

Communication

Trimeric Ruthenium Cluster-Derived Ru Nanoparticles Dispersed in MIL-101(Cr) for Catalytic Transfer Hydrogenation

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Abstract: The synthesis of highly dispersed metal nanoparticles supported on metal–organic frameworks has been widely studied as a means to provide high-performance heterogeneous catalysts. Here, a Ru-nanoparticles-supported MIL-101(Cr) catalyst was prepared via a diamine and oxo-centered trimeric ruthenium cluster ($[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}$), Ru_3 cluster sequential grafting, followed by alcohol reduction. Ethylenediamine (ED) acted as the linker, coordinating with unsaturated sites on both MIL-101(Cr) and the Ru_3 cluster to produce $\text{Ru}_3\text{-ED-MIL-101(Cr)}$, after which selective alcohol reduction process provided the Ru/ED-MIL-101(Cr) catalyst. The synthesized Ru/ED-MIL-101(Cr) catalyst contained small, finely dispersed Ru nanoparticles, and the structural integrity of ED-MIL-101(Cr) was maintained. The Ru/ED-MIL-101(Cr) catalyst was tested for the transfer hydrogenation of benzene using isopropanol as the hydrogen source, where it was shown to outperform other Ru-based catalysts.

Keywords: metal–organic framework; trimeric ruthenium cluster; Ru nanoparticle; transfer hydrogenation



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1. Introduction

Metal-organic frameworks (MOFs) are crystalline porous materials consisting of metal ions or clusters connected by organic linkers [1,2]. Because of their exceptional characteristics, such as high surface area, large pore volume, and tunable pore structures, they have attracted significant attention in a wide range of applications, including catalysis [3–6], gas adsorption and separation [7,8], and sensing [9].

MOFs can also serve as robust host materials for diverse guest molecules, such as clusters, complexes, nanoparticles, and enzymes [10–12]. Metal nanoparticle-supported MOFs have emerged as representative heterogeneous catalysts exhibiting excellent catalytic performance. The incorporation of metal species by simple impregnation often suffers from the deposition of metal precursors at the outer surface of MOFs, which inevitably causes either particle aggregation or a broad size distribution of nanoparticles [13]. To avoid this issue, several synthetic methods, such as the ship-in-bottle strategy [14], bottle-around-ship strategy [15], double solvent method [16], and in situ encapsulation method [17] have been developed. Diamine grafting utilizing free amine groups for the anchoring of metal salts via coordinating diamines to coordinatively unsaturated sites (CUS) of MOFs has received significant attention for its ability to prepare highly dispersed metal nanoparticle-supported MOF catalysts [18,19].

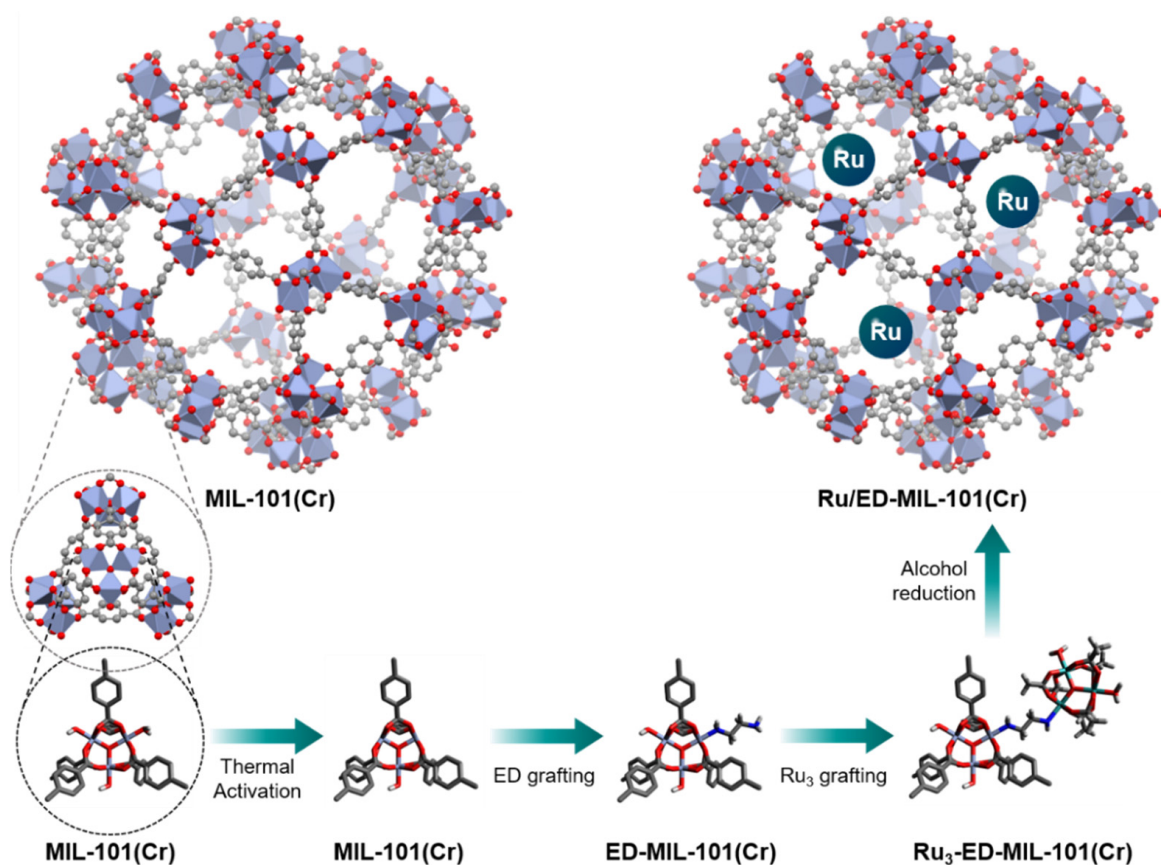
In this study, we present an extended version of the diamine grafting method as a means to prepare highly dispersed Ru nanoparticles in an MOF structure. The previous method used acidic solution to induce the ionic interaction between $-\text{NH}_3^+$ group and anionic metal salts [18], which limits the types of metal precursor and solvent. Here, the strong coordination of diamine molecules with the CUS of MOF and trimeric metal cluster

