# Supporting Information for

# Crystal Epitaxy Confined Pd, Ti-Bimetallic Sites in MFI Zeolite for Benzylalcohol Oxidation

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# 1. Materials and methods

1.1 Synthesis of Pd@S1 and Pd/TS-1@S1 catalysts

The empirical synthetic composition of Pd@S1 zeolite was in the following molar composition: 1.0 TEOS: 0.4 TPAOH: 35 $H_2O$: 0.0065 $[Pd(NH_2CH_2CH_2NH_2)_2]Cl_2$. Typically, the synthetic Pd@S1 zeolite was prepared by dissolving 8.27 g tetrapropylammonium hydroxide solution (TPAOH, Sinopharm, 25 wt%) and 12.9 g of tetraethyl orthosilicate (TEOS, Sinopharm, AR) in 9.32 g of water. The resulting transparent solution was stirred overnight at room temperature, obtaining silicalite-1 zeolite gels. The $[Pd(NH_2CH_2CH_2NH_2)_2]Cl_2$ solution was prepared by adding 0.35 mL ethylenediamine (EDA, Lingfeng, 99 wt%) and 0.046 g $PdCl_2$ (J&K Chemicals, 99 wt%) successively to 5 mL $H_2O$ mixture, the resulted metal precursor solution was added to the above gel dropwise under vigorous stirring for 30 min and the clear solution was obtained. Finally, the resultant gel was transferred to a 50 mL Teflon-lined autoclave and reacted 3 days at 443 K under static conditions.

The TS-1 zeolite synthesis conditions are consistent with silicalite-1 zeolite, and titanium tetraisopropanolate as titanium source (TIPT, Macklin, 97 wt%) was added 2 h after TEOS was added to the gel and stirred overnight. The empirical synthetic composition of TS-1 zeolite was in the following molar composition: 1.0 TEOS: 0.25 TPAOH: 0.04 TIPT: 35 $H_2O$. And the Pd/TS-1@S1 catalyst was synthesized by 0.8 g of calcined TS-1@S1 was added to the 10 mL $[Pd(NH_2CH_2CH_2NH_2)_2]Cl_2$ solution (0.0079 M), and the resulting solution was stirred at room temperature for 24 h. Among

them, for the synthesis of TS-1@S1 catalysts, the silicalite-1 precursor solution was prepared by dissolving 1.23 g of tetrapropylammonium hydroxide aqueous solution, 2.4 g ethanol (EtOH, Sinopharm, AR) and 2.5 g of TEOS in 12.95 g water, the resulting transparent solution was stirred overnight at room temperature. Afterwards, 0.5 g calcined TS-1 zeolite was added to the resulting solution as seed, sonicated for 10 min, and stirred at 368 K with 500 rpm for 24 h.

1.2 Synthesis of Pd@TS-1@S1 catalysts

For the synthesis of Pd@TS-1@S1, the Pd@TS-1 was served as core zeolite for the secondary growth under the same synthetic conditions with the above TS-1@S1. And Pd@TS-1 catalyst was synthesized with the molar composition of 1.0 $SiO_2$: 0.4 TPAOH: 0.04 TIPT: 35 $H_2O$: 0.0065 $[Pd(NH_2CH_2CH_2NH_2)_2]Cl_2$ under the modified hydrothermal synthetic conditions with the above Pd@S1 by in a typical synthesis procedure.

The all as-synthesized zeolites were centrifuged, washed with deionized water several times to a neutral pH, and then dried at 353 K in an air oven overnight, followed by calcination in air at 823 K for 6 h. Prior to some tests, some necessary calcined samples were reduced following the $H_2$ atmosphere at 473 K for 2 h.

