Reduction of RuO_2 nanoparticles supported on silica by organic molecules: a strategy for nanoparticle redispersion

ELECTRONIC SUPPORTING INFORMATION

Gabriel Fraga[a,b,c], Muxina Konarova[c], Laurence Massin[d], Athukoralalage Don K Deshan[a,b], Darryn Rackemann[a,b], Bronwyn Laycock[c], Steven Pratt[c], Nuno Batalha[d,*]

[a] Centre for Agriculture and the Bioeconomy, Queensland University of Technology, Brisbane, QLD, 4000 Australia

[b] School of Mechanical, Medical, and Process Engineering, Faculty of Engineering, Queensland University of Technology, Brisbane, Queensland 4000, Australia

[c] School of Chemical Engineering, Faculty of Engineering, Architecture and Information Technology, The University of Queensland, St Lucia, QLD 4072, Australia

[d] Université de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR5256 CNRS-UCB Lyon 1, 2 Avenue Albert Einstein, 69626, Villeurbanne Cedex, France

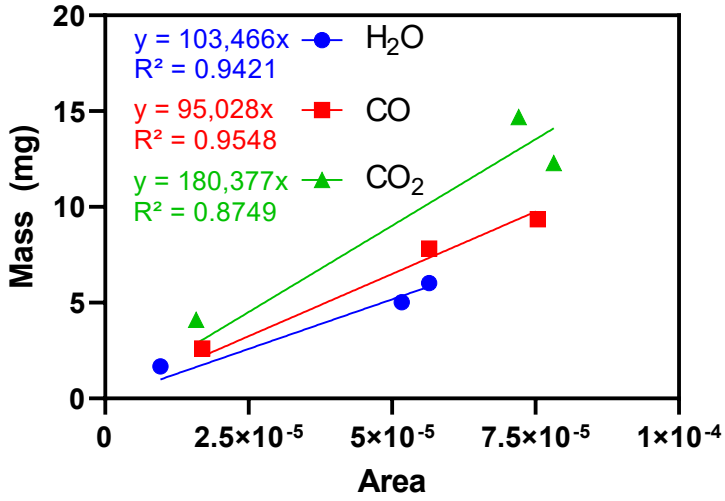


Figure S1. Calibration of mass using the decomposition of $(COO)_2Ca \cdot H_2O$. Area based on integration over time (signal x time).

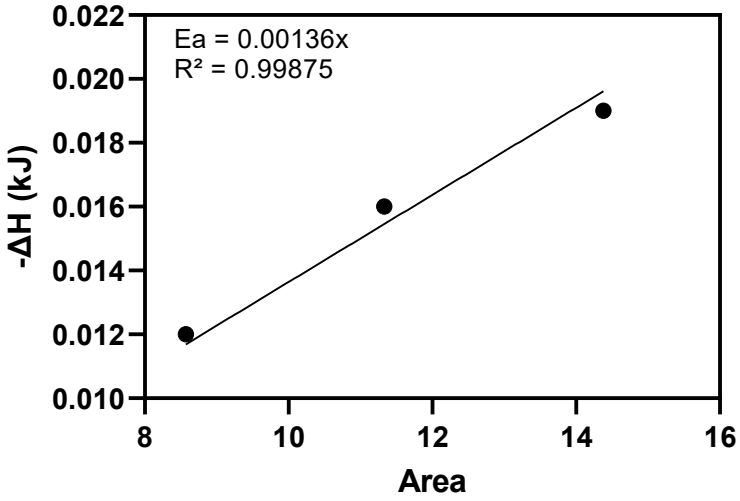


Figure S2. Calibration of ΔH using Pt/γ-Al_2O_3 with 3, 4 and 5% weight Pt. Area based on integration over time (signal x time).

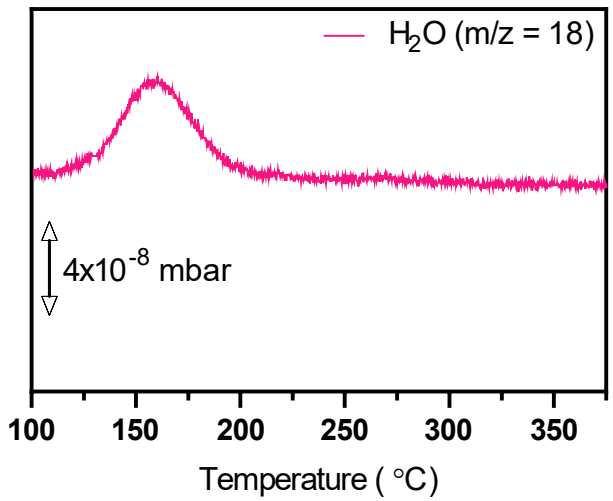


Figure S3. MS analysis of H_2O (m/z = 18) obtained by reduction of RuO_2/SiO_2 with $5\%H_2/N_2$.

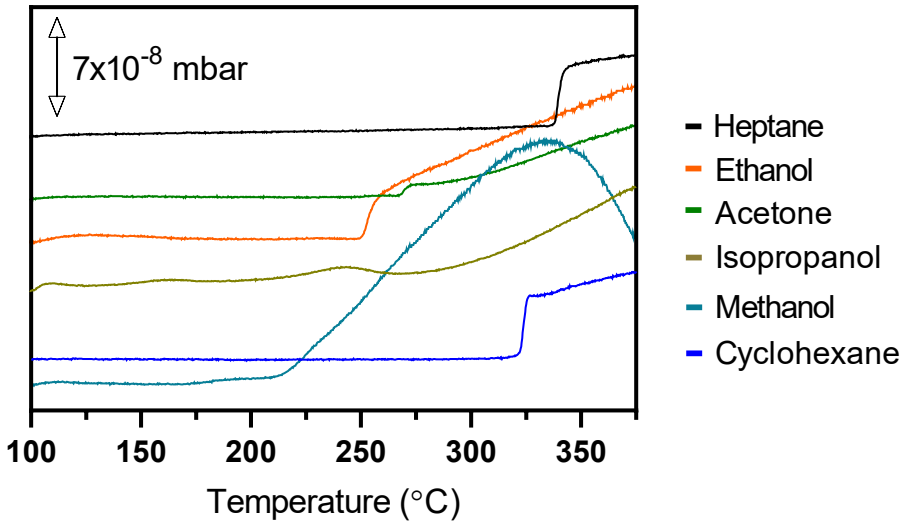


Figure S4. MS analysis of H_2 (m/z = 2) obtained by reduction of RuO_2/SiO_2 with different organic molecules.

