Correlating Fischer-Tropsch activity to Ru nanoparticle surface structure as probed by high-energy X-ray diffraction

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Experimental Details

A. Catalyst Synthesis

Polyvinylpyrrolidone (PVP, $M_n = 10\ 000$ g/mol, Sigma Aldrich) stabilized Ru nanoparticles were synthesized by using 1,4-butanediol or $H_2$ as the reducing agent. The Ru precursors included ruthenium(III) chloride hydrate ($RuCl_3.nH_2O$, Alfa Aesar) and ruthenium(III) acetylacetonate ($Ru(acac)_3$, Aldrich). The reduction by 1,4-butanediol was carried out similar to an earlier procedure described for Rh$^{[1]}$. In a typical catalyst synthesis (PVP/Ru molar ratio of 20), 30 mg of $Ru(acac)_3$ and 0.17 g of PVP were dissolved in 2 mL of tetrahydrofuran (THF, Sigma Aldrich) and 3 mL of 1,4-butanediol (Sigma-Aldrich). The mixture was then added to 27 mL of 1,4-butanediol, which was preheated at 225 °C, followed by refluxing in a $N_2$ atmosphere for 2 h. The resulting black mixture was washed thoroughly with acetone and diethyl ether. After collecting the Ru nanoparticles by centrifugation, they were redispersed in 1.5 mL distilled water. In cases where reduction was carried out in hydrogen, first 40 mg of $RuCl_3.xH_2O$ and 0.22 g of PVP were dissolved in 1 mL of distilled water in a 10 mL autoclave. The autoclave was then pressurized with 20 bar $H_2$ followed by heating to $145\ °C$ for 2 h under vigorous stirring. The resultant black mixture was washed, collected by centrifugation, and redispersed in 3 mL distilled water.

B. Catalyst Characterization

The concentration of the Ru nanoparticles dispersed in water was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis performed on a Goffin Meyvis SpectroCirus apparatus.

Transmission electron micrographs (TEM) were made with a FEI Tecnai 20 electron microscope equipped with a LaB6 filament and operating at an acceleration voltage of $200\ kV$. A small amount of the nanoparticles was mixed with ethanol, dispersed over a carbon-coated Cu grid and finally dried in air. The average particle size and the standard deviation were determined by measuring at least 150 particles.

FTIR spectra of adsorbed CO were collected using a heated attenuated total reflectance (HATR) flow cell from Spectra-Tech ARK with a Si 45° crystal (cutoff at 1500 cm$^{-1}$) in a Nicolet Protégé 460 FTIR spectrometer equipped with a liquid-nitrogen cooled MCT detector. Prior to the IR measurement, the Ru nanoparticles dispersed in water were re-reduced in an autoclave at $150\ °C$ with $20\ bar\ H_2$ for 2 h under vigorous stirring. The Ru particles were then spin-coated onto the Si crystal under a $N_2$ atmosphere. The coated Si crystal was mounted and sealed in the ATR cell under a $N_2$ atmosphere. The sample was dried by flowing 5 mL/min of He at $80\ °C$ for 30 min. CO was introduced in the cell by using a flow of 2.5 mL/min. After an isothermal period at $50\ °C$ for 0.5 h, the cell was heated to $150\ °C$. FTIR spectra were recorded 5 min after reaching $150\ °C$ in absorbance mode at a resolution of 4 cm$^{-1}$. A total of 32 scans were measured in this way, followed by subtraction of the background spectrum of the Si crystal.

X-ray Absorption Spectra (XAS) were recorded in a home-built transmission cell for liquid samples at the Dutch Belgium Beamline (DUBBLE) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). A droplet of the liquid containing the Ru nanoparticles was placed between Kapton windows. XAS spectra were collected in fluorescence mode at the Ru K edges with a 9-channel solid-state detector. Energy selection was done by a double crystal Si(111) monochromator. EXAFS analysis was performed with EXCURVE931 on $k^2$-weighted unfiltered raw data using the curved wave theory. Phase shifts were derived from ab initio calculations using Hedin-Lundqvist exchange potentials and Von Barth ground states as implemented in EXCURVE98. In a typical experiment, 200 µL of 140 µmol $Ru/mL\ H_2O$ of sample was transferred into the XAS cell. The cells were then transferred to the beamline and the EXAFS spectra were recorded at room temperature.

