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Ordered Mesoporous Nitrogen Dope Carbon Synthesized from Aniline for Stabilization of Ruthenium Species in CO₂ Hydrogenation to Formate

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Abstract: The hydrogenation of CO₂ to produce formic acid has garnered increasing interest as a means to address climate change and promote the hydrogen economy. This research investigates the nanocasting technique for the synthesis of ordered mesoporous nitrogen-doped carbon (MNC-An). KIT-6 functioned as the silica template, while aniline served as the nitrogen-carbon precursor. The resultant MNC-An exhibits cubic Ia3D geometry, possesses significant mesoporosity, and has a high nitrogen content, which is essential for stabilizing ruthenium single atoms. The catalyst exhibited a specific activity of 252 mmol_{FA}g_{cat}^{−1} following a 2 h reaction at 120 °C. Moreover, the catalyst exhibited exceptional relative activity during five recycling experiments while preserving its catalytic efficacy. The atomically dispersed ruthenium and its Ru³⁺ oxidation state demonstrated perseverance both before and after the treatment. The results indicated that the synthesized catalyst possesses potential for the expedited commercialization of CO₂ hydrogenation to produce formic acid. The elevated carbon yield, along with excellent thermal stability, renders it a viable substrate for attaching and stabilizing atomically dispersed ruthenium catalysts.

Keywords: CO₂ hydrogenation; formic acid; heterogeneous catalysis; ruthenium; mesoporous N-doped carbon



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1. Introduction

Hydrogen is increasingly in demand as a clean fuel, serving as an alternative to traditional fossil fuels, which are major contributors to greenhouse gas emissions, particularly carbon dioxide (CO₂) [1]. Conventional metal hydrides, such as LiBH₄, are commonly used for hydrogen storage, but require a significant amount of energy for hydrogen release. In contrast, liquid organic hydrogen carriers (LOHCs) have emerged as a more efficient alternative to conventional liquefaction and compression methods [2]. Recently, techno-economic analysis and life cycle assessments of formic acid production from CO₂ utilization have provided insights into its potential as an efficient hydrogen storage medium due to its cost efficiency [3,4]. Additionally, formic acid's low flammability, safety, and energy-related applications have further driven its increasing demand and production capacity [5–7]. Recently, direct formic acid fuel cells (DFAFCs) have been used for clean power generation [8]. However, the extreme molecular stability of CO₂ highlights the need to explore catalytic alternatives for formic acid production on an industrial scale [9].

Single-atom catalysts (SACs) on inorganic or molecular frameworks can bridge the gap between homogeneous and heterogeneous catalysts, allowing for easy separation while maintaining high activity. To stabilize the single isolated active site during the

reaction condition, various types of supports have previously been utilized for the CO₂ hydrogenation to formate [10–21]. Among the previous published supporting materials, porous organic polymers (POPs) and covalent triazine frameworks (CTFs) have been identified as potential anchoring supports for atomically dispersed catalysts [22,23]. The robustness of these supports to anchor SACs stems from their skeletal structures, which allow for control over their chemical and geometric properties through the building blocks used. Recently, Kim et al. demonstrated the use of a CTF-based catalyst in a pilot plant, achieving over 100 h of continuous reaction [4]. However, conventional POPs and CTFs generally have pore sizes below 2 nm, which poses challenges related to mass transfer limitations [24,25]. Efforts to enlarge pore sizes have sometimes resulted in a reduction in pyridinic N, which plays a key role in stabilizing the catalyst [26,27]. Thus, the synthesis of highly mesoporous carbon with a high pyridinic N content is an urgent need in this field.

Ordered mesoporous carbon (OMC) is a promising support material for atomically dispersed catalysts due to its tunable porosity and high surface area. Additionally, OMC is well suited for surface functionalization and exhibits excellent electronic and thermal properties [28]. Various methods for synthesizing OMC have been explored, including the use of SBA-15 as a template to create replica-based structures [29]. More recent research has shown that doping OMC with nitrogen using melamine as the nitrogen source improves lithium storage performance compared to pristine OMC [30]. Our previous work has demonstrated that nitrogen sites serve as efficient binding sites for atomically dispersed ruthenium [10,26,27,31–34]. Furthermore, we synthesized mesoporous nitrogen-doped carbons (MNCs) using various precursors, highlighting the critical role of precursor choice in determining catalytic activity [32]. Despite these advancements, few studies have employed nanocasting techniques to synthesize nitrogen-doped OMCs using different precursors for CO₂ hydrogenation to formate. Precursors with high carbon content and stability during thermal treatment result in higher carbon yield and more robust mesoporous structures [35–37]. Therefore, exploring different precursors for nitrogen-doped OMCs through nanocasting synthesis is essential to achieve controlled mesoporous supports with high carbon yield, robust structure, and enhanced stability for catalytic applications in CO₂ hydrogenation to formate.

