

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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The presence of biogenic or process-derived impurities poses a major problem on the efficient catalytic hydrogenation of biomass-derived levulinic acid to γ -valerolactone; hence, studies on their influence on catalyst stability are now required. Herein, the influence of sulfuric acid as feed impurity on the performance of Ru-based heterogeneous catalysts, including Ru/ZrO₂ and mono- and bimetallic Ru-on-carbon catalysts in dioxane as solvent, was investigated. The carbon-supported Ru catalysts proved to be very sensitive to minor amounts of sulfuric acid. In stark contrast, Ru/ZrO₂ showed a remarkable stability in the presence of the same impurity, which is attributed to the sulfate-ion adsorption capacity of the support. Preferential sulfate adsorption onto the surface of ZrO₂ effectively protects the Ru active phase from deactivation by sulfur poisoning. A simple catalyst regeneration strategy was effective in removing adsorbed impurities, allowing efficient catalyst recycling.

γ -Valerolactone (GVL) is expected to take a central role in future biorefinery operations, given the many different applications that are envisaged for this renewable platform molecule.^[1–4] GVL is typically obtained through levulinic acid (LA) hydrogenation, which can be derived directly from lignocellulosic biomass. The LA-to-GVL process has thus attracted considerable attention of both researchers and industries, with numerous studies reporting on active and selective catalysts for this conversion. Catalyst stability is equally important, yet has received rather limited attention.^[5,6] The highly polar, liquid-phase conditions under which LA hydrogenation reactions are

typically conducted are rather demanding for the supported metal catalysts used for this reaction. Catalyst deactivation, either by coking, sintering, or phase transformation, is therefore a major concern.^[7,8] For example, Abdelrahman et al. studied catalyst deactivation in the aqueous-phase hydrogenation using the (clean) LA process and could discern both reversible and irreversible loss of activity for Ru supported on C, TiO₂, SiO₂, and Al₂O₃.^[9] The general issue of catalyst deactivation can be further compounded by the possibility of deactivation through poisoning by impurities when actual biomass-derived LA feeds are used. In general, downstream catalytic biomass conversion reactions can be impacted by biogenic or externally introduced impurities. Examples of the former include deactivation of Pt-based catalysts by fatty-acid impurities in glycerol aqueous phase reforming^[10] or deactivation of Pd- or Ru-based catalysts by methionine in the hydrogenation of bio-based substrates.^[11] Indeed, even low-level contamination with elemental S, N, or Cl can have a detrimental influence on the hydrogenation ability of a metal catalyst.^[6] Similarly, contaminants introduced externally during previous processing steps can also poison or foul a catalyst used in further downstream upgrading. For example, LA can be obtained from different biomass sources by hydrolysis/(de)hydration of the carbohydrate fraction using various mineral acids (e.g., HCl or H₂SO₄), with the latter being preferred owing to its lower price.^[12] Trace-to-minor levels of these mineral acids, as well as formic acid (itself co-produced with LA), can remain in the LA feed and will influence catalyst stability. Although sulfur poisoning of the Ru active phase is well-established,^[13–15] the influence of process-derived impurities on subsequent catalytic steps, for example liquid-phase hydrogenation reactions, has been only sparsely studied.^[6] Furthermore, the severity of inhibition or deactivation shown by such impurities will be greatly influenced by several factors including the type of S-containing impurity (oxidation state of S in particular), impurity concentration, and process conditions such as solvent, reactive atmosphere, and temperature under which the Ru catalyst will be employed. Arena studied the effect of impurities on the hydrogenation of glucose to sorbitol,^[15] a study that was later extended by Elliot et al.^[16] A more recent example reported by Wang et al. showed that S-containing species in bio-oil could poison the Ru/TiO₂ catalyst used for hydrogenation.^[17] Lange et al. in turn reported on catalyst deactivation during LA hydrogenation, noting S, Ni, and Fe accumulation on a PtRu/ZrO₂ catalyst.^[6,18] Furthermore, Braden et al. demonstrated that H₂SO₄ had a detrimental effect on Ru/C catalysts for the hydro-

