

Electronic supplementary information

Immobilization of trimeric ruthenium cluster in mesoporous chromium terephthalate and its catalytic application

*Sanil E. Sivan,^a Kyung-Ryul Oh,^a Ji-Woong Yoon,^a Changho Yoo^a and Young Kyu Hwang^{*a}*

^a Chemical & Process Technology Division, Korea Research Institute of Chemical Technology (KRICT),
Daejeon 34114, Republic of Korea. E-mail: ykhwang@kRICT.re.kr

Chemicals and materials

All reagents, 5-hydroxymethylfurfural (HMF, Aldrich, 99.9%), 2,5-diformylfuran (DFF, Aldrich, 97%), Benzyl alcohol (Aldrich, 99%), Benzaldehyde (Aldrich, 99%), chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich, 99%), ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, Aldrich), 1,4-butanediamine (Aldrich, 99%), benzene-1,4-dicarboxylic acid (Aldrich, 99%), glacial acetic acid (Aldrich, 99%), sodium acetate trihydrate (Aldrich), hydrofluoric acid (HF, Aldrich, 48wt% in H_2O), ammonium fluoride (Junsei, 97%), ethyl alcohol (Samchun chemical, 95%), methyl alcohol (Samchun chemical, 95%), acetone (Samchun chemical, 95%), toluene anhydrous (Aldrich, 99.8%), diethyl ether (Samchun chemical, 99%), and chloroform (Samchun chemical, 99%) were used as purchased without further purification.

Synthesis of MIL-101(Cr)

MIL-101 (Cr) was prepared by hydrothermal reaction of 1,4-dicarboxylic acid (1 mmol) with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 mmol), HF (0.25 mmol), and H_2O (267 mmol) at 493 K for 8 h. These reactions produced a highly crystallized green powder of the chromium terephthalate. The as-synthesized MIL-101 (Cr) was further purified by the following two-step processes using hot ethanol and 5wt% of aqueous NH_4F solutions. A first activation treatment was performed using two subsequent solvent treatments with hot water at 95 °C for 5 h and hot ethanol at 75 °C for 3 h until no detection of colored impurities in the mother liquor solution. In the second activation treatment, the material was purified by dispersing in 150 mL of an aqueous solution of 30 mM NH_4F at 95 °C for 10 h. After cooling, the precipitate was filtered and washed five times with 200 mL of hot water (60 °C) to remove traces of NH_4F .

Synthesis of BD-MIL-101(Cr)

1 g of MIL-101(Cr) dehydrated at 423 K for 12 h under vacuum, was suspended in 100 mL of anhydrous ethanol. To this suspension, 2 mmol of 1,4-butanediamine was added and the resulting mixture was refluxed at 78 °C for 10 h. The product was recovered by filtration, washed with plenty of anhydrous ethanol, and finally dried at 100 °C for 12 h. The content of the amine group was examined by the elemental analysis and was found to be 1.67 mmol/g.

Ethylenediamine functionalization MIL-101(Cr)

1 g of MIL-101(Cr) dehydrated at 423 K for 12 h under vacuum, was suspended in 100 mL of anhydrous toluene. To this suspension, 3 mmol of ethylenediamine was added and the resulting mixture was refluxed at 110 °C for 12 h. The product was recovered by filtration, washed with deionized water-ethanol mixture, and finally dried at 100 °C for 12 h. The content of the amine group was examined by the elemental analysis and was found to be 2.1 mmol/g.

Synthesis of $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}$ cluster

$[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}$ cluster was synthesized as reported elsewhere with a slight modification.¹ A mixture of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (22.9 mmol), sodium acetate trihydrate (88.2 mmol), glacial acetic acid (150 mL), and ethanol (150 mL) was charged into a 500 mL round-bottom flask. The brown-colored solution was refluxed for 4 h (during refluxing the solution color changed to deep forest green). After cooling to room temperature, the solution was filtered and discarded the insoluble residues. The solvent was removed by rotary evaporation under vacuum conditions. The resulting oily residue was dissolved in a minimum amount of methanol and precipitated by adding an excess amount of acetone and filtered off. The resulting powder was further washed with acetone and diethyl ether. The product obtained was a crude form of the

cluster, which contains sodium chloride as the by-product. A highly pure sample was obtained by the repeated recrystallization by dissolving the crude powder in a minimum amount of premixed methanol/acetone (1:1) cooled to -40 °C (acetonitrile/dry-ice bath) and finally collected the precipitate by filtration from cold solution. Anal. Calculated for $[\text{Ru}_3\text{O}(\text{OOCCH}_3)_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}$: C, 21.3; H, 3.44. Found: C, 20.8; H, 3.5.

