

Supporting Information

Straightforward Synthesis of Hierarchically Porous Nitrogen-Doped Carbon via Pyrolysis of Chitosan/Urea/KOH Mixtures and Its Application as a Support for Formic Acid Dehydrogenation Catalysts

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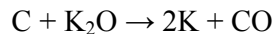
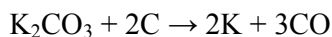
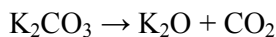
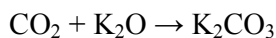
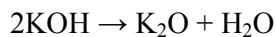
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- Number of pages: 7
- Number of figures: 4
- Number of tables: 2

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- Chemical reactions during activation with KOH

Chemical activation with KOH involves the following reactions.³⁶



- Calculation method of conversion

The conversion of formic acid was calculated as follows.⁴¹

$$\text{Conversion [\%]} = P_{\text{atm}} V / (2RTn_{\text{FA}}) \times 100$$

where P_{atm} is the atmospheric pressure (101325 Pa), V is the produced H_2 and CO_2 mixture gas volume, R is the universal gas constant ($8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$), T is the room temperature (298 K), and n_{FA} is the initial mole of formic acid.

- Supporting tables and figures

Table S1. Synthesis conditions of KIE-8 samples.

Sample code	KOH/chitosan	Urea/chitosan	Pyrolysis
	weight ratio [-]	weight ratio [-]	temperature [°C]
KIE-8-a	0	0	800
KIE-8-b	1.33	0	800
KIE-8-c	0	6	800
KIE-8-d	1.33	6	700
KIE-8-e	1.33	6	800
KIE-8-f	1.33	6	900
KIE-8-g	1.33	6	1000

Table S2. Catalytic activity comparison of various heterogeneous catalysts for formic acid dehydrogenation.

Catalysts	Additive	Temperature [°C]	TOF ^a	TOF ^b	TOF ^c	TOF ^d	TOF ^e	TOF ^f	Reference
			initial 10 min	initial 20 min	initial 15% conv.	initial 20% conv.	initial 30% conv.	Full conv.	
Pd/KIE-8	HCOONa	25	280.7	238	320	296	269	-	This work
Pd/CN	-	25	-	-	752	-	-	-	[39]
CoAuPd/Vulcan XC-72	-	25	80	-	-	-	-	-	[40]
PdAgMnO _x /N-SiO ₂	-	25	-	-	-	330	-	-	[41]
AuPd/C-L-7.5	HCOONa	25	-	-	-	-	1153	-	[42]
Au@Pd/N-mrGO	-	25	-	89.1	-	-	-	-	[43]
CoAuPd/DNA- rGO	-	25	-	85	-	-	-	-	[44]
(Co ₆)AgPd/RGO	HCOONa	50	-	-	-	-	-	2739	[45]
Pd/C	HCOONa	60	-	-	-	-	-	7256	[46]
Pd/N-MSC-30	HCOONa	60	-	-	-	-	-	8414	[47]

TOF was calculated ^a at initial 10 min of reaction time (TOF = mole of produced hydrogen gas per hour/mole of metal catalyst), ^b at initial 20 min of reaction time, ^c at initial 15 % conversion, ^d at initial 20 % conversion, ^e at initial 30 % conversion, ^f at full conversion.

