

Readily available Ti-Beta as efficient catalyst for greener and sustainable production of campholenic aldehyde

Supporting Information

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A. Experimental

1 Chemicals

α -pinene oxide, isocarveol, dodecane, acetonitrile (CAN), toluene, cyclohexane, N,N-dimethylacetamide (DMA), bis(cyclopentadienyl) titanium dichloride were purchased from Sigma-Aldrich.

CP-811 zeolite was purchased from Zeolyst.

2 Catalyst preparation

1 Ti-beta-F

Ti-beta-F was synthesized in fluoride medium following the method described in the literature [1].

2. Dealumination of beta zeolite:

5 g of CP-811 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$) were added to 100 mL of HNO_3 solution (13M). The solution was heated up at 100°C under stirring for 20h. The dealuminated sample was washed extensively with water until pH=7 and dried overnight at 100°C. The sample was characterized by ICP, DRX, IR (KBr).

3. Ti-Beta-PS preparation

3 grams of dealuminated Beta zeolite was milled in a ball mill with 300 mg of bis(cyclopentadienyl) titanium dichloride 97% (Cp_2TiCl_2)(2%Ti). The weight of zirconium beads was 5 x grams of zeolite. Then the samples were screened (removed zirconium beads) at room temperature and 50 rpm. The dried sample was calcined in a combustion furnace to 550°C (10°C/min ramp rate), first under nitrogen flow (3h), and subsequently under air (3h). Gas flow rates of 75 ml min^{-1} were employed. The calcined sample was characterized by DRX, ICP, and UV Visible.

4. Post-synthesis treatment of Ti-Beta-PS

- Preparation of Ti-Beta-PS-HT

1 g of calcined Ti-Beta-PS was soaked into 20 ml distilled water and the solution was stirred at 80°C for 15 hours. The solid sample was recovered by filtration and washed with 1200ml distilled water. The solid was dried overnight at 60°C and it was calcined at 550°C for 6h in air.

- Preparation of Ti-Beta-PS-Na

1 g of calcined Ti-Beta-PS was soaked into 1.0 M NaNO_3 solution (50 ml) and the solution was stirred at 80°C for 15 hours. The solid sample was recovered by filtration and washed with 200 ml of distilled water. The solid was dried overnight at 60°C and it was calcined at 550°C for 6h in air [2, 3].

- Preparation of Ti-Beta-PS-Li.

1 g of calcined Ti-Beta-PS was soaked into 1.0 M LiNO_3 solution (50 ml) and the solution was stirred at 80°C for 12 hours. The solid sample was recovered by filtration and

washed with 200 ml of distilled water. The solid was dried overnight at 60°C, then it was calcined at 550°C for 6 h in air.

3 Characterization Techniques

XRD analysis was carried out with a Philips X'PERT diffractometer equipped with a proportional detector and a secondary graphite monochromator. Data were collected stepwise over the $2^{\circ} \leq 2\theta \leq 20^{\circ}$ angular region, with steps of $0.02^{\circ} 2\theta$, 20s/step accumulation time and $\text{CuK}\alpha$ ($\lambda=1.54178 \text{ \AA}$) radiation.

Si, Al, Ti, Li and Na contents were obtained by means of atomic absorption spectroscopy (Spectra AA 10 Plus, Varian).

UV/Vis spectra were registered with Cary 5000 UV-Vis-NIR spectrophotometer (Agilent).

FTIR spectra were recorded with a Thermo Nicolet 8700 FTIR spectrophotometer and a conventional quartz infrared cell connected to a vacuum dosing system. The catalyst powder was pressed into self-supporting wafers (10 mg) and activated at 250 °C in vacuum for 1 h, before the adsorption experiments. Adsorption of deuterated acetonitrile (4–200 mbar) was performed at room temperature with a calibrated volume (1.55 cm³), followed by time-controlled evacuation at the same temperature. In all cases, FTIR spectra of the unloaded catalyst sample were recorded as reference spectra. IR bands at 2004 and 1880 cm⁻¹ on the reference sample were used for normalisation of the spectra. Deconvolution of the IR spectra was done with the ORIGIN software program and Gaussian-type curves were considered.

Field-emission scanning electron microscopy (FESEM) micrographs were recorded on a ZEISS Ultra 55 microscope operating at 2 kV, with a 2×10^{-9} A beam current and 2.5 mm as the working distance.