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generation of LA in water,^[14] whereas a RuRe/C bimetallic catalyst was less active but remained stable in the presence of the same impurity. Recent work of Hausoul et al., furthermore, showed H₂SO₄ to be detrimental for the activity of P-based porous polymers loaded with Ru complexes in the selective dehydrogenation of formic acid, a co-product of LA from hydrolysis of hydroxymethylfurfural (HMF).^[19] We previously showed that Ru/ZrO₂ outperformed benchmark LA hydrogenation catalysts, such as Ru/C and Ru/TiO₂, in terms of stability in the hydrogenation of analytical-grade LA in an organic solvent.^[20] In this work, we found that Ru/ZrO₂ also performs remarkably well in the hydrogenation of LA to GVL in the presence of H₂SO₄ impurities.

Under batch hydrogenation conditions of 423 K and 50 bar H₂, H₂SO₄ was added to an analytical-grade LA feed in dioxane, a typical aprotic organic solvent, which we have used as a GVL mimic. This H₂SO₄ additive greatly affected the performance of the benchmark commercial Ru/C catalyst, as was previously noted.^[21,22] Indeed, minor amounts of H₂SO₄ (i.e., 0.025–0.1 wt% with respect to the total weight feed) significantly reduced the hydrogenation activity of Ru/C, with GVL yields nearly decreasing to zero in reaction mixtures containing 0.1 wt% H₂SO₄ after 1 h (Figure S1 in the Supporting Information). For a combination of Ru/C and acidic Amberlyst resin in the LA-to-GVL process, deactivation of Ru/C was also noted and attributed to poisoning by S compounds originating from decomposition of the resin.^[23]

Building upon the previous study by Braden et al., who demonstrated improved stability of RuRe/C against H₂SO₄ in water,^[14] we also tested this catalyst as well as RuMo/C catalysts (prepared using the same experimental procedure^[14]), of which RuMo/C contains a more oxophilic promoter. GVL production rates for the three C-supported catalysts showed that the RuRe/C candidate indeed performed better in the presence of 0.1 wt% of H₂SO₄ under 50 bar H₂ and 423 K in dioxane as solvent (Figure 1). Notably, Ru/C (S/bulk Ru molar ratio of 4) yielded only 30% GVL even after 100 h of reaction and with moderate GVL selectivity (64%; LA conversion of 47%), attributed to the formation of by-products (α - and β -angelicalac-

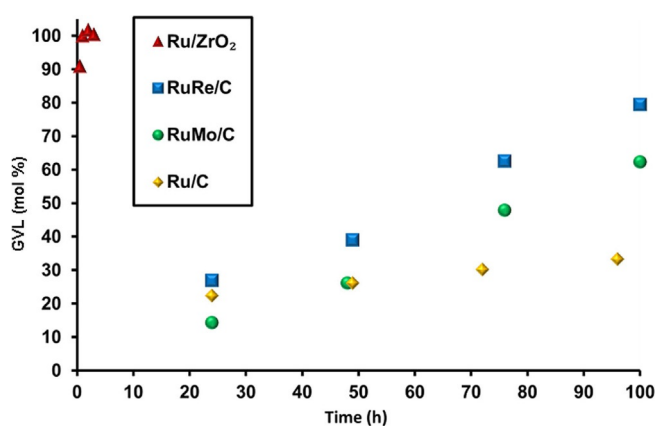


Figure 1. GVL yields as function of time over different Ru-based catalysts. Conditions: 10 wt% LA, LA/Ru molar ratio = 350, 423 K, 50 bar H₂, and 0.1 wt% H₂SO₄ in dioxane.

tone, dihydro-5-methylthiophenone, and 4-oxo-ethyl ester pentanoic acid). For comparison, full conversion with 94% yield to GVL is reached after 1 h using Ru/C and analytical-grade LA under otherwise identical conditions. The RuMo/C (LA/Mo = 170, S/Ru = 4, S/Mo = 1.9) and RuRe/C (LA/Re = 325, S/Ru = 4, S/Re = 3.7) catalysts were found to be fully selective for GVL, showing steadily increasing LA conversions with GVL yields reaching 60% and 80%, respectively, after 100 h. Remarkably, and in stark contrast with the mono- and bimetallic carbon-supported Ru catalysts, Ru/ZrO₂ (S/Ru = 4) showed full, quantitative conversion and >99% selectivity to GVL after only 1 h of reaction time in the presence of H₂SO₄. In the case of Ru/ZrO₂ after 0.5 h of reaction, the GVL yields with and without H₂SO₄ impurities were 96% and 91%, respectively.

