Supporting information

Zirconium Phosphate Supported-Silver Nanoparticles for Selective Hydrogenation of Nitrobenzene into Azoxybenzene Compounds

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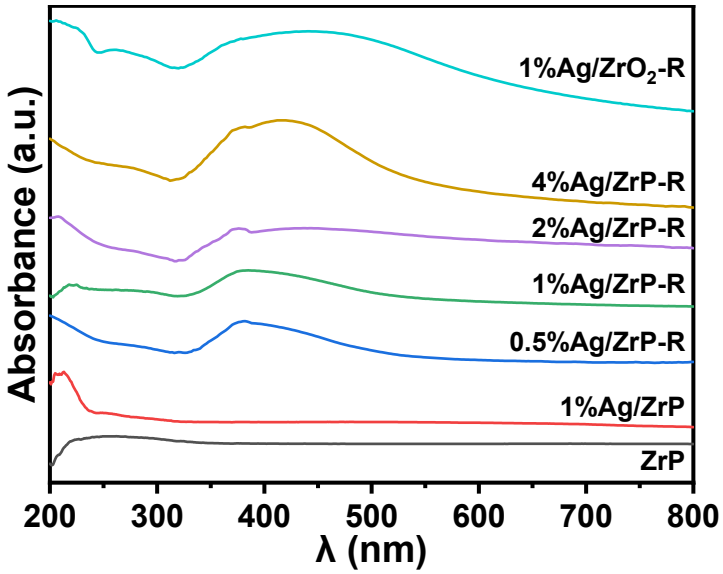

Fig. S1 UV-Vis DRS of the catalysts.

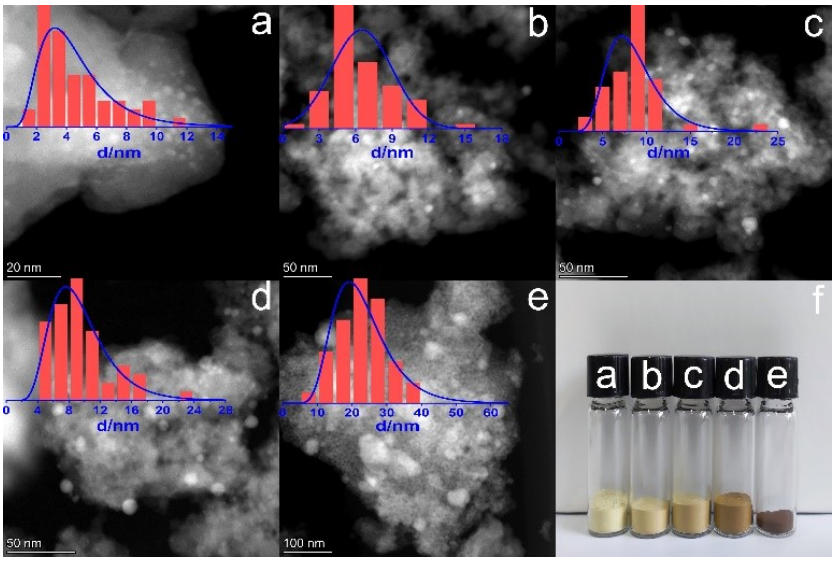

Fig. S2 HAADF-STEM images and particle size distributions of a) 0.5%Ag/ZrP-R, b) 1%Ag/ZrP-R, c) 2%Ag/ZrP-R, d) 4%Ag/ZrP-R and e) 1%Ag/ZrO_2-R. f) The appearance of catalysts.