1.3 Characterization methods

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE diffractometer equipped with a copper radiation source and an energy resolved LynxXEye detector ($\lambda$ = 1.5418 Å, voltage: 40 kV and current: 40 mA). The PXRD

patterns for phase verification were collected under the condition of 2$\theta$ angle range: 5-50°, step size: 0.02° at speed: 0.1°/s. The surface morphology of zeolite was monitored by scanning electron microscopy (SEM) on Zeiss Sigma 300 under accelerated voltage of 3 kV and energy spectrum model of Oxford Xplore 50. The high-resolution image and element mapping of zeolite was performed on a transmission electron microscopy (TEM) FEI talos F200 $G^2$ under the super-X energy spectrum model. The general chemical composition of the obtained samples was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on the Agilent 5110 spectrometer. X-ray photoelectron spectroscopy (XPS) of metallic species in the spent catalysts was carried out on the Thermo Scientific K-Alpha instrument. $N_2$ sorption was performed on a Micromeritics ASAP 2020 HD88 apparatus at 77 K. Before the tests, the calcined zeolitic catalyst was degassed at 573 K for 4 h. The specific surface area and pore volume were evaluated using the BET model with the adsorption branches and pore distribution was calculated by the DFT model, respectively. The FT-IR spectra of the zeolites were recorded on a Nicolet IS5 spectrometer in the fixed range of 4000-400 $cm^{-1}$. The UV-Vis spectra of the zeolites were collected on a PerkinElmer Lambda 950 in the wavelength range of 200-800 nm.

1.4 Catalytic performance evaluation

In a typical reaction, 40 mg zeolitic catalyst was mixed with 3 mL acetonitrile (Sinopharm, AR) with stirring in a 50 mL Shrek tube. Sequentially, 1 mmol benzylalcohol (Macklin, AR) was introduced to the above mixture at 373 K and calculated amount of 1.5 mmol $H_2O_2$ (Lingfeng, 30 wt%). The obtained product was

monitored by gas chromatography (Fuli 9790 Plus) equipped with a hydrogen flame detector and RB-PLOT Q capillary chromatography columns (30 m × 320 μm × 0.5 μm). The relative contents of benzyl alcohol, benzaldehyde, and toluene were quantitative analyzed by their portion in empirical peak areas.

$$\text{Yield of benzaldehyde (\%)} = \frac{L_{Benzaldehyde}}{L_{Benzaldehyde} + L_{Benzylalcohol} + L_{Toluene}} \times 100$$

$$\text{Selectivity of benzaldehyde (\%)} = \frac{L_{Benzaldehyde}}{L_{Benzaldehyde} + L_{Toluene}} \times 100$$

## 2. Figures

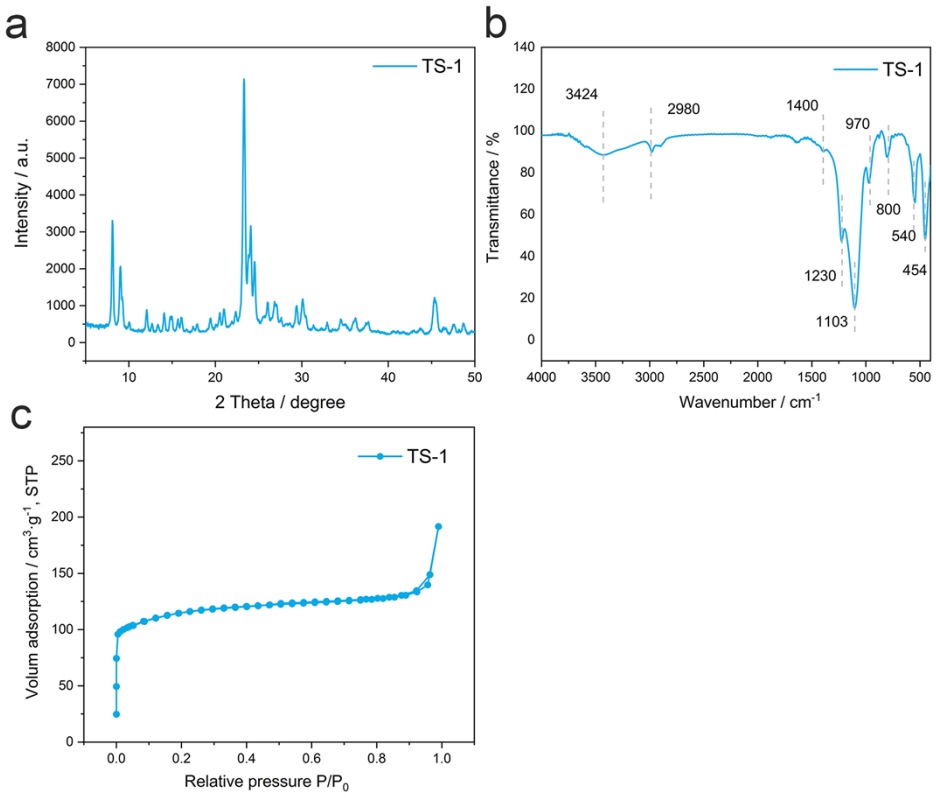


**Fig. S1** Physicochemical properties of catalytic materials. a) PXRD patterns of as made TS-1 zeolite, b) FT-IR spectra of as-made TS-1, c) $N_2$ isothermal sorption profiles of TS-1 at 77 K.