4 Catalytic activity test

Reactions were monitored by GC-FID (Shimadzu, GC Plus ultra 2010) equipped with a HP-Innowax column (0.25µm*0.25mm*60m) and GC-MS (Shimadzu, GCMS-QP2010 Ultra). Dodecane was used as internal standard and calibration curves were established.

2 Microwave batch reactor

A serie of experiment were performed under microwave heating in a Biotage® Initiator+ equipment. For a typical experiment, the desired amount of zeolite, 2 mmol of α-PO and solvent were added in a microwave reaction vial of 2 mL. The vial was sealed and the reaction medium was heated up at the desired temperature for a determined time (min). At the end of reaction, internal standard, dodecane, was added to the reaction medium, the catalyst was filtered and a sample was analysed by GC.

3 Fixed bed reactor

The catalytic experiments were performed in a 10 mm internal diameter downflow stainless steel double jacket fixed bed reactor at temperature between 130-160°C, under 6-8 bars, and contact times between 0.00315-0.00483 h. Under these conditions, the reaction occurs in the liquid phase and the conditions of plug flow reactor (PFR) are fulfilled. The condition of turbulent flow generally ensures the absence of temperature, velocity and concentration gradients in the radial direction. We used 0.1-0.6 g of catalyst with particle sizes 0.20-0.40 mm, and silicagel (0.20-0.40 mm) was employed as stuffing. The temperature was controlled by thermal oil heating what ensured a homogenous temperature control among all the catalytic bed. The α -pinene oxide solution was pumped through the reactor with a Gilson piston pump, and the pressure was controlled with a BPR (Back Pressure Regulator) valve.

B. Characterisation of the Beta-zeolite samples.

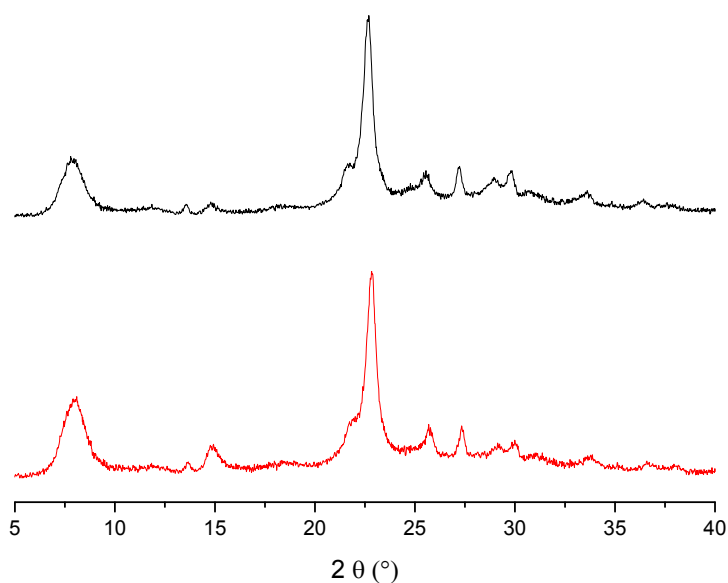


Figure S1. XRD patterns Al-Beta (-) and dealuminated-Beta (-).

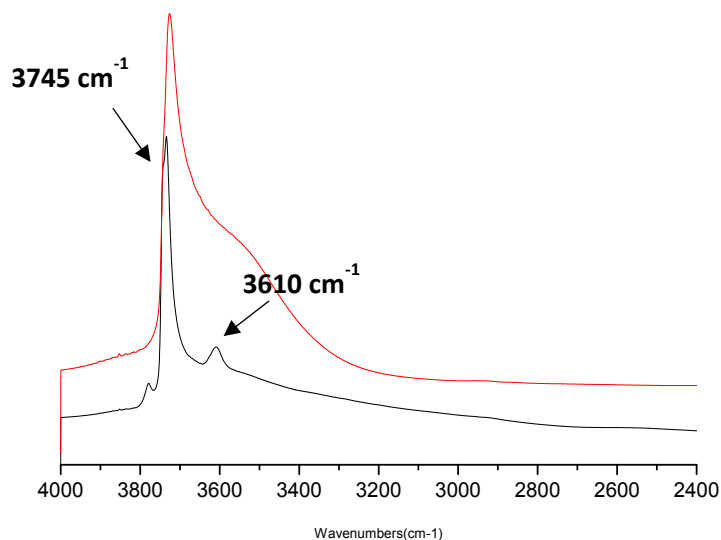


Figure S2. FT-IR spectra for Al-Beta (-) and dealuminated-Beta (-).

