1. Experimental

a. Materials

USY zeolites (2.5 ≤ Si/Al ≤ 30) were supplied by Zeolyst International, H-beta (Si/Al = 75) was obtained from SüdChemie München and NH_4^+-MOR (Si/Al = 5.8) was purchased from Zeocat. Microcrystalline cellulose, Avicel PH-101, was obtained from Sigma-Adrich, as was the carbon supported Ru (5%) hydrogenation catalyst. H_2SO_4 (96%), H_3PO_4 (85%), HCl (37%) and all other chemicals were commercially supplied. Water content of all the substrates and catalysts was determined by thermogravimetric analysis (TGA) under an inert N_2 atmosphere with a TGA Q500 from TA Instruments before use and the weight of each component and yield calculations were adjusted accordingly.

b. Cellulose ball milling procedure

Ball-milling of cellulose was carried out in batches of 25g cellulose using seven ZrO_2 balls (mass of 7.5 g and diameter of 1.8 cm) in a 500 mL ZrO_2 bottle, for 24 one hour sessions. This assured that the cellulose temperature never exceeded 323K and therefore no thermal decomposition of the cellulose occurred during ball milling. The resulting cellulose feed was extensively characterised and this data was published earlier.[1,2]

c. Catalytic reactions

In a typical hydrolytic hydrogenation of cellulose, the acid catalyst, zeolite or Ru/C catalyst and water were loaded in a 100ml reactor (Parr Instruments Co.). The reactor was then flushed with N_2 to remove O_2. The mixture was stirred at 750 rpm and heated to 463K. The reactor was pressurized with 50 bar H_2 when the reaction temperature was reached. This moment was chosen as the reaction starting time. Samples were taken during the reaction, which were quickly cooled in an ice bath and centrifuged. The product mixture was then derivatised to trimethylsilylethers and analysed on a Hewlett Packard 5890 GC equipped with an HP 7673 autosampler, a 50m CP-Sil-5CB column and a FID. Product yields are expressed in C mol% and are calculated as follows: yield(%) = [moles C in product / total moles C loaded in reactor] x 100%. Selected samples were also analyzed after filtration over a 0.45µm PTFE filter by an Agilent 1200 Series HPLC equipped with a Varian Metacarb 67C column (300 x 6.5 mm) and a RI detector. Water was used as mobile phase. The conversion of cellulose was determined by dissolved organic carbon (DOC) analysis of the product mixture.

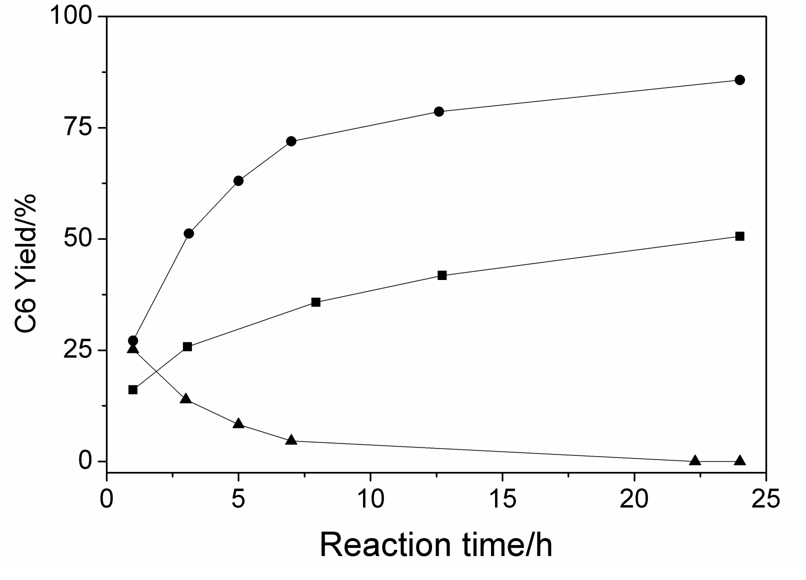
2. Preparation of Ru/zeolite catalysts

Zeolite materials that were obtained in the Na-form were refluxed overnight in aqueous NH_4OH to convert them to the NH_4-form. Zeolite materials in the H-form were converted to the NH_4-form by stirring overnight in NH_4OH at room temperature.

The NH_4-form was then exchanged with an appropiate amount of $Ru(NH_3)_6Cl_3$ by stirring overnight. Analysis of the supernatans confirmed that >99% of Ru was exchanged onto the zeolite in a single step. After the exchange, the zeolites were washed over a büchner until the washing water was Cl^-free as determined by $AgNO_3$. The zeolites were then dried at 60°C in an oven for several hours. At this point the originally white zeolite powder turned pink by the formation of Ru_{red}.[3] The dried powder was then pelletized (250-500µm) and loaded into a quartz tube. The tube was then inserted into an oven and a flow of N_2 was sent over the powder. Temperature was increased to 200°C to desorb all the water from the zeolite. Temperature was then further increased to 350°C and the flow of N_2 was changed to H_2 and the temperature was increased to 400°C to reduce the Ru. TPD/TPD experiments confirmed that this procedure converts all of the Ru to its metallic form.

3. Kinetics of selected reaction from Table 1

Figure S5. Hydrolytic hydrogenation of BMC with HCl (0.97 10-3M) and (•) Ru(0.2)/H-USY, (■) Ru(1.8)/H-USY and (▲) Pt(0.2)/H-USY. 'C6 yield' comprises both the hexitol and the glucose yield.



The figure shows the increased selectivity of the system when decreasing the Ru-loading from 1.8 wt% to 0.2 wt%, due to the near-elimination of hydrogenolysis side reactions. In these two reactions, glucose hydrogenations is all but complete throughout every stage of the reaction, meaning that the C6 yield is effectively equal to the hexitol yield. The same is not true for the HCl-Pt(0.2)/H-USY reaction. In this reaction, glucose is the main C6 product (hexitol yield < 1.5% for all samples taken), making the C6 yield effectively equal to the glucose yield. This shows that the Pt-H-USY catalyst is almost inactive for glucose hydrogenation. Instead of glucose acid degradation products (5-HMF, levulinic acid, formic acid, …), the main byproducts are C2-C5 polyols with varying degree of hydroxylation, showing that the Pt/H-USY catalyst is active in the liquid-phase reforming of glucose, as already noted by Palkovits *et al.*[4]

4. Sorption of glucose and sorbitol on H-USY

Glucose and sorbitol solutions (50ml) are prepared with a concentration of 2.5 10^{-4}M. A 1 ml sample is taken and analyzed on GC. 0.5g of H-USY (Si/Al = 30) is added to the solution and the mixture is stirred for 4h at room temperature. The fluid is centrifuged and again a 1ml sample is taken and analyzed.

5. References

1. J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs and B. Sels, *Chem. Commun.*, 2010, **46 (20)**, 3577-3579.
2. S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L. Zhang, G. Van Tendeloo, P. A. Jacobs, B. F. Sels, *ChemSusChem*, 2010, **3**, 698 –701.
3. C. Madhusudhan, M. Patil and M. Good, *Inorg. Chem.*, 1979, **18 (9)**, 2384-2389.
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