Electronic Supplementary Material (ESI) for RSC Advances.

Ru coordinated with BINAP in knitting aryl network polymers for heterogeneous asymmetric hydrogenation of methyl acetoacetate

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Catalysts Preparation

Benzene, biphenyl, methanol and dichloromethane (DCM) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. $FeCl_3$ (anhydrous) were obtained from National Medicines Co., Ltd. 1,3,5-triphenylbenzene and formaldehyde dimethyl acetal (FDA) were purchased from Aladdin Company. All solvents were analytical grade and were purified by distillation under Ar_2 atmosphere before use. Unless otherwise noted, all manipulations were carried out under Ar_2 atmosphere either in a glove-box or using standard Schlenk techniques.

Synthesis of KAP-1

In a glove box, $FeCl_3$ (anhydrous 4.866g, 30mmol) was added to a solution of BINAP (0.249 g, 0.4 mmol), benzene (0.781 g, 10 mmol) and FDA (2.283 g, 30 mmol) in 20ml DCM. The mixture was firstly stirred at 35 ℃ for 4 h to form original network, and then heated at 80 ℃ for 68 h. The precipitate was filtered under inert atmosphere with methanol (1500 mL) and DCM (500 mL), then washed with methanol and DCM in a

Soxhlet for each 12 h under inert atmosphere. KAP-1 was finally dried under reduced pressure at 60 ℃ for 24 h.

Synthesis of KAP-2

In a glove box, $FeCl_3$ (anhydrous 3.244 g, 20 mmol) was added to a solution of BINAP (0.249 g，0 .4 mmol), biphenyl (0.771 g, 5 mmol) and FDA (1.522 g, 20 mmol) in 14mL DCM. The mixture was firstly stirred at 35 ℃ for 4 h to form original network, and then heated at 80 ℃ for 68 h. The precipitate was filtered under inert atmosphere with methanol (1500 mL) and DCM (500 mL), then washed with methanol and DCM in a Soxhlet for each 12 h under inert atmosphere. KAP-2 was finally dried under reduced pressure at 60 ℃ for 24 h.

Synthesis of KAP-3

In a glove box, $FeCl_3$ (anhydrous 2.433 g, 15 mmol) was added to a solution of BINAP (0.249 g, 0.4 mmol), 1,3,5-triphenylbenzene (0.766 g, 2.5 mmol) and FDA (1.141 g, 15 mmol) in 10 mL DCM. The mixture was firstly stirred at 35 ℃ for 4 h to form original network, and then heated at 80 ℃ for 68 h. The precipitate was filtered under inert atmosphere with methanol (1500 mL) and DCM (500 mL), then washed with methanol and DCM in a Soxhlet for each 12 h under inert atmosphere. KAP-3 was finally dried under reduced pressure at 60 ℃ for 24 h.

Characterization

Nitrogen isotherms at 77.3 K were measured using micromeritics ASAP 2420. The samples were outgassed at 120 ℃ for 10 h. The pore size distributions were calculated using density functional method (DFT). Thermogravimetric analysis (TGA) was measured using NETZSCH STA 449F3, and the samples were heated from 40 ℃ to 1000 ℃ at the rate of 10 ℃/min under air. Transmission electron microscope (TEM) images were taken on a JEM-2100 with an accelerating voltage of 200 kV. Polymer morphologies were investigated on a JSM-7800F scanning electron microscope (SEM). Solid-state NMR spectra were obtained on a VARIAN infinity plus spectrometer. The ^{31}P MAS NMR spectra were recorded with a 2.5 mm probe at a frequency of 161.8 MHz under a magic angle spinning rate of 10 kHz and a delay of 3 s. The chemical shifts were referenced to 85% H_3PO_4. ^{13}C MAS NMR spectra were recorded under a magic angle spinning rate of 6 kHz.

Catalytic process

Dichloro(η^6-benzene)ruthenium(Ⅱ) dimer, ($[RuCl_2(benene)]_2$): This ruthenium (Ⅱ) complex was synthesized according the previous published procedure.[1] Hydrated ruthenium(Ⅲ)chloride (1.065 g, 4.07 mmol) was dissolved in 50mL of 90% (V/V) ethanol. After dropwise addition of excess 1,3-cyclohexadiene (5.0 mL), the mixture was heated at 85 ℃ for 4 h under ambient conditions. The red production was

collected by filtration, washed with amount of ethanol, and dried under vacuum.

In a glove box, 3.60 mg $[RuCl_2(benzene)]_2$ was dissolved in 6 mL DMF, followed by the addition of 0.50 g KAP-1 in 12 mL DCM. After stirring at room temperature for 24 h, Ru/KAP-1 catalyst was obtained under reduced pressure at 85 ℃ for 6 h. Other catalysts Ru/KAP-2, Ru/KAP-3, and Ru/KAP-4 were prepared in the same way. Notably, the theoretical BINAP/Ru (molar ratios) of all the catalysts was 10.

As a typical run for asymmetric hydrogenation of β-keto esters, Ru/KAP-1 catalyst (0.03 g, 0.00086 mmol), methyl acetoacetate (0.20 g, 1.72 mmol) and anhydrous methanol (2mL) were added into a 30 mL autoclave in a glove box. After the reactor was purged with H_2 for 4 times, its pressure of H_2 was finally adjusted to desired value and heated from room temperature to the reaction temperature of 80 ℃, stirred for 10 h. The catalyst was separated by centrifugation, and the product was analyzed by gas chromatography (Agilent 7890B gas chromatography equipped with a flame ionization detector and a Cyclosil-B capillary column).

For recycling the catalyst, the catalyst was separated by centrifugation (performed in a glove box), washed with methanol (3×2 mL), then the catalyst was used directly for the next catalytic reaction.

Table S1. Texture parameters for materials and their supported catalysts.

