Electronic Supplementary Information

Efficient catalysts of zeolite nanocrystals with a preferred orientation to nanofibers

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EXPERIMENTAL SECTION

1. Synthesis of nanocrystal zeolites. Nano-sized zeolite seeds were synthesized by controlling various crystallization conditions. The Y-zeolite seeds were prepared from the precursor solution with molar composition of $1Al_2O_3$: $4.35SiO_2$: 2.4TMAOH: 1.2TMABr: $0.048Na_2O$: 249 H_2O. The products were obtained by crystallization at 120°C for 72 h.

2. Grafting of nanocrystal zeolites on titania fibers. 2 g of TiO_2 fibers were immersed with aqueous ammonia solution (250 mL, pH = 10.5) for 0.5 h. After separation, the fibers were modified with 1 M NaCl solution [50 mL, including 0.5% of Poly(diallydimethylammonium chloride), PDDA] for about 0.5 h. The residual PDDA was removed by rinsing with aqueous ammonia solution three times. The modified TiO_2 fibers were then dispersed into 50 mL of aqueous ammonia solution (including 0.5 g of zeolite seeds). Subsequently TiO_2 nanofibers were collected by centrifugation with 4000 rpm for 15 mins.

3. Zeolite crystals growth. The synthesis solution for Y-zeolite@NFs was prepared with the molar composition: $1Al_2O_3$: $4.35SiO_2$: 2.4TMAOH: 1.2TMABr: $0.048Na_2O$: $500H_2O$, which was corresponded to the H_2O amount of 200 g. 2 g nanofibers grafted with the zeolite seeds were added into the solution. The suspension was stirred for 4 h, and then transferred into reactors. Crystallization was conducted at 120°C for 48 h. The obtained precipitates were recovered by filtration and washed with water. Finally, the solid products were dried at 80°C, followed by calcination at 550°C for 5 h.

4. Catalysis. The activities of Y-zeolite@NFs were assessed by acetalization of cyclohexanone and carboxylation of benzyl alcohol. The acetalization of cyclohexanone was conducted as follows. 10 mmol cyclohexanone and 100 mmol methanol were charged with 0.1 g of catalyst in a 50 ml-flask. Prior to the reaction, air was carefully removed by purging with argon and the reaction was conducted at 60°C under stirring. In the carboxylation of benzyl alcohol, 30 ml of dimethyl carbonate, benzyl alcohol (2.0 mmol), and 0.1 g catalysts were added in a 50 ml-flask. Air was carefully removed by purging with Argon prior to the reaction. The reaction was conducted at 60°C under stirring. The reaction mixture were analyzed by a Gas Chromatography (Agilent, HP6890) with a HP-5 column.

5. Characterization. The crystal structures of the samples were analyzed on an X-ray diffractometer (XRD, Philips Panalytical X'Pert Pro) using Cu Kα radiation at 40 kV and 40 mA, the scanning speed was 5°/min. TEM images were obtained with a JEOL JEM-2100 transmission electron microscope operating at an accelerating voltage of 200 kV. All the samples were dispersed in 95% ethanol and deposited onto a copper micro-grid coated with a carbon film. The field emission scanning electron microscopy (FESEM) was utilized to directly observe the morphology with a JEOL JSM-7001f at 10 kV. The IR spectra were recorded on Nicolet Nexus 870 IR spectrophotometer with the spectral range of 4000 - 400 cm^{-1} with a resolution of 4 cm^{-1}

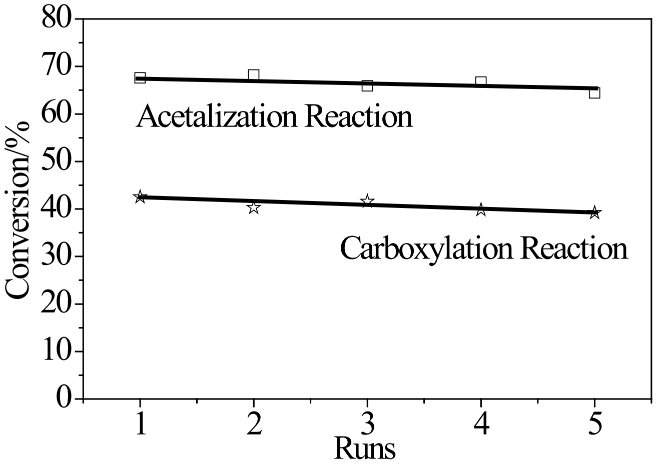


Figure S1. Test of the reusability of the Y-zeolite@NFs catalyst for the acetalization of cyclohexanone with methanol and the carboxylation of benzyl alcohol with DMC. The catalyst was used for five runs with each run lasting 24 hours.

