Supporting Information for

Novel DMF-mediated formation of cyclic intermediates facilitating dicyclopentadiene epoxidation over Ti-BEA/H₂O₂

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1. Experimental

1.1 Materials preparation

Al-BEA molecular sieve (Sinopec Catalyst Co.,Ltd. Changling Division). Nitric acid (HNO₃, 65%, Tianjin Damao Chemical Reagent Partnership Enterprise (Limited Partnership)), Titanium tetrachloride (TiCl₄, 99.0%, Shanghai Aladdin Biochemical Technology Co., Ltd.), Ethyl alcohol (99.9%, Beijing InnoChem Science & Technology Co., Ltd.).

1.2 Catalyst preparation

Preparation of DeAl-BEA: Al-BEA zeolites were used as raw materials, prepared by acid de-aluminization method. Al-BEA was stirred and mixed with a 13 mol/L HNO₃ solution at a mass ratio of 1:41 and stirred at 100 °C for 24 hours to remove skeletal aluminium. Subsequently, the mixture was filtered and washed with deionised water until reaching a neutral pH. It was then dried at 110 °C for four hours. The resulting solid was stirred with a 0.1 mol/L HNO₃ solution (prepared by diluting 65 wt.% nitric acid) in accordance with a mass ratio of 1:10. This was stirred at 80 °C for two hours to remove non-skeletal aluminium. Subsequently, the mixture was filtered at 110 °C for four hours to remove non-skeletal aluminium. Subsequently, the mixture was filtered and washed washed water was filtered and washed washed until reaching a neutral pH with deionized water. It was then dried at 110 °C for four hours and calcined at 550 °C for three hours. This process yielded DeAl-BEA zeolites with nested hydroxyl defects.

Preparation of Ti-BEA: Ti-BEA zeolites were prepared by the liquid-phase post insertion of titanium method ¹⁻³, TiCl₄ was chosen as the titanium source, and anhydrous

ethanol was used as the solvent, and the steps of preparation were as follows: Firstly, ethanol and TiCl₄ were combined and stirred for 20 minutes at 60 degrees Celsius in order to produce $Ti(Cl)_{4-n}(OEt)_n$ (0<n<4). Subsequently, DeAl-BEA zeolites were added to the mixed solution of ethanol and TiCl₄ (the molar ratio of TiCl₄ to Si atoms in DeAl-BEA was 0.02). The volumetric mass ratio of ethanol to DeAl-BEA was 20, and the solution was stirred for two hours at 60 °C. At the conclusion of the heating period, the solvent was removed via rotary evaporation (60 °C, -0.1 MPa), and the resulting material was dried for four hours at 110 °C. Finally, Ti-BEA zeolites were obtained through calcination at 550 °C for 3 hours.

1.3 Characterizations

XRD: X-ray powder diffraction was conducted using an Empyrean X-ray diffractometer manufactured by Philips. The test conditions included the use of Cu K α rays with $\lambda = 1.5406$ nm, a 2 θ scanning range of 5° to 35°, and the calculation of relative crystallinity as the peak area at 2 $\theta = 22.5^{\circ}$. This value was taken to be 100% for the relative crystallinity of Al-BEA zeolites.

XRF: X-ray fluorescence spectroscopy was conducted using a ZSX100E X-ray fluorescence spectrometer manufactured by Rigaku. The samples were initially pressed into slices and subsequently tested. The excitation voltage was set at 40 kV, while the excitation current was set at 250 mA. The samples were tested using a tungsten target. XPS: X-ray photoelectron spectroscopy was conducted using an ESCALAB 250 X-ray photoelectron spectrometer from Thermo Fisher Scientific, with monochromatic Al Kα

X-rays at an energy of 1486.6 eV and a power of 150 W. The C1s peak of the contaminated carbon (284.8 eV) was employed to correct for the charge potential shift, and the OriginPro2022 software was utilized for split-peak fitting of the spectra.

UV-Vis: The ultraviolet-visible spectroscopic analysis was conducted to examine the optical properties of the samples. The analysis of UV-visible diffuse reflectance spectra was conducted using a Cary300 UV spectrophotometer produced by Agilent. The test conditions were as follows: the samples were tested at room temperature and under normal pressure, after pressing the film, with a scanning range from 190 to 800 nm.

BET: The characterisation and analysis of N₂ adsorption and desorption was conducted using an Autosorb 6B static nitrogen adsorbent, manufactured by Quantachrome. The test conditions were as follows: the sample was loaded and heated to 300°C, then evacuated to 1.33×10^{-2} Pa. The sample was then purified at constant temperature and pressure for 4h, after which it was characterised under liquid nitrogen at a temperature of -196°C. The specific surface area was calculated using the BET formula, and the sample was deemed to be null. The specific surface area was calculated using the BET formula, and the sample was found to have an empty volume calculated by the adsorption amount under the condition of p/p0 ≤ 0.98 .

TEM: Tecnai-F20 G2 transmission electron microscope from FEI was used for the transmission electron microscope, and the test conditions were that the accelerating voltage was 200 kV, and the samples to be tested were first dispersed in anhydrous ethanol on a multivacuum microgrid, and then selected areas were focused for observation after drying.

SEM: A Quanta 200F electron scanning electron microscope from FEI was used as the scanning electron microscope.

