Supplementary Information for

Efficient amine-assisted hydrogenation of CO_2 into methanol collectively catalysed by ruthenium single sites and ensembles in a unified catalyst

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Section 1. Chemicals and characterization

All chemicals were obtained from commercial suppliers at analytical grade and used as received without further purification. Acetone, tert-butanol (t-BuOH), and Ethanol were purchased form Sinopharm Chemical Reagent Co., LTD. Cyclohexylmethanol was purchased from ShangHai Macklin Biochemical Co., LTD. Morpholine, α-Al_2O_3 (0.2 μm), 1,4-dioxane, N-formylmorpholine (NFM), Cesium carbonate, cyclohexylaldehyde and cyclohexanecarboxylic acid were obtained from Shanghai Aladdin Bio-Chem Technology Co., LTD. Ru-Macho (R) was obtained from Sigma-Aldrich Co., LTD. Cyclohexylamide was obtained from Alfa Aesar. Deuterium gas (8 MPa, 100L) was purchased from specialty gases suppliers.

De-ionized water was obtained by reversed osmosis (the specific resistance of 18.25 MΩ·cm) followed by ion-exchange and filtration. Powder X-ray diffractions (PXRD) patterns of the samples were collected on a D8-Advance Bruker AXS diffractometer with Cu kα (λ = 1.5418 Å) radiation at room temperature. Inductively coupled plasma Optical Emission Spectrometer (ICP-OES) measurements were carried on SPECTRO ARCOS II. Transmission electron microscopy (TEM) images were recorded on Talos F200x microscope. The aberration-corrected HAADF-STEM measurements were taken on a Spectra 300 instrument at 300 keV. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a thermo ESCALAB 250 high-performance electron spectrometer using monochromatized Al Ka (hν = 1486.6 eV) as the excitation source. Ru K-edge X-ray absorption spectroscopy (XAS) was performed at the beamline BL14W1 station of the Shanghai

Synchrotron Radiation Facility (SSRF). The CO pulse titration used to determine the metal dispersion of Ru/Al_2O_3 catalysts was performed on a Micromeritics AutoChem II 2920 apparatus equipped with a thermal conductivity detector (TCD). CO probe diffuse reflection infrared fourier transform spectroscopy (CO probe DRIFTS) was conducted on NICOLET 6700 equipped with a liquid-nitrogen-cooled mercruy-cadmium-telluride infrared detector and an in situ Praying Mantis diffuse reflection reaction cell.

Section 2. Preparation of Al_2O_3-based Ru catalysts

Preparation of Ru-1: The synthesis method of the catalyst is a typical impregnation method. Firstly, 1 g of α-Al_2O_3 was dispersed in 20 mL of acetone with continuous stirring. Then, 60 mg of Ru-Macho(R) was weighed and dispersed in 20 mL of acetone by ultrasonic treatment for half an hour. After that, the latter was added into the acetone solution containing the α-Al_2O_3 support, and stirred at room temperature for 4 h. The mixture was then heated to 60 ℃ and stirred until the acetone was completely evaporated. The resulting light yellow solid was grounded and placed in a ceramic boat. The boat was placed in a tube furnace and gas replacement was carried out for 1 hour in a nitrogen atmosphere (80 mL/min) to remove air. The sample was then heated to 200 ℃ at a rate of 5 ℃/min and kept there for 2 h in a nitrogen atmosphere (80 mL/min), followed by natural cooling to room temperature to obtain the Ru-1 catalyst.

Preparation of Ru-2: The preparation method of the Ru-2 catalyst was similar to that of Ru-1, except that it is calcined in air using a muffle furnace. Typically, 1 g of α-Al_2O_3 was dispersed in 20 mL of acetone with continuous stirring. Then, 60 mg of Ru-Macho(R) was weighed and dispersed in 20 mL of acetone by ultrasonic treatment for half an hour. After that, the latter was added into the acetone solution containing the α-Al_2O_3 support, and stirred at room temperature for 4 h. The mixture was then heated to 60 ℃ and stirred until the acetone was completely evaporated. The resulting light yellow solid was grounded and placed in a ceramic boat. The boat was placed in a muffle furnace. The sample was then heated to 200 ℃ at a rate of 5 ℃/min and kept

there for 2 h, followed by natural cooling to room temperature to obtain the Ru-2 catalyst.