Grafting of $[\text{Ru}_3\text{O}(\text{OOCCH}_3)_6(\text{H}_2\text{O})_3]^+$ cluster on BD-MIL-101(Cr)

1 g of 1,4-butanediamine grafted MIL-101(Cr) (1.67 mmol diamine equivalent) was added into a solution of 3 mmol of Ru_3 cluster in 100 mL anhydrous methanol. The resulting mixture was stirred at 45 °C under vigorous stirring for 24 h. The solid was separated by filtration, washed with plenty of methanol until the filtrate become colorless, and finally dried at 100 °C for 12 h.

Material Characterizations

The as-synthesized MIL-101(Cr), $[\text{Ru}_3\text{O}(\text{OOCCH}_3)_6(\text{H}_2\text{O})_3]\text{CH}_3\text{COO}$ cluster, BD-MIL-101(Cr), and Ru_3 cluster@BD-MIL-101(Cr) materials were characterized with various physiochemical characterization techniques. Powder X-ray diffraction patterns of all the samples were recorded by a Rigaku diffractometer (D/MAX IIIB, 2 kW) using Ni-filtered $\text{Cu K}\alpha$ -radiation (40 kV, 30mA, $\lambda = 1.5406 \text{ \AA}$) and a graphite crystal monochromator. The morphology of the materials was analyzed using a scanning electron microscope (SEM, Carl Zeiss Sigma HD). Transmission electron microscopy (TEM) images and corresponding energy-dispersive X-ray spectroscopy (EDS) map images were obtained by a TEM (FEI tecnai GS-20 S-Twin) at an accelerating voltage of 200 kV. Specific surface areas were measured by N_2 adsorption and desorption isotherms at liquid nitrogen temperature using a sorption analyzer (Micromeritics, Tristar 3000). All samples were degassed by heating at 150 °C for 12 h under vacuum ($<10^{-5}$ Torr)

before measurements. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method in the P/P_0 range of 0.05 – 0.2. The pore size distribution was determined by the argon sorption technique using the non-local density functional theory (NLDFT) method. Thermogravimetric (TGA) analyses were carried out under nitrogen (20 mL min^{-1}) with a Perkin-Elmer electro balance TGA-7 at a heating rate of 5 min^{-1} up to $600 \text{ }^\circ\text{C}$. Before TGA analysis the samples were kept under a saturated NH_4Cl atmosphere in a closed chamber for 24 h.

FTIR spectra were recorded on a Nicolet FTIR spectrometer (MAGNA-IR 560) using KBr pellets. Temperature-dependent FTIR spectra of the bare Ru_3 cluster were recorded at different temperatures on a Nicolet FTIR spectrometer (MAGNA-IR 560). The KBr pellet of the sample (for making the pellet, 0.2 g of KBr and 0.01 g Ru_3 cluster was mixed thoroughly and 30 mg of the mixture was used to make the pellet) was treated at each designated temperature for 3 h under N_2 flow (10 mL/min.) in a specially designed IR cell before measuring the IR spectra. The CO adsorbed FTIR spectra measurements were performed using a Nicolet Is-50 instrument having a mercury cadmium telluride detector. The self-supported wafer (about 10 mg) of the sample was placed in a quartz cell equipped with CaF_2 windows. The cell was connected to a vacuum line for the evacuation and calcination steps and also for the introduction of CO into the IR cell. The sample was activated in the IR cell at $150 \text{ }^\circ\text{C}$ for 6 h under vacuum (3.0×10^{-6} torr) before performing the CO adsorption. After the thermal treatment, the sample was cooled to approximately $-173 \text{ }^\circ\text{C}$ using liquid N_2 . The incremental addition of CO molecules in the cell was made possible via a calibrated volume (3.99 cm^3) connected to a pressure gauge for the control of the probe pressure (0.01-2.0 torr).

