Supplementary Information

Ruthenium on phosphorus-modified alumina as effective and stable catalyst for catalytic transfer hydrogenation of furfural

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Transmission electron microscopy (TEM)

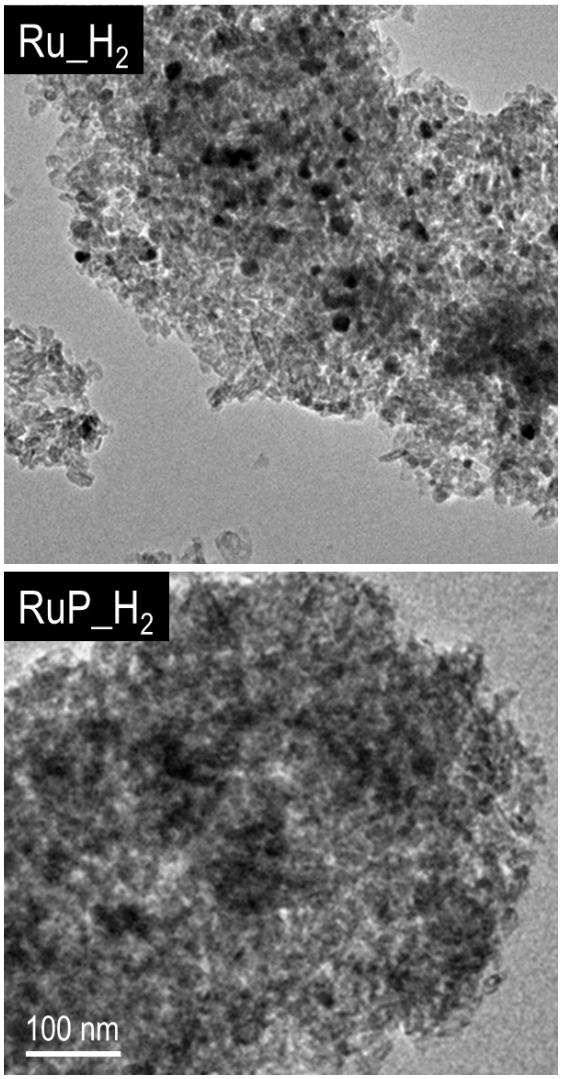

Figure S1. TEM micrographs of Ru_H_2 and RuP_H_2. The same scale bar applies for both images.

Particles of ca. 10 nm diameter are observed in the case of Ru_H_2, while hardly any particle is discernible in the case of RuP_H_2 in agreement with XRD (Figure 1 in main text) and EXAFS data (Figure 2 in main text).

X-ray powder diffraction (XRPD)

2θ (°)	FWHM (-)	crystallite size (nm)	Average size (nm)	Error on average (nm)
38.55	0.7952	10.6	**11.1**	**±0.6**
42.30	0.6567	12.9		
44.19	0.8160	10.5		
58.45	0.8695	10.5		

Table S1. Crystallite size of Ru_H_2 was obtained using the Scherrer equation. Peak maxima and full width half maximum (FWHM) were obtained by peak fitting using Gaussian function. The four peaks were obtained by subtraction of the diffractogram of Al_2O_3 from that of Ru_H_2 followed by baseline correction.

X-ray absorption near edge structure spectroscopy (XANES)