Figure S1. Pore size distribution of (a) KAP-1, (b) KAP-2, (c) KAP-3.

Figure S2. SEM image of (a) KAP-1, (b) KAP-2, (c) KAP-3.

Figure S3. TEM images and EDS on TEM of Ru/KAP-1.

Figure S4. TEM images and EDS on TEM of Ru/KAP-2.

Figure S5. TEM images and EDS on TEM of Ru/KAP-3.

Figure S6. The ^{31}P MAS NMR spectra of Ru/KAP-1. The ^{31}P MAS NMR spectra was recorded with a 2.5 mm probe at a frequency of 161.8 MHz under a magic angle spinning rate of 7 kHz and a delay of 3 s.

Figure S7. The effect of H_2 pressure on the yield and ee values in hydrogenation of methyl acetoacetate catalyzed by Ru/KAP-1. All the reactions were carried out with S/C=2000 (0.00086 mmol of Ru was used) and 2 mL methanol as solvent at 80 °C for 10 h under various H_2 pressure.

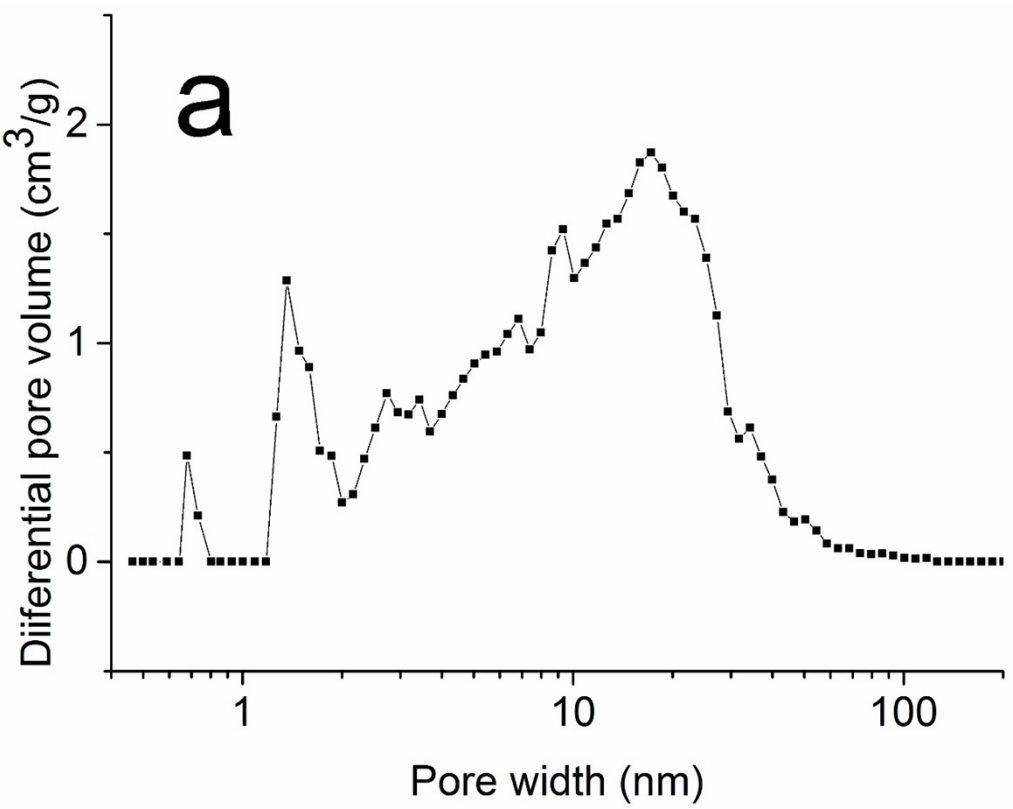
Figure S8. The effect of temperature on the yield and ee values in hydrogenation of methyl acetoacetate catalyzed by Ru/KAP-1. All the reactions were carried out with S/C=2000 (0.00086 mmol of Ru was used) and 2 mL methanol as solvent at 2 MPa for 10 h under various reaction temperature.

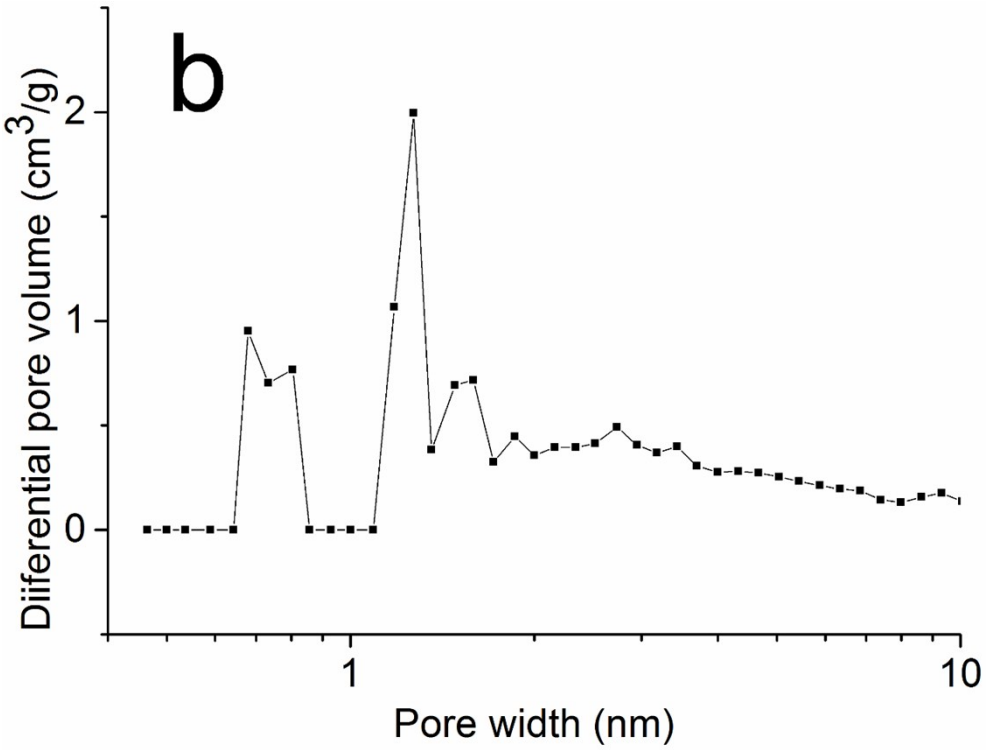
Figure S9. The effect of S/C molar ratios on the yield and ee values in hydrogenation of methyl acetoacetate catalyzed by Ru/KAP-1. All the reactions were carried out under a H_2 pressure of 2 MPa and 0.00086 mmol of Ru at 80 °C for 10 h with various methyl acetoacetate amounts (0.86-5.16 mmol).

