Supporting Information

Modulated electronic structure of Pd nanoparticles on $Mg(OH)_2$ for selective benzonitrile hydrogenation into benzylamine at low temperature

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Table of Contents

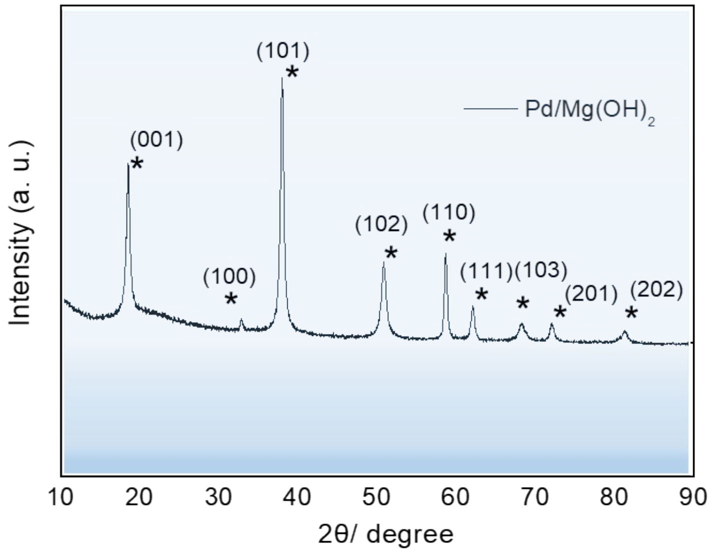


Fig. S1. XRD of the synthesized $Mg(OH)_2$.

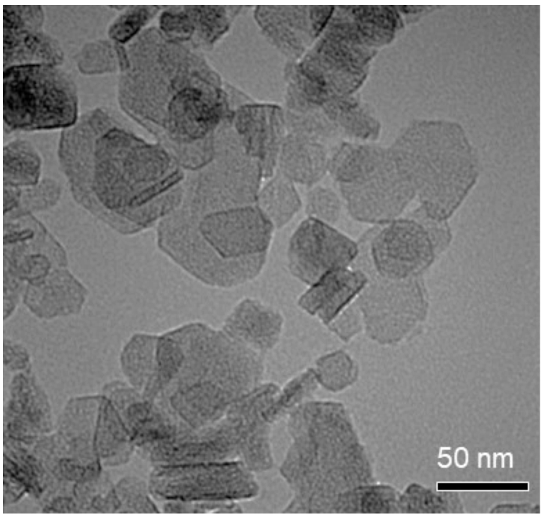


Fig. S2. TEM image of the synthesized $Mg(OH)_2$.

