An In Situ XAS Study of the Cobalt Rhenium Catalyst for Ammonia Synthesis

Karina Mathisen · Karsten Granlund Kirste · Justin S. J. Hargreaves · Said Laassiri · Kate McAulay · Andrew R. McFarlane · Nicholas A. Spencer

Published online: 12 February 2018 © The Author(s) 2018. This article is an open access publication

Abstract
A cobalt rhenium catalyst active for ammonia synthesis at 400 °C and ambient pressure was studied using in situ XAS to elucidate the reducibility and local environment of the two metals during reaction conditions. The ammonia reactivity is greatly affected by the gas mixture used in the pre-treatment step. Following H₂/Ar pre-treatment, a subsequent 20 min induction period is also observed before ammonia production occurs whereas ammonia production commences immediately following comparable H₂/N₂ pre-treatment. In situ XAS at the Co K-edge and Re LIII-edge show that cobalt initiates reduction, undergoing reduction between 225 and 300 °C, whereas reduction of rhenium starts at 300 °C. The reduction of rhenium is near complete below 400 °C, as also confirmed by H₂-TPR measurements. A synergistic co-metal effect is observed for the cobalt rhenium system, as complete reduction of both cobalt and rhenium independently requires higher temperatures. The phases present in the cobalt rhenium catalyst during ammonia production following both pre-treatments are largely bimetallic Co–Re phases, and also monometallic Co and Re phases. The presence of nitrogen during the reduction step strongly promotes mixing of the two metals, and the bimetallic Co–Re phase is believed to be a pre-requisite for activity.

Keywords Ammonia · Cobalt · Rhenium · In situ XAS

1 Introduction
Since the development of the Haber Bosch Process at the beginning of the twentieth Century, considerable effort has been made to reduce the severity of the process by developing new efficient catalytic materials operational under milder reaction conditions [1–5]. The current industrial catalyst which is based on promoted iron is operated at high pressure (ca. 100–300 atm.) and moderate temperatures (ca. 400 °C) to ensure acceptable industrial ammonia production rates [6]. Amongst the materials developed as alternatives to the iron based system, Re based catalysts display comparatively high catalytic activity [7]. The catalytic activity of such Re based catalysts was found only to be stabilized when cobalt was added as a promoter to the bulk Re (atomic ratio of 4:1 Re:Co), whereas rapid deactivation over time was observed in the case of the non-promoted system [8]. The stability of the cobalt rhenium phase was correlated in the literature to the formation of a stable active rhenium nitride phase upon the ammonolysis step employed in its preparation. Subsequently, more recent work from McAulay et al. [9] has demonstrated that highly active cobalt rhenium catalysts can be prepared without an ammonolysis stage. Interestingly, a pronounced influence of pre-treatment gas mixture was reported in the catalytic activity of this material with 75% H₂ in N₂ leading to more active catalyst than when applying 75% H₂ in Ar. Furthermore, an induction period of 20 min was observed before the catalytic activity developed in the case of the H₂ in Ar pre-treated catalyst [9]. Although, post-reaction analysis did not reveal any relevant structural changes in cobalt rhenium upon the different pre-treatments,
subtle changes, not easily detected by classical characterization techniques, might be responsible for these differences.

In situ X-ray absorption spectroscopy (XAS) has been reported in the literature as an efficient tool for studying the rhenium cobalt catalyst used in the Fischer–Tropsch Process [10–15]. Since XAS is an element specific probe, information related to the local environment of each constituent, Co or Re, can be obtained in an independent manner [16]. The Near Edge (XANES) region is highly sensitive to local environment and oxidation state, meaning fingerprinting with carefully selected reference compounds can reveal initial information about the state of the elements involved. From the extended fine structure region (EXAFS) structural information, inaccessible by standard characterization techniques, might be responsible for these differences.

As for the structural modeling of the catalyst, under an atmosphere of 75% H2 in Ar (BOC, 99.98%) at a total gas feed of 60 ml min−1. Prior to reaction, the cobalt rhenium material was activated under an atmosphere of 75% H2 in N2 (BOC, 99.98%) at a total gas feed of 60 ml min−1 at 600 °C for 2 h. Ammonia production applying a 60 ml min−1 flow of 75% H2 in Ar at 400 °C was determined by measurement of the decrease in conductivity of a 200 ml 0.0018 M H2SO4 solution through which the reactor effluent stream was flowed.

2.2 Denitridation

The reactivity of cobalt rhenium was probed, using 0.3 g of catalyst, under an atmosphere of 75% H2 in Ar (BOC, 99.98%) at a total gas feed of 60 ml min−1. Prior to reaction, the cobalt rhenium material was activated under an atmosphere of 75% H2 in N2 (BOC, 99.98%) mixture at a total gas feed of 60 ml min−1 at 600 °C for 2 h. Ammonia production applying a 60 ml min−1 flow of 75% H2 in Ar at 400 °C was determined by measurement of the decrease in conductivity of a 200 ml 0.0018 M H2SO4 solution through which the reactor effluent stream was flowed.

2.3 Temperature Programmed Reduction

The reducibility of cobalt rhenium samples was studied by temperature programmed reduction (TPR). 40 mg of sample was pre-treated under 5.0 vol% O2 in He using a flow rate of 50 ml min−1 at 600 °C for 2 h, and then cooled down to ambient temperature. Thereafter, the TPR experiment was performed under a mixture of gases composed of 5.0 vol% H2 in He using a total gas feed of 50 ml min−1 with a temperature ramp rate of 5 °C min−1.

