Electronic Supplementary Material (ESI) for Chemical Science
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Electronic Supplementary Information (ESI) for

Sodium Hydroxide-Assisted Growth of Uniform Pd Nanoparticles on Nanoporous Carbon MSC-30 for Efficient and Complete Dehydrogenation of Formic Acid under Ambient Conditions

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1. Chemicals and Materials

All chemicals were commercial and used without further purification. Potassium tetrachloropalladate (K_2PdCl_4, Wako Pure Chemical Industries, Ltd., >97%), sodium borohyride ($NaBH_4$, Sigma-Aldrich, 99%), sodium hydroxide (NaOH, Chameleon Reagent, >98%), Maxsorb MSC-30 (Nanoporous Carbon, Kansai Coke and Chemicals Co. Ltd.), Vulcan XC-72R (Carbon, specific surface area = 240 m^2 g^{-1}, Cabot Corp., USA), aluminum oxide (Al_2O_3 nanoparticles, ~150 mesh, specific surface area = 155 m^2 g^{-1}, Sigma-Aldrich), formic acid (FA, HCOOH, Kishida Chemicals Co. Ltd., >98%), sodium formate dehydrate (SF, HCOONa, Sigma-Aldrich, 99.5%) were used as received. De-ionized water with a specific resistance of 18.2 MΩ·cm was obtained by reverse osmosis followed by ion-exchange and filtration (RFD 250NB, Toyo Seisakusho Kaisha, Ltd., Japan).

2. Instrumentation

Laboratory powder X-ray diffraction patterns were collected for synthesized catalysts on a Mac Science MXP3 V diffractometer with Ni filtered Cu-Kα radiation (λ = 0.15406 nm) (40 kV, 20 mA). The surface area measurements were performed with N_2 adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp-max) after dehydration under vacuum at 120 °C for 12 h. X-ray photoelectron spectroscopic (XPS) measurements were conducted on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg Kα source (10 kV, 10 mA). The argon sputtering experiments were carried out under the conditions of background vacuum of 3.2×10^{-6} Pa and sputtering acceleration voltage of 2 kV and sputtering current of 10 mA. The charging potential of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) at 284.6 eV. The TEM and HAADF-STEM images and EDX spectra were recorded on Transmission electron microscope (TEM, TECNAI G^2 F20) with operating voltage at 200 kV equipped with energy-dispersive X-ray detector (EDX). After purging the reactor with argon three times, the decomposition of formic acid was carried out, and the generated gas was collected, which was analyzed by GC-8A (molecular sieve 5A, Ar as carrier gas) and GC-8A (Porapack N, He as carrier gas) analyzers (Shimadzu).

3. Syntheses of Catalysts

3.1 Syntheses of Pd/MSC-30 catalysts: The Pd nanocatalyst supported by MSC-30 was synthesized by a facile sodium hydroxide-assisted reduction method. Typically, 100 mg of MSC-30 carbon powder was ultrasonically dispersed in 2.5 mL of water and subsequently mixed with an aqueous solution of K_2PdCl_4 (0.30 M, 0.30 mL). The resulted aqueous suspension was further homogenized under sonication condition for half an hour. Then, 0.50 mL of 2.0 M NaOH solution was added into the above obtained solution with vigorous stirring, followed by an immediate addition of 20 mg of $NaBH_4$ dissolved in 0.50 mL water, resulting in the generation of catalyst as a dark suspension. The mixture was stirred for another half an hour at room temperature to fully deposit the metallic nanoparticles onto the support. Finally, the desired catalyst Pd/MSC-30 was collected by centrifuging and washed with de-ionized water three times and then dried in vacuum at room temperature.

For comparison, the catalyst was also prepared using the same synthetic procedure without the addition of NaOH.

3.2 Syntheses of Pd/XC-72R and Pd/Al_2O_3 catalysts: The Pd/XC-72R and Pd/Al_2O_3 catalysts were prepared following the same synthetic procedure as that for Pd/MSC-30 catalyst prepared with NaOH except that the XC-72R or Al_2O_3 nanoparticles was used instead of MSC-30, respectively.

4. Catalytic Activity Characterization

4.1 Procedure for the decomposition of formic acid: Reaction apparatus for measuring the H_2/CO_2 evolution from the FA/SF system is the same as previously reported.[1] In general, a mixture of as-synthesized catalyst and distilled water (2 mL) was placed in a two-necked round-bottomed flask (30 mL), which was placed in a water bath at a preset temperature (25-50 °C) under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (temperature kept constant at 25 °C during measurements). The reaction started when 1.5 mL of the mixed aqueous solution containing FA (6.0 M) and SF with different molar ratios was injected into the mixture using a syringe. The molar ratios of Pd/FA were theoretically fixed at 0.01 for all the catalytic reactions. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.