In this study, ordered mesoporous nitrogen-doped carbon (MNC) was synthesized using KIT-6 as a silica template, with aniline serving as both the carbon and nitrogen source. Based on our previously published study, we assumed that aniline would be more suitable than melamine as a nanocasting precursor because melamine, which undergoes step-growth polymerization, exhibited a less ordered mesopore structure due to hindered infiltration into the silica template [32,38–42]. Additionally, the higher glass transition temperature of polyaniline, compared to polypyrrole and polyacrylonitrile, is expected to result in a higher carbon yield after carbonization [43–45]. After preparing the polyaniline-based OMCs, we confirmed the durability of the support through catalytic activity and stability tests in a batch reaction, achieving a specific activity of 252 mmol_{FA}g_{cat}^{−1} over two hours, with remarkable relative activity maintained throughout five cycles. Ultimately, the catalyst preserved its single-atom sites and oxidation state.

2. Results and Discussion

2.1. Characterization of Support Material

Figure 1 depicts the standard procedure for the nanocasting technique used in the synthesis of ordered MNCs. Nanocasting employs ordered mesoporous inorganic solids as hard templates. The advantages of MNCs include well-defined pore channels and a high density of nitrogen sites, which are crucial for stabilizing active metals. In this study, KIT-6, characterized by a cubic Ia3d structure, was used as an inorganic mesoporous silica template, prepared according to our previous publication [32]. Aniline was polymerized with the assistance of FeCl₃ and incorporated into the KIT-6 pore structure, resulting in a replica-based structure referred to as MNC-An. Figure S1 depicts the typical polymerization route for the aniline.

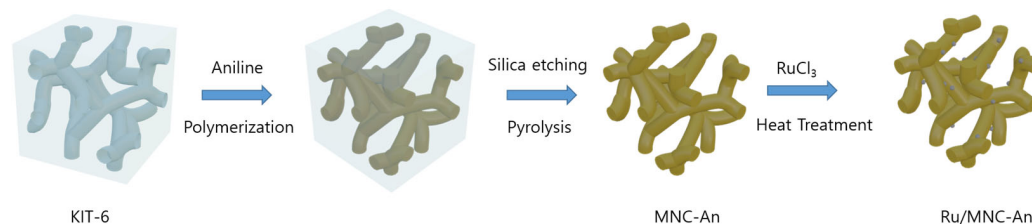


Figure 1. Schematic illustration for synthesis of MNC-An using nanocasting.

Figure 2a displays the HR-TEM image of MNC-An, illustrating its orderly mesoporous architecture, which closely mirrors the original structure of KIT-6, as documented in our recent publication [32]. The SAXS analysis in Figure 2b reveals distinct reflection peaks at 1.1° and 1.3° , confirming the presence of the cubic Ia3d phase, originating from KIT-6. This confirms the effective replication of the cubic structure onto the carbon support using KIT-6 as a template. The unit cell parameter of MNC-An was determined to be 19.67 nm, compared to 21.73 nm for KIT-6 (Table S1), indicating that the synthesized carbon underwent shrinkage, thereby corroborating the successful formation of the carbon replica structure.

