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# Mechanism of formation of Co-Ru nanoalloys: the key role of Ru on the reduction pathway of Co

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## Keywords

Bimetallic nanoparticles, *in situ* studies, formation mechanism, EXAFS, SAXS

## Abstract

The chemical synthesis of alloy nanoparticles requires adequate conditions to obtain co-reduction instead of separate reduction of the two metal cations. The mechanism of formation of bimetallic cobalt-ruthenium nanoalloys by reducing the metal salts in an alcohol medium was explored to draw general rules to extrapolate to other systems. The relative kinetics of reduction of both metal cations were studied by UV-visible and *in situ* Quick-X-ray absorption spectroscopies as well as H<sub>2</sub> evolution. The addition of Co(II) ions does not influence the reduction kinetics of Ru(III) but adding Ru(III) to a Co(II) solution promotes the reduction of cobalt cations. Indeed, while CoO is formed when reaching the boiling temperature of the solvent for the monometallic system, a direct reduction of Co is observed at this temperature without formation of the oxide for the bimetallic one. The co-reduction of the metal cations results in the formation of bimetallic nanoplatelets, the size of which can be tuned by changing the Ru content.

## 1. Introduction

Metal nanocrystals (NC) display intriguing properties, which are often different from their bulk counterparts, due to the high specific surface area and quantum size effects. The immense progress that has been made over the past 20 years to synthesize them by liquid phase processes with precise control over the size and shape opens broad perspectives of applications in magnetism, optics, electronics, and catalysis.<sup>1-9</sup> The development of bimetallic NC is a step forward: they often do not display only a combination of the monometallic properties but also synergetic or new ones<sup>10-13</sup> which are particularly valuable in catalysis.<sup>13-15</sup> However, their synthesis is also trickier. It is generally performed by co-reduction of the two metal salts, thermal decomposition of organometallic precursors, seeded growth or galvanic replacement reaction.<sup>10</sup> The polyol method has revealed an interesting one among the co-reduction processes. This method refers to the reduction of metal salts in a poly-alcohol that acts as the solvent, the reduction as well as a complexing agent.<sup>16</sup> In this synthesis method, which can be extended to the reduction in monoalcohol media, the relative reduction kinetics of the two metal salts can be varied by changing the nature of the counterions and the solvent used, as well as the addition of ligands.<sup>17-21</sup> Even two non-miscible metals, for example Cu and Ag<sup>22</sup> or Ru and Cu,<sup>23</sup> could form nanoalloys.

Ru<sup>24</sup> and Co<sup>25</sup> nanoparticles (NPs) are widely used in catalysis and, by combining them into nanoalloys, we can expect strong improvement of their catalytic properties. For instance a small amount of Ru is added to Co-based Fischer Tropsch catalysts to enhance their stability.<sup>26</sup> The Co<sub>98.5</sub>Ru<sub>1.5</sub> composition was identified by DFT calculations as one of the most promising candidate among 348 screened bimetallic catalysts nanoalloys for the amination of octan-1-ol using ammonia. This was further validated by experiments.<sup>27</sup> Co and Ru can also be associated to achieve catalysts with a better activity towards water splitting<sup>28</sup> or towards hydrolysis of ammonia borane<sup>29</sup> due to induced lattice strains which modulate the electronic structure. Moreover, the addition of Co to Ru can result in the emergence of magnetic properties<sup>30</sup> which is valuable for recovering unsupported nanocatalysts. Recently, we also demonstrated that the addition of a small quantity of a noble metal such as Ru ([Ru]/[Ru+Co] = 2.5 mol%) was mandatory for the formation of monodisperse Co nanorods with controlled shapes in polyol medium. A Ru nucleus was found at the exact center of each nanorod, demonstrating the role of Ru as a nucleating agent. Depending on the reaction conditions, Ru

NPs could also be present at the particle surface.<sup>31, 32</sup> These Co nanorods are very active towards the acceptorless dehydrogenation of primary alcohols and show better catalytic stability during recycling than nanorods which are not decorated with Ru.

We also recently evidenced that  $\text{Co}_x\text{Ru}_{100-x}$  alloy nanoplatelets show better catalytic activity towards the acceptorless dehydrogenation of alcohols than their monometallic counterparts.<sup>33</sup> The synthetic method consisted in co-reducing acetylacetonate Co(II) and Ru(III) precursors in octan-1-ol at the boiling point. Co and Ru are theoretically miscible elements in the bulk state.<sup>34</sup> In a first approximation, metal ions displaying similar redox potential are more likely to form an alloy. Yet, it is not the case for Co and Ru ( $E^0(\text{Ru}^{3+}/\text{Ru}) = 0,39 \text{ V vs. SHE}$ ) and  $E^0(\text{Co}^{2+}/\text{Co}) = -0,28 \text{ V vs. SHE}$ ).<sup>35</sup> Although redox potential values can serve as a guide to assess the reducibility of metal species, they are given at standard conditions (25 °C and 1 atm), conditions that differ significantly from those used in the synthesis. Moreover, ligands coordinated to the metal center also influence the redox potential value and the solvent potential plays a role in the kinetics of reduction.<sup>11</sup> Depending on the solvent and metal salt precursor, we obtained either bimetallic nanoparticles or a mixture of monometallic ones.<sup>33</sup> The formation of homogeneous structures necessitates either the simultaneous reduction of the two metal ions which nucleate and grow together to generate alloy nanocrystals,<sup>11, 36</sup> the formation of a core shell structure followed by interdiffusion or a dissolution-reprecipitation process. Understanding the reaction pathway and the key parameters controlling the atomic arrangement (leading either to segregation or mixing) is of the utmost importance to tailor NPs with tunable properties. For this purpose, we have studied the kinetics of reduction of the ions, taken either separately or together to assess the possible influence of one metal on the other and the nature of the intermediate species formed during the reaction. The three compositions previously published ( $\text{Co}_x\text{Ru}_{100-x}$  with  $x = 20, 50$  and  $80$ ) were studied to assess whether the ratio of Co to Ru had an influence. Different complementary techniques have been used to follow the reaction: UV-visible spectroscopy, *in situ* X-ray Absorption Fine Structure (XAFS), Small Angle X-Ray Scattering (SAXS) and  $\text{H}_2$  flow metering (molecular hydrogen being generated as a side product during the reaction). The observation of the species and of their reduction *in situ* is critical as the intermediate species that form at a given temperature can be metastable and transform when freezing aliquots to analyze them at ambient temperature. The combination of all these data gives a thorough

understanding of the influence of one metal on the reduction pathway of the other one and leads to the proposition of a formation mechanism for the nanoalloys.

## 2. Experimental

### 2.1. Chemicals

Ru acetylacetonate, Ru(acac)<sub>3</sub>, (Alfa Aesar, 97%), Na acetylacetonate monohydrate, Na(acac)·H<sub>2</sub>O, (Sigma Aldrich, 97 %) and octan-1-ol (AlfaAesar, > 99%) were used as purchased. Co acetylacetonate, Co(acac)<sub>2</sub>, (Sigma Aldrich, 97 %) was dried in an oven for at least one night at 50 °C before use.

### 2.2. *Ex situ* synthesis

The preparation of the Co<sub>x</sub>Ru<sub>100-x</sub> samples has been reported elsewhere.<sup>33</sup> Briefly, Ru(acac)<sub>3</sub> and Co(acac)<sub>2</sub> are dissolved at room temperature (RT) in octan-1-ol with the targeted molar ratio and a global metallic concentration of 16.3 mmol.L<sup>-1</sup> and flushed with Ar. The solution is then heated up to the boiling point, *ca.* 190°C, at a rate of 10°C·min<sup>-1</sup>. After 90 minutes under reflux, the solution is cooled down to RT. The nanoparticles are recovered by centrifugation at 20 000 rpm and washed twice with absolute ethanol and once with acetone.