4.2 Durability testing of the catalysts: For testing the durability of the catalyst Pd/MSC-30 prepared with NaOH, 0.34 mL of pure FA (9.0 mmol) was subsequently added into the reaction flask after the completion of the first-run decomposition of FA/SF. Such test cycles of the catalyst for the decomposition of FA were carried out for 5 runs at 50 °C by adding aliquots of pure FA.

4.3 Stability of the catalysts: After the reaction, the catalyst Pd/MSC-30 prepared with NaOH were separated from the reaction solution by centrifugation and dried under vacuum at room temperature for the PXRD and TEM analyses.

5. Calculation Methods

The turnover frequency (TOF) reported here is an apparent TOF value based on the number of Pd atoms in catalyst, which is calculated from the equation as follow:

$$TOF = \frac{P_{atm} V_{gas} / RT}{2\, n_{Pd} t} \tag{S2}$$

Where P_{atm} is the atmospheric pressure (101325 Pa), V_{gas} is the final generated volume of H_2/CO_2 gas, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), n_{Pd} is the total mole number of Pd atoms in catalyst and t is the completion time of the reaction in hour.

Table S1. Catalytic activities for dehydrogenation of formic acid catalyzed by outstanding heterogeneous and homogeneous catalysts.

Catalyst	Solvent/medium	Temp. (°C)	CO evolution	TOF (h^{-1})[a]	Ref.
Heterogeneous					
Pd/MSC-30	**Aqueous HCOONa**	**50**	**No**	**2623**	**This work**
		25	**No**	**750**	**This work**
Au/ZrO_2 NCs	5HCOOH/2NEt_3	50	No	1593[b]	2
		25	No	252[b]	
$Ag_{42}Pd_{58}$	Aqueous	50	No	382[b]	3
Ag@Pd/C	Aqueous	20	No	192	4
$Co_{0.30}Au_{0.35}Pd_{0.35}$	Aqueous	25	No	80[b]	5
Pd/C with citric acid	Aqueous HCOONa	25	No	64	6
PdAu/C-CeO_2	Aqueous HCOONa	92	145 ppm	113.5	7
PdAu@Au/C	Aqueous HCOONa	92	30 ppm	21.4	8
Pd-S-SiO_2	Aqueous	85	No	719	9
AuPd@ED-MIL-101	Aqueous HCOONa	90	Yes	106	1
Homogeneous					
$RuBr_3 \cdot xH_2O$, 3 equiv. PPh_3[c]	5HCOOH/2NEt_3	40		3630[b]	10
$RuCl_2(PPh_3)_3$	5HCOOH/2NEt_3	40		2688[b]	11
$[Fe(BF_4)_2] \cdot 6H_2O$, 2 equiv. PP_3[d]	Propylene Carbonate	40	≤10 ppm	1942	12
		80	≤20 ppm	5390	
[Ir(Cp*)(dhbp)][e]	Aqueous	50	No	1240[b]	13
		90	No	14000[b]	
$[RuCl_2(benzene)]_2$, 6 equiv. dppe[f]	*N,N*-dimethyl-*n*-hexylamine	40		900	14
$[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2]^{4+}$[g]	Aqueous HCOONa	RT	No	426[b]	15

[a] TOF values were calculated according to the amount of released H_2 in overall testing time, [b] Initial TOF values calculated at the initial stages of the catalytic reactions, [c] PPh_3 = triphenylphosphine, [d] PP_3 = tris[2-diphenylphosphino)ethyl]phosphine, [e] Cp* = η^5-pentamethylcyclopentadienyl, dhbp = 4,4'-dihydroxy-2,2'-bipyridine, [f] dppe = 1,2-bis(diphenylphosphino)ethane, [g] bpm = 2,2'-bipyrimidine, bpy = 2,2'-bipyridine.