High-energy X-ray diffraction (XRD) experiments were performed at the 11-ID-B beamline (Advanced Photon Source, Argonne National Laboratory) using X-rays of energy of $90.48\ keV$ ($\lambda = 0.1372\ \text{Å}$) as described in ref. [2] Prior to the measurements, the Ru nanoparticles dispersed in water were re-reduced at $150\ °C$ with $20\ bar\ H_2$ for 2 h in an autoclave under vigorous stirring. After reduction, the PVP stabilized Ru particles were loaded on to carbon nanofibers by impregnation and dried in an oven overnight at $100\ °C$. The supported Ru particles were then loaded into glass capillaries and measured at room temperature. Bulk Ru (from Alfa Aesar; 99.9% purity; crystallite grain size of $\sim 1000\ \text{nm}$) was used as a reference material. The
processing of XRD data and derivation of G(r) values was performed using the RAD program.[3] The hcp-model based PDFs were computed using the PDFFIT program.[4] Reverse Monte Carlo (RMC) simulations was performed using the RMC++ program.[5]

C. Catalytic Activity Measurements

Prior to reaction, an amount of catalyst (50 µmol Ru) was dispersed in 3 mL of deionized water and re-reduced in a 10 mL stainless steel autoclave at 150°C with 20 bar H₂ for 2 h under vigorous stirring. After reduction, the autoclave was cooled to room temperature in an ice bath before releasing the pressure. The liquid phase FTS was carried out at 30 bar for 24 h in the same autoclave. The autoclave was flushed with CO for 3 times, before being pressurized with CO followed by H₂ to 30 bar (molar ratio H₂/CO = 2). The autoclave was sealed and the autoclave body was heated to 150°C with a band heater controlled by a temperature controller. After 24 h, the reaction was terminated by immersing the autoclave into an ice bath.

The gas phase products were analyzed with an Interscience Compact GC system, equipped with an Al₂O₃/KCl column and a flame ionization detector (FID). For analysis, the gas cap was flushed through a 6-way valve allowing injection onto the GC columns. Methane, ethane, ethylene, propane and propylene were analyzed against a standard gas mixture. For analysis of the liquid phase, an extraction was carried out with diethyl ether containing p-cymene as an internal standard. The organic phase containing the products was then analyzed with a GC (QP5050, Shimadzu) equipped with a Rxi-5ms capillary column (30 m × 0.25 mm × 0.5 µm) and a flame ionization detector (FID). Identification and quantification of linear alkanes (C₆ to C₁₆), alcohols (C₄ to C₁₂) and aldehydes (C₄ to C₁₂) was established with reference compounds and p-cymene as the internal standard. The identity of the products was also verified with a GC-MS equipped (GC-MS, QP5050, Shimadzu) with a Rxi-5ms capillary column.

The different turnover frequency (TOF) were calculated based on the number of moles of carbon being formed in the products according to the following formula:

\[
r = \frac{\text{total mol C formed in all products}}{\text{mass of Ru} \times \text{reaction time}}
\]

\[
\text{TOF}_{\text{surface}} = \frac{\text{total mol C formed in all products}}{\left(\text{mol Ru}_{\text{surface atoms}}\right) \times \text{reaction time}}
\]

\[
\text{TOF}_{\text{CN10 + 11}} = \frac{\text{total mol C formed in all products}}{\text{mol Ru} \times x_{\text{CN10 + 11}} \times \text{reaction time}}
\]

with the \(\text{mol Ru}_{\text{surface atoms}} = \text{mol Ru} \times D\), and \(x_{\text{CN10 + 11}} = x_{\text{CN10}} + x_{\text{CN11}}\). Where \(x_{\text{CN10}}\) and \(x_{\text{CN11}}\) are the fraction of Ru atoms with coordination number 10 and 11 determine form the RMC model.

Dispersion was calculated assuming spherical shapes by using the formula given by Scholten et al.[6]

\[
D = 10^{21} \times \frac{6 \times M \times \rho_{\text{site}}}{d_p \times N_{\text{Av}} \times \rho_{\text{metal}}}
\]

with \(M\) being the atomic weight of Ru, \(\rho_{\text{site}}\) the surface density (16.3 Ru atom/nm²), \(\rho_{\text{metal}}\) the density of metal (12.3 g/cm³), \(d_p\) the Ru particle size and \(N_{\text{Av}}\) the Avogadro’s number. Hydrocarbons selectivity includes alkanes and alkenes and oxygenates selectivity aldehydes and alcohols.
Computational Methods