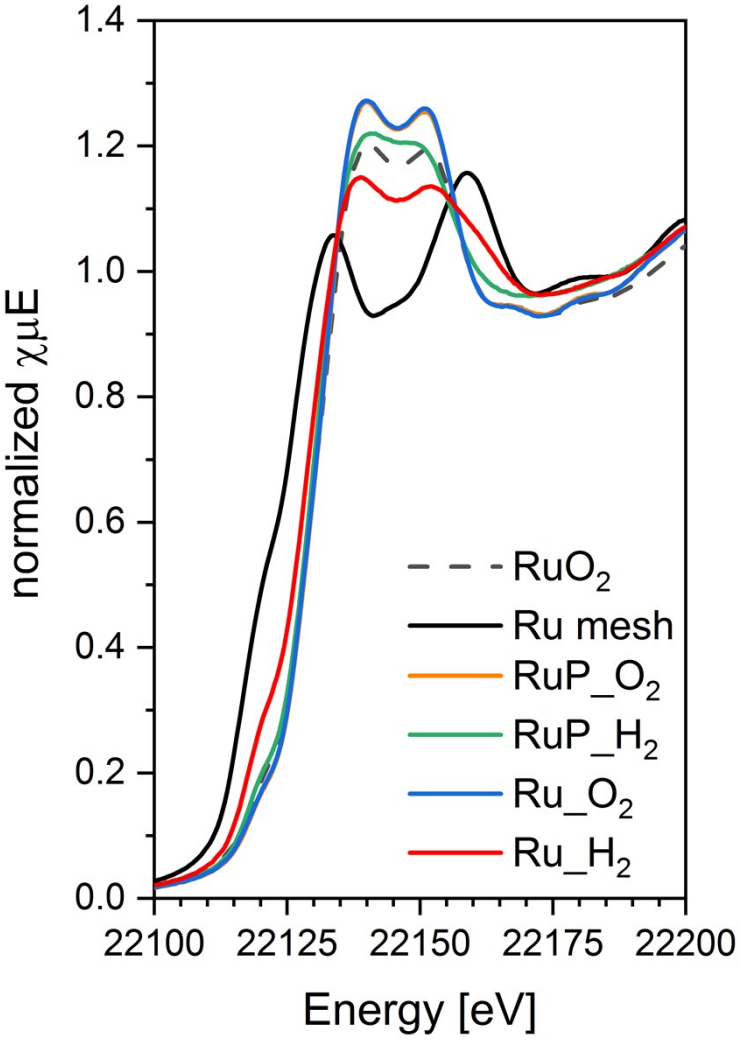

Figure S2. Ru K-edge XANES spectra of the various Ru catalysts and of the RuO_2 and Ru mesh references.

Pyridine adsorption using infrared spectroscopy

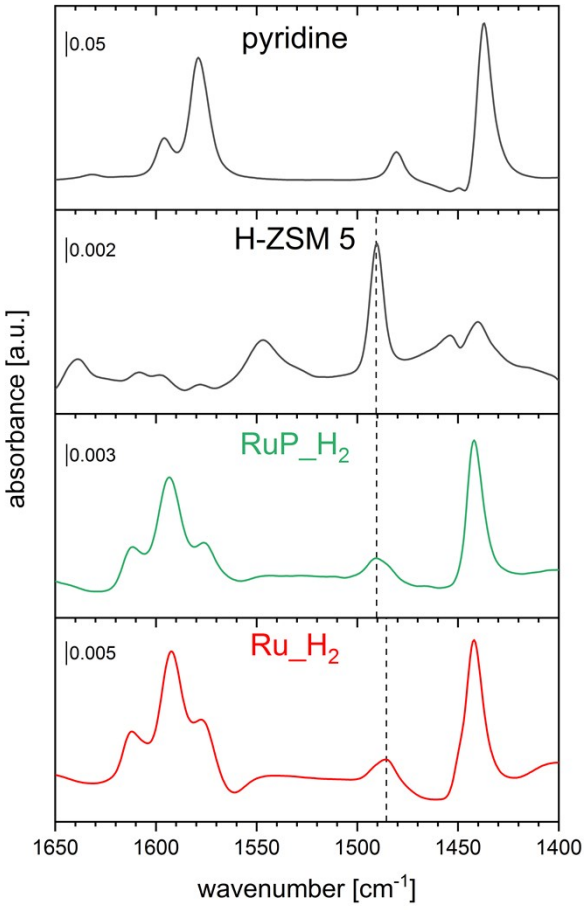

Figure S3. ATR-IR spectra of pyridine adsorbed on the indicated samples and of a solution of pyridine in cyclohexane (10 mM).

