

Beamtime Report
SNBL BM01B
01-01-989

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In this work, comparison of the role of activation under $H_2:N_2$ gas mixtures compared to $H_2:Ar$ on the $CoRe_4$ phase was undertaken. In laboratory based studies undertaken in Glasgow it is known that there is an induction period related to the use of the latter mixture whereas in the case of $H_2:N_2$ catalysts display immediate high activity and result in materials which are more active than their $H_2:Ar$ pre-treated analogues. Particular emphasis was placed upon obtaining high quality Co edge data. The ammonia synthesis *in-situ* XAS/XRD experiments was undertaken at both the Re LIII and Co K-edges in pre-treatments of 2% H_2 in N_2 or Argon. This concentration of hydrogen is significantly lower than the reactions conditions initially used during laboratory testing (3:1 $H_2:N_2$), but due to our beamtime being moved up gases could not be ordered in time.

It was initially believed that an amorphous nitride phase, forming in $H_2:N_2$, was accountable for activity in the $CoRe_4$ system, however our *in situ* XAS analysis reveal that the active phase is in fact metallic Re^0 and Co^0 with a high degree of nanoalloying occurring in the system. The N_2/H_2 pre-treatment affects the reducibility of rhenium, but the active phase is quite similar for both protocols. We have strong indications of the $Co(II) \rightarrow Co^0$ step initiating reduction, however our initial studies used a very low concentration of H_2 . Our findings suggest that the microstructure of the nanoalloy changes during reaction conditions, possibly due to cobalt segregation. We also find that the Re-Re coordination numbers are greater in $H_2:N_2$ PT, indicating larger particles forming during this protocol and significantly less bimetallic Co/Re interaction (see Figure).

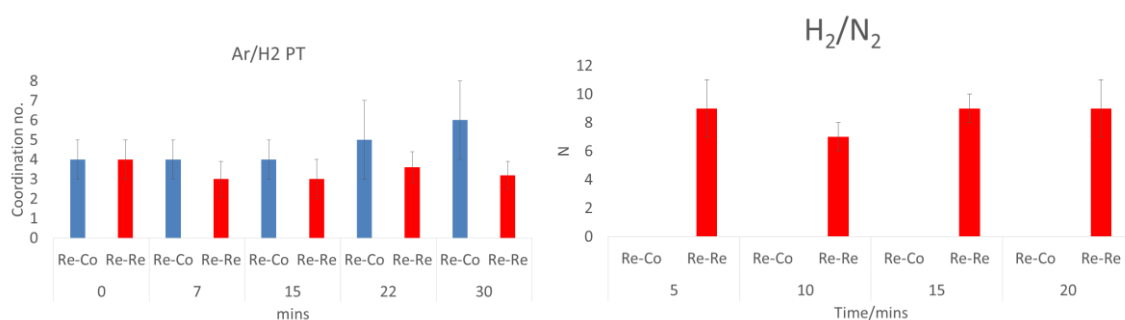


Figure 1: Changes in Re-Co and Re-Re absorption pair coordination numbers in reaction gas following H_2/Ar pre-treatment.

A cycling experiment was undertaken, treating the sample stepwise with gas components, which revealed that $Co^0 \rightarrow Co(II)$ re-oxidation occurs instantly when removing H_2 from the feed (see figure below). Re-introducing H_2 leads to a significant increase in ammonia production (see raw MS data below), possibly due to a very active nitride phase forming. Following this,

catalytic measurements were undertaken with N₂ pre-treatment, which also yields a highly active material.

