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Electronic Supplementary Information:

Regulating the size and spatial distribution of Pd nanoparticles supported by the defect engineered Metal-Organic Framework HKUST-1 and applied in the aerobic oxidation of cinnamyl alcohol

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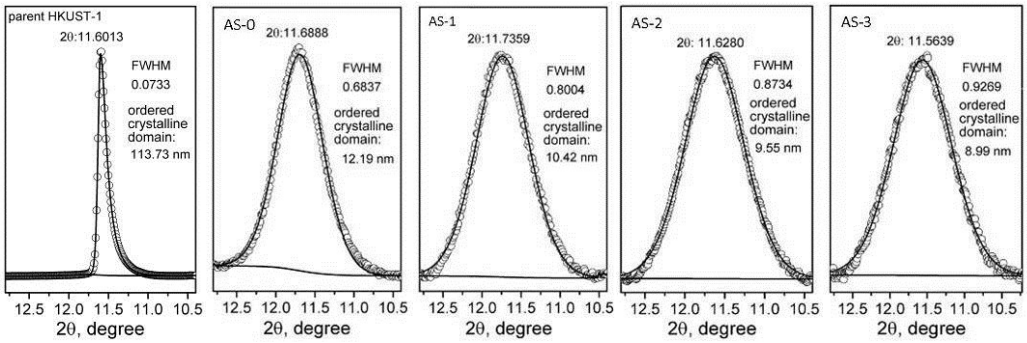

Fig. S1 Mean size of ordered crystalline domains calculated by Scherrer Equation $\tau = K\lambda/(B\cos\theta)$, ($K = 0.94$, $\lambda = 0.15406$ nm) for parent HKUST-1, AS-0, AS-1, AS-2 and AS-3.