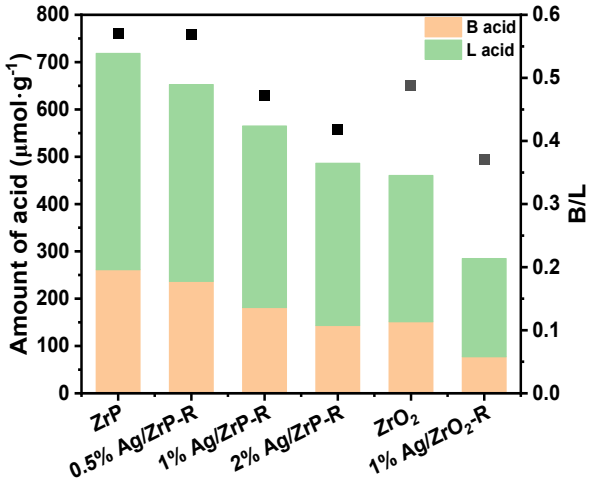

Fig. S3 Quantitative analysis of py-IR spectra of the catalysts. The solid square points denote the ratio of B/L. B=Brønsted acid. L =Lewis acid.

Table S1 Catalytic performance of 1%Ag/ZrP-R in different solvents.

Entry	Solvent	T(℃)	t(min)	Conv. (%)[a]	Sel. (%)			
					AN	AZB	AOB	NSB
1	MeOH	20	3	99	-	-	99	-
2[b]	MeOH	20	30	-	-	-	-	-
3[c]	MeOH	20	30	-	-	-	-	-
4	THF	20	30	-	-	-	-	-
5	1,4-dioxane	20	30	-	-	-	-	-
6	CH_3CN	20	30	28	-	56	43	-
7	EtOH	20	30	57	-	3	96	-
8	H_2O	20	30	41	6	2	16	75

[a]Reaction conditions unless otherwise noted: 1.7 mmol NB, 2.5 mmol $NaBH_4$, 75 mg 1%Ag/ZrP-R, 5 mL solvent, stirring rate: 400 rpm. [b]Reaction was carried out without catalyst. [c]ZrP was used as a catalyst.

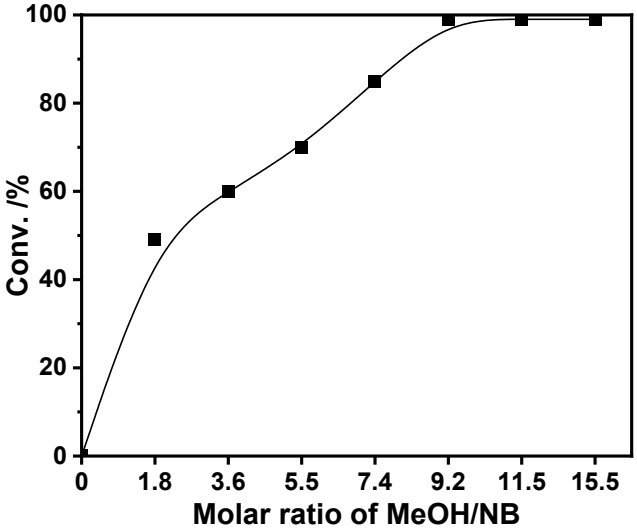

Fig. S4 Catalytic performance of 1%Ag/ZrP-R with varying mass of MeOH. Reaction conditions unless otherwise noted: 1.7 mmol NB, 2.5 mmol $NaBH_4$, 75 mg 1%Ag/ZrP-R, stirring rate: 400 rpm.

Table S2 Catalytic performance of 1%Ag/ZrP-R using different reductants.[a]

					Sel.(%)			
Entry	Reductants	T(°C)	t(min)	Conv.(%)	AN	AZB	AOB	NSB
1	IPA[b]	20	60	-	-	-	-	-
2	HCOOH[c]	20	10	-	-	-	-	-
3	H_2[d]	120	240	-	-	-	-	-
4	Hydrazine	20	10	5	-	-	-	99
5	$NaBH(AcO)_3$	20	30	-	-	-	-	-
6	$TBABH_4$[e]	20	20	78	-	18	82	-
7	$NaBH_4$	20	3	99	-	1	99	-

[a]Reaction conditions unless otherwise noted: 1.7 mmol NB, 2.5 mmol reductant, 75 mg 1%Ag/ZrP-R, 5 mL MeOH, stirring rate: 400 rpm. [b]IPA denoted isopropyl alcohol. [c]10 mmol HCOOH was used. [d]3 MPa H_2. [e]$TBABH_4$ denoted tetrabutylammonium borohydride.