enabled the molecular level isolation of metal species in the MOF pores [20], and subsequent microwave alcohol reduction process selectively reduced Ru_3 clusters into Ru nanoparticles. The prepared Ru-nanoparticle-supported MOF catalyst was analyzed to confirm the structural integrity of the parent MOF and the level of dispersion of Ru nanoparticles. Subsequently, it was tested for the catalytic transfer hydrogenation reaction, utilizing a green hydrogen source instead of gaseous hydrogen under mild reaction conditions [3,4,21,22], where it showed higher turnover numbers (TONs) than other Ru catalysts.

2. Results and Discussion

2.1. Stepwise Synthesis of Ru/ED-MIL-101(Cr)

MIL-101(Cr) has been widely utilized as a host material by virtue of its high surface area, large pore size, thermal and chemical stability, and large number of CUS [23]. Scheme 1 shows the stepwise process involved in the synthesis of Ru/ED-MIL-101(Cr). The prepared MIL-101(Cr) was thermally activated to remove water molecules coordinated to CUS and then grafted using ethylenediamine (ED). ED molecules selectively bind to the CUS of MIL-101(Cr) to produce ED-MIL-101(Cr). ED-MIL-101(Cr) contains free amine groups on its uncoordinated ED molecules, which can further bind to the incoming metal precursor via coordination bonds [18]. To achieve this method, thermally activated Ru_3 clusters with Ru CUS were dissolved in ethanol and grafted onto ED-MIL-101(Cr). The Ru_3 cluster used in this study is known to be easily reduced through heating with alcohol [24]. Thus, to selectively reduce the incorporated Ru_3 cluster while maintaining the MIL-101(Cr) structure, the obtained Ru_3 -ED-MIL-101(Cr) was dispersed in isopropanol and microwaved at 120 °C, resulting in the formation of Ru/ED-MIL-101(Cr).



Scheme 1. Stepwise synthesis processes for Ru/ED-MIL-101(Cr). Atom colors: Cr (pale purple), Ru (dark cyan), C (dark grey), O (red), N (blue), and H (white).

2.2. Characterization of MIL-101(Cr) and Its Derivatives

The prepared MIL-101(Cr), ED-MIL-101(Cr), Ru₃-ED-MIL-101(Cr), and Ru/ED-MIL-101(Cr) were analyzed using various physicochemical characterizations. Figure 1a shows that the synthesized MIL-101(Cr) exhibits the reported crystallinity of MIL-101(Cr) [25]. This crystallinity was almost maintained after successive ED grafting, Ru₃ cluster grafting, and alcohol reduction. The thermogravimetric analysis (TGA) patterns of the four materials (saturated by water) indicate that they have similar thermal stabilities up to ~370 °C, with MOF water contents in the following order (highest to lowest): MIL-101(Cr), ED-MIL-101(Cr), Ru/ED-MIL-101(Cr), and Ru₃-ED-MIL-101(Cr) (Figure 1b). The slightly increased water content of Ru/ED-MIL-101(Cr) compared with that of Ru₃-ED-MIL-101(Cr) can be explained by the removal of organic ligands from the Ru₃ cluster after reduction, thereby increasing the free pore volume. The same trend was observed in the N₂ isotherm results (Figure 1c). The amount of N₂ uptake in the MOFs was in the same order as that of their water contents observed in TGA. In pore size distribution plots (Figure 1d), the pore volume at 2–3 nm of MIL-101(Cr) was reduced after the grafting of ED and Ru₃ clusters, which demonstrates that the ED molecules and Ru₃ clusters were incorporated into the mesopores of MIL-101(Cr).

