

Supporting information

Solvent-free liquid phase *tert*-butylation of phenol over hierarchical ZSM-5 zeolites for the efficient production of 2,4-ditert-butylphenol

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Experimental Section

I. Synthesis of materials

The hierarchical zeolites were synthesized according to the methods described in the literature.¹ In a typical synthesis procedure (Si/Al=50), 3.2 g of pluronic P123 (EO₂₀PO₇₀EO₂₀, MW=5800) was added to 18 g distilled water under continuous stirring to get a homogeneous solution. Then, 0.2 g aluminum isopropoxide and 10.4 g tetraethylorthosilicate (TEOS) were added to the solution, subsequently. The resultant mixture was stirred vigorously for 2 hours. After that, 4.1 g tetrapropylammonium hydroxide (TPAOH, 25% in water) was added dropwise into the sol. The molar ratio of the resultant sol was SiO₂: 0.01Al₂O₃: 0.1TPAOH: 0.11P123: 20H₂O. Stirring was continued to form a solidified gel and the whole stirring process was carried out at 40 °C. The resultant wet gel was aged at 60 °C for about 8 h and subsequently, dried at 90 °C for at least 12 h until the mass of solid gel became unchanged. Then, this as-prepared gel was crystallized by SAC method at 160 °C for 18 h. The product was washed and filtrated repeatedly for several times and then dried at 100 °C overnight. Finally, the product was calcined at 600 °C for 10 h in air to remove the organic templates and the obtained product was labeled as HZ50. Similarly, depending on the designated Si/Al molar ratios in the precursor gels, sample HZ30, HZ100, and HZ200 were also prepared.

For comparison, conventional ZSM-5 with the Si/Al ratio of 50 was purchased from Nanjing Jinling Petrochemical Co., Ltd. Before catalysis tests, all catalysts were ion-exchanged three times with NH₄⁺ using a 10% NH₄NO₃ solution and then calcined again in air at 550 °C for 5 h to convert them into the H⁺ form.

II. Characterization

Powder X-ray diffraction (XRD) were recorded by using a Rigaku D/Max 2200PC diffractometer with CuK α radiation (40 kV and 40 mA) with a scanning rate of 4°min⁻¹ over the 2 θ range of 5–50°. The nitrogen adsorption isotherms were measured on the Micromeritics Tristar 3000 and Micromeritics ASAP 2020 porosimeters at 77 K for mesoporosity and microporosity, respectively. The surface area, micropore and mesopore distributions were calculated according to the BET and BJH theories. SEM micrographs of uncoated powders were obtained on the field emission scanning electron microscopy Hitachi S4800. Transmission electron microscopy was performed with a JEOL-2010F.

The acidic properties of the obtained materials were carried out by temperature programmed desorption of ammonia (NH₃-TPD) on a Micromeritics Autochem TP5080 instrument equipped with a thermal conductivity detector (TCD). The 100 mg sample was pretreated at 550 °C in a flow of N₂ (30 ml/min) for 30 min, followed by ammonia loading at 100 °C for 15 min. Then, N₂ was passed through the sample for 30 min to remove free and weakly adsorbed NH₃. And desorption of NH₃ was monitored in the range of 100–550 °C at a ramp rate of 10 °C /min.

III. Catalytic tests

The solvent-free liquid phase *tert*-butylation of phenol was carried out in a three-necked round-bottom flask with magnetic stirrer and a temperature-controlled heating jacket under N₂ atmosphere. A chilled water reflux condenser and an injector pump were equipped to minimize the evaporation of TBA. To obtain accurate calculation of conversion, acetophenone was used as the internal standard for phenol. In a typical reaction, 0.3 g of the catalyst, 4.7 g of phenol, and 1 g of acetophenone were mixed with continuous stirring until the reaction temperature reached 120 °C. Subsequently, 11.8 ml of TBA was dosed in the reactor at the ramp rate of 2 ml/h by the injector pump. Liquid samples were withdrawn using a micro-syringe after reaction 24 h and analyzed by GC–MS (Agilent, 6890/5973N). Since the reactant TBA was in excess, conversion was calculated based on the phenol.

References

- 1 J. Zhou, Z. Hua, Z. Liu, W. Wu, Y. Zhu and J. Shi, *Acs Catal.*, 2011, **1**, 287.