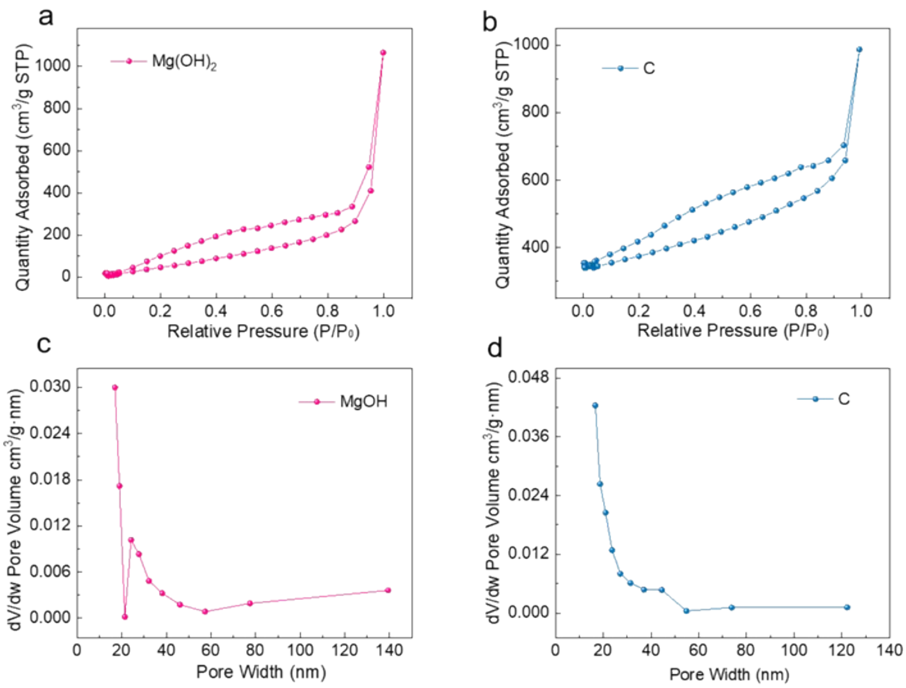


Fig. S3. (a) Nitrogen adsorption/desorption isotherm plot of the (a) $Mg(OH)_2$ and (b) C supports. Pore size distribution of the (c) $Mg(OH)_2$ and (d) C supports obtained from BET testing.

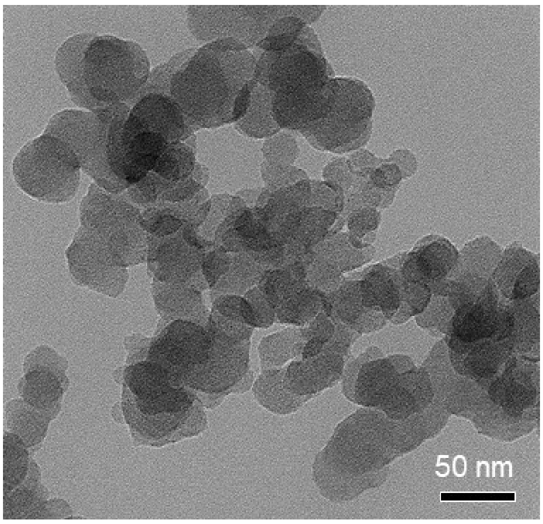


Fig. S4. TEM image of the synthesized carbon black.

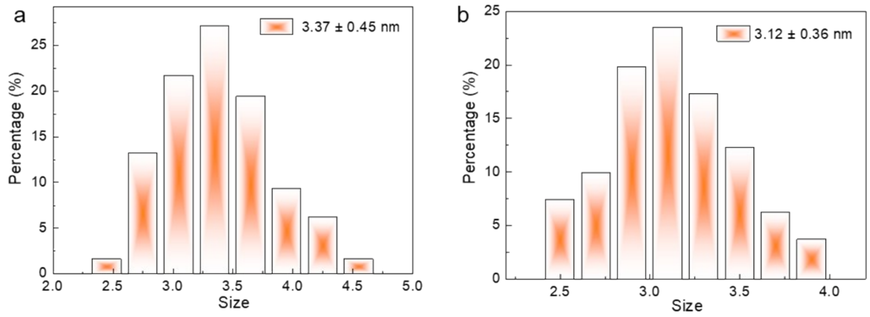


Fig. S5. Size distribution of (a) $Pd/Mg(OH)_2$ and (b) Pd/C catalysts.

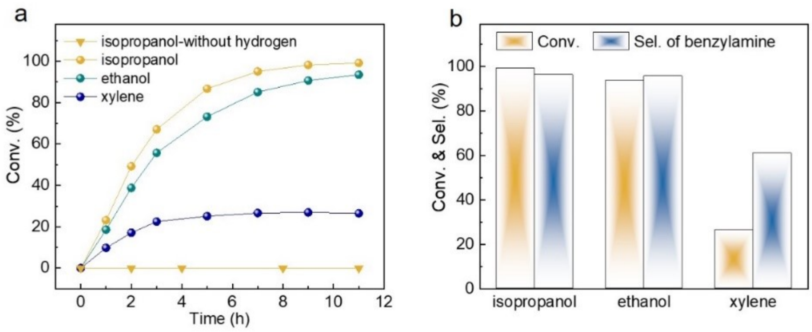


Fig. S6. Catalytic performance in different solvent. (a) Comparison on activity of different solvent. (b) Comparison on selectivity of different solvent at 11 h reaction. **Reaction condition:** 0.5 mmol of benzonitrile, 2 mL of solvent, 20 mg of catalyst, 30 °C, 1 MPa of H_2, or 0.5 mmol of benzonitrile, 2 mL of isopropanol, 20 mg of catalyst, 30 °C, 1 MPa of N_2.

