Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting information

Alkali Metal Cation-Anchored Hydrated Hydroxide Complex as Catalytic Active Site for Efficient Liquid-phase Aerobic Oxidation of Benzyl Alcohol

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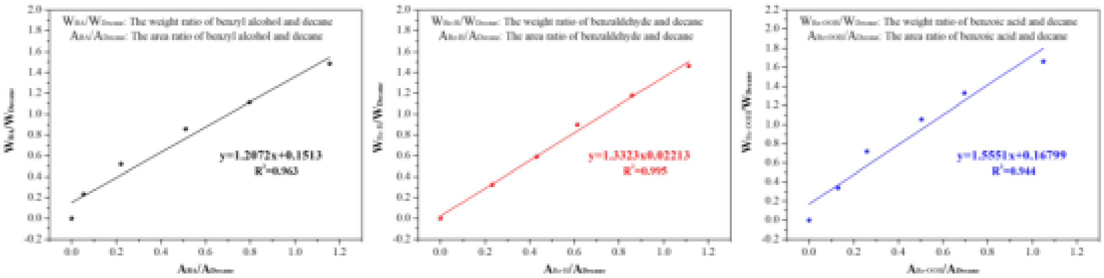
Materials

Lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), rubidium hydroxide (RbOH), Cesium hydroxide monohydrate ($CsOH•H_2O$), toluene, cyclohexane, n-heptane, acetonitrile, ethanol, methanol and benzyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemical reagents were directly used without any isolation or purification.

Experimental

General procedure for alkali metal hydroxide catalytic oxidation of benzyl alcohol. Catalytic experiments were carried out at atmospheric pressure and 80 °C, in a 25 ml, three-necked batch reactor fitted with a reflux condenser, oil bath, thermocouple and magnetic stirrer. Typically, 100 µl benzyl alcohol (1 mmol), *n*-decane (100 µl) which is used as internal standard, and 2 mmol of NaOH, were added to 10 mL of toluene. The reaction mixture was stirred at 80 °C and flushed with pure oxygen at a rate of 30 mL min^{-1} with vigorous stirring. After the reaction, the reaction solution is neutralized with hydrochloric acid. The products were quantified by GC-MS analysis (Varian GCMS- CP-3800). The typical GC-MS analysis program was as follows: initial column temperature 60 °C, to 280 °C at 20 °C / min, and hold for 2 min. The standard curves of substrate (benzyl alcohol, black) and products (benzaldehyde, red and benzoic acid, blue) verse internal standard (*n*-decane) are presented below:



To investigate the effect of the type of alkali metal used, the reaction was conducted under the same conditions, except different alkali metal hydroxides were used (LiOH, NaOH, KOH, RbOH and CsOH).

To investigate the effect of the water additive, the reaction was conducted under the same conditions, except that different volumes (0, 10, 20, 30, 40, 50, 100 and 200 μL) of water were added to the reaction mixture. In the deuterium isotope experiments, the reaction procedure was the same as above, except that H_2O was replaced with D_2O.

Characterization

Fluorescence was measured by using a FluorMax-4 fluorimeter (Horiba, Japan). ^{1}HNMR spectra were obtained using Bruker DPX-400 or Bruker DPX-500 spectrometer. Chemical shifts were reported in ppm from $CDCl_3$ and CD_3OD-d_4 with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

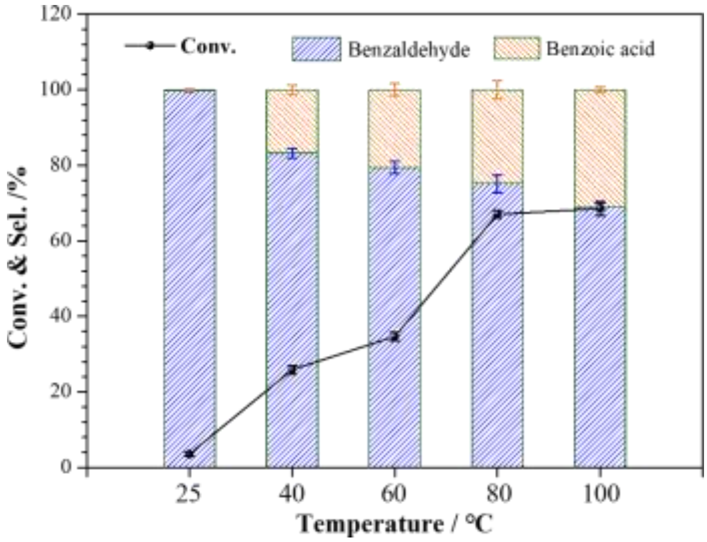


Figure S1. The effect of reaction temperature on the oxidation of benzyl alcohol using a NaOH Catalyst. Reaction condition: 2 mmol NaOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), x °C, p = 1 atm, O_2 bubbling rate (30 ml/min), time 1 h.

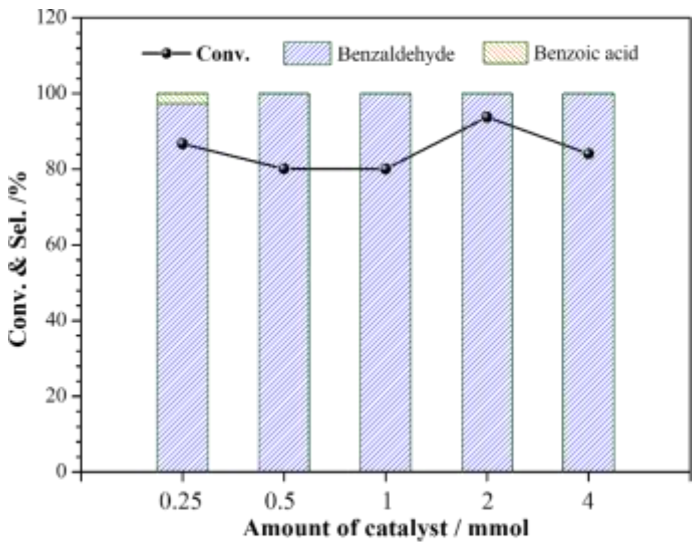


Figure S2. The effect of catalyst concentration on the oxidation of benzyl alcohol using a CsOH catalyst. Reaction condition: x mmol CsOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), 80 °C, p = 1 atm, O_2 bubbling rate (30 ml/min), time 1 h.