The ATR-IR spectrum of pyridine adsorbed on H-ZSM 5 displays two clear bands at 1546 and 1490 cm^{-1} that are associated with the pyridinium ion. While molecularly adsorbed pyridine on Lewis acid sites can contribute to the latter signal, its intensity and peak shape reveal that it is predominantly due to Brønsted acid sites. The spectrum obtained on RuP_H_2 exhibits the same signal (1490 cm^{-1}) but much weaker, while the signal observed for Ru_H_2 is clearly shifted to 1485 cm^{-1} assigned to Lewis acid sites.

^{27}Al Magic angle spinning nuclear magnetic resonance (^{27}Al MAS-NMR)

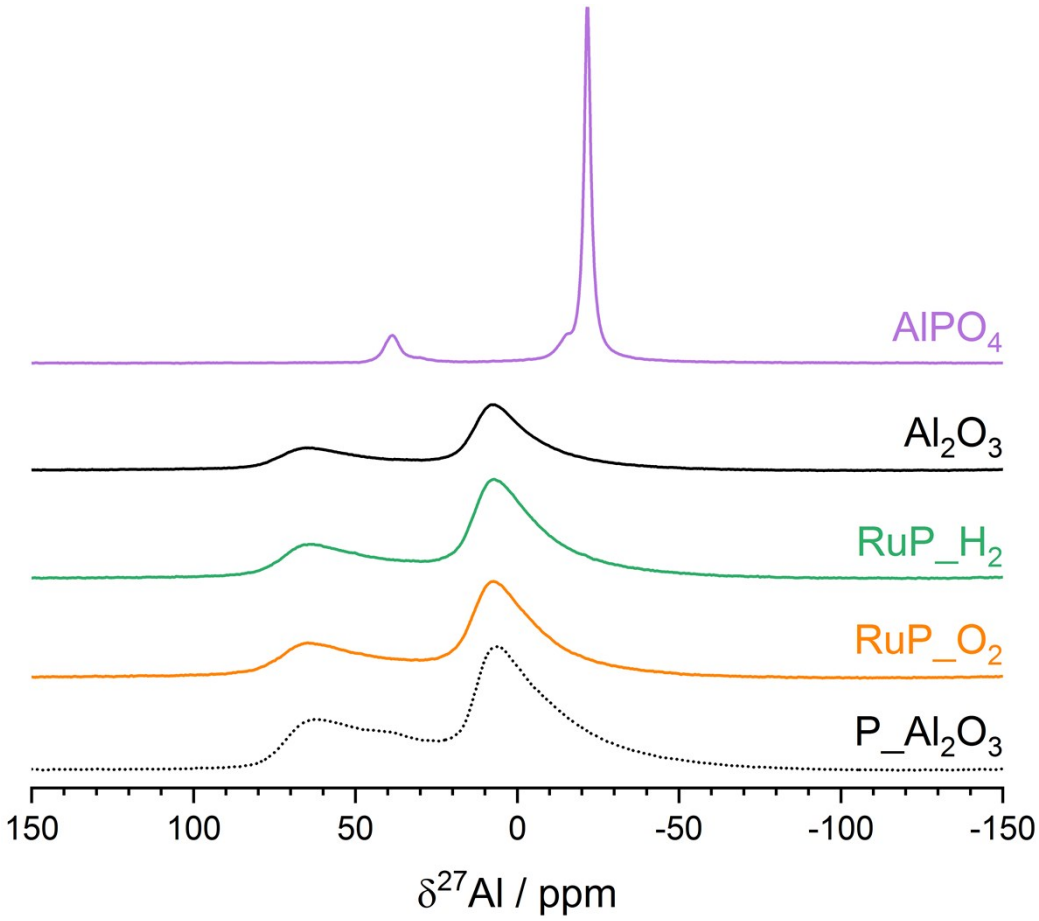

Figure S4. ^{27}Al MAS-NMR spectra of RuP_H_2, RuP_O_2 and of reference materials.