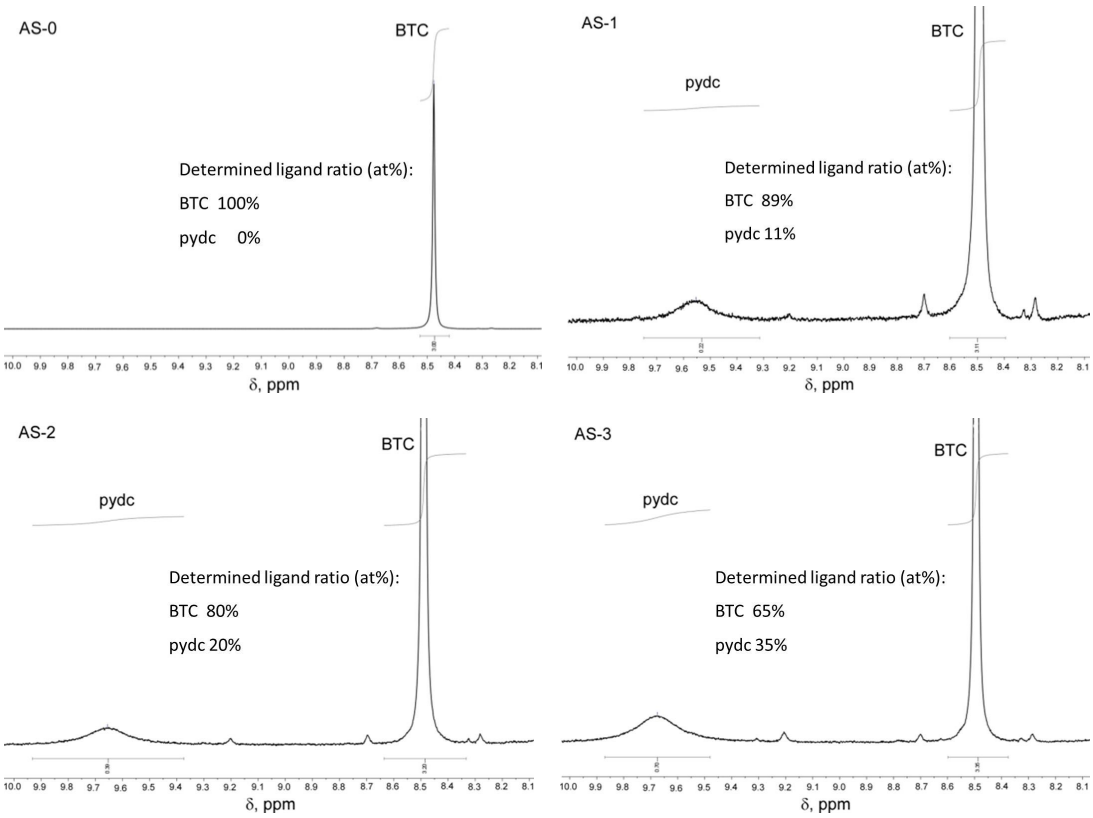

Fig. S2 The ^{1}H-NMR results for the AS-0, AS-1, AS-2 and AS-3 samples to determine the incorporated amount of pydc. Before the measurements, the samples were solvent-exchanged by acetone for five times and then activated at 403 K for 4 h.