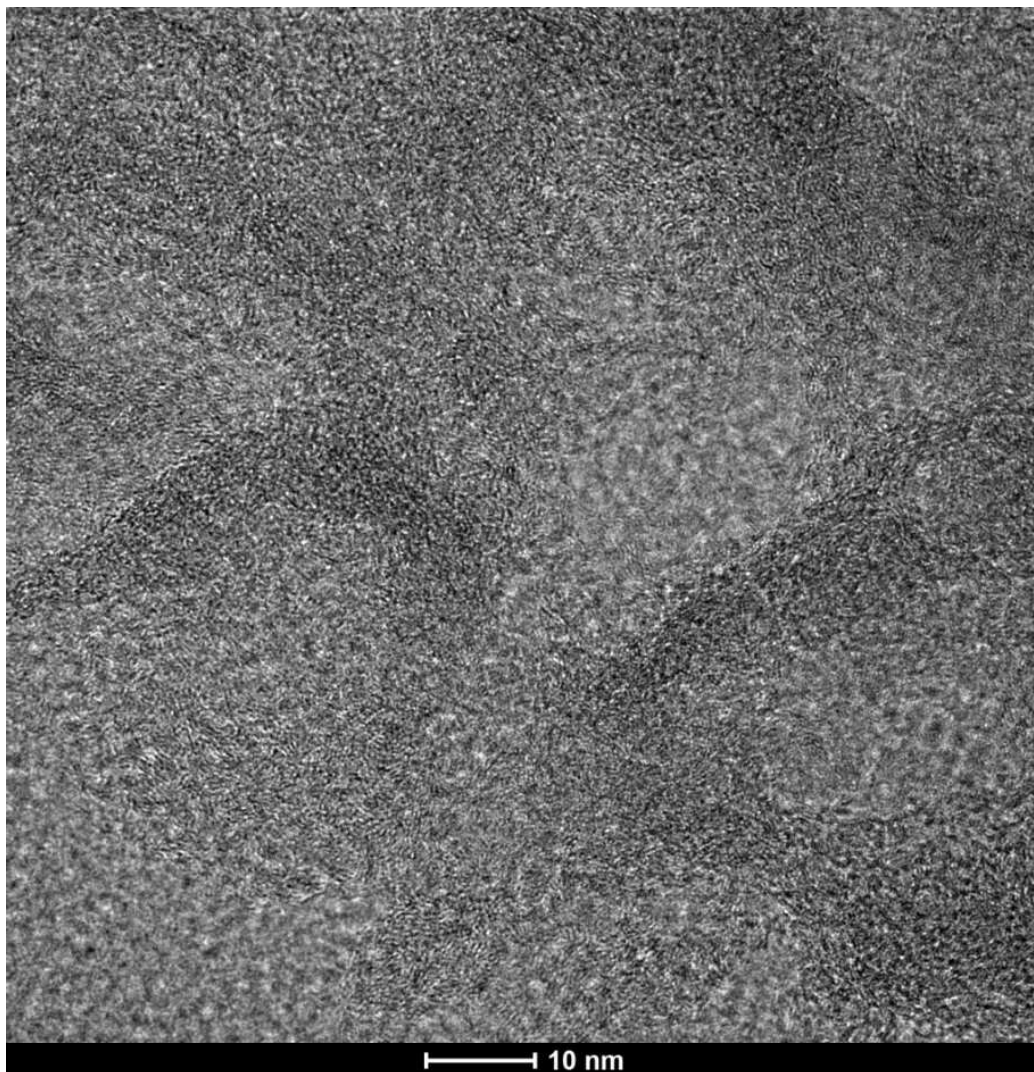


Figure S1. A high magnification TEM image of KIE-8-c (scale bar: 10 nm).