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra (DLD) photoelectron spectrometer operated at 15 kV and 10 mA at a pressure of about 5×10^{-9} Torr using Al K α as the exciting source (15 kV, 15 mA) (all the binding energy values are calibrated by using C 1s signal at 284.8 eV). Elemental analysis (EA) was performed to determine the nitrogen content of the amine-functionalized MIL-101(Cr). The Ru concentrations in the materials were analyzed by the ICP-AES technique (Thermo scientific Icap 6500 duo inductively coupled plasma-atomic emission spectrometer).

Catalytic test and product analysis

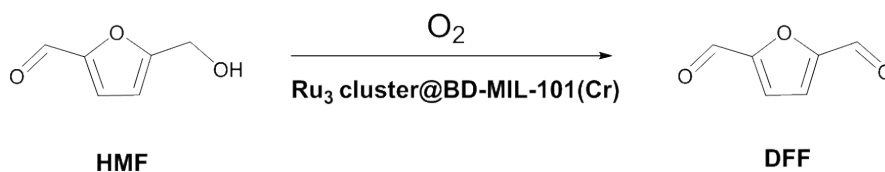
The catalytic reactions were carried out in a high-pressure stainless-steel autoclave reactor fitted with a 100 mL Teflon bomb. The temperature and stirring speed were controlled by electronic controllers equipped with the reactor. Prior to each reaction, the MIL-101(Cr) derived catalyst was activated at 150 °C under vacuum overnight to generate Ru CUS. In a typical reaction, the reactor was charged with 0.15 g of HMF, 0.1 g of decane (internal standard), a catalytic amount of Ru₃ cluster-based catalyst (HMF/Ru₃ cluster mole ratio fixed to 37.5), and 22 g anhydrous toluene. Before starting the reaction, the reactor was purged three times with oxygen. The reactions were carried out at 130 °C for 24 h under 30 bar oxygen pressure with a stirring speed of 500 rpm. After the reaction, the reactor was cooled, depressurized, and filtered off the catalyst. The reaction solution was further filtered by using a syringe membrane filter (13 mm to 0.45 μ m; Whatman) and used for the quantitative analysis (for the quantification of HMF and DFF) by using gas chromatography equipped with a DB-624 column.

To extract the adsorbed product [toluene insoluble products such as 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA), 5-formyl-2-furancarboxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA)] on the catalyst, the recovered catalyst was further dispersed in a known amount of anhydrous methanol, stirred for 5 min and separated the catalyst. The methanol solution was further filtered by using a syringe membrane filter (13 mm to 0.45 μm ; Whatman) and used for the quantitative analysis by using high-performance liquid chromatography (HPLC) {Bio-Rad Aminex HPX-87 H pre-packed column, 0.010 M CF_3COOH (mobile phase), 60 $^\circ\text{C}$ (column temp.), 0.5 mL/min (flow rate), 254 nm (UV detector wavelength)}. In all the reactions, the collective yield of methanol soluble products such as HMFCFA, FFCA, and FDCA obtained from the HPLC analysis was less than 1%.

The HMF conversion and product yields were calculated using the following formula.

$$\text{Conversion (\%)} = \frac{(\text{Initial mole of HMF}) - (\text{Final mole of HMF})}{\text{Initial mole of HMF}} \times 100$$

$$\text{Product yield (\%)} = \frac{\text{Mole of product formed}}{\text{Initial mole of HMF}} \times 100$$



Scheme S1. Reaction scheme of HMF oxidation to DFF.