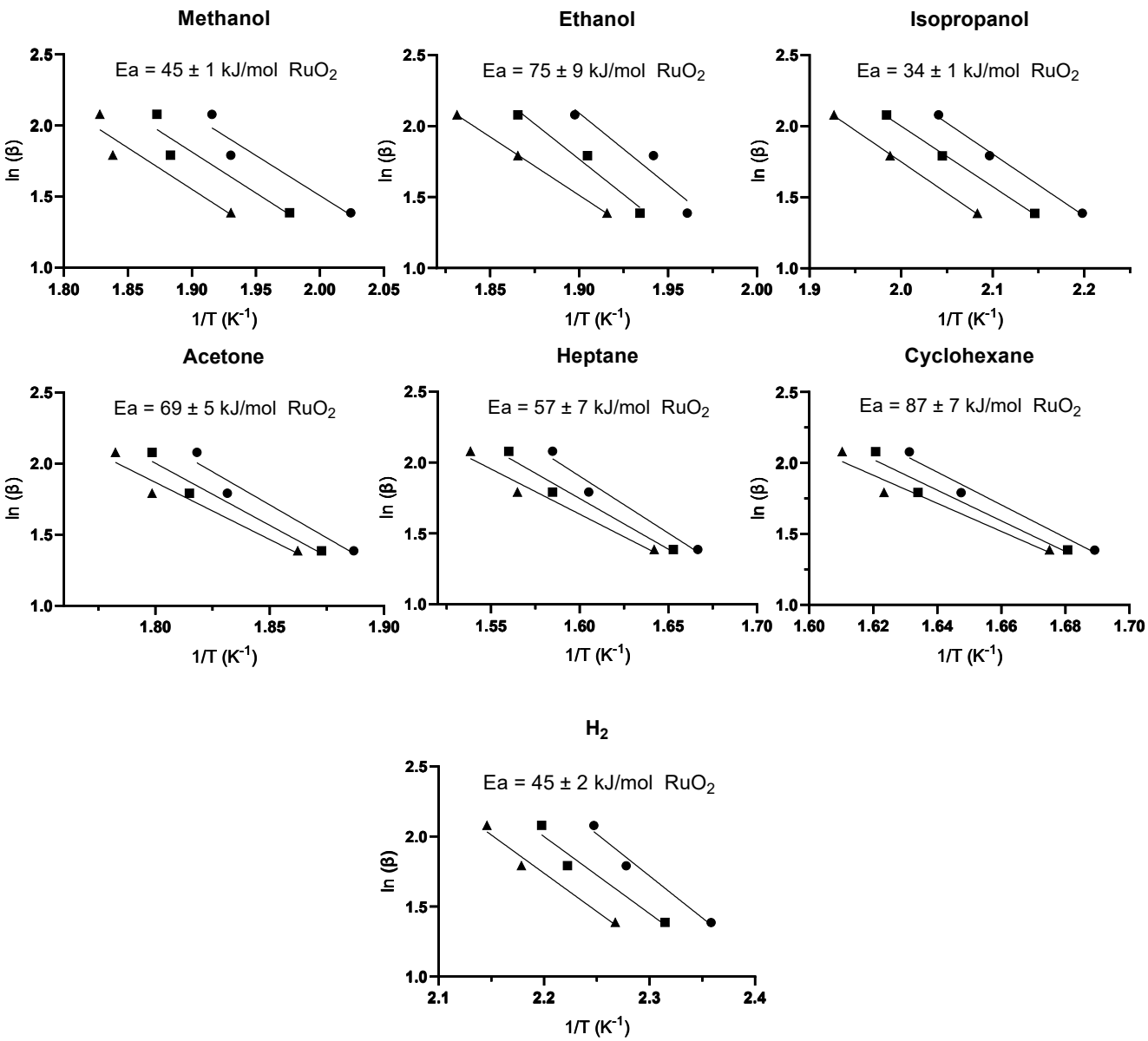


Figure S5. Flynn-Wall-Ozawa plots for activation energy (E_{app}) of reduction of RuO_2/SiO_2 using seven different reducing agents and calculated activation energy.

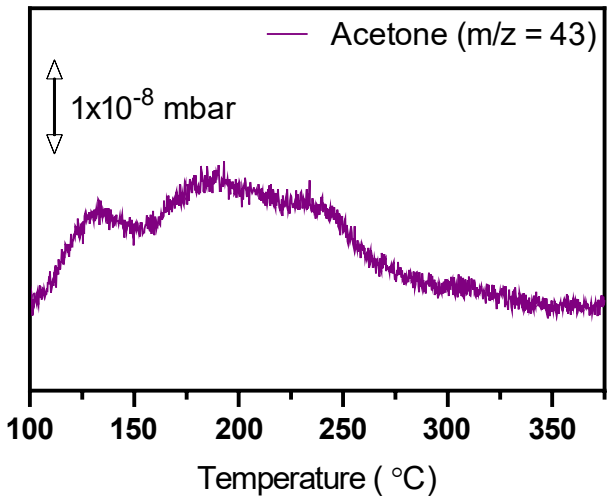


Figure S6. MS analysis of acetone (m/z = 43) obtained by reduction of RuO_2/SiO_2 with isopropanol.