2.4 XAS Data Collection

Cobalt K-edge and rhenium LIII-edge XAS data was collected in transmission mode at the Swiss-Norwegian Beamlines (SNBL, BM1B) at the European Synchrotron Radiation Facility (ESRF). The data was collected in the 16-bunch filling mode, providing a maximum current of 90 mA. A bending magnet collects the white beam from the storage ring to the beamline. BM01B is equipped with a Si(111)
The incident and transmitted intensities ($I_0$ and $I_0 + I_2$) were detected with ion chambers filled with, $I_0$ (17 cm) 50% $N_2 + 50%$ He, and $I_1$ and $I_1$ (30 cm) with 85% $N_2 + 15%$ He at the cobalt edge. Post-ammonolysis samples (CoN$_2$, ReN$_2$ and CoReN$_2$), cobalt references (CoO, Co$_3$O$_4$) and rhenium references (ReO$_3$, KReO$_4$ and NH$_4$ReO$_4$) placed in aluminium sample holders were also collected ex situ and were mixed with boron nitride for optimum absorption. The cobalt XAS data were measured in continuous step scan and were mixed with boron nitride for optimum absorption. The sample weight, cell thickness and gas flow were kept constant. The cobalt rhenium catalyst was mixed with boron nitride, pressed into wafers and sieved. Sieved samples (above 375 μm) were then placed inside 0.9 mm quartz capillaries with quartz wool on either side. The capillary was heated by a blower placed directly under the sample, and the exhaust was continuously sampled using a Tristar Mass spectrometer.

The cobalt XAS data were measured in continuous step scan from 7600 to 8300 eV with a step size of 0.5 eV and counting time 300 ms. The rhenium LIII-edge data was collected from 7600 to 8300 eV with a step size of 0.5 eV and counting time 200 ms. For all in situ measurements, great care was taken to ensure that similar conditions were applied for both edges and hence sample weight, cell thickness and gas flow were kept constant. The cobalt rhenium catalyst was mixed with boron nitride, pressed into wafers and sieved. Sieved samples (above 375 μm) were then placed inside 0.9 mm quartz capillaries with quartz wool on either side. The capillary was heated by a blower placed directly under the sample, and the exhaust was continuously sampled using a Tristar Mass spectrometer.

Samples were studied using two protocols with pre-treatments either in 75% $H_2$ in Ar or 75% $H_2$ in $N_2$ at 600 °C for 2 h using a 10 °C min$^{-1}$ temperature ramp rate with a total gas flowrate of 10 ml min$^{-1}$. EXAFS step scans were collected continuously following the protocol shown in Figure S.1 with XRD patterns being collected at the end points. After the pre-treatment, samples were cooled to 400 °C and the reaction gas was switched to 75% $H_2$ in $N_2$. EXAFS step scans were collected continuously. A setup with pneumatic switching valves and a secondary by-pass line was employed to prevent gas build-up during switching between gases.

### 2.5 XAS Data Refinements

The XAS data was binned (edge region −30 to 50 eV; pre-edge grid 10 eV; XANES grid 0.5 eV; EXAFS grid 0.05 Å$^{-1}$) and background subtracted, and the EXAFS part of the spectrum extracted to yield the $\chi_{\text{exp}}^k(k)$ using Athena software from the IFFEFITT package. The XANES spectra were normalised from 30 to 150 eV above the edge, while the EXAFS spectra were normalised from 150 eV to the end point [20]. The data were carefully deglitched and truncated at the end of the EXAFS spectra when needed. The smooth background $\mu_0(E)$ was checked and corrected to achieve the maximum overlap with total absorption $\mu(E)$. Athena uses the Autobk algorithm to determine the background and normalise $\mu(E)$ data. Edge step normalisation was used, meaning that the difference between $\mu(E)$ and $\mu_0(E)$ was divided by an estimation of $\mu_0(E_0)$. A line was regressed to the data in the region below the edge and subtracted from the data. A quadratic polynomial was then regressed to the data above the edge and extrapolated back to $E_0$ [20]. For cobalt the threshold energy ($E_0$) was set to be at the mid-point (0.5) of the normalised absorption edge step ensuring it was chosen after any pre-edge or shoulder features. For rhenium samples $E_0$ was determined to be the first inflection point in the first derivative spectra, as there are no pre-edges or shoulder features. All XANES spectra are energy corrected against the corresponding reference foil (Co = 7709 eV, Re = 10,535 eV).

XANES is invaluable for distinguishing between valence states of transition metals and is highly sensitive towards changes in the electronic states and or the local environment. At every stage of the process, attempts were made to fit the experimental spectra to reference compounds, including corresponding foils, using the linear combination feature in the Athena package [20]. The normalised data were fitted from −20 eV below the edge and 60 eV above the edge, allowing also the $E_0$ value to be fitted, due to the ambiguity in selecting this value resulting from pre-edge features. All fits with unreasonable Δ$E_0$ values (±2.5 eV) were excluded. The maximum number of standards was set to three and the most relevant were chosen on the basis of the statistical goodness of fit.

EXAFS least-squares refinements were carried out using DL-EXCURV [21], which conducts the curve fitting of the theoretical $\chi^0(k)$ to the experimental $\chi^\text{exp}(k)$ using the curved wave theory. The fit parameter reported for each refinement procedure is given by the statistical R-factor, defined as:

$$R = \sum \frac{1}{\sigma_i} \left( \frac{\chi_i^\text{exp}(k) - \chi_i^\text{th}(k)}{\chi_i^\text{th}(k)} \right) \times 100\%$$

Ab initio phase shifts for both edges were also calculated within DL-EXCURV and verified using reference compounds. The amplitude reduction factor (AFAC) was extracted from the following reference compounds: Co$_3$O$_4$ and NH$_4$ReO$_4$ for the oxidized cobalt rhenium phase, while Co-foil and Re-foil were used for the reduced phase. The least-squares refinements were carried out in typical wave number k range 2–8.5 Å$^{-1}$ for cobalt and k range 3.5–9.5 Å$^{-1}$ for rhenium using a k$^3$ weighting scheme.