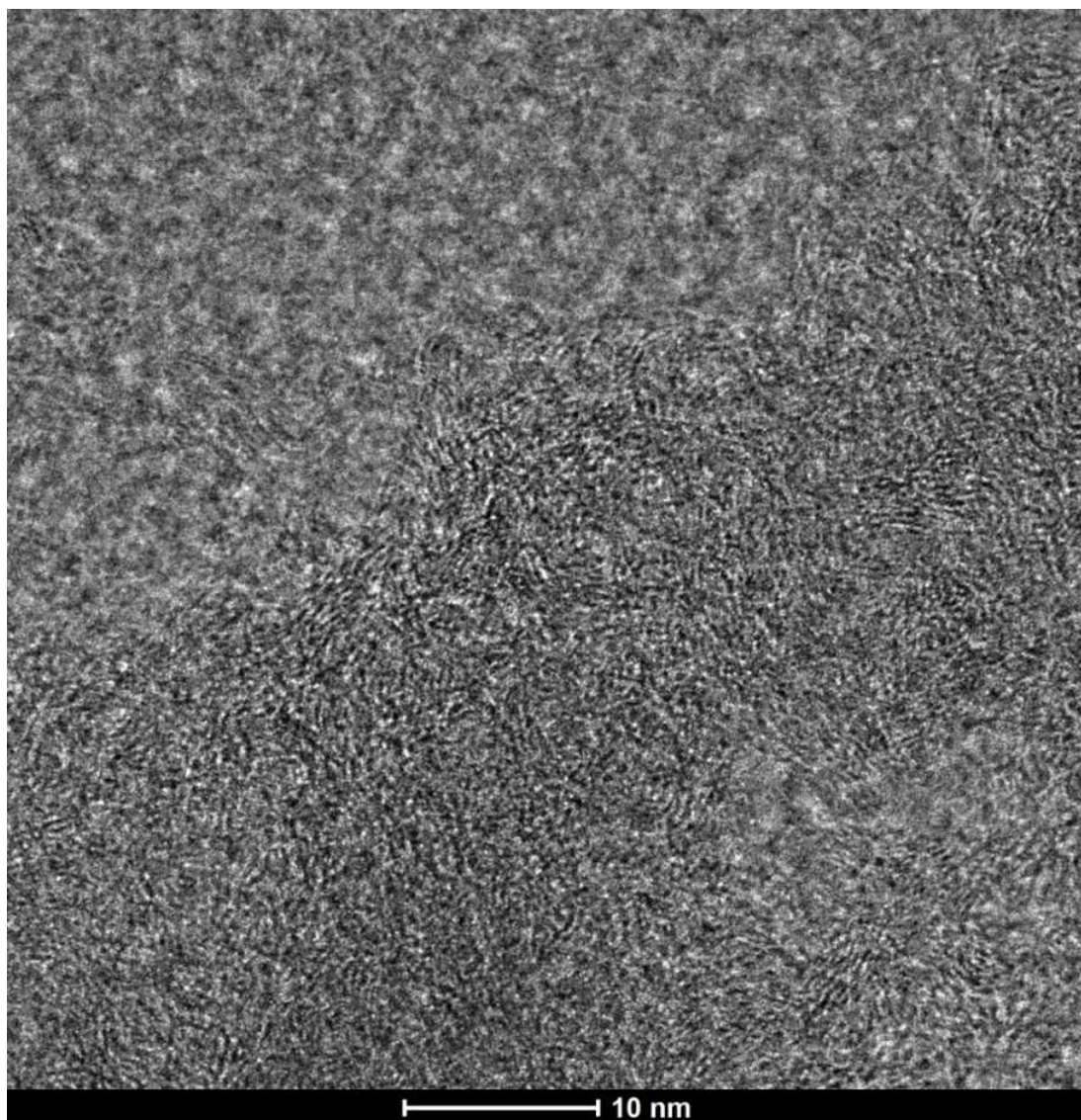


Figure S2. A high magnification TEM image of KIE-8-f (scale bar: 10 nm).