Table S1. Texture parameters for materials and their supported catalysts.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)
KAP-1	1280	1.94

KAP-2	1125	0.78
KAP-3	1282	0.92
Ru/KAP-1	1268	1.74
Ru/KAP-2	1110	0.81
Ru/KAP-3	1210	0.92





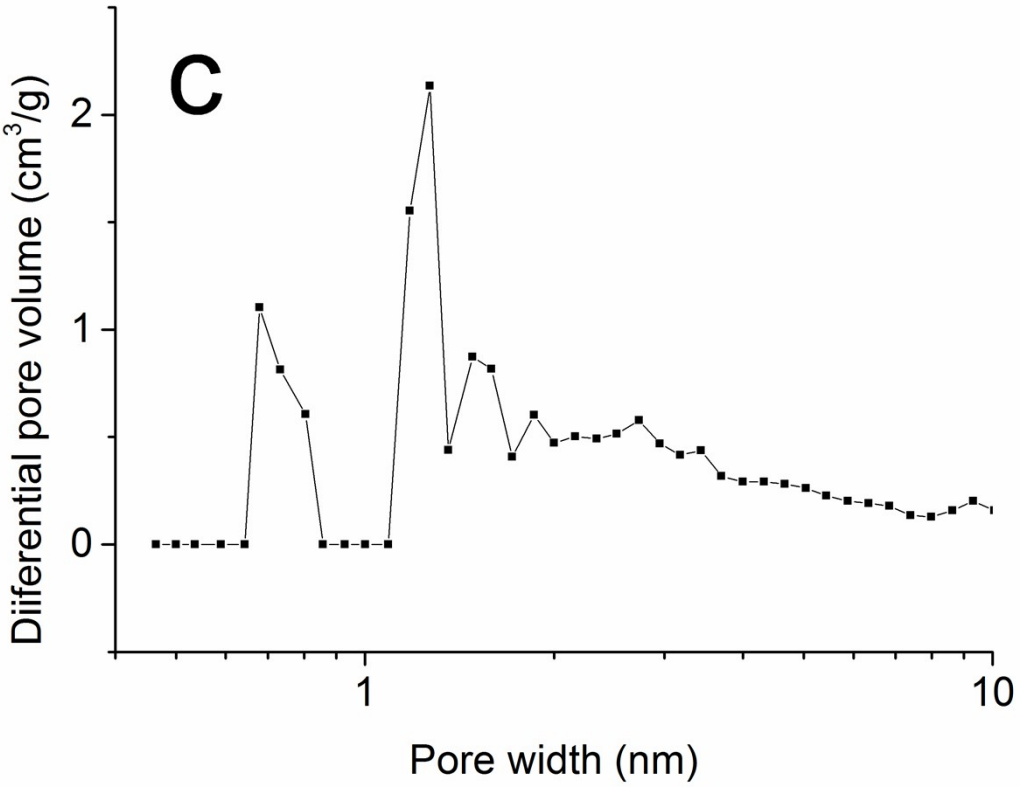
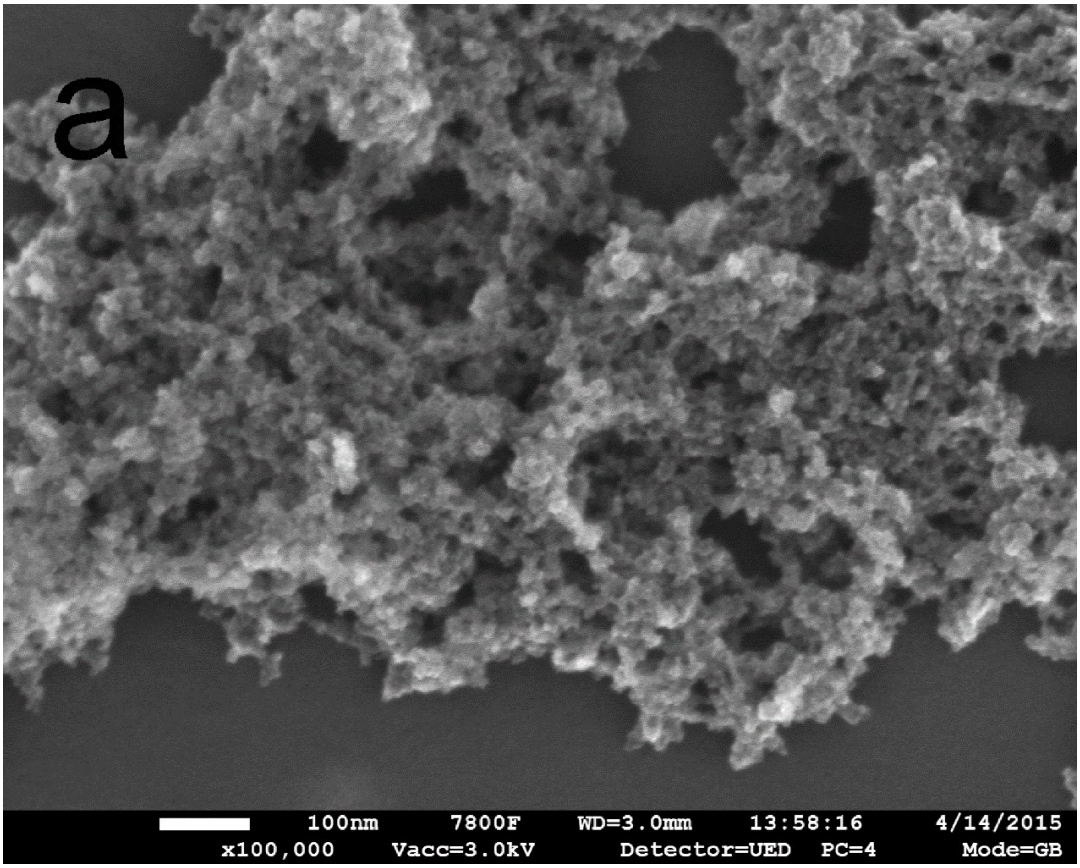