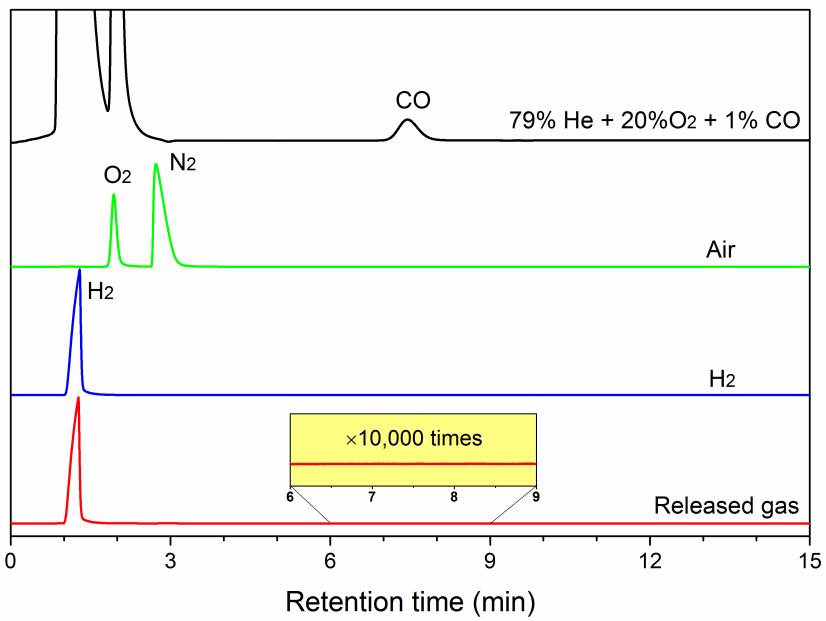

Figure S1. Gas chromatograms of CO, air and H_2 as reference gases and the released gas from the decomposition of FA/SF in the presence of Pd/MSC-30 catalysts prepared with NaOH (n_{Pd}/n_{FA}= 0.01, 50 °C), showing the presence of H_2 and absence of CO in the released gas.

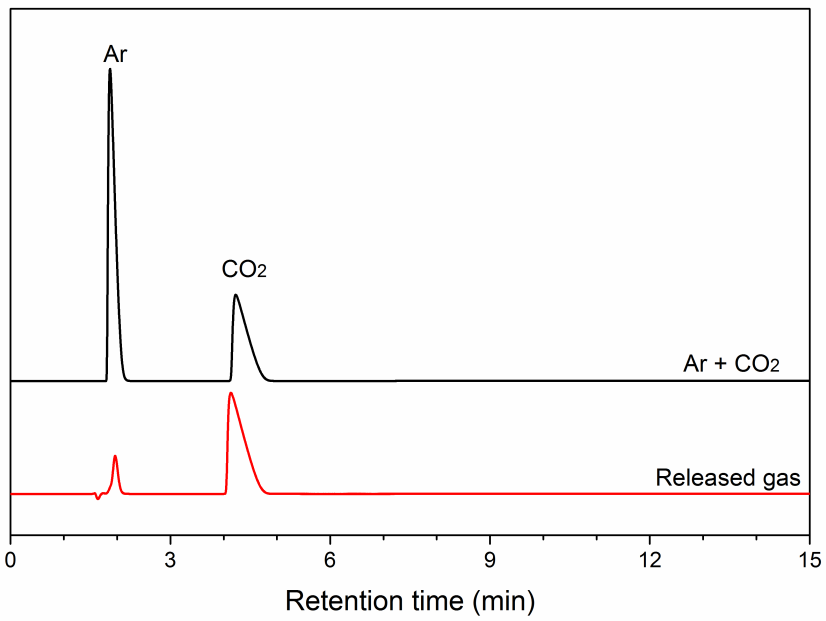

Figure S2. Gas chromatograms of CO_2 as reference gas and the released gas from the decomposition of FA/SF in the presence of Pd/MSC-30 catalysts prepared with NaOH (n_{Pd}/n_{FA}= 0.01, 50 °C), showing the presence of CO_2 in the released gas.

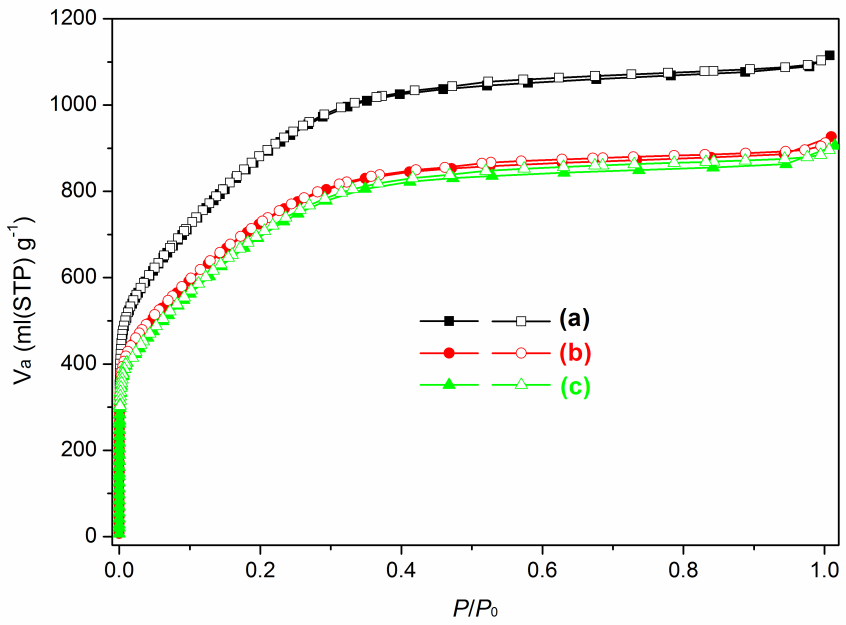

Figure S3. N_2 sorption isotherms of (a) MSC-30, and Pd/MSC-30 catalysts prepared (b) with and (c) without NaOH at 77 K. Filled and open symbols represent adsorption and desorption branches, respectively. The BET surface areas of MSC-30, and Pd/MSC-30 catalysts prepared with and without NaOH are 3012, 2490 and 2364 m^2 g^{-1}, respectively, while their pore volumes are 1.7008, 1.4150 and 1.3772 cm^3 g^{-1}, respectively, as determined by N_2 sorption isotherms. The surface of carbon materials is heterogeneous because of its non-crystalline character and the possible presence of different functional groups. It has been suggested that surface heterogeneity may influence the pore filling process in such a way that it proceeds via a continuous pore filling, leading to the observed N_2 isotherms.