### 3 Results

#### 3.1 Cobalt Rhenium Starting Material

The original catalyst was labelled according to the original synthesis molar ratio between the cobalt and rhenium.
(CoRe₄). However, in order to elucidate the real composition of the material ICP-MS was performed and such analysis revealed the actual molar composition to be CoRe₁.₆. The loss of rhenium from the sample may be attributed to volatilization of rhenium during the calcination stage at 700 °C in air prior to reaction. From here on in within this manuscript the cobalt rhenium catalyst will be labelled as CoRe₁.₆.

Figure 1 shows the Co K-edge and Re L₃-edge normalised XANES of the CoRe₁.₆ starting material compared to reference compounds. The fresh CoRe₁.₆ does not show similarities to the oxides and instead the local cobalt surrounding is more comparable to the cobalt phosphate reference. Comparing E₀ values, it is clear cobalt is present as a Co(III)/Co(II) mixture in the fresh catalyst prior to pre-treatment. The XANES (Fig. 1) of the CoRe₁.₆ starting material resembles strongly the NH₄ReO₄ reference compound in also exhibiting similar absorption edge values to the Re(VII) references.

The EXAFS (Figure S.2) further confirms the above as refinements show an average coordination of four Co–O pairs at 1.96 Å. EXAFS refinements of the fresh CoRe₁.₆ yield 3.4 Re–O absorption pairs at 1.70 Å which is slightly shorter than those previously reported for tetrahedrally coordinated ReO₄⁻ (1.74 Å in Bi/Re/O compounds), and longer than the Re=O double bonds reported from X-ray diffraction of organo-rhenium (VII) oxides (1.67 Å) [22]. By comparison the octahedral Re–O₉ bond lengths are typically found at 1.89 Å [23]. A second Re–O shell with a multiplicity of 3 is found at 2.15 Å, which appears to be too long to be octahedrally coordinated ReO₆⁻². However similar Re–O bonds are also reported in the EXAFS studies of the oxides of Re/Bi mentioned above [23]. Hence it can be concluded that both cobalt and rhenium are present in a highly oxidised state in CoRe₁.₆ prior to pre-treatment (Table 1).

### 3.2 Denitridation

To obtain a first indication of the role of pre-treatment in the possible formation of an active CoReₓNₓ nitride phase during the induction time, denitridation of N₂/H₂ pre-treated CoRe₁.₆ was undertaken using H₂/Ar. Pre-treatment was undertaken using 75% H₂ in N₂ at 600 °C for 2 h. The subsequent H₂/Ar reaction profile, presented in Figure S.3, displayed an overall drop in conductivity of 42 μS cm⁻¹ which corresponded to a total ammonia production of ~35 μmoles of ammonia over 200 min of reaction, after which no further ammonia production was observed. Table 2 displays observed rates of ammonia production for selected nitrides
and also the equivalent cobalt rhenium material previously reported (which is denoted as CoRe₄, representing its synthesis ratio) under comparable reaction conditions (400 °C, ambient pressure, 75% H₂ in N₂). The low amount of ammonia generated in the absence of dinitrogen gas feed suggests a very low content of N being stored within the CoRe₁.₆ system, and possibly results from residual N stored on the surface.

3.3 Reducibility of the Cobalt Rhenium System

The active form of the cobalt rhenium system is typically obtained after reduction during the pre-treatment step at high temperature. The reducibility of CoRe₁.₆ and Co₂O₃ was evaluated using H₂ TPR (Fig. 2). The reduction of Co₂O₃ started at a temperature as low as 200 °C and was characterized by two reduction steps. A small peak around 230 °C can be observed which has been assigned in the literature to the reduction of Co³⁺ to Co²⁺ with the second peak occurring at higher temperature being attributed to the reduction of Co²⁺ to Co⁰ [24, 25]. The reduction profile of CoRe₁.₆ started at slightly higher temperature than the Co₂O₃ and was characterized by a single reduction step with a maximum located at 325 °C. Hydrogen spillover from rhenium to cobalt oxide is widely accepted to promote the reduction of cobalt oxide which could explain the profile reduction of the CoRe₁.₆ [26, 27].

### Table 1

| Sample | Shell | N  | R (Å)  | 2σ² (Å²) | EF (eV) | R (%) | Δk |
|--------|-------|----|--------|----------|---------|-------|----|
| CoRe₁.₆ | Co–O  | 4(1) | 1.96(2) | 0.003(9) | -2(2) | 58    | 2–8 |
| Re–O  | 3.4(3) | 1.70(4) | 0.003(1) | -6(2) | 28    | 2–13 |
| Re–O  | 3(1)  | 2.15(2) | 0.02(1)  |        |       |       |     |
| CoRe₂Nₓ | Co–Co | 4.6(7) | 2.46(8) | 0.018(3) | -5.0(9) | 29    | 2–10|
| Co–Re | 2.0(8) | 2.66(1) | 0.011(7) |        |       |       |     |
| CoRe₃Nₓ | Re–N  | 0.4(2) | 1.76(3) | 0.01(1)  | -6(1) | 16    | 3.5–9.5|
| Co–Re | 3.0(5) | 2.57(1) | 0.022(3) |        |       |       |     |
| CoRe₄Nₓ | Re–Re | 3.1(8) | 2.65(0) | 0.018(5) |        |       |     |
| CoNₓ | Co–Co | 4.0(8) | 2.50(1) | 0.013(3) | -8(2) | 43    | 2–11 |
| Re–N  | 0.6(5) | 1.79(3) | 0.014(18) | 3(2) | 47    | 3.5–9 |
| Re–Re | 7(2)  | 2.67(2) | 0.032(8) |        |       |       |     |
| Co-foil | Co–Co | 12    | 2.496(7) | 0.0132(8) | -16(1) | 33    | 2–12 |