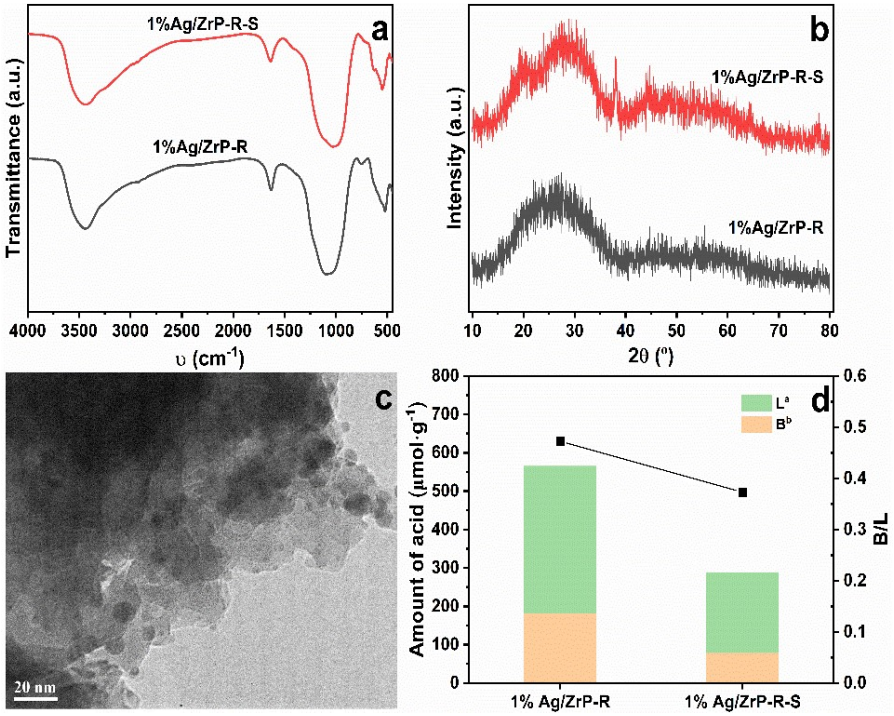

Fig. S5 a) The FT-IR spectra and b) XRD patterns of fresh and used 1%Ag/ZrP-R, c) HRTEM images of 1%Ag/ZrP-R-S and d) FT-IR spectra of pyridine adsorbed on the fresh and spent catalysts. 1%Ag/ZrP-R-S denoted the spent catalyst after 10 catalytic cycles.

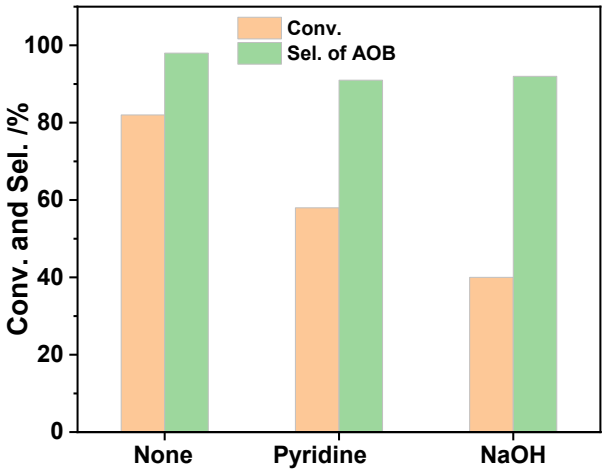

Fig. S6 The effect of base treatment on catalytic performance of 1%Ag/ZrP-R. The catalysts were pretreated with 0.1M methanol solution of NaOH or pyridine for 30 min and then washed with MeOH and H_2O for 3 times prior to reaction. Reaction conditions unless otherwise noted: 1.7 mmol NB, 2.5mmol $NaBH_4$, 75mg 1%Ag/ZrP-R, 5 mL MeOH, stirring rate: 400 rpm.