### 2.3. Characterization techniques

UV-Visible spectra were recorded on a Perkin Elmer Lambda 1050 spectrometer equipped with a three-detectors module to work in the 175 - 3300 nm wavelength domain. The spectra were recorded using a quartz Suprasil™ demountable cell with an optical path length of 0.2 mm. The kinetics of reduction of Ru(III) was followed by this technique for solutions containing (i) 16.3 mM of Ru(acac)<sub>3</sub> and (ii) 8.15 mM of both Ru(acac)<sub>3</sub> and Co(acac)<sub>2</sub> in octan-1-ol. For this purpose, aliquots were taken every 10 °C during the heating ramp and at different times of the stage at 190°C.

The oxidation state and the local environment of metal species in the precursor solutions of Ru, Co<sub>x</sub>Ru<sub>100-x</sub> (x=20, 50 and 80) and Co has been followed *in situ* during the heating ramp from RT to boiling temperature by time-resolved X-ray Absorption Spectroscopy

at SOLEIL Synchrotron facility on the Quick-EXAFS ROCK beamline using a specially designed PEEK cell (see Figure S2). The heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  up to the boiling temperature, as for the *ex situ* experiments, gave a non satisfactory signal to noise ratio. Consequently, the temperature was raised stepwise with an lower average heating rate of  $5^{\circ}\text{C}\cdot\text{min}^{-1}$ . Moreover, the boiling temperature of the solution is close to  $190\text{ }^{\circ}\text{C}$  but the setup did not permit to stay for a long time at this temperature as a cooling system limited the evaporation of the solvent but did not prevent it completely. The plateau was thus set at  $180\text{ }^{\circ}\text{C}$  instead of  $190\text{ }^{\circ}\text{C}$ . The heating profile is given in Figure S3.

The dimension of the cell has been optimized for recording Quick-EXAFS spectra at the Co K edge (Optical Path (OP) = 0.6 cm) and at the Ru K edge (OP = 8 cm) for the same solution. For this purpose, the cell installed on the motorized rotation stage is rotated to align either the short OP or the long one to the X-rays beam for data collection in transmission mode. More details on the PEEK cell and sample environment used for the *in situ* Quick-EXAFS monitoring are given in Supplementary information S2.1. Using the so-called edge jumping capability of the beamline,<sup>37</sup> Si(111) and Si(220) Quick-EXAFS monochromators together with the respective B<sub>4</sub>C and Pd harmonic rejection mirror stripes were exchanged in less than 35 s for recording Co and Ru K edge data, respectively. Ionization chambers filled with N<sub>2</sub> and a mixture of N<sub>2</sub> and Ar were used for measuring the intensities of photons at the Co and Ru K edges, respectively. A Co foil ( $E_0 = 7709\text{ eV}$ ) and a RuO<sub>2</sub> pellet ( $E_0 = 22135.6\text{ eV}$ ) previously calibrated on a Rh foil ( $E_0 = 23\ 220\text{ eV}$ ) were measured simultaneously to the sample spectra with a third ionization chamber for energy calibration. The typical time resolution for kinetic monitoring was 10 s corresponding to the merge of 20 consecutive recorded Quick-EXAFS spectra, each being acquired at 2 Hz oscillation frequency of the Quick-EXAFS monochromators (250ms/spectrum with ascending Bragg angles). The corresponding powders, obtained following the procedure described in section 2.2, have also been analyzed.

The spectra were normalized using the graphic interface *normal\_gui*<sup>38</sup> written in Python and dedicated to spectra measured on ROCK for a massive and quick normalization allowing the reconstruction of a matrix of experience. Multivariate-Curve Resolution with Alternative-Least Squares (MCR-ALS) methodology<sup>39</sup> using the *MCR-ALS gui 2.0* developed by R. Tauler *et al.* on the Matlab® platform<sup>40</sup> was used for isolating from the experience matrix the concentration profiles of the species participating to the reaction and their associated XAS spectra. The use

of MCR-ALS applied for XAS analysis is extensively described in the literature.<sup>41-44</sup> The analysis of the spectra was performed using Demeter (Athena and Artemis programs).<sup>45</sup>

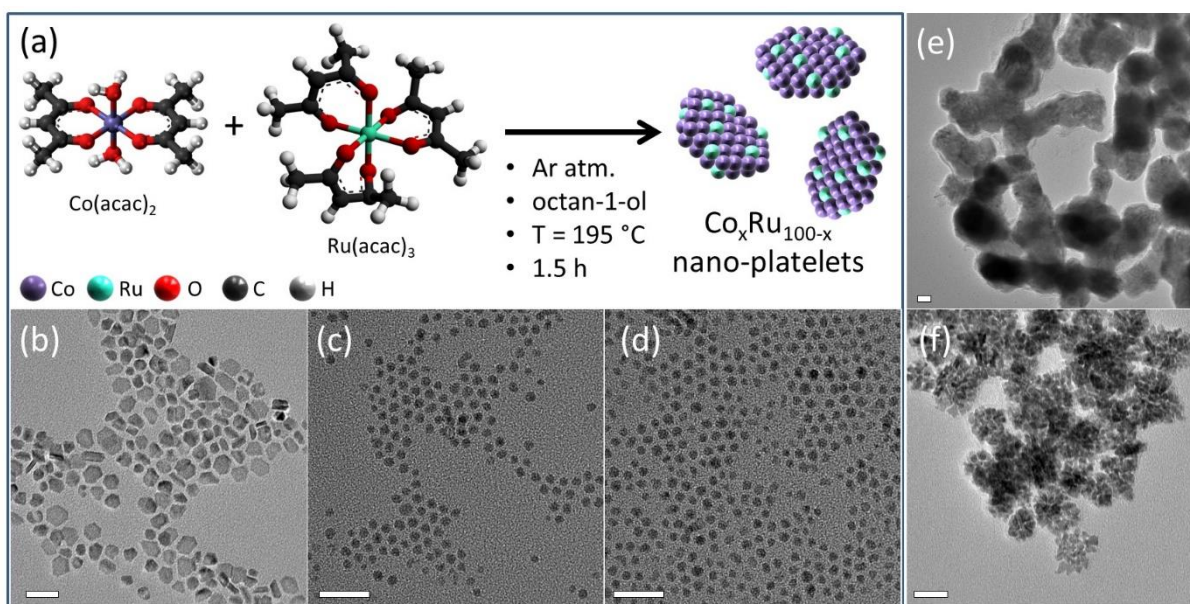
For measurements of NPs produced *ex situ*, pellets were prepared by carefully mixing the as-prepared powders with boron nitride (weight ratio of NPs to BN of *ca.* 1:2 and 1:5 for Ru and Co<sub>80</sub>Ru<sub>20</sub>, respectively).. Before recording the XAS data, a scan of the sample in x and y orthogonal directions was carried out at a fixed monochromator energy in order to check the pellet homogeneity.

The SAXS data were acquired on a homemade laboratory instrument with a Mo X-ray generator.<sup>46</sup> The samples were recorded in a cell with Kapton windows in the q range from 0.01 to 0.2 Å<sup>-1</sup>. Calibration of the q range was performed using dodecanol while absolute intensity was obtained using a Lupolen standard. Analysis of the data was performed using Sasview free software.<sup>47</sup>

The evolution of H<sub>2</sub> during particle synthesis was measured using a Bronkhorst flowmeter linked to a micro-computer. Considering the acceptorless dehydrogenation mechanism for octan-1-ol: C<sub>7</sub>H<sub>15</sub>CH<sub>2</sub>OH = C<sub>7</sub>H<sub>15</sub>CHO + H<sub>2</sub>, conversion of the alcohol can be calculated by measuring the volume of generated H<sub>2</sub>, assuming that the perfect gas law is verified.