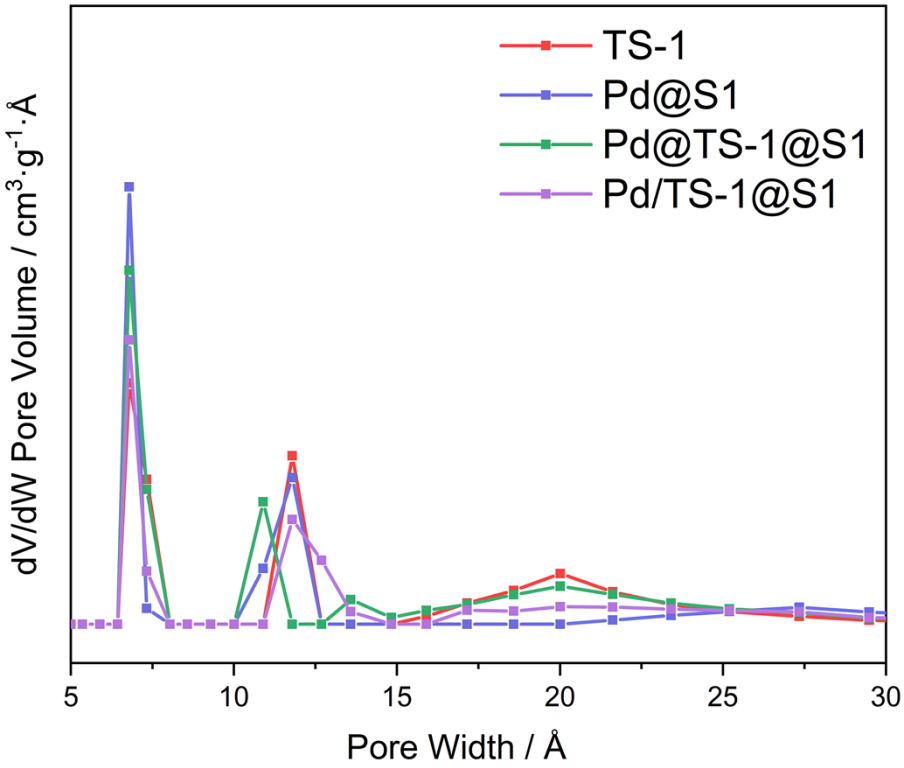


**Fig. S2** The pore size distribution of different types of calcined **MFI** zeolites according to the DFT model.

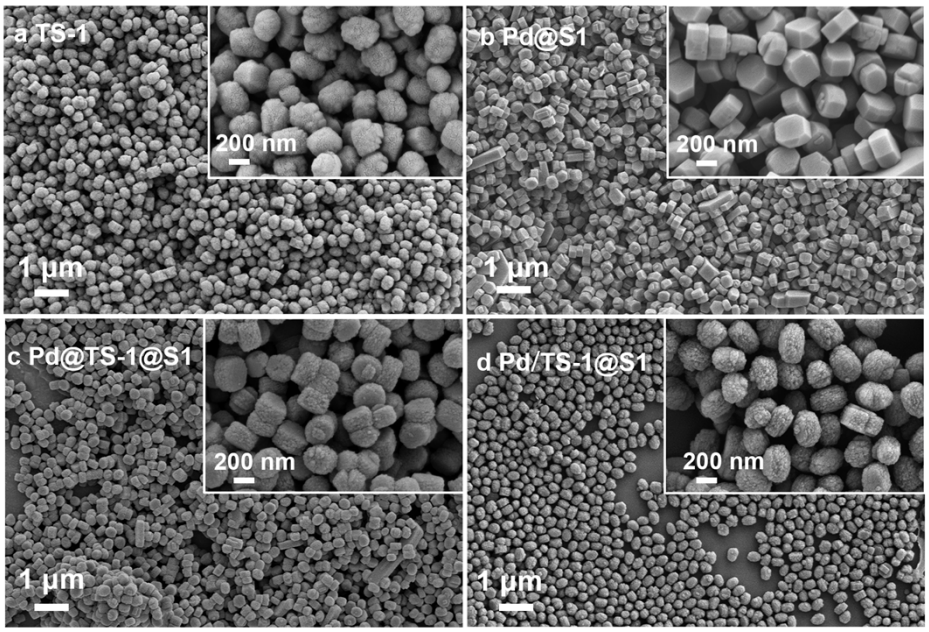


**Fig. S3** The SEM morphology of metal-containing zeolite (higher magnification view).

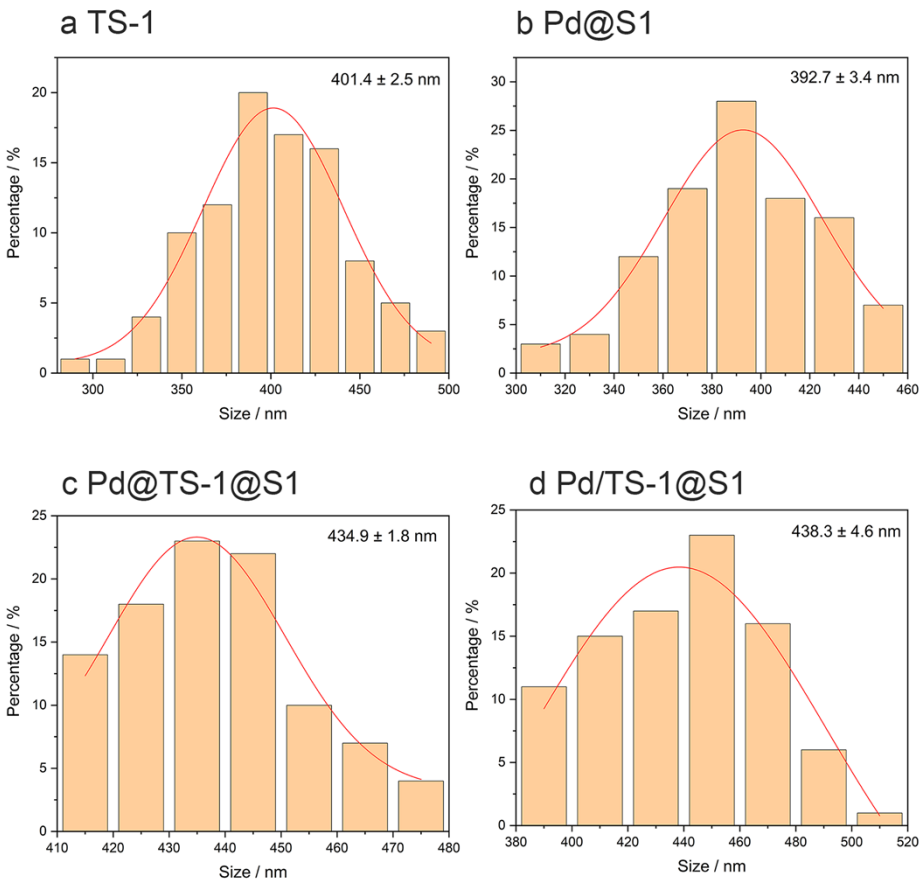


