Steam reforming of ethanol over Co$_3$O$_4$–Fe$_2$O$_3$ mixed oxides

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**Abstract**

Co$_3$O$_4$, Fe$_2$O$_3$ and a mixture of the two oxides Co–Fe (molar ratio of Co$_3$O$_4$/Fe$_2$O$_3$ = 0.67 and atomic ratio of Co/Fe = 1) were prepared by the calcination of cobalt oxalate and/or iron oxalate salts at 500 °C for 2 h in static air using water as a solvent/dispersing agent. The catalysts were studied in the steam reforming of ethanol to investigate the effect of the partial substitution of Co$_3$O$_4$ with Fe$_2$O$_3$ on the catalytic behaviour. The reforming activity over Fe$_2$O$_3$, while initially high, underwent fast deactivation. In comparison, over the Co–Fe catalyst both the H$_2$ yield and stability were higher than that found over the pure Co$_3$O$_4$ or Fe$_2$O$_3$ catalysts. DRIFTS-MS studies under the reaction feed highlighted that the Co–Fe catalyst had increased amounts of adsorbed OH/water; similar to Fe$_2$O$_3$. Increasing the amount of reactive species (water/OH species) adsorbed on the Co–Fe catalyst surface is proposed to facilitate the steam reforming reaction rather than decomposition reactions reducing by-product formation and providing a higher H$_2$ yield.

1. Introduction

Currently, there is a significant drive to move away from the use of non-renewable fossil fuels, i.e. petroleum, natural gas and coal, for energy production due to the associated environmental problems such as the production of air pollutants and greenhouse gas emissions [1]. One of the most attractive options to replace fossil fuel derived hydrocarbons is to use hydrogen coupled with, for example, fuel cell technology. Although significant amounts of hydrogen are produced by the steam reforming of natural gas, the production of hydrogen from alternative, sustainable sources is highly desirable with one such process being the steam reforming of bioethanol which is produced via biomass fermentation processes. Due to the potential of this process, the steam reforming of ethanol to produce hydrogen has been widely investigated [2,3].

A wide range of catalysts have been studied for the steam reforming of ethanol including solid oxides, transition metals and noble metals as well as multi metallic catalysts [3]. Although noble metals exhibit high activity and stability towards ethanol steam reforming (ESR), their use is undesirable due to their high cost. For non-noble metal catalysts, Ni and Co have been reported to exhibit the best performance for ethanol steam reforming favouring C–C bond cleavage and a high selectivity for H$_2$ production [1]. Co-based catalysts have been actively researched for the process as less methane and...
more hydrogen is generated compared with Ni-based catalysts. However, the deactivation of Co-based catalysts as a result of sintering and/or carbon deposition over the catalyst surface has hindered the wider use of these catalysts for steam reforming reactions [4]. Consequently, most of the studies investigating cobalt catalysts for ethanol steam reforming have been in the area of improving their activity and, importantly, stability while concomitantly reducing the formation of undesired by-products, in particular coke.

The addition of promoters such as noble metals [5,6], Ni, Cu, Na, Mn, Cr and Fe [4,7–14] to Co catalysts has been investigated for their effect on the activity and stability for ethanol steam reforming. In particular, promotion with Fe has been reported to improve activity and H2 yield over Co/Z-Al2O3 and Co/SrTiO3 catalysts [4,14] and Co/ZnO supported catalysts [8]. In the latter, Fe promoted Co/ZnO also exhibited improved water gas shift (WGS) activity at low temperatures. Unsup-ported CoOx catalysts have also been reported to be active for steam reforming of ethanol [11,15–18] with 1% Fe doped onto CoOx also showing a promoting effect with lower CH4 and CO formed compared to CoOx. In most reports the addition of Fe to Co catalysts enhances the dehydrogenation of ethanol and increases the transformation of acetaldehyde selectively without promoting formation of by-products, such as methane and coke [4,12,14,16]. The promoting effect of Fe has been attributed to the formation of Co–Fe solid solutions [11], Co–Fe alloys [8] and close contact between the Co and Fe (no new phases detected) [14]. The interaction between the Co and Fe in the catalysts is likely related to the preparation method with solid solutions and alloys formed from co-precipitation and co-impregnation methods respectively while close contact was reported for sequential impregnation of Fe onto Co/ZnO catalyst.

In this study, the catalysts have been prepared by a simple, one pot synthesis procedure producing a mixed Co–Fe oxide catalyst (1:1 atomic ratio) following decomposition of the oxalate precursors in air. No solid solution formation is expected from this method [19] hence the promoting effect is expected to result from close contact between separate oxide phases. Contact between the phases is expected to be enhanced with partial substitution of Co with Fe as opposed to doping with Fe. As a reference, a physical mixture of CoOx and FeOx (Co–Fe-Physical) was prepared from grinding together the individual oxides and this catalyst was tested under the same reaction conditions.

2. Experimental

2.1. Catalyst preparation

Pure cobalt oxide (Co3O4) and iron oxide (Fe2O3) samples were prepared by the calcination of cobalt (II) oxalate dihydrate, Co(C2O4)·2H2O (Sigma–Aldrich) and iron (II) oxalate dihydrate, Fe(C2O4)·2H2O (Sigma–Aldrich), respectively. The oxalate samples were calcined for 2 h in static air at 500 °C in a muffle furnace after ramping from room temperature at 5 °C min−1.