### 3. Results

The nanoalloys were prepared using a simple soft chemistry route relying on the use of a long-chain alcohol that has a dual role: the solvent and a mild reducing agent allowing the reduction of Co(II) and Ru(III) species into their zero-valent state (see Figure 1a). The obtained particles correspond to hexagonal platelets (see Figure 1b-d) and HAADF – STEM coupled to EDX analyses reveals the formation of alloys as reported in a previous study.<sup>33</sup> In contrast, large aggregates are isolated for pure Co and nanoflowers corresponding to the agglomeration of particles with a size of a few nanometers were obtained for pure Ru (see Figures 1e and 1f). Clearly, the combination of the two metals allows for the formation of Co<sub>x</sub>Ru<sub>100-x</sub> particles with well-defined morphologies but the reaction mechanism has to be clarified.



**Figure 1.** (a) Synthetic scheme for the formation of the  $\text{Co}_x\text{Ru}_{100-x}$  nanoalloys and TEM images of (b)  $\text{Co}_{80}\text{Ru}_{20}$ , (c)  $\text{Co}_{50}\text{Ru}_{50}$ , (d)  $\text{Co}_{20}\text{Ru}_{80}$ , (e) pure Co and (f) pure Ru samples. The scale bar corresponds to 20 nm.

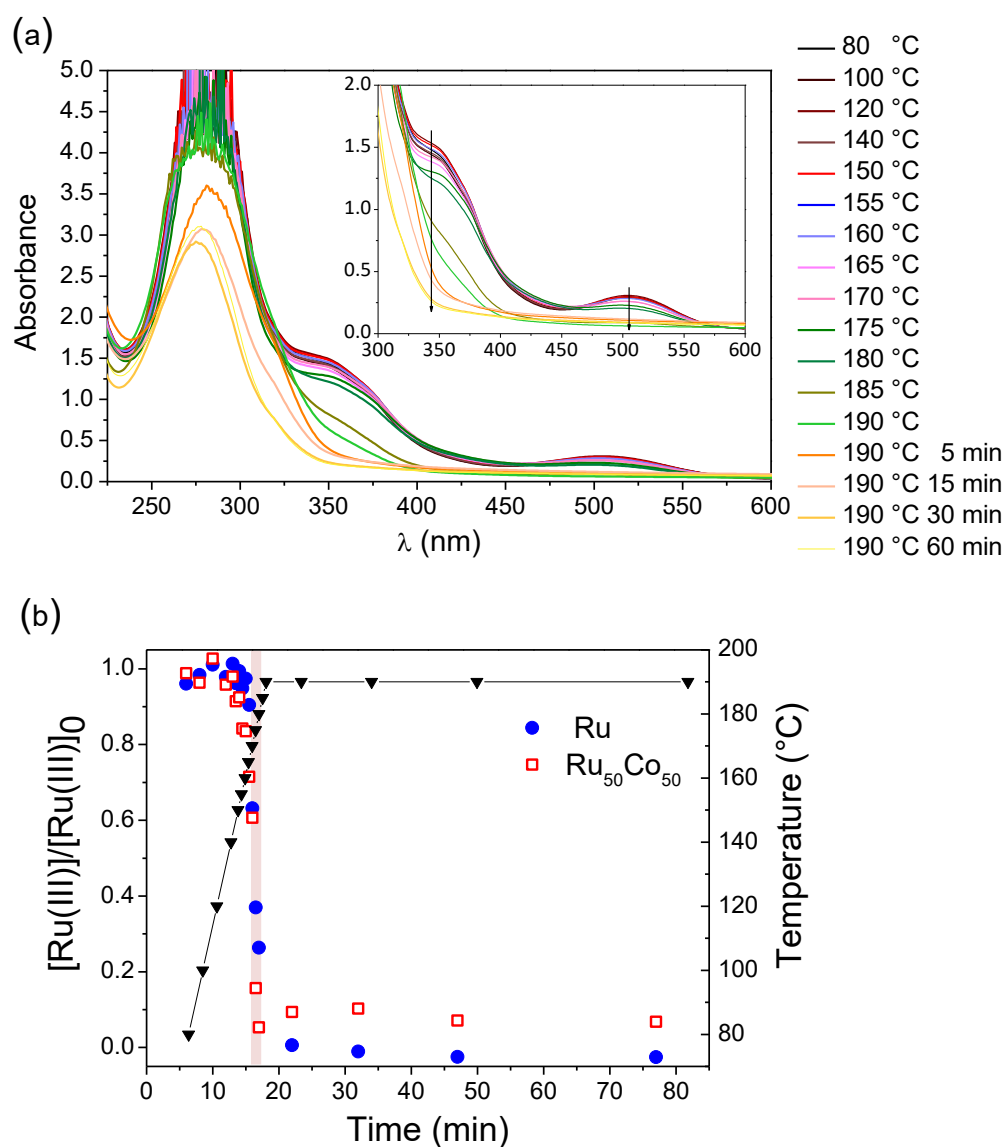
### 3.1 UV-visible spectroscopy

First, UV-visible characterization was carried out to quantitatively follow the reduction of the metal species. The spectra of  $\text{Na}(\text{acac})$ ,  $\text{Co}(\text{acac})_2$  and  $\text{Ru}(\text{acac})_3$  and the peak attributions are given in Figure S1 and Table S1 in the supplementary information (SI). For the  $\text{Co}(\text{acac})_2$  complex, only the transitions of the solvent and the  $\pi \rightarrow \pi^*$  transition of the acac ligand are visible. Spin-allowed but Laporte-forbidden transitions are normally expected but are not seen easily because molar absorption coefficient values are well lower than those associated with spin- and Laporte-allowed electronic transitions.<sup>48</sup> Consequently, the kinetics or reduction of  $\text{Co}(\text{II})$  could not be monitored by this technique. On the contrary, for the  $\text{Ru}(\text{acac})_3$  complex, three peaks with high molar absorption coefficient are detected (see SI, section S1), as already reported.<sup>49</sup> Aside the transition at 271 nm associated with the acac ligand, two other peaks due to metal to ligand or ligand to metal charge transfer transitions are visible at 349 and 506 nm. The UV-visible spectra of an equimolar solution of  $\text{Ru}(\text{acac})_3$  and  $\text{Co}(\text{acac})_2$  in octan-1-ol collected during the rise and at the plateau at the final temperature are given in Figure 2a. A clear evolution is observed: with reaction time, the intensity of the two charge transfer peaks decreases until disappearing while that of the peak at 271 nm, attributed to the acac ligand, decreases in a much lower extent. The  $\text{Ru}(\text{III})$  concentration was deduced from the absorbance



value of the peak at 506 nm, using the Beer-Lambert law and the molar extinction coefficient determined previously (see Table S1).

The temporal evolution of the Ru(III) concentration for two reactive solutions, Ru(acac)<sub>3</sub> in octanol and an equimolar mixture of Ru(acac)<sub>3</sub> and Co(acac)<sub>2</sub>, are given in Figure 2b. At 80°C, the Ru(III) concentration for these two solutions is close to the theoretical value of 16.3 and 8.15 mM for Ru and Co<sub>50</sub>Ru<sub>50</sub>, respectively. The evolution is very similar for the two systems: a similar sharp decrease of the Ru concentration with time is observed after *ca.* 16-17 minutes (170-185 °C temperature range). This clearly evidences that the presence of Co(II) species does not influence the kinetics of reduction of Ru(III).



**Figure 2.** (a) UV-visible spectra obtained during heating an equimolar solution of Ru(acac)<sub>3</sub> and Co(acac)<sub>2</sub> in octan-1-ol. Inset: magnification in the 300 nm – 600 nm range. (b) Evolution of the relative Ru(III) concentration during the synthesis of Ru (●) and Co<sub>50</sub>Ru<sub>50</sub> (□) NPs deduced from the absorbance value at 506 nm and associated temperatures (▼) at which the aliquots were taken.

UV-visible spectroscopy gave a good insight into Ru(III) reduction but provided no information on the reduction of Co(II) species. Thus, *in situ* X-ray Absorption Spectroscopy (XAS) experiments at the Ru and Co K-edges were carried out to accurately study the kinetics of metallic ions reduction taken separately or together.

