

Experiment Report

Potassium K-edge XANES studies to understand the nature of alkali promoters in catalytic ethanol steam reforming (129712)

Alkali promoters, such as potassium, strongly influence catalytic performance in innumerable reactions, including supported Co-catalysed ethanol steam reforming. The location and nature of potassium within these catalysts are not fully understood and change under reaction conditions. Therefore, we performed potassium K-edge XANES of catalysts with different potassium doping levels after successive ethanol steam reforming reaction stages. The aim was to identify potassium dispersion, speciation (i.e. nitrate/carbonate/oxide) and information on its short-range structure.

The measured samples comprised reference materials with structural potassium and potassium-doped surfaces. **Table 1** summarises the measured samples along with their respective energy ranges.

Table 1: Summary of investigated samples.

No.	Sample	Energy range [eV]
1.	KCl	3550-3720
2.	K/zeolit-5	3550-3720
3.	K _x CoO ₂	3550-3720
4.	KAlO ₂	3550-3720
5.	KFeO ₂	3550-3720
6.	K ₂ Fe ₂₂ O ₃₄	3550-3720
7.	O,5K/FeO	3550-3720, 7000-7650
8.	0,5K/Fe ₂ O ₃	3550-3720, 7000-7650
9.	0,5K/Fe ₃ O ₄	3550-3720, 7000-7650
10.	0,5K/Fe ₃ O ₄ (red)	3550-3720, 7000-7650
11.	0,5K/Al ₂ O ₃	3550-3720
12.	0,5K/ZrO ₂	—
13.	0,5K/CeO ₂	3550-3720
14.	0,5K10Fe/Al ₂ O ₃	3550-3720, 7000-7650
15.	0,5K10Fe/ZrO ₂	3550-3720, 7000-7650

16.	0,5K10Fe/ZrO ₂ (red)	3550-3720, 7000-7650
17.	0,5K10Fe/CeO ₂	3550-3720, 7000-7650
18.	0,5K10Fe/CeO ₂ (red)	3550-3720, 7000-7650
19.	0,1KNO ₃ +Co ₃ O ₄	3550-3720, 7650-8200
20.	0,1K/Co ₃ O ₄	3550-3720, 7650-8000
21.	0,1K/Co ₃ O ₄ (red)	3550-3720, 7650-8000
22.	0,1K/Co ₃ O ₄ +20 min ESR	3550-3720, 7650-8000
23.	0,1K/Co ₃ O ₄ +40 min ESR	3550-3720
24.	0,1K/Co ₃ O ₄ +60 min ESR	3550-3720
25.	0,1K/Co ₃ O ₄ +120 min ESR	3550-3720
26.	0,5KNO ₃ +Co ₃ O ₄	3550-3720, 7650-8200
27.	0,5K/Co ₃ O ₄	3550-3720, 7650-8000
28.	0,5K/Co ₃ O ₄ (red)	3550-3720
29.	0,5K/Co ₃ O ₄ +20 min ESR	3550-3720
30.	0,5K/Co ₃ O ₄ +40 min ESR	3550-3720
31.	0,5K/Co ₃ O ₄ +60 min ESR	3550-3720, 7650-8000
32.	0,5K/Co ₃ O ₄ +120 min ESR	3550-3720

The measurements consisted of mounting the samples on the measurement holder without any on-site preparation. All planned samples and measurements were performed according to the experimental procedure.

Figure 1 presents the key measured spectra of the investigated samples, derived from the ethanol steam reforming reactor after different reaction times, with 0.1 and 0.5 wt.% potassium loading, along with iron-based reference materials and other reference materials. We observed a clear difference in the potassium structural and chemical environments between the samples at different stages of preparation before the catalytic test and after different times on stream (Figure 1A and 1 B). One unforeseen problem that appeared during the spectral analysis was the presence of a fine structure characteristic of the KCl structure, even in samples that should not have contained any chloride ions and that were prepared with due diligence to exclude external contamination.

The results are under evaluation and have not been included in a publication draft so far.