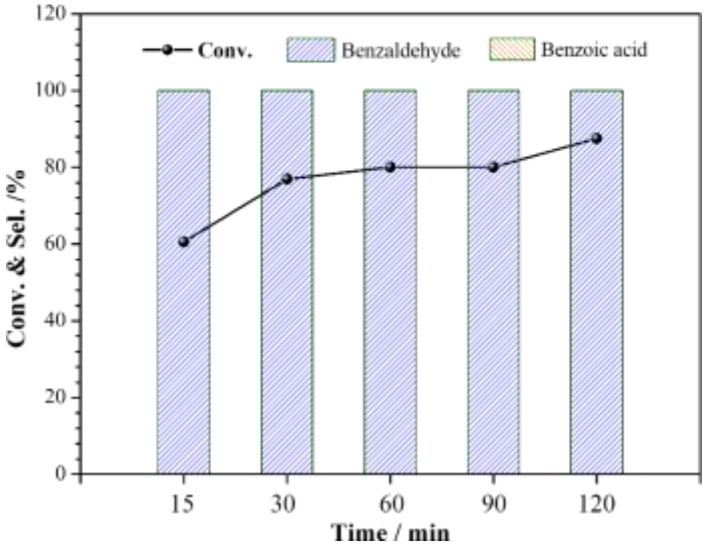


Figure S3. The effect of reaction time on the oxidation of benzyl alcohol using a CsOH catalyst. Reaction condition: 1 mmol CsOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), 80 °C, p = 1 atm, O_2 bubbling rate (30 ml/min), time x min.

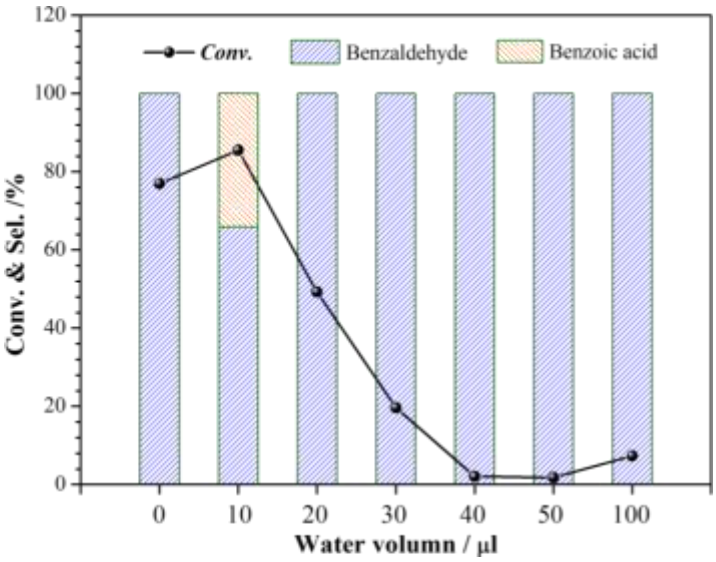


Figure S4. The effect of water additives on the oxidation of benzyl alcohol using a CsOH catalyst. Reaction condition: 1 mmol CsOH, 10 ml toluene, x µl H_2O, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), 80 °C, p = 1 atm, O_2 bubbling rate (30 ml/min), time 30 min.

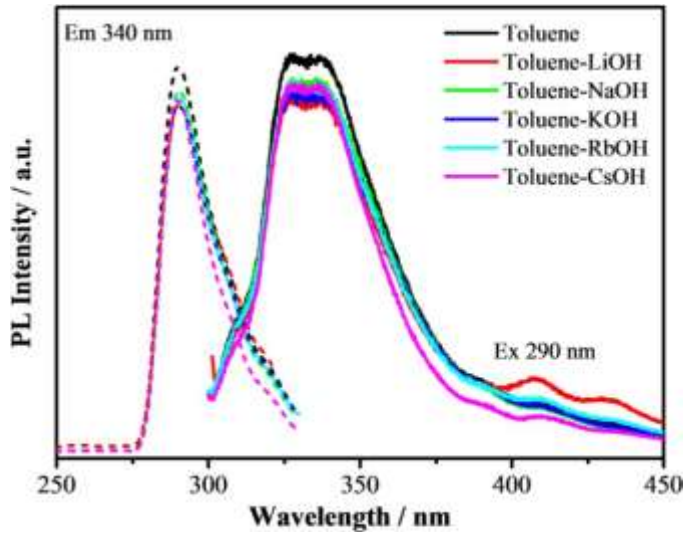


Figure S5. Excitation and photoluminescence spectra of the mixture of MOH (M represented alkali metal cations, Li^+, Na^+, K^+, Rb^+ and Cs^+) and toluene.