Using Ru/ZrO₂, the amount of H₂SO₄ added was increased from 0.1 to 0.25 wt% (representing an increase of the S/Ru molar ratio from 4 to 10 and an increase in the S/Zr molar ratio from 0.05 to 0.125) at fixed LA/Ru molar ratio. This increase resulted in a slight decrease in the GVL yield to 90%, however full selectivity for GVL was maintained (Figure 2). It is

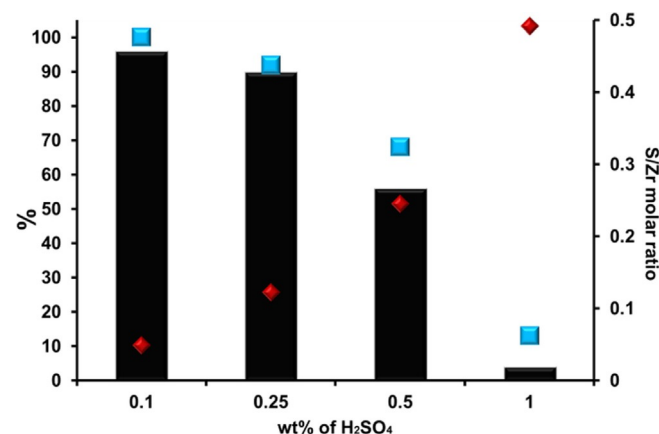


Figure 2. GVL yields obtained (black bars; left axis) with Ru/ZrO₂ catalysts with varying concentrations of added H₂SO₄. Blue squares denote LA conversion (on the left axis); red diamonds denote molar S/Zr ratio (on the right axis). Conditions: 10 wt% LA, LA/Ru molar ratio = 350, 423 K, 50 bar H₂, and 3 h in dioxane.

only when the H₂SO₄ incorporation reached 0.5 wt% (S/Ru of 20 and S/Zr of 0.25) that a clear decrease in GVL yield to 55% was observed, suggesting an upper limit of H₂SO₄ sensitivity for the Ru/ZrO₂ catalyst. In this case, reaction products other than GVL (around 10 mol% combined) were detected and identified as 3-methyldihydro-2(3H)-thiophenone and α - and β -angelicalactone, among others. A H₂SO₄ concentration of 1.0 wt% resulted in almost complete catalyst inhibition, giving very low LA conversion and GVL yields. Reactions were also run with Ru/ZrO₂ and 0.25 wt% H₂SO₄ at lower temperatures (323 and 373 K). Expectedly, lower activity was seen at 373 K, with the reaction run for 3 h in the presence of 0.25 wt% H₂SO₄ showing a GVL yield 15 times lower than that for the same reaction without H₂SO₄ (Table S1 in the Supporting Information). Furthermore, significant amounts of α -angelicalactone were obtained in reactions run at 373 K with 0.25 wt%

H₂SO₄, showing that the subsequent hydrogenation step is certainly impeded. Interestingly, without H₂SO₄, significant amounts of 4-hydroxypentanoic acid (4-HPA) were detected in reaction mixtures at 373 K, suggesting that the subsequent lactonization to GVL was limited in dioxane at this temperature. Reactions were thus run under standard reaction conditions (423 K) to obtain high selectivities to GVL, wherein no 4-HPA was detected. No activity was observed at 323 K with or without H₂SO₄.