Catalytic transfer hydrogenation of furfural without catalyst pre-reduction: selectivity towards furfuryl alcohol

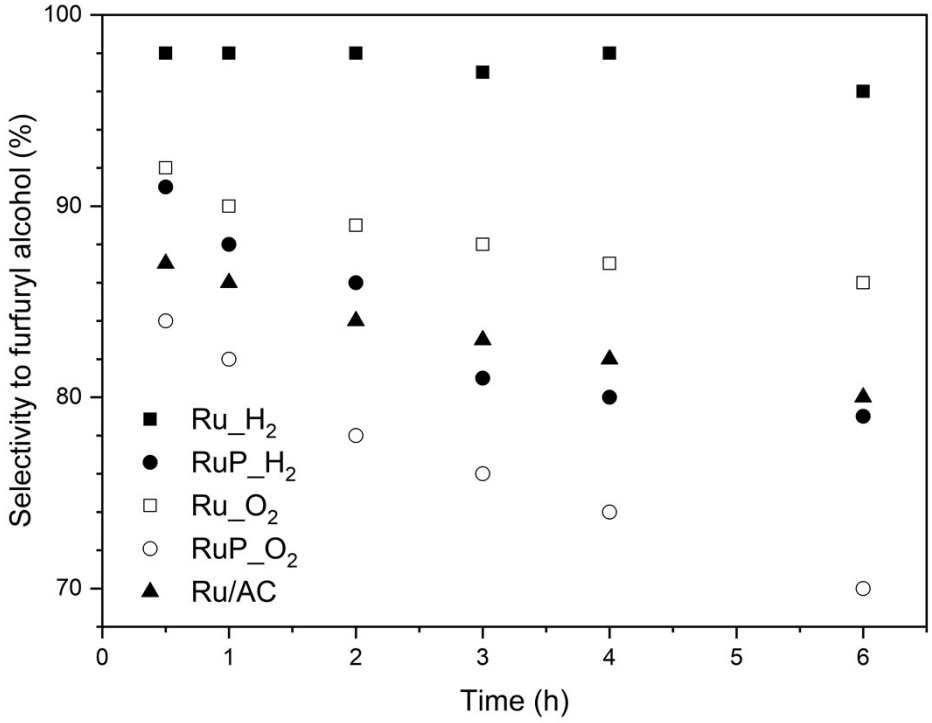

Figure S5. Selectivity to furfuryl alcohol under catalytic transfer hydrogenation conditions.