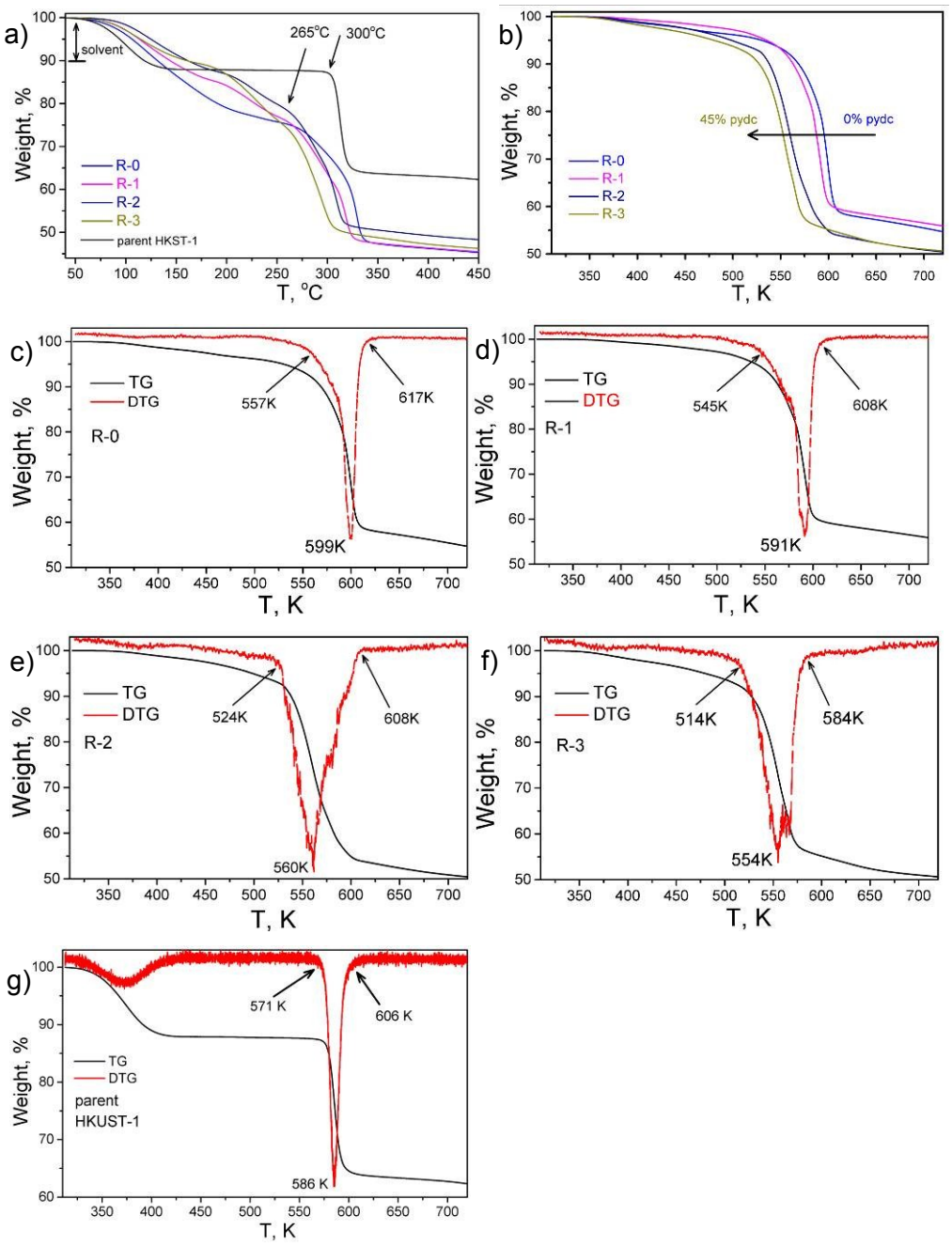

Fig. S3 a) TG plots of freshly-prepared R-0 to R-3 samples and parent HKUST-1; b) TG plots of R-0 to R-3 samples pre-activated at 403 K. DTG plots for c) R-0 pre-activated at 403 K, d) R-1 pre-activated at 403 K, e) R-2 pre-activated at 403 K, f) R-3 pre-activated at 403 K and g) as-synthesized parent HKUST-1. The heating ramp was 5 K/min.

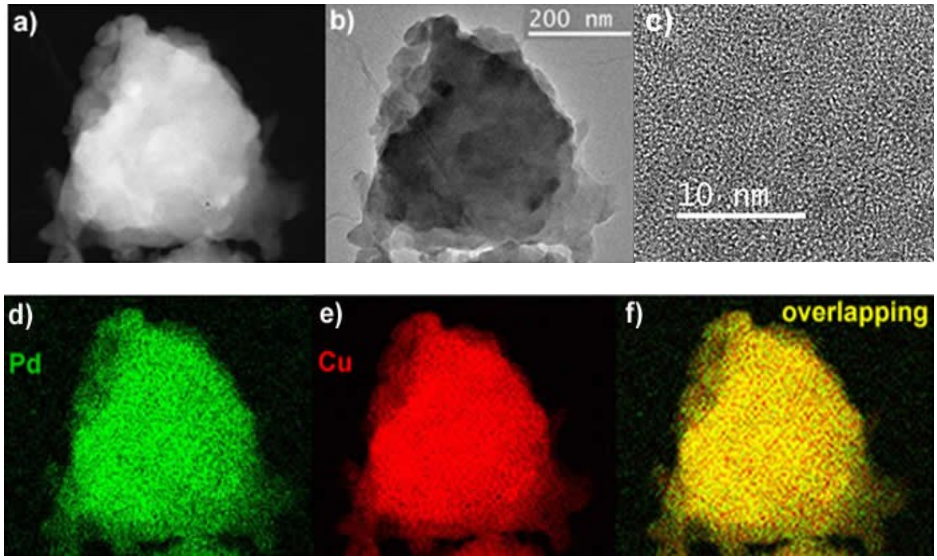

Fig. S4 a) STEM-HAADF image, b) TEM image, c) magnified TEM image, d) palladium mapping, e) copper mapping and f) palladium and copper overlapping for as-synthesized AS-0 (0% pydc) sample.