*The EXAFS refinements give information about multiplicity (N), bonding distance (R) and thermal vibration (Debye–Waller factor, 2σ²). EF is the refined correction of Fermi energy in vacuum, compared to E₀. The standard deviation in the last significant digit as calculated by DL-excurv is given in parentheses. The deviation for 2σ² is ± 20%. The Fit index is defined as FI = σ_{i}[1/σ_{i}(|Δχ_{exp}(k)| − Δχ_{th}(k))] × 100% and gives indication of the quality of fit in k-space.

### Table 2

| Materials  | Pre-treatment | Reaction conditions | Rate (μmol g⁻¹ h⁻¹) | Reference |
|------------|---------------|---------------------|----------------------|-----------|
| Co₃Mo₃N   | H₂/N₂         | H₂/N₂               | 652                  | [4]       |
| Ni₃Mo₃N   | H₂/N₂         | H₂/N₂               | 400                  | [1]       |
| CoRe₄     | H₂/N₂         | H₂/N₂               | 943                  | [9]       |
| CoRe₃     | H₂/N₂         | H₂/N₂               | 844                  | [9]       |
| CoRe₁₆    | H₂/N₂         | H₂/Ar               | a                    | This paper |

*Rate not determined, deactivation after 2 h of reaction.

---

**Fig. 2** Temperature programmed reduction (TPR) profiles of CoRe₁.₆ catalyst (lower profile) and Co₂O₃ (upper profile) under H₂ flow.
3.4 Effect of Different Pre-treatments; H₂/Ar or H₂/N₂

Selected normalised XANES (at 150 °C intervals, including relevant changes) of CoRe₁.₆ during pre-treatment in 75% H₂ in N₂ and 75% H₂ in Ar from ambient temperature to 600 °C are shown in Fig. 3. The figure also presents the reduction profiles determined from linear combination of all XANES spectra. The Co^{II}/Co⁰ reduction occurs quite steeply, is initiated around 200 °C, and clearly occurs before the reduction of Re^{VII}/Re⁰, which starts at 300 °C for both pre-treatments as seen in Fig. 3. The starting point for the first reduction step for cobalt is somewhat lower for the H₂/Ar pre-treatment. Typically complete reduction of rhenium requires much higher temperatures [28], hence these results suggest a cooperative effect between rhenium

Fig. 3 Selected normalized XANES (150 °C intervals) during pre-treatments in H₂/Ar and H₂/N₂, XANES for Co K-edge (top left) and Re L_{III}-edge (top right), and reduction profiles from linear combination of all normalized (30–150 eV) XANES in Athena (bottom)
and cobalt, similar to the hydrogen spillover effect which has been reported for the Pt–Re system [29]. Both elements are reduced to the metallic state between 500 and 600 °C. Other studies have also suggested the role of rhenium being to be the promotion of reduction of cobalt [15]. However, in the current study it is clear that cobalt initiates reduction of rhenium in the CoRe₁.₆ during both H₂/Ar and H₂/N₂ pre-treatments.

The normalised XANES of CoRe₁.₆ after the two pre-treatments compared to references at the Co K-edge and Re L₃-edge are shown in Figs. 4 and 5 respectively. Both the shape of the XANES and the obtained E₀ values confirm that the metals are present in the metallic state, however the cobalt data show two small features in the white line region (Fig. 4), whereas the cobalt foil shows one broad feature. These two smaller white line features are also reported in the cobalt XANES for the PtCo/Al₂O₃ system after in situ H₂ reduction, hence it would seem indicative of bimetallic Co–M interaction [30]. We cannot rule out re-oxidation in air of the post-ammonolysis samples as they were collected ex situ. The normalised rhenium XANES for the CoRe₁.₆ clearly appear at a lower E₀ value also displaying a lower white line intensity (Fig. 4) when compared to CoReₓNₓ and ReNₓ prepared by ammonolysis. This would confirm that rhenium in CoRe₁.₆ is fully reduced, whereas rhenium is partially re-oxidised in the post-ammonolysis references. There are clear similarities between the features observed in the XANES independent of pre-treatment for both edges, indicating that there are largely similar local metal surroundings at this point.

For the EXAFS analysis, attention was directed towards analysis of the structure of the cobalt rhenium phase and more precisely the mixing and bimetallic nature of the material during the pre-treatment and ammonia synthesis. The degree of bimetallic mixing is obtained by comparing the obtained average coordination of the first absorption shell which for the cobalt edge will comprise Co–Co and/or Co–Re, and similarly Re–Re and/or Re–Co at the rhenium edge. As EXAFS sees sums of contributions both absorption pairs will be present on respective edges if the material consists of a mixture of mono- and bimetallic phases. However, as these shells exhibit different bond distances the contributions should be resolved in EXAFS refinements. In a bimetallic system the degree of mixing is often best obtained from the minority element, which in our case is Co [31]. This can be exemplified by the following relationship Cᵣₑ × Nᵣₑ−Co = Cᵦₒ × Nᵦₒ−Re, where Cᵣₑ and Cᵦₒ are the concentrations of each metal, which means that heteroatomic
bonds will be better visualized at the element of low concentration in bimetallic phases [30]. However, due to rhenium being a heavy absorber optimising the dilution for XAS data collection was challenging, which in turn led to in situ cobalt data being of reduced quality. Another challenge in this study is obtaining reliable information about rhenium as a backscatterer due to the fact that a large part of the EXAFS signal lies in the high k-region, and the data in this study utilises a k-window of 3.5–9.5 Å⁻¹ as the resolution beyond this value is limited by the in situ conditions.