Table S1. ICP analysis of Al-Beta and dealuminated-Beta.

| Sample | Si% | Al% | Si/Al |
|-------------------|-------|------|-------|
| Al-Beta | 34,69 | 3,39 | 9,85 |
| dealuminated-Beta | 41.06 | 0,02 | 2046 |

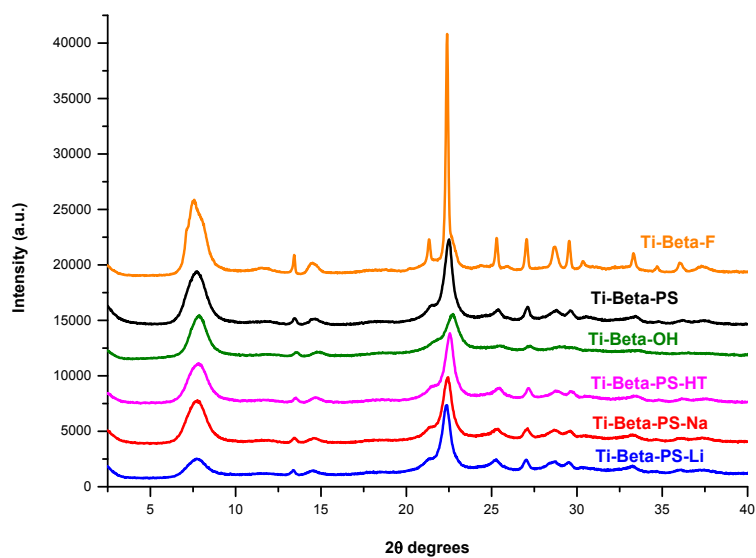


Figure S4. XRD patterns of the different Ti-Beta samples.

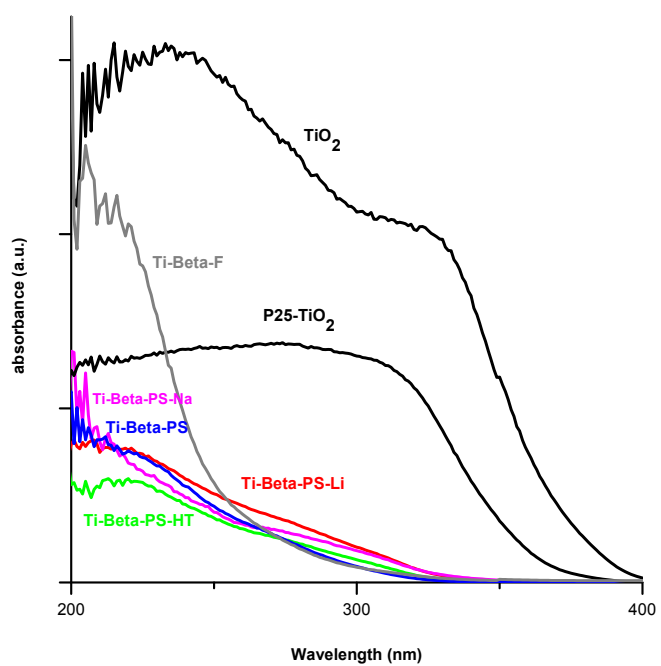


Figure S3. DRUV-Vis spectra obtained for Ti-Beta-F (-), Ti-Beta-PS (-), Ti-Beta-PS-Na (-), Ti-Beta-PS-Li (-), Ti-Beta-PS-HT (-) and TiO_2 (-).

