Electronic Supplementary Material (ESI) for RSC Advances.

Efficient hydrogenation of aromatic aldehydes to corresponding benzyl alcohols over Ni-B/MIL-101

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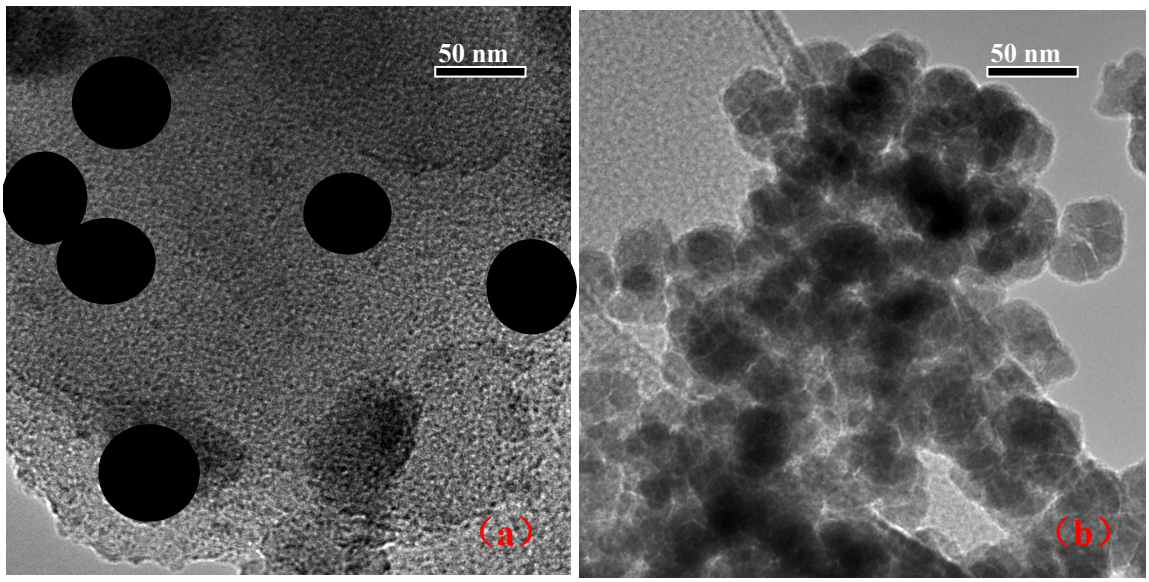

Fig.S1 (a) Ni-B/MIL-101 and (b) Ni-B/SiO_2

Table S1 The characterized results of Pd/Al_2O_3

Sample	surface area (m^2/g)	Pore volume(cm^3/g)	Pd loading [a] (wt%)	Particle size[b] (nm)	Pd dispersion[c] (%)	Binding energy [d] (eV)
Ni-B/MIL-101	145.2	0.44	0.48	7.8 ± 2.3	12.8	335.4

[a] Loading of palladium on the catalyst is measured by ICP-AES,
[b] Particle size of palladium is derived from TEM,
[c] Calculated from the H_2-chemisorption,
[d] Binding energy of palladium is characterized by XPS.