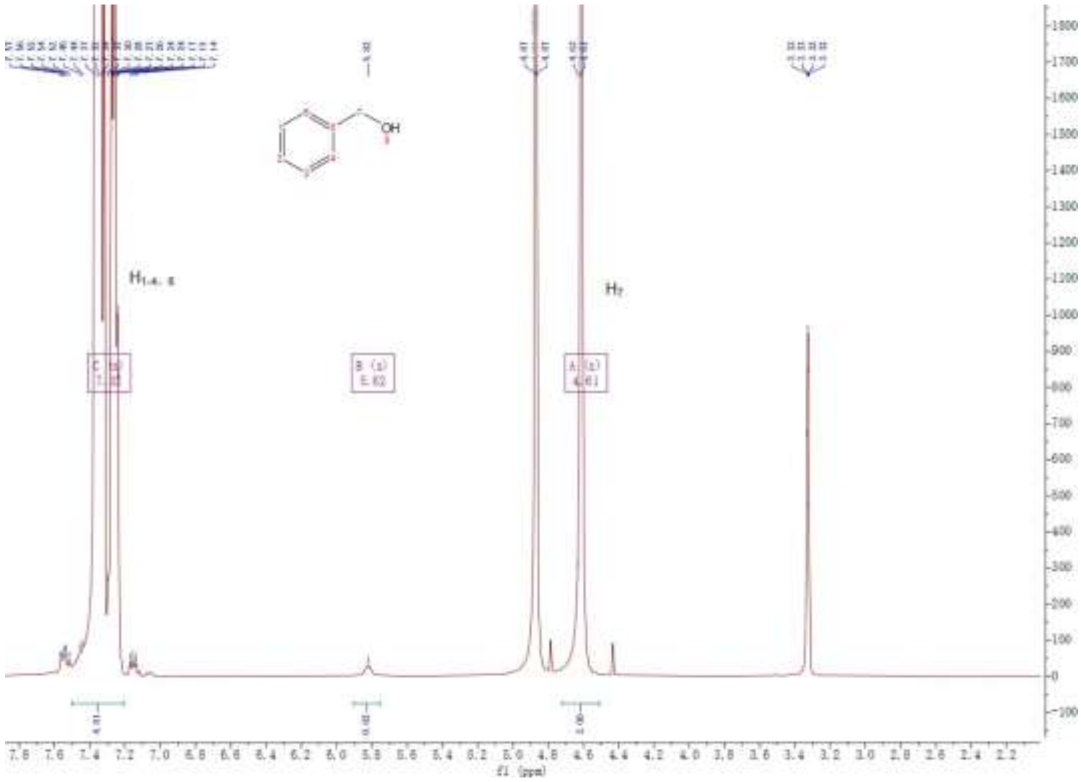


Figure S6. ^{1}H-NMR spectra of $PhCH_2OH$.

^{1}H NMR (500 MHz, Methanol-d4) δ 7.50 – 7.20 (m, 4H), 5.82 (s, 0H), 4.61 (s, 1H).

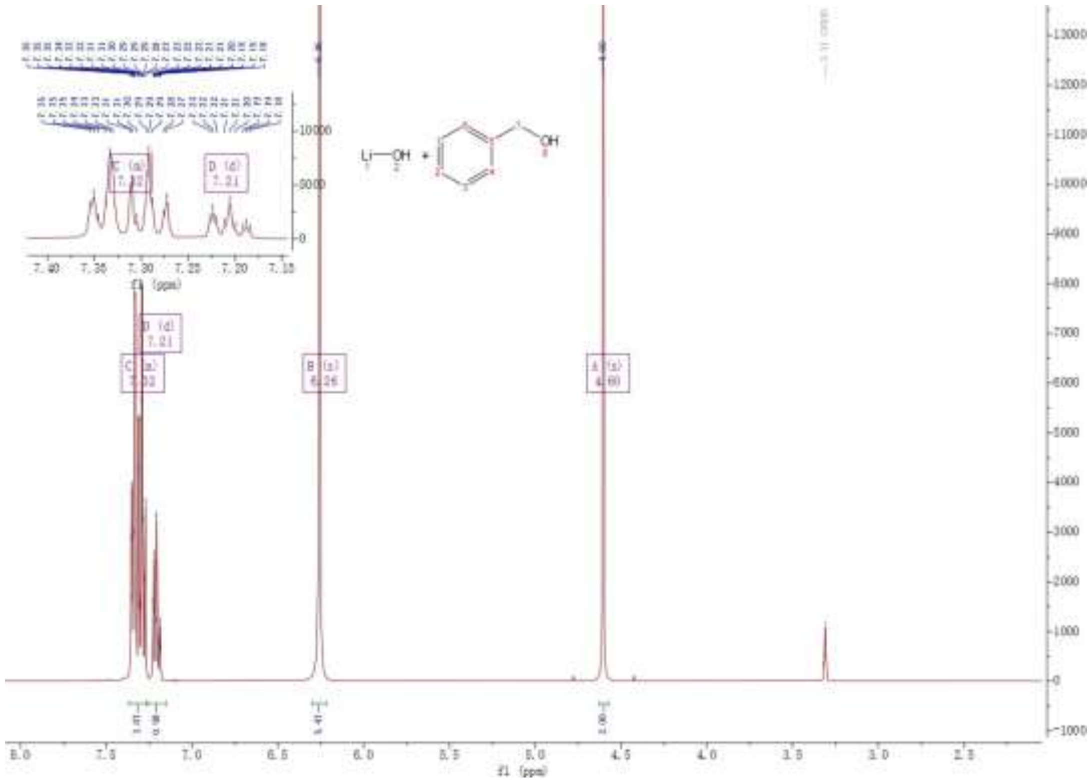


Figure S7. ^{1}H-NMR spectra of $PhCH_2OH$ with LiOH.

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.37 – 7.25 (m, 2H), 7.21 (d, J = 7.1 Hz, 0H), 6.26 (s, 3H), 4.60 (s, 1H).