**Fig. S4** The particle size distribution of the prepared zeolite catalysts.

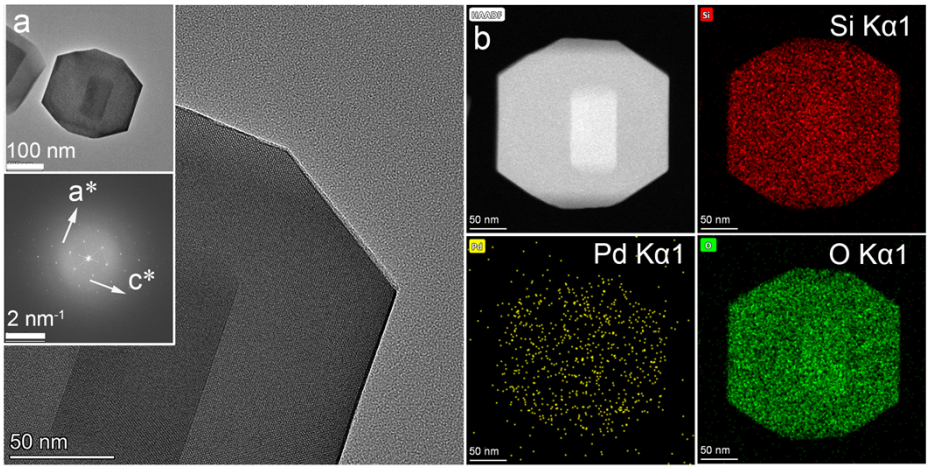


**Fig. S5** Typical TEM images and element mapping of as-made Pd@S1. a) High-resolution TEM images of the encircled area in Pd@S1. b) Element mapping of Si, O, Pd in the as-made Pd@S1, respectively.