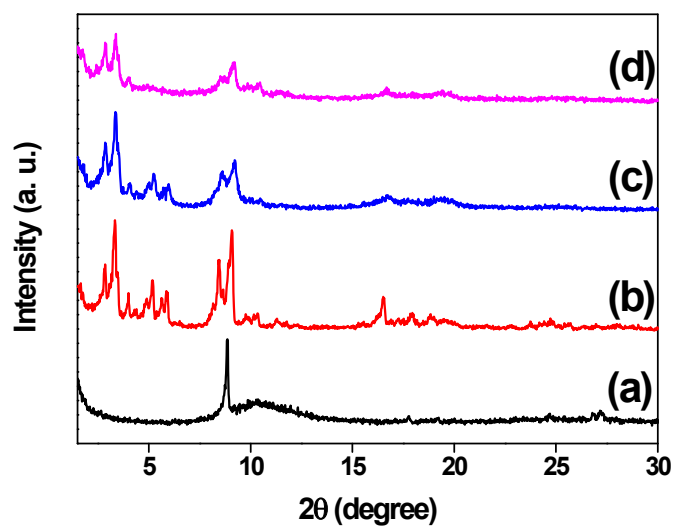


Figure S1. PXRD patterns of (a) Ru₃ cluster, (b) MIL-101(Cr), (c) BD-MIL-101(Cr) and (d) Ru₃ cluster@BD-MIL-101(Cr).

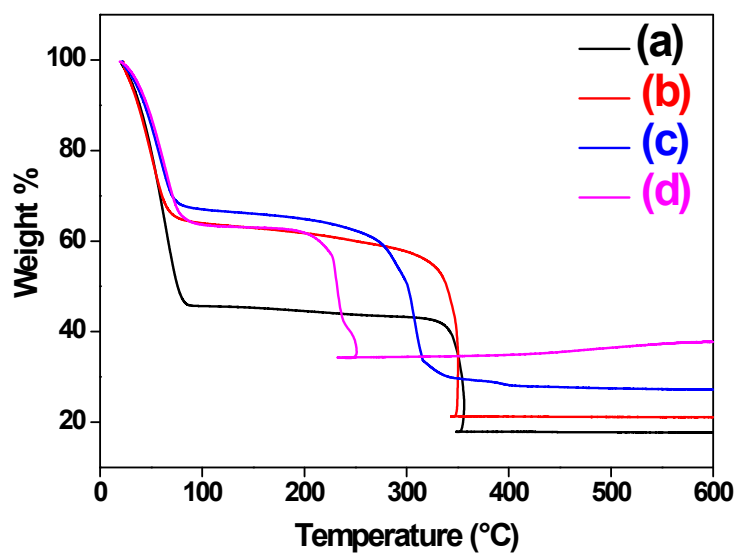


Figure S2. TGA patterns of (a) MIL-101(Cr), (b) BD-MIL-101(Cr), (c) Ru₃ cluster@BD-MIL-101(Cr), and (d) Ru₃ cluster.

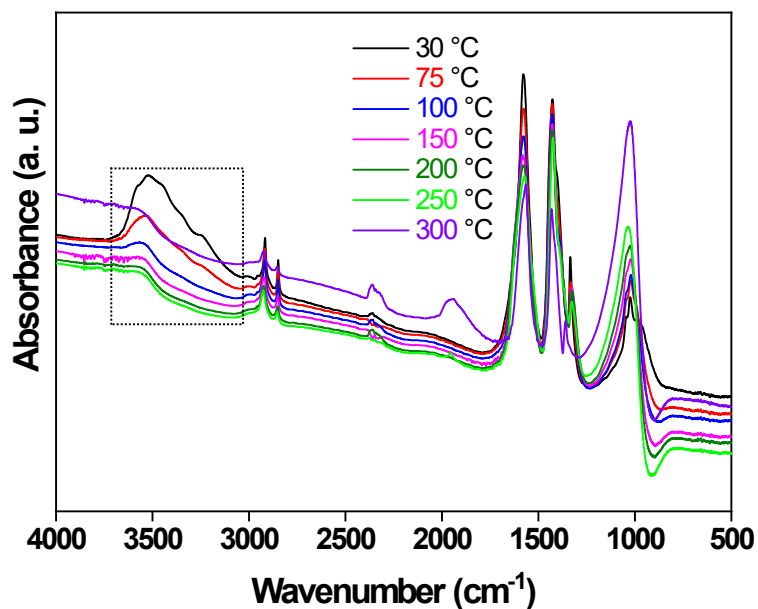


Figure S3. Temperature dependent FTIR spectra of Ru₃ cluster.