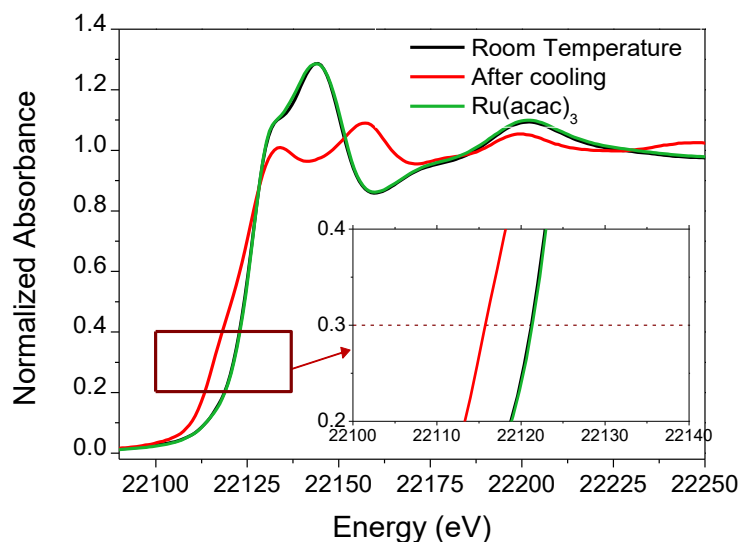
### 3.2. X-ray Absorption Spectroscopy (XAS)

#### 3.2.a) Kinetics of reduction of Ru(III) species

The XAS spectrum at the Ru K edge of the Ru(acac)<sub>3</sub> powder and of the Co<sub>20</sub>Ru<sub>80</sub> precursor solution before heating (*Room Temperature*) and after *in situ* heating for 15 min at the boiling temperature and cooling (*after cooling*) are plotted in Figure 3. The spectra of the Ru(acac)<sub>3</sub> powder and of the solution before heating are similar, indicating that no reduction of Ru(III) species has occurred at room temperature in octan-1-ol nor modification of the Ru environment. The spectrum of the solution obtained after heating for 15 minutes at the boiling point and cooled down to room temperature is very similar to that of a Ru(0) foil.<sup>50</sup> The edge is shifted towards lower energy compared to the previous spectra, indicating the reduction of Ru(III) during the heating stage. The shift in energy is maximum at a normalized absorbance of *ca.* 0.3 (see inset in Figure 3.a). Consequently, this energy value will be further used to follow the reduction of Ru species.

The precursor solutions with the Ru, Co<sub>20</sub>Ru<sub>80</sub>, Co<sub>50</sub>Ru<sub>50</sub> and Co<sub>80</sub>Ru<sub>20</sub> compositions were all analyzed by XAS at the Ru K-edge *in situ* during the heating ramp using the afore-mentioned specific cell designed for this study (see section S2.1 in supplementary information). The results obtained for the Co<sub>20</sub>Ru<sub>80</sub> composition are displayed in Figure S4. The quantitative evolutions of both the edge at 0.3 normalized absorbance and white line intensity are given in Figures S5 and S6, respectively. A similar evolution is observed for all the solutions, irrespective of the Co concentration. First, both the rising edge position and the white line intensity at *ca.* 22148.5 eV remain nearly invariant until the temperature of the solution get

close to the boiling temperature, *i.e.* *ca.* 160 - 170 °C. Second, the position of the edge at 0.3 normalized absorbance shifts abruptly towards lower energy as the reaction proceeded to higher temperatures whereas the white line intensity decreases concomitantly, indicating a decrease of the oxidation state of Ru at the end of the heating ramp.



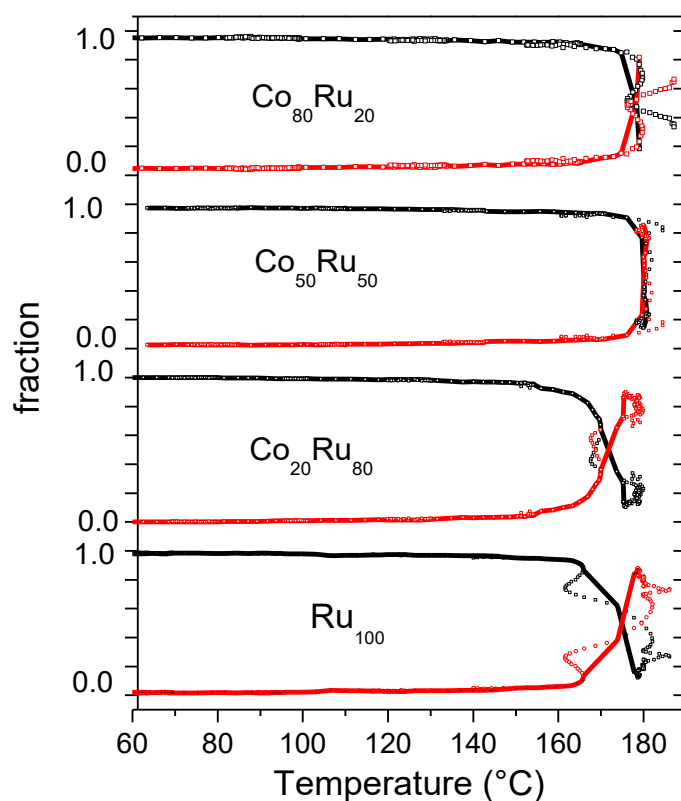
**Figure 3.** Normalized XAS spectra of the  $\text{Co}_{20}\text{Ru}_{80}$  reactive solution at the Ru K edge (at room temperature and after cooling) and of the  $\text{Ru}(\text{acac})_3$  powder. The inset is an enlargement of the plot to show the difference of energy value at a normalized absorbance of 0.3.

Owing to the high number of spectra obtained with Quick-EXAFS, chemometric analysis was carried out, using a combination of Principal Component Analysis (PCA) and Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) methods, which are detailed in SI (section S2.2). The latter method is particularly powerful for solving the mixture problem by isolating, from time-resolved spectroscopic data sets obeying to the Beer-Lambert law, the spectra of pure species and their corresponding concentration profiles.<sup>39</sup> Irrespective of the solution composition, the PCA analysis indicates that only two Ru species are present in our system. No intermediate species was identified. Common spectra of the two species for the four sets of data were obtained by a Column-Wise matrix Augmentation (CWA) strategy (see SI). They are shown in Figure S7. The spectrum of the first Ru(III) species is similar to the one of the  $\text{Ru}(\text{acac})_3$  solution while the second one, characteristic of metallic Ru, is slightly different from the last ones obtained *in situ* because the reduction is not totally achieved after 15 minutes heating at the boiling temperature. These latter can be reconstructed by a

combination of the spectra of the first and second pure species obtained by MCR-ALS as shown in Figure S8.

The evolutions of the fraction of Ru(III) and Ru(0) species as a function of temperature for the four compositions are given in Figure 4. The profiles of the four solutions are similar and strongly related to the previously shown evolution of the rising edge position at 0.3 (normalized absorbance) and white line intensity (Figures S5 and S6). A quick reduction of Ru(III) to Ru(0) is observed near the boiling temperature, from 160 °C for the Ru rich compositions and 170 °C for the Co rich ones. It is reminded that the heating ramp was not linear with temperature oscillations due to overshooting, giving the non-monotonous evolution. During this step of quick evolution of the Ru species (160 °C to boiling temperature), a small decrease in temperature does not completely stop the reduction but rather slows it down. However, the general profile drawn in Figure 4 is very similar to that obtained by UV and can be thus relied on.

From the above results, three important conclusions can be drawn: i) the evolution described here is similar to that already observed by UV-visible spectroscopy; the slight differences in reduction temperature being explained by the different ramping rate used for EXAFS (5 °C min<sup>-1</sup>) and for UV-visible spectroscopy experiments (10 °C min<sup>-1</sup>); ii) the presence of Co in the system has a very limited impact on the reduction kinetics of Ru(III) and iii) the reduction of Ru(III) to Ru(0) occurs directly, without the formation of any intermediate species.