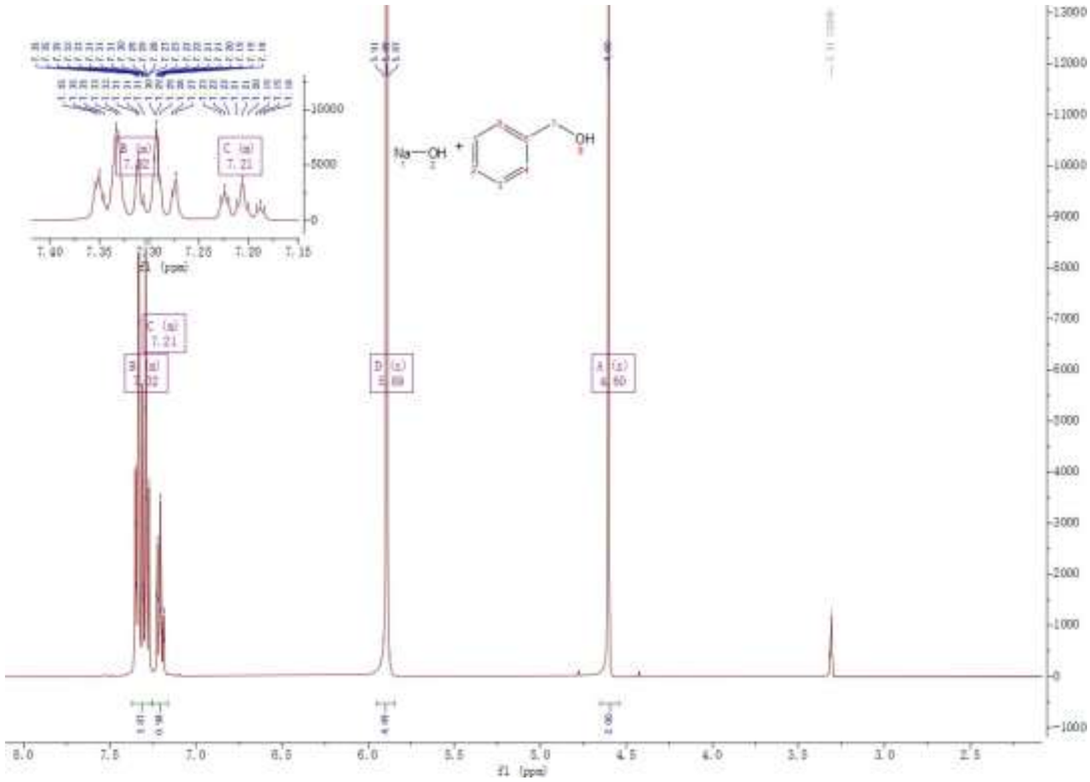


Figure S8. ^{1}H-NMR spectra of $PhCH_2OH$ with NaOH.

^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 7.37 – 7.25 (m, 2H), 7.25 – 7.15 (m, 0H), 5.89 (s, 3H), 4.60 (s, 1H).

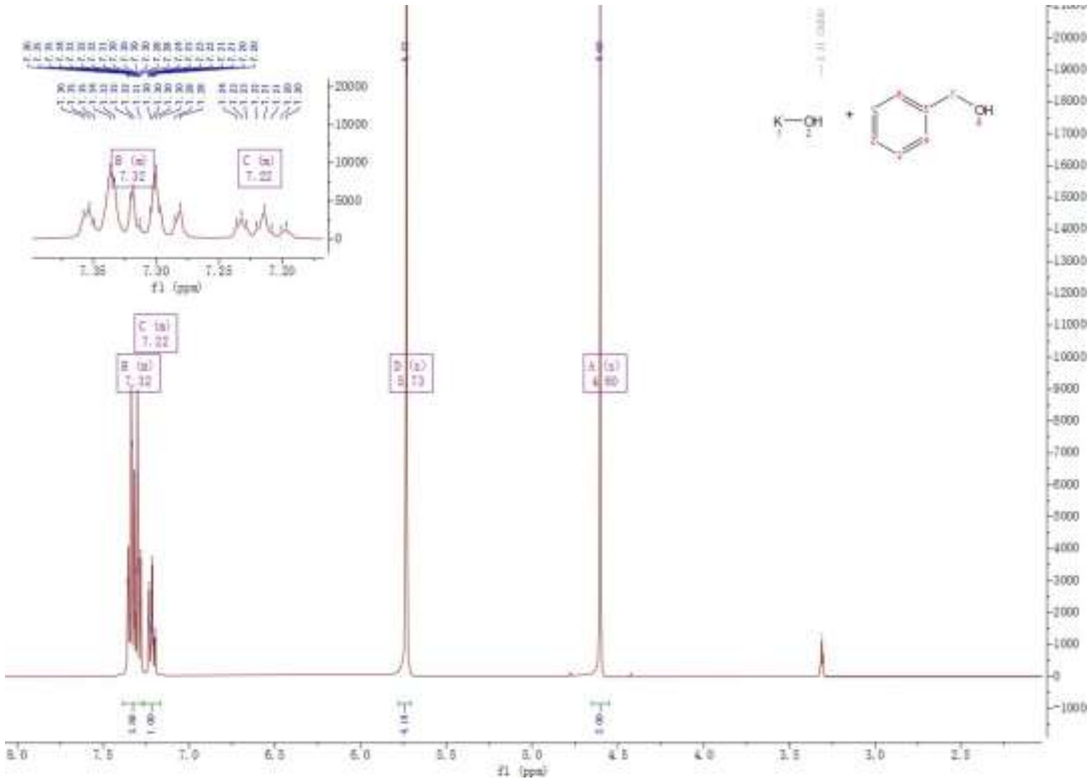


Figure S9. ^{1}H-NMR spectra of $PhCH_2OH$ with KOH.

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.38 – 7.26 (m, 2H), 7.26 – 7.18 (m, 0H), 5.73 (s, 2H),4.60 (s,1H).

