

Hydrothermally stable ruthenium-zirconium-tungsten catalyst for cellulose hydrogenolysis to polyols

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Abstract: In this work, we describe a catalytic material based on a zirconium-tungsten oxide with ruthenium for the hydrogenolysis of microcrystalline cellulose under hydrothermal conditions. With these catalysts, polyols can be produced with high yields. High and stable polyol yields were also achieved in recycling tests. A catalyst with 4.5 wt% ruthenium in total achieved a carbon efficiency of almost 100%. The prepared Zr-W oxide is mesoporous and largely stable under hydrothermal conditions (493 K and 65 bar hydrogen). A decomposition into the components ZrO_2 and WO_3 could be observed at temperatures of 1050 K in air.

Introduction

Using of biomass for the production of chemicals is one of the solutions to replace fossil raw materials. It solves part of the problem of global warming. As it is the most frequent occurring biological raw material, cellulose has been the focus of research the past years.

The depolymerization of cellulose to soluble oligosaccharides up to glucose is usually the first step in order for the utilization of cellulose as a raw material for chemicals. Herein the application of mineral acids shows good results.^[1] These have the disadvantage that mineral acids are contained in the product mixtures in a homogeneous phase and complicated further processes steps. The use of solid acid catalysts has therefore been proposed as alternative approach.^[2]

Many different solid acids like zeolites, sulfated zirconia, silica (SBA15) and others were tested.^[3-5,33,34,35]

All these studies have in common that the de-polymerization of cellulose in water starts only at higher temperatures. Under these conditions the final de-polymerization product – glucose – tends to isomerization and dehydration Fructose by isomerization of glucose formed, leads via retro aldol reaction to 1,2-propandiol as main product.^[30,31] The dehydration products 5-HMF and other furans leads to unwanted polymerization products.^[7,8] A solution is the fast hydrogenation of the glucose molecule to sorbitol at nickel or ruthenium catalysts^[3] or the production of short chain polyols like ethylene glycol via retro aldol reaction and hydrolysis. The retro aldol reaction is catalysed by tungsten species.^[9-11] An effective catalyst to produce ethylene glycol or 1,2-propandiol from cellulose contains a hydrogenation function (e.g. nickel or ruthenium) and a function for the C-C cleavage (retro aldol

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 E-mail: lucas@tc2.tu-darmstadt.de reaction e.g. tungsten compound). It should be mentioned at this point that the resulting polyols could promote the solvolysis of the cellulose in the presence of mineral or solid acids.^[42,43] In addition to the activity and the selectivity achieved, the long-term stability under harsh hydrothermal conditions is the decisive criterion for the evaluation of the catalysts. For zeolites and supported metal catalysts several studies were published about hydrothermal stability in hot liquid water.^[37-39] The main reason for deactivation of zeolite based catalyst in hot water is the dealumination and hydrolysis of siloxane bonds.^[37] The stability of the zeolites can be increased by modification of the H-form (e.g., lanthanium or cerium). Unfortunately, the acidity decreases.^[40]

Further materials with excellent hydrothermal stability are carbon materials, zirconia, titandioxid and mixed oxides.^[37] Furthermore, sintering of metal particles is a problem that these systems have in common

In a previous work, we found that because of the high reaction temperature, leaching of tungsten can occur.^[12,13] The ruthenium – tungsten catalyst with activated carbon as support material^[12] showed a loss of activity after six reaction runs due to the release of tungsten.

This is consistent with results from the literature.^[7,14,15] Thereafter, tungsten bronzes are responsible for C-C cleavage. These HxWO₃ compounds act homogeneously catalytically and are formed from the tungsten components of the catalyst. To compensate the resulting loss of activity, authors give Tungstic acid to the reaction mixture.^[14,15]

A review, published by Tao Zhang, provides a comprehensive overview of transformation of cellulose to polyols with a short section on catalyst recycling.^[33] A further study describes, among other things, problems with the catalyst stability in the conversion of biomass.^[36]

