Supplementary Materials

Sustainable Solvent-Free Selective Oxidation of Benzyl Alcohol Using Ru(0) Supported on Alumina

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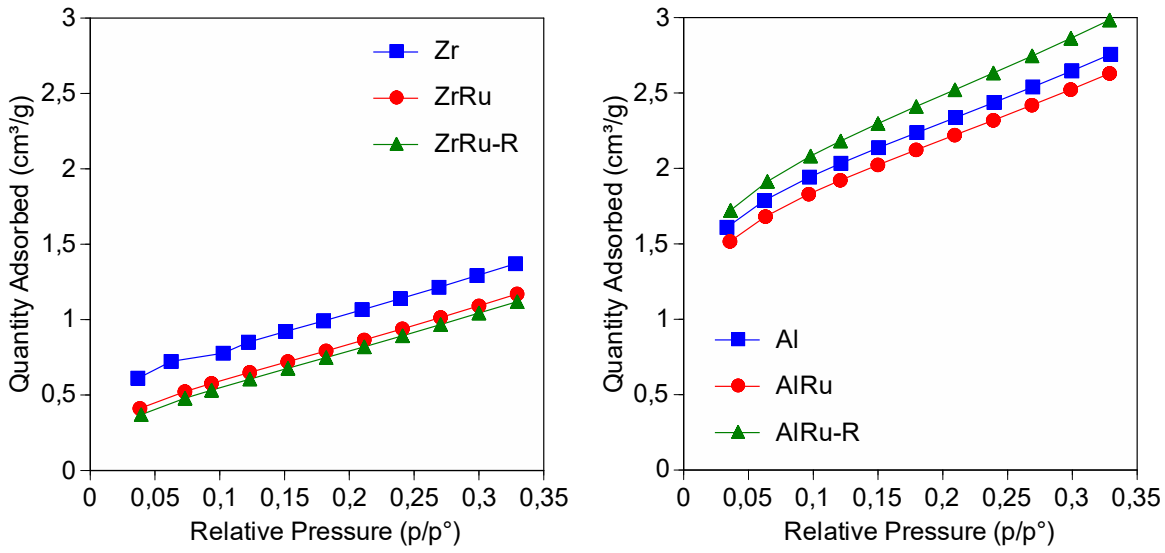

Figure S1. Adsorption isotherms for the investigated samples.

Table S1. TOF values of the catalysts.

Sample	TOF (h^{-1})[a]	TOF (h^{-1})[b]
ZrRu	3	100
ZrRu-R	4	180
AlRu	1	91
AlRu-R	6	178

[a]: moles of Ru in the catalyst, determined from the used amount of Ru in preparing the catalysts (nominal).

[b]: moles of Ru in the catalyst, estimated by the dispersion obtained by XPS analysis.

Table S1 shows the TOF values of the catalysts. Results are strongly dependent over the effective active-site utilization factor and for this reason we have reported the values of the two extremes, using the nominal moles of Ru or the moles estimated by the dispersion obtained by XPS analysis.

