Influence of Sulfuric Acid on the Performance of Ruthenium-based Catalysts in the Liquid-Phase Hydrogenation of Levulinic Acid to γ-Valerolactone

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1. Experimental section

1.1. Materials

All chemicals were used as received without any further purification. For the catalytic tests: levulinic acid (98%) and 1,4-dioxane (99+%; containing 0.05% of H₂O), both from Alfa Aesar. Anisole (99%) (used as an internal standard) and alpha-angelica lactone (98%) were purchased from Acros Organics. Sulfuric acid (>95%) was purchased from Fisher chemical. For the preparation of the monometallic catalyst, the Ru precursor and support were: ruthenium(III) nitrosyl nitrate (RuNO(NO₃)₃/Ru 31.3%) from Alfa Aesar and ZrO₂ (monoclinic) Daiichi Kikenso RC-100 from Degussa. For the preparation of the bimetallic RuRe/C and RuMo/C catalysts, the following chemicals were used: Ru₅%/C was obtained from Aldrich and used as received, a perrhenic acid (HReO₄) aqueous solution (75-80%) from Alfa Aesar and ammonium molybdate tetrahydrate (99%) [(NH₄)₆Mo₇O₂₄·4H₂O] from Sigma-Aldrich. Acetone (>99%) used for washing the catalyst was purchased from Interchema.

1.2. Catalyst preparation

The 1 wt.% Ru catalyst supported on monoclinic ZrO₂ was prepared using a wet impregnation procedure as previously reported.¹ First, the support was crushed and then dried for 2 h at 393 K, after which the support was dispersed in distilled water with stirring (450 rpm) for 30 min. 10 mL of the precursor solution was added to the suspended support dropwise after which the mixture was allowed to stir for 1 h. After elimination of the water under vacuum at 333 K, the catalyst was dried at 333 K overnight, calcined at 773 K for 3.5 h with a heating ramp of 5 K min⁻¹ under a N₂ flow of 100 mL min⁻¹, followed by its reduction at 723 K, for 5 h, under a H₂ flow of 80 mL min⁻¹. The bimetallic catalysts (Ru₅%Re₁₀%/C and Ru₅%M₀₁₀%/C) were prepared according to a literature procedure:² 2 g of commercial Ru₅%/C were dried at 393 K for 2 h, after which the solid was dispersed in 50 mL of distilled water for 30 min at 400 rpm. After that, a solution of 20 mL containing the precursor of the second metal (either HReO₄ or (NH₄)₆Mo₇O₂₄·4H₂O) was added and the mixture stirred for 3 h at 400 rpm. After elimination of the water under vacuum at 333 K, the catalyst was dried at 393 K overnight, calcined at 773 K for 3 h with a heating ramp of 5 K min⁻¹ under a N₂ flow of 100 mL min⁻¹, followed by its reduction at 723 K for 5 h under a H₂ flow of 80 mL min⁻¹. The solid was finally passivated with an O₂:N₂ mixture of 1:99 for 60 min.
1.3. Catalyst testing, regeneration, and product analysis

LA hydrogenation experiments were carried out in a 50 mL Parr batch autoclave at a temperature of 423 K, a H$_2$ pressure of 50 bar, and a stirring speed of 1250 rpm. It was previously shown that in this setup, LA conversion is essentially independent of the stirrer speed if above 900 rpm. In a typical reaction, the batch autoclave reactor was loaded with the catalyst, substrate and solvent. Then, the autoclave was purged three times with argon after which the reaction mixture was heated to reaction temperature and charged with H$_2$. This was taken as the starting point of the reaction; during the reaction samples were taken regularly, filtered and 1 wt.% of anisole was added as internal standard. At the end of the reaction, the autoclave was cooled rapidly to room temperature in an ice bath, after which the remaining H$_2$ was released. The catalyst was separated by filtration (filters of 0.45 µm), washed with acetone or hot distilled water (323 K), and dried overnight at 333 K in air. The reaction products were analyzed using a Shimadzu GC-2010A gas chromatograph equipped with a CPWAX 57-CB column (25 m × 0.2 mm × 0.2 µm) and FID detector, using authentic samples for calibration. GC-MS measurements were performed on a Shimadzu GC-2010 using a VF5-ms column, coupled to a Shimadzu GCMS-QP2010 mass spectrometer. The majority of the tests were performed using 1,4-dioxane (27 g) as a solvent, 10 wt.% of levulinic acid (3 g, 25.8 mmol) over a series of supported Ru catalysts. For all three catalysts (Ru$_{1\%}$/ZrO$_2$, Ru$_{5\%}$Re$_{10\%}$/C and Ru$_{5\%}$Mo$_{10\%}$/C), the amount of catalyst added to the reaction medium was such that a molar LA to Ru ratio of 350 was obtained (0.75 g for the Ru/ZrO$_2$ and 0.15 g for the Ru/C or RuM/C – M for Re or Mo). As for the bimetallic catalysts, the second metal (M) to LA molar ratios were 320 in the case of RuRe/C, and 170 in the case of RuMo/C.