The mixed FeOx and CoOx oxide sample (Co–Fe) was prepared using 11.3 g iron (II) oxalate dihydrate, Fe(C2O4)·2H2O (Sigma–Aldrich) and 11.4 g cobalt (II) oxalate dihydrate, Co(C2O4)·2H2O (Sigma–Aldrich) dissolved in approximately 10 cm3 doubly deionised (18 MΩ) water at room temperature until a homogeneous paste was obtained. This paste was dried at 100 °C in an oven for 20 h before being calcined in static air at 500 °C for 2 h after ramping from room temperature at 5 °C min−1. The catalyst obtained contained 40 mol % CoOx + 60 mol% FeOx which gives an atomic ratio of Co/Fe = 1. The physical mixture (Co–Fe-Physical) with the same composition as the Co–Fe sample was prepared by grinding together the calcined CoOx and FeOx.

2.2. Characterization techniques

X-ray diffraction was carried out using a PANanalytical X’Pert Pro X-ray diffractometer equipped with a Cu Kα, X-ray source and the X-ray detector set to 40 kV and 40 mA. Under ambient conditions, a Spinaker PW3064 sample stage was used. Identification of the diffraction peaks was undertaken using the PCPDFWIN database.

Temperature programmed reduction (TPR) experiments were performed in a fixed-bed quartz U-tube reactor using 20 mg of the fresh catalyst. The sample was exposed to 5% H2/Ar (20 cm3 min−1) and heated from room temperature to 1000 °C at a heating rate of 15 °C min−1 and hydrogen consumption (m/z: 2) was monitored during the temperature ramp using a Hiden Analytical HPK20 quadrupole mass spectrometer with a capillary inlet.

Temperature programmed oxidation (TPO) measurements were performed to assess the amount of carbon deposited on the catalysts after 2 h of reaction. 50 mg of the used catalyst was ramped from 30 to 800 °C at a heating rate of 10 °C min−1 in 5% O2/Ar (50 cm3 min−1) while monitoring the evolution of carbon dioxide (m/z: 44) and carbon monoxide (m/z: 28) using a Hiden Analytical HPK20 quadrupole mass spectrometer with a capillary inlet.

Temperature programmed desorption of ammonia (NH3- TPD) was obtained from samples (100 mg) pre-reduced using 40 cm3 min−1 of 25% H2/Ar at 400 °C for 1 h. After cooling to 40 °C in Ar (30 cm3 min−1), the samples were exposed to 0.4% NH3/Ar (50 cm3 min−1) for 2 h and then the sample was flushed with Ar (50 cm3 min−1) for 30 min. The NH3-TPD measurements were carried out with a heating rate of 10 °C min−1 from 40 to 800 °C under a flow of Ar (50 cm3 min−1). Desorption of ammonia (m/z: 16) was monitored using a Hiden Analytical HPK20 quadrupole mass spectrometer with a capillary inlet.

BET surface area measurements were performed at liquid nitrogen temperature using an automatic ASAP-2010 sorptometer (Micromeritics). The catalyst samples were outgassed at 200 °C for 1 h prior to each measurement.

Transmission electron microscopy (Philips TECNAI F20 Transmission electron microscope) at 200 kV was performed to analyse the morphology of the samples. The catalysts were suspended following ultrasonic agitation for ~2 min in ethanol and the suspension then deposited onto copper grids before the ethanol was evaporated. Elemental analysis of catalyst samples was carried out using EDX on STEM imaging.

Raman analysis, of the fresh catalysts and used catalysts after 15 h of reaction at 500 °C under the ESR feed, was carried out using an Avalon Ramanstation fiberoptic system with a
785 nm laser; spectra were accumulated for 2 min with a resolution of 2 cm\(^{-1}\).

2.3. **Catalytic reaction**

Before exposure to the reaction feed, the catalyst was heated from room temperature to 400 °C at a heating rate of 10 °C min\(^{-1}\); in Ar at 60 cm\(^3\) min\(^{-1}\) followed by reduction for 1 h at 400 °C in 25% H\(_2\)/Ar at 80 cm\(^3\) min\(^{-1}\). Following the reduction, the feed was changed to Ar (60 cm\(^3\) min\(^{-1}\)) and the temperature ramped from 400 to 500 °C at a heating rate of 10 °C min\(^{-1}\). At 500 °C, the water/ethanol/Kr/Ar feed (mole ratio of 1/3/0.6/11.4) at 80 cm\(^3\) min\(^{-1}\) was introduced to the catalyst bed (200 mg of catalyst diluted with 500 mg SiC) held in a quartz reactor (13 mm internal diameter) under atmospheric pressure; Kr was added to the feed as an internal standard for determination of the carbon balance. The liquid water–ethanol mixture was delivered by a syringe-free liquid pump from Valco Instruments Co. Inc. into an evaporator heated at 100 °C. The output gas mixture was analysed on-line by gas chromatography (Clarus 500, PerkinElmer) with TCD and FID (coupled with a methaniser) detectors.

The stoichiometric ethanol steam reforming reaction is shown below (Eq. (1)):

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2
\]

(1)

The hydrogen yield (H\(_2\) Y %), ethanol conversion (Ethanol conv. %) and selectivity of carbon-containing products (S %) are defined as:

H\(_2\) Y % = \((\text{moles of hydrogen produced} \times 100)/(6 \times \text{moles of ethanol fed})\)

Ethanol conv. % = \((\text{moles of ethanol converted} \times 100)/(\text{moles of ethanol fed})\)

S % of product A = \((N \times \text{moles of A produced} \times 100)/(2 \times \text{moles of ethanol converted})\)

where \(N\) is the number of carbon atoms in the product A.

