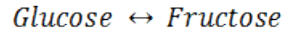


Supplementary Information

1. Thermodynamic data

The isomerization of glucose into fructose using can be represented as:



The equilibrium constant K_{eq} and equilibrium conversion were calculated as follows:

$$K_{eq} = \frac{[\text{Fructose}]}{[\text{Glucose}]} \quad (1)$$

$$\text{Conversion} = \frac{K_{eq}}{(1+K_{eq})} \quad (2)$$

$$\Delta G_T^o = -RT \ln(K_{eq}) \quad (3)$$

$$\Delta G_T^o = \Delta H_T^o - T \Delta S_T^o \quad (4)$$

$$\Delta H_T^o = \Delta H_\theta^o + \Delta c_p^o (T - \theta) \quad (5)$$

$$\Delta S_T^o = \Delta S_\theta^o + \Delta c_p^o \ln\left(\frac{T}{\theta}\right) \quad (6)$$

Where $\theta = 298.15$ K, the reference temperature, and the heat capacity (c_p) is considered to be constant. Thus, combining equations 4,5, and 6 above:

$$\Delta G_T^o = \Delta H_\theta^o + \Delta c_p^o (T - \theta) + \frac{T}{\theta} (\Delta G_\theta^o - \Delta H_\theta^o) - T \Delta c_p^o \ln\left(\frac{T}{\theta}\right) \quad (7)$$

Microcalorimetric data from work by Tewari (1) at $T = 298.15$ K shows that:

$$\Delta G^o = 0.35 \pm 0.05 \text{ kJ/mol}$$

$$\Delta H^o = 2.78 \pm 0.20 \text{ kJ/mol}$$

$$\Delta c_p^o = 0.076 \pm 0.03 \text{ kJ/mol K}$$

From these data, and equations 2 and 3, the following plot is generated as a function of temperature, using the upper and lower bounds of Δc_p^o for the dotted lines.