In search of tungsten compounds that are stable under hydrothermal conditions, references to zirconium tungsten oxides were found. In literature, under hydrothermal conditions produced tungsten and zirconia containing material can be found.^[26-28] The hydrothermal preparation after Hui^[26] produced well crystalline ZrW₂O₈ ^[16,17] grains for the photocatalytic water splitting with low BET surface of 3.58 m²/g. In this work, preparation conditions were also described leading to amorphous material. The surface acidic properties of tungstated zirconia catalysts and ZrW2O8 are used in the paraffin isomerization, cracking, alkylation, hydration of cyclohexene and in the esterification of fatty acids.[18-22] The use of tungstated zirconia in the aqueous hydrolysis of cellobiose [23] and cellulose [24] has been reported. Good yields of lactic acid and 2.5-hexanedione were observed with tungstated zirconia.^[25]. Good yields of ethylene glycol from cellulose were obtained with a WO₃-ZrO₂ catalyst in combination with Ru/C.^[32]

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Results and Discussion

With the chosen preparation method – using only small amounts of hydro chloric acid – a support material (Zr-W-oxide) was obtained that is similar to a polymorph of zirconium tungstate hydrate described in literature.^[29]



Figure 1. XRD Patterns for Zr-W-oxide (a), 3Ru/Zr-W-oxide (b) and 3Ru/Zr-W-oxide after 10 recycling runs (c) with a measurement artefact around 50 degrees, 3Ru/Zr-W-oxide (-25W) (d), 3Ru/Zr-W-oxide (+25W) (e).

No x-ray reflexes were found that could be attributed to ZrW_2O_8 , WO_3 or ZrO_2 (Fig. 1a). The mesoporous material in this work, the so-called Zr-W-oxide has a comparatively high BET-surface area of 75 m²/g, with a pore volume of 0.26 g/cm³ and a small fraction of micro pores (Table 1).

The ratio between tungsten and zirconium is according to REM-EDX measurement 2:1 (Table 2).

In the temperature programmed reduction experiments (Fig. 2) it was shown that, the material has a well-defined reduction peak with a maximum at 1050 K. The addition of ruthenium does not affect the XRD results (Fig. 1b). The BET surface area and the average pore radius are slightly increased (Table 1). This may be related to the reduction in the hydrogen stream at 523 K. The reduction peak of the tungsten is shifted slightly towards low temperatures of 1034 K. In addition, a reduction peak for ruthenium at 391 K can be observed.

In order to determine the optimum of zirconium to tungsten ratio, the amount of Na_2WO_4 used was varied during preparation. Two different materials were obtained.

Zr-W-oxide (-25W) with 25 % less tungsten addition and Zr-Woxide (+25W) with 25 % more tungsten addition during the preparation. For these materials, a similar pattern can be seen in XRD results. In case of a lower tungsten content, XRD shows very poor reflexes (Fig. 1d) and in case of a higher tungsten content, reflexes are clearly visible (Fig. 1e). The pattern is in this case very similar to the polymorph of zirconium tungstate hydrate described in literature.^[29] But also here: No x-ray reflexes were found that could be attributed to ZrW_2O_8 , WO_3 or ZrO_2 . For the catalysts with the different ruthenium contents, the catalytic activity (Table 4) was determined in tests under standard conditions. These standard conditions have proved to be the optimum in experiments with ruthenium and tungsten-containing catalysts and facilitate comparability with the results of our previous investigations (Table 4, last line).^[13,14] The ruthenium content has a significant influence on conversion and product spectrum. As ruthenium content increases from 2.0 wt% to 4.5 wt%, cellulose conversion drops from 90% to 72%.

Table 1. Results of N2-physisorption measurement.

catalyst ^[a]	BET surface [m²/g]	Pore volume ^[a] [cm ³ /g]	Micropore area ^[b] [m²/g]	Pore diam. ^[c] [Å]
Zr-W-oxide	75.5	0.26	7.0	113
2Ru/Zr-W-oxide	80.4	0.25	6.7	131
3Ru/Zr-W-oxide	79.1	0.25	6.5	132
4.5Ru/Zr-W-oxide	78.0	0.24	5.2	129
3Ru/Zr-W-oxide after Run#10 3Ru/Zr-W-oxide hw ^[d]	92.8 88.1	0.27 0.26	5.1 9.5	130 130
3Ru/ZrW2O8 AE ^[e]	0.3	0.0005	0	(44)
3Ru/Zr-W-oxide(-25W)	37.8	0.06	1.4	15
3Ru/Zr-W-oxide(+25W)	49.9	0.09	4.2	17