2.4. **Diffuse reflectance infra-red Fourier transform spectroscopy-mass spectroscopy analysis (DRIFTS-MS)**

The DRIFTS setup consisted of an in-situ high temperature diffuse reflectance IR cell (Spectra-Tech) fitted with ZnSe windows which was modified in house to behave as a plug flow reactor [20]. All DRIFT spectra were recorded using a Bruker Vertex 70 spectrometer using an average of 256 scans and a resolution of 4 cm\(^{-1}\). Analysis of the gas from the outlet of the DRIFTS cell was performed with a Hiden Analytical HPR20 quadrupole mass spectrometer (QMS) with a capillary inlet. Reagents and products were monitored by the following \(m/z\) values: 2 (for H\(_2\)), 15 (for CH\(_4\)), 18 (for H\(_2\)O), 26 and 27 (for ethylene), 28 (for CO\(_2\)), 29 (for acetaldehyde), 31 (for ethanol), 43 (for acetone) and 44 (for CO\(_2\)).

Prior to reaction, the catalyst (~50 mg) was pre-reduced under 25% H\(_2\)/Ar (20 cm\(^3\) min\(^{-1}\)) for 1 h at 400 °C. After reduction, the temperature was lowered to 100 °C and the reduced catalyst taken as a background spectrum. A gas feed of 20 cm\(^3\) min\(^{-1}\) containing ethanol/water/Kr/Ar (mole ratio of 1/3/0.6/11.4) was fed over the catalyst at 100 °C for 1 h thereafter the temperature was increased to 500 °C at 10 °C min\(^{-1}\). The catalyst was held at 500 °C for 1 h under the reaction feed. The liquid water–ethanol-inert mixture was delivered by a 3-way mixing valve and evaporator (Bronkhorst) with the evaporation temperature held at 100 °C.

3. **Results and discussion**

3.1. **Catalytic behaviour**

Co\(_3\)O\(_4\), Fe\(_2\)O\(_3\), Co–Fe-physical and Co–Fe samples were tested for activity in the steam reforming of ethanol. Fig. 1 shows the %ethanol conversion and %H\(_2\) yield and Table 1 summarises the %selectivity to carbon-containing compounds as a function of time on stream at 500 °C. Fe\(_2\)O\(_3\) exhibited some initial activity for the steam reforming of ethanol at 500 °C with a H\(_2\) yield of 60% and selectivity to CO\(_2\) of 36.1% with CO (39.5%) and undetected carbon (23.1%) also formed. The Fe\(_2\)O\(_3\) catalyst underwent rapid deactivation with an initial ethanol conversion of 90% after 0.75 h on stream dropping to 10% after 6 h of reaction. While initial activity for the steam reforming of ethanol (H\(_2\) and CO\(_2\) formation) was observed, with time on stream, the H\(_2\) yield decreased more rapidly than the ethanol conversion with an increase in the selectivity towards acetaldehyde. In addition, no methane was observed over this

![Fig. 1 – %Ethanol conversion and % hydrogen yield as a function of reaction time in ethanol steam reforming over Co\(_3\)O\(_4\) ( ), Co–Fe-physical (△), Co–Fe (□) and Fe\(_2\)O\(_3\) (×) at 500 °C, ethanol:water = 1:3, 200 mg catalyst and a total flow of 80 cm\(^3\) min\(^{-1}\).](image-url)
catalyst indicating that little acetaldehyde (or ethanol) decomposition occurred.

Co₃O₄ was more active than Fe₂O₃ with a H₂ yield of 73% at 100% conversion of ethanol. This catalyst also deactivated with time on stream although at a slower rate than that found for Fe₂O₃. The %selectivity towards C₁ vs C₂ products over the Co₃O₄ catalyst demonstrated that this catalyst has higher activity for C–C bond breaking compared with Fe₂O₃ with initial %selectivity to CO₂, CO and CH₄ considerable higher than acetaldehyde with no ethylene formation observed at 500 °C. While no ethylene in the gas phase was observed over Co₃O₄, the selectivity to undetected carbon was higher than over the Fe₂O₃ catalyst which suggests that over the Co₃O₄ catalyst coke deposition could be the cause of the deactivation.

The physical mixture of Co₃O₄ and Fe₂O₃, while also exhibiting initial complete conversion of ethanol (as for the Co₃O₄ catalyst) importantly showed a lower selectivity to undetected carbon compared with either of the two pure oxides, in addition a decrease in CH₄ formation was also observed. Ethanol conversion over the physically mixed catalyst decreased at a slower rate compared to over the Co₃O₄ catalyst while the %H₂ yield was found to decrease at a similar rate over both catalysts. As there was no promotional effect on the pathways for H₂ production from physically mixing the two oxides, this suggests that these reactions occur over the Co₃O₄. However, contact between the two oxides did provide a synergetic effect in terms of reducing by-product formation (both methane and coke).

The Co–Fe sample, which was prepared from static air calcination of an aqueous paste of Co and Fe oxalate precursors, exhibited the highest hydrogen yield (80%) and greater selectivity to CO₂ and CO compared with the pure oxides and the physical mixture. Addition of Fe₂O₃ to the Co₃O₄ catalyst was also observed to lower the selectivity to methane and undetected carbon by-products over and above the enhancement found for the physical mixture. The average value for the selectivity to undetected carbon was 8.2% for Co–Fe compared with 28.5% for Co₃O₄ and 14.3% for the physical mixture.

A comparison of the ethanol steam reforming activity over Co/Al₂O₃, Fe/Al₂O₃ and a physical mixture of the two catalysts was reported by Kazama et al. [14]. Therein, it was shown that Co/Al₂O₃ was more active with respect to ethanol conversion and more stable and had higher H₂ and CO₂ yields compared with the Fe/Al₂O₃ catalyst which exhibited low ethanol conversion and low H₂ yield with fast deactivation over 3 h of reaction at 550 °C. This is comparable to the results obtained over the Fe₂O₃ catalyst in this study where fast deactivation was observed. As found for the unsupported Fe₂O₃, the supported Fe catalyst also showed increased selectivity to acetaldehyde as the catalyst deactivated. In contrast with the present study, the physical mixture of Co/Al₂O₃ and Fe/Al₂O₃ exhibited higher ethanol conversion and higher H₂ yields compared with the individual Co/Al₂O₃ and Fe/Al₂O₃ catalysts showing a clear promotion of Fe on the activity of the Co-based catalyst [14].