Strong and essentially irreversible deactivation of Ru-based hydrogenation catalysts by S-containing impurities was attributed in different examples to strong chemisorption of sulfur species on Ru active sites.^[24,25] For instance, Na₂S in water deactivated a Ru/Al₂O₃ catalyst, which was attributed to adsorption of sulfide on the Ru active sites.^[15] For the Ru/C catalyst, deactivation in the presence of Na₂SO₄ or dimethylsulfoxide in supercritical water was attributed to irreversible sulfate bonding to Ru^[26] and Ru sulfide formation, respectively.^[6,27] With the sensitivity of the active Ru phase toward sulfur poisoning being well appreciated, the results presented above suggest that the ZrO₂ support acts as a sulfate scavenger of finite capacity. Spent Ru/ZrO₂ catalysts, recovered after reaction with 0.1 and 0.5 wt % H₂SO₄ and with subsequent acetone washing, were analyzed by Fourier transform-infrared (FTIR) spectroscopy. Figure 3a shows that (bidentate) sulfate bands between 1400–1000 cm⁻¹, absent in fresh Ru/ZrO₂, are clearly evident in the spent catalysts. The broad bands located at around 1400–

1340 and 1200–1000 cm⁻¹ are respectively assigned to S=O and S–O stretching vibration modes of the sulfate present on the surface of ZrO₂.^[28–30] In comparison with fresh Ru/ZrO₂, two new (weak) bands appeared at approximately 1450 and 1530 cm⁻¹ in the spent catalysts, ascribed to the vibration of C–H groups, indicating some deposition of organic species as well.^[31,32] Indeed, (weak) C–H stretching vibrations for the purported organic compounds could be observed in the spent catalysts (Figure 3a, inset). FTIR analysis after CO adsorption, however, showed the $\nu_{\text{S=O}}$ sulfate bands to be slightly shifted to lower wavenumbers, showing that the quantity of organic molecules deposited must be low, as the contact between CO and surface sulfate species was not inhibited. Complementary analysis of spent, acetone-washed Ru/ZrO₂ catalysts by inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed the presence of 1.7 wt % S (relative to the total weight of the sample) on the spent catalyst after the 3 h reaction with 0.25 wt % H₂SO₄ in the LA feed (Table S2).

It is well known that sulfation can promote the surface acidity of ZrO₂. Indeed, sulfated ZrO₂ materials are extensively used as solid acids and are typically prepared through precipitation of ZrO₂ precursors, followed by impregnation of sulfate (using H₂SO₄ or Na₂SO₄), and finally calcination.^[33–35] Considering the present study, sulfate must be incorporated only on the surface of already-crystalline ZrO₂ (Ru/ZrO₂) and at a relatively lower concentration during reactions. The acidity of the catalysts before and after reaction was then evaluated by temperature-programmed desorption of NH₃ (TPD-NH₃). Figure 3b shows that the bare (monoclinic) ZrO₂ support exhibits some surface acidity, with a total amount of acid sites of 0.25 mmol_{NH₃} g⁻¹, in agreement with literature values.^[33] Impregnation of Ru on ZrO₂ had a pronounced effect on acidity as the fresh Ru/ZrO₂ catalyst showed an intense desorption peak that increased the total amount of acid sites to 0.43 mmol_{NH₃} g⁻¹, which was attributed to various amounts of Lewis-acidic Ru centers and/or generation of oxygen-deficient sites.^[36,37] Compared to the fresh Ru/ZrO₂ catalyst, a noticeable increase of the intensity of the broad peak in the TPD-NH₃ profile in the range of 373–515 K was observed for the spent Ru/ZrO₂ material (after reaction with 0.5 wt % H₂SO₄ and acetone wash), suggesting an increase in the amount of weak acid sites exclusive to ZrO₂. The overall strength of the acid sites also increased, as seen from the shifting of T_{max} from 513 to 550 K (total amount acid sites of 0.45 mmol_{NH₃} g⁻¹), suggesting promotion of acidity by sulfate. The presence of surface sulfate was furthermore confirmed by the progressive increase in the signal at around 775 K, owing to the oxidation of surface-bound NH₃ to N₂ by sulfate groups at high temperatures under O₂-free conditions.^[35] These findings are clearly in line with the FTIR spectroscopy results and a number of studies on sulfation of ZrO₂.^[28–30,33–35]