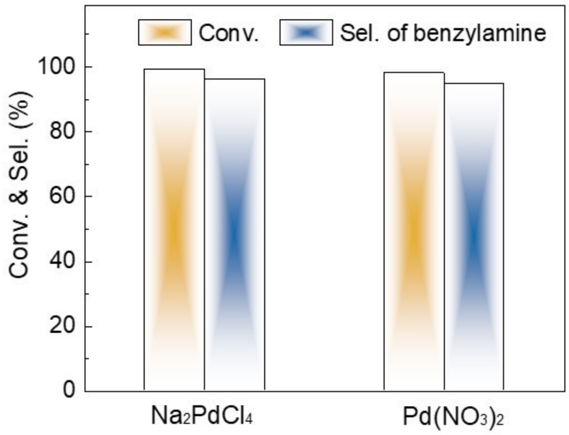


Fig. S7. Comparison between the different metal precursor. **Reaction conditions**: 0.5 mmol of benzonitrile, 2 mL of isopropanol, 20 mg of catalyst, 30 °C, 1 MPa of H_2.

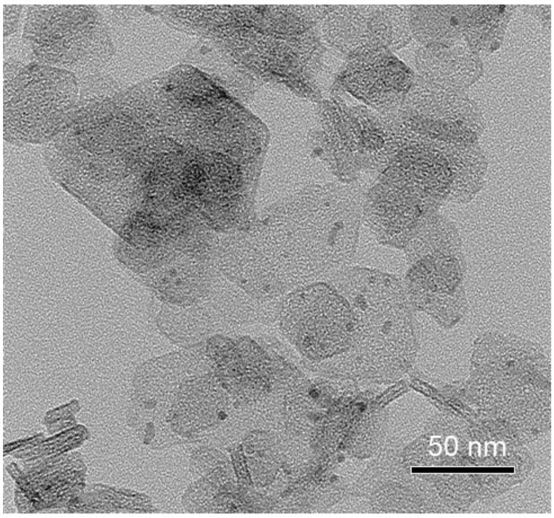


Fig. S8. TEM image of the used $Pd/Mg(OH)_2$.

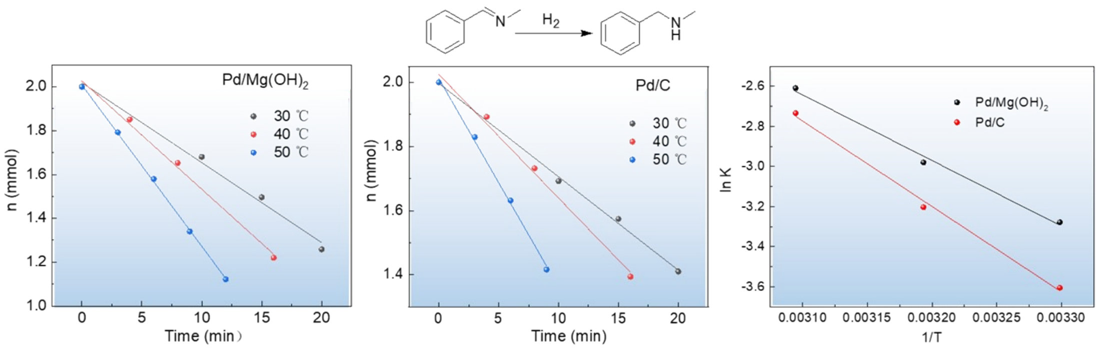


Fig. S9. Apparent activation energy calculation for *N*-benzylidenemethanamine hydrogenation. **Reaction condition**: 2 mmol of *N*-benzylidenemethanamine, 5 mg of catalyst, 2 mL of isopropanol, 1 MPa of H_2.