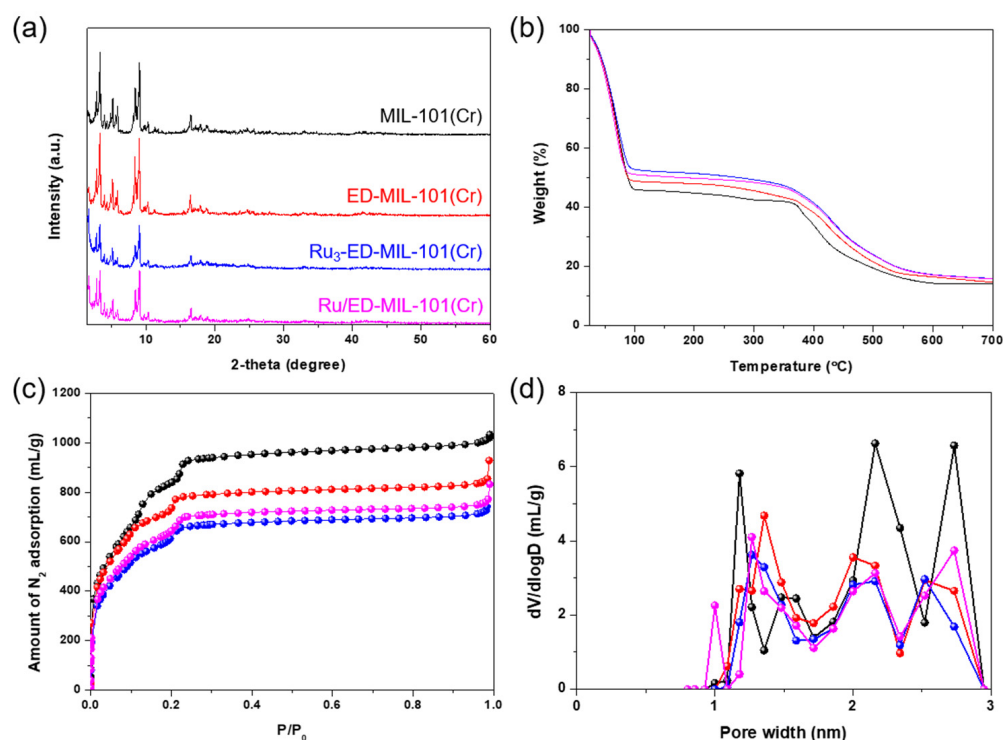


Figure 1. (a) PXRD patterns, (b) TGA plots, (c) N₂ isotherms, and (d) pore size distributions (using the DFT method) of MIL-101(Cr) (black), ED-MIL-101(Cr) (red), Ru₃-ED-MIL-101(Cr) (blue), and Ru/ED-MIL-101(Cr) (pink).

Table 1 summarizes the elemental composition and textural properties of the synthesized MIL-101(Cr) and its derivatives. The Brunauer–Emmett–Teller (BET) surface areas of MIL-101(Cr), ED-MIL-101(Cr), Ru₃-ED-MIL-101(Cr), and Ru/ED-MIL-101(Cr) were 3121, 2681, 2258, and 2366 m²/g, respectively, and their pore volumes were 1.6, 1.4, 1.3, and 1.3 cm³/g, respectively. ED-MIL-101(Cr) contains 2.8 wt% of nitrogen, confirming the successful grafting of ED molecules; this corresponds to 2.0 mmol/g of amine contents and half the number of free amine groups and indicates that approximately one ED molecule was coordinated to the Cr trimer of MIL-101(Cr), considering the potential amount of Cr CUS (3.0 mmol/g) [18]. The Ru content in Ru₃-ED-MIL-101(Cr) was 1.98 wt%, which is calculated to 0.20 mmol Ru/g and 0.065 mmol Ru₃ cluster/g, indicating that approximately 6.5 mol% of free amine groups were grafted by Ru₃ clusters. After reduction,

Ru/ED-MIL-101(Cr) had 2.03 wt% of Ru, implying that the Ru content in the Ru₃-ED-MIL-101(Cr) was almost maintained in Ru/ED-MIL-101(Cr) following the microwave alcohol reduction process.