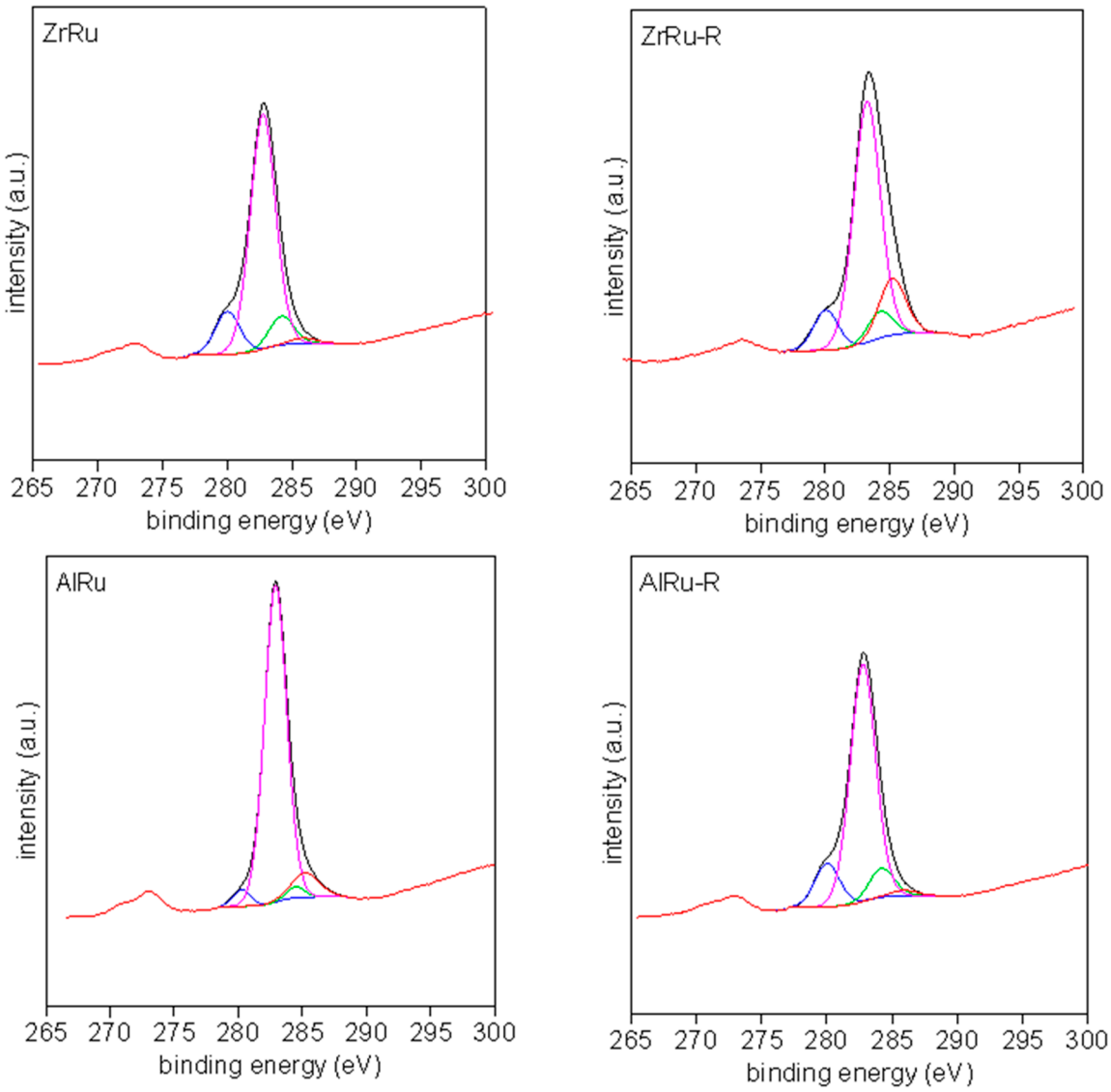

Figure S2. XPS spectra of C 1s + Ru 3d.

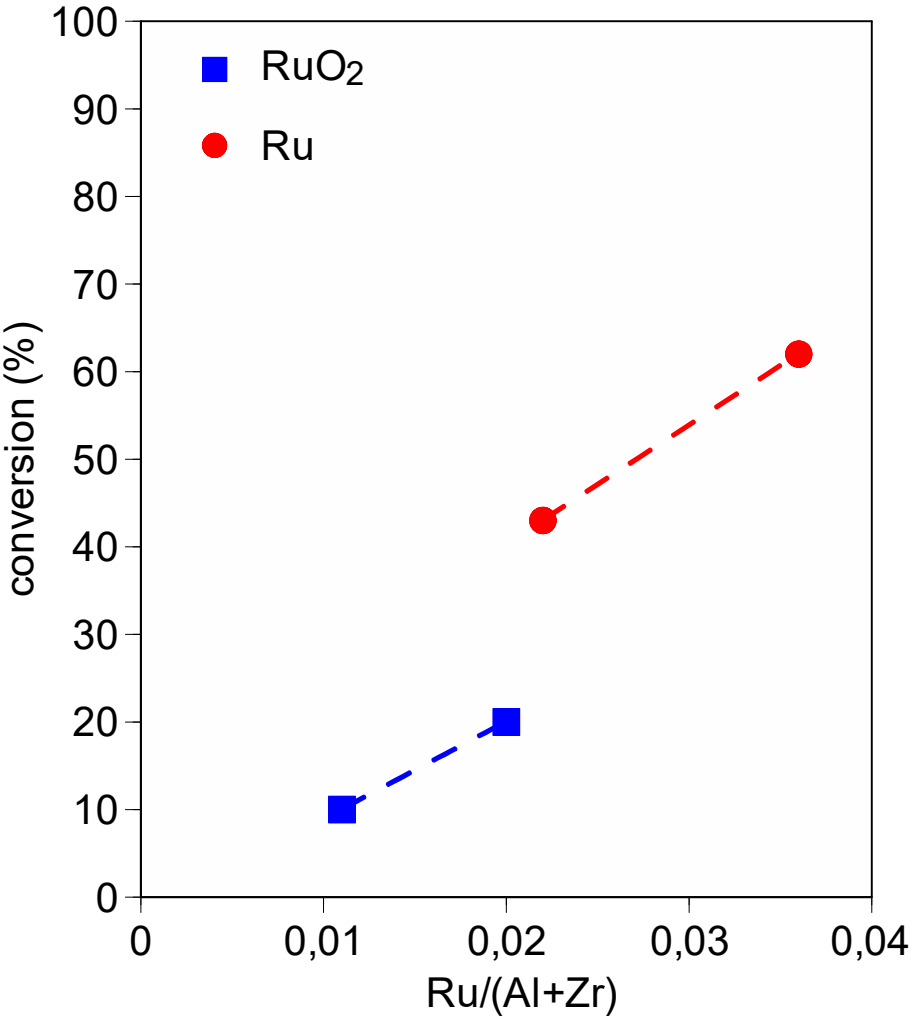

Figure S3. Dependence of conversion of benzyl alcohol to benzaldehyde on ruthenium dispersion on the support.

