Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Ultrafinely Dispersed PdNanoparticles ona CN@MgO Hybrid asa Bifunctional Catalyst for BioderivedCompounds Upgrading

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Contents

Experimental section

Synthesis of nitrogen doped carbon coated MgO supportsCN@MgO. In a typical process, 2 g glucosaminehydrochloride (GAH) was firstly dissolved in 15 mL deionized water in a crucible (50 mm in diameter) with sttirring, afterwards 0.5 g MgO nanopowder were added in. The crucible was heated to 80 ^{o}C in an oil bath with stirring until a dried dark black product was obtained (Figure S1 A for detailed color change process of the above mixture with stirring under heating and Figure S1 B the IR spectras comparison of GAH and the obtained mixture). Afterwards, it was transferred into a nitrogen furnace, calcined at 1000 ^{o}C for 1 h with a heating rate of 10 ^{o}C/min while keeping a N_2 flow of 400 mL/min, until it was cooled to room temperature, the black product was ground into powder, finally, the CN@MgO(where the mass ratio of MgO in CN@MgOwas 0.4)was obtained. For another two supportsCN@MgO-1and CN@MgO-2 (where the mass ratio of MgO in CN@MgO were 0.25 and 0.6, respectively), only the mass ratio of the precursors GAH and MgO were changed to 2/0.33 and 2/0.8, respectively.

Synthesis of nitrogen doped carbon CN. Moderate amount of the as prepared CN@MgO was dissolved in an excess diluted HCl solution, after 24 hours' magnetic stirring at room temperature, filter the solution with deionized water for several times until the pH of the filtrate reached 7, indicating a complete removal of the residual acid. Then a black solid was obtained and it was dried in an oven at 70 ^{o}C overnight, finally the black solid was gently ground to obtain a black powder, nitrogen doped CN was obtained.

Synthesis ofPd/CN@MgO, Pd/CN, Pd/MgO, and Pd/(CN+MgO) catalysts.In a typical synthesis, 0.2 g CN@MgO was dispersed in 20 mL deionized water in a beaker by shaking it in the ultrasonic sound condition, and then 2 mL $PdCl_2$ aqueous solution (0.01 g/mL) was added into, 10 minutes later, 10 mL newly prepared $NaBH_4$solution(1 mg/mL)was added into the solution, and kept shaking the solution for 30 minutes. All the process above was done in the ultrasonic sound condition. Later, filter the solution and wash the residue (black solids) with deionized water for several times. After being dried in an oven overnight, the catalyst was ready to be used. The rest catalysts Pd/CN, Pd/MgO and Pd/(CN+MgO)were synthesized in the same method as in the fabricating the Pd/CN@MgO catalyst except that replacing the support CN@MgO with CN, MgO and CN+MgO, respectively.As toPd/(CN+MgO), quantitive CNand MgO was mixed according to the mass ratio of CN/MgO in Pd/CN@MgO catalyst.For the above Pd/CN@MgO, Pd/CN, Pd/MgO and Pd/(CN+MgO)catalysts, the theoretically loading of Pd was 5.66% in mass ratio, and the actual loading of Pd from ICP analysis were 5.5 %, 4.6 %, 6.0 % and 5.4 %, respectively.

Catalytic aldol condensation between furfural and acetone. All aldol reactions were carried out in a 150 mL stainless-steel autoclave with an external temperature and stirring controller. In a typical experiment, a catalyst (20 mg) was first added into a beaker with 40 mL deionized water followed by ultrasound treatment to better disperse nanoparticles in the solution as possible. Afterwards, the solution with well-dispersed nanoparticles were transferred into the autoclave followed by adding 0.31 g furfural and 1.69 g acetone (Molar ratio 1:9). Then the reactor was purged with N_2 for 3 times, then sealed tight and pressurized to 0.1 MPa N_2, when the temperature was heated to 120 ^oC, stirring was startedto give a 1 h of reaction. Afterwards, the reactor was carefully vented and the reaction mixture was extracted with ethyl acetate (~40 mL). The furfural conversion and product selectivity were confirmed by GC with cetane as an internal standard.In a series of aldol condensation reactions, reaction parameters such as molar ratio of acetone/furfural, N_2 pressure, reaction temperature, and reaction time were studied with the same processing procedures descibed above.