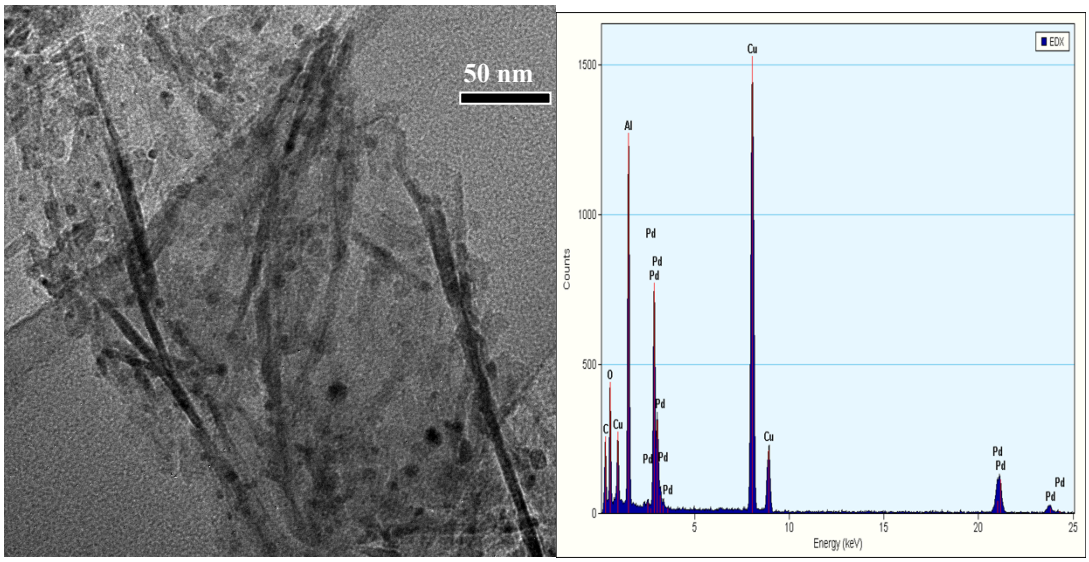

Fig. S2 The TEM image and EDX spectra of Pd/Al_2O_3

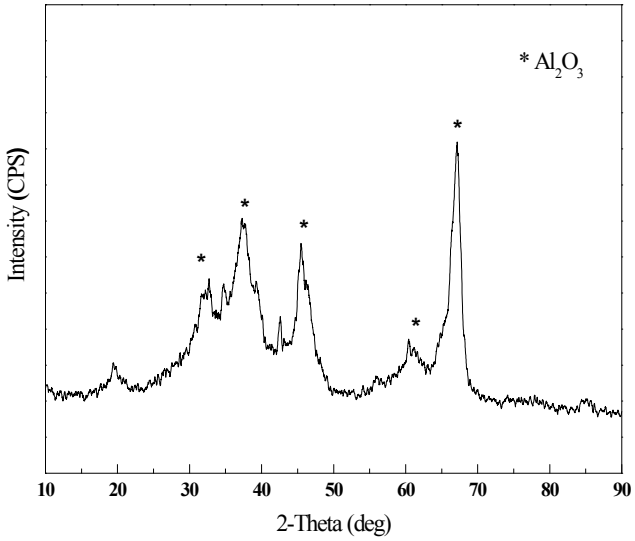

Fig. S3 The XRD patterns of Pd/Al_2O_3

Al_2O_3 phase are observed, while no visible Pd phase can be observed from the XRD patterns of Pd/Al_2O_3 due to the fact that Pd was either well dispersed or had a low content on the support.

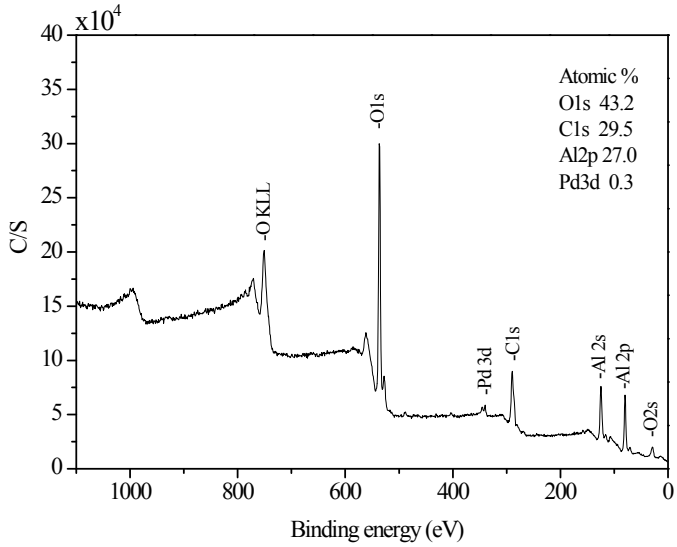

Fig. S4 XPS spectra of Pd/Al_2O_3

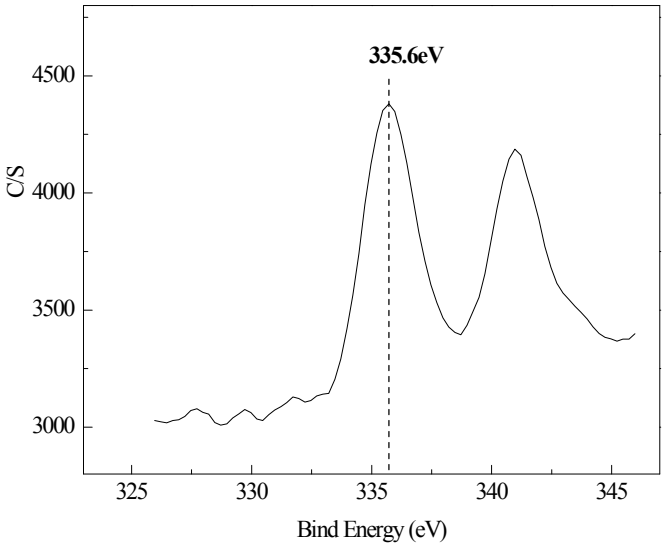

Fig. S5 Pd 3d XPS spectra of Pd/Al_2O_3

Table S2 The catalytic performance of the catalysts

Catalyst	Conversion/%	Selectivity / %			
		Methylcyclohexane	Toluene	Benzyl alcohol	Other
Pd/Al_2O_3	92.2	45.2	37.2	20.6	1.0
$Ni\text{-}B/SiO_2$	46.0	2.5	13.5	75.4	8.6
Ni-B/MIL-101	90.0	0.0	0.0	98.5	1.5

Reaction conditions: reaction temperature (80℃), catalyst amount (1.3mmol, based on the metal species), substrate (30mmol), methanol (100 mL), hydrogenation pressure (1.5MPa), reaction time (2h).