1. Tewari, Y., *Applied Biochemistry and Biotechnology* **1990**, *23*, 187.

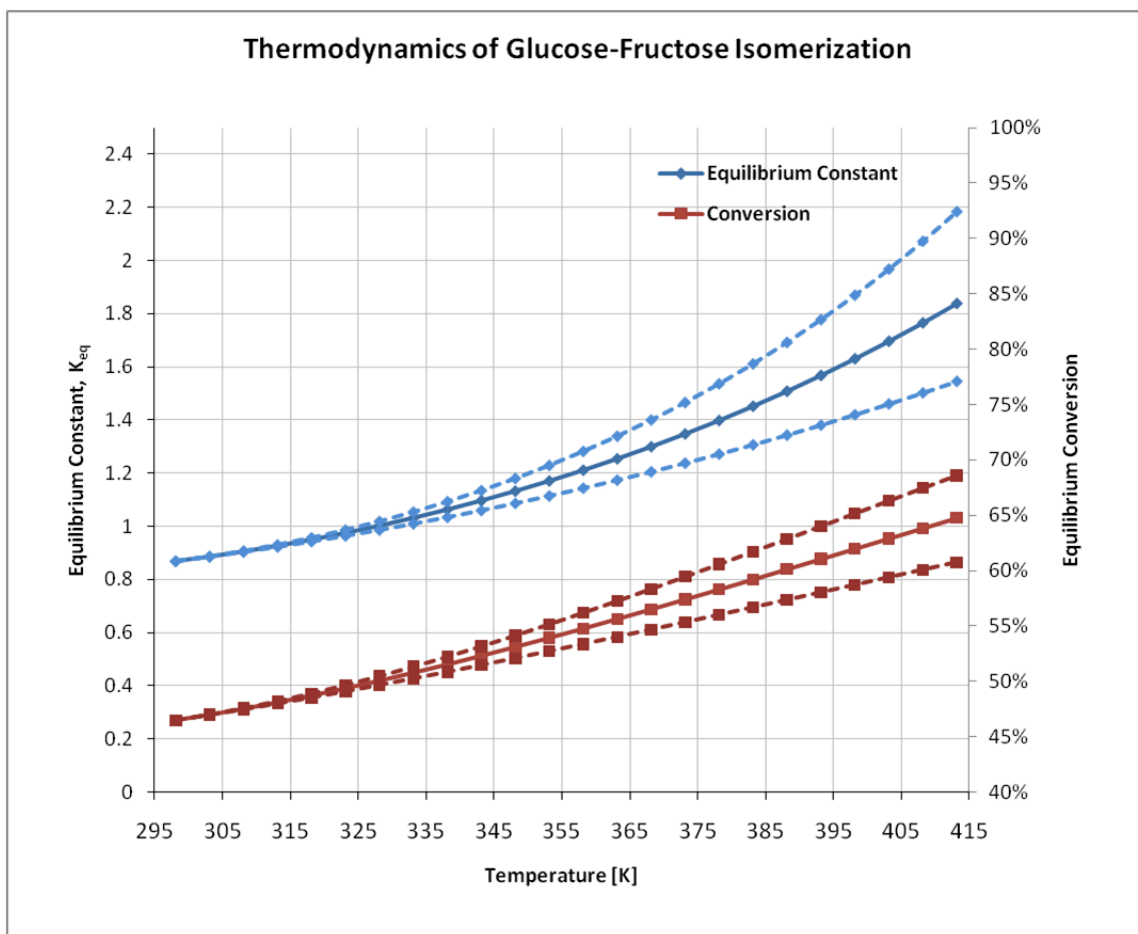


Figure S1. Thermodynamic data of glucose to fructose isomerization based on data from Tewari (1).

2. Synthesis of materials

Synthesis of Ti-Beta

Ti-Beta zeolite has been prepared as follows: 7.503 g of tetraethylammonium hydroxide solution (Sigma-Aldrich, 35% (w/w) in water) was diluted with 15 g of water. Then, 7.016 g of tetraethylorthosilicate (Sigma-Aldrich, 98% (w/w)) and 0.201 g of titanium (IV) isopropoxide (Sigma-Aldrich, 97% (w/w)) were added to the solution. The mixture was stirred until complete hydrolysis of the tetraethylorthosilicate and titanium (IV) isopropoxide was obtained. Next, the solution was allowed to reach the desired water ratio by complete evaporation of ethanol, isopropanol, and some water. Finally, 0.670 g of HF solution (Mallinckrodt, 52% (w/w) in water) was added resulting in a thick gel. The gel composition was $\text{SiO}_2 / 0.021 \text{ TiO}_2 / 0.54 \text{ TEAOH} / 0.53 \text{ HF} / 6.6 \text{ H}_2\text{O}$. This gel was transferred to a Teflon-lined stainless steel autoclave and heated at 413 K for 14 days. The solid was recovered by filtration, extensively washed with water, and dried at 373 K overnight. The solid was calcined at 853 K for 6 h to remove the organic content located within the crystalline material. The solid material shows the Beta zeolite topology (see Ti-Beta XRD pattern in Fig. S3). UV-vis diffuse reflectance spectrum of the calcined sample shows the

presence of a unique band at ~200-250 nm, which can be assigned to Ti tetrahedrally coordinated into the zeolite framework (see Ti-Beta in Fig. S2).

Synthesis of Sn-Beta

Sn-Beta zeolite was prepared as follows: 7.57 g of tetraethylammonium hydroxide solution (Sigma-Aldrich, 35% (w/w) in water) was diluted with 15 g of water. Next, 7.011 g of tetraethylorthosilicate (Sigma-Aldrich, 98% (w/w)) and 0.121 g of tin (IV) chloride pentahydrate (Sigma-Aldrich, 98% (w/w)) were added to the solution. The mixture was stirred until complete hydrolysis of the tetraethylorthosilicate, and then allowed to reach the desired water ratio by complete evaporation of ethanol and some water. Finally, 0.690 g of HF solution (Mallinckrodt, 52% (w/w) in water) was added, resulting in a thick gel. The gel composition was $\text{SiO}_2 / 0.01 \text{ SnCl}_4 / 0.55 \text{ TEAOH} / 0.54 \text{ HF} / 7.52 \text{ H}_2\text{O}$. This gel was transferred to a Teflon-lined stainless steel autoclave and heated at 413 K for 40 days. The solids were recovered by filtration, extensively washed with water, and dried at 373 K overnight. The solid was calcined at 853 K for 6 h to remove the organic content located in the crystalline material.

