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Supporting Information

Interfacial electronic effects of palladium nanocatalysts on the by-product ammonia selectivity during nitrite catalytic reduction

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Figure captions:

Fig. S1 (a, c) TEM images and (b, d) Pd nanoparticle size distributions of Pd-EtOH@MIL-101 and Pd-C12T@MIL-101, respectively.

Fig. S2 XPS spectra of support MIL-101 and Pd-based catalysts.

Fig. S3 S 2p level XPS spectrum of Pd-C12T@MIL-101.

Fig. S4 Adsorption behavior of (a) nitrite and (b) ammonia by Pd@MIL-101, Pd-EtOH@MIL-101 and Pd-C12T@MIL-101.

Fig. S5 (a) Nitrite reduction (solid symbols) and ammonia yield (hollow symbols) over ethanolic solvothermal treated Pd@MIL-101 at different temperature, respectively ((■, □) 20℃, (●, ○) 40℃, (▲, △) 60℃,(▼,▽)80℃). (b) Corresponding ammonia selectivity at different ethanolic solvothermal treatment temperature. (c) Catalytic nitrite reduction over vacuum treated Pd-EtOH@MIL-101. (d) Corresponding ammonia selectivity.

Fig. S6 Effect of reaction temperature on nitrite catalytic reduction over Pd@MIL-101 (top), Pd-EtOH@MIL-101 (middle) and Pd-C12T@MIL-101(bottom). (a, c and e) nitrite degradation curves and (b, d and f) corresponding regression curves.

Table captions:

Table S1 The rate constant *k* of nitrite catalytic reduction over Pd-based catalysts at different temperature.

Experimental methods

Ethanolic solvothermal treated Pd@MIL-101 at different temperature

Typically, 200 mg of as-synthesized Pd@MIL-101 and 40 ml of anhydrous ethanol were added to a 100 ml of round-bottom flask and sonicated for ca. 10 min. After that, the suspension was stirred at 20, 40, 60, and 80 ℃ for 12 h, respectively. The green solid was collected by filtration and washed with amounts of ethanol, and then dried at room temperature under an inert flow of argon.

High temperature vacuum treated Pd-EtOH@MIL-101

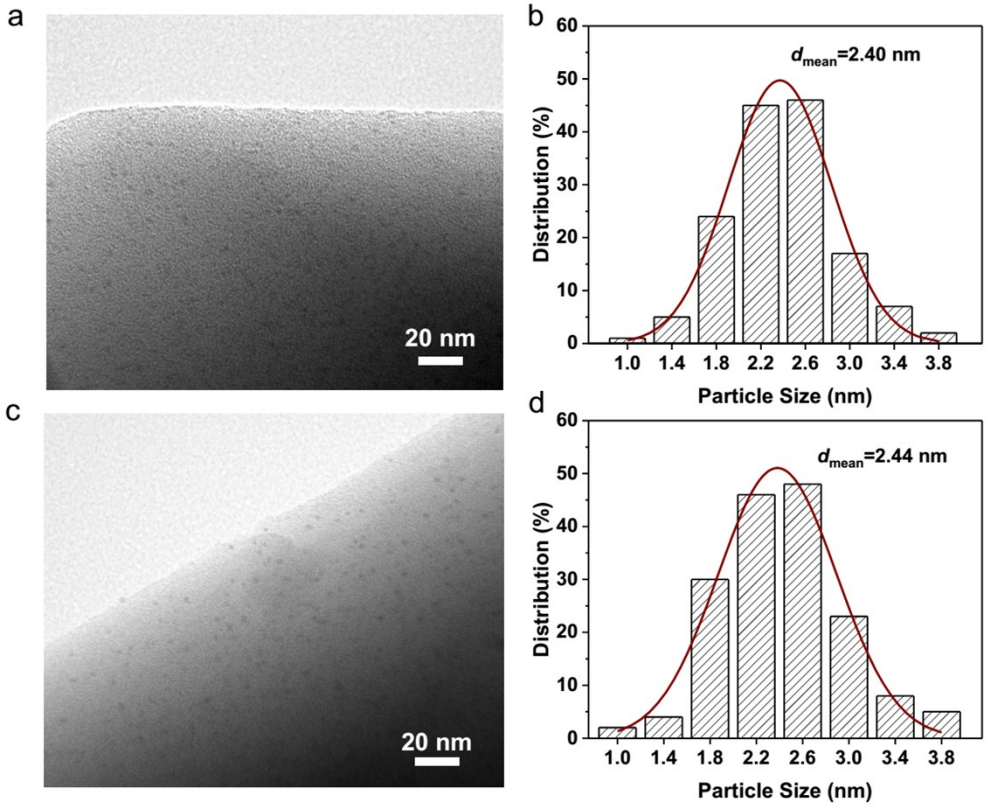
Typically, 200 mg of as-synthesized Pd-EtOH@MIL-101 catalyst was placed and dried in a vacuum oven at 70 ° C for 48 hours.