1.4. Catalyst characterization

Thermal gravimetric analysis (TGA) was performed with a Perkin–Elmer Pyris 1 apparatus. The sample was initially heated to 423 K for 1 h with a temperature ramp of 10 K min$^{-1}$ in a 20 mL min$^{-1}$ flow of Ar to exclude physisorbed water and acetone, followed by a ramp of 5 K min$^{-1}$ to 873 K in a 10 mL min$^{-1}$ flow of O$_2$ to burn off any organic deposits formed. N$_2$ physisorption isotherms were recorded to determine surface areas and pore volumes with a Micromeritics Tristar 3000 setup operating at 77 K. The samples were outgassed prior to performing the measurement for 20 h at 573 K in a N$_2$ flow. Surface areas were determined using the Brunauer–Emmett–Teller (BET) theory, while micropore volumes (cm$^3$ g$^{-1}$) were determined by
t-plot analysis for t between 3.5 and 5.0 Å to ensure inclusion of the minimum required pressure points.

Fourier-transform infrared (FT-IR) spectra in transmission mode were recorded on a Perkin-Elmer 2000 instrument. Samples were pressed under 3.5 tons for 15 s to achieve self-supporting wafers (25-30 mg/13 mm diameter). The wafer was positioned in a well-sealed cell with CaF$_2$ window and posteriorly activated at 473 K (5 K min$^{-1}$ heating rate) under high vacuum (10$^{-6}$ bar) for 1 h. Subsequently, the cell was cooled down to 85 K. Spectra were taken upon CO (10% in He, purity 99.9%) adsorption on the sample, at increasing pressures. The activation temperature was chosen relatively low to prevent the decomposition of the compounds that might have become attached to the surface of the sample during reaction.

The overall acidity of the catalyst materials was determined by temperature-programmed desorption of ammonia (TPD-NH$_3$) on a Micromeritics ASAP 2920 instrument. In a typical experiment, the sample (200 mg) in a quartz reactor was dried in a He flow by heating (5 K min$^{-1}$) from room temperature to 773 K. Subsequently, the sample was cooled to 373 K and NH$_3$ pulses (10 vol. % in Ar) were applied at this temperature to eliminate physisorbed NH$_3$. The sample was then heated to 873 K at 5 K min$^{-1}$ to induce desorption under flowing He. The desorbed NH$_3$ was quantified using a thermal conductivity detector (TCD), obtained by integrating the desorption peaks to determine the distribution of acid sites in the 373-773 K range. The total amount of NH$_3$ desorbed was taken as the total amount of acid sites. The total sulfur content in catalyst samples was quantified by using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectro Acros) after dissolution in aqua regia.
Figure S1. GVL yields obtained (black bars) with commercial Ru/C as function of added H$_2$SO$_4$ (blue squares denote LA conversion; red diamonds molar S/Ru). Experimental conditions: 10 wt.% LA, LA/Ru=500, 423 K, 50 bar H$_2$, and 1 h in dioxane.
Figure S2. GVL yields over time as function of recycling with Ru/ZrO₂ and in the presence of 0.1 wt.% of H₂SO₄. Catalyst treatment after reaction according to Method B: recovered catalyst washed with hot water after each run. Conditions: 10 wt.% LA in dioxane, LA/Ru=350, S/Zr=0.05, 423 K, 50 bar H₂, and 3 h in dioxane.
Table S1. LA conversion and GVL yields as function of time using the Ru/ZrO\(_2\) catalyst at 373 K. Conditions: 10 wt.% LA, LA/Ru molar ratio = 350, 50 bar H\(_2\), and 0.25 wt.% H\(_2\)SO\(_4\) in dioxane.

| Time (h) | Without H\(_2\)SO\(_4\)\(^a\) | With H\(_2\)SO\(_4\) | 4-Hydroxy-pentanoic acid (mol %)\(^b\) | \(\alpha\)-Angelica lactone yield (mol %) |
|----------|-------------------------------|----------------------|----------------------------------------|----------------------------------------|
| 1        | 22                            | 18                   | 5                                      | 14                                     |
| 2        | 45                            | 20                   | 15                                     | 15                                     |
| 3        | 79                            | 18                   | 31                                     | 14                                     |

\(^a\) Average of two runs.
\(^b\) Response factor used for quantification by GC-FID the same as the one used for LA. Confirmed by \(^1\)H-NMR spectroscopy using D\(_2\)O as solvent.

Table S2. Total sulfur concentration of various spent Ru/ZrO\(_2\) catalyst samples as analyzed by ICP-AES.

| Sample                                                                 | Wt. % total sulfur relative to the total mass of sample used (%) |
|-----------------------------------------------------------------------|---------------------------------------------------------------|
| Fresh Ru/ZrO\(_2\)                                                    | 0.02                                                          |
| Ru/ZrO\(_2\) after one run with 0.25 wt.% of H\(_2\)SO\(_4\)          | 1.72                                                          |
| Ru/ZrO\(_2\) after 5\(^{th}\) recycling (Method B regeneration) with 0.1 wt.% of H\(_2\)SO\(_4\) | 0.68                                                          |
| Ru/ZrO\(_2\) after 5\(^{th}\) recycling (Method C regeneration) with 0.1 wt.% of H\(_2\)SO\(_4\) | 1.80                                                          |
2. References

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