Engineering porosity and acidity of H-Beta zeolite by dealumination for the production of 2-ethylanthraquinone *via* 2-(4'-ethylbenzoyl) benzoic acid dehydration

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Fig. S1 SEM image of nano-sized H-Beta zeolite.



Fig. S2 The structures of E-BBA dehydration over H-Beta zeolites.(Considering the clarity of structures, only the part of structures treated by high-level functional were shown, the others were omitted)



Fig. S3 XRD patterns of H-Beta and dealuminated H-Beta zeolites.



Fig. S4 ²⁹Si MAS NMR spectra of H-Beta and dealuminated H-Beta zeolites.

In the ²⁹Si MAS NMR spectra, five peaks assigned to Q4 (-112 and -116 ppm), Q3 (-107and -103 ppm), and Q2 (-99 ppm) sites were detected¹. The two peaks for Q4 sites originate from the two different stacking orders polymorph A and polymorph B known for zeolite BEA. The Q3 peaks at -103 and -107 ppm originating from Si(OSi)3(OH)1 and Si(OSi)3(OAl)1 tetrahedrons, respectively. All peaks were fitted with Gaussian functions, and the framework Si/Al ratio is calculated according to literature².

References:

- [1] Pérez-Pariente J., Sanz J., Fornés V., Corma A., J. Catal., 1990,124, 217.
- [2] M.A. Camblor, A. Corma, S.Valencia, Micropor. Mesopor. Mater., 1998, 25, 59.

	Sites	E (a.u.)	ΔE (kcal/mol)
0 1	1	-1610.7933094	0
	2	-1610.7917244	0.99
	3	-1610.7958588	-1.60
$7 \frac{5}{6} \frac{5}{1000} \frac{3}{4}$	4	-1610.7886260	2.94
	5	-1610.7831944	6.35
	6	-1610.7910402	1.42
	7	-1610.8010084	-4.83
	8	-1610.7956514	-1.47
	9	-1610.7885487	2.99
	10	-1610.7944923	-0.74

Scheme S1 Assumed intermolecular dehydration of the carboxyl of one 2-(4'-ethylbenzoyl)-benzoic acid (E-BBA) molecule with the hydrogen atoms of another E-BBA molecule in positions 1-10, and the energies for all possible products of intermolecular dehydration

In order to make the calculated results comparable, the same method as the high layer of ONIOM was used (ω B97XD/6-31+G(d,p)) to get the energies and structures of two BEA molecules intermolecular dehydration. The energies of all possible species involved in the inter-molecular dehydration have been listed in Table. And only one product, which dehydrated at No.2 position, may fit in the channel of β zeolite. It was shown in following Figure (named as Dimer-1).



Scheme S2 Theoretical calculations of the configurations of representative products generated from intra- and inter-molecular dehydrations of E-BBA.

Table S1 Micropores trafficability of H-Beta zeolite for 2-EAQ and dimer-1 of

Micropore sizes in H-Beta zeolite	Straight channels in tetragonal structure, 0.68×0.73 nm	Straight channels in monoclinic structure, 0.60×0.73 nm	Sinusoidal channels in both structures, 0.55×055 nm
2-EAQ size, nm 0.25×0.54×1.04	Yes	Yes	Yes
Dimer-1 size, nm 058×0.65×1.63	Yes	Yes	No

inter-molecular dehydrations*

* The micropore sizes of BEA zeolite are crystallographic free diameters; the molecular sizes of 2-EAQ product from intra-molecular dehydration and dimeric by-product from inter-molecular dehydration are calculated by using ONIOM (ω B97XD/6-31+G(d,p)) method.

theoretically calculated molecular sizes of both intra-The and inter-molecular dehydration products of E-BBA are compared with the crystallographic micropore diameters of H-Beta zeolite, it is easy to see that the shape-selective function of the H-Beta zeolite micropores should be a help hand to cripple the inter-molecular dehydration of E-BBA. The direct comparison of these sizes indicates that the micropores of H-Beta zeolite can exclude the formation of most inter-molecular dehydration products. Only dimer-1 is possible to diffuse out through both straight and sinusoidal channels. There is no doubt that, in order to take the advantage of the shape-selectivity of H-Beta zeolite micropores, the external surface of the zeolite should be passivated in advance.

Sample	$S_{\rm BET}^{a}$ (m ² g ⁻¹)	V_{pore}^{b} (cm ³ g ⁻¹)	$V_{\rm micro}^{\rm c}$ (cm ³ g ⁻¹)	$V_{\rm meso}{}^{\rm d}$ (cm ³ g ⁻¹)	$c_{\mathrm{B}}^{\mathrm{e}}$ (µmol _{Py} g ⁻¹)	c_{L}^{e} (µmol _{Py} g ⁻¹)
HB	522	0.59	0.08	0.51	111	124
HB0.3	607	0.63	0.06	0.57	107	99
HB0.6	556	0.58	0.08	0.50	60	27
HB2.0	538	0.61	0.05	0.56	4	12

Table S2 Characterization data of H-Beta and dealuminated H-Beta zeolites

^a BET method applied to the Ar isotherm.

^b Volume of Ar adsorbed at $p/p_0=0.99$.

^c *t*-plot method applied to the Ar isotherm.

^d $V_{\text{meso}} = V_{\text{pore}} - V_{\text{micro}}$.

^e Concentration of Brønsted (c_B) and Lewis (c_L) acid sites derived from the IR study of adsorbed pyridine (Py).

Compared with parent sample HB, the BET surface area increased for all treated samples, but the degree of increased BET surface area was opposite with the concentration of acid, viz., HB0.3>HB0.6>HB2.0. Associated with the NMR results, most of the extra-framework aluminium species at low concentration of acid was eliminated; while further increasing the concentration of acid will dissolve the framework aluminium species which would block the channel again. Therefore, it exhibited in the opposition of degree of increased BET surface area with the concentration of acid.