The ability of ZrO₂ to scavenge S-containing compounds was previously observed for SO₂^[38] and H₂S.^[39] For H₂S, a comparison of Ru/C and Ru/ZrO₂ showed the formation of Ru sulfides and fast catalyst deactivation on Ru/C, and both sulfide and sulfate formation and slower deactivation for Ru/ZrO₂.^[39] The scavenging function of the ZrO₂ support is demonstrated

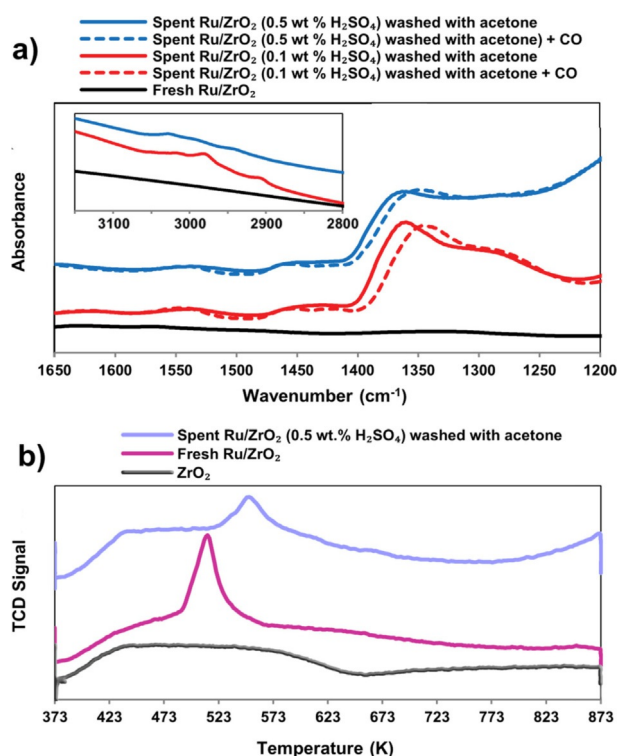


Figure 3. a) FTIR spectra of dehydrated fresh and spent Ru/ZrO₂ in the ν (sulfate) region in the absence (473 K, ca. 10⁻⁵ mbar) and presence of CO (85 K, ca. 1 mbar); inset shows C–H stretching vibrations in spent Ru/ZrO₂ catalysts only. b) TPD-NH₃ profiles of the bare ZrO₂ support, and fresh and spent Ru/ZrO₂ catalysts pretreated at 773 K under He.

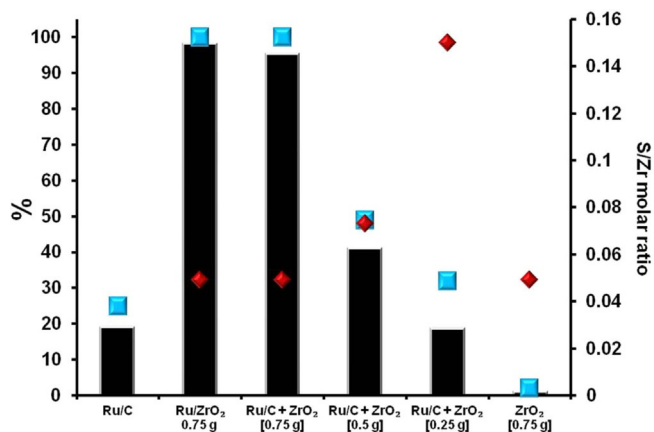


Figure 4. GVL yields (black bars; left axis) as function of catalyst composition in the presence of 0.1 wt% of H₂SO₄. Blue squares denote LA conversion (left axis); red diamonds denote S/Zr molar ratio at fixed Ru/C composition (right axis); values in brackets indicate the weight of ZrO₂ present in the reaction mixture. Catalyst Ru/ZrO₂ was used with 0.75 g total weight; i.e., no further ZrO₂ was added. Conditions: 10 wt% LA, LA/Ru = 350, 423 K, 50 bar H₂, and 3 h in dioxane.