[a] Total pore volume < 270 Å. [b] t-Plot Method. [c] Medium pore diameter (BJH method). [d] catalyst pre-treated four hours without cellulose in hot water under standard reaction conditions. [e] catalyst was prepared based on a commercial support material (ZrW₂O₈; AlfaAesar).

This is strongly correlated with the measured acidity of the catalysts (Table 3).

It can also be formulated that the acidity of the support diminishes with increasing ruthenium surface coverage. Ruthenium dispersion is nearly constant for catalysts with different ruthenium content. A dispersion value of 2.9% is low, but also explains the low formation of sorbitol and the higher formation of ketones with the catalysts. A higher ruthenium dispersion, but also a lower acidity and thus a lower conversion, can be observed in case of the catalysts with a varied Zr / W content. The catalysts with the nominal W/Zr ratio > 2 show a higher EG yield (35% compared to 30%). This can possible be explained by soluble tungsten species. Overall, the differences in product yields and conversion are not very large due to the variation of the W / Zr ratio. A comparison of long-term stability should provide further insights into W/Zr system.

Table 2. Results of REM-EDX and XRF measurements.									
catalyst ^[a]	Ru	Zr	W	W/Zra ^[a]	W/Zr ^[a]				
	[at.%]	[at.%]	[at.%]	REM-EDX	XRF				
Zr-W-oxide ^[b]	-	33.3	66.7	2.01	1.76				
3Ru/Zr-W-oxide	7.4	31.9	60.8	1.91	1.76				
3Ru/Zr-W-oxide									
after Run#10	5.4	38.6	53.8	1.40	1.47				
3Ru/Zr-W-oxide hw ^[c]	n.m.	n.m.	n.m.	n.m.	1.63				

[a] Atomic ratio. [b] The W/Zr atomic ratio derived from the amounts used in the preparation is 1.66. [c] Catalyst pre-treated four hours without cellulose in hot water under standard reaction conditions.

The decrease in the cellulose conversion is accompanied by a significant increase in the yield of polyols from 37 to 45%. In this context, the decrease in ketone yields, which are the precursors of the polyols, is also notified. The yield of ketones is very high (>5%) compared to Ru/W/AC catalyst systems (0.4%) - hinting to the fact that the hydrogenation activity of the catalysts is lower. It was to be expected that the hydrogenation rate with the ruthenium content increases. The jump in carbon efficiency coefficients (CEL) from 92 to near 100% was unusual. The reason might be that only small amounts of cellulose were converted to 5-HMF, which is prone to polymerise and build humins under the reaction conditions.^[8] We obtained a yield of free HMF of approximately < 0.07% in all experiments with Ru/Zr-W-oxide catalysts, only about a quarter of what we found with Ru/W/AC catalysts in previous experiments.^[12] It is also noticeable that only small amounts of sorbitol are formed - a further indication that the hydrogenation activity of the catalysts is comparatively low. In comparison, the catalyst with the support ZrW_2O_8 (AlfaAesar) shows very low yields to polyols.

 $\label{eq:table_state} \begin{array}{l} \textbf{Table 3.} \ \text{Results of CO-chemisorption and NH_3-TPD measurement in comparision to cellulose conversion (X) and ethylene glycol yield <math display="inline">(Y_{EG})^{[D]}. \end{array}$

catalyst	D _{Ru} ^[a] [%]	NH₃-TPD [mmol/g]	X _{Cell} [%]	Y _{Polyols} [%]
Zr-W-oxide	-	0.141	· ·	-
2Ru/Zr-W-oxide	2.9	0.106	90.5	37.2
3Ru/Zr-W-oxide	2.9	0.100	81.9	43.5
4.5Ru/Zr-W-oxide	2.8	0.077	72.2	45.1
3Ru/Zr-W-oxide after Run#10	2.8	0.085	-	-
3Ru/Zr-W-oxide (-25W)	5.6	0.033	65.1	43.3
3Ru/Zr-W-oxide (+25W)	4.5	0.037	70.8	48.6

[a] Ruthenium dispersion. [b] extracted from table 3.