Promotion of Co₃O₄ catalysts with Fe has also been reported by de la Pena et al. [11]. Using a reaction temperature of 400 °C and an ethanol: water ratio of 1:6, Co₃O₄ doped with 1 wt% Fe and Fe incorporation into the Co₃O₄ spinel structure forming a solid solution (FeₓCo₃₋ₓO₄ with 0 < x < 0.60) exhibited enhanced H₂ selectivities and low CO and CH₄ formation. The concentration of Fe incorporated into the solid solution affected the activity and selectivity of the reaction.

<table>
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<th>CO</th>
<th>CH₄</th>
<th>CH₂CH₂</th>
<th>CH₃CHO</th>
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Table 1 – %Selectivity to carbon-containing products in the ethanol steam reforming over the Fe₂O₃, Co₃O₄, Co–Fe–Physical and Co–Fe catalysts as a function of time on stream at 500 °C, ethanol:water = 1:3, 200 mg catalyst and a total flow of 80 cm³ min⁻¹.
with Fe ≥ 0.15 showing lower ethanol conversion and higher selectivities towards acetaldehyde. High selectivity for acetaldehyde was also observed over pure Fe/Al₂O₃ [14] and Fe₂O₃ catalysts in this work. Of interest is that in the catalyst preparation [11], NaOH was used as the precipitating agent with appreciable amounts (compared with the Fe content) of Na detected on the catalysts. Na has been reported to be a promoter for Co catalysts reducing coke formation possibly having an additional effect on these catalysts [21].

### 3.2. Characterization of catalysts

Fig. 2 shows the XRD diffraction patterns of Co₃O₄, Fe₂O₃, Co–Fe-Physical and Co–Fe samples. The Co₃O₄ sample is consistent with the cubic structure of Co₃O₄ (PDF-#: 76-1802) [22] while the Fe₂O₃ sample shows hematite to be the main crystalline phase (PDF-#: 89-0599) [23]. Both the physical mixture (Co–Fe-Physical) and the mixed oxide sample Co–Fe, contained peaks due to both Fe₂O₃ hematite and cubic Co₃O₄. No other phases/shift in peak positions were observed by XRD in this study which suggests that no extensive solid solution was formed between the two oxides as a result of this preparation method. However, low concentration of solid solution formation cannot be discounted as for a Co/ZnO catalyst promoted with 1% Fe, XRD did not identify any different phases yet cobalt–iron alloy formation was observed from HRTEM and EELS techniques [7, 8]. However, Gabal et al. characterised the cobalt and iron phases in a cobalt–iron oxalate mixture with calcination temperature and showed that, after the initial dehydration, decomposition of Fe₃O₄·2H₂O was followed by decomposition of Co₃O₄·2H₂O to form Co₃O₄–Fe₂O₃ by 265 °C with Co₃O₄–Fe₂O₃ being thermally stable up to 920 °C. Of relevance to this study, a solid solution, CoFe₂O₄, was only detected at calcination temperatures of 1000 °C [19], therefore, using the preparation method described, herein (mixing the respective oxalates in water at room temperature followed by calcination in air at 500 °C) a solid solution is not expected to form between Co and Fe.

Fig. 3 shows TEM images of Co₃O₄, Fe₂O₃, Co–Fe-Physical and Co–Fe samples. The average particle size of the Co₃O₄ catalyst (Fig. 3A) was 10–50 nm which is smaller than that of the Fe₂O₃ catalyst, 50–150 nm (Fig. 3B). The size difference between the particles is clear in the micrograph of the Co–Fe Physical sample (Fig. 3C), where the size of the individual Fe₂O₃ and Co₃O₄ particles in the physical mixture are comparable to that measured for the pure oxide samples despite the catalyst being prepared by grinding together the two oxides. EDX analysis of the particles in the physical mixture confirmed that the larger particles contained only Fe and the smaller particles contained only Co. For the Co–Fe sample, (Fig. 3D) the particle size was in the range of 10–50 nm, which was similar to the particle size of the pure Co₃O₄ catalyst.

However, it was not possible to distinguish (by EDX) separate particles of Fe₂O₃ or Co₃O₄ in contrast with the physical mixture. This demonstrates that while separate phases are shown by the XRD, the two phases are in intimate contact within a given particle rather than the oxides forming separate distinct particles. These results indicate that grinding the two oxides together as in the Co–Fe-Physical sample, while providing some improvement in selectivity, does not form the same degree of contact between the two oxides as observed in the Co–Fe sample which results in a more significant reduction in by-product formation. In addition to greater contact between the oxides in the Co–Fe sample, the surface area was also increased substantially from 18 m² g⁻¹ for Co₃O₄ and 13.5 m² g⁻¹ for Fe₂O₃ to 29.3 m² g⁻¹ for the Co–Fe catalyst.

Raman spectra of the fresh Co₃O₄ and Fe₂O₃ catalysts show characteristic peaks due to both oxides with bands at 484, 522, 612 cm⁻¹ for Co₃O₄ and 292, 410, 493 and 612 cm⁻¹ for Fe₂O₃ [25, 26] (Fig. 4). The Raman spectrum of the Co–Fe fresh catalyst showed peaks of Co₃O₄ with only very weak Fe₂O₃ features at 292 cm⁻¹ observed which suggests that the Co₃O₄ could be covering the Fe phase in the Co–Fe catalyst. This is consistent with the observation by Casanovas et al. wherein, using HRTEM, they observed that in promoted Co/ZnO catalysts (1% Fe, Na, Cu, Cr or Ni), the Co-alloy particles were sometimes covered by Co₃O₄ [8].