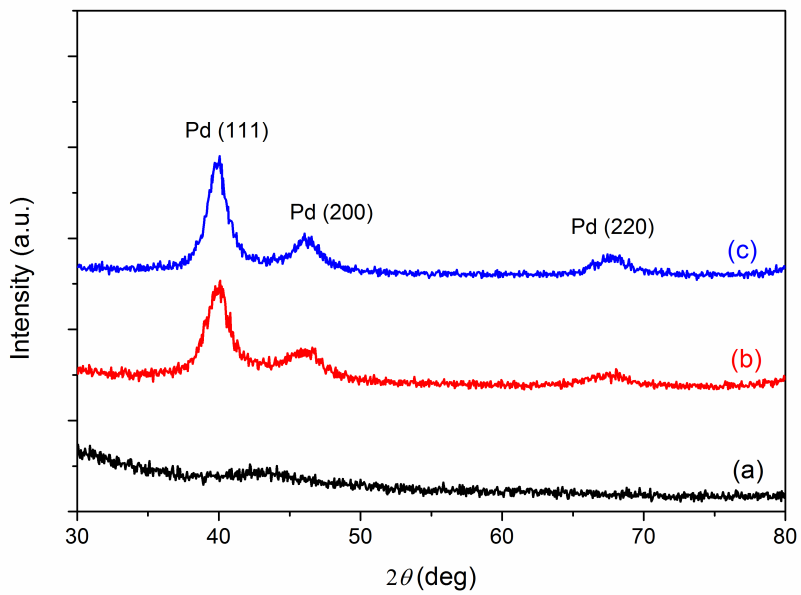

Figure S4. PXRD patterns of (a) MSC-30, and Pd/MSC-30 catalysts prepared (b) with and (c) without NaOH.

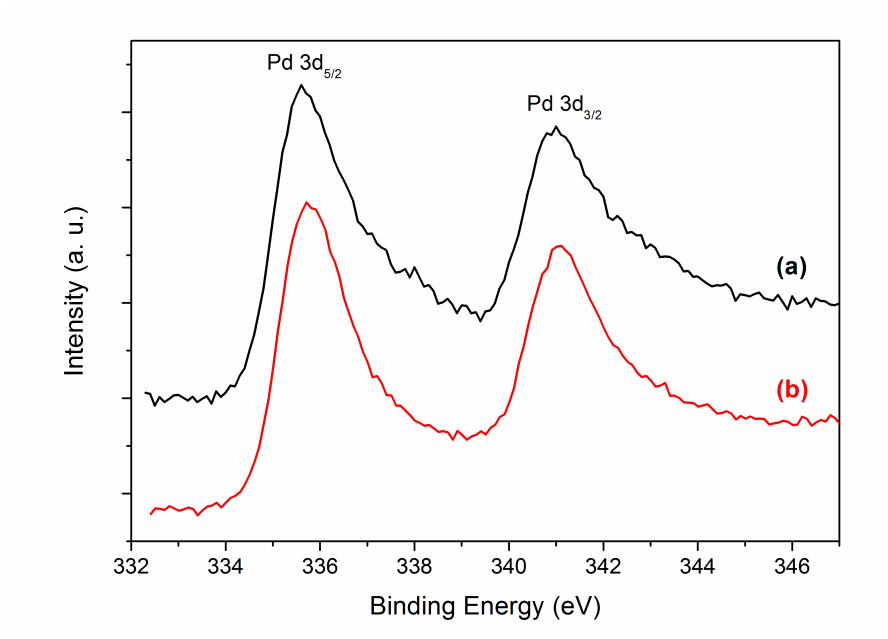

Figure S5. XPS spectra of Pd element in Pd/MSC-30 catalysts prepared (a) with and (b) without NaOH.