Figure S1 Pore size distribution of (a) KAP-1, (b) KAP-2, (c) KAP-3.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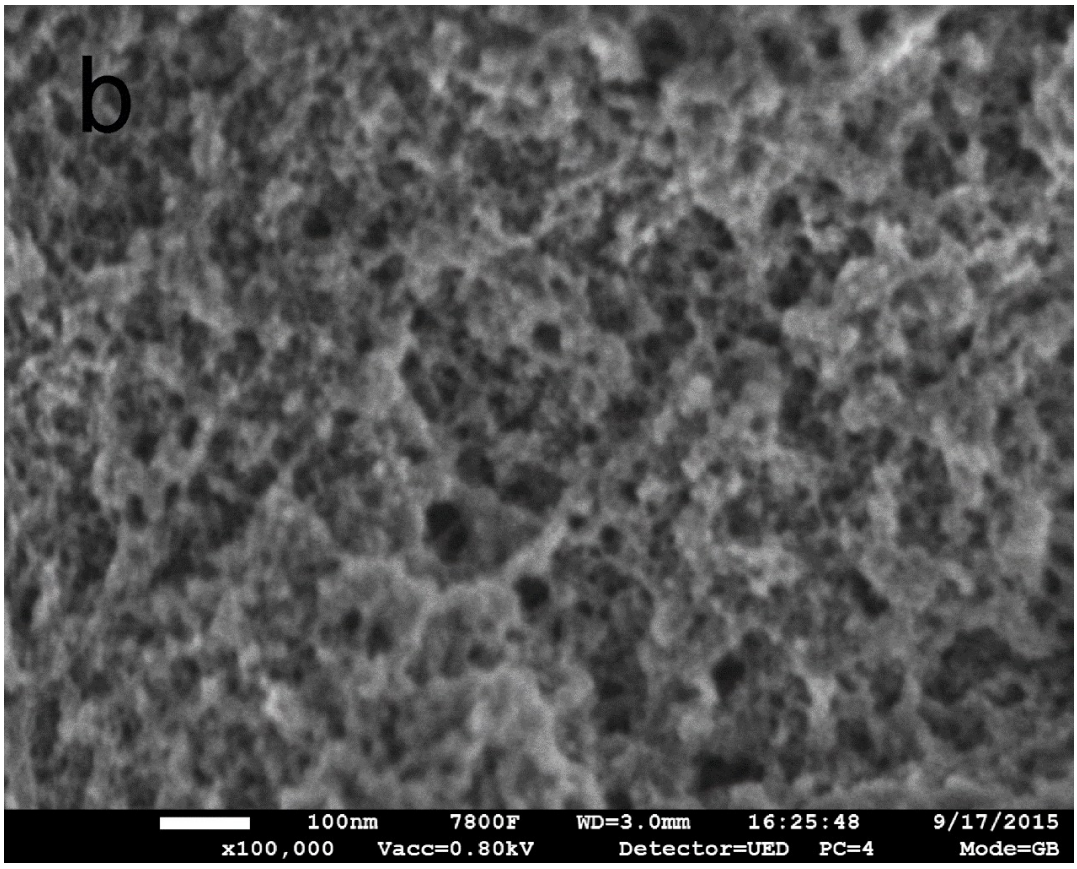