In order to compute the activation energy for CO dissociation on models representative for the surface of 5.2 nm Ru nanoparticles, Density Functional Theory (DFT) calculations were performed using the Vienna Ab initio simulation package (VASP)\cite{7}. The projector-augmented wave (PAW)\cite{8} method was used in conjunction with a Perdew-Becke-Ernzerhof (PBE) exchange-correlation functional\cite{9}. The kinetic cutoff energy for the plane waves was set to 500 eV. As such computations are prohibitively expensive for a 5.2 nm Ru nanoparticle, we extracted relevant parts out of the model nanoparticle (size roughly 1.5 nm, typically 150 atoms). Such particles were treated as a cluster. In order to retain as much as possible the original structure of the nanoparticle around the reaction center, the Ru atoms outside a sphere with a diameter of 1 nm around the Ru surface atom which binds the CO molecule were frozen. As the size of the periodic cell was approximately 20 Å in each direction, it was sufficient to only use the Γ-point in the calculations. In the calculations, all the degrees of freedom were optimized using the conjugate-gradient algorithm, as implemented in VASP. The transition states were found by optimizing the highest image, as found by a nudged elastic band calculation, by means of a quasi-Newton optimization scheme. In order to check the nature of the extrema on the potential energy surface, frequency calculations were performed using the finite difference technique. The initial and final states of the elementary reaction paths were found to be local minima, while the transition states were checked to have a single imaginary frequency with a corresponding eigenvector in the direction of the reaction path.
<table>
<thead>
<tr>
<th>Ru Particle Size$^b$</th>
<th>Reducing Agent$^c$</th>
<th>Reduction Temperature ($^\circ$C)</th>
<th>Ru Source</th>
<th>Ru Conc.$^d$ (µmol/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 ± 0.4</td>
<td>H$_2$</td>
<td>145</td>
<td>RuCl$_3$</td>
<td>35.6</td>
</tr>
<tr>
<td>2.3 ± 0.3</td>
<td>Polyol</td>
<td>195</td>
<td>RuCl$_3$</td>
<td>35.8</td>
</tr>
<tr>
<td>2.7 ± 0.3</td>
<td>Polyol</td>
<td>165</td>
<td>Ru(acac)$_3$</td>
<td>35.9</td>
</tr>
<tr>
<td>3.4 ± 0.5</td>
<td>Polyol</td>
<td>175</td>
<td>Ru(acac)$_3$</td>
<td>34.1</td>
</tr>
<tr>
<td>3.7 ± 0.5</td>
<td>Polyol</td>
<td>195</td>
<td>Ru(acac)$_3$</td>
<td>33.2</td>
</tr>
<tr>
<td>4.3 ± 0.6</td>
<td>Polyol</td>
<td>215</td>
<td>Ru(acac)$_3$</td>
<td>29.0</td>
</tr>
<tr>
<td>5.2 ± 0.8</td>
<td>Polyol</td>
<td>225</td>
<td>Ru(acac)$_3$</td>
<td>32.6</td>
</tr>
</tbody>
</table>

[a] Ru nanoparticles synthesis parameters: PVP/Ru molar ratio = 20, $M_n$(PVP) = 10 000, re-dispersed in 1.5 mL H$_2$O. [b] Average particle size and standard deviation determined by TEM analysis. [c] Polyol: 1,4-Butanediol as reducing agent, H$_2$: 20 bar H$_2$ as reducing agent. [d] Determined from ICP-AES for the synthesized Ru nanoparticles re-dispersed in 1.5 mL H$_2$O (theoretical concentration: 50 µmol/mL). Data from Ref. [10].
**Table S2**: Fit parameters of $k^3$-weighted EXAFS data.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Ru Particle Size (nm)</th>
<th>EXAFS fit parameters(^{[b]})</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>$\Delta \sigma^2$ (Å$^2$)</th>
<th>$E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru foil</td>
<td></td>
<td>Ru-Ru</td>
<td>12</td>
<td>2.68</td>
<td>0.004</td>
<td>-7.9</td>
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<tr>
<td>1.2</td>
<td></td>
<td>Ru-Ru</td>
<td>6.1</td>
<td>2.64</td>
<td>0.005</td>
<td>-6.1</td>
</tr>
<tr>
<td>2.3</td>
<td></td>
<td>Ru-O</td>
<td>1.4</td>
<td>1.99</td>
<td>0.002</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ru-Ru</td>
<td>6.9</td>
<td>2.67</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td></td>
<td>Ru-O</td>
<td>1.1</td>
<td>1.97</td>
<td>0.002</td>
<td>-3.3</td>
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<tr>
<td></td>
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<td>Ru-Ru</td>
<td>7.5</td>
<td>2.67</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
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<td>Ru-O</td>
<td>1.0</td>
<td>1.93</td>
<td>0.004</td>
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<td></td>
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<td>Ru-Ru</td>
<td>8.7</td>
<td>2.67</td>
<td>0.007</td>
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</tr>
</tbody>
</table>

\(^{[a]}\) From Ref. 10.