The resulting product solution was brown and the product stuck to all parts of the batch. In comparison the yield of free 5-HMF was very high at 0.6%.

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Information about the catalyst stability can be obtained by recycling experiments. The procedure for the recycling experiments are described in the experimental section. The recycling experiments started with a half gram of the catalyst 3Ru/Zr-W-oxide. After seven four-hour cycles, a cycle of eight hours duration followed. Thereby the cellulose was fully converted and the catalyst separated. Thus, 75% of the initial catalyst mass could be recovered. On one hand, the loss of 25% of the catalyst can be explained by the elimination of catalyst-components under the hydrothermal conditions; on the other hand, a loss of catalyst due to the recycling itself is possible. As shown in Table 2, the tungsten zirconium atomic ratio (at the surface; REM-EDX) changes from 1.9 to 1.4. However, in the centrifuged and decanted reaction solutions, small amounts of catalyst together with cellulose precipitated over time.



Figure 2. TPR profiles of Zr-W-oxide (___) and 3Ru/Zr-W-oxide (- -)

What can be said about the catalyst activity during recycling? As shown in Figure 3 and Table 5, the CEL was nearly constant at 90% after two runs. The increase during the first experiments results from the transfer and accumulation of unreacted cellulose by the recycling process. The overall selectivity to polyols was nearly constant at 65%. The EG selectivity decreased from 44 to 28%, while selectivity to 1,2-propandiole, 1,2-butandiole and sorbitol increased.

In the subsequent eighth cycle, fresh and accumulated cellulose was completely converted after a longer time of reaction. This results in an apparent CEL of 108%. After cycle eight the catalyst recovered after being washed and dried and was used in the reaction again. For this, the amount of cellulose and water were adjusted to the lower catalyst mass (0.2688g). The results can also be found in Figure 3 and Table 5 under Run#9 and #10. The carbon efficiency achieved is comparable to the previous experiments. Concerning ethylene glycol, an increase in the selectivity from 27% to 34% was achieved. This value is close to the selectivity in the first cycles. Part of the activity changes during recycling and can be attributed to catalyst losses.