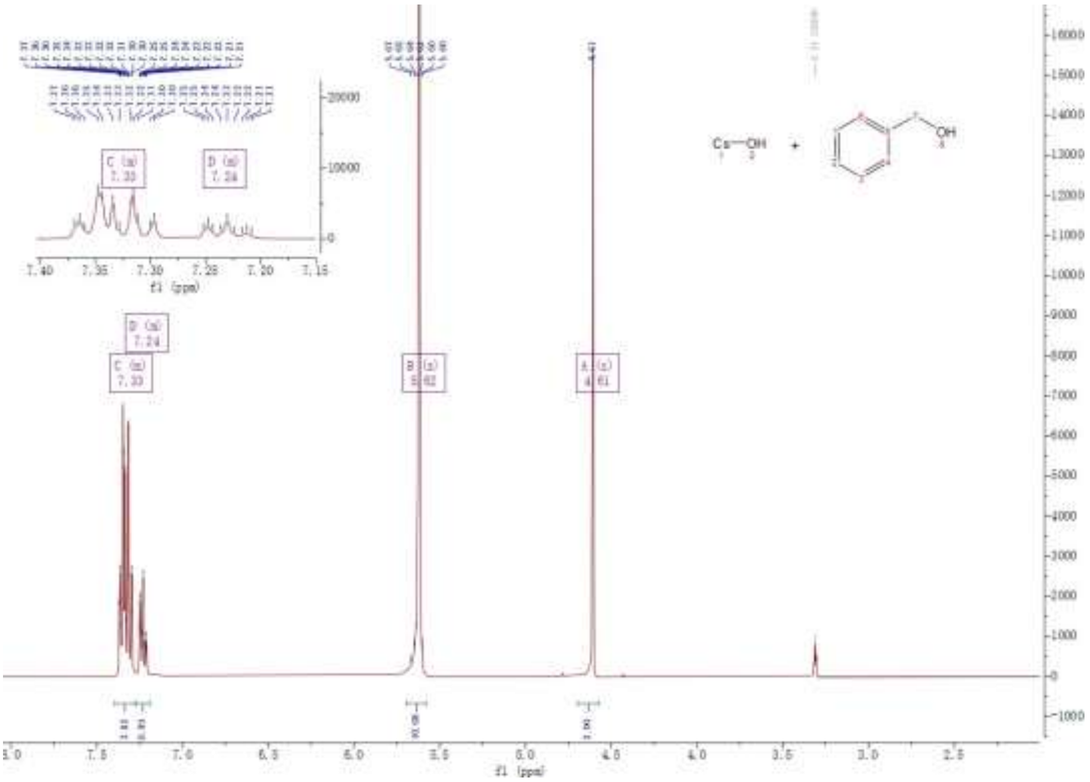


Figure S10. ^{1}H-NMR spectra of $PhCH_2OH$ with CsOH.

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.39 – 7.28 (m, 2H), 7.28 – 7.17 (m, 1H), 5.62 (s, 6H), 4.61 (s, 1H).

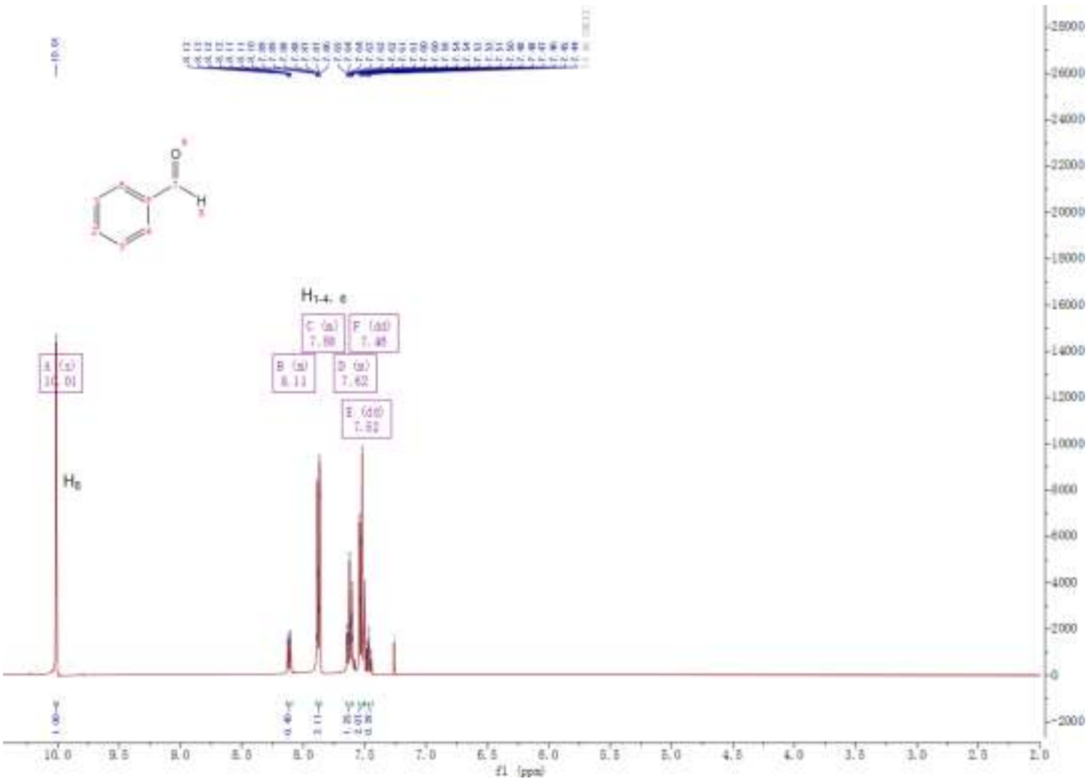


Figure S11. ^{1}H-NMR spectra of PhCHO.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.01 (s, 1H), 8.14 – 8.09 (m, 0H), 7.90 – 7.86 (m, 2H), 7.66 – 7.59 (m, 1H), 7.52 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.46 (dd, *J* = 8.4, 7.1 Hz, 0H).

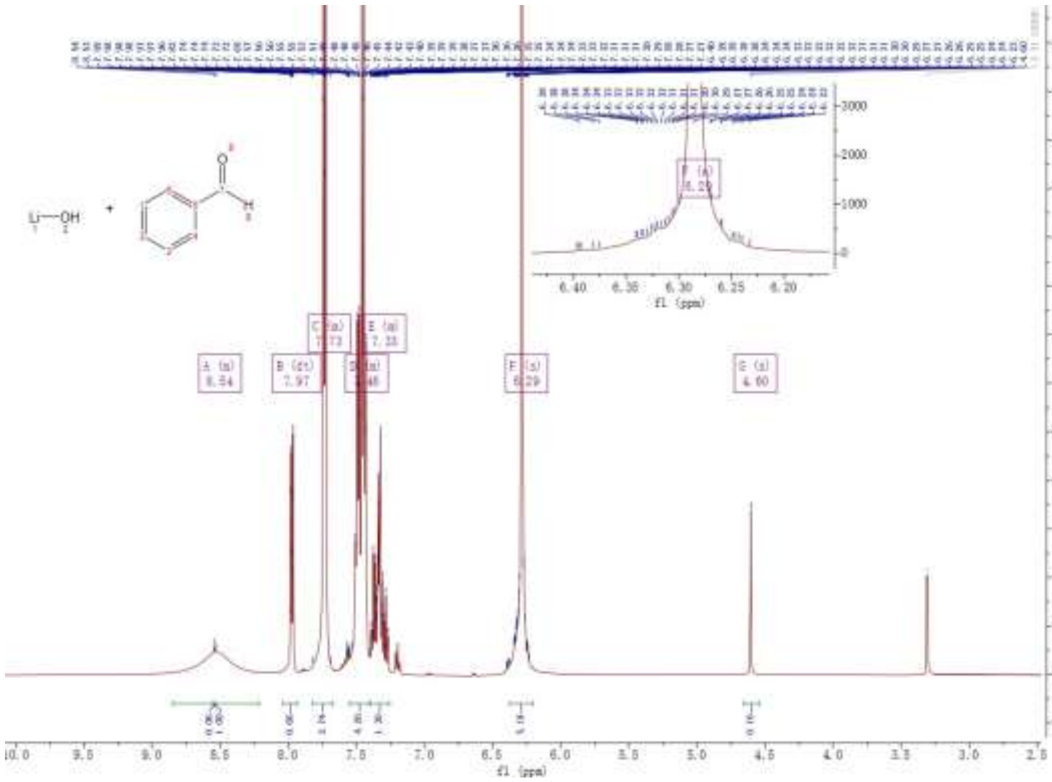


Figure S12. ^{1}H-NMR spectra of PhCHO with LiOH.