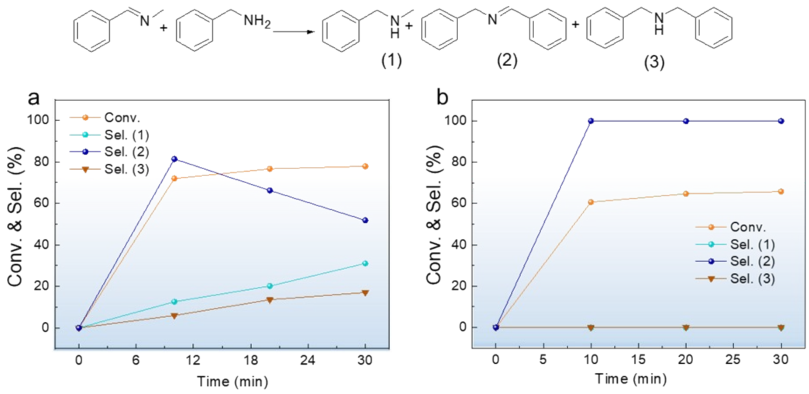


Fig. S10. *N*-benzylidenemethanamine hydrogenation in the presence of benzylamine on (a) $Pd/Mg(OH)_2$ and (b) Pd/C. **Reaction condition:** 1 mmol of *N*-benzylidenemethanamine, 1 mmol of benzylamine, 5 mg of catalyst, 2 mL of isopropanol, 30 °C, 1 MPa of H_2.

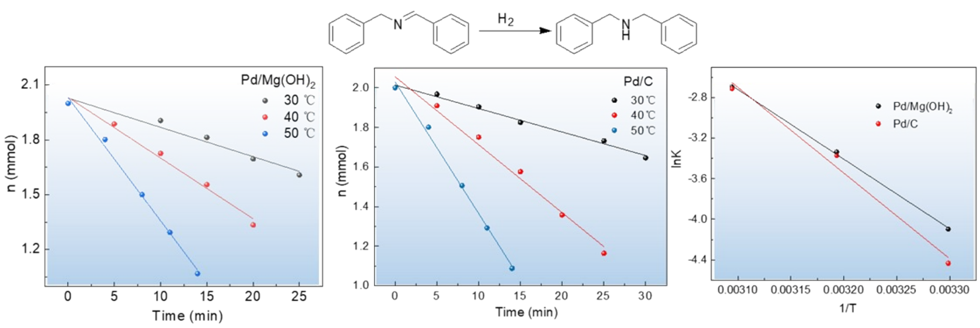


Fig. S11. Apparent activation energy calculation for *N*-benzylidenebenzylamine hydrogenation. **Reaction condition:** 1 mmol of *N*-benzylidenebenzylamine, 5 mg of catalyst, 2 mL of isopropanol, 1 MPa of H_2.

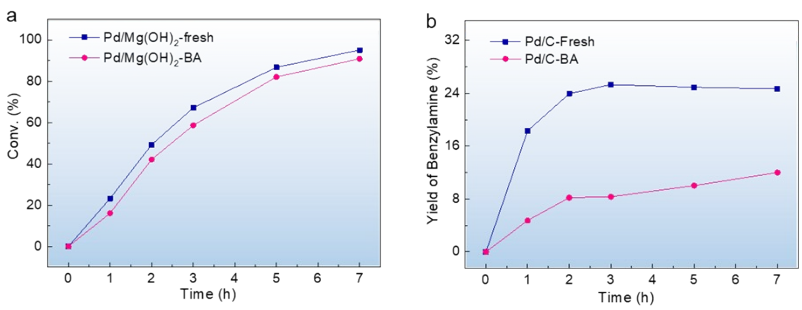


Fig. S12. Benzonitrile hydrogenation on (a) fresh Pd/Mg$(OH)_2$ and benzylamine treated Pd/Mg$(OH)_2$, and (b) fresh Pd/C and benzylamine treated Pd/C. **Reaction condition**: 0.5 mmol of benzonitrile, 2 mL of isopropanol, 20 mg of catalyst, 30 °C, 1 MPa of H_2.

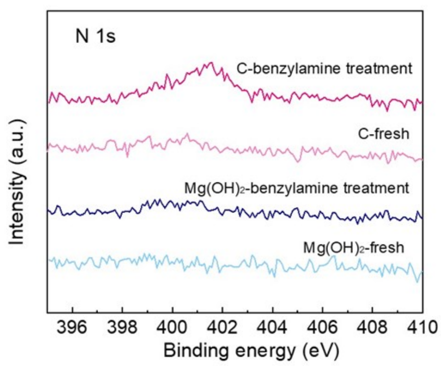


Fig. S13. N 1s spectrum of the fresh and the benzylamine treated supports.