Nitrite catalytic reduction experiments

Nitrite reduction experiments were performed in a 100 ml home-build sealed semi-batch reactor with a pair of gas inlet and outlet. The reaction temperature and stirring rate were controlled by a water bath with magnetic stirring. Typically, 95 ml of ultrapure water was added into the reactor under stirring at ca. 500 rpm and bubbled with a flow of H_2 (50 ml/min) at atmosphere pressure for 30 min to remove the dissolved oxygen of water. Afterwards, 30 mg of ethanolic soaking treated Pd@MIL-101or high temperature vacuum treated Pd-EtOH@MIL-101 catalyst pre-dispersed in 4 ml of water was introduced into the reactor with a syringe, and a flow of CO_2 (50 ml/min) was also bubbled into the water at the same time to maintained the pH value of hydrogenation system at 5.5 ± 0.5. The H_2 pressure and flow rate remained constant throughout the experiment. Nitrite was then added into the reactor to obtain the initial nitrite concentration of 7.0 $mg \cdot L^{-1}$ as N and start the reaction. During the experiment, samples were withdrawn at the regular time intervals and filtered by 0.22 μm membranes for concentration determination.

Adsorption experiments

All the adsorption experiments were carried out under N_2 replaced H_2 at 25℃, and other experimental processes were same as those of catalytic nitrite reduction experiments. It should be pointed out that the initial ammonia concentration was 1.0 mg·L-1 as N in the ammonia absorption experiment.



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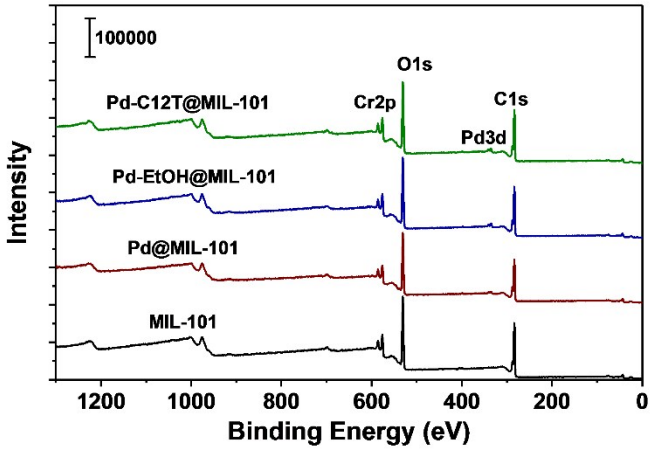


Fig. S2 XPS survey spectra of support MIL-101 and Pd-based catalysts.

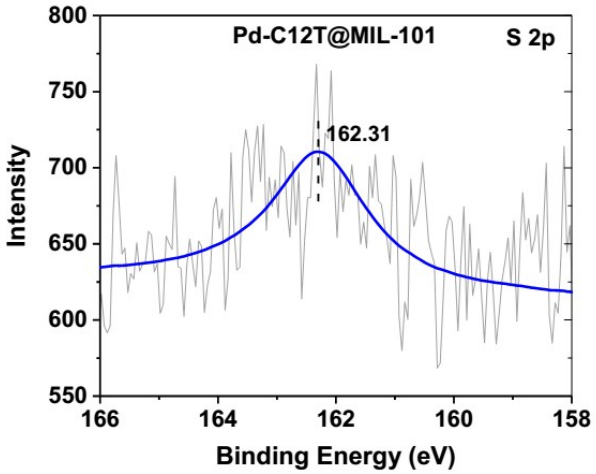


Fig. S3 S 2p level XPS spectrum of Pd-C12T@MIL-101.

