

Supporting Information

Intensifying strategy of ionic liquid for Pd-based catalysts in anthraquinone hydrogenation

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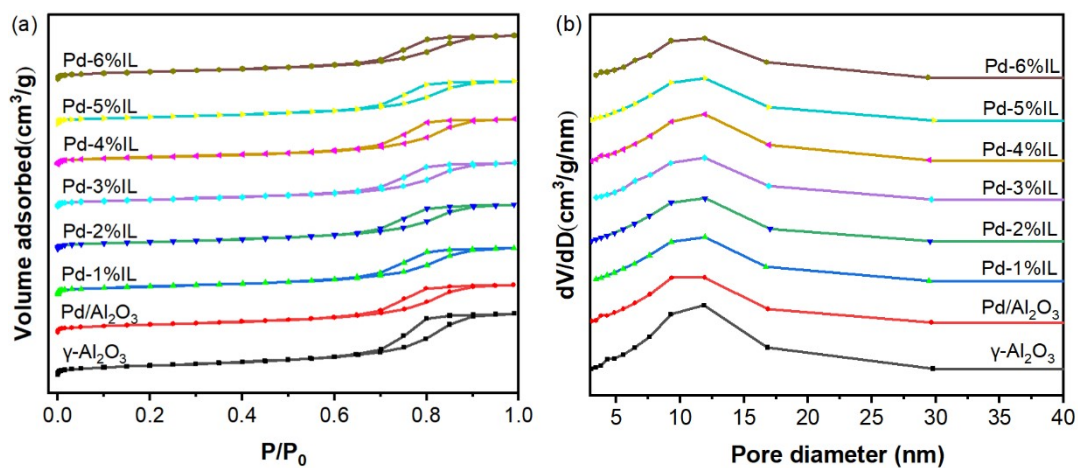


Fig. S1 (a) N_2 adsorption-desorption isotherms and (b) the pore size distributions of catalyst samples (Barrett-Joyner-Halenda (BJH) method was used to calculate the pore volume and the pore size distribution. Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area.)

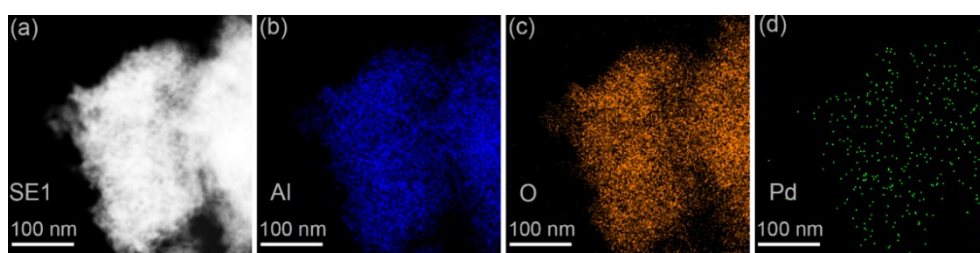


Fig. S2 (a) STEM image of Pd/Al_2O_3 catalyst; (b)-(d) elemental mapping images of Al (blue), O (orange) and Pd (green), respectively