herein by a set of experiments using a physical mixture of Ru/C and ZrO₂ with 0.1 wt% H₂SO₄, run for 3 h with a fixed amount of Ru and variable amounts of ZrO₂ (LA/Ru = 350; Figure 4). The GVL yields obtained using physical mixtures of Ru/C and ZrO₂ were similar to that obtained with Ru/ZrO₂ after one single run. This is in stark contrast to the low LA conversion and GVL yield obtained with Ru/C alone. Variation of the ZrO₂ loading then expectedly shows a decrease in GVL yield with further increase in the S/Zr molar ratio. The fact that ZrO₂ is able to effectively scavenge sulfate under conditions that otherwise lead to Ru deactivation (in the absence of ZrO₂) therefore implies that the scavenging process is much faster than the reaction pathway that otherwise leads to S poisoning of Ru through H₂SO₄ decomposition.

With the better performance of Ru/ZrO₂ catalyst attributed to the surface sulfation of the support, we further assessed its capability for reuse. In a first set of experiments, the spent catalyst was subjected to washing with acetone only, with subsequent drying at 333 K, as previously performed for recycle runs with analytical-grade LA.^[20] Using this regeneration method, catalytic activity was rapidly and almost completely lost within two cycles of reuse (Figure 5, Method A). This deactivation is in line with an expected depletion of scavenging capacity upon consecutive use. As the scavenging capacity of ZrO₂ needs to be restored after each run, a new regeneration method was adopted that involved washing of the recovered catalyst with hot (boiling) water, followed by a mild drying at 333 K overnight. This regeneration strategy was very effective, with catalyst recycling possible for up to four cycles without any significant loss of catalytic activity or selectivity (Figure 5, Method B)—even in the presence of 0.1 wt% of H₂SO₄. The first signs of deactivation were only noticed in the fifth run, shown by a decrease in the GVL yields from 93% to 84%. GVL yields as function of time and number of reuse cycles, allowing for comparisons to be made at lower conversions, are provided in Figure S2. Interestingly, an increase in GVL yield was observed

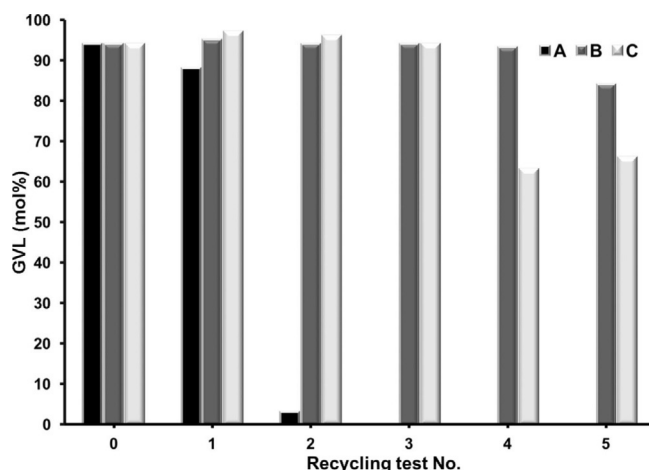


Figure 5. GVL yields as function of recycling with Ru/ZrO₂ and in the presence of 0.1 wt% of H₂SO₄. Method A: recovered catalyst washed with acetone after each run; Method B: recovered catalyst washed with hot water after each run; Method C: 10 wt% of water added to the feed, recovered catalyst washed with acetone after each run. Conditions for each method: 10 wt% LA in dioxane, LA/Ru = 350, S/Zr = 0.05, 423 K, 50 bar H₂, and 3 h in dioxane.

after the first reuse of the fresh catalyst, as similarly observed in the hydrogenation of analytical-grade LA.^[20] This suggests that some in situ activation of the catalysts occurs; thereafter, stable performance was then seen upon recycling.