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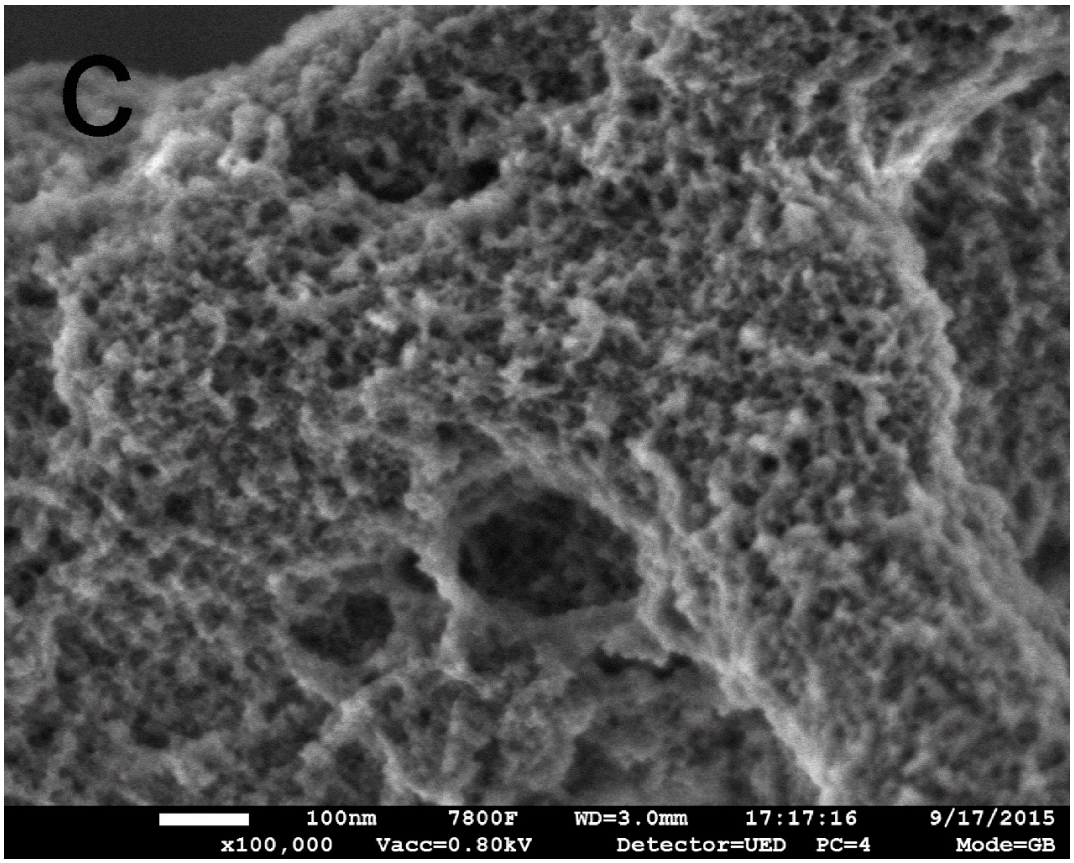
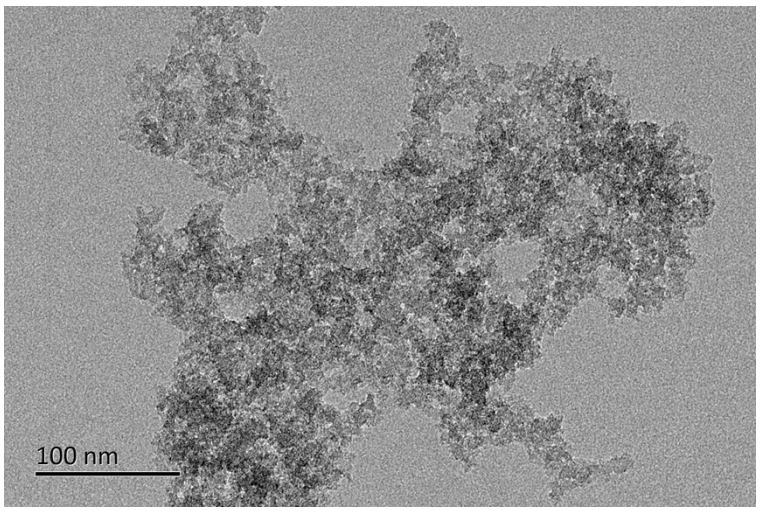
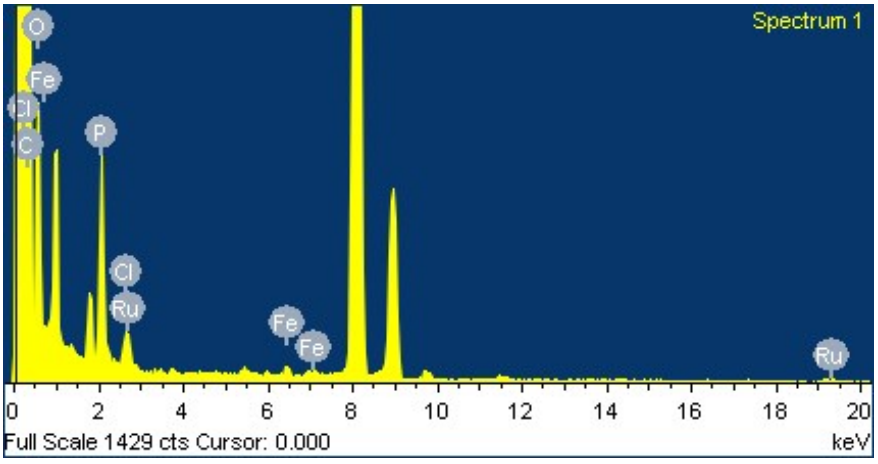