Preparation of Ru-3: Typically, 1 g of α-Al_2O_3 was dispersed in 20 mL of acetone with continuous stirring. Then, 60 mg of Ru-Macho(R) was weighed and dispersed in 20 mL of acetone by ultrasonic treatment for half an hour. After that, the latter was added into the acetone solution containing the support, and stirred at room temperature for 4 h. The mixture was then heated to 60 ℃ and stirred until the acetone was completely evaporated. The resulting light yellow solid was grounded and placed in a ceramic boat. The boat was placed in a tube furnace and gas replacement was carried out for 1 hour in a nitrogen atmosphere (80 mL/min) to remove air. The sample was then heated to 300 ℃ at a rate of 5 ℃/min and kept there for 2 h in a 10% H_2/Ar atmosphere (200 mL/min), followed by natural cooling to room temperature to obtain the Ru-3 catalyst.

Section 3. Catalyst evaluation.

Calculation of catalytic conversion, yield and selectivity: The typical sampling process was conducted by ^{1}H NMR test with t-BuOH as external standard. Generally, 200 uL reaction solution was transferred to 400 uL D_2O solution containing 0.04 mmol t-BuOH, then the mixture was further tested by ^{1}H NMR. The catalytic conversion, yield and selectivity was calculated based on ^{1}H NMR results.

Catalytic N-formylation of morpholine: Typically, in a batch reactor, 100 mg of catalyst and 0.5 mmol of cesium carbonate were added to the 50 mL reaction vessel lined with 15 mL of 1,4-dioxane as the solvent and 10 mmol of morpholine as the substrate. After the inert atmosphere of reaction vessel was purged several times with CO_2 and H_2, 2 MPa CO_2 and 2 MPa H_2 were added as the reaction atmosphere, and the reaction was carried out with continuous stirring at 120 ℃.

Catalytic selective hydrogenation of N-formylmorpholine: Typically, in a batch reactor, 100 mg of catalyst and 0.5 mmol of cesium carbonate were added to the 50 mL reaction vessel lined with 15 mL of 1,4-dioxane as the solvent and 10 mmol of N-formylmorpholine as the substrate. After the inert atmosphere of reaction vessel was purged several times with H_2, 4 MPa H_2 are added as the reaction atmosphere, and the reaction was carried out with continuous stirring at 120 ℃.

Catalytic recycling process of two-step reaction via Ru-2 catalyst: Typically, in a batch reactor, 100 mg of catalyst and 0.5 mmol of cesium carbonate were added to the 50 mL reaction vessel lined with 15 mL of 1,4-dioxane as the solvent and 10 mmol of morpholine as the substrate. After the inert atmosphere of reaction vessel was purged

several times with CO_2 and H_2, 2 MPa CO_2 and 2 MPa H_2 were added as the reaction atmosphere, and the reaction was carried out with continuous stirring at 120 ℃ for 36 h. After that, the catalyst was centrifuged and washed with acetone for several times. The solid was further heated at 200 ℃ for an hour and reloaded to reaction solution. Then, the reaction mixture went through hydrogenation process for 12 h under 4 MPa H_2 at 120 ℃. At the end of hydrogenation process, methanol was distilled and the left reaction mixture was submitted to another two reaction cycle.

Catalytic hydrogenation of Cyclohexylmethanol, cyclohexanecarboxylic acid and Cyclohexylamide: Typically, in a batch reactor, 100 mg of catalyst, 0.5 mmol of cesium carbonate and 10 mmol of substrates were added to the 50 mL reaction vessel lined with 15 mL of 1,4-dioxane as the solvent. After the inert atmosphere of reaction vessel was purged several times with H_2, 4 MPa H_2 are added as the reaction atmosphere, and the reaction was carried out with continuous stirring at 120 ℃.

Calculation of intrinsic TOF value: Firstly, the amount of intrinsic active sites was calculated via Ru loading and Ru dispersion. Then, the reaction time interval for N-formylation and amide hydrogenation was 2 h and 0.5 h respectively, where the substrate conversion was controlled under 20 %.

Section 4. Characterization details.