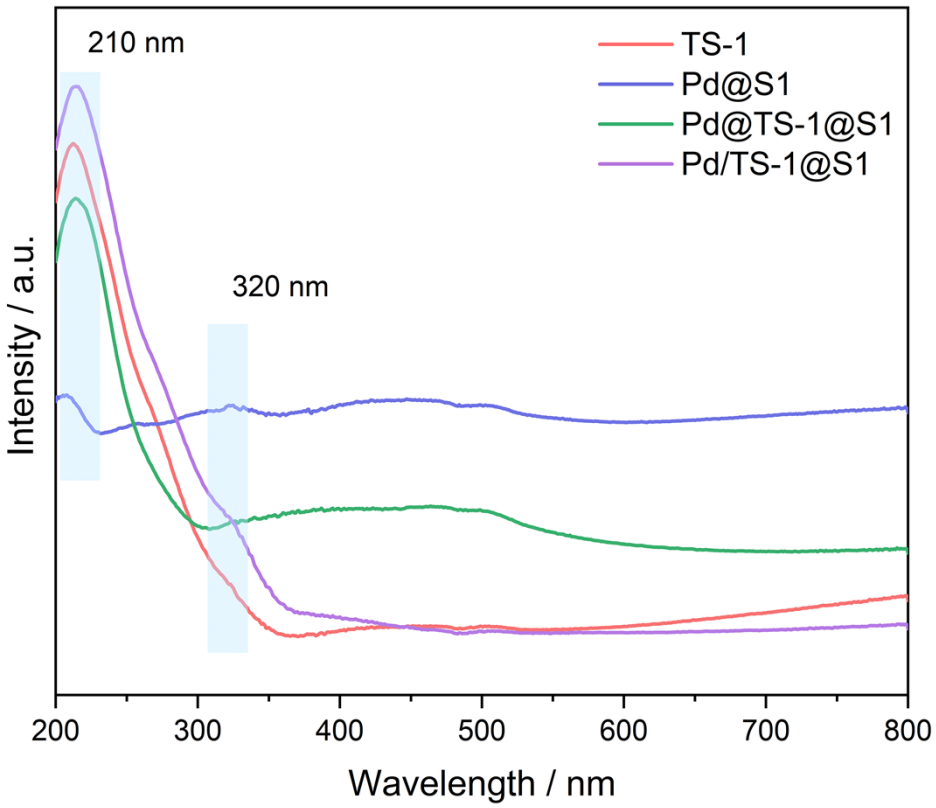


**Fig. S6** UV-Vis spectra of as-made zeolite catalysts.

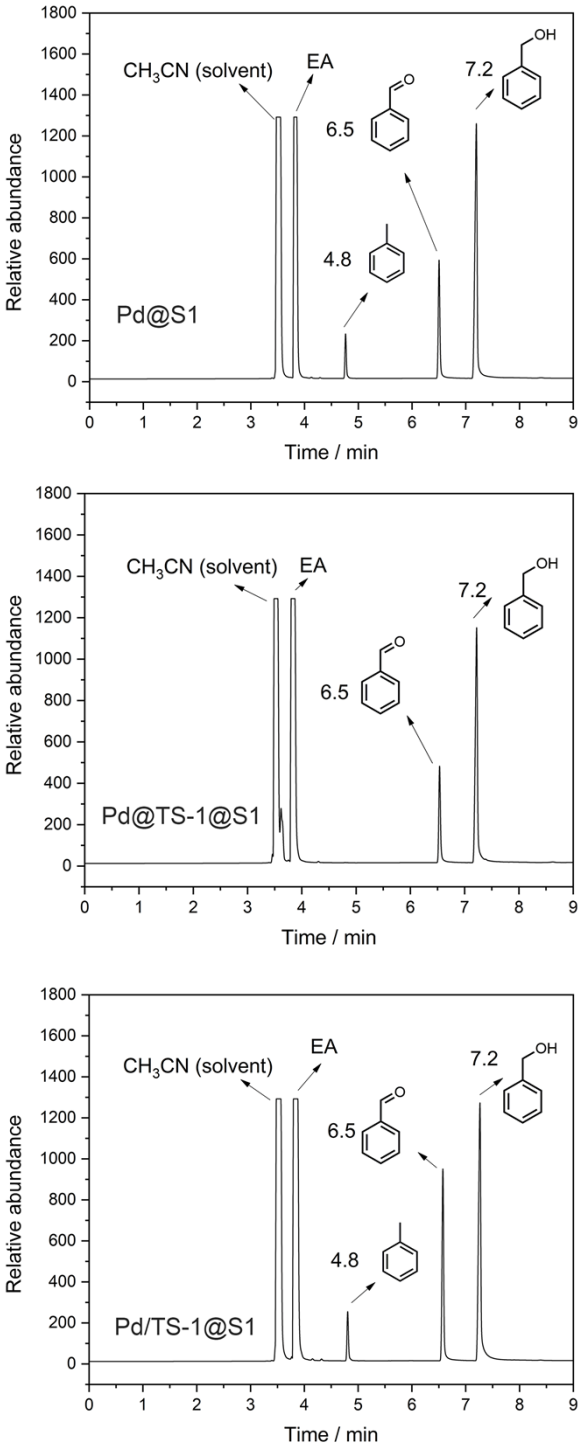


**Fig. S7** The gas chromatogram spectra of the final products (The final products were extracted by ethyl acetate solution).

# 3. List of tables

**Table S1**. The content of elements by ICP-OES

| Entry | Si wt% | Ti wt% | Pd wt% |
|---|---|---|---|
| Pd@S1 | 42.71 | / | 0.94 |
| TS-1 | 38.85 | 1.59 | / |
| Pd@TS-1@S1 | 40.36 | 0.86 | 0.96 |
| Pd/TS-1@S1 | 43.92 | 1.10 | 0.96 |

**Table S2.** Physical adsorption parameters of calcined zeolite catalysts.

| Entry | Surface area ($m^2/g$) | | | Pore Volume ($cm^3/g$) | | |
|---|---|---|---|---|---|---|
| | BET[a] | Langmuir[b] | Single point[c] | Total[d] | Micropore[d] | Mesopore[d] |
| TS-1 | 381.2 | 600.7 | 391.7 | 0.22 | 0.13 | 0.09 |