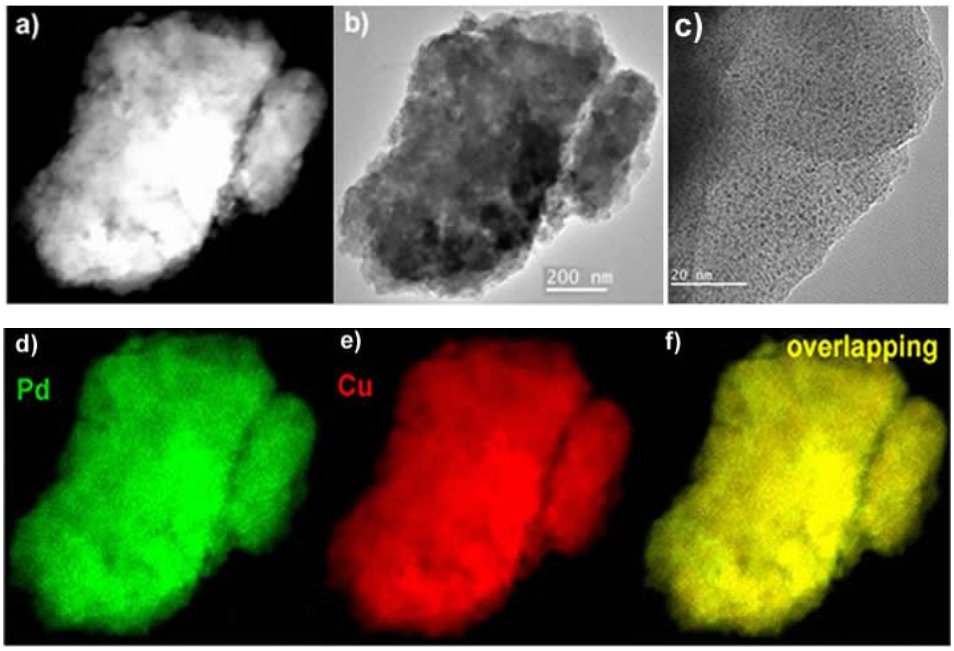

Fig. S5 a) STEM-HAADF image, b) TEM image, c) magnified TEM image, d) palladium mapping, e) copper mapping and f) palladium and copper overlapping for as-synthesized AS-2 (30% pydc) sample.

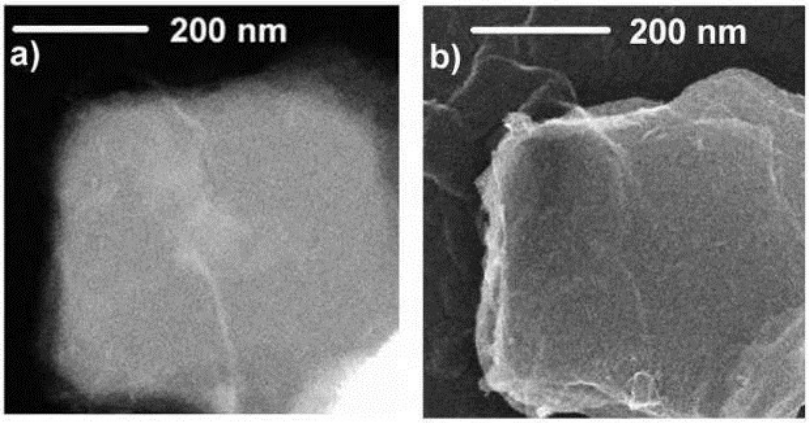

Fig. S6 a) STEM-HAADF, b) SEI images of parent HKUST-1.

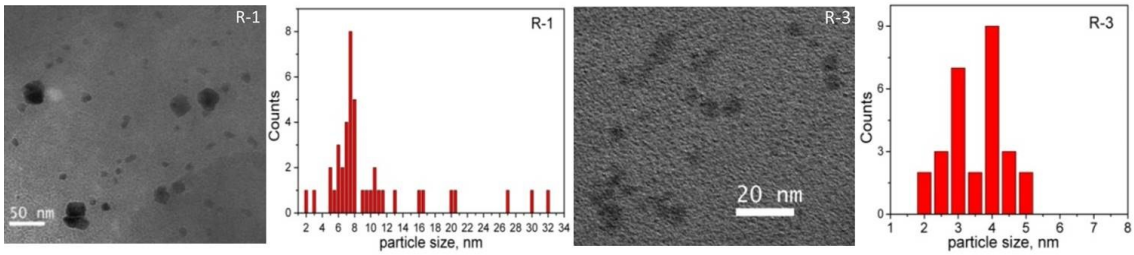

Fig. S7 TEM images and Pd NPs size distributions for R-1 (15% pydc) and R-3 (45% pydc).

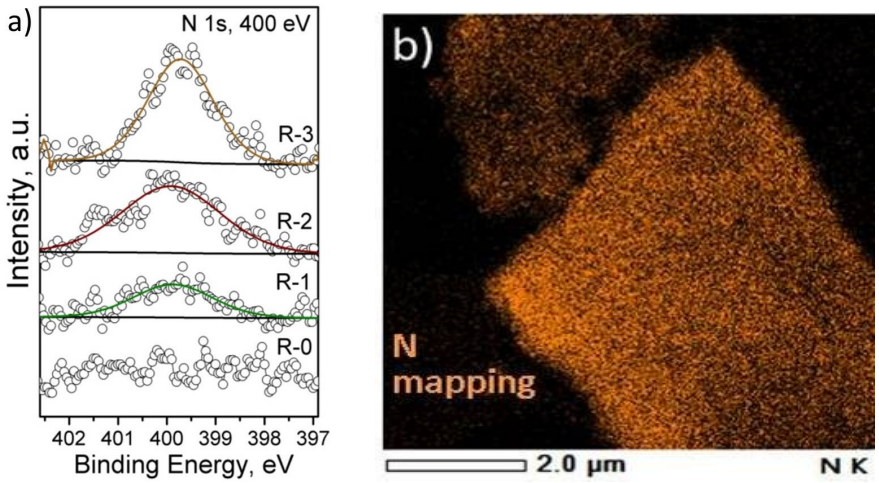

Fig. S8 a) XP N 1s regions of R-0, R-1, R-2 and R-3. N 1s signal exclusively originates from pydc incorporation. b) EDS elemental mapping of N for R-2 (30% pydc feeding ratio).