**Figure 4.** Evolution of the molar fraction of the Ru(III) (in black) and Ru(0) (in red) species during the heating ramp for the precursor solutions of (a)  $\text{Co}_{80}\text{Ru}_{20}$ , (b)  $\text{Co}_{50}\text{Ru}_{50}$ , (c)  $\text{Co}_{20}\text{Ru}_{80}$ , and (d) Ru. The points are the experimental data whereas the lines give the evolution profile.

The recovered solids (after 1h30 heating under reflux) have also been characterized by EXAFS. Figure S9 shows the Ru EXAFS Fourier transformed moduli while Table 1 gives the fitted parameters for pure Ru and the powder containing 20 % Ru. For both samples, the number of O neighbouring atoms is close to 1, indicating a limited oxidation of Ru, probably at the surface. The number of Ru neighbours in the first shell of pure Ru NPs is similar to that found by G. Viau *et al.*<sup>51</sup> for 1.9 nm particles synthesized in polyol. For random distribution of cobalt and ruthenium in the  $\text{Co}_{80}\text{Ru}_{20}$  alloyed sample, 4 more Co neighbours than Ru ones should be found. Herein the best simulation evidences a nearly equal number of Co and Ru as first neighbours (a constrain of 4 more Co than Ru leads to a r-factor of 0.024, far higher than the one found by refining the two number of neighbours independently). This suggests that the

particles are not totally homogeneous, in line with previously published results<sup>33</sup>. This will be further discussed when analyzing the EXAFS data at the Co K-edge.

**Table 1.** EXAFS fitting parameters at the Ru K-edge for the spectra of Ru and Co<sub>80</sub>Ru<sub>20</sub> powders obtained in the laboratory ( $S_0^2 = 0.9$ ;  $E_0 = 22130.0$  eV). The fits were made between  $R = 1$  and  $3 \text{ \AA}$ ; from  $k = 4$  to  $16$  with  $dk = 2$  (Kaiser Bessel).

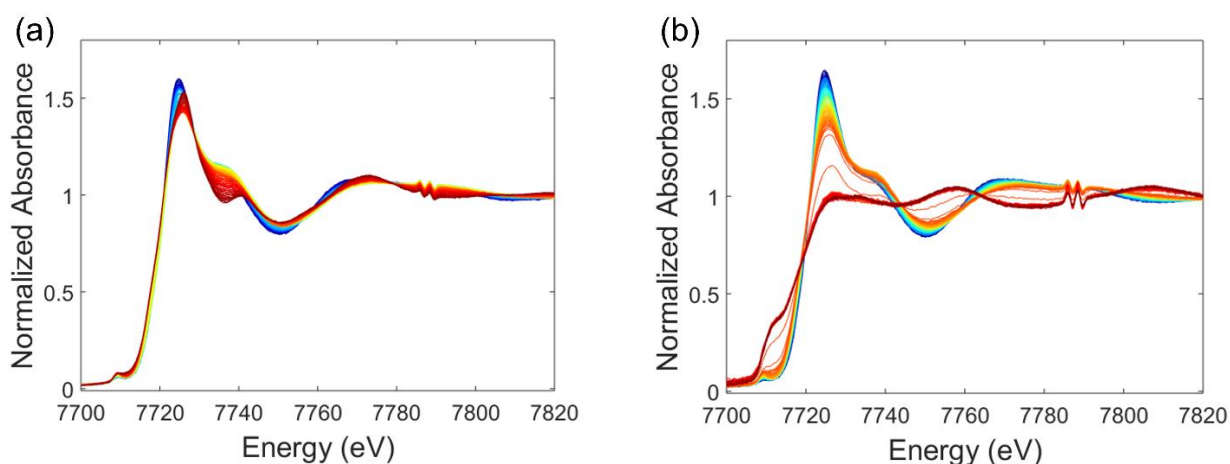
Backscatter	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\text{\AA}^2$ ) $\times 10^3$
<b>Ru NPs</b>			
Ru	$8.4 \pm 0.6$	$2.68 \pm 0.01$	$6 \pm 1$
O	$0.9 \pm 0.4$	$1.96 \pm 0.01$	$11 \pm 4$
r-factor = 0.0063	$\chi^2 = 481$ ; $\chi^2_{\text{red}} = 43.7$	$N_{\text{ind}} = 17$	$N_{\text{var}} = 6$
<b>Co<sub>80</sub>Ru<sub>20</sub> NPs</b>			
Ru	$5.2 \pm 0.2$	$2.65 \pm 0.01$	$6 \pm 1$
Co	$4.6 \pm 1.3$	$2.59 \pm 0.02$	$11 \pm 1$
O	$1.3 \pm 0.2$	$1.97 \pm 0.01$	$12 \pm 2$
r-factor = 0.003	$\chi^2 = 46$ ; $\chi^2_{\text{red}} = 5.75$	$N_{\text{ind}} = 17$	$N_{\text{var}} = 9$

*r-factor*: overall fit quality factor,  $\chi^2$  ( $\chi^2_{\text{red}}$ ): (reduced) chi-square goodness-of-fit test,  $N_{\text{ind}}$ : maximum number of independent points in the data,  $N_{\text{var}}$ : number of variables in the fit

### 3.2.b) Kinetics of reduction of Co(II) species

A solution of Co(acac)<sub>2</sub> alone in octan-1-ol as well as the solutions containing Co(acac)<sub>2</sub> and Ru(acac)<sub>3</sub> in different proportions were also analyzed by *in situ* XAS at the Co K-edge upon heating. The obtained spectra are given in Figure 5 for Co and Co<sub>80</sub>Ru<sub>20</sub> solutions and Figure S10 for all the compositions. The evolutions, as the temperature rises, of the energy for a normalized absorbance of 0.3 and of the white line intensity are given in Figures S11 and S12, respectively. The spectra are similar for all the compositions at the beginning but the evolution differs between the solution containing Co cations only and those containing also Ru cations. In the first case, only a slight decrease of the white line intensity and a slight continuous decrease of less than 2 eV of its energy position are observed during the heating step and for the first minutes at the boiling temperature (see Figures S11 and S12). The absence of a significant variation in energy of the rising edge indicates that no modification of the cobalt oxidation state occurs. In the presence of Ru, the intensity of the white line decreases much more and the shoulder in the rising edge is much more marked (Figure 5b). The shape of the spectra in the solutions containing ruthenium after heating is characteristic of a Co(0) species

and, for those solutions, a 2 step process is observed. From RT to *ca.* 160°C, only the white line significantly decreases in intensity from *ca.* 1.6 to 1.4 with no marked change of the rising edge position, whereas an abrupt shift of edge position and of the white line intensity occurs above 160°C to the values characteristic of metallic cobalt. These findings clearly indicate that Ru triggers Co(II) reduction.