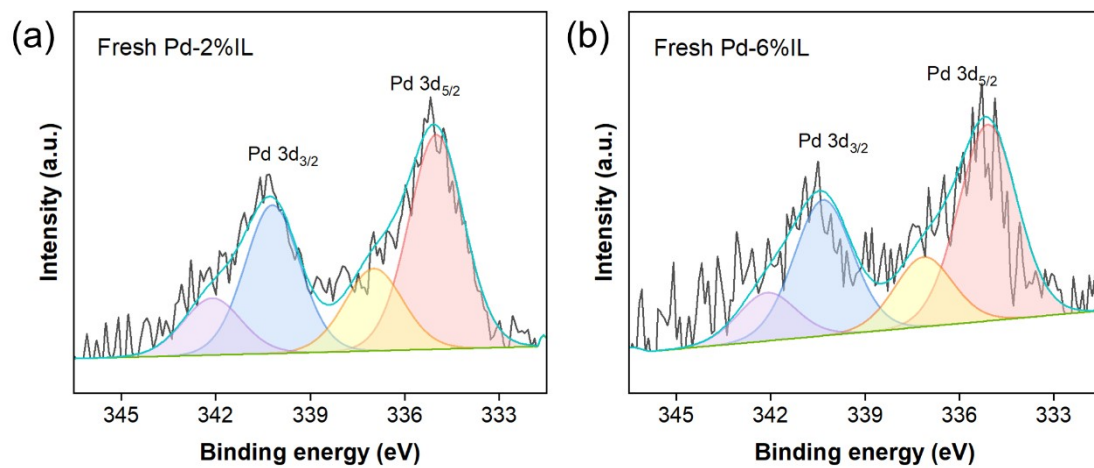


Fig. S3 XPS Pd 3d spectra of (a) fresh Pd-2%IL and (b) fresh Pd-6%IL

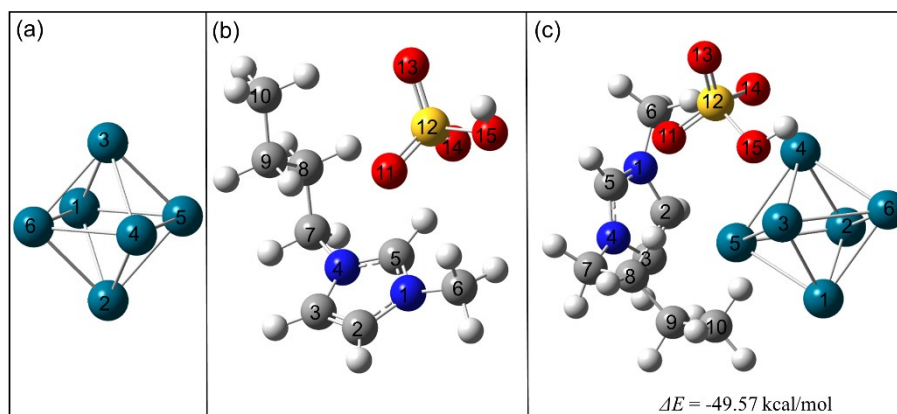


Fig. S4 The stable structures and serial number of (a) Pd₆ cluster, (b) IL and (c) Pd₆-IL.

Carbon, hydrogen, oxygen, nitrogen, sulfur, palladium atoms are depicted in gray, white, red, blue, orange and green, respectively.

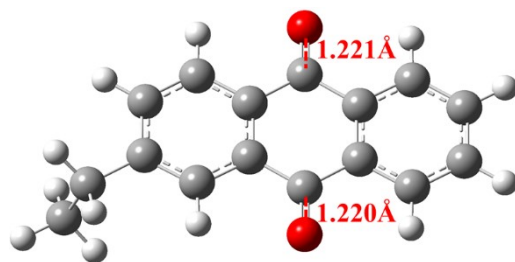


Fig. S5 The stable structure of EAQ. Carbon, hydrogen, oxygen, are depicted in gray, white and red, respectively.

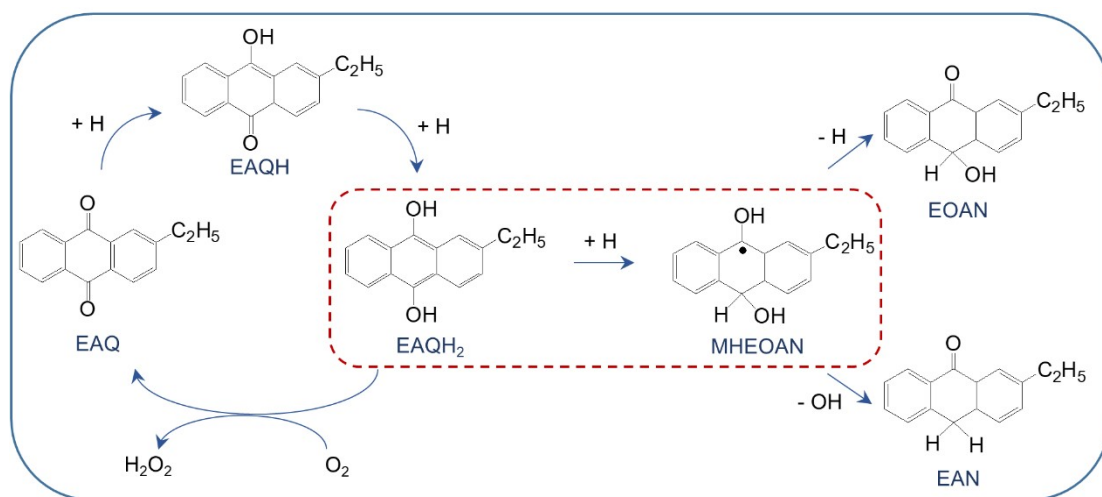


Fig. S6 Reaction paths of 2-ethyl-anthraquinone hydrogenation [1, 2].