\(^{[b]}\) Only first Ru-O and Ru-Ru shells fitted; $\Delta k = 2.5–13.4$ Å$^{-1}$; estimated errors in R: ± 0.01 Å, N: ± 20%, and $\Delta \sigma^2$: ± 10%.
Table S3: Properties of Ru nanoparticles derived from XRD-PDF measurements.^[a]

<table>
<thead>
<tr>
<th>Ru Particle Size (nm)</th>
<th>CN&lt;sub&gt;average&lt;/sub&gt;[b]</th>
<th>Atomic PDF of first coordination sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FWHM (Å)</td>
</tr>
<tr>
<td>1.2</td>
<td>8.2</td>
<td>0.45</td>
</tr>
<tr>
<td>3.4</td>
<td>9.7</td>
<td>0.42</td>
</tr>
<tr>
<td>3.7</td>
<td>10.0</td>
<td>0.38</td>
</tr>
<tr>
<td>5.2</td>
<td>10.4</td>
<td>0.33</td>
</tr>
<tr>
<td>Polycrystalline Ru</td>
<td>-</td>
<td>0.30</td>
</tr>
</tbody>
</table>

[a] Atomic pair distribution function (PDF) extracted from high energy XRD data, and fitting performed by RMC. Ru nanoparticles were re-reduced at 150°C under 20 bar H<sub>2</sub> for 2 h. [b] Average coordination number determined from the RMC model. [c] ΔFWHM = FWHM - FWHM<sub>polycrystalline Ru</sub>. 
Figure S1. Electron micrographs and particle size distributions. (a) 1.2 nm, (b) 2.3 nm, (c) 2.7 nm, (d) 3.4 nm, (e) 3.7 nm, (f) 4.3 nm and (g) 5.2 nm.
Figure S2. Experimental (○) and fitted model (red lines) for (a) FT EXAFS functions and (b) $k^3$-weighted EXAFS oscillations of Ru-1.2, Ru-2.3, Ru-3.7 and Ru-5.2 after polyol and H$_2$ reduction steps.
Figure S3. CO adsorption FTIR spectra measured at 150°C. Prior to measurements, Ru particles were re-reduced in an autoclave at 150°C with 20 bar H₂.

Two main features can be observed in these spectra: a strong band centered at 1990-2015 cm⁻¹ region with a shoulder at 2050 cm⁻¹ and a weak broad band in the 1900-1950 cm⁻¹ region. The IR spectrum for Ru-1.2 shows an additional band centered around 2116 cm⁻¹. For the assignment of the bands, we follow the work of Chin et al. [11]: bridge-bonded CO at 1900 to 1950 cm⁻¹, linearly bonded CO at 1990-2015 cm⁻¹, dicarbonyl CO species adsorbed on Ru⁰ at 2050 cm⁻¹ and CO adsorbed on Ru⁺⁺ at 2116 cm⁻¹. A notable finding is that the band assigned to linearly adsorbed CO sites undergoes a red shift when the nanoparticle size is decreased from 4.3 to 1.2 nm. The red shift is greatest when the average particle size decreases from 2.3 nm (2009 cm⁻¹) to 1.2 nm (1990 cm⁻¹). CO is still linearly bonded when the band shift from 2009 to 1990 cm⁻¹, within the range usually observed for linearly bonded CO [11]. Therefore, the shift is best explained by stronger adsorption of CO. It is also seen that a shoulder appears at 2050 cm⁻¹ with decreasing particle size, which is due to Ru-dicarbonyl species. These surface complexes are likely due to CO adsorption on very low coordinated Ru surface atoms such as corner sites. The increase of this band is greatest when the particle size is decreased from 2.3 to 1.2 nm. This is consistent with the decrease in coordination number for smaller particles as determined by EXAFS. The very weak band at 2116 cm⁻¹ is due to the presence of a small amount of oxidic Ru species on Ru-1.2.
**Figure S4.** Atomic PDF data and fitting using *hcp* and RMC model. Experimental data (symbols) for polycrystalline Ru and 5.2 nm Ru particles. (a) Fitting performed using *hcp-lattice constrained* model (red line) and green circles indicating poor fitting for the 5.2 nm Ru. (b) RMC model fitting (blue line) and *hcp* model fitting (red line).
**Figure S5.** Low-$r$ part of the experimental PDFs for various Ru nanoparticles.
Figure S6. Coordination number distribution for various Ru nanoparticles. Distributions were derived from truncated hcp particle (grey bars) and RMC refined Ru particle models (red bars). (a) 1.2 nm, (b) 3.4 nm, (c) 3.7 nm and (d) 5.2 nm.
Figure S7. Surface view of RMC generated Ru particle models. The surface atoms with different coordination numbers are highlighted in different colors. (a) 1.2 nm, (b) 3.4 nm, (c) 3.7 nm and (d) 5.2 nm.
Figure S8. Different surface atomic configurations on the 5.2 nm Ru RMC model.
References