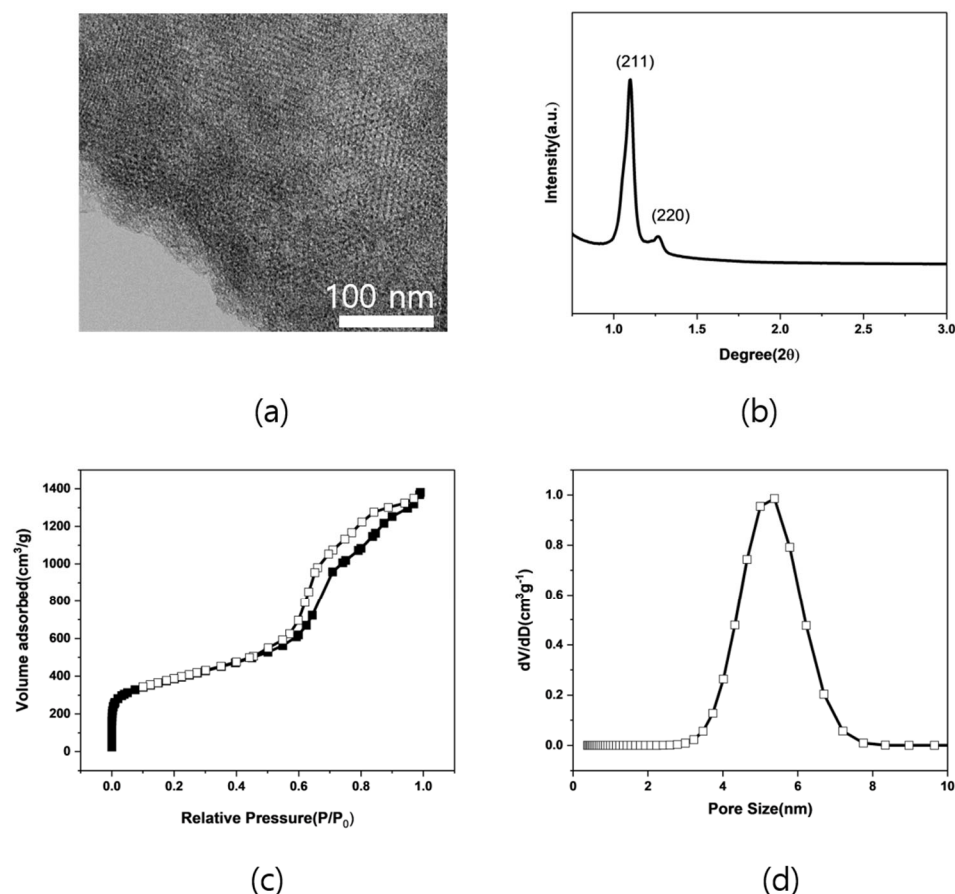


Figure 2. HRTEM (a), SAXS pattern (b), N_2 adsorption–desorption isotherm (c) and GCMC pore size distribution (d) for MNC-An. Closed and open symbols in Figure 2c indicate the adsorption and desorption.

A N_2 physisorption analysis was conducted to assess the morphological properties of MNC-An. Figure 2c shows a distinct capillary condensation phase at elevated relative pressure (P/P_0), indicating the presence of large, channel-like mesopores. The surface area of the support was measured at $1371 \text{ m}^2/\text{g}$, as shown in Table 1, with a total pore volume (TPV) of $2.13 \text{ cm}^3/\text{g}$. These results confirm the successful use of KIT-6 as a rigid

template for synthesizing highly porous, ordered mesoporous nitrogen-doped carbon derived from polyaniline. The pore size distribution of the support, determined by the GCMC method, revealed a peak pore size of 5.38 nm, further confirming the successful formation of mesopores within the nitrogen-doped carbon structure. The mesoporous architecture, with its high surface area and pore volume, is expected to enhance mass transport and catalytic activity in our reactions. Moreover, the NLDFT analysis for the pore size distribution has also been reported (Figure S2).

Table 1. Physiochemical properties of MNC-An.

Sample	Surface Area [m ² /g]	Total Pore Volume [cm ³ /g]	GCMC Pore Size [nm]
MNC-An	1371	2.13	5.38

The carbon support was further analyzed using wide-angle XRD (Figure 3a). The XRD patterns displayed broad peaks at 20–22.5° and 42.5°, indicating the presence of amorphous carbon. A pronounced peak at approximately 26° (002) suggested the presence of graphitic carbon. Raman spectroscopy is essential for evaluating the degree of amorphousness in the structure. The Raman analysis of MNC-An (Figure 3b) revealed an ID/IG ratio of around 1.09, indicating a high presence of surface defects in the nitrogen-doped carbon material. In carbon-based mesoporous replicas, a greater number of N-dopant sites is typically associated with increased levels of amorphousness. A study on MNC synthesized from melamine, which had the highest nitrogen content, similarly showed a high ID/IG ratio [32].