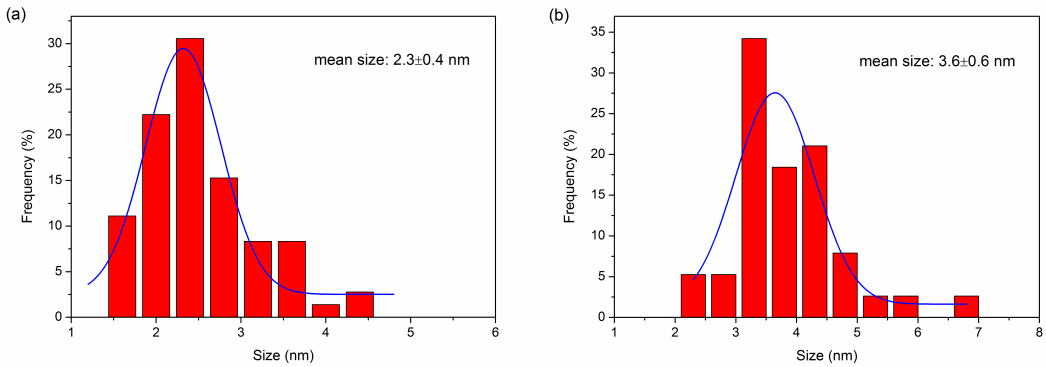

Figure S6. Particle size distribution histograms of Pd/MSC-30 catalysts prepared (a) with and (b) without NaOH.

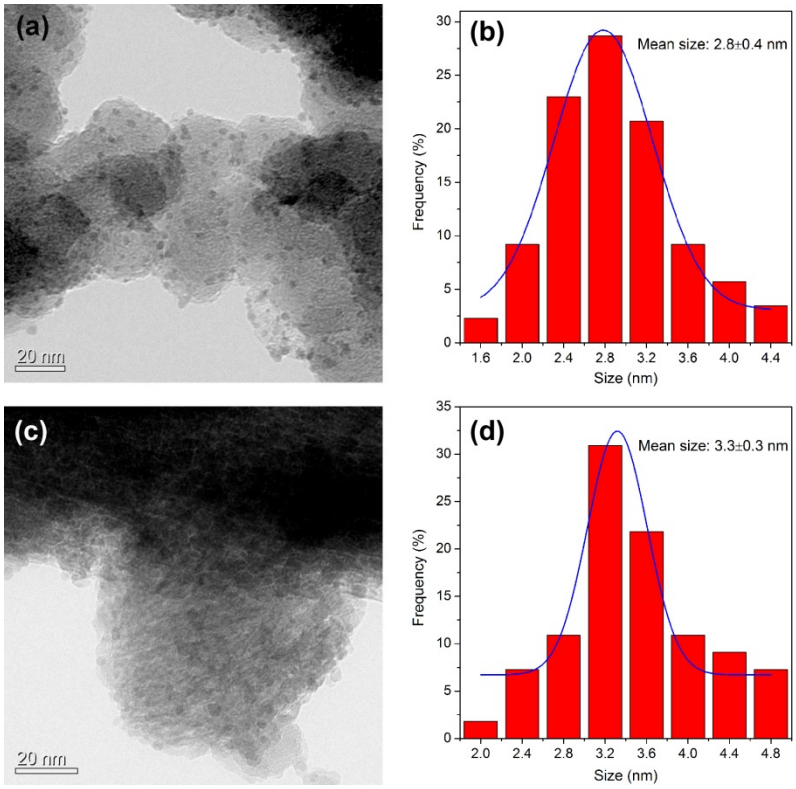

Figure S7. TEM images and corresponding particle size distribution histograms of (a, b) Pd/XC-72R and (c, d) Pd/Al_2O_3 catalysts prepared with NaOH.

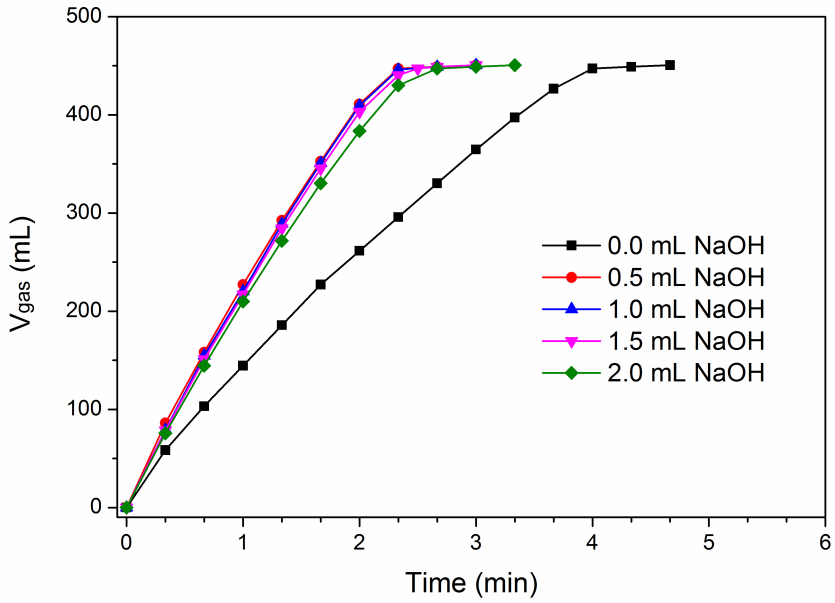

Figure S8. Volume of the generated gas (CO_2 + H_2) versus time for the dehydrogenation of FA/SF (1:1) over Pd/MSC-30 (n_{Pd}/n_{FA}= 0.01, 50 °C) prepared with different amounts of 2.0 M NaOH solution added in 2.8 mL precursor solution (K_2PdCl_4, 0.09 mmol).