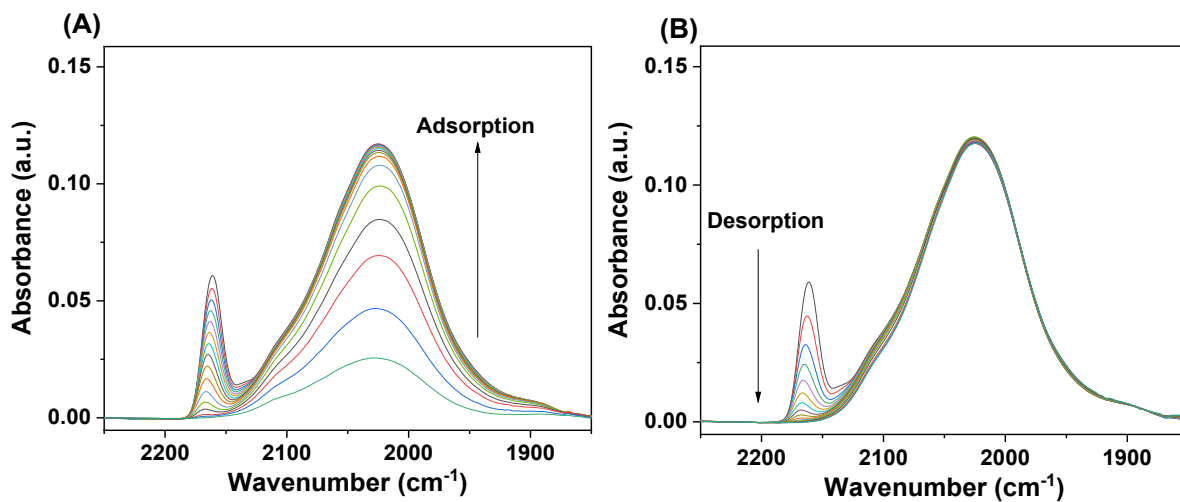


Figure S4. FTIR spectra of Ru₃ cluster/SiO₂ recorded at -173 °C during CO adsorption (A) and desorption (B) under vacuum.

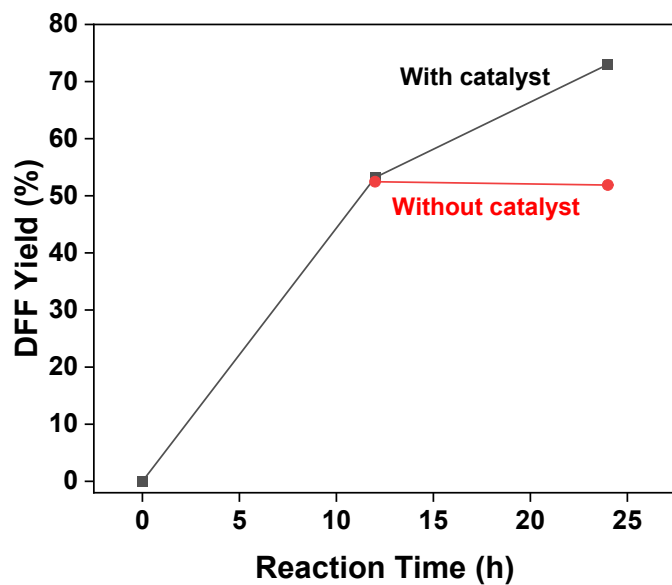


Figure S5: Hot filtration experiment.