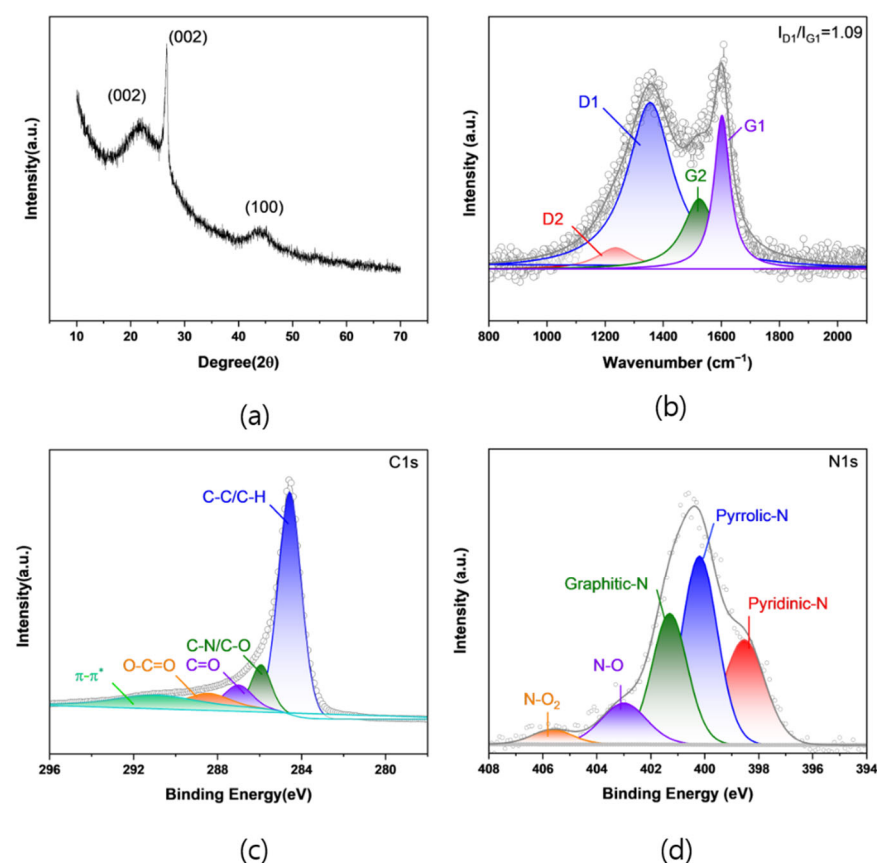


Figure 3. XRD pattern (a), Raman analysis (b), XPS C1s (c) and N1s (d) deconvolution for MNC-An.

Elemental analysis was conducted to determine the overall elemental composition of the nitrogen-doped carbon material (Table 2). The MNC-An sample contained 4.27% nitrogen, a critical component for stabilizing ruthenium within the nitrogen-doped carbon matrix. The quantification analysis based on XPS spectra also showed that a similar ratio

of nitrogen is present in the prepared supporting materials (Table S2). Carbon yield is also another important criterion for potential industrial applications. The carbon yield of MNC-An was observed to exceed 70%, demonstrating the effectiveness of the nanocasting synthesis method, which is known for improving carbon yield. It is determined that higher glass transition temperature than previous investigated polymer would offer the increased carbon yield [43–45]. Table S3 provides a detailed comparison with previously reported literature in terms of support yield. This comparison highlights the significance of using aniline as the precursor, which results in one of the highest support yields among the reported works for synthesizing NDC.

Table 2. Elemental analysis of MNC-An.

Sample	C (At. %)	N (At. %)	H (At. %)	O (At. %)	Carbon Yield (%)
MNC-An	81.20	4.27	1.00	4.13	70

XPS analysis was conducted to elucidate the chemical surface properties of the support. Prior to analysis, the spectra were calibrated using the adventitious carbon peak at 284.6 eV. The deconvolution of the C1s spectra, as shown in Figure 3c, revealed peaks corresponding to C-C/C-H (284.6 eV), C-N/C-O (285.92 eV), C=O (287 eV), O-C=O (288.44 eV), and π - π^* (291 eV). Simultaneously, the N1s spectra (Figure 3d) were deconvoluted into five distinct peaks representing different nitrogen species: pyridinic-N, pyrrolic-N, graphitic-N, N-O, and N-O₂ at 398.7, 400.2, 401.6, 403.9, and 405.1 eV, respectively. The relative quantities of these nitrogen species were 23.75% pyridinic-N and 36.90% pyrrolic-N (Table 3). Both pyridinic-N and pyrrolic-N are crucial for stabilizing the ruthenium catalyst, as confirmed by DFT calculations [26,32,33].

Table 3. Relative type of N-species inside MNC-An support measured from XPS and ruthenium content of fresh catalyst calculated from ICP-OES.

Sample	Total N (at. %)	Pyridinic-N (%)	Pyrrolic-N (%)	Graphitic-N (%)	N-O (%)	N-O ₂ (%)	Ru Content (%)
MNC-An	4.27	23.75	36.90	25.48	10.36	3.54	1.6

2.2. Catalytic Performance of Ru Supported on MNC-An

Figure S1 illustrates the conventional pathway for aniline polymerization. The Ru/MNC-An catalyst was synthesized following the procedure shown in Figure 1 and subsequently heat-treated at 400 °C in a nitrogen atmosphere for two hours to stabilize the active ruthenium species. Ruthenium chloride achieved complete reduction before reaching 400 °C, as reported in our previous study [32].

The ruthenium concentration in the newly synthesized catalyst was quantified via ICP-OES, revealing a loading of 1.60 wt.% (Table 3). A batch reaction was performed to assess the catalytic activity, followed by five recycling tests to evaluate the catalyst's stability. During the initial 2 h reaction cycle, the catalyst achieved a specific activity of 252 mmol_{FA}g_{cat}^{−1} at a reaction temperature of 120 °C and a pressure of 80 bar. The catalyst consistently maintained its relative activity across five recycling tests, exhibiting a specific activity of 255 mmol_{FA}g_{cat}^{−1} after the fifth cycle (Figure 4). The detailed experimental data are presented in Table S4. A detailed comparison of catalytic stability for CO₂ hydrogenation was conducted using previously published literature [10–21,26,27,31–34]. As shown in Table S3, our Ru/MNC-An catalyst demonstrated superior catalytic stability compared to other catalytic systems. This confirms that aniline was successfully employed as a precursor for nanocasting-based mesoporous NDC supporting materials due to the sufficient amount of doped nitrogen. Moreover, the proposed catalytic mechanism for CO₂ hydrogenation to formate on Ru/MNC-An is presented in Figure S3. First, HCO₃[−] is formed through the reaction of CO₂ and H₂ in the presence of water and triethylamine. H₂ dissociates on the

surface of the ruthenium active metal, and H^+ binds with HCO_3^- . With the assistance of triethylamine, formate is produced after water is released during the reaction [10,13,31].

