Electronic Supplementary Information

Nitrided ITQ-2 as an efficient Knoevenagel condensation catalyst

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Catalyst Preparation. NH₄-ZSM-5 (Si/Al = 14) and H-Y (Si/Al = 15) were obtained from Tosoh and PQ, respectively. MCM-22 (Si/Al = 17), ITQ-2 (Si/Al = 19) and SBA-15 (Si/Al = 20) were prepared according to the procedures described in the literature.^{1,2} Nitridation was performed following the procedures reported by Hammond et al.³ Approximately 1.0 g of the protonated microporous or mesoporous material was placed within a down-flow quartz reactor, heated under flowing He (60 ml min⁻¹) from room temperature to 673 K with a ramping rate of 0.5 K min⁻¹ and held at the same temperature for 6 h in order to make each material dehydrated. After shifting the flowing gas to a pure NH₃ stream (300 ml min⁻¹), the temperature was increased to 1123 K with a ramping rate of 1.5 K min⁻¹. The furnace was maintained at this temperature for 4 - 12 h and cooled down under flowing He (60 ml min⁻¹). Finally, all nitrided materials prepared here were kept under vacuum to a residual pressure of 10^{-3} Torr, prior to their use as base catalysts. For comparison, a commercially available magnesium oxide (99.99%, Aldrich) was calcined in air at 823 K for 2 h to remove adsorbed H₂O and CO₂ and then used as a reference catalyst.

Characterisation. Powder X-ray diffraction (XRD) patterns were measured on a PANalytical X'Pert diffractometer (CuK_{α} radiation) with an X'Celerator detector. Crystal morphology and average size were determined by a JEOL JSM-6510 scanning electron microscope. The N₂ sorption experiments were performed on a Mirae SI nanoPorosity-XQ analyzer. Elemental analysis was carried out on a Jarrell-Ash Polyscan 61E inductively coupled plasma spectrometer in combination with a Perkin-Elmer 5000 atomic absorption

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spectrophotometer. The nitrogen contents of the catalysts were determined using a Vario EL III elemental organic analyzer. The ²⁹Si MAS NMR spectra at a spinning rate of 6.0 kHz were measured on a Varian Inova 300 spectrometer at a ²⁹Si frequency of 59.590 MHz. The spectra were obtained with an acquisition of 1000-2500 pulse transients, which was repeated with a $\pi/2$ rad pulse length of 7.0 µs and a recycle delay of 30 s. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VG ESCALAB 220 iXL spectrometer employing an Mg K_a Xray source (1253.6 eV) with a background pressure of 4×10^{-9} Torr. Typically, 20 scans were accumulated and all binding energies are referenced, within an accuracy of ± 0.2 eV, to the C(1s) line at 284.6 eV from adventitious carbon. The IR spectra were collected on an ABB Bomem MB 104 FT-IR spectrometer using self-supporting zeolite wafers of approximately 12 mg (1.3 cm diameter). Prior to IR measurements, the samples were pretreated under vacuum at 773 K for 2 h inside a home-built IR cell with CaF₂ windows. The CO₂ temperature-programmed desorption (TPD) profiles were recorded on a fixed bed, flow-type apparatus linked to a Pfeiffer Prisma QMS 200 mass spectrometer detecting ion peaks at $m/z^+ = 44$ (CO₂⁺). About 0.1 g of sample was activated in flowing He (50 ml min⁻¹) at 823 K for 2 h. Then, pure CO₂ (10 ml min⁻¹) was passed over the sample at room temperature for 0.5 h. The treated sample was subsequently purged with He at the same temperature for 1 h to remove physisorbed CO₂. Finally, the TPD was performed in flowing He (30 ml min⁻¹) from room temperature to 923 K with a ramping rate of 10 K min⁻¹.

Catalysis. The Knoevenagel condensation reactions were carried out under an inert atmosphere (N₂) in a round bottom flask equipped with a magnetic stirrer and a reflux condenser. The flask containing a mixture of a particular type of aldehyde (5 mmol) (e.g., benzaldehyde, 2-naphthaldehyde, phenanthrene-9-carboxaldehyde, 1-pyrenecarboxaldehyde and 2-hydroxy-1-naphthaldehyde), ethyl cyanoacetate (5 mmol) and toluene (30 ml) was electrically heated. Once the mixture reached the desired temperature (353 or 373 K), 200 mg of catalyst was added into the flask. Water formed during the reaction was removed using a Dean-Stark trap. A small portion (*ca*. 0.1 ml) of sample was periodically withdrawn by a filtering syringe and analyzed by a HP 7890A gas chromatograph equipped with a flame ionization detector and HP-5 capillary column (30 m \times 0.25 mm). After 24 h reaction time, the used catalyst was recovered by filtration, washed repeatedly with copious acetone (0. 2 g solid/500 ml solvent), dried at 353 K within a vacuum oven and then employed for the reusability test.

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Fig. S1 Powder X-ray diffraction patterns of the proton form of a) ITQ-2, b) MCM-22, c) ZSM-5 and d) Y before (bottom) and after (top) nitridation at 1123 K for 12 h on pure NH₃ stream (300 ml min⁻¹).

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Fig. S2 ²⁹Si MAS NMR spectra of the proton form of a) ITQ-2, b) MCM-22, c) ZSM-5, d) Y and e) SBA-15 before (bottom) and after (top) nitridation at 1123 K for 12 h on NH_3 stream (300 ml min⁻¹).

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Fig. S3 N(1s) XPS spectra of nitrided catalysts prepared in this work: a) N(11.0)-ITQ-2, b) N(7.2)-MCM-22, c) N(6.0)-ZSM-5, d) N(6.4)-Y and e) N(6.1)-SBA-15. The values in parentheses of the catalyst identification are nitrogen contents in wt%.

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Fig. S4 IR spectra of the proton form of a) ITQ-2, b) MCM-22, c) ZSM-5, d) Y and e) SBA-15 before (bottom) and after (top) nitridation at 1123 K for 12 h on NH₃ stream (300 ml min⁻¹).

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Fig. S5 CO₂ TPD profiles for a) N(11.0)-ITQ-2, b) N(7.2)-MCM-22, c) N(6.0)-ZSM-5, d) N(6.4)-Y, e) N(6.1)-SBA-15 and MgO. The values in parentheses of the catalyst identification are nitrogen contents in wt%.





Fig. S6 Pore size distribution curve for a commercially available MgO (99.99%, Aldrich) calculated from its N_2 desorption branch isotherm using the BJH formalism.

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Scheme S1 Synthesis of 3-oxo-3*H*-benzo[*f*]chromene-2-carbonitrile via the Knoevenagel condensation between 2-hydroxy-1-naphthaldehyde with ethyl cyanoacetate.