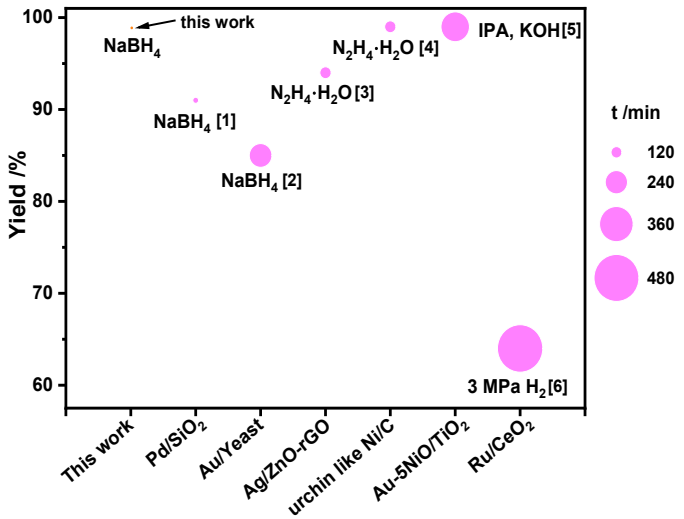

Fig. S7 Comparison of the 1%Ag/ZrP-R catalyst and reported catalytic systems in selective hydrogenation of NB into AOB. The reference numbers were shown in parenthesis.

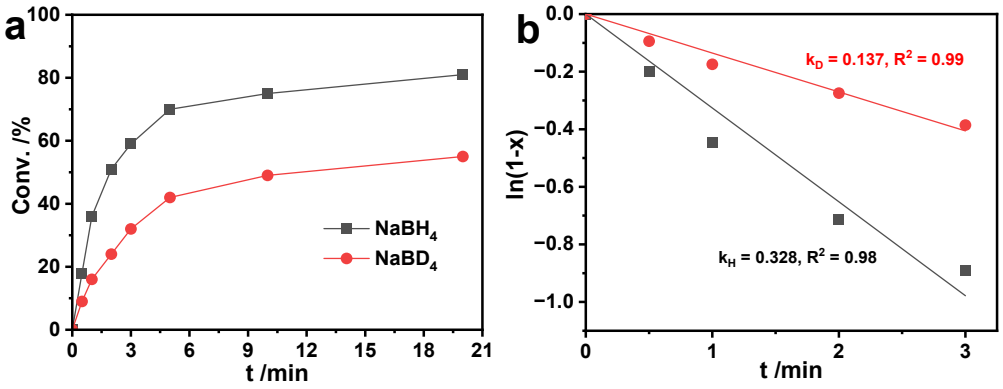

Fig. S8 Kinetic analysis of the 1%Ag/ZrP-R-catalyzed reduction of NB with $NaBH_4$ or $NaBD_4$. a) NB conversion as a function of reaction time and b) kinetic isotope effect in NB hydrogenation with either $NaBH_4$ or $NaBD_4$ as a reductant. Reaction conditions: -15°C, 1.7 mmol NB, 2.5 mmol $NaBH_4$ or $NaBD_4$, 75 mg 1%Ag/ZrP-R, 5 mL MeOH, stirring rate: 400 rpm.