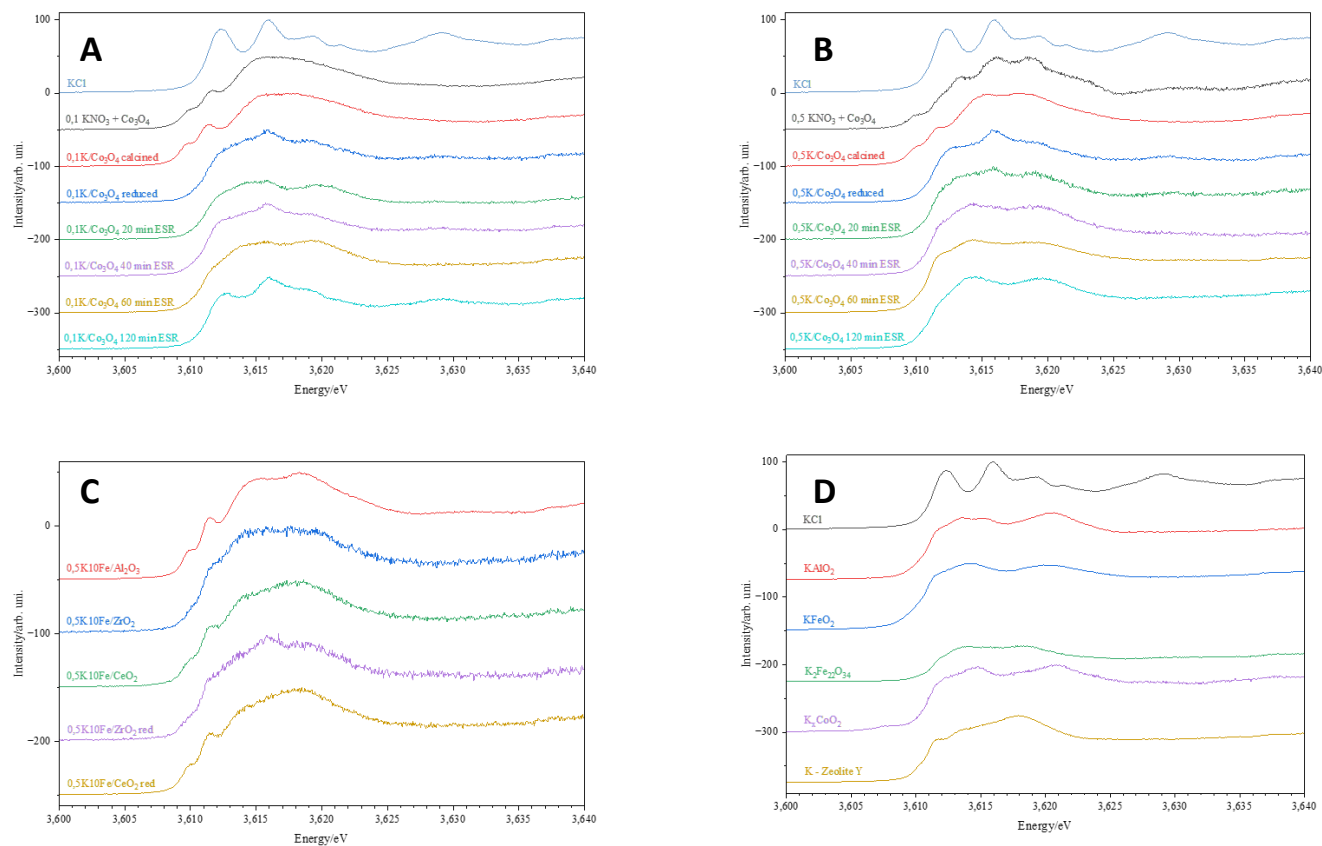


Figure 1 K-edge XANES spectra of the investigated samples derived from the ethanol steam reforming reactor after different times of reaction with A) 0.1 wt.% and B) 0.5 wt.% potassium loading, along with C) iron-based reference materials and D) other reference materials.