Table S3 The influence of temperature on the reaction

Temperature ℃	Conversion/%	Selectivity / %			
		Methylcyclohexane	Toluene	Benzyl alcohol	Other
60	74.0	0.0	0.0	96.5	3.5
80	90.0	0.0	0.0	98.5	1.5
100	100.0	0.0	0.0	99.4	0.6
120	100.0	0.0	3.2	96.0	0.8
200	100.0	0.0	15.5	82.0	2.5
260	100.0	0.0	30.1	66.5	2.4
280	92.0	0.0	45.1	52.6	2.3
300	80.2	0.0	53.1	44.5	2.4
320	55.0	0.0	64.4	33.3	2.3
340	20.0	2.0	75.3	18.5	5.2

Reaction conditions: catalyst amount (1.3mmol, based on the metal species), substrate (30mmol), methanol (100 mL), hydrogenation pressure (1.5MPa), reaction time (2h).

Thus, 100℃ was chosen to be the best reaction temperature for the present reaction.

Table S4 The influence of hydrogenation pressure on the reaction

Pressure/ MPa	Conversion/%	Selectivity / %			
		Methylcyclohexane	Toluene	Benzyl alcohol	Other
1	96.8	0.0	0.0	98.8	1.2
1.5	100.0	0.0	0.0	99.4	0.6
2	100	0.8	1.2	97.5	0.5
3	100	2.4	8.4	88.6	0.6

Reaction conditions: reaction temperature (100℃), catalyst amount (1.3mmol, based on the metal species), substrate (30mmol), methanol (100 mL), reaction time (2h).

Thus, 1.5 MPa was chosen to be the best hydrogen pressure for the present reaction.

Table S5 The influence of reaction time on the reaction

Reaction time / h	Conversion/%	Selectivity / %			
		Methylcyclohexane	Toluene	Benzyl alcohol	Other
1	86.5	0.0	0.0	98.0	2.0
1.5	95.6	0.0	0.0	98.8	1.2
2	100.0	0.0	0.0	99.4	0.6
2.5	100.0	0.4	5.6	93.5	0.5

Reaction conditions: reaction temperature (100℃), catalyst amount (1.3mmol, based on the metal species), substrate (30mmol), methanol (100 mL), hydrogenation pressure (1.5MPa).

Thus, 2 h was chosen to be the best reaction time for the present reaction.

Table S6 The influence of Ni precursor on the reaction

Ni precursor	Conversion/%	Selectivity / %			
		Methylcyclohexane	Toluene	Benzyl alcohol	Other
NiCl	100.0	0.0	0.0	99.4	0.6
$NiNO_3$	100.0	0.0	0.0	91.6	8.4

Reaction conditions: reaction temperature (100℃), catalyst amount (1.3mmol, based on the metal species), Substrate (30mmol), methanol (100 mL), hydrogenation pressure (1.5MPa), reaction time (2h).

All in all, as can be found, the conversion of benzaldehyde and selectivity towards toluene reached to 100.0% and 99.3% at the optimum conditions (reaction temperature (80℃), catalyst amount (1.3mmol, based on the metal species), substrate (30mmol), methanol (100 mL), hydrogenation pressure (1.5MPa), reaction time (2h))

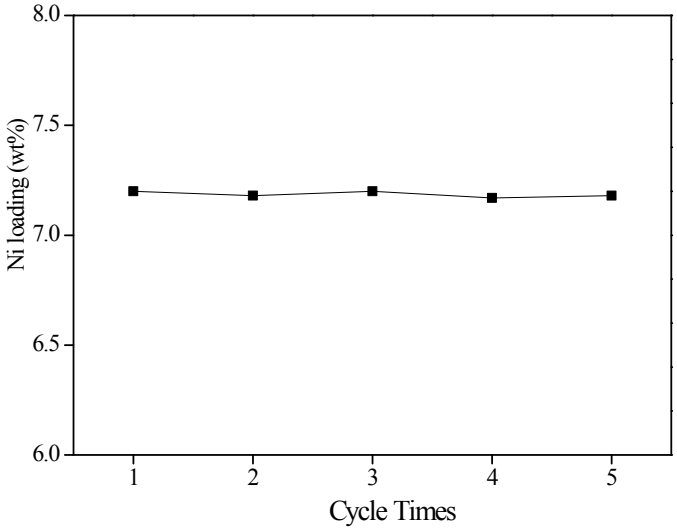

Fig. S6 The Ni loading of Ni-B/MIL-101 for consequent 5 runs