Sequential aldol condensation followed by catalytic hydrogenation. All reactions were carried out in a 150 mL stainless-steel autoclave. Typically, before starting the condensation reaction, the reactor was initially loaded with with reaction mixture of 20 mg Pd/CN@MgO, 0.31 g furfural and 1.69 g acetone in 40 mL deionized water, and air was purged out with N_2 for three times. The reactor was then in an atmosphere of 0.1 MPa N_2, when heated to 120^oC, the stirring was started. Aldol condensation was stopped after 1 h of reaction, and the reactor was cooled to room temperature. The following hydrogenation reaction was started by a similar purging procedure with H_2 andthen pressurized to 1.0 MPa, then the reactor was again heated to 120 ^oC, and then stirring was started to let the hydrogenation run for 3 h. Afterwards, the reactor was cooled to room temperature quicklly in water and carefully vented, the reaction mixture was extracted with ethyl acetate (~ 40 mL). The furfural conversion and product selectivity were confirmed by GC with cetane as an internal standard.

Recycling of Pd/CN@MgO towards the hydrogenation of monomer.In a typical reaction,0.1 g of the monomer substrate, 40 mgcatalystand 20 mL water were all added in a 50 mL three-necked flask, and ultrasound treatment was performed to better disperse the mixture. Afterwards, the reaction mixture was subjected to 0.1 MPa H_2at 80 ^oC for 1.5 h under magnetic stirring. Finally, the products were extracted with ethyl acetateand the final conversion and prduct selectivity was confirmed by GC with cetane as an internal standard.As to the recyling procedure,the catalyst Pd/CN@MgO was recycled by centrifugation and washed with ethanol three times, then dried overnight.For each of the recycles, the amount of substrate was reduced in mass proportion with the recycled catalyst, and the hydrogenation procedure was repeated as illustrated above.

Figure S1. A) Color change process of the mixture of GAH and MgO with stirring under heating (80 °C). As can be seen in the preparation process, we found that through the slow oligomerization of GAH with the gradual color change when heating, MgO was uniformly wrapped by the polymerized GAH. Finally, only dark brown polymerized GAH wrapped MgO was seen. B) IR spectras of GAH and the final dark brown product. From the decreasing peak intensity around ~ 1040 cm^{-1} which is to C-O stretching vibration, demonstrating GAH was polymerized during heating (80 °C) with MgO.

