Electronic Supplemental Information to

Doping Pd/SiO₂ with Na⁺: changing the reductive etherification of C=O to furan ring hydrogenation of furfural in ethanol

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Table S1. Pd loading, particle size and textural properties of Pd/SiO_2 and $Pd-Na/SiO_2$ catalysts

Catalyst	Pd ^a	SSA ^b	V_{total}^{c}	\mathbf{D}^{d}	
	(wt.%)	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(nm)	
Pd-SiO ₂	2.2	227	1.0	8.7	
Pd-Na/SiO ₂	2.0	155	1.3	4.6	

- a. Determined by ICP.
- b. Calculated by N_2 adsorption with BET method.
- c. Determined from the adsorption amount of nitrogen at $P/P_0 = 0.99$.
- d. Average size of NPs determined by TEM investigation.

Table S2.	Catalytic	hydrogenation	of fu	ırfural	in	ethanol	over	Pd/SiO_2	under	different
temperatu	re and H ₂	pressure. ^a								

Tener	TT	Correct	Sel. (%) ^b					
Temp.	H_2	Conv.	FFF				THF	
(°C)	(MPa)	(%)	EFE	FDA	THFDA	ΓА	А	
80	0.3	91	35	30	2	19	5	
100	0.3	100	58	0	0	7	9	
120	0.5	100	50	0	14	10	8	
120	1	100	7	0	22	0	26	

^a Reaction conditions: 100 mg of catalyst; reaction time 1 h.

^b In some cases, other products (not shown) due to the decomposition of EFE were detected.

Table S3. The activities of furfural acetalization with ethanol over SiO_2 , alkaline-treated
SiO_2 and Pd/SiO_2 catalysts. Reaction conditions: 10 mL of 0.24 M FAL ethance
solution; 120 °C; 100 mg catalyst; 30 min.

Sample	Conv. (%)
SiO ₂	51
SiO ₂ -Na	0
SiO ₂ -K	0
Pd/SiO ₂	44
Pd-Na/SiO ₂	0
Pd-K/SiO ₂	0

Table S4. Catalytic hydrogenation results of 180 μ L of FDA in 10 mL of ethanol over Pd/SiO₂ in presence of 20 μ L of furfural or furfuryl alcohol for 10 min under 120 °C and 0.3 MPa H₂ pressure.

Additivo	FDA Conv.	Sel. (%)				
Additive	(%)	EFE	THEFE	THFDA	THFA	
Fufural (FAL)	91	34	11	29	8	
Furfuryl alcohol (FA)	12	22	10	60	-	



Figure S1. The Na 1s XPS spectra of Pd/SiO_2 and $Pd-Na/SiO_2$ catalysts.

Figure S2. Catalytic hydrogenation of furfural in isopropanol over Pd(-Na)/SiO₂ catalyst. Reaction conditions: 10 mL of 0.24 M FAL ethanol solution; 120 °C; 0.3 MPa H₂; 100 mg catalyst.



Figure S3. Catalytic hydrogenation of furfural over Pd-K/SiO₂ catalyst. Reaction conditions: 10 mL of 0.24 M FAL ethanol solution; 120 °C; 0.3 MPa H₂; 100 mg catalyst.