CO probe DRIFTS test: The catalysts was pretreated with 10 % H_2/Ar atomosphere at 200 ℃ for 1 h. Then the catalysts was transferred to Praying Mantis diffuse reflection reaction cell. The background was recorded under N_2 atomosphere. The gas inlet was switched to Carbon Monoxide and the spectrum was recorded after 24 min. Then, CO was totally purged with nitrogen after 30min, and the final adsorbed state was recorded. The Ru single site (Ru_1) percentage was calculated as follow:

$$isolated\ Ru\ （Ru_1）\% = \frac{S(Ru-(CO)_2)/2}{S(Ru-(CO)_2)/2 + S(Ru-(CO))}$$

where S(Ru-(CO)) represents the area of one linear adsorbed CO on metallic ruthenium in Fig. 1f, and S(Ru-$(CO)_2$) represents the area of two linear adsorbed CO on single Ru site.

Calculation method for Ru species dispersio: Typically, the metal dispersion (D) was determined by CO pulse titration with an extinction coefficient of 1, while this coefficient for Ru_1 site and Ru_e site was 2 and 1 respectively according to CO probe DRIFTS test, where each Ru_1 and Ru_e site absorbed two CO and one CO molecule respectively. Therefore, the dispersion should be calculated w.r.t the percentage metal species as follow:

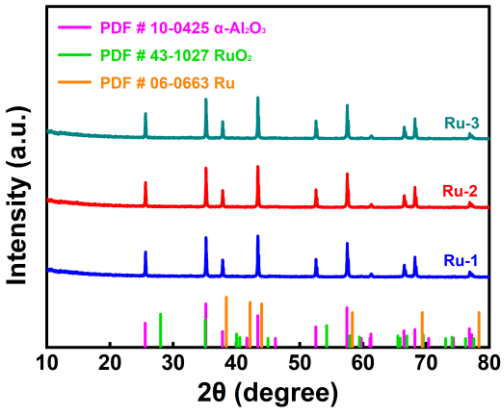
$$[D] = D * (Ru_1\% * 2 + (1 - Ru_1\%))$$

where [D] represents the Ru dispersion calculated with an extinction coefficient of 1 via CO pulse titration.

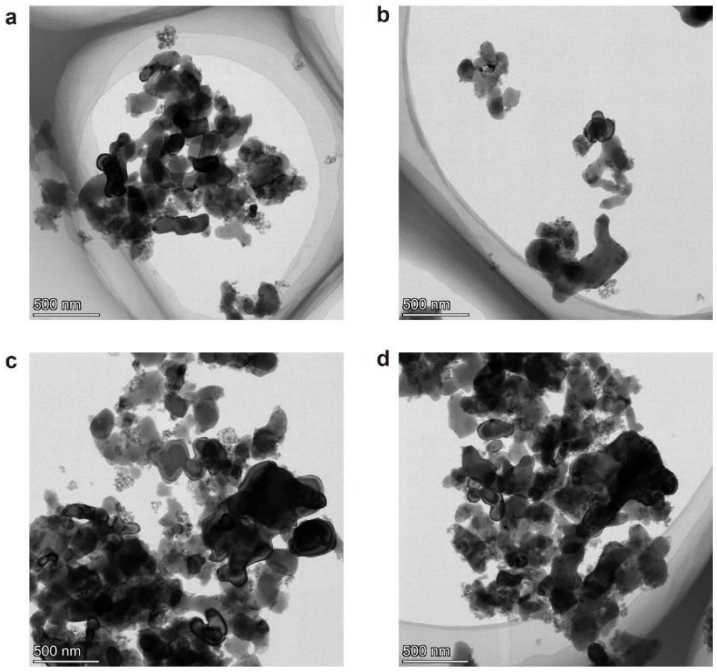
Section 5. Computational details

Density Functional Theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP). The calculations employed the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional to calculate the exchange and correlation energy. The projector augmented wave (PAW) method was employed to describe ion-electron interactions. A plane-wave cut-off energy of 450 eV was used. The DFT-D3 correction was included to account for van der Waals (vdW) interactions. Two models were constructed in this study, including Ru_8-cluster supported on $Al_2O_3(100)$ surface (marked as Ru-ensemble) and $(CH_3)_3P$-coordinated single Ru atom supported on $Al_2O_3(100)$ (marked as Ru-SAC). The $Al_2O_3(100)$ facet, cleaved from the α-Al_2O_3 bulk, was used as the substrate due to its low surface energy. The exposed Al sites in Al_2O_3 surface was covered with hydroxyl group to passivate the Al sites. A nearly spherical Ru_{10} cluster was cleaved from the metal Ru bulk, and 2 atoms were removed from the cluster to form a surface in contact with Al_2O_3. Then the Ru_8 cluster was placed on the passivated $Al_2O_3(100)$ facet to construct the Ru-cluster model. The Ru-SAC model was constructed by doping single atom Ru in the passivated $Al_2O_3(100)$ facet. A trimethylphosphine ($(CH_3)_3P$) ligand coordinated to Ru atom to simulate the coordination environment. A vacuum layer of 15 Å in the z direction was used to prevent interaction between periodic images. For structure relaxation, the convergence criteria for force and energy were set to 0.03 eV $Å^{-1}$ and 10^{-4} eV, respectively. The CI-NEB method was employed to locate the transition state and calculate the reaction barrier for the water