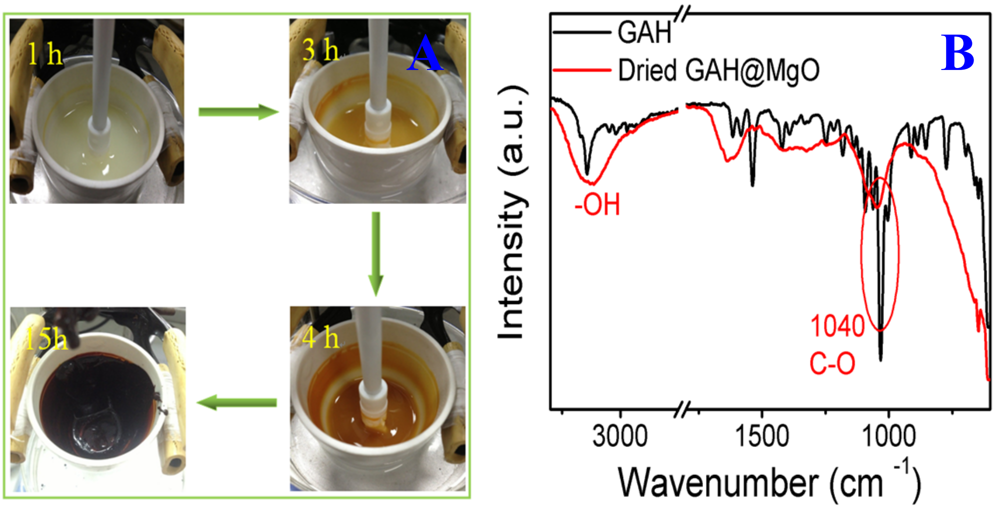


Figure S2. TGA spectras of the synthesized CN@MgOwith different mass ratio of CN to MgO in O_2 flow, which were obtained by changing the mass ratio of precursors GAH and MgO. For simplicity, the supports are simplified as CN@MgO, CN@MgO-1, CN@MgO-2, respectively. Where we can see the mass ratio of MgO in each hybrid are about 0.4, 0.25 and 0.6,respectively.

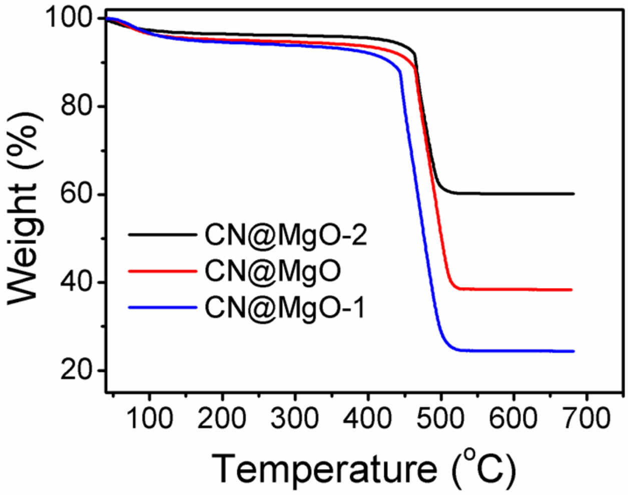


Figure S3. HRTEM image of Pd/CN@MgO clearly showing theuniform deposited Pd nanoparticles.

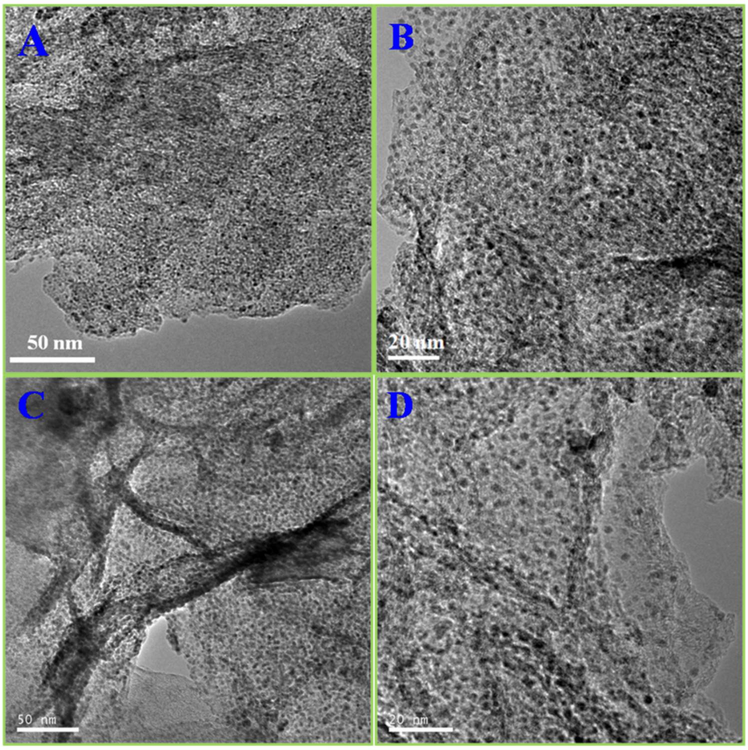


Figure S4. A) Pictures of contact angle of CN with water and its dipersion in water; B) Water dispersions of MgO and CN@MgO, showing thehydrophilic property of CN@MgO.