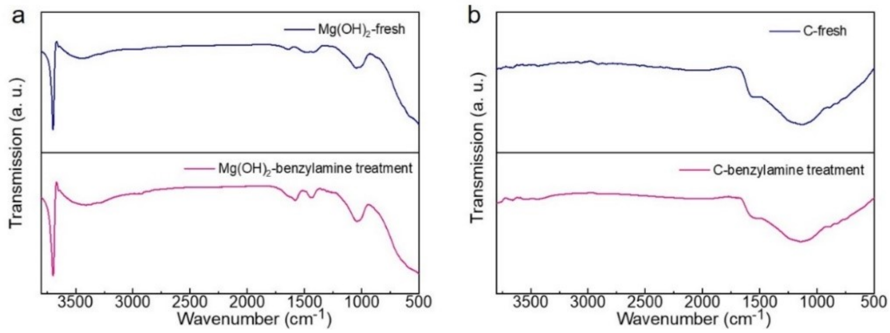
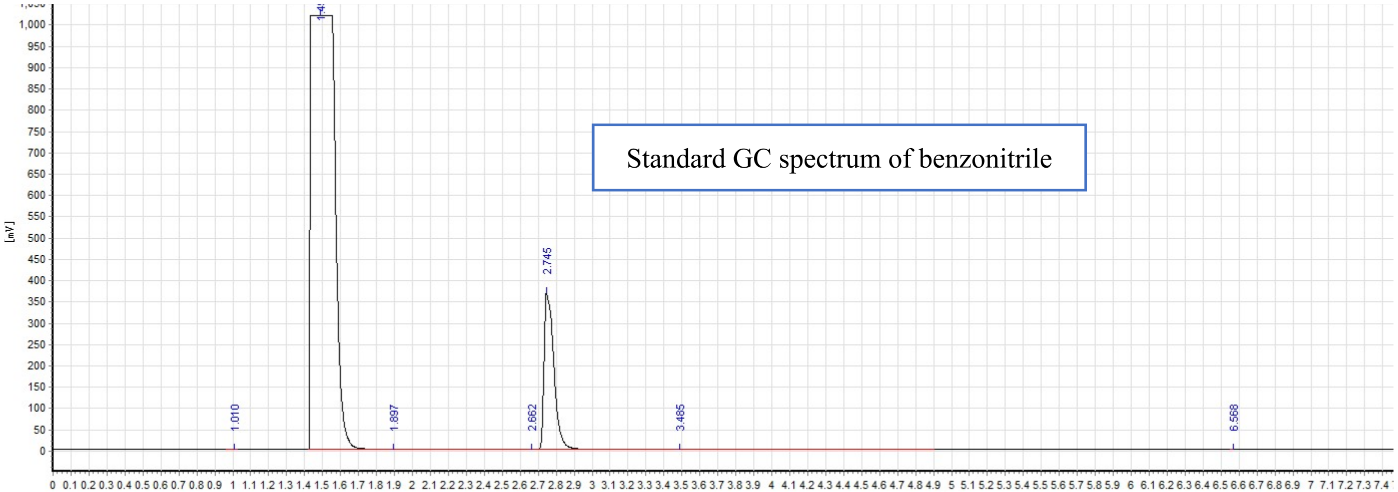