The catalysts were pre-reduced in-situ in the catalytic testing prior to exposure to the reaction feed. To study the effect of the reduction on the oxides, temperature programmed reduction (TPR) was performed. Fig. 5 shows the TPR profiles for the Co₃O₄, Fe₂O₃ and Co–Fe catalysts. The reduction profile of Co₃O₄ contained two main peaks, one at 360 °C corresponding to the reduction of Co³⁺ to Co²⁺ and another at 473 °C corresponding to the reduction of Co³⁺ to Co⁰ [27]. The reduction profile of Fe₂O₃ has three peaks, the first at 417 °C, the second at 636 °C and the third broad peak at ~835 °C. The first peak corresponds to the reduction of Fe₂O₃ to Fe₃O₄ while the second and the third peaks correspond to the transformation of Fe₃O₄ to Fe⁰ which proceeds through FeO [28].

The reduction profile of the mixture Co–Fe, showed three main peaks at 350 °C, 460 °C and 660 °C with a small feature around 535 °C and a shoulder around 740 °C. The first peak corresponds to the reduction of Co³⁺ to Co²⁺, which occurs at the same temperature as in the Co₃O₄ catalyst, while the other peaks are associated with overlapping features from the reduction of Co²⁺ to Co⁰, Fe₃O₄ to Fe₃O₄ and Fe₃O₄ to Fe⁰. The presence of Fe in the Co₃O₄ catalyst had little effect on the reduction temperature of Co species in contrast to supported Co/Al₂O₃ catalysts where addition of Fe enhanced Co reducibility [12]. In the case of the Co–Fe catalyst, TPR analysis showed that the reduction process was completed by ~775 °C.

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**Fig. 2** – XRD patterns of Fe₂O₃ (A), Co–Fe-physical (B), Co–Fe (C) and Co₃O₄ (D).
which is significantly lower than that found for pure Fe₂O₃ (985 °C) indicating a notable improvement in the reducibility of Fe₂O₃ in the mixture compared to the pure oxide. Increased reducibility of Co₃O₄ in the mixed sample aiding the higher temperature reduction of Fe₂O₃ to Fe metal has also been observed by Homs et al. [11] in iron promoted cobalt-based catalysts. However, TPR analysis of the Co–Fe catalyst reduction show that by 400 °C (the temperature used to activate catalyst prior to catalytic testing), the Co will be a mixture of Co₃O₄, CoO and, possibly, Co metal.

Characterisation of promoted Co catalysts suggests that addition of Fe improves the reduction of Co₃O₄ to Co⁰ [12] and thus allows the catalyst to maintain an optimal balance between Co⁰ and Co₃O₄ with Co₃O₄ reported to be the active phase for ethanol dehydrogenation and Co⁰ for acetaldehyde reforming [8,16,29]. However, both CoO and Co⁰ have been reported to co-exist in active ethanol steam reforming catalysts for both unsupported [16,17] and supported Co₃O₄ catalysts [30] with ease of exchange between metallic and oxidised cobalt suggested to be key for the activity. Following reduction at 400 °C, Fe would be present as Fe₂O₃ (possibly some Fe₃O₄); however, under the feed conditions, further reduction of Fe (and Co) could occur [31].

With rapid deactivation of the catalysts observed and the formation of undetected carbon, temperature programmed oxidation (TPO) of the catalysts after 2 h on stream at 500 °C was carried out (Fig. 5). Analysis of the CO₂ peak areas shows that the highest amount of CO₂ was formed from Co₃O₄ in comparison with the pure Fe₂O₃. The CO₂ peak positions in the TPO profiles of Co₃O₄ and Co–Fe are similar which suggests that the nature of the coke formed over these samples is not altered by the presence of Fe in Co–Fe. However, after 2 h of reaction, the amount of deposited coke on the Co₃O₄ is approximately three times higher that found on the Co–Fe sample which correlates well with the decrease in the undetected carbon in Table 1 and the relative deactivation profiles of the two catalysts. It should be noted that the Fe₂O₃ catalyst had the least amount of coke deposited and the peaks in the TPO profile occur at lower temperatures than found in the cobalt containing samples, i.e. showing the presence of more easily oxidisable coke.

Raman spectra of the used catalysts (recorded ex-situ after 15 h of reaction) are shown in Fig. 6. The used Co₃O₄ catalyst, showed no bands due to cobalt oxide species after reaction; however, two new bands at 1596 and 1310 cm⁻¹ were observed and assigned to stretching mode of sp² carbon of ordered graphitic carbon (G band) and disordered carbon species (D band), respectively [10,32,33]. The spectrum of the Co–Fe used catalyst had the same graphitic bands (position and intensity) as observed over the Co₃O₄ catalyst which suggests that coke formation occurs on cobalt species rather than on Fe. The lack

Fig. 4 – Raman spectra of fresh catalysts Fe₂O₃ (A), Co–Fe (B) and Co₃O₄ (C); bands due to Fe₂O₃ (●) and Co₃O₄ (○).
of bands due to cobalt oxide species suggest that either the coke is covering the cobalt or that the Co is reduced to Co$^0$ during reaction.