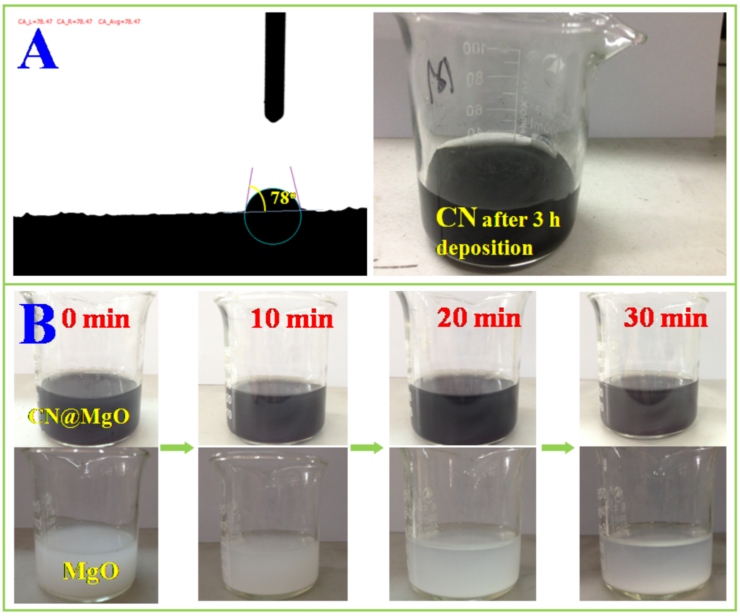


Figure S5. CO_2-TPD of the catalyst supports.

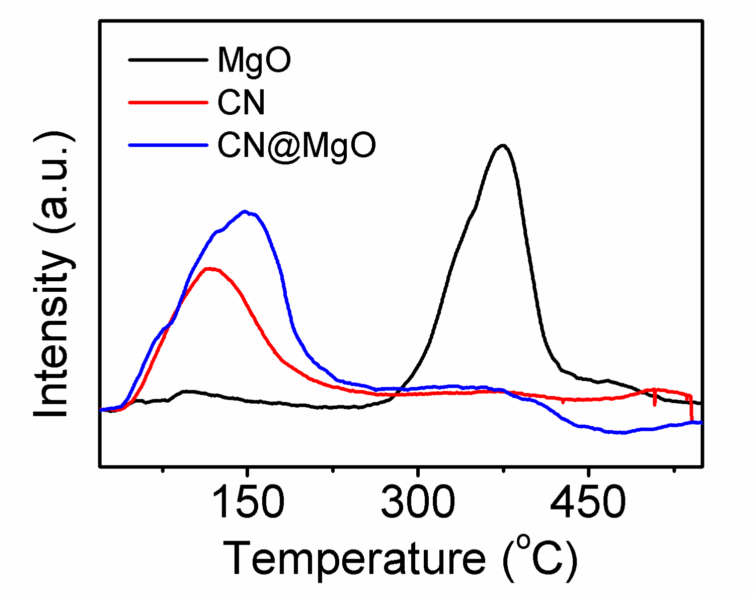


Figure S6. TEM images of Pd/(CN+MgO) showing average Pd particle size of ~4.0 nm together with apparent aggregation of Pd NPs.

