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## Binary iron cobalt oxide silica membrane for gas separation

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## ABSTRACT

This work investigates the preparation, characterisation and performance of binary iron/cobalt oxide silica membranes by sol–gel synthesis using tetraethyl orthosilicate as the silica precursor, and cobalt and iron nitrates. It was found that cobalt and iron oxides were generally dispersed homogeneously in the silica structure, with the exception of a few minor patches rich in cobalt oxide. The sol–gel synthesis affected the micro-structural formation of binary metal oxide silica matrices. Increasing the iron content favoured condensation reactions and the formation of siloxane bridges, and consequently larger average pore sizes which lead to low He/N<sub>2</sub> permselectivity values below 20. In the case of high cobalt content, a higher silanol to siloxane ratio was observed with tighter pore size tailoring, as evidenced by higher He/N<sub>2</sub> permselectivities reaching 170. The binary metal oxide and silica interfaces proved to follow a molecular sieving mechanism characterised by activated transport where the permeance of the smaller gas molecules (He and H<sub>2</sub>) increased with temperature up to 500 °C, whilst the permeance of larger gas molecules (CO<sub>2</sub> and N<sub>2</sub>) decreased.

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## 1. Introduction

The sol–gel method is a very versatile technique generally employed to prepare high quality silica derived membranes for gas separation at high temperatures. Embedding metal oxides into silica membranes generally does not affect the micro-structural pore formation thus conferring good gas permeation and separation performances. The preferred choices for doping silica matrices include oxides of nickel [1,2], cobalt [3] and palladium [4], in addition to zirconia [5–7], titania [8], niobia [9,10] and alumina [11,12]. Adding metal oxides also provide functionalities to the membranes which otherwise are not available with pure silica.

Examples of functionalities include superior stability under steam exposure of cobalt oxides silica membranes using tetraethyl orthosilicate (TEOS) as the silica precursor [13]. Battersby et al. [14] reported that cobalt silica matrices remained microporous in wet gas streams, whilst pure silica xerogels were greatly affected by closing small pores and opening large pores leading to mesoporous structures. In some cases, the metal oxide can aid the transport of gases by changing adsorption properties for gases such as H<sub>2</sub> for nickel oxide silica amorphous materials [15–16]. In other cases, the oxidation state of cobalt oxide in silica xerogels can be modulated by adding cationic surfactants [17]. In another example, Miller et al.

[18] recently reported the unusual effect of reversible redox effect on gas permeation of cobalt oxide doped on ethoxy polysiloxane (ES40) silica precursor.

Another important functionality of metal oxides is the pore size control and stability to other substances. For instance, Uhlmann et al. [19] exposed cobalt oxide silica membranes to H<sub>2</sub>S and found that sulphur did not react with cobalt oxide, thus clearly indicating that the silica and cobalt oxide interface had pore sizes below the kinetic diameter of H<sub>2</sub>S ( $d_k=3.6$  Å). The stability of cobalt oxide silica membranes was also proven for 2000 h under thermal cycling tests up to 500 °C for a scaled-up module containing 8 membrane tubes [20]. In addition, cobalt oxide silica membranes showed excellent performance for the H<sub>2</sub> separation even at higher temperatures of 600 °C [21], a temperature which would lead to thin film densification in the case of pure silica membranes. Very recently, it was proven for the first time that cobalt oxide silica are robust in the preparation of membranes via rapid thermal processing [22,23], where membranes were manufactured in a single day instead of the conventional slow thermal processing of up to 10–14 days.

The structural tailorability of cobalt oxides makes them the preferred metal oxide doping material in silica membranes. Nevertheless, Darmawan et al. [24] recently incorporated iron oxide into silica matrices, producing microporous materials. Iron nitrate has a good solubility, adequate for applying in the sol–gel method [25], leading to the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (magnetite) in the silica matrix [26]. Iron oxides also showed excellent dispersion with small

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particle sizes [27], which tend to confer stronger oxide and matrix interactions [28]. On this basis, the reported properties of iron oxide should justify its potential as a dope material embedded in silica matrices. However, there is a serious mismatch between the coefficient of thermal expansion between silica and iron oxides [29], which is concerning thin silica films containing iron oxides may crack, thus rendering membranes ineffective.

To address this problem, this work pursues a strategy of binary metal oxide doping by investigating the effect of binary iron and cobalt oxides into silica membranes. Currently there is only a single publication into binary metal oxide doping using cobalt and palladium silica membranes [30]. Palladium is an expensive noble metal, and its replacement with the abundant and cost effective iron oxide is desirable in economic terms. Therefore, this work investigates the physicochemical properties of bulk xerogels prepared via the sol-gel method and containing varying ratios of iron to cobalt oxides. In addition, the silica membrane performance with varying Fe/Co ratios are tested for single gas permeation for helium, hydrogen, carbon dioxide and nitrogen at temperatures ranging from 200 to 500 °C.