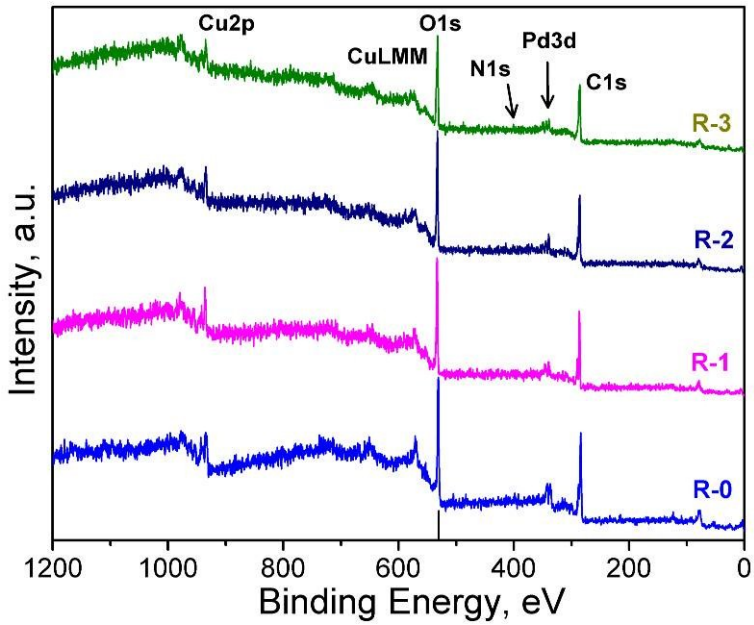

Fig. S9 XPS survey scans of R-0, R-1, R-2 and R-3.

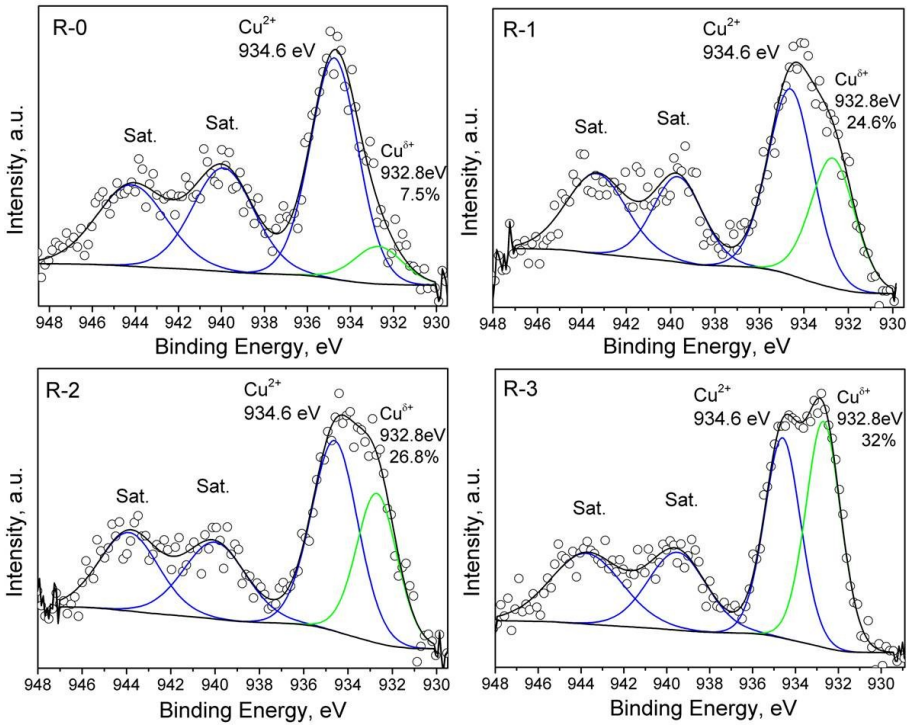

Fig. S10 XP Cu 2p region of R-0, R-1, R-2 and R-3.