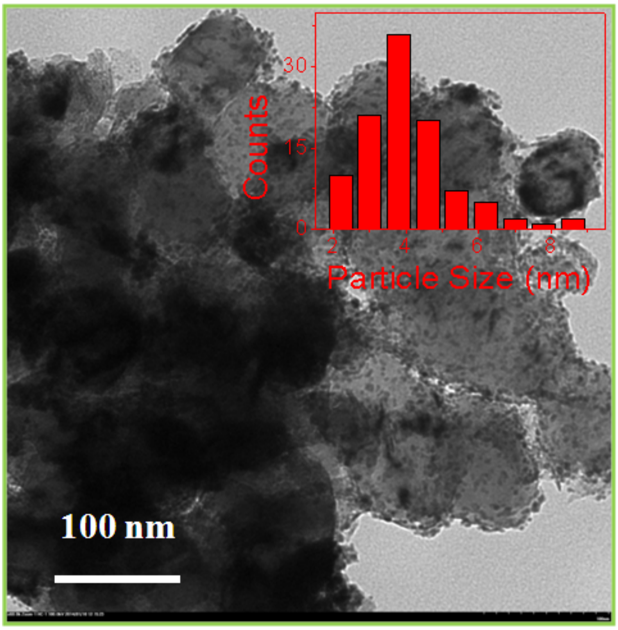


Figure S7. HR-TEM images and particle size distribution of Pd@CN$_{0.132}$,shwoing local aggregations of Pd nanoparticles and a relatively large mean particle size of ~ 4.9 nm, adapted from ref.[1].

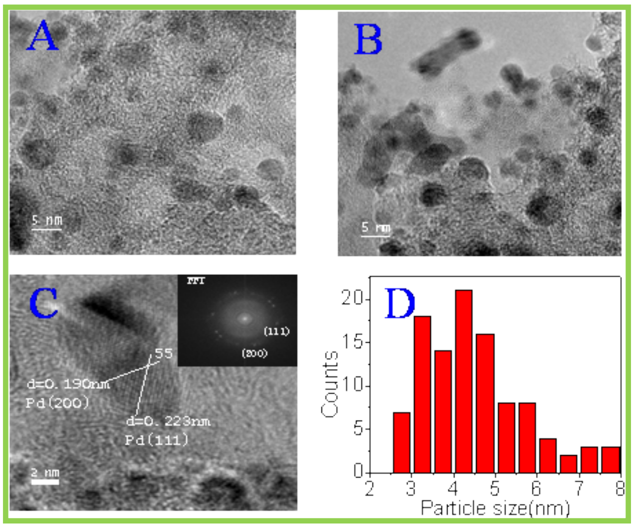


Figure S8. N$_2$adsorption/desorption isotherms of Pd/MgO, Pd/(CN+MgO) and Pd/CN@MgO.