Figures

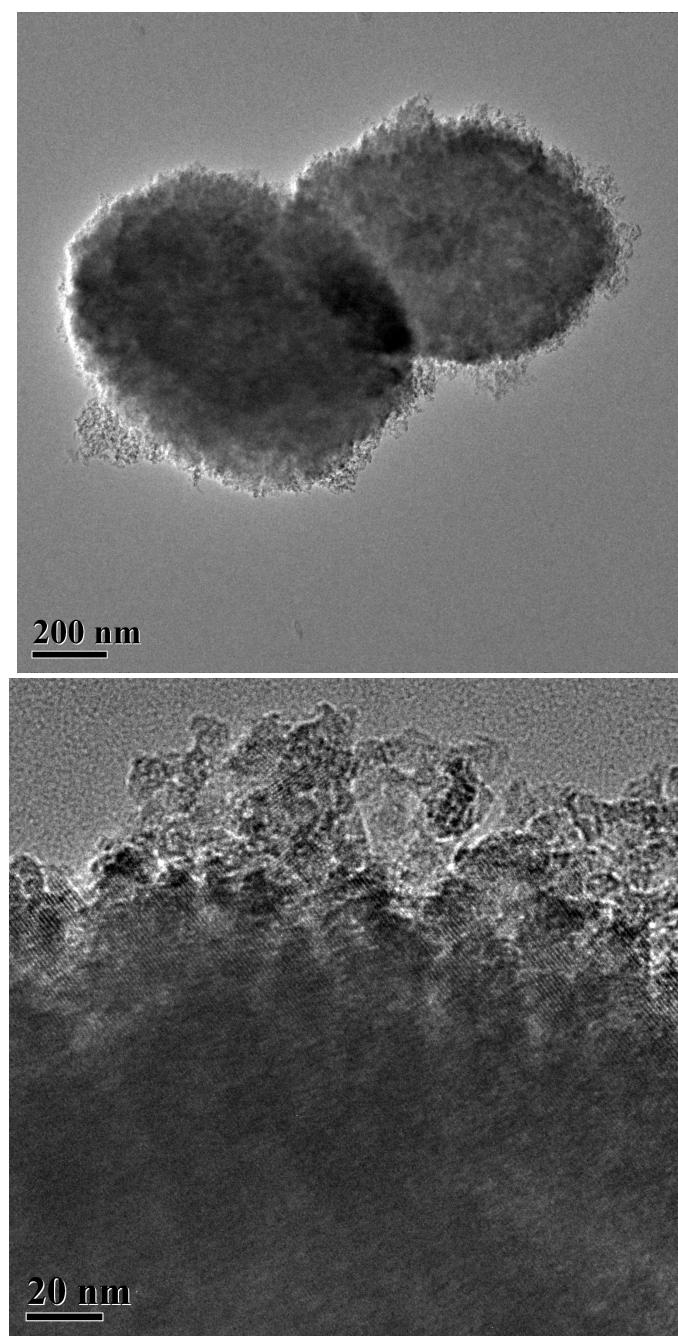


Fig. S1 Representative HR-TEM images of hierarchical zeolite HZ50.

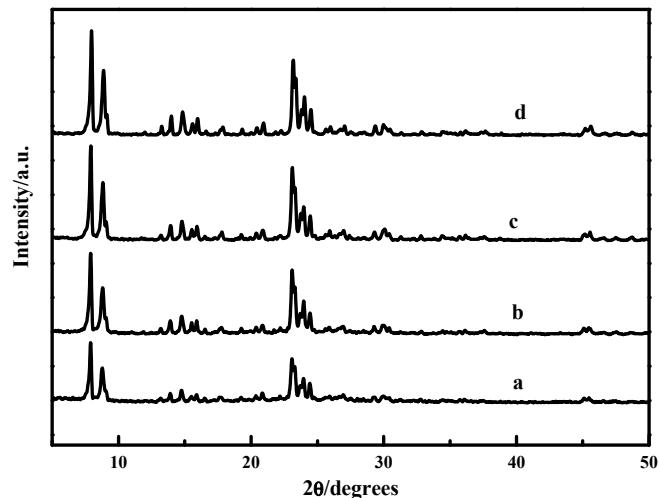


Fig. S2 Powder XRD patterns of (a) HZ30, (b) HZ50, (c) HZ100, (d) HZ200.

Table S1 The maximum desorption temperature (°C) for strong and weak acid sites of the catalysts obtained from NH₃-TPD curves.