Given that the addition of water into reaction mixtures is known to improve LA hydrogenation activity in organic solvents^[40,41] and that we observe a beneficial effect of regeneration by a hot water wash, we then aimed to combine these two effects and performed a set of reactions adding 10 wt% water to the feed. Catalyst regeneration then involved only an acetone wash of the recovered catalyst and subsequent drying (Figure 5, Method C). Indeed, a clear effect of the added water was seen, as catalyst activity was maintained for four runs. Upon further reuse, a distinct and sudden drop in GVL yield to 60% was observed. TGA analysis of the five-time-recycled Ru/ZrO₂ showed a 4% weight loss, which can be attributed to deposition of carbonaceous materials with a concomitant decrease in BET surface area from 94 to 79 m²g⁻¹. The recycling results indicate that the catalyst can be efficiently and simply regenerated using Method B. The first results on Method C look promising and indeed suggest a beneficial effect of water not only on activity but also on stability against H₂SO₄ impurities; however, the cause of the sudden drop in activity needs to be further studied.

To correlate catalytic performance, deactivation, and the effect of the various regeneration methods within the context of surface sulfate formation and efficiency of sulfate removal, and Ru speciation, CO FTIR spectroscopy measurements were likewise performed. Compared to fresh Ru/ZrO₂ (Figure 6a), all samples treated with 0.1 wt% H₂SO₄ (Figures 6b–d) generally show enhanced Lewis acidity as evidenced by the presence of a CO vibration peak at about 2195–2185 cm⁻¹. These results imply that washing the spent catalyst with hot water (in the case of five-times-recycled Ru/ZrO₂ using Method B, Figure 6c) seems to remove most, but not all, of the deposited sulfate