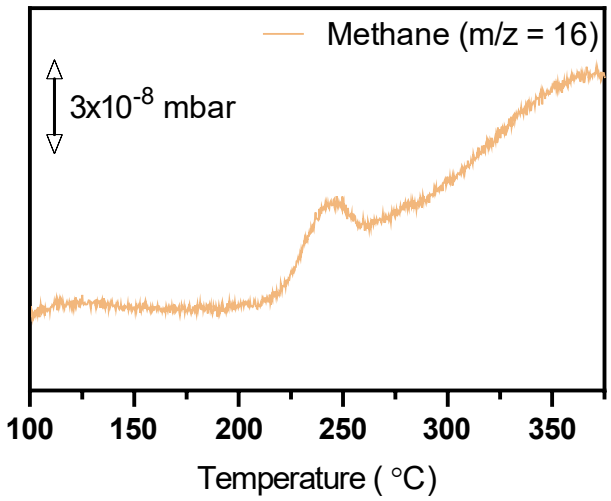


Figure S7. MS analysis of methane (m/z = 16) obtained by reduction of RuO_2/SiO_2 with ethanol.

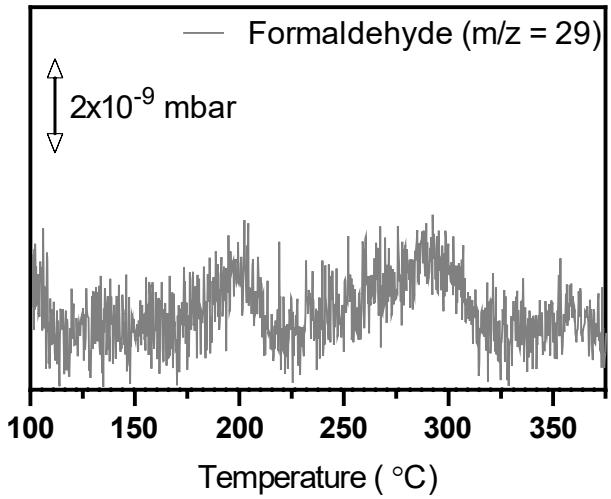


Figure S8. MS analysis of formaldehyde (m/z = 29) obtained by reduction of RuO_2/SiO_2 with methanol.

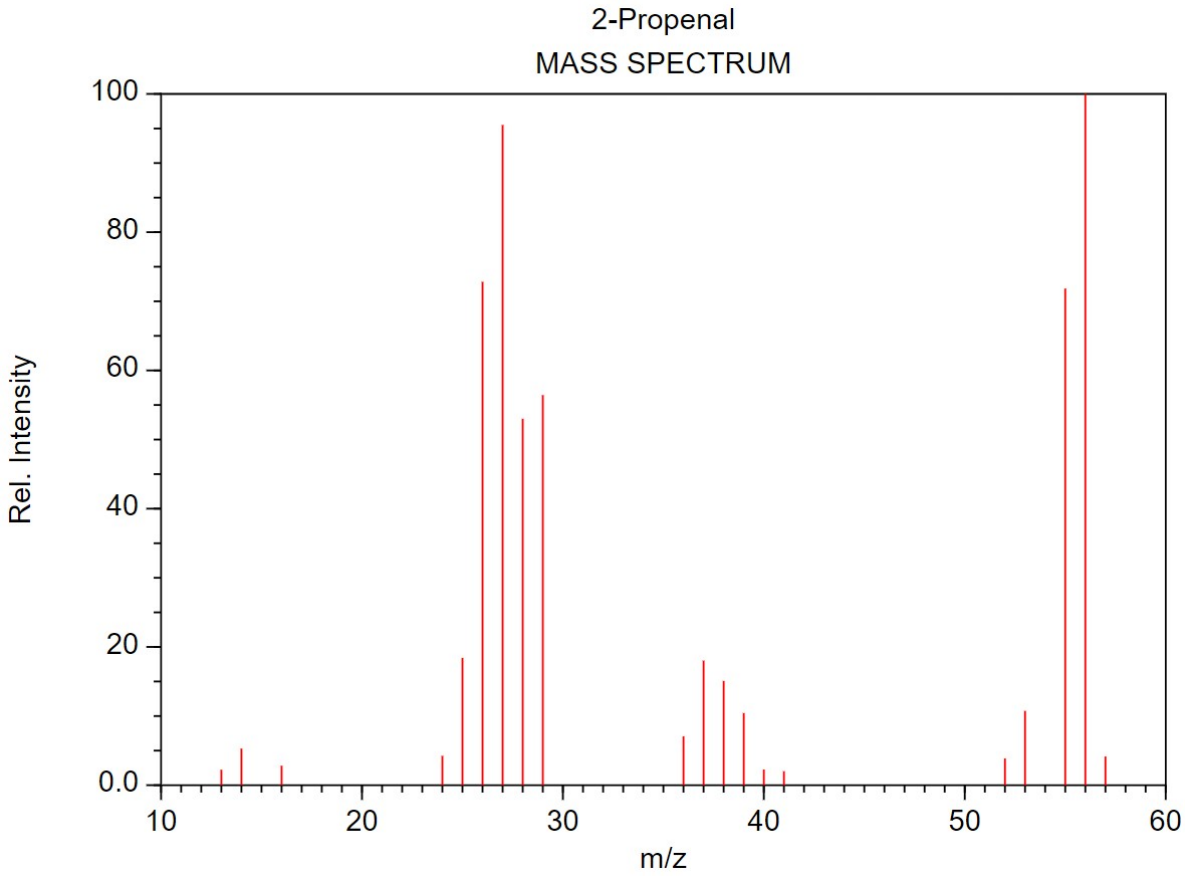


Figure S9. Mass spectrum of acrolein (2-propenal), from the NIST Standard Reference Database 69: *NIST Chemistry WebBook.*