## 2. Experimental

### 2.1. Sol-gel synthesis and characterisation

The metal to silicon ratio chosen in this investigation is 1:4 (25 mol%), which is in the range for the best microporous structures as reported by Yacou et al. [20] for cobalt oxide silica matrices. A series of samples were prepared by changing the Fe/Co oxide ratio, though the total metal to silicon ratio was kept constant at 1:4. Briefly, Fe/Co oxide sols were synthesised by the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in ethanol and 30% aqueous  $H_2O_2$  with iron nitrate nonahydrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) and cobalt nitrate hexahydrate ( $Co(NO_3)_2 \cdot 6H_2O$ ). An initial molar ratio of 255 EtOH: 4 TEOS: 1 Metal Nitrate Hydrate:  $9H_2O_2$ :  $40H_2O$  was mixed and vigorously stirred for 3 h in an ice-cooled bath. The molar concentration of the iron and cobalt ( $x:y$ ) was varied between 0:1 (0/100) and 1:0 (100/0). Hence, the total concentration of the two metals was always 1 mol in the sol. Blank samples of iron oxide silica ( $x=1$  and  $y=0$ ) and cobalt oxide silica ( $x=0$  and  $y=1$ ) were prepared for comparison purposes with the binary metal doped silica structures. Sol samples were dried in a temperature controlled oven at 60 °C and atmospheric conditions to form xerogels. The xerogel samples were crushed finely and calcined at ramp rates from 1.5 °C  $min^{-1}$  to 600 °C in air atmosphere with a 2.5 h holding time at the desired temperature.

Nitrogen adsorption was studied at 77 K using a Micromeritics Tristar 3020 to determine the BET surface area and pore volume. The samples were initially degassed for 24 h to pressures of  $\sim 2$  Pa at 200 °C. Fourier transform infrared analysis (FTIR) was carried out on a Shimadzu IRAffinity-1 with a Pike MIRacle ATR attachment. Spectra in the relevant regions of silica and metal oxides were taken over a wavelength range of 1300–520  $cm^{-1}$ . Scanning electron microscopy (SEM) images of platinum coated samples were obtained with a JSM-7001F field emission microscope operated at an accelerating voltage of 10 kV with a Si(Li) energy dispersive X-ray spectrometer. The EDX spectra were acquired using an EX-64175-JMH EDX system at 20 kV and 10 mm distance. The EDX spectra were analysed with an Integrated JEOL Analyses Station Software (version 3.8).

### 2.2. Membrane preparation and testing

Iron cobalt oxide silica thin film layers were coated on ceramic tubular supports 10 cm in length and 1.4 cm external diameter provided by the Energy Centre of the Netherlands (ECN). These supports have high quality  $\gamma$ -alumina interlayers with an intrinsic pore size distribution centred  $\sim 4$  nm, with a very low defect density above 10 nm [21,31], which were coated on  $\alpha$ -alumina substrates. The tubular supports were dip-coated with the binary iron cobalt oxide silica sol using a controlled immersion time of 1 min, and immersion/withdrawal speed of 10  $cm\ min^{-1}$ . Each layer was calcined at 600 °C in air, and held for 2.5 h with a heating and cooling rate of 1 °C  $min^{-1}$ . A total of 4 layers were coated onto the alumina support.

The performance of iron cobalt oxide silica membranes was measured by single gas permeation using a custom-made setup (Fig. 1) with a membrane housing module. The temperature of the module was controlled by a furnace with an external PID temperature controller. The membrane tube was sealed using graphite ferrules and stainless steel pressure fitting before being placed inside the module. The single gas permeation was carried out in dead-end mode, where the retentate line was closed and the permeate line was open to atmospheric pressure. The feed pressure of gases in the membrane module was measured by a pressure gauge.

The membrane was then heated and tested for single gas permeance with helium (He), hydrogen ( $H_2$ ), nitrogen ( $N_2$ ) and carbon dioxide ( $CO_2$ ) at decreasing temperatures ranging from 500 °C to 100 °C at 50 °C increments with a trans-membrane pressure of 400 kPa. The gas flow rates in the permeate stream were measured by a bubble flow metre. The permeance of gas

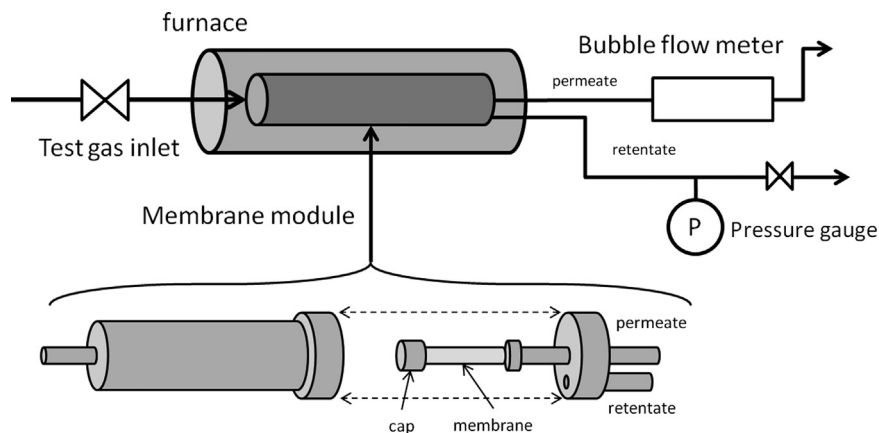


Fig. 1. Permeation setup.

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