Fig. S2 SEM image of (a) KAP-1, (b) KAP-2, (c) KAP-3.





Spectrum processing:

Peaks possibly omitted: 8.043, 8.903, 9.706 keV

Quantitation method: Cliff Lorimer thin ratio section.

Processing option: All elements analyzed (Normalised)

Number of iterations = 2

Standardless

Element	Weight%	Atomic%
C K	97.44	98.68
O K	1.12	0.85
P K	0.97	0.38
Cl K	0.13	0.05
Fe K	0.08	0.02
Ru K	0.26	0.03
Totals	100.00	

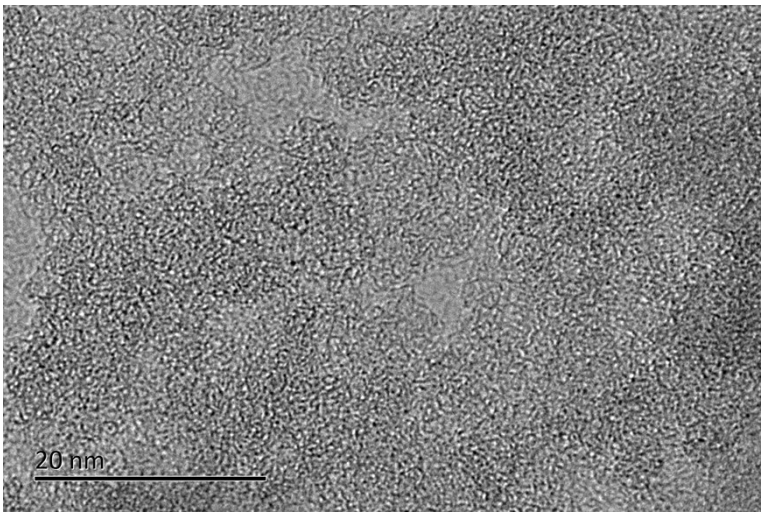
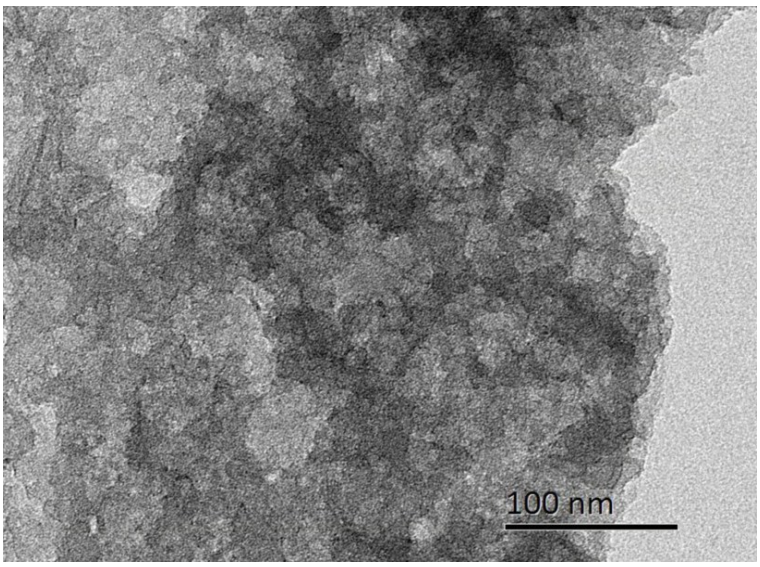
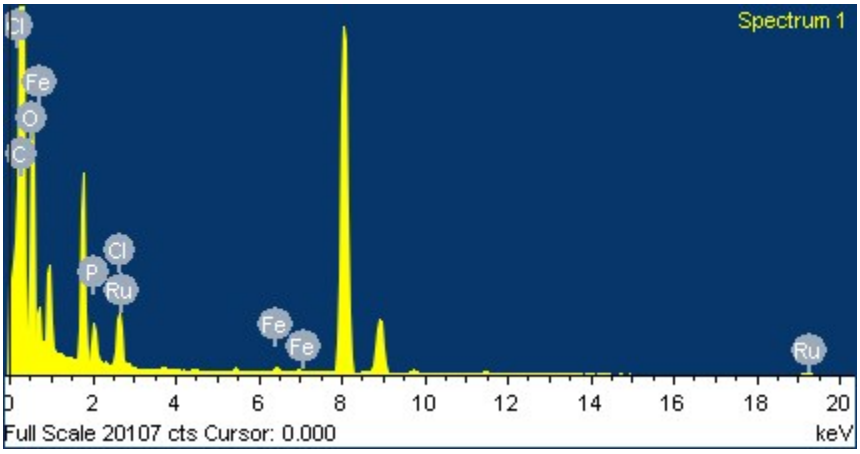


Figure S3. TEM images and EDS on TEM of Ru/KAP-1.





Spectrum processing:

Peaks possibly omitted: 3.699, 5.415, 8.043, 8.430, 8.903, 9.710, 11.419 keV

Quantitation method: Cliff Lorimer thin ratio section.

Processing option: All elements analyzed (Normalised)

Number of iterations = 3

Standardless

Element	Weight%	Atomic%
C K	96.30	97.73
O K	2.53	1.93
P K	0.38	0.15
Cl K	0.43	0.15
Fe K	0.06	0.01
Ru K	0.30	0.04
Totals	100.00	

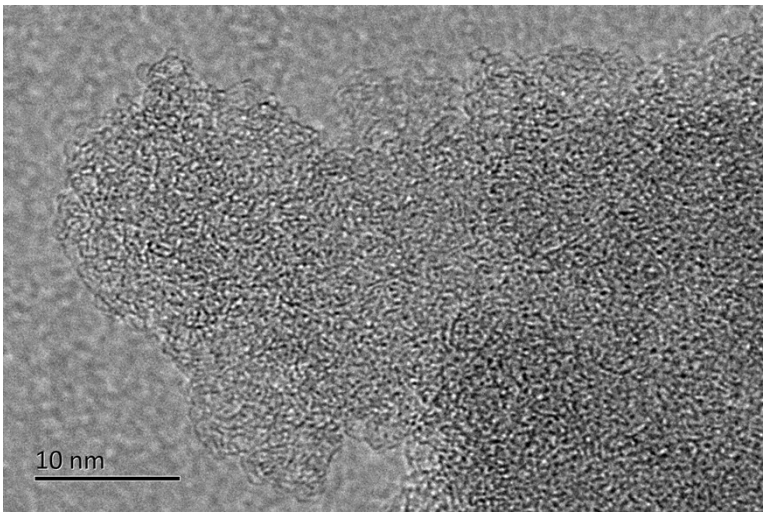
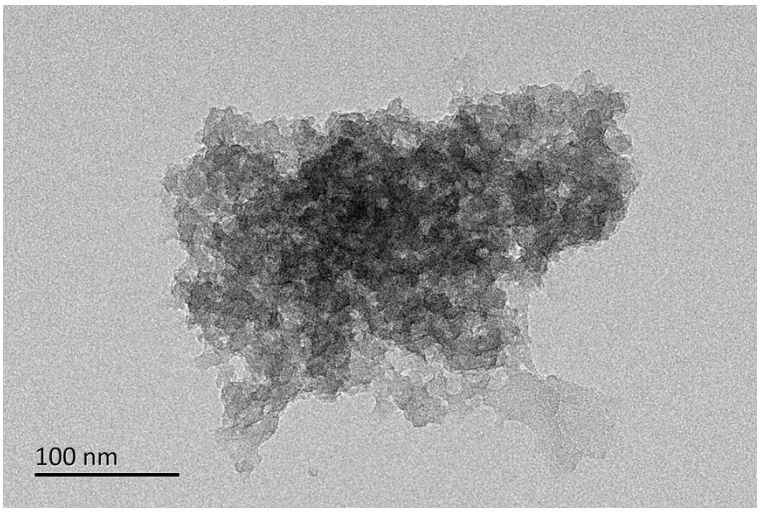