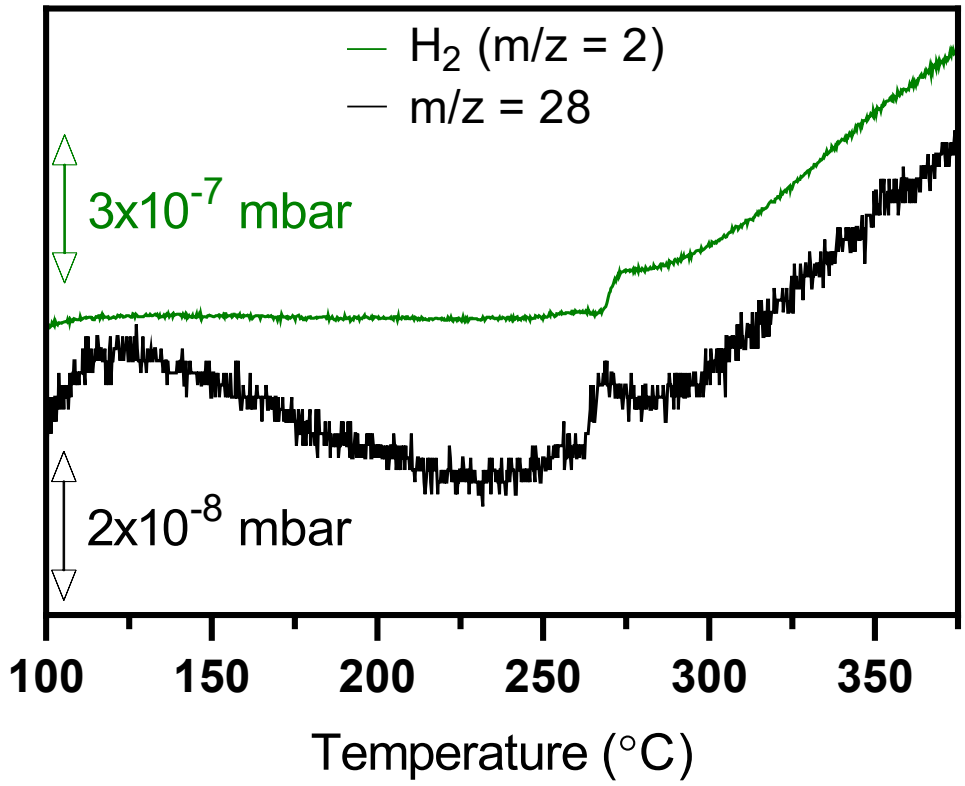


Figure S10. Superposed spectra of H_2 (M/z = 2) and M/z = 28 obtained by reduction of RuO_2/SiO_2 with acetone.

Determination of the enthalpy of reaction for the reduction RuO_2 through the oxidation and oxidative dehydrogenation of the multiple reducing agents

The enthalpy of reduction ($\Delta H_{reduction}$) of RuO_2 to Ru promoted by the oxidation (OXI) and oxidative dehydrogenation (ODH) of acetone, isopropanol, methanol, ethanol, cyclohexane, and heptane was calculated using the equations S1 and S2. The chemical equations for the reduction of RuO_2 to Ru through OXI and ODH of each reducing agent are represented in equations S3 to S13. Finally, the thermodynamic constants and reaction temperatures used to estimate the enthalpy of reduction are represented in Table S1.

Enthalpy of reduction under standard conditions

$$\Delta Hr^0\left(\frac{kJ}{mol_{RuO_2}}\right) = \frac{\sum^{Products} \nu_i.\Delta Hf^0{}_i - \sum^{Reagents} \nu_i.\Delta Hf^0{}_i}{\nu_{RuO_2}} \qquad \textbf{Eq. S1}$$

Where:

ΔHr^0, represents the enthalpy of reaction under standard conditions;

ΔHf^0, is the enthalpy of formation of compound i (Table S1);

ν_i, is the number of moles of compound i (equation S3 to S13);

Enthalpy of reduction at reduction temperature

$$\Delta Hr\left(\frac{kJ}{mol_{RuO_2}}\right) = \Delta Hr^0 + \frac{\left(\sum^{Products} \nu_i.Cp_i - \sum^{Reagents} \nu_i.Cp_i\right)}{\nu_{RuO_2}}(T_{reduction} - 25) \qquad \textbf{Eq. S2}$$

Where:

ΔHr, represents the enthalpy of reaction at reduction temperature;

ΔHr^0, represents the enthalpy of reaction under standard conditions (Equation S1);

ν_i, is the number of moles of compound i; (equation S3 to S13).

Cp_i, is the specific heat capacity of compound i; (Table S1).

$T_{reduction}$, is the temperature at which the reduction occurs (Table S1).

Table S1. Thermodynamic parameters.

Compound	Formula	$T_{reduction}$ (°C)	ΔH_f^0 (kJ/mol) [a]	Cp (J/mol.K)
Ruthenium oxide, solid	RuO_2	-	-314.15 [b]	56.42
Ruthenium, solid	Ru	-	0	24.05
Water, gas	H_2O	-	-241.8	33.55
Carbon Monoxide, gas	CO	-	-110.5	29.12
Carbon Dioxide, gas	CO_2	-	-393.5	37.2
Hydrogen, gas	H_2	159	0	28.84
Acetone, gas	C_3H_6O	261	-248.4	75
Isopropanol, gas	C_3H_7OH	193	-272.6	89.3
Methanol, gas	CH_3OH	233	-205	116
Ethanol, gas	C_2H_5OH	244	-234.8	65.6
Heptane, gas	C_7H_{16}	332	-187.6	166
Cyclohexane, gas	C_6H_{12}	322	-123.4	106
Acetaldehyde, gas	C_2H_4O	-	-170.7	89.05
Cyclohexene, gas	C_6H10	-	-5	105
1-heptene, gas	C_7H_{14}	-	-63	180.5
Formaldehyde, gas	CH_2O	-	-115.9	35.34
Acrolein, gas	C_2H_4O	-	-84.0	71.28

[a] Except where indicated, reference is: Hussein Y. Afeefy, Joel F. Liebman, and Stephen E. Stein, "Neutral Thermochemical Data" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, https://doi.org/10.18434/T4D303.

[b] Cordfunke, E. H. P.; Konings, R. J. M., Thermochim. Acta 1988, 129 (1), 63-69.

Table S2. Average Ru particle size quantified using Scherrer equation.

