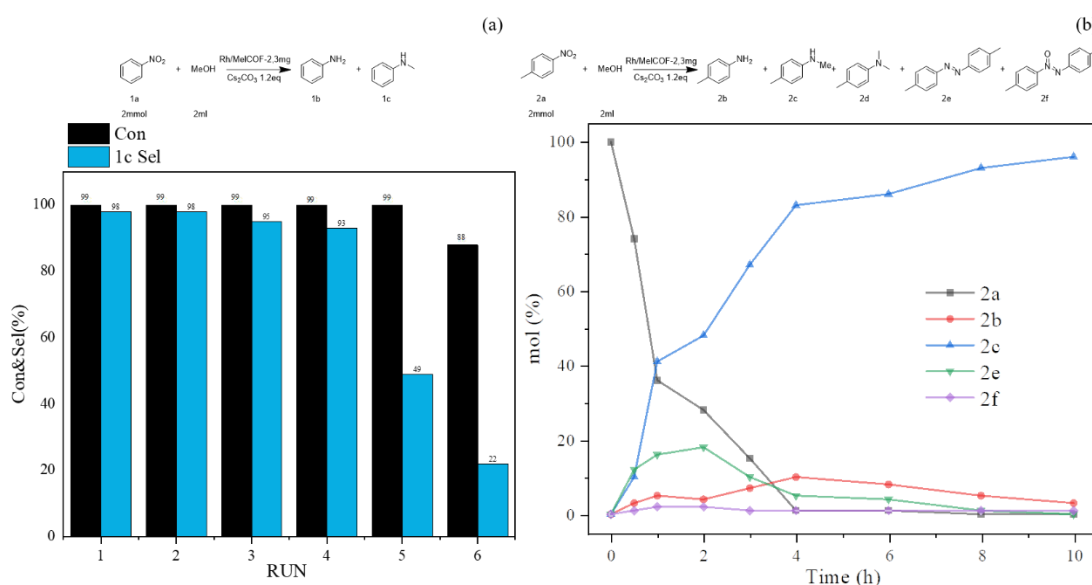


<sup>a</sup> Reaction conditions: 3 mg Rh/MelCOF-2 catalyst, 2 mmol substrates, 2 mL MeOH, 2.4 mmol Cs<sub>2</sub>CO<sub>3</sub>, 130 °C, 16 h. Conversion and selectivity were determined by GC. The types of products were confirmed by GCMS and <sup>1</sup>H NMR.

Then the reusability of Rh/MelCOF-2 catalyst was tested for N-monomethylation reaction of

1a (**Figure 5a**). The catalyst recycle ability test was carried out under the optimized reaction conditions, and when every single reaction was finished, the reaction samples were analyzed using GC. Then the residue was centrifugally precipitated and the reaction solution was extracted, afterward, methanol is added to the remaining solid-liquid mixture, and again the centrifugal precipitation is carried out which is repeated until no color showed according to TLC. In this case, the next catalyst recycle test could be carried out according to the standard procedure, the reaction mixture is loaded into the tube and carried out for the next run. As shown in **Figure 5a**, the catalyst can be successfully recycled 4 times without losing significant catalytic reactivity and product selectivity. In the fifth cycle, although the conversion still kept over 99%, the selectivity of 1c decreased to 49%, which is probably due to the decrease of catalyst performance and the decrease in the reaction rate from 1b to 1c.

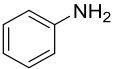

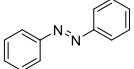
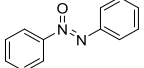
Under the optimized reaction conditions, the reaction curve of p-methylnitrobenzene 2a showed that 2a was rapidly consumed within 4 hours to form 2c (**Figure 5b**). In the early stage of the reaction, the intermediate compound 2e gradually increased and reached the highest amount within 2 hours and then decreased gradually after 2 hours. Interestingly, another intermediate compound 2f continuously stays at a low level with the emergence of 2e. The intermediate amine 2b also slowly increased to the maximum in 4 h, which is consistent with the result that the starting material 2a was completely consumed at 4 h. Then the intermediates compound 2b, 2e was gradually transformed into 2c, which was consistent with the observed selectivity.