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		Yield [%] ^[b]								
X [%]	CEL [%]	EG	PG	BD	Sor	Σ Polyols	Ketones	Gaseous	Others	рН
90.5	92.4	25.5	4.8	4.0	0.4	37.2	9.8	1.0	40.6	2.80
81.9	91.8	30.0	4.2	4.4	0.9	43.5	6.8	0.8	26.6	2.88
72.2	100	31.9	4.5	4.5	0.8	45.1	5.7	1.3	22.4	2.87
100	90.8	29.9	11.2	5.7	4.6	58.8	0.8	1.6	27.7	2.94
65.1	100	30.0	3.7	3.8	1.6	43.3	5.0	0.9	19.4	2.92
70.8	100	34.9	4.0	4.5	1.3	48.6	4.7	1.0	19.0	2.88
84.9	34.2	0.9	0.1	0.2	0.8	5.1	5.0	3.0	20.4	2.12
1										
	X [%] 90.5 81.9 72.2 100 65.1 70.8 84.9	X [%] CEL [%] 90.5 92.4 81.9 91.8 72.2 100 100 90.8 65.1 100 70.8 100 84.9 34.2	X [%] CEL [%] Yield [%/EG 90.5 92.4 25.5 81.9 91.8 30.0 72.2 100 31.9 100 90.8 29.9 65.1 100 30.0 70.8 100 34.9 84.9 34.2 0.9	X [%] CEL [%] Yield [%] ^[b] 90.5 92.4 25.5 4.8 81.9 91.8 30.0 4.2 72.2 100 31.9 4.5 100 90.8 29.9 11.2 65.1 100 30.0 3.7 70.8 100 34.9 4.0 84.9 34.2 0.9 0.1	X [%] CEL [%] Yield [%] ^[b] 90.5 92.4 25.5 4.8 4.0 81.9 91.8 30.0 4.2 4.4 72.2 100 31.9 4.5 4.5 100 90.8 29.9 11.2 5.7 65.1 100 30.0 3.7 3.8 70.8 100 34.9 4.0 4.5 84.9 34.2 0.9 0.1 0.2	X [%] CEL [%] Yield [%] ^b EG PG BD Sor 90.5 92.4 25.5 4.8 4.0 0.4 81.9 91.8 30.0 4.2 4.4 0.9 72.2 100 31.9 4.5 4.5 0.8 100 90.8 29.9 11.2 5.7 4.6 65.1 100 30.0 3.7 3.8 1.6 70.8 100 34.9 4.0 4.5 1.3 84.9 34.2 0.9 0.1 0.2 0.8	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	X [%] CEL [%] Yield [%] ^[b] BG PG BD Sor Σ Polyols Ketones 90.5 92.4 25.5 4.8 4.0 0.4 37.2 9.8 81.9 91.8 30.0 4.2 4.4 0.9 43.5 6.8 72.2 100 31.9 4.5 4.5 0.8 45.1 5.7 100 90.8 29.9 11.2 5.7 4.6 58.8 0.8 65.1 100 30.0 3.7 3.8 1.6 43.3 5.0 70.8 100 34.9 4.0 4.5 1.3 48.6 4.7 84.9 34.2 0.9 0.1 0.2 0.8 5.1 5.0	X [%] CEL [%] Yield [%] ^[b] 90.5 92.4 25.5 4.8 4.0 0.4 37.2 9.8 1.0 81.9 91.8 30.0 4.2 4.4 0.9 43.5 6.8 0.8 72.2 100 31.9 4.5 4.5 0.8 45.1 5.7 1.3 100 90.8 29.9 11.2 5.7 4.6 58.8 0.8 1.6 65.1 100 30.0 3.7 3.8 1.6 43.3 5.0 0.9 70.8 100 34.9 4.0 4.5 1.3 48.6 4.7 1.0 84.9 34.2 0.9 0.1 0.2 0.8 5.1 5.0 3.0	X [%] CEL [%] Yield [%] ^[b] BG PG BD Sor Σ Polyols Ketones Gaseous Others 90.5 92.4 25.5 4.8 4.0 0.4 37.2 9.8 1.0 40.6 81.9 91.8 30.0 4.2 4.4 0.9 43.5 6.8 0.8 26.6 72.2 100 31.9 4.5 4.5 0.8 45.1 5.7 1.3 22.4 100 90.8 29.9 11.2 5.7 4.6 58.8 0.8 1.6 27.7 65.1 100 30.0 3.7 3.8 1.6 43.3 5.0 0.9 19.4 70.8 100 34.9 4.0 4.5 1.3 48.6 4.7 1.0 19.0 84.9 34.2 0.9 0.1 0.2 0.8 5.1 5.0 3.0 20.4

[a] under standard conditions as described. [b] EG = ethylene glycol, PG = propylene glycol, BD = 1,2-butanediol, Sor = Sorbitol, Σ Polyols = total C2...C6 diols and sugar alcohols, Ketones = 1-hydroxy-2-propanone and 1-hydroxy-2-butanone, Gaseous = CH4, CO and CO2, Others = summary of all other peaks in GC (ketones, acids, furanes, esters, alcohols - identified by GC/MS), pH = pH of the solution after the reaction. [c] after 8 h reaction time standard conditions 3 h. [d] catalyst was prepared based on a commercial support material (ZrW₂O₆; AlfaAesar). [e] Preparation published in a previous work. [12]