Results from EXAFS analysis of references prepared by ammonolysis (CoRe₅Nx, CoNx and ReNx) are shown in Table 1 and Figure S.2 confirming that the process has led to the reduction to the metallic state in all three samples. Bimetallic mixing is confirmed for CoRe₅Nx where coordination numbers of 4.6 for Co–Co and 2.0 for Co–Re are found at the cobalt edge, while average coordination numbers at the rhenium edge are 3.1 for Re–Re and 3.0 for Re–Co. The bond-distance obtained for the Co–Co bond in CoRe₅Nx is 2.47 Å, which is slightly shorter than that obtained for the Co-foil (2.49 Å), and the Re–Re bond length is 2.65 Å, which is shorter than that of Re-foil (2.74 Å). From refinements, the Co–Re bond length is 2.66 Å, while the corresponding Re–Co bond length at the rhenium edge is 2.57 Å. Shorter Re–Re bonds were also reported by Rønning et al. for the Co–Re/Al₂O₃ system where, similar to our findings, they found the Re–Co bond length to be 2.54 Å [15]. These numbers do in fact confirm bimetallic Co–Re mixing occurs in the sample, however as relatively high multiplicity Co–Co and Re–Re absorption pairs are found during refinements, one cannot exclude the possibility that pure Co and Re phases occur in the sample. Nitride formation, suggested by the partially oxidised rhenium from XANES for this sample, is confirmed by a Re–N shell at 1.76 Å. The low average Re–N multiplicity of 0.4 and high Re–Re/Co coordination suggests there is still a large degree of metallic rhenium in this sample. A Re–N shell with average coordination of 0.6 is also found in the ReNx sample at 1.79 Å, in addition to the Re–Re shell at 2.67 Å. For the CoNx sample, only the Co–Co shell at 2.50 Å with an average coordination of 4 is found in the refinement.
EXAFS of CoRe$_{1.6}$ after the two different pre-treatments clearly confirms that the presence of nitrogen during pre-treatment is a prerequisite for extensive bimetallic Co–Re mixing in CoRe$_{1.6}$ (Table 3). While there are clear similarities in the EXAFS and Fourier Transform spectra at the rhenium edge (Fig. 7), there are clear differences in the cobalt EXAFS (Fig. 6). Cobalt, being the minor constituent in the sample, is the element which would be more sensitive to the degree of mixing. A large degree of Co–Re bimetallic mixing is observed in CoRe$_{1.6}$ after pre-treatment in 75% H$_2$ in N$_2$, yielding coordination numbers of 3.2 for Co–Re and 3 for Re–Co at 2.51 Å. As observed for the post-ammonolysis samples, CoRe$_{1.6}$ also exhibits Co–Co (1.7, at 2.45 Å) and Re–Re (5, at 2.71 Å) backscattering pairs, suggesting pure cobalt and rhenium phases are also present. It is worth noting that the lack of second or third metal–metal scattering shells in these samples indicates a high degree of disorder in the system. Typically a second Re-metal distance is found at 3.56 Å in bulk rhenium, which is absent in the CoRe$_{1.6}$ system. This again is reflected in the XRD patterns (Figure S.5), which show a degree of amorphous background. It should be noted that attempts to introduce a Re–N shell at low R-value led to a decrease in fit-factor. Reasonable fit-values could not be obtained and the shell was therefore omitted.

Table 3  EXAFS least squares refinements of CoRe$_{1.6}$ after 2 h pre-treatment at 600 °C in either H$_2$/N$_2$ or H$_2$/Ar and during ammonia synthesis at 400 °C for both Co K-edge and Re L$_{III}$-edge from in situ XAS (AFAC transferred from Co-foil = 0.79 and Re-foil = 0.8)