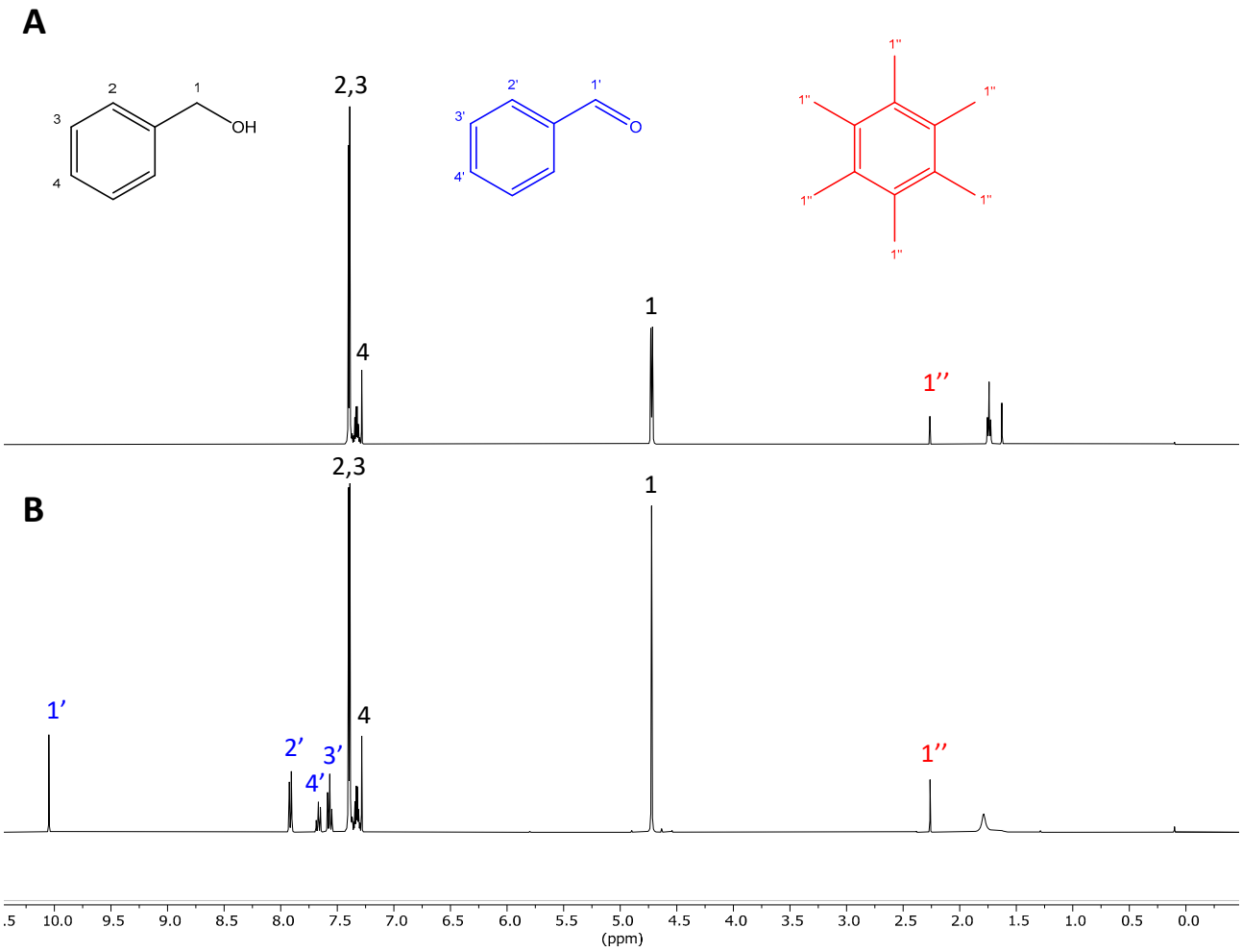

Figure S4. Representative 1H-NMR spectra A) before and B) after reaction with AlRu-R (reaction conditions: 1 ml of benzyl alcohol, 200 mg of catalyst, 90 °C for 24 h, 10 mg of hexamethylbenzene as internal standard).

^{1}H NMR spectroscopy has been used for the quantitative analysis of the conversion and selectivity of benzyl alcohol oxidation to benzaldehyde. The ^{1}H NMR spectrum of benzyl alcohol shows a multiplet at 7.43-7.29 ppm bearing to the protons of the aromatic ring (signals 2, 3 and 4 in Figure S3), and a singlet at 4.72 ppm corresponding to the methylene group (signal 1). In addition, signal at 2.30 ppm (1'') due to hexamethylbenzene, used as internal reference, is found. The formation of the benzaldehyde give rise to new sets of signals. Specifically, the signal at 10 ppm is attributed to the proton resonance of the aldehyde group (signal 1') and from 7.87 to 7.51 ppm the signals related to benzyl group (signals 2', 3' and 4'). A detailed analysis of the ^{1}H NMR spectrum does not reveal formation of any other reaction products with exception of benzaldehyde, indicating that the reaction is completely selective.