The Raman spectrum of the used Fe$_2$O$_3$ catalyst did not exhibit any bands due to Fe$_2$O$_3$ and no new bands were observed which suggests that any carbon laydown over this catalyst (undetected carbon in Table 1) is not graphitic but more likely from adsorbed ethoxy/acetate/carbonate species (see DRIFT spectra in Section 3.3). The Raman spectrum of the used Fe$_2$O$_3$ catalyst and the weak TPO profile suggests other deactivation processes to be the cause of the very rapid loss of activity observed over Fe$_2$O$_3$.

While Raman spectroscopy showed the same nature and amount of carbon formation on Co$_3$O$_4$ and Co–Fe samples, TPO analysis (and the amount of undetected carbon) showed the Co–Fe samples to have reduced coke formation compared with the Co$_3$O$_4$ catalyst. NH$_3$-TPD was performed to assess the concentration and strength of acidic sites on these catalysts. While NH$_3$-TPD can distinguish sites by sorption strength, it cannot differentiate between Brønsted and Lewis-acid sites. In supported catalysts, basic supports are preferred in ethanol steam reforming as they do not favour ethanol dehydration to ethylene. According to Tanabe et al. [35] the strength of solid acid sites within TPD profiles can be classified by the temperature at which NH$_3$ desorbs with NH$_3$ desorbing from weak acid sites between 120 and 300°C, moderate acid sites between 300 and 500°C and strong acid sites between 500 and 650°C.

NH$_3$-TPD profiles for Co$_3$O$_4$, Fe$_2$O$_3$ and Co–Fe fresh catalyst after reduction for 1 h at 400°C are reported in Fig. 5. The NH$_3$-TPD profile of Fe$_2$O$_3$ exhibited one broad peak (40–340°C) with a maximum at 200°C. The broad nature of the peak indicates the presence of sites with a range of acid strength on this catalyst. For both Co$_3$O$_4$ and Co–Fe, the TPD profile contains two peaks, in the case of Co$_3$O$_4$ the peaks were at 104°C and 240°C, while in the case of Co–Fe the peaks were at 104°C and 390°C (with a third small feature at 240°C) indicating the presence of two well defined acid sites in each case. The weak acid site corresponding to the peak at 104°C is common to both samples and could be responsible for formation of the graphitic coke as detected by Raman spectroscopy. Following addition of Fe to the sample, the second peak at 240°C which is observed over Co$_3$O$_4$ is depleted with the formation of new sites of moderate acidic strength (peak at 390°C). The nature of the acid sites change upon addition of Fe$_2$O$_3$ to Co$_3$O$_4$ and consideration of the total acid site concentration from the area under the peaks, showed that the concentration of acid sites was greatest over Fe$_2$O$_3$ then Co–Fe and then Co$_3$O$_4$. Since the total number of acid sites does not follow the trend in the deactivation rate/amount of coke deposited on the catalyst, this suggests that specific sites are active for coke formation over the Co$_3$O$_4$ catalyst. The reduction of the peak at 240°C following incorporation of Fe and lower coke deposition over this catalyst, suggests that loss of these acidic sites on the Co–Fe catalyst could be responsible for the reduced carbon laydown observed.

3.3. DRIFTS-MS study

The reaction network in the steam reforming of ethanol is complex with many reactions leading to intermediates and side products, such as ethylene, acetaldheyde, acetone, methane, ethane, and coke [21]. Co$_3$O$_4$, Fe$_2$O$_3$ and the Co–Fe catalysts exhibit differing activities and product selectivities for the steam reforming of ethanol with the Co–Fe catalyst exhibiting higher hydrogen yield with lower CH$_4$ and lower coke formation when compare with the Co$_3$O$_4$ catalyst (Table 1 and Fig. 1). In-situ DRIFTS-MS during a temperature ramp to 500°C under the steam reforming feed over Co$_3$O$_4$, Fe$_2$O$_3$ and the Co–Fe samples was performed to probe the evolution of gas phase species whilst monitoring the surface adsorbed species to investigate the promotional effect of Fe$_2$O$_3$ on Co$_3$O$_4$.

For all three catalysts, 100% conversion of ethanol was achieved at 500°C which is comparable to the results obtained in a plug flow reactor (Table 1 and Fig. 1) [36]. However, in the low temperature region (100–400°C) the MS profiles over the three catalysts showed the formation of hydrogen (Fig. 7B), carbon oxides (Fig. 7C, D), ethylene (Fig. 7E), acetaldheyde (Fig. 7F), methane (Fig. 7G) and acetone (Fig. 7H) with the
relative proportions and temperature at which products/intermediates were formed found to vary with the catalyst. Conversion of ethanol begins at a lower temperature over Co$_3$O$_4$, $\sim$150 °C compared with $\sim$280 °C for Fe$_2$O$_3$ and $\sim$220 °C for Co–Fe (Fig. 7A). Initial low temperature formation of ethylene over Fe$_2$O$_3$ (upon switching to the feed at 100 °C) could be the cause of the initial higher ethanol conversion observed which recovers as the temperature increased.

While ethanol conversion begins at a lower temperature over Co$_3$O$_4$, between 400 and 500 °C the ethanol conversion profile changes exhibiting slower conversion at higher temperatures; this is not observed for Fe$_2$O$_3$ or the Co–Fe catalyst. The two stages of conversion of ethanol over Co$_3$O$_4$ is also evident in the product profiles which exhibit second peaks at higher temperatures.