X-ray diffraction confirmed that the solid material has the Beta zeolite topology (Fig. S3). The UV-vis diffuse reflectance spectrum of the calcined sample shows the presence of a unique band at ~200-250 nm, that can be assigned to Sn tetrahedrally coordinated into the zeolite framework (Fig. S2). SEM EDS measurements for the Sn-Beta sample show an atomic ratio Si:Sn of 96:1.

Synthesis of TS-1

TS-1 sample was synthesized following the method reported in the patent literature (2). TS-1 was crystallized from a clear solution prepared by mixing titanium butoxide (TNBT, Sigma-Aldrich), tetraethylorthosilicate (Sigma-Aldrich), tetrapropylammonium hydroxide (Sigma-Aldrich, 1 M) and distilled water. The mixture was stirred until complete hydrolysis of the tetraethylorthosilicate and titanium butoxide was obtained, then allowing complete evaporation of ethanol, butanol and some water until the desired water ratio was reached. The gel composition was $\text{SiO}_2 / 0.03 \text{ TiO}_2 / 0.44 \text{ TPAOH} / 30 \text{ H}_2\text{O}$. The TS-1 reaction mixture was charged into Teflon-lined autoclaves and allowed to crystallize at 448 K for 5 days. The autoclave was rotated at 50 rpm. After cooling, the solid was recovered by filtration, extensively washed with water, and dried at 373 K overnight. The material was calcined at 853 K for 6 h to remove the organic content located within the crystalline material.

Synthesis of Ti-MCM-41

The Ti-MCM-41 sample was synthesized as follows: a solution of hexadecyltrimethylammonium bromide (C_{16}TABr) was prepared (1.93 g of C_{16}TABr in 15.1 g of water). Then, 6.42 g of tetramethylammonium hydroxide solution (Sigma-Aldrich, 25% (w/w)) was added. After homogenization, 7.015 g of tetraethylorthosilicate (Sigma-Aldrich, 98% (w/w)) and 0.19 g of titanium (IV) isopropoxide (Sigma-Aldrich, 97% (w/w)) were added to the solution. The mixture was stirred until complete hydrolysis of the tetraethylorthosilicate and titanium (IV) isopropoxide was obtained. Next, complete evaporation of ethanol, isopropanol, and some water was allowed until the desired water ratio was reached. The final

2. Tamarasso M, Perego G, Notari B (1983) *U.S. Patent 4,410,501*

composition was: 1.0 SiO₂ / 0.02 TiO₂ / 0.16 C₁₆TABr / 0.26 TMAOH / 24.8 H₂O. The homogeneous gel was sealed in Teflon-lined stainless steel autoclaves and heated at 408 K under static conditions during 48 h. The solid was recovered by filtration, extensively washed with water, and dried at 373 K overnight. The solid was calcined at 853 K for 6 h to remove the organic content located within the ordered material.

Synthesis of Sn-MCM-41

The Sn-MCM-41 sample was synthesized as follows: a solution of hexadecyltrimethylammonium bromide (C₁₆TABr) was prepared (1.46 g of C₁₆TABr in 4.3 g of water). Then, 6.34 g of tetramethylammonium hydroxide solution (Sigma-Aldrich, 25% (w/w)) was added. After homogenization, 0.088 g SnCl₄·5H₂O (Sigma-Aldrich, 98% (w/w)) and 3.76 g of colloidal silica solution (Sigma-Aldrich, Ludox AS-40) were added with continuous stirring. The final composition was: 1.0 SiO₂ / 0.01 SnCl₄ / 0.16 C₁₆TABr / 0.35 TMAOH / 25 H₂O. The homogeneous gel was sealed in Teflon-lined stainless steel autoclaves and heated at 408 K under static conditions during 48 h. The solid was recovered by filtration, extensively washed with water, and dried at 373 K overnight. The solid was calcined at 853 K for 6 h to remove the organic content located within the ordered material.

3. Characterization

Powder X-ray diffraction (XRD) patterns were collected by using a Scintag XDS 2000 diffractometer using Cu K α radiation. Scanning electron microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) measurements were recorded on a LEO 1550 VP FE SEM at an electron high tension (EHT) of 10 kV. UV-Vis measurements were recorded using a Cary 3G spectrophotometer equipped with a diffuse reflectance cell.