| Sample | Shell | N  | R (Å)   | $2σ^2$ (Å$^2$) | EF (eV) | R (%) | Δk |
|--------|-------|----|---------|----------------|--------|-------|----|
| CoRe$_{1.6}$ H$_2$/N$_2$ 600 °C | Co–Co | 1.7(6) | 2.45(1) | 0.011(7) | −6.3(8) | 39 | 2–8.5 |
|       | Co–Re | 3.2(9) | 2.51(1) | 0.020(6) |         |       |    |
|       | Re–Co | 3(1)  | 2.51(2) | 0.042(9) | −7(2)   | 49 | 3.5–9.5 |
|       | Re–Re | 5(3)  | 2.71(3) | 0.05(2)  |         |       |    |
| CoRe$_{1.6}$ H$_2$/Ar 600 °C | Co–Co | 9(2)  | 2.46(1) | 0.049(5) | −3(1)   | 36 | 2–8.5 |
|       | Re–Co | 1.7(8) | 2.51(1) | 0.031(9) | −9(1)   | 47 | 3.5–9.5 |
|       | Re–Re | 7(3)  | 2.73(1) | 0.05(1)  |         |       |    |
| H$_2$/N$_2$ PT 10 min | Co–Co | 5(1)  | 2.47(1) | 0.029(5) | −6.1(8) | 29 | 2–8.5 |
|       | Co–Re | 2.1(7) | 2.52(1) | 0.010(7) |         |       |    |
|       | Re–Co | 3(2)  | 2.54(6) | 0.05(2)  | −7(2)   | 45 | 3.5–9.5 |
|       | Re–Re | 4(1)  | 2.66(1) | 0.027(7) |         |       |    |
| H$_2$/N$_2$ PT 60 min | Co–Co | 2.7(8) | 2.509(7) | 0.013(7) | −4.0(8) | 37 | 2–8.5 |
|       | Co–Re | 2.7(7) | 2.486(8) | 0.005(5) |         |       |    |
|       | Re–Co | 0.9(6) | 2.48(1) | 0.013(9) | −8(2)   | 45 | 3.5–9.5 |
|       | Re–Re | 5(2)  | 2.70(1) | 0.029(8) |         |       |    |
| H$_2$/Ar PT 10 min | Co–Co | 5.4(9) | 2.460(9) | 0.026(4) | −1(1)   | 29 | 2–8.5 |
|       | Co–Re | 1.2(5) | 2.56(2) | 0.013(6) | −9(1)   | 42 | 3.5–9.5 |
|       | Re–Co | 5(2)  | 2.68(1) | 0.030(8) |         |       |    |
| H$_2$/Ar PT mins | Co–Co | 4.7(8) | 2.452(8) | 0.024(4) | −1(1)   | 29 | 2–8.5 |
|       | Co–Re | 2(2)  | 2.62(8) | 0.07(5)  |         |       |    |
|       | Re–Co | 0.7(3) | 2.531(9) | 0.002(6) | −11(1)  | 36 | 3.5–9.5 |
|       | Re–Re | 5(2)  | 2.743(9) | 0.026(6) |         |       |    |

PT refers to pre-treatment and the times given correspond to reaction times under ammonia synthesis conditions.

For CoRe$_{1.6}$ pre-treated in 75% H$_2$ in Ar, attempts to introduce a Co–Re coordination shell were unsuccessful, yielding only a Co–Co shell at 2.46 Å with average coordination number of 9. At the rhenium edge, a Re–Co shell could be fitted, with average coordination of 1.7 at 2.51 Å. The major contribution to the signal is the Re–Re shell at 2.73 Å with average coordination number of 7. Clearly, the degree of mixing is greatly influenced by the pre-treatment, as the presence of nitrogen ensures bimetallic Co–Re pair formation. Average coordination numbers for the two pre-treatments of CoRe$_{1.6}$ are displayed in Fig. 8.

3.5 Structural Changes During Ammonia Synthesis

Following pre-treatment, CoRe$_{1.6}$ was cooled to 400 °C where ammonia synthesis was carried out for 2 h in 75% H$_2$ in N$_2$. The mass spectrometer (MS) signal is shown in Fig. 9, confirming the 20 min lag-time before ammonia production starts for the sample pre-treated in H$_2$/Ar, as has already been reported [9]. For CoRe$_{1.6}$ pre-treated in H$_2$/N$_2$ (reaction gas) ammonia production starts immediately. At this stage, as we have already established that the two pre-treatments affect the degree of Co–Re mixing and it is of interest to establish whether the observed lag-time can be explained by structural changes observable in in situ XAS. Following
pre-treatment, CoRe1.6 was cooled to 400 °C where ammonia synthesis was carried out for 2 h in 75% H₂ in N₂.

The normalised XANES at both edges taken after 10 and 60 min under ammonia synthesis reaction conditions are displayed in Figs. 4 and 5. No changes appear to occur in the cobalt XANES when compared to the spectra after the pre-treatment. The XANES are also similar independently of pre-treatment. Interestingly, when examining
the rhenium normalised XANES, it is clear that the white line of the CoRe$_{1.6}$ sample pre-treated in H$_2$/Ar shows an increase in intensity 10 and 60 min into ammonia synthesis. The intensity of the white line for Re L$_{III}$-edge XANES is caused by the transition from 2p$_{3/2}$ to 5d, and typically the higher the oxidation state, the higher the white line. It is often regarded as difficult to extract quantitative information from variations in white line intensity for the rhenium L$_{III}$-edge. However it seems clear that the observed change in electronic state of the Re species is not correlated with a similar change in the Co species. Hence, the change seems to occur in a pure Re-phase, and corresponds to the material becoming active for ammonia synthesis. The observed increase in intensity could possibly be an effect of partial oxidation of rhenium. However attempts to fit a Re–N shell for this sample were not successful.

Results from EXAFS refinements (Table 3), show that the Co–Re mixing observed in the sample pre-treated in H$_2$/N$_2$ also remains during ammonia synthesis at 400 °C. After 10 min 2.1 Co–Re distances are fitted at 2.52 Å, and corresponding three Re–Co distances are found at 2.54 Å at the rhenium edge. After 60 min, 2.7 Co–Re distances remain at 2.48 Å, but at the rhenium edge only 0.9 is found at 2.48 Å. This could suggest some reorganisation of the nanostructure of the material and possible segregation of species occurs during reaction. There is a small shortening of the Co–Re/Re–Co average distance. During time on stream, Co–Co is reduced from 5 to 2.7 in multiplicity, and this shell undergoes an elongation from 2.47 to 2.51 Å. Similarly, the Re–Re bond is slightly elongated from 2.66 to 2.70 Å, but remains at 4–5 in average coordination number during the process. Experimental and calculated EXAFS and Fourier Transforms for CoRe$_{1.6}$ following pre-treatment in H$_2$/N$_2$ after 10 and 60 min of reaction time show only minor changes (Figs. 10, 11).