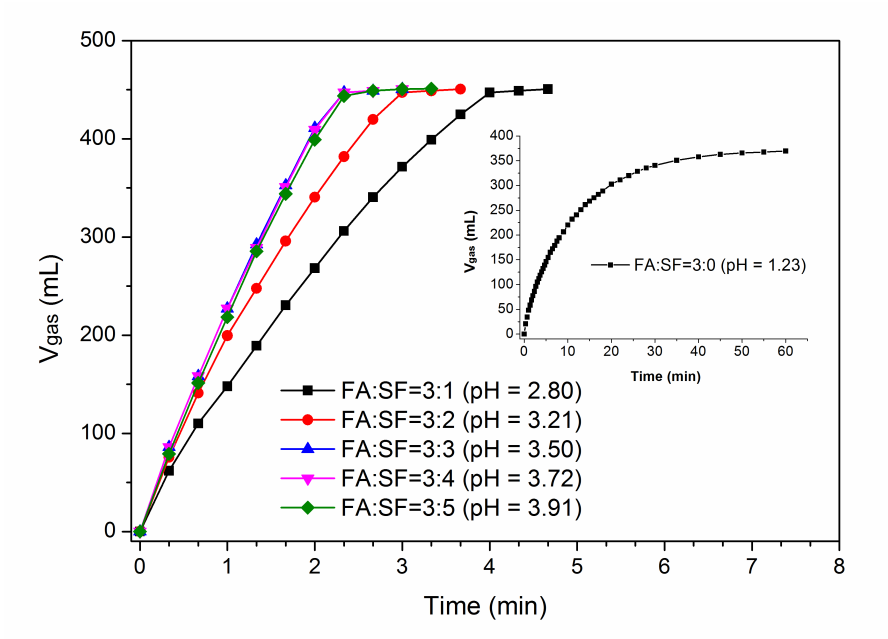

Figure S9. Volume of the generated gas (CO_2 + H_2) versus time for the dehydrogenation of FA/SF with different FA/SF molar ratios over Pd/MSC-30 prepared with NaOH (n_{Pd}/n_{FA}= 0.01, 50 °C). The pH values of FA/SF solutions with different FA/SF molar ratios are given in brackets.

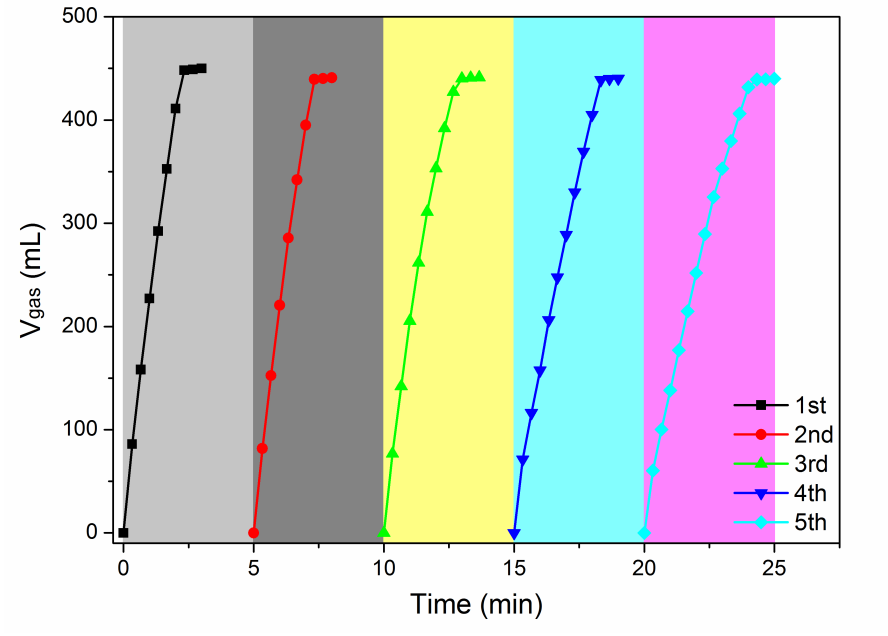

Figure S10. Durability test for the dehydrogenation of FA/SF (1:1) over Pd/MSC-30 prepared with NaOH (n_{Pd}/n_{FA}= 0.01, 50 °C).