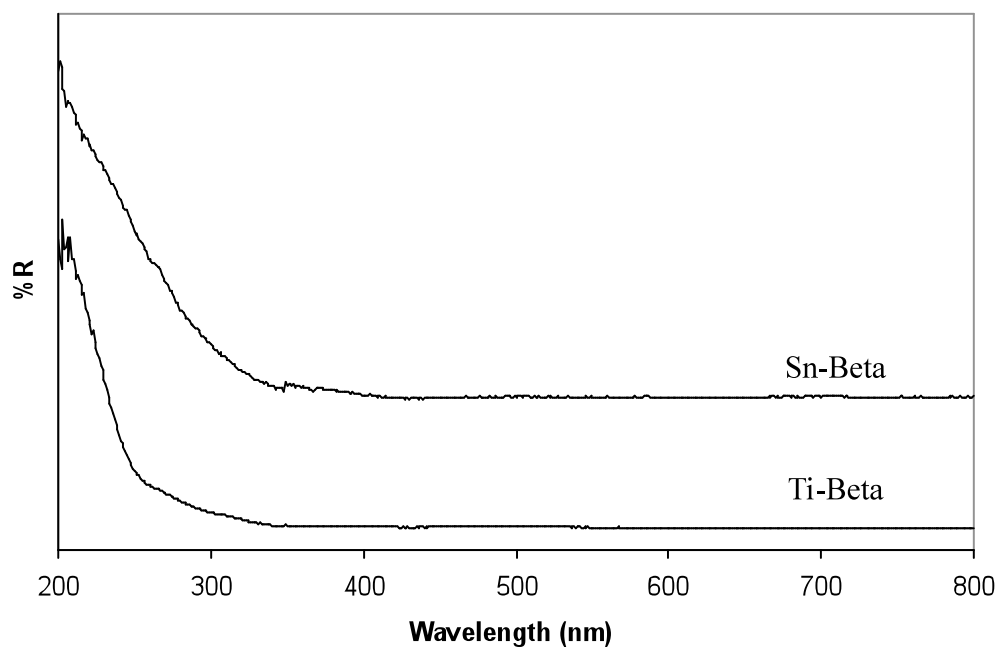


Figure S2 UV-vis diffuse reflectance spectra of Sn-Beta and Ti-Beta.