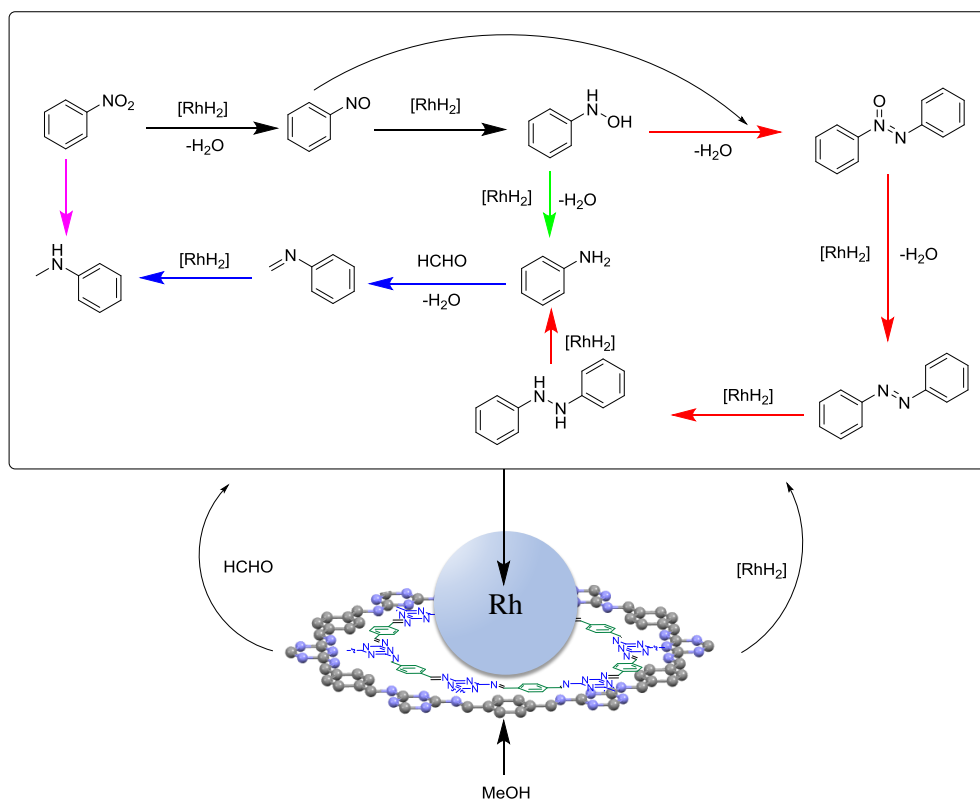
**Figure 5.** (a) Durability Test for N-mono-methylation of Nitrobenzene in One-Pot to Produce N-Methylaniline, (b) Time-dependence of the N-methylation of 1-methyl-4-nitrosobenzene with methanol catalyzed by Rh/MelCOF-2.

**Table 3.** Validation of Mono-N-methylation of Nitrobenzene to Generate N-methylaniline as a Possible Reaction Intermediate in One-Pot

Entry	Substrate	mol (%)			
		1b	1c	1e	1f

1		55	45	0	0
2		0	>99	0	0
3		58	33	9	0
4		30	9	60	1

Then, to support the hydrogen borrowing mechanism and determine that the reaction intermediates are involved in the reaction, 1b, 1c, 1e, and 1f are used as the substrates for the reaction under the optimized conditions. It is found that 1b and 1e are all reaction intermediates, and once 1c is produced, it is difficult to reverse the reaction. According to the reported kinds of literature, it is speculated that the hydrogen transfer reduction of nitrobenzene to aniline occurs in two ways, and then N-methylaniline is synthesized by N-methylation of aniline. One way is that nitrobenzene is reduced to N-phenylhydroxylamine by intermediate nitrosamine with the help of hydrogen transfer, which is directly dehydrated to aniline. The other path is the reductive coupling of nitrosamine with N-phenylhydroxylamine to get azobenzene by oxidation of azobenzene, which is further reduced to aniline by 1,2-diphenylhydrazine. From the analysis of mechanical inquiry dynamics, the second path plays a major role in it. Then, as previously reported, aniline was dehydrogenated with methanol to form the intermediate N-phenylmethylimine, and then continued to be reduced to N-methylaniline (**Figure 6**).



**Figure 6.** Proposed mechanistic pathways for the transfer hydrogenation, reduction and N-monomethylation of nitrobenzene to aniline using methanol as a hydrogen source.