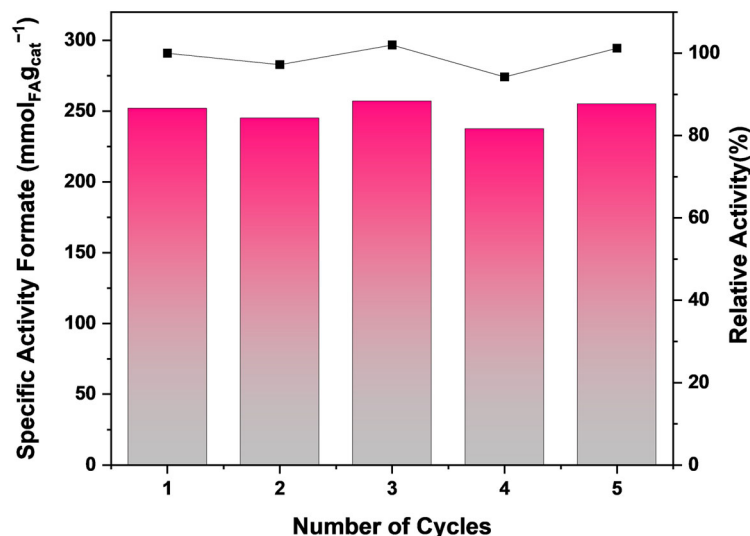


Figure 4. Stability Test of Ru/MNC-An over five cycles (reaction conditions: 120 °C, 80 bar pressure; H_2 : CO_2 (1:1), 1MTEA, 2 h reaction).

MNC-An, synthesized with a high nitrogen content, effectively stabilized the active ruthenium species through pyridinic-N and pyrrolic-N. This highlights the importance of MNC support synthesis based on the selection of precursors with high pyridinic-N and pyrrolic-N content. Additionally, the inclusion of iron chloride during aniline polymerization is crucial, as it acts as an oxidizing agent, facilitating the polymerization process, controlling the molecular weight of the polymer, and doping the polyaniline [46–48].

2.3. Physicochemical Properties of Fresh and Spent Ru/MNC-An

High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were used to examine both fresh and spent catalyst samples, focusing on the catalyst's architecture and the condition of ruthenium. Figure 5a,b show that both the fresh and used catalysts retain a characteristic mesoporous architecture, similar to the support. HAADF-STEM analysis (Figure 5c,d) indicated that ruthenium remained in a distinct single-atom state both before and after the reaction. Heat treatment effectively stabilized the catalyst, ensuring the stability of ruthenium throughout the process. Our previous research demonstrated that heat treatment promotes the migration of ruthenium to pyridinic-N or pyrrolic-N sites, which have a strong affinity for Ru, thereby stabilizing the ruthenium catalyst [32,34].

XPS analysis was conducted on both fresh and spent catalysts to evaluate the oxidation state of ruthenium (Figure 5d,e). Our recent study identified a ruthenium binding energy of 463.01 eV (Ru 3p_{3/2}), indicative of the Ru³⁺ oxidation state, which is known for its high activity in oxidation reactions [34]. Consistent with these findings, the Ru/MNC-An catalyst exhibited a binding energy of 462.95 eV, confirming the presence of ruthenium in the Ru³⁺ oxidation state.

The XPS N1s spectra of both fresh and spent catalysts were analyzed to identify the nitrogen species present (Figure 6a,b). It was found that both catalysts predominantly contained pyridinic-N and pyrrolic-N, similar to the MNC support. The calculated N1s species are shown in Figure 7, with pyridinic-N and pyrrolic-N being the most prominent nitrogen species in both samples. Both fresh and spent catalysts showed negligible variation in binding energy, with values for pyridinic-N (398.7 eV), pyrrolic-N (400.2 eV), graphitic-N (401.6 eV), N-O (403.9 eV), and N-O₂ (405.1 eV). Furthermore, the relative nitrogen content of the nitrogen species, as evaluated through XPS deconvolution (Figure 7), indicates that

pyridinic nitrogen and pyrrolic nitrogen both exceed 20% and 34% in the fresh and spent catalysts, respectively.