Table 1. Elemental composition and textural properties of the prepared materials.

Materials	Textural Properties ^a		Amount of N ^b		Amount of Ru ^c	
	S _{BET} (m ² /g)	V ^t (cm ³ /g)	wt%	mmol/g	wt%	mmol/g
MIL-101(Cr)	3121	1.6	-	-	-	-
ED-MIL-101(Cr)	2681	1.4	2.8	2.0	-	-
Ru ₃ -ED-MIL-101(Cr)	2258	1.3	2.7	1.9	1.98	0.20
Ru/ED-MIL-101(Cr)	2366	1.3	2.7	1.9	2.03	0.20

^a Obtained by N₂ isotherms. ^b Analyzed using EA. ^c Analyzed using ICP-AES.

Scanning electron microscopy (SEM) micrographs of the synthesized MIL-101(Cr) and its derivatives are shown in Figure S1. All images show truncated octahedral shapes, again confirming the structural integrity of MIL-101(Cr) after each process. Figure 2a–d shows the transmission electron microscopy (TEM) and scanning TEM (STEM) images of Ru₃-ED-MIL-101(Cr) and Ru/ED-MIL-101(Cr). The Ru₃-ED-MIL-101(Cr) particles exhibited a neat surface, indicating that the Ru₃ clusters were incorporated at the molecular level without aggregation. In contrast, Ru/ED-MIL-101(Cr) contained uniform small nanoparticles with an average particle size of 1.9 nm (Figure S2). Furthermore, energy-dispersive X-ray spectroscopy (EDS) maps indicate that N, Cr, and Ru are dispersed over the entirety of the Ru/ED-MIL-101(Cr) particles (Figure 2e), indicating that Ru nanoparticles are incorporated into pores whereas ED molecules remain within the MIL-101(Cr) structure. The absence of Ru peaks in the powder X-ray diffraction (PXRD) patterns of Ru/ED-MIL-101(Cr) (Figure 1a) also verifies that the Ru nanoparticles are very small. These results confirm that small Ru nanoparticles were encapsulated in the ED-MIL-101(Cr) structure with a high dispersion level via Ru₃ cluster grafting and subsequent alcohol reduction.

The samples were further analyzed using in situ Fourier transform infrared (FTIR) spectroscopy to observe changes in functional groups during each synthesis process (Figure 3a). Upon ED grafting, stretching vibrational peaks for the N–H (3100–3350 cm^{−1}) and C–H (2800–3000 cm^{−1}) groups appeared. The aliphatic C–H stretching peaks were slightly changed after Ru₃ cluster grafting due to the presence of acetate groups in the Ru₃ cluster. A reduced intensity with a slight shift of the N–H peaks was also observed, which can be ascribed to the coordination bond of free amines with the Ru center of the Ru₃ cluster used for grafting.

To further confirm the oxidation state of the Ru species, X-ray photoelectron spectroscopy (XPS) analysis was conducted. Figure 3 shows the Ru 3p XPS spectra of Ru₃ clusters, Ru₃-ED-MIL-101(Cr), Ru/ED-MIL-101(Cr), and commercial Ru/C that was pre-reduced by hydrogen at 400 °C. The XPS spectrum of the Ru₃ cluster showed Ru 3p_{1/2} and Ru 3p_{3/2} peaks at 485.8 and 463.4 eV, which can be assigned to the Ru³⁺ oxidation state. Ru₃-ED-MIL-101(Cr) exhibited almost the same binding energies, confirming retention of the Ru³⁺ oxidation state after grafting onto ED-MIL-101(Cr). Ru/ED-MIL-101(Cr) showed peaks at 485.3 and 462.9 eV; the same binding energies were obtained from commercial Ru/C, clearly proving that the Ru₃ cluster was reduced into Ru⁰ after microwave alcohol reduction. This characterization demonstrates the successful grafting of the Ru₃ cluster and its selective reduction, which produces well-dispersed Ru nanoparticles within ED-MIL-101(Cr) pores.