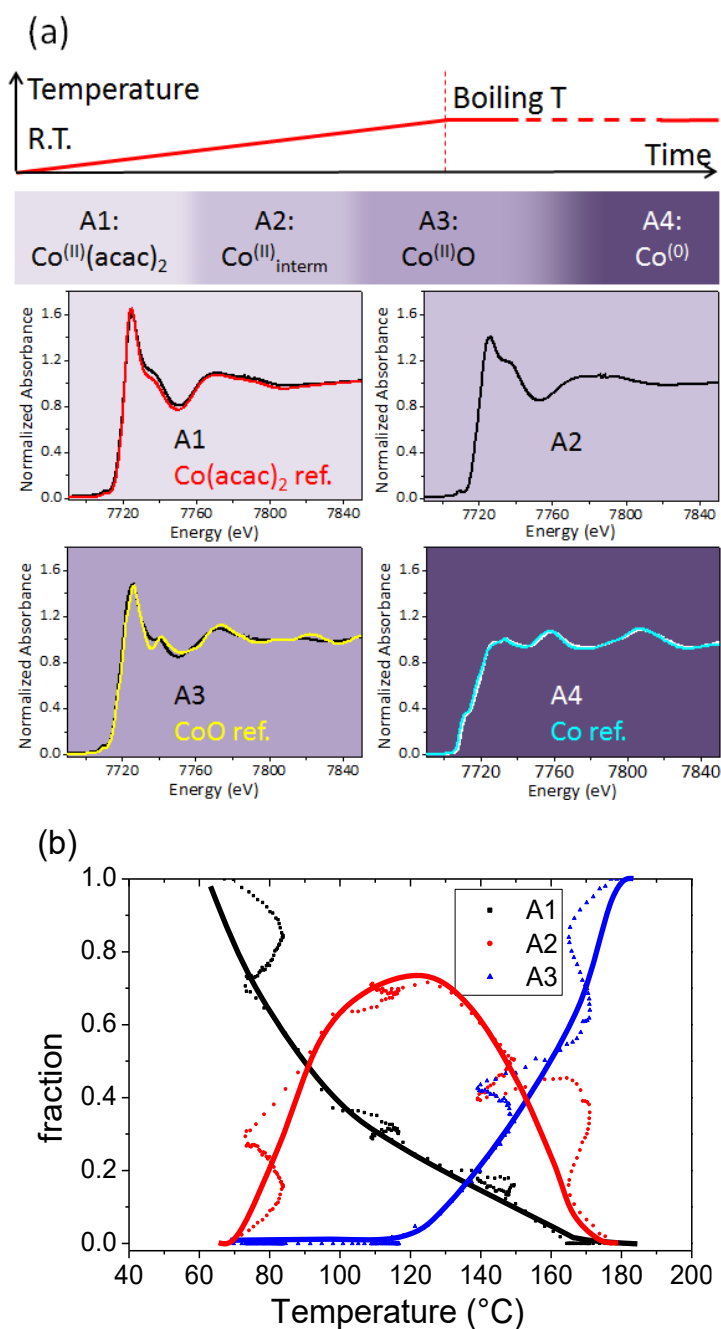
**Figure 5.** Normalized spectra at the Co K-edge obtained when heating the precursor solutions of Co (a) and Co<sub>80</sub>Ru<sub>20</sub> (b) NPs (the colour evolves from blue at the beginning of the experiment to red at the end).

Thus, the *in situ* Co K-edge XAS monitoring of the reaction clearly evidences that for pure Co, the reduction of Co(II) cations has not occurred after heating for about 15 min at the boiling temperature (and subsequent cooling) contrary to what happens when adding Ru species. This can be seen in Figure S13 where the obtained spectrum is very close to that of the CoO reference. However, it is possible to reduce it to metallic Co if the reaction proceeds for longer time, typically 1h30.

The data of the solution containing only Co(acac)<sub>2</sub> was first analyzed. The PCA method was used to determine the number of species formed during heating. A set of 3 species has to be considered to account for the observed experimental data (see Figure S14). The spectra of species obtained by MCR-ALS are given in Figure 6a and their EXAFS signals in Figure S15. The evolution of each of these species during heating is plotted in Figure 6b. Note that the spectrum at the Co K-edge for the powder obtained for 1h30 at 190°C is also presented as A4

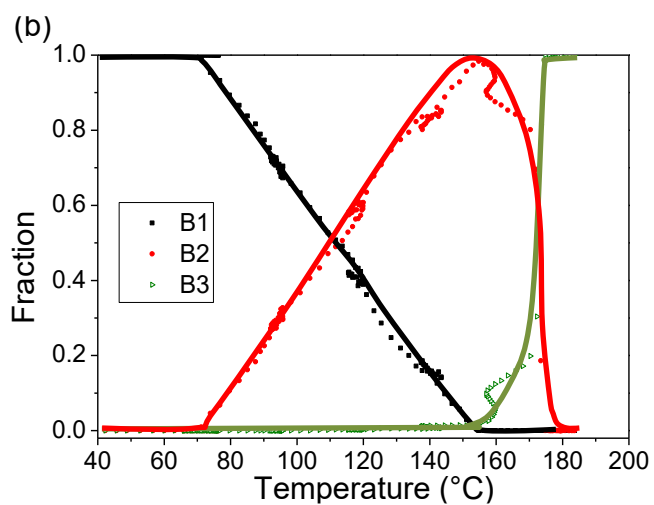
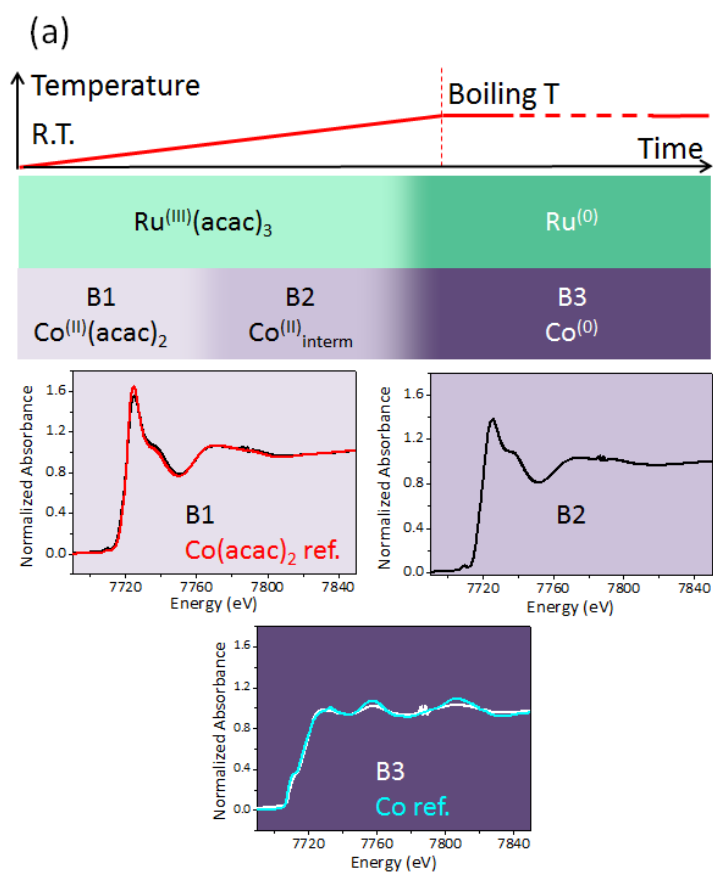
in Figure 6a. In this manner, a complete picture of the different species generated during the course of the reaction can be obtained. The spectrum of the first Co pure species in octan-1-ol before heating (at RT), denoted A1, is nearly identical to that of the  $\text{Co}(\text{acac})_2$  solid precursor. As for pure  $\text{Ru}(\text{acac})_3$ , this shows that there is no reduction of Co(II) at RT (*vide supra*) and no significant modification of the Co environment. Next, an intermediate A2 species appears at 70 °C and predominates at 90 °C. The X-ray absorption spectrum of A2 differs from the  $\text{Co}(\text{acac})_2$  and CoO references. The distance between Co and the O in the first shell is decreased of *ca.* 0.1 Å compared to that obtained for A1 (see Figure S15b). We assume that, during heating, there is a partial replacement of acac ligands by octan-1-ol molecules in the first coordination sphere of the Co(II) metal center or formation of polymeric species of Co(II) acetylacetonate. Then, a third species (A3) is generated between 120 and 160 °C and it is the only Co-containing species present when reaching the boiling temperature. Its X-ray absorption spectrum at the Co K-edge is close to that of the CoO reference (see Figure 6) with consistent in-phase EXAFS oscillations (see SI, Figure S15a). The existence domain of species A3 at temperatures above 120°C explains the reason for the EXAFS oscillations of this CoO-like species being not well defined compared to the RT bulk crystalline reference. This is related to the damping of the EXAFS oscillations associated with the increase of the thermal contribution of the Debye Waller factors of the different neighbours shells. The powder obtained after 1h30 heating under reflux (species A4) is then similar to the Co(0) reference.