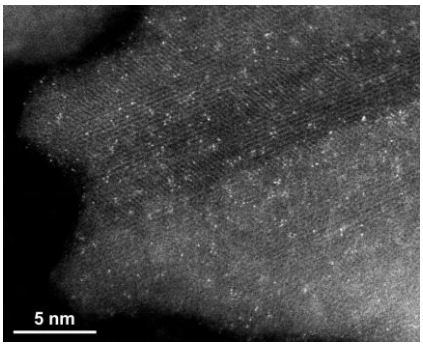
dissociation step.



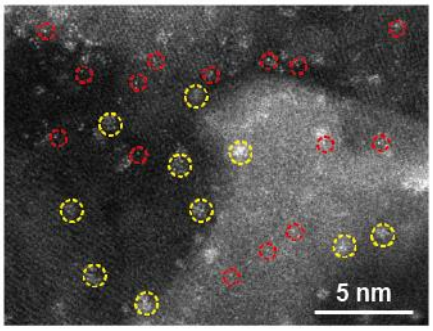
Supplementary Fig. 1. The Powder XRD patterns of as-synthesized three Ru catalysts.



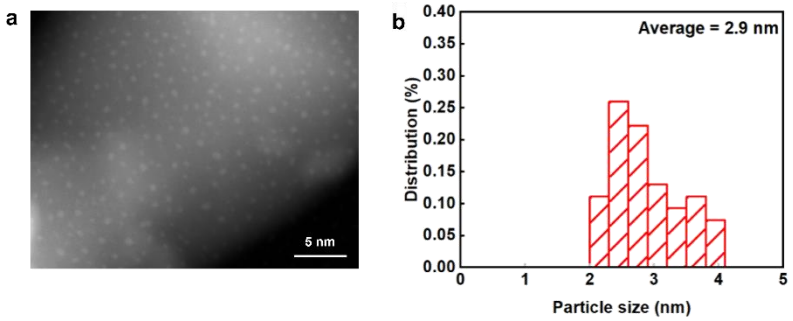
Supplementary Fig. 2. The TEM morphologies for (a) commercial α-Al_2O_3 support, (b) Ru-1, (c) Ru-2 and (d) Ru-3, demonstrating identical morphology.



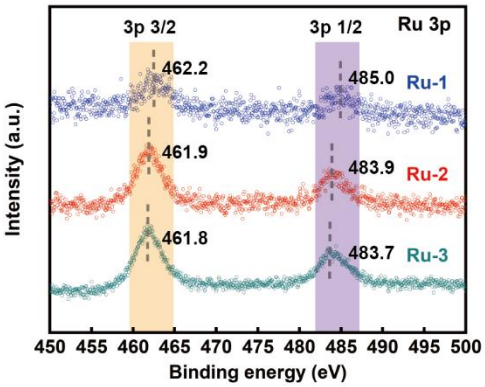
Supplementary Fig. 3. The aberration-corrected HAADF-STEM image of Ru-1.



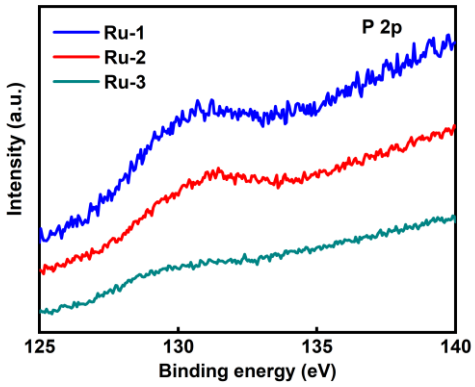
Supplementary Fig. 4. The aberration-corrected HAADF-STEM image of Ru-2.