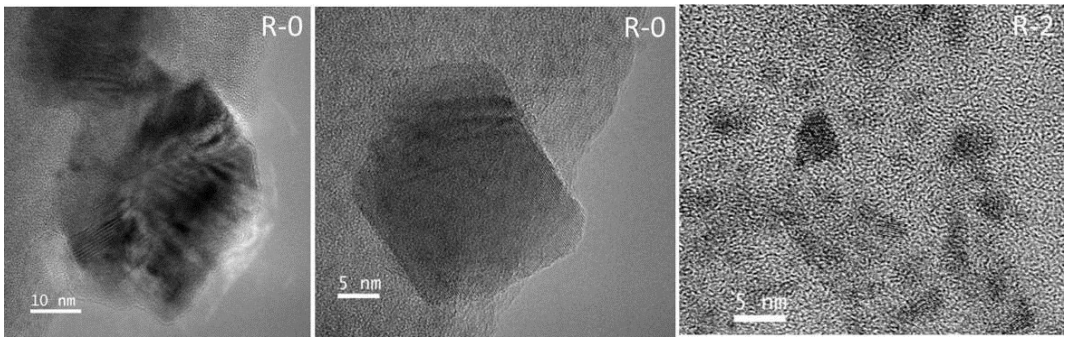

Fig. S11 Magnified TEM images for R-0 and R-2 samples.

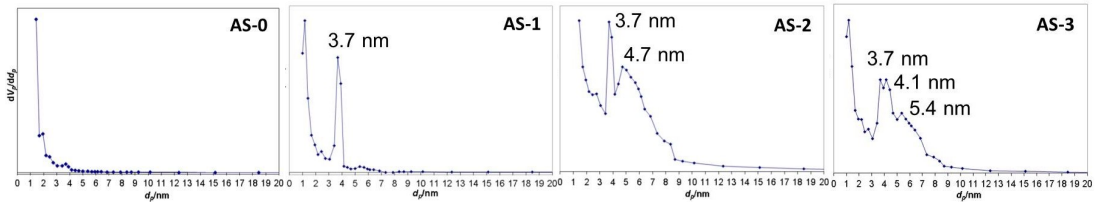

Fig. S12 BJH plots derived from N_2 physisorption isotherms of the as-synthesized samples. Before the measurements, the samples were solvent-exchanged by acetone for five times and then activated at 403 K for 4 h.

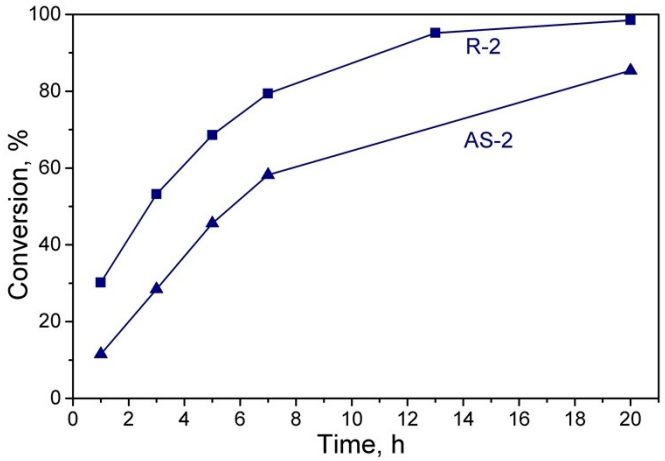

Fig. S13 Cinnamyl alcohol oxidation using AS-2 and R-2 as catalysts.

