Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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Structure Elucidation of the Highly Active Titanosilicate Catalyst Ti-YNU-1**

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Supporting information 1: N_2 Adsorption data

Specific surface area and Pore volume were obtained based on the following N_2 adsorption isotherms (Figure 1).

Specific surface area (Langmuir): Ti-YNU-1, 654 $m^2 g^{-1}$; 3D Ti-MWW, 548 $m^2 g^{-1}$.

Pore volume: Ti-YNU-1, 0.20 mL g^{-1}; 3D Ti-MWW, 0.16 mL g^{-1}.

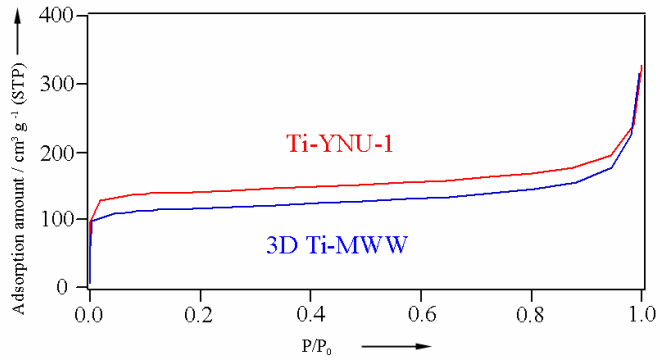

Figure 1 N_2 adsorption isotherms of Ti-YNU-1 and 3D Ti-MWW

Supporting information 2: the calibrated selected area ED pattern

Au particles were spattered on the carbon grid as an internal standard in order to calibrate the camera length. After calibrating the camera length from the gold ring, the unit cell parameters were obtained from the selected area electron diffraction in Figure 2, which is consistent with the data from the powder XRD examination (shown in Table 1).

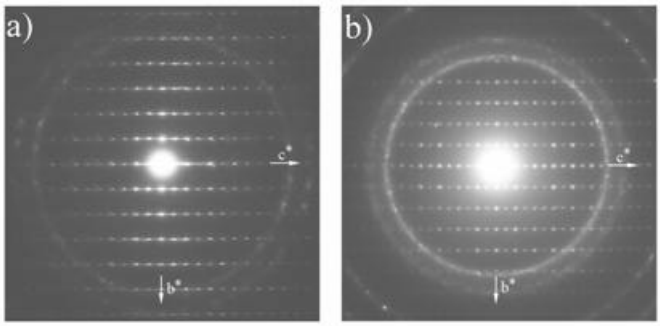

Figure 2 The selected area ED pattern of a) 3D Ti-MWW and b) Ti-YNU-1 with Debye –Scherrer ring from gold for calibration.

Table1: The calculated unit cell parameters from powder XRD and ED for 3D Ti-MWW and Ti-YNU-1.

Sample	unit cell parameters (from powder XRD)	unit cell parameters (from ED)
3D Ti-MWW	a = 14.263Å c = 25.098 Å	a = 14.1Å c = 25.0Å
Ti-YNU-1	a = 14.238Å c = 27.571Å	a = 14.2Å c = 27.5Å

Supporting information 3: simulated HRTEM images of 3D MWW

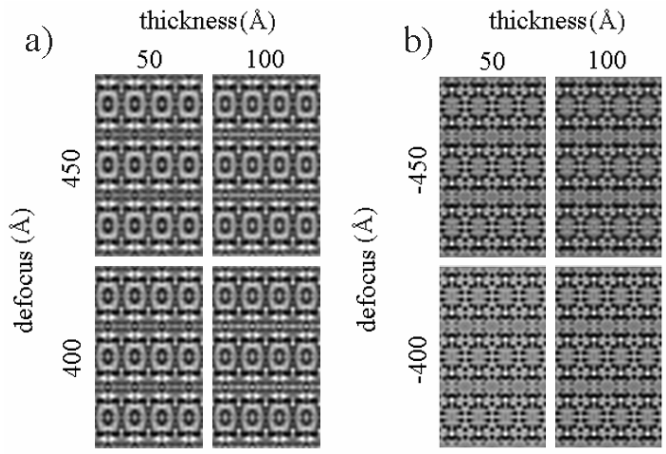

Figure 3 Simulated HRTEM images of 3D MWWW under a) over-focus condition and b) under-focus condition by multislice method along [100] incident direction.

Supporting information 4: the simulated Powder XRD pattern of Ti-YNU-1

Using the proposed Ti-YNU-1 structure, the Powder XRD pattern was simulated by Crystal Diffract_X program. The simulated Powder XRD pattern in Figure 4 fits the experimental pattern quite well.