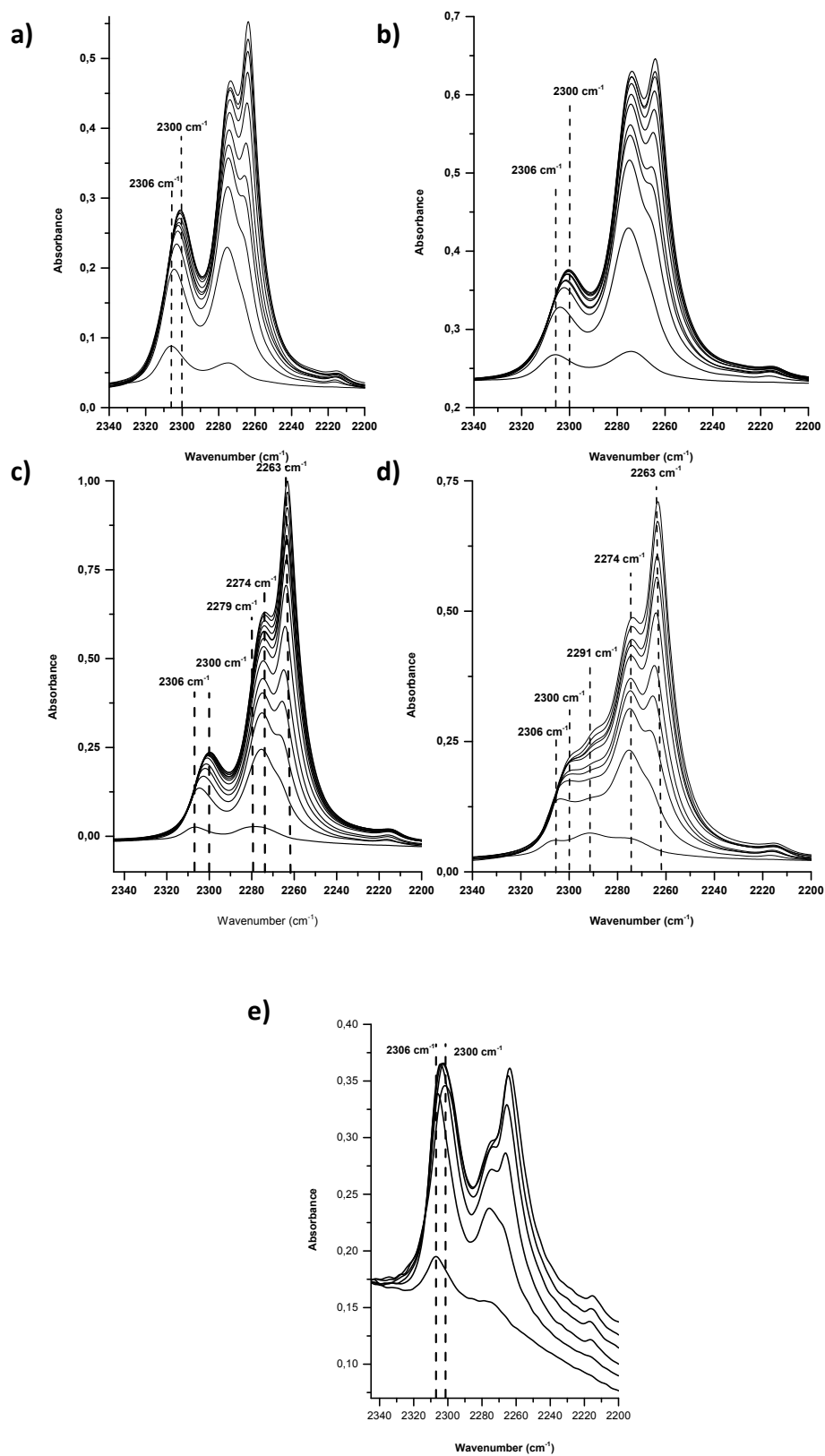


Figure S5. IR spectra at increasing acetonitrile coverage from 4 to 200 mBar on (a) Ti-Beta-PS, (b) Ti-Beta-PS-HT, (c) Ti-Beta-PS-HT-Na, (d) Ti-Beta-PS-HT-Li and (e) Ti-Beta-F samples.