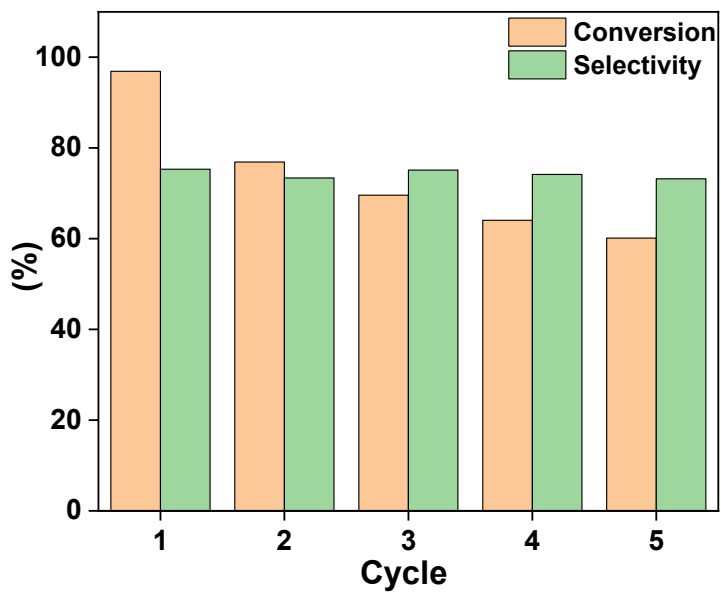


Figure S6. Catalyst recyclability test (HMF to DFF oxidation). Reaction condition: 130 °C, 24 h, 20 bar O₂, Solvent- Toluene anhydrous (22 g), HMF (0.15 g), Catalyst (0.1 g), Internal standard- Decane (0.1 g).

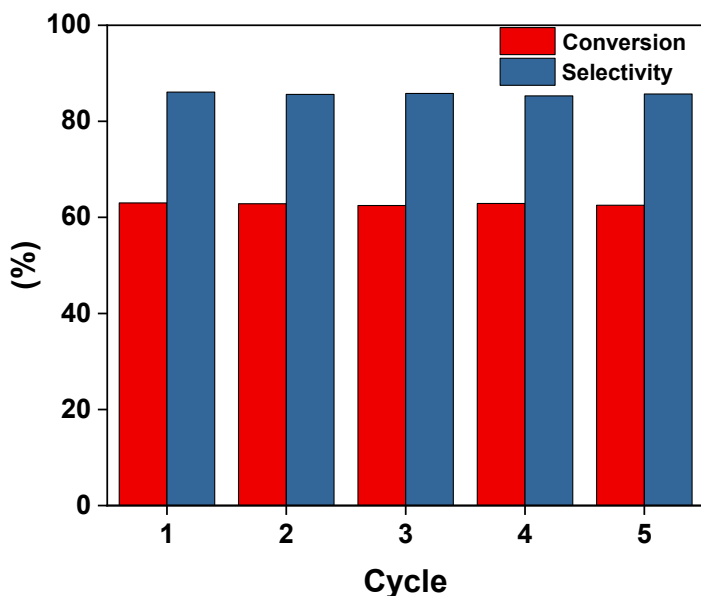


Figure S7. Catalyst recyclability test (Benzyl alcohol to Benzaldehyde oxidation). Reaction condition: 80 °C, 16 h, 20 bar O₂, Solvent- Toluene anhydrous (25 g), Benzyl alcohol (0.130 g), Catalyst (0.1 g), Internal standard- Decane (0.12 g).

To prove the robustness of the newly developed Ru₃ cluster@BD-MIL-101(Cr) catalyst in this study by avoiding the catalyst deactivation due to the deposition of humins observed when HMF was used as the reactant, we opted to perform the benzyl alcohol oxidation. The results of the recycling experiments of benzyl alcohol oxidation to benzaldehyde are depicted in Figure S7. As can be seen from the Figure, no significant decrease in the benzyl alcohol conversion and

benzaldehyde selectivity was observed up to the five cycles in the catalyst recyclability tests. These results clearly indicate the robustness of the Ru₃ cluster@BD-MIL-101(Cr) catalyst.