_		Selectivit	y [%] ^[b]								
Run#t	CEL [%]	EG	PG	BD	Sor	HDL	Σ Polyols	Ketones	Gaseous	Others	pН
1	66.6	44.4	6.1	7.5	0.9	2.3	62.9	5.7	1.7	20.1	2.97
2	79.0	37.6	11.3	8.0	2.5	3.6	65.7	3.0	1.6	22.5	3.02
3	89.4	37.1	11.7	7.3	4.0	3.8	67.3	2.3	1.7	21.2	3.14
4	90.3	33.8	11.2	6.5	6.2	4.0	65.1	1.6	2.0	23.3	3.15
5	89.6	31.2	13.1	7.1	7.1	4.7	66.8	1.4	2.0	21.9	3.14
6	88.0	29.8	12.7	6.4	6.3	4.7	64.5	2.5	1.7	24.0	3.19
7	88.4	28.7	13.0	6.3	6.2	4.9	63.7	3.0	1.6	24.6	3.20
8 ^[c]	108.3	27.1	14.9	7.2	6.4	5.8	65.3	0.3	1.9	24.9	3.06
9 ^[d]	74.0	34.3	12.7	6.6	5.3	3.1	66.3	1.6	2.2	22.7	3.05
10 ^[e]	93.8	34.7	13.0	6.6	4.8	3.3	65.8	0.2	1.8	22.9	2.94

[a] under standard conditions as described. [b] EG = ethylene glycol, PG = propylene glycol, BD = 1,2-butanediol, Sor = Sorbitol, Σ Polyols = total C2...C6 diols and sugar alcohols, Ketones = 1-hydroxy-2-propanone and 1-hydroxy-2-butanone, Gaseous = CH4, CO and CO2, Others = summary of all other peaks in GC (ketones, acids, furanes, esters, alcohols - identified by GC/MS), pH = pH of the solution after the reaction. [c] 8 h reaction time for full conversion of cellulose. [d] With reduced catalyst mass (0.2688g) from recycling#8 and accordingly reduced cellulose and water amount after 4 h reaction time. [e] Same as [d] and 4 h reaction time.

The significant change in the product distribution from the first to the second cycle - fewer retro aldol reaction products (ethylene glycol), more isomerization (1,2-propandiole as a product of the retro aldol reaction of fructose) and hydrogenation products (e.g. sorbitol)- can't be explained simply by catalyst lost. The decrease of retro aldol reaction products (e.g. ethylene glycol) and the increase in selectivity of sorbitol can be explained by tungsten losses.^[12]

The catalyst recovered after Run # 10 was examined for changes. Interestingly, sintering of the ruthenium particles did not play an important role. The ruthenium dispersion of the fresh and of the catalyst after recycling tests was almost the same (2.9%). The acidity decreased significantly (15%) during the recycling tests, which seems to be associated with the loss of tungsten (Table 3 and 2). Compared to data from the literature, however, this loss is not very high. Lercher et al. published for different HBEA zeolites the loss of acid sites in hot liquid water.^[41] For example, the number of acidic sites of HBEA150 decreased from 0.150 mmol/g to 0.115 mmol/g after 48 hours in hot liquid water at 433 K, a loss of almost 25%. Compared to this, the loss in the investigated Zr-W systems at 493 K (50h) in a real reaction system is low. This

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also applies to the pore system. HBEA150 lost about 50% of the micropores in hot water, while the catalyst 3Ru/Zr-W-oxide loses little pore volume.



Figure 3. Results of the recycling experiments under standard conditions as described. EG = ethylene glycol, PG = propylene glycol, BD = 1,2-butanediol, Total polyols = total 1,2-C2...C6 diols, Other GC = summary of all other peaks in gaschromatography (ketones, acids, furanes, esters, alcohols – identified by GC/MS. **a**) after 8 h reaction time. **b**) Recycling test with reduced cellulose mass – adapted to the catalyst mass found after experiment #8. Results of the recycling experiments under standard conditions as described.

The N₂-physisorption measurement shows a significant larger surface area for the recycled catalyst (93 m²/g instead of 79 m²/g). A comparison test, in which fresh catalyst was treated under standard conditions once without cellulose for 4 hours, showed also an increase in the surface area in the same order of magnitude (Table 1). This is an indication that residues of the





preparation were washed out. According to experience made in the recycling test, the solution was left to sediment. This reduced the catalyst losses from 4 wt% to 2 wt%. Via REM-EDX measurements a change in the W/Zr atomic ratio from 1.9 to 1.4 could be observed as described above. This statement applies, due to the REM-EDS method only for the surface of the sample. The atomic ratio in the bulk (Table 2; XRF) does not decrease so drastically from 1.76 to 1.47. The described four-hour hot water treatment changes the W/Zr atomic ratio from 1.76 to 1.63. This result is consistent with the measured mass loss and the change in the pore system of the catalyst.