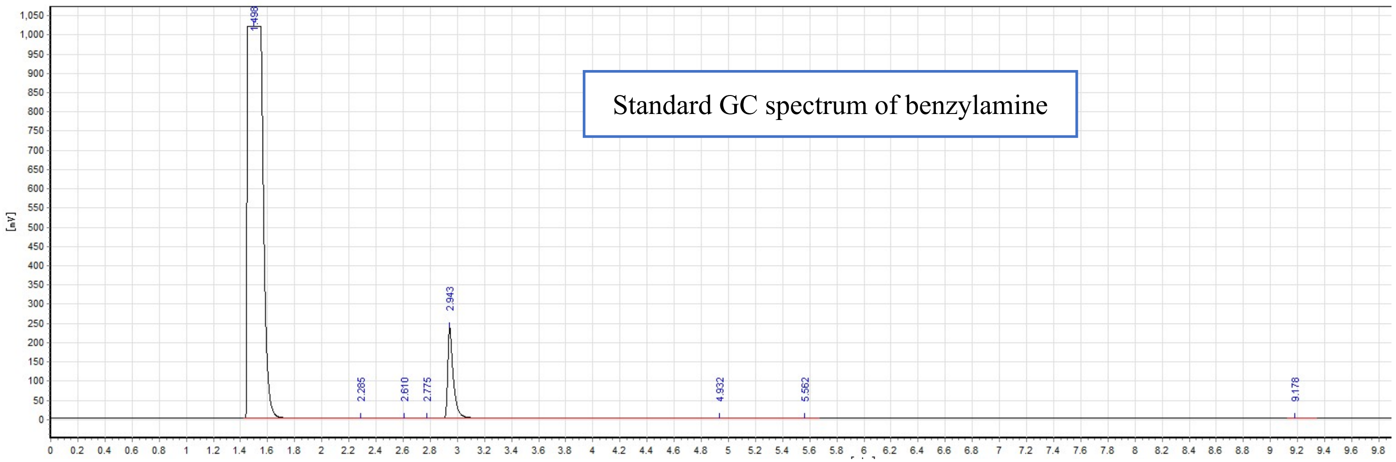
Fig. S14. FTIR characterization on the fresh and the benzylamine treated supports.

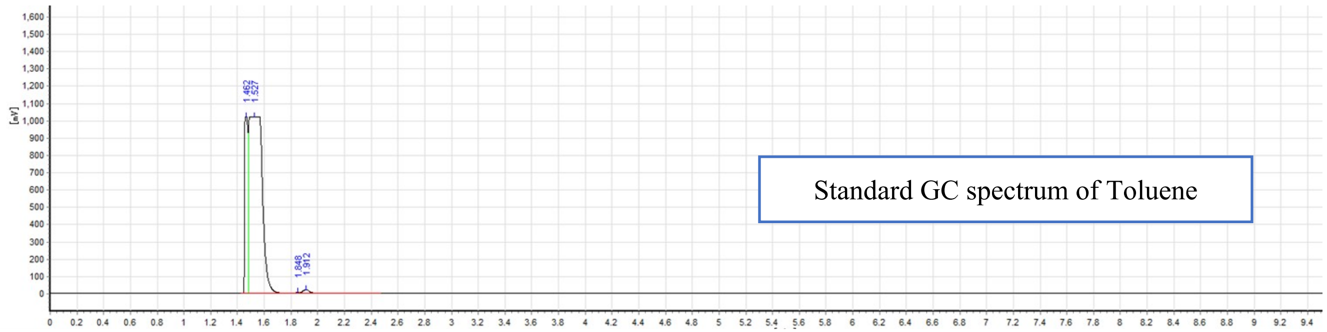
Table S1. Comparison on performance of benzonitrile hydrogenation in the reported literature