Figure S4. TEM images and EDS on TEM of Ru/KAP-2.



Spectrum processing:

Peaks possibly omitted: 8.043, 8.900, 9.726, 11.470 keV

Quantitation method: Cliff Lorimer thin ratio section.

Processing option: All elements analyzed (Normalised)

Number of iterations = 3

Standardless

Element	Weight%	Atomic%
C K	95.46	97.12
O K	3.26	2.49
P K	0.54	0.21
Cl K	0.33	0.11
Fe K	0.07	0.02
Ru K	0.33	0.04
Totals	100.00	

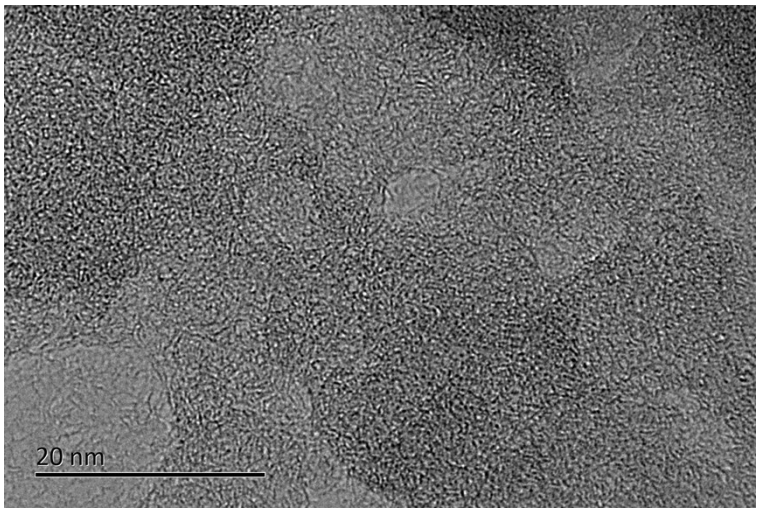


Figure S5. TEM images and EDS on TEM of Ru/KAP-3.

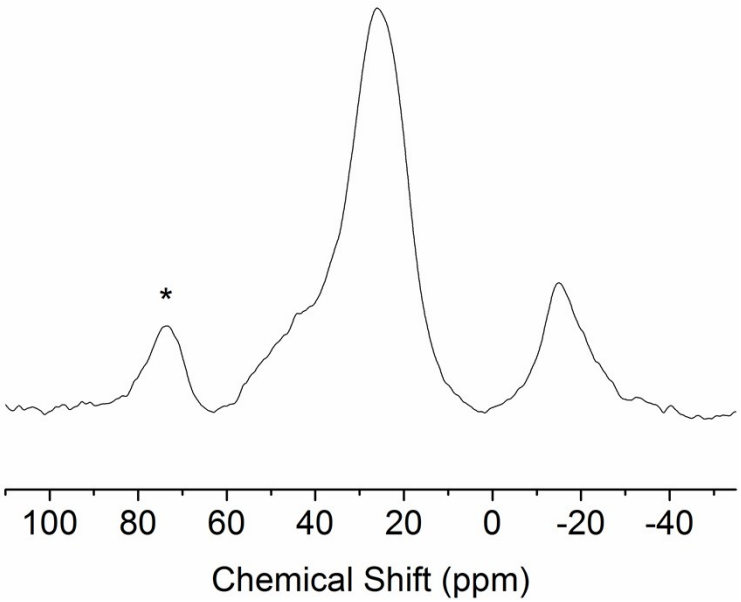


Figure S6.