^{1}H NMR (501 MHz, Methanol-d_4) δ 8.84 – 8.21 (m, 1H), 7.97 (dt, *J* = 7.0, 1.5 Hz, 0H), 7.80 – 7.70 (m, 2H), 7.54 – 7.42 (m, 3H), 7.40 – 7.26 (m, 1H), 6.29 (s, 4H), 4.60 (s, 0H).

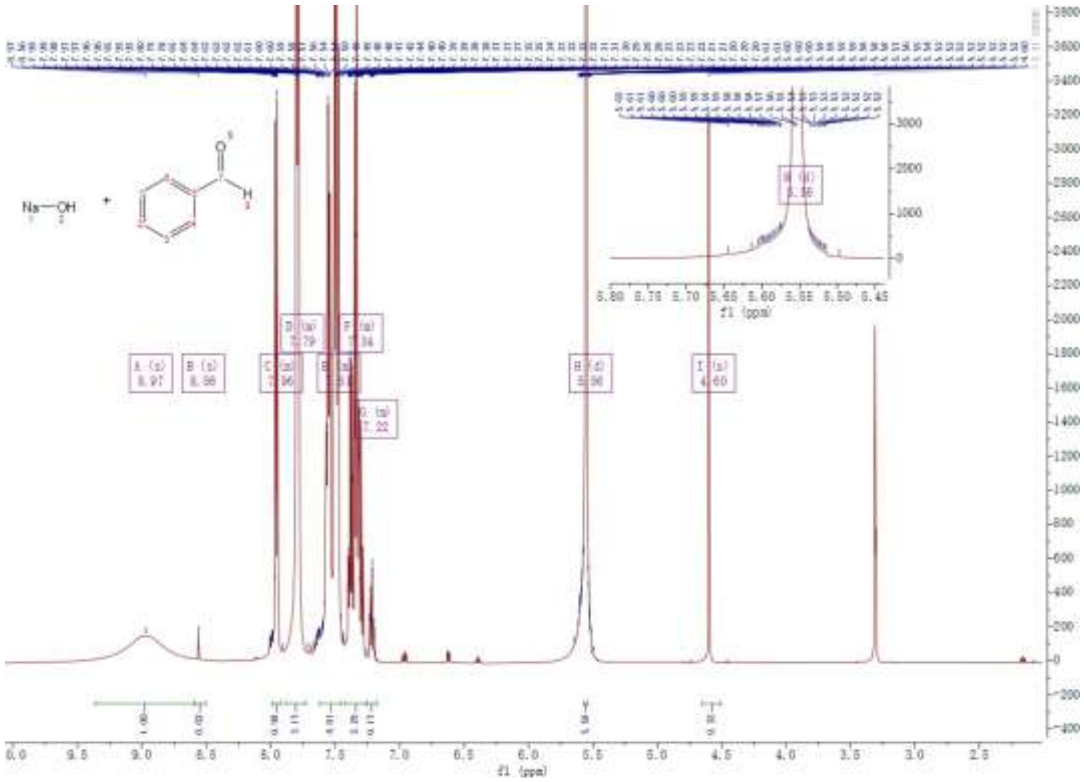


Figure S13. ^{1}H-NMR spectra of PhCHO with NaOH.

^{1}H NMR (501 MHz, Methanol-d_4) δ 8.97 (s, 1H), 8.56 (s, 0H), 8.02 – 7.90 (m, 1H), 7.90 – 7.72 (m, 2H), 7.61 – 7.43 (m, 3H), 7.43 – 7.26 (m, 1H), 7.27 – 7.16 (m, 0H), 5.56 (d, *J* = 1.4 Hz, 4H), 4.60 (s, 0H).