Fig. 4 shows the XPS of the 3Ru/Zr-W-oxide in fresh state and after the recycling tests. The changes in the tungsten signals are not very large. The ratio of the summarized signal intensity between WO₃ and WO₂ changes from 44 to 56 (fresh catalyst) toward 57 to 43 (after recycling). As noted in the REM-EDX and XRF investigations, the atomic ratio W/Zr changes significantly. From 1.4 for the fresh catalyst to 1 for the recycled catalyst.

The XRD measurements showed no significant changes in the location and the width of the reflexes (Figure 1). A decomposition into WO_3 and ZrO_2 was observed only after a treatment in air at 1050 K for 12 h.

Conclusions

A ruthenium catalyst based on zirconium and tungsten, which is of interest for the reaction under hydrothermal conditions, has been successfully developed and tested. In addition to good yields of polyols, the carbon efficiency coefficients reached nearly 100% for the catalyst with 4.5 wt% Ruthenium - under these harsh conditions a particular highlight.

This is probably achieved by a slight tendency to form 5-HMF and its subsequent polymerization to form humines. A decisive advantage of the investigated system is its stability under the chosen conditions in any case - 50 hours at 493 K in hot compressed water under hydrogen pressure with a constant selectivity of 65 % to polyols. The hydrogenation efficiencies are weaker compared to other similar catalysts based on ruthenium. This results in lower ethylene glycol yields and higher yields of 1,2-propandiol. This disadvantage could be compensated by optimization of the catalyst preparation. In particular, the calcination temperature, which has a decisive influence on the activity and selectivity of Zr/W systems, should be optimized in further studies.^[32]

Experimental Section

Catalyst preparation

The carrier for the catalysts was prepared in accordance with.^[26] For this purpose, 100 ml of ZrOCl₂ aqueous solution (0.15 mol/L; AlfaAesar) and 200 ml of a Na₂WO₄ aqueous solution (0.125 mol/L; AlfaAesar; 0.09375 mol/L in case of Zr-W-oxide(-25W); 0.156 mol/L in case of Zr-W-oxide(+25W)) were added dropwise to 50 ml of deionized water in a beaker

at 333 K with constant stirring. After half an hour, 50 ml of 1.5 mol/L HCl aqueous solution was added dropwise to the mixture. The slurry was stirred for four hours at 333 K. The partially evaporated white slurry (100 mL) was transferred in a Teflon-lined Parr autoclave (300 mL), purged three times with Argon and heated under 15 bar Argon for 20 h at 473 K to carry out the hydrothermal conversion. The now blue suspension was removed and aged for two days at room temperature. The colour changed to light blue. After the aging, the product was filtered and washed with deionized water until it was free of chloride ions and dried for 10 h at 376 K. Finally, the light green powder was crushed and sieved to particle less than 200 μ m and heated under airflow at 873 K for 6 hours in a quartz tube. 6.3 g light yellow powder were obtained.

To each of three fractions (2g) of the powder different concentration of ruthenium (III) nitrosyl nitrate solution (AlfaAesar) was added via incipient wetness method. Catalysts containing 2 wt%, 3 wt% and 4.5 wt% ruthenium were obtained. After drying at 376 K for 2 hours, the catalyst was heated to 623 K under hydrogen flow for 2 h.

Materials with the variation in the Zr/W ratio were loaded in the same manner with 3 wt% ruthenium.

