

Green Chemistry

Electronic Supporting Information

**Reductive Splitting of Hemicellulose with Stable Ruthenium-
loaded USY Zeolite**

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More information about the used zeolite catalysts

The faujasite (FAU) zeolite topology, including zeolite Y and USY, is a well-studied class of zeolites in catalysis due to their easy adjustable nature and their intense use in oil refinery.¹⁻⁴ As a consequence, these classic zeolites have already been studied in a wide range of biomass-related reactions showing excellent performances.⁵⁻¹² This present work explores commercial USY zeolites with a variety in properties resulting from different post-synthetic modifications (see Tables 2 and S1). USY19 is prepared by a mild steaming procedure of zeolite Y at elevated temperature, leading to a mainly microporous USY zeolite with a low mesopore volume. During the steaming procedure, aluminium is extracted from the framework leading to an increased framework Si/Al ratio.¹³ These extracted aluminium species are deposited as extra-framework aluminium (EFAl) in and around the zeolite crystal.¹⁴ Earlier research on the reductive splitting of cellulose showed that such species have a negative influence on the conversion of cellulose¹⁵ as they are deposited on Brønsted acid sites.¹⁴⁻¹⁶ Therefore, we also investigated some zeolite samples which underwent an acid washing step whereby, dependent on the harshness of the washing step, a part to all EFAl is removed. For example, USY9 is a more severely steamed Y zeolite subjected to a mild acid washing step. Due to the severe steaming of this zeolite sample, illustrated by the much higher mesopore volume and lower Brønsted acidity compared to USY19, only part of the EFAl species is removed by the mild washing (Table S1). Besides these two samples, also two other severely steamed but extensively washed zeolite samples are used, USY6 and USY3, with high Si/Al, low Brønsted acidities and low EFAl content (Table S1). The latter sample was submitted to two severe steaming steps leading to the lowest Brønsted acidity of the zeolite samples under study (see Table 2).

Table S1. Bulk and framework Si/Al and distribution of framework and extra-framework aluminium in the used USY zeolites based on data from ref. ¹⁵.

| Sample code | Si/Al | | Al distribution (%) | |
|-------------|-------|-----------|---------------------|-------------------|
| | bulk | framework | FAI ^a | EFAl ^b |
| USY19 | 2.6 | 4.4 | 59 | 41 |
| USY9 | 6.0 | 10.0 | 58 | 42 |
| USY6 | 15.0 | 16.7 | 85 | 15 |
| USY3 | 30.0 | 34.9 | 85 | 15 |

^a FAI: framework aluminium; ^b EFAl: extra-framework aluminium

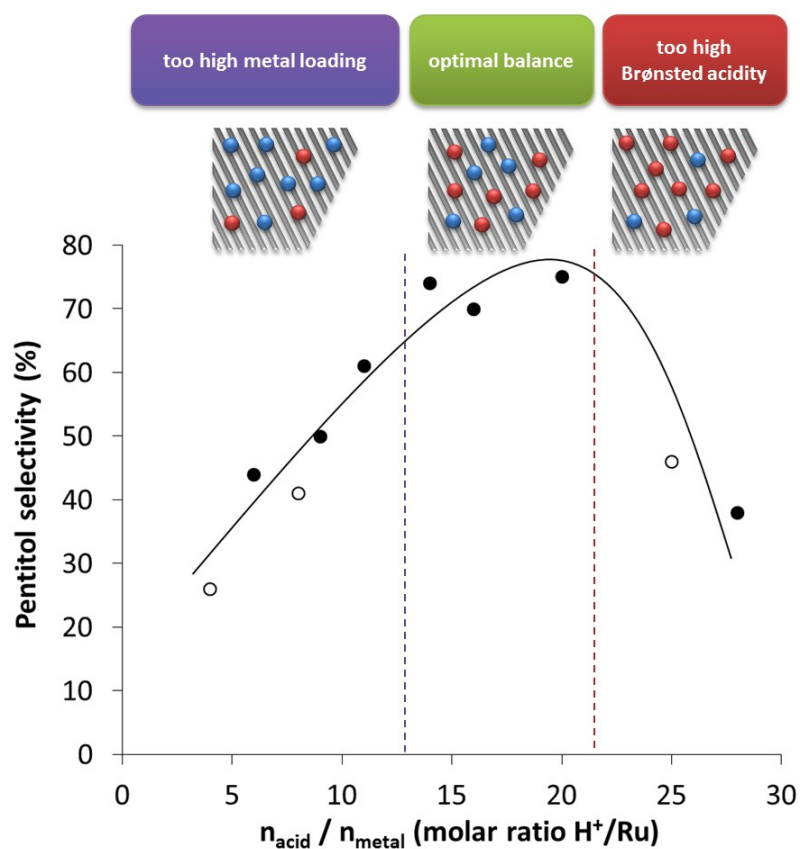


Figure S1. Effect of the acid/metal balance on the pentitol yield. Filled symbols represent USY9 catalysts with different Ru loading and the open symbols represent the other Ru/USY catalysts from Table 4.