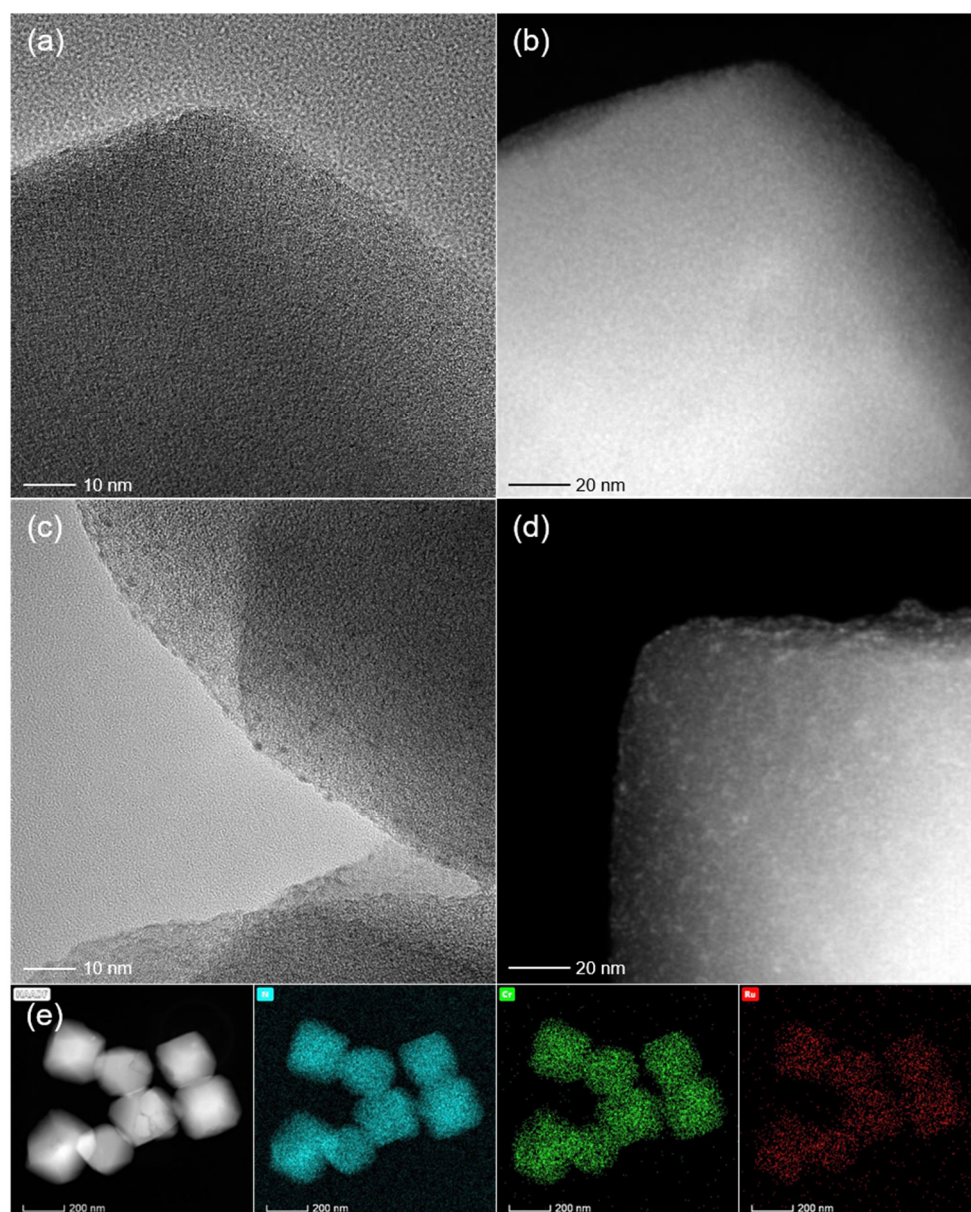


Figure 2. (a) TEM and (b) STEM images of $\text{Ru}_3\text{-ED-MIL-101(Cr)}$. (c) TEM and (d) STEM images of Ru/ED-MIL-101(Cr) . (e) EDS maps of Ru/ED-MIL-101(Cr) . N (cyan), Cr (green), and Ru (red) are indicated.