**Figure 6.** (a) Spectra at the Co K-edge of the species A1, A2 and A3 extracted with the MCR-ALS method during heating a solution of  $\text{Co}(\text{acac})_2$  in octan-1-ol and of the powder (A4) obtained after 1h30 heating at the boiling temperature. Spectra at the Co K-edge of the  $\text{Co}(\text{acac})_2$ ,  $\text{CoO}$  and  $\text{Co}$  are also given for comparison purposes. (b) Speciation diagram for the A1, A2 and A3 species. as a function of temperature. The points are experimental data and the lines give the general tendency.

The key result is that, without Ru and for a reaction time of a few minutes at the boiling temperature, the reaction ends with the formation of a CoO-like phase while reduction of Co(II) to Co(0) has not occurred. During the 1h30 stage at the boiling temperature, the CoO phase transforms into metal Co, following a mechanism which is not under the scope of this study.



**Figure 7.** (a) Spectra at the Co K-edge of the species B1, B2 and B3 extracted with the MCR-ALS method during heating a solution of  $\text{Co}(\text{acac})_2$  and  $\text{Ru}(\text{acac})_3$  in octan-1-ol for the  $\text{Co}_{80}\text{Ru}_{20}$  composition. Spectra at the Co K-edge of the  $\text{Co}(\text{acac})_2$  and Co are also given for comparison purposes. (b) Speciation diagram for the species B1, B2 and B3 as a function of temperature, tendency extracted from Figure S20.

MCR-ALS treatment (see Figure S16) was similarly done for the  $\text{Co}_x\text{Ru}_{100-x}$  bimetallic particles ( $x = 20, 50, 80$ ). Three components (including the initial species) were also deduced. They are called B1, B2 and B3 (see Figure 7a and S15). The first MCR-ALS species are similar irrespective of the Co to Ru ratio, including pure Co, i.e. A1 and B1 are similar. Regarding the 2<sup>nd</sup> species, the spectra isolated for  $\text{Co}_{80}\text{Ru}_{20}$ ,  $\text{Co}_{50}\text{Ru}_{50}$  and  $\text{Co}_{20}\text{Ru}_{80}$  are superimposable and in close relationship with the one isolated for pure Co composition indicating that a common cobalt intermediate species is formed irrespective of the ruthenium content. In other words, it means that species A2 and B2 are close and correspond probably to Co centers with a partial replacement of acac ligands by octan-1-ol molecules or formation of clusters, as proposed above. A very noticeable result is that species B3 differs strongly from species A3 (without Ru). In the case of pure Co, A3 is close to CoO and reduction to Co(0) necessitates much more than 15 min at the boiling temperature whereas for  $\text{Co}_x\text{Ru}_{100-x}$  alloys, B3 is characteristic of metallic Co as displayed in Figure 7 and S15. The slight differences in the shape of the XANES spectra for  $\text{Co}_{80}\text{Ru}_{20}$ ,  $\text{Co}_{50}\text{Ru}_{50}$ ,  $\text{Co}_{20}\text{Ru}_{80}$  and Co foil is ascribed to the replacement of cobalt by ruthenium.

The Co speciation diagram for the  $\text{Co}_{80}\text{Ru}_{20}$  sample is given in Figure 7b, and in Figure S17, together with those of the  $\text{Co}_{50}\text{Ru}_{50}$  and  $\text{Co}_{20}\text{Ru}_{80}$  materials. They are very similar for the bimetallic samples irrespective of the Co to Ru ratio. However, they are also very different from that obtained for pure Co (Figure 6a). For bimetallic particles, the initial species disappears progressively between 70 and 150 °C whereas the intermediate species 2 appears. It is interesting to note that this intermediate species B2 does not evolve towards CoO and is, on the contrary, stable in the temperature range at which CoO forms for pure Co ( $T > 120$  °C). B2 then transforms into Co(0) between 160 °C and the boiling temperature, the same range observed for the reduction of Ru in our system. This effect of Ru as a promotor of reduction of Co is well known in the preparation of catalysts used for the Fischer Tropsch reaction.<sup>52</sup>

Small Angle X-Ray Scattering (SAXS) experiments carried out on aliquots confirmed the formation of particles in this range (see S3 in the supplementary information).

The fitting parameters for the Co<sub>80</sub>Ru<sub>20</sub> powder are given in Table 2 (see Figure S16 for the fits). Co atoms have in majority Co atoms in their first coordination shell. The EXAFS fitting parameters of the Co<sub>80</sub>Ru<sub>20</sub> establish that Ru atoms are surrounded by as much Ru than Co atoms and that Co atoms are surrounded by 17.5 more atoms of Co than Ru, much more than the expected 4 to 1 stoichiometry. This means that Co and Ru are not homogeneously distributed throughout the sample. This confirms the results reported in a previous paper<sup>33</sup> which enlightened the presence of platelets of two different compositions Co<sub>50</sub>Ru<sub>50</sub> and Co<sub>86</sub>Ru<sub>14</sub>. O atoms are also found. The powder is thus partly oxidized as shown by XPS, previously published.<sup>33</sup> It is noteworthy that the total number of atoms in the first shell is 11.1 for Ru and 8.6 atoms for Co, which would mean that the Co-rich nanoplatelets would be smaller than the Co<sub>50</sub>Ru<sub>50</sub> composition or that Ru would be more in the core of the NP but it is difficult to link this figure to the size of the nanoplatelets as they are not isotropic and that N is an average on the two populations.

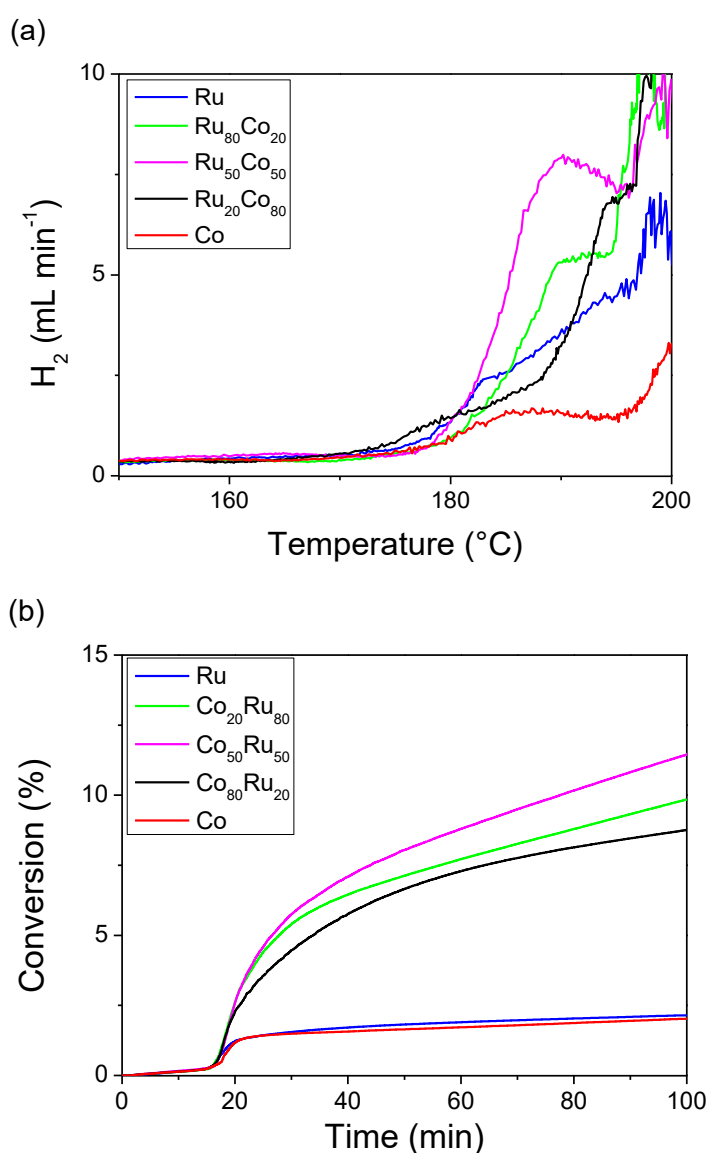
**Table 2.** EXAFS fitting parameters at the Co K-edge for the spectra of the Co<sub>80</sub>Ru<sub>20</sub> powder obtained in the laboratory.  $S_0^2 = 0.86$ ;  $E_0 = 7716.6$  eV. The fits were made between  $R = 1$  and  $3 \text{ \AA}$ ; from  $k = 4.4$  to  $10.8$  with  $dk = 2$  (Kaiser Bessel).