#### 4. Conclusions

In conclusion, we successfully synthesized and fully characterized two kinds of novel Rh/MelCOF catalysts, and realized the highly selective synthesis of N-methylamine by only using methanol as the methylation and hydrogenation source, and nitroarene as the raw material. Two kinds of Rh/MelCOF carrier materials were prepared by a simple heating and stirring method, and the relatively narrow pore size distribution was concentrated in 1.5 nm-5.7 nm. Rh is anchored uniformly on the two COF materials. According to XPS, it is found that the strong coordination bond of MelCOF has a strong interaction with Rh, which makes the catalyst have the catalytic performance of carrier and rhodium chloride to carry out the mono-N-methylation of nitroaromatic hydrocarbons. A series of functionalized nitroaromatic hydrocarbons with electron-donating and electron-withdrawing substituents, including heterocyclic or sterically hindered derivatives, have been effectively converted to corresponding N-methylamines with good to excellent yields under low catalyst support using  $\text{Cs}_2\text{CO}_3$ . On the other hand, according to the study of the reaction path, the reaction path here is different from the previously reported mechanism, and the reaction path with azobenzene as an intermediate is faster and much more selective. With the help of Rh/MelCOF, it is widely used to realize the high-value conversion of nitroaromatic compounds to a variety of N-methylamines. The synthesis process using methanol as methylation and hydrogenation source is more economical and green. Currently, we are focusing modify and improve the stability of these novel COF-supported heterogeneous catalysts and exploring their more applications in challenging organic transformations.

#### Acknowledgment

This work was supported financially by the National Key R&D Program of China (2018YFB1501500), National Natural Science Foundation of China (51976225).

#### Author contributions

J. G. L., B. Y and L. L. M supervised and designed the research. M. Y. Z. performed the experiments and data analysis. M. Y. Z. wrote the original manuscript. J. G. L. reviewed and corrected the manuscript. All authors discussed the results and assisted during manuscript preparation.

#### Competing interests.

The authors declare no competing financial interests.

#### Data availability

Data supporting the findings of this study are available from the corresponding authors upon reasonable request.

#### Additional information.

Correspondence and requests for materials should be addressed to J. G. L. or L. L. M.

#### References.

1. Irrgang, T. and R. Kempe, *Transition-Metal-Catalyzed Reductive Amination Employing Hydrogen*. Chem. Rev., 2020. **120**(17): p. 9583-9674.
2. Corma, A. and P. Serna, *Chemoselective hydrogenation of nitro compounds with supported gold catalysts*. Science, 2006. **313**(5785): p. 332-334.
3. Corma, A., et al., *Transforming nonselective into chemoselective metal catalysts for the hydrogenation of substituted nitroaromatics*. J. Am. Chem. Soc., 2008. **130**(27): p. 8748-8753.
4. Westerhaus, F.A., et al., *Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis*