Catalysts	HZ30	HZ50	HZ100
The maximum desorption temperature for strong acid sites	348	359	367
The maximum desorption temperature for weak acid sites	186	182	154

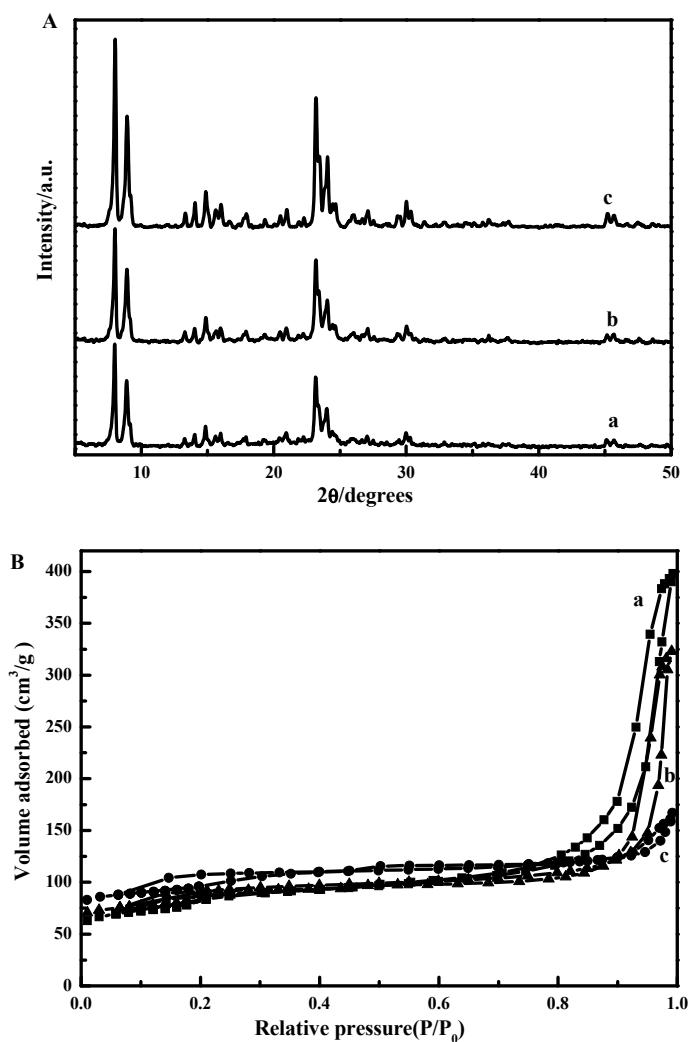


Fig. S3 Hydrothermal stability under 70% steam in N₂ at 973 K for 12 h of the representative samples, A: X-ray diffraction patterns; B: N₂ adsorption isotherms of (a) HZ30, (b) HZ50 and (c) HZ100.

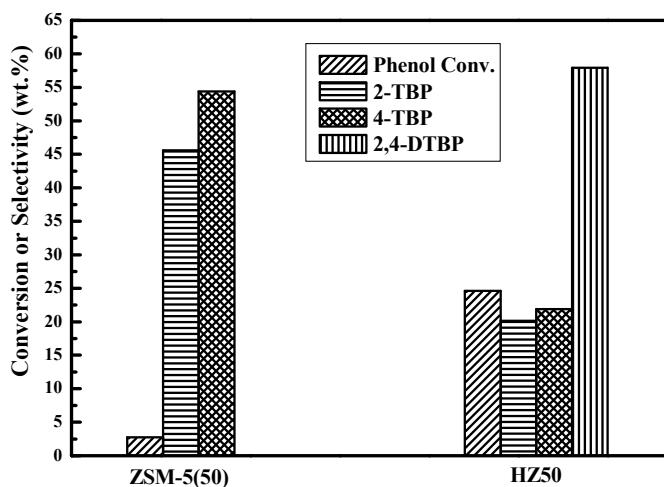


Fig. S4 Conversion and selectivity of the phenol alkylation using different types of solid acidic catalysts.

Table S2 Effect of TBA/phenol mole ratio on the phenol conversion and product selectivity.

TBA: Phenol mole ratio	Conversion Phenol (%)	Product selectivity (%)		
		2-TBP	4-TBP	2,4-DTBP
2	11.3	16.2	17.1	66.7
2.5	19.1	8.2	9.9	81.9
4	32.2	7.2	9.2	83.6