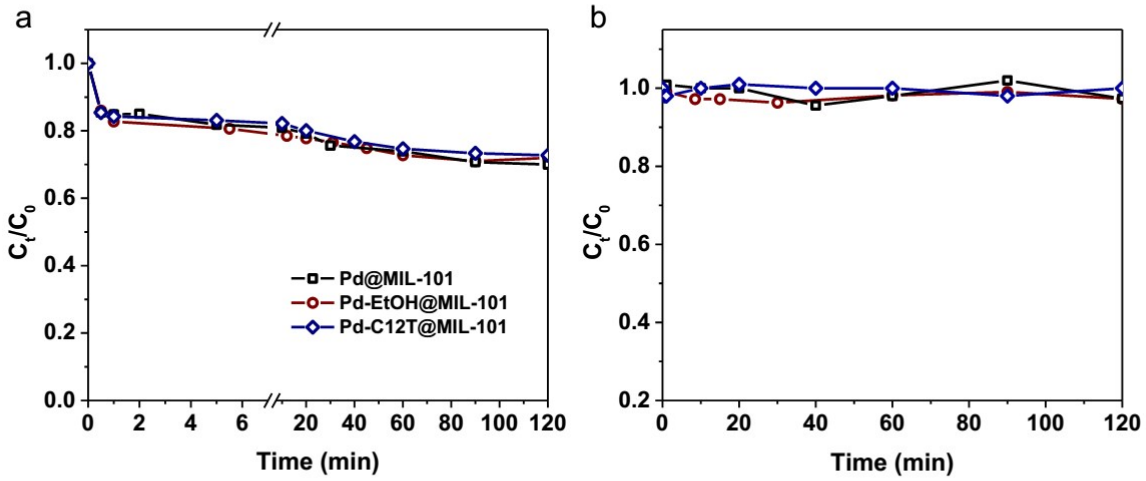
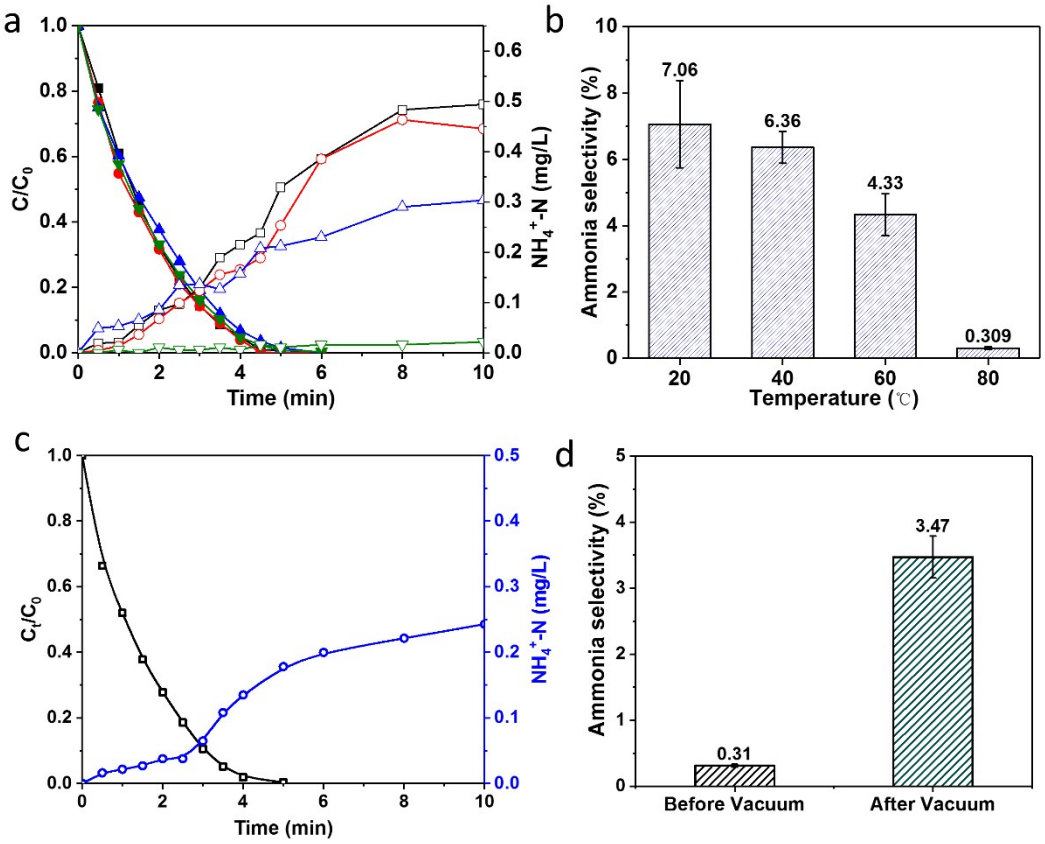


Fig. S4 Adsorption behavior of (a) nitrite and (b) ammonia by Pd@MIL-101, Pd-EtOH@MIL-101 and Pd-C12T@MIL-101. ($C_{NO2-,\ initial}$ 7.0 mg/L as N, $C_{NH4+,\ initial}$ 1.0 mg/L as N, CO_2 flow rate 50ml/min, N_2 flow rate 50ml/min, temperature 25℃)