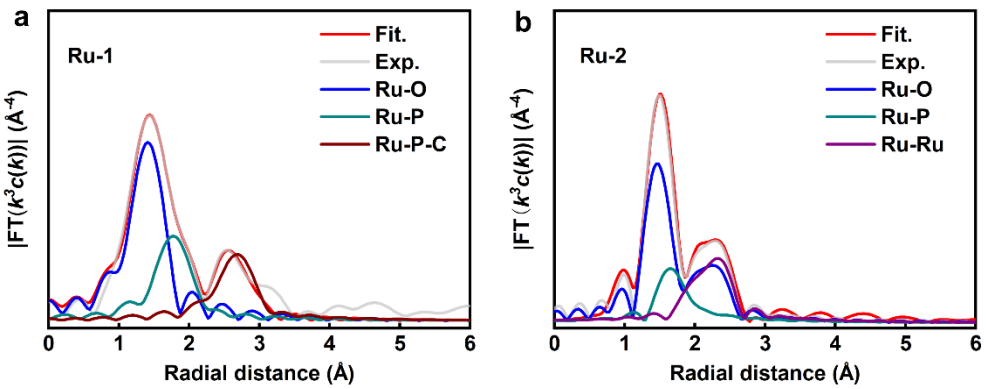
Supplementary Fig. 5. (a) The aberration-corrected HAADF-STEM image of Ru-3 and (b) corresponding particle size distribution of Ru nanoparticles in (a).



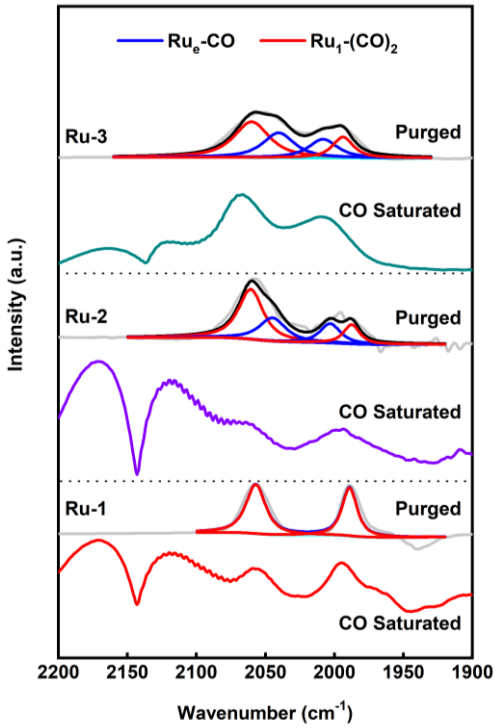
Supplementary Fig. 6. The high resolution Ru 3p XPS spectrum of the three Ru catalysts.



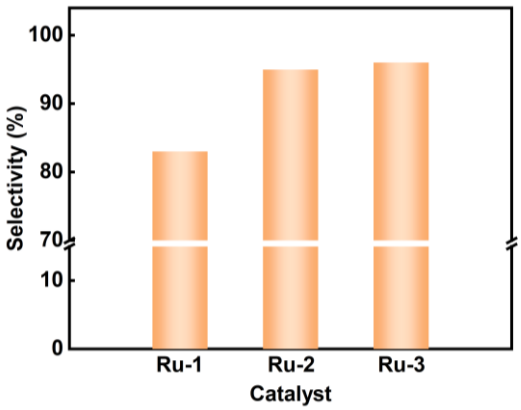
Supplementary Fig. 7. The high-resolution XPS spectra of P 2p in three Ru catalysts.



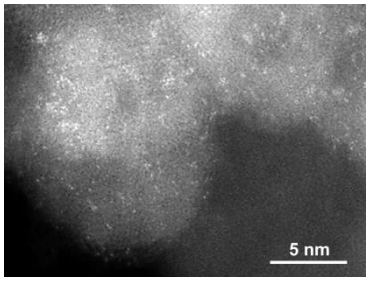
Supplementary Fig. 8. EXAFS fitting curves of Ru species for (a) Ru-1 and (b) Ru-2.