| Pd@S1 | 355.6 | 569.2 | 359.9 | 0.20 | 0.13 | 0.07 |
| Pd@TS-1@S1 | 394.4 | 636.8 | 404.6 | 0.23 | 0.13 | 0.10 |
| Pd/TS-1@S1 | 360.8 | 570.8 | 363.1 | 0.21 | 0.13 | 0.08 |

***Note***: [a] Calculated by the BET method, [b] Calculated by the Langmuir method, [c] Single point surface area at $P/P_0 = 0.29$, [d] Calculated by the *t*-plot method.

**Table S3**. Comparative catalytic study over various zeolite catalysts on benzylalcohol

| Entry | Catalyst | Oxidizer | Yield [a] / % | Yield [b] / % | Sel [a] / % |
|---|---|---|---|---|---|
| 1 | Pd@S1 | $H_2O_2$ | 25.8 | 7.1 | 78.1 |
| 2 | Pd@TS-1@S1 | $H_2O_2$ | 27.4 | 0 | >99 |
| 3 | Pd/TS-1@S1 | $H_2O_2$ | 31.5 | 8.1 | 79.3 |

***Note*:** [a] Main product benzaldehyde, [b] main product toluene and the reaction condition: 1 mmol benzylalcohol, 1.5 mmol $H_2O_2$, 3 mL $CH_3OH$, 40 mg catalyst, 100 ℃ and 12 h.