Catalytic transfer hydrogenation of furfural after *in situ* reduction

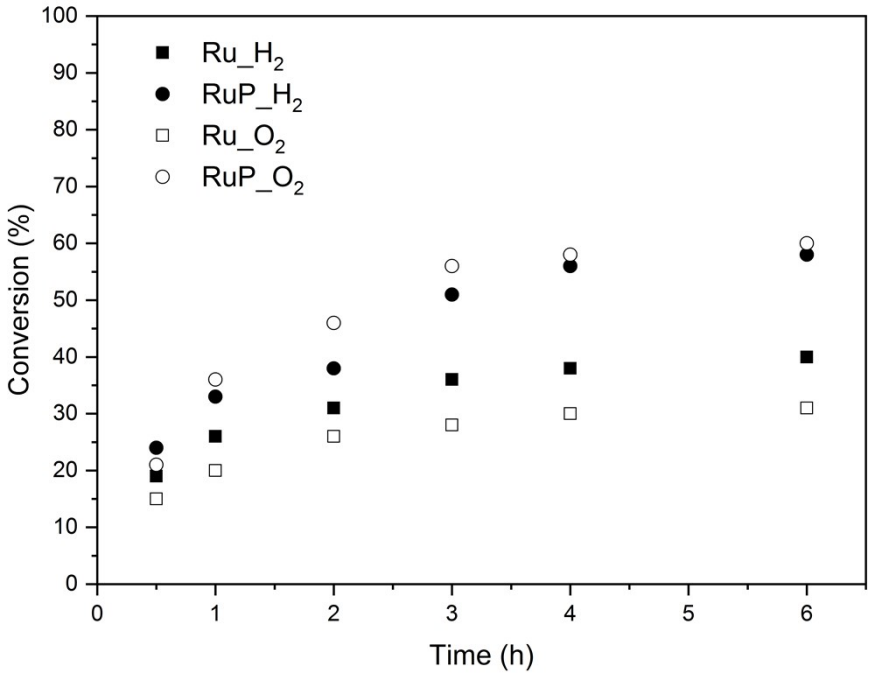

Figure S6. Conversion of furfural under catalytic transfer hydrogenation conditions. Materials were pre-reduced *in situ* before introduction of furfural in the reactor.

Operando XANES

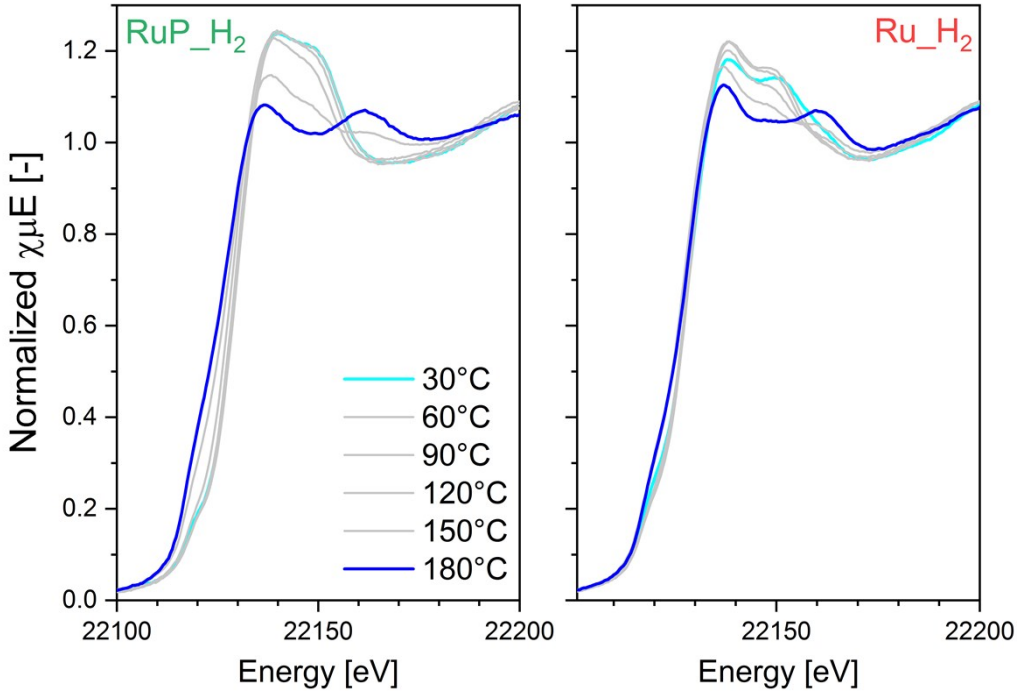

Figure S7. Operando Ru K-edge XANES spectra of RuP_H_2 and Ru_H_2 recorded during furfural hydrogenation at various temperatures.