Catalyst characterization

N₂-Physisorption measurements performed using were bv Quantachromes Quadrasorb MP. The Powder XRD measurements were recorded using StoeCie (Ge[111]-Monochromator, CuKa1-Radiation, I = 1,54060 Å, Detektor: Mythen1K), REM-EDX measurements (Jeol JSM 6400 with EDAX Apollo) and X-ray flourescence measurements with Olympus GoldXpert XRF analyser. Temperature-programmed reduction measurements was carried out on a TPD/R/O 1100 from Thermo Fisher Scientific. Ruthenium dispersion was determined with CO-chemisorption also in the TPD/R/O 1100 equipment. Typically, 100 mg catalyst were pretreated in hydrogen at 623 K for one hour and after cooling down to room temperature CO was pulsed in the hydrogen flow over the catalyst. The CO concentration was monitored with a TCD. The ruthenium dispersion D_{Ru} is the ratio of ruthenium amount and the amount of chemisorbed CO in percent. NH₃-TPD experiments was carried out in a self-assembled quartz reactor. The sample (approximately 100 mg) was calcined at 623 K or at 873 K under a flow of 10 cm3 /min of nitrogen. After cooling down to 373 K the sample was saturated under flow with 2% of ammonia in nitrogen, subsequently 2 hours flushed with pure nitrogen and heated up to 873 K with 10 K/min under 50 ml/min nitrogen flow. The desorption of ammonia was monitored with a FTIR-detector (Thermo Antaris IGS with 2 m gas cell). XPS were taken on a SSX 100 ESCA Spectrometer with monochromated AI Ka radiation source (aperture slot 0.25 * 1.0mm). The high resolution spectra were collected with 50 eV and 0.054 eV resolution.

Catalytic experiments

Typically, 0.5 g of the catalyst, 5 g microcrystalline cellulose (Merck; item 1.02331.500) and 100 g deionized water are filled in a 300 ml stainless steel autoclave (Parr instruments), purged with argon, 25 bar hydrogen was added to the solution and the mixture was heated under stirring (1000 rpm) up to 493 K. As the solution reached the desired temperature, the pressure was increased from 42 bar to 65 bar with hydrogen. Notice that, the measured gas phase temperature (approx. 425 K) is lower than the liquid phase temperature. As a result, the partial pressure of the hydrogen is roughly 59 bar. The pressure in the reactor is kept constant at 65 bar via a backpressure regulator. The spent hydrogen was fed from an external tank. The pressure drop in this tank was recorded during the reaction. Therefore, it is possible to determine the amount of hydrogen consumed in the reaction. The rate of hydrogen consumption is constant to about 50%

cellulose conversion and then slows. After three hours (four hours in case of the recycling experiments) the autoclave was cooled down to room temperature and the gas phase was analysed via gas-phase FTIR analyser (Thermo Antaris IGS). The aqueous phase together with the rest of cellulose was filtered and the products analysed via GC and HPLC as described in ^[13]. Only the twenty main products were individually quantified. For the other products a mean quantification factor based on 1,2-butandiole was used. The conversion rate (X) of the cellulose was determined by weighing the dry filter cake.

In this work the yield of products (Y_i) are calculated as the ratio of moles of carbon in the different products and the moles of carbon in cellulose. The carbon efficiency coefficient (CEL) is the ratio between the sum of carbon found in the analysed products and the carbon in the converted cellulose.

The recycling experiments started with the above-described procedure. Since at the end of the reaction cellulose was not completely reacted, it was separated from the product solution together with the catalyst. For that purpose the slurry was centrifuged, the product solution was decanted and weighed for the mass balance. The product yields are based on the mass of the removed solution. The wet unconverted cellulose and the catalyst were re-transferred in the batch together with fresh cellulose and water. It is clear that the amount of cellulose with the uncomplete conversion in the following recycle experiments rises. This procedure prevent re-oxidation of the catalyst. The selectivity shown in the recycling experiments is the ratio between the individual product yield and the sum over all analysed product yields.

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Keywords: Cellulose • Hydrogenolysis • Polyols • Tungstenzirconia catalyst • Hydrothermally stable

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Solid acid and effective: based on ruthenium, zirconium and tungsten, a hydrothermal stable catalyst for cellulose conversion has been developed. In recycling experiments, a consistently high yield of polyols was achieved. The carbon efficiency achievable with the Ru/Zr-W-oxide is nearly 100%.

Martin Lucas*, Katarina Fabičovicova and Peter Claus

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