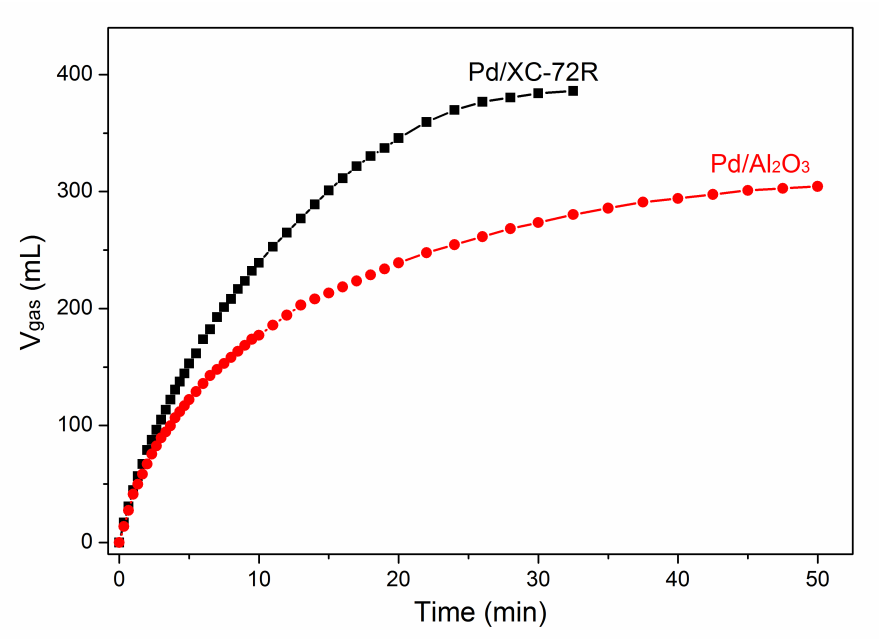

Figure S11. Volume of the generated gas (CO_2 + H_2) versus time for the dehydrogenation of FA/SF (1:1) over Pd/XC-72R and Pd/Al_2O_3 synthesized with NaOH (n_{Pd}/n_{FA} = 0.01, 50 °C).

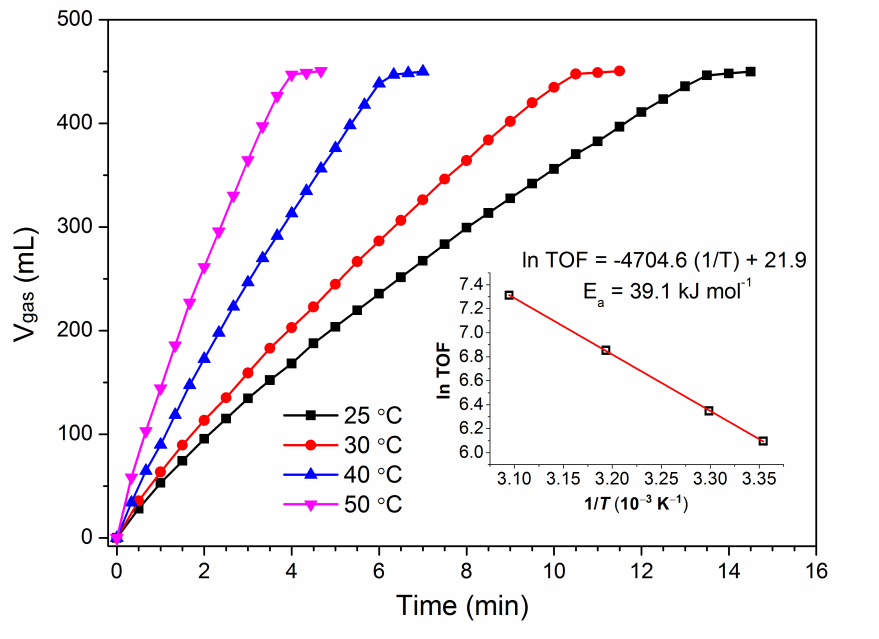

Figure S12. Volume of the generated gas (CO_2 + H_2) versus time for the dehydrogenation of FA/SF (1:1) at different temperatures over Pd/MSC-30 prepared without NaOH (n_{Pd}/n_{FA} = 0.01). Inset: Arrhenius plot (ln(TOF) vs. 1/*T*).