By comparison, experimental and calculated EXAFS spectra of the sample pre-treated in H$_2$/Ar are shown in Figs. 12 and 13, and while there appears to be only small changes at the cobalt edge, the changes in the local rhenium surroundings are more apparent. The lack of Co–Re mixing is still present following the pre-treatment in H$_2$/Ar and during subsequent H$_2$/N$_2$ reaction at 400 °C, with only 4.6 Co–Co distances being fitted at 2.46 Å after 10 min of reaction at the cobalt edge (Fig. 14). After 60 min, the 4.6 Co–Co distances remain at 2.45 Å, but adding a second Co–Re contribution at 2.62 Å with average coordination of 2 improves the fit. However, the uncertainties and specifically the Debye–Waller factor are questionable suggesting
the major contribution is still in fact only Co–Co. At the rhenium edge, the major contribution is still Re–Re with average coordination of 5 during reaction, although the bond elongates from 2.68 to 2.73 Å. A low coordinated (1.2 and 0.7) Re–Co interaction remains at 2.56–2.53 Å during the reaction. Refinements reveal the Co–Re mixing to be irreversible, but as the Re–Co shell is present, some mixing is obtained also after pre-treatment in H₂/Ar. A comparison of the Fourier Transformed EXAFS spectra for the pre-treatment and time on stream is shown in Figures S.6 and S.7.

4 Discussion

4.1 Effect of Pre-treatment on the Phases Formed in Cobalt Rhenium

The in situ XAS results can be summarised as follows: the presence of Co–Co, Co–Re and Re–Re interatomic distances indicate there to be a mixture of phases in the CoRe₁.₆ system during ammonia synthesis, with both Co–Re bimetallic species, and monometallic Re and Co-species being evident. The lack of a second metal–metal
absorption shell in the analysis of both Co K-edge and Re L_{III}-edge EXAFS indicate a high degree of disorder in the major phase. The fraction of bimetallic phase has been calculated after the method of Shibata et al. [32] based on the average coordination number (N) of Re–Co and Co–Re shells and the total coordination number (N_{Re-Re} + N_{Re-Co} + N_{Co-Co} + N_{Co-Re}) to follow the amount of bimetallic phase, as shown in Fig. 15. After pre-treatment in H_2/N_2, the major contribution is the Co–Re bimetallic particles and pure Re-species with some Co-species also present.

After pre-treatment in H_2/Ar the major contribution is Co and Re phases, with only a very small presence of Co–Re bimetallic phase. The higher refined sum of first shell multiplicities for CoRe_{1.6} after pre-treatment in H_2/Ar also indicates a larger particle size for this catalyst. This is in accordance with previous findings on supported Co/Re systems where the role of rhenium is to prevent cobalt agglomeration via promotion of reduction at lower temperatures [10]. Clearly, the latter is true for the CoRe_{1.6} system for pre-treatments in both H_2/N_2 and H_2/Ar, as cobalt
undergoes complete reduction starting at a temperature as low as 250 °C. However, the choice of pre-treatment atmosphere clearly affects the Co–Re alloying process, which is significantly inhibited in H₂/Ar.

4.2 Can In Situ-XAS Reveal Mechanistic Aspects of Cobalt Rhenium During Ammonia Synthesis?

It is assumed that the activity of cobalt rhenium for ammonia synthesis is governed by activation of N₂ by the active phase, and that the activity of the sample pre-treated in H₂/N₂ is superior to that pre-treated in H₂/Ar, even after the lag. From the in situ EXAFS analysis it is clear that the sample pre-treated in H₂/N₂ has better mixture of the Co–Re pair, or consists of more of the bimetallic phase. Significant nitride formation as a result of H₂/N₂ pre-treatment can also be excluded, as a Re–N/Co–N shell was not found in EXAFS refinements at any stage. This is further confirmed by XANES and variations in E₀, which revealed that both Co and Re are completely reduced at all stages. This also correlates with the denitridation of the N₂/H₂ pre-treated CoRe₁.₆ sample measuring the ammonia production in H₂/Ar at 400 °C (Figure S.3). Assuming nitrogen is stored in the material one would expect ammonia production to occur for some time, however this is not observed suggesting a surface reaction mechanism. It should be noted that during fitting procedures, attempts were made to add both a Re–N and Co–N shell around 1.75–1.80 Å to the CoRe₁.₆ at each stage of reaction. For the sample treated in H₂/N₂ addition of such a shell at the rhenium edge lowered the R-factor by up to 10%, but very low multiplicities and/or negative Debye–Waller factors were obtained. Such a reduction of the R-factor was also observed for CoRe₁.₆ for both pre-treatments after 60 min in reaction gas. It is possible that a signal in this lower R-range stems from nitrogen inclusion species (M–Nₖ) in the metal phase or traces of surface nitrogen species (M–Nₘₖ), however we believe the average coordination number could be limited by the particle size of the CoRe₁.₆ phase.

Fig. 14 Average coordination numbers (N) from EXAFS analysis for CoRe₁.₆ during ammonia synthesis after pre-treatment at 600 °C in H₂/N₂ (left) or H₂/Ar (right) at the Co K-edge and the Re L₃-edge

Fig. 15 The fraction of bimetallic phase determined at the Re L₃-edge and Co K-edge
5 Conclusions