Reducing Agent	β	**Ru particle size (nm)**
H_2	0.89361	10.0
Heptane	1.89792	4.7
Acetone	2.03901	4.4
Ethanol	3.52039	2.5
Methanol	1.98717	4.5
Isopropanol	1.58640	5.6
Cyclohexane	1.53816	5.8

Scherrer Equation:

$$\tau = \frac{K \times \lambda}{\beta \times \cos\theta}$$

Where: K is the shape factor (0.94), λ is the X-ray wavelength (1.54178 Å), β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle (21.95°).

Determination of the Ru equivalent particle size from HR-TEM particle size of RuO_2

For the calculation, the particles were assumed to be of spherical shape.

Table S3. Calculation of Ru equivalent diameter from RuO_2

RuO_2	
Diameter - nm (from HR-TEM measurements)	16.2
Volume (nm^3)	2,229.7
Density (g/nm^3)[a]	6.97E-21
Mass of Oxide (g)	1.55E-17
Mw Ru/ Mw RuO_2	0.76
Ru	
Mass Pure Metal (g)	1.18E-17
Density (g/nm^3)*	1.22E-20
Volume (nm^3)	967.5
$D_{equivalent}$ (nm)	**12.3**

[a] From Sigma-Aldrich catalogue.

Table S4. Atomic concentrations quantified by XPS of RuO_2/SiO_2 and after reduction with different reducing agents.

	Atomic %				Ru/C	Ru/Si	Si/O
	C (1s)	O (1s)	Si (2p)	Ru (3d)			
Raw	1.4	66.2	32.2	0.19	0.13	0.006	0.486
Hydrogen	2.1	65.4	32.2	0.36	0.17	0.011	0.492
Ethanol	1.6	65.9	32.0	0.46	0.28	0.014	0.485
Isopropanol	2.9	64.8	32.1	0.23	0.08	0.007	0.495
Heptane	1.1	66.0	32.6	0.32	0.29	0.010	0.494
Methanol	1.0	66.2	32.5	0.32	0.33	0.010	0.490
Cyclohexane	1.2	66.2	32.1	0.45	0.38	0.014	0.485
Acetone	1.3	66.3	32.0	0.43	0.34	0.013	0.483

Table S5. Deconvolution of XPS Ru 3d XPS peaks for RuO_2/SiO_2 and reduced samples. Si 2p peak was used as the reference (103.7 eV). Deconvolution in Figure S12.

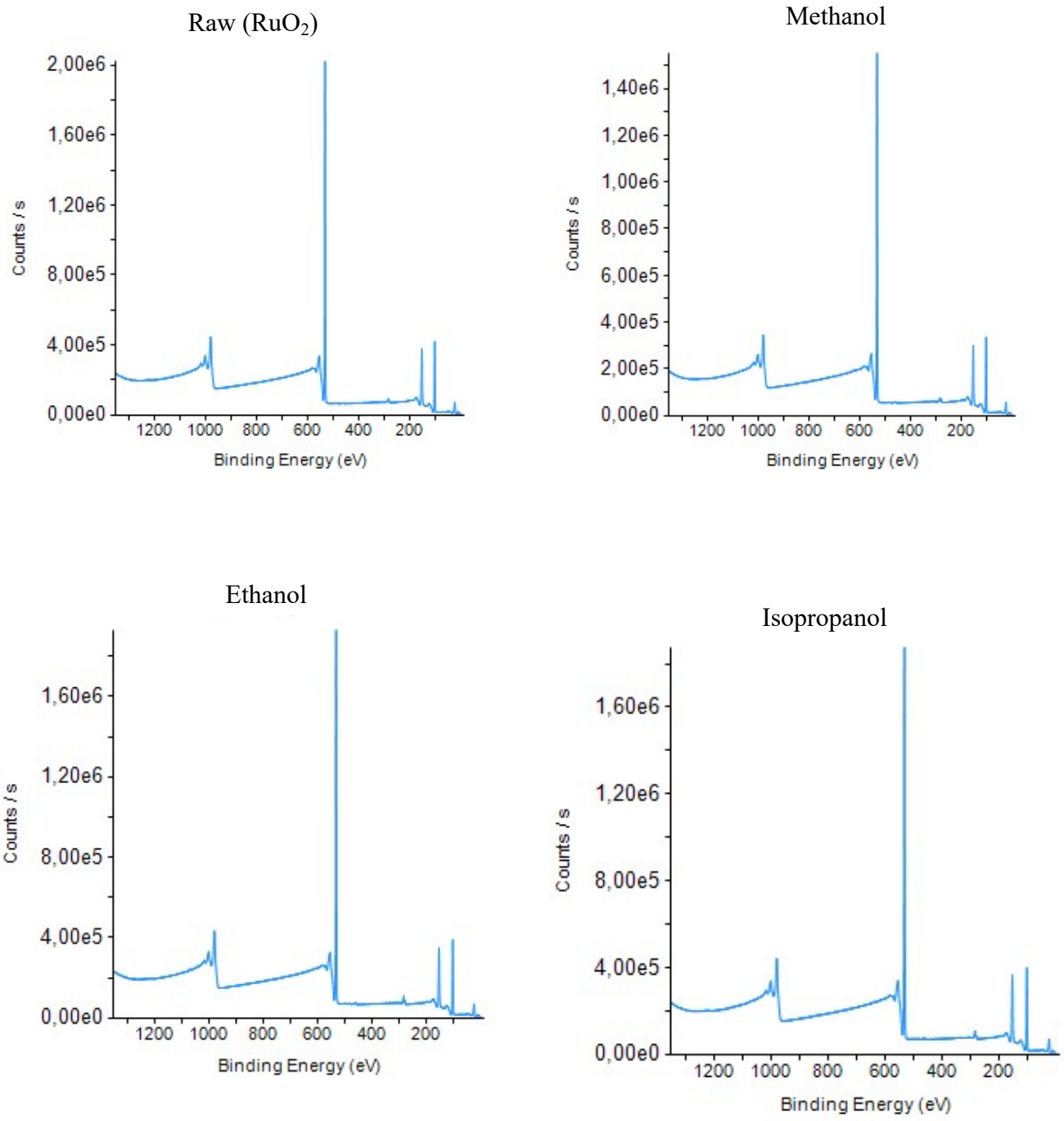
	Ru^0		Ru^{4+}		Ru^{4+} (Sat)	
	Binding Energy (eV)	Area (%)	Binding Energy (eV)	Area (%)	Binding Energy (eV)	Area (%)
Raw	-	-	280.5	79.8	282.8	20.2
Hydrogen	280.1	56.6	281.2	31.1	282.7	12.4
Ethanol	280.1	50.4	281.1	38.1	283.0	11.4
Isopropanol	280.0	32.4	281.0	51.1	282.8	16.5
Heptane	279.9	64.7	280.9	29.6	282.6	5.7
Methanol	279.8	52.5	280.7	39.8	282.6	7.7
Cyclohexane	279.8	23.9	280.5	70.0	282.8	6.1
Acetone	280.0	65.3	281.1	26.3	282.7	8.4