Over Co-based catalysts, the ethanol steam reforming reaction pathway has been proposed to occur via the dehydrogenation of ethanol to acetaldehyde (Eq. (2)) followed by reforming of acetaldehyde in combination with the WGS reaction to form CO$_2$ + H$_2$ (Eq. (3)) with acetaldehyde proposed as the major intermediate [8]. Over Co$_3$O$_4$, Fe$_2$O$_3$ and Co–Fe catalysts, acetaldehyde began to be observed at $\sim$150 °C (Fig. 7F); however, the temperature at which the maximum in acetaldehyde formation occurred varied from 270 °C over Co$_3$O$_4$ to

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**Fig. 7 — Reaction profile during temperature ramp from 100 °C to 500 °C and steady state at 500 °C under ethanol water feed (1:3 molar ratio) over Co$_3$O$_4$ (black line), Fe$_2$O$_3$ (grey line) and Co–Fe (light grey line) for conversion of ethanol (A), formation of H$_2$ (B), CO$_2$ (C), CO (D), ethylene (E), acetaldehyde (F), methane (G) and acetone (H).**
350 °C for Fe2O3 and 370 °C for the Co–Fe catalyst. Co3O4 was found to have the highest activity for the transformation of acetaldehyde. However, as the temperature increased from 400 to 500 °C, acetaldehyde was observed to form again (Fig. 7F). Over the Fe2O3 and Co–Fe catalysts acetaldehyde was still detected for the first ~10 min while at 500 °C.

Acetaldehyde can undergo decomposition reactions (Eq. (4)) as well as reforming reactions (Eq. (5)), with both pathways forming CO (which can react further to CO2 + H2 via WGS). Products from the transformation of acetaldehyde also include H2 (via reforming) or methane (via decomposition). The amount of methane formed over the Co3O4 catalyst was significantly higher compared with the Fe2O3 catalyst (Fig. 7H). This is not consistent with previous reports where Co catalysts exhibited low methane formation under ethanol steam reforming conditions [37]. Co catalysts have also been reported to have low methanation activity at low to moderate temperatures [38] so it is likely that this methane found together with CO and H2 comes via ethanol decomposition (Eq. (6)).

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \\
\text{CH}_3\text{CHO} & \rightarrow \text{CH}_4 + \text{CO} \\
\text{CH}_3\text{CHO} + \text{H}_2\text{O} & \rightarrow 2\text{CO} + 3\text{H}_2 \\
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2
\end{align*}
\]

The high selectivity towards methane over Co3O4 suggests that ethanol or acetaldehyde decomposition pathways are favoured compared with reforming reactions whereas over the Fe2O3 catalysts, the low methane suggests that reforming reactions are favoured. However, it was noted that the H2 and CO2 signals over Fe2O3 decrease over the 1 h period at 500 °C (Fig. 7B and C). Although Fe2O3 catalysts form less methane than Co3O4 at low temperatures. While comparable species are observed on the Fe2O3 and Co3O4 catalysts, the relative intensity of the adsorbed water to acetate bands varied significantly with the water/OH bands observed over the Fe catalyst resembling the spectrum of Fe2O3 under H2 and cooled to 100 °C before introduction of the feed. Spectra have been corrected for contributions due to gas phase ethanol.

**Fig. 8** — DRIFT spectra recorded at 100 °C: Fe2O3 (dark grey spectrum), Co–Fe (black) and Co3O4 (light grey spectrum) under ethanol/water feed (1:3 molar ratio). Catalysts were pre-reduced at 400 °C under H2 and cooled to 100 °C before introduction of the feed. Spectra have been corrected for contributions due to gas phase ethanol. Over Co–Fe compared with Co3O4 or Fe2O3 oxides alone. The change in activity for ethylene conversion could be responsible for the reduced coke formation observed over the mixed metal catalyst (Table 1).

Fig. 8 shows DRIFT spectra of Co3O4 and Fe2O3 at 100 °C under the ethanol/water feed referenced to the respective reduced catalysts before exposure to the feed. On the Fe2O3 catalyst under the feed at 100 °C, bands due to adsorbed water (bands between 3700–3000 and 1646 cm⁻¹), acetyl species, a band at 1685 cm⁻¹ (shoulder to higher wavenumber of the 1646 cm⁻¹ which can form from dehydrogenation of acetaldehyde) [40] and ethoxy species, bands at 1082 and 1045 cm⁻¹, were observed [29,41]. Bands due to acetate species were also observed at 1545 and carbonates at 1525 cm⁻¹ [40]. The Co3O4 spectrum at 100 °C has similar adsorbed species to Fe2O3 with water, acetyl and acetate species observed. The major difference between the Co3O4 and Fe2O3 catalysts is the lack of ethoxy bands on the Co3O4 and the presence of additional, although weak, acetate bands between 1450 and 1330 cm⁻¹ which suggests that ethanol adsors and is oxidised to acetate on Co3O4 at low temperatures. While comparable species are observed on the Fe2O3 and Co3O4 catalysts, the relative intensity of the adsorbed water to acetate bands varied significantly with the water/OH bands observed over the Fe catalyst at 100 °C being significantly more intense compared with the acetate/carbonate bands while for the Co3O4 catalyst, these bands are of more comparable intensities (Fig. 8). The DRIFT spectrum of the Co–Fe catalyst resembles the spectrum of Fe2O3 at 100 °C (Fig. 8) with comparable relative intensities of the adsorbed water and ethoxy bands.

On ramping the temperature to 500 °C under the ethanol/water feed, the ethoxy/acetate species and water/OH surface coverage decrease over all catalysts although at differing rates which is in line with the MS results where different temperature ranges for the formation/reaction of intermediates/by-products was observed over the catalysts.