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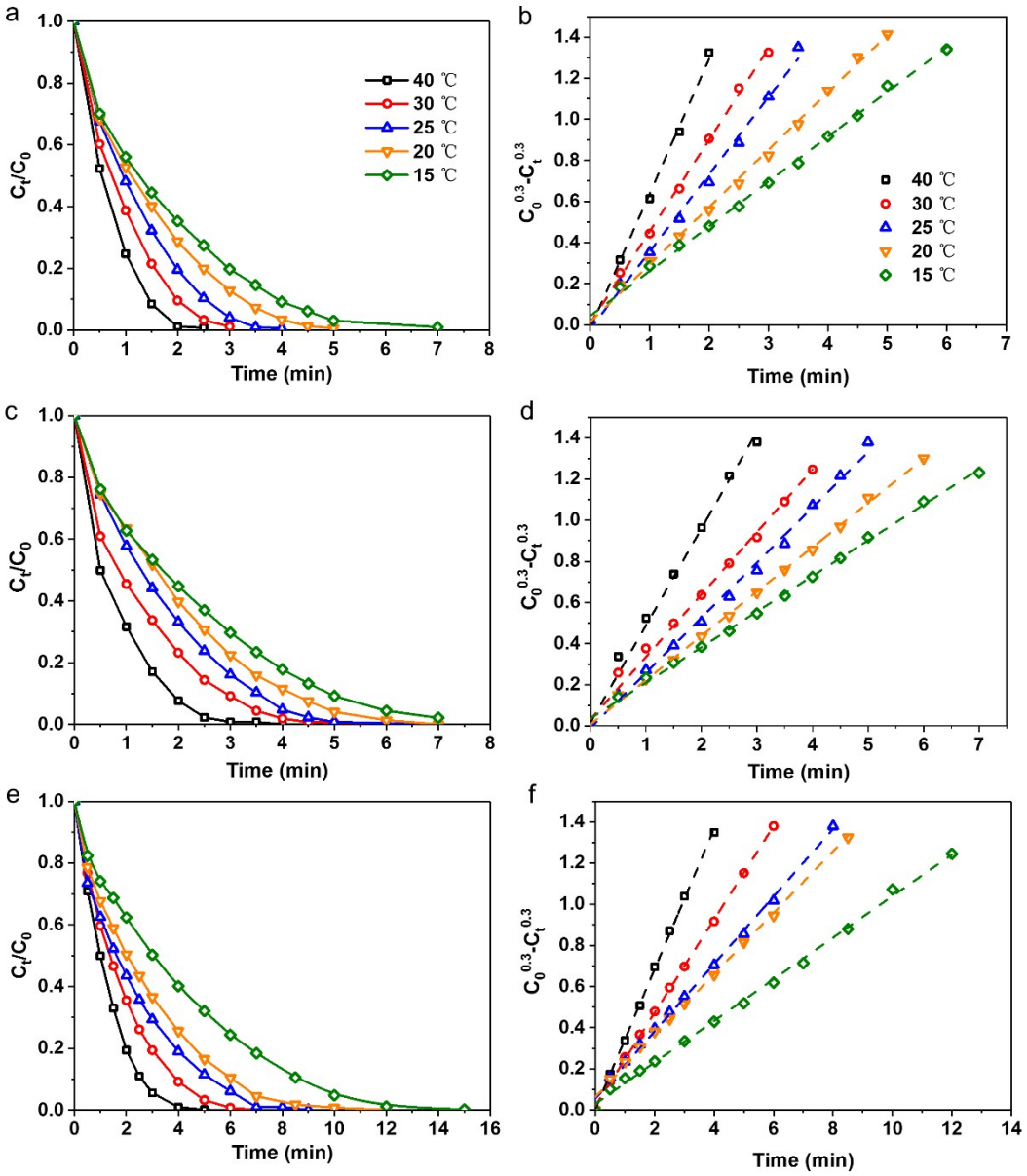

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Table S1

The rate constant *k* of nitrite catalytic reduction over Pd-based catalysts at different temperature.

Temperature	Pd@MIL-101			Pd-EtOH@MIL-101			Pd-C12T@MIL-101		
	slope[a]	*k*[b]	R^2	slope	*k*	R^2	slope	*k*	R^2
15	0.218	0.727	0.997	0.173	0.577	0.998	0.101	0.337	0.997
20	0.279	0.930	0.997	0.215	0.717	0.999	0.149	0.497	0.996
25	0.376	1.253	0.994	0.268	0.893	0.996	0.164	0.547	0.996
30	0.445	1.483	0.998	0.304	1.013	0.994	0.227	0.757	0.999
40	0.655	2.183	0.997	0.471	1.570	0.995	0.341	1.137	0.999

[a] Calculated from Fig. S6.

[b] Represent the rate constant, unit:($mg^{0.3} \cdot L^{-0.3} \cdot min^{-1}$).