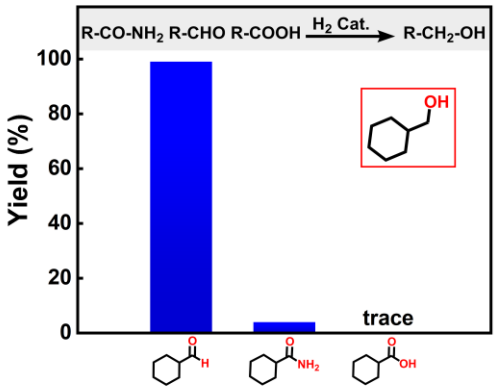
Supplementary Fig. 9. The CO-probe DRIFTS results of three Ru catalysts after CO saturation and purge with Argon.



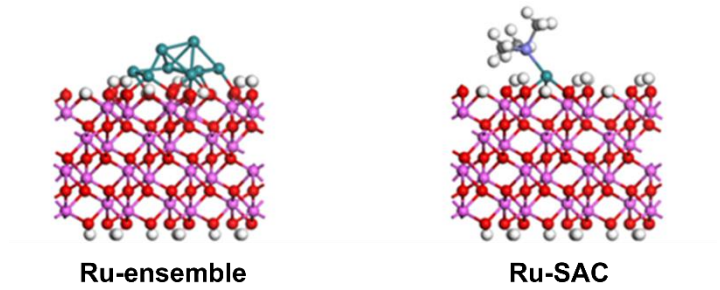
Supplementary Fig. 10. The selectivity of N-formylmorpholine in N-formylation reaction catalyzed by different catalysts in Fig. 2b. The only by-product is formic acid.



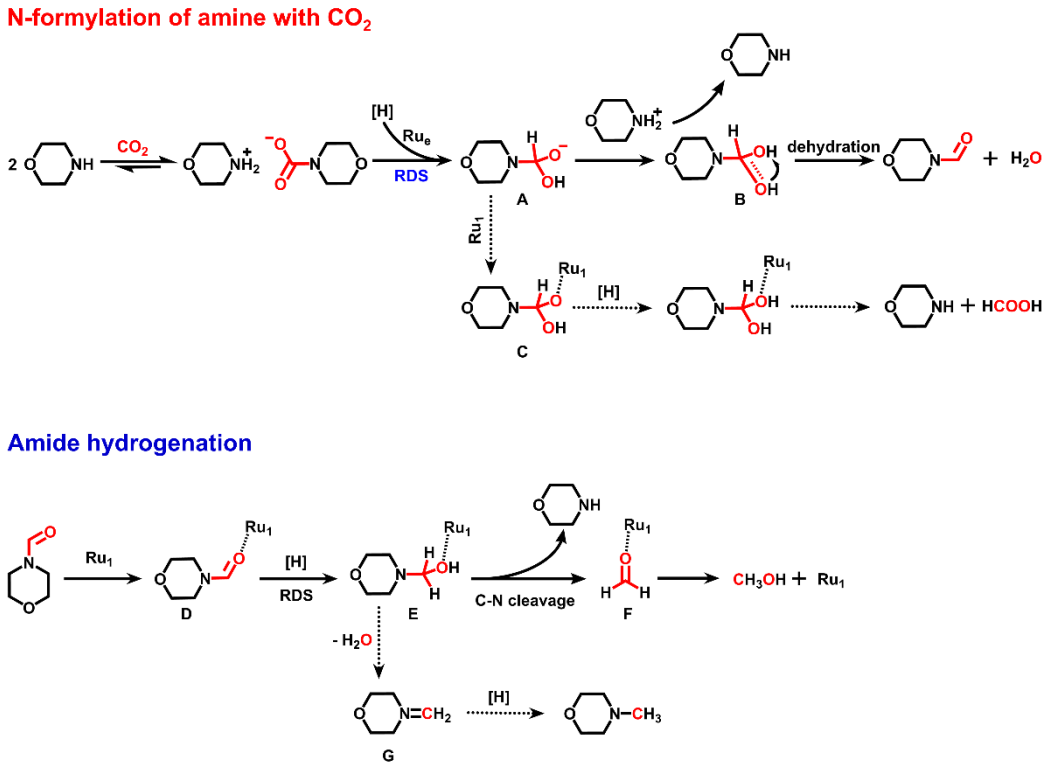
Supplementary Fig. 11. The aberration-corrected HAADF-STEM image of Ru-2 after consecutive N-formylation and hydrogenation reactions for 144 h.