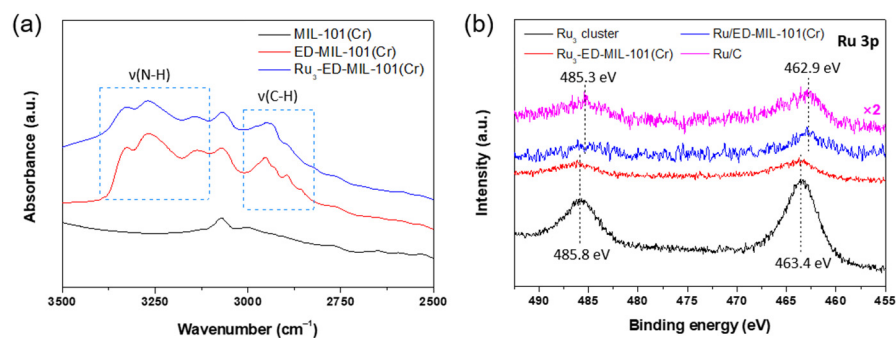


Figure 3. (a) In situ FTIR spectra of MIL-101(Cr) (black), ED-MIL-101(Cr) (red), and $\text{Ru}_3\text{-ED-MIL-101(Cr)}$ (blue) measured at $150\text{ }^\circ\text{C}$. (b) Ru 3p XPS spectra of Ru_3 clusters (black), $\text{Ru}_3\text{-ED-MIL-101(Cr)}$ (red), Ru/ED-MIL-101(Cr) (blue), and Ru/C (pink).

2.3. Catalytic Transfer Hydrogenation of Benzene Using Isopropanol over Ru Catalysts

The resulting Ru/ED-MIL-101(Cr) was tested for its applicability to the catalytic transfer hydrogenation of benzene, using isopropanol as the hydrogen source. The hydrogenation of benzene can theoretically produce 1,3-cyclohexadiene, cyclohexene, and cyclohexane. Thermodynamically, however, partial hydrogenation is not favorable because cyclohexane has lower Gibbs free energy (75 kJ/mol) than other products [26]. Ru is well known for its hydrogenation and dehydrogenation abilities, therefore, it is also an excellent catalyst for transfer hydrogenation [27]. Isopropanol is among the most widely used hydrogen sources for transfer hydrogenation and can be produced from biomass feedstocks [28,29]. As such, the use of isopropanol as the hydrogen source instead of hydrogen gas is considered sustainable.

Table 2 shows the catalytic results obtained over various Ru catalysts. Both the Ru₃ cluster and Ru₃ clusters pre-reduced by hydrogen at 250 °C exhibited low TONs of 49 and 7, respectively. In a previous study, the Ru₃ cluster was used as a catalyst for allylic alcohol isomerization, where ethanol solvent was dehydrogenated to acetaldehyde, and the Ru₃ cluster was reduced to Ru⁰ and aggregated into nanoparticles during the reaction [30]. Therefore, the high activity of the Ru₃ cluster relative to the pre-reduced Ru₃ cluster in the transfer hydrogenation of benzene can be ascribed to the in situ formation of smaller Ru nanoparticles from Ru₃ clusters. RuCl₃·xH₂O showed low activity (TON = 11) compared with RuO₂·xH₂O (TON = 91). RuO₂ is known to be active in transfer hydrogenation, becoming reduced to metallic Ru during the reaction [31]. Commercial Ru/C showed a much higher TON value of 169 due to the presence of highly dispersed Ru nanoparticles with a size of 2–3 nm. Notably, the synthesized Ru/ED-MIL-101(Cr) exhibited the best catalytic activity, achieving TON = 192 and 94% yield. Although high cyclohexane yield could be obtained from benzene hydrogenation in many reports, the research on the transfer hydrogenation of benzene has rarely been studied. Tang et al. obtained 25% of cyclohexane yield out of the maximum theoretical yield of 33% over NiCo/CeO₂ catalyst by using glycerol as the hydrogen donor at 160 °C [32]. The high catalytic activity of Ru/ED-MIL-101(Cr) can be attributed to the high dispersion of small Ru nanoparticles (1.9 nm) in the MIL-101(Cr) structure. Additionally, the window sizes (1.2 and 1.6 nm) and cage sizes (2.9 and 3.4 nm) of MIL-101(Cr) do not interfere with the diffusion of benzene (kinetic diameter = 0.585 nm) [33] and isopropanol (kinetic diameter = 0.46 nm) molecules [34]. The Ru/ED-MIL-101(Cr) catalyst was collected after catalytic reaction and characterized by PXRD (Figure S3), which confirmed that the structural integrity of MIL-101(Cr) was maintained after reaction.

Table 2. Catalytic transfer hydrogenation of benzene to cyclohexane using isopropanol as the hydrogen source over various Ru catalysts.

Entry	Catalysts	Yield (%)	TON
1	Ru ₃ cluster	24.0	49
2	Ru ₃ cluster, pre-reduced	3.4	7
3	RuCl ₃ ·xH ₂ O	5.4	11
4	RuO ₂ ·xH ₂ O	44.5	91
5	Ru/C	82.6	169
6	Ru/ED-MIL-101(Cr)	93.9	192

Reaction conditions: 2 mmol benzene, 30 mL isopropanol, 0.01 mmol Ru catalyst, 120 °C, 18 h.