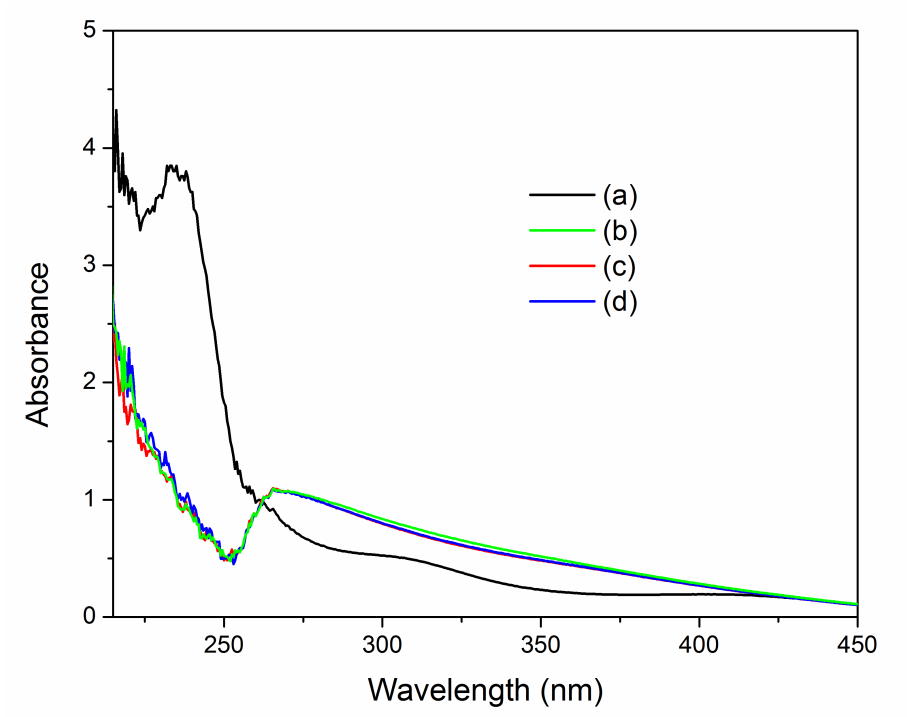

Figure S13. UV-Vis spectra of aqueous K_2PdCl_4 solution (a) in the absence and presence of NaOH with [NaOH]/[K_2PdCl_4] ratios of (b) 10, (c) 20 and (d) 30.

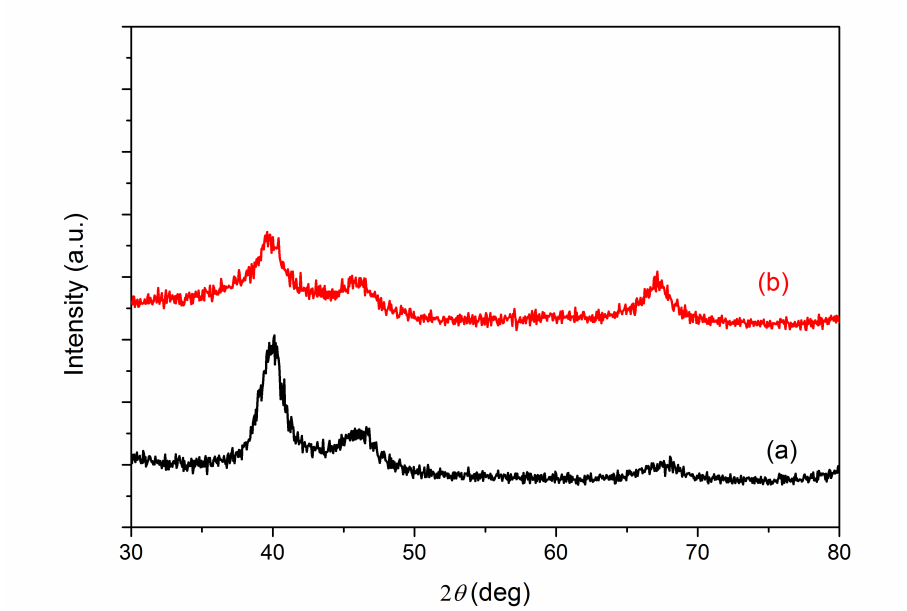

Figure S14. PXRD patterns of Pd/MSC-30 catalyst prepared with NaOH (a) before and (b) after catalysis.

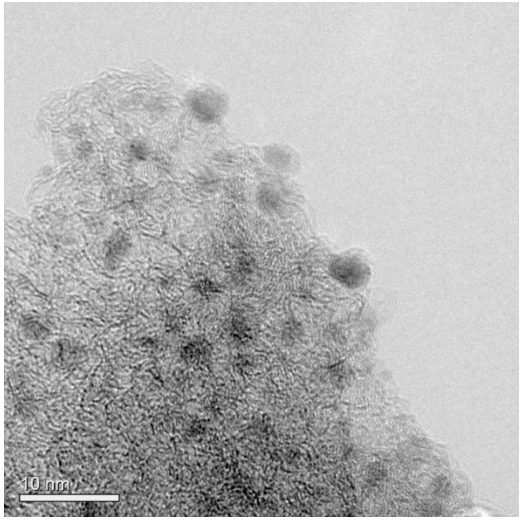

Figure S15. TEM image of Pd/MSC-30 catalyst prepared with NaOH after catalysis.

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