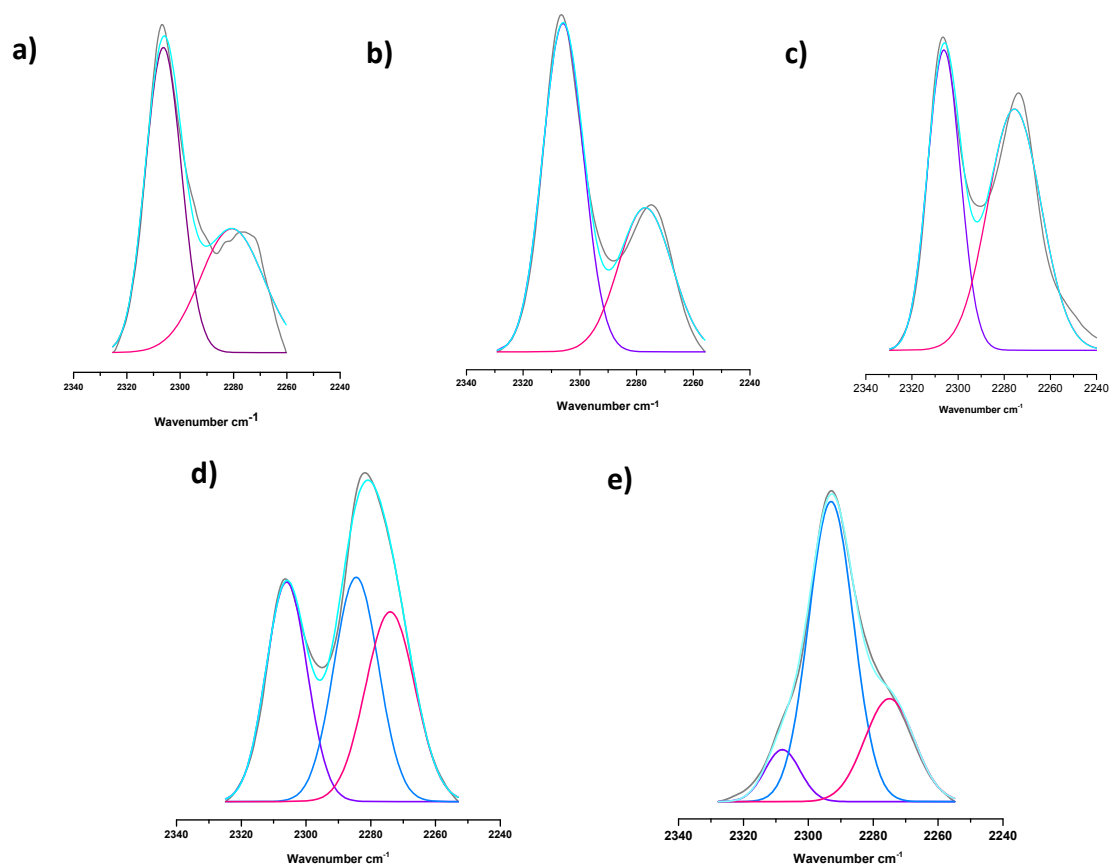


Figure S6. Deconvolution of the IR spectra with the ORIGIN software program for CD_3CN adsorption for the different Ti-Beta-PS samples after desorption for 4 minutes (a) Ti-Beta-F, (b) Ti-Beta-PS, (c) Ti-Beta-PS-HT, (d) Ti-Beta-PS-Na and (e) Ti-Beta-PS-Li samples.

Table S2.

| Catalyst | S_{BET} , m^2/g | Micro.Vol. (cm^3/g) | Total Vol. (cm^3/g) |
|----------------------|--|---------------------------------------|---------------------------------------|
| Ti-Beta-PS | 556 | 0.168 | 0.946 |
| Ti-Beta-PS-HT | 542 | 0.165 | 0.811 |
| Ti-Beta-PS-Na | 543 | 0.165 | 0.835 |
| Ti-Beta-PS-Li | 557 | 0.165 | 1.194 |

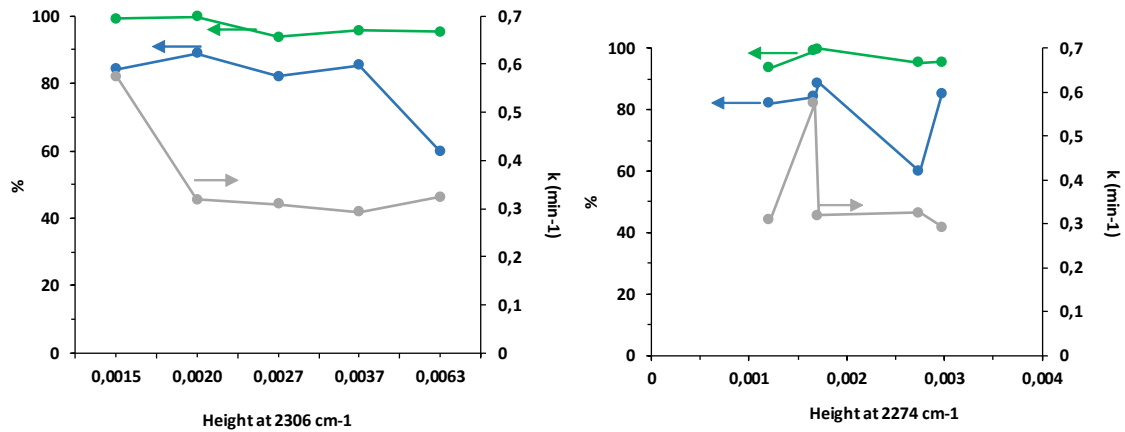


Figure S7. Correlation between the height of Lewis acid sites at 2306 cm^{-1} and Brønsted acid sites at 2274 cm^{-1} and the (●) CA selectivity, (●) α -PO conversion (●) Kinetic constant.