A CoRe$_{1.6}$ catalyst active for ammonia production at 400 °C and ambient pressure following a reduction step at 600 °C in either H$_2$/N$_2$ or H$_2$/Ar was investigated in situ using XAS and XRD. Specifically the reduction profiles were targeted depending on pre-treatment mixture and the nature of the active species during ammonia synthesis reaction conditions analysed. While both pre-treatments render the material active, the H$_2$/Ar reduction step results in a 20 min lag-time also observed during in situ measurements. Rhenium XANES reveal a synergistic effect and similar reduction profiles for both pre-treatments, with Co initiating reduction and Re being near completely reduced within the 300–375 °C interval. The only observable difference is in the cobalt XANES, where slight differences are observed between the two pre-treatments as the profile of the H$_2$/Ar pre-treatments initiates at a lower temperature. The two pre-treatments result in the formation of Co–Re bimetallic alloys and pure Co and Re monometallic phases. The bimetallic Co–Re phase is the major component following pre-reduction in H$_2$/N$_2$ while the latter is the major component in the active material following H$_2$/Ar pre-treatment. Clearly the presence of nitrogen in the reduction step promotes a high degree of bimetallic Co–Re mixing confirmed by Co–Re/Re–Co absorption shells at both edges. EXAFS confirms restructuring of the pure Re and Co phases following H$_2$/Ar pre-treatment only after 60 min during time on stream in H$_2$/N$_2$. Formation of the bimetallic Co–Re phase coincides with the observed lag-time both during catalytic experiments and in situ conditions.

Acknowledgements We acknowledge the Norwegian University of Science and Technology and the Norwegian Research Council for grants supporting the Swiss-Norwegian Beamlines (SNBL) and the Anders Jahre fund for promotion of science. The assistance of beamline scientists M. Brunelli and W. van Beek is very much appreciated. We are also grateful to the EPSRC for supporting this work through grants EP/L02537X/1 and EP/J018384/1.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Bion N, Can F, Cook J, Hargreaves JSJ, Hector AL, Levenson W, McFarlane AR, Richard M, Sardar K (2015) Appl Catal A: Gen 504:44
2. Hayashi F, Kitano M, Yokoyama T, Hara M, Hosono H (2014) ChemCatChem 6:1317
3. Jacobsen CJIH, Dahl S, Clausen BS, Bahn S, Logadottir A, Nordskov JK (2001) J Am Chem Soc 123:8404
4. Kojima R, Aika K-I (2001) Appl Catal A: Gen 218:121
5. McKay D, Hargreaves JSJ, Rico JL, Rivera JL, Sun XL (2008) J Solid State Chem 181:325
6. Schloegl R (2003) Angew Chem Int Ed 42:2004
7. Kojima R, Aika K-I (2001) Appl Catal A: Gen 209:317
8. Alexander AM, Hargreaves JSJ, Mitchell C (2013) Top Catal 56:1963
9. McAulay K, Hargreaves JSJ, McFarlane AR, Price DJ, Spencer NA, Bion N, Can F, Richard M, Greer HF, Zhou WZ (2015) Catal Commun 68:53
10. Bazin D, John L (2002) Catal Lett 84:169 182
11. Das TK, Jacobs G, Patterson PM, Conner WA, Li J, Davis BH (2003) Fuel 82:805
12. Jacobs G, Chaney JA, Patterson PM, Das TK, Davis BH (2004) Appl Catal A: Gen 264:203
13. Jacobs G, Ji Y, Davis BH, Cronauer D, Kropf AJ, Marshall CL (2007) Appl Catal A 333:177
14. Ronning M, Tsakoumis NE, Voronov A, Johnsen RE, Norby P, van Beek W, Borg Ø, Ryter E, Holmen A (2010) Catal Today 155:289
15. Ronning M, Nicholson DG, Holmen A (2001) Catal Lett 72:141
16. Koningsberger DC, Mojet BL, van Dorssen GE, Ramaker DE (2000) Top Catal 10:143
17. Voronov A, Tsakoumis NE, Hammer N, van Beek W, Emeric H, Ronning M (2014) Catal Today 229:23
18. Bakken V, Bergene E, Ryter E, Swang O (2010) Catal Lett 135:21
19. Tsakoumis NE, Voronov A, Ronning M, Beek WV, Borg Ø, Ryter E, Holmen A (2012) J Catal 291:138
20. Ravel B, Newville M (2005) J Synchrotron Radiat 12:537
21. Tomic S, Searle BG, Wander A, Harrison NM, Dent AJ, Moselmans JFW, Inglesfield JE, CCLRC Technical Report 2005, Council for the Central Laboratory of the Research Councils, UK
22. Romao CC, Kuhn FE, Herrmann WA (1997) Chem Rev 97:3197
23. Crompton TE, Moselmans JFW, Greaves C (2005) J Mater Chem 15:164
24. Schanke D, Vada S, Blekkan EA, Hilmen AM, Hoff A, Holmen A (1995) J Catal 156:85
25. Steen Ev, Sewell GS, Makhsoxe RA, Micklethwaite C, Manstein H, de Lange M, O’Connor CT (1996) J Catal 162:220
26. Hilmen AM, Schanke D, Holmen A (1996) Catal Lett 38:143
27. Kumar N, Payzant EA, Jothimurugesan K, Spivey JJ (2011) Phys Chem Chem Phys 13:14735
28. Fung AS, Tooley PA, Kelley MJ, Koningsberger DC, Gates BC (1991) J Phys Chem 95:225
29. Sa J, Kartusch C, Makosch M, Paun C, van Bokhoven JA, Kleymenov E, Szlachetko J, Nachtgael M, Manyar HG, Hardacre C (2011) Chem Commun 47:6590
30. Gucci L, Bazin D, Kovács I, Borkó L, Schay Z, Lynch J, Parent P, Lafon C, Steffler G, Koppány Z, Sajo I (2002) Top Catal 20:129
31. Frenkel AI, Machavariani VS, Rubshtein A, Rosenberg Y, Voronel A, Stern EA (2000) Phys Rev B 62:9364
32. Shibata T, Bunker BA, Zhang Z, Meisel D, Vardeman CF, Gezelter JD (2002) J Am Chem Soc 124:11989