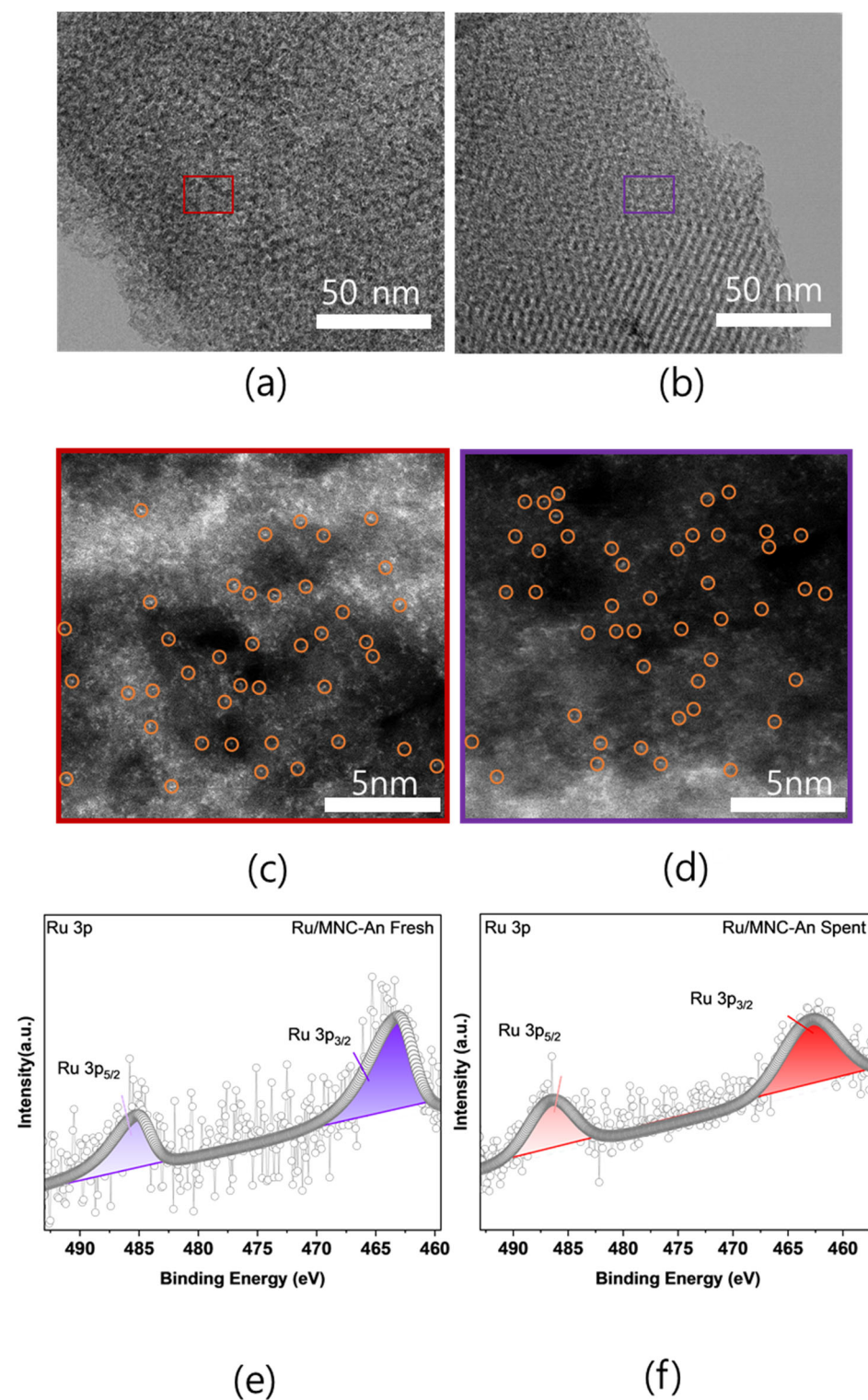


Figure 5. HRTEM and HAADF-STEM of fresh catalyst Ru/MNC-An (a,c), spent catalyst (b,d). Red and purple boxes indicate the area where HAADF-STEM images were acquired. XPS Ru(3P) of fresh (e) and spent (f) catalyst.