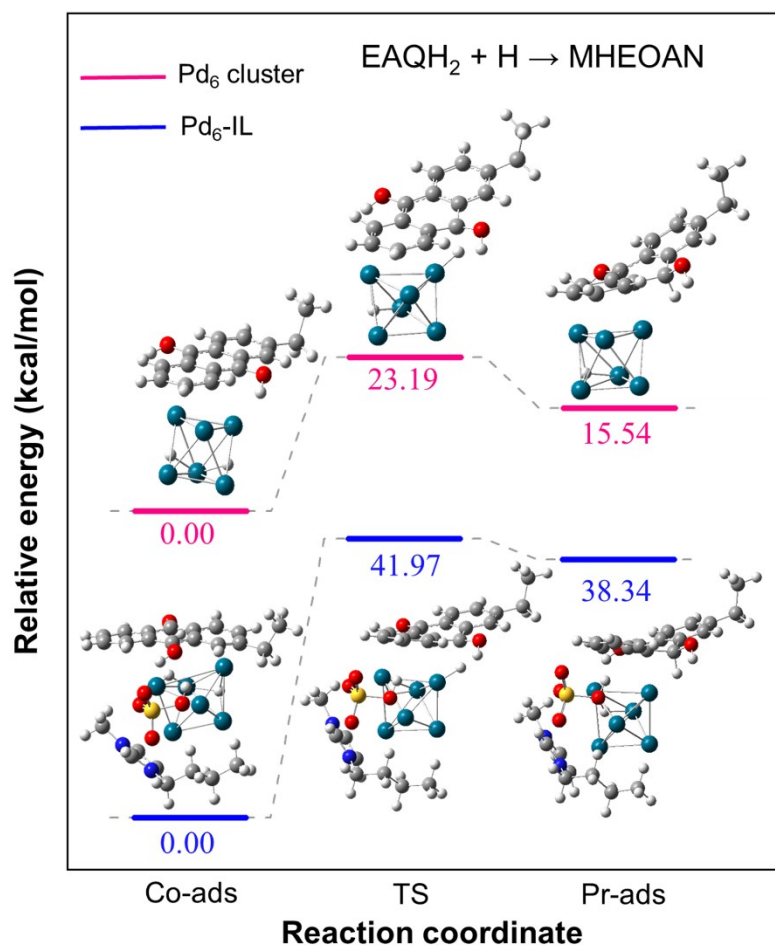


Fig.S7 The unwanted reaction pathway (EAQH₂ + H → MHEOAN) with the optimized structure in the illustration: Co-adsorbed reactants (Co-ads), transition state (TS), product-adsorbed (Pr-ads). Carbon, hydrogen, oxygen, nitrogen, sulfur, palladium atoms are represented in gray, white, red, blue, orange and green balls, respectively

Table S1 Actual load of Pd in catalysts by ICP-AES

Catalyst	Pd content (wt%)
Pd/Al ₂ O ₃	0.26
Pd-1%IL	0.24
Pd-2%IL	0.25
Pd-3%IL	0.24
Pd-4%IL	0.25
Pd-5%IL	0.28
Pd-6%IL	0.28

Table S2 STY of H₂O₂ for Pd/Al₂O₃ and Pd-4%IL catalysts with different reaction time

Sample	STY (g g _{Pd} ⁻¹ h ⁻¹)		
	15 min	30 min	45 min
Pd/Al ₂ O ₃	743	684	512
Pd-4%IL	1229	837	604

Table S3 Charge distribution of major atoms in IL before and after adsorption of Pd₆

	Atom number	IL (e)	Pd ₆ -IL (e)
Cation	N1	-0.307	-0.273
	C2	0.204	0.069
	C3	0.174	0.053
	N4	-0.304	-0.270
	C5	0.518	0.514
	C6	0.297	0.297
	C7	0.177	0.177
	C8	0.065	0.095
	C9	-0.015	0.007
	C10	0.044	0.078
Anion	O11	-0.626	-0.577
	S12	1.162	1.236
	O13	-0.549	-0.485
	O14	-0.605	-0.573
	O15	-0.236	-0.192
Total charge of major atoms		-0.001	0.156

(N1 to O15 are respectively the first to the fifteenth atoms in IL shown in Fig.S4.)

References

- [1] A. Li, Y.H. Wang, J. Ren, J.L. Zhang, W. Li, C.L. Guo, Enhanced catalytic activity and stability over P-modified alumina supported Pd for anthraquinone hydrogenation, *Appl Catal a-Gen*, 593 (2020).
- [2] T. Kamachi, T. Ogata, E. Mori, K. Iura, N. Okuda, M. Nagata, K. Yoshizawa, Computational exploration of the mechanism of the hydrogenation step of the anthraquinone process for hydrogen peroxide production, *The Journal of Physical Chemistry C*, 119 (2015) 8748-8754.