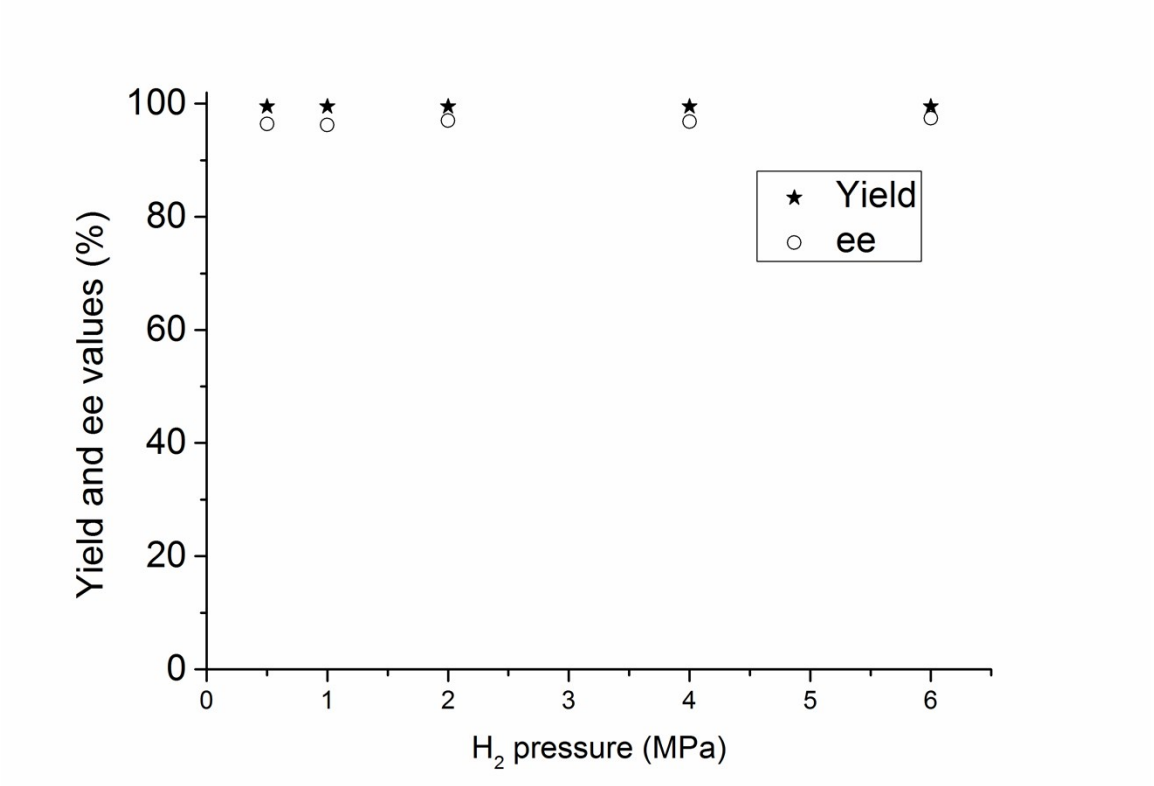


Figure S7

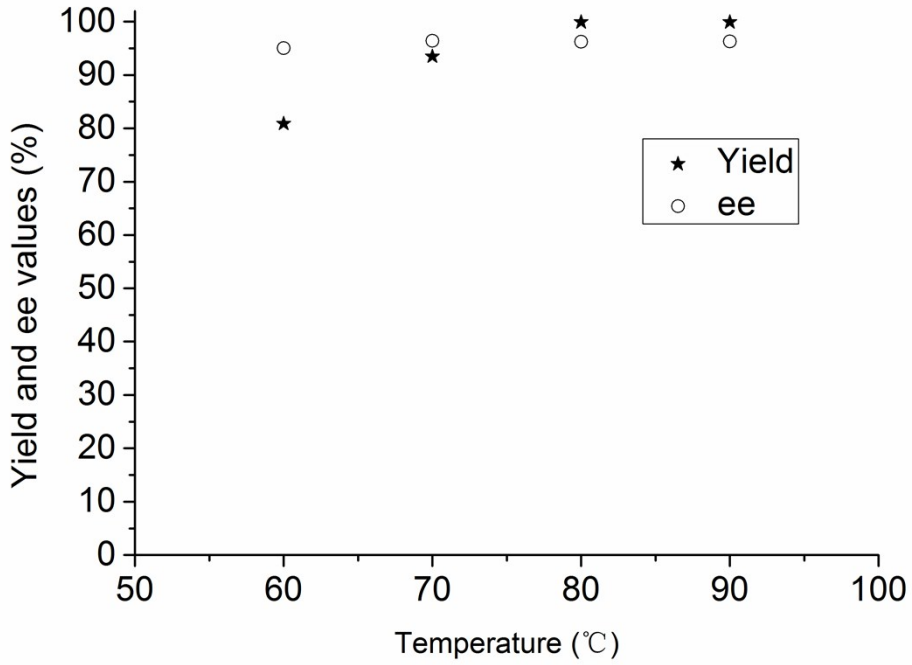


Figure S8.

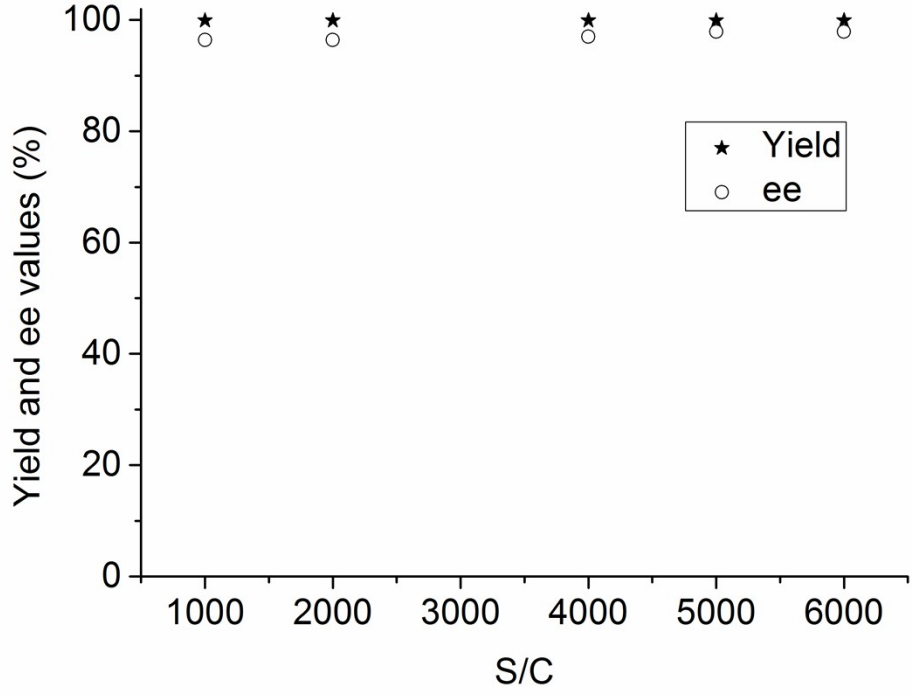


Figure S9.

Reference:

1 M. Myahkostupov and F. N. Castellano, Inorg. Chem., 2011, 50, 9714.