Table S6. Deconvolution of XPS C 1d XPS peaks for RuO_2/SiO_2 and reduced samples. Si 2p peak was used as the reference (103.7 eV). Deconvolution in Figure S12

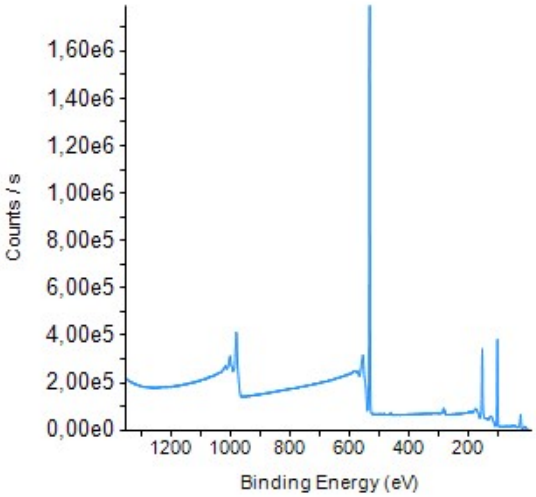
	C-C	C-O	C=O

	Binding Energy (eV)	Area (%)	Binding Energy (eV)	Area (%)	Binding Energy (eV)	Area (%)	Binding Energy (eV)	Area (%)
Raw	284.5	44.4	285.7	44.8	288.1	10.8	-	-
Hydrogen	284.6	45.6	285.7	34.2	287.2	11.1	288.8	9.0
Ethanol	285.0	52.3	286.1	40.6	-	-	288.7	7.1
Isopropanol	284.5	43.2	285.7	39.5	287.3	13.4	288.8	4.8
Heptane	284.8	58.9	286.2	30.4	-	-	288.0	10.7
Methanol	284.8	53.4	285.8	31.7	287.6	14.8	-	-
Cyclohexane	284.7	39.6	285.8	41.7	286.9	11.4	288.6	7.2
Acetone	284.5	37.2	285.4	34.7	286.7	17.4	288.6	10.8

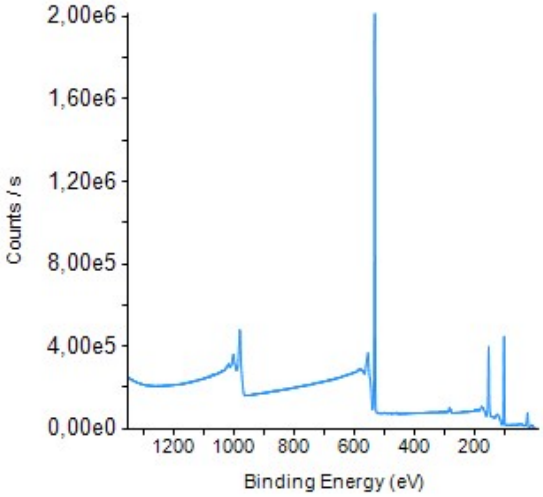
Figure S11. The wide XPS spectra of RuO_2/SiO_2 and after reduction with different reducing agents.