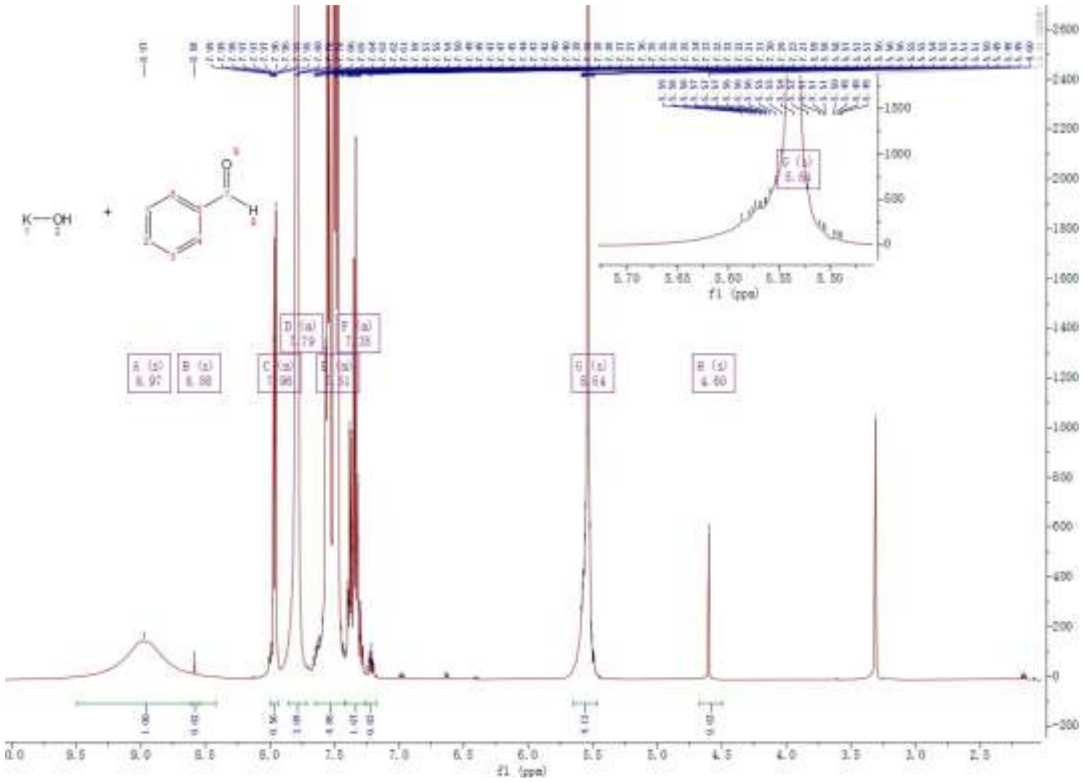


Figure S14. ^{1}H-NMR spectra of PhCHO with KOH.

^{1}H NMR (501 MHz, Methanol-d_4) δ 8.97 (s, 1H), 8.58 (s, 0H), 8.02 – 7.91 (m, 0H), 7.88 – 7.70 (m, 2H), 7.65 – 7.44 (m, 3H), 7.44 – 7.26 (m, 1H), 5.54 (s, 3H), 4.60 (s, 0H).

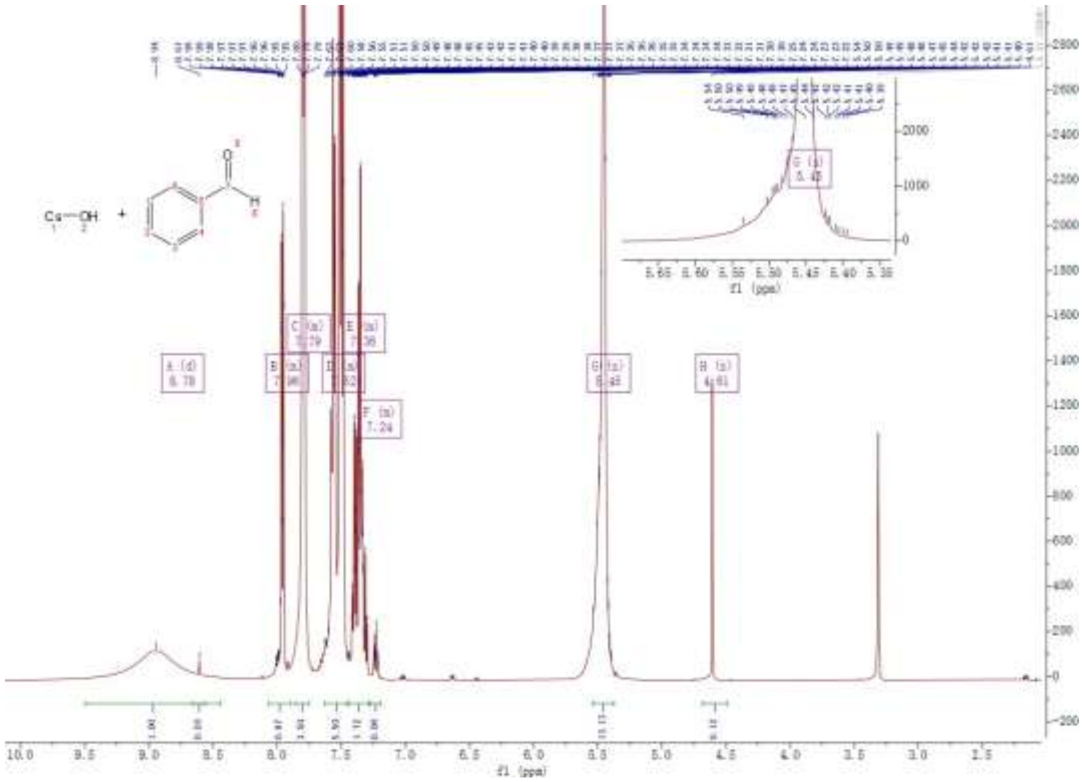


Figure S15. ^{1}H-NMR spectra of PhCHO with CsOH.

^{1}H NMR (501 MHz, Methanol-d_4) δ 8.78 (d, J = 168.4 Hz, 1H), 8.00 – 7.91 (m, 0H), 7.91 – 7.74 (m, 2H), 7.67 – 7.46 (m, 2H), 7.44 – 7.28 (m, 1H), 7.29 – 7.15 (m, 0H), 5.45 (s, 7H), 4.61 (s, 0H).

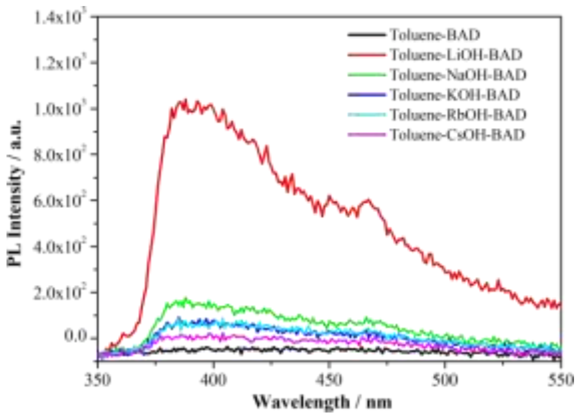


Figure S16. Photoluminescence spectra of catalytic system (mixture of toluene, BAD and MOH, M represented alkali metal cations, Li^{+}, Na^{+}, K^{+}, Rb^{+} and Cs^{+}) of hydroxide.

Table S1. Effect of reaction temperature on the catalytic performance for the selective oxidation of benzyl alcohol using a NaOH catalyst.[a]

Entry	Temperature / °C	Time / h	Conv./%	Sel./%	
				Benzyl alcohol	Benzoic acid
1	25	1	-	-	-
2		2	3.51	99.9	0.1
3	40	1	12.2	87.8	12.2
4		2	25.5	83.2	16.8
5	60	1	22.7	84.0	16.0
6		2	34.4	79.0	21.0
7	80	1	44.0	78.5	21.5
8		2	67.2	75.6	24.3
9	100	1	48.6	72.3	27.7
10		2	68.9	69.4	30.6

[a]Reaction condition: 2 mmol NaOH, 10 ml toluene, 100 µl benzaldehyde, 100 µl decane (used as internal standard), X °C, p = 1 atm, O_2 bubbling rate (30 ml/min).