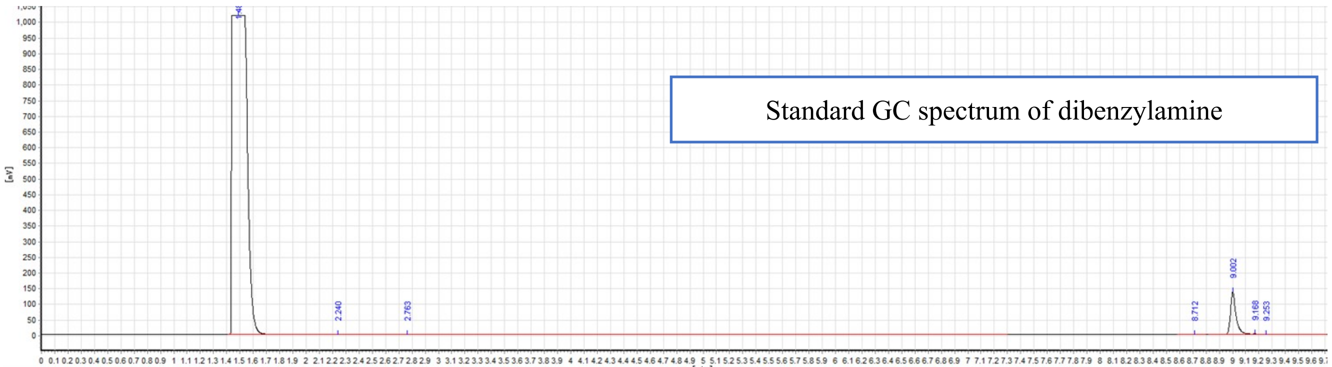
No.	Catalyst	T (℃)，pH_2 (bar)	Solvent	Additive	X_{BN} (%)	S_{BA} (%)	Ref.
1	Pd/C	30 ℃, 6 bar,	H_2O/dichloromethane	NaH_2PO_4	95.0	95.0	1
2	Raney Ni	100, 40	Methanol	None	n. a.	76.0	2
3	Sn-Pt/SiO_2	60, 4	Ethanol	None	100	20	3
4	Pt/Al_2O_3	100, 15	Methanol	Dibenzyl-hydrazine	40	40	4
5	Pd/Al_2O_3	80 ℃, 10 bar,	2-Propanol	None	50.0	94.0	5
6	Pd/MCM-41	50, 20	n. a.	CO_2 (10MPa)	90.2	90.9	6
7	Ni/Al_2O_3	80, 40	H_2O, hexane, ethanol	CO_2 (10 MPa)	97.0	94.4	7
8	Co/Phen@-Al_2O_3-800	85, 5	i-PrOH	NH_3 (aq.)	98.0	98.0	8
9	Co@NC-700	110, 10	Methanol	NH_3 (aq.)	n. a.	94.9 (yield)	9
10	Co_2P	130, 40	2-Propanol	NH_3 (aq.)	n. a.	93.0 (yield)	10
11	Ni@mSiO_2@LDH	100, 20	H_2O	None	100	76.1	11
12	$Ru_{3\text{-}CO}$/K-Alu C	70 ℃, 1	Dehydrated 1,4-dioxane/n-nonane	None	>99.0	93.0	12
13	12Cu-MgO	240, H_2/Benzontrile = 7.5	n. a.	None	98.0	70.0	13
14	Pd/γ-Al_2O_3 and Pd/ η-Al_2O_3	90, 15	n. a.	None	100	>90.0%	14
15	Pd/Al_2O_3	80, n.a.	n. a.	None	60	100	15
16	**Pd/$Mg(OH)_2$**	**30, 10**	**2-Propanol**	**None**	**99.2**	**96.1**	**This work**