Fit of FT-EXAFS spectra

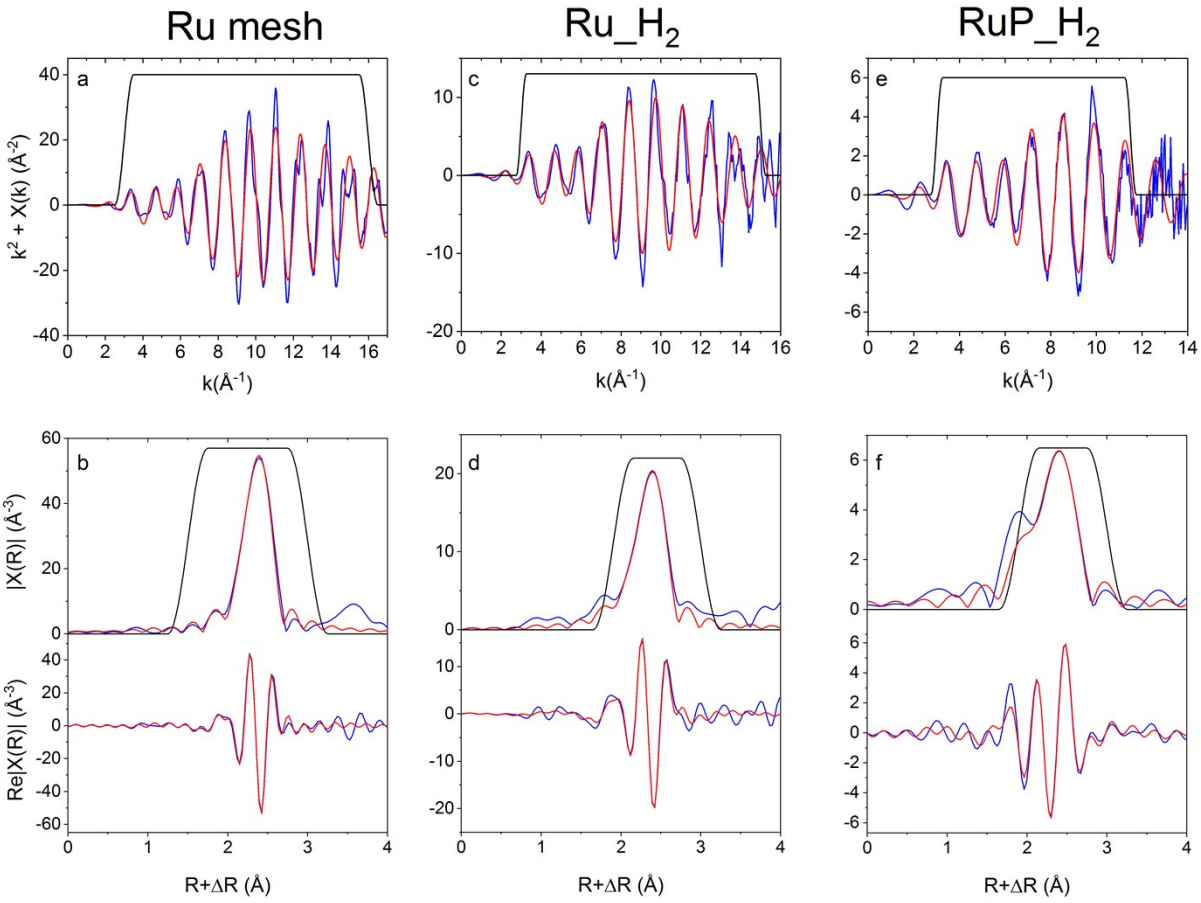

Figure S8. Operando Ru K-edge QEXAFS spectra obtained during furfural hydrogenation in Ar-saturated 2-propanol solution at 180°C and 16 bar. Spectra are the result of averaging of 60 spectra. (a, b) Ru mesh, (c, d) Ru_H_2 sample, (e, f) RuP_H_2 sample. (a,c,e) k^2-weighted $\chi(k)$, (b,d,f) magnitude $|\chi(R)|$ and real part $Re|\chi(R)|$ of the non-phase corrected Fourier transform spectra. Experimental data is shown in blue, fit results in red and fit window in black.