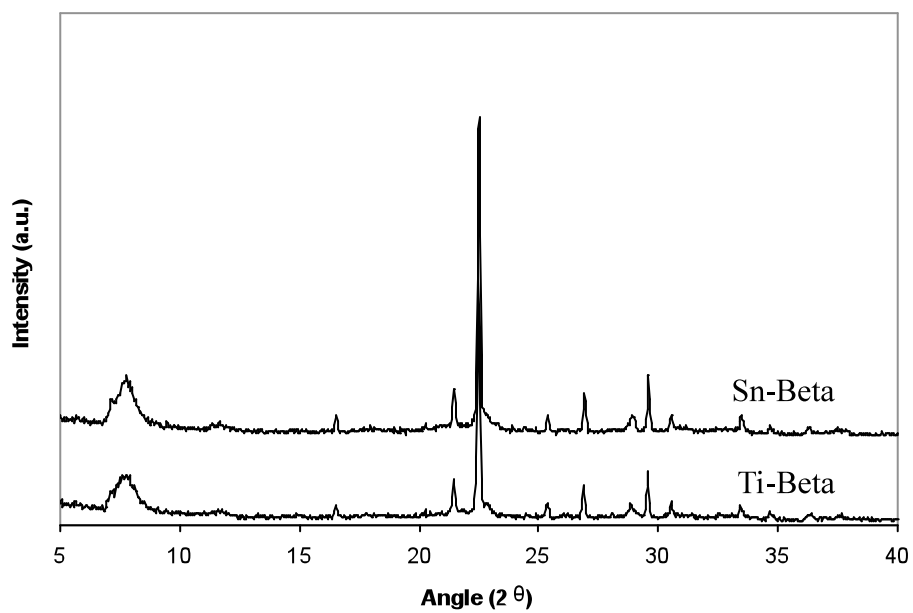
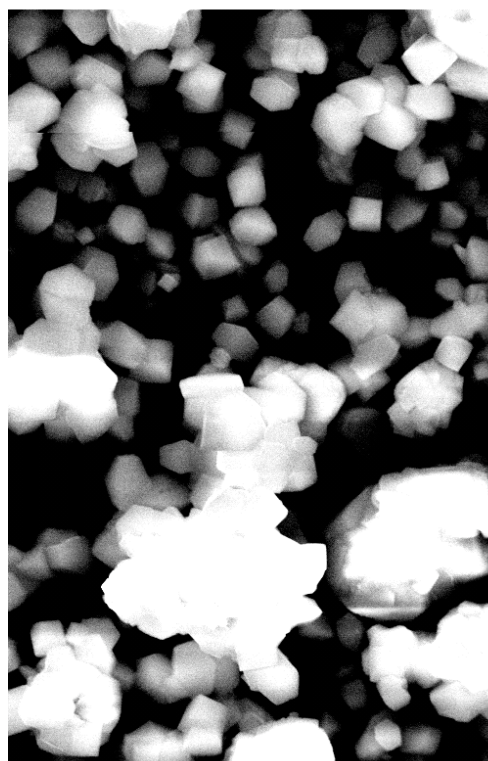
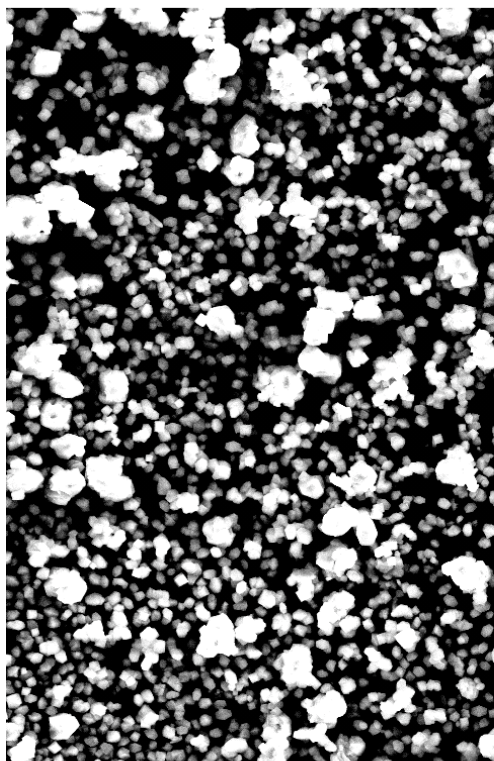


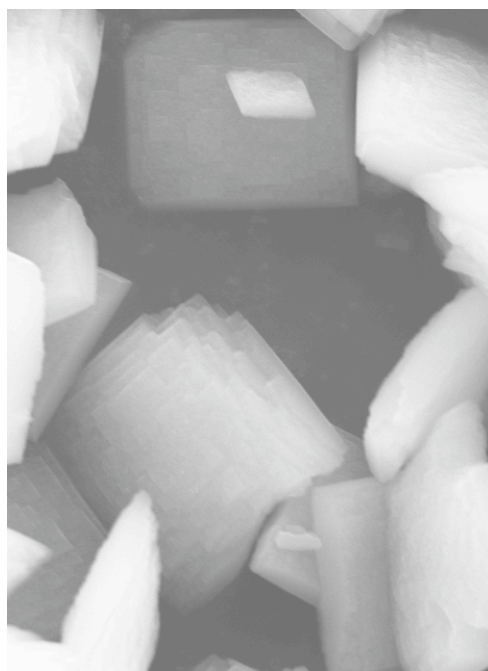
Figure S3 X-ray powder diffraction patterns of Ti-Beta and Sn-Beta.



50 μ m



200 μ m



3 μ m



20 μ m

Figure S4 SEM images of Ti-Beta zeolite (top) and Sn-Beta (bottom).

Table S1 Metal content in each solid material

Material	Metal	Si/M ^[a]
TS-1	Ti	34.7
Ti-Beta	Ti	53.8
Ti-MCM-41	Ti	64.4
Sn-Beta	Sn	96.0
Sn-MCM-41	Sn	71.8

^[a] Measured by Energy Dispersive X-ray Spectroscopy (EDS)