Supplementary Fig. 12. The catalytic yield of different carbonyl analogs with Ru-2 catalyst after 12h. The selectivity was calculated based on the amount of cyclohexyl methanol over all products.



Supplementary Fig. 13 Side view of the models for the Ru cluster and single atom supported by Al_2O_3 layers, corresponding to Ru_e and Ru_1, respectively. Colour code: Ru: green; P: purple; Al: pink; N: blue; C: grey; O: red; H: white.



Supplementary Fig. 14. The proposed reaction mechanism of Ru-2 catalyzed N-formylation and amide hydrogenation reaction.

Supplementary Table 1. The ICP-OES results of Ru loading in corresponding samples.

Sample	Ru loading (wt%)
Ru-1	0.67%
Ru-2	0.74%
Ru-3	1.04%

Supplementary Table 2. EXAFS fitting parameters at the Ru K-edge for various samples. (S_0^2=0.86)

Sample	Path	C.N.	R (Å)	$\sigma^2 \times 10^{-3}$ (Å^2)	ΔE (eV)	R factor
Ru foil	Ru-Ru	12*	2.67±0.01	4.1±0.3	-5.1±1.0	0.0057
RuO_2	Ru-O	6.1±0.7	1.97±0.01	3.5±0.7	-5.2±1.6	0.012
	Ru-Ru	2.6±0.6	3.11±0.01	4.5±0.9		
	Ru-Ru	10.8±1.7	3.55±0.01			
Ru-2	Ru-O	3.6±0.8	2.14±0.01	3.2±1.1	11.1±1.7	0.010
	Ru-P	1.2±0.8	2.48±0.02	1.9±4.4		
	Ru-Ru	3.0±1.0	2.69±0.01	4.2±2.4		
Ru-1	Ru-O	3.2±0.7	1.941±0.022	5.5±2.2	-3.1±2.9	0.009
	Ru-P	1.1±0.3	2.304±0.028			

Data reduction, data analysis, and EXAFS fitting were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages[1] that utilizes the FEFF6 program[2] to fit the EXAFS data. The energy calibration of the sample was conducted through a standard Ru foil, which as a reference was simultaneously measured. A linear function was subtracted from the pre-edge region, then the edge jump was normalized using Athena software. The χ(k) data were isolated by subtracting a smooth, third-order polynomial approximating the absorption background of an isolated atom. The *k3*-weighted *χ(k)* data were Fourier transformed after applying a. Hanning window function (Δk = 1.0). For EXAFS modeling, The global amplitude EXAFS (*CN*, *R*, σ^2 and ΔE_0) were obtained by nonlinear fitting, with least-squares refinement, of the EXAFS equation to the Fourier-transformed data in *R*-space, using Artemis software, EXAFS of the Ru foil is fitted and the obtained

amplitude reduction factor S_0^2 value (0.86) was set in the EXAFS analysis to determine the coordination numbers (*CNs*) in the Ru-C/O/P scattering path in sample.

Supplementary Table 3. The statistical percentage of Ru_1 and Ru_e in Ru-1, Ru-2 and Ru-3 catalysts.

Sample	**Ru content (wt%)**	**Ru_1 dispersion based on CO-drifts (%)**	**Ru dispersion (%)**
Ru-1	0.67	100.0	99.5
Ru-2	0.74	44.8	69.5
Ru-3	1.14	37.8	59.4

Supplementary Table 4. The tested metal dispersion (*D*) from CO-pulse titrition with extinct coefficient of 1 and calculated metal dispersion [*D*] w.r.t CO-DRIFTS determined extinct coefficient, where the revised extinct coefficient for Ru_1 site and Ru_e site was 2 and 1 respectively.

Sample	**D (%)**	**[D] (%)**
Ru-1	49.7	99.5
Ru-2	47.9	69.5
Ru-3	42.8	59.4

$$[D] = D * (Ru_1\% * 2 + (1 - Ru_1\%))$$

The [D] represented the calculated actual distribution of suface active species with revised extinct coefficient.

References

1. Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchrotron Radiat.***12**, 537-541 (2005).
2. Zabinsky, S. I., Rehr, J. J., Ankudinov, A., Albers, R. C. & Eller, M. J. Multiple-scattering calculations of X-ray-absorption spectra. *Phys. Rev. B* **52**, 2995-3009 (1995).