Wave length: 1.5406Å

The instrumental broadening type: Gaussian 0.2

Unit cell: a = 14.187Å, b =14.191Å, c = 27.542Å, a = 90.008°, ß = 89.992° , ? = 120.020°

Particle size: 1 µm

Percent strain: 0

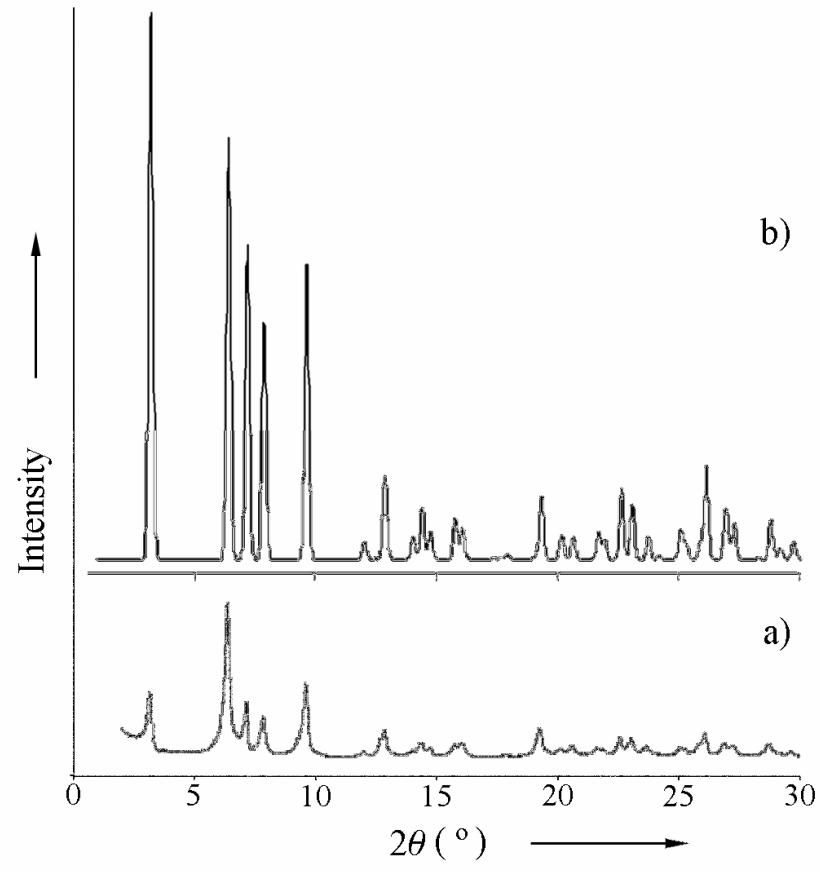

Figure 4: The a) experimental and b) simulated XRD pattern of Ti-YNU-1.

Supporting information 5:

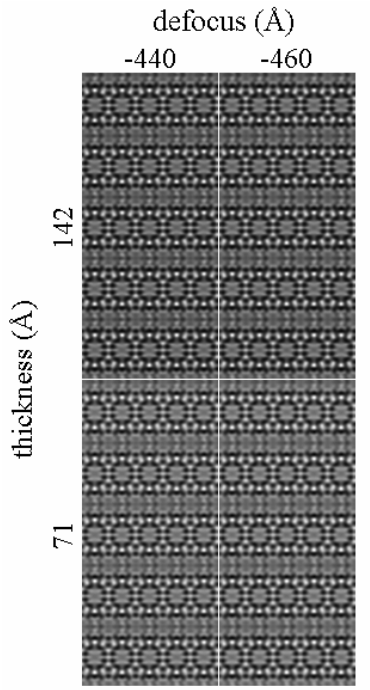

Figure 5 Simulated HREM images for the new structure with 12 MR by multislice method along [100] incident direction (super cell 5x5x5).

Supporting information 6: Computer simulation

In both the empirical and potential work, the starting model was taken to be purely siliceous MWW. This was always optimised in P1 symmetry - at no stage in the simulation was symmetry enforced. To generate the initial YNU cell, the optimised MWW cell was taken and the Q2 species were added at the mid-point of the cell. The cell was expanded by 2.5 angstroms to accommodate these species but the cell parameters was free to relax during the bulk empirical potential and first-principle calculations to generate purely siliceous YNU candidate structures. These structures were used for substitution calculations, whereby a single Ti replaces a Si site in the perfect YNU cell.

Dual substitution of the pillar sites by a Ti-$(OH)_2$ group was considered, which results in a further lattice expansion in *c* of ~ 0.3Å (i.e. ~2.9Å larger than Si-MWW). The probability of such an event occurring however is extremely low, because of the strong calculated thermodynamic incentive to segregate coupled with the experimentally observed low Ti:Si ratio of ~1:240. When a single Ti is introduced into a 3x3x3 supercell, upon relaxation the cell parameters are essentially unchanged from the purely Si-YNU-1 case.

The possibility of a partially interrupted structure was considered, where a proportion of the pillar sites are vacated. The absent T sites give rise to under-coordinated oxygen atoms that are assumed to form silanol species under basic conditions. Using a 3x3x3 supercell with approximately 20% of pillar sites vacated gave rise to a structure that again had almost identical *c* parameter to that of 'perfect' Si-YNU. Although the structure is thermodynamically

stable (measured relative to pure Si-FAU), the silanol species were found to be in extremely close proximity. It is thermodynamically favorable for the groups to condense, leading to a continuous network of bonds. The barrier for this internal condensation process is likely to be rather low, therefore it seems unlikely that interruptions will occur in high concentrations.