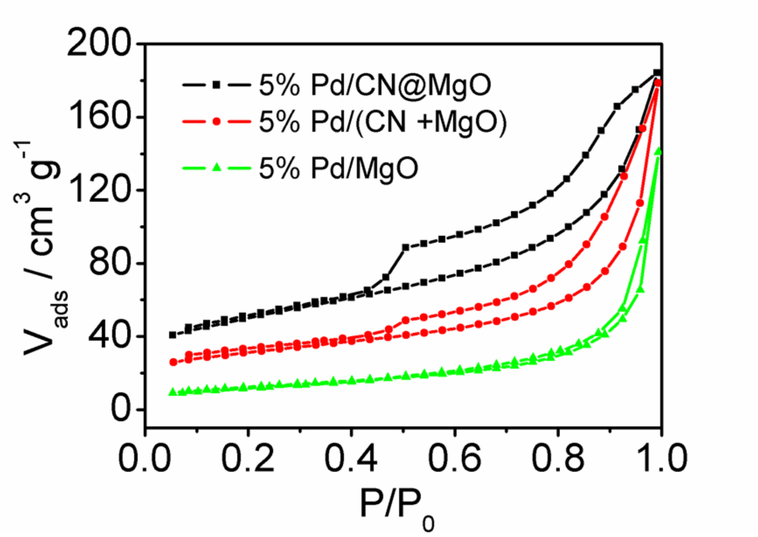
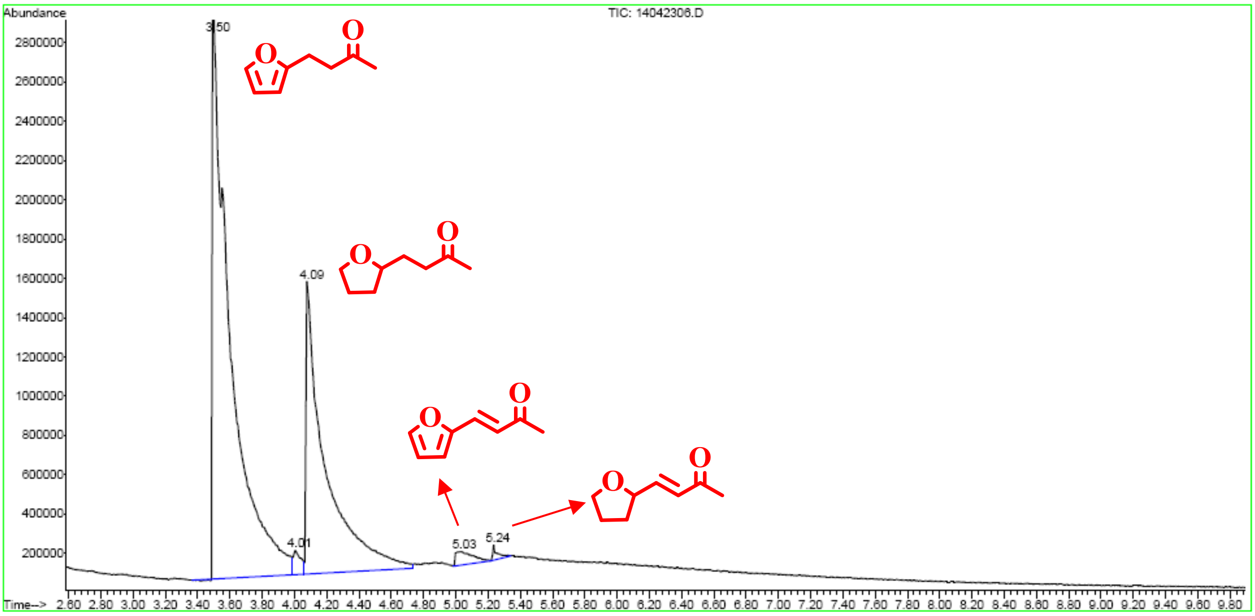
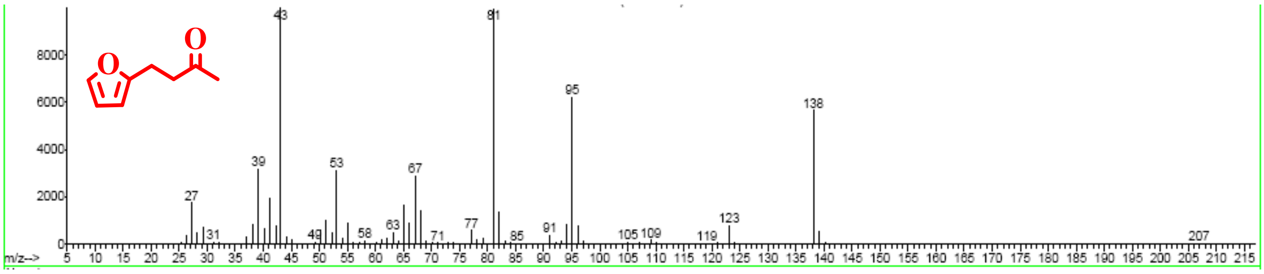