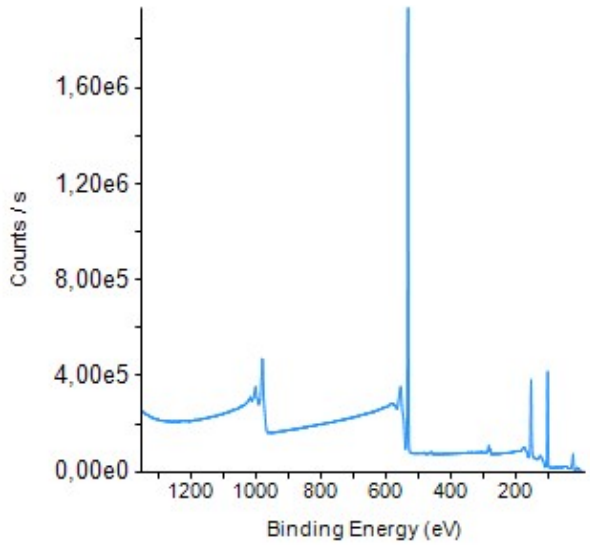
Acetone



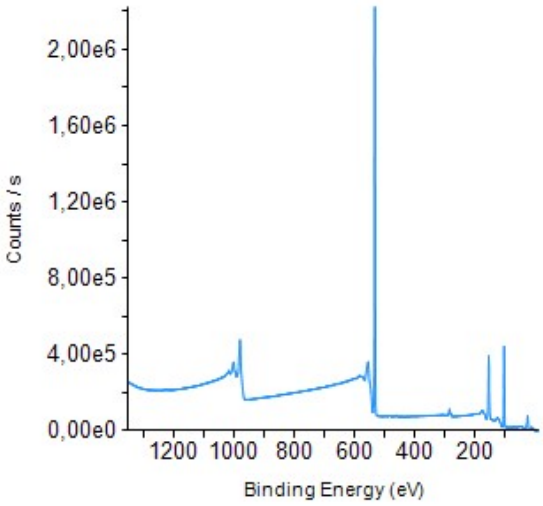
Heptane



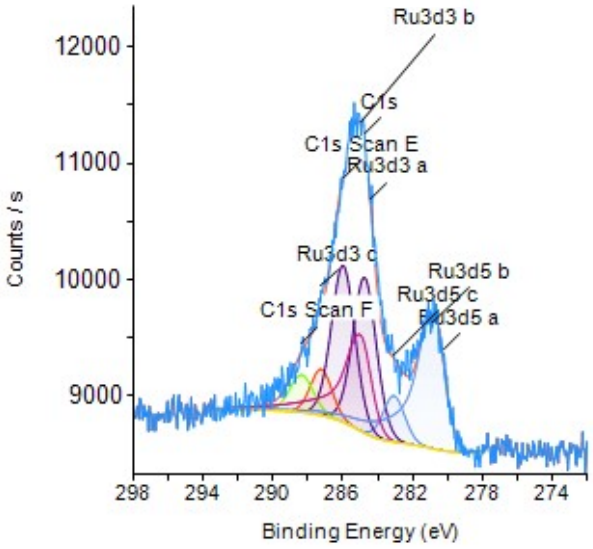
Cyclohexane



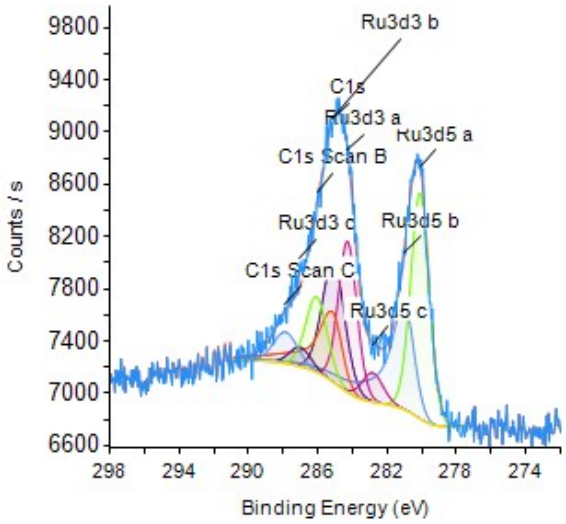
H_2



Raw (RuO_2)



Methanol



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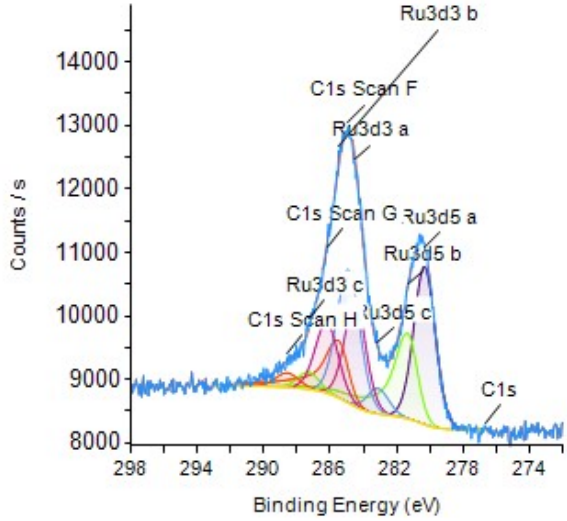
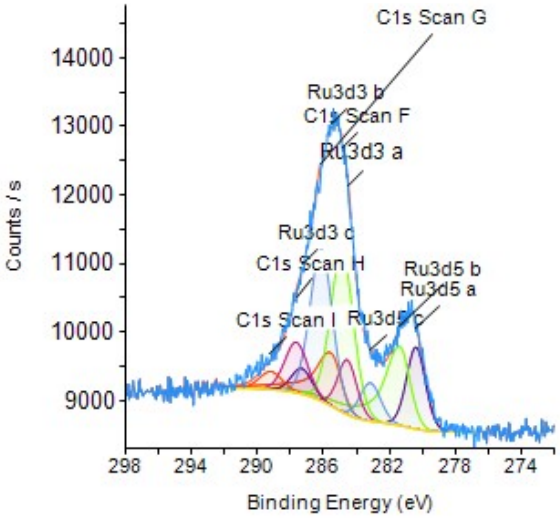