The acetone peak was observed in the gas chromatography (GC) spectrum, demonstrating that benzene was reduced by transfer hydrogenation using isopropanol as the hydrogen source. In addition, in all cases, cyclohexane was detected as the sole product; i.e., cyclohexene was not produced. Cyclohexenes can be produced by adding water or by improving the hydrophilicity of the catalyst to inhibit further hydrogenation [27,35]. The dehydrogenation of isopropanol (+54 kJ/mol) [36] is a more energy-demanding reaction than hydrogenation of benzene (−208 kJ/mol) and cyclohexene (−120 kJ/mol) [26], indicating that isopropanol dehydrogenation is the rate-determining step in our reaction.

system. Therefore, in situ generated hydrogen can immediately hydrogenate intermediate cyclohexene over Ru nanoparticles to achieve 100% cyclohexane selectivity.

3. Materials and Methods

3.1. Materials

Chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%), terephthalic acid (99%), ED (99%), toluene anhydrous (99.8%), ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 99.0%), benzene anhydrous (99.8%), cyclohexane anhydrous (99.5%), 2-propanol (99.5%), and 5% Ru/C were purchased from Sigma-Aldrich, Burlington, MA, USA. Ammonium fluoride (NH_4F , 97.0%) was purchased from JUNSEI, Tokyo, Japan. Ethyl alcohol (EtOH , 99%), diethyl ether ($(\text{CH}_3)_2\text{O}$, 99%), chloroform (99%), and glacial acetic acid (99.7%) were purchased from Samchun, Seoul, Korea. All reagents were used as received without further purification.

3.2. Syntheses of Ru_3 Cluster (μ_3 -oxo-hexakis(μ -acetato)tri(aqua)triruthenium(III) acetate, $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}$)

The Ru_3 cluster was synthesized following reported procedures with a slight modification [37]. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ of 4.75 g and sodium acetate trihydrate of 12 g were added to a mixture of 300 mL glacial acetic acid/ethanol (50:50 in volume ratio) in a 500 mL round bottom flask. The mixture was refluxed overnight and cooled to room temperature. Then, the solution was filtered to remove undissolved solid, and the solvent was removed by rotary evaporation. A small amount of methanol was added to the resulting oily residue, and it was precipitated by adding an excess amount of acetone, followed by filtration. The resulting powder was further washed with diethyl ether. To increase the purity of the sample, the recrystallization process was repeated by dissolving the powder in methanol/acetone (1:1 in volume ratio) and cooling to -40°C in acetonitrile/dry ice bath. Finally, the material was collected by filtration from the cold solution. Anal. calculated for $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}$, calculated; C, 21.3; H, 3.44, Ru, 38.6, found; C, 20.8; H, 3.5, Ru, 39.5.

3.3. Synthesis of MIL-101(Cr)

MIL-101(Cr) was synthesized following a previously reported method [38]. Deionized water of 600 mL, terephthalic acid of 20.75 g, 5 M HF solution of 6.25 mL, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ of 50 g were added to a Teflon-lined autoclave and hydrothermally treated at 220°C in an oven for 11 h with stirring. Subsequently, the hot reactor was immediately removed from the oven and cooled down using cold water for 2.5 h; then, the green slurry was filtered through a 38 μm Buchner funnel to remove any remaining terephthalic acid. The product was further treated overnight with hot water containing 30 mM NH_4F at 85°C and for 3 h using hot ethanol at 70°C ; purification by centrifugation at 7000 rpm was conducted for 10 min after each treatment.

3.4. Synthesis of ED-MIL-101(Cr)

Amine grafting of MIL-101(Cr) was conducted following a previously reported method [18]. MIL-101(Cr) was dehydrated at 150°C for 12 h under vacuum conditions, and 1 g of dehydrated MIL-101(Cr) was dispersed in 30 mL of toluene. Then, 1.5 mmol of ED was added, and the mixture was refluxed for 12 h. After cooling to room temperature, the resulting product was filtered, washed with toluene and an excess amount of ethanol, and dried overnight at 100°C .

3.5. Synthesis of Ru_3 -ED-MIL-101(Cr)

A Ru_3 cluster of 50 mg was dissolved in 20 mL of ethanol. Then, 1 g of ED-MIL-101(Cr) was added to the solution and stirred at 40°C for 24 h. The resulting mixture was filtered and then washed using excess amounts of ethanol. The resulting solid was dried overnight at 70°C .

3.6. Synthesis of Ru/ED-MIL-101(Cr)

Ru₃-ED-MIL-101(Cr) of 0.5 g was dispersed in 50 mL of isopropanol and heated at 120 °C for 1 h under microwave conditions. Following this treatment, the sample was filtered, washed with isopropanol and dried overnight at 70 °C.