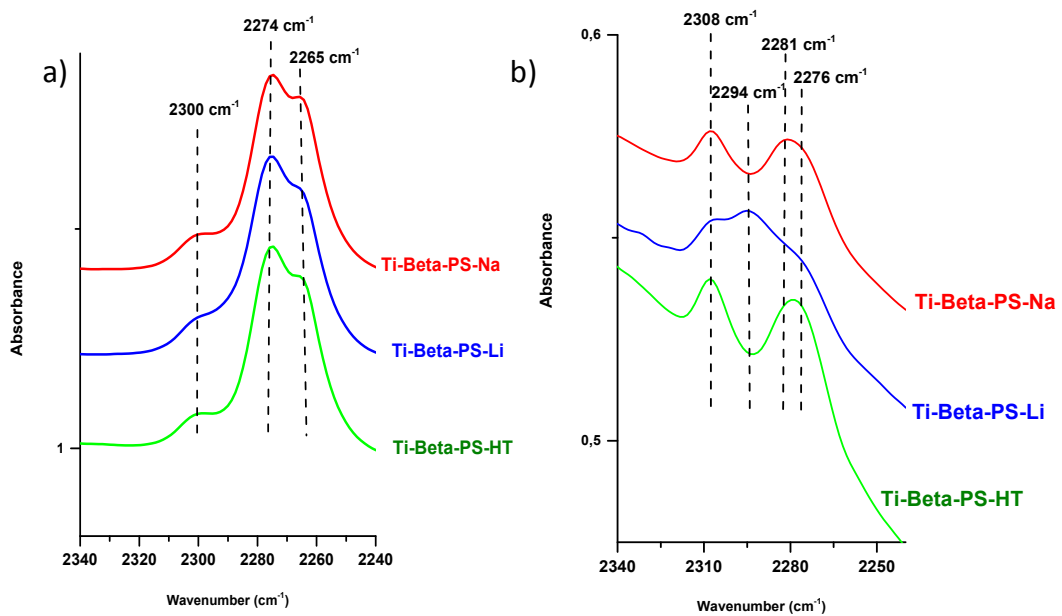


Figure S8. CD_3CN adsorption/desorption profile for the different Ti-Beta-PS samples, (a) maximum coverage and (b) after desorption for 4 minutes.

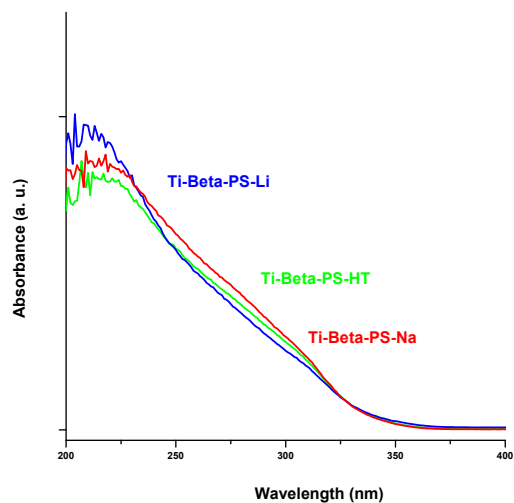


Figure S9. DRUV-Vis spectra obtained for Ti-Beta-PS-HT-Na (-), Ti-Beta-PS-HT-Li (-) and Ti-Beta-PS-HT (-).

References

1. O. de la Torre, M. Renz, A. Corma, *Applied Catalysis A: General*, 2010, **380**, 165.
2. R. Otomo, R. Kosugi, Y. Kamiya, T. Tatsumi and T. Yokoi, *Catal. Sci. Technol.*, 2016, **6**, 2787.
3. Taarning Esben, Saravanamurugan Shunmugavel, Spangsborg Holm Martin, Xiong Jianmin, West Ryan M., and Christensen Claus Hviid, *ChemSusChem*, 2009, **2**, 625.