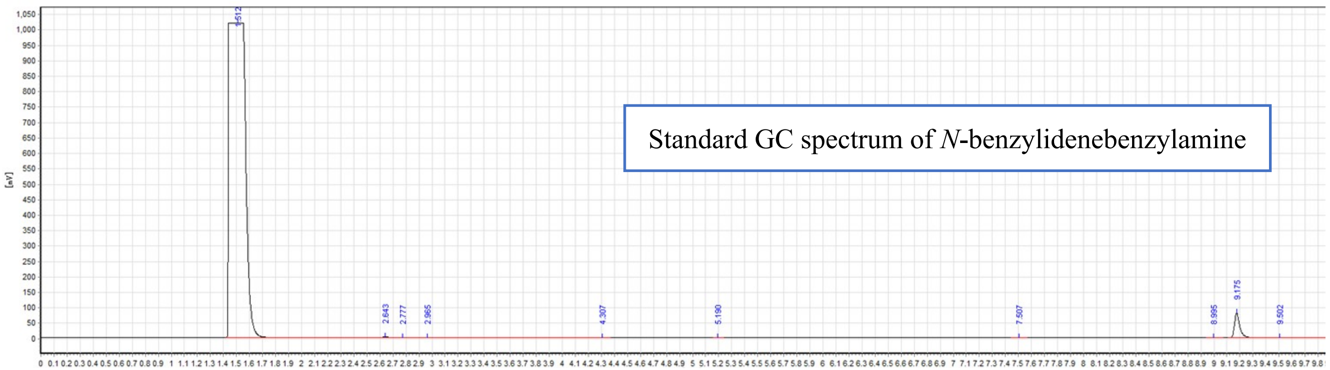
GC spectrums

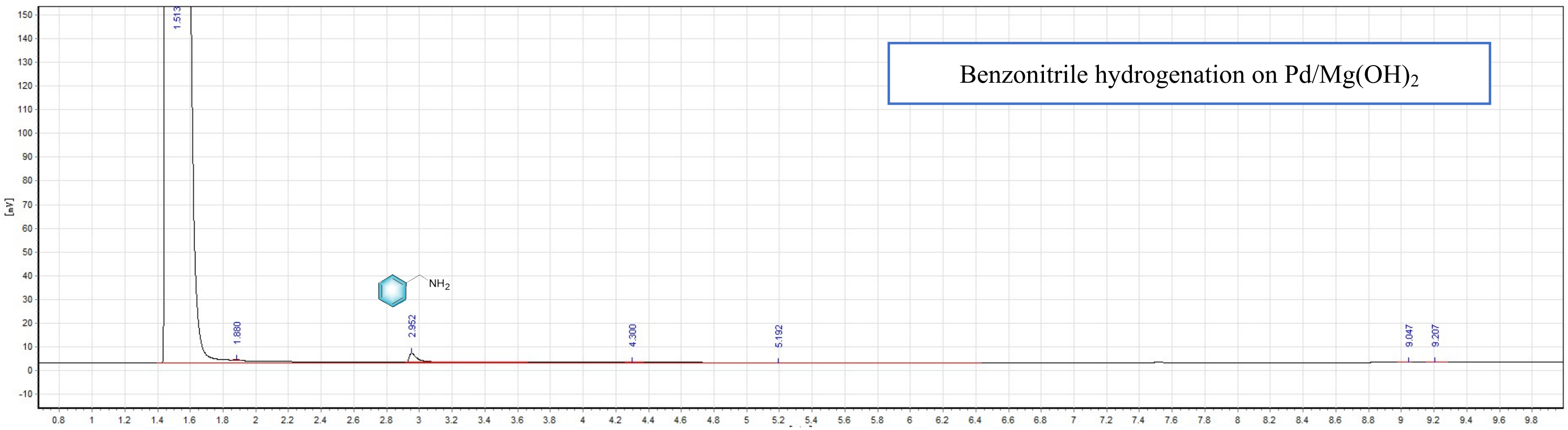





Standard GC spectrum of Toluene


Standard GC spectrum of dibenzylamine

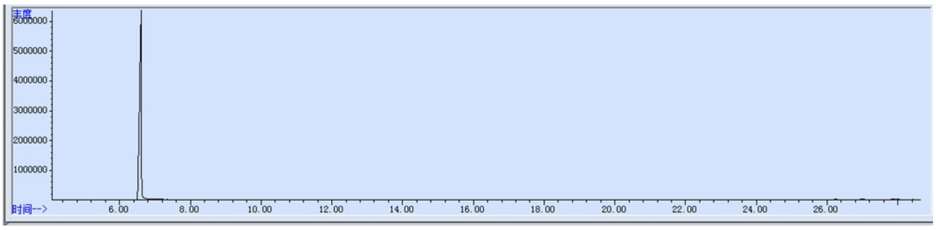

Standard GC spectrum of *N*-benzylidenebenzylamine

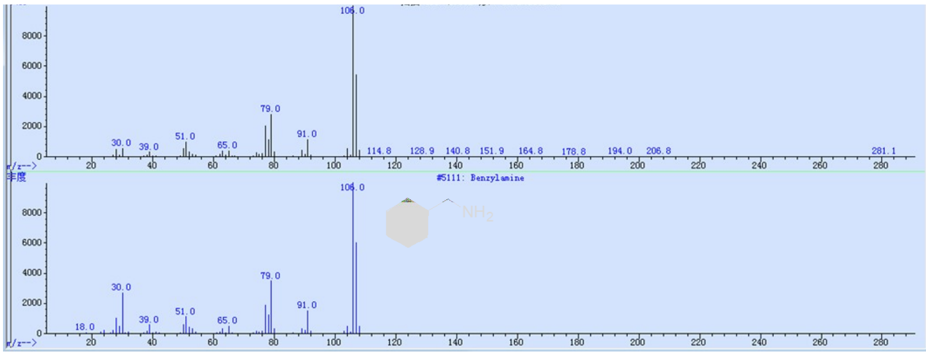


Benzonitrile hydrogenation on Pd/Mg(OH)$_2$
NH$_2$
[µV]
1.513
1.880
2.952
4.300
5.192
9.047
9.207

GCMS spectrum

GCMS standard spectrum of benzylamine





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