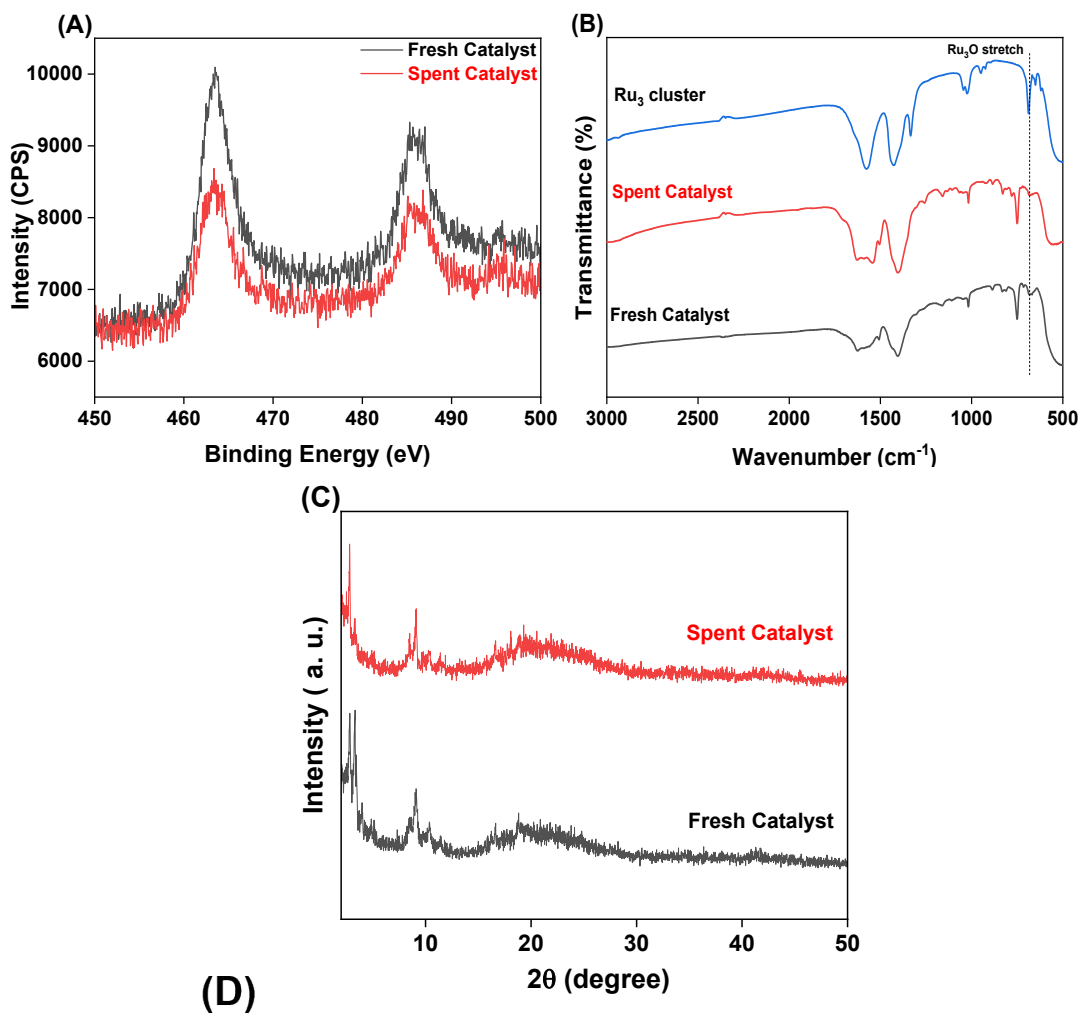
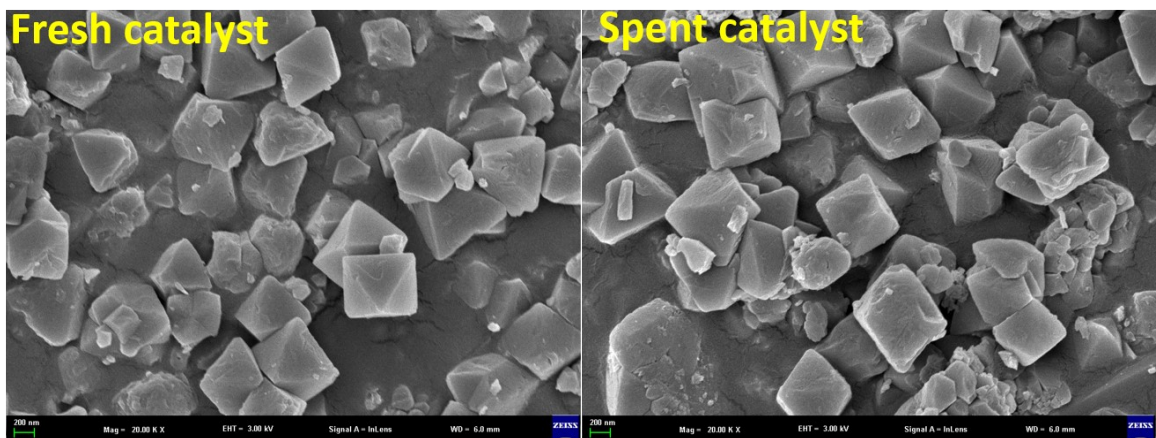


Figure S8:
Comparison
of (A) XPS
(Ru 3p)



region), (B) FT-IR, (C) PXRD, and (D) SEM of the fresh and spent catalyst after the 5th cycle of the HMF oxidation recycle test.