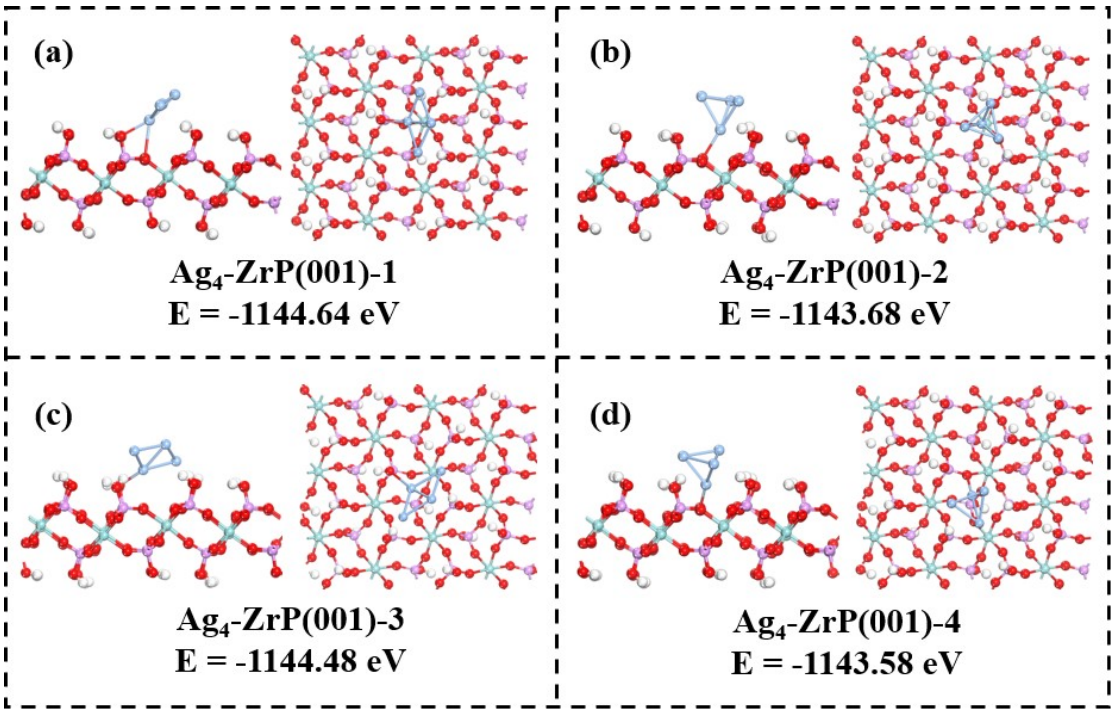

Figure S9. Calculated different structures of Ag_4 clusters stabilized over ZrP. Red: O atoms; white: H atoms; plum: P atoms; light green: Zr atoms; light blue: Ag atoms, respectively.

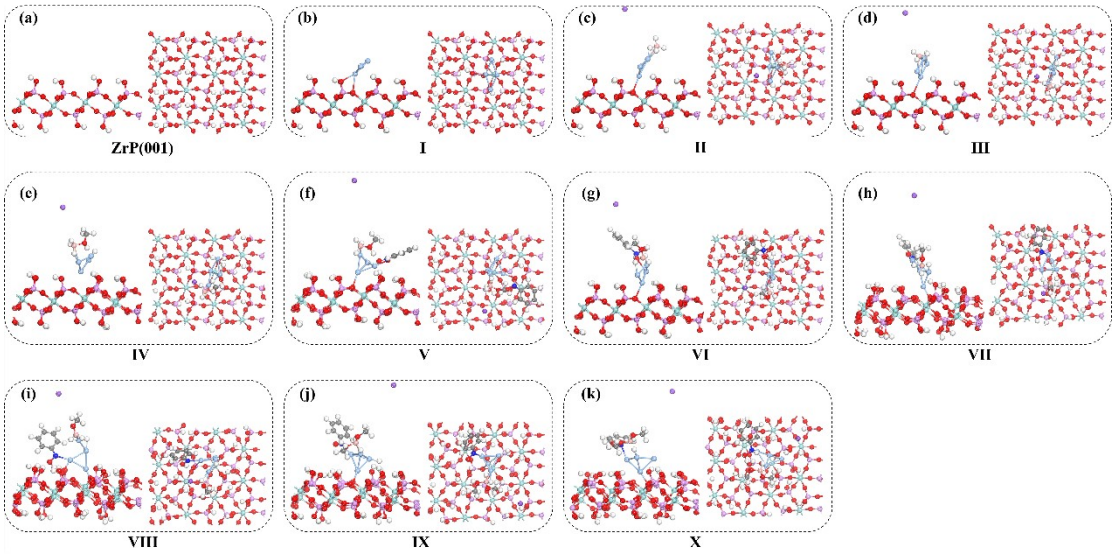

Figure S10. Calculated structure of (a)ZrP and (b-k) the key states within the NB selective hydrogenation to AOB at Ag_4-ZrP (001) surface. Red: O atoms; white: H atoms; grey: C atoms; blue: N atoms; pink: B atoms; purple: Na atoms; plum: P atoms; light green: Zr atoms; light blue: Ag atoms, respectively.

References

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