Isopropanol



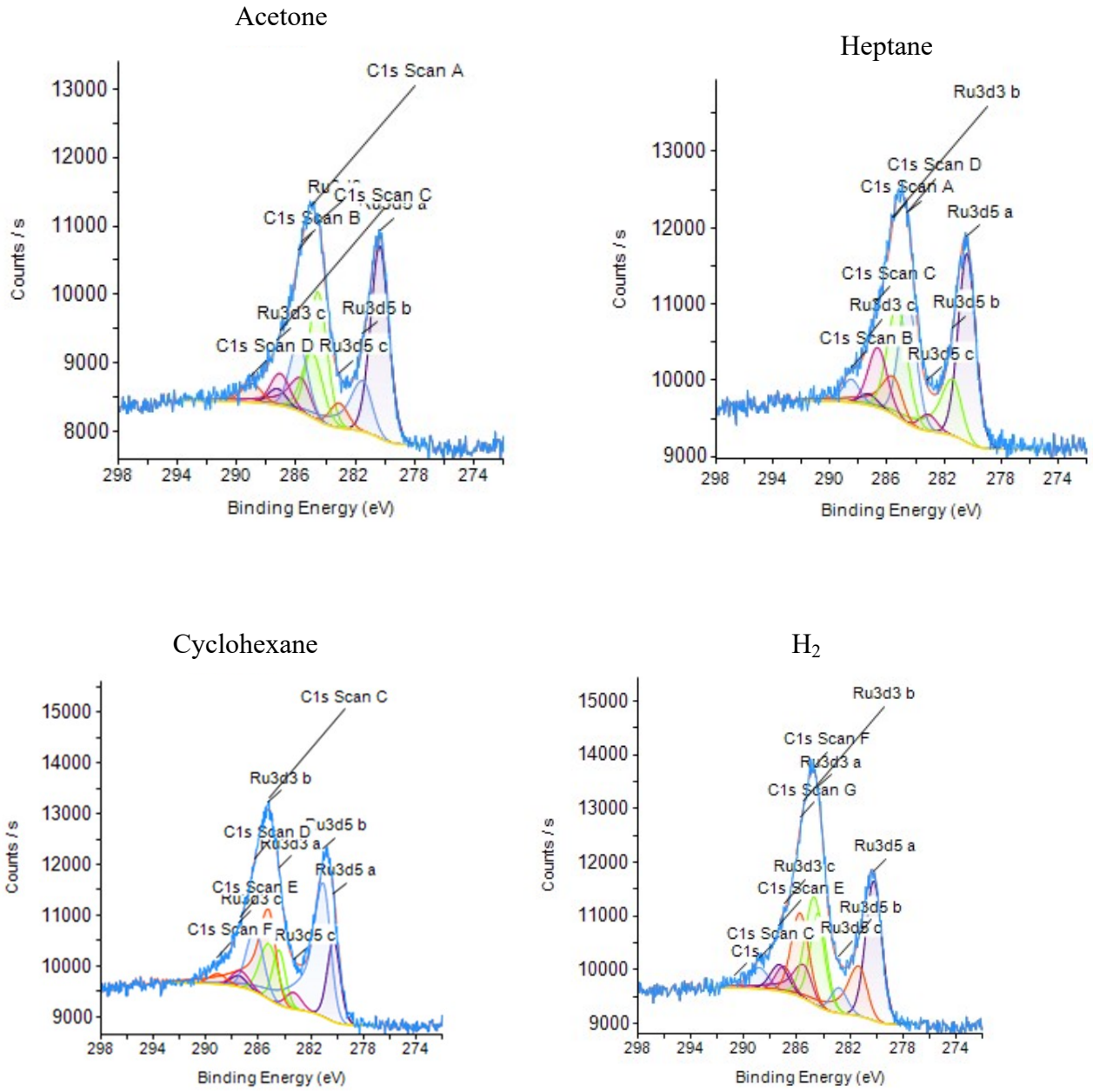


Figure S12. The C1s and Ru3d XPS spectra of RuO_2/SiO_2 and after reduction with different reducing agents.

Table S7. Area, FWHM, BE, Δ spin-orbit, and $\frac{A\,(Ru_{3d5/2})}{A(Ru_{3d3/2})}$ for the deconvolution of Ru 3d region .Si 2p peak was used as the reference (103.7 eV). Deconvolution in Figure S12

		Area	FWHM (eV)	BE (eV)	Δ spin-orbit	Area ratio Ru 3d 5/2 / Ru3d3/2
Raw	Ru3d5/2 a	-	1.2	280.22		
	Ru3d3/2 a	-	1.2	284.39		
	Ru3d5/2 b	2938.21	1.5	280.83	4.17	1.5
	Ru3d3/2 b	1968.61	1.5	285.00		
	Ru3d5/2 c	620.8	1.5	283.07	4.17	1.5
	Ru3d3/2 c	415.94	1.5	287.24		
Hydrogen	Ru3d5/2 a	4060.78	1.5	280.21	4.17	1.5
	Ru3d3/2 a	2720.73	1.5	284.38		
	Ru3d5/2 b	2230.70	1.5	281.33	4.17	1.5
	Ru3d3/2 b	1492.59	1.5	285.50		
	Ru3d5/2 c	739.28	1.5	282.83	4.17	1.5
	Ru3d3/2 c	495.32	1.5	287.00		
Ethanol	Ru3d5/2 a	4073.94	1.6	280.32	4.17	1.5
	Ru3d3/2 a	2729.54	1.6	284.49		
	Ru3d5/2 b	3094.21	1.4	281.34	4.17	1.5
	Ru3d3/2 b	2073.14	1.4	285.51		
	Ru3d5/2 c	661.27	1.6	283.13	4.17	1.5
	Ru3d3/2 c	443.06	1.6	287.30		
Isopropanol	Ru3d5/2 a	1740.71	1.4	280.39	4.17	1.5
	Ru3d3/2 a	1166.25	1.4	284.56		
	Ru3d5/2 b	2745.64	1.5	281.38	4.17	1.5
	Ru3d3/2 b	1839.59	1.5	285.55		
	Ru3d5/2 c	889.00	1.5	283.15	4.17	1.5
	Ru3d3/2 c	595.64	1.5	287.32		
Heptane	Ru3d5/2 a	3861.30	1.5	280.40	4.17	1.5
	Ru3d3/2 a	2587.07	1.5	284.57		
	Ru3d5/2 b	1767.31	1.5	281.40	4.17	1.5
	Ru3d3/2 b	1184.11	1.5	285.57		
	Ru3d5/2 c	342.24	1.5	283.12	4.17	1.5
	Ru3d3/2 c	229.29	1.5	287.29		
Methanol	Ru3d5/2 a	2346.30	1.3	280.11	4.17	1.5
	Ru3d3/2 a	1572.03	1.3	284.28		
	Ru3d5/2 b	1776.81	1.3	280.99	4.17	1.5
	Ru3d3/2 b	1190.45	1.3	285.16		
	Ru3d5/2 c	345.27	1.5	282.85	4.17	1.5
	Ru3d3/2 c	231.34	1.5	287.02		
Cyclohexane	Ru3d5/2 a	2018.90	1.2	280.27	4.17	1.5
	Ru3d3/2 a	1352.66	1.2	284.44		
	Ru3d5/2 b	5909.22	1.3	281.07	4.17	1.5
	Ru3d3/2 b	3959.14	1.3	285.24		
	Ru3d5/2 c	513.39	1.5	283.34	4.17	1.5
	Ru3d3/2 c	343.97	1.5	287.51		
Acetone	Ru3d5/2 a	4381.64	1.5	280.35	4.17	1.5

Ru3d3/2 a	2935.70	1.5	284.52		
Ru3d5/2 b	1765.87	1.5	281.50	4.17	1.5
Ru3d3/2 b	1183.15	1.5	285.67		
Ru3d5/2 c	563.85	1.5	283.10	4.17	1.5
Ru3d3/2 c	377.78	1.5	287.27		