Table S2. Catalytic performance of NaOH catalysts with the addition of different volume of water for the selective oxidation of benzyl alcohol.[a]

Entry	H_2O / µl	Time / h	Conv./%	Sel./%	
				Benzaldehyde	Benzoic acid
1	0	1	44.0	78.5	21.5
2	10	1	78.2	68.7	31.3
3	20	1	83.1	74.1	25.9
4	30	1	66.3	64.9	35.1
5	40	1	38.0	90.1	9.9
6	50	1	38.3	94.8	5.2
7	100	1	10.6	>99	-
8	100	1	5.8	>99	-

[a]Reaction condition: 2mmol NaOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), 80 °C, pressure =1 atm, O_2 bubbling rate (30 ml/min).

Table S3. Effect of solvents on the catalytic performance for the selective oxidation of benzyl alcohol.[a]

Entry	Solvents	Time / h	Conv./%	Sel./%	
				Benzaldehyde	Benzoic acid
1	Toluene	2	67.3	75.6	24.3
2	cyclohexane	2	71.9	20.8	79.2
3	n-Heptane	2	>99	10.2	89.8
4	Acetonitrile	2	6.38	>99	-
5	Ethanol	2	3.63	>99	-
6	Methanol	2	4.32	>99	-

[a]Reaction condition: 2mmol NaOH, 10 ml solvent, 100 µl benzyl alcohol, 100 µl *n*-decane (used as internal standard), 80 °C, pressure =1 atm, O_2 bubbling rate (30 ml/min).

Table S4. Catalytic performance of MOH catalysts for the selective oxidation of benzyl alcohol.[a]

Entry	Catalyst	Time / h	Conv./%	Sel./%	
				Benzaldehyde	Benzoic acid
1	LiOH	1	4.3	>99	-
2	NaOH	1	44.0	78.5	21.5
3	KOH	1	75.9	74.1	25.9
4	RbOH	1	>99	94.9	5.1
5	CsOH	1	>99	97.5	2.5

[a]Reaction condition: 2mmol MOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl *n*-decane (used as internal standard), 80 °C, pressure =1 atm, O_2 bubbling rate (30 ml/min).

Table S5. Catalytic performance of LiOH catalysts with the addition of different volume of water for the selective oxidation of benzyl alcohol.[a]

Entry	H_2O / µl	Time / h	Conv./%	Sel./%	
				Benzaldehyde	Benzoic acid
1	0	2	4.8	>99	-
2	10	2	5.6	>99	-
3	20	2	7.1	>99	-
4	30	2	8.3	>99	-
5	40	2	9.6	>99	-
6	50	2	11.7	>99	-
7	100	2	11.76	>99	-

[a]Reaction condition: 2mmol LiOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl *n*-decane (used as internal standard), 80 °C, pressure =1 atm, O_2 bubbling rate (30 ml/min).

Table S6. The effect of catalyst concentration on the oxidation of benzyl alcohol using a CsOH catalyst.[a]

Entry	Catalyst	Amount / mmol	Conv./%	Sel./%	
				Benzaldehyde	Benzoic acid
1	CsOH	0.25	86.0	97.4	2.6
2	CsOH	0.5	79.5	100	0
3	CsOH	1	79.4	100	0
4	CsOH	2	93.0	100	0
5	CsOH	4	83.4	100	0

[a]Reaction condition: x mmol CsOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), 80 °C, p = 1 atm, O_2 bubbling rate (30 ml/min), time = 1h.

Table S7. The effect of reaction time on the oxidation of benzyl alcohol using a CsOH catalyst.[a]

Entry	Catalyst	Time / min	Conv./%	Sel./%	
				Benzaldehyde	Benzoic acid
1	CsOH	15	60.1	100	0
2	CsOH	30	76.3	100	0
3	CsOH	60	79.4	100	0
4	CsOH	90	79.4	100	0
5	CsOH	120	86.8	100	0

[a]Reaction condition: 1 mmol CsOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), 80 ℃, p = 1 atm, O_2 bubbling rate (30 ml/min), time = x min.

Table S8. The effect of water additives on the oxidation of benzyl alcohol using a CsOH catalyst.[a]

Entry	Catalyst	Additive	Amount / µl	Conv./%	Sel./%	
					Benzaldehyde	Benzoic acid
1	CsOH	H_2O	0	76.3	100	0
2	CsOH	H_2O	10	84.8	65.9	34.1
3	CsOH	H_2O	20	48.9	100	0
4	CsOH	H_2O	30	19.5	100	0
5	CsOH	H_2O	40	2.1	100	0
6	CsOH	H_2O	50	1.8	100	0
7	CsOH	H_2O	100	7.3	100	0

[a]Reaction condition: 1 mmol CsOH, 10 ml toluene, 100 µl benzyl alcohol, 100 µl decane (used as internal standard), 80 ℃, p=1 atm, O_2 bubbling rate (30 ml/min), time = 30 min, H_2O x µl.

Table S9. Catalytic performance of MOH catalysts for the selective oxidation of benzaldehyde.[a]

Entry	Catalyst	Time / h	Conv./%	Sel./%	
				Benzyl alcohol	Benzoic acid
1	-	1	-	-	-
2		2	-	-	-
3	LiOH	1	-	-	-
4		2	-	-	-
5	NaOH	1	33.9	50.6	49.4
6		2	39.2	43.7	56.3
7	KOH	1	5.8	39.7	60.3
8		2	7.2	35.0	64.9
9	RbOH	1	-	-	-
10		2	-	-	-
11	$CsOH \cdot H_2O$	1	-	-	-
12		2	-	-	-

[a]Reaction condition: 2 mmol MOH, 10 ml toluene, 100 µl benzaldehyde, 100 µl *n*-decane (used as internal standard), 80 °C, pressure =1 atm, O_2 bubbling rate (30 ml/min).