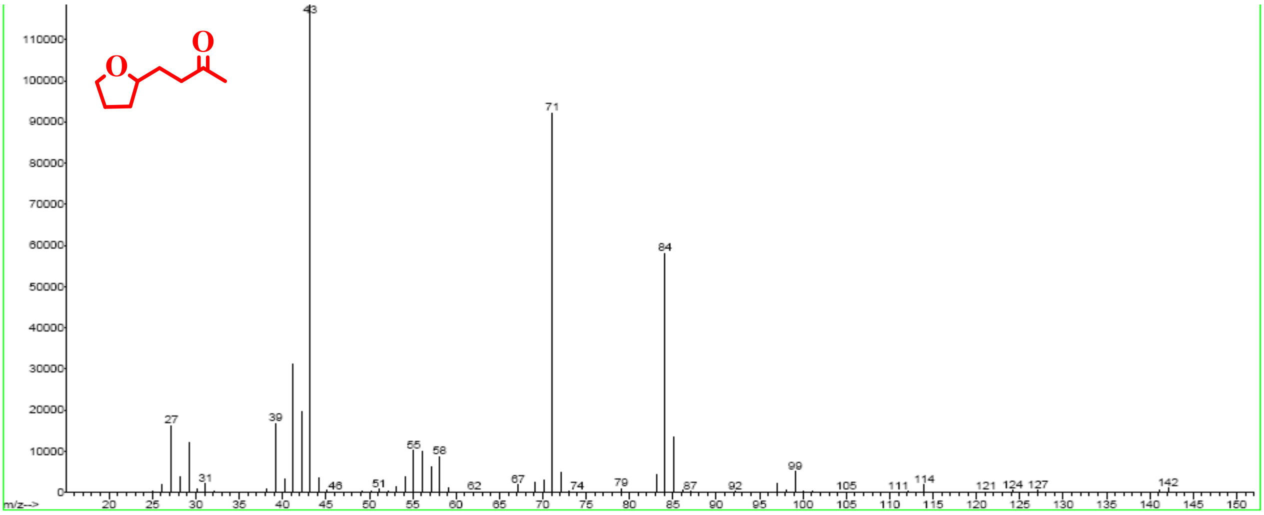
Figure S9. Identification of the products in the monomer hydrogenation process by GC-MS.

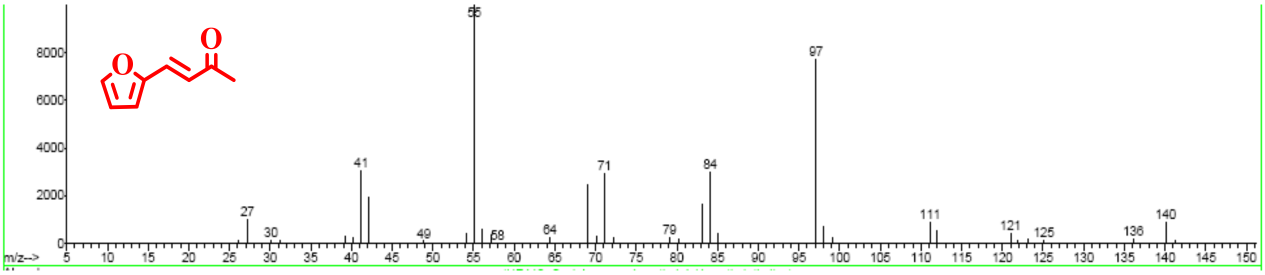
GC chromatogram



MS chromatogram







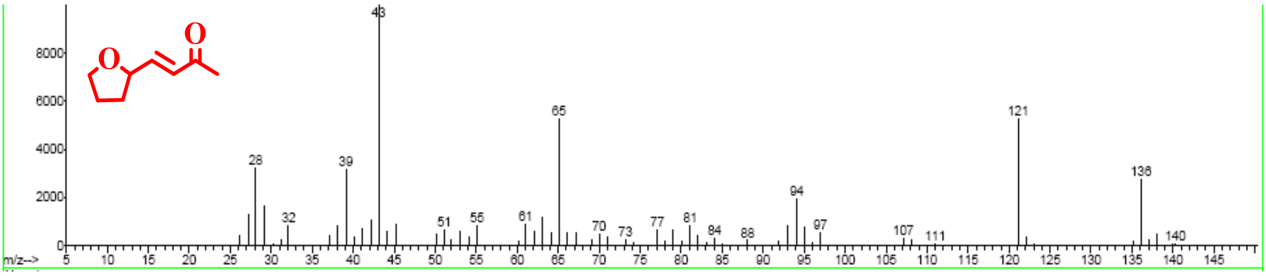


Figure S10. XRD patterns of the synthesized A) Pd/CN@MgOand B) Pd/MgO catalysts before and after a tandem reaction. Reaction condition: aldol condensationbetween furfural and acetone was performed in 0.1 MPa N_2, 120 ^{o}C for 1 h in 40 mL water, followed by a hydrogenation process at 120 ^{o}C under 1.0 MPa H_2.