OH-IR: Fourier Transform Infrared Spectroscopy A Nicolet 6700 Fourier Transform Infrared (FT-IR) spectrometer manufactured by Thermo Fisher Scientific was selected for the infrared hydroxyl test.

1.4 Theoretical calculations

In this work, the BEA zeolite crystal was used as the basic model and catalyst was constructed by replacing one Si atom in BEA pore with Ti atom, forming a tetrahedral Ti-(O-Si)₄ active center structure with four bridging oxygen atoms. All theoretical computations based on spin-polarized density functional theory (DFT) ⁴ were conducted by Vienna Ab initio Simulation Package (VASP) ^{5, 6}. The ion-electron interactions were treated by projector augmented wave (PAW) method ⁷. Generalized gradient approximation (GGA)⁸ of the Perdew-Burke Enzerhor (PBE) functional⁹ was used to describe the exchange-correlation function. The plain-wave cutoff energy was set to 450 eV and DFT-D3 scheme ¹⁰ was employed to consider the long-range van der Waals correction. The first Brillouin zone was sampled by Gamma point only due to the large enough lattice. The convergence criteria of energy and force for all structural optimization and energy calculation were set to 10⁻⁴ eV and 0.02 eV Å⁻¹, respectively. The Bader population was used for charge analysis by the code developed by Henkelman et al.¹¹. The LOBSTER program was employed to calculate Crystal Orbital Hamilton Population (COHP) to analysis bonding states of a specific bond ¹².

2. Supporting Figures



Scheme S1. DCPD structural formula.



Fig. S1. XRD spectra of Al-BEA, DeAl-BEA, and Ti-BEA samples.



Fig. S2. UV-Vis spectra of Ti-BEA samples.



Fig. S3. XPS spectrum of the Ti-BEA sample.

sieve samples.							
entry	catalyst	crystallinity ^{a/%}	Si/Al ^b	bulk Si/Ti ^b	surface Si/Ti ^c		
1	Al-BEA	100	9.73	—	—		
2	DeAl-BEA	99	>500	—	—		
3	Ti-BEA	96	>500	39.39	81.59		
^a XRD. ^b XRF. ^c XPS.							

Table S1. Relative crystallinity and elemental analysis of different molecular

Table S2. Morphological distribution of titanium in X-ray photoelectron spectra

and UV-vis spectra.

		Ti species content		T'			
entry	catalyst	from XPS/%		11 species content from UV-VIS/%			
		459.0 eV	460.1 eV	215 nm	270 nm	320 nm	
1	Ti-BEA	34.3	65.7	80.9	14.4	4.7	



Fig. S4. N₂ adsorption and desorption curve spectra of Al-BEA, DeAl-BEA, and Ti-

BEA samples.



Fig. S5. FT-IR spectra of Al-BEA, DeAl-BEA, and Ti-BEA samples in the region

of hydroxyl stretching vibrations.



Fig. S6. Transmission electron microscopy of Al-BEA, DeAl-BEA, and Ti-BEA

samples.



Fig. S7. Scanning electron microscope of Al-BEA, DeAl-BEA, and Ti-BEA

samples.



Fig. S8. Calculation of the charge change of the carbonyl O atom upon coordination

of DMF to the active Ti(IV) species of Ti-BEA.



Fig. S9. DCPD epoxidation reaction pathway.



Fig. S10. DFT model presentation.



Fig. S11. (a) S_{1,2-DCPDMO} in different solvent systems (as a function of time). (b) S_{5,6-DCPDMO} in different solvent systems (as a function of time). (c) S_{DCPDDO} in different solvent systems (as a function of time). (d) S_{other} in different solvent systems (as a

function of time).



Fig. S12. Calculation of the charge change of the Ti atom of Ti-BEA upon

coordination of DMF to the active Ti(IV) species of Ti-BEA.

	solvent	Conversion S		Selectivity of	Selectivity of product/%		
entry		of	1,2-	5,6-	DODDO	- 41	
		DCPD/%	DCPDMO	DCPDMO	DCPDDO	other	
1	methanol	76.2	52.5	16.2	8.3	23.0	
2	ethanol	75.8	48.4	20.0	9.8	21.8	
3	n-propanol	83.2	47.9	19.9	10.1	22.1	
4	i- propanol	78.4	51.3	18.5	10.3	19.9	
5	n-butyl alcohol	73.0	46.5	27.3	7.2	19.0	
6	i-butyl alcohol	78.8	54.1	15.3	10.8	19.8	
7	t-butyl alcohol	83.6	55.3	17.9	11.0	15.8	
8	acetonitrile	82.0	63.0	20.1	9.6	7.3	
9	acetone	91.4	36.1	20.7	12.8	30.4	
10	1,4-dioxane	86.9	34.0	30.6	9.6	25.8	
11	tetrahydrofuran	93.2	12.6	12.1	9.3	66.0	
12	trichloromethane	12.6	39.0	22.1	11.2	27.7	
13	N,N-dimethylformamide	98.4	74.6	18.8	6.6	0	
14	N-methylformamide	95.3	67.2	23.6	9.2	0	
15	dimethylsulfoxide	18.9	71.1	28.9	0	0	

Table S3. DCPD epoxidation reaction results for different solvents

reaction time: 8 h

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