- of molecularly defined complexes. *Nat. Chem.*, 2013. **5**(6): p. 537-543.
- Jagadeesh, R.V., et al., *MOF-derived cobalt nanoparticles catalyze a general synthesis of amines*. *Science*, 2017. **358**(6361): p. 326-332.
  - Irrgang, T. and R. Kempe, *Transition-Metal-Catalyzed Reductive Amination Employing Hydrogen*. *Chem. Rev.*, 2020. **120**(17): p. 9583-9674.
  - Liu, J.G., et al., *Facile synthesis of controllable graphene-co-shelled reusable Ni/NiO nanoparticles and their application in the synthesis of amines under mild conditions*. *Green Chem.*, 2020. **22**(21): p. 7387-7397.
  - Liu, J.G., Y.P. Song, and L.L. Ma, *Earth-abundant Metal-catalyzed Reductive Amination: Recent Advances and Prospect for Future Catalysis*. *Chem. Asian J.*, 2021. **16**(17): p. 2371-2391.
  - Fatemeh, N.H., et al., *N-methylation versus oxidative addition using MeI in the reaction of organoplatinum(II) complexes containing pyrazine ligand*. *J. Organomet. Chem.*, 2019. **880**: p. 232-240.
  - Jiang, X., et al., *A General Method for N-Methylation of Amines and Nitro Compounds with Dimethylsulfoxide*. *Chem. Eur. J.*, 2014. **20**(1): p. 58-63.
  - Ricci, A., *Modern amination methods*. 2008: John Wiley & Sons.
  - van der Waals, D., et al., *Ruthenium-Catalyzed Methylation of Amines with Paraformaldehyde in Water under Mild Conditions*. *Chemsuschem*, 2016. **9**(17): p. 2343-2347.
  - Zhu, L., et al., *Methylation of aromatic amines and imines using formic acid over a heterogeneous Pt/C catalyst*. *Catal. Sci. Technol.*, 2016. **6**(16): p. 6172-6176.
  - Qiao, C., et al., *Copper(II)-Catalyzed Selective Reductive Methylation of Amines with Formic Acid: An Option for Indirect Utilization of CO<sub>2</sub>*. *Org. Lett.*, 2017. **19**(6): p. 1490-1493.
  - Ting, K.W., et al., *Catalytic Methylation of m-Xylene, Toluene, and Benzene Using CO<sub>2</sub> and H<sub>2</sub> over TiO<sub>2</sub>-Supported Re and Zeolite Catalysts: Machine-Learning-Assisted Catalyst Optimization*. *ACS Catal.*, 2021. **11**(9): p. 5829-5838.
  - Li, Y.H., et al., *Catalytic Methylation of C-H Bonds Using CO<sub>2</sub> and H<sub>2</sub>*. *Angew. Chem. Int. Ed.*, 2014. **53**(39): p. 10476-10480.
  - Li, Y.H., et al., *Selective Methylation of Amines with Carbon Dioxide and H<sub>2</sub>*. *Angew. Chem. Int. Ed.*, 2013. **52**(46): p. 12156-12160.
  - Li, Y.H., et al., *A General Catalytic Methylation of Amines Using Carbon Dioxide*. *Angew. Chem. Int. Ed.*, 2013. **52**(36): p. 9568-9571.
  - Jacquet, O., et al., *CO<sub>2</sub> as a C-1-building block for the catalytic methylation of amines*. *Chemical Science*, 2013. **4**(5): p. 2127-2131.
  - Bobbink, F.D., S. Das, and P.J. Dyson, *N-formylation and N-methylation of amines using metal-free N-heterocyclic carbene catalysts and CO<sub>2</sub> as carbon source*. *Nat. Protoc.*, 2017. **12**(2): p. 417-428.
  - Wei, H.S., et al., *FeOx-supported platinum single-atom and pseudo-single-atom catalysts for chemoselective hydrogenation of functionalized nitroarenes*. *Nat. Commun.*, 2014. **5**.
  - Wang, L., H. Neumann, and M. Beller, *Palladium-Catalyzed Methylation of Nitroarenes with Methanol*. *Angew. Chem. Int. Ed.*, 2019. **58**(16): p. 5417-5421.
  - Jagadeesh, R.V., et al., *Nanoscale Fe<sub>2</sub>O<sub>3</sub>-Based Catalysts for Selective Hydrogenation of Nitroarenes to Anilines*. *Science*, 2013. **342**(6162): p. 1073-1076.
  - Gonzalez-Lainez, M., et al., *Effective N-methylation of nitroarenes with methanol catalyzed by a functionalized NHC-based iridium catalyst: a green approach to N-methyl amines*. *Catal. Sci. Technol.*, 2020. **10**(10): p. 3458-3467.
  - Goyal, V., et al., *Commercial Pd/C-Catalyzed N-Methylation of Nitroarenes and Amines Using*