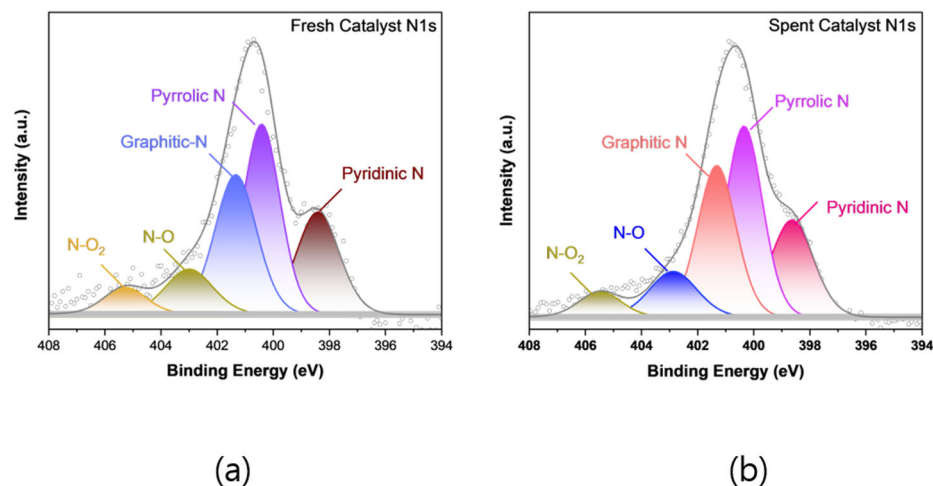


Figure 6. Deconvoluted N1s spectra of fresh (a) and spent (b) catalysts.

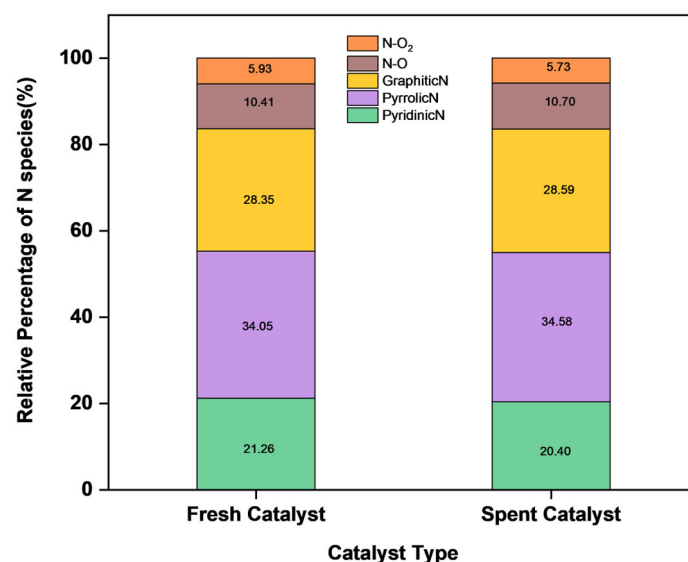


Figure 7. Deconvoluted N1s spectra of fresh and spent catalysts.

3. Materials and Methods

3.1. Materials

All reagents were used directly without further purification. Anhydrous iron (III) chloride (FeCl_3), aniline, hydrofluoric acid (HF), ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), aniline, and sulfuric acid were purchased from Sigma Aldrich (St. Louis, MO, USA). Meanwhile, aqueous methanol, hydrochloric acid (HCl), triethylamine (TEA), and acetone were obtained from Samchun Chemical (Seoul, Republic of Korea). All gases (CO_2 and H_2) were supplied by Sinyang gas Industries (Cheongju, Republic of Korea).

3.2. Preparation

MNC-An: KIT-6 was prepared based on our previous report [32]. The as-synthesized KIT-6 was degassed at 120 °C for 12 h before further use. Infiltration was carried out twice to polymerize aniline on the KIT-6. The first infiltration was conducted as follows: 1 g of FeCl_3 was dissolved in 1 mL ethanol, and then this solution was infiltrated into the KIT-6 pore. The obtained yellow powder was dried at 80 °C for 2 h under vacuum, followed by the addition of 0.66 mL aniline, and the sample was kept at room temperature overnight. The sample was cured at 350 °C under a nitrogen atmosphere for 120 min at a rate of 5 °C/min. The second infiltration was carried out using the same procedure

with a 0.8 lower dose than the first infiltration. The sample was subjected to two stages of calcination under nitrogen flow: at 350 °C at a rate of 5 °C/min and then halted for 120 min; and then the temperature was increased to 800 °C with a ramping rate of 2 °C/min and halted for 120 min. Finally, the silica template and FeCl₃ were removed by a mixture of concentrated HF (48%), 2M HCl, and EtOH with the same volume ratio. The mixture was stirred intensely at room temperature for 120 min, and then transferred to vacuum filtration to obtain the residue after washing with acetone and water. The as-synthesized carbon support was denoted as MNC-An.

Ru/MNC-An: Here, 200 mg of MNC-An was dispersed in 32 mL methanol. Then, the mixture was refluxed at 80 °C for 24 h after adding 8 mL of ruthenium solution with 0.5 mg/mL Ru. The black powder was filtered and washed with acetone and methanol after cooling to room temperature. The powder was dried overnight in a vacuum at 80 °C. After that, the catalyst was subjected to a two-hour calcination process at 400 °C, with a ramping rate of 2 °C/min. Lastly, the powder that was obtained was allowed to dry at room temperature in a glass desiccator.