Influence of the reaction temperature on the bifunctional reaction and its optimal acid/metal balance

The acid/metal ratio and the pentitol selectivity/yield is strongly dependent on the reaction conditions (especially pressure and temperature). In this part, we will systematically perform this exercise for the temperature.

Arrhenius law foresees faster reaction upon increasing the temperature. Reactions with AX in presence of USY9 were carried out in the temperature range of 140 °C to 190 °C. In addition, it is reported that the autoprotolysis of water generates more protons at higher temperatures,^{17, 18} predicting the requirement of a higher hydrogenation activity to preserve the optimal acid/metal balance. The influence of the temperature is presented in Figure S2.

The maximum pentitol yield first increases by increasing the temperature from 140 °C to 160 °C up to 75%, as depicted in Figure S2. This increase is mainly due to restricted hydrolysis at the lower temperature showing a lot of XO in the product mixtures of all reactions at 140 °C, even at the lower Ru loadings. This indicates that despite the amorphous nature of hemicellulose, and the consequently very fast dissolution, still relative harsh conditions, *viz.* temperatures of at least 150 - 160 °C, are needed to ensure efficient hydrolysis of the oligomers. Temperatures above 160 °C are accompanied with a gradual drop in maximum pentitol yield, due to the dominance of dehydration reactions, to a value as low as 20% at 190 °C. At such high temperatures, C5-sugars are too fast liberated whereby, irrespective the metal loading, strong acid catalysed dehydration, rearrangement and condensation reactions occur given their very high reactivity at such high temperatures. This is probably the reason for the moderate yields obtained in the heterogeneous systems in Table 1. Therefore, a temperature range of 160 to 175 °C seems to be optimal for the reductive splitting of hemicellulose.

Figure S2 summarizes the pentitol yield obtained at the different temperatures in function of the Ru loading. For all temperatures, typical acid/metal balance pattern is evident showing an optimal Ru loading for the USY9 zeolite. As predicted, higher Ru loadings are required to maximize the pentitol yield with increasing temperature. Remarkably, the deficiency in pentitol yield at higher temperatures (175 and 190 °C) is slightly different than at lower temperatures (140 and 160 °C). In both cases, at too low acid/metal balances, sugar dehydration products are dominant due to a build-up of free sugars. At low acid/metal balances and low temperatures (140 and 160 °C), a hampered hydrolysis can be observed as mostly XO are present in the product pool. However, at higher temperatures (and low acid/metal balances) mostly hydrogenolysis products are observed (short polyols). As hydrogenolysis is an energy demanding reaction, it will mainly occurs at higher temperatures and only minorly at lower temperatures whereby consecutively only small amounts of short polyols are observed at these lower temperatures.

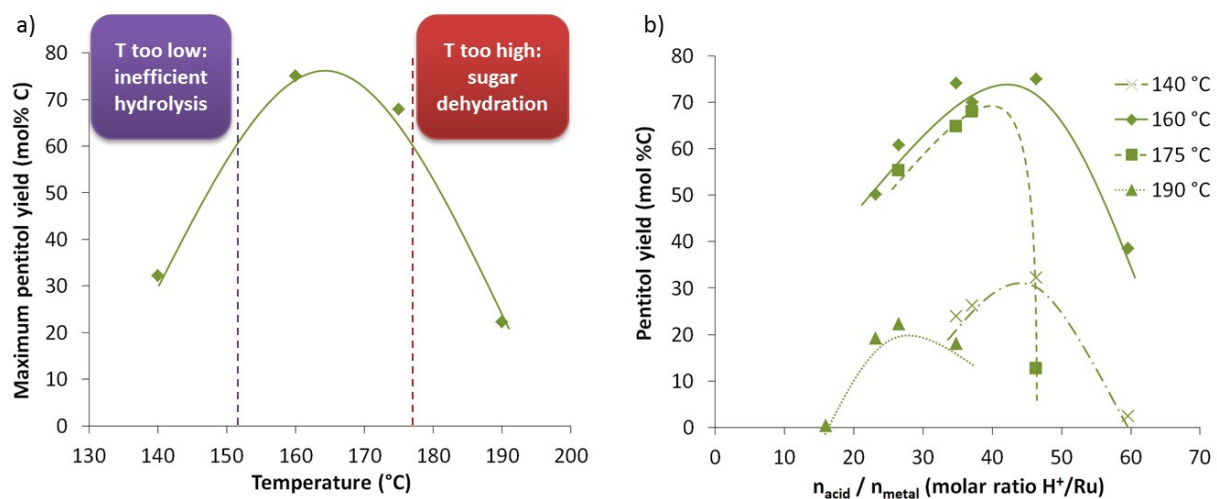


Figure S2. Influence of the reaction temperature on the reductive splitting of arabinoxylan: a) influence on the maximum obtained pentitol yield for different Ru/USY9 catalysts; b) effect of the reaction temperature on the pentitol yield of USY9 loaded with various amounts of ruthenium.

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