- Methanol as Both C1 and H<sub>2</sub> Source*. J. Org. Chem., 2019. **84**(23): p. 15389-15398.
26. Jamil, M.A.R., et al., *N-Methylation of amines and nitroarenes with methanol using heterogeneous platinum catalysts*. J. Catal., 2019. **371**: p. 47-56.
  27. Zhang, S.C., J.J. Ibrahim, and Y. Yang, *A pincer ligand enabled ruthenium catalyzed highly selective N-monomethylation of nitroarenes with methanol as the C1 source*. Org. Chem. Front., 2019. **6**(15): p. 2726-2731.
  28. Reed-Berendt, B.G., N. Mast, and L.C. Morrill, *Manganese-Catalyzed One-Pot Conversion of Nitroarenes into N-Methylarylamines Using Methanol*. Eur. J. Org. Chem., 2020. **2020**(9): p. 1136-1140.
  29. Wang, J.Q., et al., *Selective mono-N-methylation of nitroarenes with methanol catalyzed by atomically dispersed NHC-Ir solid assemblies*. J. Catal., 2020. **389**: p. 337-344.
  30. Paul, B., et al., *Tandem Transformation of Nitro Compounds into N-Methylated Amines: Greener Strategy for the Utilization of Methanol as a Methylating Agent*. Chemsuschem, 2017. **10**(11): p. 2370-2374.
  31. Wang, J., et al., *Selective mono-N-methylation of nitroarenes with methanol catalyzed by atomically dispersed NHC-Ir solid assemblies*. J. Catal., 2020. **389**: p. 337-344.
  32. González-Lainez, M., et al., *Effective N-methylation of nitroarenes with methanol catalyzed by a functionalized NHC-based iridium catalyst: a green approach to N-methyl amines*. Catal. Sci. Technol., 2020. **10**(10): p. 3458-3467.
  33. Huang, S., et al., *Bimetallic Bis-NHC-Ir(III) Complex Bearing 2-Arylbenzo[d]oxazolyl Ligand: Synthesis, Catalysis, and Bimetallic Effects*. Organometallics, 2020. **39**(19): p. 3514-3523.
  34. Zhang, S., J.J. Ibrahim, and Y. Yang, *A pincer ligand enabled ruthenium catalyzed highly selective N-monomethylation of nitroarenes with methanol as the C1 source*. Org. Chem. Front., 2019. **6**(15): p. 2726-2731.
  35. Goyal, V., et al., *Commercial Pd/C-Catalyzed N-Methylation of Nitroarenes and Amines Using Methanol as Both C1 and H<sub>2</sub> Source*. J. Org. Chem., 2019. **84**(23): p. 15389-15398.
  36. Wang, L., H. Neumann, and M. Beller, *Palladium-Catalyzed Methylation of Nitroarenes with Methanol*. Angew. Chem. Int. Ed., 2019. **58**(16): p. 5417-5421.
  37. Reed-Berendt, B.G., N. Mast, and L.C. Morrill, *Manganese-Catalyzed One-Pot Conversion of Nitroarenes into N-Methylarylamines Using Methanol*. E. J. Org. Chem., 2020. **2020**(9): p. 1136-1140.
  38. Jamil, M.A.R., et al., *N-Methylation of amines and nitroarenes with methanol using heterogeneous platinum catalysts*. J. Catal., 2019. **371**: p. 47-56.
  39. Cote, A.P., et al., *Porous, crystalline, covalent organic frameworks*. Science, 2005. **310**(5751): p. 1166-1170.
  40. Colson, J.W., et al., *Oriented 2D Covalent Organic Framework Thin Films on Single-Layer Graphene*. Science, 2011. **332**(6026): p. 228-231.
  41. Lin, S., et al., *Covalent organic frameworks comprising cobalt porphyrins for catalytic CO<sub>2</sub> reduction in water*. Science, 2015. **349**(6253): p. 1208-1213.
  42. Jin, E.Q., et al., *Two-dimensional sp<sup>2</sup> carbon-conjugated covalent organic frameworks*. Science, 2017. **357**(6352): p. 673-676.
  43. Evans, A.M., et al., *Seeded growth of single-crystal two-dimensional covalent organic frameworks*. Science, 2018. **361**(6397): p. 52-57.
  44. Gropp, C., et al., *Design of higher valency in covalent organic frameworks*. Science, 2020. **370**(6515): p. 424.
  45. Liu, J.G., N. Wang, and L.L. Ma, *Recent Advances in Covalent Organic Frameworks for Catalysis*.



Chem. Asian J., 2020. **15**(3): p. 338-351.

46. Ding, S.Y., et al., *Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki-Miyaura Coupling Reaction*. J. Am. Chem. Soc., 2011. **133**(49): p. 19816-19822.

47. Liu, J.G., et al., *Palladium Nanoparticles on Covalent Organic Framework Supports as Catalysts for Suzuki-Miyaura Cross-Coupling Reactions*. ACS Appl. Nano Mater., 2021. **4**(6): p. 6239-6249.

48. Sadhasivam, V., M. Mariyappan, and A. Siva, *Porous Triazine Containing Covalent Organic Polymer Supported Pd Nanoparticles: A Stable and Efficient Heterogeneous Catalyst for Sonogashira Cross-Coupling and the Reduction of Nitroarenes*. Chemistryselect, 2018. **3**(47): p. 13442-13455.

49. Wu, Y., et al., *A pi-electronic covalent organic framework catalyst: pi-walls as catalytic beds for Diels-Alder reactions under ambient conditions*. Chem. Commun., 2015. **51**(50): p. 10096-10098.

50. Rao, M.R., et al., *Conjugated Covalent Organic Frameworks via Michael Addition-Elimination*. J. Am. Chem. Soc., 2017. **139**(6): p. 2421-2427.

51. Kishi, K. and Y. Ehara, *Interaction of acetic acid with ethylenediamine on a Ni (111) surface studied by XPS*. Surf. Sci., 1986. **176**(3): p. 567-577.