Over Fe2O3, as the temperature increases, there was an initial increase in the intensity of the water and ethoxy bands up to a temperature of 200 °C (Fig. 9). Above 200 °C, bands due...
to water and ethoxy species began to decrease with further increases in temperature with ethoxy bands no longer observed above 350 °C and water bands no longer observed above 400 °C. At 400 °C, a new band is observed at 1743 cm⁻¹ which could be due to the formation of acetaldehyde or acetone (υ(C=O)). Other bands to aid the assignment were not distinguishable and hence unambiguous assignment from the DRIFT spectra was not possible. This new band, however, increases in intensity up to a temperature of 500 °C over Fe₂O₃ after which it remains constant. Once this species is formed, it is strongly adsorbed on the catalyst surface. The temperature at which the 1743 cm⁻¹ band is observed corresponds with the reaction of acetaldehyde to form acetone; temperature at which the maximum acetaldehyde is formed in the gas phase (Fig. 7). Using TPD experiments of acetaldehyde and acetone adsorbed over Co/ZrO₂ and Co/CeO₂ catalysts, Song et al. showed that acetone had a stronger interaction with the surface; products from acetone conversion were also observed over a much greater temperature range than acetaldehyde [39]. Most of the acetaldehyde desorption features were in the temperature range of 300–350 °C while with acetone, products were formed between 250 and 550 °C. This suggests that the band at 1743 cm⁻¹ could be due to acetone strongly adsorbed on the catalyst surface. As well as the band at 1743 cm⁻¹, as the temperature increases, the bands at 1541, 1458 and 1345 cm⁻¹ due to acetate/carbonte species increase. At 500 °C, the Fe₂O₃ catalyst surface has adsorbed acetone and acetate/carbonte species.

Fig. 9 – DRIFT spectra of Fe₂O₃ under ethanol/water feed (1:3 molar ratio) from 100 to 500 °C (heating rate 10 °C min⁻¹). Grey arrows highlight species which grow with increasing temperature.

Fig. 10 – DRIFT spectra of Co₃O₄ under ethanol/water feed (1:3 molar ratio) from 100 to 500 °C (heating rate 10 °C min⁻¹). Grey arrows highlight species which grow with increasing temperature.
Over Co$_3$O$_4$, at 100 °C, water/OH bands and acetyl bands are much weaker than over Fe$_2$O$_3$ and no ethoxy bands were observed (Fig. 10). No change in the adsorbed species occurred between 100 and 200 °C. The bands due to adsorbed water began to decrease above 250 °C and were no longer observed above 350 °C; 100 °C lower than over the Fe$_2$O$_3$ catalyst. MS data for the conversion of ethanol with increasing temperature profile (Fig. 7A) showed a decrease in the ethanol conversion rate between 400 and 500 °C which corresponds with the temperature range where water is no longer adsorbed on the Co$_3$O$_4$ catalyst. This suggests that with the increasing temperature, the extent of conversion of ethanol through reforming and decomposition reactions could be altered with decomposition becoming more significant at higher temperature when water/OH is no longer adsorbed on the catalyst. Over Co$_3$O$_4$ at 250 °C, (as opposed to 400 °C for the Fe$_2$O$_3$ catalyst) a band at 1745 cm$^{-1}$ assigned to acetone was observed. This band increases slightly at 300 °C and then remains constant, decreasing above 450 °C to a weak band which is still present at 500 °C. Co$_3$O$_4$ has a higher activity than Fe$_2$O$_3$ for transformation of acetone. Co$_3$O$_4$ catalyst also shows a decrease in acetate/carbonate bands with increasing temperature and like Fe$_2$O$_3$, at 500 °C, has only bands due to acetone and acetate/carbonate species.

DRIFT spectra of the Co–Fe catalyst under ethanol/water feed with increasing temperature are shown in Fig. 11. The DRIFT spectrum of Co–Fe at 100 °C has the same water and ethoxy bands as the Fe$_2$O$_3$ catalyst (Fig. 8). As the temperature is ramped to 500 °C the following changes are observed:

(i) water/OH bands initially increase in intensity with increasing temperature and are no longer observed at 450 °C as for the Fe$_2$O$_3$ catalyst;
(ii) ethoxy bands are no longer observed by 300 °C which is at a lower temperature compared to Fe$_2$O$_3$ (350 °C);
(iii) at 350 °C, the band associated with acetone formation (1745 cm$^{-1}$ band) is detected which is at an intermediate temperature between Co$_3$O$_4$ (250 °C) and Fe$_2$O$_3$ 400 °C;
(iv) acetone and acetate/carbonate species are present on all three catalysts at 500 °C under the feed.

Interestingly, coke formation from the build up of acetate/carbonate species has been proposed over catalysts under the ESR conditions; [42] however all the catalysts have comparable intensity bands due to acetate/carbonate bands at 500 °C with very different amounts/nature of carbon deposited (Table 1). The higher H$_2$ yield over the Co–Fe catalyst compared with the pure oxides may be related to the increase in water/OH species adsorbed on the catalyst at lower temperatures. The higher concentration of OH species on the Co phase in Co–Fe would favour reforming activity rather than decomposition reactions which are favoured over the pure Co$_3$O$_4$ catalyst at these temperatures therefore increasing the selectivity to H$_2$ over methane, for example.

4. Conclusions

The Co–Fe sample exhibited not only higher H$_2$ yield but also reduced by-product formation compared with the pure oxides and the physical mixture. The DRIFT-MS study highlighted that properties of the individual oxides were maintained in the Co–Fe catalyst in particular the adsorption properties of Fe$_2$O$_3$ (water/OH present on the catalyst to higher temperatures) which is a result of the preparation method used; formation of separate cobalt and iron phases in intimate contact. Increasing the amount of reactive species (higher ratio of water to ethoxy/acetate species at higher temperatures) adsorbed on the Co–Fe catalyst surface compared with the Co$_3$O$_4$ catalyst is proposed to facilitate reforming over decomposition reactions reducing by-product formation and providing a higher H$_2$ yield.
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