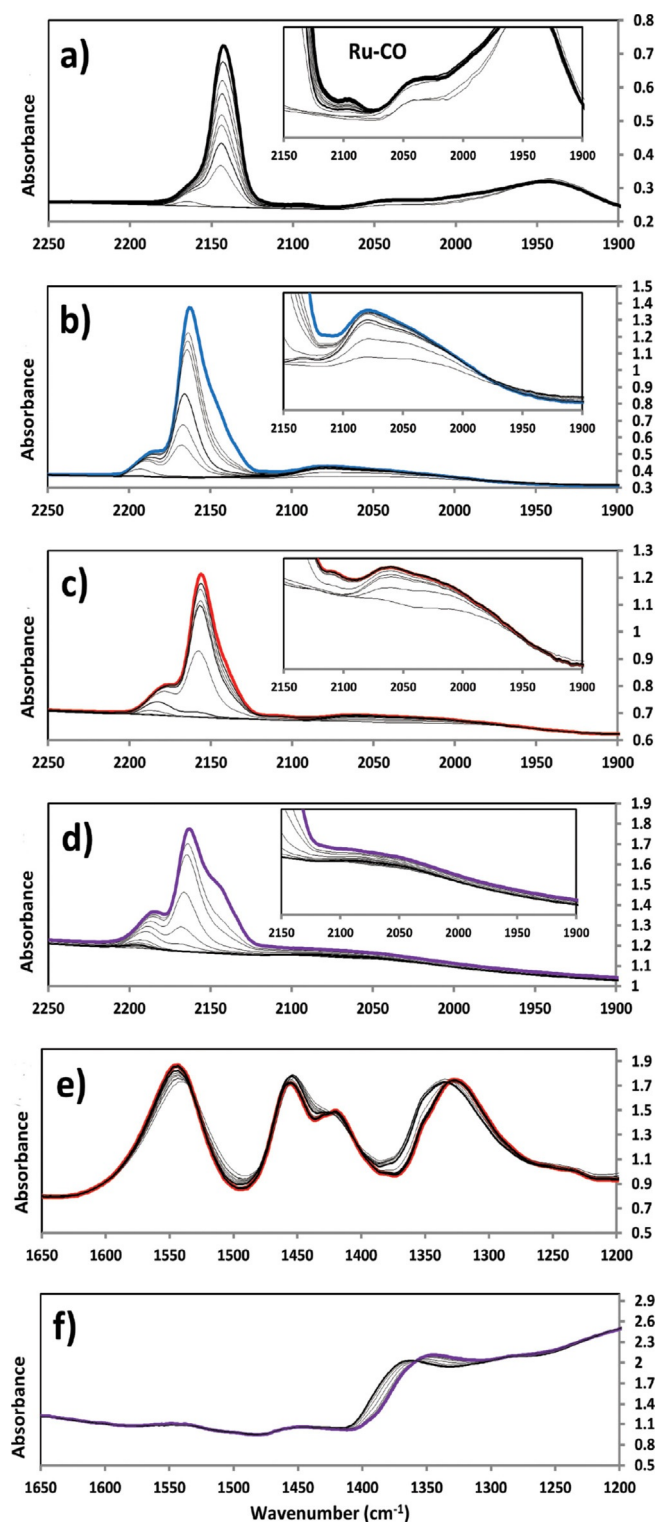


Figure 6. Stepwise, low-temperature CO FTIR spectra (CO region) of a) fresh Ru/ZrO₂ (main image) and spent Ru/ZrO₂ (inset) catalysts after reaction with 0.1 wt% H₂SO₄; b) acetone-washed samples after one single run (Method A); c) 5-times-recycled, washed with hot water after each run (Method B); d) 5-times-recycled, water added in situ, washed with acetone after each run (Method C); e) sulfate region of spectra from (c); and f) sulfate region of spectra from (d). The sulfate region of spectra from b) is shown in Figure 3 a.

species. Moreover, surface sulfate bands are indeed present in both singly used, acetone-washed samples (Method A; Figure 3 a) and five-times-recycled samples (treated according to Method B; Figure 6 e, or Method C; Figure 6 f). Based on the intensity of the CO vibration on Lewis acid sites (LAS) at about 2195–2185 cm⁻¹, using Method C resulted in a more acidic Ru/ZrO₂ (Figure 6 d) than Method B (Figure 6 c) after undergoing the same number of recycling runs. The fresh sample (Figure 6 a, inset) shows that the Ru⁰–CO interaction at approximately 2040 cm⁻¹ is mostly present, whereas one or both of the two interactions (Ru⁰–CO and Ru^{δ+}–CO bands at approximately 2075 cm⁻¹)^[42,43] are present in both singly used, five-times-recycled, and hot water-washed samples (Figure 6 b and c, insets). Sulfur analyses of the recycled catalysts confirm that Method B is more efficient (although it is not completely effective) than Method C in removing the adsorbed S species during recycling, showing a lower total S content of 0.68 wt% for Method B compared to 1.8 wt% for Method C (Table S2, Supporting Information). Interestingly the Ru–CO bands in spectra of samples subjected to Method C do not seem to be significantly altered after the washing process. This suggests that any species deposited do not appear to be covering the Ru active sites and that ZrO₂ indeed protects the Ru from deactivation. Previous reports show that surface sulfates can be reduced into sulfides (e.g., under reductive and acidic reaction conditions), which could eventually react and poison the Ru active sites.^[14] A more efficient removal of the adsorbed sulfate species, for instance by optimization of the hot-water-wash procedure, is therefore key to sustained catalytic activity. Indeed, if the capacity is reached and the catalyst is used again, the deactivation is attributed to direct interaction of new and some previously deposited sulfate acting as poisons for Ru.

In conclusion, it has been shown that Ru/C, as demonstrated previously, is very sensitive to minor amounts of H₂SO₄, which inhibit the selective hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL) under batch conditions of 423 K and 50 bar H₂. Bimetallic systems helped to improve the resistivity of the monometallic system; however, the GVL productivity remained very low. In strong contrast, the Ru/ZrO₂ catalyst showed excellent performance in the presence of H₂SO₄ owing to the ability of ZrO₂ to act as a scavenger for sulfate species, effectively protecting Ru from S poisoning. Importantly, Ru/ZrO₂ showed excellent stability after multiple reuse cycles when adopting a suitable regeneration method, such as a hot water wash followed by mild drying. The results obtained thus provide valuable insights into the (in)sensitivity of common hydrogenation catalysts toward impurities, such as sulfuric acid, using different solvents and catalyst supports, as well as interesting potential solutions for the use of real biomass feeds.

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