3.3. Characterization

High-resolution transmission electron microscopy (HRTEM) using the Titan80-300, equipped with a Cs-corrector (FEI, Hillsboro, OR, USA), and scanning transmission electron microscopy (STEM) were both performed. In order to determine the structure of the silica, the Nanopi instrument from Rigaku was used to perform small-angle X-ray scattering (SAXS) within the $2\theta = 0.045\text{--}3^\circ$ range. Raman analysis using a Renishaw CCD camera excited by an Ar laser and wide-angle X-ray diffraction (XRD) using a Bruker instrument D8 advance (Shimadzu Instruments, Kyoto, Japan) were both used to investigate the carbon structure. The sample's textural qualities were examined using the BELSOPR max (Microtrac BEL, Osaka, Japan). A degassing step was performed on the sample overnight at 120 °C to eliminate any moisture before the measurement. Using the Brunauer–Emmett–Teller (BET) equation in the 0.05–0.3 P/P₀ range, the surface area was calculated, and the pore size distribution was obtained using non-local density function theory (NLDFT). To better understand the sample's surface chemical characteristics, X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe from Ulvac-PHI, Chigasaki, Japan) was used. The sample surface was cleaned using Ar-ion sputtering before the measurement, and the spectra that were obtained were calibrated at 284.6 eV using adventitious carbon. Thermo Scientific Flash 2000 (Carlsbad, CA, USA), an elemental analyzer, was used to measure the overall elemental content. Thermo Scientific's iCAP6000 (Carlsbad, CA, USA), an inductively coupled plasma, was used to assess the sample's Ru concentration. Finally, the YL 9100 Plus high-performance liquid chromatography system (YL instruments Co. Ltd., Anyang, Republic of Korea) was used to ascertain the formic acid content.

3.4. Operational Procedure for the CO₂ Hydrogenation Reaction

In a batch reactor, 62 mg of catalyst was initially mixed with 40 mL of 1M TEA. Afterwards, a 1:1 ratio of CO₂ to H₂ was maintained as the gases were charged into the reactor up to 80 bar. Vibrant stirring at 300 rpm was used to bring the reactor temperature up to 120 °C, with a ramping rate of 3 °C/min. After 2 h, the reaction was halted and the temperature of the reactor was lowered using a fan. Filtration was used to retrieve the catalyst, and 0.2 µm filter paper was used to collect the liquid product for FA measurement. Analytical chromatography (HPLC) with an eluent of 5 mM H₂SO₄ and a flowrate of 0.6 mL/min was used to quantify the FA content.

3.5. Stability Test Procedure

Five cycles were performed in the recycle test. To begin, 62 mg of catalyst was mixed with TEA using equal pressure of CO₂ and H₂ gas with vigorous stirring. The catalyst was filtered out after the reaction and then dried in a vacuum at 80 °C overnight. After that, the dry powder went through the next cycle.

4. Conclusions

This study focused on the synthesis of ordered mesoporous carbon using KIT-6 as a hard template and polyaniline as a nitrogen–carbon precursor (MNC-An). The synthesis yielded over 70% carbon, demonstrating the practicality of this method for producing nitrogen-doped carbon. The mesoporous and ordered structure of MNC-An, replicated from KIT-6, was confirmed by HRTEM and SAXS analysis. Physisorption analysis indicated larger capillary condensation at high relative pressures, suggesting the presence of large mesopores, which was further corroborated by the NLDFT pore size distribution, showing mesopores > 5 nm. Elemental analysis revealed over 4% nitrogen content, while XPS analysis of N1s confirmed the presence of stable binding sites, specifically pyridinic and pyrrolic-N sites, which are essential for stabilizing ruthenium. The catalyst demonstrated high catalytic activity, with specific activity of $252 \text{ mmol}_{\text{FA}} \text{g}_{\text{cat}}^{-1}$ and maintained nearly same relative activity after five recycling tests, indicating excellent stability. HAADF-STEM analysis revealed that the ruthenium remained in a single-atom state before and after the reaction, and XPS analysis confirmed the maintenance of the Ru^{3+} oxidation state of the ruthenium. The N1s analysis of both fresh and spent catalysts showed minimal change in N-species, underscoring the robustness of the MNC-An support. The high carbon yield and stable catalytic performance highlight the potential of mesoporous nitrogen-doped carbon (MNC-An) as a practical and efficient catalyst support for CO_2 hydrogenation to formic acid.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14100720/s1>, Figure S1: Typical aniline polymerization route; Figure S2: NLDFT analysis of support MNC-An comprising both microporous and mesoporous volume; Figure S3: Detailed mechanism of CO_2 hydrogenation to formate over $\text{Ru}/\text{MNC-An}$; Table S1: Unit Cell parameter; Table S2: Calculation of elements through the XPS analysis in MNC-An support; Table S3: Catalytic activities of previously reported CO_2 hydrogenation to formate catalysts; Table S4: Detailed Recycling test for each $\text{Ru}/\text{MNC-An}$ cycle.

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Conflicts of Interest: The authors declare no conflicts of interest.

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