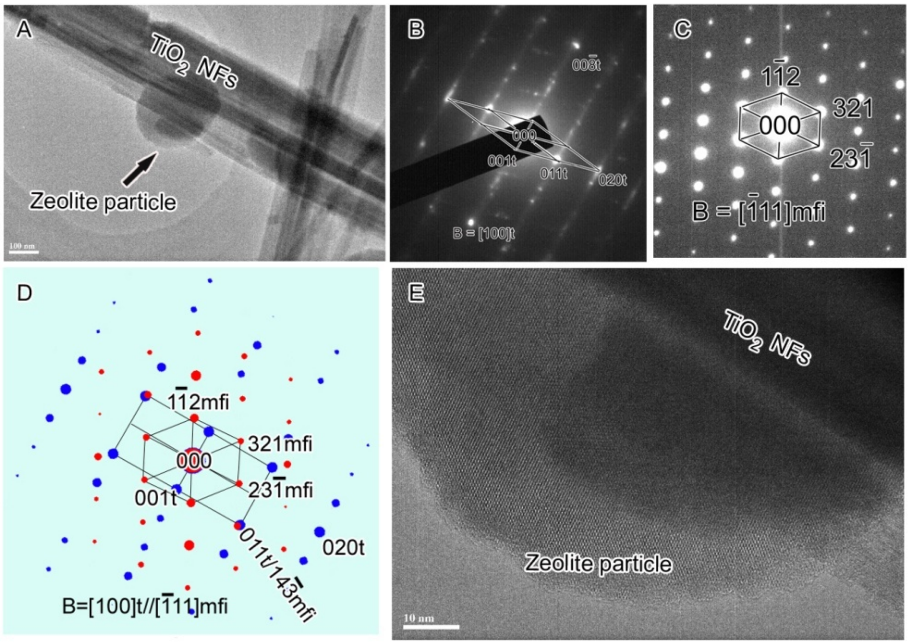
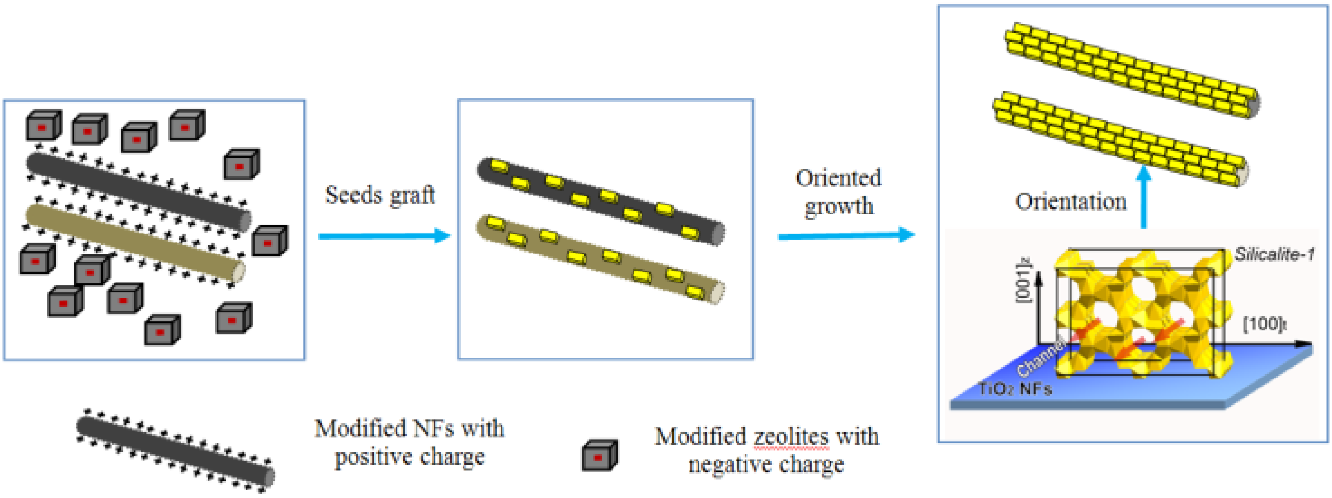


Figure S2 TEM micrographs of TiO_2 NFs (t) grafted with MFI-type nanozeolites (MFI). (A) Bright field image (scale bar is 100 nm); (B) Electron diffraction pattern (EDP) of TiO_2 substrate taken at $[100]_t$ direction. It is noticed that the strong diffraction spot $(011)_t$ is from the close-packed plane; (C) EDP of MFI-type zeolite particle taken at $[02\bar{1}]_{MFI}$ direction. The particle is well-crystallized and very intensive diffraction is observed; (D) simulated composited EDPs of both TiO_2 and MFI-type zeolite indicating a very good matching between plane $(011)_t$ and $(14\bar{3})_{MFI}$. The interplanar distances of the planes are 0.35 nm and 0.33 nm, respectively; and (E) HRTEM image showing good planar fringe of MFI-type zeolite on the substrate of TiO_2 (scale bar is 10 nm). There is a close crystallographic registry between TiO_2 and MFI-type zeolite as proved by TEM experimental evidence, that is, $[100]_t//[\bar{1}11]_{MFI}$ and $(011)_t//(14\bar{3})_{MFI}$.



Scheme 1. A schematic process for orient growth of MFI-type zeolite on TiO_2 nanofibers.