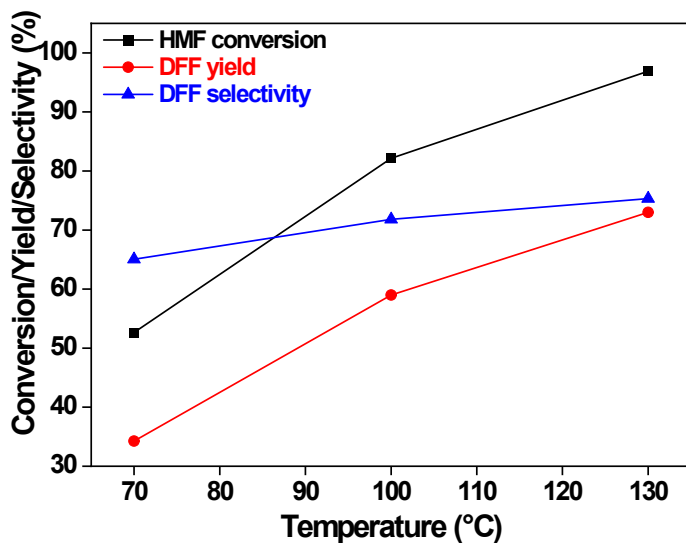


Figure S9. Effect of temperature on the catalytic activity of Ru₃ cluster@BD-MIL-101(Cr) catalyst.

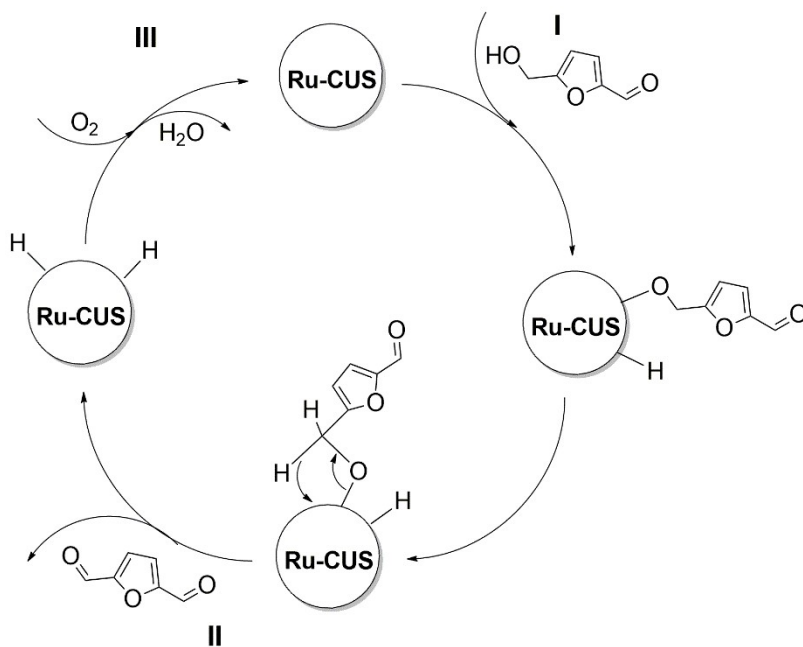


Figure S10. Proposed reaction mechanism for HMF to DFF oxidation over Ru₃ cluster@BD-MIL-101(Cr) catalyst (For better clarity, only the Ru-CUS in the Ru₃ cluster@BD-MIL-101(Cr) catalyst are represented in the figure).

Reference

1. J. C. Goeltz, S. D. Golver, J. Hauk and C. P. Kubiak, *Inorganic Syntheses*, edited by Thomas. B. Rauchfuss, 2010, **35**, 156.