Backscatter	N	R (Å)	$\sigma^2 (\text{Å}^2) \times 10^3$
Co <sub>80</sub> Ru <sub>20</sub> NPs			
Ru	$0.4 \pm 0.8$	$2.58 \pm 0.01$	$9 \pm 4$
Co	$7.0 \pm 0.6$	$2.50 \pm 0.03$	$7 \pm 1$
O	$1.2 \pm 0.9$	$2.00 \pm 0.04$	$15 \pm 5$
r-factor = 0.003	$\chi^2 = 928$ ; $\chi^2_{\text{red}} = 185$	$N_{\text{ind}} = 10$	$N_{\text{var}} = 5$

### 3.3. Gas phase evolution

When heating the reactive solution to the boiling temperature, the formation of gas was observed. The formation of H<sub>2</sub> was attested by micro-GC (see Figure S22a, section 4 in the SI). Its evolution was monitored with a gas flow meter during the synthesis of the different Co<sub>x</sub>Ru<sub>100-x</sub> compounds. The instantaneous hydrogen flow is plotted in Figure 8a and the calculated conversion (see the experimental part for details) in Figure 8b. During heating, H<sub>2</sub> formation is observed from *ca.* 170°C (corresponding to *ca.* 17 min reaction time with the

ramping rate used), irrespective of the Ru composition studied, confirming that the reduction of the metal species begins at this same temperature for all the samples. The quantity of H<sub>2</sub> formed at 190 °C (see Figure 8a) is the lowest for Co only and the highest for the Co<sub>50</sub>Ru<sub>50</sub> composition. After this reduction stage, the formed nanoparticles catalyze the conversion of octan-1-ol mainly into octanal (see Figure S22b), giving a second rise in the H<sub>2</sub> formation plot. The nanoalloys were found to be better catalysts for this reaction than pure Co or Ru (see Figure 8a) as already demonstrated for octan-2-ol<sup>33</sup> even if conversion and selectivity were lower for the primary alcohol than for the secondary one.



**Figure 8.** (a) Instantaneous H<sub>2</sub> flow measured during the synthesis of the Co<sub>x</sub>Ru<sub>100-x</sub> NPs and (b) calculated octan-1-ol conversion using the total volume of evolved H<sub>2</sub>.

#### 4. Discussion

The results obtained clearly establish that the addition of Co(II) to a solution of Ru(III) does not influence much the kinetics of reduction of Ru(III) which occurs between 160 and 180°C as demonstrated by UV-visible and X-ray absorption spectroscopies. On the contrary, the presence of Ru(III) favors the reduction of Co(II), whatever the Ru(III) atomic percentage between 20 and 80 %. Indeed, a co-reduction of Co(II) and Ru(III) is observed in the 160 – 180 °C range for mixed solutions whereas the precipitation of solid CoO (as attested by EXAFS and SAXS) is observed in this same temperature range for pure Co solutions. In this monometallic solution, the reduction of CoO requires a prolonged reaction time at the boiling temperature. It is noteworthy that CoO is not identified as an intermediate species when Ru(III) is added.

The effect of noble metals such as Ru as a promoter of the reduction of Co(II) is well known and widely used in heterogeneous catalysis where noble metals in very small amounts (Ru/Co < 0.08 at.) are often added to prepare Co-based Fisher Tropsch catalysts.<sup>53</sup> Even if the reduction conditions are very different for these catalysts (thermal treatment of metal species on oxide substrates), Ru was shown to enhance the reducibility of Co<sub>3</sub>O<sub>4</sub> to CoO and that of CoO to Co as well as to decrease the average Co cluster size,<sup>52</sup> which is in line with our results. CoO was not identified as an intermediate species but Ru may promote the reduction of the Co(II) species B2 or CoO might form as a transient species within a too short time scale and/or too small quantity to be observed. Other studies showed that the reduction of Ru(IV) impregnated on Co<sub>3</sub>O<sub>4</sub> resulted in the concomitant formation of CoO and Ru(III) further reduced into Ru(0) at the surface of CoO nanoparticles enabling hydrogen activation for the further reduction of Ru/CoO species to the metallic state in an autocatalytic process.<sup>44</sup> It was also reported that reducing Ru complexes in a basic polyol medium involves the formation of molecular ruthenium hydrides which decompose to form Ru clusters with molecular dihydrogen release.<sup>53, 54</sup> The formation of Co nanorods from Co(laurate)<sub>2</sub> in 1,2-butanediol in the presence of Ru(III) cations was also shown to proceed in two steps involving both the release of H<sub>2</sub>.<sup>31</sup> In this study, the first H<sub>2</sub> production event at 150 °C was associated with the reduction of Ru(III) through the decomposition of hydrides formed *in situ* and the second one to the catalytic dehydrogenation of the polyol solvent by the formed Co nanorods. The

evolution of H<sub>2</sub> in our study is similar: a first H<sub>2</sub> production event occurs as the metal cations are reduced and a second more intense one when the particles are formed. A few H<sub>2</sub> is detected for Co alone but in a lower extent. This H<sub>2</sub> could be involved in the reduction of Co during the stage at the boiling temperature. For the compositions containing Ru, the H<sub>2</sub> is released in higher quantity, explaining the reduction of Co(II) concomitantly to Ru(III). When the particles are formed, they then catalyze the dehydrogenation of the alcohol solvent and then generate more H<sub>2</sub>. A synergetic catalytic effect is then observed for mixed compositions.

## 5. Conclusion

Coupling various techniques such as UV-visible and X-ray absorption spectroscopies as well as chromatography or X-ray scattering techniques permits to follow the reduction of species and the modification of the environments of metal centers as well as the fate of the by-products in the liquid and gas phases. A good insight into the mechanism of formation of metal nanoparticles in solution can be then achieved. Depending on the metal ions, the reduction can be straightforward (for Ru(III) for example) or can involve the formation of intermediate species (formation of CoO for solutions containing only Co(II) metal cations, for example). The addition of a more reducible noble metal salt to a solution containing a transition metal salt can trigger its reduction, resulting in a quasi-simultaneous reduction of the two metal cations which leads to the formation of an alloy. In our system, our results suggest that the reducing agent is not only the solvent but also *in situ* generated H<sub>2</sub>. More generally, this work opens perspectives for the formation of other nanoalloys of interest, using *in situ* generated H<sub>2</sub>.

## Authors contribution

B. A., T. B. G. and N. H. have made the synthesis of the nanoalloys under the supervision of L. S. and J.-Y. P.. B.A. has made the first synthesis in ITODYS and carried out the UV-visible spectroscopy measurements under the supervision of J. B.. T. B. G. and N. H. have made the chromatography experiments. O. T. has made the SAXS measurements. L. B. has designed the cell for *in situ* XAS experiments. B. A., S. N., J.-Y. P., V. B. and L. S. have carried out the XAS experiments in SOLEIL, L. S. has made the EXAFS treatment while V. B. has carried out PCA and MCR-ALS analysis. M. G., J. P., J.-Y. P. and L. S. have debated about the experiments and their interpretation.

## Conflicts of interest

There are no conflicts to declare.

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