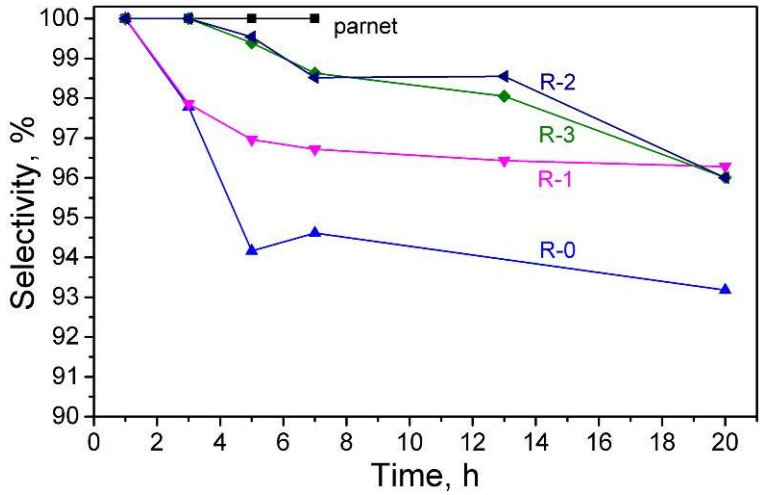

Fig. S14 Selectivity to cinnamaldehyde as a function of time for cinnamyl alcohol oxidation.

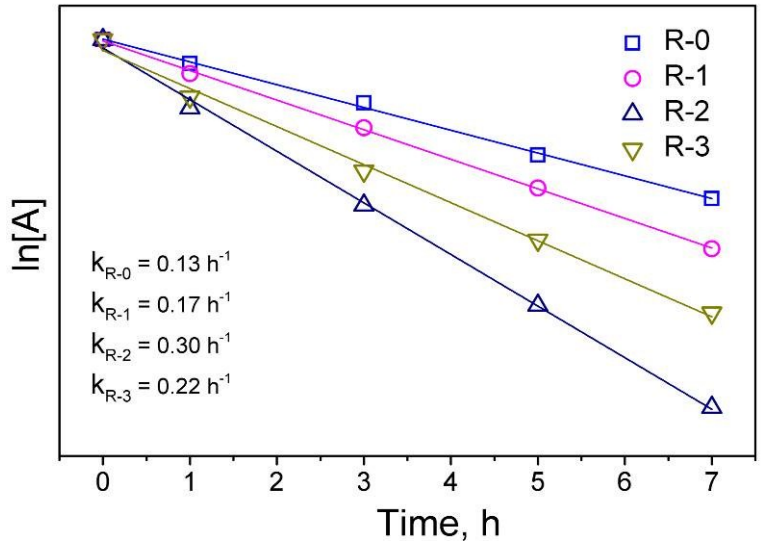

Fig. S15 Reaction order and rate constant determination by plotting ln[A] with respect to time for R-0, R-1, R-2 and R-3. The oxidation of cinnamyl alcohol is determined to be a first-order reaction. The reaction rate constant k is calculated by $\ln[A] = -kt + \ln[A_0]$, where [A], $[A_0]$, k, and t are reactant concentration, initial reactant concentration, rate constant and reaction time, respectively.

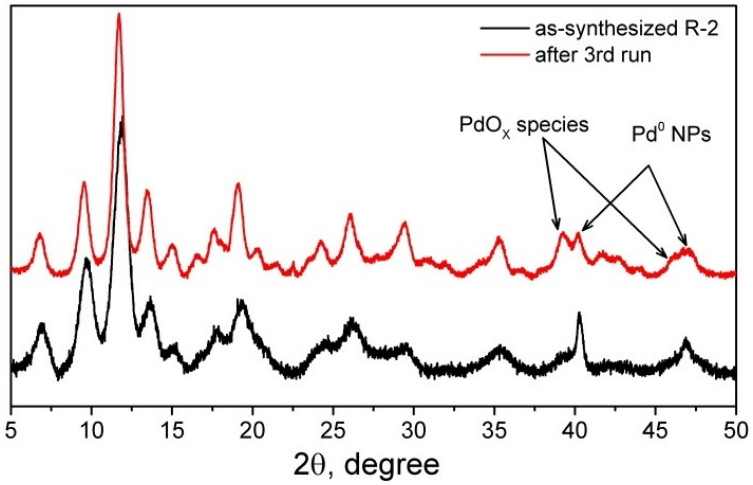

Fig. S16 Powder XRD patterns of R-2, freshly synthesized and after the third cycle.

Table S1. Effect of stirring speed on the conversion of cinnamyl alcohol.

Stirring speed (rpm)	300	500	700	1000
Conversion (%)	62.86	82.30	88.05	87.85

Reaction conditions: 50 mg R-2, 1 mmol cinnamyl alcohol, 20 mL toluene, 393 K, 5 bar O_2 pressure, 7h.