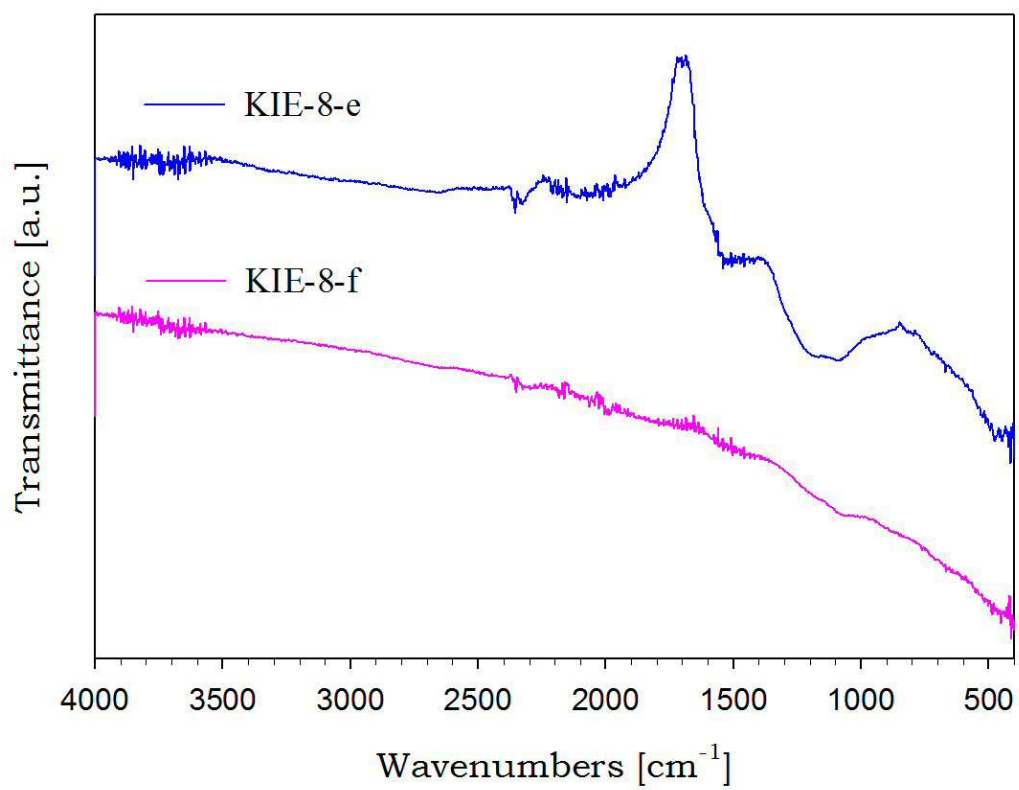


Figure S3. FTIR spectra of KIE-8-e and KIE-8-f.

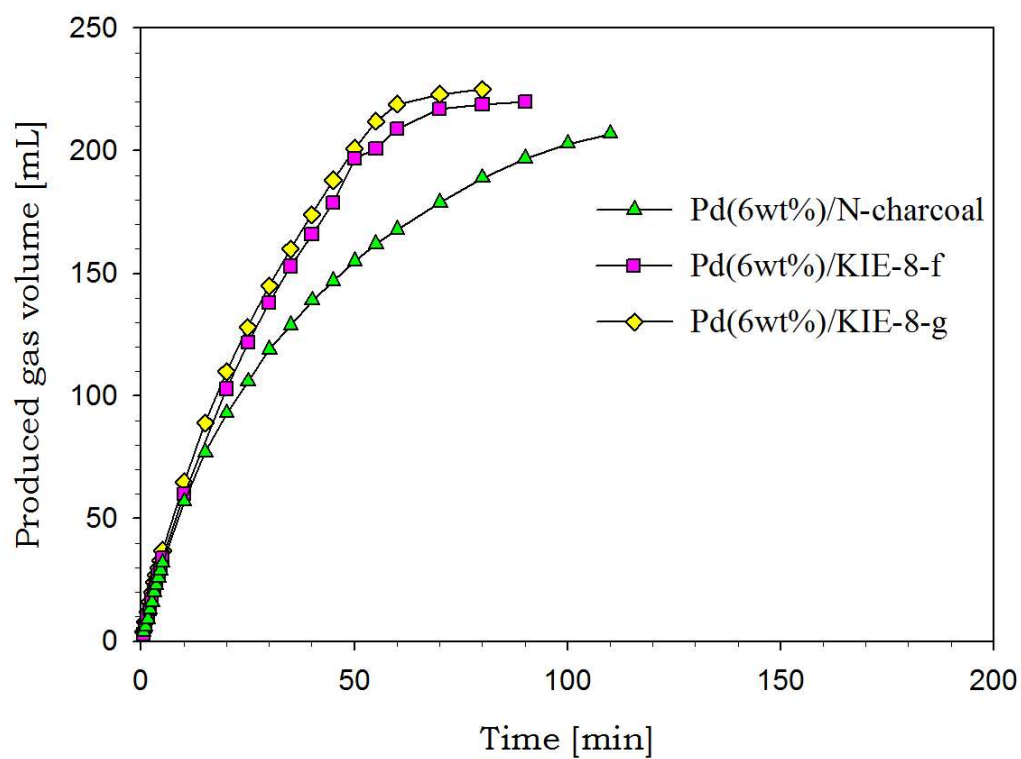


Figure S4. Comparison of formic acid dehydrogenation activity of Pd/KIE-8 with Pd/N-activated charcoal.