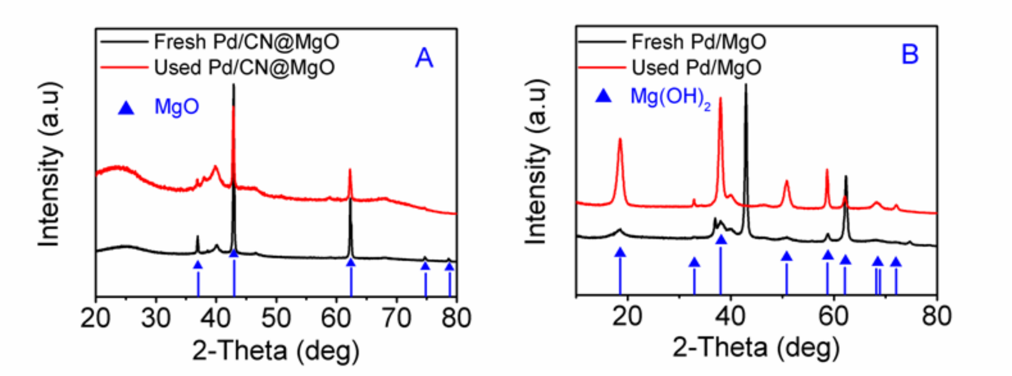


Table S1. Elemental analysis results of CN@MgO support.

Entry	Sample	Element (%)		
		C	H	N
1	CN@MgO	48.69	0.82	2.33

Table S2.BET specific area, pore volume and average pore size of the catalyst supports determined by nitrogen sorption measurements.

Sample	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore size (nm)
MgO	40	0.10	23
CN	84	0.3	14
CN@MgO	92	0.21	9

Table S3. Effects of different reaction parameters on aldol condensation of furfural and acetone using Pd/CN@MgOcatalyst.

Entry	Molarratio (F/A)	N_2 pressure (Mpa)	Temperature (°C)	Time (h)	Conversion (%)	Sel. (%)		
						Monomer	Dimer	Others
1	1:9	1.5	80	3	98	82	18	0
2	1:9	0.1	80	3	>99	87	13	0
3	1:1	0.1	80	3	44	58	38	4
4	2:1	0.1	80	3	45	46	47	7
5	1:9	0.1	50	3	84	84	11	5
6	1:9	0.1	120	3	>99	90	10	0
7	1:9	0.1	120	2	>99	89	11	0
8	1:9	0.1	120	1	>99	90	10	0
9	1:9	0.1	120	0.5	95	87	13	0

All runs were carried out in 40 mL H_2O with c(furfural)= 0.081mol·L^{-1} while keeping the molar ratio of furfural/acetone 1:9 and the mass ratio of organic/ catalyst 100:1.

Table S4. Catalytic products of aldol condensation of furfural and acetone followed by hydrogenation withPd/CN@MgOcatalysts with different mass ratio of CN and MgO. The results showed both furfural conversion and products selectivity were worse than what was performed using Pd/CN@MgO as the most desired catalyst, showing the significant influence of the catalyst support on the overall catalytic activity, although with the same components CN and MgO, but if contents between were changed, the results may be much different.

Entry	Cat.[a]	Conv. (%)	Sel. (%)				
			1	3	7	8	Others
1	Pd/CN@MgO-1	91	16	71 (1)	0	9	3
2	Pd/CN@MgO-2	95	33	57	3	7	0

[a]Theoretically synthesized with 5.66wt% Pd in mass ratio. All runs were carried out in 40 mL H_2O with c(furfural)=0.081 mol·L^{-1} while keeping the molar ratio of furfural/acetone 1:9 and the mass ratio of organic/catalyst 100:1. Condensation in 0.1MPa N_2, 120 °C for 1 h; Hydrogenation in 1.0MPa H_2, 120 °C for 3 h.While the brackets are the corresponding alcohols.

1. X. Xu, Y. Li, Y. Gong, P. Zhang, H. Li and Y. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 16987-16990.