3.7. Characterization

PXRD patterns were obtained using a diffractometer (Rigaku, Tokyo, Japan, D/MAX 2200V) emitting Ni-filtered Cu K α radiation (40 kV, 40 mA, λ = 1.5406 Å) at a scan rate of 4°/min. N₂ adsorption and desorption isotherms were obtained at −196 °C (Micromeritics, Norcross, GA, USA, Tristar 3000). The samples were activated at 150 °C for 12 h under vacuum conditions (<10^{−5} Torr) prior to analysis. The specific surface area was determined using the BET method, and the pore volume was obtained following the single-point method at P/P₀ = 0.995. The pore size distribution was determined using the density functional theory (DFT) method. TGA was performed using a thermal analyzer (Scinco, Seoul, Korea, TGA-N 1000). The samples were heated at a heating rate of 5 °C/min from 25 to 700 °C under a constant flow of N₂ at 30 mL/min. Prior to TGA, the samples were kept under a saturated NH₄Cl atmosphere in a closed chamber for 24 h. For in situ FTIR measurements, the samples were pelletized and evacuated for 30 min at 150 °C under He flow (20 mL/min). In situ FTIR spectra were obtained using an FTIR spectrometer (Nicolet, Champaign, IL, USA, MAGNA-IR 560) equipped with an in situ IR cell with KBr windows.

SEM images were obtained at an acceleration voltage of 10 kV (Tescan, Brno, Czech Republic, VEGA-II LSU). TEM and STEM images with corresponding EDS maps were obtained using a TEM (FEI tecnai, Stanford, CA, USA, GS-20 S-Twin) at an accelerating voltage of 200 kV. XPS analysis was conducted using an AXIS SUPRA X-ray photoelectron spectrometer (225 W, Al K α , 15 kV, 10 mA). Spectra were calibrated using the C 1 s peak at 284.8 eV. C, H, and N elemental analysis was conducted using a Thermo Finnigan Flash 1112, Waltham, MA, USA. The Ru concentrations in the materials were analyzed by inductively coupled plasma–atomic emission spectrometry (ICP–AES) using a Thermo Fisher Scientific iCAP 6500Duo, Waltham, MA, USA. Prior to analysis, the powder samples were completely digested in HCl/HNO₃ (3:1 vol%) solution using Xpert microwave (Berghof, Eningen unter Achalm, Germany) with Teflon containers.

3.8. Catalytic Transfer Hydrogenation of Benzene Using Isopropanol

Catalytic transfer hydrogenation was performed in a 50 mL autoclave. Typically, 2 mmol of benzene, 30 mL of isopropanol (392 mmol), and 0.5 mol% of Ru catalyst were added to the reactor. The reaction proceeded by heating to 120 °C with stirring at 300 rpm for 18 h. Following the reaction, the reactor was cooled to room temperature and the reaction solution was filtered to separate the used catalyst. A small amount of decane was added to the filtered liquid product as the external standard. The resulting solution was analyzed using GC (flame ionization detector and DB-624 column).

4. Conclusions

In summary, we developed an effective method for preparing highly dispersed Ru nanoparticles in the pores of ED-MIL-101(Cr). For this strategy, the CUS of MIL-101(Cr) was grafted by ED molecules, followed by Ru₃ cluster grafting, and microwave alcohol reduction. The crystallinity and porosity of MIL-101(Cr) were almost maintained after each process, and the encapsulated Ru nanoparticles were shown to be small and well dispersed throughout the pores of ED-MIL-101(Cr). The Ru/ED-MIL-101(Cr) exhibited a higher catalytic activity than other Ru catalysts in terms of the transfer hydrogenation of benzene to afford cyclohexane using isopropanol as the hydrogen source under mild conditions.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal12091010/s1>, Figure S1: SEM images of (a) MIL-101(Cr), (b) ED-MIL-101(Cr), (c) Ru₃-ED-MIL-101(Cr), and (d) Ru/ED-MIL-101(Cr); Figure S2: Particle size distribution of Ru nanoparticles in Ru/ED-MIL-101(Cr) observed by TEM and Figure S3: The PXRD patterns of Ru/ED-MIL-101(Cr) before (black) and after reaction (red).

Author Contributions: Conceptualization, Y.K.H.; methodology, K.-R.O. and S.E.S.; formal analysis, K.-R.O.; investigation, K.-R.O. and S.E.S.; writing—original draft preparation, K.-R.O.; writing—review and editing, C.Y., D.-Y.H. and Y.K.H.; funding acquisition, Y.K.H. All authors have read and agreed to the published version of the manuscript.

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

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